Pheromone Synthesis, Part 203[+]

Pheromonal and Kairomonal Activities Can Be Separated: Synthesis and Bioactivity Studies of Pine Bast Scale Sex Pheromones and Their Analogues

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*New syntheses were achieved to secure matsuone (**1**), the pheromone of the pine scale* Matsucoccus matsumurae*, that of* M. feytaudi *(**2**), and that of* M. josephi *(**3**). Five analogues (**4** – **8**) of **1**, **2**, and **3** were synthesized and their bioactivities studied. The pheromone analogue **7** showed relatively strong pheromonal activity toward* M. josephi*, while it was inactive as a kairomone toward the predator* Elatophilus hebraicus*. Similarly, analogue **8** acted as a pheromone for* M. feytaudi*, but it did not attract any of its local predators. The* M. feytaudi *pheromone **2** exhibited strong kairomonal activity toward* E. hebraicus*, but was not active as a pheromone mimic to attract* M. josephi*.*

KEYWORDS:

kairomones · natural products · pheromones · structure – activity relationships

Introduction

Pine bast scales of the genus *Matsucoccus* are troublesome pests in pine forests. In 1989, the pioneering work of Lanier, Silverstein and their respective co-workers culminated in the isolation of and structural proposal for the female sex pheromone matsuone (**1**) (Figure 1) of the red pine scale *M. resinosae* and the Japanese pine scale (*M. matsumurae*).[1] Its absolute configuration as shown in **1** was assigned in 1991 by Kallmerten and his co-workers on the basis of their enantioselective synthesis of **1**.[2] We, as well as others, also reported enantioselective syntheses of **1**.[3–6] The second pine bast scale pheromone to be clarified in 1990 was that produced by the maritime pine scale (*M. feytaudi*) (**2**).[7] We synthesized the four stereoisomers of **2**,[8, 9] and studies of their bioactivities by Jactel et al. established **2** as the naturally occurring pheromone.[10] The third one, identified in 1993, was the pheromone of the Israeli pine scale (*M. josephi*) (**3**).[11] Our synthesis of its enantiomers[12] was followed by their GC comparison with the natural pheromone, and the major component of the pheromone was found to possess the absolute configuration as depicted in **3**.[13] As evident from the structures **1** – **3**, these *Matsucoccus* pheromones share the same *R*-configured chiral diene part, while the opposite parts of the molecules determine their species specificity.

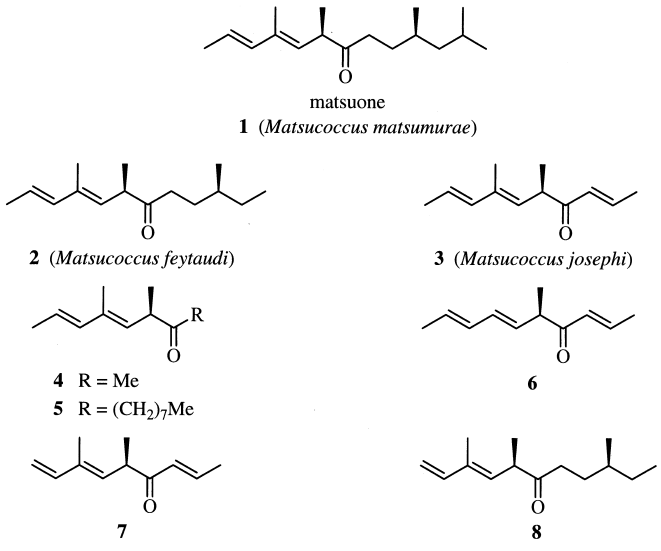

Figure 1. *Structures of the pine bast scale pheromones and their analogues.*

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In 1996, Dunkelblum et al. reported that the predator *Elatophilus hebraicus* was attracted by the sex pheromone **3** of its prey, *M. josephi*.[14] This is an example of kairomonal attraction of natural enemies by the sex pheromones of their prey insects. Surprisingly, however, *E. hebraicus*, but not *M. josephi*, was also attracted by the pheromones **1** and **2**, although *M. matsumurae* and *M. feytaudi*, which emit these pheromones, do not occur in Eastern Mediterranean countries such as Israel. This means that the kairomone receptor of *E. hebraicus* may be sensitive to the chiral diene part of the molecules **1** – **3**, while flexible against the structural change in the parts characterizing the species specificity of the *Matsucoccus* pheromones. It may be possible then to find a pheromone analogue that works only as the pheromone for *M. josephi*, with no kairomonal activity toward *E. hebraicus*. This would enable us to trap only the pest pine scale *M. josephi*, without luring and decreasing the population of its natural enemy, *E. hebraicus*. Therefore, we undertook an attempt to design and synthesize the five pheromone analogues **4** – **8**, and indeed, the mimic **7** was found to show strong pheromonal activity toward *M. josephi* with no kairomonal activity toward *E. hebraicus*, as detailed below. The biological implications of the present work are outlined in Figure 2.

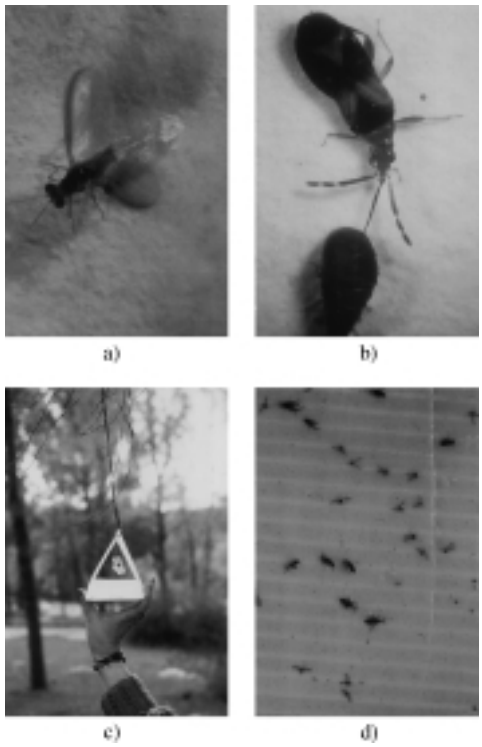

Figure 2. *a)* M. josephi *male (2 – 3 mm in length); b)* E. hebraicus *(4 – 5 mm in length) feeding on female* M. josephi *(3 – 4 mm in length); c) pheromone trap; d) sticky plate with trapped* M. josephi *males and adult* E. hebraicus.

Results and Discussion

Because the racemates of the pheromones **1** – **3** are known to be bioactive,[1, 10, 13] extreme care is not necessary to achieve highly enantioselective syntheses of the pheromones and their analogues. The methods employed in the present synthesis, which do not guarantee high stereochemical purities of the final products, afforded them in 80 – 90 % stereochemical purities (see below).

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was born in Seoul, Korea, in 1935 as the son of a Japanese Christian pastor. He obtained his B.Sc. (1957, agricultural chemistry), M.Sc. (1959, biochemistry), and Ph.D. (1962, organic chemistry) degrees from the University of Tokyo where he was promoted to the positions of assistant professor (1962), associate professor (1968), and full professor (1978). In 1995 he moved to the Science University of Tokyo as a professor. His research interests include the enantioselective synthesis of pheromones and other bioactive molecules, biotransformations, and chemical ecology. He has been honored by awards from the Japan Academy (1981, in the presence of the late Emperor Hirohito), the International Society of Chemical Ecology (1996, Silver Medal), and the American Chemical Society (1999, Ernest Guenther Award in the Chemistry of Natural Products).

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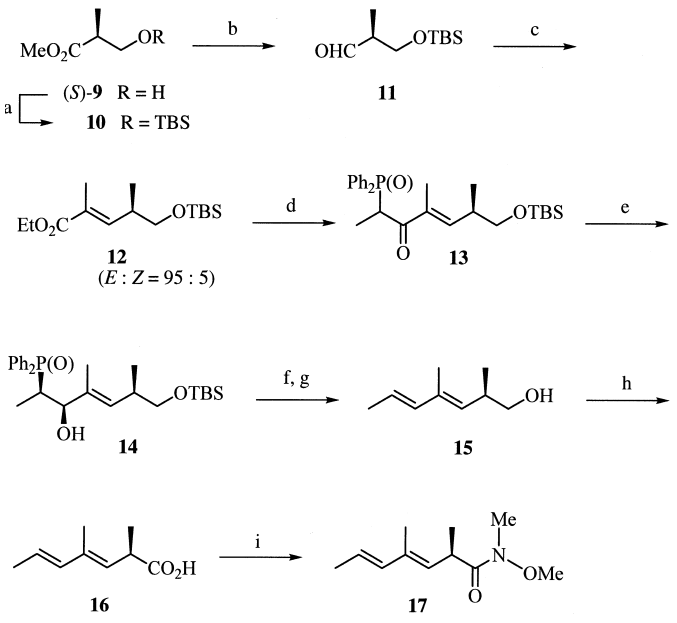
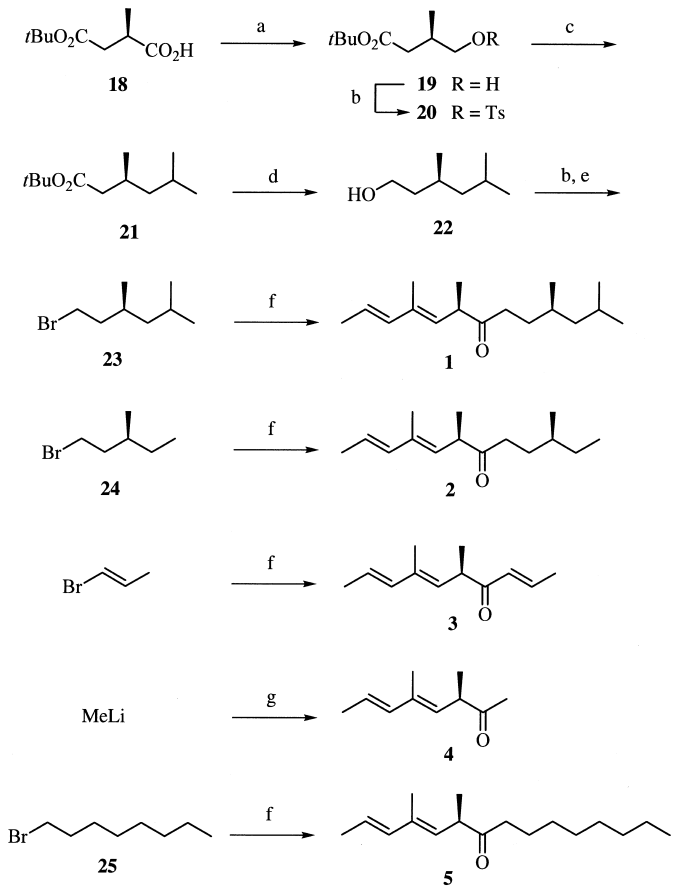
Synthesis of the *Matsucoccus* Pheromones 1 – 3 and Their Analogues 4 and 5

For the synthesis of **1** – **5**, the coupling of the Weinreb amide **17**[15] (Scheme 1) with various organometallic reagents was adopted as the key step, because this strategy enables the preparation of different pheromone analogues. The key intermediate **17** was synthesized from commercially available methyl (*S*)-2-methyl-3-hydroxypropanoate (**9**) (Scheme 1). The *tert*-butyldimethylsilyl ether **10** derived from **9** was reduced with diisobutylaluminum hydride at $-78\,^{\circ}C$ to give aldehyde **11**, which was subjected to Wittig olefination to give the known unsaturated ester **12** ($E/Z = 95:5$ as judged by ^1H NMR analysis).[16] Conversion of **12** to the chiral dienol **15** by the olefination method of Buss and Warren[17] was achieved according to Lin and Xu,[5] who prepared **15** from the methyl ester corresponding to **12** with a *tert*-butyldiphenylsilyl protective group instead of the TBS group of the ethyl ester **12**. Our sample of pure **15** (as judged by GC) exhibited a positive rotation, $[\alpha]_D^{25} = +43.5$ ($CHCl_3$), which was considerably larger than the previously reported value, $[\alpha]_D = +29.0$ ($CHCl_3$).[5] The crude acid **16** obtained by oxidation of **15** with PDC was treated with *N*,*O*-dimethylhydroxylamine under standard conditions to give the desired Weinreb amide **17**. The overall yield of **17** was 18 % based on (*S*)-**9** (9 steps).

Scheme 2 summarizes the synthesis of the pheromones and analogues **1** – **5** by the coupling between the amide **17** and organometallic reagents. For the synthesis of matsuone (**1**), a Grignard reagent had to be prepared from the (*S*)-bromide **23**.



