Preparation of the Versatile Chiron, (*R*)- and (*S*)-12-(Tetrahydropyranyloxy)-3-methyldodecanol: Application to the Syntheses of Methyl Branched Insect Pheromones

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A convenient chemoenzymatic synthesis for the title methyl branched chiron has been developed starting from 10-undecenoic acid (**1**). Thus, **1** was converted to 1-(tetrahydropyranyloxy)-10-undecan-2-one (**4**) which on reaction with triethyl phosphonoacetate and subsequent functionalization led to the racemic chiron **7**. This was resolved *via C. rugosa* lipase-catalyzed acetylation and subsequently used for the syntheses of some chiral insect pheromones. Thus, (*S*)-**7** was mesylated, reduced with LAH and acetylated to give the pheromone (*R*)-10-methyldodecan-1-yl acetate (**I**), while its oxidation to the aldehyde **10** followed by Wittig reaction with methylenephosphorane, depyranylation, and hydrogenation gave the alcohol **12**. Its tosylation, detosylation, and Hg^{2+}-catalyzed hydration furnished (*R*)-10-methyltridecan-2-one (**II**). Likewise, Wittig reaction of (*R*)-**10** with a suitable phosphorane and similar protocol as above afforded the alcohol **14**. Its tosylate was coupled with 3-butenylmagnesium bromide to furnish pheromone (*S*)-14-methyloctadecene (**III**).

Chirality due to methyl branching is abundant amongst several naturally occurring secondary metabolites. This structural feature *i.e.* $R_1CH(Me)$- (R_1 = Et, *n*-Pr, *n*-Bu, *etc.*) is particularly predominant amongst insect pheromones,[1] many of which are of economic significance. As a consequence, considerable effort has been directed toward the synthesis of these *via* chiron and asymmetric routes. In view of the above, formulation of an efficient strategy for this class of compounds especially from easily accessible material seems a desirable attribute.

An approach to the synthesis of methyl branched insect pheromones would be to prepare a bifunctional methyl branched chiron preferably in its enantiomeric forms and derivatize it to the desired target compounds. In view of the fact that most of the insect pheromones in this class contain at least a C_{12}-chain, the title chiron, 12-(tetrahydropyranyloxy)-3-methyldodecanol (**7**) seems best suited for the above purpose. Hence, in continuation of our efforts[2–4] in this field, we devised a biocatalytic protocol for **7** which was subsequently used for the syntheses of several methyl branched pheromones possessing different alkyl chains (R_1 = Et, *n*-Pr and *n*-Bu) *viz.* (*R*)-10-methyldodecyl acetate (**I**), (*R*)-10-methyltridecanone (**II**) and (*S*)-14-methyloctadecene (**III**). Compounds **I**, **II**, and **III** constitute the pheromones of lesser tea tortrix moth,[5] southern corn rootworm,[6] and peach leafminer moth,[7] respectively. Compared to the existing syntheses[8–10] of these pheromones, the present divergent route for all of these targets seems most practical.

Thus, the undecenol derivative **2**, available[11] from 10-undecenoic acid (**1**) was subjected to Hg^{2+}-catalyzed hydration to furnish **3**. Its oxidation to the ketone **4** followed by Wittig–Horner reaction with triethyl phosphonoacetate gave the conjugated ester **5** as a mixture of geometrical isomers. However, since this was of no consequence to our synthesis, its isomeric composition was not determined. After catalytic hydrogenation, the ester **6** was reduced with LAH to afford (±)-**7**. In order to obtain both the enantiomers of **7** with good %ee, we decided to explore its enzymatic transacetylation with vinyl acetate. For this purpose, *Candida rugosa* lipase (CRL) was chosen after initial screening of the commercially available lipases. Consequently, all the other reaction conditions, *viz.* solvent and degree of conversion, were optimized for maximum enantioselectivity with the same catalyst. At 40% conversion, the acetate (*S*)-(**8**) (>96% ee) and the resolved (*R*)-**7** (71% ee) were produced. A second acetylation of the partially resolved **7** led to (*R*)-**7** with 97.7% ee. For the estimation of its optical purity, compound **7** was oxidized with PDC/DMF and depyranylated to furnish the corresponding ω-hydroxy carboxylic acid. This was then converted to the diastereomeric amide with optically pure (*R*)-phenylethylamine and analyzed with capillary GLC. The %ee of the acetate **8** was likewise analyzed after hydrolysis to (*S*)-**7**. The GLC retention times (t_R) for the (*R*)- and (*S*)-enantiomers of **7** were 65.7 min and 68.1 min, respectively, under the condition specified in the Experimental Section.

