CH_2O), 3.8 (m, 1 H, CNH), 4.12 (m, 1 H, CHO), 7.0 and 7.2 (m, 10 H, arom).

(4*S*,5*S*)-4-Benzyl-3-(*tert*-butoxycarbonyl)-5-((2*R*)-2-carboxy-3-phenylpropyl)-2,2-dimethyl-1,3-oxazolidine (14). To a suspension of PtO_2 (55 mg, 0.24 mmol) in H_2O, previously reduced with H_2 (1 atm, 1 h), was added a solution of 13 (90 mg, 0.2 mmol) in dioxane (2 mL). The mixture was warmed to 50 °C, and oxygen was bubbled through it for 36 h. Ethyl acetate (5 mL) was added, the aqueous phase was adjusted to pH 3 with 1 M HCl, and the organic layer was separated. After a second extraction with ethyl acetate (5 mL), the organic layer was washed with brine and dried on anhydrous Na_2SO_4. After evaporation of the solvent, column chromatography on silica gel (hexane/ethyl acetate, 1/4) gave product 14 (67 mg, 62% yield); mp 63–67 °C; IR (neat) ν 3100–2700, 2980, 1730, 1640 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.58 (bs, 15 H, t-Bu and Me), 1.8–2.4 (m, 5 H, 2 CH_2 or CH), 2.8 (m, 1 H, CH_2Ph) 3.0–3.4 (m, 4 H CH_2Ph and CH), 3.8 (m, 1 H, CHN), 4.05 (m, 1 H, CHO), 7.2 (m, 10 H, arom), 10.6 (bs, 1 H, OH); MS *m/e* 454 ($M^+ + 1$), 453, 381, 361, 328, 264, 220, 91, 57 (base). Anal. Calcd for $C_{27}H_{35}NO_5$: C, 71.50; H, 7.78; N, 3.09; O, 17.64. Found: C, 71.05; H, 7.69; N, 3.00.

(2*R*,4*S*,5*S*)-*N*,2-Dibenzyl-5-((*tert*-butoxycarbonyl)-amino)-4-hydroxy-6-phenylhexanamide (15). Triethylamine (0.28 g, 0.28 mmol) was added to a solution of the acid 14 (63 mg, 0.14 mmol) in CH_2Cl_2 (1 mL). BOP (62 mg, 0.14 mmol) was added, followed by benzylamine (21 mg, 0.2 mmol). After 3 h of stirring to room temperature, CH_2Cl_2 (5 mL) was added and the mixture was washed with 3 M HCl (1 mL) and 10% $NaHCO_3$ (1 mL). After the organic layer was dried over anhydrous Na_2SO_4, the solvent was evaporated and the crude product was dissolved in MeOH (2 mL). Boron trifluoride acetic acid complex (0.2 mL) was added, and the mixture stirred at room temperature for 5 h. Solid Na_2CO_3 (0.1 g) was added, and the mixture was stirred for 30 min. After filtration on Celite, the filtration cake was washed with ethyl acetate and the organic layer was dried on anhydrous Na_2SO_4. After evaporation of the solvent, column chromatography on silica gel (hexane/ethyl acetate, 1/1) gave product 15 (40 mg, 57%): mp 179–181 °C; IR (neat) ν 3350, 3260, 3010, 2980, 1700, 1645, 1540, 1480 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.41 (s, 9 H, t-Bu), 1.81 (m, 2 H, CH_2), 1.9 (bs, 1 H, OH), 2.3–2.9 (m, 4 H, CH_2Ph), 3.61 (m, 1 H, CHN), 3.75 (m, 1 H, CHN), 4.15 (m, 1 H, CHO), 4.4 (m, 2 H, CH_2N), 4.96 (bm, 1 H, NH), 5.91 (bm, 1 H, NH), 7.0–7.4 (bm, 15 H, arom); MS *m/e* 502 (M^+), 488, 91 (base); HRMS calcd for $C_{31}H_{38}N_2O_4$ 502.6539, found 502.6557.

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Supplementary Material Available: ^1H and ^{13}C NMR spectra of 4 and 5 (6 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Synthesis of 7-Methyl-3-propyl-2(*E*),6(*E*)-nonadienyl Acetate, a Terpenoid Compound in the Male Square-Necked Grain Beetle *Cathartus quadricollis* (Guér.)

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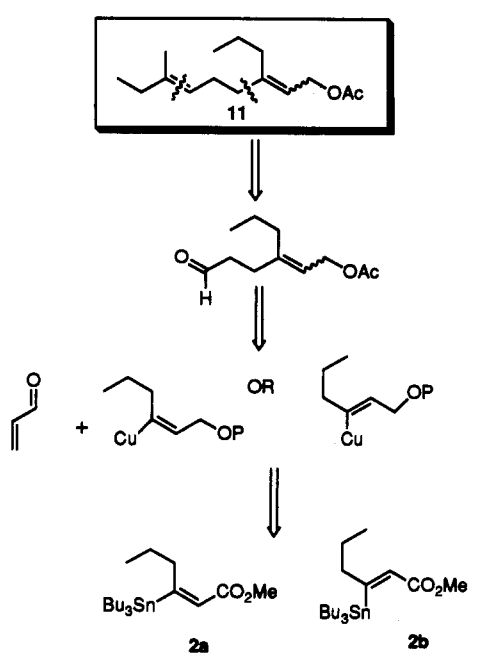
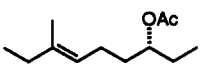
Introduction

