atmosphere of H_2 (65 psi) in a Parr hydrogenator apparatus for 48 h. The catalyst was removed by suction filtration and the filtrate concentrated under reduced pressure. The residue was purified by flash chromatography (1:3 hexanes/EtOAc) to provide 0.091 g (99%) of **23** as a clear colorless oil: $[\alpha]^{23}_D$ = 25.5° (c = 1.0, $CHCl_3$); ^1H NMR (300 MHz) δ 5.05 (ddd, J = 8.5, 3.9, 3.3 Hz, 1 H), 4.86 (dd, J = 8.5, 1.7 Hz, 1 H), 4.29 (ddd, J = 8.1, 6.3, 4.8 Hz, 1 H), 4.16 (dd, J = 8.6, 6.3 Hz, 1 H), 3.90 (dd, J = 8.6, 4.8 Hz, 1 H), 3.79 (d, J = 11.8 Hz, 1 H), 3.73 (J = 8.1, 1.7 Hz, 1 H), 3.52 (d, J = 11.8 Hz, 1 H), 3.29 (s, 3 H), 2.62 (dd, J = 16.0, 3.9 Hz, 1 H), 1.80 (br s, 1 H), 1.78 (dd, J = 16.0, 3.3 Hz, 1 H), 1.42 (s, 3 H), 1.36 (s, 3 H); ^{13}C NMR (75 MHz) δ 154.0, 109.7, 99.1, 73.3, 72.9, 72.3, 68.7, 67.5, 48.5, 30.4, 26.7, 25.0; IR ν 1805 cm^{-1}; mass spectrum m/z 304.1165 ($C_{13}H_{20}O_8$ requires 304.1158), 289, 273, 257, 153, 11, 101, 95, 43.

Methyl 3-Deoxy-7,8-*O*-(1-methylethylidene)-α-D-*manno*-octos-2-ulo-2,6-pyranoside, Cyclic Carbonate (25). To a solution of DMSO (0.086 g, 1.1 mmol) in CH_2Cl_2 (4 mL) at −78 °C was added oxalyl chloride (0.070 g, 0.55 mmol). The solution was stirred for 15 min, and alcohol **23** (0.0834 g, 0.274 mmol) dissolved in CH_2Cl_2 (5 mL) was added dropwise. After 15 min at −78 °C, triethylamine (0.17 g, 2.2 mmol) was added, and the solution was stirred for 0.5 h while warming to rt. The reaction mixture was poured into saturated $NaHCO_3$ (5 mL), and the mixture was extracted with ether (3 × 10 mL). The combined organic extracts were washed with saturated $NaHCO_3$ (5 mL), dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by flash chromatography (3:2 hexanes/EtOAc) to furnish 0.067 g (80%) of **25** as a clear colorless oil; $[\alpha]^{23}_D$ +40.3° (c = 1.0, $CHCl_3$); ^1H NMR (300 MHz) δ 9.48 (s, 1 H), 5.04 (ddd, J = 8.5, 3.6, 2.9 Hz, 1 H), 4.91 (dd, J = 8.5, 1.7 Hz, 1 H), 4.41 (ddd, J = 8.1, 6.2, 4.6 Hz, 1 H), 4.23 (dd, J = 8.6, 6.2 Hz, 1 H), 3.98 (dd, J = 8.6, 4.6 Hz, 1 H), 3.82 (dd, J = 8.1, 1.7 Hz, 1 H), 3.32 (s, 3 H), 2.60 (dd, J = 16.2, 3.6 Hz, 1 H), 1.95 (dd, J = 16.2, 2.9 Hz, 1 H), 1.45 (s, 3 H), 1.39 (s, 3 H); ^{13}C NMR (75 MHz) δ 197.4, 153.3, 109.9, 98.6, 72.8, 72.5, 71.2, 70.5, 67.0, 51.1, 30.9, 26.8, 24.9; IR ν 1805 cm^{-1}; mass spectrum m/z 287.0759 [$C_{12}H_{15}O_8$ ($M^+ - CH_3$) requires 287.0767], 273, 111, 101, 95, 43.

Methyl 3-Deoxy-7,8-*O*-(1-methylethylidene)-α-D-*manno*-octos-2-ulo-2,6-pyranosonic Acid (26). A mixture of **25** (0.014 g, 0.045 mmol) and Ag_2O (0.011 g, 0.045 mmol) in 2 N NaOH (0.11 mL) and 50% aqueous EtOH (0.4 mL) was stirred for 24 h at rt with the exclusion of light. The solids were removed by filtration through a pad of Celite, and the filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography on purified cellulose (1:1 $CHCl_3$/MeOH) to deliver 0.13 g (96%) of **26** as a white solid: $[\alpha]^{23}_D$ = +43.4° (c = 0.3, H_2O); ^1H NMR (300 MHz, D_2O) δ 4.41 (m, 1 H), 4.24 (dd, J = 9.0, 6.1 Hz, 1 H), 4.08 (dd, J = 9.0, 4.6 Hz, 1 H), 4.02 (m, 1 H), 3.91 (d, J = 2.2 Hz, 1 H), 3.56 (d, J = 8.2 Hz, 1 H), 3.15 (s, 3 H), 2.00 (dd, J = 13.4, 5.1 Hz, 1 H), 1.76 (dd, J = 13.4, 12.8 Hz, 1 H), 1.44 (s, 3 H), 1.39 (s, 3 H); ^{13}C NMR (75 MHz, D_2O) δ 175.3, 109.6, 100.7, 73.4, 72.7, 67.4, 66.5, 65.4, 50.5, 34.8, 25.7, 24.2; IR (film) ν 1690 cm^{-1}; mass spectrum 277.0929 [$C_{11}H_{17}O_8$ ($M^+ - CH_3$) requires 277.0923], 262, 201, 44.

3-Deoxy-α-D-*manno*-2-octulopyranosonic Acid, Ammonium Salt [(+)-KDO] (1). The pH of a solution of **26** (0.139 g, 0.52 mmol) in water (2 mL) was adjusted to <2 with Dowex 50 W (H^+), and the mixture was heated with stirring at 80–85 °C for 1.5 h. The pH was adjusted to 10 with NH_4OH (5%) and the solution stored at 0 °C for 24 h. The pH of the solution was then adjusted to 7 with Dowex 50 W (H^+), and the water was removed by lyophilization. The crude (+)-KDO was then purified by sequential chromatography on cellulose (MeOH/$CHCl_3$/H_2O (10:10:1)) followed by passage of the resulting solution through Sephadex G-10. The combined filtrates were concentrated in vacuo to afford 0.059 g (44%) of the ammonium salt of **1** as a white solid that was identical (mp, mixed mp, ^1H and ^{13}C NMR, $[\alpha]_D$, and TLC) with a commerical sample purchased from Sigma Chemical Co: mp = 121.5–123 °C (lit.[25] mp = 121.5–123 °C); $[\alpha]^{23}_D$ = +42.4° [c = 1.7, H_2O (lit.[25] $[\alpha]^{23}_D$ = +41.5°, c = 1.7, H_2O)]; ^1H NMR (500 MHz, D_2O) δ 4.5 (m, 0.5 H), 4.3 (m, 0.2 H), 4.1–3.9 (m, 1.3 H), 3.8–3.6 (m, 2.1 H), 3.7–3.5 (m, 1.9 H), 2.6 (m, 0.3 H), 2.1 (m, 0.3 H), 2.0–1.8 (m, 1.4 H); ^{13}C NMR (125 MHz, D_2O) δ 177.5, 176.9, 176.7, 175.4, 104.2, 103.0, 97.3, 96.4, 85.5, 85.0, 73.5, 72.5, 71.5, 71.4, 71.1, 70.9, 70.7, 69.7, 69.3, 69.2, 69.0, 67.6, 67.4, 66.5, 66.5, 66.3, 66.3, 66.2, 65.7, 65.3, 63.8, 63.1, 62.9, 62.8, 44.6, 43.5, 35.0, 33.7, 33.6.

