Stereoselective Synthesis of the Bis-tetrahydrofuran Fragment (C-1–C-9) of Asteltoxin

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An 18-step synthesis of the chiral bis-tetrahydrofuran fragment **2** of asteltoxin **1** is described. This synthesis proceeds under practically complete substrate stereocontrol, starting with compound **5a**. From there the chirality centers of **2** are generated with >95% ds each by using a sequence of Claisen rearrangement, chelate Cram Grignard addition, and osmylation reactions. The current synthesis affords **2** in racemic form. The key intermediate **8** was also synthesized with ee > 96%, which should provide access to **2** in both enantiomeric forms.

Introduction

Asteltoxin (**1**), a metabolite of *Aspergillus Stellatus* Curzi,[1] is an ATPase inhibitor with a toxicity toward mammals comparable to that of aflatoxin B_1.[2] For about a decade **1** has been an attractive synthetic target particularly due to the complex structure of its chiral bis-tetrahydrofuran segment which, in form of the triol **2**, is generated from **1** by ozonolysis and reductive workup.[3] Triol **2** houses an extreme density of functional groups and chirality centers: six out of its seven skeletal carbons (C-3–C-9) are chiral and/or carry functional groups. So far, two syntheses of **1** have been reported, one of which leads to racemic[4] or partially racemic[5] and one to optically pure material.[6] The chiral fragment **2**, on the other hand, has been prepared in the form of the racemate[3] and of the (+)-enantiomer.[7] It is unclear whether the toxicity of **1** stems primarily from the chiral or the achiral part of the molecule; therefore, the synthesis of **2** is attractive also from the physiological point of view.

We report a totally stereocontrolled synthesis of **2** which rests on the principles of acyclic stereoselection.[8] The retrosynthetic analysis (Scheme 1) shows that the diol unit at C-3/4 in **I** may be considered as equivalent to a double bond (= **II**); this triggers a retro-Claisen type rearrangement (**III** ⇒ **IV**) generating the quaternary center at C-6[9] plus a carboxyl group which is suitable for the one carbon chain elongation (**III** → **II**) to introduce C-9. In this way the bis-allylic alcohol (*R*)-**IV** emerges as a key intermediate.

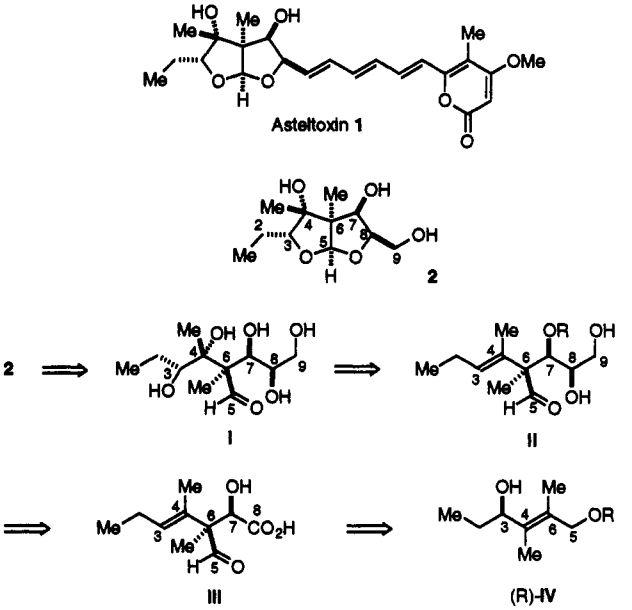
Results and Discussion

The starting material of our synthesis was the symmetrical diol **3a** (Scheme 2), easily available from 2,3-dimethyl-1,3-butadiene.[10] Monoprotection of **3a** furnished the derivatives **3a–d** which were converted into the alcohols **5a-c** via the corresponding aldehydes **4a–c**. The benzoate **4b** afforded only very low yields in the Grignard addition; $EtTi(OiPr)_3$ did not lead to a satisfactory result either (21%), contrary to literature reports[11] (Table 1).

Table 1. Yields of Ethyl Anion Addition to 5a–c

4	Et-Met	yield of 5 (%)
a	EtMgBr	80
b	$EtTi(OiPr)_3$	21
b	EtMgBr	9
c	EtMgBr	80

Scheme 1. Retrosynthetic Considerations



For obtaining enantiomerically enriched alcohol **5** there are two options: either to perform the organometallic addition **4** → **5** under chiral catalysis or to resolve racemic **5** into the enantiomers. In the latter case Sharpless' epoxidation[12] appeared to be the method of choice. However, it turned out that the efficiency of this protocol was highly dependent on the protective group R. Thus, **5a** was unstable under the conditions, and **5c** gave relatively low enantiomeric excesses. In the case of **5b** the ee values strongly varied with the stoichiometric ratio of *t*BuOOH.

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(1) Kruger, G. J.; Steyn, P. S.; Vleggaar, R.; Rabie, C. J. *J. Chem. Soc. Chem. Commun.* **1979**, 441.
(2) Vleggaar, R. *Pure Appl. Chem.* **1986**, *58*, 239.
(3) Schreiber, S. L.; Satake, K. *J. Am. Chem. Soc.* **1983**, *105*, 6723.
(4) Schreiber, S. L.; Satake, K. *J. Am. Chem. Soc.* **1984**, *106*, 4186.
(5) Schreiber, S. L.; Satake, K. *Tetrahedron Lett.* **1986**, *27*, 2575.
(6) Tadano, K. I.; Yamada, H.; Idogaki, Y.; Ogawa, S.; Suami, T. *Tetrahedron Lett.* **1988**, *29*, 655; *Tetrahedron* **1990**, *46*, 2353.
(7) Yamamura, S.; Nishiyama, S.; Kanai, H.; Tadano, K. I. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 1322.
(8) Bartlett, P. A. *Tetrahedron* **1980**, *36*, 1.
(9) The synthesis in refs 6 and 7 also used a Claisen rearrangement for this purpose, however, either on a cyclic substrate[8] or on an acyclic one without any stereocontrol.[7]
(10) Sweeting, O. J.; Johnson, J. R. *J. Am. Chem. Soc.* **1946**, *68*, 1057.
(11) Reetz, M. T. *Top. Curr. Chem.* **1982**, 106, 1; *Chem. Ber.* **1985**, *118*, 1421.
(12) Sharpless, K. B.; Gao, Y.; Hanson, R. M.; Klunder, J. M.; Ko, S. Y.; Masamune, H. *J. Am. Chem. Soc.* **1987**, *109*, 5765.

