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# Pheromone synthesis. Part 259: Synthesis of seven methyl-branched hydrocarbons as the pheromone candidates for female Korean apricot wasp, *Eurytoma maslovskii*☆

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ABSTRACT

Seven new methyl-branched hydrocarbons were synthesized, which were the pheromone candidates of the female Korean apricot wasp (*Eurytoma maslovskii*). They are (*Z*)-15-methyl-7-nonacosene (**1**), (*Z*)-17-methyl-7-hentriacontene (**2**), 3,7-dimethylheptacosane (**3**), 8,12-dimethyltriacontane (**4**), 8,18-dimethyltriacontane (**5**), 3,7,11-trimethylnonacosane (**6**), and 3,7,17-trimethylnonacosane (**7**). All of them were synthesized as stereoisomeric mixtures, employing short and simple routes. Hydrocarbon **7** was synthesized via 4,8-dimethyldecanal (**71**, tribolure), the red flour beetle pheromone. The hydrocarbons **1**,**2**,**3** and **6** were identified by GC–MS analysis as the components (with unknown stereochemistry) of the female-specific secretion of *E. maslovskii*.

## 1. Introduction

In 1959 when the first insect pheromone bombykol [(10*E*,12*Z*)-10,12-hexadecadien-1-ol] was discovered, its bioactivity against male silkworm moth was thought to be entirely due to that single compound.[2] At present it is generally believed that a pheromone is composed of plural components. A recent example of such multicomponent pheromones is the male pheromone of the dried bean beetle, which is a mixture of six components.[3] In the cases of multi-component pheromones, identification of the each component is not always easy. All of the candidate components must be synthesized, and the synthetic components should be compared with the natural ones by GC–MS analysis as well as by bioassay. Usually, female- and male-secretions are compared, and the sex-specific components are found out, and they will be studied further. Accordingly, it is important to develop a quick and reliable synthetic methods for the components, even as stereoisomeric mixtures, to facilitate and speed up the identification of the bioactive components. Herein are described short and simple syntheses of various methyl-branched hydrocarbons as pheromone candidates.

The wasp *Eurytoma maslovskii* (Hymenoptera: Eurytomidae) is the most serious pest in Korean apricot orchards, causing up to 30% fruit damage in recent years. The cuticular extract of its females was shown to be pheromonally active and seven candidate structures **1**–**7** (Fig. 1) were proposed for the female pheromone components by GC–MS analysis (C.Y. Yang, manuscript in preparation), referring to Howard's paper on the identification of insect hydrocarbons by MS.[4] The present paper reports the synthesis of the stereoisomeric mixtures of **1**–**7**. Four of them (**1**, **2**, **3** and **6**) were identical with the natural components by GC–MS comparison. The synthesis of **1**–**7** must be of interest to those who are engaged in the study of methyl-branched hydrocarbons as semiochemicals.[5,6]

## 2. Results and discussion

The structures **1**–**7** of the target hydrocarbons indicate that they can be classified into four groups: (A) methyl-branched (*Z*)-alkenes (**1** and **2**), (B) dimethylated alkanes where the two methyl groups are separated by three methylene groups (**3** and **4**), (C) dimethylated alkanes whose methyl groups are separated by nine methylene groups (**5**), and (D) trimethylated alkanes (**6** and **7**). Details of the synthesis of **1**–**7** will be discussed in the order as shown above.

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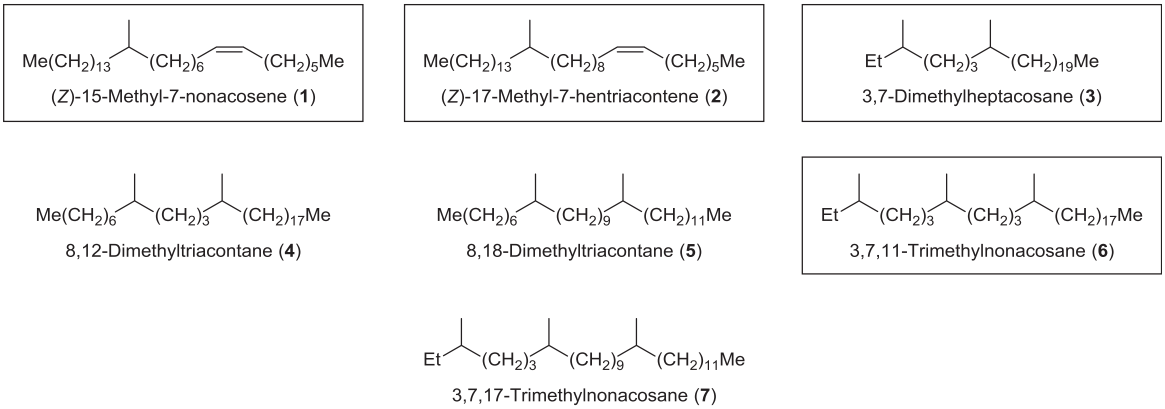


**Fig. 1.** Candidate structures **1**–**7** for the female-specific hydrocarbons of the Korean apricot wasp, *Eurytoma maslovskii*.

## 2.1. Synthesis of 1 and 2

Fig. 2 shows the retrosynthetic analysis of **1** and **2**, which differ only in the number of the methylene spacers between the methyl-branched position and the (*Z*)-double bond. Accordingly, they can be synthesized in a similar fashion, employing aldehyde **A** and bromide **B** or **C** as the building blocks, and connecting the two by Grignard reaction. Racemic aldehyde **A** can be prepared from commercially available (±)-citronellol (**8**). By using either (*R*)- or (*S*)-**8**, the enantiomers of **1** and **2** can be prepared readily. Citronellol enantiomers are versatile starting materials for natural products synthesis.[7]

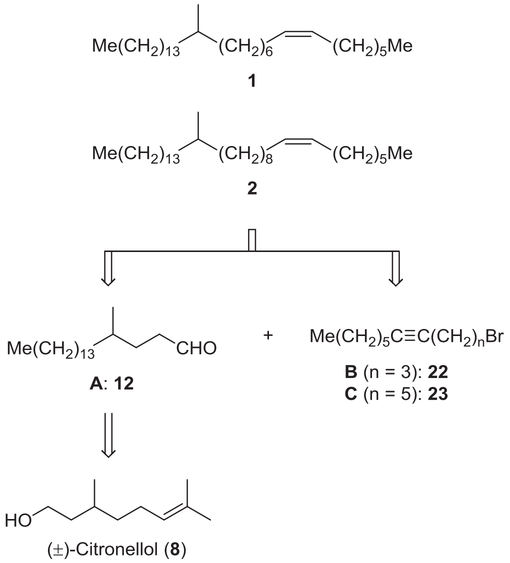


**Fig. 2.** Retrosynthetic analysis of **1** and **2**.

Scheme 1 summarizes the synthesis of (±)-**1** and (±)-**2**. (±)-Citronellol (**8**) was tosylated, and the resulting **9** was treated with *n*-$C_{12}H_{25}MgBr$ in the presence of $Li_2CuCl_4$ to give **10**. The crude **10** was dihydroxylated with $OsO_4$ and *N*-methylmorpholine-*N*-oxide (NMO). The product was purified by $SiO_2$ chromatography followed by recrystallization to give crystalline diol **11**. Cleavage of the diol **11** with $HIO_4$ in THF afforded oily **12** in 23% overall yield based on **8** (four steps).

Other two building blocks **22** (=**B**) and **23** (=**C**) were synthesized from 1-octyne (**13**). Alkylation of **13** with bromide **14** or **15** using *n*-BuLi as the base effected chain-elongation to give **16** or **17**. Then **16** or **17** was treated with TsOH in MeOH to give alcohol **18** or **19**. The corresponding tosylate **20** or **21** was converted to the desired bromide **22** or **23** by treatment with LiBr in DMF. The overall yield of **22** was 23% based on **13** (four steps), while that of **23** was 26% based on **13** (four steps).

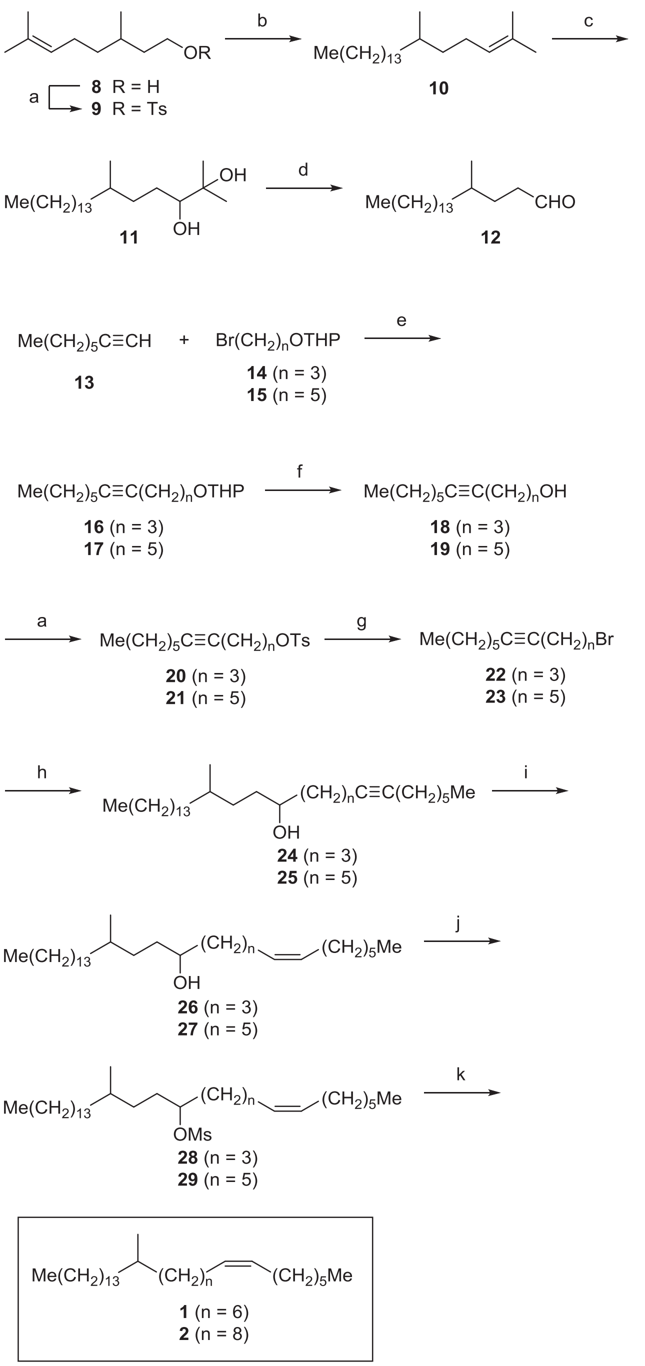
The next stage was the coupling of the aldehyde **12** with the bromide **22** or **23** by means of the Grignard reaction. Accordingly, **12** was treated with the Grignard reagent prepared from **22** or **23** to give alkynol **24** or **25** as diastereomeric mixtures. Semi-hydrogenation of **24** or **25** with Lindlar's Pd catalyst gave (*Z*)-alkenol **26** or **27**. The corresponding mesylate **28** or **29** was reduced with $LiAlH_4$ to give the target hydrocarbon **1** or **2**. The yield of **1** was 48% based on **12** (four steps), while that of **2** was 28% based on **12** (four steps).