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Registry No. 1, 10149-14-1; 4, 110-00-9; 5, 119947-92-1; 6, 136089-33-3; 9, 119947-93-2; α-11, 136089-34-4; β-11, 136172-78-6; α-12, 120052-41-7; β-12, 119948-02-6; 13, 136089-35-5; 14 (isomer 1), 136089-36-6; 14 (isomer 2), 136089-39-9; 15, 119947-94-3; 16, 119947-95-4; 18, 119947-96-5; 19, 119947-97-6; 20, 119947-98-7; 21, 136089-37-7; 22, 119947-99-8; 23, 119948-00-4; 25, 136089-38-8; 26, 119948-01-5; BOC-ON, 58632-95-4; ethyl chloroformate, 541-41-3; benzyl chloromethyl ether, 3587-60-8; trichloroacetyl isocyanate, 3019-71-4.

Supplementary Material Available: ^1H and/or ^{13}C NMR spectra for all new compounds described in the Experimental Section for which there is no combustion analysis (26 pages). Ordering information is given on any current masthead page.

Total Synthesis of (−)-Colletol

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The first total synthesis of the unsymmetrical bis-macrolide (−)-colletol is described. The synthesis involves a Lewis acid mediated addition of triphenylallylstannane to aldehyde **14** to set the C_{12} stereochemistry. The penultimate step utilized macrolactonization to assemble the 14-membered ring. The natural product was prepared in 12 linear steps and 12% overall yield.

Colletol (**1**) was first isolated from the fermentation broth of *Colletotrichum capsici* in 1973 along with three other related metabolites, colletodiol (**2**), colletoketol (**3**) and colletallol (**4**).[1] Although no biological activity was

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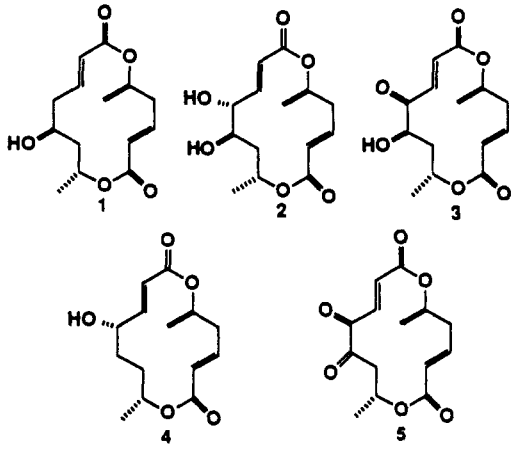
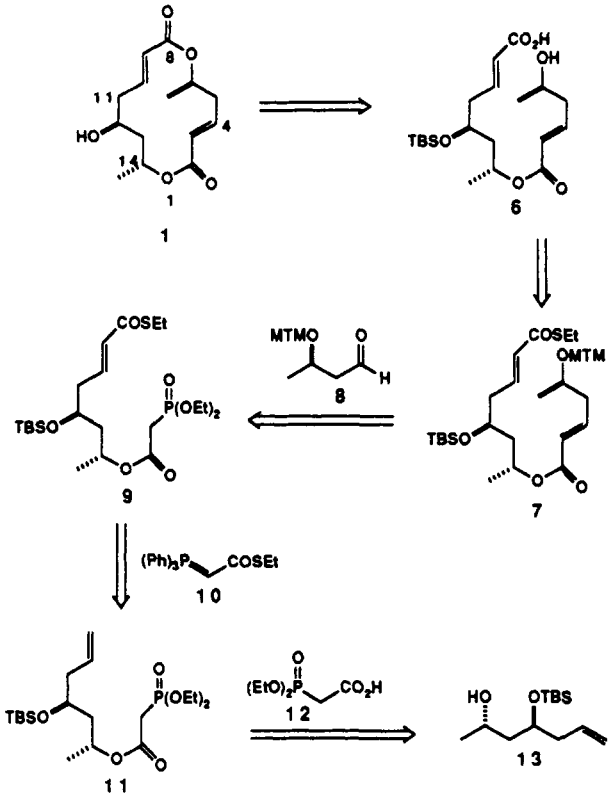


reported, this class of compounds was considered novel since they were the first reported unsymmetrical (bis)-macrolactones. Further interest in this family was stimulated in 1980 when Ronald reported the isolation of grahamimycin A_1 (5), which displayed potent activity against 36 species of bacteria, 10 species of algae, and 5 fungi.[2] Apparently due to their limited availability from biological sources, colletodiol, colletol, and colletallol have not yet been tested for biological activity. The promising biological activity and unique structures present this family of fungal metabolites as attractive synthetic targets; however, synthetic work in this area has been limited. Seebach[3] and Mitsunobu[4] have reported syntheses of colletodiol, but both of these approaches were compromised by poor yields in the penultimate macrolactonization step. Recent work in this area has resulted in the synthesis of two related macrolides. Mitsunobu has reported the synthesis of 11-*epi*-colletodiol, which completes a formal total synthesis of grahamimycin A_1.[5] Also, Zwanenburg completed the synthesis of (-)-colletallol in 26 steps and 1.6% overall yield.[6] In 1989, we reported a general synthetic strategy toward such macrolactones which resulted in the total synthesis of colletodiol.[7] This approach represented an improvement over the previous syntheses in that the macrolactonization event was realized in an 83% yield and the natural product was delivered in an overall yield of 8.2%. We now report an extension of this methodology to the first total synthesis of (-)-colletol.