Scheme 1. *Synthesis of the Weinreb amide **17**. a) TBSCl, imidazole, DMF, 98%; b) iBu$_2$AlH, hexane/CH$_2$Cl$_2$; c) Ph$_3$P=C(Me)CO$_2$Et, C$_6$H$_6$, 83% (based on **10**); d) Ph$_2$P(O)Et, nBuLi, THF, 98%; e) NaBH$_4$, CeCl$_3$·7H$_2$O, EtOH; then chromatography on SiO$_2$, 66%; f) NaH, DMF; g) TBAF, THF, 90% (based on **14**); h) PDC, DMF; i) HNMe(OMe)·HCl, EDC·HCl, DMAP, iPr$_2$NEt, CH$_2$Cl$_2$, 38% (based on **15**). DMAP = 4-(dimethylamino)pyridine; EDC = 1-ethyl-3-(3-dimethylamino)-propyl carbodiimide; PDC = pyridinium dichromate; TBAF = tetrabutylammonium fluoride; TBS = tert-butyldimethylsilyl.*



Scheme 2. *Synthesis of the pheromones **1**–**3** and their analogues **4** and **5**. a) BH$_3$·Me$_2$S, THF, 93%; b) TsCl, C$_5$H$_5$N; c) iPrMgCl, Li$_2$CuCl$_4$, THF, 52% (based on **19**); d) LiAlH$_4$, Et$_2$O, 77%; e) LiBr, Me$_2$CO, 70% (based on **22**); f) 1) Mg, THF; 2) **17**, 89, 90, 80, and 81% for **1**, **2**, **3**, and **5**, respectively; g) **17**, THF, 67%. Ts = toluene-4-sulfonyl.*

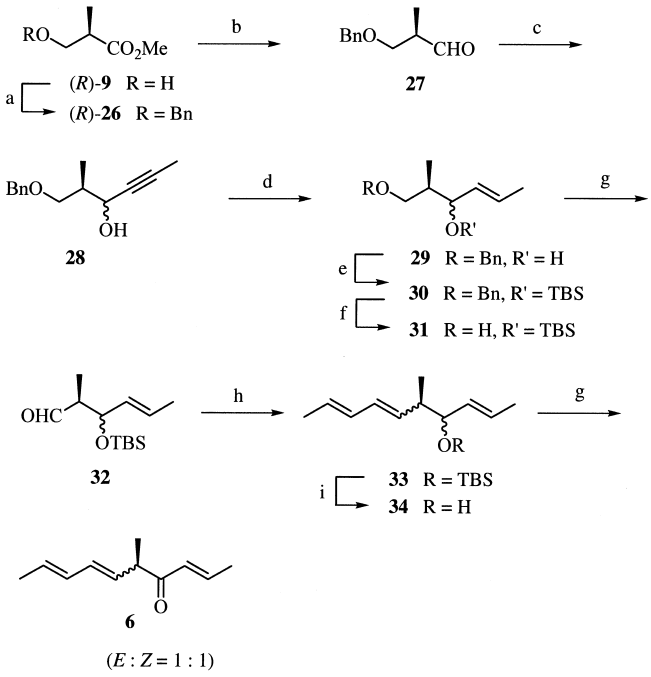
We employed the commercially available (*R*)-configured half ester **18**[18] as the starting material for the preparation of **23**. Reduction of **18** with borane gave the alcohol **19**, whose tosylate **20** was treated with isopropylmagnesium chloride in the presence of dilithium tetrachlorocuprate[19] to give **21**. Reduction of **21** with lithium aluminum hydride gave **22**, which was converted to the bromide **23** by standard methods. Transformation of **23** to the corresponding Grignard reagent was followed by its treatment with the Weinreb amide **17** to give (2*E*,4*E*,6*R*,10*S*)-**1** in 23% overall yield based on **18** (7 steps) or 16% overall yield based on **9** (10 steps). Our sample of **1** showed $[\alpha]_D^{21} = -284$ ($CDCl_3$), whereas for our previous sample a value of $[\alpha]_D^{22} = -316$ ($CDCl_3$) was reported.[3] Since there was no danger of racemization at C-10, the present sample of **1** must be diastereomerically impure at C-6. It therefore seems that the present synthetic route to **1** employing the Weinreb process suffers from slight racemization at the stereogenic center (C-6) next to the carbonyl group.

The pheromone **2** of *M. feytaudi* was synthesized by treatment of the amide **17** with the Grignard reagent prepared from (*S*)-3-methylpentyl bromide (**24**).[20] The specific rotation of **2** was $[\alpha]_D^{26} = -266$ ($CDCl_3$), whereas the reported value was $[\alpha]_D^{22} = -336$ ($CDCl_3$).[8] Since **24** was pure, the purity at C-6 of **2** was thought to be imperfect. The synthesis of the pheromone **3** of *M. josephi* was achieved by treatment of the amide **17** with (*E*)-propenylmagnesium bromide, and the product exhibited $[\alpha]_D^{22} = -426$ (*n*-pentane). Because the reported rotation value of **3** was $[\alpha]_D^{26} = -466$ (*n*-pentane),[12] the present sample of **3** was not completely enantiomerically pure.

The two pheromone analogues **4** and **5** were also prepared by treatment of the amide **17** with methyllithium and octylmagnesium bromide, respectively. Their specific rotations were $[\alpha]_D^{25} = -373$ ($CHCl_3$) (**4**) and $[\alpha]_D^{27} = -173$ ($CHCl_3$) (**5**).

Synthesis of the 7-Demethyl Analogue 6 of the *M. josephi* Pheromone

Scheme 3 summarizes the synthesis of the 7-demethyl analogue **6** of the *M. josephi* pheromone. In this case, the diene part of the molecule **6** was attached to the chiral part in a later stage of the synthesis by a Wittig reaction. We chose the commercially available (*R*)-hydroxy ester **9** as the starting material, and it was converted to the benzyl ether **26** by treatment with benzyl trichloroacetimidate and triflic acid.[21] Reduction of **26** with diisobutylaluminum hydride gave **27**, which was treated with 1-lithiopropyne to furnish **28**. The acetylenic alcohol **28** was then reduced with lithium aluminum hydride to give the desired alkenol **29** with (*E*)-olefin geometry. After protecting the secondary hydroxy group of **29** as its TBS ether, the benzyl protective group of **30** was removed by reduction with sodium,



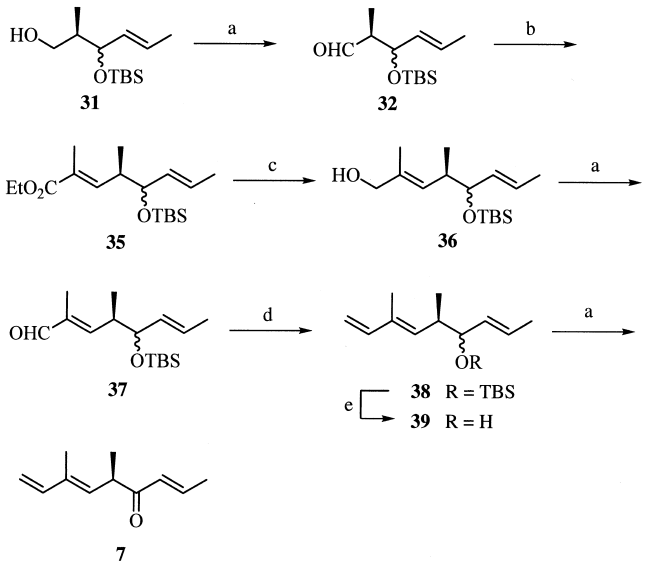
Scheme 3. *Synthesis of the pheromone analogue **6**. a) $CCl_3C(=NH)OBn$, TfOH, CH_2Cl_2, 85 %; b) iBu_2AlH, hexane/CH_2Cl_2; c) $MeC{\equiv}CH$, nBuLi, HMPA/THF, 54 % (based on **26**); d) $LiAlH_4$, Et_2O, 98 %; e) TBSCl, imidazole, DMF, quant.; f) Na, NH_3, THF, 83 %; g) $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2, 48 % (for **6**); h) (E)-MeCH=$CHCH_2P(O)Ph_2$, nBuLi, HMPA/THF, 31 % (based on **31**); i) TBAF, THF, quant. HMPA = hexamethylphosphoramide; Tf = trifluoromethanesulfonyl.*

dissolved in liquid ammonia, to give **31**. Oxidation of **31** under Swern conditions yielded the crude aldehyde **32**, which was immediately treated with the carbanion derived from (*E*)-2-butenyldiphenylphosphane oxide.[22] After the eliminative olefin formation,[22] the product **33** was obtained as a 1:1 mixture of the *E*/*Z* isomers at C-6. Removal of the TBS protective group of **33** was followed by Swern oxidation of the resulting alcohol **34** to give the pheromone analogue **6**, $[\alpha]_D^{24} = -278$ ($CHCl_3$), in 5.6 % overall yield based on (*R*)-**9** (10 steps).

Synthesis of the Nor-Analogue 7 of the *M. josephi* Pheromone

The analogues **7** and **8** are chain-shortened mimics of the natural pheromones **3** and **2**, respectively. The intermediate **32**, which was employed in the synthesis of **6**, was used as the chiral part of the pheromone analogue **7**. The crude aldehyde **32** was obtained by Swern oxidation of **31** and converted to the unsaturated ester **35** by a Wittig reaction (Scheme 4).

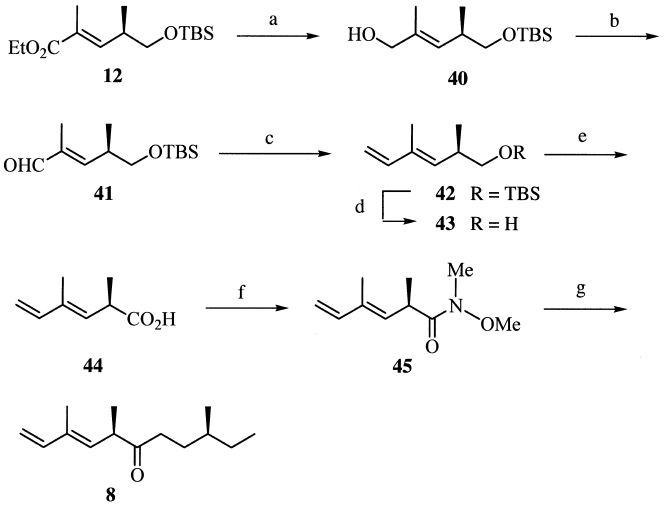
Reduction of **35** with diisobutylaluminum hydride furnished the allylic alcohol **36**. This was oxidized under Swern conditions to give aldehyde **37**. Methylenation of **37** by a Wittig reaction afforded triene **38**, whose TBS protective group was removed to furnish alcohol **39**. Swern oxidation of **39** gave the pheromone analogue **7**, $[\alpha]_D^{24} = -259$ ($CHCl_3$), in 13 % overall yield based on **32** (6 steps).



Scheme 4. *Synthesis of the pheromone analogue **7**. a) $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2, 55 % (for **7**); b) $Ph_3P{=}C(Me)CO_2Et$, C_6H_6, 32 % (based on **31**); c) iBu_2AlH, hexane/CH_2Cl_2, 98 %; d) $Ph_3P(Me)Br$, nBuLi, THF, 73 % (based on **36**); e) TBAF, THF, quant.*

Synthesis of the Nor-Analogue 8 of *M. feytaudi* Pheromone

The analogue **8** was synthesized via the nor-analogue **45** of the Weinreb amide **17** that was employed for the synthesis of **1** – **5**. The ester **12**, used as the precursor to **17**, was reduced with diisobutylaluminum hydride to furnish alcohol **40** (Scheme 5).



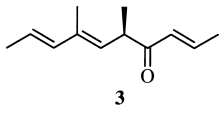
Scheme 5. *Synthesis of the pheromone analogue **8**. a) iBu_2AlH, hexane/CH_2Cl_2, 95 %; b) $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2; c) $Ph_3P(Me)Br$, nBuLi, THF, 69 % (based on **40**); d) TBAF, THF, 88 %; e) PDC, DMF; f) HNMe(OMe) · HCl, EDC · HCl, DMAP, iPr_2NEt, CH_2Cl_2, 42 % (based on **43**); g) **24**, Mg, THF, 87 %.*

Swern oxidation of **40** afforded aldehyde **41**, which was subjected to Wittig methylenation to give diene **42**. Deprotection of the TBS protective group of **42** was followed by PDC oxidation of the resulting **43** to yield the dienoic acid **44**. The corresponding Weinreb amide **45** was treated with the Grignard

reagent prepared from (*S*)-3-methylpentyl bromide to give the desired pheromone analogue **8**, $[\alpha]_D^{24} = -340$ ($CHCl_3$), in 21% overall yield based on **12** (7 steps).