Racemic (*Z*)-15-methyl-7-nonacosene (**1**, 1.12 g) was obtained as a colorless oil. Its *Z*/*E* ratio was ca. 95:5, judging from its $^{13}C$ NMR spectrum (see 4.13). The overall yield of **1** was 11% based on (±)-citronellol (**8**, eight steps), or also 11% based on 1-octyne (**13**, eight steps). Racemic (*Z*)-17-methyl-7-hentriacontene (**2**, 653 mg) was also obtained as a colorless oil. Its *Z*/*E* ratio was ca. 94:6, judging from its $^{13}C$ NMR spectrum (see 4.14). The overall yield of **2** was 6% based on **8** (eight steps), or 7% based on **13** (eight steps). The synthetic **1** and **2** were identified with the naturally occurring **1** and **2** by GC–MS comparison. Details will be published later by Yang.

## 2.2. Synthesis of 3 and 4

Fig. 3 shows the retrosynthetic analysis of **3** and **4**, which possess in common the three-methylene spacer between the two methyl-branching positions. They can be synthesized by the Wittig reaction between **D** and **E** or **F** and **G**. The building blocks **E** and **G** can be synthesized from (±)-citronellal (**30**).

Scheme 2 summarizes the synthesis of **3** and **4** as stereoisomeric mixtures. Addition of *n*-$C_{18}H_{37}MgBr$ or *n*-$C_{16}H_{33}MgBr$ to (±)-citronellal (**30**) gave alcohol **31** or **32**. The hydroxy group of **31** or **32** was removed by reduction of the corresponding mesylate **33** or **34** with $LiAlH_4$ to give alkene **35** or **36**. Oxidation of the alkene **35** or **36** with $SeO_2$ in the presence of *t*-BuOOH gave aldehyde **37** or **38**. Treatment of **37** with $Ph_3P{=}CH_2$ afforded **39**, while that of **38** with *n*-$C_5H_{11}CH{=}PPh_3$ furnished **40**. Finally, the dienes **39** and **40** were hydrogenated over Pd–C to give the desired 3,7-dimethylheptacosane (**3**, 867 mg) and 8,12-dimethyltriacontane (**4**, 1.28 g), respectively, both as colorless oils. The overall yield of **3** was 10% based on (±)-citronellal (**30**, six steps), while that of **4** was 13%. 3,7-Dimethylheptacosane (**3**) was identified with the



**Scheme 1.** Synthesis of **1** and **2**. Reagents: (a) TsCl, $C_5H_5N$ (quant.); (b) $Me(CH_2)_{11}MgBr$, $Li_2CuCl_4$, THF; (c) $OsO_4$, NMO, acetone, *t*-BuOH, $H_2O$ (29%, two steps); (d) $HIO_4 \cdot 2H_2O$, THF (78%); (e) *n*-BuLi, THF, HMPA; (f) TsOH, MeOH (46% for **18**, two steps; 36% for **19**, two steps); (g) LiBr, DMF (51% for **22**, two steps; 72% for **23**, two steps); (h) Mg, THF, then **12** (80% for **24**; 68% for **25**); (i) $H_2$, Lindlar Pd, quinoline, cyclohexane (quant. for **26**; 91% for **27**); (j) MsCl, $C_5H_5N$, $CH_2Cl_2$ (quant.); (k) $LiAlH_4$, THF (60% for **1**; 46% for **2**).

naturally occurring **3** by GC–MS comparison. Another female-produced hydrocarbon was shown to be different from **4** by GC–MS comparison. Details will be published later by Yang.

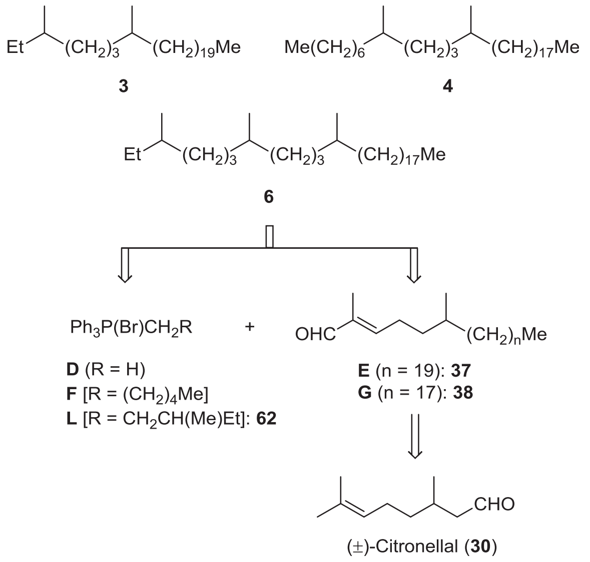
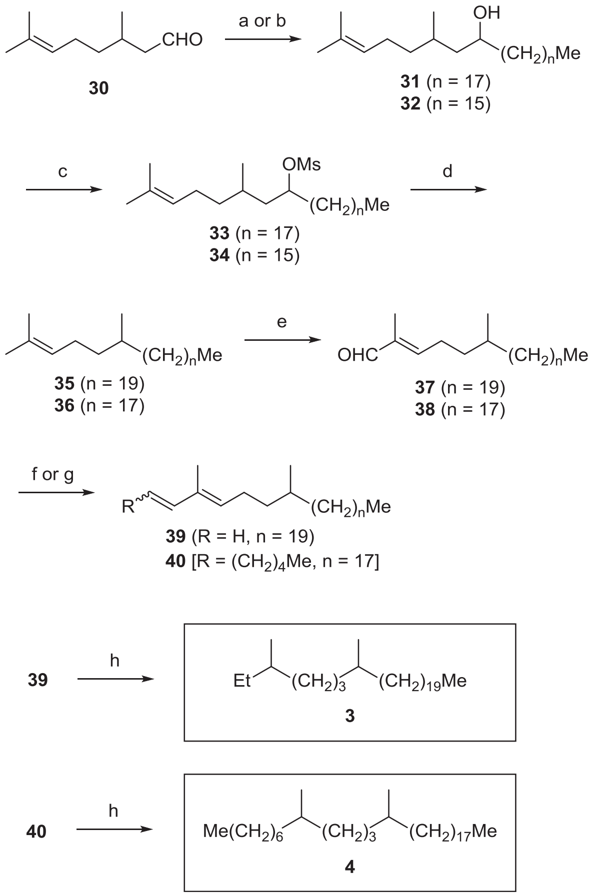


**Fig. 3.** Retrosynthetic analysis of **3**, **4** and **6**.



**Scheme 2.** Synthesis of **3** and **4**. Reagents: (a) $Me(CH_2)_{17}MgBr$, THF (96% of **31**); (b) $Me(CH_2)_{15}MgBr$, THF (92% of **32**); (c) MsCl, $C_5H_5N$ (99%); (d) $LiAlH_4$, THF (87% for **35**; 85% for **36**); (e) $SeO_2$, *t*-BuOOH, $CH_2Cl_2$ (27% for **37**; 36% for **38**); (f) $Ph_3P(Br)Me$, *n*-BuLi, THF (45% of **39**); (g) $Ph_3P(Br)(CH_2)_5Me$, *n*-BuLi, THF (51% of **40**); (h) $H_2$, Pd–C, hexane (99% for **3**; 96% for **4**).

## 2.3. Synthesis of 5

Because **4** was not the structure of another female-produced hydrocarbon of *E. maslovskii*, Yang proposed 8,18-dimethyltriacontane (**5**) as its candidate structure. Fig. 4 shows the retrosynthetic analysis of **5**. The target alkane **5** can be obtained by reducing ketone **H**. Alkylation of β-keto ester **I** with **J** followed by alkaline hydrolysis gives **H**. The β-keto ester **I** can be prepared by dianion alkylation of methyl acetoacetate with **K**. Both **J** and **K** will be synthesized from (±)-citronellol (**8**).

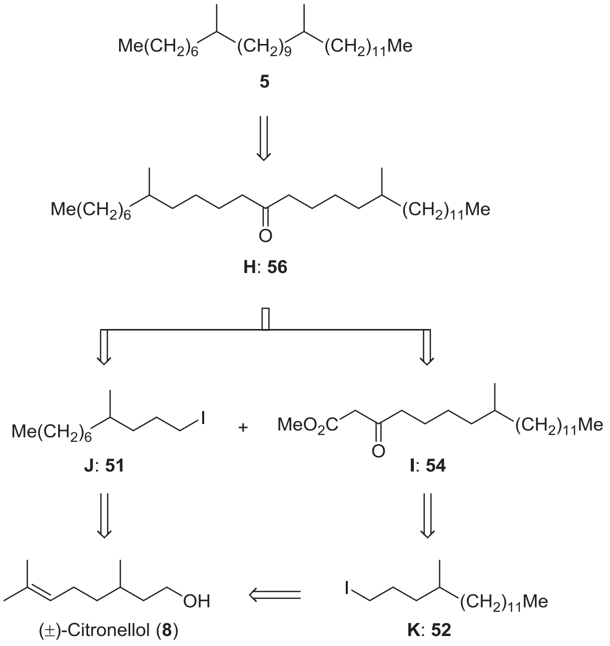


**Fig. 4.** Retrosynthetic analysis of **5**.

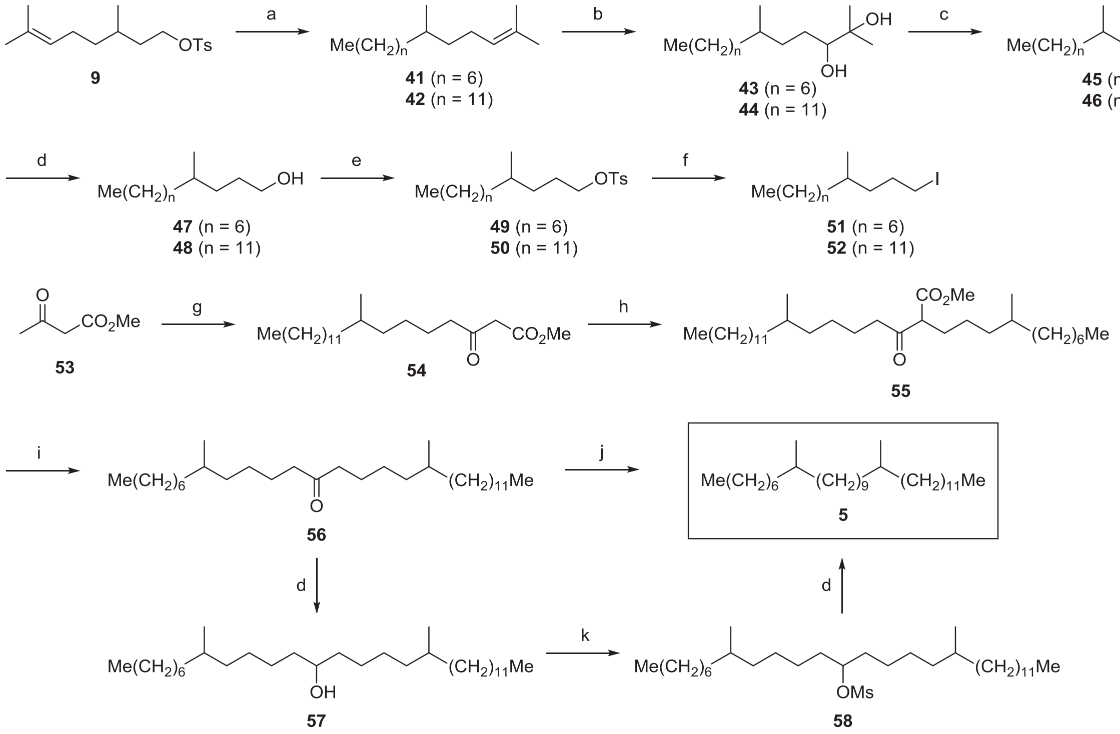
Synthesis of a stereoisomeric mixture of **5** is summarized in Scheme 3. First, (±)-citronellyl tosylate (**9**) was converted to the two iodides **51** and **52** in the following manner. Chain-elongation of **9** with either *n*-$C_5H_{11}MgBr$ or *n*-$C_{10}H_{21}MgBr$ gave **41** or **42**. Dihydroxylation of **41** or **42** with $OsO_4$ furnished **43** or **44**. Cleavage of **43** or **44** with $HIO_4$ yielded aldehyde **45** or **46**, which was reduced with $LiAlH_4$ to give the corresponding alcohol **47** or **48**. The tosylates **49** and **50** were treated with NaI to give the desired iodides **51** and **52**, respectively. Next, the carbon-chain of **5** was constructed by alkylating methyl acetoacetate (**53**). The dianion derived from **53** by treatment with NaH and *n*-BuLi was alkylated with **52** to give a new β-keto ester **54**. Further alkylation of **54** with **51** in the presence of $K_2CO_3$ furnished **55**, which was saponified (KOH) with concomitant decarboxylation to give ketone **56**.

