A New Synthesis of the Central Substructure of Botryococcenes

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The green, freshwater alga, *Botryococcus braunii*, is well-known for its ability to produce large quantities of hydrocarbons termed botryococcenes with the general formula C_nH_{2n-10} (n = 30−37).[1] Concentrations in the senescent phase of *B. braunii* are reported in the 70−90% range of its dry weight.[1−3] The alga, *B. braunii*, has received considerable interest because of its high potential to be a liquid fuel in the future. Botryococcene terpenoids are frequently found in many petroleum-rich deposits. In addition, botryococcane (perhydrobotryococcene) has been also discovered in the crude petroleum oils of Duri and Minas (Sumatra).[4] Botryococcane was also identified in a suite of coastal bitumens from 10 different stranding sites between Kingston, South Australia and Portland, Victoria.[5] The plain structure of the natural product C_{34}-botryococcene **1** was suggested by Cox and co-workers on the basis of chemical, spectral, and biosynthetic evidence.[6] The absolute stereochemistry of the two chiral centers in the methylenecyclohexane ring of braunicene **2** was elucidated by Poulter and co-workers.[7] The most influential reports on the structural elucidation of C_{34}-botryococcene **1** by chemical and spectroscopic means were White's 1986 and 1992 publications.[8] Recently, a new compound, 1,6,17,21-octahydrobotryococcene (**3**), has also been identified in sediment from Sacred Lake, Mount Kenya.[9]

Two independent syntheses of C_{34}-botryococcene **1** by White[10] and C_{30}-botryococcene **4** by Lee and Maxwell[11] have also appeared recently.

A key to the synthesis of botryococcenes lies in the efficient and stereoselective construction of the *E*-double bond, the C-13 methyl group, and the C-10 quaternary carbon center of the central substructure, which are common to all members of botryococcenes.

We now describe the synthesis of the central substructures such as **5** and **6** in a diastereomerically pure form. Our synthetic route to **6** is tactically different from those reported by White,[10] and Lee and Maxwell.[11]

The known allylic alcohol **8**,[12] readily prepared in 83% overall yield from methyl (*R*)-3-hydroxy-2-methylpropionate **7**, was epoxidized by means of Sharpless asymmetric epoxidation to yield 2,3-epoxy alcohol **9**[13] in 83% yield (98% ee). The optical purity of the epoxide **9** was also confirmed at the latter stage. Subsequent standard tosylation of **9** gave the 2,3-epoxy alcohol tosylate **10** in 74% yield.

Although a number of groups have contributed to methodology for the transformation of type **9** and **10** compounds into the allylic alcohol of type **11**,[14] some of these methods are still impractical in cases where the protective groups in the substrate tosylate are rather acid-labile and/or if research quantities of the allylic alcohol **11** are needed. Recently, Williams and co-workers reported the first total synthesis of (+)-breynolide via the MEM ether of allylic alcohol **11** which, in turn, was synthesized from 2,3-epoxy alcohol **9** in high yield by iodination with triphenylphosphine−iodine−imidazole followed by reductive elimination with *tert*-butyllithium.[13] Synthesis of some allylic alcohols from the corresponding 2,3-epoxy-1-iodoalkanes by treatment with *n*-butyllithium in place of *tert*-butyllithium was also reported by Marshall and co-workers.[14e] We recently developed a convenient and simple procedure for the transformation of the 2,3-epoxy alcohol tosylates into the corresponding allylic alcohols of type **11** by one-pot treatment with potassium iodide, followed by zinc dust and ammonium chloride, under mild reaction conditions.[15] Following this protocol, the tosylate **10** was converted into the allylic alcohol **11** in 92% isolated yield (de >98%; Mosher's ester). Acetylation of **11** followed by ozonolysis gave an aldehyde which, without purification, was treated with [(methoxycarbonyl)ethylidene]triphen-

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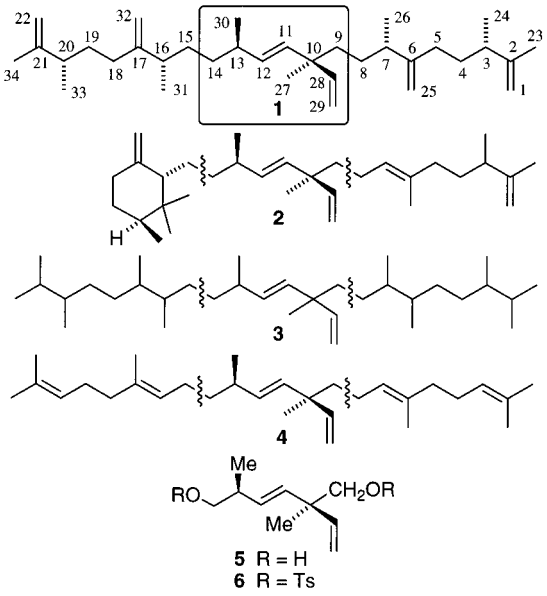
ylphosphorane to afford the α,β-(*E*)-unsaturated ester **14** in 79% yield from **11**. Although the stereochemistry and configuration of the α,β-enoate **14** was inferred from ^{1}H NMR analysis, the structure was unequivocally ascertained by a single-crystal X-ray analysis. Selective hydrolysis of the acetyl group in **14** with sodium carbonate in methanol gave the alcohol **15** in 83% yield which, on treatment with methanesulfonyl chloride and pyridine in the presence of a catalytic amount of 4-(dimethylamino)pyridine, yielded the rather labile mesylate **16** in 86% yield. Although the mesylate **16** could be synthesized in two steps from the mesylate **13** by exposure to ozone followed by [(methoxycarbonyl)ethylidene]triphenylphosphorane, the isolated yield of **16** was very low due to loss of the product during chromatographic purification.

