Enantioselective Synthesis of Alkyl-Branched Alkanes. Synthesis of the Stereoisomers of 7,11-Dimethylheptadecane and 7-Methylheptadecane, Components of the Pheromone of *Lambdina* Species

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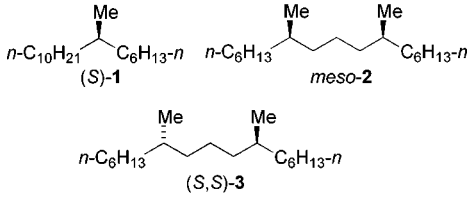
The stereoisomers of 7,11-dimethylheptadecane and 7-methylheptadecane have been synthesized. The key step used has been the intramolecular hydride transfer from a secondary γ-benzyloxy group with defined absolute stereochemistry to a cation generated by Lewis acid treatment of the suitable tertiary $Co_2(CO)_6$-complexed propargylic alcohol. The application of this method provided stereochemically defined α-alkyl-γ-hydroxy-acetylenes that after hydrogenation and further reductive elimination of the hydroxyl group yielded *sec*-alkyl hydrocarbons.

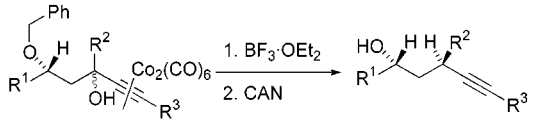
Introduction

Compounds having stereochemically defined alkyl-branched hydrocarbon chains are widespread in nature.[1] This fact is particularly important when enantiomerically active pheromones are considered.[2] (*S*)-7-Methylheptadecane (**1**) and/or *meso*-7,11-dimethylheptadecane (**2**) have been established as the bioactive female pheromone components in *Lambdina athasaria* (spring hemlock looper moth),[3] *Lambdina pellucidaria* (pitch pine looper moth),[4] *Lambdina fiscellaria fiscellaria* (Hulst),[5] and *Lambdina fiscellaria lugubrosa* (Hulst).[6] Racemic (±)-**1** and a mixture of *meso*-**2** and (±)-**3** have been synthesized and found to be bioactive.[4] The stereocontrolled syntheses of (*R*)-**1**, (*S*)-**1**, *meso*-**2**, (*S*,*S*)-**3,** and (*R*,*R*)-**3** have very recently been reported and showed that the pheromone components are (*S*)-**1** and *meso*-**2.**[7]

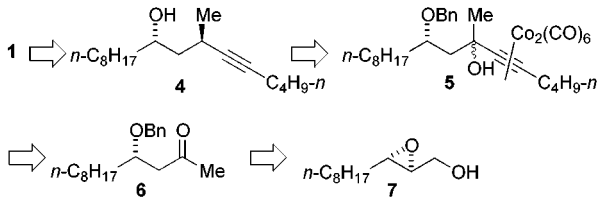


Recently, we reported on a very efficient protocol to perform the stereocontrolled reduction of tertiary propargylic alcohols by an intramolecular hydride transfer from a stereochemically defined benzyloxy group located at the bis-homo propargylic position (Scheme 1).[8] The main synthetic advantage of our method is that we can obtain *sec*-dialkyl acetylenes with absolute stereochemical control. In this paper, we report on our studies directed to the enantiomeric synthesis of methyl- and 3-methylene-interrupted dimethylalkanes and particularly the stereoisomers of 7,11-dimethylheptadecane and 7-methylheptadecane, taking synthetic advantage of the procedure outlined above.

Scheme 1



Scheme 2



Results and Discussion

Synthesis of Alkyl-Branched Alkanes. Our strategy for the controlled synthesis of stereochemically defined alkyl-substituted alkanes is based on the retrosynthetic analysis outlined in Scheme 2. We considered the synthesis of **1** from the bis-homopropargylic alcohol **4**, that in accordance with the above-mentioned reductive procedure may be obtained from the $Co_2(CO)_6$-acetylenic diols **5**. In this diastereomeric mixture, the only stereochemical requirement is a defined configuration at the benzyloxy position, that of the propargylic position being irrelevant. Retrosynthetic cleavage of such carbinols afforded, via an acetylide addition, the methyl ketone **6** as a potential precursor. The stereochemistry of the necessary benzyloxy group could be secured through the

(1) (a) *Dictionary of Natural Products*; Chapman & Hall: New York, 1998; Vol. 11 (4th Suppl.). (b) Faulkner, D. J. *Nat. Prod. Rep.* **1999**, *16*, 155, and references therein.

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(6) Gries, R.; Gries, G.; Krannitz, S. H.; Li, J.; King, G. G. S.; Slessor, K. N.; Borden, J. H.; Bowers, W. W.; West, R. J.; Underhill, E. W. *J. Chem. Ecol.* **1993**, *19*, 1009.

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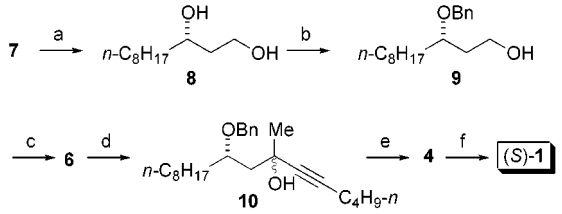
Scheme 3[a]



[a] Key: (a) Red-Al, THF, 0 °C, 93%; (b) (i) $PhCH(OMe)_2$, CSA (cat.), CH_2Cl_2, rt, (ii) DIBAL-H, CH_2Cl_2, 0 °C, 84% overall; (c) (i) SO_3·Py, DMSO, Et_3N, CH_2Cl_2, rt, (ii) MeMgCl, THF, −78 °C, (iii) PCC, CH_2Cl_2, rt, 74% overall; (d) $LiC{\equiv}CC_4H_9$-*n*, THF, −78 °C; (e) (i) $Co_2(CO)_8$, CH_2Cl_2, rt; (ii) BF_3·OEt_2, CH_2Cl_2, −20 °C, (iii) CAN, acetone, 0 °C, 75% overall; (f) (i) H_2, Pd/C, EtOAc, (ii) MsCl, Et_3N, CH_2Cl_2; 0 °C, (iii) $LiAlH_4$, THF, reflux, 73% overall.