Reduction of **56** by Wolff-Kishner reaction under the Huang Minlon conditions ($N_2H_4 \cdot H_2O$ and KOH) yielded **5**, although in a low yield of 18%. The low yield might have been due to the hindered nature of the carbonyl group of **56**, which is located at nearly the center of a very lengthy $C_{30}$-chain. Otherwise, it might have been due to the hydrophobic nature of the substrate with a long hydrocarbon chain, causing aggregation in the protic solvents.[8] A better yield was realized by the three-step procedure as follows. Reduction of **56** with $LiAlH_4$ afforded alcohol **57**, which was converted to the corresponding mesylate **58**, and reduced again with $LiAlH_4$ to give **5** in 52% yield based on **56**. In sum total 910 mg of 8,18-dimethyltriacontane (**5**) was synthesized as a colorless oil. The overall yield of **5** via the mesylate **58** was 10% (via **51**) or 16% (via **52**) based on **9** (12 steps). 8,18-Dimethyltriacontane (**5**) was not identical with the natural hydrocarbon by GC–MS comparison. Yang therefore proposed 3,7,11-trimethylnonacosane (**6**) as the structure of the natural hydrocarbon.

## 2.4. Synthesis of 6

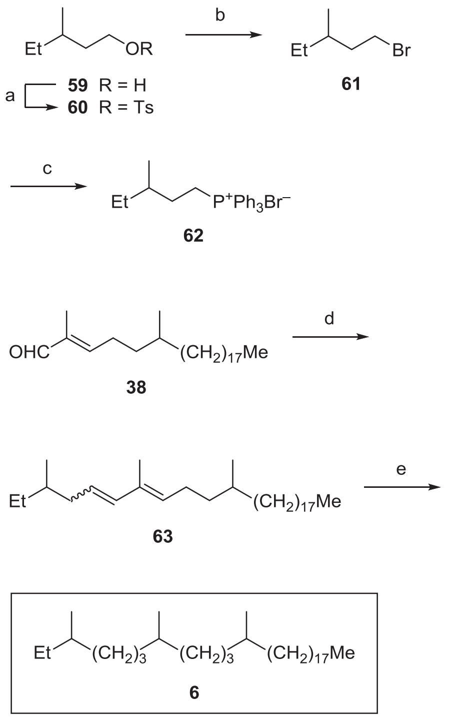
Retrosynthetic analysis of **6** is shown in Fig. 3. The intermediate **G** (=**38**) employed in the synthesis of **4** is also useful for the synthesis of **6**. The Wittig reaction between aldehyde **G** and a phosphorane derived from phosphonium salt **L** will be the key reaction.

Scheme 4 summarizes the synthesis of **6**. Commercially available (±)-3-methyl-1-pentanol (**59**) was chosen as the starting material for the phosphonium salt **62**. The alcohol **59** was tosylated, and the resulting **60** was treated with LiBr in DMF to give bromide



**Scheme 3.** Synthesis of **5**. Reagents: (a) *n*-$C_5H_{11}MgBr$ for **41** and *n*-$C_{10}H_{21}MgBr$ for **42**, $Li_2CuCl_4$, THF; (b) $OsO_4$, NMO, *t*-BuOH, acetone, $H_2O$ (71% for **43**; 99% for **44**); (c) $HIO_4 \cdot 2H_2O$, THF (84% for **45**; 85% for **46**); (d) $LiAlH_4$, THF (91% for **47**; 85% for **48**; 79% for **5**); (e) TsCl, $C_5H_5N$ (quant.); (f) NaI, DMF (66% for **51**; 80% for **52**); (g) NaH, *n*-BuLi, THF, **52** (73%); (h) $K_2CO_3$, acetone, DMF, **51** (98%); (i) KOH, EtOH, $H_2O$ (86%); (j) $N_2H_4 \cdot H_2O$, KOH, $HO(CH_2)_2O(CH_2)_2OH$ (18%); (k) MsCl, $C_5H_5N$ (73%).

**61**. A solution of **61** and $Ph_3P$ in xylene was heated to give phosphonium salt **62** (=**L**) as crystals. Treatment of **62** with *n*-BuLi in THF was followed by addition of aldehyde **38** to give diene **63** as a mixture (ca. 2:1) of its (5*E*/5*Z*)-isomers. Hydrogenation of **63** over Pd–C in hexane furnished a stereoisomeric mixture of 3,7,11-trimethylnonacosane (**6**, 1.83 g) as a colorless oil. The overall yield of **6** was 13% based on (±)-citronellal (**30**, six steps), or 24% based on **59** (five steps). GC–MS comparison of synthetic **6** with the natural hydrocarbon proved their identity. It was therefore concluded that the structure of the problematic hydrocarbon was **6** instead of the previously proposed **4** and **5**.



**Scheme 4.** Synthesis of **6**. Reagents: (a) TsCl, $C_5H_5N$, DMAP (quant.); (b) LiBr, DMF (76%); (c) $Ph_3P$, xylene, 125 °C, 18 h (67%); (d) **62**, *n*-BuLi, THF (47%); (e) $H_2$, Pd–C, hexane (99%).

### 2.5. Synthesis of 7

It was also possible that 3,7,17-trimethylnonacosane (**7**) was the naturally occurring hydrocarbon, because **7** might show virtually the same MS as that of **6**. Synthesis and GC–MS analysis of **7** was therefore executed so as to clarify the matter. Fig. 5 shows the retrosynthetic analysis of **7**, which is similar to that of **5** in Fig. 4. The trimethylalkane **7** can be obtained by reduction of ketone **L**, which is to be synthesized by alkylation of the β-keto ester **I** (**54**) with iodide **M**. The red flour beetle pheromone (tribolure) **N** can readily be converted to **M**. Synthesis of the stereoisomers of tribolure **N** was recently reported by us starting from the enantiomers of citronellal (**30**).[9]

Synthesis of a stereoisomeric mixture of **7** is summarized in Scheme 5. Conversion of commercially available (±)-2-methyl-1-butanol (**64**) to a stereoisomeric mixture of 2,6,10-trimethyl-2-dodecene (**69**) was carried out according to our previous method for the synthesis of the stereoisomers of **69**.[9] Accordingly, **64** furnished iodide **66** via tosylate **65**. Treatment of **66** in dry $Et_2O$ with 2 equiv of *t*-BuLi generated 2-methylbutyllithium, which attacked citronellal (**30**) to give **67** in 92% yield. The corresponding mesylate **68** was reduced with $LiAlH_4$ to give **69**, Dihydroxylation of **69** with $OsO_4$ and NMO yielded glycol **70**. Treatment of **70** with $HIO_4$ in THF gave a stereoisomeric mixture of 4,8-dimethyldecanal(tribolure) **71** in 36% overall yield based on **64** (seven steps).

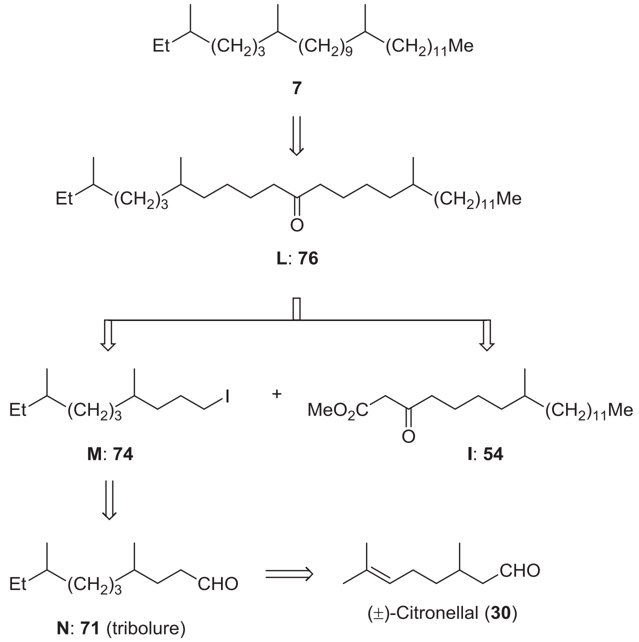


**Fig. 5.** Retrosynthetic analysis of **7**.

Reduction of **71** with $LiAlH_4$ gave **72**, whose tosylate **73** was treated with NaI to afford iodide **74**. Alkylation of the β-keto ester **54** with **74** in the presence of $K_2CO_3$ in acetone/DMF gave **75**. Alkaline hydrolysis and decarboxylation of **75** furnished ketone **76**. Its reduction to **77** was followed by mesylation, giving **78**. Finally, reduction of **78** with $LiAlH_4$ in THF gave the target hydrocarbon **7** (1.57 g) as an oil. Its MS was very similar to but slightly different from that of **6**. Co-injection experiment by GC–MS analysis indicated that the naturally occurring hydrocarbon was not **7** but **6**.