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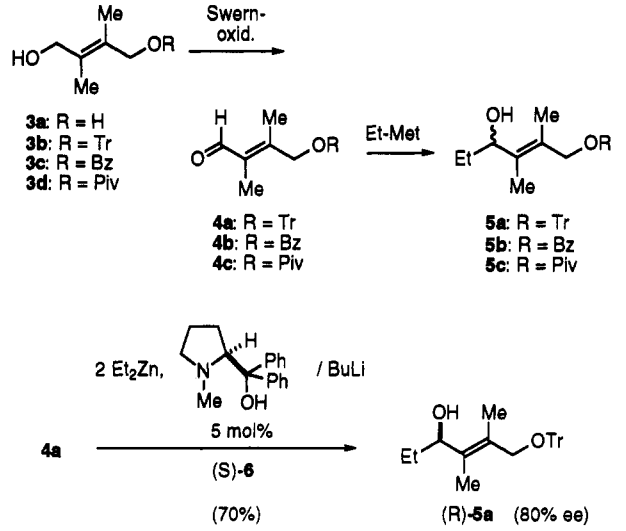
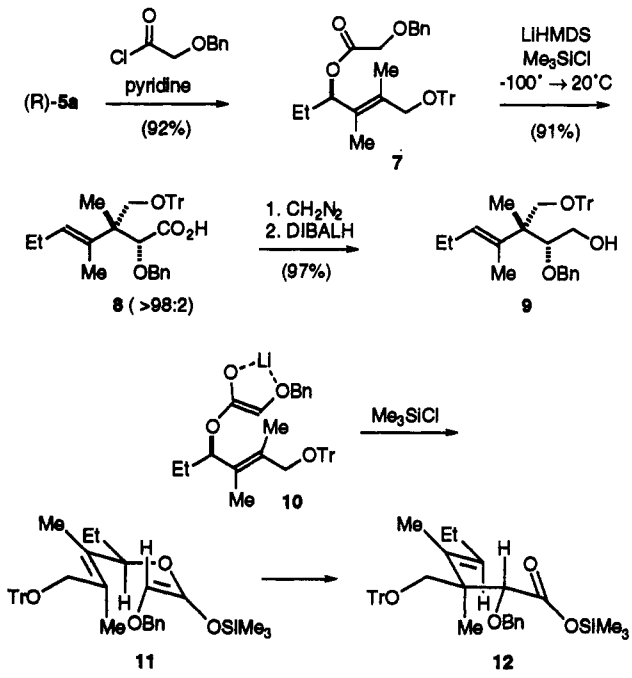
Scheme 2



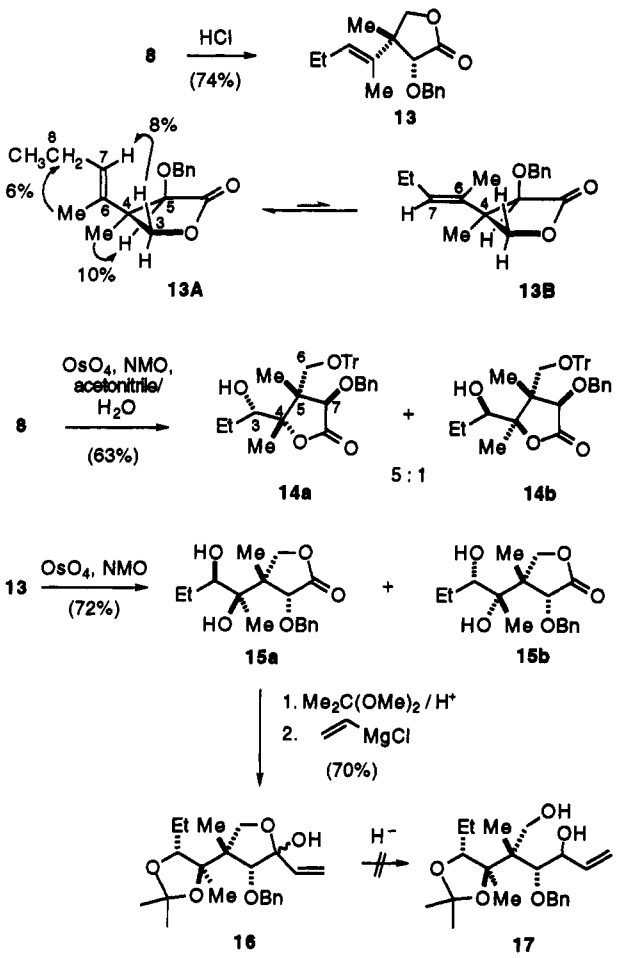
Scheme 3



Under optimized conditions (0.8 mol equiv of tBuOOH) (*R*)-**5b** could be obtained in 32% yield, based on racemate, with an ee of 97%. However, this result was not satisfactory in view of the poor accessibility of **5b** from **3c** (vide supra).

Therefore, we tried the second alternative and added diethylzinc to **4a** under the conditions described by Soai.[13] Catalyst (*S*)-**6** furnished (*R*)-**5a** with 80% ee (determined *via* the Mosher ester)[14] which we considered as sufficient to carry on with the synthesis. (*R*)-**5a** was submitted to a Claisen-type rearrangement (Scheme 3) according to the version by Burke and Kallmerten.[15] Acylation of **5a** with (benzyloxy)acetyl chloride led to the ester **7** which was smoothly rearranged to **8** as a single diastereomer. By recrystallization the optical purity of **8** was raised to >98% ee, as shown by 500-MHz ^{1}H-NMR spectroscopy of the corresponding alcohol **9** using a chiral shift reagent (Eutfc$_3$). The stereoselectivity of the Claisen rearrangement remarkably hinged on the trityl protective group. With TBDPS instead of Tr both yield (83%) and stereocontrol (86:14 mixture of epimers) were much lower. The stereochemical course of the rearrangement can be interpreted in terms of a chelated enolate **10** with defined (*E*)-geometry of the double bond. After O-silylation to **11** the rearrangement proceeds via the familiar cyclohexane-type chair transition state to form silyl ester **12** which is hydrolyzed to **8** on aqueous workup.

Scheme 4

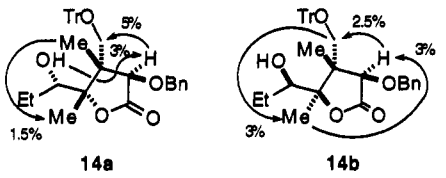


To assign the relative configuration at the newly formed quaternary center **8** was cyclized to lactone **13** and analyzed by DNOE (Scheme 4). The strong interaction between 4-Me and H-5 confirms the configuration shown, and the high DNOE between H-7 and H-3α indicates that the preferred conformation is **13A**. Rotamer **13B** is obviously disfavored by severe nonbonding repulsions between the 6-Me and the 5-OBn groups.

The availability of the optically pure key intermediate **8** should in all likeliness also provide access to optically pure **2** in form of either enantiomer,[16] as no racemization can henceforth occur of the quaternary chiral center at C-4. For the sake of convenience we carried on with racemic material and studied the osmylation of the trisubstituted double bond. This reaction was performed with both the acid **8** and the lactone **13**. Under standard

(13) Soai, K.; Ookawa, A.; Kaba, T.; Ogawa, K. *J. Am. Chem. Soc.* **1987**, *109*, 7111.
(14) Dale, J. A.; Mosher, H. S. *J. Am. Chem. Soc.* **1973**, *95*, 512.
(15) (a) Burke, S. D.; Fobare; W. F.; Pacofsky, G. J. *J. Org. Chem.* **1983**, *48*, 5221. (b) Kallmerten, J.; Gould, Th. J. *Tetrahedron Lett.* **1983**, *24*, 5177.