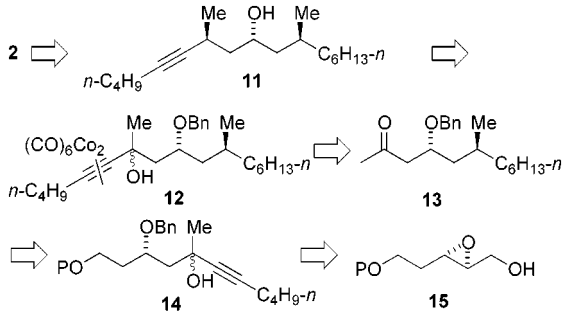
2,3-epoxy alcohol **7** easily available by the use of the Katsuki−Sharpless asymmetric epoxidation.[9]

The known epoxide **7**[10] was regioselectively opened to the corresponding 1,3-diol **8** using Red-Al as the reducing agent (Scheme 3).[11] To differentiate both hydroxyl groups and to introduce the necessary benzyloxy group at the secondary position, we protected the diol as the benzylidene acetal. Reductive opening of the cyclic ether with DIBAL-H provided the benzyl protected secondary alcohol **9** as the major regioisomer (5:1).[12] To obtain the necessary tertiary propargylic alcohol, the primary alcohol in **9** was oxidized to the corresponding aldehyde that after addition of the suitable alkyl Grignard reagent and new oxidation provided the desired methyl ketone **6**. The simple addition of the lithium acetylide derived from 1-hexyne provided the desired diastereomeric mixture **10**. Although the stereochemistry at the propargylic position is irrelevant for our purposes, it should be pointed out that a slight enrichment of one diastereosiomer was obtained (ca. 1.5:1).

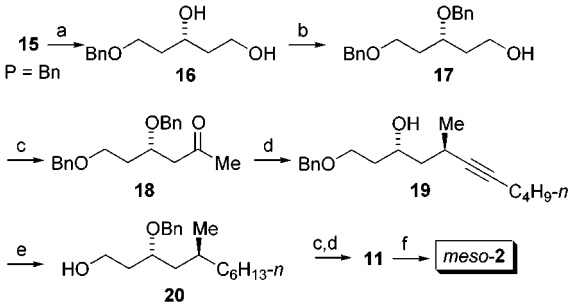
With the propargylic alcohol mixture **10** in our hands, we were ready to apply our intramolecular reduction procedure. We first complexed the carbon−carbon triple bond as the corresponding $Co_2(CO)_6$-acetylene derivative **5**. This Co-complex was then submitted to acidic treatment with BF_3·OEt_2 and further demetalated under oxidative conditions, providing the bis-homopropargylic alcohol **4** as the only detected stereoisomer. Finally, and to obtain the natural compound, the acetylene was hydrogenated to the saturated chain, and the hydroxyl group was eliminated via the mesylation and further hydride reduction to afford (*S*)-7-methylheptadecane (**1**) $[\alpha]^{25}_D = +0.29$ (*c* 5.13, hexane) [lit.[7] $[\alpha]^{25}_D = +0.275$ (*c* 5.02, hexane)].

Synthesis of 3-Methylene-Interrupted Dialkyl-Branched Alkanes. The achievement of the enantiomeric synthesis of **1** prompted us to speculate over the iterative application in both directions of the above-described reduction, taking a central benzyloxy group as the stereochemical director. In this sense, the stereocontrolled synthesis of *meso*-**2** could be envisioned from a secondary alcohol such as **11**, available by application of our methodology to a complexed tertiary carbinol such as **12** (Scheme 4). Thus, the synthesis of an additional tertiary alcohol forces us to perform the first reductive process over a substrate with an additional protected hydroxyl group **14**, this molecule being easily available from the corresponding 2,3-epoxy alcohol **15** by a similar methodology to that outlined earlier.

Scheme 4



Scheme 5[a]



[a] Key: (a) Red-Al, THF, 0 °C, 88%; (b) (i) DHP, CH_2Cl_2, $OPCl_3$, 0 °C, (ii) $PhCH_2Br$, NaH, *n*-Bu_4NI (cat.), THF, rt, (iii) MeOH, HCl (cat.), rt, 73% overall; (c) (i) SO_3·Py, DMSO, Et_3N, CH_2Cl_2, rt, (ii) MeMgCl, THF, −78 °C, (iii) PCC, CH_2Cl_2, rt, 76% overall; (d) (i) $LiC{\equiv}CC_4H_9$-*n*, THF, −78 °C, (ii) $Co_2(CO)_8$, CH_2Cl_2, rt, (iii) BF_3·OEt_2, CH_2Cl_2, −20 °C, (iv) CAN, acetone, 0 °C, 77% overall; (e) (i) H_2, Pd/C, EtOAc, rt, (ii) $PhCH(OMe)_2$, CSA (cat.), CH_2Cl_2, (iii) DIBAL-H, CH_2Cl_2, 0 °C, 81% overall; (f) (i) H_2, Pd/C, EtOAc, rt, (ii) MsCl, Et_3N; CH_2Cl_2; 0 °C, (iii) $LiAlH_4$, THF, reflux, 71% overall.

The application to the known epoxide **15**[13] (P = Bn) of a methodology similar to that described above yielded the free alcohol **19** with the stereochemically well-defined methyl group located at the α-position relative to the triple bond (Scheme 5). Interestingly, it should be pointed out that in this case we had to apply a different procedure to locate the benzyloxy group at the secondary position since the DIBAL-H reduction of the benzylidene derivative of **16** provided the primary benzyl ether as the major product. Thus, we had to obtain **17** from **16** by a consecutive series of protecting group manipulations, namely monoprotection of the primary alcohol as the THP-ether, benzyl ether formation of the secondary carbinol and cleavage of the primary ether.

The hydrogenation of **19** permitted simultaneously the cleavage of the benzyl-protecting group and reduction of the triple bond to the corresponding saturated chain. The resulting diol was protected as the benzylidene derivative that after reduction with DIBAL-H provided **20**, having the necessary secondary benzyloxy group (to induce a new intramolecular reduction) and the free primary

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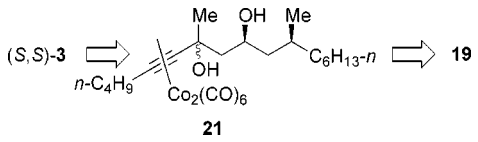
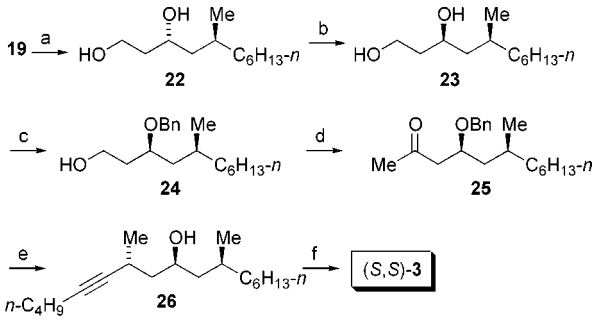
Scheme 6



