Registry No. **1a**, 75414-38-9; **1b**, 13007-49-3; **1c**, 52080-38-3; **1d**, 52152-86-0; **2a**, 111718-45-7; **2b**, 125302-92-3; **2c**, 125302-93-4; **2d**, 125409-16-7; **3a**, 111819-59-1; **3b**, 125409-10-1; **3c**, 125409-13-4; **3d**, 125409-17-8; **4a**, 125409-08-7; **4b**, 125409-11-2; **4c**, 125409-14-5; **4d**, 125409-18-9; **5a**, 125409-09-8; **5b**, 125409-12-3; **5c**, 125409-15-6; **5d**, 125409-19-0; **6**, 125302-94-5; cyclopentadiene, 542-92-7.

Supplementary Material Available: The ^1H NMR spectra of all the Diels–Alder adducts (19 pages). Ordering information is given on any current masthead page.

Stereoselective Synthesis of a Nonracemic Hydronaphthalene Subunit of Kijanolide

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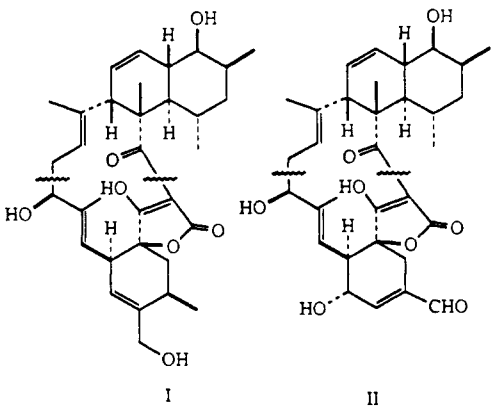
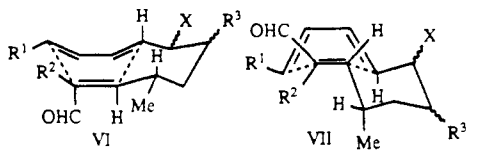
Lewis acid catalyzed Diels–Alder cyclization of the tetraenal **15** affords the endo product, hydronaphthalene **16**, with high diastereoselectivity. Nonracemic **15** is prepared by addition of dienyne **5** to resolved (2*S*,4*S*)-5-[(*tert*-butyldimethylsilyl)oxy]-2,4-dimethylpentanal followed by oxidation to ketone **7**, reduction first with *ent*-Chirald–LAH and then with Red-Al (Aldrich) and homologation of the derived aldehyde **12** by a Horner–Emmons protocol. Hydronaphthalene **16** is a subunit of the antitumor antibiotic natural products kijanimicin and tetrocarin A.

The novel macrocyclic compounds kijanolide (I) and tetronolide (II) are the aglycons of the antitumor antibiotics kijanimicin and tetrocarcin A.[1,2] To date only three representatives of this family have been identified.[3] Nonetheless these structures have elicited a great deal of interest as targets of synthesis.[4] Several years ago we showed that (*all-E*)-2,8,10-undecatrienals with a methyl substituent at C-4 (III) undergo facile Diels–Alder cyclization to endo products of type IV rather than the diastereomers V (eq 1).[5] The observed diastereoselectivity

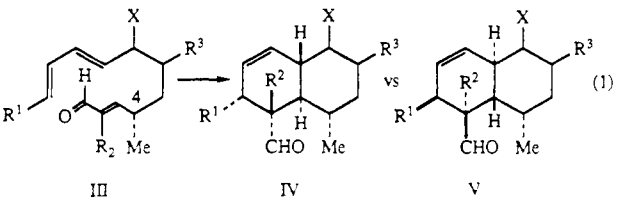


I II



VI VII

Figure 1. Endo chair cyclization pathways for 4-methyl-2,8,10-undecatrienals.



III IV V (1)

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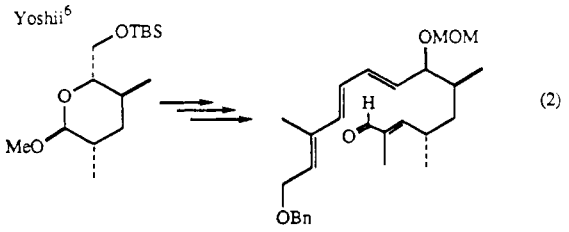
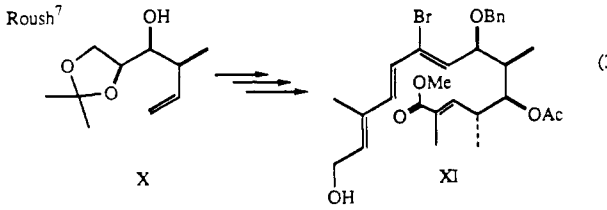
was attributed to the endo transition state VI in which the C-4 methyl substituent adopts an equatorial orientation in the chair-like conformation of the four-carbon tether (Figure 1). The alternative chair endo arrangement VII places this substituent in the less favorable axial orientation. This directing effect is also seen with more substituted tethers (R^3 = Me, X = OBn). These findings establish the feasibility of assembling hydronaphthalene subunits of kijanolide and tetronolide by an intramolecular Diels–Alder strategy. Indeed after our report on the synthesis of racemic XIII and its cyclization to IV (R^1 = C(Me)=CHCH$_2$OBn, R^2 = Me, R^3 = β-Me, X = β-OBn), Yoshii[6] and Roush[7] described routes to nonracemic 2,8,10-undecatrienal IX (eq 2) and the ester XI (eq 3) and



(2)

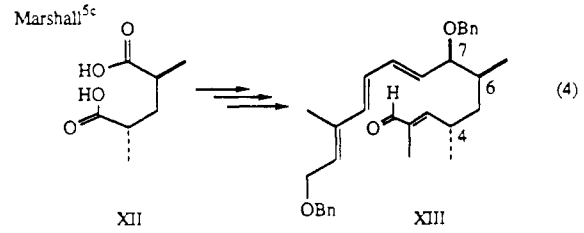
VIII IX



(3)

X XI

the subsequent cyclization of these polyenes to hydronaphthalene subunits of I and II. Yoshii's synthesis of aldehyde IX utilized the carbohydrate-derived acetal VIII. Roush prepared ester XI from the adduct X of glyceraldehyde acetonide and a nonracemic crotylboronate by a sequence which features diastereoselective transformations of acyclic intermediates. Our route to tetraenal XIII employed racemic 2,4-dimethylglutaric acid as the starting material[5c] (eq 4). Both XIII and its C-7 epimer were produced as an inseparable 1:1 mixture. The present work



(4)

XII XIII

was undertaken to develop an efficient synthesis of nonracemic diastereomerically homogeneous XIII and to examine both Lewis acid and thermal Diels–Alder cyclizations leading to a potential hydronaphthalene subunit of kijanolide (I).

