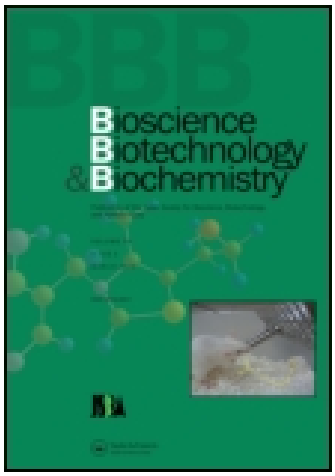

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Synthesis of (+)-(1S,2S,5R,6S)-1-Hydroxysamin from l-(+)-Arabinose

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Synthesis of (+)-(1*S*,2*S*,5*R*,6*S*)-1-Hydroxysamin from L-(+)-Arabinose

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As a model for the synthesis of optically active 6-aryl-2-aryloxy-1-hydroxy-3,7-dioxabicyclo-[3.3.0]octanes, which are 1,2-dioxygenated furofuran lignans, the most important intermediate, (+)-(1*S*,2*S*,5*R*,6*S*)-1-hydroxysamin (1), was synthesized from L-(+)-arabinose.

Key words: samin; lignan; furofuran lignan

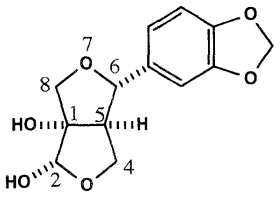
Some 1,2-dioxygenated furofuran lignans have been isolated.[1,2] The interesting biological activities of these lignans have been reported,[2] as well as other types of furofuran lignans. Synthesis of the optically active 1,2-dioxygenated furofuran lignan was achieved by Ishibashi and Taniguchi by optical resolution of β-vinyl-γ-butyrolactone as the starting material.[3a] Our efforts were directed to a more efficient synthesis of this type of lignans. Since many 1,2-dioxygenated furofuran lignan analogs, (±)-6-aryl-2-aryloxy-1-hydroxy-3,7-dioxabicyclo[3.3.0]octanes, have been synthesized by glycosidation of (±)-6-aryl-1,2-dihydroxy-3,7-dioxabicyclo[3.3.0]octanes with phenol,[4] an effective synthesis of optically active 6-aryl-1,2-dihydroxy-3,7-dioxabicyclo[3.3.0]octane needs to be achieved to synthesize of the optically active 6-aryl-2-aryloxy-1-hydroxy-3,7-dioxabicyclo[3.3.0]octane. This report describes the synthesis of (+)-(1*S*,2*S*,5*R*,6*S*)-1-hydroxysamin (**1**) from L-(+)-arabinose as a model for synthesis of the optically active 6-aryl-2-aryloxy-1-hydroxy-3,7-dioxabicyclo[3.3.0]octane type of lignans.

It seemed that the combination of γ-butyrolactone **2**, which had been prepared from L-(+)-arabinose,[5] with piperonal (**3**) might lead to hemiacetal **1**. It could be expected that the C5 carbon of lactone **2** would be transformed to the C2 carbon of hemiacetal **1**. Silane reduction[6] would be suitable for converting the carbonyl carbon in lactone **2** to the C4 carbon in the furofuran ring. The C4 position of lactone **2** would allow methylenation after oxidation at this position. The required oxygens might be introduced to the resulting double bond to give oxygens at the C1 and 7 positions of the furofuran ring. Clearly, the C6 carbon of the furofuran ring can be derived from the aldehyde carbon of piperonal (**3**) (Fig.).

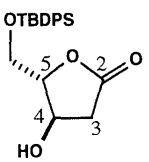
Results and Discussion

γ-Butyrolactone **2** was prepared from L-(+)-arabinose by the Marquez method[5] in a 21% overall yield in 4 steps. Aldol condensation of this γ-butyrolactone with piperonal (**3**) by lithium diisopropylamide gave a mixture of *erythro* and *threo* adduct **4** in a 44% yield. The ratio of *erythro*/*threo* was 4/1. Employing potassium diisopropylamide instead of lithium diisopropylamide as the base gave only the *erythro* adduct in a 24% yield. Such high *erythro* selectivity in the aldol condensation of γ-butyrolactone with benzaldehyde has been previously observed.[7] The existence of an intramolecular hydrogen bond between the hydrogen of the benzylic hydroxy group and the oxygen of the carbonyl group resulted in the *erythro* and *threo* isomers taking a six-membered ring in a chair conformation. 1′-H and 3-H of the *erythro* isomer were axial-equatorial, while those of the *threo* isomer were *trans* diaxal. The coupling constant between 1′-H and 3-H of the *erythro* isomer was reportedly smaller than that of the *threo* isomer,[8] the coupling constant between 1′-H and 3-H of *erythro* adduct **4** being 4.0 Hz and that of the *threo* adduct being 5.8 Hz. The observation of NOE between 3-H and 5-H in **4** confirmed the stereochemistry of the C3 position. Protection of the hydroxy group at the C4 position of γ-butyrolactone **2** prevented us from obtaining an aldol adduct. Aldol condensation of the 4-benzyloxy[9] and 4-[(triethylsilyl)oxy]γ-butyrolactone corresponding to **2** with piperonal (**3**) did not proceed to the recovery of 4-benzyloxy and 4-[(triethylsilyl)oxy]γ-butyrolactone and piperonal.

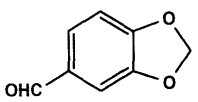
Protecting the two hydroxy groups of aldol adduct **4** with *tert*-butyldimethylsilyl groups by using *tert*-butyldimethylsilyltrifluoromethane sulfonate[10] allowed separation of the *erythro* (79%) and *threo* (18%) isomers by silica gel column chromatography. Resulting *erythro* silyloxy lactone **5** was reduced to a hemiacetal by diisobutylaluminum hydride.



1: (+)-1-Hydroxysamin



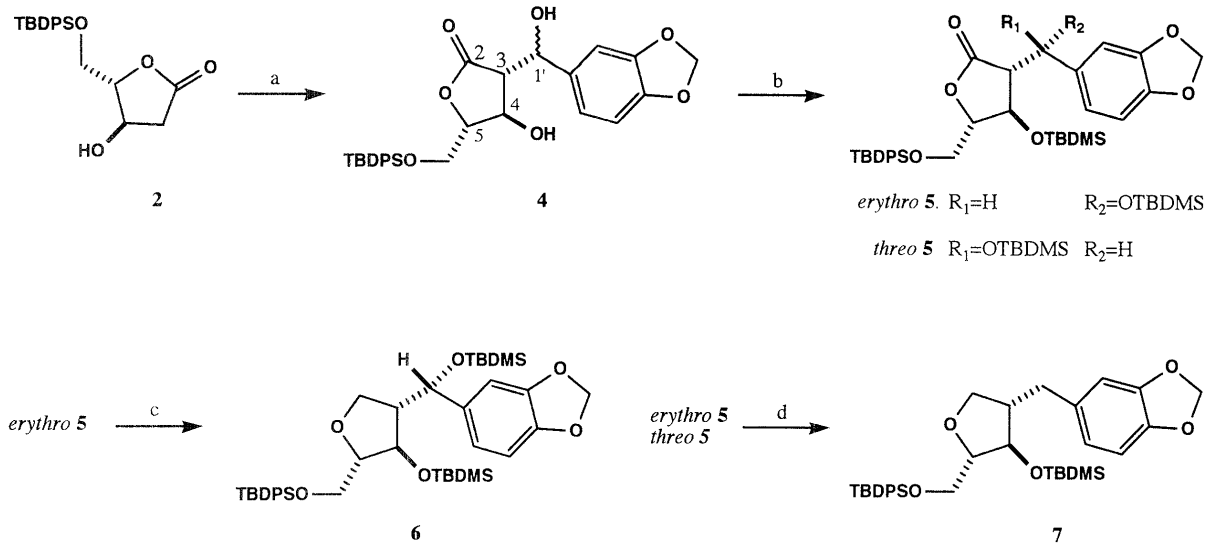
2[5]



3

Fig.

† To whom correspondence should be addressed.



Scheme 1. Synthesis of Tetrahydrofuran Derivative **7**.

(a) LDA or KDA, THF, piperonal (**3**). −75°C; (b) TBDMSOTf, 2,6-lutidine, CH_2Cl_2, 0°C; (c) (1) DIBAH, toluene, −75°C; (2) Et_3SiH, $BF_3 \cdot OEt_2$, CH_2Cl_2, −20°C; (d) (1) DIBAH, toluene, −75°C; (2) Et_3SiH, $BF_3 \cdot OEt_2$, CH_2Cl_2, 2°C.

Without purification, this hemiacetal was exposed to silane reduction under the influence of triethylsilane and a catalytic amount of boron trifluoride etherate in dichloromethane[6] at −20°C, reducing only the hemiacetal position to provide disilyloxy tetrahydrofuran **6** in a 28% yield from *erythro* **5**, with the hemiacetal being recovered. An increase of temperature to 2°C permitted both reduction of the hemiacetal position and of the benzylic position to provide silyloxy tetrahydrofuran **7** in a 71% yield from a mixture of *erythro*/*threo* silyloxy lactone **5**. The hydroxy group at the benzylic position was necessary to construct the furofuran ring. However, the need for an acceptable yield of **7** forced us to continue using **7** because the introduction of a hydroxy group to the benzylic position was assumed to be possible later. Reduction of the benzylic hydroxy group by hydride and Lewis acid is known to be possible[11] (Scheme 1).