Retrosynthetic Analysis

Our retrosynthetic analysis of (-)-colletol is outlined in Scheme I. The penultimate step was expected to be macrolactonization[8] of the hydroxy acid **6**, which would be derived from deprotection of the MTM protected thioester **7**. We envisioned the C_3–C_4 trans olefin as arising from Horner–Emmons coupling of the phosphonate **9** with MTM-protected (*R*)-3-hydroxybutanal **8**. The aldehyde **8** would be obtained from DIBAL reduction of MTM-protected (*R*)-ethyl 3-hydroxybutanoate, which can easily obtained from naturally occurring (*R*)-polyhydroxybutyrate. The other trans olefin at C_9–C_{10} could then be produced by reaction of ylide **10** with the aldehyde derived

Scheme I. Retrosynthetic Analysis of (-)-Colletol



from oxidative cleavage of the homoallylic alcohol **11**. The thioester was chosen for two reasons. First, the Wittig reaction occurs with only moderate selectivity for the trans olefin (4:1); however, since the unsaturated thioester is a very good Michael acceptor, the olefin geometry can be equilibrated to yield the more thermodynamically stable trans olefin simply by exposure to catalytic amounts of 4-(dimethylamino)pyridine.[9] Secondly, the thioester acts as a masked carboxylic acid which can be released at the appropriate time under mild reaction conditions without cleavage of the other ester function present. The phosphonate could be prepared from Mitsunobu esterification of the homoallylic alcohol **13** with the readily available phosphono acid **12**. The homoallylic alcohol was envisioned to arise from chelation-controlled addition of an allylstannane to the appropriately protected chiral aldehyde. We have been investigating the addition of allylstannanes to chiral aldehydes for some time and have been able to produce high diastereomeric ratios of the desired anti homoallylic alcohols under appropriate reaction conditions.[10]

Total Synthesis of (-)-Colletol

The synthetic scheme began with the preparation of optically pure (*S*)-ethyl 3-hydroxybutyrate. We initially employed the yeast reduction of ethyl acetoacetate used by Seebach;[11] however, during the course of this work our attention was drawn to the Noyori procedure using a chiral ruthenium–BINAP catalyst.[12] We have found this pro-

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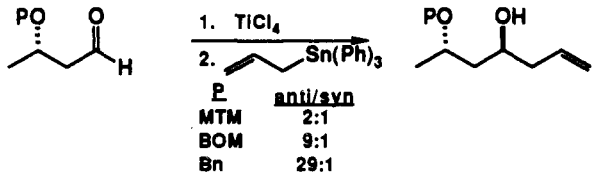
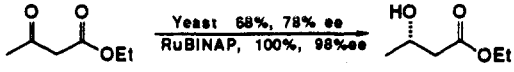
Scheme II

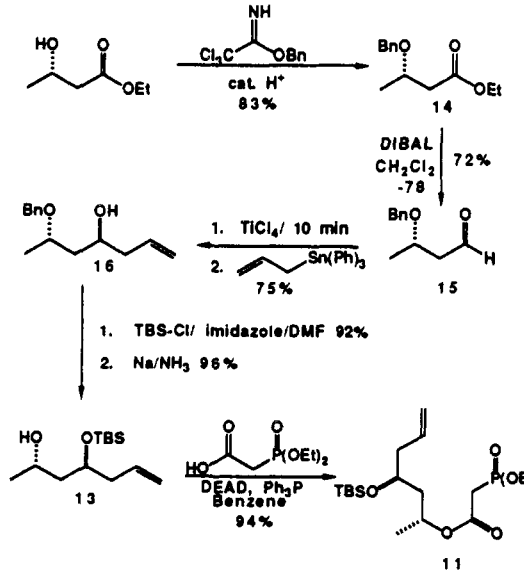


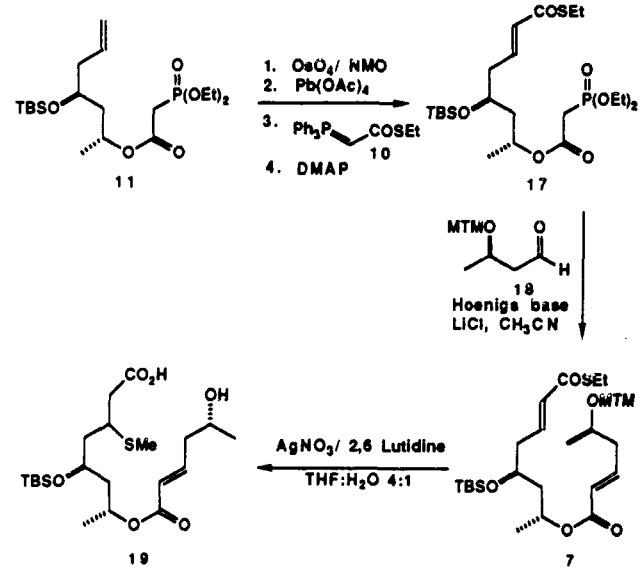
P	anti/syn
MTM	2:1
BOM	9:1
Bn	29:1

cedure superior to the yeast reduction in yield and optical purity of the hydroxy ester. For example, yeast reduction



of ethyl acetoacetate produced the hydroxy ester in 68% yield and 78% ee. Conversely, the Noyori procedure resulted in quantitative conversion to the hydroxy ester with 98% ee. In addition, the Noyori method proved to be a much simpler procedure operationally. The next transformation involved protection of the hydroxyl group, reduction to the aldehyde, and addition of triphenylallylstannane. Previous work in our laboratories had shown that to realize high levels of diastereofacial selectivity in Lewis acid mediated additions of stannanes to 3-alkoxy aldehydes two requirements must be met: (a) the protecting group must permit effective bidentate chelation between the aldehyde carbonyl and the ether oxygen and (b) the protecting group must be sufficiently bulky to force the methyl substituent into an axial position in the six-ring chelate formed upon bidentate complexation of the Lewis acid.[10] Three protecting groups were surveyed: (methylthio)methyl ether (MTM), (benzyloxy)methyl ether (BOM), and benzyl ether (Bn). The results are tabulated in Scheme II.[13] The protecting group of choice was benzyl (Bn), which allowed preparation of the homoallylic alcohol in a 29:1 anti:syn ratio. The requisite (*S*)-ethyl β-(benzyloxy)butyrate was prepared in 83% yield using the Iversen reagent[14a,b] 2,2,2-trichloracetimidate according to the general procedure of Widmer.[14c,d] Half-reduction of the ester at low temperature followed by the addition of triphenylallylstannane gave the anti homoallylic alcohol **16** in 75% yield. The next key step involved Mitsunobu esterification of the C-6 hydroxyl group; however, it was first necessary to protect the C-4 hydroxyl and then deprotect the C-6 benzyl group such that differential esterification could be achieved. The choice of protecting group at the C-4 hydroxyl was very important because the group of choice must be able to withstand the following seven synthetic transformations yet also must be removable under very mild conditions that would not cleave the very pH sensitive macrolactone. The group of choice was a *tert*-butyldimethylsilyl ether, which was installed in 92% yield. Removal of the benzyl group using sodium metal in liquid ammonia produced the alcohol **13** in 96% yield. The molecule was now properly protected to effect the Mitsunobu esterification.[15] The choice of solvent proved to be key to the success of this reaction, which would not go to completion in THF or diethyl ether. However, using benzene as solvent, the reaction was complete within 1 hour and after chromatography the phosphonate **11** was isolated in 80% yield. Attempts to oxidatively cleave the terminal olefin using ozone were unsatisfactory and led to only trace amounts of the desired aldehyde. Alternatively, catalytic osmylation followed by oxidative cleavage of the resulting diol with lead tetraacetate produced the crude aldehyde in good yield. Exposure of the crude aldehyde to the stabilized Wittig reagent **10** in refluxing chloroform yielded the unsaturated thioester in 79% yield for three steps as a 1:4 mixture of cis/trans olefins. Exposure of this mixture to catalytic 4-(dimethylamino)pyridine resulted in quantitative conversion to the all-trans thioester **17**. Coupling





of the phosphonate with aldehyde **18** under Roush–Masamune conditions[16] was uneventful and produced the MTM-protected thioester **7** in 82% yield. Unfortunately, attempts to simultaneously deprotect the MTM and the thioester led to predominantly the methylthio adduct **19**. This side reaction could be minimized by carefully monitoring the reaction by thin layer chromatography and working it up immediately upon disappearance of starting material and then resubjecting the pure hydroxy thioester to the same reaction conditions. This sequence of events proved to be somewhat cumbersome and an alternative procedure was desired. Since deprotection of the hydroxy