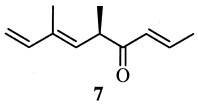
Summary of Biological Activities of 1 – 8

Although detailed biological results will be published separately,[23] it is appropriate here to summarize them briefly. As we already reported, all of the three *Matsucoccus* pheromones **1** – **3** showed strong kairomonal activity toward the predator *Elatophilus hebraicus*.[13] Attractive action on the males of the Israeli pine bast scale *M. josephi* was only observed with the natural pheromone **3**, whereas **1** and **2** showed no pheromonal activity at all. The pheromone mimic **4** had practically no activity, while **5** possessed moderate kairomonal activity, but both were inactive as a pheromone for *M. josephi*. The mimic **6** showed weak pheromonal activity but no kairomonal activity. The analogues **7** and **8** were active as pheromones for *M. josephi* and *M. feytaudi*, respectively, while they had no kairomonal activity. Figure 3 summarizes the biological results. The analogue **7** shows strong



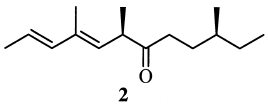
3

natural pheromone and kairomone



7

strong pheromonal activity with no kairomonal activity



2

strong kairomonal activity with no pheromonal activity

Figure 3. *Summary of the bioactivities of the synthetic compounds* ***2****,* ***3****, and* ***7****.*

pheromonal activity without any kairomonal activity. This compound may be useful to trap only the pest *M. josephi* without disturbing its predator *E. hebraicus*. The *M. feytaudi* pheromone **2** shows strong kairomonal activity toward *E. hebraicus* without any pheromonal activity toward *M. josephi*, and thus can trap only the predator. The naturally occurring pheromone **3** of *M. josephi* works both as the pheromone and the kairomone. In conclusion, the two different bioactivities of the pheromone **3** could be separated to create a new compound **7** that showed only the pheromonal activity toward *M. josephi*.

Experimental Section

General: Boiling points and melting points were uncorrected. IR spectra were recorded on a Jasco IRA-102 spectrometer. ^{1}H NMR spectra were obtained on a Jeol JNM-EX 90A (90 MHz) or Bruker DPX 300 (300 MHz) instrument with the solvent peak as internal standard (TMS: $\delta_H = 0.00$, $CHCl_3$: $\delta_H = 7.26$, C_6D_6: $\delta_H = 7.15$). ^{13}C NMR spectra were recorded on a Bruker DPX 300 spectrometer (75 MHz) with the solvent peak as internal standard ($CDCl_3$: $\delta_C = 77.0$, C_6D_6: $\delta_C = 128.0$). Mass spectra (MS) were recorded with a Jeol JMS-SX 102A or a Hitachi M-80B spectrometer. Optical rotation was measured with a Jasco DIP-1000 instrument, CD spectra with a Jasco J-725 spectrometer. Column chromatography was conducted on E. Merck silica gel 60, thin-layer chromatography with E. Merck silica gel plates 60 F_{254}, thickness 0.25 mm.

(*S*)-3-*tert*-Butyldimethylsilyloxy-2-methylpropanal (11): Diisobutylaluminum hydride (0.95 M in hexane, 58 mL, 55 mmol) was added to a stirred solution of **10**[16] (10.0 g, 43.1 mmol) in dichloromethane (100 mL) at $-78\,^\circ$C under argon. After stirring for 20 min at $-78\,^\circ$C, saturated aqueous Rochelle's salt solution was added and the temperature was gradually raised to room temperature. Water and diethyl ether were added to the reaction mixture, the organic phase was separated and the aqueous phase was extracted with diethyl ether. The combined organic phases were washed with water and brine, dried over $MgSO_4$, and concentrated under reduced pressure to give 9.5 g (quant) of **11** as a colorless oil. This was used for the next step without further purification. IR (film): $\tilde{\nu}_{max} = 2720$ (m, CHO), 1730 (s, C=O), 1260 cm^{-1} (s, Si–Me); ^{1}H NMR (90 MHz, $CDCl_3$): $\delta = 0.01$ (s, 6H, $SiMe_2$), 0.83 (s, 9H, *t*Bu), 1.03 (d, $J = 7$ Hz, 3H, 2-Me), 2.25 – 2.70 (m, 1H, 2-H), 3.78 (dd, $J = 1.0$, 5.8 Hz, 2H, 3-H), 9.68 (d, $J = 1.5$ Hz, 1H, CHO).

Ethyl (2*E*,4*R*)-5-*tert*-butyldimethylsilyloxy-2,4-dimethyl-2-pentenoate (12): $Ph_3P{=}C(Me)CO_2Et$ (18.7 g, 51.7 mmol) was added to a stirred solution of the crude **11** (9.5 g, ca. 46.9 mmol) in benzene (200 mL), and the mixture was stirred for 19 h at room temperature. Saturated aqueous ammonium chloride was added, the organic phase was separated, and the aqueous phase was extracted with diethyl ether. The combined organic phases were washed with water and brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel (100 g, hexane/ethyl acetate, 50:1) to give 10.2 g (83% based on **10**) of **12** as a colorless oil. The *E*/*Z* ratio of **12** (95:5) was determined by ^{1}H NMR analysis. $n_D^{22} = 1.4482$; $[\alpha]_D^{27} = +2.67$ ($c = 1.42$, $CHCl_3$) [ref. [16]: $[\alpha]_D^{20} = +2.06$ ($c = 1.36$, $CHCl_3$)]; IR (film): $\tilde{\nu}_{max} = 1715$ (s, C=O), 1650 (w, C=C), 1260 (s, Si-Me), 1085 cm^{-1} (s, C-O); ^{1}H NMR (90 MHz, $CDCl_3$): $\delta = 0.00$ (s, 6H, $SiMe_2$), 0.83 (s, 9H, *t*Bu), 0.97 (d, $J =$ 7 Hz, 3H, 4-Me), 1.25 (t, $J = 7$ Hz, 3H, $CO_2CH_2CH_3$), 1.83 (d, $J = 1.5$ Hz, 3H, 2-Me), 2.60 (dq, $J = 14$, 7 Hz, 1H, 4-H), 3.48 (d, $J = 7$ Hz, 2H, 5-H), 4.15 (q, $J = 7$ Hz, 2H, CO_2CH_2), 5.66 – 5.82 (m, 1H, *cis*-3-H), 6.53 (dq, $J = 14$, 1.2 Hz, 1H, *trans*-3-H).

(4*E*,6*R*)-4,6-Dimethyl-7-*tert*-butyldimethylsilyloxy-2-diphenylphosphaneoxido-4-hepten-3-one (13): *n*-Butyllithium (1.65 M in *n*-hexane, 30.0 mL, 49.5 mmol) was added to a stirred solution of ethyldiphenylphosphane oxide[17] (10.8 g, 46.9 mmol) in THF (150 mL) at $-78\,^\circ$C under argon. To this solution, **12** (11.2 g, 39.0 mmol) in THF (50 mL) was added, and the mixture was stirred for 90 min at $-78\,^\circ$C under argon. Water was added and the temperature was gradually raised to room temperature. Ethyl acetate was added, the organic phase was separated, and the aqueous phase was extracted with ethyl acetate. The combined organic phases were washed with water and brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel (100 g, hexane/ethyl acetate, 10:1) to give 15.5 g (98% based on consumed **12**) of **13** as a gummy white solid with the recovery of **12** (1.6 g). $[\alpha]_D^{21} = -2.46$ ($c = 0.61$, $CHCl_3$); IR (film): $\tilde{\nu}_{max} =$ 1655 (s, C=O), 1585 (w, aromatic), 1250 (s, Si–Me), 1190 (s, P=O), 1115 cm^{-1} (s, C–O); ^{1}H NMR (90 MHz, $CDCl_3$): $\delta = 0.00$ (s, 6H, $SiMe_2$), 0.85 (s, 9H, *t*Bu), 0.97 (d, $J = 7$ Hz, 3H, 6-Me), 1.25 – 1.54 (m, 3H, 1-Me), 1.58 (s, 3H, 4-Me), 2.56 (dq, $J = 12$, 7 Hz, 1H, 6-H), 3.20 – 3.56 (m, 2H, 7-H), 4.18 – 4.63 (m, 1H, 2-H), 6.22 – 6.57 (m, 1H, 5-H), 7.30 – 8.07 (m, 10H, aromatic); elemental analysis (%): calcd for $C_{27}H_{39}O_3PSi$ (470.66): C 68.90, H 8.35; found: C 69.10, H 8.30; HR-MS: calcd for $C_{27}H_{39}O_3PSi$ 470.2406; found 470.2405.

(4*E*,6*R*)-4,6-Dimethyl-7-*tert*-butyldimethylsilyloxy-2-diphenylphosphaneoxido-4-hepten-3-ol (14): $CeCl_3 \cdot 7H_2O$ (11.3 g, 30.4 mmol) was added to a solution of **13** (14.3 g, 30.4 mmol) in anhydrous ethanol (200 mL) at $-78\,^{\circ}C$. Sodium tetrahydroborate (1.15 g, 30.4 mmol) was added and the stirring was continued for 3 h. Then water was added and the temperature was gradually raised to room temperature. The solution was then concentrated under reduced pressure. Ethyl acetate was added to the residue, the organic phase was separated, and the aqueous phase was extracted with ethyl acetate. The combined organic phases were washed with water and brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel (400 g, hexane/ethyl acetate, 2:1) to give 9.41 g (66%) of *syn* product **14** and 3.07 g (21%) of the *syn*/*anti* mixture as colorless oils. **14**: $[\alpha]_D^{21} = +2.68$ ($c = 0.68$, $CHCl_3$); IR (film): $\tilde{\nu}_{max} = 3300$ (s, O–H), 1590 (w, aromatic), 1255 (s, Si–Me), 1155 (s, P=O), 1115 cm^{-1} (s, C–O); ^1H NMR (90 MHz, $CDCl_3$): $\delta = 0.00$ (s, 6H, $SiMe_2$), 0.85 (s, 9H, *t*Bu), 0.92 – 1.36 (m, 6H, 1-Me, 6-Me), 1.68 (d, $J = 2$ Hz, 3H, 4-Me), 2.36 – 2.95 (m, 1H, 6-H), 3.16 – 3.77 (m, 4H, 2-H, 7-H, OH), 3.98 – 4.29 (m, 1H, 3-H), 4.96 – 5.17 (m, 1H, 5-H), 7.36 – 7.94 (m, 10H, aromatic); HR-MS: calcd for $C_{27}H_{41}O_3PSi$ 472.2563, found 472.2560.

(2*R*,3*E*,5*E*)-2,4-Dimethyl-3,5-heptadien-1-ol (15): A solution of **14** (7.69 g, 16.3 mmol) in dry DMF (100 mL) was added to a suspension of NaH (60% suspension in mineral oil, 3.00 g, 75.0 mmol) in dry DMF (100 mL). The mixture was stirred at room temperature for 48 h, and then water and diethyl ether were added. The phases were separated, and the aqueous phase was extracted with diethyl ether. The combined organic solution was washed with water, saturated aqueous ammonium chloride, and brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was diluted with THF (100 mL), and a solution of tetrabutylammonium fluoride (1.0 M in THF, 32.6 mL, 32.6 mmol) was added. The mixture was stirred for 20 h at room temperature, then poured into water, and extracted several times with diethyl ether. The ether solution was washed with water and brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel (50 g, hexane/ethyl acetate, 20:1) to give 2.06 g (90%) of **15** as a colorless oil. $n_D^{23} = 1.4891$; $[\alpha]_D^{25} = +43.5$ ($c = 1.02$, $CHCl_3$) [ref. [5]: $[\alpha]_D = +29.0$ ($c = 0.1$, $CHCl_3$)]; gas – liquid chromatography (column: Chirasil-DEX CB, (0.25 mm × 25 m); at 80 – 150 °C, +2 °C min^{-1}; carrier gas: He, pressure 90 kPa): $t_r = 20.0$ min (99.8%, (*R*)-isomer), $t_r = 20.9$ min (0.2%, (*S*)-isomer). The enantiomeric purity of (*R*)-**15** was therefore 99.6% *ee*. IR (film): $\tilde{\nu}_{max} = 3350$ (s, O–H), 3040 (m, olefinic C–H), 1625 (m, C=C), 965 cm^{-1} (s, olefinic C–H); ^1H NMR (90 MHz, $CDCl_3$): $\delta = 0.96$ (d, $J = 7$ Hz, 3H, 2-Me), 1.69 – 1.88 (m, 7H, 4-Me, 7-Me, OH), 2.69 (dq, $J = 11$, 7 Hz, 1H, 2-H), 3.22 – 3.57 (m, 2H, 1-H), 5.12 (d, $J = 10$ Hz, 1H, 3-H), 5.63 (dq, $J = 16$, 7 Hz, 1H, 6-H), 6.09 (d, $J = 16$ Hz, 1H, 5-H); HR-MS: calcd for $C_9H_{16}O$ 140.1202, found 140.1210.

(2*R*,3*E*,5*E*)-2,4-Dimethyl-3,5-heptadienoic acid (16): Pyridinium dichromate (13.7 g, 36.4 mmol) was added to a solution of **15** (1.00 g, 7.13 mmol) in dry DMF (100 mL). The mixture was stirred at room temperature for 10 h, and then water was added. The phases were separated, and the aqueous phase was extracted with diethyl ether. The combined organic phases were washed with water and brine, dried over $MgSO_4$, and concentrated under reduced pressure to give 1.10 g (quant) of **16** as a colorless oil. This was used for the next step without further purification. IR (film): $\tilde{\nu}_{max} = 3500$ (m, COO–H), 1665 cm^{-1} (s, C=O); ^1H NMR (90 MHz, $CDCl_3$): $\delta = 1.25$ (d, $J = 6.9$ Hz, 3H, 2-Me), 1.62 – 1.86 (m, 6H, 4-Me, 7-H) 3.20 – 3.75 (m, 1H, 2-H), 5.25 – 6.30 (m, 3H, 3-H, 5-H, 6-H).