α-(Benzyloxy)acetaldehyde, prepared by Swern oxidation[8] of 2-(benzyloxy)ethanol followed by nonaqueous workup to prevent hydration, afforded a separable 95:5 mixture of (*E*)- and (*Z*)-crotonic esters 1 in 94% yield upon Wittig condensation with α-(triphenylphosphorylidene)-acetate in CH_2Cl_2. Reduction with DIBAH and Swern oxidation[8] of the resulting alcohol 2 gave the aldehyde 3 in 95% overall yield. Aldehyde 3 condensed with the ylid derived from the TIPS propargyltriphenylphosphonium Wittig reagent to give an 88:12 inseparable mixture of *E*-dienyne 4 and the *Z* isomer in 99% yield. Desilylation with Bu_4NF afforded the alkyne 5 nearly quantitatively as a 9:1 mixture of *E* and *Z* isomers. Lithiation of 5 with *n*-BuLi followed by addition of (2*S*,4*S*)-5-[(*tert*-butyldimethylsilyl)oxy]-2,4-dimethylpentanal[5d] gave rise to a 1:1 mixture of diastereomeric alcohols 6 in 94% yield. This mixture was converted to ketone 7 in 95% yield upon Swern oxidation.[8] The *E*,*E*-ketone 7 was readily separated from the small amount of *E*,*Z* isomer impurity through column chromatography. Reduction of ketone 7 with L-Selectride (Aldrich) at −78 °C led to a ca. 4.5:1 inseparable mixture of alcohol stereoisomers.[9] The major product was presumed to be the 5*S* isomer **8b** from consideration of the Felkin transition state for the hydride reduction (Figure 2).[10] Hoping to improve this ratio we examined the reduction of ketone 7 with various hydride reagents (Table I).

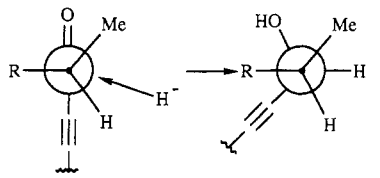


Figure 2. Preferred reduction pathway for ketone 7.

Table I. Hydride Reductions of Ketone 7

hydride	conditions[a]	*T*, °C	yield, %	**8b**/**8a**
L-Selectride	A	−78	83	4.5:1[b]
LS-Selectride	B	−100	70	2:1[c]
(*S*)-Alpine-Hydride	C	−78	76	2:1[c]
(*S*)-BINAL-H	D	−78	76	2.5:1[c]
(*R*)-BINAL-H	D	−78	65	1.5:1[c]
Li(O-tBu)$_3$AlH	E	−78	57	1.5:1[c]
(S)-Alpine-Borane	F	23	34	5:1[c]
(R)-Alpine-Borane	G	23	70	1:17[b]
Chirald–LiAlH$_4$	H	−78	89	1:11[b]
ent-Chirald–LiAlH$_4$[d]	I	−78	90	13:1[b]

[a] A = 0.02 M reagent in THF, 1.5 h; B = 0.16 M reagent in THF, 2.5 h; C = 1.1 M reagent in THF, 12 h; D = 0.07 M reagent in THF, 14 h; E = 0.25 M reagent in THF, 2 h; F = 0.5 M reagent in THF, 36 h; G = neat reagent, 20 h; H = 0.24 M reagent in Et_2O, 15 h; I = 0.018 M reagent in Et_2O, 5 h. [b] Ratios determined by ^1H NMR analysis of the *O*-methyl mandelate derivatives (see text). [c] Ratios determined by ^1H NMR analysis of the alcohols (see text). [d] (1*R*,2*S*)-4-(Dimethylamino)-3-methyl-1,2-diphenyl-2-butanol (see Acknowledgments).

Isomer ratios could be approximated by comparison of the OH doublets at 1.97 and 1.99 ppm in the ^1H NMR spectra of the crude alcohol products **8a** and **8b**. A more precise analysis was possible through conversion of the reduction product mixture to the *O*-methyl mandelic esters 18 and 19.[11] These esters showed clearly resolved doublets

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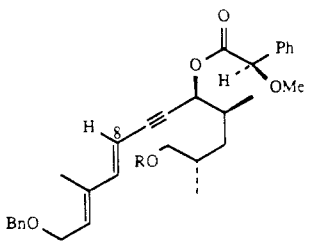
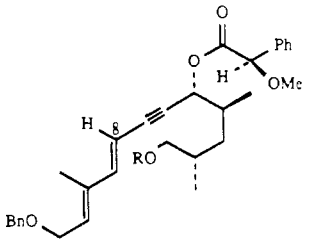


18 H-8 = 6.62 ppm



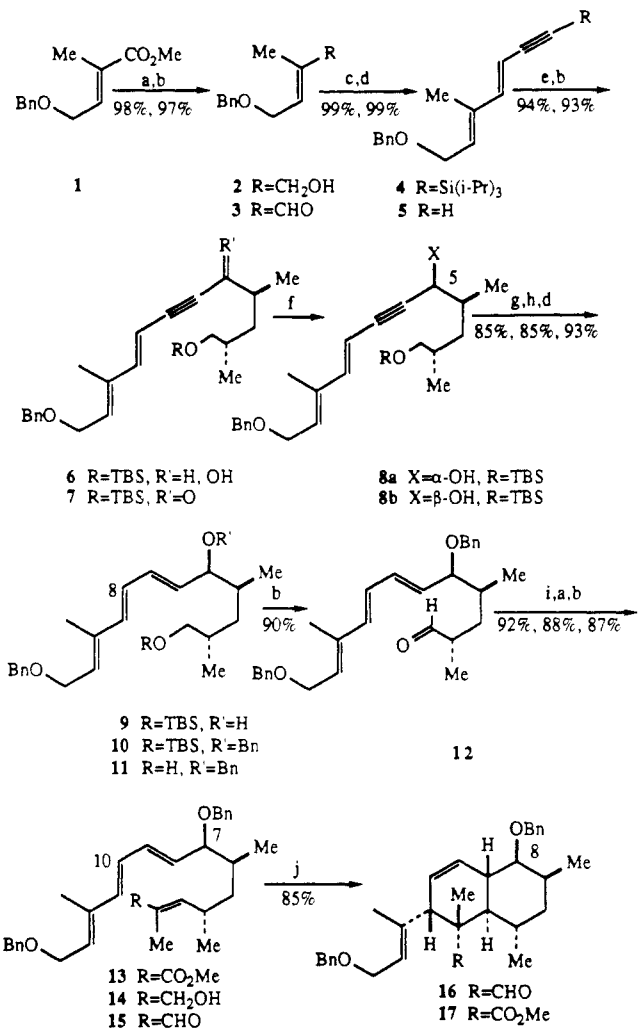
19 H-8 = 6.49 ppm

at 6.62 and 6.49 ppm resulting from the C-8 vinylic protons of the diastereoisomers. The relative chemical shifts of these protons supports the assigned absolute configuration of the carbinyl centers.[11]