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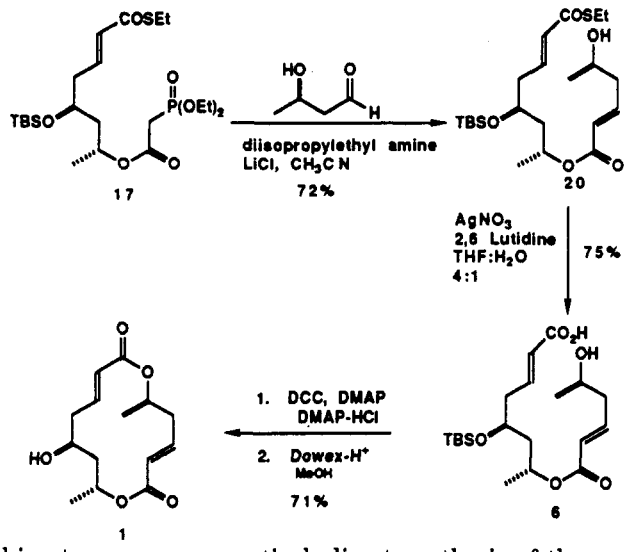

thioester was very practical, direct synthesis of the unprotected hydroxy thioester could result in an efficient synthesis of the hydroxy acid. A survey of the literature revealed that the unprotected (*R*)-3-hydroxybutanal had been synthesized; however, experimental details were not available. Fortunately, half-reduction of (*R*)-ethyl 3-hydroxybutyrate using DIBAL at low temperatures produced the aldehyde although in poor isolated yield. However, addition of the *crude* material to phosphonate **17** under Roush–Masamune conditions delivered the hydroxy thioester **20** in 72% yield. Hydrolysis of the thioester was then effected under identical conditions as employed previously to produce the hydroxy acid **6** in 75% yield. The stage was now set for the key macrolactonization step. Subjection of the hydroxy acid to appropriate macrolactonization conditions[8] afforded the macrolactone, which was deprotected to yield (-)-colletol (**1**) in 71% yield for two steps. The synthetic material was identical to a natural sample by ^{1}H NMR, TLC R_f, IR, and melting point. An X-ray crystal structure confirmed the absolute stereochemistry of the macrolactone. The route described furnishes synthetic (-)-colletol in 12 linear steps and 12% overall yield. We are currently investigating the possibility that colletol and its related metabolites could serve as potential spore germination autoinhibitors as suggested by Schreiber et al.[17]

Experimental Section

All reactions were carried out under an atmosphere of nitrogen. Solvents were purified according to the guidelines in *Purification of Common Laboratory Chemicals* (Perrin, Armarego, and Perrin, Pergamon: Oxford, 1966). Reagent grade AcOH, MeOH, and acetone were purchased and used without further purification. Ethanol-free chloroform was prepared by washing 100 mL of reagent grade chloroform 3 × 100 mL of water, drying with anhydrous K_2CO_3, and distilling from P_2O_5. Yields were calculated for material judged homogeneous by TLC and NMR. TLC was performed on Merck kieselgel 60 F_{254} plates, visualizing with a 254-nm UV lamp and staining with an ethanol solution of 12-molybdophosphoric acid. Column chromatography was performed with W.G. Grace Davisil 62 silica gel, slurry packed in glass columns. Capillary GC analyses were carried out on J and W DB-5 columns 30 m in length with a film thickness of 1 μm with He as the carrier gas (80 psi) and a flame ionization detector. Melting points are uncorrected.

Preparation of (*S*)-Ethyl 3-Hydroxybutyrate. $(RuCl_2CO\text{-}D)_n$ (113.34 mg, 0.4 mmol) and (*S*)-BINAP (300 mg, 0.482 mmol) were added to an oven-dried Schlenk flask in an inert atmosphere (N_2 drybox). The vessel was charged with a degassed mixture of toluene (17 mL) and triethylamine (0.416 mL, 5.76 mmol) and refluxed for 8 h. The reaction was allowed to cool to room temperature and the solvent was removed in vacuo to yield an orangish red solid. Ethyl acetoacetate (40.0 g, 0.307 mol) was dissolved in 60 mL of dry ethanol and the resulting mixture was degassed via three freeze–thaw cycles and subsequently added to the schlenk vessel. The solution was then heated to reflux to yield a burnt-orange solution which was transferred to a Parr high pressure autoclave and subjected to 1400 psi of H_2. This solution was allowed to stir slightly above room temperature for 60 h. The solvent was removed in vacuo and the liquid was Kugelrohr distilled to yield 39.8 g (0.301 mol, 98%) of a colorless liquid: $[\alpha]_D$ +41.5° (*c* 4.7, $CHCl_3$, 98% ee); R_f 0.15 (20% EtOAc/hexanes); 300-MHz ^{1}H NMR ($CDCl_3$) δ 4.19 (q, *J* = 7.2 Hz, 3 H), 3.15 (br s, 1 H), 2.4 (dd, *J* = 4.2, 20.8 Hz, 1 H), 2.40 (dd, *J* = 8.1, 24.6 Hz, 1 H), 1.28 (t, *J* = 7.2 Hz, 3 H), 1.20 (d, *J* = 6.3 Hz, 3 H); 75-MHz ^{13}C NMR ($CDCl_3$) δ 173.8, 65.1, 61.6, 43.7, 23.4, 15.1; IR (neat) 3420, 2980, 2930, 1720, 1450, 1370, 1290, 1160, 1080, 1025, 945, 920, 840. Anal. Calcd for $C_6H_{12}O_3$: C, 54.55; H, 9.0. Found: C, 54.34; H, 9.41.