***N*-Methyl-*N*-methoxy-(2*R*,3*E*,5*E*)-2,4-dimethyl-3,5-heptadienamide (17)**: *N*,*O*-dimethylhydroxylamine hydrochloride (835 mg, 8.56 mmol), *N*,*N*-diisopropylethylamine (1.49 mL, 8.56 mmol), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (1.37 g, 7.13 mmol), and solid 4-dimethylaminopyridine (3 mg) were added to a solution of crude **16** (1.10 g, ca. 7.13 mmol) in dichloromethane (100 mL) at 0 °C. After stirring for 2 h at 0 °C, water was added, and the temperature was gradually raised to room temperature. The organic phase was separated, and the aqueous phase was extracted with diethyl ether. The extracts were combined and washed with water, dilute HCl, saturated aqueous $NaHCO_3$, and brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel (10 g, hexane/ethyl acetate, 5:1) to give 541 mg (38%) of **17** as a colorless oil. $n_D^{24} = 1.4931$; $[\alpha]_D^{20} = -98.4$ ($c = 1.05$, $CHCl_3$); IR (film): $\tilde{\nu}_{max} = 1665$ (s, C=O), 965 cm^{-1} (s, olefinic C–H); ^1H NMR (90 MHz, $CDCl_3$): $\delta = 1.09$ (d, $J = 7$ Hz, 3H, 2-Me), 1.71 (d, $J = 1.1$ Hz, 3H, 7-Me), 1.78 (d, $J = 1.1$ Hz, 3H, 4-Me), 3.17 (s, 3H, NMe), 3.66 (s, 3H, OMe), 3.83 (dq, $J = 16$, 7 Hz, 1H, 2-H), 5.41 (d, $J = 9$ Hz, 1H, 3-H), 5.63 (dq, $J = 16$, 7 Hz, 1H, 6-H), 6.08 (d, $J = 16$ Hz, 1H, 5-H); elemental analysis (%): calcd for $C_{11}H_{19}O_2N$ (197.27): C 66.97, H 9.71, N 7.10; found: C 66.58, H 9.98, N 6.82; HR-MS: calcd for $C_{11}H_{19}O_2N$ 197.1416; found 197.1409.

***tert*-Butyl (*R*)-4-hydroxy-3-methylbutanoate (19)**: Borane – dimethyl sulfide complex (2.00 M in THF, 13.3 mL, 26.6 mmol) was added to a stirred solution of **18** (5.00 g, 26.6 mmol) in THF (100 mL) at $-20\,^{\circ}C$ under argon. The mixture was then warmed to room temperature and stirred for 24 h. After the reaction mixture was cooled to 0 °C, water and potassium carbonate (8.0 g) were added to the mixture, the organic phase was separated, and the aqueous phase was extracted with diethyl ether. The combined organic phases were washed with water and brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by distillation to give 4.32 g (93%) of **19** as a colorless oil. B.p. 92 – 93 °C (5 Torr); $n_D^{26} = 1.4280$; $[\alpha]_D^{28} = +4.70$ ($c = 1.05$, $CHCl_3$); IR (film): $\tilde{\nu}_{max} = 3430$ (s, O–H), 1725 (s, C=O), 1155 cm^{-1} (s, C–O); ^1H NMR (90 MHz, $CDCl_3$): $\delta = 0.96$ (d, $J = 6.8$ Hz, 3H, 3-Me), 1.45 (s, 9H, CO_2*t*Bu), 1.64 (br, 1H, OH), 1.72 – 2.42 (m, 3H, 2-H, 3-H), 3.40 – 3.63 (m, 2H, 4-H); elemental analysis (%): calcd for $C_9H_{18}O_3$ (174.24): C 62.04, H 10.41; found: C 61.65, H 10.24.

***tert*-Butyl (*R*)-(4-toluenesulfonyloxy)-3-methylbutanoate (20)**: TsCl (4.47 g, 23.4 mmol) was added to an ice-cooled stirred solution of **19** (3.14 g, 18.0 mmol) in dry pyridine (60 mL), and stirring was continued for 20 h at 0 °C. Water and diethyl ether were added to the mixture, the organic phase was separated, and the aqueous phase was extracted with diethyl ether. The extracts were combined and washed with water, saturated aqueous $CuSO_4$, water, saturated aqueous $NaHCO_3$, and brine, dried over $MgSO_4$, and concentrated under reduced pressure to give 6.62 g (quant) of **20** as a colorless oil. This was used for the next step without further purification. IR (film): $\tilde{\nu}_{max} = 1730$ (s, C=O), 1600 (m, aromatic), 1360 (s, SO_2), 1180 cm^{-1} (s, SO_2); ^1H NMR (90 MHz, $CDCl_3$): $\delta = 0.96$ (d, $J = 6.5$ Hz 3H, 3-Me), 1.42 (s, 9H, *t*Bu), 1.98 – 2.10 (m, 3H, 2-H, 3-H), 2.46 (s, 3H, aromatic Me), 3.90 (d, $J = 5.5$ Hz, 2H, 4-H), 7.34 (br. d, $J = 8.4$ Hz, 2H, aromatic *m*-H), 7.79 (br. d, $J = 8.4$ Hz, 2H, aromatic *o*-H).

***tert*-Butyl (*S*)-3,5-dimethylhexanoate (21)**: A solution of crude **20** (6.62 g, ca. 20.2 mmol) in THF (120 mL) was added to a stirred solution of isopropylmagnesium chloride (2.00 M in THF, 45.0 mL, 90.1 mmol) at $-78\,^{\circ}C$ under argon. A solution of dilithium tetrachlorocuprate (0.50 M in THF, 15.0 mL, 7.5 mmol) was added to this mixture at $-78\,^{\circ}C$ under argon. The mixture was then gradually warmed to 0 °C and stirred for 14 h. Saturated aqueous ammonium chloride solution was added to the mixture, and the temperature was raised to room temperature. The mixture was stirred for several minutes and filtered through Celite. The organic phase was separated, and the aqueous phase was extracted with diethyl ether.

The extracts were combined and washed with water and brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by distillation to give 1.86 g (52% based on **19**) of **21** as a colorless oil. B.p. 118–120 °C (55 Torr); $n_D^{25} = 1.4186$; $[\alpha]_D^{28} = -3.59$ ($c = 0.86$, $CHCl_3$); IR (film): $\tilde{\nu}_{max} = 1725$ (s, C=O), 1150 cm^{-1} (s, C–O); ^1H NMR (90 MHz, $CDCl_3$): $\delta = 0.86$ (d, $J = 6.3$ Hz, 3H, 3-Me), 0.88 (d, $J = 6.3$ Hz, 3H, 6-H), 0.89 (d, $J = 6.3$ Hz, 3H, 5-Me), 0.96–1.35 (m, 2H, 4-H), 1.43 (s, 9H, CO_2tBu), 1.51–2.27 (m, 4H, 2-H, 3-H, 5-H); elemental analysis (%): calcd for $C_{12}H_{24}O_2$ (200.32): C 71.95, H 12.08; found: C 71.38, H 12.23.

(*S*)-3,5-Dimethyl-1-hexanol (22): A solution of **21** (1.86 g, 9.29 mmol) in diethyl ether (30 mL) was added dropwise to a stirred slurry of $LiAlH_4$ (706 mg, 18.6 mmol) in dry diethyl ether (50 mL) at 0 °C. The mixture was stirred at room temperature for 3 h. Excess $LiAlH_4$ was destroyed by careful addition of water (1 mL), 15% aqueous NaOH (1 mL), and water (3 mL). The mixture was diluted with diethyl ether, filtered through Celite, and the filtrate was concentrated under reduced pressure. The residue was purified by distillation to give 930 mg (77%) of **22** as a colorless oil. B.p. 98–100 °C (40 Torr); $n_D^{25} = 1.4265$; $[\alpha]_D^{24} = -8.67$ ($c = 0.55$, $CHCl_3$) [ref. [5]: $[\alpha]_D = -8.5$ ($c = 3.5$, $CHCl_3$)]; IR (film): $\tilde{\nu}_{max} = 3350$ (s, O–H), 1055 cm^{-1} (s, C–O); ^1H NMR (90 MHz, $CDCl_3$): $\delta = 0.85$ (d, $J = 6.4$ Hz, 3H, 3-Me), 0.87 (d, $J = 6.4$ Hz, 6H, 5-Me, 6-H), 0.96–1.86 (m, 6H, 2-H, 3-H, 4-H, 5-H), 3.54–3.82 (m, 3H, 1-H, OH).

(*S*)-3,5-Dimethylhexyl bromide (23): TsCl (3.19 g, 16.8 mmol) was added to an ice-cooled stirred solution of **22** (1.68 g, 12.9 mmol) in dry pyridine (40 mL), and the stirring was continued for 20 h at 0 °C. Water and diethyl ether were added to the mixture, the organic phase was separated, and the aqueous phase was extracted with diethyl ether. The extracts were combined and washed with water, saturated aqueous $CuSO_4$, water, saturated aqueous $NaHCO_3$, and brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was diluted with acetone (80 mL). Lithium bromide (1.68 g, 19.4 mmol) was added to the solution, and the mixture was heated under reflux for 2 h with stirring. Water and diethyl ether were added to the mixture, the organic phase was separated, and the aqueous phase was extracted with diethyl ether. The combined organic phases were washed with water and brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by distillation to give 1.75 g (70%) of **23** as a colorless oil. B.p. 96–98 °C (68 Torr); $n_D^{24} = 1.4426$; $[\alpha]_D^{24} = +2.40$ ($c = 0.93$, $CHCl_3$); IR (film): $\tilde{\nu}_{max} = 2975$ (s, C–H), 2930 (s, C–H), 2880 (s, C–H), 1465 (s, C–H), 1385 (s, C–H), 1365 (m, C–H), 1250 cm^{-1} (m, C–H); ^1H NMR (90 MHz, $CDCl_3$): $\delta = 0.63–1.02$ (m, 9H, 3-Me, 5-Me, 6-H), 1.03–2.02 (m, 6H, 2-H, 3-H, 4-H, 5-H), 3.46 (br.t, $J = 7.2$ Hz, 2H, 1-H); HR-MS: calcd for $C_8H_{17}Br$ 192.0514; found 192.0530. Due to the high volatility of **23**, no correct combustion analysis data could be obtained.

(2*E*,4*E*,6*R*,10*S*)-4,6,10,12-Tetramethyl-2,4-tridecadien-7-one (1): (*S*)-3,5-dimethylhexylmagnesium bromide was prepared from **23** (1.11 g, 5.73 mmol) and magnesium (167 mg, 6.87 mmol) in dry THF (10 mL) under argon. This reagent was added dropwise to a solution of **17** (113 mg, 0.57 mmol) in dry THF (10 mL) at −20 °C under argon. After stirring for 2 h at room temperature, dilute HCl was added to the mixture, the organic phase was separated, and the aqueous phase was extracted with diethyl ether. The combined organic phases were washed with water, saturated aqueous $NaHCO_3$, and brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel (10 g, hexane/ethyl acetate, 150:1) to give 128 mg (89%) of **1** as a colorless oil. $n_D^{23} = 1.4749$ [ref. [3]: $n_D^{22} = 1.4766$]; $[\alpha]_D^{21} = -284$ ($c = 0.87$, $CDCl_3$) [ref. [3]: $[\alpha]_D^{22} = -316$ ($c = 0.47$, $CDCl_3$)]; CD ($c = 0.000320$, *n*-hexane): $\Delta\varepsilon$ (λ) = −13.7 (296), +15.2 (239 nm); IR (film): $\tilde{\nu}_{max} = 1710$ (s, C=O), 1635 (w, C=C), 960 cm^{-1} (s, olefinic C–H); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.79$ (d, $J = 6.4$ Hz, 3H, 10-Me), 0.81 (d, $J = 6.5$ Hz, 3H, 13-Me), 0.84 (d, $J = 6.6$ Hz, 3H, 12-Me), 0.91–1.69 (m, 6H, 9-H, 10-H, 11-H, 12-H), 1.13 (d, $J = 6.8$ Hz, 3H, 6-Me), 1.76 (dd, $J = 6.6$, 1.3 Hz, 3H, 1-H), 1.81 (d, $J = 1.1$ Hz, 3H, 4-Me), 2.39 (t, $J = 7.5$ Hz, 2H, 8-H), 3.49 (dq, $J = 9.9$, 6.8 Hz, 1H, 6-H), 5.19 (d, $J = 9.8$ Hz, 1H, 5-H), 5.65 (dq, $J = 15.5$, 6.6 Hz, 1H, 2-H), 6.06 (dd, $J = 15.5$, 1.0 Hz, 1H, 3-H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 12.9$, 16.5, 18.2, 19.4, 22.2, 23.3, 25.1, 29.9, 31.0, 38.4, 46.4, 46.5, 124.1, 128.6, 135.3, 135.5, 212.1. These spectral data were in good accord with those reported in refs. [3, 4]. Elemental analysis (%): calcd for $C_{17}H_{30}O$ (250.42): C 81.54, H 12.08; found: C 81.32, H 12.34.

