Stereocontrolled Total Synthesis of Hemibrevetoxin B

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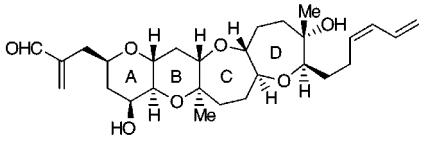
The stereocontrolled total synthesis of hemibrevetoxin B (**1**) has been achieved in 56 steps and 0.75% overall yield from D-mannose. The intramolecular reaction of γ-alkoxyallylstannane with aldehyde is a key step for the present total synthesis. Thus, the BF_3·OEt_2-mediated reaction of **24** gave **6** as a sole product. We encountered difficulty in the synthesis of γ-alkoxyallylstannane **30** from the corresponding allyl ether **29** in which the γ-alkoxy substituent became sterically quite bulky. This problem was solved by developing the acetal cleavage method for the synthesis of γ-alkoxyallylstannanes. The cyclization of **38** proceeded smoothly to give the key intermediate **5** in a highly stereoselective manner. Construction of the α-vinyl aldehyde and (*Z*)-diene moieties were performed using Nicolaou's protocol.

Introduction

In recent years there has been an explosion of interest in biologically active natural products of marine origin.[1] Much attention has been paid to the synthesis of polycyclic ethers due to their unusual structures, biological activities, and rarity in nature.[2] Hemibrevetoxin B (**1**), which has a 6,6,7,7-tetracyclic ether skeleton including 10 stereocenters, an α-vinyl aldehyde, and a (*Z*)-diene moiety, was isolated from the cultured cells of the red tide organism *Gymnodinium breve* by Shimizu in 1989.[3]



Hemibrevetoxin B (1)

The unique structural features have attracted the attention of synthetic chemists, and a number of strategies have been investigated.[4] The first total synthesis of hemibrevetoxin B (**1**) was accomplished by Nicolaou in 1992,[5] and the second was achieved by us in 1995.[6] More recently, the Nakata[7] and Mori[8] groups have also reported the total and formal total syntheses of **1**, respectively. The serious drawback of our previous synthesis[6] was that the conversion of allyl ether to γ-alkoxyallylstannane in a certain stage resulted in only 16% yield (*vide post* **30**), although good yields were obtained in the other steps. Now, we have found a new method for the synthesis of γ-alkoxyallylstannanes, and by using this method the problem has been solved. Herein we describe in detail the stereocontrolled total synthesis of hemibrevetoxin B (**1**).

Strategy and Retrosynthetic Analysis

During the past several years we have been studying the stereoselective synthesis of medium-sized cyclic ethers via the intramolecular reaction of an allylic stannane with an aldehyde.[9] This methodology is recognized to be one of the most powerful methods for the synthesis of oxepane derivatives.[10] For example, the reaction of monocyclic ether **2** with BF_3·OEt_2 gave quantitatively the cyclic ether **3** as the sole product (Scheme 1).[9a,b] The characteristic features of this reaction are not only the high yield and high stereoselectivity but also the presence of a hydroxy and a vinyl group attached to the newly formed cyclic ether skeleton. Further manipulation based on these two functional groups can lead to aldehyde and γ-alkoxyallylstannane side chains, thus the repeated use of the cyclization produced the 6,7,7,6-tetracyclic ether **4** which is a part of brevetoxin

† Institute for Chemical Reaction Science.

(1) For recent reviews, see: (a) Shimizu, Y. *Chem. Rev.* **1993**, *93*, 1685−1698. (b) Yasumoto, T.; Murata, M. *Chem. Rev.* **1993**, *93*, 1897−1909.

(2) For recent reviews, see: (a) Alvarez, E.; Candenas, M.-L.; Pérez, R.; Ravelo, J. L.; Martín, J. D. *Chem. Rev.* **1995**, *95*, 1953−1980. (b) Nicolaou, K. C. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 589−607.

(3) Prasad, A. V. K.; Shimizu, Y. *J. Am. Chem. Soc.* **1989**, *111*, 6476−6477.

(4) (a) Feng, F.; Murai, A. *Chem. Lett.* **1992**, 1587−1590. (b) Kadota, I.; Matsukawa, Y.; Yamamoto, Y. *J. Chem. Soc., Chem. Commun.* **1993**, 1638−1641. (c) Feng, F.; Murai, A. *Chem. Lett.* **1995**, 23−24. (d) Feng, F.; Murai, A. *Synlett* **1995**, 863−865. (e) Ishihara, J.; Murai, A. *Synlett* **1996**, 363−365. (f) Nakata. T.; Nomura, S.; Matsukura, H.; Morimoto, M. *Tetrahedron Lett.* **1996**, *37*, 217−220. (g) Matsukura, H.; Morimoto, M.; Nakata. T. *Chem. Lett.* **1996**, 487−488. (h) Gleason, M. M.; McDonald, F. E. *J. Org. Chem.* **1997**, *62*, 6432−6435.

(5) (a) Nicolaou, K. C.; Reddy, K. R.; Skokotas, G.; Sato, F.; Xiao, X.-Y. *J. Am. Chem. Soc.* **1992**, *114*, 7935−7936. (b) Nicolaou, K. C.; Reddy, K. R.; Skokotas, G.; Sato, F.; Xiao, X.-Y.; Hwang, C.-K. *J. Am. Chem. Soc.* **1993**, *115*, 3558−3575.

(6) For a preliminary communication, see: Kadota, I.; Park, J.-Y.; Koumura, N.; Pollaud, G.; Matsukawa, Y.; Yamamoto, Y. *Tetrahedron Lett.* **1995**, *36*, 5777−5780.

(7) Morimoto, M.; Matsukura, H.; Nakata, T. *Tetrahedron Lett.* **1996**, *37*, 6365−6368.

(8) Mori, Y.; Yaegashi, K.; Furukawa, H. *J. Am. Chem. Soc.* **1997**, *119*, 4557−4558.

(9) (a) Yamamoto, Y.; Yamada, J.; Kadota, I. *Tetrahedron Lett.* **1991**, *32*, 7069−7072. (b) Gevorgyan, V.; Kadota, I.; Yamamoto, Y. *Tetrahedron Lett.* **1993**, *34*, 1313−1316. (c) Kadota, I.; Kawada. M.; Gevorgyan, V.; Yamamoto, Y. *J. Org. Chem.* **1997**, *62*, 7439−7446.

(10) (a) Suzuki, T.; Sato, O.; Hirama, M.; Yamamoto, Y.; Murata, M.; Yasumoto, T.; Harada, N. *Tetrahedron Lett.* **1991**, *32*, 4505−4508. (b) Ravelo, J. L.; Regueiro, A.; Martín, J. D. *Tetrahedron Lett.* **1992**, *33*, 3389−3392. (c) Kadota, I.; Matsukawa, Y.; Yamamoto, Y. *J. Chem. Soc., Chem. Commun.* **1993**, 1638−1641. (d) Alvarez, E.; Díaz, M. T.; Pérez, R.; Ravelo, J. L.; Regueiro, A.; Vera, J. A.; Zurita, D.; Martín, J. D. *J. Org. Chem.* **1994**, *59*, 2848−2870. (e) Yamamoto, Y.; Kadota, I. *Bull. Soc. Chim. Belg.* **1994**, *103*, 619−629. (f) Oguri, H.; Hishiyama, S.; Oishi, T.; Hirama, M. *Synlett* **1995**, 1252−1254.

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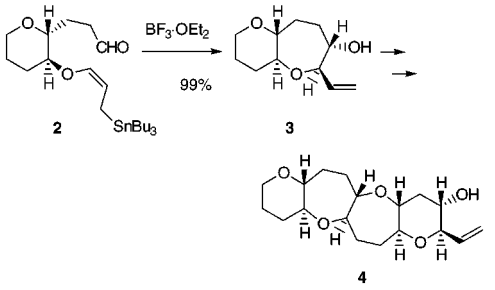
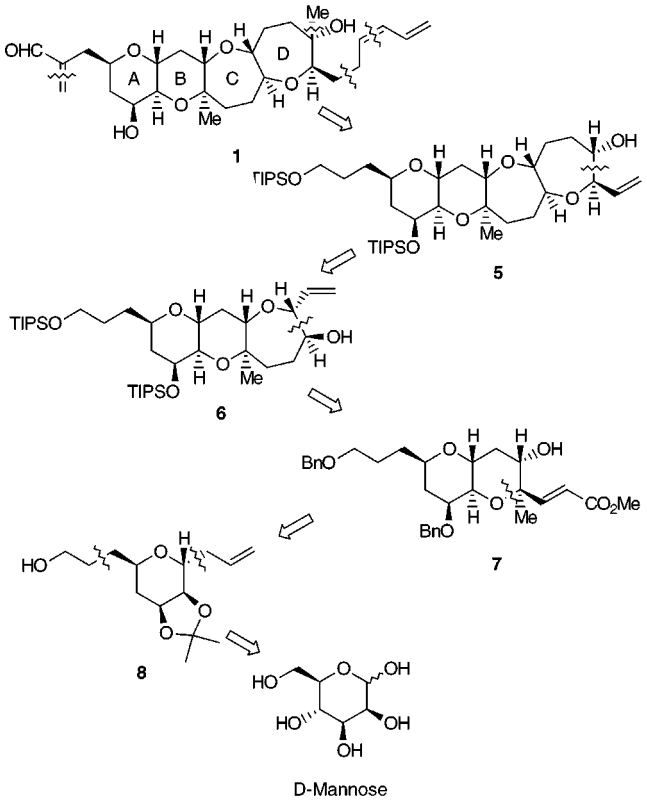
Scheme 1



Scheme 2. Retrosynthetic Analysis of Hemibrevetoxin B (1)



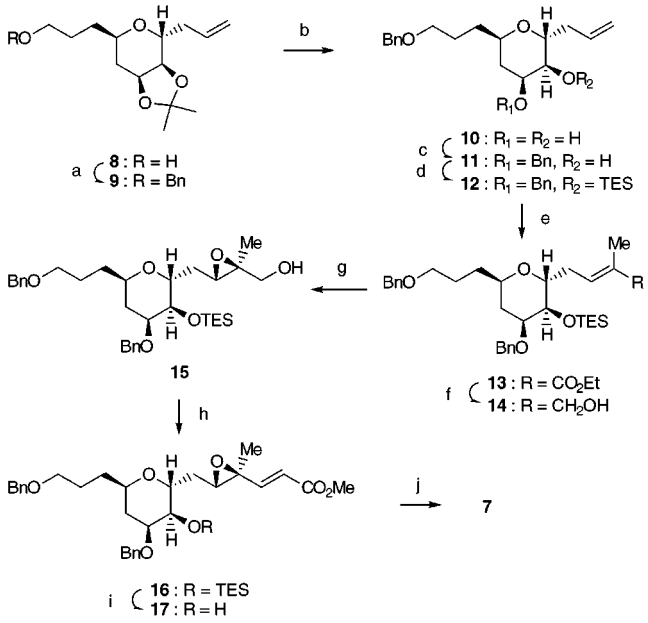
B. Encouraged by these successful results, we examined the retrosynthetic analysis of hemibrevetoxin B (**1**) as illustrated in Scheme 2.

Since constructions of the α-vinyl aldehyde and (*Z*)-diene moieties have been developed by Nicolaou,[5] we focused our efforts on the synthesis of the potential precursor **5**. Sequential retrosynthetic disassembly of the bis-oxepane ring system of **5** based on the allylic tin methodology mentioned above allowed the generation of the intermediate **7** via **6**. The B ring of **7** was then retrosynthetially broken by an epoxide opening−ring closure reaction leading to the known starting material **8**,[11] which can be derived from D-mannose.

Synthesis of the AB Ring System

The preparation of AB ring system was carried out primarily based on a modification of Nicolaou's method (Scheme 3).[11] Thus, protection of the primary alcohol of

Scheme 3[a]



[a] Conditions: (a) BnBr, KH, THF, rt, 98%; (b) HCl, MeOH, rt, 100%; (c) (i) Bu_2SnO, MeOH, reflux; (ii) BnBr, CsF, DMF, rt, 94%; (d) TESCl, imidazole, DMF, rt, 99%; (e) (i) O_3, CH_2Cl_2, −79 °C, then Ph_3P, rt; (ii) $Ph_3P{=}C(Me)CO_2Et$, benzene, reflux, 91%; (f) DIBALH, CH_2Cl_2, −78 °C, 87%; (g) (+)-DET, $Ti(O^iPr)_4$, ^{t}BuOOH, 4A molecular sieves, CH_2Cl_2, −20 °C; (h) (i) SO_3·py, DMSO, Et_3N, CH_2Cl_2, rt; (ii) $Ph_3P{=}CHCO_2Me$, benzene, reflux, 82% from **14**; (i) TBAF, THF, rt, 100%; (j) CSA, CH_2Cl_2, rt, 81%.

8 as a benzyl ether led to **9**, followed by methanolysis of the acetonide group to give the diol **10** quantitatively. Allylic alcohol **14** was produced in five steps as shown in Scheme 3. Sharpless asymmetric epoxidation of **14** using (+)-diethyl tartrate (DET) as a chiral auxiliary gave the epoxide **15**, which was converted to ester **17** as illustrated in Scheme 3. Cyclization of the hydroxy epoxide **17** with camphorsulfonic acid gave **7** to complete synthesis of the AB ring system.