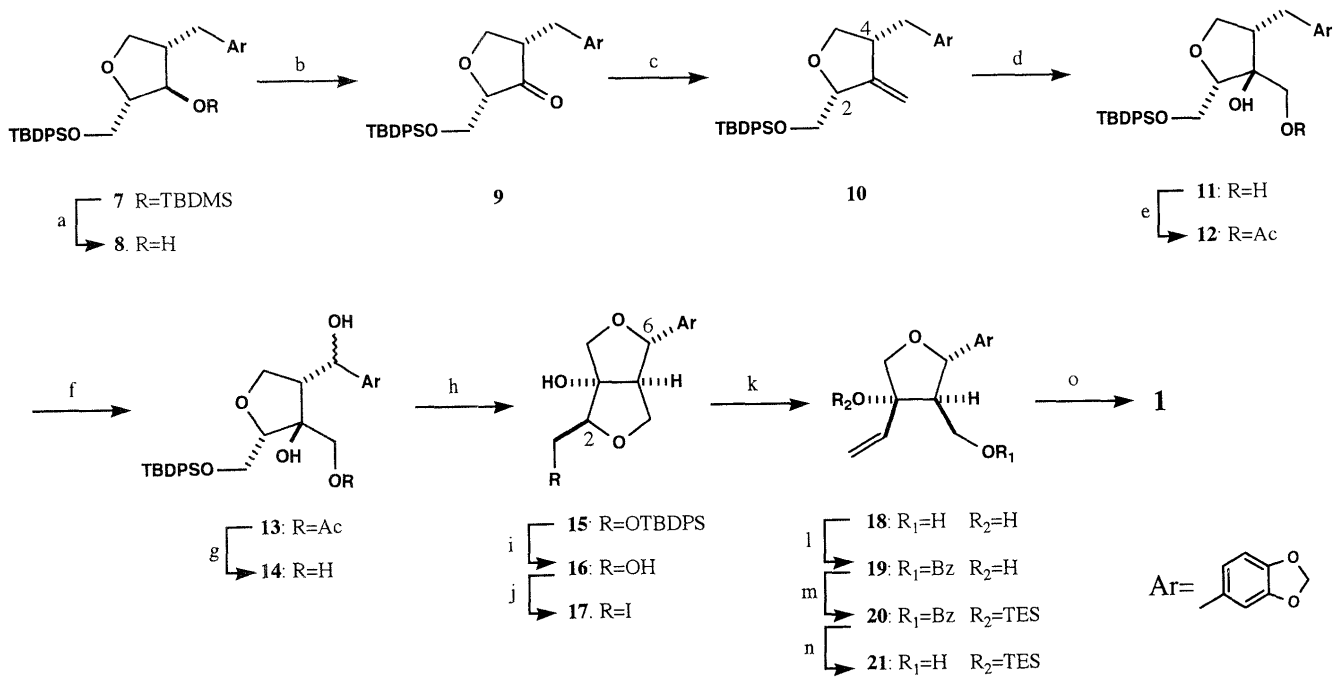
Selective desilylation of the *tert*-butyldimethylsilyl group by conc. hydrochloric acid in tetrahydrofuran, methanol, and water (86% yield) and subsequent pyridinium chlorochromate oxidation[12] gave ketone **9** in a 94% yield. Neither Wittig reaction[13] nor Peterson olefination[14] was effective on ketone **9**. The methylenation of ketone **9** was achieved by employing the Tebbe reagent[15] at −40°C in tetrahydrofuran in an 87% yield. The presence of NOE between 2-H and 4-H of **10** revealed no isomerization to the *trans* isomer. Stereoselective osmium tetroxide-*N*-methylmorpholine *N*-oxide oxidation[16] to olefin **10** was achieved at 0°C in a quantitative yield. Stereoselectivity was decreased by increasing the temperature. At room temperature, desired glycol **11** was obtained in an 86% yield together with an undesired glycol in a 6% yield.

After acetylating the primary hydroxy group of glycol **11** in acetic anhydride in the presence of 4-dimethylaminopyridine (88% yield), resulting monoacetate **12** was treated with *N*-bromosuccinimide and a catalytic amount of benzoyl peroxide[17] in refluxing tetrachlorocarbon. The crude product was applied to silica gel column chromatography to afford benzyl alcohol **13** as a diastereomeric mixture with a 4:1 ratio in a 47% yield (based on 61% conversion). When the two hydroxy groups of glycol **11** were protected as dimethylacetal, the introduction of the hydroxy group to the benzylic position also proceeded in a 23% yield. However, deprotection of the 1,2-diol failed. Deacetylation of **13** with potassium carbonate gave triol **14** in a 90% yield. Treatment of this triol **14** with a catalytic amount of *p*-toluenesulphonic acid in dichloromethane led to formation of furofuran **15** as a single isomer in a 96% yield. The product was identical to the desired isomer in 6*S* form from the chemical shift of 5-*H* of 2.61 ppm.[3]

The next stage was the construction of a hemiacetal moiety in the furofuran ring, leading to 1-hydroxysamin (**1**). As indicated earlier, conversion of the C2 carbon of **15** to the hemiacetal C2 carbon of **1** was effective.

After desilylating **15** with tetra-*n*-butylammonium fluoride[18] (84% yield), resulting diol **16** was subjected to iodination by iodine, imidazole, and triphenylphosphine[19] in refluxing toluene to afford iodide **17** in a 72% yield. Dihydroxy olefin **18** was produced by reductive ring opening with zinc[20] in refluxing ethanol in a 93% yield. Protection of the primary and tertiary hydroxy groups as a benzoyl ester and triethylsilyl ether, respectively, and subsequent treatment of **20** with potassium carbonate in methanol gave hydroxy olefin **21** in a 76% overall yield from **18**. Cleavage of the terminal double bond of **21** was then carried out with osmium tetroxide-*N*-methylmorpholine *N*-oxide[16] followed by periodate-mediated cleavage of the glycol. The resulting product was treated with tetra-*n*-butylammonium fluoride to reveal (+)-(1*S*,2*S*,5*R*,6*S*)-1-hydroxysamin (**1**) as a single isomer in a 38% overall yield from olefin **21**. The existence of NOE between 2-H and 8β-H shows the stereochemistry at the C-2 position to be *S*.[21] The fact that NOE was observed between 6-H and 4β,8β-H revealed the stereochemistry of the C-6 position to be *S* (Scheme 2).

An important intermediate for the synthesis of the 1,2-dioxygenated furofuran lignan, (+)-(1*S*,2*S*,5*R*,6*S*)-1-hydroxysamin (**1**), was synthesized from L-(+)-arabinose by 25 steps in a 0.3% overall yield. This is a new pathway to construct a 1,2-dioxygenated furofuran ring.



Scheme 2. Synthesis of 1-Hydroxysamin **1**.

(a) Conc. HCl, THF, MeOH, H_2O, r.t.; (b) PCC, CH_2Cl_2, r.t.; (c) Tebbe reagent, pyridine, THF, −40°C; (d) OsO_4, NMO, aq. acetone, *tert*-BuOH, 0°C; (e) Ac_2O, DMAP, r.t.; (f) (1) NBS, $(BzO)_2$, CCl_4, reflux; (2) silica gel column chromatography; (g) K_2CO_3, MeOH, r.t.; (h) *p*-TsOH, CH_2Cl_2, r.t.; (i) *n*-Bu_4NF, THF, r.t.; (j) I_2, imidazole, Ph_3P, toluene, reflux; (k) Zn, EtOH, reflux; (l) BzCl, Et_3N, CH_2Cl_2, r.t.; (m) TESOTf, 2,6-lutidine, CH_2Cl_2, r.t.; (n) K_2CO_3, MeOH, r.t.; (o) (1) OsO_4, NMO, acetone, *tert*-BuOH, H_2O, r.t.; (2) $NaIO_4$, EtOAc, H_2O, r.t.; (3) *n*-Bu_4NF, THF.

Experimental

All melting point (mp) data are uncorrected. NMR data were measured by JNM-GSX270, JNM-EX400, and JEOL α500 spectrometers, while IR spectra were determined with a Shimadzu FTIR-8100 spectrometer. EIMS and FABMS spectra were measured with Hitachi M-80B and JEOL HX-110 spectrometers, respectively, and optical resolution was evaluated with HORIBA SEPA-200 equipment. The silica gel used was Wakogel C-300 (Wako, 200–300 mesh), and preparative TLC was conducted with Merck silica gel $60F_{254}$ (0.5 mm thickness, 20 × 20 cm).

(3R,4R,5S)-5-[(tert-Butyldiphenylsilyl)oxy]methyl-4-hydroxy-3-[(1S)-1-hydroxy-1-(3,4-methylenedioxyphenyl)methyl]dihydro-2(3H)-furanone (*erythro* **4**). To a mixture of potassium *tert*-butoxide (1.69 g, 15.1 mmol) and diisopropylamine (1.98 ml, 15.1 mmol) in tetrahydrofuran (75 ml) was added *n*-butyllithium (9.21 ml, 1.64 M in hexane, 15.1 mmol) at −10°C under nitrogen gas, the resulting mixture being stirred at −10°C for 15 min and then cooled to −75 °C. Lactone **2** (2.8 g, 7.56 mmol) in tetrahydrofuran (15 ml) was added. After stirring at −75°C for 30 min, piperonal (1.13 g, 7.53 mmol) in tetrahydrofuran (5 ml) was added. The reaction mixture was stirred at −75°C for 2 h before addition of saturated aqueous NH_4Cl solution. The organic solution was separated, washed with brine, and dried (Na_2SO_4). Concentration followed by silica gel column chromatography (ethyl acetate/benzene = 1/9) gave *erythro* isomer **4** (0.94 g, 1.81 mmol, 24%) as a colorless oil. $[\alpha]_D^{20}$ −29.0 (*c* 1.0, $CHCl_3$). 270 MHz ^{1}H-NMR δ_H ($CDCl_3$): 1.06 (9H, s, $(CH_3)_3CSi$), 2.40–2.62 (1H, br., O*H*), 2.97 (1H, dd, *J* = 8.6, 4.0 Hz, 3-*H*), 3.85 (1H, dd, *J* = 11.8, 3.8 Hz, TBDPSOCH_2), 3.97 (1H, dd, *J* = 11.8, 3.4 Hz, TBDPSOCH_2), 4.17 (1H, ddd, *J* = 8.6, 3.8, 3.4 Hz, 5-*H*), 4.75 (1H, dd, *J* = 8.6, 8.6 Hz, 4-*H*), 5.28 (1H, d, *J* = 4.0 Hz, ArC*H*(OH)), 5.97 (2H, s, OCH_2O), 6.80–6.91 (3H, m, Ar*H*), 7.37–7.45 (6H, m, Ar*H*), 7.65–7.70 (4H, m, Ar*H*). 67.5 MHz ^{13}C-NMR δ_C ($CDCl_3$): 19.24, 26.72, 56.30, 61.81, 67.81, 70.07, 83.07, 101.24, 106.06, 108.55, 118.70, 127.80, 127.83, 129.90, 132.68, 133.03, 134.58, 135.59, 135.68, 147.32, 148.18, 173.95. IR ($CHCl_3$) ν_{max}: 3603, 3137, 3075–2780, 1778, 1505, 1491, 1445, 1429, 1250, 1221–1211, 1113, 1042, 733–785, 704, 669 cm^{-1}. FABMS *m/z*: 543 ($M+Na^+$, 100). HRMS (FAB) *m/z* ($M+Na^+$): calcd. for $C_{29}H_{32}O_7SiNa$, 543.1815; found, 543.1819.