(3*S*,8*E*,9*R*,10*E*)-3,7,9-Trimethyl-8,10-dodecadien-6-one (2): This compound was prepared under the same conditions as described for the preparation of **1** by employing (*S*)-3-methylpentyl bromide (**24**)[20] (594 mg, 3.60 mmol), magnesium (105 mg, 4.32 mmol), and the amide **17** (71 mg, 0.36 mmol) to give 72 mg (90%) of **2** as a colorless oil. $n_D^{24} = 1.4740$ [ref. [8]: $n_D^{22} = 1.4796$]; $[\alpha]_D^{26} = -266$ ($c = 0.85$, $CDCl_3$) [ref. [8]: $[\alpha]_D^{22} = -336$ ($c = 0.55$, $CDCl_3$)]; CD ($c = 0.000441$, *n*-hexane): $\Delta\varepsilon$ (λ) = −11.7 (296), +13.1 (239 nm); IR (film): $\tilde{\nu}_{max} = 1715$ (s, C=O), 1620 (w, C=C), 970 cm^{-1} (s, olefinic C–H); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.81$ (d, $J = 6.3$ Hz, 3H, 10-Me), 0.85 (t, $J = 7.2$ Hz, 3H, 12-Me), 1.11 (d, $J = 6.8$ Hz, 3H, 6-Me), 1.20–1.63 (m, 5H, 9-H, 10-H, 11-H), 1.76 (dd, $J = 6.5$, 1.3 Hz, 3H, 1-H), 1.80 (d, $J = 1.2$ Hz, 3H, 4-Me), 2.36–2.41 (m, 2H, 8-H), 3.48 (dq, $J = 9.8$, 6.8 Hz, 1H, 6-H), 5.17 (d, $J = 9.8$ Hz, 1H, 5-H), 5.66 (dq, $J = 15.5$, 6.6 Hz, 1H, 2-H), 6.05 (dd, $J = 15.5$, 1.5 Hz, 1H, 3-H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 11.3$, 12.9, 16.5, 18.2, 18.8, 29.2, 30.3, 34.0, 38.5, 46.3, 124.1, 128.6, 135.3, 135.5, 212.1. These spectral data were in good accord with those reported in refs. [8, 9]. Elemental analysis (%): calcd for $C_{15}H_{26}O$ (222.37): C 81.02, H 11.79; found: C 81.05, H 11.59.

(2*E*,5*R*,6*E*,8*E*)-5,7-Dimethyl-2,6,8-decatrien-4-one (3): This compound was prepared under the same conditions as described for the preparation of **1** by employing (*E*)-1-propenyl bromide (850 mg, 7.03 mmol), magnesium (208 mg, 8.56 mmol), and the amide **17** (150 mg, 0.76 mmol) to give 108 mg (80%) of **3** as a colorless oil. $n_D^{22} = 1.5072$ [ref. [12]: $n_D^{27} = 1.5068$]; $[\alpha]_D^{22} = -426$ ($c = 1.18$, *n*-pentane) [ref. [12] $[\alpha]_D^{26} = -466$ ($c = 1.16$, *n*-pentane)]; CD ($c = 0.000494$, *n*-hexane): $\Delta\varepsilon$ (λ) = −4.70 (343), +3.20 (259), −6.39 (235), +0.105 (219), −0.281 (212 nm); IR (film): $\tilde{\nu}_{max} = 1695$ (s, C=O), 1670 (s, C=C), 1630 (s, C=C), 965 cm^{-1} (s, olefinic C–H); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.15$ (d, $J = 6.8$ Hz, 3H, 5-Me), 1.76 (dd, $J = 1.3$, 6.6 Hz, 3H, 10-H), 1.80 (d, $J = 1.1$ Hz, 3H, 7-Me), 1.85 (dd, $J = 1.6$, 6.9 Hz, 3H, 1-H), 3.60 (dq, $J = 9.7$, 6.8 Hz, 1H, 5-H), 5.23 (d, $J = 9.7$ Hz, 1H, 6-H), 5.66 (dq, $J = 15.5$, 6.6 Hz, 1H, 9-H), 6.06 (dq, $J = 15.5$, .3 Hz, 1H, 8-H), 6.15 (dq, $J = 15.4$, 1.6 Hz, 1H, 3-H), 6.88 (dq, $J = 15.4$, 6.9 Hz, 1H, 2-H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 12.8$, 16.6, 18.19, 18.22, 44.6, 124.0, 128.5, 129.7, 135.4, 135.5, 142.5, 200.3. These spectral data were in good accord with those reported in ref. [12]. Elemental analysis (%): calcd for $C_{12}H_{18}O$ (178.27): C 80.85, H 10.18; found: C 80.74, H 10.40.

(3*R*,4*E*,6*E*)-3,5-Dimethyl-4,6-octadien-2-one (4): This compound was prepared under the same conditions as described for the preparation of **1** by employing the amide **17** (113 mg, 0.57 mmol) and methyllithium (1.02 M in diethyl ether, 2.00 mL, 1.95 mmol) to give 66 mg (67%) of **4** as a colorless oil. $n_D^{24} = 1.4807$; $[\alpha]_D^{25} = -373$ ($c = 0.77$, $CHCl_3$); IR (film): $\tilde{\nu}_{max} = 1720$ (s, C=O), 1625 (w, C=C), 970 cm^{-1} (s, olefinic C–H); ^1H NMR (300 MHz, C_6D_6): $\delta = 1.08$ (d, $J = 6.8$ Hz, 3H, 3-Me), 1.60 (d, $J = 1.2$ Hz, 3H, 5-Me), 1.62 (dd, $J = 7.5$, 1.4 Hz, 3H, 8-Me), 1.73 (s, 3H, 1-H), 3.15 (dq, $J = 10.5$, 6.8 Hz, 1H, 3-H), 5.29 (d, $J = 9.8$ Hz, 1H, 4-H), 5.49 (dq, $J = 15.5$, 6.6 Hz, 1H, 7-H), 5.98 (dd, $J = 15.5$, 1.1 Hz, 1H, 6-H); ^{13}C NMR (75 MHz, C_6D_6): $\delta = 13.5$, 17.2, 18.9, 28.2, 47.8, 124.4, 129.9, 136.4, 136.7, 207.6; HR-MS: calcd for $C_{10}H_{16}O$ 152.1202; found 152.1200. Due to the high volatility of **4**, no correct combustion analysis data could be obtained.

(2*E*,4*E*,6*R*)-4,6-Dimethyl-2,4-pentadecadien-7-one (5): This compound was prepared under the same conditions as described for the preparation of **1** by employing octyl bromide **25** (603 mg, 3.12 mmol), magnesium (86 mg, 3.54 mmol), and the amide **17** (41 mg, 0.21 mmol) to give 42 mg (81%) of **5** as a colorless oil. $n_D^{25} = 1.4689$; $[\alpha]_D^{27} = -173$ ($c = 0.94$, $CHCl_3$); IR (film): $\tilde{\nu}_{max} = 1715$ (s, C=O), 1620 (w, C=C), 965 cm^{-1} (s, olefinic C–H); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.80$ (t, $J = 6.3$ Hz, 3H, 15-H), 1.06 (d, $J = 6.6$ Hz, 3H, 6-Me), 1.15–1.32 (m, 12H, 9, 10, 11, 12, 13, 14-H), 1.69 (dd, $J = 6.6$, 1.3 Hz, 3H, 1-H), 1.74 (d, $J = 1.3$ Hz, 3H, 4-Me), 2.29–2.49 (m, 2H, 8-H), 3.46 (dq, $J = 9.9$, 6.8 Hz, 1H, 6-H), 5.19 (d, $J = 9.8$ Hz, 1H, 5-H), 5.65 (dq, $J = 15.5$, 6.6 Hz, 1H, 2-H), 6.06 (dd, $J = 15.5$, 1.0 Hz, 1H, 3-H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 12.8$, 14.0, 16.4, 18.1, 22.6, 23.7, 29.07, 29.15, 29.3, 31.8, 40.7, 46.3, 124.0, 128.6, 135.3, 135.4, 211.7; elemental analysis (%): calcd for $C_{17}H_{30}O$ (250.42): C 81.54, H 12.08; found: C 81.34, H 12.01.

Methyl (*R*)-3-benzyloxy-2-methylpropanoate (26): Triflic acid (0.20 mL, 2.26 mmol) was added to a stirred solution of (*R*)-**9** (10.0 g, 84.6 mmol) and benzyl trichloroacetimidate[21] (32.0 g, 127 mmol) in dichloromethane (100 mL). The solution was stirred at room temperature for 15 h. The reaction was quenched with saturated aqueous $NaHCO_3$. The organic phase was separated, and the aqueous phase was extracted several times with dichloromethane. The extracts and the organic layer were combined and washed with water, saturated aqueous $NaHCO_3$, and brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel (400 g, hexane/ethyl acetate, 100:1) to give 15.0 g (85%) of **26** as a colorless oil. A sample was further purified by distillation. B.p. 102–105 °C (2 Torr); $n_D^{23} = 1.4921$; $[\alpha]_D^{23} = -11.5$ ($c = 5.15$, $CHCl_3$) [ref. [21] $[\alpha]_D^{20} = -11.6$ ($c = 1.0$, $CHCl_3$)]; IR (film): $\tilde{\nu}_{max} = 1745$ (s, C=O), 1605 (w, aromatic), 1590 (w, aromatic), 1500 (m, aromatic), 1100 cm^{-1} (s, C–O); ^1H NMR (90 MHz, $CDCl_3$): $\delta = 1.18$ (d, $J = 7.1$ Hz, 3H, 2-Me), 2.78 (sextet, $J = 7.1$ Hz, 1H, 2-H), 3.63 (dd, $J = 6.9$, 15.5 Hz, 1H, 3-H_a), 3.69 (s, 3H, CO_2Me), 3.79 (dd, $J = 6.9$, 15.5 Hz, 1H, 3-H_b), 4.52 (s, 2H, benzylic CH_2), 7.32 (br. s, 5H, aromatic).

(*R*)-3-Benzyloxy-2-methylpropanal (27): A solution of diisobutylaluminum hydride (0.95 M in hexane, 95.0 mL, 90.3 mmol) was added to a stirred solution of **26** (17.4 g, 83.5 mmol) in dry dichloromethane (180 mL) at −78 °C under argon. After stirring for 20 min at −78 °C, saturated aqueous Rochelle's salt solution was added, and the temperature was gradually raised to room temperature. Water and diethyl ether were added to the mixture, the organic phase was separated, and the aqueous phase was extracted with diethyl ether. The combined organic phases were washed with water and brine, dried over $MgSO_4$, and concentrated under reduced pressure to give 15.7 g (quant) of **27** as a colorless oil. This was used for the next step without further purification. IR (film): $\tilde{\nu}_{max} = 2740$ (m, CHO), 1725 (s, C=O), 1605 (w, aromatic), 1590 (w, aromatic), 1500 (m, aromatic), 1100 cm^{-1} (s, C–O); ^1H NMR (90 MHz, $CDCl_3$): $\delta = 1.14$ (d, $J = 7.2$ Hz, 3H, 2-Me), 2.45–2.90 (m, 1H, 2-H), 3.40–3.85 (m, 2H, 3-H), 4.52 (s, 2H, benzylic CH_2), 7.32 (br. s, 5H, aromatic), 9.72 (d, $J = 2.1$ Hz, 1H, CHO).

(2*R*,3*RS*)-1-Benzyloxy-2-methyl-4-hexyn-3-ol (28): *n*-Butyllithium (3.04 M in *n*-hexane, 41.2 mL, 125 mmol) was added to a stirred solution of propyne (6.5 g, 162 mmol) in dry THF (200 mL) at −78 °C under argon. After the mixture had been stirred for 1 h at 0 °C, HMPA (20 mL) was added at −40 °C under argon, and the mixture was stirred for 10 min. After crude **27** (15.7 g, ca. 88.1 mmol) in THF (50 mL) was added to this solution at −40 °C under argon, the temperature was gradually raised to room temperature, and the mixture was stirred for 14 h. Water was added to the mixture, the organic phase was separated, and the aqueous phase was extracted with diethyl ether. The combined organic phases were washed with water, saturated aqueous $NaHCO_3$, and brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel (250 g, hexane/ethyl acetate, 50:1) to give 9.9 g (54% based on **26**) of **28** as a colorless oil. An analytical sample was further purified by distillation. B.p. 120–130 °C (1 Torr); $n_D^{23} = 1.4482$; $[\alpha]_D^{24} = -33.5$ ($c = 1.37$, $CHCl_3$); IR (film): $\tilde{\nu}_{max} = 3450$ (s, O–H), 2250 (w, C≡C), 1605 (w, aromatic), 1590 (w, aromatic), 1500 (m, aromatic), 1100 cm^{-1} (s, C–O); ^1H NMR (90 MHz, $CDCl_3$): $\delta = 0.91$ (d, $J = 6.8$ Hz, 1.5H, 2-Me), 1.03 (d, $J = 7.0$ Hz, 1.5H, 2-Me), 1.84 (d, $J = 2.0$ Hz, 3H, 6-Me), 2.03 (m, 1H, 2-H), 3.00 (d, $J = 5.0$ Hz, 1H, OH), 3.38–3.82 (m, 2H, 6-H), 4.30–4.50 (m, 1H, 3-H), 4.53 (s, 2H, benzylic CH_2), 7.33 (br. s, 5H, aromatic); elemental analysis (%): calcd for $C_{14}H_{18}O_2$ (218.30): C 77.03, H 8.31; found: C 77.28, H 8.35.