Preparation of (*S*)-Ethyl 3-(Benzyloxy)butyrate (14). To a stirring solution of (*S*)-ethyl 3-hydroxybutyrate (2 g, 15.13 mmol) and benzyl trichloroacetimidate (7.6 g, 30.26 mmol) in 150 mL of cyclohexane:methylene chloride (2:1) was added 0.2 mL of triflic acid. This solution was allowed to stir at room temperature for 36 h and then extracted with aqueous $NaHCO_3$. The organic layer was separated and the aqueous layer was washed three times with 100-mL portions of CH_2Cl_2. The organic layers were combined, dried over Na_2SO_4, and concentrated in vacuo. The resulting solid was filtered and washed with hexanes. The filtrate was concentrated in vacuo and the resulting oil was chromatographed over a 5 × 15 cm silica gel column (slurry packed with hexanes), eluting with a solvent gradient from hexanes through 15% EtOAc/hexanes. The product-containing fractions were concentrated to yield **14** (2.8 g, 83% yield): $[\alpha]_D$ +15.98° (*c* 2.49, $CHCl_3$); R_f = 0.42 (20% EtOAc/hexanes); 300-MHz ^{1}H NMR ($CDCl_3$) δ 7.3–7.2 (m, 5 H), 4.53 (AB q, 2 H), 4.13 (dq, *J* = 7.2, 1.3 Hz, 2 H), 4.0–3.96 (m, 1 H), 2.64 (dd, *J* = 14.9, 7.3 Hz, 1 H), 2.42 (dd, *J* = 15.0, 5.8 Hz, 1 H) 1.27 (t, *J* = 7.2 Hz, 3 H), 1.26 (d, *J* = 6.2 Hz, 3 H); 75-MHz ^{13}C NMR ($CDCl_3$) δ 172.17, 139.35, 129.07, 128.38, 128.27, 72.77, 71.59, 61.12, 42.88, 20.62, 14.98; IR (neat) 3025, 2900, 1730, 1495, 1450, 1370, 1300, 1260, 1180, 1130, 1085, 1025, 945, 910, 845, 785, 735, 695. Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.27; H, 8.1. Found: C, 70.91; H, 7.73.

Preparation of (*S*)-3-(Benzyloxy)butanal (15). To a stirring solution of compound **14** (2 g, 9 mmol) in CH_2Cl_2 at -90 °C was added 7.2 mL of diisobutylaluminum hydride (1.5 M in toluene) via syringe pump over 1 h. After 2 h, the reaction was quenched with methanol (4 mL) and allowed to warm to room temperature. The mixture was poured into a saturated solution of Rochelle salts and stirred for 8 h. The organic layer was separated and the aqueous phase was extracted three times with 100-mL portions of ethyl acetate. The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The resulting oil was chromatographed over a 3 × 15 cm silica gel column (slurry packed with hexanes), eluting with a solvent gradient from hexanes through 15% EtOAc/hexanes. The product-containing fractions were concentrated to yield compound **3** (1.15 g, 6.46 mmol, 72% yield): $[\alpha]_D$ +39.07° (*c* 3.88, $CHCl_3$); R_f = 0.27 (20% EtOAc/hexanes); 300-MHz ^{1}H NMR ($CDCl_3$) δ 9.7 (dd, *J* = 2.6, 2.4 Hz, 1 H), 7.4–7.2 (m, 5 H), 4.5 (AB q, 2 H), 4.06 (sextet, *J* = 6.3 Hz, 1 H), 2.7 (ddd, *J* = 16.4, 7.4, 2.5 Hz, 1 H), 2.49 (ddd, *J* = 16.4, 4.9, 1.8 Hz, 1 H), 1.28 (d, *J* = 6.2 Hz, 3 H); 75-MHz ^{13}C NMR ($CDCl_3$) δ 201.2, 138, 128.5, 128.2, 127.5, 70.4, 70.1, 50.3, 19.6; IR (neat), 3060, 3030, 2970, 2925, 2860, 2620, 1720, 1495, 1450, 1375, 1340, 1205, 1100, 1055, 1025, 735, 695.

Preparation of (4*S*,6*S*)-4-Hydroxy-6-(benzyloxy)-1-heptene (16). To a stirring solution of aldehyde **15** (1.00 g, 5.62 mmol) in CH_2Cl_2 (28 mL) at -78 °C was added $TiCl_4$ (1.07 g, 5.62 mmol, 0.615 mL), and the resulting yellow solution was allowed to stir for 10 min. To this solution was added triphenylallylstannane (4.30 g, 11.24 mmol) dissolved in 5 mL of CH_2Cl_2 over a period of 15 min. After 4 h, the reaction was quenched by the addition of 10 mL of a saturated solution of $NaHCO_3$ and allowed to warm to room temperature. The mixture was then diluted with

(17) Schreiber, S. L.; Kelly, S. E.; Porco, J. A.; Sammakia, T.; Suh, E. M. *J. Am. Chem. Soc.* **1988**, *110*, 6210.

CH_3CN (50 mL) and stirred with KF (2 g, 34.48 mmol) for several hours. The mixture was diluted with ether and after a small aliquot had been taken for capillary VPC analysis, the solution was filtered through a 3-cm pad of Celite. The organic layer was separated and the aqueous layer was extracted three times with 100-mL portions of ethyl acetate. The organic layers were combined, dried over Na_2SO_4, and concentrated in vacuo. The resulting oil was chromatographed over a 2 × 15 cm silica gel column (slurry packed with hexanes) eluted with hexanes through 20% ethyl acetate/hexanes. The product-containing fractions were combined and concentrated to yield 0.92 g (75%) of a colorless oil: R_f = 0.29, R_f of minor isomer 0.26 (20% ethyl acetate/hexanes); capillary GC (DB-5, 200–250 °C, 2.5°/min) (major) 7.29 min, (minor) 7.50 min (29:1 anti:syn); $[\alpha]_D$ +45.2° (c 3.12, $CHCl_3$); 300-MHz ^1H NMR ($CDCl_3$) δ 7.2–7.4 (m, 5 H), 5.83 (ddt, J = 11.6, 15.8, 6.2 Hz, 1 H), 5.11 (dd, J = 0.5, 15.8 Hz, 1 H), 5.06 (dd, J = 1.5, 11.6 Hz, 1 H), 4.55 (AB q, 2 H), 3.98 (quintet, J = 6.2 Hz, 1 H), 3.87 (sextet, J = 6.2 Hz, 1 H), 2.78 (br s, 1 H), 2.21 (t, J = 6.9 Hz, 2 H), 1.64 (t, J = 6.3 Hz, 2 H), 1.25 (d, J = 6.3 Hz, 3 H); 75-MHz ^{13}C NMR ($CDCl_3$) δ 138.4, 135.0, 128.3, 127.6, 127.5, 117.3, 72.5, 70.5, 67.5, 42.5, 42.1, 19.3; IR (neat), 3440 (broad), 3080, 3030, 2970, 2930, 1640, 1450, 1370, 1085, 1065, 910, 730, 695. Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.33; H, 9.15. Found: C, 76.51; H, 9.14.