Scheme 7[a]



[a] Key: (a) H_2, Pd/C, EtOAc, rt, 100%; (b) (i) MsCl, Et_3N, CH_2Cl_2, (ii) KOAc, 18-crown-6 (cat.), Be, reflux, (iii) MeOH, NaH, CH_2Cl_2, 0 °C, 77% overall; (c) (i) $PhCH(OMe)_2$, CSA (cat.), CH_2Cl_2, (ii) DIBAL-H, CH_2Cl_2, 0 °C 82% overall; (d) (i) SO_3·Py, DMSO, Et_3N, CH_2Cl_2, (ii) MeMgCl, THF, −78 °C, (iii) PCC, CH_2Cl_2, 0 °C, 75% overall; (e) (i) LiC≡CC_4H_9-*n*, THF, −78 °C; (ii) $Co_2(CO)_8$, CH_2Cl_2, rt, (iii) BF_3·OEt_2, CH_2Cl_2, −20 °C, (iv) CAN, acetone, 0 °C, 73% overall; (f) (i) H_2, Pd/C, EtOAc, rt, (ii) MsCl, Et_3N; CH_2Cl_2; 0 °C, (iii) $LiAlH_4$, THF, reflux, 70% overall.

alcohol to homologate the chain. With the iteration of the former sequence of reactions the free alcohol **11** was obtained without any contamination of stereoisomers. Finally, the reductive elimination of the hydroxyl group provided *meso*-**2**, identical in all aspects to the natural product.

Although it has been established that the bioactive pheromone components are (*S*)-**1** and *meso*-(**2**) our methodology would also be ideal for the synthesis of the other diastereoisomers of **2**. Thus, addressing our attention over the synthesis of (*S*,*S*)-**3** should be easily resolved by application of above-described method to the epimeric alcohols **21** that should be available from **19** after inversion of the configuration at the carbinol center (Scheme 6).

To perform the necessary inversion at the secondary carbinol center, the acetylenic alcohol **19** was submitted to hydrogenation (Scheme 7). In one step, concomitant benzyl ether cleavage and triple bond hydrogenation provided the diol **22**. Simultaneous mesylation of the diol system and further treatment with sodium acetate provided the corresponding diacetates with inverted configuration at the secondary center. Basic hydrolysis of both esters yielded the diol **23** as a pure stereoisomer, verified by comparison with **22** and the corresponding diacetates. After this point, an iterative application of the series of reactions used above led to (7*S*,11*S*)-dimethylheptadecane [(*S*,*S*)-**3**] $[\alpha]^{25}_D = +1.63$ (*c* 1.52, hexane) [lit.[7] $[\alpha]^{22}_D = +1.77$ (*c* 1.41, hexane)].

Conclusions

The Lewis acid treatment of tertiary $Co_2(CO)_6$-propargylic alcohols having a stereochemically defined benzyloxy group at the γ-benzyl position yielded after cobalt demetalation *sec*-dialkyl bis-homopropargylic alcohols in good yields. The hydrogenation of the acetylene and the reductive elimination of the alcohol group provided an excellent way to achieve the synthesis of alkyl branched alkanes with perfect control of the stereochemistry. With the application of this intramolecular reductive process the enantiomeric synthesis has been accomplished of the pheromone component of some species of *Lambdina*, structurally characterized as methyl-substituted linear alkanes. Although the presented methodology has been described only for one enantiomeric series, the alternative choice of the tartrate auxiliary in the Katsuki−Sharpless asymmetric epoxidation step reaction for the synthesis of the starting epoxy alcohols permits us to control the absolute configuration in the final product. The application of the described methodology could be a way to gain access to the enantiomeric series of many other natural compounds having alkyl-substituted hydrocarbons in their structures.

Experimental Section

Materials and Methods. ^1H and ^{13}C NMR spectra were recorded at 400 and 75 MHz, respectively, and chemical shifts are reported relative to internal Me_4Si. Optical rotations were determined for solutions in chloroform or *n*-hexane. Column chromatography was performed on Merck silica gel, 60 Å and 230−400 mesh. Compounds were visualized by use of UV light and/or 2.5% phosphomolybdic acid in ethanol with heating. All solvents were purified by standard techniques.[14] Reactions requiring anhydrous conditions were performed under argon. Anhydrous magnesium sulfate was used for drying solutions.

Preparation of (3*S*)-Undecane-1,3-diol (8). To a solution of **7**[10] (0.30 g, 1.61 mmol) in dry THF (8 mL) was slowly added Red-Al (1.2 mL, 3.4 M solution in toluene, 4.03 mmol) at 0 °C under argon. The reaction mixture was stirred for 2.5 h, after which time TLC showed no remaining epoxide. Then water (3 mL) and HCl (5% w/v in water) (6 mL) were sequentially added, and the mixture was stirred until clear phases were reached (0.5 h). The phases were separated, and the aqueous phase was extracted with Et_2O. The combined organic phases were washed with saturated aqueous $NaHCO_3$ and brine, dried, filtered, concentrated, and purified by column chromatography to yield **8** (0.28 g, 93% yield) as a colorless oil: $[\alpha]^{25}_D = -0.25$ (*c* 2.40, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 0.85 (t, $J = 6.3$ Hz, 3H), 1.90−1.38 (br s, 11H), 1.38−1.50 (m, 3H), 1.52−1.72 (m, 2H), 3.30 (br s, 2H), 3.81 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 14.12 (q), 22.62 (t), 25.53 (t), 29.24 (t), 29.55 (t), 29.63 (t), 31.84 (t), 37.74 (t), 38.21 (t), 61.50 (t), 72.29 (d); IR (film) $\tilde{\nu}_{max}$ (cm^{-1}) 3347, 2926, 2855, 1466; MS *m*/*z* (relative intensity) 188 $(M)^+$ (0.1), 187 $(M - 1)^+$ (0.2), 141 (18), 83 (17), 75 (100). Anal. Calcd for $C_{11}H_{24}O_2$: C, 70.16; H, 12.85. Found: C, 70.16; H, 12.97.

Preparation of (3*S*)-3-(Phenylmethoxy)undecan-1-ol (9). To a stirred solution of **8** (0.16 g, 0.85 mmol) in dry CH_2Cl_2 (8 mL) were sequentially added a catalytic amount of CSA (21 mg, 0.085 mmol) and benzaldehydedimethyl acetal (179 μL, 1.17 mmol) at room temperature. The reaction mixture was stirred for 1 h, after which time TLC showed complete conversion to the benzylidene derivative. Then, Et_3N was added until pH ≈ 7, and the mixture was stirred for 5 min and evaporated under reduced pressure.