Next, regio- and stereoselective transformation of the mesylate **16** into the desired α-vinyl-β,γ-enoate **21** was examined. Extensive stereochemical and mechanistic studies by the present authors,[16] Corey,[17] Trost,[18] Fleming,[19] Goering,[20] Marshall,[21] and Marino[22] on the substitution reaction of acetates, benzoates, and mesylates of allylic alcohols and of vinyloxiranes with organocopper and organocopper-Lewis acid reagents have shown that an anti S_N2' pathway is highly favored for substitution. In addition, as shown in Scheme 3, it has been well documented by the present authors that the highly anti S_N2'-selective nature of the reaction of γ-(mesyloxy)-α,β-enoates such as **17** with alkylcopper reagents (sp^3 carbon reagents) can be used to relay the stereochemistry at the γ-position to an α-position to yield alkylation products such as **18** via preferred conformation **B** in acyclic systems.[23]

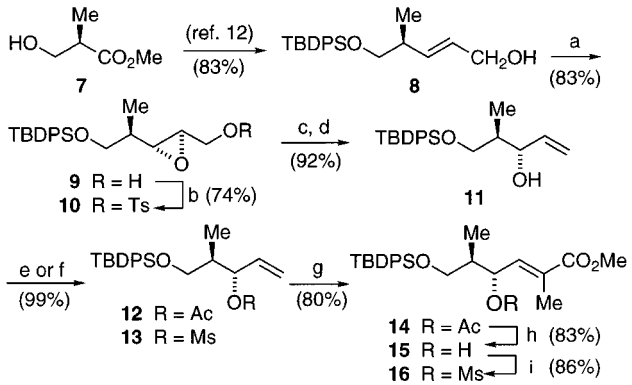
While seemingly straightforward, it was found that the conversion of the mesylate **16** into **21** by the use of ordinary sp^2 carbon organocopper reagents was rather more difficult than first envisioned.[24] In conjunction with the optimization process, the solvent, metal (Cu- and Zn-salts), vinyllithium, and vinylmagnesium halide were screened to maximize the expected anti S_N2' reaction. Some results are summarized in Table 1.

Scheme 1



1: C_{34}-Botryococcene; **2**: Braunicene; **3**: 1,6.17, 21-octahydrobotryococcene; **4**: C_{30}-botryococcene

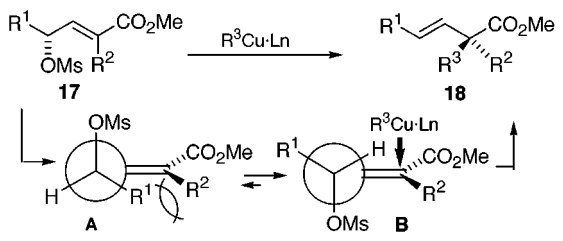
Scheme 2



Abbreviations: TBDPS = *t*-BuPh$_2$Si; Ts = 4-methylbenzenesulfonyl; Ms = methanesulfonyl.

Reagents and conditions: a) diisopropyl D-tartrate - Ti(OPr^i)$_4$ - Bu^{t}OOH, CH_2Cl_2, - 20 °C; b) TsCl-pyridine - 4-DMAP; c) KI in DMF, 55 °C, 1 h; d) Zn - NH_4Cl, 0 °C, 30 min; e) Ac_2O-pyridine - 4-DMAP, 0 °C, 2 h; f) MsCl - pyridine, rt, 3 h; g) i. ozone in *n*-hexane-$CHCl_3$ (1 : 1), - 78 °C; ii. Zn powder (2 equiv), 0 °C, 30 min; iii. Ph_3P=C(Me)CO_2Me; h) Na_2CO_3 in MeOH, rt, 8 h; i) MsCl - pyridine - 4-DMAP in CH_2Cl_2, 0 °C, 24 h.

Scheme 3



The reaction of the mesylate **16** with ordinary vinylcopper reagents or their Lewis acid complexes in THF at −78 °C yielded only the reduction product **19** as a 50:50 mixture of diastereomers (Scheme 4 and entries 1 and 2, Table 1). Similarly, the treatment of the mesylate **16** with a vinylcopper reagent, prepared from vinylzincate and cuprous cyanide, afforded exclusively the reduction product **19** (entry 3, Table 1). The drawback in these reactions has been remedied partially by the use of

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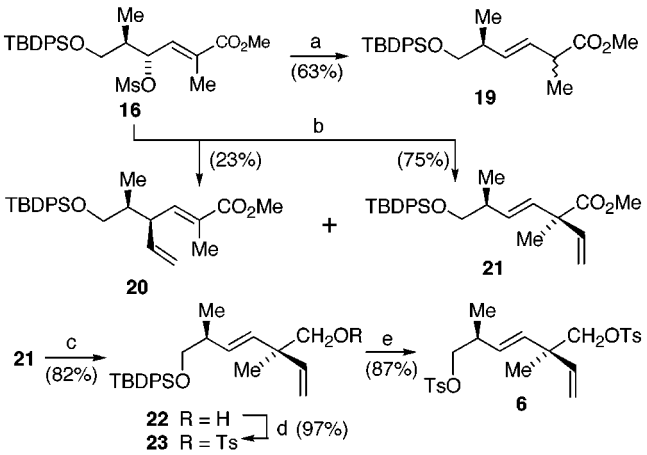
Table 1. Vinylcopper-Mediated Reactions of γ-(Mesyloxy)-α,β-enoate 16