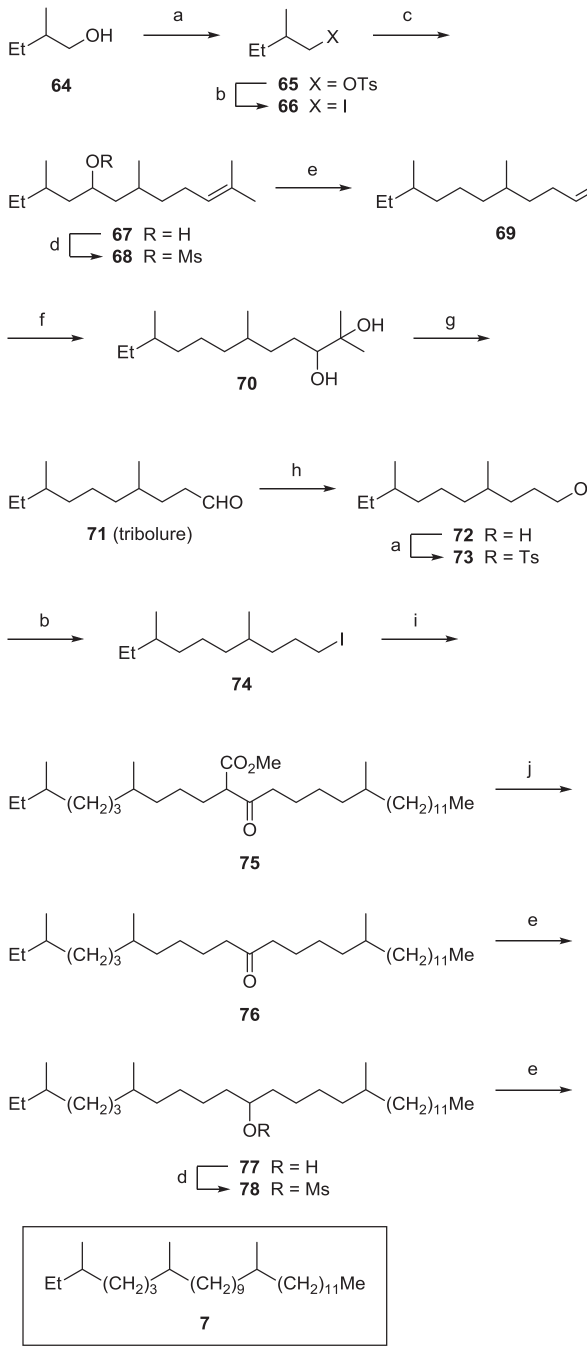
## 3. Conclusion

The present synthesis of the hydrocarbons **1**–**7** and their GC–MS comparison with the female-specific hydrocarbons of the Korean apricol wasp (*E. maslovskii*) enabled the identification of the naturally occurring secretions as **1**, **2**, **3** and **6**. Unfortunately, however, their various blend combinations caught no males of *E. maslovskii* in field tests in Korea (April and May, 2016). Further studies are necessary to identify *E. maslovskii* pheromone. Details of biological studies including GC–MS co-injection experiments will be published in due course by C.Y. Yang.

## 4. Experimental

### 4.1. General

Melting points are uncorrected values. Refractive indices were measured on an Atago EMT-1 refractometer. IR spectra were measured on a Jasco FT/IR-410 spectrometer. $^1H$ NMR spectra (400 MHz, TMS at $\delta$=0.00 as the internal standard) and $^{13}C$ NMR spectra (100 MHz, $CDCl_3$ at $\delta$=77.0 as the internal standard) were recorded on a Jeol JNM-ECZ 400S/L1 spectrometer. GC–MS were measured on Agilent Technologies 5975 inert XL. HRMS were recorded on Jeol JMS-T100 GCV or Jeol JMS-700V. Column chromatography was carried out on Merck Kieselgel 60 Art 1.00734. All the compounds are stereoisomeric mixtures if they are chiral.



**Scheme 5.** Synthesis of **7**. Reagents: (a) TsCl, $C_5H_5N$ (quant.); (b) NaI, DMF (78% for **66**, 86% for **74**); (c) 2 equiv *t*-BuLi, $Et_2O$; then **30** (92%); (d) MsCl, $C_5H_5N$ (quant.); (e) $LiAlH_4$, THF (82% for **69**, 99% for **77**, 81% for **7**); (f) $OsO_4$, NMO, *t*-BuOH, $Me_2CO$, $H_2O$ (83%); (g) $HIO_4 \cdot 2H_2O$, THF (73%); (h) $LiAlH_4$, $Et_2O$ (91%); (i) **54**, $K_2CO_3$, $Me_2CO$, DMF (83%); (j) KOH, EtOH, $H_2O$ (71%).

### 4.2. 2,6-Dimethyl-2-icosene (10)

(±)-Citronellol (**8**, 8.0 g, 53 mmol) in dry $C_5H_5N$ (30 mL) was treated with TsCl (11.5 g, 72 mmol) with stirring and ice-cooling (0–5 °C) for 1 h. Subsequent work-up gave 17.9 g (quant.) of **9**, $\nu_{max}$ (film): 2963 (s), 2925 (s), 1598 (m), 1362 (s), 1189 (s), 1176 (s), 946 (s), 890 (m), 815 (m), 764 (m), 664 (s). A Grignard reagent was prepared from *n*-$C_{12}H_{25}Br$ (19.1 g, 76.5 mmol) and Mg (2.0 g, 82 mmol) in dry THF (20 mL). A solution of **9** (17.9 g, 53 mmol) in dry THF (30 mL) was added to the stirred and cooled Grignard reagent at −70 °C under argon. A solution of $Li_2CuCl_4$ in THF (0.1 M, 3 mL, 0.3 mmol) was added to the stirred mixture at −70 °C. The mixture was stirred at −60 to −70 °C for 2 h, and left to stand overnight with gradual raise of the temperature. Usual work-up gave 22.4 g of crude **10** as an oil, $\nu_{max}$ (film): 2956 (s), 2925 (s), 2853 (s), 1465 (m), 1377 (m), 1072 (m), 721 (m), 676 (w). The oily **10** was used in the next step without further purification.

### 4.3. 2,6-Dimethylicosane-2,3-diol (11)

A solution of $OsO_4$ (1% in *t*-BuOH, 10 mL, 0.1 g) and aqueous *N*-methylmorpholine *N*-oxide (50% NMO, 36.5 g, ca. 156 mmol) were added to a stirred solution of crude **10** (22.4 g, 53 mmol) in *t*-BuOH (140 mL), acetone (340 mL) and $H_2O$ (85 mL). The brown-colored mixture was stirred at room temperature for 4 d. Subsequently, $Na_2SO_3$ (22.4 g) was added, and the mixture was stirred for 30 min. It was then concentrated in vacuo. The residue was diluted with water, and extracted with EtOAc. The EtOAc extract was washed with water and brine, dried ($MgSO_4$), and concentrated in vacuo. The residue was chromatographed over $SiO_2$ (120 g). Fractions eluted with hexane/EtOAc (4:1) was recrystallized from acetone to give 5.38 g (29%) of **11** as rods, mp 55–56 °C; $\nu_{max}$ (Nujol): 3411 (br s), 1088 (m), 719 (m); $\delta_H$($CDCl_3$): 0.88 (3H, d, *J* 6), 0.89 (3H, t, *J* 6), 1.16 (3H, s), 1.22 (3H, s), 1.22–1.50 (31H, m, peak at 1.26), 1.96 (1H, br s), 2.10 (1H, br. d), 3.32–3.36 (1H, m). HRMS calcd for $C_{22}H_{46}O_2Na$: 365.3390, found: 365.3390.

### 4.4. 4-Methyloctanal (12)

$HIO_4 \cdot 2H_2O$ (4.0 g, 17.5 mmol) was added to a stirred and ice-cooled solution of **11** (5.38 g, 15.7 mmol) in THF (50 mL). The mixture was stirred at 0–5 °C for 30 min, diluted with ice-water, and extracted with hexane. The hexane extract was washed with water, $NaHCO_3$ solution and brine, dried ($MgSO_4$), and concentrated in vacuo. The residue was chromatographed over $SiO_2$ (30 g). Elution with hexane/EtOAc (30:1) gave 3.47 g (78%) of **12** as a colorless oil, $n_D^{20}$=1.4512; $\nu_{max}$ (film): 2925 (s), 2853 (s), 2711 (m), 1729 (s), 1466 (s), 1378 (m), 1038 (w), 721 (m); $\delta_H$ ($CDCl_3$): 0.88 (3H, d, *J* 7.6), 0.91 (3H, t, *J* 7.2), 1.08–1.15 (1H, m), 1.20–1.35 (26H, br s), 1.36–1.48 (2H, m), 2.38–2.46 (2H, m), 9.77 (1H, t, *J* 2); GC–MS [column: HP-5MS, 5% phenylmethylsiloxane, 0.25 mm i.d.×30 m; carrier gas, He; press, 60.7 kPa; temp: 70–230 °C (+10 °C/min)]: $t_R$ 18.33 min (97.1%); MS (70 eV, EI): *m/z*: 282 (<1) [$M^+$], 264 (4), 238 (13), 223 (5), 210 (10), 182 (9), 125 (10), 111 (26), 95 (53), 85 (66), 82 (66), 69 (56), 57 (100), 56 (70), 55 (60), 43 (56), 41 (49). HRMS calcd for $C_{19}H_{38}O$: 282.2943, found: 282.2922.

### 4.5. 4-Undecyn-1-ol (18)

3-Bromo-1-propanol (13.9 g, 100 mmol) was converted to the corresponding THP ether **14** (28.1 g) by treatment with DHP (9.0 g, 107 mmol) and $TsOH \cdot H_2O$ (0.2 g) in $Et_2O$ (70 mL). A solution of *n*-BuLi (1.6 M in hexane, 52 mL, 82 mmol) was added dropwise to a stirred and cooled solution of **13** (9.0 g, 82 mmol) in dry THF (70 mL) and dry HMPA (7 mL) at −60 to −50 °C under argon. The mixture was warmed to 0 °C and again cooled to −78 °C. A solution of **14** (28.0 g, ca. 100 mmol) in dry THF (10 mL) was added through a syringe to the stirred and cooled mixture at −78 to −60 °C. The mixture was left to stand to reach room temperature, and then stirred and heated at 40–50 °C for 1 h. After cooling, it was diluted with water, and extracted with hexane. The hexane extract was washed with water and brine, dried ($MgSO_4$), and concentrated in vacuo to give crude **16** (31.8 g) as an oil, $\nu_{max}$ (film): 2939 (s), 2871 (s), 1200 (m), 1136 (s), 1120 (s), 1076 (m), 1035 (s), 986 (m), 870 (m), 816 (m). $TsOH \cdot H_2O$ (1.0 g) was added to a solution of **16** (31.8 g) in MeOH (170 mL), and the solution was left to stand overnight at room temperature. It was then stirred and heated under reflux for

1 h, and concentrated in vacuo. The residue was diluted with water, and extracted with hexane. The hexane solution was washed with water and brine, dried ($MgSO_4$), and concentrated in vacuo. The residue was distilled to give **18** (6.31 g, 46% based on **13**, two steps), bp 105–108 °C/3 Torr; $n_D^{22}$=1.4602; $\nu_{max}$ (film): 3342 (br m), 2930 (s), 2858 (s), 1058 (m); $\delta_H$ ($CDCl_3$): 0.89 (3H, t, *J* 6.4), 1.20–1.40 (7H, m), 1.42–1.52 (2H, m), 1.68–1.80 (2H, m), 2.10–2.18 (2H, m), 2.26–2.32 (2H, m), 3.77 (2H, t, *J* 6.8); GC–MS (same conditions as those used for **12**): $t_R$ 10.83 min (97.1%); MS (70 eV, EI); *m*/*z*: 168 (6) [$M^+$], 139 (4), 125 (7), 107 (10), 97 (100), 83 (54), 81 (43), 79 (71), 67 (53), 55 (46), 41 (36). HRMS calcd for $C_{11}H_{20}O$: 168.1514, found: 168.1505.