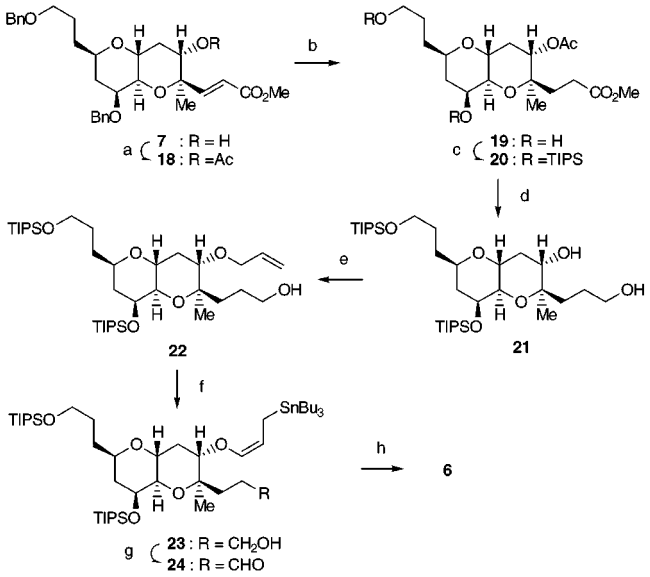
Construction of the C Ring

The stereocontrolled synthesis of the C ring is shown in Scheme 4. The secondary hydroxy group of **7** was protected as an acetate to give **18**, debenzylation and hydrogenation of which afforded the diol **19** in high yield. The free OH groups were protected with triisopropylsilyl triflate to give the bis-silyl ether **20** quantitatively. Reduction of **20** with $LiAlH_4$ afforded the diol **21** in 100% yield. Selective protection of the primary alcohol followed by allylation of the secondary alcohol and selective cleavage of the TES ether under mild acidic conditions gave the allyl ether **22**. Generation of the corresponding allylic anion by using excess *sec*-BuLi/TMEDA followed by trapping with *n*-Bu_3SnCl afforded **23**, which was oxidized to produce the cyclization precursor **24**.

Aldehyde **24** was then subjected to the cyclization by treatment with $BF_3{\cdot}OEt_2$ at −78 °C to give the desired tricyclic ether **6** in 94% yield with high stereoselectivity. Although the stereochemistry of **6** was not confirmed at this stage, we presumed it from the preliminary study described in Scheme 1. The observed high stereoselectivity can be explained by the well-accepted acyclic

(11) (a) Nicolaou, K. C.; Hwang, C.-K.; Duggan, M. E. *J. Am. Chem. Soc.* **1989**, *111*, 6682−6690. (b) Nicolaou, K. C.; Veale, C. A.; Hwang, C.-K.; Hutchinson, J.; Prasad, C. V. C.; Ogilvie, W. W. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 299−303.

Scheme 4[a]



[a] Conditions: (a) Ac_2O, pyridine, DMAP, CH_2Cl_2, rt, 97%; (b) H_2, $Pd(OH)_2$−C, MeOH, rt, 99%; (c) TIPSOTf, 2,6-lutidine, DMF, rt to 70 °C, 100%; (d) $LiAlH_4$, ether, 0 °C, 100%; (e) (i) TESCl, Et_3N, CH_2Cl_2, −15 °C; (ii) allyl bromide, KH, THF, rt; (iii) Amberlyst-15, EtOH, rt, 96%; (f) *sec*-BuLi, TMEDA, THF, −78 °C, then $^nBu_3SnCl$, −78 °C to rt, 69%; (g) SO_3·py, DMSO, Et_3N, CH_2Cl_2, rt, 90%; (h) BF_3·OEt_2, CH_2Cl_2, −78 °C, 94%.

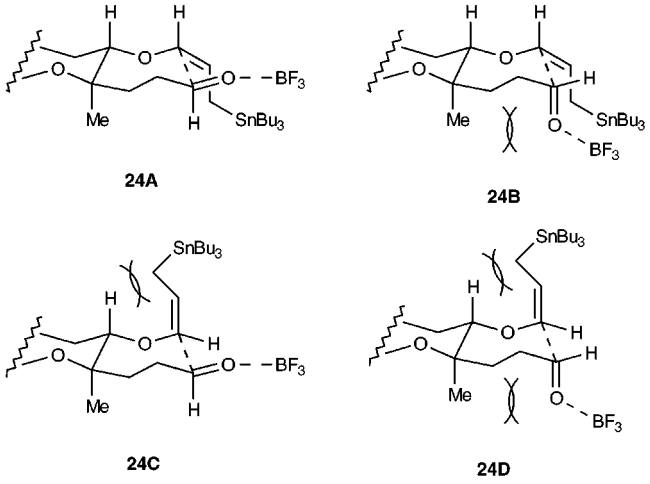


Figure 1. Presumed transition states of the cyclization of **24**.

transition state model (Figure 1).[12] To avoid the 1,3-diaxial repulsion, the allylic stannane moiety and the carbonyl oxygen of the substrate are oriented to a pseudo-equatorial position (**24A**) leading to **6**. All of the other transition state structures (**24B**, **C**, and **D**) do not contribute to the reaction because of the significant steric repulsion of the axially oriented groups, as depicted in Figure 1.[13]

Synthesis of the D Ring and Completion of the Total Synthesis

Acetylation of **6** followed by ozonolysis and Wittig reaction afforded α,β-unsaturated ester **26** via **25**, quantitatively (Scheme 5). Further elaboration of **26** was carried out using the similar methodology as shown in Scheme 4 to provide **29**. In contrast to earlier results in the synthesis of compound **23**, the usual allylic anion formation followed by trapping with *n*-Bu_3SnCl afforded **30** in only 16% yield along with the recovered starting material. Deprotonation of the sterically bulky allylic ether **29** would possibly be quite slow, and the decomposition of the resulting allylic anion would compete if a prolonged reaction time was employed. This problem prompted us to develop a new synthesis of γ-alkoxyallylstannanes.

Scheme 6 shows the general synthetic sequence for the γ-alkoxyallylstannanes via an acetal cleavage.[14] We have found that the combined use of trimethylsilyl iodide (TMSI) and hexamethyldisilazane (HMDS) is the best choice for the cleavage of mixed acetals[15,16] having the tributylstannyl group. The acetals are easily prepared by acid-catalyzed reaction of the corresponding alcohols and γ-methoxyallylstannane **31**.[17] As demonstrated in Table 1, the reaction of secondary alcohol **32**, prepared quantitatively by selective protection of the primary hydroxy group of **21** with pivaloyl chloride (PvCl)/pyridine, with **31** in the presence of a catalytic amount of CSA proceeded smoothly to give the mixed acetal **33** as a 1:1 diastereomeric mixture. It should be noted that the use of an excess of **31** is required to obtain the mixed acetals in high yield, otherwise a significant amount of symmetric acetal is formed as a byproduct. Treatment of **33** with TMSI and HMDS afforded the desired enol ether **34** in 83% yield. Interestingly, only (*Z*)-allylic stannane was produced, perhaps due to the coordination of ether oxygen to a tin atom. Encouraged by this success, the acetal methodology was used to introduce the allylic stannane moiety efficiently into tricyclic ether **35** (Table 1). It is notable that both of acetal formation and cleavage were not affected by the bulkiness of the substrates.

The final sequence of the synthesis is shown in Scheme 7. Removal of the pivalate protecting group with DIBALH led to **30**, which was oxidized to furnish the aldehyde **38**. The BF_3·OEt_2-mediated cyclization of **38** afforded the tetracyclic ether **5** as a sole product in 98% yield. Again, perfect stereoselectivity was observed in the cyclization step. The introduction of a methyl group at the D ring was performed using Murai protocol.[4a] Thus, Swern oxidation of **5** followed by treatment with MeMgBr in toluene at −78 °C gave an 86:14 mixture of the desired isomer **39** and its epimer **40**. As reported by Nicolaou, the reaction carried out in ether gave poor selectivity (ca. 1:1).[5] The major product **39** was isolated by chromatography, and the tertiary alcohol was protected with *tert*-butyldimethylsilyl triflate (TBSOTf)/2,6-lutidine to give **41**. Ozonolysis of **41** followed by Wittig reaction gave **42**, hydrogenation of which followed by $LiAlH_4$ reduction

(12) For representative studies on the reaction of allylstannanes with aldehydes, see: (a) Yamamoto, Y.; Yatagai, H.; Naruta, Y.; Maruyama, K. *J. Am. Chem. Soc.* **1980**, *102*, 7109−7110. (b) Denmark, S. E.; Weber, E. J. *J. Am. Chem. Soc.* **1984**, *106*, 7970−7971. For recent reviews, see: (c) Yamamoto, Y.; Asao, N. *Chem. Rev.* **1993**, *93*, 2207−2293 and references therein. (d) Nishigaichi, Y.; Takuwa, A.; Naruta, Y.; Maruyama, K. *Tetrahedron* **1993**, *49*, 7395−7426.

(13) For a detailed discussion of this reaction, see ref 9c.

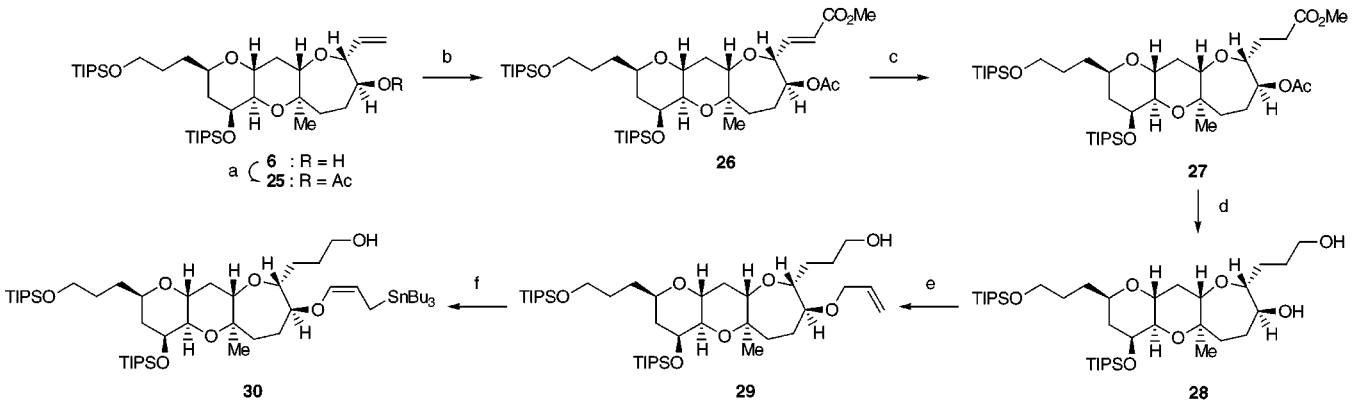
(14) For a preliminary report, see: Kadota, I.; Sakaihara, T.; Yamamoto, Y. *Tetrahedron Lett.* **1996**, *37*, 3195−3198.

(15) Miller, R. D.; McKean, D. R. *Tetrahedron Lett.* **1982**, *23*, 323−326.

(16) For other examples of this type of transformation, see: (a) (HC(OMe)$_3$/TsOH) Wohl, R. A. *Synthesis* **1974**, 38−40. (b) ($AlCl_3$/Et_3N) Barbot, F.; Miginiac, P. *Helv. Chim. Acta* **1979**, 1451−1457. (c) ($(CO)_5MnSiMe_3$) Marsi, M.; Gladysz, J. A. *Organometallics* **1982**, *1*, 1467−1473. (d) ($TiCl_4$/DBU) Fleet, G. W. J.; James, K.; Lunn, R. J. *Tetrahedron Lett.* **1986**, *27*, 3053−3056. (e) (*i*-Bu_3Al) Naruse, Y.; Yamamoto, H. *Tetrahedron Lett.* **1986**, *27*, 1363−1366.

(17) For the synthesis of **31**, see: Koreeda, M.; Tanaka, Y. *Tetrahedron Lett.* **1987**, *28*, 143−146.-

Scheme 5[a]



[a] Conditions: (a) Ac_2O, pyridine, DMAP, CH_2Cl_2, rt, 100%; (b) (i) O_3, CH_2Cl_2, −78 °C, then Ph_3P, −78 °C to rt; (ii) $Ph_3P{=}CHCO_2Me$, CH_2Cl_2, 0 °C to rt, 99%; (c) (i) H_2, 10% Pd−C, EtOAc, rt; (d) $LiAlH_4$, ether, 0 °C, 98%; (e) (i) TESCl, Et_3N, CH_2Cl_2, −15 °C; (ii) allyl bromide, KH, THF, rt; (iii) Amberlyst-15, EtOH, rt, 94%; (f) *sec*-BuLi, TMEDA, THF, −78 °C, then $^nBu_3SnCl$, −78 °C to rt, 16%.