entry	reagent	conditions[a]	product ratio **19**:**20**:**21**	combined isolated yield, %
1	$(vinyl)_2CuMgBr{\cdot}Mg(Br)I{\cdot}BF_3$	*b*	100:0:0	63
2	$(vinyl)_2Cu(CN)(MgBr)_2$	*b*	100:0:0	63
3	$(vinyl)_3ZnMgBr{\cdot}2Mg(Br)Cl{\cdot}2LiCl + 0.5CuCN$	*c*	100:0:0	92
4	$(vinyl)_2Cu(CN)(ZnCl)_2{\cdot}2Mg(Br)Cl{\cdot}4LiCl$	*d*	0:24:27	51
5	$(vinyl)_2Zn{\cdot}2LiCl + 0.5\ CuCN$	*d*	0:19:81	70
6	$(vinyl)_2Cu(CN)(ZnCl)_2{\cdot}4LiCl$	*e*	0:24:76	98

[a] All reactions were carried out in THF under a positive pressure of argon. [b] −78 °C, 2 h. [c] −78 °C, 3 h. [d] −78 °C, 1 h, and then 0 °C, 5 h. [e] −78 °C, 0.5 h, and then 0 °C, 5 h.

Scheme 4



Abbreviations: TBDPS = *t*-$BuPh_2Si$; Ts = 4-methylbenzenesulfonyl; Ms = methanesulfonyl.
Reagents and conditions: a) $(vinyl)_2Cu(CN)Li_2$, THF, - 78 °C, 30 min; b) $(vinyl)_2Cu(CN)(ZnCl)_2{\cdot}4LiCl$, THF, - 78 °C, 30 min and then 0 °C, 5 h; c) DIBAL in toluene, - 78 °C, 30 min; d) TsCl - pyridine -4-DMAP, rt, 16 h; e) i. *n*-Bu_4NF, THF, 0 °C, 7 h; ii. TsCl - pyridine - 4-DMAP, CH_2Cl_2, 0 °C, 14 h.

copper-catalyzed vinylzinc chloride giving the S_N2 and S_N2' substitution products **20** and **21** in rather low yield (entry 4, Table 1). Finally, the substrate **16** yielded the separable substitution products **20** and **21** in acceptable yields by treatment with either divinylzinc in the presence of 0.5 equiv of CuCN or "higher order" vinylzinc cuprate (entries 5 and 6, Table 1). By the use of a reagent shown in entry 6, the desired anti S_N2' product **21** could be obtained in 75% isolated yield after flash chromatographic separation from a small amount of the S_N2 product **20**.

Conversion of **21** into the target bis-tosylate **6** via the alcohol **22** and the tosylate **23** was achieved in a direct way. The ^1H and ^{13}C NMR spectra of synthesized **6** were found to be superimposable to the authentic spectra kindly provided by Professor White.[10] Since bis-tosylate **6** has been converted into C_{34}-botryococcene **1** in an elegant manner by White,[10] synthesis of **6** constitutes a formal synthesis of C_{34}-botryococcene **1**.

In summary, synthesis of the key intermediate **6** for botryococcene terpenoids has been accomplished starting from methyl (*R*)-3-hydroxy-2-methylpropionate (**7**).

Experimental Section

General Methods. All reactions were carried out under a positive pressure of argon. All glassware and syringes were dried in an electric oven at 100 °C prior to use. All melting points are uncorrected. For flash chromatographies, silica gel 60 H (silica gel for thin-layer chromatography, Merck) or silica gel 60 (finer than 230 mesh, Merck) was employed.

(2*R*,3*R*,4*S*)-5-(*tert*-Butyldiphenylsiloxy)-2,3-epoxy-4-methyl-1-pentanol (9). To a stirred suspension of diisopropyl D-tartrate (3.05 g, 13 mmol), $Ti(O^iPr)_4$ (2.84 g, 10 mmol), and 4A molecular sieves (500 mg, activated powder) in CH_2Cl_2 (15 mL) at −20 °C under argon was added 13.3 mL (40 mmol) of a 3.0 M solution of ^{t}BuOOH in isooctane, and the whole was stirred for 30 min at −20 °C. To the above mixture was added allyl alcohol **8** (3.546 g, 10 mmol) in CH_2Cl_2 (10 mL) at −20 °C and the mixture was allowed to stand for 26 h at −20 °C. The mixture was poured into a cold mixture of $FeSO_4{\cdot}7H_2O$ (16.68 g, 60 mmol), citric acid monohydrate (12.608 g, 60 mmol), and H_2O (120 mL). The mixture was extracted with Et_2O, and the extract was washed with 5% citric acid, 5% $NaHCO_3$, and brine and dried over $MgSO_4$. Concentration under reduced pressure gave an oily residue. To a vigorously stirred solution of the above residue in Et_2O (20 mL) at 0 °C was added 30 mL of 30% NaOH. The mixture was stirred for 1 h at 0 °C and extracted with Et_2O. The extract was washed with H_2O and dried over $MgSO_4$. Concentration under reduced pressure gave an oily residue, which was purified by flash chromatography over silica gel with *n*-hexane−AcOEt (5:1) to afford the epoxy alcohol **9** (3.088 g, 83% yield) as a colorless oil. Kugelrohr distillation, 170 °C (1 mmHg); $[\alpha]^{22}_D$ +11.4 (*c* 0.666, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$) δ 0.99 (d, J = 6.9 Hz, 3 H), 1.06 (s, 9 H), 1.62−1.78 (m, 2 H), 3.67 (dd, J = 9.9, 5.0 Hz, 1 H), 3.72 (dd, J = 9.9, 5.0 Hz, 1 H), 3.91 (ddd, J = 12.9, 5.6, 2.3 Hz, 1 H), 7.34−7.46 (m, 6 H), 7.64−7.69 (m, 4 H). Anal. Calcd for $C_{22}H_{30}O_3Si$: C, 71.31; H, 8.16. Found: C, 71.33; H, 8.30.