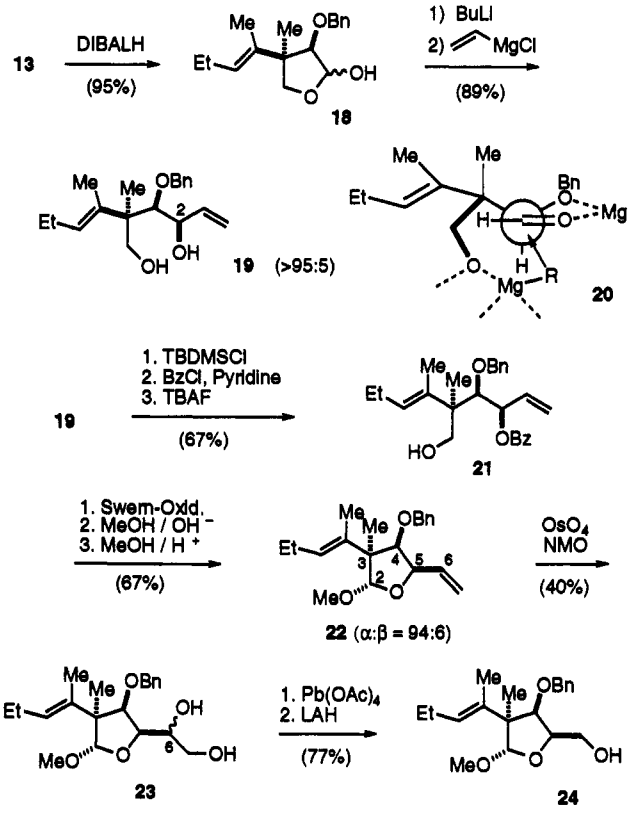
(16) Both (*R*)- and (*S*)-**7** are readily available from the corresponding prolinol derivates which are commercially available from Aldrich Co.



14a 14b

Figure 1. DNOE for **14a/b**.

Scheme 5

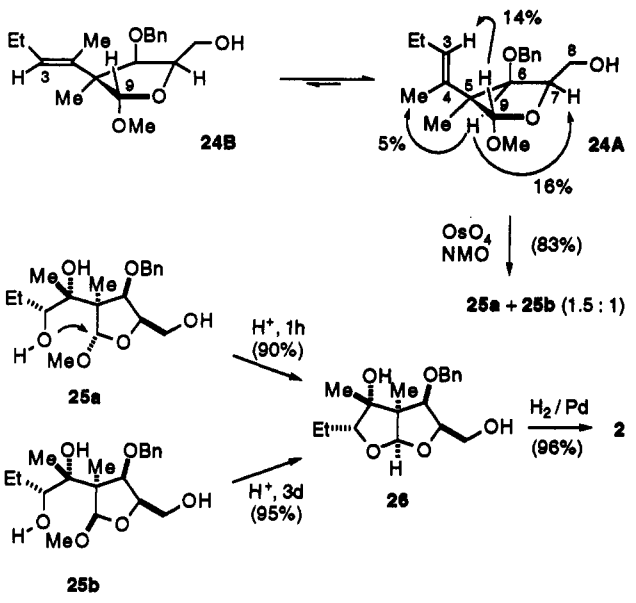


conditions 8 gave a 5:1 mixture of the lactones **14a/b**. The relative configurations of **14a/b** were again assigned by DNOE (Figure 1), with the result that the major stereoisomer (**14a**) was the one with the "wrong" configurations at C-3 and C-4.

On the other hand, osmylation of lactone **13** furnished **15a/b** as a 5:1-mixture. The stereochemistry of these isomers could not be fully clarified; the configurations in **15a/b** were tentatively assigned on the basis of the conformational arguments described above. It was assumed that the major stereoisomer (**15a**) is the one generated by an osmium tetraoxide attack on the less hindered face of **13A**. For C-1 chain elongation vinylmagnesium chloride was added to **15a** after acetonide protection of the 3,4-diol. Hemiketal **16** was obtained as a mixture of anomers, but any attempt to reduce **16** to diol **17** failed.

We therefore decided to reverse the order of the steps (Scheme 5). Lactone **13** was reduced with DIBALH to give the hemiketal **18** as an anomeric mixture. Addition of vinylmagnesium chloride only led to deprotonation of the unprotected hydroxyl function, and no addition to the latent aldehyde was observed. However, after deprotonation of **18** with 1 equiv of *n*-butyllithium the addition of vinylmagnesium chloride did occur and diol **19** was obtained as a single diastereomer. The stereochemical outcome of the reaction indicates a chelate Cram intermediate[17] **20** in which the primary alkoxide group serves as a ligand for the organometal.

Scheme 6



The next five steps were designed to convert **19** into the cyclic ketal **22**. Selective monobenzoylation of the secondary hydroxyl function was accomplished via three steps to form **21**, which was then submitted to a Swern oxidation of the primary hydroxyl group and debenzoylation of the secondary one. The hydroxy aldehyde spontaneously cyclized to the lactol which was ketalized to give **22** as a 94:6 mixture of the α and β anomers. Next the 5-vinyl group had to be degraded to a CH_2OH appendage without affecting the trisubstituted olefin in 3-position. To our surprise **22** could be osmylated to diol **23** under carefully controlled conditions in 40% yield as a 10:1 mixture of the C-6-epimers. Glycol cleavage with lead tetraacetate immediately followed by reduction of the aldehyde with lithiumaluminium hydride furnished alcohol **24** with less than 5% epimerization at C-5 at the stage of the aldehyde.

DNOE analysis of **24** revealed a strong interaction between H-3 and H-9. This indicates a conformational equilibrium between **24A** (major conformer) and **24B** (minor conformer) quite in analogy to our earlier results with the lactones **13a/b**. If **24A** also acts as the reactive conformation in the osmylation, the attack may be expected to occur from the 3-*re*-4-*si* face, due to the shielding effect of the benzyl group. In fact, diol **25** was formed with >95:5 diastereoselectivity as an 1.3:1 mixture of the anomers **25a/b**, which means that extensive anomerization occurs under the osmylation conditions (Scheme 6).

Both anomers were treated separately with acid to close the second tetrahydrofuran ring of **26** by transketalization. Anomer **25a** reacted much faster than **25b**, which indicates that the cyclization favors a S_N2-type mechanism. Anomerization was not observed under the conditions. The relative configuration of **26** was confirmed by DNOE

(17) (a) Cram, D. J.; Abd Elhafez, F. A. *J. Am. Chem. Soc.* **1952**, *74*, 5828. (b) Tatsuta, K.; Takahaski, H.; Amemiya, Y.; Kinoshita, M. *J. Am. Chem. Soc.* **1983**, *105*, 4096. (c) Reviews: Reetz, M. T. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 556. (d) Eliel, E. L. In *Asymmetric Synthesis*, Morrison, J. D., Ed.; Academic Press: New York, 1983; Vol. 2, p 125. (e) Mulzer, J.; Altenbach, H.-J.; Braun, M.; Krohn, K.; Reissig, H.-U. *Organic Synthesis Highlights*, VCH: Weinheim, 1991, p 3 and references cited therein.

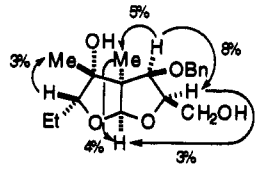


Figure 2. DNOE for **26**.

(Figure 2). Debenzylation of **26** furnished **2**, whose 500-MHz ^{1}H-NMR spectrum was identical with the 400-MHz spectrum described by Yamamura.[7]

Conclusion

In conclusion we have developed an 18-step synthesis (total yield 3%) of the racemic C-1–C-9 fragment of asteltoxin **2** from diol **3a**, which in principle is also applicable to both enantiomers of **2**. The synthesis proceeds under practically complete substrate control; i.e., the first stereocenter generated in the sequence controls all the others to follow. From **2** a number of *O*-acyl and *O*-alkyl derivatives can be made, which, together with **2**, will be tested with respect to their physiological properties.