Preparation of (4*S*,6*S*)-4-(*tert*-Butyldimethylsiloxy)-6-(benzyloxy)-1-heptene. To a stirring solution of **16** (0.500 g, 2.28 mmol) in DMF (12 mL) was added imidazole (0.310 g, 4.56 mmol) and *tert*-butyldimethylsilyl chloride (0.450 g, 2.97 mmol). The resulting solution was allowed to stir for 24 h, then diluted with ether (50 mL), and washed with H_2O (50 mL). The organic layer was separated and the aqueous layer was extracted three times with 100-mL portions of ether. The organic layers were combined, dried over Na_2SO_4, and concentrated in vacuo. The resulting oil was chromatographed over a 4 × 15 cm silica gel column (slurry packed with hexanes), eluting with 100% hexanes. The product-containing fractions were combined and concentrated in vacuo to yield 0.700 g (92%) of a colorless oil: $[\alpha]_D$ +33.98° (c 4.65, $CHCl_3$); R_f = 0.9 (20% ethyl acetate/hexanes); 300-MHz ^1H NMR ($CDCl_3$) δ 7.2–7.4 (m, 5 H), 5.83 (ddt, J = 11.6, 15.8, 6.2 Hz, 1 H), 5.09 (dd, J = 0.5, 15.8 Hz, 1 H), 5.06 (dd, J = 1.5, 11.6 Hz, 1 H), 4.55 (AB q, 2 H), 4.03 (quintet, J = 6.2 Hz, 1 H), 3.78 (sextet, J = 6.2 Hz, 1 H), 2.3 (t, J = 6.9 Hz, 2 H), 1.5–1.8 (m, 2 H), 1.24 (d, J = 6.1 Hz, 3 H), 0.92 (s, 9 H), 0.094 (s, 3 H), 0.075 (s, 3 H); 75-MHz ^{13}C NMR ($CDCl_3$) δ 138.4, 134.8, 128.3, 127.6, 127.4, 116.9, 72.0, 70.0, 68.7, 44.7, 42.6, 25.9, 20.1, -4.1, -4.6; IR (neat), 3070, 3020, 2960, 2940, 2850, 1680, 1490, 1460, 1370, 1250, 1150, 1120, 1080, 1050, 1000, 920, 830, 770, 730, 690. Anal. Calcd for $C_{20}H_{34}O_2Si$: C, 71.86; H, 10.18. Found: C, 71.89; H, 9.94.

Preparation of (4*S*,6*S*)-4-(*tert*-Butyldimethylsiloxy)-6-hydroxy-1-heptene (13). To a 100-mL, three-necked flask equipped with a mechanical stirrer, Dewar condenser, and an ammonia inlet was added (4*S*,6*S*)-[(*tert*-butyldimethylsiloxy)-6-(benzyloxy)-1-heptene (0.500 g, 1.497 mmol) dissolved in 20 mL of ethanol. The flask was then cooled to -78 °C and ammonia was condensed until a final volume of 40 mL was achieved. Small pieces of sodium wire were then added to the solution until a bright blue color was present for 1 min. At this time, solid ammonium chloride was added in portions until the solution was white. The solution was then allowed to slowly warm to room temperature over a period of 12 h, then diluted with ethyl acetate (50 mL), and washed with water (50 mL). The organic layer was separated and the aqueous layer was then extracted three times with 50-mL portions of ethyl acetate. The organic layers were combined, dried over Na_2SO_4, and concentrated in vacuo. The resulting oil was then chromatographed over a 1.5 × 15 cm silica gel column (slurry packed with hexanes), eluting with a solvent gradient from hexanes through 20% ethyl acetate/hexanes. The product-containing fractions were combined and concentrated in vacuo to yield 0.350 g (96%) of a colorless oil: $[\alpha]_D$ +15.89° (c 2.58, $CHCl_3$); R_f = 0.49 (20% ethyl acetate/hexanes); 300-MHz ^1H NMR ($CDCl_3$) δ 5.83 (ddt, J = 11.6, 15.8, 6.2 Hz, 1 H), 5.09 (dd, J = 0.5, 15.8 Hz, 1 H), 5.03 (dd, J = 1.5, 11.6 Hz, 1 H), 4.12 (quintet, J = 6.3 Hz, 1 H), 4.09 (sextet, J = 6.4 Hz, 1 H), 3.3 (br s, 1 H), 2.3 (t, J = 7.2 Hz, 2 H), 1.5–1.8 (m, 2 H), 1.14 (d, J = 6.2 Hz, 3 H), 0.86 (s, 9 H), 0.07 (s, 3 H), 0.05 (s, 3 H); 75-MHz ^{13}C NMR ($CDCl_3$) δ 134.9, 117.6, 71.4, 64.6, 43.4, 41.3, 26.1, 24.2, 19.1, -4.3, -4.6; IR (neat) 3440 (broad), 3090, 2960, 2930, 2860, 1825, 1640, 1460, 1370, 1250, 1050, 1000, 910, 830, 800, 770, 730, 660. Anal. Calcd for $C_{13}H_{28}O_2Si$: C, 63.93; H, 11.48. Found: C, 63.63; H, 11.42.

Preparation of (4*S*,6*R*)-9-(Diethoxyphosphinyl)-8-oxo-6-methyl-4-(*tert*-butyldimethylsiloxy)-7-oxo-1-nonene (11). To a stirring solution of **13** (220 mg, 0.902 mmol), diethyl (carboxymethyl)phosphonate (273 mg, 1.39 mmol), and triphenylphosphine (364 mg, 1.39 mmol) in dry benzene (15 mL) was added a solution of diethyl azodicarboxylate (242 mg, 1.39 mmol) in 5 mL of dry benzene via a dropping funnel over 1 h. After complete addition, the reaction was partially concentrated and hexanes were added until cloudiness persisted. After standing for 24 h, the solution was decanted off and the solid was washed with hexanes. The resulting solution was concentrated to yield a bright yellow solid. The solid was dissolved in 1 mL of 10% ethyl acetate/hexanes, loaded onto a 1.5 × 15 cm silica gel column (slurry packed with 10% ethyl acetate/hexanes), and eluted with a solvent gradient from 10% ethyl acetate/hexanes to 100% ethyl acetate/hexanes. The product-containing fractions were combined and concentrated to yield 372 mg (94%) of a colorless oil: $[\alpha]_D$ +13.08° (c 4.1, $CHCl_3$) R_f = 0.43 (50% ethyl acetate/hexanes); 300-MHz ^1H NMR ($CDCl_3$) δ 5.8 (m, 1 H), 5.0 (m, 3 H), 4.1 (quintet, J = 7.1 Hz, 4 H), 3.7 (t, J = 5.9 Hz, 1 H), 2.9 (d, J = 21.5 Hz, 2 H), 2.17 (m, 2 H), 1.77 (dt, J = 13.8, 6.8 Hz, 1 H), 1.57 (dt, J = 13.9, 6.2 Hz, 1 H), 1.27 (t, J = 7.1 Hz, 6 H), 1.19 (d, J = 6.3 Hz, 3 H), 0.9 (s, 9 H), 0.07 (s, 3 H), 0.05 (s, 3 H); 75-MHz ^{13}C NMR ($CDCl_3$) δ 165.0 (d, J = 6.5 Hz), 134.5, 117.2, 70.0, 69.9, 68.7, 62.5 (d, J = 6.3 Hz), 42.6, 41.5, 35.4, 33.7, 25.8, 20.2 (d, J = 36.2 Hz), 17.9, 16.3 (d, J = 6.1 Hz), -4.4, -4.8; IR (neat) 3160, 2980, 2960, 2930, 2900, 2860, 2250, 1750, 1640, 1470, 1380, 1345, 1250, 1220, 1160, 1090, 1050, 1030, 970, 900, 835, 810, 750, 650. Anal. Calcd for $C_{19}H_{39}O_6PSi$: C, 54.0; H, 9.3. Found: C, 54.16; H, 9.61.