(3*R*,2*S*,4*S*)-5-(*tert*-Butyldiphenylsiloxy)-2,3-epoxy-4-methyl-[1-(4-methylbenzenesulfonyl)oxy]pentane (10). To a stirred solution of the epoxy alcohol **9** (371 mg, 1.0 mmol) in CH_2Cl_2 (10 mL) at −78 °C were added pyridine (2.24 mL, 33 mmol), 4-(dimethylamino)pyridine (12 mg, 0.10 mmol), and TsCl (210 mg, 4.4 mmol), and the mixture was stirred for 40 h at room temperature. To the stirred mixture was added 10 mL of 5% $NaHCO_3$ at 0 °C. After 1 h, the mixture was extracted with a mixed solvent of Et_2O and CH_2Cl_2 (4:1). The extract was washed with 5% citric acid, 5% $NaHCO_3$ and brine and dried over $MgSO_4$. Concentration under reduced pressure gave an oily residue, which was purified by flash chromatography over silica gel with *n*-hexane−AcOEt (5:1) to afford the tosylate (387 mg, 74% yield) as a colorless oil. $[\alpha]^{25}_D$ +11.75 (*c* 0.511, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$) δ 0.94 (d, J = 6.9 Hz, 3 H), 1.04 (s, 9 H), 1.66 (m, 1 H), 2.44 (s, 3 H), 2.84 (dd, J = 6.6, 2.3 Hz, 1 H), 3.04 (ddd, J = 6.3, 3.6, 2.3 Hz, 1 H), 3.61 (dd, J = 10.2, 4.2 Hz, 1 H), 3.66 (dd, J = 10.2, 4.2 Hz, 1 H), 3.95 (dd, J = 11.2, 6.3 Hz, 1 H), 4.20 (dd, J = 11.2, 3.6 Hz, 1 H), 7.59−7.67 (m, 4 H), 7.30−7.48 (m, 8 H), 7.80 (d, J = 8.3 Hz, 2 H); LRMS (FAB), *m*/*z*, 525 (MH^+), 467, 437, 353 (base peak), 333, 293, 269, 239, 197, 165, 135, 97, 91, 75. HRMS (FAB), *m*/*z*, calcd for $C_{29}H_{37}O_5SSi$ (MH): 525.2131; found: 525.2113.

(2*S*,3*S*)-1-(*tert*-Butyldiphenylsiloxy)-3-hydroxy-2-methyl-4-pentene (11). A mixture of the tosylate **10** (5.16 g, 9.85 mmol), KI (4.90 g, 30 mmol), and DMF (60 mL) was heated at 55 °C under stirring for 1.5 h. The mixture was cooled to 0 °C, where zinc powder (6.14 g, 98.5 mmol) and NH_4Cl (2.63 g, 49.3 mmol) were added with stirring, and the whole was stirred at 0 °C for 30 min. The mixture was diluted with 200 mL of Et_2O, and inorganic precipitates were removed by filtration. The filtrate was successively washed with 5% citric acid, 5% $NaHCO_3$, and water and dried over $MgSO_4$. The usual workup followed by flash chromatography over silica gel with *n*-hexane−EtOAc (4:1) gave 3.22 g (92% yield) the title compound

as a colorless oil. Kugelrohr distillation, 140 °C (1 mmHg); $[\alpha]^{22}_D$ −21.2 (*c* 0.179, $CHCl_3$); de = >98% (Mosher's ester); ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.85 (d, J = 7.0 Hz, 3 H), 1.06 (s, 9 H), 1.84 (m, 1 H), 3.62 (m, 2 H), 3.80 (dd, J = 10.2, 4.3 Hz, 1 H), 4.10 (m, 1H), 5.17 (ddd, J = 10.2, 2.0, 1.3 Hz, 1 H), 5.30 (ddd, J = 16.8, 1.7, 1.3 Hz, 1 H), 5.87 (ddd, J = 16.8, 10.2, 6.3 Hz, 1 H), 7.36−7.48 (m, 6 H), 7.66−7.70 (m, 4 H). Anal. Calcd for $C_{22}H_{30}O_2Si$: C, 74.53; H, 8.53. Found: C, 74.81; H, 8.75.