Scheme 6

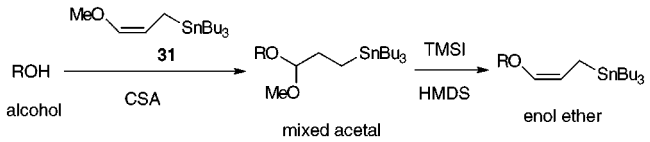
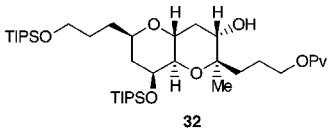
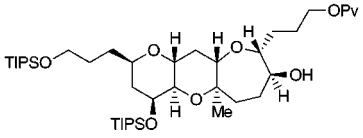


Table 1. Synthesis of the γ-Alkoxyallylstannanes via an Acetal Cleavage

alcohol	mixed acetal[a]	enol ether[b]
 **32**	**33:** 85%	**34:** 83%
 **35**	**36:** 93%	**37:** 85%

[a] 3.0 equiv of **31**, 0.2 equiv of CSA, CH_2Cl_2, rt. [b] 5.0 equiv of TMSI, 7.0 equiv of HMDS, CH_2Cl_2, −15 °C.

afforded **44** via **43**. Oxidation of **44** followed by treatment with the ylide derived from $PhSe(CH_2)_3P^+Ph_3Br^-$ and *n*-BuLi, and oxidation−*syn*-elimination using H_2O_2 and $NaHCO_3$ afforded diene **45**, selective desilylation of which gave **46**. Dess−Martin oxidation followed by treatment with Eschenmoser's salt[18] afforded **47**, which was converted to hemibrevetoxin B (**1**) by removal of the silyl protecting groups using SiF_4.[19] Synthetic hemibrevetoxin B (**1**) exhibited physical and spectroscopic data ($[\alpha]_D$, IR, and ^1H and ^{13}C NMR) identical with those of the natural product.[3]

Conclusion

The stereocontrolled total synthesis of hemibrevetoxin B (**1**) was accomplished with high stereoselectivity in 56 steps and 0.75% overall yield from D-mannose. Although the linear approach employed makes the synthesis considerably longer, the target molecule **1** was obtained in relatively high yield. The efficiency of the total synthesis exceeds those of the other synthetic routes by a factor of 15 to 25 (Nicolaou, overall 0.03% from D-mannose by 57 steps;[5] Nakata, overall 0.05% yield from geranyl acetate by 57 steps[7]). Demonstrated in this study was the power of the intramolecular reaction of γ-alkoxyallylstannanes with aldehydes as a tool for the synthesis of polycyclic ethers (see the conversion of **24** → **6** and **38** → **5**). The novel and efficient methods for synthesis of the cyclization precursors is also deserving of attention (see Scheme 6 and Table 1).

Experimental Section

General Procedure. All reactions involving air- and/or moisture-sensitive materials were carried out under argon with dry, freshly distilled solvents unless otherwise noted. Ether and THF were distilled from sodium/benzophenone ketyl. CH_2Cl_2, hexane, benzene, triethylamine, pyridine, DMF, DMSO, HMPA, tributyltin chloride, *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA), and hexamethyldisilazane (HMDS) were distilled from CaH_2. All other reagents were purchased at highest commercial quality and used without further purification. On workup, extracts were dried over $MgSO_4$.

All reactions were monitored by thin-layer chromatography on Merck precoated aluminum plates (Kieselgel 60 F_{254}, 0.2 mm) by using UV light and *p*-anisaldehyde solution as a developing reagent. Column chromatography was performed with Merck silica gel 60 (70−230 mesh ASTM), and for flash chromatography, Merck silica gel 60 (230−400 mesh ASTM) was employed. Yields refer to chromatographically and spectroscopically (^1H NMR) homogeneous materials.

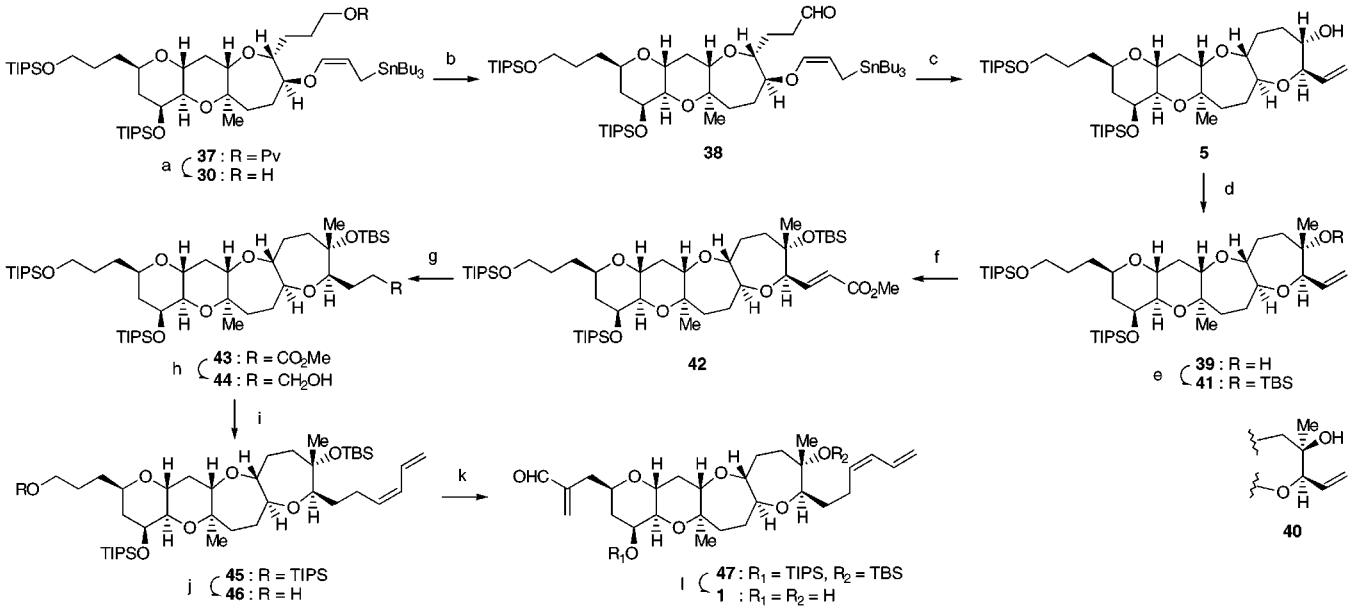
Chemical shifts are reported in delta (δ) units relative to tetramethylsilane or to the singlet at 7.26 ppm for chloroform. Coupling constants are reported in hertz (Hz).

Benzyl Ether 9. To a stirred suspension of KH (2.8 g of a 35% suspension in mineral oil, 24.9 mmol, prewashed with hexane) in THF (50 mL) at 0 °C was added dropwise a solution of **8**[11] (4.26 g, 16.6 mmol) in THF (40 mL). After 20 min, the mixture was treated with benzyl bromide (2.4 mL, 19.9 mmol). The cooling bath was removed, and the reaction mixture was stirred for another 2 h. The reaction mixture was quenched with methanol, diluted with ether, and washed with brine. The organic layer was concentrated and purified by chromatography (hexane/EtOAc, 4:1) to give **9** (5.65 g, 98%): colorless oil; R_f = 0.39 (hexane/EtOAc, 4:1); $[\alpha]^{23}_D$ +26.6° (*c* 1.60, $CHCl_3$); IR (neat) 3080, 2950, 1645 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 7.38−7.25 (m, 5H), 5.86 (dddd, *J* = 17.0, 10.0, 8.0, 8.0 Hz, 1H), 5.16−5.03 (m, 2H), 4.52 (d, *J* = 12.0, 1H), 4.47 (d, *J* = 12.0 Hz, 1H), 4.29 (ddd, 8.0, 6.0, 6.0 Hz, 1H), 3.85 (t, *J* = 6.5

(18) (a) Schreiber, J.; Maag, H.; Hashimoto, N.; Eschenmoser, A. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 330−331. (b) Takano, S.; Inomata, K.; Samizu, K.; Tomita, S.; Yanase, M.; Suzuki, M.; Iwabuchi, Y.; Sugihara, T.; Ogasawara, K. *Chem. Lett.* **1989**, 1283−1284.-

(19) Corey, E. J.; Yi, K. Y. T*etrahedron Lett.* **1992**, *33*, 2289−2290.

Scheme 7[a]



[a] Conditions: (a) DIBALH, CH_2Cl_2, −78 °C, 96%; (b) SO_3·py, DMSO, Et_3N, CH_2Cl_2, rt, 79%; (c) BF_3·OEt_2, CH_2Cl_2, −78 °C, 98%; (d) (i) $(COCl)_2$, DMSO, CH_2Cl_2, then Et_3N, −78 °C to rt; (ii) MeMgBr, toluene, −78 °C to rt, 83% (**39**:**40** = 86:14); (e) TBSOTf, 2,6-lutidine, CH_2Cl_2, rt, 85%; (f) (i) O_3, CH_2Cl_2, −78 °C, then Ph_3P, −78 °C to rt; (ii) $Ph_3P{=}CHCO_2Me$, CH_2Cl_2, rt, 82%; (g) H_2, 10% Pd−C, EtOAc, rt, 94%; (h) $LiAlH_4$, 0 °C, 93%; (i) (i) SO_3·py, DMSO, Et_3N, CH_2Cl_2, rt; (ii) $PhSe(CH_2)_3P^+Ph_3Br^-$, ^{n}BuLi, HMPA, −78 °C to rt; (iii) H_2O_2, $NaHCO_3$, THF, rt, 74%; (j) TBAF, THF, rt, 91%; (k) (i) Dess−Martin periodinane, CH_2Cl_2, rt; (ii) $Me_2(CH_2)N^+I^-$, Et_3N, CH_2Cl_2, rt, 89%; (l) SiF_4, CH_2Cl_2−CH_3CN (1:1), rt, 76%.

Hz, 1H), 3.74−3.62 (m, 2H), 3.55−3.42 (m, 2H), 2.42 (ddddd, J = 14.0, 7.0, 4.0, 1.5, 1.5 Hz, 1H), 2.24 (ddddd, J = 14.0, 8.5, 7.0, 1.5, 1.5 Hz, 1H), 2.0 (ddd, J = 14.0, 6.0, 4.5 Hz, 1H), 1.85−1.50 (m, 5H), 1.48 (s, 3H), 1.34 (s, 3H). Anal. Calcd for $C_{21}H_{30}O_4$: C, 72.80; H, 8.73. Found: C, 72.96; H, 8.92.

Diol 10. A solution of **9** (1.62 g, 4.68 mmol) in methanol (30 mL) was treated with concentrated HCl (30 μL) and stirred at room temperature. After 5 h, the resulting mixture was concentrated and purified by chromatography (hexane/EtOAc, 1:1) to give **10** (1.43, 100%): colorless needles; mp 87−88 °C (ether); R_f = 0.12 (hexane/EtOAc, 1:1); $[\alpha]^{24}_D$ +18.7° (*c* 1.05, $CHCl_3$); IR (KBr) 3600−3200, 3080, 2960, 1645 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.38−7.25 (m, 5H), 5.77 (dddd, J = 16.5, 10.5, 7.0, 7.0 Hz, 1H), 5.14−5.05 (m, 2H), 4.52 (d, J = 12.0 Hz, 1H), 4.47 (d, J = 12.0 Hz, 1H), 3.98 (ddd, J = 8.5, 6.0, 2.5 Hz, 1H), 3.88 (ddd, J = 10.5, 5.0, 3.0 Hz, 1H), 3.63 (t, J = 3.0 Hz, 1H), 3.61−3.40 (m, 3H), 2.45−2.15 (m, 4H), 1.82−1.45 (m, 6H). Anal. Calcd for $C_{18}H_{26}O_4$: C, 70.56; H, 8.55. Found: C, 70.28; H, 8.52.

Alcohol 11. A mixture of **10** (4.79 g, 15.6 mmol) and dibutyltin oxide (4.28 g, 17.2 mmol) in absolute methanol (150 mL) was refluxed for 1.5 h. The solvent was then removed in vacuo, and the residue was dried azeotropically with toluene (100 mL) and dissolved in DMF (150 mL). Benzyl bromide (2.2 mL, 18.7 mmol) and CsF (2.8 g, 18.7 mmol) were added, and the mixture was stirred at room temperature. After 12 h, the reaction mixture was diluted with ether and washed with water and brine. The organic layer was concentrated and purified by chromatography (hexane/EtOAc, 2:1) to give **11** (4.93 g, 98% based on 84% conversion) and recovered **10** (748 mg, 16%): colorless oil; R_f = 0.22 (hexane/EtOAc, 2:1); $[\alpha]^{25}_D$ +26.5° (*c* 1.96, $CHCl_3$); IR (neat) 3600−3200, 3080, 2940, 1645 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.40−7.20 (m, 10H), 5.79 (dddd, J = 17.5, 9.5, 7.0 7.0 Hz, 1H), 5.09−5.00 (m, 2H), 4.62 (d, J = 11.5 Hz, 1H), 4.54 (d, J = 11.5 Hz, 1H), 4.51 (d, J = 12.0 Hz, 1H), 4.46 (d, J = 12.0 Hz, 1H), 3.98 (ddd, J = 8.5, 6.0, 2.5 Hz, 1H), 3.77−3.69 (m, 3H), 2.41 (d, J = 3.5 Hz, 1H), 2.40−2.18 (m, 2H), 1.80−1.50 (m, 6H). Anal. Calcd for $C_{25}H_{32}O_4$: C, 75.73; H, 8.13. Found: C, 75.79; H, 8.11.