Preparation of (2*E*,5*S*,7*R*)-Ethyl 10-(Diethoxyphosphinyl)-5-(*tert*-butyldimethylsiloxy)-7-methyl-9-oxo-8-oxa-2-decenethioate (17). To a stirring solution of **11** (500 mg, 1.14 mmol) and *N*-methylmorpholine *N*-oxide (250 mg, 2.14 mmol) was added a solution of OsO_4 in THF (5 drops, 1 g/100 mL). After stirring for 24 h, the reaction was quenched with saturated aqueous $NaHSO_3$ (50 mL) and diluted with ethyl acetate. The organic layer was separated and the resulting black aqueous layer was extracted three times with 100-mL portions of ethyl acetate. The organic layers were combined, dried over Na_2SO_4, and concentrated in vacuo. The resulting solid was dissolved in 20 mL of CH_2Cl_2 and to this solution was added $Pb(OAc)_4$ (695 mg, 1.57 mmol). After stirring for 15 min, the reaction was quenched with water (10 mL). The organic layer was separated and the aqueous layer was extracted three times with 50-mL portions of ethyl acetate. The organic layers were combined, filtered through a 3-cm pad of Celite, dried over Na_2SO_4, and concentrated in vacuo. The crude oil was dissolved in 20 mL of $CHCl_3$, [carbothioethoxymethylidene]triphenylphosphorane (**10**) (415 mg, 1.14 mmol) was added, the solution was brought to reflux for 24 h and then cooled to room temperature, and (dimethylamino)pyridine (5 mg) was added. After being stirred for 24 h, the solution was partially concentrated and hexanes were added until cloudiness persisted. After being allowed to stand for 24 h, the solution was decanted off and the resulting solid was washed with hexanes. The solution was then concentrated in vacuo and the resulting solid was dissolved in 1 mL of 35% ethyl acetate/hexanes, loaded onto a 1.5 × 15 cm silica gel column slurry packed with 35% ethyl acetate/hexanes, and eluted with 100-mL portions of 0%, 10%, 30%, 50%, 75%, and 100% ethyl acetate/hexanes. The product was found in fractions 26–45 (8 mL fractions), which were combined and concentrated to yield 475 mg (79%) of a colorless oil: $[\alpha]_D$ +14.77° (c 4.63, $CHCl_3$); R_f = 0.53 (75% ethyl acetate/hexanes); 300-MHz ^1H NMR ($CDCl_3$) δ 6.8 (dt, J = 7.7, 15.5 Hz, 1 H), 6.07 (d, J = 15.7 Hz, 1 H), 4.98 (m, 1 H), 4.7 (quintet, J = 7.3 Hz, 4 H), 3.8 (m, 1 H), 2.85 (d, J = 21.5 Hz, 2 H), 2.85 (q, J = 7.4 Hz, 2 H), 2.36 (ddd, J = 5.6, 6.5, 14.2 Hz, 1 H), 2.34 (ddd, J = 6.8, 7.4, 14.2 Hz, 1 H), 1.81 (ddd, J = 5.9, 7.3, 13.9 Hz, 1 H), 1.56 (ddd, J = 5.9, 6.4, 13.7 Hz, 1 H), 1.3 (t, J = 7.4 Hz, 3 H), 1.28 (t, J = 7.1 Hz, 3 H), 1.18 (d, J = 7.0 Hz, 3 H), 0.82 (s, 9 H), 0.09 (s, 3 H), 0.06 (s, 3 H); 75-MHz ^{13}C NMR ($CDCl_3$) δ 189.7, 165 (d, J = 6.2 Hz), 141, 130.9,

69.4, 67.9, 62.6 (d, J = 6.2 Hz), 43.2, 39.5, 35.4, 33.6, 25.6, 22.9, 20.1, 17.8, 16.3 (d, J = 6.3 Hz) 14.7, −4.6, −4.8; IR (neat) 2980, 2940, 2910, 1755, 1680, 1650, 1450, 1380, 1370, 1220, 1170, 970. Anal. Calcd for $C_{22}H_{43}O_7SSiP$: C, 51.73; H, 8.43. Found: C, 51.76; H, 8.49.

Preparation of (2*E*,5*S*,7*R*,10*E*,13*R*)-Ethyl 13-Hydroxy-5-(*tert*-butyldimethylsiloxy)-7-methyl-9-oxo-8-oxatetradeca-2,10-dienethioate (20). To a stirring solution of (*R*)-ethyl 3-hydroxybutyrate (1.00 g, 7.58 mmol) in 50 mL of CH_2Cl_2 at −90 °C was added diisobutylaluminum hydride (1.5 M in toluene, 11.1 mL, 16.7 mmol) over a period of 2 h. After complete addition, 5 mL of MeOH were added over 15 min, and the solution was allowed to warm to room temperature, then poured into 300 mL of saturated Rochelle salts, and stirred for several hours. The organic layer was separated and the aqueous layer was washed three times with 100-mL portions of CH_2Cl_2. The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The resulting yellow oil was dissolved in 1 mL of CH_3CN, added to a stirring solution of phosphonate **17** (1.00 g, 1.96 mmol), lithium chloride (164 mg, 3.92 mmol), and diisopropylethylamine (505 mg, 3.92 mmol, 0.678 mL) in 40 mL of CH_3CN, and allowed to stir for 12 h. The solution was then concentrated in vacuo, applied to a 2.0 × 16 cm silica gel column (slurry packed with 10% ethylacetate/hexanes), and eluted with 100-mL portions of 10%, 20%, 35%, 50%, 75%, and 100% ethyl acetate/hexanes. The product was found in fractions 17–29 (8 mL fractions), which were combined and concentrated to yield 636 mg (73%) of a colorless oil: $[\alpha]_D$ −9.64° (c 1.12, $CHCl_3$); R_f = 0.76 (75% ethyl acetate/hexanes); 300-MHz ^1H NMR ($CDCl_3$) δ 6.93 (dt, J = 7.5, 15.1 Hz, 1 H), 6.82 (dt, J = 7.1, 15.4 Hz, 1 H), 6.09 (dt, J = 1.3, 15.6 Hz, 1 H), 5.84 (dt, J = 1.5, 15.7 Hz, 1 H) 5.03 (m, 1 H), 3.94 (m, 1 H), 3.82 (m, 1 H), 2.89 (q, J = 7.5 Hz, 2 H), 2.32 (m, 4 H), 1.86 (ddd, J = 5.2, 8.1, 14.2 Hz, 1 H), 1.60 (ddd, J = 4.9, 7.1, 15.0 Hz, 1 H), 1.26 (t, J = 7.43 Hz, 3 H), 1.20 (d, J = 6.15 Hz, 3 H), 1.22 (d, J = 6.11 Hz, 3 H), 0.85 (s, 9 H), 0.023 (s, 3 H), 0.019 (s, 3 H); 75-MHz ^{13}C NMR ($CDCl_3$) δ 189.7, 165.5, 145.1, 141.2, 130.8, 123.8, 68.2, 67.9, 66.6, 43.6, 41.8, 39.6, 25.8, 23.3, 23.1, 20.1, 18.0, 14.8, −4.5, −4.6; IR (neat) 3470, 2960, 2930, 2850, 1720, 1665, 1470, 1380, 1330, 1280, 1230, 1160, 1050, 980. Anal. Calcd for $C_{22}H_{40}O_5SSi$: C, 59.46; H, 9.01. Found: C, 59.38; H, 9.10.