To a solution of the crude obtained in dry CH_2Cl_2 (6 mL) was slowly added DIBAL-H (8.5 mL, 1 M solution in cyclohexane, 8.5 mmol) at 0 °C. After this addition, the mixture was allowed to warm to room temperature for a period of 15 min with stirring and diluted with CH_2Cl_2 (20 mL), and aqueous HCl (5% w/v in water) (10 mL) was added. The resulting mixture was extracted with CH_2Cl_2. The combined organic layers were washed with saturated aqueous $NaHCO_3$ and brine, dried, filtered, concentrated, and purified by column chromatography to afford **9** (199 mg, 70% overall yield) as a colorless oil: $[\alpha]^{25}_D = +34.3$ (*c* 2.92, $CHCl_3$); ^1H NMR ($CDCl_3$)

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δ 0.89 (t, J = 6.6 Hz, 3H), 1.28 (br s, 13H), 1.48−1.83 (m, 3H), 2.15 (br s, 1H), 3.64 (m, 1H), 3.75 (m, 2H), 4.54 (dd, J = 35.3, 11.4 Hz, 2H), 7.34 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 14.1 (q), 22.7 (t), 25.1 (t), 29.3 (t), 29.6 (t), 29.8 (t), 31.9 (t), 33.5 (t), 36.0 (t), 60.6 (t), 70.9 (t), 78.4 (d), 127.7 (d), 127.8 (d), 128.0 (d), 128.4 (d), 138.5 (s); IR (film) $\tilde{\nu}_{max}$ (cm^{-1}) 3405, 2855, 1455, 1350, 1066; MS m/z (relative intensity) 278 $(M)^+$ (2), 260 $(M - H_2O)^+$ (7), 107 (28), 91 (100). Anal. Calcd for $C_{18}H_{30}O_2$: C, 77.65; H, 10.86. Found: C, 77.69; H, 10.71.

Preparation of (4*S*)-4-(Phenylmethoxy)dodecan-2-one (6). SO_3-py complex (0.27 g, 1.69 mmol) was added to a stirred mixture of **9** (150 mg, 0.54 mmol), Et_3N (0.38 mL, 2.7 mmol), dry DMSO (1.11 mL, 5.78 mmol), and dry CH_2Cl_2 (3 mL) at 0 °C. The reaction mixture was stirred until TLC showed completion of the reaction (ca. 2 h). Then the mixture was diluted with CH_2Cl_2, washed with brine, dried, filtered, and concentrated, providing the aldehyde that was suitable for use without further purification.

To a solution of the crude aldehyde in THF (5.5 mL) was added dropwise MeMgCl (0.24 mL, 3 M in THF, 0.70 mmol) at −78 °C. After the mixture was stirred for 0.5 h, saturated NH_4Cl solution (5 mL) was added, and the resulting slurrywas extracted with Et_2O. The combined organic extracts were dried, filtered, and concentrated. The residual oil was used without further purification.

To a solution of the crude diastereomeric alcohols in dry CH_2Cl_2 (6 mL) were sequentially added PCC (0.23 g, 1.08 mmol), powdered 4-Å molecular sieves, and a small amount of NaOAc (ca. 10 mg). The heterogeneous mixture was stirred for 4 h, filtered through a pad of silica gel, and concentrated. The resulting viscous oil was purified by flash column chromatography to yield **6** (116 mg, 74% yield) as a colorless oil: $[\alpha]^{25}_D$ = +15.2 (*c* 0.53, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 6.5 Hz, 3H), 1.26 (br s, 12H), 1.58 (m, 2H), 2.16 (s, 3H), 2.51 (dd, J = 15.8, 4.8 Hz, 1H), 2.75 (dd, J = 15.8, 7.5 Hz, 1H), 3.92 (dddd, J = 6.0, 6.0, 6.0, 6.0 Hz, 1H), 4.51 (dd, J = 10.6, 14.7 Hz, 2H), 7.30 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 14.1 (q), 22.6 (t), 25.1 (t), 29.2 (t), 29.5 (t), 29.6 (t), 31.2 (q), 31.8 (t), 34.3 (t), 48.6 (t), 71.5 (t), 75.6 (d), 127.6 (d), 127.8 (d), 128.3 (d), 128.4 (d), 128.8 (d), 138.5 (s), 207.9 (s); IR (film) $\tilde{\nu}_{max}$ (cm^{-1}) 2926, 2233, 1721, 1357, 1070; MS m/z (relative intensity) 290 $(M)^+$ (0.4), 152 (29), 107 (32), 91 (100). Anal. Calcd for $C_{19}H_{30}O_2$: C, 78.57; H, 10.41. Found: C, 78.52; H, 10.71.

Preparation of (9*S*,7*R*)-7-Methylheptadec-5-yn-9-ol (4). *n*-BuLi (0.22 mL, 1.9 M in hexanes, 0.41 mmol) was added to a solution of 1-hexyne (51 μL, 0.44 mmol) in dry THF (1.5 mL) at −78 °C. After the addition, the mixture was warmed to room temperature for a period of 0.5 h. Then, this mixture was cooled to −78 °C and a solution of **6** (100 mg, 0.34 mmol) in dry THF (2.5 mL) was added dropwise. The mixture was stirred at −78 °C for 1 h, whereupon it was quenched with saturated NH_4Cl solution (5 mL) and Et_2O (10 mL). The organic layer was washed with brine, dried, filtered, and concentrated to give **10** as a mixture of diastereoisomers in which one slightly predominated (ca. 1.5:1).

To a solution of **10** in dry CH_2Cl_2 (4 mL) was added $Co_2(CO)_8$ (151 mg, 0.44 mmol) at room temperature. The reaction mixture was stirred at room temperature until TLC showed complete conversion to the hexacarbonyldicobalt complex (ca. 1h). The mixture was concentrated through a pad of silica gel and concentrated to yield a brown solid that was used without any purification.

To a stirred solution of the crude $Co_2(CO)_6$ complex in dry CH_2Cl_2 (4 mL) was slowly added $BF_3{\cdot}OEt_2$ (27 μL, 0.35 mmol) at −20 °C. The reaction mixture was stirred for 10 min and poured into a saturated aqueous $NaHCO_3$ (10 mL) at 0 °C. The resulting mixture was vigorously stirred for 15 min and extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried, filtered, and concentrated to give the $Co_2(CO)_6$ complex of **4** that was employed in the next step without further purification.