### 4.6. 6-Tridecyn-1-ol (19)

5-Bromo-1-pentanol (16.7 g, 100 mmol) was converted to the corresponding THP ether **15** (29.8 g) by treatment with DHP (9.0 g, 107 mmol) and $TsOH\cdot H_2O$ (0.2 g) in $Et_2O$ (70 mL). A solution of *n*-BuLi (1.6 M in hexane, 52 mL, 82 mmol) was added dropwise to a stirred and cooled solution of **13** (9.0 g, 82 mmol) in dry THF (70 mL) and dry HMPA (7 mL) at −78 to −60 °C under argon. The mixture was then warmed up to 0 °C and again cooled to −78 °C. A solution of **15** (29.8 g, 100 mmol) in dry THF (10 mL) was added through a syringe to the stirred and cooled mixture at −78 to −60 °C. The mixture was left to stand overnight at room temperature, and then stirred and heated at 40–50 °C for 1 h. After cooling, it was diluted with water, and extracted with hexane. The hexane extract was washed with water and brine, dried ($MgSO_4$), and concentrated in vacuo to give crude **17** as an oil, $\nu_{max}$ (film): 2939 (s), 2860 (s), 1200 (m), 1136 (s), 1120 (s), 1077 (s), 1035 (s), 992 (m), 972 (m), 905 (m), 870 (m), 815 (m). $TsOH\cdot H_2O$ (1.0 g) was added to a solution of **17** (31.9 g) in MeOH (170 mL), and the solution was left to stand overnight at room temperature. It was then stirred and heated under reflux for 1 h, and concentrated in vacuo. The residue was diluted with water, and extracted with hexane. The hexane extract was washed with water and brine, dried ($MgSO_4$), and concentrated in vacuo. The residue was distilled to give **19** (5.73 g, 36% based on **13**, two steps), bp 135–138 °C/3 Torr; $n_D^{22}$=1.4648; $\nu_{max}$ (film): 3346 (br m), 2931 (s), 2859 (s), 1460 (m), 1073 (m), 1054 (m); $\delta_H$ ($CDCl_3$): 0.89 (3H, t, *J* 7.2), 1.22–1.40 (6H, m), 1.40–1.74 (9H, m), 2.10–2.24 (4H, m), 3.64 (2H, t, *J* 7); GC–MS (same conditions as those used for **12**): $t_R$ 13.34 min (84.5%) [impurities at $t_R$ 14.27 (5.1%) and 18.04 min (7.3%)]; MS (70 eV, EI): *m*/*z*: 196 (<1) [$M^+$], 178 (6), 149 (8), 135 (11), 121 (10), 109 (22), 93 (72), 79 (100), 67 (81), 55 (48), 41 (40). HRMS calcd for $C_{13}H_{24}O$: 196.1827, found: 196.1862.

### 4.7. 4-Undecynyl bromide (22)

TsCl (8.00 g, 42 mmol) was added to a stirred and ice-cooled solution of **18** (6.30 g, 37.5 mmol) in dry $C_5H_5N$ (60 mL) containing DMAP (50 mg). The mixture was stirred for 1.5 h at 0–5 °C, when $C_5H_5N\cdot HCl$ precipitated. The mixture was diluted with ice and water, and extracted with $Et_2O$. The $Et_2O$ extract was washed successively with dil HCl, water, $NaHCO_3$ solution and brine, dried ($MgSO_4$), and concentrated in vacuo to give 10.16 g (quant.) of **20** as an oil, $\nu_{max}$ (film): 2930 (s), 2858 (s), 1599 (m), 1365 (s), 1189 (s), 1177 (s), 933 (s). LiBr (7.0 g, 80 mmol) was added to a solution of **20** (10.16 g, 37.5 mmol) in dry DMF (40 mL). After the exothermic reaction, the homogeneous solution was left to stand overnight at room temperature. It was then diluted with water, and extracted with hexane. The extract was washed with water and brine, dried ($MgSO_4$), and concentrated in vacuo. The residue was distilled to give **22** (4.41 g, 51%, two steps) as a colorless oil, bp 95 °C/3 Torr; $n_D^{19}$=1.4775; $\nu_{max}$ (film): 2956 (s), 2930 (s), 2857 (s), 1457 (m), 1433 (m), 1272 (m), 1248 (m); $\delta_H$ ($CDCl_3$): 0.89 (3H, t, *J* 6.8), 1.20–1.40 (6H, m), 1.40–1.52 (2H, m), 1.94–2.04 (2H, m), 2.10–2.18 (2H, m), 2.30–2.38 (2H, m), 3.53 (2H, t, *J* 6.8); GC–MS (same conditions as those used for **12**); $t_R$ 11.77 min (98.8%); MS (70 eV, EI): *m*/*z*: 203 (11), 201 (11), 189 (5), 187 (5), 161 (5), 148 (16), 146 (16), 134 (31), 132 (31), 123 (83), 109 (41), 95 (66), 81 (100), 79 (72), 67 (90), 55 (27), 53 (27), 41 (37). HRMS calcd for $C_{11}H_{19}Br$: 230.0670, found: 230.0676.

### 4.8. 6-Tridecynyl bromide (23)

TsCl (6.50 g, 34 mmol) was added to a stirred and ice-cooled solution of **19** (5.70 g, 29 mmol) and DMAP (50 mg) in dry $C_5H_5N$ (50 mL). The mixture was stirred for 1.5 h at 0–5 °C, then diluted with ice and water, and extracted with $Et_2O$. The $Et_2O$ extract was washed successively with dil HCl, water, $NaHCO_3$ solution and brine, dried ($MgSO_4$), and concentrated in vacuo to give 8.90 g (quant.) of **21** as an oil, $\nu_{max}$ (film): 2931 (s), 2859 (s), 1599 (m), 1363 (s), 1189 (s), 1177 (s), 950 (m). LiBr (6.0 g, 69 mmol) was added to a solution of **21** (8.90 g, 34 mmol) in dry DMF (35 mL). After exothermic reaction, the homogeneous solution was left to stand overnight at room temperature. It was then diluted with water, and extracted with hexane. The extract was washed with water and brine, dried ($MgSO_4$), and concentrated in vacuo. The residue was distilled to give **23** (5.38 g, 72%, two steps) as a colorless oil, bp 120–123 °C/3 Torr; $n_D^{19}$=1.4764; $\nu_{max}$ (film): 2931 (s), 2858 (s), 1459 (m), 1435 (m), 1333 (w), 1269 (w), 1241 (w); $\delta_H$ ($CDCl_3$): 0.89 (3H, t, *J* 7.2), 1.22–1.42 (2H, m), 1.42–1.62 (6H, m), 1.82–1.92 (2H, m), 2.08–2.22 (4H, m), 3.41 (2H, t, *J* 6.8); GC–MS (same conditions as those used for **12**): $t_R$ 14.32 min (86.8%) [impurities at $t_R$ 13.30 (6.8%) and 18.03 min (3.2%)]; MS (70 eV, EI): *m*/*z*: 260 (3) [$M^+$], 258 (3) [$M^+$], 149 (8), 135 (11), 123 (19), 109 (64), 95 (80), 81 (100), 67 (97), 55 (46), 41 (33). HRMS calcd for $C_{13}H_{23}Br$: 258.0983, found: 258.1008.

### 4.9. 15-Methyl-7-nonacosyn-12-ol (24)

A Grignard reagent was prepared from **22** (2.31 g, 10 mmol) and Mg (300 mg, 12.5 mmol) in dry THF (10 mL) employing a trace amount of $I_2$ as an initiator. A solution of **12** (1.70 g, 6 mmol) in dry THF (7 mL) was added dropwise to the stirred and ice-cooled Grignard solution at 0–10 °C. After the exothermic reaction subsided, the mixture was left to stand overnight at room temperature, then acidified with dil HCl and ice, and extracted with $Et_2O$. The $Et_2O$ extract was washed successively with water, $NaHCO_3$ solution and brine, dried ($MgSO_4$), and concentrated in vacuo. The residue (4.23 g) was chromatographed over $SiO_2$ (35 g). Elution with hexane gave hydrocarbons (0.30 g). Further elution with hexane/EtOAc (30:1) gave **24** (2.09 g, 80%) as a colorless oil, which solidified in a deep freezer, $n_D^{20}$=1.4644; $\nu_{max}$ (film): 3347 (br m), 2925 (s), 2854 (s), 1465 (m), 1377 (m), 1089 (m), 1039 (m), 722 (m); $\delta_H$ ($CDCl_3$): 0.85–0.90 (9H, m), 1.06–1.14 (2H, m), 1.20–1.35 (30H, br, peak at $\delta$ 1.28), 1.35–1.65 (12H, m), 2.10–2.24 (4H, m), 3.60 (1H, br); GC–MS [column: HP-5MS, 5% phenylmethylsiloxane, 0.25 mm i.d.×30 m; carrier gas, He; press 52.6 kPa; temp: 50–300 °C (+15 °C/min)]: $t_R$ 21.32 min (93.3%); MS (70 eV, EI): *m*/*z*: 434 (<1) [$M^+$], 416 (24), 373 (16), 331 (47), 317 (9), 252 (46), 235 (18), 219 (90), 181 (69), 163 (48), 149 (43), 135 (85), 121 (76), 107 (72), 95 (100), 81 (88), 67 (74), 57 (90), 55 (93), 43 (95). HRMS calcd for $C_{30}H_{58}ONa$: 457.4380, found: 457.4380.

### 4.10. 17-Methyl-7-hentriacontyn-14-ol (25)

A Grignard reagent was prepared from **23** (2.60 g, 11 mmol) and Mg (300 mg, 12.5 mmol) in dry THF (10 mL) using a trace amount of $I_2$ as an initiator. A solution of **12** (1.70 g, 6 mmol) in dry THF (7 mL) was added dropwise to the stirred and ice-cooled Grignard solution at 0–10 °C. The reaction was exothermic. The mixture was left to stand overnight at room temperature. Work-up as described for **24** in 4.9 gave crude **25** (4.29 g). This was chromatographed over $SiO_2$ (35 g). Hydrocarbon by-products (0.61 g) were eluted with hexane. Further elution with hexane/EtOAc (30:1) gave 1.90 g (68%) of **25** as a colorless oil, which solidified in a deep freezer, $n_D^{21}$=1.4670; $\nu_{max}$ (film): 3373 (br m), 2925 (s), 2854 (s), 1465 (m), 1376 (m), 1036 (m), 772 (m); $\delta_H$ ($CDCl_3$): 0.84–0.92 (9H, m), 1.20–1.60 (48H, m, peak at 1.26), 2.10–2.20 (4H, m), 3.54–3.60 (1H, br); GC–MS (same conditions as those used for **24**): $t_R$ 23.32 min (82.5%) [impurities at $t_R$ 13.47 (3.0%), 14.98 (5.5%), 18.25 (2.5%) and 28.05 min (2.0%)]; MS (70 eV, EI): *m*/*z*: 402 (<1) [$M^+$], 359 (11), 252 (24), 219 (24), 205 (18), 191 (18), 177 (16), 163 (16), 149 (29), 135 (61), 121 (84), 109 (60), 95 (97), 81 (100), 69 (76), 67 (82), 57 (87), 55 (95), 43 (87). HRMS calcd for $C_{32}H_{62}ONa$: 485.4693, found: 485.4691.

### 4.11. (*Z*)-15-Methyl-7-nonacosen-12-ol (26)

Lindlar Pd catalyst (Aldrich 62145, 5% Pd on $CaCO_3$ poisoned with $Pb^{2+}$, 200 mg) was added to a solution of **24** (2.00 g, 4.6 mmol) and quinoline (one drop) in cyclohexane (25 mL). The mixture was stirred vigorously under $H_2$ (balloon) at 0–5 °C for 2 h, then filtered through Celite, and the catalyst and Celite were washed with $Et_2O$. The organic solution was washed successively with dil HCl, water, $NaHCO_3$ solution and brine, dried ($MgSO_4$), and concentrated in vacuo to give **26** (2.04 g, quant) as a colorless oil, $n_D^{19}$=1.4618; $\nu_{max}$ (film): 3350 (br m), 3005 (m), 2925 (s), 2852 (s), 1653 (w), 1465 (m), 1377 (m), 1073 (m), 1038 (m), 721 (m); $\delta_H$ ($CDCl_3$): 0.84–0.92 (9H, m), 1.98–2.08 (4H, m), 1.20–1.38 (39H, m, peak at 1.26), 1.38–1.50 (4H, m), 1.98–2.08 (4H, m), 3.52–3.60 (1H, br), 5.30–5.42 (2H, m); GC–MS (same conditions as those used for **24**): $t_R$ 21.04 min (96.9%); MS (70 eV, EI); *m*/*z*: 418 (13) [$(M-H_2O)^+$], 281 (10), 252 (14), 238 (10), 211 (11), 199 (12), 180 (17), 166 (22), 152 (15), 138 (70), 123 (26), 109 (62), 96 (100), 95 (96), 81 (90), 67 (78), 55 (91), 43 (73). HRMS calcd for $C_{30}H_{60}ONa$: 459.4536, found: 459.4536.