Silyl Ether 12. To a mixture of **11** (5.57 g, 14.0 mmol) and imidazole (1.90 g, 28.0 mmol) in CH_2Cl_2 at 0 °C was added TESCl (2.8 mL, 16.8 mmol), and the mixture was stirred for 2 h at 0 °C. The mixture was diluted with ether and washed with water, aqueous $NaHCO_3$, and brine. The organic layer was concentrated and purified by chromatography (hexane/EtOAc, 10:1) to give **12** (7.07 g, 99%): colorless oil; R_f = 0.28 (hexane/EtOAc, 10:1); $[\alpha]^{25}_D$ +16.7° (*c* 1.23, $CHCl_3$); IR (neat) 3070, 2960, 1645 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.40−7.20, (m, 10H), 5.78 (dddd, J = 18.0, 9.0, 7.0, 7.0 Hz, 1H), 5.07−4.98 (m, 2H), 4.56 (s, 2H), 4.51 (d, J = 12.0 Hz, 1H), 3.87 (ddd, J = 7.0, 7.0, 4.0 Hz, 1H), 3.73 (t, J = 3.0 Hz, 1H), 3.65−3.38 (m, 4H), 2.25 (dddd, J = 7.0, 7.0, 1.5, 1.5 Hz, 2H), 1.95−1.50 (m, 6H), 0.95 (t, J = 8.0 Hz, 9H), 0.60 (q, J = 8.0 Hz, 6H). Anal. Calcd for $C_{31}H_{46}O_4Si$: C, 72.90; H, 9.08. Found: C, 72.87; H, 9.11.

Unsaturated Ester 13. Ozone was passed through a solution of **12** (5.33 g, 10.4 mmol) in CH_2Cl_2 (100 mL) at −78 °C until the solution turned blue. The excess ozone was removed with a stream of oxygen, followed by addition of triphenylphosphine (4.10 g, 15.6 mmol). The mixture was allowed to warm to room temperature, concentrated, and dissolved in benzene (100 mL). To the solution of crude aldehyde was added (carboethoxyethyliden)triphenylphosphorane (7.50 g, 20.8 mmol), and the mixture was refluxed. After 1 h, the reaction mixture was concentrated and diluted with hexane. The resulting triphenylphosphine oxide was filtered off, and the solvent was removed in vacuo. The residue was purified by chromatography (hexane/EtOAc, 4:1) to give **13** (5.63 g, 91%): colorless oil; R_f = 0.42 (hexane/EtOAc, 4:1); $[\alpha]^{24}_D$ +13.7° (*c* 1.10, $CHCl_3$); IR (neat) 3050, 2970, 1715, 1650 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.40−7.20 (m, 10H), 6.80 (brt, J = 7.0 Hz, 1H), 4.58 (s, 2H), 4.50 (d, J = 12.0 Hz, 1H), 4.45 (d, J = 12.0 Hz, 1H), 4.17 (q, J = 7.0 Hz, 2H), 3.99−3.90 (m, 1H), 3.70−3.40 (m, 5H), 2.50−2.20 (m, 2H), 1.95−1.50 (m, 6H), 1.80 (d, J = 1.0 Hz, 3H), 1.26 (t, J = 7.0 Hz, 3H), 0.95 (t, J = 8.0 Hz, 9H), 0.61 (q, J = 8.0 Hz, 6H). Anal. Calcd for $C_{35}H_{52}O_6Si$: C, 70.43; H, 8.78. Found: C, 70.14; H, 8.72.

Allylic Alcohol 14. To a stirred solution of **13** (1.20 g, 2.01 mmol) in CH_2Cl_2 (30 mL) at −78 °C was added DIBALH (4.4 mL, 1.0 M in CH_2Cl_2, 4.4 mmol) dropwise. After 0.5 h, the mixture was diluted with ether and washed with aqueous sodium potassium tartrate and brine. The organic layer was

concentrated and purified by chromatography (hexane/EtOAc, 2:1) to give **14** (0.97 g, 87%): colorless oil; $R_f = 0.30$ (hexane/EtOAc, 2:1); $[\alpha]^{27}_D$ +13.9° (*c* 1.60, $CHCl_3$); IR (neat) 3600−3200, 3050, 2970, 1460 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 7.40−7.20 (m, 10H), 5.45 (brt, *J* = 7.0 Hz, 1H), 4.57 (s, 2H), 4.51 (d, *J* = 12.0 Hz, 1H), 4.46 (d, *J* = 12.0 Hz, 1H), 3.98 (brs, 2H), 3.84 (ddd, *J* = 9.0, 6.0, 4.0 Hz, 1H), 3.72 (t, *J* = 3.0 Hz, 1H), 3.64 (ddd, 9.0, 3.0, 3.0 Hz, 1H), 3.60−3.51 (m, 1H), 3.50−3.40 (m, 2H), 2.35−2.10 (m, 2H), 1.90−1.45 (m, 6H), 1.63 (brs, 3H), 0.94 (t, *J* = 8.0 Hz, 9H), 0.60 (q, *J* = 8.0 Hz, 6H). Anal. Calcd for $C_{33}H_{50}O_5Si$: C, 71.44; H, 9.08. Found: C, 71.14; H, 9.01.

Unsaturated Ester 16. A stirred mixture of powdered activated 4A molecular sieves, allylic alcohol **14** (960 mg, 1.73 mmol), and CH_2Cl_2 (20 mL) was cooled to − 20 °C and treated sequentially with (+)-diethyl tartrate (356 μL, 2.08 mmol) and titanium(IV) isopropoxide (515 μL, 1.73 mmol). After 10 min, *tert*-butyl hydroperoxide (1.2 mL, 3.0 M in 2,2,4-trimethylpentane, 3.6 mmol) was added, and the mixture was stirred for 12 h at −20 °C. The reaction mixture was diluted with ether (30 mL), and while the solution was vigorously stirred, aqueous Na_2SO_4 (3 mL) was added. After 1 h, the suspension was removed by filtration through a Celite pad. The filtrate was concentrated to give crude **15** which was used directly.

To a stirred solution of **15** (1.73 mmol) obtained above, DMSO (5 mL), and triethylamine (1.7 mL, 12.1 mmol) in CH_2Cl_2 (15 mL) at 0 °C was added sulfur trioxide pyridine complex (1.4 g, 8.65 mmol), and the mixture was stirred at room temperature. After 2 h, the reaction mixture was diluted with ether and washed with water and brine. The organic layer was concentrated to give the corresponding aldehyde which was immediately subjected to the next reaction without purification.

To the crude aldehyde in benzene (15 mL) was added methyl (triphenylphosphoranylidene)acetate (870 mg, 2.60 mmol), and the mixture was stirred at room temperature. After 11 h, the reaction mixture was concentrated and diluted with hexane. The resulting triphenylphosphine oxide was filtered off, and the solvent was removed in vacuo. The residue was purified by chromatography (hexane/EtOAc, 4:1) to give **16** (882 mg, 82%): colorless oil; $R_f = 0.28$ (hexane/EtOAc, 4:1); $[\alpha]^{28}_D$ +17.5° (*c* 1.68, $CHCl_3$); IR (neat) 3040, 2960, 1730, 1660 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 7.40−7.20 (m, 10H), 6.75 (d, *J* = 16.0 Hz, 1H), 6.01 (d, *J* = 16.0 Hz, 1H), 4.60 (d, *J* = 12.0 Hz, 1H), 4.55 (d, *J* = 12.0 Hz, 1H), 4.50 (d, *J* = 12.0 Hz, 1H), 4.46 (d, *J* = 12.0 Hz, 1H), 4.00−3.90 (m, 1H), 3.72 (s, 3H), 3.70−3.60 (m, 3H), 3.50−3.40 (m, 2H), 2.98 (t, *J* = 6.0 Hz, 1H), 2.00−1.50 (m, 8H), 1.39 (s, 3H), 0.94 (t, *J* = 8.0 Hz, 9H), 0.60 (q, *J* = 8.0 Hz, 6H). Anal. Calcd for $C_{36}H_{52}O_7Si$: C, 69.20; H, 8.39. Found: C, 69.14; H, 8.43.

Alcohol 17. To a stirred solution of **16** (4.22 g, 6.75 mmol) in THF (70 mL) was added tetrabutylammonium fluoride (8.1 mL, 1.0 M in THF, 8.1 mmol). After 1 h, the mixture was concentrated and purified by chromatography (hexane/EtOAc, 1:1) to give **17** (3.44 g, 100%): colorless oil; $R_f = 0.32$ (hexane/EtOAc, 1:1); $[\alpha]^{29}_D$ +33.2° (*c* 1.71, $CHCl_3$); IR (neat) 3600−3200, 3040, 2940, 1730, 1655 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 7.40−7.20 (m, 10H), 6.75 (d, *J* = 16.0 Hz, 1H), 6.01 (d, *J* = 16.0 Hz, 1H), 4.66 (d, *J* = 11.5 Hz, 1H), 4.51 (d, *J* = 11.5 Hz, 1H), 4.49 (s, 2H), 4.00 (ddd, *J* = 9.0, 5.0, 5.0 Hz, 1H), 3.80−3.55 (m, 3H), 3.72 (s, 3H), 3.55−3.40 (m, 2H), 2.99 (t, *J* = 6.0 Hz, 1H), 2.47 (d, *J* = 5.0 Hz, 1H), 1.95−1.50 (m, 8H), 1.40 (s, 3H). Anal. Calcd for $C_{30}H_{38}O_7$: C, 70.57; H, 7.50. Found: C, 70.16; H, 7.58.

Bicycle 7. A solution of **7** (3.44 g, 6.74 mmol) in CH_2Cl_2 (100 mL) was treated with camphorsulfonic acid (465 mg, 2.0 mmol). After 13 h, the reaction mixture was quenched with triethylamine (1 mL), concentrated, and purified by chromatography (hexane/EtOAc, 1:1) to give **7** (2.8 g, 81%): colorless oil; $R_f = 0.31$ (hexane/EtOAc, 1:1); $[\alpha]^{23}_D$ +17.6° (*c* 1.87, $CHCl_3$); IR (neat) 3600−3200, 3040, 2960, 1730, 1660 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.40−7.20 (m, 10H), 7.16 (d, *J* = 15.8, 1H), 6.15 (d, *J* = 15.8 Hz, 1H), 4.79 (d, *J* = 12.5 Hz, 1H), 4.64 (d, *J* = 12.5 Hz, 1H), 4.49 (s, 2H), 3.80−3.75 (m, 3H), 3.76 (s, 3H), 3.60 (dd, *J* = 12.0, 4.5 Hz, 1H), 3.55−3.42 (m, 2H), 3.37 (dd, *J* = 9.8, 2.5 Hz, 1H), 2.36−2.20 (m, 1H), 2.10 (ddd, *J* = 11.5, 4.5, 4.5 Hz, 1H), 1.95−1.55 (m, 6H), 1.33 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.4, 151.8, 139.2, 138.5, 128.3, 128.2, 127.6, 127.4, 127.2, 127.1, 118.9, 77.5, 73.6, 72.8, 72.6, 72.4, 70.7, 70.1, 62.5, 51.6, 34.5, 33.0, 29.1, 27.0, 14.6; HRMS (EI) calcd for $C_{30}H_{38}O_7$ 510.2618, found 510.2591. Anal. Calcd for $C_{30}H_{38}O_7$: C, 70.57; H, 7.50. Found: C, 70.13; H, 7.61.

Acetate 18. To a stirred solution of **7** (2.8 g, 5.48 mmol), pyridine (980 μL, 12 mmol), and 4-(dimethylamino)pyridine (DMAP, 20 mg) in CH_2Cl_2 (50 mL) was added acetic anhydride (1.0 mL, 11 mmol). After 20 h, the reaction mixture was concentrated and purified by chromatography (hexane/EtOAc, 2:1) to give **18** (2.95 g, 97%): colorless oil; $R_f = 0.30$ (hexane/EtOAc, 2:1); $[\alpha]^{27}_D$ +27.2° (*c* 1.60, $CHCl_3$); IR (neat) 3050, 2970, 1760, 1740, 1665 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.40−7.20 (m, 10H), 6.92 (d, *J* = 15.8 Hz, 1H), 6.13 (d, *J* = 15.8 Hz, 1H), 4.77 (d, *J* = 12.4 Hz, 1H), 4.75 (dd, *J* = 11.8, 4.6 Hz, 1H), 4.63 (d, *J* = 12.4 Hz, 1H), 4.49 (s, 2H), 3.95−3.80 (m, 3H), 3.75 (s, 3H), 3.55−3.45 (m, 2H), 3.42 (dd, *J* = 10.0, 2.7 Hz, 1H), 2.25 (ddd, *J* = 11.5, 4.7, 4.7 Hz, 2H), 2.08 (s, 3H), 1.95−1.90 (m, 2H), 1.80−1.55 (m, 4H), 1.39 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.6, 167.0, 149.9, 139.0, 138.60, 128.3, 128.2, 127.6, 127.4, 127.2, 127.1, 119.5, 75.5, 73.8, 73.4, 72.9, 72.6, 72.5, 71.8, 70.1, 62.0, 51.6, 33.0, 31.1, 29.1, 27.0, 21.1, 15.9; HRMS (EI) calcd for $C_{32}H_{40}O_8$ 552.2724, found 552.2703. Anal. Calcd for $C_{32}H_{40}O_8$: C, 69.55; H, 7.30. Found: C, 69.18; H, 7.35.