To a stirred solution of the complexed acetylene in dry acetone (4 mL) was added CAN (0.76 g, 0.25 mmol) in one portion at 0 °C. The reaction mixture was stirred at 0 °C until TLC showed completion of the reaction (ca. 5 min). The mixture was evaporated and the residue diluted with water and extracted with Et_2O. The combined organic solutions were dried, filtered, and concentrated. Flash column chromatography yielded **4** (69 mg, 75% yield overall) as a colorless oil: $[\alpha]^{25}_D$ = −22.7 (*c* 0.90, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 0.87 (t, J = 6.9 Hz, 3H), 0.89 (t, J = 6.2 Hz, 3H), 1.16 (d, J = 6.8 Hz, 3H), 1.27 (br s, 12H), 1.45 (m, 6H), 1.53 (t, J = 6.7 Hz, 2H), 2.14 (t, J = 6.7 Hz, 2H), 2.50 (m, 2H), 3.75 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 13.6 (q), 14.1 (q), 18.3 (t), 21.9 (t), 22.0 (q), 22.6 (t), 24.0 (d), 25.4 (t), 29.3 (t), 29.6 (t), 29.7 (t), 31.1 (t), 31.9 (t), 37.4 (t), 44.6 (t), 71.4 (d), 82.0 (s), 84.5 (s); IR (film) $\tilde{\nu}_{max}$ (cm^{-1}) 3358, 2928, 2856, 2291, 1074; MS m/z (relative intensity) 266 $(M)^+$ (5), 248 $(M - H_2O)^+$ (5), 153 (100). Anal. Calcd for $C_{18}H_{34}O$: C, 81.13; H, 12.86. Found: C, 81.19; H, 12.57.

Preparation of (7*S*)-7-Methylheptadecane (1). A suspension of the acetylene **4** (51 mg, 0.19 mmol) in AcOEt (2 mL) and 10% Pd−C (4 mg) was degassed at room temperature. The mixture was vigorously stirred under H_2 atmosphere for 2 h at room temperature. After removal of the catalyst by filtration, the filtrate was concentrated, and the residue was used without further purification.

To a mixture of the crude alcohol in dry CH_2Cl_2 (2 mL) and Et_3N (53 μL, 0.38 mmol) was added $MeSO_2Cl$ (22 μL, 0.29 mmol) at 0 °C. The solution was allowed to warm to room temperature and stirred for 20 min. The reaction mixture was quenched with brine (5 mL) and extracted with CH_2Cl_2. The organic layer was washed with brine, dried, filtered and concentrated under reduced pressure. The residue was used in the next step without further purification.

The crude mesylate was dissolved in dry THF (2 mL) and added to a stirred suspension of $LiAlH_4$ (7.5 mg, 0.19 mmol) in dry THF (1 mL) at room temperature. The mixture was refluxed for 12 h, after which time TLC showed complete conversion to the saturated compound. Then, the reaction mixture was cooled to 0 °C and quenched with wet Et_2O (5 mL) and aqueous HCl (5%) (5 mL). The layers were separated, and the aqueous solution was extracted with Et_2O. The combined organic layers were washed with saturated aqueous $NaHCO_3$ and brine, dried and concentrated. The residue obtained was purified by column chromatography to furnish pure **1** (35 mg, 73% yield overall) as a colorless oil: $[\alpha]^{25}_D$ = +0.29 (*c* = 5.13, hexane); ^{1}H NMR ($CDCl_3$) δ 0.84 (d, J = 6.4 Hz, 3 H), 0.88 (t, J = 6.8 Hz, 6 H), 1.00−1.40 (m, 29H); ^{13}C NMR ($CDCl_3$) δ 14.09 (q), 19.69 (q), 22.68 (t), 27.04 (t), 27.08 (t), 29.35 (t), 29.48 (t), 29.66 (t), 29.70 (t), 30.03 (t), 31.92 (t), 31.95 (t), 32.74 (d), 37.09 (t); IR (film) $\tilde{\nu}_{max}$ (cm^{-1}) 2956, 2925, 1463, 725; MS m/z (relative intensity) 254 $(M)^+$ (6), 239 (7), 168 (33), 112 (44), 57 (100). Anal. Calcd for $C_{18}H_{38}$: C, 84.95; H, 15.05. Found: C, 84.98; H, 14.77.

Preparation of (3*R*)-5-(Phenylmethoxy)pentane-1,3-diol (16). The same procedure used above to obtain **8** from **7** was applied to **15**[13] on a 0.30 g (1.61 mmol) scale, yielding **16** (0.27 g, 88% yield) as a colorless oil: $[\alpha]^{25}_D$ = +13.1 (*c* 0.45, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.69−1.78 (m, 1H), 1.78−1.90 (m, 3H), 3.14 (br s, 2H), 3.68 (m, 2H), 3.81 (m, 2H), 4.07 (m, 1H), 4.51 (s, 2H), 7.32 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 36.6 (t), 38.5 (t), 61.4 (t), 69.0 (t), 71.6 (d), 73.1 (t), 127.7 (d), 127.8 (d), 128.2 (d), 128.5 (d), 137.8 (s); IR (film) $\tilde{\nu}_{max}$ (cm^{-1}) 3384, 2925, 1656, 1453, 1091; MS m/z (relative intensity) 211 $(M + 1)^+$ (1), 192 (6), 107 (63), 91 (100). Anal. Calcd for $C_{12}H_{18}O_3$: C, 68.54; H, 8.63. Found: C, 68.54; H, 8.75.

Preparation of (3*R*)-3,5-Bis(phenylmethoxy)pentan-1-ol (17). To a stirred solution of **16** (0.25 g, 1.19 mmol) in dry CH_2Cl_2 (15 mL) were added 3,4-dihydro-2*H*-pyran (0.10 mL, 1.13 mmol) and a catalytic amount of $OPCl_3$ at 0 °C. The reaction was stirred at 0 °C until starting material was not detected by TLC (ca. 4 h). Then, Et_3N was added until pH ≈ 7, and the reaction mixture was poured into brine at room temperature. The mixture was extracted with CH_2Cl_2, and the combined organic phases were dried, filtered, and concentrated to give a mixture of mono and diprotected products, which was used in the next step without further purification.

To a stirred suspension of NaH (60% in mineral oil, 57.2 mg, 1.43 mmol) in dry THF (4 mL), at 0 °C were sequentially and slowly added a solution of the crude product in THF (1

mL), a catalytic amount of Bu_4NI, and benzyl bromide (0.2 mL, 1.67 mmol). The reaction mixture was stirred at room temperature for 24 h. Then, the mixture was diluted with Et_2O, washed with brine, dried, and concentrated.