Increasing the steric bulk of the hydride through the use of LS-Selectride led to decreased selectivity. A similar effect has been noted by Midland.[12] We next examined a number of asymmetric reducing agents in the hope of enhancing diastereoselectivity through matching of substrate and reagent preferences. (*S*)-Alpine-Hydride showed selectivity comparable to that of LS-Selectride.[13] Evidently the bulk of this reagent diminishes its effectiveness toward the branched chain ketone **7**. The *S*-selective reagent (*S*)-(−)-BINAL-H[14] afforded only a 2.5:1 predominance of the *S*-alcohol **8b**, a modest improvement over the substrate directed reduction with $Li(O\text{-}tBu)_3AlH$. Noyori has observed poor selectivity in reductions of an α-branched ynone with BINAL-H, as well.[15] (*S*)-Alpine-Borane reduced ketone **7** slowly to a 5:1 mixture favoring the *S* isomer **8b**.[16] α-Chiral ketones are preferentially reduced to anti-Cram products with electrophilic reducing agents such as boranes and alanes.[17] In the case of ketone **7** the *R* isomer is the expected anti-Cram product so the interaction with the *S*-selective reagent (*S*)-(−)-Alpine-Borane is mismatched. In contrast, (*R*)-(+)-Alpine-Borane afforded a 17:1 excess of the unwanted *R*-alcohol **8a** in 70% yield. Satisfactory results were obtained with the LAH-Darvon alcohol complex.[18] The 1*S*,2*R* amino alcohol auxiliary favored the *R*-alcohol **8a** 11:1 whereas the 1*R*,2*S* enantiomer (*ent*-Darvon alcohol) gave a 13:1 predominance of the desired *S*-alcohol **8b** in 89% yield.[19] Evidently LAH-Darvon reductions of the α-chiral ketone **7** are largely reagent controlled. In contrast, analogous reductions of β-chiral alkynones are highly dependent on substrate configuration.[20]

Hydroalanation of the foregoing 13:1 alcohol mixture with Red-Al[21] in toluene followed by aqueous quench yielded the *all-E*-trienol **9** in 92% yield. The alcohol grouping of this mixture was protected as the benzyl ether **10**. Cleavage of the TBS ether with Bu_4NF followed by

Scheme I[a]



[a] (a) DIBAH, Et_2O, −78 °C; (b) $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2; (c) $Ph_3P{=}CHC{\equiv}CSi(i\text{-}Pr)_3$; THF, −78 °C; (d) Bu_4NF, THF; (e) *n*-BuLi, THF, −78 °C; (2*S*,4*S*)-$TBSOCH_2CH(Me)CH_2CH(Me)$-CHO, THF, −40 °C; (f) see Table; (g) Red-Al, Et_2O; (h) *n*-BuLi, THF, $PhCH_2Br$, HMPA; (i) $Ph_3P{=}C(Me)CO_2Me$, CH_2Cl_2; (j) Me_2AlCl, CH_2Cl_2, −78 °C to −30 °C or 200 °C.

Swern oxidation[8] afforded aldehyde **12** in 84% overall yield. Wittig condensation then gave the *E* conjugated ester **13** in 88% yield. Enal **15** was prepared from ester **13** by a two-step protocol involving DIBAH reduction and Swern oxidation.[8]

Treatment of tetraenal **15** with Me_2AlCl at −78 °C to −30 °C afforded the hydronaphthalene **16** in 85% yield. The thermal cyclization of enal **15** at 200 °C proceeded comparably. Both samples of hydronaphthalene **16** gave nearly identical optical rotations. Thermal cyclization of conjugated ester **13** was also examined. Although the starting enoate **13** and the cyclization products exhibited the same TLC mobility in several solvent systems, the ^1H NMR spectrum indicated that the cyclization proceeded largely to the desired hydronaphthalene products. Expansion and integration of the methoxy signal indicated the presence of at least three saturated esters in the ratio 80:19:1.

Of the three cyclizations, the Lewis acid procedure on enal **15** was most efficient followed closely by the thermal protocol. In contrast, the cyclization of ester **13** yielded significant diastereomeric byproducts in accord with previous observations on analogous systems.[4c,d] In light of these previous findings we did not attempt Lewis acid promoted cyclization of enoate **13**.

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Experimental Section[22]

Methyl (*E*)-4-(Benzyloxy)-2-methyl-2-butenoate (1). To a stirred, cooled (−78 °C) solution of 10.62 g (83.7 mmol) of oxalyl chloride in 90 mL of CH_2Cl_2 was added 12.77 g (163.4 mmol) of DMSO in 20 mL of CH_2Cl_2 over 5 min. The solution was stirred for 15 min, and 5.52 g (36.3 mmol) of 2-(benzyloxy)ethanol was added in 40 mL of CH_2Cl_2. The mixture was stirred for 0.5 h followed by the addition of 25.3 mL (181.5 mmol) of triethylamine. The mixture was warmed to room temperature, diluted with 1:1 ether–hexane, filtered through anhydrous $MgSO_4$, and concentrated under reduced pressure. The crude aldehyde was dissolved in 75 mL of CH_2Cl_2 and cooled to 0 °C, and 17.79 g (51.0 mmol) of methyl α-(triphenylphosphorylidene)acetate was added. The mixture was stirred for 45 h at room temperature and concentrated under reduced pressure. The residue was carefully chromatographed on 200 g of silica gel eluting with 10% EtOAc in hexane to afford 7.15 g (90%) of (*E*)-butenoate 1 and 0.374 g (4%) of the *Z* isomer: IR (film) ν 3000, 2925, 1715, 1435, 1255, 1140 cm^{-1}; ^1H NMR (90 MHz) δ 1.80 (3 H, s, vinyl CH_3), 3.73 (3 H, s, OCH_3), 4.20 (2 H, d, J = 6 Hz, H4), 4.53 2 H, s, $PhCH_2O$), 6.85 (1 H, t, J = 6 Hz, H3), 7.33 (5 H, s, Ph). Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.88; H, 7.32. Found: C, 70.88; H, 7.35.

(*E*)-4-(Benzyloxy)-2-methyl-2-buten-1-ol (2). To a stirred, cooled (−78 °C) solution of 3.44 g (15.6 mmol) of ester 1 in 160 mL of ether was added 35.0 mL (35.0 mmol) of 1.0 M DIBAH in CH_2Cl_2. The solution was stirred for 20 min, quenched with 2 mL of methanol, and warmed to 0 °C. Saturated aqueous potassium sodium tartrate was added, and the mixture was stirred for 0.5 h at room temperature. The mixture was extracted with ether, and the combined organic layers were dried over anhydrous Na_2SO_4. Solvent was removed at reduced pressure, and the residue was chromatographed on 15 g of silica gel. Elution with 25% EtOAc in hexane afforded 2.95 g (98%) of alcohol 2: IR (film) ν 3350, 3010, 2850, 1460, 1075 cm^{-1}; ^1H NMR (90 MHz) δ 1.66 (3 H, s, vinyl CH_3), 4.00 (2 H, s, H1), 4.03 (2 H, d, J = 6 Hz, H4), 4.46 (2 H, s, $PhCH_2O$), 5.63 (1 H, t, J = 6 Hz, H3), 7.30 (5 H, s, Ph). Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 75.09; H, 8.43.