### 4.12. (*Z*)-17-Methyl-7-hentriaconten-14-ol (27)

Lindlar Pd catalyst (Aldrich 62145, 200 mg) was added to a solution of **25** (1.83 g, 3.9 mmol) and quinoline (one drop) in cyclohexane (25 mL). The mixture was stirred vigorously under $H_2$ (balloon) at 0–5 °C for 3 h, then filtered through Celite, and the catalyst and Celite were washed with $Et_2O$. The organic solution was washed successively with dil HCl, water, $NaHCO_3$ solution and brine, dried ($MgSO_4$), and concentrated in vacuo to give **27** (1.67 g, 91%) as a colorless oil, $n_D^{20}$=1.4608; $\nu_{max}$ (film): 3361 (br m), 3004 (m), 2925 (s), 2853 (s), 1653 (w), 1465 (m), 1377 (m), 1036 (m), 721 (m); $\delta_H$ ($CDCl_3$): 0.84–0.92 (9H, m), 1.06–1.14 (1H, m), 1.20–1.40 (43H, m, peak at 1.26), 1.40–1.50 (4H, m), 1.96–2.06 (4H, m), 3.52–3.60 (1H, br), 5.33–5.40 (2H, m); GC–MS (same conditions as those used for **24**): $t_R$ 22.93 min (80.6%) [impurities at $t_R$ 13.47 (3.1%), 14.71 (7.2%), 17.88 (3.2%) and 22.73 min (1.7%)]; MS (70 eV, EI): *m*/*z*: 446 (11) [$(M-H_2O)^+$], 281 (6), 252 (8), 207 (11), 194 (8), 180 (24), 166 (19), 152 (11), 138 (22), 123 (27), 109 (48), 96 (100), 81 (82), 69 (58), 57 (87), 55 (95), 43 (73). HRMS calcd for $C_{32}H_{60}ONa$: 487.4849, found: 487.4847.

### 4.13. (*Z*)-15-Methyl-7-nonacosene (1)

A solution of MsCl (1.00 g, 9 mmol) in dry $CH_2Cl_2$ (3 mL) was added to a stirred and ice-cooled solution of **26** (1.93 g, 4.4 mmol) in dry $CH_2Cl_2$ (6 mL) and dry $C_5H_5N$ (6 mL) at 0–5 °C. The mixture was left to stand overnight in a refrigerator. It was then diluted with ice and water, and extracted with $Et_2O$. The extract was washed with dil HCl, $NaHCO_3$ solution and brine, dried ($MgSO_4$), and concentrated in vacuo to give **28** (2.06 g, quant) as a colorless oil, $\nu_{max}$ (film): 3004 (w), 2925 (s), 2854 (s), 1653 (w), 1465 (m), 1358 (s), 1175 (s), 905 (s). A solution of **28** (2.06 g, 4.4 mmol) in dry THF (4 mL) was added dropwise to a stirred and ice-cooled suspension of $LiAlH_4$ (500 mg, 13 mmol) in dry THF (15 mL). The mixture was stirred and heated at 60 °C for 1 h. Subsequently, the excess $LiAlH_4$ was destroyed by dropwise addition of water to the stirred and ice-cooled mixture. It was then acidified with dil HCl and ice, and extracted with hexane. The hexane solution was washed with water and brine, dried ($MgSO_4$), and concentrated in vacuo. The residue (1.68 g) was chromatographed over $SiO_2$ (15 g). Elution with hexane gave **1** (1.12 g, 60%, two steps) as a colorless oil, $n_D^{22}$=1.4582; $\nu_{max}$ (film): 3005 (m), 2955 (s), 2926 (s), 2853 (s), 1655 (w), 1465 (m), 1403 (w), 1377 (m), 1304 (w), 1110 (w), 966 (w), 888 (w), 856 (w), 722 (m); $\delta_H$ ($CDCl_3$): 0.83 (3H, d, *J* 6.4), 0.880 (3H, t, *J* 6.0), 0.883 (3H, t, *J* 7.2), 1.04–1.12 (2H, m), 1.20–1.40 (43H, m, peak at 1.26), 1.97–2.04 (4H, m), 5.31–5.39 (2H, m); $\delta_C$ ($CDCl_3$): 14.125, 14.144, 19.73, 22.69, 22.72, 27.08, 27.12, 27.24, 29.21, 29.38, 29.40, 29.65, 29.70, 29.74, 29.77, 29.81, 29.94, 30.07, 31.81, 31.96, 32.77, 37.11, 124.91, 130.37 (signal strength 124.91/130.37=95.1:4.9); GC–MS (same conditions as those used for **24**): $t_R$ 19.70 min (97.1%); MS (70 eV, EI): *m*/*z*: 420 (5) [$M^+$], 238 (25), 223 (23), 222 (22), 210 (18), 196 (4), 182 (15), 167 (7), 153 (11), 139 (17), 125 (33), 111 (67), 97 (99), 83 (82), 69 (84), 57 (100), 55 (74), 43 (64). HRMS calcd for $C_{30}H_{60}$: 420.4695, found: 420.4712.

### 4.14. (*Z*)-17-Methyl-7-hentriacontene (2)

A solution of MsCl (1.03 g, 9 mmol) in dry $CH_2Cl_2$ (3 mL) was added to a stirred and ice-cooled solution of **27** (1.49 g, 3.2 mmol) in dry $CH_2Cl_2$ (6 mL) and dry $C_5H_5N$ (6 mL) at 0–5 °C. The mixture was left to stand overnight in a refrigerator. It was then worked up in the same manner as described for **28** in 4.13 to give **29** (1.70 g, quant) as a colorless oil, $\nu_{max}$ (film): 3003 (m), 2925 (s), 2854 (s), 1650 (w), 1465 (m), 1439 (m), 1359 (s), 1176 (s), 905 (s). A solution of **29** (1.65 g, 3.2 mmol) in dry THF (4 mL) was added dropwise to a stirred and ice-cooled suspension of $LiAlH_4$ (500 mg, 13 mmol) in dry THF (15 mL). The mixture was stirred and heated at 60 °C for 1 h. Subsequent work-up as described for **1** in 4.13 gave crude **2** (1.32 g), which was chromatographed over $SiO_2$ (12 g). Elution with hexane gave **2** (653 mg, 46%, two steps) as a colorless oil, $n_D^{22}$=1.4580; $\nu_{max}$ (film): 3005 (m), 2955 (s), 2925 (s), 2853 (s), 1654 (w), 1465 (m), 1403 (w), 1377 (m), 1304 (w), 1110 (w), 966 (w), 889 (w), 855 (w), 721 (m); $\delta_H$ ($CDCl_3$) 0.83 (3H, d, *J* 6.8), 0.88 (6H, t, *J* 6.8), 1.04–1.12 (2H, m), 1.20–1.40 (47H, m, peak at 1.26), 1.90–2.06 (4H, m), 5.30–5.40 (2H, m); $\delta_C$ ($CDCl_3$): 14.13, 19.73, 22.68, 22.71, 27.11, 27.23, 29.01, 29.33, 29.39, 29.59, 29.69, 29.73, 29.76, 29.78, 30.04, 31.81, 31.95, 32.76, 37.11, 129.90, 130.37 (signal strength 129.90/130.37=93.8:6.2); GC–MS (same conditions as those used for **24**): $t_R$ 21.05 min (94.3%) [impurity at $t_R$ 17.88 min (3.6%)]; MS (70 eV, EI): *m*/*z*: 448 (4) [$M^+$], 266 (11), 250 (12), 238 (18), 223 (12), 210 (12), 195 (4), 182 (8), 167 (7), 153 (10), 139 (14), 125 (29), 111 (59), 97 (88), 83 (76), 57 (100), 55 (71), 43 (62). HRMS calcd for $C_{32}H_{64}$: 448.5008, found: 448.5018.

### 4.15. 2,6-Dimethyl-2-hexacosen-8-ol (31)

A Grignard reagent was prepared from a solution of 1-bromooctadecane (25.0 g, 75 mmol) in dry THF (70 mL), Mg (2.0 g, 83 mmol) and a trace amount of $I_2$ in the usual manner. A solution of **30** (7.4 g, 48 mmol) in dry THF (30 mL) was added dropwise over 20 min to the stirred and ice-cooled solution of the Grignard reagent. After the addition, the mixture was left to stand overnight at room temperature. Then the mixture was quenched with ice and dil HCl, and extracted with hexane. The hexane solution was washed with water, $NaHCO_3$ solution and brine, dried ($MgSO_4$), and concentrated in vacuo. The residue (29.8 g) was chromatographed over $SiO_2$ (150 g). Elution with hexane gave hexatriacontane (6.35 g). Further elution with hexane/EtOAc (20:1) gave **31** (18.3 g, 96%) as a waxy solid, mp 38–39 °C; $\nu_{max}$ (film): 3357 (br m), 2910 (s), 2849 (s), 1651 (w), 1465 (m), 1377 (m), 1119 (m), 938 (w), 720 (m); $\delta_H$ ($CDCl_3$): 0.85–0.93 (6H, m, quint-like), 1.20–1.32 (36H, br, peak at 1.26), 1.35–1.50 (4H, m), 1.61 (3H, s), 1.68 (3H, s), 1.92–2.04 (2H, m), 3.64–3.74 (1H, m), 5.10 (1H, t, *J* 7). HRMS calcd for $C_{28}H_{56}O$: 408.4331, found: 408.4328.

### 4.16. 2,6-Dimethyl-2-tetracosen-8-ol (32)

A Grignard reagent was prepared from 1-bromohexadecane (23.0 g, 75 mmol), Mg (2.0 g, 83 mmol) and a trace amount of $I_2$ in dry THF (70 mL). A solution of **30** (7.4 g, 48 mmol) in dry THF (30 mL) was added to the Grignard reagent. Work-up of the reaction mixture in the same manner as described for **31** in 4.15 gave crude **32** (29.7 g), which was chromatographed over $SiO_2$ (150 g). After washing the column with hexane, elution with hexane/EtOAc (30:1) gave **32** (17.4 g, 92%) as a waxy solid, mp 27–29 °C; $\nu_{max}$ (film): 3357 (br m), 2955 (s), 2913 (s), 2849 (s), 1465 (m), 1377 (m), 1118 (m), 924 (w), 839 (w), 720 (m); $\delta_H$ ($CDCl_3$): 0.85–0.93 (6H, m, quint-like), 1.20–1.32 (31H, br, peak at 1.26), 1.35–1.50 (4H, m), 1.61 (3H, s), 1.68 (3H, s), 1.90–2.50 (2H, m), 3.64–3.74 (1H, m), 5.11 (1H, t, *J* 7). HRMS calcd for $C_{26}H_{52}O$ 380.4018, found: 380.4008.