(2*R*,3*RS*,4*E*)-1-Benzyloxy-2-methyl-4-hexen-3-ol (29): A solution of **28** (9.30 g, 42.6 mmol) in diethyl ether (100 mL) was added dropwise to a stirred slurry of $LiAlH_4$ (10.0 g, 263 mmol) in dry diethyl ether (500 mL) at 0 °C. The mixture was stirred at room temperature for 5 days. Excess $LiAlH_4$ was destroyed by careful addition of water (10 mL), aqueous sodium hydroxide solution (15%, 10 mL), and water (30 mL). The mixture was diluted with diethyl ether, filtered through Celite, and the filtrate was concentrated under reduced pressure. The residue was purified by chromatography on silica gel (100 g, hexane/ethyl acetate, 50:1) to give 5.02 g (53%) of **29** as a colorless oil. An analytical sample was further purified by distillation. B.p. 130–136 °C (3 Torr); $n_D^{25} = 1.4581$; $[\alpha]_D^{27} = -15.9$ ($c = 1.11$, $CHCl_3$); IR (film): $\tilde{\nu}_{max} = 3450$ (s, O–H), 1670 (w, C=C), 1590 (w, aromatic), 1500 (m, aromatic), 1100 cm^{-1} (s, C–O); ^1H NMR (90 MHz, $CDCl_3$): $\delta = 0.85$ (d, $J = 7.0$ Hz, 1.5H, 2-Me), 0.90 (d, $J = 7.2$ Hz, 1.5H, 2-Me), 1.40 (d, $J = 4.9$ Hz, 3H, 1-H), 1.80–2.20 (m, 1H, 5-H), 2.75 (d, $J = 5.6$ Hz, 0.5H, OH), 3.20 (d, $J = 3.4$ Hz, 0.5H, OH), 3.85–4.25 (m, 1H, 4-H), 4.45 (s, 2H, benzylic CH_2), 5.30–5.80 (m, 2H, 2-, 3-H), 7.30 (br. s, 5H, aromatic); elemental analysis (%): calcd for $C_{14}H_{20}O_2$ (220.31): C 76.33, H 9.15; found: C 76.27, H 9.26.

(2*E*,4*RS*,5*R*)-6-Benzyloxy-4-*tert*-butyldimethylsilyloxy-5-methyl-2-hexene (30): Imidazole (3.88 g, 57.0 mmol) and TBSCl (4.47 g, 29.7 mmol) were added to a solution of **29** (4.70 g, 21.3 mmol) in dry DMF (50 mL), and the mixture was stirred for 15 h at room temperature. Water was added, the organic phase was separated, and the aqueous phase was extracted with diethyl ether. The combined organic phases were washed with water, saturated aqueous $NaHCO_3$, and brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel (100 g, hexane) to give 7.52 g (quant) of **30** as a colorless oil. $n_D^{24} = 1.4791$; $[\alpha]_D^{26} = +0.43$ ($c = 1.08$, $CHCl_3$); IR (film): $\tilde{\nu}_{max} = 1670$ (w, C=C), 1500 (m, aromatic), 1255 (s, Si–Me), 1100 cm^{-1} (s, C–O); ^1H NMR (90 MHz, $CDCl_3$): $\delta = 0.01$, 0.02 (each s, 6H, $SiMe_2$), 0.86 (s, 9H, *t*Bu), 0.90 (d, $J = 6.8$ Hz, 3H, 5-Me), 1.66 (d, $J = 4.8$ Hz, 3H, 1-H), 1.82 (m, 1H, 5-H), 3.15–3.55 (m, 2H, 6-H), 3.95–4.20 (m, 1H, 4-H), 4.48 (s, 2H, benzylic CH_2), 5.20–5.66 (m, 2H, 2-, 3-H), 7.32 (br. s, 5H, aromatic); elemental analysis (%): calcd for $C_{20}H_{34}O_2Si$ (334.57): C 71.80, H 10.24; found: C 71.80, H 10.43.

(2*R*,3*RS*,4*E*)-3-*tert*-Butyldimethylsilyloxy-2-methyl-4-hexen-1-ol (31): A solution of **30** (4.68 g, 14.0 mmol) in dry THF (50 mL) was added dropwise to a blue solution of sodium (3.50 g, 152 mmol) in ammonia (400 mL) with stirring at −78 °C under nitrogen. After stirring for 20 min at −78 °C, ammonium chloride (5.0 g) was added, and the temperature was raised to room temperature. Water was added, the organic phase was separated, and the aqueous phase was extracted with diethyl ether. The combined organic phases were washed with water, saturated aqueous $NaHCO_3$, and brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel (60 g, hexane/ethyl

acetate, 120:1) to give 2.84 g (83%) of **31** as a colorless oil. An analytical sample was further purified by distillation. B.p. 90–95 °C (5 Torr); $n_D^{25} = 1.4472$; $[\alpha]_D^{27} = -12.5$ ($c = 1.15$, $CHCl_3$); IR (film): $\tilde{\nu}_{max} =$ 3450 (s, O–H), 1670 (w, C=C), 1255 (s, Si–Me), 1100 cm^{-1} (s, C–O); ^1H NMR (90 MHz, $CDCl_3$): $\delta = 0.02$, 0.03 (each s, total 6H, $SiMe_2$), 0.75, 0.85 (each d, $J = 7.0$ Hz, total 3H, 2-Me), 0.90 (s, 9H, *t*Bu), 1.71 (d, $J =$ 5.3 Hz, 3H, 6-H), 1.90 (m, 1H, 2-H), 3.20 (d, $J = 4.9$ Hz, 1H, OH), 3.40–4.20 (m, 3H, 1, 3-H), 5.30–5.90 (m, 2H, 4, 5-H); elemental analysis (%): calcd for $C_{13}H_{28}O_2Si$ (244.45): C 63.88, H 11.55; found: C 63.63, H 11.51.

(2*S*,3*RS*,4*E*)-3-*tert*-Butyldimethylsilyloxy-2-methyl-4-hexenal (32): A solution of dimethyl sulfoxide (0.52 mL, 7.33 mmol) in dry dichloromethane (5 mL) was added to a solution of oxalyl chloride (0.32 mL, 3.67 mmol) in dry dichloromethane (5 mL) at −60 °C. After the mixture had been stirred for 10 min at this temperature, a solution of **31** (720 mg, 2.95 mmol) in dry dichloromethane (5 mL) was added at −60 °C. Stirring was continued for 30 min at this temperature, and triethylamine (2.10 mL, 15.1 mmol) was added to the mixture, which was subsequently warmed to 0 °C. The mixture was then poured into water and extracted several times with dichloromethane. The extracts were combined and washed with water, saturated aqueous $NaHCO_3$, and brine, dried over $MgSO_4$, and concentrated under reduced pressure to give 672 mg (94%) of **32** as a colorless oil. This was used for the next step without further purification. IR (film): $\tilde{\nu}_{max} = 2720$ (m, CHO), 1730 (s, C=O), 1670 (m, C=C), 1630 (s, C=C), 1250 cm^{-1} (s, Si–Me); ^1H NMR (90 MHz, $CDCl_3$): $\delta = 0.02$, 0.03 (each s, 6H, $SiMe_2$), 0.89 (s, 9H, *t*Bu), 1.04 (d, $J = 6.8$ Hz, 3H, 2-Me), 1.88 (dd, $J = 1.8$, 6.5 Hz, 3H, 6-H), 3.00 (sextet, $J = 6.8$ Hz, 1H, 2-H), 3.56 (dd, $J = 6.2$, 9.8 Hz, 0.5H, 3-H), 3.80 (dd, $J = 6.8$, 9.8 Hz, 0.5H, 3-H), 6.21 (dq, $J = 15.7$, 1.8 Hz, 1H, 4-H), 6.88 (dq, $J = 15.7$, 6.5 Hz, 1H, 5-H), 9.85 (br. s, 1H, CHO).

(2*E*,4*EZ*,6*R*,7*RS*,8*E*)-7-*tert*-Butyldimethylsilyloxy-6-methyl-2,4,8-decatriene (33): A solution of *n*-butyllithium (1.66 M in *n*-hexane, 2.10 mL, 3.49 mmol) was added to a solution of (*E*)-2-butenyldiphenylphosphane oxide[22] (1.05 g, 4.10 mmol) in dry THF (30 mL) and HMPA (1.23 mL, 7.07 mmol) at −78 °C under argon. After the mixture had been stirred for 10 min at this temperature, a solution of crude **32** (672 mg, ca. 2.77 mmol) in dry THF (5 mL) was added at −78 °C under argon. The resulting solution was stirred at −78 °C for 10 min, at 0 °C for 30 min, and finally at room temperature for 2 h, and then poured into ice-cooled dilute HCl. The organic phase was separated, and the aqueous phase was extracted several times with diethyl ether. The extracts and the organic phase were combined and washed with water, saturated aqueous $NaHCO_3$, and brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel (6.0 g, hexane) to give 258 mg (31% based on **31**) of **33** as a colorless oil. The *E*/*Z* ratio of **33** (ca. 1:1) was determined by ^1H NMR analysis. $n_D^{25} = 1.4688$; $[\alpha]_D^{23} =$ −12.4 ($c = 1.06$, $CHCl_3$); IR (film): $\tilde{\nu}_{max} = 1670$ (w, C=C), 1255 cm^{-1} (s, Si–Me); ^1H NMR (90 MHz, $CDCl_3$): $\delta = 0.02$, 0.03 (each s, 6H, $SiMe_2$), 0.85 (s, 9H, *t*Bu), 0.93, 0.95 (d, $J = 7.1$ Hz, 3H, 6-Me), 1.65 (d, $J = 5.1$ Hz, 3H, 10-H), 1.73 (d, $J = 6.5$ Hz, 3H, 1-H), 2.05–2.20 (m, 1H, 6-H), 3.85 (br. t, $J = 5.6$ Hz, 1H, 7-H), 5.00–6.50 (m, 6H, 2-, 3-, 4-, 5-, 8-, 9-H); elemental analysis (%): calcd for $C_{17}H_{32}OSi$ (280.53): C 72.79, H 11.50; found: C 73.22, H 11.59.

(2*E*,4*RS*,5*R*,6*EZ*,8*E*)-5-Methyl-2,6,8-decatrien-4-ol (34): A solution of tetrabutylammonium fluoride (1.0 M in THF, 2.5 mL, 2.5 mmol) was added to a solution of **33** (320 mg, 1.14 mmol) in THF (10 mL). The mixture was stirred for 12 h at room temperature, then poured into water and extracted several times with diethyl ether. The extracts and the organic layer were combined and washed with water, saturated aqueous $NaHCO_3$, and brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel (4.0 g, hexane/ethyl acetate, 150:1) to give 190 mg (quant) of **34** as a colorless oil. $n_D^{24} = 1.4989$; $[\alpha]_D^{23} =$ −18.1 ($c = 1.00$, $CHCl_3$); IR (film): $\tilde{\nu}_{max} = 3400$ (s, O–H), 1670 (w, C=C), 990 (s), 970 cm^{-1} (s); ^1H NMR (90 MHz, $CDCl_3$): $\delta = 0.97$, 1.01 (d, $J =$ 7.0 Hz, 3H, 5-Me), 1.24 (br. s, 1H, OH), 1.60–1.85 (m, 6H, 1, 10-H), 2.00–2.90 (m, 1H, 5-H), 3.60–4.05 (m, 1H, 4-H), 5.00–6.50 (m, 6H, 2-, 3-, 6-, 7-, 8-, 9-H); HR-MS: calcd for $C_{11}H_{18}O$ 166.1358; found 166.1363.