(*E*)-4-(Benzyloxy)-2-methyl-2-butenal (3). To a stirred, cooled (−78 °C) solution of 873 mg (6.9 mmol) of oxalyl chloride in 15 mL of dry CH_2Cl_2 was added 1.04 g (13.4 mmol) of DMSO in 4 mL of CH_2Cl_2 over 5 min.[8] The solution was stirred for 5 min, and 1.15 g (6.0 mmol) of alcohol 2 was added in 6 mL of CH_2Cl_2. The mixture was stirred for 0.5 h followed by the addition of 4.2 mL (30.1 mmol) of triethylamine. The mixture was warmed to room temperature, poured into water, and extracted with CH_2Cl_2. The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$. Solvent was removed under reduced pressure, and the residue was chromatographed on 6 g of silica gel. Elution with 5% EtOAc in hexane afforded 1.11 g (97%) of aldehyde 3 as a yellow oil: IR (film) ν 3000, 2825, 1680, 1460, 1210 cm^{-1}; ^1H NMR (90 MHz) δ 1.73 (3 H, s, vinyl CH_3), 4.33 (2 H, d, J = 6 Hz, H4), 4.58 (2 H, s, $PhCH_2O$), 6.60 (1 H, t, J = 6 Hz, H3), 7.36 (5 H, s, Ph), 9.45 (1 H, s, CHO). Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.75; H, 7.42. Found: C, 75.86; H, 7.45.

(*E,E*)-7-(Benzyloxy)-6-methyl-1-(triisopropylsilyl)-3,5-heptadien-1-yne (4). To a stirred, cooled (0 °C) solution of 2.95 g (11.2 mmol) of triphenylphosphine in 5 mL of dry benzene was added 3.09 g (11.02 mmol) of 3-bromo-1-(triisopropylsilyl)-1-propyne. The mixture was allowed to warm to room temperature and stir for 24 h. The white solid was filtered, washed thoroughly with cold hexane, and dried at reduced pressure to afford 5.60 g (93%) of phosphonium salt: ^1H NMR (90 MHz) δ 0.86 [(21 H, s, Si(i-Pr_3)], 5.23 (2 H, d, J = 15 Hz, H1), 8.06–7.50 (15 H, m, PPh_3). To a stirred, cooled (−78 °C) suspension of 804 mg (1.50 mmol) of the above phosphonium salt in 15 mL of THF was added 1 mL (1.50 mmol) of 1.5 M *n*-BuLi in hexanes. The red mixture was stirred for 0.5 h at −40 °C, and 205 mg (1.08 mmol) of aldehyde 3 was added dropwise. The mixture was warmed to 0 °C and stirred for 1 h. Solvent was removed under reduced pressure, and the residue was chromatographed on 12 g of silica gel. Elution with 5% EtOAc in hexane afforded 391 mg (99%) of dienyne 4 as an 88:12 mixture of *E*:*Z* isomers as determined by GC analysis: IR (film) ν 3050, 2930, 2850, 1470, 1120, 1080 cm^{-1}; ^1H NMR (400 MHz) δ 1.08 [(21 H, s, Si(i-$Pr)_3$], 1.73 (3 H, s, vinyl CH_3), 4.17 (2 H, d, J = 6.6 Hz, H7), 4.51 (2 H, s, $PhCH_2O$), 5.66 (1 H, d, J = 16.0 Hz, H3), 5.77 (1 H, t, J = 6.6 Hz, H6), 6.69 (1 H, d, J = 16.0 Hz, H4), 7.34 (5 H, s, Ph). Anal. *Calcd* for $C_{24}H_{36}OSi$: C, 78.20; H, 9.84. Found: 78.30; H, 9.89.

(*E,E*)-7-(Benzyloxy)-5-methyl-3,5-heptadien-1-yne (5). To a stirred, cooled (0 °C) solution of 300 mg (0.81 mmol) of alkyne 4 in 1 mL of THF was added 2.5 mL (2.5 mmol) of 1.0 M tetra-*n*-butylammonium fluoride in THF. The mixture was warmed to room temperature, stirred for 1 h, poured into water, and extracted with ether. The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$. Solvent was removed at reduced pressure, and the residue was chromatographed on silica gel. Elution with 5% EtOAc in hexane afforded 170 mg (99%) of dienyne 5, a 9:1 mixture of *E*:*Z* isomers as determined by GC analysis. This material rapidly discolored and was best used directly: IR (film) ν 3275, 3025, 2850, 1460, 1370, 1075 cm^{-1}; ^1H NMR (400 MHz) δ 1.74 (3 H, s, vinyl CH_3), 3.00 (1 H, s, H1), 4.17 (2 H, d, J = 6.5 Hz, H7), 4.52 (2 H, s, $PhCH_2O$), 5.57 (1 H, d, J = 16.1 Hz, H3), 5.77 (1 H, t, J = 6.5 Hz, H6), 6.72 (1 H, d, J = 16.1 Hz, H4), 7.34 (5 H, s, Ph).

(2*E*,4*E*)-(8*R*,9*S*,11*S*)- and -(8*S*,9*S*,11*S*)-12-[(*tert*-Butyldimethylsilyl)oxy]-3,9,11-trimethyl-1-(benzyloxy)-2,4-dodecadien-6-yn-8-ol (6). To a stirred, cooled (−78 °C) solution of 2.00 g (9.42 mmol) of dienyne 5 in 14 mL of THF was added 3.20 mL (8.00 mmol) of 2.5 M *n*-BuLi in hexanes dropwise. The solution was warmed to −50 °C over 20 min. To this solution was added dropwise 1.40 g (5.74 mmol) of (2*S*,4*S*)-5-[(*tert*-butyldimethylsilyl)oxy]-2,4-dimethylpentanal[5e] in 14 mL of THF. The solution was stirred at −50 °C for 45 min, and then the mixture was poured into saturated aqueous $NaHCO_3$ and extracted into ether. The combined organic phases were dried over anhydrous $MgSO_4$, the solvent was removed under reduced pressure, and the residue was chromatographed on 80 g of silica gel. Elution with 10% ether–hexanes, and then 60% ether–hexanes afforded 2.47 g (94%) of a viscous yellow oil, the diastereomeric alcohols 6: $[\alpha]_D$ −5.78° (*c* 1.87, $CHCl_3$); IR (film) ν 3410, 2950, 2920, 2850, 2200, 1450, 1090, cm^{-1}; ^1H NMR (300 MHz) δ 0.03 (6 H, s, Si-$(CH_3)_2$), 0.83 (3 H, d, J = 6.6 Hz, C11-CH_3), 0.88 (9 H, s, SiC-$(CH_3)_3$), 0.95 and 0.97 (3 H, d and d, J = 5.2 and 5.1 Hz, C9-CH_3), 1.24 and 1.31 (2 H, m and m, CH_2), 1.72 (3 H, s, vinyl CH_3), 1.86–1.99 (2 H, m, methine H), 3.38 (2 H, dd, J = 3.1 and 6.4 Hz, CH_2OTBS), 4.14 (2 H, d, J = 6.6 Hz, $BnOCH_2$), 4.37 (1 H, m, CHOH), 4.50 (2 H, s, $PhCH_2$), 5.58 (1 H, d, J = 16.0 Hz, H4), 5.70 (1 H, t, J = 6.6 Hz, H2), 6.58 (1 H, d, J = 16.0 Hz, H5), 7.27–7.34 (5 H, m, aryl H).