To a stirred mixture of the crude product in MeOH (4 mL) was added concentrated HCl until pH ≈ 1 at room temperature. The reaction mixture was stirred at room temperature until TLC showed completion of the reaction (ca. 5 min), whereupon it was quenched with Et_3N until pH ≈ 7. The reaction mixture was stirred for 5 min, concentrated under reduced pressure and the crude residue obtained was chromatographed on a column to yield **17** (0.26 g, 73% yield) as a colorless oil: $[\alpha]^{25}_D = +2.6$ (*c* 0.89, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.77−2.06 (m, 4H), 2.32 (br s, 1H), 3.59 (m, 2H), 3.78 (m, 2H), 3.81 (m, 1H), 4.49 (s, 2H), 4.55 (s, 2H), 7.33 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 34.1 (t), 36.3 (t), 60.2 (t), 66.7 (t), 71.4 (t), 73.1 (t), 75.4 (d), 127.7 (d), 127.8 (d), 127.9 (d), 128.2 (d), 128.4 (d), 128.5 (d), 138.3 (s); IR (film) $\tilde{\nu}_{max}$ (cm^{-1}) 3418, 1643, 1362, 1091, 799; MS *m*/*z* (relative intensity) 301 $(M + 1)^+$ (0.1), 194 (12), 107 (26), 91 (100). Anal. Calcd for $C_{19}H_{24}O_3$: C, 75.97; H, 8.05. Found: C, 75.99; H, 7.92.

Preparation of (4*S*)-4,6-Bis(phenylmethoxy)hexan-2-one (18). The same procedure used above to obtain **6** from **9** was applied to **17** on a 0.24 g (0.80 mmol) scale, yielding **18** (0.19 g, 76% yield) as a colorless oil: $[\alpha]^{25}_D = -6.1$ (*c* 0.99, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.86 (m, 2H), 2.14 (s, 3H), 2.61 (dd, *J* = 16.0, 5.2 Hz, 1H), 2.77 (dd, *J* = 16.0, 7.2 Hz, 1H), 3.61 (m, 2H), 4.12 (m, 1H), 4.49 (m, 4H), 7.30 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 31.0 (q), 34.5 (t), 48.8 (t), 66.5 (t), 71.8 (t), 73.0 (t), 73.1 (d), 127.6 (d), 127.7 (d), 127.8 (d), 128.1 (d), 128.3 (d), 128.4 (d), 128.5 (d), 138.1 (s), 207.4 (s); IR (film) $\tilde{\nu}_{max}$ (cm^{-1}) 2861, 1716, 1496, 1361, 799; MS *m*/*z* (relative intensity) 294 $(M - H_2O)^+$ (0.7), 148 (11), 115 (28), 91 (100). Anal. Calcd for $C_{20}H_{24}O_3$: C, 76.89; H, 7.74. Found: C, 76.85; H, 7.78.

Preparation of (3*R*,5*R*)-5-Methyl-1-(phenylmethoxy)-undec-6-yn-3-ol (19). The same procedure used above to obtain **6** from **9** was applied to **18** on a 0.18 g (0.58 mmol) scale, yielding **19** (0.13 g, 77% yield overall) as a colorless oil: $[\alpha]^{25}_D = -17.9$ (*c* 0.61, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 0.89 (t, *J* = 7.1 Hz, 3H), 1.16 (d, *J* = 6.8 Hz, 3H), 1.34−1.54 (m, 5H), 1.60−1.79 (m, 3H), 2.14 (dd, *J* = 5.0, 5.0 Hz, 2H), 2.53 (m, 1H), 3.15 (br s, 1H), 3.68 (m, 2H), 3.97 (m, 1H), 4.52 (s, 2H), 7.32 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 13.6 (q), 18.4 (t), 21.7 (q), 21.9 (t), 23.2 (d), 31.1 (t), 36.5 (t), 44.5 (t), 68.6 (t), 69.7 (d), 73.2 (t), 81.4 (s), 84.5 (s), 127.6 (d), 127.8 (d), 128.2 (d), 128.4 (d), 138.1 (s); IR (film) $\tilde{\nu}_{max}$ (cm^{-1}) 3405, 2931, 2232, 1659, 1453, 1097, 782; MS *m*/*z* (relative intensity) 288 $(M)^+$ (0.8), 159 (23), 153 (13), 91 (100). Anal. Calcd for $C_{19}H_{28}O_2$: C, 79.12; H, 9.78. Found: C, 79.13; H, 9.95.

Preparation of (5*S*,3*R*)-5-Methyl-3-(phenylmethoxy)-undecan-1-ol (20). To a solution of **19** (0.12 g, 0.42 mmol) in EtOAc (4 mL) was added 10% Pd−C (12 mg) at room temperature. The resulting suspension was vigorously stirred under an atmosphere of H_2 (1 atm) for 2 h at room temperature. After removal of the catalyst by filtration through a small pad of Celite, the filtrate was concentrated and the residue used without further purification.

To a solution of the crude diol in dry CH_2Cl_2 (4 mL) were sequentially added a catalytic amount of CSA (9.8 mg, 0.04 mmol) and benzaldehydedimethyl acetal (84 μL, 0.55 mmol) at room temperature. The reaction mixture was stirred for 1 h after which time TLC showed complete reaction. Then, Et_3N was added until pH ≈ 7, stirred for 5 min, and evaporated under reduced pressure. The residue was used without further purification.

To a solution of the crude benzylidene derivative obtained in dry CH_2Cl_2 (3 mL) was slowly added DIBAL-H (4 mL, 1 M solution in cyclohexane, 4 mmol) at 0 °C. The reaction mixture was allowed to warm to room temperature over a period of 15 min. The mixture was diluted with CH_2Cl_2 (10 mL), and aqueous HCl (5%) (5 mL) was added. The resulting mixture was extracted with CH_2Cl_2. The combined organic layers were washed with saturated aqueous $NaHCO_3$ and brine, dried, filtered, concentrated and purified by column chromatography to yield **20** (98 mg, 81% yield overall) as a colorless oil: $[\alpha]^{25}_D = -7.9$ (*c* 0.76, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 0.88 (m, 6H), 1.26 (br s, 10H), 1.58−1.94 (m, 5H), 2.33 (br s, 1H), 3.74 (m, 2H), 3.80 (m, 1H), 4.54 (dd, *J* = 11.4, 11.4 Hz, 2H), 7.33 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 14.1 (q), 20.0 (q), 23.2 (t), 27.0 (t), 29.4 (d), 29.6 (t), 31.9 (t), 36.2 (t), 38.5 (t), 41.5 (t), 60.5 (t), 70.9 (t), 76.5 (d), 127.4 (d), 127.7 (d), 127.9 (d), 128.4 (d), 138.4 (s); IR (film) $\tilde{\nu}_{max}$ (cm^{-1}) 3387, 2925, 1719, 1454, 1069; MS *m*/*z* (relative intensity) 292 $(M)^+$ (2), 147 (11), 107 (27), 92 (14), 91 (100). Anal. Calcd for $C_{19}H_{32}O_2$: C, 78.03; H, 11.03. Found: C, 78.07; H, 11.06.