(3R,4R,5S)-5-[(tert-Butyldiphenylsilyl)oxy]methyl-3-[(1S)-1-[(tert-butyldimethylsilyl)oxy]-1-(3,4-methylenedioxyphenyl)methyl]-4-hydroxydihydro-2(3H)-furanone (*erythro* **5**) *and (3R,4R,5S)-5-[(tert-butyldiphenylsilyl)oxy]methyl-3-[(1R)-1-[(tert-butyldimethylsilyl)oxy]-1-(3,4-methylenedioxyphenyl)methyl]-4-hydroxydihydro-2(3H)-furanone* (*threo* **5**). To a solution of diisopropylamine (7.2 ml, 0.055 mol) in tetrahydrofuran (400 ml) was added *n*-butyllithium (34.4 ml, 1.6 M in hexane, 0.055 mol) at −10°C under nitrogen gas. After stirring at −10°C for 15 min, the solution was cooled to −75°C. To the solution was added lactone **2** (9.11 g, 0.025 mol) in tetrahydrofuran (40 ml). After 15 min at −75°C, piperonal (3.8 g, 0.025 mol) in tetrahydrofuran (20 ml) was added, and then the reaction mixture was stirred at −75°C for 1 h before addition of saturated aqueous NH_4Cl solution. The organic solution was separated, washed with brine, and dried (Na_2SO_4). Concentration followed by silica gel column chromatography (ethyl acetate/benzene = 1/9) gave diol **4** (5.49 g, 0.011 mol, 44%) in a 4:1 mixture of *erythro*/*threo* isomers as a colorless oil. 270 MHz ^{1}H-NMR δ_H ($CDCl_3$): 0.99 (1.8H, s, $(CH_3)_3CSi$), 1.06 (7.2H, s, $(CH_3)_3CSi$), 2.60 (0.8H, d, *J* = 4.0 Hz, O*H*), 2.97 (0.8H, dd, *J* = 8.6, 4.0 Hz, 3-*H*), 3.37 (0.2H, dd, *J* = 5.8, 5.8 Hz, 3-*H*), 3.74 (0.2H, dd, *J* = 8.8, 2.1 Hz, TBDPSOCH_2), 3.85 (0.8H, dd, *J* = 11.8, 3.8 Hz, TBDPSOCH_2), 3.85–3.91 (0.2H, m, TBDPSOCH_2), 3.97 (0.8H, dd, *J* = 11.8, 3.4 Hz, TBDPSOCH_2), 4.17 (0.8H, ddd, *J* = 8.6, 3.8, 3.4 Hz, 5-*H*), 4.40 (0.2H, m, 5-H), 4.48 (0.2H, d, *J* = 5.8 Hz, O*H*), 4.52–4.60 (0.2H, m, 4-*H*), 4.75 (0.8H, m, 4-*H*), 5.28 (0.8H, dd, *J* = 4.0, 4.0 Hz, ArC*H*(OH)), 5.39 (0.2H, dd, *J* = 5.8, 5.8 Hz, ArC*H*(OH), 5.95 (0.4H, s, OCH_2O), 5.97 (1.6H, s, OCH_2O), 6.80–6.91 (3H, m, Ar*H*), 7.37–7.45 (6H, m, Ar*H*), 7.65–7.70 (4H, m, Ar*H*).

To an ice-cooled solution of *erythro* and *threo* diol **4** (3.49 g, 6.70 mmol) and 2,6-lutidine (2.95 ml, 25.3 mmol) in dichloromethane (80 ml) was added *tert*-butyldimethylsilyl trifluoromethanesulfonate (4.0 ml, 17.4 mmol). The reaction solution was stirred in an ice-bath for 1 h before addition of saturated aqueous $NaHCO_3$ solution. The organic solution was separated, washed with brine, and dried (Na_2SO_4). Concentration followed by silica gel column chromatography (5% ethyl acetate/hexane) gave *erythro* disilyl ether **5** (3.98 g, 5.31 mmol, 79%) as a colorless oil and *threo* disily ether **5** (0.92 g, 1.23 mmol, 18%) as a colorless oil. *Erythro* disilyl ether **5**: $[\alpha]_D^{20}$ −53.0 (*c* 1.0, $CHCl_3$). 270 MHz ^{1}H-NMR δ_H ($CDCl_3$): −0.44 (3H, s, $(CH_3)_2Si$), −0.20 (3H, s, $(CH_3)_2Si$), −0.15 (3H, s, $(CH_3)_2Si$), −0.09 (3H, s, $(CH_3)_2Si$), 0.65 (9H, s, $(CH_3)_3CSi$), 0.72 (9H, s, $(CH_3)_3CSi$), 1.08 (9H, s, $(CH_3)_3CSi$), 2.74 (1H, dd, *J* = 3.1, 3.1 Hz, 3-*H*), 3.75 (1H, dd, *J* = 10.6, 6.4 Hz, TBDPSOCH_2), 3.86 (1H, dd, *J* = 10.6, 6.3 Hz, TBDPSOCH_2), 4.32–4.37 (2H, m, 4-*H*, 5-*H*), 5.28 (1H, d, *J* = 3.1 Hz, ArC*H*(OTBDMS)), 5.95 (2H, s, OCH_2O), 6.78–6.82 (3H, m, Ar*H*), 7.36–7.47 (6H, m, Ar*H*), 7.66–7.70 (4H, m, Ar*H*). 67.5 MHz ^{13}C-NMR δ_C ($CDCl_3$): −5.67, −5.36, −4.78, −4.71, 17.49, 18.21, 19.15, 25.30, 25.75, 26.84, 60.35, 63.78, 69.88, 72.43, 88.12, 101.06, 106.50, 108.28, 118.98, 127.79, 129.86, 132.81, 133.12, 135.55, 135.62, 135.73, 147.04, 147.93, 175.91. IR ($CHCl_3$) ν_{max}: 3075–2859,

1771, 1505–1429, 1254, 1113, 1082, 839, 787 cm^{-1}. EIMS *m/z* (20 eV): 748 (M^+-1, 0.1), 691 (60), 407 (67), 265 (100). *Anal.* Found: C, 65.44; H, 7.97. Calcd. for $C_{41}H_{60}O_7Si_3$: C, 65.73; H, 8.07. *threo* Disilyl ether **5**: $[\alpha]_D^{20}$ −33.9 (*c* 0.56, $CHCl_3$). 270 MHz ^{1}H-NMR δ_H ($CDCl_3$): −0.22 (3H, s, $(CH_3)_2Si$), 0.05 (3H, s, $(CH_3)_2Si$), 0.06 (3H, s, $(CH_3)_2Si$), 0.10 (3H, s, $(CH_3)_2Si$), 0.89 (9H, s, $(CH_3)_3CSi$), 0.93 (9H, s, $(CH_3)_3CSi$), 1.04 (9H, s, $(CH_3)_3CSi$), 3.22 (1H, dd, *J* = 7.2, 4.9 Hz, 3-*H*), 3.62 (1H, dd, *J* = 11.8, 2.7 Hz, TBDPSOCH_2), 3.78 (1H, dd, *J* = 11.8, 2.8 Hz, TBDPSOCH_2), 3.82 (1H, m, 5-*H*), 4.78 (1H, dd, *J* = 7.2, 5.3 Hz, 4-*H*), 5.16 (1H, d, *J* = 4.9 Hz, ArC*H*(OTBDMS)), 5.93 (2H, s, OCH_2O), 6.71 (1H, d, *J* = 8.2 Hz, Ar*H*), 6.89 (1H, dd, *J* = 8.2, 1.5 Hz, Ar*H*), 6.94 (1H, d, *J* = 1.5 Hz, Ar*H*), 7.57–7.66 (6H, m, Ar*H*), 7.87–7.81 (4H, m, Ar*H*). 67.5 MHz ^{13}C-NMR δ_C ($CDCl_3$), −4.98, −4.57, −4.47, −4.43, 18.04, 18.08, 19.18, 25.82, 25.88, 26.79, 54.17, 61.47, 69.59, 71.08, 83.36, 100.89, 107.64, 108.19, 121.11, 127.76, 127.78, 129.86, 129.90, 132.15, 132.94, 135.45, 135.52, 135.73, 147.08, 147.26, 173.34. CIMS *m/z* (70 eV): 748 (M^+-1, 1), 691 (36), 485 (95), 265 (100). *Anal.* Found: C, 65.61; H, 7.97. Calcd. for $C_{41}H_{60}O_7Si_3$: C, 65.73; H, 8.07.

(2S,3R,4R)-3-[(tert-Butyldimethylsilyl)oxy]-4-[1(S)-1-[(tert-butyldimethylsilyl)oxy]-1-(3,4-methylenedioxyphenyl)methyl]-2-[(tert-butyldiphenylsilyl)oxy]methyltetrahydrofuran (**6**). To a solution of *erythro* lactone **5** (0.14 g, 0.19 mmol) in toluene (10 ml) was added diisobutylaluminum hydride (0.29 ml, 1 M in toluene, 0.29 mmol) at −75°C under nitrogen gas. The reaction mixture was stirred at −75°C for 30 min. After addition of a 1 N aqueous HCl solution, the organic solution was separated, successively washed with saturated aqueous $NaHCO_3$ solution and brine, and dried (Na_2SO_4). Concentration gave a crude hemiacetal (0.14 g, 0.19 mmol) as a colorless oil.