In the investigation of the square-necked grain beetle, *Cathartus quadricollis* (Guér.), we identified (3*R*)-7-methyl-6(*E*)-nonen-3-yl acetate (quadrilure) as an aggregation pheromone produced by males.[1] The male beetles also produced another compound which was assigned the structure 7-methyl-3-propyl-2,6(*E*)-nonadienyl acetate (11) on the basis of a detailed analysis of its decoupled ^1H NMR spectra. However, the ^1H NMR spectra data did not permit an assignment of the C_2–C_3 double-bond geometry. Although this compound was apparently inactive in the laboratory bioassays, determination of its exact effects on the behavior of the beetles was difficult due to the small amount of the natural compound produced by the beetles. To establish the structure of this novel compound and to provide sufficient material for testing, we describe herein its synthesis.

Scheme I





Quadrilure

Results and Discussion

Retrosynthetic analysis of the 1,5-diene structure of 11 showed that both the 2(*E*) and the 2(*Z*) isomers could be readily synthesized by the application stannylcuprate chemistry currently under investigation in this and other laboratories.[2-5] As outlined in Scheme I, the appropri-

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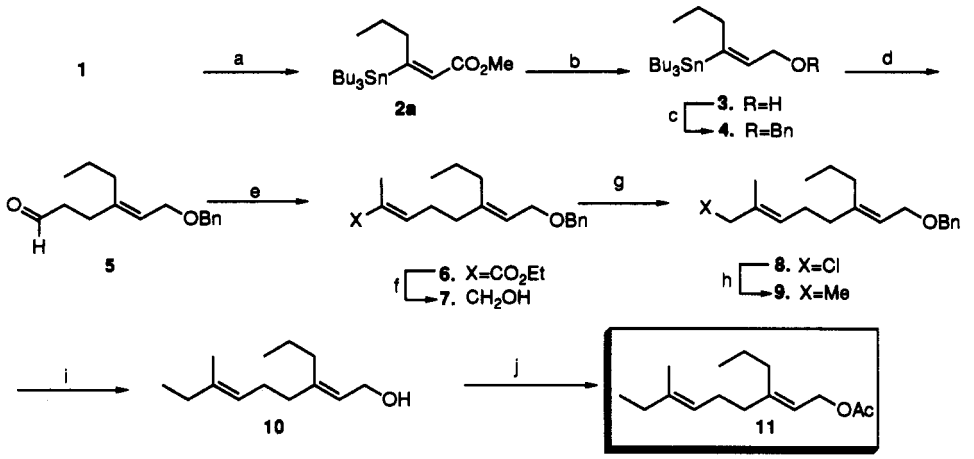
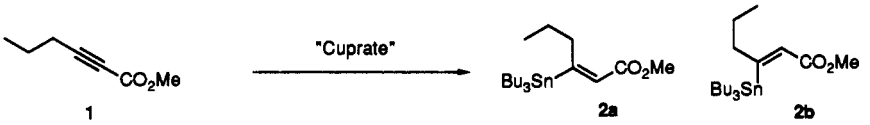
0022-3263/92/1957-5250$03.00/0

Scheme II[a]



[a] Key: (a) Bu_3SnCu-DMS; (b) DIBAL-H, THF 0 °C; (c) NaH, BnBr, DMF; (d) (i) *n*-BuLi, THF, −78 °C, (ii) (2-Th)Cu(CN)Li, THF, −78 °C, HMPA; (iii) acrolein, TMSCl, THF; (e) $(CH_3)(CO_2Et)C{=}PPh_3$, CH_2Cl_2; (f) DIBAL-H, THF; (g) NCS–DMS, CH_2Cl_2; (h) $Me_2Cu(Br)I$, THF, −78 °C; (i) Li, $EtNH_2$, −78 °C; (j) Ac_2O, Py.

Table I. Reaction of Mixed HO Stannyl Cuprates to Methyl 2-Hexynoate (1)



entry	"cuprate"	reaction condns	product ratio **2a**:**2b**	yield (%)
1	$(Bu_3Sn)(n\text{-Bu})Cu(CN)Li_2$	−50 °C, 2 h, saturated NH_4Cl/NH_4OH	15:85	80–85
2	$(Bu_3Sn)(2\text{-Th})Cu(CN)Li_2$	rt, 2 h, saturated NH_4Cl/NH_4OH	10:90	80–85
3	$(Bu_3Sn)(N\text{-imid})Cu(CN)Li_2$	rt, 2 h, saturated NH_4Cl/NH_4OH	4:96	>85

ately-protected vinyl stannyl allylic alcohols, prepared from fragments **2a** or **2b**, could be transmetallated to their corresponding vinyl cuprates and added to acrolein in a conjugate fashion, giving the required 2(*E*) and 2(*Z*) double-bond geometry, respectively. The resulting intermediate aldehydes would then serve as the template for the introduction of the second double bond at C_6–C_7.