Experimental Section

General Methods. NMR spectra were measured on a Bruker AC 250, WH 270, or AMX 500 spectrometer with TMS as an internal standard using and recorded on a ppm scale. For multiplets (m) the location of the center is given. The assignments of the ^{1}H-NMR signals in compounds **13**, **14**, **24**, and **26** were made on the basis of COSY and/or spin–spin decoupling experiments. NOE spectra were measured with the automatic Bruker program NOEMULT. Preirradiation time was 4.8 s, irradiation energy 7×10^{-7} W. Before measuring nitrogen was bubbled through the solution for 5 min to remove most of the oxygen. The enhancements were related to the integral difference of the signal in the reference spectrum and the irradiated signal. IR spectra were measured in cm^{-1} units on a Perkin-Elmer IR 580 B infrared spectrometer or a Nicolet FTIR-Interferometer system 5 SXC using KBr pellets. Mass spectra were measured on a Varian MAT 112S (CI) and a Varian MAT 711 (EI) spectrometer. The elemental analyses were determinated on a Perkin-Elmer 2400 CHN-Elementar analyzer. Optical rotations were obtained in $CHCl_3$, with a Perkin-Elmer 241 polarimeter at 589 nm and 20 °C. Melting points are corrected. HPLC seperations were performed on Nucleosil 50 with particle sizes of 5 μm (analytical) and 7 μm (preparative), with RI and UV detection. Preparative column chromatography was performed on silica gel Merck 60 (0.063–0.04 nm) using 30–50 g of silica gel per 1 g of substance. All reactions were carried out under an argon atmosphere in purified solvents with magnetic stirring and followed by TLC control (TLC plates Merck 5554).

1-[(Triphenylmethyl)oxy]-2,3-dimethyl-2(*E*)-buten-1-ol (3b). To a stirred solution of **3a**[10] (12.19 g, 105 mmol) in pyridine (1050 mL) was added trityl chloride (32.2 g, 116 mmol) in pyridine (120 mL) dropwise at 0 °C. After 20 h at room temperature the mixture was poured into ice–water (2 L) and extracted with ether (5 × 200 mL). The organic phase was dried ($MgSO_4$), concentrated under reduced pressure, and purified by chromatography (hexane/ethyl acetate (1:1)) to give **3b** (18.9 g, 50%) as colorless crystals: mp 96–98 °C; ^{1}H-NMR (250 MHz, $CDCl_3$) δ 1.2 (s, 1 H); 1.58 (s, 3 H), 1.88 (s, 3 H), 3.70 (s, 2 H), 4.12 (s, 2 H), 7.28 (m, 9 H), 7.46 (m, 6 H); ^{13}C-NMR (62.9 MHz, CD_2Cl_2) δ 16.05, 16.34, 63.92, 65.66, 86.92, 127.35, 128.18, 128.42, 129.11, 130.01, 131.84, 144.84; IR 3300, 1445, 1050, 700 cm^{-1}. Anal. Calcd for $C_{25}H_{26}O_2$: C, 83.76; H, 7.31. Found: C, 83.53; H, 7.27.

1-(Triphenylmethoxy)-2,3-dimethyl-2(*E*)-hexen-4-ol (5a). To oxalyl chloride (5.91 g, 46.9 mmol) in dichloromethane (120 mL) at –60 °C was added dimethyl sulfoxide (7.95 g, 102 mmol) in dichloromethane (20 mL) dropwise under stirring. After 10 min **3b** (15.25 g, 42.6 mmol) in dichloromethane (50 mL) was added followed by diisopropylethylamine (28.4 g, 220 mmol). After 15 min the temperature was raised to 0 °C over ca. 1 h. Water (200 mL) was added, and the mixture was extracted with ether (3 × 100 mL) after separation of the dichloromethane phase. The combined organic phases were washed with 2 N HCl (50 mL), saturated aqueous sodium bicarbonate (100 mL), and brine (100 mL), dried ($MgSO_4$), concentrated under reduced pressure, and used for the organometallic addition without further purification.

Racemic 5a. The crude aldehyde in ether (400 mL) was added dropwise to ethylmagnesium bromide (150 mL) in THF at –15 °C. After 14 h at room temperature the mixture was quenched with water (200 mL). The organic layer was separated, washed with brine (100 mL), dried ($MgSO_4$), and evaporated under reduced pressure to give racemic **5a** (15.0 g, 82% based on **3b**).

(*R*)-5a. Alcohol **3b** (10.0 g, 28 mmol) was oxidized to the aldehyde as described above and dissolved in cyclohexane (50 mL). Chiral auxiliary (*R*)-(–)-DPMPM[13] (93 mg, 2.5 mol %) in cyclohexane (10 mL) was treated dropwise with *n*-butyllithium (1.6 M in hexane, 0.21 mL) and stirred for 20 min at room temperature. To this solution was added the aldehyde, and stirring was continued for an additional 20 min. The solution was cooled to 0 °C, and diethylzinc (1.0 M in hexane, 30 mL) was added. After 24 h the mixture was quenched with 2 N HCl (30 mL) and neutralized with solid sodium bicarbonate. The organic phase was separated, washed with water (100 mL), dried ($MgSO_4$), and evaporated under reduced pressure. Chromatography (hexane/ethyl acetate (5:1)) furnished (*R*)-**5a** (10.0 g, 73%), $[\alpha]^{20}_D$ –11.36° (*c* 1.003). NMR and IR spectra were identical with those of **5a**. The optical purity was determined by converting 60 mg of the alcohol into the Mosher ester.[15] HPLC analysis showed two base-line separated peaks of relative intensity 10.9:89.1. Racemic Mosher ester gave the same peaks with an intensity of 50.15:49.85. The ee value was then 80%. **5a**: ^{1}H-NMR (250 MHz, $CDCl_3$) δ 0.88 (t, 3 H, *J* = 7.5 Hz), 1.34 (d, 1 H, *J* = 3 Hz), 1.46 (s, 3 H), 1.49 (m, 1 H), 1.58 (m, 1 H), 1.84 (s, 3 H), 3.58 (d, 1 H, *J* = 12.5 Hz), 3.62 (d, 1 H, *J* = 12.5 Hz), 4.58 (dt, 1 H, *J* = 3, 7.5 Hz), 7.28 (m, 9 H), 7.46 (m, 6 H); ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ –5.61, 10.10, 11.04, 16.05, 27.72, 64.91, 72.47, 76.48, 76.99, 77.50, 126.85, 127.70, 128.74, 128.99, 132.96, 144.40; IR 3366, 2935, 1449, 1052 cm^{-1}. Anal. Calcd for $C_{27}H_{30}O_2$: C, 83.90; H, 7.82. Found: C, 83.65; H, 7.76.