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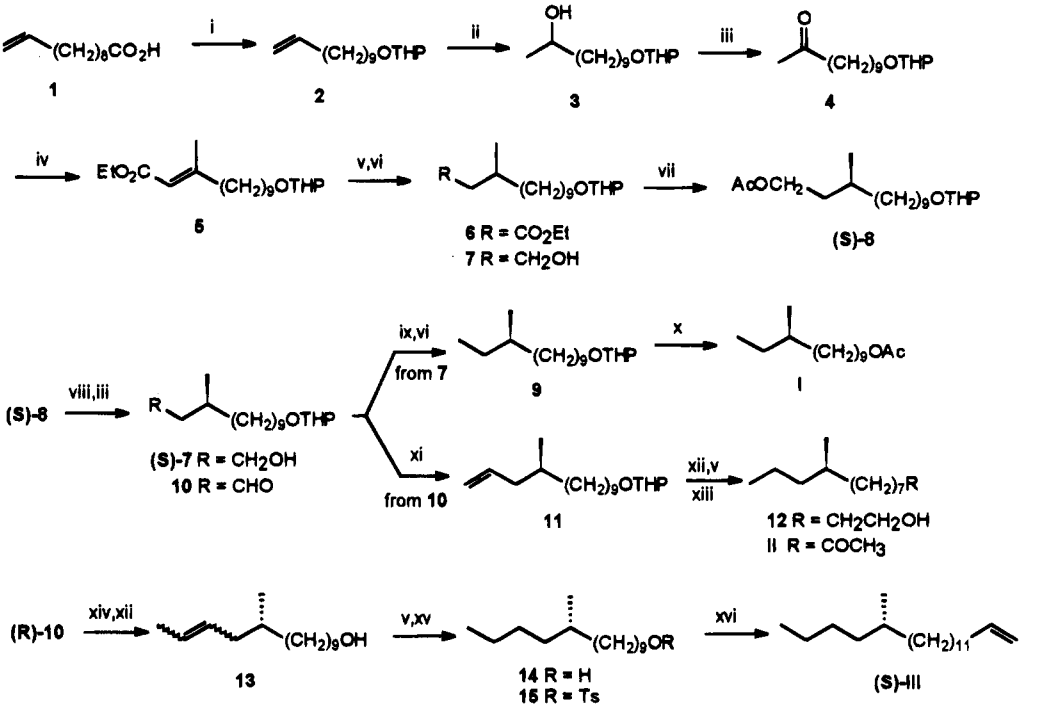
Scheme 1



[a] (i) ref 11, (ii) $Hg(OAc)_2$/THF/H_2O, (iii) PCC/NaOAc/CH_2Cl_2, (iv) NaH/$(EtO)_2P(O)CH_2CO_2Et$, (v) H_2/Pd–C/EtOH, (vi) LAH/ether, (vii) H_2C=CHOAc/CRL/diisopropyl ether, (viii) alcoholic KOH, (ix) MsCl/TEA, (x) AcCl/AcOH/Δ, (xi) CH_3PPh_3I/dimsyl anion, (xii) MeOH/PTS, (xiii) ref 12, (xiv) $EtPPh_3Br$/dimsyl anion, (xv) *p*-TsCl/Py, (xvi) H_2C=$CH(CH_2)_2Br$/Mg/CuBr/THF.