(2*E*,4*E*)-(9*S*,11*S*)-12-[(*tert*-Butyldimethylsilyl)oxy]-3,9,11-trimethyl-1-(benzyloxy)-2,4-dodecadien-6-yn-8-one (7). The procedure of Swern was followed.[8] A solution of 0.41 mL (4.65 mmol) of oxalyl chloride in 4 mL of CH_2Cl_2 was cooled to −78 °C, and 0.65 mL (9.30 mmol) of Me_2SO was added dropwise. Alcohol 6 (1.42 g, 3.10 mmol) in 3 mL of CH_2Cl_2 was then added dropwise. The mixture was stirred at −78 °C for 1.5 h followed by the addition of 2.15 mL (15.5 mmol) of Et_3N. After 30 min, the cold bath was removed, and when the suspension reached ca. 10 °C, water was added. The aqueous layer was extracted with

(22) The apparatus and methods described by G. W. Kramer, M. M. Midland, and A. B. Levy[23] were used to maintain an argon or nitrogen atmosphere in the reaction flask. Anhydrous solvents were obtained by distillation from benzophenone ketyl (diethyl ether, tetrahydrofuran), P_2O_5 (dichloromethane), calcium hydride (hexamethylphosphoramide), or sodium (benzene, toluene). Infrared absorption maxima are reported in wavenumbers (cm^{-1}) and are standardized by reference to the 1601 cm^{-1} peak of polystyrene. Proton magnetic resonance samples were prepared as dilute solutions in deuteriochloroform ($CDCl_3$). Chemical shifts (δ) are reported downfield from tetramethylsilane (Me_4Si) in parts per million (ppm) of the applied field. Peak multiplicities are abbreviated: singlet, s; doublet, d; triplet, t; quartet, q; pentuplet, p; envelope, e; multiplet, m. Coupling constants (J) are reported in hertz (Hz). Glass capillary gas chromatography was performed on a Hewlett-Packard 5890A GC equipped with a Superox 4 25M column. Combustion microanalyses were performed by Atlantic Laboratories, Norcross, GA. Analytical thin-layer chromatography (TLC) was routinely used to monitor reactions. Plates precoated with E. Merck silica gel 60 F254 of 0.25 mm thickness, supplied by Brinkmann Instruments, were used. E. Merck silica gel 60 (230–400 ASTM mesh) was employed for column chromatography according to the procedure of Still, Kahn, and Mitra.[24]

(23) Brown, H. C. *Organic Syntheses via Boranes*; Wiley: New York, 1975; pp 191–202.

(24) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

ether, and the combined organic phases were washed with brine and then dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure, and the residue was chromatographed on 60 g of silica gel. Elution with 5% ether–hexanes and then 10% ether–hexanes afforded 1.34 g (95%) of yellow liquid ketone **7**: $[\alpha]_D$ −4.80° (*c* 5.08, $CHCl_3$); IR (film) ν 3030, 2950, 2920, 2850, 2170, 1650, 1450, 1090 cm^{-1}; ^1H NMR (300 MHz) δ 0.02 (6 H, s, $Si(CH_3)_2$), 0.86 (3 H, d, J = 6.5 Hz, $CHCH_3$), 0.87 (9 H, s, $SiC(CH_3)_3$), 1.13 (3 H, d, J = 6.9 Hz, $CHCH_3$), 1.44–1.57 (3 H, m, H10 and H11), 1.75 (3 H, s, vinyl CH_3), 2.67 (1 H, m, $C(O)CHCH_3$), 3.41 (2 H, d, J = 5.7 Hz, CH_2OTBS), 4.17 (2 H, d, J = 6.3 Hz, $BnOCH_2$), 4.52 (2 H, s, $PhCH_2$), 5.65 (1 H, d, J = 16.0 Hz, H4), 5.88 (1 H, t, H2), 6.85 (1 H, d, J = 16.0 Hz, H5), 7.30–7.35 (5 H, m, aryl H); MS calcd for $C_{28}H_{42}O_3Si$ 454.2903, found 454.2920.

(2*E*,4*E*)-(8*S*,9*S*,11*S*)-12-[(*tert*-Butyldimethylsilyl)oxy]-3,9,11-trimethyl-1-(benzyloxy)-2,4-dodecadien-6-yn-8-ol (8b). To a stirred, cooled (0 °C) solution of 0.89 mL (0.89 mmol) of 1 M $LiAlH_4$ in THF in 55.0 mL of Et_2O was added 0.65 g (2.31 mmol) of α-(−)-4-(dimethylamino)-3-methyl-1,2-diphenyl-2-butanol (*ent*-Darvon alcohol) as a solution in 10.0 mL of Et_2O over 2 min. The mixture was stirred an additional 2 min at 0 °C and then cooled to −78 °C, and 338 mg (0.74 mmol) of ketone **7** was added as a solution in 10.0 mL of Et_2O over 1.0 h. This mixture was stirred for 3 h, warmed to 0 °C, and quenched with wet Et_2O. The aqueous layer was extracted with Et_2O, and the combined organic phases were washed with 1 N HCl and brine and then dried over $MgSO_4$. The solvent was removed at reduced pressure, and the resulting residue was chromatographed on silica gel. Elution with 30% ether–hexanes afforded 301 mg (89%) of a yellow oil: $[\alpha]_D$ −12.41° (*c* 2.40, C_6H_6); IR (film) 3400, 3030, 2900, 2205, 1450, 1245 cm^{-1}; ^1H NMR (300 MHz) δ 0.03 (6 H, s, $Si(CH_3)_3$, 0.83 (3 H, d, J = 6.6 Hz, $CHCH_3$), 0.88 (9 H, s, $SiC(CH_3)_3$), 0.96 (3 H, d, J = 6.7 Hz, $CHCH_3$), 1.16–1.32 (2 H, m, H10), 1.69 (1 H, m, $CHCH_3$), 1.72 (3 H, d, J = 1.0 Hz, vinyl CH_3), 1.85 (1 H, m, $CHCH_3$), 1.92 (1 H, d, J = 5.7 Hz, OH), 3.38 (2 H, m, $TBSOCH_2$), 4.14 (2 H, d, J = 6.6 Hz, $BnOCH_2$), 4.37 (1 H, m, CHOH), 4.50 (2 H, s, $PhCH_2$), 5.58 (1 H, d, J = 16.0 Hz, H4), 5.72 (1 H, m, H2), 6.58 (1 H, d, J = 16.0 Hz, H5), 7.28–7.34 (5 H, m, aryl H); MS calcd for $C_{28}H_{44}O_3Si$ 456.3060, found 456.3040. The diastereomeric ratio was found to be 13:1 through ^1H NMR analysis of the *O*-methyl mandelic esters **18** and **19**. These derivatives also establish the ee as >95% for alcohol **8b**.