Diol 19. Palladium hydroxide on carbon (270 mg) was added to a stirred solution of **18** (2.75 g, 4.98 mmol) in methanol (50 mL). A hydrogen atmosphere was introduced using a hydrogen-filled balloon by repeated evacuations (water aspirator). After 16 h, the catalyst was filtered off. The filtrate was concentrated and purified by chromatography (EtOAc) to give **19** (1.85 g, 99%): colorless oil; $R_f = 0.30$ (EtOAc); $[\alpha]^{29}_D$ +31.9° (*c* 2.29, $CHCl_3$); IR (neat) 3650−3200, 2960, 1745 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 4.84 (dd, *J* = 11.5, 4.5 Hz, 1H), 4.01 (ddd, *J* = 3.0, 2.5, 2.5 Hz, 1H), 3.90−3.80 (m, 1H), 3.78 (ddd, *J* = 12.0, 9.5, 4.5 Hz, 1H), 3.67 (t, *J* = 6.0 Hz, 2H), 3.25 (dd, *J* = 9.5, 2.5 Hz, 1H), 2.40 (t, *J* = 7.0 Hz, 2H), 2.35−2.20 (m, 1H), 2.17 (ddd, *J* = 11.0, 4.5, 4.5 Hz, 1H), 2.06 (s, 3H), 2.05−1.55 (m, 8H), 1.27 (s, 3H). Anal. Calcd for $C_{18}H_{30}O_8$: C, 57.74; H, 8.08. Found: C, 57.68; H, 8.02.

Bis-silyl Ether 20. To a stirred solution of **19** (1.71 g, 4.57 mmol) and 2,6-lutidine (1.9 mL, 16 mmol) in DMF (50 mL) at 0 °C was added triisopropylsilyl trifluoromethanesulfonate (TIPSOTf, 3.1 mL, 11.4 mmol), and the mixture was heated at 70 °C. After 17 h, the reaction was quenched with methanol at 0 °C, diluted with ether and washed with water and brine. The organic layer was concentrated and purified by chromatography (hexane/EtOAc, 4:1) to give **20** (3.14 g, 100%): colorless oil; $R_f = 0.31$ (hexane/EtOAc, 4:1); $[\alpha]^{23}_D$ +29.6° (*c* 1.43, $CHCl_3$); IR (neat) 2950, 1750 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 4.65 (dd, 12.0, 4.5 Hz, 1H), 4.24 (ddd, *J* = 3.0, 2.5, 2.5 Hz, 1H), 3.85−3.65 (m, 4H), 3.66 (s, 3H), 3.19 (dd, *J* = 9.5, 2.5 Hz, 1H), 2.60−2.25 (m, 3H), 2.19 (ddd, *J* = 11.0, 4.5, 4,5 Hz, 1H), 2.05 (s, 3H), 2.05−1.45 (m, 8H), 1.21 (s, 3H), 1.09−1.04 (m, 42H). Anal. Calcd for $C_{36}H_{70}O_8Si_2$: C, 62.93; H, 10.27. Found: C, 62.68; H, 10.23.

Diol 21. To a stirred suspension of $LiAlH_4$ (330 mg, 8.73 mmol) in ether (50 mL) at 0 °C was added dropwise a solution of **20** (4.0 g, 5.82 mmol) in ether (20 mL). After 0.5 h, the reaction mixture was quenched with a minimum amount of brine, and the mixture was stirred vigorously for 0.5 h. The resulting white precipitate was removed by filtration through a Celite pad. The filtrate was concentrated and purified by chromatography (hexane/EtOAc, 1:1) to give **21** (3.55 g, 99%): colorless oil; $R_f = 0.33$ (hexane/EtOAc, 1:1); $[\alpha]^{25}_D$ +21.5° (*c* 1.92, $CHCl_3$); IR (neat) 3600−3100, 2950 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 4.23 (ddd, *J* = 3.0, 2.5, 2.5 Hz, 1H), 3.86−3.71 (m, 2H), 3.69 (t, *J* = 6.0 Hz, 2H), 3.62 (ddd, *J* = 6.0, 6.0, 1.5 Hz, 2H), 3.51 (dd, *J* = 6.5, 4.5 Hz, 1H), 3.15 (dd, 9.5, 3.0 Hz, 1H), 2.40−2.25 (m, 1H), 2.07 (ddd, *J* = 11.5, 5.0, 5.0 Hz, 1H), 2.00 (ddd, *J* = 14.0, 7.0, 3.0 Hz, 1H), 1.90−1.35 (m, 9H), 1.17 (s, 3H), 1.09−1.04 (m, 42H). Anal. Calcd for $C_{33}H_{68}O_6Si_2$: C, 64.23; H, 11.11. Found: C, 63.82; H, 11.09.

Allyl Ether 22. To a stirred solution of **21** (3.55 g, 5.75 mmol) and triethylamine (960 μL, 6.7 mmol) in CH_2Cl_2 at −15 °C was added dropwise triethylsilyl chloride (TESCl, 1.1 mL, 6.33 mmol). After 1 h, the reaction mixture was diluted with ether and washed with water, aqueous $NaHCO_3$, and brine. The organic layer was concentrated to give the crude monosilyl ether which was used directly.

To a stirred suspension of KH (790 mg of a 35% suspension in mineral oil, 6.9 mmol, prewashed with hexane) in THF (30 mL) at 0 °C were added consecutively allyl bromide (600 mL, 6.9 mmol) and a solution of the secondary alcohol obtained above in THF (20 mL). The cooling bath was removed, and the reaction mixture was stirred for 0.5 h. The reaction was quenched with methanol at 0 °C and diluted with ether. The organic layer was washed with brine and concentrated to give crude allyl ether which was used for the next reaction without purification.

The crude allyl ether was dissolved in ethanol (50 mL) and stirred with Amberlyst-15 (200 mg) at room temperature. After 0.5 h, the resin was filtered off, and the filtrate was concentrated and purified by chromatography (hexane/EtOAc, 4:1) to give **22** (3.64 g, 96%): colorless oil; $R_f = 0.33$ (hexane/EtOAc, 4:1); $[\alpha]^{23}_D$ +34.6° (*c* 1.84, $CHCl_3$); IR (neat) 3600−3200, 2960 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 5.89 (dddd, *J* = 17.0, 10.5, 5.0, 5.0 Hz, 1H), 5.26 (dddd, *J* = 17.0, 3.0, 2.5, 2.5 Hz, 1H), 5.15 (dddd, *J* = 10.5, 3.0, 2.5, 2.5 Hz, 1H), 4.22 (ddd, *J* = 3.0, 3.0, 2.5 Hz, 1H), 4.10 (dddd, *J* = 12.5, 5.0, 1.5, 1.5 Hz, 1H), 3.90 (dddd, *J* = 12.5, 5.0, 1.5, 1.5 Hz, 1H), 3.82 (ddd, *J* = 10.5, 6.5, 3.5 Hz, 1H), 3.76−3.65 (m, 1H), 3.70 (t, *J* = 6.5 Hz, 2H), 3.60 (ddd, *J* = 6.5, 6.5, 1.0 Hz, 2H), 3.20−3.12 (m, 2H), 2.40−2.26 (m, 1H), 2.21 (ddd, *J* = 11.5, 5.0, 5.0 Hz, 1H), 2.00 (ddd, *J* = 14.0, 7.0, 3.0 Hz, 1H), 1.90−1.25 (m, 9H), 1.16 (s, 3H), 1.15−1.00 (m, 42H). Anal. Calcd for $C_{36}H_{72}O_6Si_2$: C, 65.80; H, 11.04. Found: C, 65.37; H, 11.16.

Allylic Stannane 23. To a solution of **22** (198 mg, 0.30 mmol) and TMEDA (100 μL, 0.66 mmol) in THF (3 mL) at −78 °C was added *sec*-BuLi (660 μL of a 1.0 M solution in cyclohexane, 0.66 mmol), and the resulting mixture was stirred for 1 h. To this yellow solution was added tributyltin chloride (120 μL, 0.45 mmol), and the mixture was allowed to warm to room temperature. The reaction mixture was quenched with water and extracted with ether. The organic layer was washed with brine and concentrated. The residue was purified by chromatography (hexane/EtOAc/Et_3N, 200:20:1) to give **23** (92 mg, 69% based on 46% conversion) and **22** (107 mg, 54%). For **23**: colorless oil; $R_f = 0.21$ (hexane/EtOAc, 10:1); $[\alpha]^{23}_D$ +21.4° (*c* 1.16, $CHCl_3$); IR (neat) 3600−3200, 2950, 1650 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 5.78 (d, *J* = 6.0 Hz, 1H), 4.52 (ddd, *J* = 9.0, 9.0, 6.0 Hz, 1H), 4.26−4.21 (m, 1H), 3.86−3.68 (m, 2H), 3.69 (t, *J* = 6.0 Hz, 2H), 3.63−3.55 (m, 2H), 3.36 (dd, *J* = 11.5, 6.5 Hz, 1H), 3.18 (dd, *J* = 9.5, 2.5 Hz, 1H), 2.40−2.25 (m, 1H), 2.15 (ddd, *J* = 11.5, 5.0, 5.0 Hz, 1H), 2.00 (ddd, *J* = 14.0, 7.0, 3.0 Hz, 1H), 1.85−1.25 (m, 21H), 1.21 (s, 3H), 1.09−1.04 (m, 42H), 0.88 (t, *J* = 7.0 Hz, 9H), 0.86−0.80 (m, 6H). Anal. Calcd for $C_{48}H_{98}O_6Si_2Sn$: C, 60.93; H, 10.44. Found: C, 60.67; H, 10.39.

Aldehyde 24. To a stirred solution of **23** (203 mg, 0.21 mmol), DMSO (0.5 mL), and triethylamine (153 μL, 1.1 mmol) in CH_2Cl_2 (3 mL) at 0 °C was added sulfur trioxide pyridine complex (100 mg, 0.63 mmol), and the mixture was stirred at room temperature. After 4 h, the reaction mixture was diluted with ether and washed with water and brine. The organic layer was concentrated and purified by chromatography (hexane/EtOAc/Et_3N, 200:20:1) to give **24** (179 mg, 90%): colorless oil; $R_f = 0.47$ (hexane/EtOAc, 10:1); $[\alpha]^{27}_D$ +26.4° (*c* 1.55, $CHCl_3$); IR (neat) 2950, 1735, 1650 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 9.75 (s, 1H), 5.79 (d, *J* = 6.0 Hz, 1H), 4.56 (ddd, *J* = 9.0, 9.0, 6.0 Hz, 1H), 4.26−4.20 (m, 1H), 3.86−3.68 (m, 2H), 3.69 (t, *J* = 6.0 Hz, 2H), 3.38 (dd, *J* = 11.5, 6.5 Hz, 1H), 3.18 (dd, *J* = 9.5, 2.5 Hz, 1H), 2.62−2.50 (m, 2H), 2.40−1.90 (m, 3H), 1.85−1.25 (m, 21H), 1.20 (s, 3H), 1.09−1.04 (m, 42H), 0.87 (t, *J* = 7.0 Hz, 9H), 0.86−0.80 (m, 6H). Anal. Calcd for $C_{48}H_{96}O_6Si_2Sn$: C, 61.06; H, 10.25. Found: C, 61.03; H, 10.21.

Tricycle 6. To a stirred solution of boron trifluoride etherate (200 μL, 1.66 mmol) in CH_2Cl_2 (30 mL) at −78 °C was added a solution of **24** (1.30 g, 1.38 mmol) dropwise. After the reaction mixture was stirred for 0.5 h at −78 °C, the reaction was quenched with triethylamine (2 mL). The resulting mixture was diluted with ether, washed with brine, and concentrated. The residue was dissolved in ether (5 mL) and stirred with aqueous KF (5 mL) vigorously for 1 h. The resulting white precipitate (n-Bu_3SnF) was filtered off, and the filtrate was extracted with ether. The organic layer was washed with brine and concentrated. The residue was purified by chromatography (hexane/EtOAc, 10:1) to give **6** (850 m g, 94%): colorless needles, mp 137−138 °C (hexane); $R_f = 0.20$ (hexane/EtOAc, 10:1); $[\alpha]^{27}_D$ +19.8° (*c* 1.06, $CHCl_3$); IR (KBr) 3450, 2960 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 5.80 (ddd, *J* = 17.0, 10.5, 6.5 Hz, 1H), 5.34 (brd, *J* = 17.0 Hz, 1H), 5.18 (brd, *J* = 10.5 Hz, 1H), 4.20 (ddd, *J* = 3.0, 3.0, 2.5 Hz, 1H), 4.00 (dd, *J* = 6.0, 4.5 Hz, 1H), 3.86−3.72 (m, 3H), 3.69 (t, *J* = 6.0 Hz, 2H), 3.61 (dd, *J* = 12.0, 4.0 Hz, 1H), 3.20 (dd, 9.5, 2.5 Hz, 1H), 2.37−2.20 (m, 1H), 2.08−1.90 (m, 3H), 1.85−1.74 (m, 3H), 1.70−1.47 (m, 5H), 1.23 (s, 3H), 1.14−0.98 (m, 42H). Anal. Calcd for $C_{36}H_{70}O_6Si_2$: C, 66.00; H, 10.77. Found: C, 65.80; H, 10.68.