Preparation of (*R*)-I: The (*S*)-acetate (**8**) was hydrolyzed with alkali to furnish the alcohol (*S*)-**7**. After mesylation, the resultant compound was reduced with LAH to give compound **9**. Its direct acetylation finally afforded the pheromone (*R*)-**I**.

Preparation of (*R*)-II: The above alcohol [(*S*)-**7**] was oxidized with "buffered-PCC" to furnish the aldehyde **10** which on Wittig olefination with methylidenetriphenylphosphorane led to the olefin **11**. Its depyranylation followed by hydrogenation over 10% Pd–C afforded the C_{13}-alcohol **12**. This was then converted to the title pheromone following our own method.[12] Thus, **12** was tosylated and subsequently treated with ^{t}BuOK under refluxing condition to give (*R*)-10-methyltridecene. This was then converted to **II** by Hg^{2+}-catalyzed hydration and PCC oxidation.

Preparation of (*S*)-III: For this, the (*R*)-alcohol (**7**) was oxidized to (*R*)-**10** which on Wittig reaction with ethyltriphenylphosphonium bromide and subsequent deprotection gave the alcohol **13**. After hydrogenation, the product alcohol **14** was tosylated and subsequently coupled with 3-butenylmagnesium bromide in presence of CuBr as the catalyst to produce the pheromone (*S*)-**III**. This was purified by repeated column chromatography followed by "argentation chromatography".

Based on the optical purities of our starting chirons **7** and **8**, the optical purities of the synthesized pheromones are expected to be >96%. This was further corroborated by comparison of their chirooptical data with those reported.

Experimental Section

For normal GLC analyses, 2 m × 0.5 mm column was used with N_2 flow rate 40 mL/min, while for capillary GLC the same were 50 m × 0.25 mm (split ratio 1:100) and 2 mL/min, respectively. All anhydrous reactions were carried out under Ar atmosphere with freshly dried solvent. The enzymatic reactions were carried out with the commercially available enzyme without any purification with solvents desiccated over 4 Å mol. sieve (Linde) for 48 h.

1-(Tetrahydropyranyloxy)-10-oxoundecane (4). To a stirred suspension of $Hg(OAc)_2$ (30.0 g, 0.094 mol) in H_2O (50 mL) was added compound **2** (12.0 g, 0.047 mol) in THF (50 mL). After 3 h, a solution of $NaBH_4$ (0.893 g, 0.024 mol) in aqueous NaOH (3 N, 20 mL) was introduced into the reaction mixture and stirring continued for further 2 h. The precipitated Hg was separated by decantation, the organic phase separated, and the aqueous portion extracted with EtOAc. The combined organic extract was washed with water, brine, and dried. Solvent removal followed by column chromatography of the residue over silica gel (0-20% EtOAc/hexane) gave pure **3** (7.68 g, 60%): IR 3360, 880, 820 cm^{-1}; ^{1}H-NMR δ 1.1 (d, *J* = 7 Hz, 3H), 1.3 (br s, 16H), 1.4–1.6 (m, 6H), 3.0 (br s, D_2O exchangeable, 1H), 3.3–3.8 (m, 4H), 3.9–4.0 (m, 1H), 4.51 (s, 1H). Anal. Calcd for $C_{16}H_{32}O_3$: C, 70.54; H, 11.84. Found: C, 70.77; H, 11.68.

Oxidation of **3** (7.68 g, 0.028 mol) with PCC (9.1 g, 0.042 mol) in CH_2Cl_2 (50 mL) in presence of NaOAc (0.23 g, 2.8 mmol) followed by usual isolation furnished **4** (6.6 g, 87%): IR 1740, 880, 820 cm^{-1}; ^{1}H-NMR δ 1.32 (br s, 14H), 1.4–1.6 (m, 6H), 2.0–2.3 (t containing a s at δ 2.1, 5H), 3.5–3.7 (m, 4H), 4.51 (s, 1H). Anal. Calcd for $C_{16}H_{30}O_3$: C, 71.06; H, 11.18. Found: C, 71.18; H, 11.20.