(*RS*)-6-(Trityloxy)-4,5-dimethyl-4(*E*)-hexen-3-yl *O*-Benzylglycolate ((±)-7). To (±)-**5a** (10.34 g, 26.8 mmol) in pyridine (50 mL) was added via a syringe *O*-benzylglycolic acid chloride (6.84 g, 26.8 mmol) at 0 °C. After being stirred at 20 °C for 14 h the mixture was poured on ice (50 g). The organic layer was separated, washed with brine (100 mL), dried ($MgSO_4$), and concentrated under reduced pressure to give, after chromatography (hexane/ethyl acetate (8:1)) (±)-**7** (12.4 g, 92%) as a colorless oil. The same procedure was used to prepare (*R*)-**7** from (*R*)-**5a**: $[\alpha]^{20}_D$ +4.86° (*c* 1.26); ^{1}H-NMR (250 MHz, $CDCl_3$) δ 0.87 (t, 3 H, *J* = 7.5 Hz), 1.39 (d, 3 H, *J* = 1.25 Hz), 1.66 (m, 2 H), 1.94 (d, 3 H, *J* = 1.25 Hz), 3.54 (d, 1 H, *J* = 12.5 Hz), 3.64 (d, 1 H, *J* = 12.5 Hz), 4.07 (s, 2 H), 4.62 (s, 2 H), 5.75 (t, 1 H, *J* = 7.5 Hz), 7.15–7.50 (m, 20 H); ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ 9.76, 11.81, 16.32, 25.43, 64.75, 67.25, 73.21, 86.48, 126.86, 127.70, 127.88, 127.96, 128.42, 128.70, 131.43, 137.26, 144.30, 169.71; IR 1750, 1449, 1054, 764, 747 cm^{-1}. Anal. Calcd for $C_{36}H_{38}O_4$: C, 80.87; H, 7.16. Found: C, 80.76; H, 7.06.

(*RS*)-2-(Benzyloxy)-3,4-dimethyl-3-[[(triphenylmethyl)-oxy]methyl]-4(*E*)-heptenoic Acid ((±)-8). Ester **7** (3.10 g, 5.80 mmol) in THF (100 mL) was treated dropwise at –95 °C with LiHMDS (18 mmol) in THF. After 1 h at –95 °C the mixture was cooled to –105 °C, and TMSCl (4.32 g, 40 mmol) was added via a syringe. After the mixture was stirred for 1 h, the cooling bath was removed and the mixture was stirred for another 12 h. Saturated aqueous ammonium chloride (20 mL) was added, and after additional 2.5 h at room temperature, the organic layer was separated and the aqueous layer was extracted with ether. The combined organic phases were washed with brine (100 mL), dried ($MgSO_4$), and evaporated under reduced pressure. Column chromatography (ethyl acetate) furnished **8** (2.85 g, 91%) as colorless crystals of mp 137–138 °C. Likewise, (*R*)-**7** (1.98 g, 3.70 mmol) was converted into (2*R*,3*R*)-**8**: $[\alpha]^{20}_D$ +0.62 (*c* 1.37). Repeated recrystallization from ethyl acetate/hexane furnished

material with $[\alpha]^{20}_D$ +0.70° (c 1.4): ^{1}H-NMR (250 MHz, $CDCl_3$) δ 0.95 (t, 3 H, J = 7.5 Hz), 1.24 (s, 3 H), 1.55 (s, 3 H), 2.0 (m, 2 H), 3.12 (d, 1 H, J = 10 Hz), 3.28 (d, 1 H, J = 10 Hz), 4.06 (s, 1 H), 4.26 (d, 1 H, J = 12.5 Hz), 4.54 (d, 2 H, J = 12.5 Hz), 5.3 (t, br, 1 H, J = 7.5 Hz), 6.41 (m, 2 H), 6.55 (m, 12 H), 6.71 (m, 6 H); ^{13}C-NMR (250 MHz, $CDCl_3$) δ 13.47, 13.96, 17.58, 21.47, 47.67, 66.99, 73.18, 81.67, 126.98, 127.63, 127.73, 127.86, 128.33, 128.85, 134.83, 143.86, 173.45; IR 1714, 1449, 1077, 701 cm^{-1}. Anal. Calcd for $C_{36}H_{38}O_4$: C, 80.87; H, 7.16. Found: C, 80.73; H, 7.11.

Enantiomeric Purity of Recrystallized (2*R*,3*R*)-8. Acid (+)-8 (2.00 g, 3.74 mmol) in ether (10 mL) was esterified with ethereal diazomethane. The crude methyl ester was dissolved in THF (10 mL) and reduced with DIBALH (1.6 M in toluene, 5 mL) at −30 °C for 3 h, and 2-propanol (10 mL) and then silica gel (20 g), moistened with water (10 mL), were added slowly. The mixture was stirred at 20 °C for 14 h and filtered. Ether was added, and the organic layer was separated, washed with brine (3 × 50 mL), dried ($MgSO_4$), and concentrated under reduced pressure to furnish (2*R*,3*R*)-2-*O*-benzyl-3-(1-methyl-1(*E*)-butenyl)-3-methyl-4-*O*-tritylbutane-1,2,4-triol (**9**) as colorless crystals (2.01 g, 97%): mp 123 °C; $[\alpha]^{20}_D$ −4.11° (c 1.87). Likewise, racemic **9** was prepared. The optical purity was checked by 500-MHz ^{1}H-NMR spectroscopy with a chiral shift reagent ($Eutfc_3$). The olefinic Me signal was doubled for the racemate and appeared as a single signal for the optically active compound. The limit of detection was found to be less than 2%. **9**: ^{1}H-NMR (500 MHz, $CDCl_3$) δ 1.02 (t, 3 H, J = 7.5 Hz), 1.12 (s, 3 H), 1.55 (s, 3 H), 1.66 (dd, 1 H, J = 5.2, 7.5 Hz), 2.11 (m, 2 H), 3.11 (d, 1 H, J = 8.45 Hz), 3.17 (d, 1 H, J = 8.45 Hz), 3.51 (m, 1 H), 3.58 (m, 1 H), 3.71 (dd, 1 H, J = 3.7, 7.37 Hz), 4.35 (d, 1 H, J = 8.15 Hz), 4.48 (d, 1 H, J = 8.15 Hz), 5.42 (dd, 1 H, J = 1, 6.95 Hz), 7.06 (m, 2 H), 7.24 (m, 14 H), 7.38 (m, 4 H); ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ 13.29, 14.07, 16.58, 21.48, 47.75, 62.71, 67.54, 74.39, 82.43, 86.06, 126.80, 127.55, 128.26, 128.69, 128.85, 136.00, 138.52, 144.05; IR 1790, 1449, 1071, 1026, 709 cm^{-1}. Anal. Calcd for $C_{36}H_{40}O_3$: C, 83.04; H, 7.74. Found: C, 82.73; H, 7.65.

(3*RS*,4*SR*)-2-(Benzyloxy)-3-(1-methyl-1(*E*)-buten-1-yl)-3-methyloxolan-2-one (±)-13). Acid (±)-8 (3.87 g, 7.24 mmol) in dichloromethane (20 mL) was treated at room temperature with 2 N (10 mL) for 14 h. The organic layer was washed with aqueous sodium bicarbonate (50 mL) and brine (50 mL), dried ($MgSO_4$), and evaporated under reduced pressure. Column chromatography (hexane/ethyl acetate (5:1)) furnished (±)-13 (1.47 g, 74%) as a colorless oil: ^{1}H-NMR (270 MHz, $CDCl_3$) δ 0.96 (t, 3 H, J = 8.1 Hz, H-4′), 1.14 (s, 3 H, 3-Me), 1.58 (s, 3 H, 1′-Me), 2.04 (m, 2 H, H-3′), 3.61 (s, 1 H, H-2), 4.04 (d, 1 H, J = 8.6 Hz, H-4), 4.56 (d, 1 H, J = 8.6 Hz, H-4), 4.62 (d, 1 H, J = 11.3 Hz, OCH_2Ph), 4.84 (d, 1 H, J = 11.3 Hz, OCH_2Ph), 4.99 (t, 1 H, J = 8.6 Hz, H-2′), 7,32 (m, 5 H, Ph); ^{13}C-NMR (67.9 MHz, $CDCl_3$) δ 13.43, 13.90, 21.08, 22.65, 49.03, 71.80, 75.91, 79.55, 127.80. 127.93, 128.19, 128.31, 133.62, 136.85, 174.34, IR 1788, 1110, 1010 cm^{-1}. HRMS *m/z* calcd for $C_{17}H_{22}O_3$ 274.1568, found 274.1568.