To a solution of this crude hemiacetal (0.14 g, 0.19 mmol) and triethylsilane (44 µl, 0.28 mmol) in dichlorometane (15 ml) was added boron trifluoride diethyl etherate (18 µl, 0.14 mmol) at −45°C under nitrogen gas. The reaction solution was stirred at −20°C for 1 h before addition of a saturated aqueous $NaHCO_3$ solution. The organic solution was separated, washed with brine, and dried (Na_2SO_4). Concentration followed by silica gel column chromatography (5% ethyl acetate/hexane) gave tetrahydrofuran **6** (0.04 g, 0.054 mmol, 28%) as a colorless oil. The hemiacetal (0.07 g, 0.093 mmol, 49%) was recovered. Tetrahydrofuran **6**: $[\alpha]_D^{20}$ −34.0 (*c* 1.0, $CHCl_3$). 270 MHz ^{1}H-NMR δ_H ($CDCl_3$): −0.32 (3H, s, $(CH_3)_2Si$), −0.19 (3H, s, $(CH_3)_2Si$), 0.05 (3H, s, $(CH_3)_2Si$), 0.13 (3H, s, $(CH_3)_2Si$), 0.81 (9H, s, $(CH_3)_3CSi$), 0.87 (9H, s, $(CH_3)_3CSi$), 1.06 (9H, s, $(CH_3)_3CSi$), 2.26 (1H, m, 4-*H*), 3.47 (1H, dd, *J* = 9.2, 1.9 Hz, 5-*H*), 3.63–3.71 (2H, m, TBDMSOCH_2), 3.77 (1H, dd, *J* = 9.2, 5.8 Hz, 5-*H*), 3.89 (1H, m, 2-*H*), 4.28 (1H, d, *J* = 9.5 Hz, ArC*H*(OTBDMS)), 4.33 (1H, dd, *J* = 4.1, 4.1 Hz, 3-*H*), 5.93 (2H, d, *J* = 4.9 Hz, OCH_2O), 6.66 (1H, dd, *J* = 7.3, 1.5 Hz, Ar*H*), 6.71 (1H, d, *J* = 7.3 Hz, Ar*H*), 6.76 (1H, d, *J* = 1.5 Hz, Ar*H*), 7.26–7.43 (6H, m, Ar*H*), 7.67–7.71 (4H, m, Ar*H*). 67.5 MHz ^{13}C-NMR δ_C ($CDCl_3$): −4.87, −4.51, −4.25, 17.78, 18.06, 19.16, 25.72, 25.87, 26.87, 58.56, 65.22, 68.73, 74.44, 75.50, 88.77, 100.90, 107.30, 107.66, 120.64, 127.62, 129.61, 133.43, 133.49, 135.66, 137.49, 146.88, 147.64. IR ($CHCl_3$) ν_{max}: 3073–2859, 1505, 1487, 1472, 1443, 1429, 1250, 1113, 1080, 1042, 857, 839, 704 cm^{-1}. EIMS *m/z* (20 eV): 734 (M^+-1, 0.1), 677 (39), 385 (65), 265 (100), 89 (78). *Anal.* Found: C, 66.66; H, 8.39. Calcd. for $C_{41}H_{62}O_6Si_3$: C, 66.98; H, 8.50.

(2S,3R,4S)-3-[(tert-Butyldimethylsilyl)oxy]-2-[(tert-butyldiphenylsilyl)oxy]methyl-4-(3,4-methylenedioxyphenyl)methyltetrahydrofuran (**7**). To a solution of *erythro* and *threo* lactone **5** (3.82 g, 5.10 mmol) in toluene (100 ml) was added diisobutylaluminum hydride (7.82 ml, 1 M in toluene, 7.82 mmol) at −75°C under nitrogen gas. The reaction mixture was stirred at −75°C for 30 min before addition of 1 N aqueous HCl solution. The organic solution was separated, washed with saturated aqueous $NaHCO_3$ solution and dried (Na_2SO_4). Concentration of the solvent gave a crude hemiacetal as a colorless oil (3.80 g, 5.06 mmol).

To a solution of this hemiacetal (3.80 g, 5.06 mmol) and triethylsilane (3.3 ml, 20.7 mmol) in dichloromethane (600 ml) was added boron trifluoride diethyl etherate (482 µl, 3.80 mmol) at 2°C under nitrogen gas. The reaction solution was stirred at 2°C for 1 h. After addition of saturated aqueous $NaHCO_3$ solution, the organic solution was separated, washed with brine, and dried (Na_2SO_4). Concentration followed by silica gel column chromatography (5% ethyl acetate/hexane) gave tetrahydrofuran **7** (2.18 g, 3.60 mmol, 71%) as a colorless oil. $[\alpha]_D^{20}$ −17.0 (*c* 1.0, $CHCl_3$). 270 MHz ^{1}H-NMR δ_H ($CDCl_3$): 0.01 (3H, s, $(CH_3)_2Si$), 0.02 (3H, s, $(CH_3)_2Si$), 0.86 (9H, s, $(CH_3)_3CSi$), 1.08 (9H, s, $(CH_3)_3CSi$), 2.32 (1H, m, 4-*H*), 2.47 (1H, dd, *J* = 13.5, 10.2 Hz, ArCH_2), 2.77 (1H, dd, *J* = 13.5, 5.5 Hz, ArCH_2), 3.66 (1H, dd, *J* = 8.7, 5.0 Hz, 5-*H*), 3.70–3.83 (3H, m, 2-*H*, TBDPSOCH_2), 3.88 (1H, dd, *J* = 8.7, 6.4 Hz, 5-*H*), 4.09 (1H, dd, *J* = 4.1, 4.1 Hz, 3-*H*), 5.92 (2H, s, OCH_2O), 6.56 (1H, dd, *J* = 7.6, 1.5 Hz, Ar*H*), 6.62 (1H, d, *J* = 1.5 Hz, Ar*H*), 6.71 (1H, d, *J* = 7.6 Hz, Ar*H*), 7.35–7.46 (6H, m, Ar*H*), 7.69–7.74 (4H, m, Ar*H*). 67.5 MHz ^{13}C-NMR δ_C ($CDCl_3$): −4.57, −4.43, 17.86, 19.24, 25.73, 26.87, 37.06, 50.68, 63.96, 71.30, 77.44, 87.26, 100.78, 108.19, 109.10, 121.57, 127.48, 127.55, 127.66, 129.63, 129.66, 133.30, 133.44, 134.11, 135.65, 135.70, 135.80, 145.84, 147.67. IR ($CHCl_3$) ν_{max}: 3137–2776, 1505, 1489, 1474, 1464, 1443, 1429, 1390, 1361, 1250, 1213, 1188, 1041, 941, 837, 749, 733, 704 cm^{-1}. FABMS *m/z*: 627 ($M+Na^+$, 26), 547 (11), 197 (28), 173 (36), 135 (100), 73 (82). HRMS (FAB) *m/z* ($M+Na^+$): calcd. for $C_{35}H_{48}O_5Si_2Na$, 627.2938; found, 627.2938.

(2S,3R,4S)-2-[(tert-Butyldiphenylsilyl)oxy]methyl-3-hydroxy-4-(3,4-methylenedioxyphenyl)methyltetrahydrofuran (**8**). A reaction solution of silyl ether **7** (3.58 g, 5.92 mmol) and conc. HCl (5 ml) in tetrahydrofuran (200 ml), methanol (60 ml), and H_2O (20 ml) was stood at room temperature for 5 h. After neutralization by a saturated aqueous $NaHCO_3$ solution, the mixture was concentrated. The residue was dissolved in ethyl acetate and H_2O, and the organic solution was separated and washed with brine. Drying (Na_2SO_4) and concentration followed by silica gel column chromatography (ethyl acetate/hexane = 1/3) gave alcohol **8** (2.50 g, 5.10 mmol, 86%) as a colorless oil. $[\alpha]_D^{20}$ +11.0 (*c* 1.0, $CHCl_3$). 270 MHz ^{1}H-NMR δ_H ($CDCl_3$): 1.07 (9H, s, $(CH_3)_3CSi$), 2.44 (1H, m, 4-*H*), 2.60 (1H, dd, *J* = 13.4, 9.2 Hz, ArCH_2), 2.80 (1H, dd, *J* = 13.4, 6.1 Hz, ArCH_2), 3.62 (1H, dd, *J* = 8.1, 8.1 Hz, 5-*H*), 3.74–3.79 (2H, m, 2-*H*, TBDPSOCH_2), 3.84 (1H, dd, *J* = 8.1, 5.8 Hz, 5-*H*), 3.93–4.00 (2H, m, 3-*H*, TBDPSOCH_2), 5.93 (2H, s, OCH_2O), 6.60 (1H, dd, *J* = 7.9, 1.5 Hz, Ar*H*), 6.66 (1H, d, *J* = 1.5 Hz, Ar*H*), 6.73 (1H, d, *J* = 7.9 Hz, Ar*H*), 7.39–7.44 (6H, m, Ar*H*), 7.66–7.70 (4H, m, Ar*H*). 67.5 MHz ^{13}C-NMR δ_C ($CDCl_3$): 19.16, 26.81, 36.75, 49.00, 64.54, 71.55, 77.95, 84.82, 100.78, 108.22, 108.99, 121.39, 127.70, 127.71, 129.76, 133.07, 133.14, 133.45, 135.53, 135.55, 145.90, 147.66. IR ($CHCl_3$) ν_{max}: 3673, 3137–3011, 2961–2778, 1505, 1489, 1248, 1217, 1213, 1107, 1078, 1041, 704 cm^{-1}. EIMS *m/z* (20 eV): 490 (M^+, 0.1), 433 (73), 173 (99), 135 (100). *Anal.* Found: C, 70.75; H, 7.06. Calcd. for $C_{29}H_{34}O_5Si$: C, 70.99; H, 6.98.