Ethyl 12-(Tetrahydropyranyloxy)-3-methyldodecenoate (5). To a stirred and cooled (0 °C) suspension of pentane-washed NaH (1.5 g, 0.031 mol, 50% suspension in oil) in THF (30 mL) was added triethyl phosphonoacetate (7.5 g, 0.034 mol) in THF (20 mL). After 0.5 h, the ketone **3** (6.6 g, 0.024 mol) in THF (20 mL) was added dropwise into it and the mixture stirred for 24 h at ambient temperature. The mixture was poured into ice–water and extracted with EtOAc, and the extract was washed with water and brine and finally dried. After concentration, the residue was chromatographed over silica gel (0–20% EtOAc/hexane) to furnish **5** (6.6 g, 79%): IR 1715, 1650, 880, 810 cm^{-1}; ^{1}H-NMR δ 1.1 (t, *J* = 6 Hz, 3H), 1.32 (s, 14H), 1.5–1.7 (m, 6H), 1.8 (s, 3H), 2.1–2.2 (m, 2H),

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3.3–3.87 (m, 4H), 4.1 (q, J = 7 Hz, 2H), 4.53 (s, 1H), 5.5–5.7 (m, 1H). Anal. Calcd for $C_{20}H_{36}O_4$: C, 70.55; H, 10.66. Found: C, 70.78; H, 10.68.

12-(Tetrahydropyranyloxy)-3-methyldodecanol (7). Hydrogenation of **5** (5.65 g, 0.017 mol) over 10% Pd–C in EtOH (20 mL) gave **6** (5.65 g, ~quant): IR 1735, 880, 820 cm^{-1}; ^{1}H-NMR δ 0.9 (d, J = 7 Hz, 3H), 1.14 (t, J = 7 Hz, 3H), 1.29 (s, 16H), 1.5–1.7 (m, 7H), 2.1 (d, J = 6 Hz, 2H), 3.2–3.8 (m, 4H), 4.12 (q, J = 6 Hz, 2H), 4.53 (s, 1H). Anal. Calcd for $C_{20}H_{38}O_4$: C, 70.13; H, 11.18. Found: C, 70.26; H, 11.26.

To a stirred suspension of LAH (0.626 g, 0.17 mol) in ether (70 mL) was added compound **6** (5.65 g, 0.017 mol) and the mixture gently refluxed for 3 h. It was cooled in an ice-bath, treated with aqueous saturated Na_2SO_4 to decompose excess hydride, and the mixture filtered. The filtrate on concentration furnished pure **7** (4.9 g, 99%): IR 3400, 1060, 870, 810 cm^{-1}; ^{1}H-NMR δ 0.88 (d, J = 7 Hz, 3H), 1.3 (s, 18H), 1.4–1.7 (m, 7H), 1.74 (s, D_2O exchangeable, 1H), 3.1–3.8 (m containing a t at δ 3.6, 6H), 4.51 (s, 1H). Anal. Calcd for $C_{18}H_{36}O_3$: C, 71.95; H, 12.08. Found: C, 71.87; H, 12.14.

Lipase-Catalyzed Resolution of (±)-7. A mixture of (±)-**7** (4.9 g, 0.016 mol), vinyl acetate (2.2 mL, 0.024 mol), and CRL (2.5 g, Sigma, sp act. 552 IU/mg) in diisopropyl ether (50 mL) was stirred at room temperature for 5 h till 46% conversion (GLC). Then the mixture was filtered and the filtrate concentrated under reduced pressure and chromatographed over silica gel (0–15% EtOAc/hexane) to afford (*S*)-**8** (2.3 g, 42%) and (*R*)-**7** (2.5 g, 51%).

Compound (*S*)-8: $[\alpha]^{22}$ +2.26° (c 1.33, $CHCl_3$); IR 1730, 1230, 880, 810 cm^{-1}; PMR δ 0.9 (d, J = 6 Hz, 3H), 1.3 (br s, 19H), 1.4–1.6 (m, 6H), 2.2 (s, 3H), 3.1–3.8 (m, 4H), 4.1 (t, J = 6 Hz, 2H), 4.6 (br s, 1H). Anal. Calcd for $C_{20}H_{38}O_4$: C, 70.13; H, 11.18. Found: C, 70.27; H, 11.24.