(2*E*,5*R*,6*EZ*,8*E*)-5-Methyl-2,6,8-decatrien-4-one (6): A solution of dimethyl sulfoxide (0.068 mL, 0.96 mmol) in dry dichloromethane (2 mL) was added to a solution of oxalyl chloride (0.042 mL, 0.48 mmol) in dry dichloromethane (2 mL) at −60 °C under argon. After the mixture had been stirred for 10 min at this temperature, a solution of the trienol **34** (40 mg, 0.24 mmol) in dry dichloromethane (3 mL) was added at −60 °C. Stirring was continued for 30 min at this temperature, and triethylamine (0.17 mL, 1.12 mmol) was added to the mixture which was subsequently warmed to 0 °C. The mixture was then poured into water and extracted several times with dichloromethane. The extracts were combined and washed with saturated aqueous $NaHCO_3$ and brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel (1.0 g, hexane/ethyl acetate, 400:1) to give 19 mg (48%) of **6** as a yellow oil. $n_D^{25} = 1.5055$; $[\alpha]_D^{24} = -278$ ($c =$ 0.525, $CHCl_3$); IR (film): $\tilde{\nu}_{max} = 1695$ (s, C=O), 1675 (s, C=O), 1635 (s, C=C), 995 (s), 970 (s, olefinic C–H), 955 (m), 935 cm^{-1} (m); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.17$, 1.18 (each d, $J = 7.0$ Hz, 3H, 5-Me), 1.74, 1.81 (each d, $J = 7.0$ Hz, 3H, 10-H), 1.87 (dd, $J = 1.0$, 7.0 Hz, 3H, 1-H), 3.35 (quintet, $J = 7.0$ Hz, 0.5H, 5-H), 3.74 (dq, $J = 7.0$, 9.9 Hz, 0.5H, 5-H), 5.17 (t, $J = 9.9$ Hz, 0.5H, *cis*-6-H), 5.51 (dd, $J = 7.8$, 14.4 Hz, 0.5H, *trans*-6-H), 5.60–5.85 (m, 1H, 9-H), 5.95–6.14 (m, 1.5H, *trans*-7-H, 8-H), 6.20 (dq, $J = 15.6$, 1.9 Hz, 1H, 3-H), 6.30–6.42 (m, 0.5H, *cis*-7-H), 6.90 (ddd, $J = 1.9$, 7.0, 15.6 Hz, 1H, 2-H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 16.3$, 16.7, 18.1, 18.4, 44.1, 48.1, 126.2, 127.6, 129.2, 129.6, 129.8, 129.9, 130.4, 131.1, 131.8, 132.3, 142.8, 200.1, 200.2; HR-MS: calcd for $C_{11}H_{16}O$ 164.1201; found 164.1194.

Ethyl (2*E*,4*R*,5*RS*,6*E*)-5-*tert*-butyldimethylsilyloxy-2,4-dimethyl-2,6-octadienoate (35): The alcohol **31** (1.83 g, 7.49 mmol) was oxidized under Swern conditions [$(COCl)_2$ (0.85 mL, 9.74 mmol), DMSO (1.38 mL, 19.4 mmol), Et_3N (5.22 mL, 37.5 mmol)] to the corresponding crude aldehyde **32**. $Ph_3P{=}C(Me)CO_2Et$ (94%, 3.75 g, 9.73 mmol) was added to a stirred solution of crude **32** (1.62 g, ca. 6.68 mmol) in benzene (80 mL), and the mixture was heated under reflux with stirring for 30 h. A saturated aqueous ammonium chloride solution was added, the organic phase was separated, and the aqueous phase was extracted with diethyl ether. The combined organic phases were washed with water, saturated aqueous $NaHCO_3$, and brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel (30 g, hexane/ethyl acetate, 400:1) to give 790 mg (32% based on **31**) of **35** as a colorless oil. $n_D^{25} = 1.4572$; $[\alpha]_D^{25} = +3.18$ ($c = 1.08$, $CHCl_3$); IR (film): $\tilde{\nu}_{max} = 1715$ (s, C=O), 1650 (m, C=C), 1255 cm^{-1} (s, Si–Me); ^1H NMR (90 MHz, $CDCl_3$): $\delta = 0.02$, 0.03 (each s, 6H, $SiMe_2$), 0.87 (s, 9H, *t*Bu), 0.98 (d, $J = 6.8$ Hz, 3H, 4-Me), 1.28 (t, $J = 7.0$ Hz, 3H, $CO_2CH_2CH_3$), 1.66 (d, $J = 5.1$ Hz, 3H, 8-H), 1.82 (d, $J = 1.3$ Hz, 3H, 2-Me), 2.53 (m, 1H, 4-H), 3.80–4.00 (m, 1H, 5-H), 4.18 (q, $J = 7.0$ Hz, 2H, $CO_2CH_2CH_3$), 5.20–5.75 (m, 2H, 6, 7-H), 6.63 (dq, $J = 1.3$, 9.9 Hz, 1H, 3-H); elemental analysis (%): calcd for $C_{18}H_{34}O_3Si$ (326.55): C 66.21, H 10.49; found: C 66.42, H 10.39.

(2*E*,4*R*,5*RS*,6*E*)-5-*tert*-Butyldimethylsilyloxy-2,4-dimethyl-2,6-octadien-1-ol (36): A solution of diisobutylaluminum hydride (0.95 M in hexane, 5.6 mL, 5.3 mmol) was added to a stirred solution of **35** (790 mg, 2.42 mmol) in dry dichloromethane (20 mL) at −78 °C under argon. After stirring for 30 min at −78 °C, a saturated aqueous Rochelle's salt solution was added, and the temperature was gradually raised to room temperature. Water and diethyl ether were

added to the reaction mixture. The organic phase was separated, and the aqueous phase was extracted with diethyl ether. The combined organic phases were washed with water and brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel (20 g, hexane/ethyl acetate, 50:1) to give 673 mg (98%) of **36** as a colorless oil. $n_D^{25} = 1.4633$; $[\alpha]_D^{25} = -13.1$ ($c = 1.03$, $CHCl_3$); IR (film): $\tilde{\nu}_{max} = 3350$ (s, O–H), 1670 (w, C=C), 1255 cm^{-1} (s, Si–Me); ^1H NMR (90 MHz, $CDCl_3$): $\delta = 0.00$, 0.01 (each s, total 6H, $SiMe_2$), 0.89 (s, 9H, *t*Bu), 0.93 (d, $J = 7.0$ Hz, 3H, 4-Me), 1.28 (t, $J = 7.0$ Hz, 3H, CH_2CH_3), 1.66 (d, $J = 5.1$ Hz, 3H, 8-H), 1.20, 1.24 (each br. s, total 1H, OH), 1.64 (m, 6H, 2-Me, 8-H), 2.25 – 2.60 (m, 1H, 4-H), 3.74 – 4.05 (m, 3H, 1-, 5-H), 5.16 – 5.60 (m, 3H, 3-, 6-, 7-H); elemental analysis (%): calcd for $C_{16}H_{32}O_2Si$ (284.51): C 67.55, H 11.34; found: C 67.52, H 11.17.

(2*E*,4*R*,5*RS*,6*E*)-5-*tert*-Butyldimethylsilyloxy-2,4-dimethyl-2,6-octadienal (37): A solution of dimethyl sulfoxide (0.52 mL, 7.33 mmol) in dry dichloromethane (5 mL) was added to a solution of oxalyl chloride (0.32 mL, 3.67 mmol) in dry dichloromethane (5 mL) at $-60\,^\circ C$. After the mixture had been stirred for 10 min at this temperature, a solution of **36** (600 mg, 2.11 mmol) in dry dichloromethane (5 mL) was added at $-60\,^\circ C$. Stirring was continued for 30 min at this temperature, and triethylamine (1.70 mL, 12.2 mmol) was added to the mixture which was subsequently warmed to $0\,^\circ C$. The mixture was then poured into water and extracted several times with dichloromethane. The extracts were combined and washed with water, saturated aqueous $NaHCO_3$, and brine, dried over $MgSO_4$, and concentrated under reduced pressure to give 638 mg (quant) of **37** as a colorless oil. This was used for the next step without further purification. IR (film): $\tilde{\nu}_{max} = 2370$ (m, CHO), 1690 (s, C=O), 1645 (w, C=C), 1255 cm^{-1} (s, Si–Me); ^1H NMR (90 MHz, $CDCl_3$): $\delta =$ 0.00, 0.01 (each s, 6H, $SiMe_2$), 0.87, 0.88 (each s, 9H, *t*Bu), 1.04 (d, $J =$ 7.1 Hz, 3H, 4-Me), 1.66 (d, $J = 5.4$ Hz, 3H, 8-H), 1.94 (d, $J = 1.2$ Hz, 3H, 2-Me), 2.40 – 2.90 (m, 1H, 4-H), 3.98 (br. t, $J = 5.9$ Hz, 1H, 5-H), 5.15 – 5.80 (m, 2H, 6-, 7-H), 6.25 – 6.50 (m, 1H, 3-H), 9.39 (d, $J = 2.0$ Hz, 1H, CHO).

(3*E*,5*R*,6*RS*,7*E*)-6-*tert*-Butyldimethylsilyloxy-3,5-dimethyl-1,3,7-nonatriene (38): *n*-Butyllithium (1.55 M in *n*-hexane, 2.40 mL, 3.72 mmol) was added to a stirred suspension of methyltriphenylphosphonium bromide (98%, 1.75 g, 4.80 mmol) in dry THF (20 mL) at $-78\,^\circ C$ under argon. After the mixture had been stirred for 1 h at $0\,^\circ C$, a solution of crude **37** (638 mg, ca. 2.26 mmol) in dry THF (5 mL) was added, and the reaction mixture was stirred for 2 h at $-78\,^\circ C$ under argon. Water was added, and the reaction temperature was gradually raised to room temperature. The organic phase was separated, and the aqueous phase was extracted with diethyl ether. The combined organic phases were washed with water, saturated aqueous $NaHCO_3$, and brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel (10 g, hexane) to give 431 mg (73% based on **36**) of **38** as a colorless oil. $n_D^{25} = 1.4663$; $[\alpha]_D^{23} = -20.2$ ($c = 1.12$, $CHCl_3$); IR (film): $\tilde{\nu}_{max} = 1670$ (w, C=C), 1645 (w, C=C), 1610 (m, C=C), 1255 cm^{-1} (s, Si–Me); ^1H NMR (90 MHz, $CDCl_3$): $\delta = 0.00$, 0.01 (each s, 6H, $SiMe_2$), 0.87, 0.88 (each s, 9H, *t*Bu), 0.92, 0.95 (each d, $J = 6.8$ Hz, 3H, 5-Me), 1.66 (d, $J = 4.8$ Hz, 3H, 9-H), 1.73 (s, 3H, 3-Me), 2.55 (m, 1H, 5-H), 3.87 (br. t, $J = 6.5$ Hz, 1H, 6-H), 4.82 (d, $J = 13.3$ Hz, 2H, 1-H), 5.14 – 5.75 (m, 3H, 4-, 7-, 8-H), 6.37 (dq, $J = 3.5$, 13.3 Hz, 1H, 2-H); elemental analysis (%): calcd for $C_{17}H_{32}OSi$ (280.53): C 72.79, H 11.50; found: C 72.30, H 11.52.

(2*E*,4*RS*,5*R*,6*E*)-5,7-Dimethyl-2,6,8-nonatrien-4-ol (39): This compound was prepared under the same conditions as described for the preparation of **34** by employing **38** (331 mg, 1.18 mmol) and tetrabutylammonium fluoride (1.0 M in THF, 2.0 mL, 2.0 mmol) to give 205 mg (quant) of **39** as a colorless oil. $n_D^{24} = 1.4962$; $[\alpha]_D^{23} = -16.4$ ($c = 1.02$, $CHCl_3$); IR (film): $\tilde{\nu}_{max} = 3380$ (s, O–H), 1670 (w, C=C), 1640 (w, C=C), 1605 cm^{-1} (m, C=C); ^1H NMR (90 MHz, $CDCl_3$): $\delta = 0.94$, 1.00 (each d, $J = 6.8$ Hz, 3H, 5-Me), 1.24 (d, $J = 5.1$ Hz, 1H, OH), 1.68 (d, $J = 4.8$ Hz, 3H, 1-H), 1.77 (d, $J = 1.5$ Hz, 3H, 7-Me), 2.40 – 2.90 (m, 1H, 5-H), 3.70 – 4.05 (m, 1H, 4-H), 4.96 (d, $J = 10.9$ Hz, 2H, 9-H), 5.10 – 5.80 (m, 3H, 2-, 3-, 6-H), 6.37 (dq, $J = 2.0$, 10.9 Hz, 1H, 8-H); HR-MS: calcd for $C_{11}H_{18}O$ 166.1358; found 166.1358.

(2*E*,5*R*,6*E*)-5,7-Dimethyl-2,6,8-nonatrien-4-one (7): This compound was prepared under the same conditions as described for the preparation of **6** by employing oxalyl chloride (0.050 mL, 0.573 mmol), dimethyl sulfoxide (0.10 mL, 1.41 mmol), trienol **39** (50 mg, 0.30 mmol), and triethylamine (0.20 mL, 1.43 mmol) to give 27 mg (55%) of **7** as a yellow oil. $n_D^{25} = 1.5031$; $[\alpha]_D^{24} = -259$ ($c =$ 0.515, $CHCl_3$); IR (film): $\tilde{\nu}_{max} = 1695$ (s, C=O), 1670 (s, C=O), 1630 (s, C=C), 1605 (m, C=C), 995 (m), 970 (s), 935 (m), 900 (s), 875 cm^{-1} (m); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.18$ (d, $J = 6.8$ Hz, 3H, 5-Me), 1.82 (d, $J = 1.3$ Hz, 3H, 7-Me), 1.88 (dd, $J = 6.9$, 1.7 Hz, 3H, 1-H), 3.64 (dq, $J =$ 9.7, 6.8 Hz, 1H, 5-H), 5.01 (d, $J = 10.7$ Hz, 1H, 9-H_a), 5.16 (d, $J = 17.4$ Hz, 1H, 9-H_b), 5.40 (d, $J = 9.6$ Hz, 1H, 6-H), 6.16 (dq, $J = 15.5$, 1.7 Hz, 1H, 3-H), 6.36 (ddd, $J = 17.4$, 10.7, 1.0 Hz, 1H, 8-H), 6.90 (dq, $J = 15.5$, 6.9 Hz, 1H, 2-H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 12.1$, 16.6, 18.2, 29.7, 44.6, 112.3, 129.7, 131.4, 135.7, 140.9, 142.8, 200.1; HR-MS: calcd for $C_{11}H_{16}O$ 164.1201; found 164.1212.