Prior experience with terpenoid insect pheromones led us to believe there was a greater probability that **11** possessed a 2(*E*),6(*E*) rather than the 2(*Z*),6(*E*) or 2(*Z*),6(*Z*) configuration. Though both methyl 3-(tributylstannyl)-2(*E*)- and methyl 3-(tributylstannyl)-2(*Z*)-hexenoate (**2a**) and (**2b**), respectively, were prepared, **2a** was utilized first in the reaction sequence leading to the synthesis of appropriately substituted 2(*E*),6(*E*)-nonadienyl acetate (**11**) (Scheme II).

Synthesis of 7-Methyl-3-methyl-2(*E*),6(*E*)-nonadienyl Acetate. The preparation of methyl 3-stannyl-2-(*E*)-hexenoate (**2a**) was straightforward using the method of Piers et al.[4] The addition of methyl 2-hexynoate (**1**) to Bu_3SnCu, prepared from the CuBr–DMS complex at −78 °C in THF followed by MeOH quench, gave the required α,β-unsaturated ester **2a**, in 93% yield with geometrical purity of >98%. Although **2b** could be prepared by the addition of $Bu_3SnCu(SPh)Li$ to **1** as also described by Piers,[4] we found, in our studies relating to the higher order (HO) mixed stannyl cuprates[2,5] $Bu_3Sn(R)Cu(CN)Li_2$, that the latter reagents also added to α,β-unsaturated acetylenic esters to give the predominantly the 3-stannyl-2(*Z*)-α,β-unsaturated esters (Table I). Of the three cuprates tried (R = *n*-butyl, R = 2-thienyl, and R = *N*-imidazole), the reagent with a *N*-lithioimidazole[6] ligand gave the desired **2b** in both the highest yields (>85%) and the greatest geometrical purity (>95%, *Z*). Therefore, treatment of **1** with $Bu_3Sn(N\text{-imid})Cu(CN)Li_2$[6] at −78 °C and warming the reaction to ambient temperature gave a mixture of **2a** and **2b** in a ratio of 4/96 in nearly 90% yield. The trace amount of the **2a** was easily removed by flash chromatography.

Methyl 3-(tributylstannyl)-2(*E*)-hexenoate (**2a**) was reduced to alcohol **3** with DIBAL-H and protected as its benzyl ether in a combined yield of 84%. The key reaction in this synthesis involved the coupling of **4** with acrolein. Transmetalation of the vinyltributylstannyl group of **3** to the vinyllithium species by treatment with *n*-BuLi at −78 °C and its conversion to the HO thienyl cyanocuprate[7] seemed to go smoothly. The most problematic reaction encountered in this sequence was the conjugate addition of this cuprate to acrolein. The best yields of **5** (40–50%) were obtained when trimethylsilyl chloride–HMPA[8] was used as activating agent of acrolein. Repeated attempts to increase the yield of this reaction were met with failure. It is curious that GC analysis of the crude products showed almost exclusively tetrabutylstannane and the aldehyde **5**, no other species being present.

Aldehyde **5** was treated with (carbethoxyethylidene)-triphenylphosphorane in refluxing CH_2Cl_2 to give α,β-unsaturated ester **6** (>95% *E*), in 82% yield. A trace amount of the *Z* isomer was removed by flash chromatography. Ester **6** was then reduced to alcohol **7** with DIBAL-H, which was converted to chloride **8** by treatment with the NCS–DMS complex in CH_2Cl_2 in 88% yield over two steps. The allylic chloride **8** was reacted with the cuprate

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(7) Lipshutz, B. H.; Koerner, M.; Parker, D. A. *Tetrahedron Lett.* **1987**, *28*, 945.

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reagent derived from 2.0 equiv of MeMgI and 1.0 equiv of CuBr–DMS at −78 °C to give **9** in 97% yield. When **8** was reacted with $Me_2Cu(CN)Li_2$ at −78 °C, GC analysis of the reaction showed the presence of several other products of similar molecular weights. Although this reaction was not repeated, it was assumed that a slight excess of MeLi may have been present and this led to the eliminationation of chloride ion as well as some S_N2' addition. The less reactive magnesiocuprate gave only the expected S_N2 product **9**.

The benzyl protecting group of **9** was removed with Li metal in $EtNH_2$ at −78 °C to give alcohol **10** (98% yield) which was acetylated (Py/Ac_2O) to give **11** almost quantitively. Acetate **11** was found to be identical to the natural compound by comparison of GC retention times, ^1H NMR, and mass spectral data. The synthesis of the 2(*Z*),6(*E*) isomer was, therefore, abandoned.