The above alcohol [(*R*)-**7**] (2.5 g, 0.008 mol) was subjected to a second enzymatic acetylation as above to give optically pure (97% ee) [(*R*)-**7**] (1.6 g, 32.56% based on starting (±)-**7**). $[\alpha]^{22}$ +1.29° (c 0.7, $CHCl_3$). Its spectral data were identical with the racemic sample.

***(R)*-1-(Tetrahydropyranyloxy)-10-methyldodecane (9).** Alkaline hydrolysis of (*S*)-**8** (0.55 g, 1.61 mmol) with alcoholic KOH (2 N, 10 mL) gave (*S*)-**7**: yield 0.468 g (97%); $[\alpha]^{22}$ +4.4° (c 1.12, $CHCl_3$). Its spectral data were identical with the racemic sample.

To a stirred and cooled (0 °C) mixture of (*S*)-**7** (0.468 g, 1.56 mmol) and triethylamine (0.24 g, 2.4 mmol) in CH_2Cl_2 (30 mL) was added mesyl chloride (0.2 g, 1.7 mmol). After stirring for 1 h at the same temperature, it was poured into ice–water, the organic layer separated, and the aqueous portion extracted with $CHCl_3$. The organic extract was washed with saturated NH_4Cl solution and dried. Removal of solvent gave the mesylate which (0.58 g, 98%) was directly subjected to reduction with LAH (0.268 g, 7.0 mmol) in ether (30 mL). Usual isolation and subsequent column chromatography (silica gel, 0–5% EtOAc/hexane) furnished pure (*R*)-**9** (0.179 g, 41%): IR 1470, 1180, 880, 810 cm^{-1}; ^{1}H-NMR δ 0.8–1.0 (d and t merged, 6H), 1.32 (s, 18H), 1.4–1.6 (m, 7H), 3.6–3.9 (m, 4H), 4.51 (s, 1H). Anal. Calcd for $C_{18}H_{36}O_2$: C, 75.99; H, 12.76. Found: C, 76.17; H, 12.68.

***(R)*-10-Methyldodecan-1-ol Acetate (I).** A mixture of compound (*R*)-**9** (0.179 g, 0.6 mmol), AcOH (10 mL), and AcCl (1.5 mL) was stirred at room temperature for 24 h. It was poured in ice–water and the mixture stirred for 1 h. The aqueous portion was extracted with ether, and the ether extract layer was washed with water, aqueous $NaHCO_3$ (10%), water, and brine and dried. Removal of solvent followed by preparative TLC (silica gel, 10% EtOAc/hexane) of the residue afforded the target pheromone (*R*)-**I** (0.09 g, 59%): $[\alpha]^{24}$ −5.7° (c 1.25, $CHCl_3$), (lit.[8d] $[\alpha]$ −5.93° (c 10, $CHCl_3$)); IR 1730, 1230 cm^{-1}; ^{1}H-NMR δ 0.88 (dist t, 3H), 0.96 (d, J = 7 Hz, 3H), 1.29 (m, 16H), 1..7–2.1 (m containing a s at δ 2.1, 6H), 4.12 (t, J = 7 Hz, 2H). Anal. Calcd for $C_{15}H_{30}O_2$: C, 74.32; H, 12.48. Found: C, 74.44; H, 12.39.

***(S)*-12-(Tetrahydropyranyloxy)-3-methyldodecanal (10).** Oxidation of (*S*)-**7** (2.1 g, 7.0 mmol) with PCC (2.26 g, 10.5 mmol) in CH_2Cl_2 (60 mL) in presence of NaOAc (0.074 g, 0.9 mmol) gave the aldehyde **10** (1.86 g, 89%): IR 2740, 1720, 880, 810 cm^{-1}; ^{1}H-NMR δ 0.88 (d, J = 6 Hz, 3H), 1.29 (s, 16H), 1.5–1.7 (m, 7H), 2.1–2.3 (m, 2H), 3.6–3.8 (m, 4H), 4.51 (s, 1H), 9.78 (t, J = 1.5 Hz, 1H). Anal. Calcd for $C_{18}H_{34}O_3$: C, 72.43; H, 11.48. Found: C, 72.48; H, 11.59.