(2*RS*,3*RS*,4*SR*)-3-(Benzyloxy)-2-hydroxy-3-(1-methyl-1(*E*)-buten-1-yl)-3-methyloxolane ((±)-18). Lactone (±)-13 (3.90 g, 14.22 mmol) in THF (100 mL) was treated with DIBALH (1.6 M in toluene, 11 mL, 1.2 mol equiv) at −78 °C. After 6 h, 2-propanol (10 mL) and then silica gel (20 g), moistened with water (10 mL), were added. Workup as described for **9** furnished (±)-18 as an anomeric mixture (3.91 g, 98%) after column chromatography (hexane/ethyl acetate (2:1)): ^{1}H-NMR (250 MHz, $CDCl_3$) δ 0.98 (t, 3 H, J = 7.5 Hz), 1.0 (t, 3 H, J = 7.5 Hz), 1.16 (s, 3 H), 1.32 (s, 3 H, 1st anomer), 1.62 (s, 3 H, second anomer), 1.70 (s, 3 H), 2.04 (m, 2 H), 3.54 (d, 1 H, J = 12.5 Hz), 3.58 (d, 1 H, J = 2.5 Hz), 3.75 (d, 1 H, J = 4.75 Hz), 3,88 (d, 1 H, J = 7.5 Hz), 4.04 (q, 2 H, J = 7.5 Hz), 4.62 (s, 1 H), 4.94 (dt, 1 H, J = 1.25, 7.5 Hz), 5.04 (dt, 1 H, J = 1.25, 7.5 Hz), 5.42 (d, 1 H, J = 2.5 Hz), 5.56 (dd, 1 H, J = 2.5, 12.5 Hz), 7.36 (m, 5 H); ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ 13.98, 14.27, 14.54, 21.14, 23.33, 24.00, 50.87, 52.58, 71.89, 73.51, 74.69, 84.66, 85.28, 89.90, 98.66, 102.91, 126.60, 127.21, 127.59, 127.99, 128.24, 128.45, 134.72, 136.09, 137.28; IR 3402, 1454, 1115, 1090 cm^{-1}. Anal. Calcd for $C_{17}H_{24}O_3$: C, 73.88; H, 8.75. Found: C, 73.83; H, 8.69.

(2*RS*,3*RS*,4*SR*)-3-*O*-Benzyl-2-(1-methyl-1(*E*)-buten-1-yl)-2-methylhex-5-ene-1,3,4-triol ((±)-19). Lactol (±)-18 (1.07 g, 3.87 mmol) in THF (20 mL) was treated dropwise at −78 °C with *n*-butyllithium (1.6 M in hexane, 2.5 mL). The mixture was stirred for 20 min at −35 °C. Vinylmagnesium chloride (1.6 M in THF, 7.3 mL) was added dropwise. The cooling bath was removed, and the mixture was stirred until the temperature reached 20 °C. Stirring was continued at +55 °C for another 5 h. The reaction was quenched with saturated aqueous ammonium chloride (50 mL). The organic layer was separated, and the aqueous phase was extracted with ether (2 × 50 mL). The combined organic phases were washed with brine (100 mL), dried ($MgSO_4$), and evaporated under reduced pressure. Column chromatography (hexane/ethyl acetate (3:1)) furnished (±)-19 (1.00 g, 89%) as a colorless oil: ^{1}H-NMR (250 MHz, $CDCl_3$) δ 1.00 (t, 3 H, J = 7.5 Hz), 1.16 (s, 3 H), 1.62 (s, 3 H), 2.08 (m, 2 H), 2.88 (d, 1 H, J = 5 Hz), 3.54 (dd, 1 H, J = 4.5, 12 Hz), 3.66 (dd, 1 H, J = 4.5, 12.5 Hz), 3.66 (d, 1 H, J = 2.5 Hz), 4.62 (q, 2 H, J = 12 Hz), 5.12 (dt, 1 H, J = 1.25, 12 Hz), 5.32 (t, 1 H, J = 1.25 Hz), 5.36 (m, 2 H), 5.96 (m, 1 H), 7.32 (m, 5 H); ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ 13.09, 14.08, 16.04, 21.49, 49.47, 66.62, 70.21, 75.51, 76.49, 77, 77.51, 82.97, 114.18, 127.89, 127.99, 128.46, 130.64, 153.20, 137.65, 141.33; IR 3440, 1454, 1065, 1029 cm^{-1}; HRMS *m/z* calcd for $C_{16}H_{23}O_2$ (M − C_3H_5O) 247.1698, found 247.1698.

(2*RS*,3*RS*,4*SR*)-3-*O*-Benzyl-4-*O*-benzoyl-2-(1-methyl-1(*E*)-buten-1-yl)-2-methylhex-5-ene-1,3,4-triol ((±)-21). Diol (±)-19 (3.40 g, 11.2 mmol) in dichloromethane (30 mL) was treated with imidazole (1.52 g, 22.4 mmol) at 0 °C. TBDMSCl (1.56 g, 11.5 mmol) in dichloromethane (20 mL) was added, and the mixture was stirred without further cooling for 12 h. Water (150 mL) was added, and the organic phase was separated, washed with brine (150 mL), dried ($MgSO_4$), and concentrated under reduced pressure to give, after column chromatography (hexane/ethyl acetate (5:1)), the monosilylated product (3.94 g, 84%), which was dissolved in pyridine (190 mL) and treated with benzoyl chloride (2.80 g, 20 mmol) at −10 °C. The mixture was stirred for 12 h without further cooling, quenched with ice–water (500 mL), and extracted four times with 100-mL portions of ether. The organic layer was separated, washed with 0.5 HCl (100 mL) and brine (5 × 100 mL), and concentrated under reduced pressure to furnish the 4-*O*-benzoyl-1-*O*-TBDMS derivative of **19** which was desilylated without purification. Thus, the crude material in ethanol (170 mL) was treated with PPTS (1 g) for 1 h at 50 °C. The solvent was evaporated under reduced pressure, and the residue was diluted with ether (100 mL), washed with brine (100 mL), dried ($MgSO_4$), concentrated under reduced pressure, and purified by column chromatography (hexane/ethyl acetate (8:1)) to give (±)-21 (3.07 g, 80%) as a colorless oil: ^{1}H-NMR (270 MHz, DMSO-d_6) δ 0.86 (t, 3 H, J = 7.5 Hz), 1.04 (s, 3 H), 1.88 (m, 2 H), 3.32 (d, 1 H, J = 9.45 Hz), 3.54 (d, 1 H, J = 9.45 Hz), 3.92 (s, 1 H), 4.42 (s, br, 1 H), 4.58 (d, 1 H, J = 10.8 Hz), 4.70 (d, 1 H, J = 10.8 Hz), 5.09 (m, 3 H), 5.49 (s, br, 1 H), 6,09 (m, 1 H), 7.28 (m, 6 H), 7.50 (m, 3 H), 7.96 (m, 2 H); ^{13}C-NMR (67.9 MHz, DMSO-d_6) δ 13.62, 13.78, 16.45, 20.84, 48.81, 66.44, 74.32, 74.66, 81.94, 115.61, 127.19, 127.61, 128.12, 128.77, 129.83, 135.88, 136.13, 138.72, 164.40; IR 3515, 2931, 1721, 1271, 713 cm^{-1}. Anal. Calcd for $C_{26}H_{32}O_4$: C, 76.44; H, 7.89. Found: C, 76.24; H, 7.80.