### 4.17. 2,6-Dimethyl-2-hexacosene (35)

A solution of MsCl (10.0 g, 87 mmol) in dry $CH_2Cl_2$ (10 mL) was added dropwise to a stirred and ice-cooled solution of **31** (18.0 g, 44 mmol) in $C_5H_5N$ (80 mL) containing DMAP (50 mg). The mixture was stirred at 0–5 °C for 30 min, and left to stand overnight in a refrigerator. It was then diluted with ice and water, and extracted with $Et_2O$. The extract was washed with dil HCl, $NaHCO_3$ solution and brine, dried ($MgSO_4$), and concentrated in vacuo to give **33** (21.4 g, 99%) as a colorless oil, $\nu_{max}$ (film): 2925 (s), 2853 (s), 1625 (w), 1465 (m), 1354 (m), 1175 (s), 1119 (w), 970 (m), 905 (s). This was employed in the next step without further purification. A solution of **33** (21.4 g, 44 mmol) in dry THF (30 mL) was added dropwise to a stirred and ice-cooled suspension of $LiAlH_4$ (3.4 g, 89 mmol) in dry THF (80 mL) at 5–15 °C. The mixture was stirred at 0–5 °C for 1 h, and then stirred and heated under reflux for 1 h. After cooling, water was slowly added to the stirred and ice-cooled mixture to destroy the excess $LiAlH_4$. The mixture was then acidified with dil HCl and ice, and extracted with $Et_2O$. The $Et_2O$ extract was washed with water, $NaHCO_3$ solution and brine, dried ($MgSO_4$), and concentrated in vacuo. The residue (17.1 g) was chromatographed over $SiO_2$ (80 g). Elution with hexane gave **35** (15.0 g, 87%) as a colorless oil, $n_D^{25}$=1.4565; $\nu_{max}$ (film): 2956 (s), 2925 (s), 2853 (s), 1465 (m), 1377 (m), 826 (w), 721 (m); $\delta_H$ ($CDCl_3$): 0.85 (3H, d, *J* 6.4), 0.88 (3H, t, *J* 6.8), 1.05–1.16 (2H, m), 1.18–1.45 (39H, m, peak at 1.26), 1.60 (3H, s), 1.68 (3H, s), 1.86–2.04 (2H, m), 5.10 (1H, t, *J* 6); GC–MS (same conditions as those used for **24**): $t_R$ 18.78 min (97.2%); MS (70 eV, EI): *m*/*z*: 392 (14) [$M^+$], 322 (7), 306 (7), 126 (39), 111 (46), 97 (37), 83 (43), 69 (100), 57 (73), 56 (56), 43 (49). HRMS calcd for $C_{26}H_{56}$: 392.4382, found: 392.4363.

### 4.18. 2,6-Dimethyl-2-tetracosene (36)

In the same manner as described for **33** in 4.17, MsCl (10.0 g, 87 mmol), **32** (17.0 g, 43 mmol), DMAP (50 mg) and $C_5H_5N$ (80 mL) gave **34** (20.3 g, 99%) as a colorless oil, $\nu_{max}$ (film): 2925 (s), 2853 (s), 1628 (w), 1465 (m), 1355 (m), 1175 (s), 1119 (w), 970 (m), 905 (s). This was employed in the next step without further purification.

In the same manner as described for **35** in 4.17, **34** (20.3 g, 43 mmol) and $LiAlH_4$ (3.3 g, 87 mmol) in dry THF (110 mL) yielded **36** (13.3 g, 85%) as a colorless oil after chromatographic purification over $SiO_2$ (80 g). Properties of **36**: $n_D^{25}$=1.4558; $\nu_{max}$ (film): 2956 (s), 2925 (s), 2853 (s), 1465 (m), 1377 (m), 826 (w), 721 (m); $\delta_H$ ($CDCl_3$): 0.85 (3H, d, *J* 6.4), 0.88 (3H, t, *J* 6.4), 1.04–1.16 (2H, m), 1.18–1.45 (35H, br s, peak at 1.26), 1.60 (3H, s), 1.68 (3H, s), 1.86–2.04 (2H, m), 5.10 (1H, t, *J* 6); GC–MS (same conditions as those used for **24**): $t_R$ 17.79 min (93.0%); MS (70 eV, EI): *m*/*z*: 364 (13) [$M^+$], 294 (6), 278 (5), 265 (4), 238 (3), 153 (3), 139 (5), 126 (36), 111 (45), 97 (36), 83 (43), 69 (100), 57 (73), 56 (66), 43 (50). HRMS calcd for $C_{26}H_{52}$: 364.4069. found: 364.4055.

### 4.19. (*E*)-2,6-Dimethyl-2-hexacosenal (37)

$SeO_2$ (0.27 g, 2.4 mmol) and *t*-BuOOH (70% aqueous solution, 8 mL, 59 mmol) were added to a stirred solution of **35** (7.5 g, 19 mmol) in $CH_2Cl_2$ (75 mL). The mixture was stirred at room temperature (24 °C) for 2 d. The clear solution was then washed with dil $Na_2S_2O_3$ solution to destroy excess *t*-BuOOH and $SeO_2$, and the $CH_2Cl_2$ layer was separated. The aqueous layer was extracted with $CH_2Cl_2$. The combined $CH_2Cl_2$ solution was dried ($MgSO_4$), and concentrated in vacuo. The residue (8.00 g) was chromatographed over $SiO_2$ (80 g). Elution with hexane/EtOAc (30:1) gave **37** (2.1 g, 27%) as a waxy solid, mp 37–39 °C. Further elution with hexane/EtOAc (5:1) gave 2.74 g of a complex mixture of alcohols. Properties of **37**: $\nu_{max}$ (film): 2913 (s), 2850 (s), 2708 (w), 1693 (s), 1645 (m), 1466 (s), 1378 (m); 1243 (w), 1075 (w), 1002 (w), 721 (m); $\delta_H$ ($CDCl_3$): 0.88 (3H, d, *J* 6.8), 0.90 (3H, d, *J* 6.4), 1.10–1.20 (2H, m), 1.20–1.40 (37H, br, peak at 1.26), 1.40–1.55 (2H, m), 1.75 (3H, d, *J* 1.4), 2.30–2.50 (2H, m), 6.49 (1H, t, *J* 7), 9.39 (1H, s); GC–MS (same conditions as those used for **24**): $t_R$ 20.45 min (88.5%); MS (70 eV, EI): *m*/*z*: 406 (6) [$M^+$], 388 (5), 375 (7), 348 (4), 325 (2), 207 (2), 149 (4), 126 (19), 111 (14), 97 (58), 84 (100), 71 (47), 57 (52), 55 (50), 43 (64). HRMS calcd for $C_{28}H_{54}O$: 406.4175, found: 406.4165.

### 4.20. (*E*)-2,6-Dimethyl-2-tetracosenal (38)

In the same manner as described for **37** in 4.19, $SeO_2$ (0.22 g, 2.0 mmol), *t*-BuOOH (70% aqueous solution, 8 mL, 59 mmol) and **36** (6.6 g, 18 mmol) in $CH_2Cl_2$ (75 mL) gave 8.0 g of the crude product, which was chromatographed over $SiO_2$ (75 g). Elution with hexane/EtOAc (30:1) gave **38** (2.48 g, 36%) as a colorless oil, $n_D^{24}$=1.4612; $\nu_{max}$ (film): 2924 (s), 2853 (s), 2706 (w), 1693 (s), 1646 (m), 1466 (m), 1378 (m), 1242 (w), 1070 (w), 1003 (w), 721 (m); $\delta_H$ ($CDCl_3$): 0.88 (3H, t, *J* 6.8), 0.90 (3H, d, *J* 6.4), 1.10–1.20 (2H, m), 1.20–1.40 (33H, br, peak at 1.26), 1.40–1.55 (2H, m), 1.75 (3H, s), 2.30–2.45 (2H, m), 6.47 (1H, t, *J* 7), 9.39 (1H, s); GC–MS (same conditions as those used for **24**): $t_R$ 19.21 min (90.6%); MS (70 eV, EI): *m*/*z*: 378 (5) [$M^+$], 360 (4), 347 (7), 320 (5), 139 (5), 126 (18), 111 (15), 97 (59), 84 (100), 71 (45), 57 (44), 55 (52), 43 (64). HRMS calcd for $C_{26}H_{50}O$: 378.3862, found: 378.3869.

### 4.21. (*E*)-3,7-Dimethyl-1,3-heptacosadiene (39)

A solution of *n*-BuLi in hexane (1.6 M, 8 mL, 10.8 mmol) was added to a stirred and cooled suspension of $Ph_3P(Me)Br$ (4.5 g, 12.5 mmol) in dry THF (30 mL) at −60 to −50 °C under argon. The mixture was allowed to warm up to -5 °C to give an orange-colored solution of the ylide. A solution of **37** (2.04 g, 5 mmol) in dry THF (10 mL) was added to the stirred and cooled Wittig reagent over 5 min at −60 °C. The mixture was stirred at −70 °C for 30 min and at room temperature for 1 h. It was then diluted with ice-water, and extracted with hexane/$Et_2O$. The extract was washed with water and brine, dried ($MgSO_4$), and filtered. Silica gel (10 g) was added to the filtrate, and the mixture was concentrated in vacuo. The residual slurry was transferred with hexane to the top of a column of $SiO_2$ (40 g) in hexane. Elution with hexane gave **39** (0.91 g, 45%) as a colorless oil, $n_D^{24}$=1.4684; $\nu_{max}$ (film): 3088 (w), 2925 (s), 2852 (s), 1642 (w), 1606 (w), 1466 (m), 1377 (m), 1300 (w), 1081 (w), 987 (m), 891 (m), 721 (m), $\delta_H$ ($CDCl_3$): 0.87 (3H, d, *J* 7.2), 0.88 (3H, t, *J* 7.2), 1.08–1.15 (2H, m), 1.15–1.35 (40H, br, peak at 1.26), 1.35–1.45 (2H, m), 2.05–2.20 (2H, m), 4.91 (1H, d, *J* 11), 5.06 (1H, d, *J* 17), 5.48 (1H, t, *J* 7), 6.36 (1H, dd, *J* 11, 17); GC–MS (same conditions as those used for **24**): $t_R$ 19.62 min (93.0%); MS (70 eV, EI): *m*/*z*: 404 (24) [$M^+$], 389 (4), 375 (16), 334 (6), 137 (10), 123 (100), 109 (20), 95 (72), 81 (69), 80 (65), 69 (26), 57 (39), 55 (32), 43 (48), 41 (29). HRMS calcd for $C_{29}H_{56}$: 404.4382, found: 404.4377.