Experimental Section

General Procedures. Tetrahydofuran (THF), diethyl ether (Et_2O), and dimethoxyethane (DME) were all distilled from sodium benzophenone ketyl. Diisopropylamine, triethylamine, dimethyl sulfide (DMS), hexamethylphosphoramide (HMPA), trimethylsilyl chloride (TMSCl), and dichloromethane (CH_2Cl_2) were freshly distilled from CaH_2 prior to use. Imidazole was sublimed under high vacuum (0.05 mmHg); *N*-chlorosuccinimide (NCS) was recrystallized from glacial acetic acid, washed with ice/water, and dried under high vacuum; acrolein was distilled, first at atomospheric pressure and then under vacuum (0.05 mmHg) from a round-bottom flask cooled at −30 °C and condensed at −78 °C (dry ice/acetone bath) and used immediately. Unless otherwise stated, chemicals obtained from commercial sources were used without further purification. All moisture- and air-sensitive reactions were conducted under a positive pressure of argon in glassware that was flame dried under vacuum. A nitrogen glovebag was used to weight the moisture- and oxygen-sensitive compounds. Syringes and cannulas were used to transfer oxygen- and water-sensitive liquid reagents. Unless specifically stated, standard workup refers to the combined organic extracts being washed with ice-cold brine and dried over $MgSO_4$ and the solvent removed with a rotary evaporator. Chromatography refers to flash chromatography using Merck Silica Gel 60 (mesh 230–400).

Methyl 3-(Tributylstannyl)-2(*E*)-hexenoate (2a). To a solution of LDA (26.0 mmol) at −78 °C in THF (50 mL) under argon atmosphere was added neat *n*-Bu_3SnH (6.72 mL, 25.0 mmol). After the solution was stirred for 1.5 h, CuBr–DMS complex (5.13 g, 25 mmol) was added in one portion. The brown solution was stirred at −78 °C for 1 h, and to it was added dropwise methyl 2-hexynoate (**1**) (3.15 g, 25 mmol) in THF (25 mL). The temperature was maintained at −78 °C for an additional 2 h, and the reaction was terminated with MeOH (10 mL), treated with 100 mL of saturated NH_4Cl/NH_4OH (9/1), stirred for 30 min, and extracted with Et_2O (4 × 50 mL). Standard workup followed by chromatography using ethyl acetate/hexanes (5/95) as the eluant gave **2a** (9.70, 93%) as clear oil: IR (film) 2958 (m), 1723.5, 1591, 1462, 1431, 1351, 1168, 1072, 1043, and 883 cm^{-1}; mass spectrum, CI (isobutane, rel intensity, major isotopes) 419/417 (M^+ + 1, 100/75), 387/385 (27/22), 361/359 (100/80); ^1H NMR ($CDCl_3$, ppm) 5.94 (1 H, t, J = 1.1 Hz; J_{Sn-H} = 67.0 Hz), 3.68 (3 H, s), 2.84 (2 H, tq, J = 8.0, 1.1 Hz; J_{Sn-H} = 56.0 Hz), 1.53–1.38 (8 H, bm), 1.30 (6 H, sex., J = 7.5 Hz), 0.90 (18 H, bm); ^{13}C NMR ($CDCl_3$, ppm) 174.0, 164.4, 127.4, 50.5, 37.2, 28.9 (3 C), 27.3 (3 C), 22.9, 14.0, 13.5 (3 C), 10.0 (3 C). Anal. Calcd for $C_{19}H_{38}O_2Sn$: C, 54.70; H, 9.18. Found: C, 54.68; H, 9.20.

Procedure for the Preparation of Methyl 3-(Tributylstannyl)-2(*Z*)-hexenoate (2b). From Reaction with Bu_3Sn(*N*-imid)Cu(CN)Li_2. A solution of (*N*-imid)Cu(CN)Li was prepared from freshly sublimed imidazole (0.17 g, 2.5 mmol), which was treated with *n*-BuLi (1.0 mL, 2.5 mmol, 2.5 M in hexanes) at −78 °C in THF (15 mL). After 1 h, CuCN (0.23 g, 2.5 mmol) was added and the solution warmed to rt and stirred for an additional 1 h. The resulting cloudy green solution of (*N*-imid)Cu(CN)Li was further diluted with THF (10 mL) and then added dropwise via canula to BuSnLi (2.5 mmol) in THF (10 mL) at −78 °C, prepared from Bu_2SnH (0.672 mL, 2.5 mmol) and LDA (2.52 mmol) as described above for **2a**.

After the clear light yellow solution of Bu_3Sn(*N*-imid)Cu(CN)Li_2 was stirred for 0.5 h at −78 °C, **1** (0.315 g, 2.5 mmol) in THF (5 mL) was added dropwise. The reaction temperature was maintained at −78 °C for 0.5 h and rt for 2 h. Addition of saturated NH_4Cl/NH_4OH (9/1) (50 mL) and extraction of the aqueous layer with Et_2O (4 × 50 mL), followed by standard workup, gave a mixture of **2a** and **2b** (4/96 by GC). These were easily separated by chromatography using ethyl acetate/hexanes (5/95) as the eluant. **2b** (0.87 g) eluated first, and then **2a** (trace amount) was eluated in combined yield of 89%.