(2*RS*,3*SR*,4*RS*,5*SR*)-4-(Benzyloxy)-3-(1-methyl-1(*E*)-buten-1-yl)-2-methoxy-3-methyl-5-vinyloxolane ((±)-22). Alcohol (±)-21 (2.13 g, 5.22 mmol) was oxidized to the aldehyde as described for **3b**. The crude product was dissolved in methanol (15 mL) and treated with aqueous NaOH (10 N, 5 mL) at 5 °C for 2 h. Solid ammonium chloride (5 g) was added for neutralization, and the water was removed by adding $MgSO_4$ (5 g). The solution was filtered, concentrated under reduced pressure, and diluted with methanol (30 mL). Acid-exchange resin (DOWEX 50 Wx 8, 1 g) was added, and the mixture was refluxed for 24 h, filtered, concentrated under reduced pressure, and chromatographed (hexane/ethyl acetate (6:1)) to give (±)-22 (0.996 g, 67%) as a mixture of anomers as a colorless oil: ^{1}H-NMR (250 MHz, $CDCl_3$) δ 0.95 (t, 3 H, J = 7.5 Hz), 1.00 (t, 3 H, J = 7.5 Hz), 1.08 (s, 3 H), 1.14 (s, 3 H), 1.54 (s, 3 H), 1.62 (s, 3 H), 2.06 (m, 2 H), 3.36 (s, 3 H), 3.54 (s, 3 H), 3.72 (d, 1 H, J = 3.75 Hz), 3.80 (d, 1 H, 3.75 Hz), 4.30 (d, 1 H, J = 12.5 Hz), 4.36 (d, 1 H, J = 12.5 Hz), 4.62 (d, 1 H, J = 12.5 Hz), 4.70 (dd, 1 H, J = 2.5, 7.5 Hz), 5.22 (m, 2 H), 5.26 (s, 1 H), 5.40 (d, 1H, J = 17.5 Hz), 6.01 (ddd, 1 H, J = 2.5, 10, 17.5 Hz), 7.28 (m, 5 H); ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ 14.02, 14.32, 18.79, 21.25, 45.91, 55.49, 56.94, 73.60, 78.91, 84.41, 84.68, 88.68, 108.30, 109.77, 117.95, 118.16, 127.03, 127.18, 127.36,

127.59, 128.06, 128.13, 128.60, 128.95, 134.66, 135.35, 138.27; IR 2932, 2874, 1454, 1110 cm^{-1}. Anal. Calcd for $C_{20}H_{28}O_3$: C, 75.91; H, 8.92. Found: C, 75.94; H, 8.85.

(2*RS*,3*SR*,4*RS*)-4-(Benzyloxy)-5-(hydroxymethyl)-3-(1-methyl-1(*E*)-buten-1-yl)-2-methoxy-3-methyloxolane ((±)-24). Olefin (±)-**22** (668 mg, 2.11 mmol) in THF (10 mL) and water (1 mL) was treated with *N*-methylmorpholine *N*-oxide (365 mg, 3.17 mmol) and osmium tetraoxide (0.8 M in 2-methyl-2-propanol, 1.2 mL) at 0 °C for 72 h. Dichloromethane (15 mL), sodium dithionite (1.5 g), $MgSO_4$ (3 g), and Celite (3 g) were added. The mixture was stirred at room temperature for 2 h, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (hexane/ethyl acetate (3:1)) to furnish (±)-**23** (295 mg, 40%) as a 10:1 mixture of diastereomers along with unreacted (±)-**22** (214 mg, 32%). The two diastereomers of **23** were separated by HPLC (hexane/2-propanol (9:1)) and characterized by their NMR and MS spectra.

Major diastereomer: ^{1}H-NMR (250 MHz, $CDCl_3$) δ 0.99 (t, 3H, *J* = 7.5 Hz), 1.16 (s, 3 H), 1.25 (t, 1 H, *J* = 7.5 Hz), 1.72 (s, 3 H), 2.05 (m, 3 H), 3.46 (s, 3 H), 3.72 (dd, 1 H, *J* = 5, 11.25 Hz), 3.82–3.84 (m, 2 H), 3.94 (d, 1 H, *J* = 4.75 Hz), 4.14 (dd, 1 H, *J* = 4.75, 9.75 Hz), 4.60 (s, 2 H), 5.20 (s, 1 H), 5.28 (t, 1 H, *J* = 7.5 Hz), 7.28 (m, 5 H); ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ 13.94, 14.89, 18.77, 21.37, 55.22, 56.83, 64.77, 69.66, 74.00, 87.73, 87.32, 108.44, 127.46, 127.76, 127.96, 128.47, 134.13.

Minor diastereomer: ^{1}H-NMR (250 MHz, $CDCl_3$) δ 0.80 (t, 3 H, *J* = 7.5 Hz), 1.10 (s, 3 H), 1.18 (s, br, 1 H), 1.62 (s, 3 H), 1.96 (m, 3 H), 3.28 (s, 3 H), 3.68 (dd, 1 H, *J* = 5, 11.25 Hz), 3.78 (dd, 1 H, *J* = 5, 11.25 Hz), 3.91 (d, 1 H, *J* = 5 Hz), 3.98 (m, 1 H), 4.08 (dd, 1 H, *J* = 5, 7.75 Hz), 4.50 (s, 1 H), 4,52 (d, 1 H, *J* = 11.25 Hz), 4.70 (d, 1 H, 11.25 Hz), 5.24 (t, 1 H, *J* = 7 Hz), 7.24 (m, 5 H); ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ 13.92, 15.14, 21.23, 25.43, 55.70, 57.31, 64.84, 68.88, 69.99, 74.81, 81.36, 86.02, 110.55, 127.69, 127.75, 128.43, 129.11, 133.32, 138.27.