***(S)*-1-(Tetrahydropyranyloxy)-10-methyltridec-1-ene (11).** To a stirred solution of dimsyl anion (8.0 mmol) in DMSO (30 mL) was added methyltriphenylphosphonium iodide (3.04 g, 7.5 mmol) at room temperature. After stirring for 1 h, (*S*)-**10** (1.86 g, 6.24 mmol) in THF (60 mL) was added into it at −20 °C. Stirring was continued for 4 h at the same temperature and at room temperature for 12 h. The mixture was poured in water and extracted with ether, and the ether extract was washed with water and brine. After drying, it was concentrated and the product purified by column chromatography over silica gel using 0–10% ether/hexane as the eluent to give **11** (1.55 g, 84%): IR 1640, 1000, 910, 880, 810 cm^{-1}; ^{1}H-NMR δ 0.9 (d, J = 7 Hz, 3H), 1.29 (br s, 17H), 1.4–1.6 (m, 6H), 1.8–2.1 (m, 2H), 3.5-3.8 (m, 4H), 4.5 (s, 1H), 4.8–6.2 (m, 3H). Anal. Calcd for $C_{19}H_{36}O_2$: C, 76.97; H, 12.24. Found: C, 77.15; H, 12.38.

***(R)*-10-Methyltridecan-1-ol (12).** A mixture of the above compound (1.5 g, 5.0 mmol) and PTS (0.1 g) in CH_3OH (20 mL) was stirred for 24 h. After concentration in vacuo, the residue was extracted with ether and the ether layer washed with water and brine and dried. Removal of solvent followed by column chromatography (silica gel, 0–20% ether/hexane) gave the corresponding alcohol (1.02 g, 96%): $[\alpha]^{24}$ −2.9° (c 1.4, $CHCl_3$); IR 3440, 1640, 990, 910 cm^{-1}; ^{1}H-NMR δ 0.9 (d, J = 7 Hz, 3H), 1.32 (br s, 17H), 1.8–2.0 (m, 2H), 2.86 (s, D_2O exchangeable, 1H), 3.68 (t, J = 7 Hz, 2H), 4.8–6.2 (m, 3H).

Its (1.0 g, 4.7 mmol) catalytic hydrogenation over 10% Pd–C in EtOH (20 mL) furnished **12** (0.979 g, 97%): IR 3380, 1470, 1060 cm^{-1}; ^{1}H-NMR δ 0.8–1.0 (d and t merged, 6H), 1.30 (br s, 18H), 1.5–1.9 (m, 3H), 2.21 (br s, D_2O exchangeable, 1H), 3.63 (t, J = 6 Hz, 2H). Anal. Calcd for $C_{14}H_{30}O$: C, 78.43; H, 14.11. Found: C, 78.57; H, 14.28.

***(R)*-10-Methyltridecan-2-one (II).** Compound **12** (0.95 g, 4.4 mmol) was converted[12] to (*R*)-**II** (0.63 g, 63% from **12**): bp 128 °C (bath)/5mm, (lit.[9a] bp 105–115 °C (bath/3mm)); $[\alpha]^{28}$ −1.28° (c 1.4, $CHCl_3$), (lit.[9a] $[\alpha]^{23}$ −1.4° (c 3.017, $CHCl_3$)); IR 2980, 1720 cm^{-1}; PMR δ 0.9–1.0 (t and d merged, 6H), 1.38 (br s, 17H), 2.2 (s, 3H), 2.4 (t, J = 7 Hz, 2H). Anal. Calcd for $C_{14}H_{28}O$: C, 79.58; H, 13.36. Found: C, 79.39; H, 13.48.