(2S,4S)-2-[(tert-Butyldiphenylsilyl)oxy]methyl-4-(3,4-methylenedioxyphenyl)methyldihydro-3(2H)-furanone (**9**). A reaction mixture of alcohol **8** (0.96 g, 1.96 mmol), pyridinium chlorochromate (0.67 g, 3.11 mmol) and 4A molecular sieves (2.3 g) in dichloromethane (80 ml) was stirred at room temperature for 6 h and then poured into ether (300 ml). After filtration, the filtrate was concentrated. The residue was applied to silica gel column chromatography (ethyl acetate/hexane = 1/3) to give ketone **9** (0.90 g, 1.84 mmol, 94%) as colorless crystals, mp 85–87°C. $[\alpha]_D^{20}$ +29.99 (*c* 0.6, $CHCl_3$). 270 MHz ^{1}H-NMR δ_H ($CDCl_3$): 1.05 (9H, s, $(CH_3)_3CSi$), 2.60 (1H, dd, *J* = 14.0, 11.0 Hz, ArCH_2), 2.80 (1H, m, 4-*H*), 3.13 (1H, dd, *J* = 14.0, 4.1 Hz, ArCH_2), 4.01–3.87 (3H, m, 2-*H*, TBDPSOCH_2), 4.20 (1H, dd, *J* = 8.9, 8.9 Hz, 5-*H*), 4.31 (1H, dd, *J* = 8.9, 8.9 Hz, 5-*H*), 5.93 (2H, s, OCH_2O), 6.57 (1H, dd, *J* = 7.9, 1.8 Hz, Ar*H*), 6.62 (1H, d, *J* = 1.8 Hz, Ar*H*), 6.72 (1H, d, *J* = 7.9 Hz, Ar*H*), 7.39–7.45 (6H, m, Ar*H*), 7.66–7.74 (4H, m, Ar*H*). 67.5 MHz ^{13}C-NMR δ_C($CDCl_3$): 19.05, 26.70, 32.99, 49.00, 64.65, 71.58, 80.90, 100.87, 108.32, 108.73, 121.31, 127.76, 129.76, 129.80, 132.51, 132.56, 132.72, 135.54, 135.59, 146.15, 147.78, 215.60. IR ($CHCl_3$) ν_{max}: 3074–3019, 2932–2860, 1757, 1505, 1491, 1445, 1429, 1248, 1219, 1113, 1039, 787, 704 cm^{-1}. EIMS *m/z* (20 eV): 488 (M^+, 0.4), 431 (35), 353 (81), 241 (37), 135 (100). *Anal.* Found: C, 71.20; H, 6.67. Calcd. for $C_{29}H_{32}O_5Si$: C, 71.28; H, 6.60.

(2R,4R)-2-[(tert-Butyldiphenylsilyl)oxy]methyl-3-methylene-4-(3,4-methylenedioxyphenyl)methyltetrahydrofuran (**10**). To a solution of ketone **9** (2.45 g, 5.01 mmol) and pyridine (55 µl, 0.68 mmol) in tetrahydrofuran (200 ml) was added the Tebbe reagent (11.1 ml, 0.5 M in toluene, 5.55 mmol) at −40°C under nitrogen gas. The reaction mixture was stirred at −40°C for 1 h before addition of saturated aqueous $NaHCO_3$ solution and ethyl acetate. The organic solution was separated, successively washed with 2 N aqueous HCl solution, saturated aqueous $NaHCO_3$ solution, and brine, and dried (Na_2SO_4). Concentration followed by silica gel column chromatography (ethyl acetate/hexane = 1/9) gave olefin **10** (2.13 g, 4.38 mmol, 87%) as a colorless oil. $[\alpha]_D^{20}$ −8.33 (*c* 1.0, $CHCl_3$). 270 MHz ^{1}H-NMR δ_H ($CDCl_3$): 1.08 (9H, s, $(CH_3)_3CSi$), 2.52 (1H, dd, *J* = 13.7, 10.1 Hz, ArCH_2), 2.78 (1H, dd, *J* = 13.7, 5.5 Hz, ArCH_2), 2.90 (1H, m, 4-*H*), 3.64 (1H, dd, *J* = 8.6, 6.0 Hz, 5-*H*), 3.74 (2H, d, *J* = 4.9 Hz, TBDPSOCH_2), 3.81 (1H, dd, *J* = 8.6, 6.7 Hz, 5-*H*), 4.49 (1H, m, 2-*H*), 4.93

(1H, m, CH_2=C), 4.96 (1H, m, CH_2=C), 5.92 (2H, s, OCH_2O), 6.57 (1H, dd, J=7.6, 1.5 Hz, Ar*H*), 6.63 (1H, d, J=1.5 Hz, Ar*H*), 6.71 (1H, d, J=7.6 Hz, Ar*H*), 7.36–7.46 (6H, m, Ar*H*), 7.70–7.74 (4H, m, Ar*H*). 67.5 MHz ^{13}C-NMR δ_C ($CDCl_3$): 19.18, 26.82, 38.56, 45.87, 66.66, 71.89, 82.05, 100.76, 105.76, 108.09, 109.06, 121.61, 127.60, 127.63, 129.60, 133.35, 133.51, 133.78, 135.64, 135.71, 145.82, 147.55, 151.89. IR ($CHCl_3$) ν_{max}: 3137–2778, 1505, 1489, 1445, 1429, 1248, 1221–1211, 1113, 1042, 785, 704 cm^{-1}. FABMS *m/z*: 509 (M+Na$^+$, 7), 429 (23), 199 (43), 135 (100). HRMS (FAB) *m/z* (M+Na$^+$): calcd. for $C_{30}H_{34}O_4SiNa$, 509.2124; found, 509.2125.

(*2S,3S,4S*)-*2*-[(*tert-Butyldiphenylsilyl*)*oxy*]*methyl-3-hydroxy-3-hydroxymethyl-4-*(*3,4-methylenedioxyphenyl*)*methyltetrahydrofuran* (**11**). A reaction mixture of olefin **10** (0.42 g, 0.86 mmol), *N*-methylmorpholine *N*-oxide (97%, 0.14 g, 1.16 mmol), and 2% aqueous osmium tetroxide (1 ml) in acetone (15 ml), *tert*-butyl alcohol (4 ml), and H_2O (4 ml) was stood at 0°C for 40 h under nitrogen gas in the dark. After addition of $NaHSO_3$ (2 g) in H_2O (1 ml), the mixture was filtered, and the filtrate was concentrated. The residue was dissolved in H_2O and ethyl acetate. The organic solution was separated, washed with brine, and dried (Na_2SO_4). Concentration followed by silica gel column chromatography (ethyl acetate/hexane = 1/3) gave glycol **11** (0.44 g, 0.85 mmol, 99%) as a colorless oil. $[\alpha]_D^{20}$ +5.23 (*c* 1.7, $CHCl_3$). 270 MHz ^{1}H-NMR δ_H ($CDCl_3$): 1.08 (9H, s, $(CH_3)_3CSi$), 2.35 (1H, dd, J=13.0, 13.0 Hz, ArCH_2), 2.54 (1H, m, 4-*H*), 2.84 (1H, dd, J=13.0, 3.8 Hz, ArCH_2), 3.14 (1H, s, O*H*), 3.61–3.66 (2H, m), 3.73–3.95 (5H, m), 4.07 (1H, dd, J=11.3, 4.3 Hz), 5.92 (2H, s, OCH_2O), 6.57 (1H, dd, J=7.9, 1.5 Hz, Ar*H*), 6.63 (1H, d, J=1.5 Hz, Ar*H*), 6.71 (1H, d, J=7.9 Hz, Ar*H*), 7.38–7.46 (6H, m, Ar*H*), 7.65–7.73 (4H, m, Ar*H*). 67.5 MHz ^{13}C-NMR δ_C ($CDCl_3$): 19.09, 26.73, 32.86, 50.26, 62.32, 62.77, 70.45, 86.30, 100.79, 108.19, 108.84, 121.36, 127.83, 127.90, 130.03, 130.06, 131.96, 132.17, 133.58, 135.45, 135.64, 145.89, 147.68. IR ($CHCl_3$) ν_{max}: 3852, 3436, 3075–2778, 1505, 1491, 1443, 1429, 1248, 1113, 1072, 1043, 1009, 941, 821, 704 cm^{-1}. FABMS *m/z*: 543 (M+Na$^+$, 100), 199 (17), 176 (11), 135 (44). HRMS (FAB) *m/z* (M+Na$^+$): calcd. for $C_{30}H_{36}O_6SiNa$, 543.2179; found, 543.2179.

(*2S,3S,4S*)-*3-Acetoxymethyl-2-*[(*tert-butyldiphenylsilyl*)*oxy*]*methyl-3-hydroxy-4-*(*3,4-methylenedioxyphenyl*)*methyltetrahydrofuran* (**12**). A solution of glycol **11** (0.66 g, 1.27 mmol) and 4-dimethylaminopyridine (10 mg, 0.082 mmol) in acetic anhydride (15 ml) was stirred at room temperature for 16 h. After addition of ice, the mixture was stood at room temperature for 6 h, and then ethyl acetate was added. The organic solution was separated, successively washed with saturated aqueous $NaHCO_3$ solution and brine, and dried (Na_2SO_4). Concentration followed by silica gel column chromatography (ethyl acetate/hexane = 1/2) gave acetate **12** (0.63 g, 1.12 mmol, 88%) as a colorless oil. $[\alpha]_D^{20}$ +3.62 (*c* 1.38, $CHCl_3$). 270 MHz ^{1}H-NMR δ_H ($CDCl_3$): 1.07 (9H, s, $(CH_3)_3CSi$), 2.05 (3H, s, CH_3C=O), 2.47 (1H, dd, J=11.8, 11.8 Hz, ArCH_2), 2.16–2.60 (1H, m, 4-*H*), 2.59 (1H, s, O*H*), 2.83 (1H, br.d, J=11.8 Hz, ArCH_2), 3.65 (1H, dd, J=9.7, 5.6 Hz, 5-*H*), 3.79 (2H, d, J=5.8 Hz, TBDPSOCH_2), 3.88–3.94 (1H, m, 2-*H*), 3.91 (1H, dd, J=9.7, 5.2 Hz, 5-*H*), 4.45 (2H, s, AcOCH_2), 5.92 (2H, s, OCH_2O), 6.56 (1H, dd, J=7.9, 1.8 Hz, Ar*H*), 6.61 (1H, d, J=1.8 Hz, Ar*H*), 6.71 (1H, d, J=7.9 Hz, Ar*H*), 7.36–7.42 (6H, m, Ar*H*), 7.66–7.73 (4H, m, Ar*H*). 67.5 MHz ^{13}C-NMR δ_C ($CDCl_3$): 19.06, 20.77, 26.80, 33.16, 51.50, 62.96, 64.63, 70.33, 80.18, 86.26, 100.81, 108.23, 108.87, 121.42, 127.75, 129.80, 129.82, 132.75, 132.80, 133.53, 135.55, 135.58, 145.93, 147.70, 170.84. IR ($CHCl_3$) ν_{max}: 3588, 3075–2861, 1742, 1505, 1491, 1445, 1429, 1248, 1223, 1210, 1113, 1042, 704 cm^{-1}. FABMS *m/z*: 585 (M+Na$^+$, 100), 176 (33), 135 (68). HRMS (FAB) *m/z* (M+Na$^+$): calcd. for $C_{32}H_{38}O_7SiNa$, 585.2285; found, 585.2289.