Preparation of (7*S*,11*S*,9*R*)-7,11-Dimethylheptadec-5-yn-9-ol (11). The same procedure used above to obtain **4** from **9** was applied to **20** on an 80 mg (0.28 mmol) scale, yielding **11** (49 mg, 57% yield) as a colorless oil: $[\alpha]^{25}_D = +30.3$ (*c* 0.53, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 0.88 (m, 9H), 1.16 (d, *J* = 6.8 Hz, 3H), 1.26 (br s, 13H), 1.33−1.59 (m, 6H), 2.15 (t, *J* = 5.2 Hz, 2H), 2.40 (br s, 1H), 2.53 (m, 1H), 3.86 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 13.56 (q), 14.07 (q), 18.34 (t), 19.16 (q), 21.93 (t), 22.03 (q), 22.64 (t), 23.99 (d), 26.90 (t), 28.97 (d), 29.59 (t), 31.09 (t), 31.89 (t), 37.93 (t), 44.99 (t), 45.46 (t), 69.15 (d), 82.08 (s), 84.41 (s); IR (film) $\tilde{\nu}_{max}$ (cm^{-1}) 3375, 2927, 2232, 1462, 1378; MS *m*/*z* (relative intensity) 280 $(M)^+$ (3), 191 (17), 153 (100). Anal. Calcd for $C_{19}H_{36}O$: C, 81.36; H, 12.94. Found: C, 81.35; H, 12.58.

Preparation of (7*S*,11*R*)-7,11-Dimethylheptadecane (*meso*-2). The same procedure used above to obtain **1** from **4** was applied to **11** on a 40 mg (0.14 mmol) scale, yielding *meso*-**2** (27 mg, 71% yield overall) as colorless oil: ^{1}H NMR ($CDCl_3$) δ 0.83−1.01 (m, 12H), 1.26 (m, 28H); ^{13}C NMR ($CDCl_3$) δ 14.1 (q), 19.7 (q), 22.7 (t), 24.4 (t), 27.0 (t), 29.7 (t), 31.9 (t), 32.8 (d), 37.1 (t), 37.4 (t); IR (film) $\tilde{\nu}_{max}$ (cm^{-1}) 2956, 2925, 2855, 1463, 1377, 725; MS *m*/*z* (relative intensity) 288 $(M)^+$ (3), 183 (26), 111 (21), 57 (100). Anal. Calcd for $C_{19}H_{40}$: C, 84.99; H, 15.01. Found: C, 84.99; H, 14.70.

Preparation of (5*S*,3*R*)-5-Methylundecane-1,3-diol (22). To a solution of **19** (0.20 g, 0.7 mmol) in AcOEt (7 mL) was added 10% Pd−C (20 mg) at room temperature. The resulting suspension was vigorously stirred under an atmosphere of H_2 (1 atm) for 2 h at room temperature. After removal of the catalyst by filtration, the filtrate was concentrated, and the residue was purified by flash chromatography to yield **22** (0.14 g, 100% yield) as a colorless oil: $[\alpha]^{25}_D = +6.7$ (*c* 0.97, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 0.88 (m, 6H), 1.26 (br s, 10H), 1.38−1.70 (m, 5H), 2.34 (br s, 2H), 3.86 (m, 2H), 3.97 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 14.1 (q), 19.3 (q), 22.6 (t), 26.9 (t), 29.0 (d), 29.6 (t), 31.9 (t), 37.7 (t), 39.1 (t), 45.4 (t), 61.8 (t), 69.9 (d); IR (film) $\tilde{\nu}_{max}$ (cm^{-1}) 3350, 2956, 2855, 1463, 1055; MS *m*/*z* (relative intensity) 201 $(M - 1)^+$ (0.3), 155 (15), 112 (43), 97 (11), 75 (100). Anal. Calcd for $C_{12}H_{26}O_2$: C, 71.23; H, 12.95. Found: C, 71.32; H, 12.87.

Preparation of (3*S*,5*S*)-5-Methylundecane-1,3-diol (23). To a solution of **22** (0.13 g, 0.64 mmol) in dry CH_2Cl_2 (6.5 mL) were sequentially added Et_3N (0.18 mL, 1.28 mmol) and $MeSO_2Cl$ (76 μL, 0.96 mmol) at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for 30 min, whereupon it was quenched with brine (10 mL) and extracted with CH_2Cl_2. The organic layer was washed with brine, dried, filtered, and concentrated. The resulting residue was used without any further purification.

To a suspension of KOAc (127 mg, 1.28 mmol) in benzene (3 mL) were sequentially added the crude dimesylate dissolved in benzene (5 mL) and 18-crown-6 (342 mg, 1.28 mmol) at room temperature. The mixture was refluxed with vigorous stirring for 12 h. The reaction mixture was cooled to room temperature, poured into an ice-cooled saturated NH_4Cl solution (10 mL), and extracted with AcOEt. The combined organic layers were washed with brine, dried, and concentrated to yield a crude diacetate that was used in the next step without purification.

To a suspension of NaH (77 mg, 60% in mineral oil, 1.92 mmol) in dry CH_2Cl_2 (5 mL) was slowly added dry MeOH (0.16 mL, 3.84 mmol) at 0 °C. The mixture was stirred for 10 min, and a solution of the crude diacetate dissolved in CH_2Cl_2 (2 mL) was added dropwise. The mixture was allowed to warm to room temperature and stirred for 1 h. A saturated NH_4Cl solution (5 mL) was added at 0 °C, and the mixture was

extracted with CH_2Cl_2. The combined extracts were washed with brine, dried, filtered, concentrated, and purified by column chromatography to yield **23** (99 mg, 77% overall yield) as a colorless oil: $[\alpha]^{25}_D = -5.1$ (*c* 0.48, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 0.88 (m, 6H), 1.26 (br s, 10H), 1.38 (m, 2H), 1.52−1.77 (m, 3H), 2.33 (br s, 2H), 3.87 (m, 2H), 3.97 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 14.0 (q), 20.2 (q), 22.6 (t), 26.8 (t), 29.2 (d), 29.6 (t), 31.9 (t), 36.8 (t), 38.4 (t), 45.4 (t), 61.8 (t), 70.1 (d); IR (film) $\tilde{\nu}_{max}$ (cm^{-1}) 3346, 2955, 2855, 1463, 1055; MS *m*/*z* (relative intensity) 185 $(M - HO)^+$ (0.9), 157 (12), 112 (37), 83 (28), 75 (100). Anal. Calcd for $C_{12}H_{26}O_2$: C, 71.23; H, 12.95. Found: C, 71.34; H, 13.14.