Preparation of (2*E*,5*S*,7*R*,10*E*,13*R*)-13-Hydroxy-5-(*tert*-butyldimethylsiloxy)-7-methyl-9-oxo-8-oxatetradeca-2,10-dienoic Acid (6). To a stirring solution of **20** (414 mg, 0.934 mmol) in THF:H_2O (10 mL, 4:1 volume ratio) was added 2,6-lutidine (0.75 g, 7.00 mmol) followed by silver nitrate (2.38 g, 14.0 mmol). The resulting mixture was then heated to reflux for 24 h, cooled to room temperature, acidified with acetic acid, and filtered through a pad of Celite. The resulting solution was washed with 2 × 100 mL of saturated aqueous $CuSO_4$ and then 2 × 100 mL of brine and concentrated. The resulting green oil was applied to a silica gel column (slurry packed with 10% ethyl acetate/hexanes) and eluted with 100-mL portions of 20% and 35% ethyl acetate/hexanes followed by 100-mL portions of 75:25:1 ethyl acetate/hexanes/acetic acid and 99:1 ethyl acetate/acetic acid. The product was found in fractions 29–60 (8-mL fractions), which were combined and concentrated to yield 298 mg (80%) of a colorless oil: $[\alpha]_D$ −11.78° (c 1.49, $CHCl_3$) R_f = 0.38 (toluene/dioxane/acetic acid, 20:10:1 volume ratio); 300 MHz ^1H NMR ($CDCl_3$) δ 7.12 (dt, J = 7.8, 15.4 Hz, 1 H), 6.93 (dt, J = 7.5, 14.9 Hz, 1 H), 5.85 (dt, J = 7.0, 15.7 Hz, 1 H), 5.83 (dt, J = 6.9, 15.6 Hz, 1 H), 5.04 (m, 1 H), 3.97 (m, 1 H), 3.83 (m, 1 H), 2.35 (m, 4 H), 1.85 (dt, J = 5.4, 13.9 Hz, 1 H), 1.62 (dt, J = 5.0, 14.4 Hz, 1 H), 1.24 (d, J = 4.1 Hz, 3 H), 1.21 (d, J = 4.1 Hz, 3 H), 0.86 (s, 9 H), 0.22 (s, 3 H), 0.21 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 170.94, 165.74, 148.10, 145.20, 123.99, 123.08, 68.18, 67.95, 66.75, 43.49, 41.78, 39.71, 25.75, 23.17, 20.51, 17.98, −4.56, −4.67; IR (neat) 3600–2400 (br), 2970, 2940, 1690, 1650. Anal. Calcd for $C_{20}H_{36}O_6Si$: C, 59.91; H, 8.99. Found: C, 59.82; H, 9.09.

Preparation of Colletol ((3*E*,6*R*,9*E*,12*S*,14*R*)-12-Hydroxy-6,14-dimethyl-1,7-dioxacyclotetradeca-3,9-diene-2,8-dione (1)). To a stirring solution of dicyclohexylcarbodiimide (239.6 mg, 1.25 mmol), 4-(dimethylamino)pyridine (152.5 mg, 1.25 mmol), and 4-(dimethylamino)pyridine hydrochloride (197.5 mg, 1.25 mmol) in ethanol-free chloroform (20 mL) at reflux was added a solution of **6** (100 mg, 0.25 mmol) in 5 mL of ethanol-free chloroform over a period of 16 h. The residual contents of the syringe were rinsed into a tared flask and concentrated to give 9 mg of starting hydroxy acid. The solution was cooled to room temperature and quenched with methanol (3 mL) and 10 drops of AcOH. The solution was concentrated, diluted with ether, and filtered through a pad of Celite. The solvent was removed and the resulting solid was dissolved in 1 mL of 10% ethyl acetate/hexanes and applied to a 2 × 5 cm silica gel plug rinsing with 2 × 100 mL of 10% ethyl acetate/hexanes. The solvent was removed and the resulting oil was dissolved in 10 mL of MeOH. To this stirring solution was added Dowex 50W-8 H^+ resin (50 mg), and the mixture was heated to reflux for 12 h. The mixture was cooled to room temperature, filtered, and concentrated. The resulting oil was purified by MPLC (2 × 20 cm Michel-Miller column, dry packed), eluting with 500-mL portions of 20%, 35%, 50%, and 75% ethyl acetate/hexanes, collecting 8-mL fractions. The product was found in fractions 91–132, which were combined and concentrated to give 39 mg (71%) of a white solid: mp 102 °C: $[\alpha]_D$ −38.4° (c 0.95, $CHCl_3$); R_f = 0.48 (75% ethyl acetate/hexanes); 300-MHz ^1H NMR ($CDCl_3$) δ 6.7 (ddd, J = 4.9, 9.9, 15.7 Hz, 1 H), 6.64 (ddd, J = 5.2, 11.2, 15.2 Hz, 1 H), 5.79 (ddd, J = 0.9, 1.6, 14.9 Hz, 1 H), 5.76 (ddd, J = 0.7, 1.2, 15.6 Hz, 1 H), 5.25 (ddq, J = 3.1, 6.1, 9.4 Hz, 1 H), 5.16 (ddq, J = 2.9, 6.8, 10.6 Hz, 1 H), 4.02 (dddd, J = 2.1, 5.7, 7.9, 11.9 Hz, 1 H), 2.53 (dddd, J = 1.3, 3.1, 4.6, 12.6 Hz, 1 H), 2.48 (dddd, J = 1.2, 3.3, 4.9, 12.8 Hz, 1 H), 2.30 (dt, J = 10.0, 12.1 Hz, 1 H), 2.23 (dt, J = 11.7, 13.3 Hz, 1 H), 1.97 (ddd, J = 2.3, 5.9, 16.1 Hz, 1 H), 1.49 (ddd, J = 2.8, 6.2, 12.8 Hz, 1 H), 1.35 (d, J = 6.3 Hz, 3 H), 1.34 (d, J = 6.6 Hz, 3 H); 75-MHz ^{13}C NMR ($CDCl_3$) δ 166.5, 165.1, 144.14, 143.84, 126.22, 125.16, 72.04, 68.49, 68.29, 68.26, 40.97, 39.98, 20.63, 18.24; IR ($CHCl_3$) 3480, 2980, 2930, 2860, 1715, 1655, 1318, 985, 760, 650. Anal. Calcd for $C_{14}H_{20}O_5$: C, 62.69; H, 7.46. Found: C, 62.66; H, 7.46.

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