(*2S,3S,4R*)-*3-Acetoxymethyl-2-*[(*tert-butyldiphenylsilyl*)*oxy*]*methyl-3-hydroxy-4-*[(*1R/S*)-*1-hydroxy-1-*(*3,4-methylenedioxyphenyl*)*methyl*]*tetrahydrofuran* (**13**). A reaction solution of acetate **12** (0.92 g, 1.63 mmol), *N*-bromosuccinimide (0.35 g, 1.96 mmol), and benzoyl peroxide (10 mg, 0.041 mmol) in tetrachlorocarbon (400 ml) was refluxed for 30 min under nitrogen gas. After filtration, the filtrate was concentrated. The residue was applied to silica gel column chromatography (ethyl acetate/benzene = 1/9) to give a diastereomeric mixture (82/18) of benzyl alcohol **13** (0.27 g, 0.47 mmol, 29%) as a colorless oil. Acetate **13** (0.36 g, 0.64 mmol, 39%) was recovered. When based on a 61% conversion, the yield was 47%. 400 MHz ^{1}H-NMR δ_H ($CDCl_3$): 1.06 (9H, s, $(CH_3)_3CSi$), 2.00 (3H, s, CH_3C=O), 2.41 (1H, br.s, O*H*), 2.50 (1H, br.s, O*H*), 2.68 (1H, m, 4-*H*), 3.75–3.95 (3H, m, TBDPSOCH_2 and 2-*H*), 3.99 (1H, dd, J=8.8, 8.8 Hz, 5-*H*), 4.11 (1H, dd, J=8.8, 8.8 Hz, 5-*H*), 4.52 (2H, s, AcOCH_2), 4.93 (1H, br.s, ArC*H*(OH)), 5.96 (2H, s, OCH_2O), 6.73–6.86 (3H, m, Ar*H*), 7.36–7.55 (6H, m, Ar*H*), 7.63–7.80 (4H, m, Ar*H*). 100 MHz ^{13}C-NMR δ_C ($CDCl_3$): 19.07, 20.79, 26.81, 55.54, 56.29, 62.64, 63.06, 63.43, 64.62, 66.81, 67.57, 70.92, 73.53, 78.74, 79.56, 85.28, 86.40, 101.08, 106.31, 106.48, 108.21, 119.22, 119.61, 127.76, 129.80, 129.83, 132.82, 132.98, 135.60, 136.17, 137.27, 147.02, 147.87, 170.85. IR ($CHCl_3$) ν_{max}: 3625, 3075–3011, 2780–2955, 1740, 1505, 1489, 1445, 1429, 1217, 1113, 1042, 909 cm^{-1}. FABMS *m/z*: 601 (M+Na$^+$, 52), 161 (100), 73 (48). HRMS (FAB) *m/z* (M+Na$^+$): calcd. for $C_{32}H_{38}O_8SiNa$, 601.2234; found, 601.2236.

(*2S,3S,4R*)-*2-*[(*tert-Butyldiphenylsilyl*)*oxy*]*methyl-3-hydroxy-3-hydroxymethyl-4-*[(*1R/S*)-*1-hydroxy-1-*(*3,4-methylenedioxyphenyl*)*methyl*]*tetrahydrofuran* (**14**). A reaction mixture of acetate **13** (0.17 g, 0.29 mmol) and K_2CO_3 (48 mg, 0.35 mmol) in methanol (10 ml) was stirred at room temperature for 30 min before addition of H_2O and ethyl acetate. The organic solution was separated, washed with brine, and dried (Na_2SO_4). Concentration followed by silica gel column chromatography (ethyl acetate/hexane = 1/1) gave a diastereomeric mixture (82/18) of triol **14** (0.14 g, 0.26 mmol, 90%) as a colorless oil. 400 MHz ^{1}H-NMR δ_H ($CDCl_3$): 1.07 (9H, s, $(CH_3)_3CSi$), 2.67 (1H, m, 4-*H*), 2.82 (1H, s, O*H*), 3.05 (1H, br.s, O*H*), 3.67 (1H, br.s, O*H*), 3.81–3.88 (2H, m), 3.88–3.94 (2H, m), 3.92 (1H, dd, J=8.8, 8.8 Hz, 5-*H*), 4.03 (1H, br.d, J=11.7 Hz, HOCH_2), 4.14 (1H, dd, J=8.8, 8.8 Hz, 5-*H*), 5.03 (1H, d, J=3.4 Hz, ArC*H*(OH)), 5.95 (2H, s, OCH_2O), 6.75–6.79 (2H, m, Ar*H*), 6.83 (1H, d, J=1.5 Hz, Ar*H*), 7.40–7.46 (6H, m, Ar*H*), 7.65–7.71 (4H, m, Ar*H*). 100 MHz ^{13}C-NMR δ_C ($CDCl_3$): 19.13, 26.79, 27.07, 55.90, 61.78, 62.17, 62.75, 63.02, 60.13, 66.13, 68.28, 69.89, 73.33, 79.68, 80.67, 85.17, 85.73, 101.06, 101.14, 106.34, 106.54, 108.21, 118.97, 120.02, 127.32, 127.46, 127.78, 127.88, 127.91, 129.91, 130.05, 132.16, 132.36, 132.46, 132.55, 135.06, 135.49, 135.59, 135.63, 135.71, 137.31, 146.94, 147.85, 148.08. IR ($CHCl_3$) ν_{max}: 3590, 3075–2780, 1505, 1489, 1445, 1429, 1246, 1113, 1107, 1042, 781–735, 704 cm^{-1}. FABMS *m/z*: 559 (M+Na$^+$, 76), 161 (100), 135 (48), 131 (43), 73 (73). HRMS (FAB) *m/z* (M+Na$^+$): calcd. for $C_{30}H_{36}O_7SiNa$, 559.2128; found, 559.2127.

(*1S,2S,5R,6S*)-*2-*[(*tert-Butyldiphenylsilyl*)*oxy*]*methyl-1-hydroxy-6-*(*3,4-methylenedioxyphenyl*)*-3,7-dioxabicyclo*[*3.3.0*]*octane* (**15**). A reaction solution of triol **14** (0.14 g, 0.26 mmol) and *p*-toluenesulfonic acid monohydrate (5 mg, 0.026 mmol) in dichloromethane (15 ml) was stirred at room temperature for 30 min. After addition of a few drops of triethylamine, the mixture was concentrated. The residue was applied to silica gel column chromatography (ethyl acetate/hexane = 1/3) to give furofuran **15** (0.13 g, 0.25 mmol, 96%) as a colorless oil. $[\alpha]_D^{20}$ +13.15 (*c* 0.38, $CHCl_3$). 500 MHz ^{1}H-NMR δ_H ($CDCl_3$): 1.08 (9H, s, $(CH_3)_3CSi$), 2.61 (1H, ddd, J=7.6, 7.0, 1.8 Hz, 5-*H*), 3.75 (1H, dd, J=10.1, 8.4 Hz, TBDPSOCH_2), 3.84 (1H, dd, J=9.6, 1.8 Hz, 4-*H*), 3.87 (1H, dd, J=8.4, 5.8 Hz, 2-*H*), 3.89 (1H, d, J=10.4 Hz, 8-*H*), 3.98 (1H, dd, J=9.6, 7.0 Hz, 4-*H*), 4.03 (1H, dd, J=10.1, 5.8 Hz, TBDPSOCH_2), 4.15 (1H, d, J=10.4 Hz, 8-*H*), 4.37 (1H, d, J=7.6 Hz, 6-*H*), 5.94 (2H, s, OCH_2O), 6.76 (1H, d, J=7.9 Hz, Ar*H*), 6.82 (1H, dd, J=7.9, 1.8 Hz, Ar*H*), 6.93 (1H, d, J=1.8 Hz, Ar*H*), 7.39–7.45 (6H, m, Ar*H*), 7.65–7.68 (4H, m, Ar*H*). 125 MHz ^{13}C-NMR δ_C ($CDCl_3$): 19.16 ($C(CH_3)_3$), 26.91 (CH_3), 61.85 (5-*C*), 62.64 (TBDPSOCH_2), 70.74 (4-*C*), 75.98 (8-*C*), 83.87 (2-*C*), 88.52 (6-*C*), 92.55 (1-*C*), 101.07 (OCH_2O), 106.83, 108.13, 119.83, 127.93, 127.94, 130.03, 130.09, 132.58, 132.63, 134.49, 135.47, 135.53, 147.43, 148.04. IR ($CHCl_3$) ν_{max}: 3021–2860, 1505, 1489, 1445, 1429, 1252, 1113, 1076, 1042, 938 cm^{-1}. FABMS *m/z*: 541 (M+Na$^+$, 15), 517 (16), 199 (32), 161 (100), 131 (67). HRMS (FAB) *m/z* (M+Na$^+$): calcd. for $C_{30}H_{34}O_6SiNa$, 541.2023; found, 541.2023.