***(R)*-10-Methyltetradecen-1-ol (13).** As described earlier, Wittig reaction between ethyltriphenylphosphonium bromide (3.76 g, 0.01 mol) and (*R*)-**10** (2.07 g, 0.007 mol) was carried out with dimsyl anion (0.011 mol) as the base in DMSO (15 mL)–THF (60 mL). After usual isolation and purification, the product (1.44 g, 67%) was depyranylated by refluxing its methanolic solution in presence of PTS. Usual workup and subsequent column chromatography furnished pure **13** (0.985 g, 94%): $[\alpha]^{28}$ 3.5° (c 0.4, $CHCl_3$); IR 3360, 1480, 1370, 1060 cm^{-1}; ^{1}H-NMR δ 0.9 (d, J = 7 Hz, 3H), 1.29 (br s, 17H), 1.8 (d, J = 5 Hz, 3H), 1.9–2.0 (m, 2H), 3.3 (s, D_2O exchangeable, 1H), 3.68 (t, J = 6 Hz, 2H), 5.3–5.5 (m, 2H). Anal. Calcd for $C_{15}H_{30}O$: C, 79.58; H, 13.36. Found: C, 79.72; H, 13.16.

***(S)*-10-Methyltetradecanol (14).** Hydrogenation of **13** (0.985 g, 4.4 mmol) over 10% Pd/C (0.1 g) in EtOH (20 mL) gave the alcohol **14** (0.985 g, 99%): IR 3360, 1470, 1380 cm^{-1}; ^{1}H-NMR δ 0.9–1.1 (m, 6H), 1.32 (br s, 23H), 3.3 (s, D_2O exchangeable, 1H), 3.68 (t, J = 7 Hz, 2H). Anal. Calcd for $C_{15}H_{32}O$: C, 78.87; H, 14.12. Found: C, 79.04; H, 14.18.

***(S)*-14-Methyloctadecene (III).** A solution of compound **14** (0.955 g, 4.3 mmol), pyridine (0.9 g, 11 mmol), and *p*-TsCl (0.905 g, 4.7 mmol) in CH_2Cl_2 (20 mL) was stirred for 4 h at 0 °C and then kept at −10 °C for 20 h. It was poured in water and extracted with $CHCl_3$, and the organic extract was washed with water, aqueous HCl (2 N), water, and brine and dried. Removal of solvent followed by column chromatography (silica gel, 0–10% ether/hexane) gave the tosylate **15** (1.24 g, 75%): $[\alpha]^{28}$ 1.75° (c 0.8, $CHCl_3$); IR 3030, 1600, 1480, 1380, 1180 cm^{-1}; ^{1}H-NMR δ 0.9 (m, 6H), 1.2 (s, 23H), 2.4 (s, 3H), 4.0 (t, J = 6 Hz, 2H), 7.2–7.6 (m, 2H), 7.65–8.1 (m, 2H).

To a stirred and cooled (−20 °C) solution of 3-butenylmagnesium bromide [prepared from 3-butenyl bromide (0.635 g, 4.7 mmol) and Mg (0.114 g, 4.7 mmol)] in THF (30 mL) was

added CuBr (0.65 g, 0.45 mmol) followed by **15** (1.2 g, 3.1 mmol) in THF (10 mL). After stirring for 3 h at the same temperature, the reaction was quenched with aqueous saturated NH_4Cl solution. The ethereal layer was separated, dried, and concentrated. The residue was purified first by column chromatography over silica gel (hexane) and subsequently by "argentation chromatography" to afford pure **II** (0.5 g, 60%): $[\alpha]^{22}$ 1.17° (*c* 1.02, hexane) (lit.[10a] $[\alpha]^{21}$ 1.21° (*c* 3.07, hexane)); IR 1640, 990, 910 cm^{-1}; ^1H-NMR δ 0.9 (m, 6H), 1.28 (br s, 27H), 2.3 (m, 2H), 4.8–6.2 (m, 3H). Anal. Calcd for $C_{19}H_{38}$: C, 85.63; H, 14.37. Found: C, 85.54; H, 14.48.

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