The combined diastereomers of (±)-**23** (342 mg, 0.96 mmol) in dichloromethane (4 mL) were treated with lead tetraacetate (487 mg, 1.1 mmol) for 45 min at 0 °C. THF (4 mL) and lithiumaluminum hydride (190 mg, 5 mmol) were added at 0 °C. After 10 min water (20 mL) was added, and the mixture was extracted with ether (5 × 20 mL). The organic layer was washed with brine (50 mL), dried ($MgSO_4$), and evaporated under reduced pressure to give, after column chromatography (hexane/ethyl acetate (3:1)) (±)-**24** (236 mg, 77%) as an oily 15:1-mixture of the α/β-anomers. α-Anomer: ^{1}H-NMR (250 MHz, $CDCl_3$) δ 1.00 (t, 3 H, *J* = 7.5 Hz, H-4′), 1.20 (s, 3 H, 3-Me), 1.70 (s, 3 H, 1′-Me), 2.08 (m, 2 H, H-3′), 2.22 (s, br, 1 H, OH), 3.48 (s, 3 H, OMe), 3.82 (m, 3 H, 4-H, H-6), 4.32 (q, 1 H, *J* = 5 Hz, H-5), 4.46 (d, 1 H, *J* = 11.25 Hz, OCH_2Ph), 4.56 (d, 1 H, *J* = 11.25 Hz, OCH_2Ph), 5.20 (s, 1 H, H-2), 5.30 (t, 1 H, *J* = 7 Hz, H-2′), 7.28 (m, 5 H, Ph); ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ 13.97, 14.93, 18.81, 21.36, 55.37, 56.89, 62.21, 74.09, 78.57, 88.02, 108.13, 127.51, 127.81, 127.98, 128.43, 134.04; IR 3440, 1454, 1114, 1028 cm^{-1}; HRMS *m/z* calcd for $C_{19}H_{28}O_4$ 320.1987, found 320.1981.

(2*RS*,3*RS*,4*SR*)-4-(Benzyloxy)-3-[(1*SR*,2*SR*)-1,2-dihydroxy-1-methylbutyl]-5-(hydroxymethyl)-2-methoxy-3-methyloxolane ((±)-25a and -b). The anomeric mixture of (±)-**24** (200 mg, 0.64 mmol) in acetonitrile (10 mL) and water (2 mL) was osmylated for 3 d at 50 °C as described for the conversion of **22** into **23** to furnish 188 mg (83%) of a 1.3:1 mixture of (±)-**25a** and **-b** as colorless needles (mp 82–83 °C), which were separated by HPLC as described for **23**.

Major anomer (25a): ^{1}H-NMR (250 MHz, $CDCl_3$) δ 1.0 (t, 3 H, *J* = 7.5 Hz), 1.01 (s, 3 H), 1.08 (s, 3 H), 1.21 (m, 1 H), 1.40 (m, 1 H), 1.71 (m, 1 H), 1.83 (d, 1 H, *J* = 5 Hz), 2.0 (m, 1 H), 3.44 (s, 3 H), 3.52 (m, 1 H), 3.92 (m, 2 H), 4.22 (s, br, 1 H), 4.36 (m, 1 H), 4.62 (m, 1 H), 5.32 (s,1 H), 5.36 (s, 5 H), 7.32 (s, 5 H); ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ 11.02, 16.79, 17.18, 20.86, 24.93, 55.53, 65.56, 61.21, 74.54, 74.70, 77.51, 78.41, 80.37, 86.28, 88.62, 91.35, 107.12, 111.36, 127.18, 127.94, 128.33, 128.47, 128.78, 136.83.

Minor anomer (25b): ^{1}H-NMR (250 MHz, $CDCl_3$) δ 1.01 (t, 3 H, *J* = 7.5 Hz), 1.08 (s, 3 H), 1,26 (s, 3 H), 1.56 (m, 2 H), 1.78 (s, br, 1 H), 2.08 (s, br, 1 H), 3.46 (s, 3 H), 3.96 (m, 3 H), 4.32 (m, 2 H), 4.62 (d, 1 H, *J* = 10 Hz), 4.74 (d, 1 H, *J* = 10 Hz), 5.62 (s, br, 1 H), 7.32 (m, 5 H); ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ 11.20, 16.89, 23.07, 23.67, 30.27, 56.42, 57.72, 60.48, 61.12, 74.86, 78.39, 79.04, 80.35, 90.37, 105.06, 107.09, 127.14, 128.09, 128.46, 128.76, 136.15.

(1*RS*,3*RS*,4*RS*,5*RS*,6*RS*,7*RS*)-2,8-Dioxa-4-(benzyloxy)-5,6-dimethyl-7-ethyl-6-hydroxyl-3-(hydroxymethyl)bicyclo[3.3.0]octane ((±)-26). Anomer (±)-**25a** (87 mg, 0.24 mmol) in dichloromethane (2 mL) was treated with camphorsulfonic acid monohydrate (5 mg) at room temperature for 1 h. The solvent was removed under reduced pressure, and the residue was purified by column chromatography (ethyl acetate) to give (±)-**26** (70 mg, 90%) as an amorphous solid. Likewise, anomer (±)-**25b** (72 mg, 0.20 mmol) was converted into (±)-**26** (reaction time 3 d, 95%): ^{1}H-NMR (250 MHz, $CDCl_3$) δ 1.01 (t, 3 H, *J* = 7.5 Hz, CH_3CH_2), 1.24 (s, 3 H, 5-Me, 1.26 (s, 3 H, 6-Me), 1.50 (m, 2 H, CH_3CH_2), 1.64 (s, 1 H, 6-OH), 2.06 (dd, 1 H, *J* = 3, 7.5 Hz, CH_2OH), 3.62 (d, 1 H, *J* = 3 Hz, H-4), 3.88 (m, 1 H, CH_2OH), 3.96 (m, 1 H, CH_2OH), 4.22 (m, 1 H, H-3), 4.34 (dd, 1 H, *J* = 5, 7.5 Hz, H-7), 4,54 (d, 1 H, *J* = 11.25 Hz, OCH_2Ph), 4.62 (d, 1 H, *J* = 11.25 Hz, OCH_2Ph), 5.21 (s, 1 H, H-1), 7.32 (m, 5 H, Ph); ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ 11.20, 16.98, 17.15, 21.20, 61.18, 62.07, 74.67, 80.88, 83.34, 86.25, 88.61, 111.33, 127.16, 127.81, 128.46, 137.18; IR 3488, 3368, 1105, 1024 cm^{-1}; HRMS *m/z* calcd for $C_{18}H_{26}O_5$ 322.1780, found 322.1779.

(1*RS*,3*RS*,4*RS*,5*RS*,6*RS*,7*RS*)-2,8-Dioxa-4,6-dihydroxy-5,6-dimethyl-7-ethyl-3-(hydroxymethyl)bicyclo[3.3.0]octane ((±)-2). Benzyl ether (±)-**26** (100 mg, 0.31 mmol) in methanol (3 mL) was hydrogenated over 10% Pd/C (20 mg) under a hydrogen balloon at room temperature for 24 h. The mixture was filtered and evaporated under reduced pressure to give (±)-**2** (98 mg, 96%) as an amorphous solid, whose ^{1}H-NMR spectrum was superimposable with the one described by Yamamura:[7] ^{1}H-NMR (500 MHz, $CDCl_3$) δ 1.04 (t, 3 H, *J* = 7.5 Hz), 1.11 (s, 3 H), 1.41 (s, 3 H), 1.55 (m, 2 H), 1.80 (s, br, 1 H), 3.23 (s, br, 1 H), 3.99 (m, br, 2 H), 4.10 (dd, 1 H, *J* = 5, 12.5 Hz), 4.24 (m, 1 H), 4.29 (dd, 1 H, *J* = 5, 12.5 Hz), 4.51 (m, br, 1 H), 5.34 (s, 1 H); ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ 11.22, 15.49, 18.21, 22.01, 61.39, 62.46, 80.24, 80.82, 81.68, 89.98.

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Supplementary Material Available: Spectral data for **14a**, **14b**, **15a**, **15b**, and **1b** and NMR spectra of **13**, **19**, **24**, and **26** (10 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.