Acetate 25. The experimental procedure followed was as described for compound **18**. For **25**: colorless oil; $R_f = 0.32$ (hexane/EtOAc, 10:1); $[\alpha]^{26}_D$ +25.6° (*c* 1.30, $CHCl_3$); IR (neat) 2950, 1745 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 5.80 (ddd, *J* = 17.0, 10.5, 5.0 Hz, 1H), 5.36 (ddd, *J* = 17.0, 1.5, 1.5 Hz, 1H), 5.15 (ddd, *J* = 10.5, 1.5, 1.5 Hz, 1H), 5.00 (brd, *J* = 7.0 Hz, 1H), 4.24−4.17 (m, 2H), 3.86−3.71 (m, 2H), 3.70 (t, *J* = 6.0 Hz, 2H), 3.56 (dd, *J* = 12.0, 4.5 Hz, 1H), 3.20 (dd, *J* = 9.5, 2.5 Hz, 1H), 2.40−2.27 (m, 1H), 2.11 (s, 3H), 2.06−1.47 (m, 11H), 1.14−0.98 (m, 42H). Anal. Calcd for $C_{38}H_{72}O_7Si_2$: C, 65.47; H, 10.41. Found: C, 65.08; H, 10.09.

Unsaturated Ester 26. Ozone was passed through a solution of **25** (1.48 g, 2.12 mmol) in dichloromethane (50 mL) at −78 °C until the solution turned blue. The excess ozone was removed with a stream of oxygen, followed by addition of triphenylphosphine (1.1 g, 4.2 mmol). The mixture was allowed to warm to room temperature, concentrated, and dissolved in CH_2Cl_2 (50 mL). To the solution of crude aldehyde was added methyl (triphenylphosphoranylidene)acetate (1.4 g, 4.2 mmol), and the mixture was stirred at room temperature. After 17 h, the reaction mixture was concentrated and diluted with hexane. The resulting triphenylphosphine oxide was filtered off, and the solvent was removed in vacuo. The residue was purified by chromatography (hexane/EtOAc, 4:1) to give **26** (1.60 g, 100%): colorless oil; $R_f = 0.44$ (hexane/EtOAc, 4:1); $[\alpha]^{26}_D$ +9.8° (*c* 1.50, $CHCl_3$); IR (neat) 2950, 1730, 1660 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 6.88 ((dd, *J* = 15.0, 4.0 Hz, 1H), 6.13 (dd, *J* = 15.0, 2.0 Hz, 1H), 5.04 (brd, *J* = 6.5 Hz, 1H), 4.36 (ddd, *J* = 4.0, 2.0, 2.0 Hz, 1H), 4.24−4.19 (m, 1H), 3.87−3.75 (m, 1H), 3.75−3.67 (m, 1H), 3.74 (s, 3H), 3.70 (t, *J* = 6.0 Hz, 2H), 3.56 (dd, *J* = 12.0, 4.5 Hz, 1H), 3.20 (dd, *J* = 10.0, 2.5 Hz, 1H), 2.40−2.25 (m, 1H), 2.12 (s, 3H), 2.04−1.47 (m, 11H), 1.24 (s, 3H), 1.12−1.00 (m, 42H); HRMS (EI) calcd for $C_{37}H_{67}O_9Si_2$ (M − C_3H_7) 711.4324, found 711.4368. Anal. Calcd for $C_{40}H_{74}O_9Si_2$: C, 63.62; H, 9.88. Found: C, 63.32; H, 9.69.

Saturated Ester 27. A catalytic amount of 10% palladium on carbon was added to a stirred solution of **26** (465 mg, 0.62 mmol) in EtOAc (7 mL). A hydrogen atmosphere was introduced using a hydrogen-filled balloon by repeated evacuations (water aspirator). After 16 h, the catalyst was filtered off. The filtrate was concentrated and purified by chromatography (hexane/EtOAc, 4:1) to give **27** (469 mg, 100%): colorless oil; $R_f = 0.37$ (hexane/EtOAc, 4:1); $[\alpha]^{24}_D$ +20.6° (*c* 1.00, $CHCl_3$); IR (neat) 2950, 1745 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 4.87 (brd, *J* = 6.0 Hz, 1H), 4.22−4.18 (m, 1H), 3.86−3.71 (m, 2H), 3.70 (t, *J* = 6.0 Hz, 2H), 3.66 (s, 3H), 3.58 (ddd, *J* = 10.0, 4.0, 1.0 Hz, 1H), 3.34 (dd, *J* = 12.0, 4.5 Hz, 1H), 3.18 (dd, *J* = 9.5, 2.5 Hz, 1H), 2.45−2.25 (m, 3H), 2.08 (s, 3H), 2.05−1.40 (m, 13H), 1.19 (s, 3H), 1.15−1.00 (m, 42H). Anal. Calcd for $C_{40}H_{76}O_9Si_2$: C, 63.45; H, 10.12. Found: C, 63.16; H, 10.05.

Diol 28. The experimental procedure followed was as described for compound **21**. For **28**: colorless needles; mp 137−139 °C (hexane); $R_f = 0.34$ (hexane/EtOAc, 1:1); $[\alpha]^{26}_D$

+18.2° (*c* 1.52, $CHCl_3$); IR (neat) 3600−3100, 2950 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 4.20 (ddd, J = 3.0, 2.5, 2.5 Hz, 1H), 3.85−3.72 (m, 3H), 3.69 (t, J = 6.0 Hz, 2H), 3.66 (ddd, J = 6.0, 6.0, 1.5 Hz, 2H), 3.50−3.43 (m, 1H), 3.44 (dd, J = 12.0, 4.0 Hz, 1H), 3.20 (dd, J = 9.5, 2.5 Hz, 1H), 2.40−2.23 (m, 1H), 2.05−1.93 (m, 3H), 1.85−1.40 (m, 14H), 1.20 (s, 3H), 1.10−1.00 (m, 42H). Anal. Calcd for $C_{37}H_{74}O_7Si_2$: C, 64.67; H, 10.85. Found: C, 64.38; H, 10.65.

Allyl Ether 29. The experimental procedure followed was as described for compound **22**. For **29**: colorless oil; R_f = 0.20 (hexane/EtOAc, 4:1); IR (neat) 3600−3200, 2950 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 5.90 (dddd, J = 17.0, 10.0, 5.5, 5.5 Hz, 1H), 5.27 (dddd, J = 17.0, 1.5, 1.5, 1.5 Hz, 1H), 5.16 (dddd, J = 10.0, 1.5, 1.5, 1.5 Hz, 1H), 4.21−4.16 (m, 1H), 4.00 (dddd, J = 12.5, 5.5, 1.5, 1.5 Hz, 1H), 3.81 (dddd, J = 12.5, 5.5, 1.5, 1.5 Hz, 1H), 3.80−3.59 (m, 7H), 3.52 (dd, J = 12.0, 4.5 Hz, 1H), 3.45 (brd, J = 6.0 Hz, 1H), 3.17 (dd, J = 9.5, 3.0 Hz, 1H), 2.38−2.20 (m, 1H), 2.02−1.40 (m, 15H), 1.19 (s, 3H), 1.10−1.00 (m, 42H).

Pivalate 32. To a stirred solution of **21** (100 mg, 0.16 mmol) and pyridine (26 μL, 0.32 mmol) in CH_2Cl_2 (1 mL) at 0 °C was added pivaloyl chloride (23 μL, 0.19 mmol), and the mixture was stirred for 20 h at room temperature. The mixture was diluted with ether, washed with water and brine, and concentrated. The residue was purified by chromatography (hexane/EtOAc, 4:1) to give **32** (12 mg, 100%): colorless oil; R_f = 0.28 (hexane/EtOAc, 4:1); $[\alpha]^{20}_D$ +21.5° (*c* 3.16, $CHCl_3$); IR (neat) 2943, 1730 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 4.26−4.21 (m, 1H), 4.08−3.93 (m, 2H), 3.82 (ddd, J = 10.5, 7.0, 4.0 Hz, 1H), 3.77 (dd, J = 10.5, 6.0 Hz, 1H), 3.69 (t, J = 6.0 Hz, 2H), 3.56−3.46 (m, 1H), 3.15 (dd, J = 9.5, 2.5 Hz, 1H), 2.39−2.23 (m, 1H), 2.08 (ddd, J = 11.5, 5.0, 5.0 Hz, 1H), 1.98 (ddd, J = 14.0, 7.0, 3.0 Hz, 1H), 1.85−1.40 (m, 9H), 1.20 (s, 9H), 1.17 (s, 3H), 1.09−1.04 (m, 42). Anal. Calcd for $C_{38}H_{76}O_7Si_2$: C, 65.09; H, 10.92. Found: C, 65.07; H, 10.77.

Mixed Acetal 33. To stirred solution of **32** (112 mg, 0.16 mmol) and **31**[17] (170 μL, 0.48 mmol) in CH_2Cl_2 (1 mL) was added camphorsulfonic acid (CSA, 4 mg, 0.016 mmol). After 1 h, the reaction was quenched with triethylamine and filtered through Al_2O_3. The filtrate was concentrated and purified by chromatography (hexane/EtOAc/Et_3N, 200:10:1) to give **33** (144 mg, 85%) as a 1:1 diastereomeric mixture: colorless oil; R_f = 0.12 and 0.18 (hexane/EtOAc, 20:1); IR (neat) 2955, 1731 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 4.50 (t, J = 5.0 Hz, 0.5H), 4.48 (t, J = 5.0 Hz, 0.5H), 4.35−4.13 (m, 2H), 4.10−3.70 (m, 5H), 3.54 (dd, J = 6.5, 4.5 Hz, 1H), 3.27 (s, 1.5H), 3.24 (dd, J = 9.5, 2.5 Hz, 1H), 3.19 (s, 1.5H), 2.70−2.50 (m, 1H), 2.10−1.15 (m, 22H), 1.04−0.92 (m, 15H). Anal. Calcd for $C_{54}H_{110}O_8Si_2Sn$: C, 61.05; H, 10.44. Found: C, 60.89; H, 10.66.

Enol Ether 34. To a stirred solution of **33** (50 mg, 0.047 mmol) and hexamethyldisilazane (50 μL, 0.24 mmol) in CH_2Cl_2 (1 mL) at −15 °C was added trimethylsilyl iodide (TMSI, 20 mL, 0.14 mmol). After 1.5 h, the reaction was quenched with aqueous $NaHCO_3$ and extracted with ether. The organic layer was washed with brine, concentrated, and purified by chromatography (hexane/EtOAc/Et_3N, 200:10:1) to give **34** (40 mg, 83%): colorless oil; R_f = 0.28 (hexane/EtOAc, 20:1); $[\alpha]^{21}_D$ +32.9° (*c* 1.04, $CHCl_3$); IR (neat) 2956, 1732, 1651 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 5.76 (brd, J = 6.0 Hz, 1H), 4.71 (ddd, J = 9.0, 9.0, 5.0 Hz, 1H), 4.30−4.10 (m, 3H), 4.05−3.80 (m, 3H), 3.52 (dd, J = 11.5, 4.5 Hz, 1H), 3.25 (dd, J = 10.0, 2.5 Hz, 1H), 2.70−2.55 (m, 1H), 2.45 (ddd, J = 12.0, 5.0, 5.0 Hz, 1H), 2.05−1.40 (m, 24H), 1.37 (s, 3H), 1.32 (s, 9H), 1.25−1.20 (m, 42H), 1.15−1.04 (m, 6H), 1.06 (t, J = 7.0 Hz, 9H). Anal. Calcd for $C_{53}H_{106}O_7Si_2Sn$: C, 61.79; H, 10.37. Found: C, 61.41; H, 10.24.

Pivalate 35. The experimental procedure followed was as described for compound **32**. **35**: colorless oil; R_f = 0.39 (hexane/EtOAc, 4:1); $[\alpha]^{20}_D$ +14.8° (*c* 2.03, $CHCl_3$); IR (neat) 3452, 2943, 1730 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.24−4.18 (m, 1H), 4.14−4.00 (m, 2H), 3.86−3.66 (m, 5H), 3.48−3.35 (m, 2H), 3.20 (dd, J = 9.5, 2.5 Hz, 1H), 2.40−2.24 (m, 1H), 2.05−1.40 (m, 15H), 1.19 (s, 12H), 1.12−1.02 (m, 42H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.7, 85.7, 79.5, 75.3, 72.9, 72.6, 67.7, 64.2, 63.2, 62.4, 38.7, 36.5, 35.0, 33.0, 31.2, 30.6, 29.4, 28.3, 27.2, 25.3, 18.3, 18.3, 18.1, 16.1, 12.4, 12.0. Anal. Calcd for $C_{42}H_{82}O_8Si_2$: C, 65.41; H, 10.72. Found: C, 64.97; H, 10.41.

Mixed Acetal 36. The experimental procedure followed was as described for compound **33**. **36**: colorless oil; R_f = 0.28 (hexane/EtOAc, 10:1); IR (neat) 2925, 1732 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.37−4.29 (m, 1H), 4.22−4.17 (m, 1H), 4.06 (t, J = 6.2 Hz, 2H), 3.85−3.55 (m, 6H), 3.40 (dd, J = 12.5, 4.5 Hz, 1H), 3.26 (s, 1.5H), 3.23 (s, 1.5H), 3.19 (dd, J = 9.5, 2.5 Hz, 1H), 2.35−2.20 (m, 1H), 2.05−1.25 (m, 31H), 1.19 (s, 12H), 1.10−1.05 (m, 42H), 0.89 (t, J = 7.2 Hz, 9H), 0.85−0.80 (m, 6H). Anal. Calcd for $C_{58}H_{116}O_9Si_2Sn$: C, 61.52; H, 10.32. Found: C, 61.28; H, 10.02.