Preparation of (3*S*,5*S*)-5-Methyl-3-(phenylmethoxy)-undecan-1-ol (24). The same procedure used above to obtain **9** from **8** was applied to **23** on a 81 mg (0.4 mmol), yielding **24** (94 mg, 82% overall yield) as a colorless oil: $[\alpha]^{25}_D = +36.5$ (*c* 0.62, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 0.88 (t, $J = 5.6$ Hz, 6H), 1.26 (br s, 11H), 1.48 (m, 2H), 1.69 (m, 1H), 1.89 (m, 1H), 3.70−3.85 (m, 3H), 4.54 (dd, $J = 28.9$, 10.6 Hz, 2H), 7.33 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 14.1 (q), 19.9 (q), 22.7 (t), 26.9 (t), 29.2 (d), 29.6 (t), 31.9 (t), 35.8 (t), 37.5 (t), 41.0 (t), 60.7 (t), 70.7 (t), 77.0 (d), 127.7 (d), 127.9 (d), 128.4 (d), 128.5 (d), 128.6 (d), 138.3 (s); IR (film) $\tilde{\nu}_{max}$ (cm^{-1}) 3388, 2926, 1454, 1377, 1056; MS *m*/*z* (relative intensity) 292 $(M)^+$ (0.4), 247 (5), 107 (17), 92 (11), 91 (100). Anal. Calcd for $C_{19}H_{32}O_2$: C, 78.03; H, 11.03. Found: C, 78.09; H, 10.89.

Preparation of (4*S*,6*S*)-6-Methyl-4-(phenylmethoxy)-dodecan-2-one (25). The same procedure used above to obtain **6** from **9** was applied to **24** on a 90 mg (0.31 mmol) scale, yielding **17** (71 mg, 75% yield overall) as a colorless oil: $[\alpha]^{25}_D = +8.7$ (*c* 0.36, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 0.87 (m, 6H), 1.26 (br s, 10H), 1.56 (m, 3H), 2.16 (s, 3H), 2.52 (dd, $J = 15.8$, 4.7 Hz, 1H), 2.72 (dd, $J = 15.8$, 7.3 Hz, 1H), 3.97 (m, 1H), 4.50 (s, 2H), 7.31 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 14.1 (q), 20.1 (q), 22.7 (t), 26.8 (t), 29.5 (d), 29.6 (t), 31.2 (q), 31.9 (t), 36.9 (t), 42.2 (t), 48.8 (t), 71.4 (t), 74.1 (d), 127.6 (d), 127.7 (d), 127.9 (d), 128.3 (d), 128.4 (d), 138.4 (s), 207.9 (s); IR (film) $\tilde{\nu}_{max}$ (cm^{-1}) 2955, 2855, 1721, 1454, 1069; MS *m*/*z* (relative intensity) 304 $(M)^+$ (0.1), 198 (11), 180 (19), 107 (26), 91 (100). Anal. Calcd for $C_{20}H_{32}O_2$: C, 78.90; H, 10.59. Found: C, 78.72; H, 10.49.

Preparation of (9*S*,11*S*,7*R*)-7,11-Dimethylhectadec-5-yn-9-ol (26). The same procedure used above to obtain **4** from **6** was applied to **25** on a 61 mg (0.2 mmol) scale, yielding **26** (41 mg, 73% yield overall) as a colorless oil: $[\alpha]^{25}_D = -22.4$ (*c* 0.18, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 0.89 (m, 9H), 1.16 (d, $J = 6.8$ Hz, 3H), 1.26 (br s, 13H), 1.33−1.82 (m, 6H), 2.15 (t, $J = 5.8$ Hz, 2H), 2.52 (m, 2H), 3.85 (m, 1H);^{13}C NMR ($CDCl_3$) δ 13.58 (q), 14.09 (q), 18.36 (t), 20.36 (q), 21.95 (t), 21.99 (q), 22.66 (t), 24.01 (d), 26.79 (t), 29.33 (d), 29.68 (t), 31.09 (t), 31.92 (t), 36.53 (t), 44.97 (t), 45.20 (t), 69.58 (d), 82.11 (s), 84.51 (s); IR (film) $\tilde{\nu}_{max}$ (cm^{-1}) 3380, 2856, 2232, 1598, 1071; MS *m*/*z* (relative intensity) 280 $(M)^+$ (3), 205 (15), 153 (100). Anal. Calcd for $C_{19}H_{36}O$: C, 81.36; H, 12.94. Found: C, 81.41; H, 12.74.

Preparation of (7*S*,11*S*)-7,11-Dimethylheptadecane (3). The same procedure used above to obtain **4** from **6** was applied to **26** on a 31 mg (0.11 mmol) scale, yielding **3** (21 mg, 70% yield overall) as a colorless oil: $[\alpha]^{25}_D = +1.63$ (*c* 1.52, hexane); ^{1}H NMR ($CDCl_3$) δ 0.83−1.15 (m, 12H), 1.26 (m, 28H); ^{13}C NMR ($CDCl_3$) δ 14.1 (q), 19.6 (q), 22.7 (t), 24.5 (t), 27.3 (t), 29.7 (t), 31.9 (t), 32.8 (d), 37.1 (t), 37.4 (t); IR (film) $\tilde{\nu}_{max}$ (cm^{-1}) 2956, 2855, 1463, 1377, 725; MS *m*/*z* (relative intensity) 288 $(M)^+$ (3), 183 (25), 112 (40), 71 (85), 57 (100). Anal. Calcd for $C_{19}H_{40}$: C, 84.99; H, 15.01. Found: C, 84.88; H, 14.83.

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Supporting Information Available: ^{1}H NMR and ^{13}C NMR spectra for all new compounds described in the Experimental Section. This information is available free of charge via the Internet at http://pubs.acs.org.

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