From Reaction with Bu_3Sn(*n*-Bu)Cu(CN)Li_2. To a solution of BuSnLi (2.5 mmol), prepared from Bu_3SnH (0.672 mL, 2.5 mmol) and LDA (2.5 mmol) as described above, in THF (10 mL) at −78 °C was added quickly, via canula, *n*-BuCu(CN)Li (2.6 mmol) prepared from Cu(CN) (0.24 g, 2.6 mmol) and *n*-BuLi (1.04 mL, 2.6 mmol, 2.5 M in hexanes) at −78 °C in THF (20 mL). The solution of Bu_3Sn(*n*-Bu)Cu(CN)Li_2 was stirred for 0.5 h, and **1** (0.315 g, 2.5 mmol) in THF (5 mL) was added dropwise. After the mixture was stirred for an additional 2 h at −50 °C, saturated NH_4Cl/NH_4OH (50 mL) was added and the mixture warmed to 0 °C and extracted with Et_2O (4 × 50 mL). Standard workup gave the crude product as a mixture of **2a** and **2b** (15/85 by GC analysis). Chromatography using ethyl acetate/hexanes (5/95) as the eluant gave **2b** (0.76g, 87%) and **2a** (0.11 g, 13%) in a combined yield of 83%.

From Reaction with Bu_3Sn(2-Th)Cu(CN)Li_2. To a solution of Bu_3SnLi (2.5 mmol), prepared from Bu_3SnH (0.57 mL, 2.5 mmol) and LDA (2.5 mmol) at −78 °C in THF (20 mL), was added (2-Th)Cu(CN)Li (10.5 mL, 2.6 mmol, 0.25 M in THF), and this was stirred for 0.50 h. To Bu_3Sn(2-Th)Cu(CN)Li_2 was added dropwise **1** (0.315 g, 2.5 mmol) in THF (5 mL), and the resulting solution was stirred for 0.5 h. The reaction was warmed to rt and stirred at this temperature for 2 h. Saturated NH_4Cl/NH_4OH (50 mL) was added and the mixture extracted with Et_2O (4 × 50 mL). Standard workup gave the crude product as a mixture of **2a** and **2b** (10/90, by GC analysis). Chromatography using ethyl acetate/hexanes (5/95) as the eluant gave **2b** (0.73g, 90%) and **2a** (0.084 g, 10%) in a combined yield of 81%.

2b: IR (film) 2855–2871 (m), 1709, 1596, 1463, 1434, 1327, 1199, and 1061 cm^{-1}; mass spectrum CI m/e (isobutane, rel intensity, major isotopes) 417/419 (M^+ + 1, trace amount), 361/359 (100/74); ^1H NMR ($CDCl_3$, ppm) 6.35 (1 H, t, J = 1.5 Hz, J_{Sn-H} = 108.0 Hz), 3.72 (3 H, s), 2.35 (2 H, td, J = 7.5, 1.5 Hz; J_{Sn-H} = 44.0 Hz), 1.50–1.35 (8 H, bm), 1.35–1.23 (6 H, sex., J = 7.5 Hz), 0.98–0.84 (18 H, m); ^{13}C NMR ($CDCl_3$, ppm) 176.0, 168.2, 128.1, 51.3, 42.6, 29.2 (3 C), 27.4 (3 C), 22.4, 13.7, 13.6 (3 C), 11.1(3 C).

3-(Tributylstannyl)-2(*E*)-hexen-1-ol (3). To a solution of **2a** (9.5 g, 22.7 mmol) in THF (50 mL) under an argon atmosphere at −40 °C was added dropwise neat DIBAL-H (9.0 mL, 50 mmol). The reaction was warmed to 0 °C over a 2-h period, poured into a 25% aqueous solution of tartaric acid (250 mL), and extracted with Et_2O (4 × 50 mL). Standard workup, followed by chromatography using ethyl acetate/hexanes (2/8) as the eluant, gave **3** (8.3 g, 94%) as a clear oil: IR (film) 3302 (b), 2955 (b), 1464, 1376, 1072, 1019, 960, and 873 cm^{-1}; mass spectrum CI m/e (isobutane, rel intensity, major isotopes) 391/389 (M^+ + 1, trace amount), 373/371 (trace amount), 333/331 (30/25), 291/289 (100/80); ^1H NMR ($CDCl_3$, ppm) 5.75 (1 H, bt, J = 6.5 Hz; J_{Sn-H} = 68.0 Hz), 4.23 (2 H, t, J = 6.5 Hz), 2.24 (2 H, T, J = 7.5 Hz; J_{Sn-H} = 58.0 Hz), 1.60–1.40 (6 H, bm), 1.4–1.26 (8 H, bm), 0.93–0.84 (18 H, bm); ^{13}C NMR ($CDCl_3$, ppm) 148.0, 139.4, 58.9, 35.6, 29.1 (3 C), 23.4, 13.8, 13.5 (3 C), 9.7 (3 C). Anal. Calcd for $C_{18}H_{38}OSn$: C, 55.55; H, 9.84. Found: C, 55.74; H, 9.92.