(2*S*,3*S*)-3-Acetoxy-1-(*tert*-butyldiphenylsiloxy)-2-methyl-4-pentene (12). To a stirred solution of the alcohol **11** (266 mg, 0.75 mmol) in CH_2Cl_2 (10 mL) were added pyridine (0.36 mL, 4.5 mmol), 4-(dimethylamino)pyridine (9 mg, 0.08 mmol), and acetic anhydride (0.17 mL, 2.25 mmol) at 0 °C, and the mixture was stirred for 2 h at room temperature. To the stirred mixture was added 10 mL of 5% $NaHCO_3$ at 0 °C. After 30 min, the mixture was extracted with Et_2O, and the extract was washed with 5% citric acid, 5% $NaHCO_3$, and brine and dried over $MgSO_4$. Concentration under reduced pressure gave an oily residue, which was purified by flash chromatography over silica gel with *n*-hexane−AcOEt (20:1) to afford the acetate **12** (294 mg, 99% yield) as a colorless oil. Kugelrohr distillation, 150 °C (1 mmHg); $[\alpha]^{22}_D$ −6.17 (*c* 0.486, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.94 (d, J = 6.9 Hz, 3 H), 1.05 (s, 9 H), 1.99 (s, 3 H), 2.06−1.94 (m, 1 H), 3.57 (d, J = 5.6 Hz, 2 H), 5.20 (ddd, J = 10.2, 1.7, 1.0 Hz, 1 H), 5.25 (ddd, J = 17.2, 1.7, 1.0 Hz, 1 H), 5.35 (dd, J = 6.9, 6.9 Hz, 1 H), 5.73 (ddd, J = 17.2, 10.2, 6.6 Hz, 1 H), 7.33−7.48 (m, 6 H), 7.59−7.70 (m, 4 H). Anal. Calcd for $C_{24}H_{32}O_3Si$: C, 72.68; H, 8.13. Found: C, 72.52; H, 8.01.

(2*S*,3*S*)-1-(*tert*-Butyldiphenylsiloxy)-3-[(methanesulfonyl)oxy]-2-methyl-4-pentene (13). To a stirred solution of the alcohol **11** (20 mg, 0.0565 mmol) in THF (0.5 mL) were added pyridine (0.1 mL) and methanesulfonyl chloride (0.02 mL) at −78 °C, and the mixture was stirred for 3 h at room temperature. To the above mixture was added 10 mL of 5% $NaHCO_3$ at 0 °C. After 30 min, the mixture was extracted with Et_2O−AcOEt (4:1), and the extract was washed with 5% citric acid, 5% $NaHCO_3$, and brine and dried over $MgSO_4$. Concentration under reduced pressure gave the title compound **13** (24 mg, 98%) as a rather labile oil. $[\alpha]^{23}_D$ −5.58 (*c* 0.203, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.91 (d, J = 7.0 Hz, 3 H), 0.89 (s, 9 H), 2.15 (m, 1 H), 2.95 (s, 3 H), 3.54 (dd, J = 10.0, 6.5 Hz, 1 H), 3.64 (dd, J = 10.0, 5.1 Hz, 1 H), 5.25 (dd, J = 7.5, 6.5 Hz, 1 H), 5.35−5.46 (m, 3 H), 5.85 (ddd, J = 18.0, 10.5, 8.4 Hz, 1 H), 7.3−7.5 (m, 6 H), 7.6−7.7 (m, 4 H). Due to its instability, the mesylate **13** was used directly for the next step.

Methyl (4*S*,5*R*,2*E*)-4-Acetoxy-6-(*tert*-butyldiphenylsiloxy)-2,5-dimethyl-2-hexenoate (14). Ozone was bubbled through a solution of the vinyl acetate **12** (3.0 g, 8.47 mmol) in 20 mL of *n*-hexane−$CHCl_3$ (1:1) at −78 °C until a blue color persisted. Zinc powder (1 g, 16 mmol) was added to the mixture, and the mixture was stirred for 30 min during which time it was allowed to warm to 0 °C. To the mixture at 0 °C was added [(methoxycarbonyl)ethylidene]triphenylphosphorane (19 g, 54.4 mmol), and the mixture was stirred for 18 h. The mixture was concentrated under reduced pressure to leave a semisolid, which was purified by flash chromatography over silica gel eluting with *n*-hexane−EtOAc (5:1) to give the enoate **14** (2.83 g, 80% yield). mp 90 °C (colorless crystals from *n*-hexane:Et_2O = 3:1); $[\alpha]^{16}_D$ −22.1 (*c* 0.797, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.94 (d, J = 6.8 Hz, 3 H), 1.05 (s, 9 H), 1.95 (s, 3 H), 1.99 (d, J = 1.4 Hz, 3 H), 3.55 (dd, J = 10.0, 5.4 Hz, 1 H), 3.62 (dd, J = 10.0, 5.1 Hz, 1 H), 3.74 (s, 3 H), 5.64 (dd, J = 9.5, 7.6 Hz, 1 H), 6.53 (dd, J = 9.5, 1.4 Hz, 1 H), 7.25−7.46 (m, 6 H), 7.62−7.66 (m, 4 H). Anal. Calcd for $C_{27}H_{36}O_5Si$: C, 69.20; H, 7.74. Found: C, 68.98; H, 7.77.