(2*E*,4*R*)-5-*tert*-Butyldimethylsilyloxy-2,4-dimethyl-2-penten-1-ol (40): A solution of diisobutylaluminum hydride (0.95 M in *n*-hexane, 75.0 mL, 71.3 mmol) was added to a stirred solution of **12** (9.0 g, 31.4 mmol) in dry dichloromethane (200 mL) at $-78\,^\circ C$ under argon. After stirring for 30 min at $-78\,^\circ C$, a saturated aqueous Rochelle's salt solution was added, and the temperature was gradually raised to room temperature. Water and diethyl ether were added to the reaction mixture. The organic solution was separated, and the aqueous phase was extracted with diethyl ether. The combined organic phases were washed with water and brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel (150 g, hexane/ethyl acetate, 50:1) to give 7.28 g (95%) of **40** as a colorless oil. $n_D^{24} =$ 1.4519; $[\alpha]_D^{24} = -17.6$ ($c = 1.09$, $CHCl_3$) [ref. [16]: $[\alpha]_D^{20} = -11.1$ ($c =$ 1.61, $CHCl_3$)]; IR (film): $\tilde{\nu}_{max} = 3350$ (s, O–H), 1260 cm^{-1} (s, Si–Me); ^1H NMR (90 MHz, $CDCl_3$): $\delta = 0.03$ (s, 6H, $SiMe_2$), 0.90 (s, 9H, *t*Bu), 0.95 (d, $J = 6.8$ Hz, 3H, 4-Me), 1.50 (br. s, 1H, OH), 1.69 (d, $J = 1.8$ Hz, 3H, 2-Me), 2.30 – 2.80 (m, 1H, 4-H), 3.37 (dd, $J = 6.8$, 12 Hz, 1H, 5-H_a), 3.46 (dd, $J = 6.8$, 12 Hz, 1H, 5-H_b), 4.00 (s, 2H, 1-H), 5.19 (dq, $J = 9.7$, 1.8 Hz, 1H, 3-H).

(2*E*,4*R*)-5-*tert*-Butyldimethylsilyloxy-2,4-dimethyl-2-pentenal (41): A solution of dimethyl sulfoxide (2.27 mL, 32.0 mmol) in dry dichloromethane (15 mL) was added to a solution of oxalyl chloride (1.39 mL, 15.9 mmol) in dry dichloromethane (15 mL) at $-60\,^\circ C$. After the mixture had been stirred for 10 min at this temperature, a solution of **40** (2.79 g, 11.4 mmol) in dry dichloromethane (30 mL) was added at $-60\,^\circ C$. Stirring was continued for 30 min at this temperature, and triethylamine (7.94 mL, 57.0 mmol) was added to the mixture, which was subsequently warmed to $0\,^\circ C$. The mixture was then poured into water and extracted several times with dichloromethane. The extracts were combined and washed with water, saturated aqueous $NaHCO_3$, and brine, dried over $MgSO_4$, and concentrated under reduced pressure to give 2.86 g (quant) of **41** as a colorless oil. This was used for the next step without further purification. IR (film): $\tilde{\nu}_{max} = 2720$ (m, CHO), 1690 (s, C=O), 1645 (m, C=C), 1260 cm^{-1} (s, Si–Me); ^1H NMR (90 MHz, $CDCl_3$): $\delta = 0.03$ (s, 6H, $SiMe_2$), 0.88 (s, 9H, *t*Bu), 1.07 (d, $J = 6.7$ Hz, 3H, 4-Me), 1.78 (d, $J =$ 1.1 Hz, 3H, 2-Me), 2.70 – 3.05 (m, 1H, 4-H), 3.56 (d, $J = 6.8$ Hz, 2H, 5-H), 6.31 (dq, $J = 9.7$, 1.1 Hz, 1H, 3-H), 9.40 (s, 1H, CHO).

(2*R*,3*E*)-1-*tert*-Butyldimethylsilyloxy-2,4-dimethyl-3,5-hexadiene (42): *n*-Butyllithium (1.57 M in *n*-hexane, 9.0 mL, 14.1 mmol) was added to a stirred solution of methyltriphenylphosphonium bromide (98%, 5.70 g, 15.6 mmol) in dry THF (60 mL) at −78 °C under argon. After the mixture had been stirred for 1 h at 0 °C, a solution of crude **41** (2.86 g, ca. 11.8 mmol) in dry THF (30 mL) was added, and the reaction mixture was stirred for 2 h at −78 °C under argon. Water was added, and the reaction temperature was gradually raised to room temperature. The organic phase was separated, and the aqueous phase was extracted with diethyl ether. The combined organic phases were washed with water, saturated aqueous $NaHCO_3$, and brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel (50 g, hexane) to give 1.90 g (69% based on **40**) of **42** as a colorless oil. $n_D^{24} = 1.4578$; $[\alpha]_D^{24} = -22.9$ ($c = 1.03$, $CHCl_3$); IR (film): $\tilde{\nu}_{max} = 1650$ (m, C=C), 1615 (m, C=C), 1265 cm^{-1} (s, Si–Me); ^1H NMR (90 MHz, $CDCl_3$): $\delta = 0.03$ (s, 6H, $SiMe_2$), 0.89 (s, 9H, *t*Bu), 0.98 (d, $J = 6.7$ Hz, 3H, 2-Me), 1.78 (d, $J = 1.1$ Hz, 3H, 4-Me), 2.50 – 2.85 (m, 1H, 2-H), 3.38 (dd, $J = 6.9$, 12 Hz, 1H, 1-H_a), 3.49 (dd, $J = 6.9$, 12 Hz, 1H, 1-H_b), 4.96 (d, $J = 10$ Hz, 1H, 6-H_a), 5.10 (d, $J = 17$ Hz, 1H, 6-H_b), 5.26 (d, $J = 10$ Hz, 1H, 3-H), 6.36 (dd, $J = 10$, 17 Hz, 1H, 5-H); elemental analysis (%): calcd for $C_{14}H_{28}OSi$ (240.46): C 69.93, H 11.74; found: C 70.26, H 11.98.

(2*R*,3*E*)-2,4-Dimethyl-3,5-hexadien-1-ol (43): A solution of tetrabutylammonium fluoride (1.0 M in THF, 2.5 mL, 2.5 mmol) was added to a solution of **42** (417 mg, 1.73 mmol) in THF (5 mL). The mixture was stirred for 4 h at room temperature, then poured into water, and extracted several times with diethyl ether. The extracts and the organic layer were combined and washed with water, saturated aqueous $NaHCO_3$, and brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel (5.0 g, hexane/ethyl acetate, 150:1) to give 193 mg (88%) of **43** as a colorless oil. $n_D^{27} = 1.4838$; $[\alpha]_D^{27} = +37.3$ ($c = 1.03$, $CHCl_3$); IR (film): $\tilde{\nu}_{max} = 3350$ (s, O–H), 1645 (m, C=C), 1610 cm^{-1} (m, C=C); ^1H NMR (90 MHz, $CDCl_3$): $\delta = 0.99$ (d, $J = 6.7$ Hz, 3H, 2-Me), 1.46 (s, 1H, OH), 1.80 (d, $J = 1.5$ Hz, 3H, 4-Me), 2.55 – 3.00 (m, 1H, 2-H), 3.41 (dd, $J = 6.6$, 14 Hz, 1H, 1-H_a), 3.52 (dd, $J = 6.8$, 14 Hz, 1H, 1-H_b), 4.98 (d, $J = 10$ Hz, 1H, 6-H_a), 5.14 (d, $J = 17$ Hz, 1H, 6-H_b), 5.25 (d, $J = 10$ Hz, 1H, 3-H), 6.39 (dd, $J = 10$, 17 Hz, 1H, 5-H); HR-MS: calcd for $C_8H_{14}O$ 126.1045; found 126.1038. Due to the volatility of **43**, correct combustion analysis data could not be obtained.

(2*R*,3*E*)-2,4-Dimethyl-3,5-hexadienoic acid (44): This compound was prepared under the same conditions as described for the preparation of **16** by employing **43** (410 mg, 3.25 mmol) and pyridinium dichromate (98%, 6.24 g, 16.3 mmol) to give 516 mg (quant) of **44** as a colorless oil. This was used for the next step without further purification. IR (film): $\tilde{\nu}_{max} = 3400$ (m, OH), 1710 (s, C=O), 1650 (m, C=C), 1615 cm^{-1} (m, C=C); ^1H NMR (90 MHz, $CDCl_3$): $\delta = 1.30$ (d, $J = 6.7$ Hz, 3H, 2-Me), 1.84 (d, $J = 1.2$ Hz, 3H, 4-Me), 3.30 – 3.70 (m, 1H, 2-H), 5.00 (d, $J = 10$ Hz, 1H, 6-H_a), 5.18 (d, $J = 16$ Hz, 1H, 6-H_b), 5.55 (d, $J = 10$ Hz, 1H, 3-H), 6.40 (dd, $J = 10$, 16 Hz, 1H, 5-H).

***N*-Methyl-*N*-methoxy-(2*R*,3*E*)-2,4-dimethyl-3,5-hexadienamide (45)**: This compound was prepared under the same conditions as described for the preparation of **17** by employing crude **44** (516 mg, ca. 3.68 mmol), *N*,*O*-dimethylhydroxylamine hydrochloride (380 mg, 3.90 mmol), *N*,*N*-diisopropylethylamine (0.68 mL, 3.90 mmol), 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide hydrochloride (685 mg, 3.57 mmol), and 4-dimethylaminopyridine (5 mg) to give 248 mg (42% based on **43**) of **45** as a colorless oil. $n_D^{25} = 1.4908$; $[\alpha]_D^{28} = -117$ ($c = 1.15$, $CHCl_3$); IR (film): $\tilde{\nu}_{max} = 1665$ (s, C=O), 1640 (m, C=C), 1610 cm^{-1} (m, C=C); ^1H NMR (90 MHz, $CDCl_3$): $\delta = 1.21$ (d, $J = 6.7$ Hz, 3H, 2-Me), 1.82 (d, $J = 1.1$ Hz, 3H, 4-Me), 3.18 (s, 3H, NMe), 3.65 (s, 3H, OMe), 3.70 – 4.10 (m, 1H, 2-H), 4.99 (d, $J = 10$ Hz, 1H, 6-H_a), 5.13 (d, $J = 17$ Hz, 1H, 6-H_b), 5.56 (d, $J = 10$ Hz, 1H, 3-H), 6.38 (dd, $J = 10$, 17 Hz, 1H, 5-H); elemental analysis (%): calcd for $C_{10}H_{17}O_2N$ (183.25): C 65.54, H 9.35, N 7.64; found: C 65.28, H 9.53, N 7.60; HR-MS: calcd for $C_{10}H_{17}O_2N$ 183.1259; found 183.1262.

(3*E*,5*R*,9*S*)-3,5,9-Trimethyl-1,3-undecadien-6-one (8): This compound was prepared under the same conditions as described for the preparation of **1** by employing (*S*)-3-methylpentyl bromide **24** (1.0 g, 6.06 mmol), magnesium (175 mg, 7.20 mmol), and the amide **45** (110 mg, 0.60 mmol) to give 109 mg (87%) of **8** as a colorless oil. $n_D^{24} = 1.4745$; $[\alpha]_D^{24} = -340$ ($c = 1.12$, $CHCl_3$); IR (film): $\tilde{\nu}_{max} = 1710$ (s, C=O), 1635 (m, C=C), 1600 (m, C=C), 985 (s, olefinic C–H), 895 (s), 870 cm^{-1} (m); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.82$ (d, $J = 6.2$ Hz, 3H, 9-Me), 0.84 (t, $J = 7.1$ Hz, 3H, 11-Me), 1.15 (d, $J = 6.8$ Hz, 3H, 5-Me), 1.20 – 1.63 (m, 5H, 8-, 9-, 10-H), 1.83 (d, $J = 1.2$ Hz, 3H, 3-Me), 2.40 (t, $J = 7.2$ Hz, 2H, 7-H), 3.52 (dq, $J = 9.8$, 6.8 Hz, 1H, 5-H), 5.02 (d, $J = 11$ Hz, 1H, 1-H_a), 5.17 (d, $J = 17$ Hz, 1H, 1-H_b), 5.35 (d, $J = 9.8$ Hz, 1H, 4-H), 6.36 (dd, $J = 9.8$, 17 Hz, 1H, 2-H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 11.3$, 12.1, 16.5, 18.9, 29.3, 30.3, 34.0, 38.7, 46.4, 112.4, 131.5, 135.8, 140.8, 211.9; elemental analysis (%): calcd for $C_{14}H_{26}O$ (208.34): C 80.71, H 11.61; found: C 80.58, H 11.81.

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