1-(Benzyloxy)-3-(tributylstannyl)-2(*E*)-hexene (4). To a suspension of NaH (0.865g, 21.6 mmol, 60% in oil, washed free of oil with pentane (3 × 10 mL)) in DMF (25 mL) at 0 °C under argon was added **3** (7.0 g, 18.0 mmol), in DMF (10 mL) followed by neat benzyl bromide (2.25 mL, 18.9 mmol) dropwise via syringe. The mixture was stirred for 10 h at rt, poured into water (200 mL), and extracted with Et_2O (4 × 50 mL). Usual workup followed by chromatography using ethyl acetate/hexanes (3/97) as the eluant gave **4** (7.66 g, 89%) as a clear oil: IR (film) 2930 (b), 1454, 1376, 1357, 1097, and 1071 cm^{-1}; mass spectrum CI (iso-

butane, rel intensity, major isotopes) 479/477 ($M^+ + 1$, trace amount), 423/421 (trace amount) 291/289 (100/80); ^1H NMR ($CDCl_3$, ppm) 7.30 (5 H, bm), 5.74 (1 H, tt, J = 6.0, 1.0 Hz, J_{Sn-H} = 68.0 Hz), 4.50 (2 H, s), 4.13 (2 H, d, J = 7.5 Hz), 2.22 (2 H, t, J = 7.5, J_{Sn-H} = 58.0 Hz), 1.53–1.43 (6 H, bm), 1.32 (8 H, bm), 0.88 (18 H, m); ^{13}C NMR ($CDCl_3$, ppm) 148.9, 138.6, 136.9, 128.3 (2 C), 127.8 (2 C), 127.5, 72.0, 66.3, 35.8, 29.1 (2 C), 27.4 (2 C), 23.4, 13.9, 13.6 (2 C), 9.7 (2 C). Anal. Calcd for $C_{25}H_{44}OSn$: C, 62.65; H, 9.25. Found: C, 62.85; H, 9.32.

6-(Benzyloxy)-4-propyl-4(*E*)-hexenal (5). Stannane **4** (4.85 g, 10.0 mmol) under an argon atmosphere, deoxygenated by two cycles of evacuation of the flask with oil pump vacuum and purging with argon, was dissolved in THF (50 mL) and cooled to −78 °C. *n*-BuLi (4.86 mL, 11 mmol, 2.5 M in hexane) was added dropwise, and after 2 h (2-thienyl)CuCNLi (46.0 mL, 11.5 mmol, 0.25 M in THF) was added via a syringe over a 10-min period. The brown cuprate solution was stirred for 30 min, and HMPA (3.5 mL, 20 mmol) was added followed by the dropwise addition of solution of acrolein (1.0 mL, 15 mmol) and TMSCl (1.9 mL, 15 mmol) in THF (10 mL). After 2 h the reaction contents were poured into a mixture of 1 N HCl (50 mL) and Et_2O (50 mL) and stirred for 0.5 h. The Et_2O layer was seperated and the aqueous layer extracted with Et_2O (3 × 50 mL). Standard workup followed by chromatography using ethyl acetate/hexanes (1/9) as the eluant gave **5** (1.2 g, 49%) as a slightly yellow oil: IR (film) 2930, 2868, 2720, 1723, 1665, 1454, 1354, 1090, 737, and 698; mass spectrum CI (isobutane, rel intensity) 247 ($M^+ + 1$, 20), 245 (33), 229 (20) 202 (100), 155 (30); ^1H NMR ($CDCl_3$, ppm) 9.78 (1 H, t, J = 1.2 Hz), 7.30 (5 H, m), 5.38 (1 H, t, J = 7.5 Hz), 4.50 (2 H, s), 4.02 (2 H, d, J = 7.5 Hz), 2.55 (2 H, tm, J = 7.5 Hz), 2.35 (2 H, t, J = 7.5 Hz), 2.00 (2 H, t, J = 7.0 Hz), 1.37 (2 H, sex., J = 7.5 Hz), 0.86 (3 H, t, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$, ppm) 201.4, 141.8, 138.2, 128.0 (2 C), 127.5 (2 C), 127.2, 122.0, 71.9, 66.0, 41.7, 32.6, 28.5, 21.3, 13.6. Anal. Calcd for $C_{16}H_{22}O_2$: C, 77.01; H, 9.01. Found: C, 77.27; H, 8.97.