Methyl (4*S*,5*R*,2*E*)-6-(*tert*-Butyldiphenylsiloxy)-2,5-dimethyl-4-hydroxy-2-hexenoate (15). A mixture of the acetate **14** (1.0 g, 2.14 mmol), powdered Na_2CO_3 (900 mg, 8.56 mmol), and MeOH (60 mL) was stirred at room temperature for 8 h. The inorganic precipitates were removed by filtration. The filtrate was concentrated under reduced pressure to leave an oily residue. Water (10 mL) was added to the residue, and the whole was extracted with EtOAc−Et_2O (2:1). The extract was washed with water and dried over $MgSO_4$. Usual workup followed by flash chromatography over silica gel with *n*-hexane−EtOAc (1:4) gave 756 mg (83% yield) of the title compound **15** as a colorless oil. $[\alpha]^{16}_D$ −37.8 (*c* 0.880, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.79 (d, J = 7.3 Hz, 3 H), 1.07 (s, 9 H), 1.90 (d, J = 1.6 Hz, 3 H), 1.83−1.98 (m, 1 H), 3.67 (dd, J = 10.2, 7.3 Hz, 1 H), 3.73 (d, J = 3.3 Hz, 1 H), 3.75 (s, 3 H), 3.83 (dd, J = 10.2, 4.0 Hz, 1H), 4.50 (ddd, J = 9.2, 7.9, 3.3 Hz, 1 H), 6.72 (dq, J = 9.2, 1.6 Hz, 1 H), 7.37−7.52 (m, 6 H), 7.63−7.72 (m, 4 H); LR-MS (FAB), *m*/*z*, 427 (MH^+), 409, 379, 339, 269, 251, 239, 229, 213, 199 (base peak), 197, 165, 153, 135. HR-MS (FAB), *m*/*z*, calcd for $C_{25}H_{35}O_4Si$: 427.2304; found 427.2286. Anal. Calcd for $C_{25}H_{34}O_4Si$: C, 70.39; H, 8.03. Found: C, 70.12; H, 8.07.

Methyl (4*S*,5*R*,2*E*)-6-(*tert*-Butyldiphenylsiloxy)-2,5-dimethyl-4-[(methanesulfonyl)oxy]-2-hexenoate (16). To a stirred solution of alcohol **15** (1.0 g, 2.34 mmol) in CH_2Cl_2 (30 mL) were added pyridine (1.90 mL, 23.44 mmol), 4-(dimethylamino)pyridine (29 mg, 0.23 mmol), and methanesulfonyl chloride (0.90 mL, 11.72 mmol) at −78 °C, and the mixture was stirred for 24 h at 0 °C. To the stirred mixture was added 10 mL of 5% $NaHCO_3$ at 0 °C, and the whole was stirred for 30 min. The mixture was extracted with Et_2O, and the extract was washed with 5% citric acid, 5% $NaHCO_3$, and H_2O and dried over $MgSO_4$. Concentration under reduced pressure followed by recrystallization from cold hexane−Et_2O (3:1) gave 1.01 g (86% yield) of the title compound **16** as colorless crystals. Mp 87−88 °C; $[\alpha]^{20}_D$ −6.15 (*c* 0.156, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.91 (d, J = 7.0 Hz, 3 H), 1.07 (s, 9 H), 2.00 (d, J = 1.3 Hz, 3 H), 2.11 (m, 1 H), 2.88 (s, 3 H), 3.52 (dd, J = 10.5, 5.9 Hz, 1 H), 3.69 (dd, J = 10.5, 4.6 Hz, 1 H), 3.77 (s, 3 H), 5.63 (dd, J = 9.7, 6.5 Hz, 1 H), 6.68 (dd, J = 9.7, 1.4 Hz, 1 H), 7.26−7.44 (m, 6 H), 7.61−7.69 (m, 4 H). Anal. Calcd for $C_{26}H_{36}O_6SSi$: C, 61.88; H, 7.19. Found: C, 61.60; H, 7.29.

Methyl (5*S*,3*E*)-6-(*tert*-Butyldiphenylsiloxy)-2,5-dimethyl-3-hexenoate (19). To a stirred suspension of CuCN (105 mg, 1.17 mmol) in dry THF (15 mL) at −78 °C under argon was added a 1.0 M THF solution of vinylmagnesium bromide (2.34 mL, 2.34 mmol). After 10 min, to the stirred mixture was added the mesylate **16** (148 mg, 0.293 mmol) in dry THF (2 mL) at −78 °C, and the mixture was stirred for 30 min at −78 °C. The reaction was quenched with a 1:1 mixed solution of sat. NH_4Cl (2 mL) and 28% NH_4OH (2 mL) at −78 °C. The mixture was extracted with Et_2O, and the extract was washed with H_2O and dried over $MgSO_4$. Concentration under reduced pressure gave an oily residue, which was purified by flash chromatography over silica gel. Elution with *n*-hexane−AcOEt (20:1) gave 76 mg (63% yield) of the β,γ-unsaturated ester **19** as a colorless oil. $[\alpha]^{30}_D$ −4.1 (*c* 0.13, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.02 (d, J = 6.9 Hz, 3 H), 1.04 (s, 9 H), 1.23 (d, J = 6.9 Hz, 3 H), 2.35 (m, 1 H), 3.10 (m, 1 H), 3.50 (m, 2 H), 3.65 (s, 1.5 H), 3.66 (s, 1.5 H), 5.44−5.59 (m, 2 H), 7.25−7.45 (m, 6 H), 7.63−7.24 (m, 4 H). LRMS (FAB) *m*/*z*, 411 (MH^+), 409, 353, 333, 243, 213 (base peak), 199, 135, 95. HRMS (FAB) *m*/*z*, calcd for $C_{25}H_{35}O_3Si$ (MH^+) 411.2355; found: 411.2362.