Enol Ether 37. The experimental procedure followed was as described for compound **34**. For **37**: colorless oil; R_f = 0.28 (hexane/EtOAc, 10:1); $[\alpha]^{19}_D$ −11.9° (*c* 1.34, $CHCl_3$); IR (neat) 2925, 1732, 1651 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.67 (br d, J = 6.0 Hz, 1H), 4.53 (ddd, J = 9.0, 9.0, 6.0 Hz, 1H), 4.06 (t, J = 6.5 Hz, 2H), 3.85−3.55 (m, 6H), 3.20 (dd, J = 9.5, 2.5 Hz, 1H), 2.35−2.20 (m, 1H), 2.00−1.25 (m, 29H), 1.19 (s, 12H), 1.10−1.05 (m, 42H), 0.89 (t, J = 7.2 Hz, 9H), 0.88−0.80 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.5, 139.7, 106.7, 84.9, 83.7, 79.6, 72.8, 72.6, 67.6, 64.2, 63.2, 62.35, 38.7, 26.5, 34.9, 33.3, 31.8, 30.6, 29.5, 29.2, 27.4, 27.2, 25.4, 25.0, 18.3, 18.1, 15.7, 13.8, 12.4, 12.0, 9.4, 6.4. Anal. Calcd for $C_{57}H_{112}O_8Si_2Sn$: C, 62.22; H, 10.26. Found: C, 62.87; H, 10.33.

Alcohol 30. To a stirred solution of **37** (464 mg, 0.42 mmol) in CH_2Cl_2 (5 mL) at −78 °C was added DIBALH (1.1 mL, 1.0 M in CH_2Cl_2, 1.1 mmol) dropwise. After 0.5 h, the mixture was diluted with ether and washed with aqueous sodium potassium tartrate and brine. The organic layer was concentrated and purified by chromatography (hexane/EtOAc/Et_3N, 200:50:1) to give **30** (408 mg, 96%): colorless oil; R_f = 0.20 (hexane/EtOAc, 4:1); $[\alpha]^{22}_D$ −21.0° (*c* 1.51, $CHCl_3$); IR (neat) 3600−3200, 2943, 1651 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.68 (brd, J = 6.0 Hz, 1H), 4.54 (ddd, J = 9.6, 8.5, 6.2 Hz, 1H), 4.23−4.18 (m, 1H), 3.85−3.57 (m, 8H), 3.43 (dd, J = 12.1, 4.4 Hz, 1H), 3.20 (dd, J = 9.8, 2.6 Hz, 1H), 2.35−2.20 (m, 1H), 2.05−1.23 (m, 29H), 1.20 (s, 3H), 1.10−1.00 (m, 42H), 0.90 (t, J = 7.2 Hz, 9H), 0.88−0.82 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.6, 106.5, 84.7, 83.9, 79.2, 76.8, 72.6, 72.4, 67.4, 65.7, 63.1, 62.4, 62.2, 36.4, 34.7, 33.1, 31.9, 30.4, 29.3, 29.2, 29.1, 27.3, 24.7, 18.2, 17.9, 15.5, 15.1, 13.6, 12.2, 11.9, 9.2, 6.2. Anal. Calcd for $C_{52}H_{104}O_7Si_2Sn$: C, 61.44; H, 10.31. Found: C, 61.64; H, 10.18.

Aldehyde 38. The experimental procedure followed was as described for compound **24**. For **38**: colorless oil; R_f = 0.46 (hexane/EtOAc, 4:1); $[\alpha]^{23}_D$ −16.1° (*c* 1.10, $CHCl_3$); IR (neat) 2943, 1728, 1651 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.76 (s, 1H), 5.67 (brd, J = 6.0 Hz, 1H), 4.55 (ddd, J = 9.5, 8.6, 6.0 Hz, 1H), 4.23−4.18 (m, 1H), 3.85−3.57 (m, 8H), 3.38 (dd, J = 12.1, 4.4 Hz, 1H), 3.20 (dd, J = 9.9, 2.5 Hz, 1H), 2.59 (ddd, J = 17.0, 8.0, 8.0 Hz, 1H), 2.46 (ddd, J = 17.0, 8.0, 8.0 Hz, 1H), 2.35−2.20 (m, 1H), 2.00−1.25 (m, 27H), 1.18 (s, 3H), 1.10−1.00 (m, 42H), 0.89 (t, J = 7.2 Hz, 9H), 0.87−0.83 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.0, 139.6, 106.9, 84.6, 83.1, 79.5, 76.9, 72.8, 72.5, 67.5, 63.2, 62.2, 40.8, 36.5, 34.9, 33.1, 30.5, 29.4, 29.2, 28.1, 27.3, 24.9, 18.3, 18.2, 18.0, 15.7, 13.7, 12.4, 12.0, 9.4, 6.3. Anal. Calcd for $C_{52}H_{102}O_7Si_2Sn$: C, 61.58; H, 10.14. Found: C, 61.65; H, 10.19.

Tetracycle 5. The experimental procedure followed was as described for compound **6**. For **5**: colorless needles; mp 94−95 °C (hexane); R_f = 0.14 (hexane/EtOAc, 4:1); $[\alpha]^{23}_D$ +29.6° (*c* 1.19, $CHCl_3$); IR (KBr) 3600−3200, 2943 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.91 (ddd, J = 17.0, 10.5, 6.0 Hz, 1H), 5.32 (ddd, J = 17.0, 1.5, 1.5 Hz, 1H), 5.20 (ddd, J = 10.5, 1.0, 1.0 Hz, 1H), 4.21−4.17 (m, 1H), 3.85−3.65 (m, 5H), 3.60−3.40 (m, 3H), 3.23 (dd, J = 12.2, 3.8 Hz, 1H), 3.18 (dd, J = 9.5, 2.6 Hz, 1H), 2.37−2.21 (m, 1H), 2.18−2.09 (m, 1H), 2.05−1.46 (m, 14H), 1.19 (s, 3H), 1.08−1.00 (m, 42H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.8, 115.9, 87.2, 84.8, 83.9, 82.5, 77.3, 74.1, 73.0, 72.7, 67.7, 63.2, 62.7, 37.2, 36.5, 33.0, 30.6, 29.7, 29.4, 29.3, 28.9, 18.3, 18.0, 16.2, 12.4, 12.0. Anal. Calcd for $C_{40}H_{76}O_7Si_2$: C, 66.25; H, 10.56. Found: C, 66.19; H, 10.59.

Alcohol 39. To a stirred solution of DMSO (13 μL, 0.18 mmol) in CH_2Cl_2 (0.5 mL) at −78 °C was added oxalyl chloride

(10 μL, 0.11 mmol). After this mixture was stirred for 10 min, a solution of **5** (26 mg, 0.036 mmol) in CH_2Cl_2 (0.5 mL) was added dropwise, and the resulting mixture was stirred for 0.5 h at that temperature. Triethylamine (50 μL, 0.36 mmol) was then added, and the resulting mixture was allowed to warm to room temperature with stirring. The mixture was diluted with ether and washed with water and brine. The organic layer was concentrated to give the crude ketone which was used for the next reaction without purification: R_f = 0.49 (hexane/EtOAc, 4:1); IR (neat) 2943, 1720, 1637 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.77 (ddd, *J* = 17.2, 10.6, 4.6 Hz, 1H), 5.46 (ddd, *J* = 17.2, 1.8, 1.8 Hz, 1H), 5.25 (ddd, *J* = 10.6, 1.8, 1.8 Hz, 1H), 4.37 (ddd, *J* = 4.6, 2.0, 2.0 Hz, 1H), 4.24−4.18 (m, 1H), 3.86−3.72 (m, 2H), 3.70 (t, *J* = 4.6, 2.0, 2.0 Hz, 2H), 3.56 (ddd, *J* = 9.5, 9.5, 4.1 Hz, 1H), 3.46 (dd, *J* = 12.1, 3.9 Hz, 1H), 3.22 (dd, *J* = 7.3, 2.5 Hz, 1H), 3.12 (ddd, *J* = 7.7, 7.7, 4.8 Hz, 1H), 2.86 (dd, *J* = 12.1, 10.5 Hz, 1H), 2.40−1.50 (m, 15H), 1.18 (s, 3H), 1.10−1.04 (m, 42H).

To a solution of the crude ketone in toluene (1 mL) at −78 °C was added methylmagnesium bromide (14 μL, 3.0 M in ether, 0.042 mmol), and the mixture was stirred for 1 h at that temperature. The reaction was quenched with water and extracted with ether. The organic layer was washed with brine and concentrated. The residue was purified by chromatography (hexane/EtOAc, 4:1) to give **39** (19 mg, 71%) and **40** (3 mg, 11%). For **39**: colorless oil; R_f = 0.18 (hexane/EtOAc, 4:1); $[\alpha]^{20}_D$ +36.7° (*c* 1.83, $CHCl_3$); IR (neat) 3600−3200, 2942 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.88 (ddd, *J* = 17.2, 10.6, 5.3 Hz, 1H), 5.28 (ddd, *J* = 17.2, 1.8, 1.8 Hz, 1H), 5.19 (ddd, *J* = 10.6, 1.8, 1.8 Hz, 1H), 4.21−4.17 (m, 1H), 3.85−3.73 (m, 3H), 3.69 (t, *J* = 6.0 Hz, 2H), 3.50−3.32 (m, 2H), 3.24 (ddd, *J* = 12.1, 3.9 Hz, 1H), 3.18 (dd, *J* = 9.8, 2.5 Hz, 1H), 2.46−1.45 (m, 16H), 1.18 (s, 3H), 1.10−1.03 (m, 45H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.7, 115.5, 87.9, 86.0, 84.9, 82.4, 77.3, 74.5, 73.0, 72.7, 67.7, 63.2, 62.6, 37.4, 36.5, 33.0, 30.6, 29.7, 29.4, 29.1, 24.5, 18.3, 18.0, 16.2, 12.4, 12.0. Anal. Calcd for $C_{41}H_{78}O_7Si_2$: C, 66.62; H, 10.64. Found: C, 66.26; H, 10.30. For **40**: colorless oil; R_f = 0.32 (hexane/EtOAc, 4:1); $[\alpha]^{20}_D$ +30.4° (*c* 1.29, $CHCl_3$); IR (neat) 3600−3200, 2942 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.94 (ddd, *J* = 17.2, 10.6, 5.3 Hz, 1H), 5.33 (ddd, *J* = 17.2, 1.8, 1.8 Hz, 1H), 5.27 (ddd, *J* = 10.6, 1.8, 1.8 Hz, 1H), 4.21−4.17 (m, 1H), 3.85−3.71 (m, 3H), 3.69 (t, *J* = 6.0 Hz, 2H), 3.54−3.36 (m, 2H), 3.22 (dd, *J* = 11.9, 3.9 Hz, 1H), 3.17 (dd, *J* = 10.1, 2.6 Hz, 1H), 2.36−1.46 (m, 16H), 1.18 (s, 3H), 1.16 (s, 3H), 1.10−1.01 (m, 42H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.6, 117.2, 89.3, 85.8, 83.9, 82.8, 77.3, 74.6, 73.0, 72.7, 67.6, 63.2, 62.6, 37.2, 36.6, 33.0, 30.6, 29.4, 29.2, 25.7, 18.3, 18.0, 15.8, 12.4, 12.0. Anal. Calcd for $C_{41}H_{78}O_7Si_2$: C, 66.62; H, 10.64. Found: C, 66.75; H, 10.54.

Silyl Ether 41. A stirred solution of **39** (102 mg, 0.14 mmol) and 2,6-lutidine (49 μL, 0.42 mmol) in CH_2Cl_2 (2 mL) was treated with *tert*-butyldimethylsilyl trifluoromethanesulfonate (TBSOTf, 71 μL, 0.31 mmol) at room temperature. After 9 h, the reaction mixture was diluted with ether and washed with water and brine. The organic layer was concentrated and purified by chromatography (hexane/EtOAc, 20:1) to give **41** (101 mg, 85%): colorless oil; R_f = 0.20 (hexane/EtOAc, 20:1); $[\alpha]^{20}_D$ +35.3° (*c* 1.40, $CHCl_3$); IR (KBr) 2943 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.89 (ddd, *J* = 17.2, 10.6, 3.8 Hz, 1H), 5.27 (ddd, *J* = 17.2, 2.0, 2.0 Hz, 1H), 5.12 (ddd, *J* = 10.6, 2.0, 2.0 Hz, 1H), 4.21−4.16 (m, 1H), 3.86−3.71 (m, 3H), 3.69 (t, *J* = 6.0 Hz, 2H), 3.46−3.28 (m, 2H), 3.24 (dd, *J* = 12.1, 3.8 Hz, 1H), 3.17 (dd, *J* = 9.8, 2.5 Hz, 1H), 2.37−1.45 (m, 16H), 1.18 (s, 3H), 1.08−1.02 (m, 45H), 0.94 (s, 9H), 0.08 (s, 3H), 0.05 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.9, 114.1, 87.6, 86.2, 85.1, 82.4, 77.3, 77.2, 72.9, 72.6, 67.6, 63.2, 62.6, 37.5, 37.4, 36.4, 33.1, 30.5, 29.7, 29.4, 28.9, 25.7, 24.7, 18.3, 18.2, 18.0, 16.2, 12.4, 12.0, −2.2, −2.3. Anal. Calcd for $C_{47}H_{92}O_7Si_3$: C, 66.14; H, 10.88. Found: C, 66.12; H, 10.71.