(*1S,2S,5R,6S*)-*1-Hydroxy-2-hydroxymethyl-6-*(*3,4-methylenedioxyphenyl*)*-3,7-dioxabicyclo*[*3.3.0*]*octane* (**16**). A solution of silyl ether **15** (0.13 g, 0.25 mmol) and tetra-*n*-butylammonium fluoride (0.35 ml, 1 M in tetrahydrofuran, 0.35 mol) in tetrahydrofuran (10 ml) was stirred at room temperature for 30 min before addition of saturated aqueous NH_4Cl solution and ethyl acetate. The organic solution was separated, washed with brine, and dried (Na_2SO_4). Concentration followed by silica gel column chromatography (hexane/ethyl acetate = 1/9 and ethyl acetate) gave diol **16** (0.06 g, 0.21 mmol, 84%) as a colorless oil. $[\alpha]_D^{20}$ +18.99 (*c* 1.0, $CHCl_3$). 400 MHz ^{1}H-NMR δ_H ($CDCl_3$): 2.04 (1H, br.s, O*H*), 2.60 (1H, m, 5-*H*), 2.75 (1H, br.s, O*H*), 3.80–3.85 (2H, m, CH_2OH), 3.89 (1H, dd, J=9.3, 2.2 Hz, 4-*H*), 3.90 (1H, d, J=10.3, 8-*H*), 3.92 (1H, dd, J=8.6, 4.3 Hz, 2-*H*), 4.02 (1H, dd, J=9.3, 6.8 Hz, 4-*H*), 4.06 (1H, d, J=10.3 Hz, 8-*H*), 4.40 (1H, d, J=7.3 Hz, 6-*H*), 5.95 (2H, s, OCH_2O), 6.77 (1H, d, J=7.8 Hz, Ar*H*), 6.82 (1H, d, J=7.8 Hz, Ar*H*), 6.91 (1H, s, Ar*H*).

100 MHz ^{13}C-NMR δ_C ($CDCl_3$): 60.42, 61.72, 69.98, 74.67, 85.33, 88.30, 91.48, 101.04, 106.73, 108.01, 120.00, 133.75, 147.36, 147.86. IR ($CHCl_3$) ν_{max}: 3596, 3026–2874, 1505, 1491, 1445, 1252, 1042, 740, 735 cm^{-1}. EIMS *m/z* (20 eV): 280 (M^+, 100), 176 (70), 151 (73). HRMS (EI) *m/z* (M^+): calcd. for $C_{14}H_{16}O_6$, 280.0968; found, 280.0957.

(1S,2R,5R,6S)-1-Hydroxy-2-iodomethyl-6-(3,4-methylenedioxyphenyl)-3,7-dioxabicyclo[3.3.0]octane (**17**). A reaction mixture of diol **16** (0.1 g, 0.36 mmol), triphenylphosphine (0.28 g, 1.07 mmol), imidazole (75 mg, 1.10 mmol), and iodine (0.18 g, 0.71 mmol) in toluene (50 ml) was heated under refluxing conditions for 50 min. After addition of H_2O, the organic solution was separated, washed with brine, and dried (Na_2SO_4). Concentration followed by silica gel column chromatography (ethyl acetate/hexane = 1/9) gave iodide **17** (0.1 g, 0.26 mmol, 72%) as colorless crystals, mp 142–145°C. $[\alpha]_D^{20}$ +37.50 (*c* 0.4, $CHCl_3$). 400 MHz ^{1}H-NMR δ_H ($CDCl_3$): 2.43 (1H, br.s, O*H*), 2.69 (1H, m, 5-*H*), 3.29 (2H, d, *J* = 7.3 Hz, CH_2I), 3.80 (1H, d, *J* = 10.3 Hz, 8-*H*), 3.85 (1H, dd, *J* = 9.8, 1.8 Hz, 4-*H*), 3.97 (1H, dd, *J* = 7.3, 7.3 Hz, 2-*H*), 4.00 (1H, dd, *J* = 9.8, 6.8 Hz, 4-*H*), 4.11 (1H, d, *J* = 10.3 Hz, 8-*H*), 4.40 (1H, d, *J* = 7.3 Hz, 6-*H*), 5.95 (2H, s, OCH_2O), 6.77 (1H, d, *J* = 8.3 Hz, Ar*H*), 6.81 (1H, dd, *J* = 8.3, 1.5 Hz, Ar*H*), 6.90 (1H, d, *J* = 1.5 Hz, Ar*H*). 100 MHz ^{13}C-NMR δ_C ($CDCl_3$): −0.98, 63.13, 69.48, 74.74, 85.26, 88.44, 92.29, 101.14, 106.64, 108.17, 119.84, 133.64, 147.54, 148.05. IR ($CHCl_3$) ν_{max}: 3592, 3022–3011, 2874, 2342, 1505, 1491, 1447, 1252, 1221, 1211, 1042, 785, 731 cm^{-1}. FABMS *m/z*: 413 (M + Na^+, 45), 176 (100), 136 (65), 69 (74). HRMS (FAB) *m/z* (M + Na^+): calcd. for $C_{14}H_{15}O_5INa$, 412.9862; found, 412.9863.

(2S,3R,4S)-4-Hydroxy-3-hydroxymethyl-2-(3,4-methylenedioxyphenyl)-4-vinyltetrahydrofuran (**18**). A reaction mixture of iodomethylfurofuran **17** (60 mg, 0.15 mmol) and zinc (38 mg, 0.58 mmol) in ethanol (20 ml) was heated under refluxing conditions for 2 h. After filtration, the filtrate was concentrated, and the residue was dissolved in H_2O and ethyl acetate. The organic solution was separated, washed with brine, and dried (Na_2SO_4). Concentration followed by silica gel TLC (ethyl acetate/hexane = 1/1) gave diol **18** (36 mg, 0.14 mmol, 93%) as colorless crystals, mp 92–93°C. $[\alpha]_D^{20}$ −45.31 (*c* 0.64, $CHCl_3$). 400 MHz ^{1}H-NMR δ_H ($CDCl_3$): 2.40 (1H, m, 3-*H*), 2.48 (1H, br.s, O*H*), 3.66 (1H, dd, *J* = 10.8, 5.4 Hz, CH_2OH), 3.75 (1H, dd, *J* = 10.8, 7.8 Hz, CH_2OH), 3.90 (1H, d, *J* = 9.2 Hz, 5-*H*), 3.98 (1H, d, *J* = 9.2 Hz, 5-*H*), 4.59 (1H, d, *J* = 8.3 Hz, 2-*H*), 5.36 (1H, d, *J* = 10.7 Hz, C=CH_2), 5.53 (1H, d, *J* = 17.6 Hz, C=CH_2), 5.95 (2H, s, OCH_2O), 6.17 (1H, dd, *J* = 17.6, 10.7 Hz, C*H*=CH_2), 6.76 (1H, d, *J* = 7.8 Hz, Ar*H*), 6.82 (1H, d, *J* = 7.8 Hz, Ar*H*), 6.97 (1H, s, Ar*H*). ^{13}C-NMR δ_C ($CDCl_3$): 60.34, 60.75, 77.89, 81.74, 82.84, 101.02, 106.73, 108.04, 115.31, 119.78, 135.30, 137.37, 147.28, 147.93. IR ($CHCl_3$) ν_{max}: 3632, 3590, 3092–3013, 2884, 1505, 1489, 1447, 1252, 1042, 936 cm^{-1}. EIMS (*m/z*, 20 eV): 264 (M^+, 100), 215 (59), 151 (98), 135 (73). HRMS (EI) *m/z* (M^+): calcd. for $C_{14}H_{16}O_5$, 264.0995; found, 264.0989.

(2S,3R,4S)-3-Benzoyloxymethyl-4-hydroxy-2-(3,4-methylenedioxyphenyl)-4-vinyltetrahydrofuran (**19**). To an ice-cooled solution of diol **18** (33 mg, 0.12 mmol) and triethylamine (25 µl, 0.18 mmol) in dichloromethane (10 ml) was added benzoyl chloride (21 µl, 0.18 mmol). The reaction mixture was stirred at room temperature for 1 h. After addition of saturated aqueous $NaHCO_3$ solution, the organic solution was separated, washed with brine, and dried (Na_2SO_4). Concentration followed by silica gel TLC (ethyl acetate/benzene = 1/4) gave benzoate **19** (40 mg, 0.11 mmol, 92%) as a colorless oil. $[\alpha]_D^{20}$ +16.66 (*c* 0.72, $CHCl_3$). 400 MHz ^{1}H-NMR δ_H ($CDCl_3$): 2.67 (1H, m, 3-*H*), 3.96 (1H, d, *J* = 9.5 Hz, 5-*H*), 4.05 (1H, d, *J* = 9.5 Hz, 5-*H*), 4.43 (1H, dd, *J* = 11.5, 6.1 Hz, CH_2OBz), 4.45 (1H, dd, *J* = 11.5, 6.6 Hz, CH_2OBz), 4.73 (1H, d, *J* = 7.8 Hz, 2-*H*), 5.34 (1H, dd, *J* = 10.7, 1.0 Hz, C=CH_2), 5.53 (1H, d, *J* = 17.1, 1.0 Hz, C=CH_2), 5.92 (1H, d, *J* = 3.9 Hz, OCH_2O), 5.93 (1H, d, *J* = 3.9 Hz, OCH_2O), 6.10 (1H, dd, *J* = 17.1, 10.7 Hz, C*H*=CH_2), 6.74 (1H, d, *J* = 8.3 Hz, Ar*H*), 6.88 (1H, dd, *J* = 8.3, 1.5 Hz, Ar*H*), 7.02 (1H, d, *J* = 1.5 Hz, Ar*H*), 7.38–7.42 (3H, m, Ar*H*), 7.85–7.88 (2H, m, Ar*H*). ^{13}C-NMR δ_C ($CDCl_3$): 57.97, 63.06, 78.41, 81.73, 84.36, 101.03, 107.02, 108.04, 115.89, 120.25, 128.35, 129.51, 129.60, 133.12, 134.82, 136.54, 147.41, 147.98, 166.25. IR ($CHCl_3$) ν_{max}: 3592, 3031–2955, 2894, 1719, 1505, 1489, 1449, 1275, 1250, 1119, 1042, 938 cm^{-1}. EIMS (*m/z*, 20 eV): 368 (M^+, 23), 176 (100), 149 (41), 105 (49). HRMS (EI) *m/z* (M^+): calcd. for $C_{21}H_{20}O_6$, 368.1258; found, 368.1264.