(2*E*,4*E*,6*E*)-(8*S*,9*S*,11*S*)-12-[(*tert*-Butyldimethylsilyl)oxy]-3,9,11-trimethyl-1-(benzyloxy)-2,4,6-dodecatrien-8-ol (9). The propargylic alcohol **8** (530 mg, 1.16 mmol) in 15 mL of ether was cooled to 0 °C, and 1.10 mL (3.48 mmol) of 3.4 M Red-Al in toluene was added dropwise over 40 min. Stirring was continued for 45 min at 0 °C and for 1.75 h at room temperature. The mixture was quenched at 0 °C by the dropwise addition of saturated aqueous Rochelle's salt and was then extracted into ether. The combined organic phases were dried over anhydrous $MgSO_4$, and the solvent was removed under reduced pressure. The resulting residue was chromatographed on silica gel. Elution with 30% ether–hexanes afforded 488 mg (92%) of yellow liquid alcohol **9**: $[\alpha]_D$ +4.16° (*c* 2.14, $CHCl_3$); IR (film) ν 3420, 3040, 2960, 2930, 2860, 1460, 1100 cm^{-1}; ^1H NMR (300 MHz) δ 0.02 (6 H, s, $Si(CH_3)_2$), 0.84 and 0.86 (6 H, d and d, J = 1.5 and 1.7 Hz, $CHCH_3$), 0.87 (9 H, s, $Si(CH_3)_3$), 1.16–1.21 (2 H, m, CH_2), 1.70 (2 H, m, $CHCH_3$), 1.76 (3 H, s, vinyl CH_3), 3.33–3.43 (2 H, m, CH_2OTBS), 3.94 (1 H, m, CHOBn), 4.14 (2 H, d, J = 6.7 Hz, $BnOCH_2$), 4.50 (2 H, s, $PhCH_2$), 5.65–5.74 (2 H, m, H2 and H4), 6.23–6.27 (3 H, m, H5, H6, H7), 7.26–7.34 (5 H, m, aryl H); MS calcd for $C_{28}H_{46}O_3Si$ 458.3216, found 458.3209.

(2*E*,4*E*,6*E*)-(8*S*,9*S*,11*S*)-12-[(*tert*-Butyldimethylsilyl)oxy]-3,9,11-trimethyl-1,8-bis(benzyloxy)-2,4,6-dodecatriene (10). To a stirred, cooled (−78 °C) solution of 1.20 g (2.61 mmol) of alcohol **9**, dissolved in 2 mL of THF, was added 1.04 mL (2.61 mmol) of 2.5 M *n*-BuLi in hexanes, followed by 0.47 mL (3.95 mmol) of benzyl bromide and 0.91 mL (5.23 mmol) of HMPA, all within 5 min. The suspension was stirred at −78 °C for 30 min, the cold bath was removed, and stirring was continued for 72 h. The solution was poured into water and extracted into ether. The combined organic phases were washed with brine and dried over anhydrous $MgSO_4$, and the solvent was removed under reduced pressure. The residue was chromatographed on 50 g of silica gel. Elution with 10% ether–hexanes afforded 1.22 g (85%) of a yellow oil, the dibenzyl ether **10**: $[\alpha]_D$ −4.97° (*c* 3.65, CH_2Cl_2); IR (film) ν 3040, 2960, 2940, 2860, 1455, 1100 cm^{-1}; ^1H NMR (300 MHz) δ 0.01 (6 H, s, $Si(CH_3)_2$), 0.81 and 0.85 (6 H, d and d, J = 6.4 and 4.2 Hz, $CHCH_3$), 0.87 (9 H, s, $SiC(CH_3)_3$), 1.12–1.24 (2 H, m, CH_2), 1.60–1.90 (2 H, m, $CHCH_3$), 1.78 (3 H, s, vinyl CH_3), 3.33 (2 H, m, CH_2OTBS), 3.54 (1 H, m, CHOBn), 4.16 (2 H, d, J = 6.7 Hz, $BnOCH_2$), 4.30 and 4.55 (2 H, AB q, J_{AB} = 12.0 Hz, $CHOCH_2Ph$), 4.51 (2 H, s, $PhCH_2O$), 5.59–5.69 (2 H, m and m, H2 and H4), 6.20–6.28 (3 H, m, H5, H6, H7), 7.27–7.34 (10 H, m, aryl H). Anal. Calcd for $C_{35}H_{52}O_3Si$: C, 76.59; H, 9.55. Found: C, 76.41; H, 9.52.

(6*E*,8*E*,10*E*)-(2*S*,4*S*,5*S*)-5,12-Bis(benzyloxy)-2,4,10-trimethyl-6,8,10-dodecatrien-1-ol (11). To a solution of silyl ether **10** (1.0 g, 1.81 mmol) in 3.0 mL of THF at 0 °C was added 3.6 mL (3.6 mmol) of 1 M tetrabutylammonium fluoride in THF followed 20 min later by an additional 1.8 mL (1.8 mmol). After 3 h at room temperature the solution was poured into water and extracted into ether. The combined organic phases were dried over anhydrous $MgSO_4$, and the solvent was removed under reduced pressure. The residue was chromatographed on 21 g of silica gel. Elution with 10%, then 25%, and finally 50% ether–hexanes afforded 0.73 g (93%) of a viscous yellow oil, alcohol **11**: $[\alpha]_D$ −4.75° (*c* 2.84, CH_2Cl_2); IR (film) ν 3400, 3030, 2960, 2920, 2860, 1450, 1060 cm^{-1}; ^1H NMR (300 MHz) δ 0.85 (6 H, d, J = 6.7 Hz, $CHCH_3$'s), 1.14–1.23 (2 H, m, H3), 1.34–1.77 (2 H, m, $CHCH_3$), 1.78 (3 H, d, vinyl CH_3), 3.43 (2 H, m, CH_2OH), 3.56 (1 H, m, CHOBn), 4.16 (2 H, d, J = 6.7 Hz, $BnOCH_2$), 4.29 and 4.55 (2 H, AB q, J_{AB} = 11.9 Hz, OCH_2Ph), 4.51 (2 H, s, $PhCH_2O$), 5.58–5.66 (1 H, m, H9), 5.69 (1 H, t, J = 6.8 Hz, H11), 6.17–6.28 (3 H, m, H6, H7, H8), 7.26–7.34 (10 H, m, aryl H). Anal. Calcd for $C_{29}H_{38}O_3$: C, 80.14; H, 8.81. Found: C, 80.16; H, 8.84.