Methyl (4*S*,5*S*,2*E*)-6-(*tert*-Butyldiphenylsiloxy)-2,5-dimethyl-4-ethenyl-2-hexenoate (20) and Methyl (2*S*,5*S*,3*E*)-6-(*tert*-Butyldiphenylsiloxy)-2,5-dimethyl-2-ethenyl-3-hexenoate (21). To a stirred solution of LiCl (81 mg, 9.36 mmol) in dry THF (15 mL) at −78 °C under argon were successively added a 1.0 M ethereal solution of $ZnCl_2$ (9.35 mL, 9.36 mmol), a 0.6 M THF solution of vinyllithium (15.6 mL, 9.36 mmol), and CuCN (419 mg, 4.68 mmol). After 10 min, to the stirred mixture was added the mesylate **16** (1.18 g, 2.34 mmol) in dry THF (10 mL) at −78 °C, and the mixture was stirred for 30 min at −78 °C and for 5 h at 0 °C. The reaction was quenched with a 1:1 mixed solution of sat. NH_4Cl (20 mL) and 28% NH_4OH (20 mL) at −78 °C. The mixture was extracted with Et_2O, and the extract was washed with H_2O and dried over $MgSO_4$. Concentration under reduced pressure gave an oily residue, which was purified by flash chromatography over silica gel. Elution with *n*-hexane−AcOEt (20:1) gave 775 mg (75% yield) of the β,γ-unsaturated ester **21** as a colorless oil and further elution afforded 243 mg (23% yield) of the α,β-unsaturated ester **20** as a colorless oil. **20**: $[\alpha]^{24}_D$ −33.1 (*c* 0.324, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.92 (d, J = 6.9 Hz, 3 H), 1.05 (s, 9 H), 1.76 (m, 1 H), 1.85 (d, J = 1.7 Hz, 3 H), 3.29 (m, 1 H), 3.49 (dd, J = 9.9, 5.6 Hz, 1 H), 3.52 (dd, J = 9.9, 5.9 Hz, 1 H), 3.73 (s, 3 H), 5.03 (d, J = 16.2 Hz, 1 H), 5.04 (d, J = 10.3 Hz, 1 H), 5.66 (ddd, J = 16.2, 11.2, 8.2 Hz, 1 H), 6.74 (dd, J = 10.3, 1.7 Hz, 1 H), 7.32−7.45 (m, 6 H), 7.60−7.67 (m, 4 H); LR-MS (FAB), *m*/*z*, 437 (MH^+), 435, 405, 379, 359, 213 (base peak), 199, 183, 135. HR-MS

(FAB), *m*/*z*, calcd for $C_{27}H_{37}O_3Si$: 437.2512; found: 437.2537. Anal. Calcd for $C_{27}H_{36}O_3Si$: C, 74.27; H, 8.31. Found: C, 74.13; H, 8.26. **21**: Kugelrohr distillation, 150 °C (1 mmHg); $[\alpha]^{20}_D$ −1.57 (*c* 0.510, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.02 (d, *J* = 6.9 Hz, 3 H), 1.04 (s, 9 H), 1.39 (s, 3 H), 2.42 (m, 1 H), 3.51 (m, 2 H), 3.66 (s, 3 H), 5.10 (dd, *J* = 17.5, 0.7 Hz, 1 H), 5.12 (dd, *J* = 10.9, 1.0 Hz, 1 H), 5.51 (dd, *J* = 15.8, 6.9 Hz, 1 H), 5.70 (dd, *J* = 15.8, 1.0 Hz, 1 H), 6.06 (dd, *J* = 17.5, 10.9 Hz, 1 H), 7.33−7.47 (m, 6 H), 7.64−7.67 (m, 4 H). Anal. Calcd for $C_{27}H_{36}O_3Si$: C, 74.27; H, 8.31. Found: C, 74.19; H, 8.53.

(2*S*,5*S*,3*E*)-6-(*tert*-Butyldiphenylsiloxy)-2,5-dimethyl-2-ethenyl-3-hexen-1-ol (22). To a stirred solution of the ester **21** (655 mg, 1.5 mmol) in CH_2Cl_2 (15 mL) at −78 °C under argon was added a 1.02 M solution of DIBAL in toluene (3.09 mL, 3.15 mmol), and the mixture was stirred for 30 min at −78 °C. The mixture was poured into a cold solution of saturated NH_4Cl (10 mL) at 0 °C. The mixture was made acidic with 30 mL of saturated citric acid and extracted with Et_2O−CH_2Cl_2 (4:1). The extract was washed with 5% $NaHCO_3$ and water and dried over $MgSO_4$. Concentration under reduced pressure gave an oily residue, which was purified by flash chromatography over silica gel with *n*-hexane−AcOEt (15:1) to give the alcohol **22** (505 mg, 82% yield) as a colorless oil. Kugelrohr distillation, 150 °C (1 mmHg); $[\alpha]^{20}_D$ −6.95 (*c* 1.09, $CHCl_3$); IR ($CHCl_3$) 3600, 3060, 2960, 2930, 2850, 1460, 1415, 1380, 1360, 1105, 1025, 980, 920, 800, 610 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.00 (d, *J* = 6.9 Hz, 3 H), 1.05 (s, 9 H), 1.12 (s, 3 H), 1.37 (t, *J* = 6.6 Hz, 1 H), 2.40 (m, 1 H), 3.39 (m, 2 H), 3.50 (m, 2 H), 5.09 (dd, *J* = 17.5, 1.3 Hz, 1 H), 5.13 (dd, *J* = 10.9, 1.3 Hz, 1 H), 5.42 (d, *J* = 16.2 Hz, 1 H), 5.49 (dd, *J* = 16.2, 5.6 Hz, 1 H), 5.81 (dd, *J* = 17.5, 10.9 Hz, 1 H), 7.33−7.46 (m, 6 H), 7.63−7.72 (m, 4 H). Anal. Calcd for $C_{26}H_{36}O_2Si$: C, 76.42; H, 8.88. Found: C, 76.12; H, 9.08.