Unsaturated Ester 42. The experimental procedure followed was as described for compound **26**. For **42**: colorless oil; R_f = 0.31 (hexane/EtOAc, 10:1); $[\alpha]^{20}_D$ +36.3° (*c* 1.39, $CHCl_3$); IR (KBr) 2945, 1728, 1661 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.03 (dd, *J* = 15.6, 3.1 Hz, 1H), 6.07 (dd, *J* = 15.6, 2.0 Hz, 1H), 4.22−4.16 (m, 1H), 4.02−3.97 (m, 1H), 3.85−3.71 (m, 2H), 3.74 (s, 3H), 3.69 (t, *J* = 6.0 Hz, 2H), 3.44−3.30 (m, 2H), 3.22 (dd, *J* = 12.1, 3.8 Hz, 1H), 3.17 (dd, *J* = 9.7, 2.2 Hz, 1H), 2.34−2.10 (m, 2H), 2.05−1.48 (m, 14H), 1.17 (s, 3H), 1.10−1.02 (m, 45H), 0.87 (s, 9H), 0.09 (s, 9H), 0.08 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.0, 146.9, 120.1, 86.4, 86.3, 84.6, 82.6, 77.3, 77.2, 72.9, 72.6, 67.6, 63.2, 62.6, 51.4, 37.3, 36.4, 33.0, 30.5, 29.5, 29.4, 28.9, 25.7, 25.0, 18.2, 18.0, 16.0, 12.4, 12.0, −2.2, −2.4. Anal. Calcd for $C_{49}H_{94}O_9Si_3$: C, 64.57; H, 10.39. Found: C, 64.82; H, 10.35.

Saturated Ester 43. The experimental procedure followed was as described for compound **27**. For **43**: colorless oil; R_f = 0.27 (hexane/EtOAc, 10:1); $[\alpha]^{21}_D$ +29.8° (*c* 1.29, $CHCl_3$); IR (neat) 2943, 1744 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.22−4.16 (m, 1H), 3.85−3.63 (m, 4H), 3.67 (s, 3H), 3.36−3.25 (m, 2H), 3.25−3.12 (m, 3H), 2.46 (ddd, *J* = 15.6, 8.5, 5.5 Hz, 1H), 2.34 (ddd, *J* = 15.6, 15.6, 8.5 Hz, 1H), 2.20−1.46 (m, 18H), 1.18 (s, 3H), 1.10 (s, 3H), 1.15−1.00 (m, 42H), 0.83 (s, 9H), 0.06 (s, 3H), 0.05 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.1, 87.4, 86.5, 84.7, 82.5, 77.3, 77.0, 72.9, 72.6, 67.6, 63.2, 62.6, 51.5, 37.4, 36.4, 33.0, 31.6, 30.5, 29.4, 28.8, 25.8, 25.7, 23.9, 18.2, 18.0, 16.2, 12.4, 12.0, −2.2, −2.3. Anal. Calcd for $C_{49}H_{96}O_9Si_3$: C, 64.42; H, 10.59. Found: C, 64.51; H, 10.67.

Alcohol 44. The experimental procedure followed was as described for compound **21**. For **44**: solid; R_f = 0.37 (hexane/EtOAc, 4:1); $[\alpha]^{20}_D$ +30.1° (*c* 1.31, $CHCl_3$); IR (KBr) 3600−3200, 2945 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.21−4.17, (m, 1H), 3.85−3.62 (m, 6H), 3.42−3.13 (m, 5H), 2.38−1.45 (m, 20H), 1.19 (s, 3H), 1.10 (s, 3H), 1.10−1.00 (m, 42H), 0.83 (s, 9H), 0.07 (s, 3H), 0.06 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 88.4, 86.5, 84.8, 82.5, 77.2, 77.1, 72.9, 72.6, 67.6, 63.2, 62.8, 62.6, 37.4, 36.4, 33.0, 30.5, 30.2, 29.5, 29.4, 28.8, 26.4, 25.7, 23.8, 18.2, 18.0, 16.2, 12.3, 12.0, −2.2, −2.3.

Diene 45. To a stirred solution of **44** (44 mg, 0.050 mmol), DMSO (50 μL), and triethylamine (35 μL, 0.15 mmol) in CH_2Cl_2 (1 mL) at 0 °C was added sulfur trioxide pyridine complex (24 mg, 0.15 mmol), and the mixture was stirred at room temperature. After 1 h, the reaction mixture was diluted with ether and washed with water and brine. The organic layer was concentrated and purified by chromatography (hexane/EtOAc, 10:1) to give the corresponding aldehyde (36 mg, 81%): colorless oil; R_f = 0.29 (hexane/EtOAc, 10:1).

To a stirred suspension of $PhSe(CH_2)_3P^+Ph_3Br^-$ (49 mg, 0.09 mmol) in THF (1 mL) at −78 °C was added *n*-BuLi (52 μL, 1.57 M in hexane, 0.082 mmol). After this mixture was stirred for 0.5 h, HMPA (14 μL) and a solution of the aldehyde obtained above in THF (0.5 mL) were sequentially added, and the resulting mixture was allowed to warm to room temperature. After 0.5 h, the reaction was quenched with water and extracted with ether. The organic layer was washed with brine and concentrated.

To a solution of the crude selenide in THF (1 mL) were added $NaHCO_3$ (84 mg, 1.0 mmol) and H_2O_2 (0.3 mL of 30% solution), and the mixture was stirred for 4 h at room temperature. The reaction mixture was diluted with ether and washed with water and brine. The organic layer was concentrated and purified by chromatography (hexane/EtOAc, 10:1) to give **45** (34 mg, 91%): colorless oil; R_f = 0.49 (hexane/EtOAc, 10:1); $[\alpha]^{23}_D$ +20.3° (*c* 1.60, $CHCl_3$); IR (neat) 2943 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.65 (ddd, *J* = 16.9, 10.8, 10.8 Hz, 1H), 6.03 (t, *J* = 10.8 Hz, 1H), 5.48−5.37 (m, 1H), 5.30 (d, *J* = 16.9 Hz, 1H), 5.10 (d, *J* = 10.8 Hz, 1H), 4.22−4.17 (m, 1H), 3.85−3.72 (m, 2H), 3.69 (t, *J* = 6.0 Hz, 2H), 3.34−3.14 (m, 5H), 2.40−1.30 (m, 20H), 1.16 (s, 3H), 1.10−1.03 (m, 45H), 0.83 (s, 9H), 0.06 (s, 3H), 0.05 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 132.7, 132.1, 129.7, 117.1, 86.9, 86.3, 85.1, 82.4, 77.3, 72.9, 72.6, 67.6, 63.2, 62.6, 37.5, 36.4, 33.2, 30.5, 30.1, 29.6, 29.4, 28.8, 25.7, 24.7, 24.0, 18.3, 18.2, 18.0, 16.3, 12.4, 12.0, −2.2, −2.3.

Alcohol 46. The experimental procedure followed was as described for compound **17**. For **46**: colorless oil; R_f = 0.20 (hexane/EtOAc, 4:1); $[\alpha]^{21}_D$ +23.8° (*c* 0.95, $CHCl_3$); IR (neat) 3600−3200, 2943 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.65 (ddd, *J* = 16.9, 11.0, 11.0 Hz, 1H), 6.03 (t, *J* = 11.0 Hz, 1H), 5.49−5.39 (m, 1H), 5.20 (d, *J* = 16.9 Hz, 1H), 5.10 (d, *J* = 11.0 Hz, 1H), 4.21−4.17 (m, 1H), 3.90−3.73 (m, 2H), 3.70−3.60 (m, 2H), 3.33−3.14 (m, 5H), 2.45−1.30 (m, 20H), 1.17 (s, 3H), 1.10−

1.04 (m, 24H), 0.83 (s, 9H), 0.06 (s, 3H), 0.05 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 132.7, 132.1, 129.7, 117.1, 86.9, 86.3, 85.1, 82.2, 72.8, 67.5, 63.0, 62.8, 37.5, 36.7, 32.9, 30.8, 30.2, 30.1, 29.6, 28.7, 25.7, 24.7, 23.9, 18.2, 18.0, 16.3, 12.4, −2.2, −2.3. Anal. Calcd for $C_{42}H_{78}O_7Si_2$: C, 67.15; H, 10.47. Found: C, 67.56; H, 10.36.

Aldehyde 47. A stirred solution of **46** (19 mg, 0.025 mmol) in CH_2Cl_2 (0.5 mmol) was treated with Dess−Martin periodinane (32 mg, 0.075 mmol). After 0.5 h of stirring, the reaction mixture was diluted with ether and washed with aqueous $Na_2S_2O_3$, $NaHCO_3$, and brine. The organic layer was concentrated to give crude aldehyde which was used directly.

To a solution of the crude aldehyde obtained above and triethylamine (70 μL, 0.5 mmol) in CH_2Cl_2 (0.5 mmol) was added methylenedimethylammonium chloride (24 mg, 0.13 mmol), and the mixture was stirred for 15 h at room temperature. The reaction mixture was diluted with ether and washed with water and brine. The organic layer was concentrated and purified by chromatography (hexane/EtOAc, 10:1) to give **47** (17 mg, 89%): colorless oil; R_f = 0.20 (hexane/EtOAc, 10:1); $[\alpha]^{21}_D$ +45.2° (*c* 0.60, $CHCl_3$); IR (neat) 2945, 1695 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.54 (s, 1H), 6.65 (ddd, *J* = 16.9, 10.5, 10.5 Hz, 1H), 6.31 (s, 1H), 6.08 (s, 1H), 6.03 (t, *J* = 10.5 Hz, 1H), 5.49−5.39 (m, 1H), 5.20 (d, *J* = 16.9 Hz, 1H), 5.09 (d, *J* = 10.5 Hz, 1H), 4.24−4.20 (m, 1H), 4.00−3.82 (m, 2H), 3.39 (dd, *J* = 14.7, 11.8 Hz, 1H), 3.30−3.14 (m, 4H), 2.40−1.30 (m, 18H), 1.16 (s, 3H), 1.13−1.05 (m, 24H), 0.83 (s, 9H), 0.06 (s, 3H), 0.05 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.6, 148.2, 135.7, 132.8, 132.1, 129.7, 117.1, 86.9, 86.2, 85.1, 82.3, 72.7, 70.9, 67.6, 62.7, 37.5, 36.8, 32.9, 31.8, 30.1, 29.7, 28.8, 25.7, 24.7, 24.0, 18.3, 18.1, 16.2, 12.4, −2.1, −2.3; HRMS (FAB) calcd for $C_{43}H_{76}O_7Si_2Na$ (M + Na) 783.5028, found 783.4989.

Hemibrevetoxin B (1). A cooled (0 °C) solution of **47** (6.7 mg, 8.8 μmol) in a 1:1 mixture of CH_2Cl_2−CH_3CN (1 mL) was stirred under SiF_4 gas introduced using a balloon by repeated evacuations (water aspirator). After 1.5 h, the reaction was quenched with aqueous $NaHCO_3$ and extracted with EtOAc. The extract was washed with brine, concentrated, and purified by chromatography (hexane/EtOAc, 1:1) to give **1** (3.3 mg, 76%): colorless oil; R_f = 0.12 (hexane/EtOAc, 1:1); $[\alpha]^{22}_D$ +102° (*c* 0.09, $CHCl_3$) {lit.[3] $[\alpha]^{22}_D$ +115° (*c* 0.1, $CHCl_3$)}; IR (neat) 3600−3200, 2929, 1670 cm^{-1}; ^{1}H NMR (500 MHz, CD_2Cl_2) δ 9.52 (s, 1H), 6.69 (dddd, *J* = 16.9, 11.1, 10.1, 1.1 Hz, 1H), 6.37 (d, *J* = 0.9 Hz, 1H), 6.09 (d, *J* = 0.9 Hz, 1H), 6.04 (t, *J* = 11.0 Hz, 1H), 5.50−5.44 (m, 1H), 5.21 (d, *J* = 16.9 Hz, 1H), 5.10 (d, *J* = 10.1 Hz, 1H), 4.01−3.98 (m, 1H), 3.94−3.88 (m, 1H), 3.75 (ddd, *J* = 11.0, 10.1, 4.6 Hz, 1H), 3.35−3.30 (m, 2H), 3.26 (dd, *J* = 11.9, 4.1 Hz, 1H), 3.20 (dd, *J* = 9.6, 2.8 Hz, 1H), 3.16 (dd, *J* = 14.7, 9.9 Hz, 1H), 2.46 (dd, *J* = 14.5, 5.0 Hz, 1H), 2.34−2.29 (m, 2H), 2.28−2.26 (m, 1H), 2.22−2.14 (m, 1H), 1.97−1.30 (m, 14H), 1.19 (s, 3H), 1.07 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.9, 148.4, 136.4, 133.1, 132.6, 130.0, 117.3, 87.2, 86.3, 85.4, 82.6, 78.4, 74.7, 72.5, 71.0, 66.7, 62.9, 38.6, 37.9, 33.9, 33.2, 31.9, 30.7, 30.0, 29.3, 25.1, 23.7, 17.0; HRMS (FAB) calcd for $C_{28}H_{43}O_7$ (M + H) 491.3009, found 491.2965.

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