(6*E*,8*E*,10*E*)-(2*S*,4*S*,5*S*)-5,12-Bis(benzyloxy)-2,4,10-trimethyl-6,8,10-dodecatrienal (12). The procedure of Swern[8] was followed. A solution of 58 μL (0.66 mmol) of oxalyl chloride in 1.5 mL of CH_2Cl_2 was cooled to −78 °C and 94 μL (1.32 mmol) of Me_2SO was added dropwise. The alcohol **11** (250 mg, 0.57 mmol) in 1.0 mL of CH_2Cl_2 was then added dropwise. The mixture was stirred at −78 °C for 40 min followed by the addition of 240 μL (1.71 mmol) of Et_3N. After 15 min, the cold bath was removed, and when the suspension reached ca. 10 °C, water was added. The aqueous layer was extracted with ether, and the combined organic phases were washed with brine and then dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure, and the residue was chromatographed on silica gel. Elution with 20% ether–hexanes afforded 218 mg (88%) of aldehyde **12** as a yellow oil: $[\alpha]_D$ −4.95° (*c* 2.04, $CHCl_3$); IR (film) ν 3020, 2970, 2900, 2840, 2700, 1710, 1440, 1360, 1050 cm^{-1}; ^1H NMR (300 MHz) δ 0.89 (3 H, d, J = 6.7 Hz, $CHCH_3$), 1.05 (3 H, d, J = 6.9 Hz, $CHCH_3$), 1.55 (2 H, m, H3), 1.81 (3 H, s, vinyl CH_3), 1.83 (1 H, m, H4), 2.43 (1 H, m, H2), 3.59 (1 H, m, H5), 4.18 (2 H, d, J = 6.7 Hz, H12), 4.29 and 4.57 (2 H, AB q, J_{AB} = 11.9 Hz, OCH_2Ph), 4.53 (2 H, s, $PhCH_2O$), 5.59–5.67 (1 H, m, H9), 5.70–5.75 (1 H, m, H11), 6.23–6.32 (3 H, m, H6, H7, H8), 7.27–7.36 (10 H, m, aryl H), 9.59 (1 H, s, CHO); MS calcd for $C_{28}H_{36}O_3$ 432.2664, found 432.2661.

(2*E*,8*E*,10*E*,12*E*)-(4*S*,6*S*,7*S*)-Methyl 7,14-Bis(benzyloxy)-2,4,6,12-tetramethyltetradeca-2,8,10,12-tetraenoate (13). To a stirred, cooled (0 °C) solution of 160 mg (0.37 mmol) of trienal **12** in 0.60 mL of CH_2Cl_2 was added 250 mg (0.74 mmol) of methyl α-(triphenylphosphorylidene)propionate. After 45 min the mixture was warmed to room temperature and stirred for 45 h. The mixture was poured into water and extracted into ether. The combined organic phases were washed with brine and dried over $MgSO_4$, and the solvent was removed under reduced pressure. The residue was chromatographed on silica gel. Elution with 20% ether–hexanes afforded 163 mg (88%) of the methyl ester **13**: $[\alpha]_D$ +16.51° (*c* 6.70, $CHCl_3$); IR (film) ν 3090, 3060, 3020, 2950, 2920, 2850, 1700, 1450, 1260, 1100 cm^{-1}; ^1H NMR (300 MHz) δ 0.87 (3 H, d, J = 6.8 Hz, $CHCH_3$), 0.93 (3 H, d, J = 6.6 Hz, $CHCH_3$), 1.07–1.17 (2 H, m, H5), 1.48–1.57 (2 H, m, $CHCH_3$), 1.7 (3 H, d, J = 1.4 Hz, vinyl CH_3), 1.79 (3 H, s, vinyl CH_3), 2.54–2.60 (1 H, m, H3), 3.55 (1 H, dd, J = 5.8 and 8.3 Hz, CHOBn), 3.72 (3 H, s, CH_3CO_2), 4.17 (2 H, d, J = 6.7 Hz, $BnOCH_2$), 4.28 and 4.54 (2 H, AB q, J_{AB} = 12.1 Hz, OCH_2Ph), 4.52 (2 H, s, $PhCH_2O$), 5.57–5.65 (1 H, m, H11), 5.69–5.73 (1 H, m, H13), 6.17–6.37 (3 H, m, H8, H9, H10), 6.51–6.58 (1 H, m, H3), 7.25–7.35 (10 H, m, aryl H); MS calcd for $C_{33}H_{42}O_4$ 502.3083, found 502.3088.

(2*E*,8*E*,10*E*,12*E*)-(4*S*,6*S*,7*S*)-7,14-Bis(benzyloxy)-2,4,6,12-tetramethyl-2,8,10,12-tetradecatetraen-1-ol (14). To a stirred, cooled (−78 °C) solution of 208 mg (0.41 mmol) of ester **13** in 13 mL of ether was added 0.90 mL (0.90 mmol) of 1 M DIBAH in hexanes dropwise. Stirring was continued for 30 min at −78 °C, and the reaction was quenched with saturated aqueous Rochelle's salt solution. The solution was extracted into ether, washed with brine, and dried over anhydrous $MgSO_4$, and the solvent was removed under reduced pressure. The residue was chromatographed on silica gel. Elution with 40% ether–hexanes afforded 187 mg (95%) of alcohol **14**: $[\alpha]_D$ −18.50° (*c* 1.91 $CHCl_3$); IR (film) ν 3400, 3020, 2950, 2900, 2840, 1445, 1060, 980 cm^{-1}; ^1H NMR (300 MHz) δ 0.89 (6 H, d, *J* = 6.7 Hz, $CHCH_3$), 1.08 (2 H, m, CH_2), 1.44 (1 H, m, $CHCH_3$), 1.60 (3 H, d, *J* = 1.1 Hz, vinyl CH_3), 1.80 (3 H, s, vinyl CH_3), 2.47 (1 H, m, H4), 3.60 (1 H, dd, *J* = 5.5 and 8.3 Hz, CHOBn), 3.94 (2 H, s, CH_2OH), 4.17 (2 H, d, *J* = 6.7 Hz, $BnOCH_2$), 4.31 and 4.56 (2 H, AB q, J_{AB} = 12.1 Hz, OCH_2Ph), 4.53 (2 H, s, $PhCH_2O$), 5.18 (1 H, d, *J* = 9.4 Hz, H3), 5.61–5.74 (2 H, m, H11 and H13), 6.19–6.30 (3 H, m, H8, H9, H10), 7.25–7.36 (10 H, m, aryl H); MS calcd for $C_{32}H_{42}O_3$ 474.3134, found 474.3133.