(2*S*,5*S*,3*E*)-6-(*tert*-Butyldiphenylsiloxy)-2,5-dimethyl-2-ethenyl-1-[(4-methylbenzenesulfonyl)oxy]-3-hexene (23). To a stirred solution of the alcohol **22** (347 mg, 0.85 mmol) in CH_2Cl_2 (5 mL) were added pyridine (0.96 mL, 11.87 mmol), 4-(dimethylamino)pyridine (30 mg, 0.25 mmol), and 4-methylbenzenesulfonyl chloride (1.06 g, 5.54 mmol) at −78 °C, and the mixture was stirred for 16 h at room temperature. The reaction was quenched with 5% $NaHCO_3$ (30 mL) at 0 °C, and the whole was stirred for 1 h at room temperature. The mixture was extracted with Et_2O, and the extract was washed with 5% citric acid, 5% $NaHCO_3$, and H_2O and dried over $MgSO_4$. Concentration under reduced pressure gave an oily residue, which was purified by flash chromatography over silica gel with *n*-hexane−AcOEt (15:1) to give 464 mg (97% yield) of the title compound **23** as a colorless oil. $[\alpha]^{20}_D$ −3.12 (*c* 0.961, $CHCl_3$);^{1}H NMR (270 MHz, $CDCl_3$) δ 0.96 (d, *J* = 6.6 Hz, 3 H), 1.02 (s, 9 H), 1.10 (s, 3 H), 2.33 (m, 1 H), 2.42 (s, 3 H), 3.44 (dd, *J* = 9.9, 6.3 Hz, 1 H), 3.47 (dd, *J* = 9.9, 6.3 Hz, 1 H), 3.78 (d, *J* = 9.2 Hz, 1 H), 3.81 (d, *J* = 9.2 Hz, 1 H), 4.99 (dd, *J* = 17.5, 1.0 Hz, 1 H), 5.05 (dd, *J* = 10.9, 1.0 Hz, 1 H), 5.30 (d, *J* = 15.8 Hz, 1 H), 5.41 (dd, *J* = 15.8, 6.6 Hz, 1 H), 5.70 (dd, *J* = 17.5, 10.9 Hz, 1 H), 7.63 (m, 4 H), 7.25−7.45 (m, 8 H), 7.75 (m, 2 H); LR-MS (FAB), *m*/*z*, 563 (MH^+), 561, 505, 391, 353, 333, 293, 269, 239, 197, 165, 135 (base peak), 93, 91, 55, 41. HR-MS, *m*/*z* calcd for $C_{33}H_{43}O_4SiS$: 563.2651; found: 563.2654.

(2*S*,5*S*,3*E*)-1,6-Bis[(4-methylbenzenesulfonyl)oxy]-2,5-dimethyl-2-ethenyl-3-hexene (6). To a stirred solution of the silyl ether **23** (93 mg, 0.17 mmol) in THF (3 mL) were added 0.18 mL (0.18 mmol) of a 1.0 M THF solution of tetrabutylammonium fluoride at 0 °C, and the mixture was stirred for 7 h at room temperature. To the mixture was added 10 mL of H_2O, and the mixture was extracted with $CHCl_3$. The extract was washed with water and dried over $MgSO_4$. Concentration under reduced pressure gave an oily residue, which was dissolved in 4 mL of CH_2Cl_2. To a stirred CH_2Cl_2 solution were added pyridine (0.50 mL, 6.18 mmol), 4-(dimethylamino)pyridine (10 mg, 0.08 mmol), and 4-methylbenzenesulfonyl chloride (157 mg, 0.83 mmol) at 0 °C. After 14 h, to the stirred mixture was added 5 mL of 5% $NaHCO_3$ at 0 °C, and the whole was stirred for 1 h. The mixture was extracted with Et_2O−CH_2Cl_2 (1:4), and the extract was washed with 5% citric acid, 5% $NaHCO_3$, and H_2O and dried over $MgSO_4$. Concentration under reduced pressure gave an oily residue, which was purified by flash chromatography over silica gel with *n*-hexane−AcOEt (2:1) to give the title compound **6** (69 mg, 87% yield) as a colorless oil: $[\alpha]^{20}_D$ +5.94 (*c* 1.310, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.95 (d, *J* = 6.8 Hz, 3 H), 1.06 (s, 3 H), 2.45 (s, 6 H), 2.46 (m, 1 H), 3.77 (s, 2 H), 3.78 (dd, *J* = 9.5, 6.7 Hz, 1 H), 3.84 (dd, *J* = 9.4, 6.4 Hz, 1 H), 4.97 (dd, *J* = 17.5, 0.9 Hz, 1 H), 5.06 (dd, *J* = 10.7, 0.9 Hz, 1 H), 5.21 (dd, *J* = 15.9, 7.0 Hz, 1 H), 5.34 (dd, *J* = 15.9, 0.8 Hz, 1 H), 5.64 (dd, *J* = 17.5, 10.8 Hz, 1 H), 7.35 (m, 4 H), 7.76 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.52, 21.18, 21.65, 36.35, 42.81, 73.97, 75.63, 114.96, 127.89, 129.86, 130.78, 132.95, 133.16, 134.10, 140.63, 144.81. The ^{1}H and ^{13}C NMR spectra were found to be identical with those of authentic spectra of Professor White.

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Supporting Information Available: Copies of ^{1}H NMR spectra of compounds **6**, **10**, **13**, **19**, **20**, and **23** and ^{13}C NMR spectrum of **6** (7 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.

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