Ethyl 8-(Benzyloxy)-2-methyl-6-propyl-2(*E*),6(*E*)-octadienoate (6). A mixture of aldehyde **5** (0.615 g, 2.6 mmol) and (carbethoxyethylidene)triphenylphosphorane (1.12 g, 2.9 mmol) in dry CH_2Cl_2 (15 mL) was refluxed for 6 h under an argon atmosphere. The solvent was evaporated in vacuo, and the resulting slurry was diluted with hexanes (20 mL) and filtered through a pad of Celite and the precipitate rinsed with portions of hexanes (5 × 20 mL). The solvent was evaporated in vacuo and the oil chromatographed using ethyl acetate/hexanes (1/9) as the eluant to give geometrically pure **6** (0.700 g, 82%) as clear oil: IR (film) 2930, 2869, 1709, 1649, 1453, 1366, 1268, and 1091 cm^{-1}; mass spectrum CI (isobutane, rel intensity) 331 ($M^+ + 1$, trace amount), 223 (100), 149 (20); ^1H NMR ($CDCl_3$, ppm) 7.40 (5 H, m), 6.75 (1 H, t, J = 7.0 Hz), 5.42 (1 H, t, J = 6.5 Hz), 4.50 (2 H, s), 4.17 (2 H, q, J = 7.0 Hz), 4.05 (2 H, d, J = 6.5 Hz), 2.30 (2 H, q, J = 8.0 Hz), 2.15 (2 H, t, J = 8.0 Hz), 2.02 (2 H, t, J = 7.0 Hz), 1.84 (3 H, d, J = 1.0 Hz), 1.40 (2 H, sex., J = 7.5 Hz), 1.28 (3 H, t, J = 7.0 Hz), 0.87 (3 H, t, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$, ppm) 168.0, 143.0, 141.3, 138.3, 128.2 (2C), 127.9, 127.6 (2C), 127.4, 121.8, 71.9, 66.2, 60.2, 35.1, 27.1, 21.5, 14.1, 13.9, 12.2. Anal. Calcd for $C_{21}H_{30}O_3$: C, 76.31; H, 9.16. Found: C, 76.19; H, 9.04.

8-(Benzyloxy)-2-methyl-6-propyl-2(*E*),6(*E*)-octadien-1-ol (7). To a solution of **6** (0.50 g, 1.5 mmol) in THF (10 mL) at 0 °C under argon was added dropwise DIBAL-H (3.75 mL, 3.75 mmol, 10 M in THF). The mixture was stirred for 2 h, poured into 25 mL of 25% aqueous tartaric acid solution, and extracted with Et_2O (4 × 20 mL). Standard workup followed by chromatography using ethyl acetate/hexanes (25/75) as the eluant gave **7** (0.41 g, 95%) as clear oil: IR (film) 3415, 2958 (bm), 1710, 1659, 1452, 1378, and 1070 (m) cm^{-1}; mass spectrum CI (isobutane, rel intensity) 289 ($M^+ + 1$, trace amount), 271 (3), 253 (2), 241 (trace amount), 213 (2), 181 (25), 163 (100), 135 (5), 123 (20); ^1H NMR ($CDCl_3$, ppm) 7.30 (5 H, m), 5.39 (2 H, m), 4.50 (2 H, s), 4.02 (2 H, d, J = 6.5 Hz), 3.97 (2 H, s), 2.16 (2 H, m), 2.08 (2 H, m), 2.02 (2 H, t, J = 7.0 Hz), 1.66 (3 H, s), 1.37 (2 H, sex., J = 7.5 Hz), 0.86 (3 H, t, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$, ppm) 143.7, 138.4, 135.0, 128.2 (2C), 127.7 (2C), 127.4, 125.3, 121.4, 71.9, 68.5, 66.3, 36.2, 32.5, 25.9, 21.6, 13.9, 13.5. Anal. Calcd for $C_{19}H_{28}O_2$: C, 79.11; H, 9.79. Found: C, 79.42; H, 9.90.

8-(Benzyloxy)-1-chloro-2-methyl-6-propyl-2(*E*),6(*E*)-octadiene (8). To a solution of NCS (0.180 g, 1.35 mmol) in dry CH_2Cl_2 (10 mL) at 0 °C under argon atmosphere was added dropwise DMS (0.15 mL, 2.0 mmol) and the slurry cooled to −20 °C. To this was added dropwise alcohol **7** (0.262 g, 1.0 mmol) in CH_2Cl_2 (5 mL). The mixture was warmed to 0 °C and after 6 h poured into water (25 mL) and extracted with Et_2O (4 × 30 mL). Standard workup followed by chromatography using ethyl acetate/hexanes (5/95) as the eluant gave **8** (0.250 g, 93%) as a clear oil: IR (film) 2930, 2868, 1453, 1377, 1263, 1090, 1027, 736, and 697 cm^{-1}; mass spectrum CI (isobutane, rel intensity, major isotopes) 289 ($M^+ + 1$, 5), 271 (3), 253 (7), 201/199 (33/100), 163 (43); ^1H NMR ($CDCl_3$, ppm) 7.30 (5 H, m), 5.52 (1 H, t, J = 6.5 Hz), 5.40 (1 H, t, J = 7.0 Hz), 4.50 (2 H, s), 4.04 (2 H, d, J = 6.5 Hz), 4.00 (2 H, s), 2.17 (2 H, m), 2.07 (2 H, m), 2.00 (2 H, t, J = 7.5 Hz), 1.56 (3 H, s), 1.37 (2 H, sex., J = 7.5 Hz), 0.86 (3 H, t, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$, ppm) 143.3, 138.5, 131.8, 130.2, 128.2 (2C), 127.6 (2C), 127.4, 121.7, 71.9, 66.3, 52.2, 35.8, 32.6, 26.4, 21.6, 14.0, 13.9.