(2*E*,8*E*,10*E*,12*E*)-(4*S*,6*S*,7*S*)-7,14-Bis(benzyloxy)-2,4,6,12-tetramethyl-2,8,10,12-tetradecatetraenal (15). Tetraenol **14** (124 mg, 0.26 mmol) was oxidized by the method of Swern[8] with 30 μL (0.34 mmol) of oxalyl chloride, 50.0 μL (0.69 mmol) of Me_2SO, and 180.0 μL (1.30 mmol) of triethylamine in 5 mL of CH_2Cl_2 as described above. Purification by chromatography on silica gel eluted with 20% ether–hexanes afforded 93.0 mg (76%) of aldehyde **15**: $[\alpha]_D$ −17.5° (*c* 1.20, $CHCl_3$); IR (film) ν 3010, 2950, 2910, 2840, 1675, 1445, 1060 cm^{-1}; ^1H NMR (300 MHz) δ 0.87 (3 H, d, *J* = 6.8 Hz, $CHCH_3$), 0.99 (3 H, d, *J* = 6.6 Hz, $CHCH_3$), 1.17 (2 H, m, CH_2), 1.57 (1 H, m, $CHCH_3$), 1.67 (3 H, d, *J* = 1.3 Hz, vinyl CH_3), 2.76 (1 H, m, $CHCH_3$), 3.56 (1 H, m, CHOBn), 4.16 (2 H, d, *J* = 6.7 Hz, $BnOCH_2$), 4.26 and 4.55 (2 H, AB q, J_{AB} = 12.1 Hz, OCH_2Ph), 4.51 (2 H, s, $PhCH_2O$), 5.56–5.65 (1 H, m, H11), 5.70 (1 H, m, H13), 6.18–6.33 (4 H, m, H3, H8, H9, H10), 7.27–7.34 (10 H, m, aryl H), 9.35 (1 H, s, CHO); MS calcd for $C_{32}H_{40}O_3$ 472.2977, found 472.2985.

(3*S*,4*S*,4a*S*,5*S*,7*S*,8*S*,8a*S*)-8-(Benzyloxy)-4,5,7-trimethyl-3-[(*E*)-3-(benzyloxy)-1-methyl-1-propenyl]-3,4,4a,5,6,7,8,8a-octahydronaphthalene-4-carboxaldehyde (16). A. Catalyzed Cyclization. To a stirred, cooled (−78 °C) solution of 33 mg (0.070 mmol) of tetraenal **15** (azeotropically dried with benzene) in 3.0 mL of CH_2Cl_2 was added 80 μL (0.080 mmol) of 1.0 M Me_2AlCl in hexanes. The mixture was stirred for 1 h at −78 °C, warmed slowly over 2 h to −30 °C, and stirred an additional 2 h. The reaction was quenched by the addition of saturated aqueous $NaHCO_3$ and extracted into CH_2Cl_2. The combined organic phases were washed with brine, and dried over anhydrous $MgSO_4$, and the solvent was removed under reduced pressure. The residue was chromatographed on 4 g of silica gel. Elution with 5% ether–hexanes afforded 28 mg (85%) of the hydronaphthalene **16**: $[\alpha]_D$ −40.6° (*c* 1.10, $CHCl_3$); IR (film) ν 3020, 2950, 2900, 2850, 1710, 1445, 1375, 1080 cm^{-1}; ^1H NMR (300 MHz) δ 0.67 (3 H, d, *J* = 5.8 Hz, $CHCH_3$), 1.01 (3 H, d, *J* = 7.1 Hz, $CHCH_3$), 1.09 (3 H, s, C4-CH_3), 1.41 (1 H, m, $CHCH_3$), 1.55–1.67 (2 H, m, CH_2), 1.61 (3 H, s, vinyl CH_3), 2.17 (1 H, m, H8a), 2.4 (2 H, m, H3 and H4a), 3.27 (1 H, dd, *J* = 11.0 and 5.1 Hz, H8), 4.03 (2 H, m, $BnOCH_2$), 4.38 and 4.64 (2 H, AB q, J_{AB} = 11.3 Hz, OCH_2Ph), 4.48 (2 H, s, $PhCH_2O$), 5.40 (1 H, ddd, *J* = 10.2, 4.6, 2.6 Hz, H2), 5.50 (1 H, ddd, *J* = 6.3, 1.0, 1.0 Hz, $BnOCH_2CH$), 6.13 (1 H, ddd, *J* = 10.2, 1.7, 1.7 Hz, H1), 7.27–7.39 (10 H, m, aryl H), 9.44 (1 H, s, CHO). Anal. Calcd for $C_{32}H_{40}O_3$: C, 81.32, H, 8.53. Found: C, 81.17; H, 8.57.

B. Thermal Cyclization. A solution of 47 mg (0.10 mmol) of tetraenal **15** in 10 mL of toluene containing a single crystal of BHT was placed in a thick-wall tube and degassed. The tube was sealed and heated at 200 °C in an oil bath for 40 h. The tube was cooled to room temperature and opened, solvent was removed under reduced pressure, and the residue was chromatographed on silica gel with 15% ether–hexanes to afford 38 mg (81%) of the hydronaphthalene **16**: $[\alpha]_D$ −40.8° (*c* 2.40, $CHCl_3$). The infrared and ^1H NMR spectra of this material were identical with those of a sample prepared as described in part A.

Methyl (3*S*,4*S*,4a*S*,5*S*,7*S*,8*S*,8a*S*)-8-(Benzyloxy)-4,5,7-trimethyl-3-[(*E*)-3-(benzyloxy)-1-methyl-1-propenyl]-3,4,4a,5,6,7,8,8a-octahydronaphthalene-4-carboxylate (17). A solution of 74 mg (0.15 mmol) of tetraenoate **13** in 30 mL of toluene containing a single crystal of BHT was placed in a thick-wall tube and degassed. The tube was sealed and heated at 210 °C in an oil bath for 48 h. The tube was cooled to room temperature and opened, solvent was removed under reduced pressure, and the residue was chromatographed on silica gel. Elution with 5% ether–hexanes afforded 66 mg (89%) of ester **17**: IR (film) ν 3020, 2900, 1715, 1445, 1245, 1085 cm^{-1}; ^1H NMR (300 MHz) δ 0.67 (3 H, d, *J* = 6.5 Hz, $CHCH_3$), 1.00 (3 H, d, *J* = 7.1 Hz, $CHCH_3$), 1.20 (3 H, s, C4-CH_3), 1.55 (3 H, d, *J* = 3.0 Hz, vinyl CH_3), 2.08 (1 H, m, H8a), 3.28 (1 H, dd, *J* = 5.2 and 10.9 Hz, H8), 3.47 (3 H, s, CO_2Me), 4.00 (2 H, m, $BnOCH_2$), 4.37 and 4.62 (2 H, AB q, J_{AB} = 11.4 Hz, OCH_2Ph), 4.48 (2 H, s, $PhCH_2O$), 5.37–5.40 (2 H, m, H2 and $BnOCH_2CH$), 6.12 (1 H, m, H1), 7.27–7.36 (10 H, m, aryl H). Although this material appeared as a single spot upon TLC analysis in several solvent systems, expansion and integration of the methoxy signal at 3.47 ppm in the ^1H NMR spectrum indicated the presence of at least three compounds in the ratio 80:19:1.

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Supplementary Material Available: ^1H NMR spectra of **5–7**, **8b**, **9**, **12–15**, and **17** (10 pages). Ordering information is given on any current masthead page.