(2S,3R,4S)-3-Benzoyloxymethyl-4-[(triethylsilyl)oxy]-2-(3,4-methylenedioxyphenyl)-4-vinyltetrahydrofuran (**20**). To a solution of alcohol **19** (36 mg, 0.098 mmol) and 2,6-lutidine (0.1 ml, 0.86 mmol) in dichloromethane (10 ml) was added triethylsilyl trifluoromethanesulfonate (0.1 ml, 0.44 mmol). The resulting reaction mixture was stirred at room temperature for 30 min before addition of saturated aqueous $NaHCO_3$ solution. The organic solution was separated, washed with brine, and dried (Na_2SO_4). Concentration followed by silica gel TLC (ethyl acetate/hexane = 1/4) gave silyl ether **20** (39 mg, 0.081 mmol, 83%) as a colorless oil. $[\alpha]_D^{20}$ +7.69 (*c* 0.78, $CHCl_3$). 400 MHz ^{1}H-NMR δ_H ($CDCl_3$): 0.62 (6H, q, *J* = 7.8 Hz, $(CH_3CH_2)_3Si$), 0.96 (9H, t, *J* = 7.8 Hz, $(CH_3CH_2)_3Si$), 1.87 (1H, ddd, *J* = 9.3, 7.6, 5.6 Hz, 3-*H*), 4.06 (1H, d, *J* = 8.5 Hz, 5-*H*), 4.09 (1H, d, *J* = 8.5 Hz, 5-*H*), 4.28 (1H, dd, *J* = 11.5, 7.6 Hz, CH_2OBz), 4.40 (1H, dd, *J* = 11.5, 5.6 Hz, CH_2OBz), 4.59 (1H, d, *J* = 9.3 Hz, 2-*H*), 5.30 (1H, d, *J* = 10.7 Hz, CH=CH_2), 5.42 (1H, d, *J* = 17.6 Hz, CH=CH_2), 5.90 (1H, d, *J* = 9.3 Hz, OCH_2O), 5.91 (1H, d, *J* = 9.3 Hz, OCH_2O), 6.08 (1H, dd, *J* = 17.6, 10.7 Hz, C*H*=CH_2), 6.71 (1H, d, *J* = 7.8 Hz, Ar*H*), 6.82 (1H, dd, *J* = 7.8, 2.0 Hz, Ar*H*), 6.94 (1H, d, *J* = 2.0 Hz, Ar*H*), 7.33–7.34 (2H, m, Ar*H*), 7.49–7.53 (1H, m, Ar*H*), 7.72–7.75 (2H, m, Ar*H*). 100 Hz ^{13}C-NMR δ_C ($CDCl_3$): 6.36, 6.93, 58.17, 62.56, 76.52, 82.56, 83.51, 100.97, 107.17, 108.01, 115.32, 120.50, 128.11, 129.55, 129.83, 132.85, 135.26, 138.35, 147.29, 147.86, 166.20. IR ($CHCl_3$) ν_{max}: 3020–2878, 1717, 1505, 1489, 1451, 1275, 1250, 1213, 1124, 1042, 758 cm^{-1}. FABMS *m/z*: 505 (M + Na^+, 96), 171 (77), 105 (100), 87 (75). HRMS (FAB) *m/z* (M + Na^+): calcd. for $C_{27}H_{34}O_6SiNa$, 505.2023; found, 505.2019.

(2S,3R,4S)-4-[(Triethylsilyl)oxy]-3-hydroxymethyl-2-(3,4-methylenedioxyphenyl)-4-vinyltetrahydrofuran (**21**). A reaction mixture of benzoate **20** (37 mg, 0.077 mmol) and K_2CO_3 (12 mg, 0.087 mmol) in methanol (8 ml) was stirred at room temperature for 24 h. Ethyl acetate and H_2O were then added. The organic solution was separated, washed with brine, and dried (Na_2SO_4). Concentration followed by silica gel TLC (ethyl acetate/hexane = 1/3) gave alcohol **21** (29 mg, 0.077 mmol, 100%) as a colorless oil. $[\alpha]_D^{20}$ −20.30 (*c* 1.13, $CHCl_3$). 400 MHz ^{1}H-NMR δ_H ($CDCl_3$): 0.62 (6H, q, *J* = 7.8 Hz, $(CH_3CH_2)_3Si$), 0.97 (9H, t, *J* = 7.8 Hz, $(CH_3CH_2)_3Si$), 1.97 (1H, br.s, O*H*), 2.47 (1H, ddd, *J* = 9.8, 8.3, 4.4 Hz, 3-*H*), 3.59 (1H, br.dd, *J* = 10.4, 4.4 Hz, CH_2OH), 3.74 (1H, dd, *J* = 10.4, 8.3 Hz, CH_2OH), 4.01 (1H, d, *J* = 8.3 Hz, 5-*H*), 4.03 (1H, d, *J* = 8.3 Hz, 5-*H*), 4.43 (1H, d, *J* = 9.8 Hz, 2-*H*), 5.34 (1H, dd, *J* = 10.7, 1.0 Hz, CH=CH_2), 5.19 (1H, dd, *J* = 17.5, 1.0 Hz, CH=CH_2), 5.95 (2H, s, OCH_2O), 6.17 (1H, dd, *J* = 17.5, 10.7 Hz, C*H*=CH_2), 6.76 (2H, s, Ar*H*), 6.90 (1H, s, Ar*H*). 100 MHz ^{13}C-NMR δ_C ($CDCl_3$): 6.31, 6.89, 60.39, 60.43, 75.94, 81.29, 83.31, 101.04, 106.63, 108.09, 115.37, 119.81, 135.37, 138.56, 147.34, 147.98. IR ($CHCl_3$) ν_{max}: 3520, 3027–2878, 1611, 1505, 1447, 1250, 1402, 729 cm^{-1}. FABMS *m/z*: 401 (M + Na^+, 47), 171 (100), 87 (61). HRMS (FAB) *m/z* (M + Na^+): calcd. for $C_{20}H_{30}O_5SiNa$, 401.1760; found, 401.1759.

(1S,2S,5R,6S)-1,2-Dihydroxy-6-(3,4-methylenedioxyphenyl)-3,7-dioxabicyclo[3.3.0]octane ((+)-*1-hydroxysamin*) (**1**). A reaction solution of olefin **21** (15 mg, 0.040 mmol), osmium tetroxide (2% in H_2O, 0.25 ml), and *N*-methylmorpholine *N*-oxide (97%, 6 mg, 0.050 mmol) in acetone (2.8 ml), *tert*-butanol (0.7 ml), and H_2O (0.7 ml) was stirred at room temperature for 16 h under nitrogen gas in the dark. After addition of $NaHSO_3$ (1 g) in H_2O (5 ml), the mixture was filtered and the filtrate was concentrated. The resulting residue was dissolved in H_2O and ethyl acetate, before the ethyl acetate solution was separated.

To the ethyl acetate solution (10 ml) was added sodium periodate (0.15 g, 0.70 mmol) in H_2O (10 ml). The resulting mixture was vigorously stirred at room temperature for 3 h. The ethyl acetate solution was separated, washed with brine, and dried (Na_2SO_4).

After concentration of the ethyl acetate solution, the residue was dissolved in tetrahydrofuran (5 ml). To this solution was added tetra-*n*-butylammonium fluoride (50 µl, 1 M in tetrahydrofuran, 0.050 mmol). After stirring at room temperature for 30 min, saturated aqueous NH_4Cl solution and ethyl acetate were added. The organic solution was separated, washed with brine, and dried (Na_2SO_4). Concentration followed by silica gel TLC (ethyl acetate/hexane = 1/1) gave (+)-1-hydroxysamin (**1**) (4 mg, 0.015 mmol, 38%) as a colorless oil. $[\alpha]_D^{20}$ +74.76 (*c* 0.21, $CHCl_3$). 400 MHz ^{1}H-NMR δ_H ($CDCl_3$): 2.59 (1H, m, 5-*H*), 3.16 (1H, br.s, O*H*), 3.27 (1H, br.s, O*H*), 3.72 (1H, d, *J* = 9.8 Hz, 8β-*H*), 3.77 (1H, dd, *J* = 9.3, 2.0 Hz, 4β-*H*), 4.27 (1H, d, *J* = 9.8 Hz, 8α-*H*), 4.31 (1H, dd, *J* = 9.3, 6.8 Hz, 4α-*H*), 4.48 (1H, d, *J* = 6.8 Hz, 6-*H*), 5.22 (1H, s, 2-*H*), 5.95 (2H, s, OCH_2O), 6.77 (1H, d, *J* = 7.8 Hz, Ar*H*), 6.84 (1H, dd, *J* = 7.8, 1.5 Hz, Ar*H*), 6.96 (1H, d, *J* = 1.5 Hz, Ar*H*). 100 MHz ^{13}C-NMR δ_C ($CDCl_3$): 59.55 (5-*C*), 68.91 (4-*C*), 77.78 (8-*C*), 88.99 (6-*C*), 92.43 (1-*C*), 97.88 (2-*C*), 101.11 (OCH_2O), 106.79, 108.14, 119.83, 134.28, 147.45, 148.04. NOESY 2-H/8β-H, 6-H/4β-H and 8β-H. IR ($CHCl_3$) ν_{max}: 3715,

3604, 3027–2857, 1505, 1491, 1447, 1252, 1042 cm^{-1}. EIMS (m/z, 20 eV): 266 (M^+, 100), 176 (40), 151 (97). HRMS (EI) m/z (M^+): calcd. for $C_{13}H_{14}O_6$, 266.0789; found, 266.0783.

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