1-(Benzyloxy)-7-methyl-3-propyl-3(*E*),6(*E*)-nonadiene (9). To cuprate $Me_2CuMgBr(I)$, at −78 °C under argon, prepared from CuBr–DMS (0.335 g, 2.0 mmol) and MeMgI (1.1 mL, 4.0 mmol, 3.0 M in THF) in THF (10 mL) at −40 °C for 1 h, was added dropwise allylic chloride **8** (0.25 g, 0.86 mmol) in THF (5 mL). After 0.5 h, saturated NH_4Cl/NH_4OH (25 mL) was added and extracted with Et_2O (4 × 25 mL). Standard workup followed by chromatography using ethyl acetate/hexanes (5/95) as the eluant gave **9** (0.238 g, 97%) as a clear oil: IR (film) 2930, 2870, 1664, 1454, 1376, 1203, 1072, 1007, 734, and 697 cm^{-1}; mass spectrum CI (isobutane, rel intensity) 286 ($M^+ + 1$, trace amount), 179 (100); ^1H NMR ($CDCl_3$, ppm) 7.30 (5 h, m), 5.40 (1 H, t, J = 7.0 Hz), 5.10 (1 H, tq, J = 6.5, 1.2 Hz), 4.50 (2 H, s), 4.03 (2 H, d, J = 6.5 Hz), 2.05 (8 H, m), 1.58 (3 H, s), 1.38 (2 H, sex., J = 7.5 Hz), 0.97 (3 H, t, J = 7.5 Hz), 0.86 (3 H, t, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$, ppm) 144.3, 138.8, 137.1, 128.3 (2 C), 127.8 (2 C), 127.5, 122.7, 121.4, 72.0, 66.5, 36.9, 32.8, 32.4, 26.6, 21.8, 15.9, 14.1, 12.8. Anal. Calcd for $C_{20}H_{30}O$: C, 83.85; H, 10.56. Found: C, 84.01; H, 10.58.

7-Methyl-3-propyl-3(*E*),6(*E*)-nonadien-1-ol (10). To $EtNH_2$ (~5 mL) at −78 °C under argon containing Li (25 mg) was added benzyl ether **9** (0.220 g, 0.77 mmol) in THF (2 mL). After 10 min, the blue color reappeared, solid NH_4Cl (0.200 g) was added, and the excess Li was removed with forceps. Standard workup followed by chromatography using ethyl acetate/hexanes (2/8) as the eluant gave alcohol **10** (0.148 g, 98%) as a clear oil: IR (film) 3330, 2930, 2871, 1664, 1455, 1378, and 1001 cm^{-1}; mass spectrum CI (isobutane, rel intensity) 196 ($M^+ + 1$, trace amount), 179 (100); ^1H NMR ($CDCl_3$, ppm) 5.42 (1 H, t, J = 7.0 Hz), 5.10 (1 H, tq, J = 6.5, 1.2 Hz), 4.15 (2 H, d, J = 7.0 Hz), 2.20–1.90 (8 H, m), 1.59 (3 H, s), 1.40 (2 H, sex., J = 7.5 Hz), 0.98 (3 H, t, J = 7.5 Hz), 0.89 (3 H, t, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$, ppm) 143.8, 137.2, 123.8, 122.5, 59.2, 36.8, 32.6, 32.3, 26.6, 21.9, 15.9, 14.0, 12.8. Anal. Calcd for $C_{13}H_{24}O$: C, 79.52; H, 12.33. Found: C, 79.34; H, 12.22.

7-Methyl-3-propyl-2(*E*),6(*E*)-nonadienyl Acetate (11). To alcohol **10** (0.100 g, 0.51 mmol) in CH_2Cl_2 (5 mL) was added pyridine (2.0 mL), acetic anhydride (0.10 g, 1.0 mmol), and a few crystals of DMAP. The mixture was stirred overnight (10 h), poured into ice-cold water, and extracted with Et_2O (4 × 20 mL). Standard workup followed by chromatography using ethyl acetate/hexanes (5/95) as the eluant gave **11** (0.120 g, 99%) as a clear oil: IR (film) 2932, 2873, 1742, 1460, 1369, 1231, and 1023 cm^{-1}; mass spectrum CI (isobutane, rel intensity) 238/239 ($M^+ + 1$, trace amount), 179 ($M^+ - C_2H_3O_2$, 100); EI m/e (rel intensity) 178 (4), 149 (9), 135 (9), 121 (12), 108 (7), 93 (11), 83 (60), 82 (29), 81 (20), 79 (20), 68 (21), 67 (31), 55 (100), 53 (15); ^1H NMR ($CDCl_3$, ppm) 5.35 (1 H, t, J = 7.0 Hz), 5.08 (1 H, tq, J = 6.0, 1.2 Hz), 4.58 (2 H, d, J = 7.0 Hz), 2.15–2.02 (9 H, m), 1.98 (2 H, t, J = 7.5 Hz), 1.59 (3 H, s), 1.40 (2 H, sex., J = 7.5 Hz), 0.97 (3 H, t, J = 7.5 Hz), 0.89 (3 H, t, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$, ppm) 170.9, 146.1, 137.3, 122.3, 118.7, 61.2, 36.8, 32.7, 32.3, 26.4, 21.8, 21.0, 15.9, 13.9, 12.7. Anal. Calcd for $C_{15}H_{26}O_2$: C, 75.58; H, 10.99. Found: C, 75.36; H, 11.20.

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