### 4.22. (6*EZ*,8*E*)-8,12-Dimethyl-6,8-triacontadiene (40)

In the same manner as described for **39** in 4.21, a Wittig reagent was prepared form $Ph_3P[(CH_2)_5Me]Br$ (5.1 g, 12 mmol) and *n*-BuLi (1.6 M, 8 mL, 12.8 mmol) in dry THF (30 mL) under argon. A solution of **38** (2.4 g, 6.4 mmol) in dry THF (10 mL) was added to the cooled Wittig reagent. Subsequent work-up including $SiO_2$ (50 g) chromatography gave **40** (1.43 g, 51%) as a colorless oil, $n_D^{26}$=1.4680; $\nu_{max}$ (film): 2956 (s), 2925 (s), 2852 (s), 1650 (w), 1465 (m), 1377 (m), 1305 (w), 962 (m), 721 (m); $\delta_H$ ($CDCl_3$): 0.82–0.94 (9H, m), 1.14–1.45 (43H, br, peak at 1.26), 1.72 (1.8H, s), 1.76 (1.2H, s), 1.94–2.16 (3.4H, m), 2.18–2.26 (0.6H, m), 5.22–5.42 (1.5H, m), 5.50–5.60 (0.5H, m), 5.75–5.82 (0.5H, d, *J* 8) 6.02–6.06 (0.5H, d, *J* 16); $\delta_C$ ($CDCl_3$): 12.41, 14.08, 14.13, 16.68, 19.61, 22.60, 22.72, 25.66, 25.71, 27.05, 27.09, 29.40, 29.47, 29.73, 30.05, 31.56, 31.60, 31.96, 32.49, 32.89, 36.88, 36.94, 36.98, 37.01, 127.53, 129.63, 129.91, 130.87, 132.39, 132.84, 132.29, 134.78; GC–MS (same conditions as those used for **24**): $t_R$ 20.97 (28.0%), 21.63 min (66.8%) (total 94.8%. These are the *E*/*Z*-isomers); MS of **40** with $t_R$=20.97 min (70 eV, EI): *m*/*z*: 446 (55) [$M^+$], 347 (11), 193 (18), 165 (18), 151 (13), 137 (14), 123 (34), 109 (38), 95 (68), 81 (100), 57 (61), 43 (75); MS of **40** with $t_R$=21.63 min (70 eV, EI): *m*/*z*: 446 (22) [$M^+$], 431 (4), 375 (3), 361 (14), 347 (9), 320 (4), 306 (7), 193 (29), 165 (32), 138 (26), 109 (35), 95 (73), 81 (100), 57 (53), 43 (66). HRMS calcd for $C_{32}H_{62}$: 446.4852, found: 446.4835.

### 4.23. 3,7-Dimethylheptacosane (3)

10% Pd–C (150 mg) was added to a solution of **39** (867 mg, 2.1 mmol) in hexane (8 mL). The suspension was stirred vigorously under $H_2$ (balloon) for 1.5 h at room temperature. Then the mixture was transferred to the top of a column of $SiO_2$ (5 g) in hexane. Elution with hexane gave **3** (867 mg, 99%) as a colorless oil, $n_D^{24}$=1.4510; $\nu_{max}$ (film): 2957 (s), 2925 (s), 2852 (s), 1464 (m), 1377 (m), 1304 (w), 1153 (w), 1077 (w), 1011 (w), 967 (w), 890 (w), 769 (w), 721 (m); $\delta_H$ ($CDCl_3$): 0.82–0.90 (12H, m), 1.00–1.16 (4H, m), 1.16–1.44 (44H, br, peak at 1.32); $\delta_C$ ($CDCl_3$): 11.42, 14.13, 19.23, 19.29, 19.72, 19.78, 22.73, 23.08, 24.54, 27.14, 29.41, 29.51, 29.61, 29.74, 30.08, 31.63, 31.98, 32.80, 32.83, 36.84, 37.00, 37.04, 37.12, 37.21, 37.45, 37.50; GC–MS (same conditions as those used for **24**): $t_R$ 19.15 min (93.9%); MS (70 eV, EI): *m*/*z*: 407 (<1) [$(M-H)^+$], 393 (3), 379 (9), 309 (13), 308 (11), 280 (3), 253 (1), 239 (2), 225 (2), 211 (3), 197 (3), 183 (3), 169 (4), 155 (4), 141 (6), 127 (28), 113 (11), 99 (14), 97 (21), 85 (57), 71 (80), 57 (100), 43 (59), 41 (31). HRMS calcd for $C_{29}H_{60}$: 408.4695, found: 408.4694.

### 4.24. 8,12-Dimethyltriacontane (4)

In the same manner as described for **3** in 4.23, **40** (1.32 g, 3.5 mmol) in hexane (10 mL) was hydrogenated over 10% Pd–C (150 mg) to give **4** (1.28 g, 96%) as a colorless oil, $n_D^{27}$=1.4514; $\nu_{max}$ (film): 2925 (s), 2849 (s), 1465 (s), 1377 (m), 1304 (w), 1154 (w), 1077 (w), 934 (w), 891 (w), 721 (m), $\delta_H$ ($CDCl_3$): 0.84 (6H, d, *J* 6.4), 0.88 (6H, t, *J* 6.8), 1.02–1.12 (4H, m), 1.20–1.40 (50H, br, peak at 1.26); $\delta_C$ ($CDCl_3$): 14.13, 19.72, 19.79, 22.73, 24.50, 27.14, 29.41, 29.45, 29.71, 29.74, 30.08, 31.97, 32.79, 32.81, 37.10, 37.20, 37.42, 37.48; GC–MS (same conditions as those used for **24**): $t_R$ 20.71 min (93.3%); MS (70 eV, EI): *m*/*z*: 450 (<1) [$M^+$], 435 (4), 351 (14), 280 (7), 197 (15), 183 (3), 169 (5), 155 (5), 141 (7), 126 (16), 113 (14), 99 (16), 97 (16), 85 (59), 71 (79), 57 (100), 43 (65), 41 (27). HRMS calcd for $C_{32}H_{66}$: 450.5165, found; 450.5154.

### 4.25. 2,6-Dimethyl-2-tridecene (41)

In the same manner as described for **10** in 4.2, **9** (12.5 g, 40 mmol) was treated with $n$-$C_5H_{11}MgBr$ prepared from $n$-$C_5H_{11}Br$ (8.8 g, 80 mmol) and Mg (2.0 g, 83 mmol) in THF (50 mL) in the presence of $Li_2CuCl_4$ in THF (0.1 M, 3 mL, 0.3 mmol) to give 9.02 g of crude **40** as a colorless oil, $\nu_{max}$ (film): 2959 (s), 2925 (s), 2855 (s), 1459 (m), 1377 (m), 1057 (w), 984 (w), 828 (w), 723 (w). The oily **41** was used in the next step without further purification.

### 4.26. 2,6-Dimethyl-2-octadecene (42)

In the same manner as described for **10** in 4.2, **9** (12.5 g, 40 mmol) was treated with $n$-$C_{10}H_{21}MgBr$ prepared from $n$-$C_{10}H_{21}Br$ (15.5 g, 70 mmol) and Mg (1.8 g, 75 mmol) in THF (65 mL) in the presence of $Li_2CuCl_4$ in THF (0.1 M, 3 mL, 0.3 mmol) to give 17.2 g of crude **42** as a colorless oil, $\nu_{max}$ (film): 2597 (s), 2925 (s), 2854 (s), 1466 (m), 1377 (m), 1058 (w), 826 (m), 721 (w). The oily **42** was used in the next step without further purification.

### 4.27. 2,6-Dimethyltridecane-2,3-diol (43)

In the same manner as described for **11** in 4.3, crude **41** (9.02 g, 40 mmol) in *t*-BuOH (80 mL), acetone (180 mL) and $H_2O$ (44 mL) was oxidized with a solution of $OsO_4$ (1% in *t*-BuOH, 15 mL, 150 mg) and *N*-methylmorpholine *N*-oxide (50% NMO in $H_2O$, 30 g, 120 mmol). The mixture was stirred for 3 d at room temperature, and worked up to give 6.93 g (71%) of **43** as a slightly tan-colored oil, $n_D^{25}$=1.4490; $\nu_{max}$ (film): 3405 (br. m), 2956 (s), 2925 (s), 2855 (s), 1465 (m), 1378 (m), 1165 (m), 1073 (m); $\delta_H$ ($CDCl_3$): 0.84–0.94 (6H, m), 1.06–1.20 (2H, m), 1.16 (3H, s), 1.21 (3H, s), 1.20–1.65 (15H, m, peak at 1.26) 2.10–2.22 (1H, br), 2.25–2.36 (1H, br), 3.28–3.36 (1H, m). HRMS calcd for $C_{15}H_{32}O_2$: 244.2402, found: 244.2405.

### 4.28. 2,6-Dimethyloctadecane-2,3-diol (44)

In the same manner as described for **43** in 4.27, **42** (17.2 g, 40 mmol) was oxidized with $OsO_4$ and NMO to give 12.5 g (99%) of **44**, a portion of which crystallized as small needles, mp 47–48 °C; $\nu_{max}$, (Nujol): 3410 (br s), 1331 (m), 1085 (s), 966 (m), 719 (m); $\delta_H$ ($CDCl_3$): 0.85–0.92 (6H, m), 1.08–1.18 (2H, m), 1.16 (3H, s), 1.21 (3H, s), 1.20–1.46 (25H, m, peak at 1.26), 2.03 (1H, s), 2.14–2.20 (1H, m), 3.30–3.70 (1H, m). HRMS calcd for $C_{20}H_{42}O_2$: 314.3185, found: 314.3188.

### 4.29. 4-Methylundecanal (45)

In the same manner as described for **12** in 4.4, **43** (6.93 g, 28.4 mmol) was treated with $HIO_4 \cdot 2H_2O$ (6.84 g, 30 mmol) in THF (65 mL) to give 4.37 g (84%) of **45** after $SiO_2$ (50 g) chromatography and elution with hexane/EtOAc (30:1). The aldehyde **45** was obtained as a colorless oil, $n_D^{24}$=1.4430; $\nu_{max}$ (film): 2957 (s), 2926 (s), 2855 (s), 2713 (m), 1728 (s), 1465 (m), 1379 (m), 1037 (w), 723 (w); $\delta_H$ ($CDCl_3$): 0.87 (3H, d, *J* 6), 0.88 (3H, t, *J* 6.4), 1.08–1.18 (1H, m), 1.20–1.36 (11H, br, peak at 1.26), 1.38–1.49 (2H, m), 1.60–1.72 (1H, m), 2.34–2.50 (2H, m), 9.77 (1H, t *J* 2); GC–MS (same conditions as those used for **12**): $t_R$ 9.75 min (93.4%); MS (70 eV, EI): *m*/*z*: 183 (<1) [$(M-1)^+$], 140 (20), 125 (22), 112 (23), 95 (29), 85 (54), 82 (36), 71 (35), 69 (46), 57 (91), 56 (100), 43 (59), 41 (64). HRMS calcd for $C_{12}H_{24}O$: 184.1827, found: 184.1827.

### 4.30. 4-Methylhexadecanal (46)

In the same manner as described for **45** in 4.29, **44** (12.5 g, 40 mmol) was treated with $HIO_4{\cdot}2H_2O$ (10.0 g, 44 mmol) in THF (100 mL) to give 8.61 g (85%) of **46** after $SiO_2$ (60 g) chromatography and elution with hexane/EtOAc (30:1). The aldehyde **46** was obtained as a colorless oil, $n_D^{25}$=1.4426; $\nu_{max}$ (film): 2955 (s), 2925 (s), 2853 (s), 2711 (w), 1729 (s), 1466 (m), 1379 (w), 1040 (w), 721 (w); $\delta_H$ ($CDCl_3$): 0.87 (3H, d, *J* 6.4), 0.88 (3H, t, *J* 6.4), 1.08–1.18 (1H, m), 1.20–1.35 (21 H, br, peak at 1.26), 1.38–1.48 (2H, m), 1.62–1.72 (1H, m), 2.34–2.50 (2H, m), 9.77 (1H, t, *J* 2); GC–MS (same conditions as those used for **12**): $t_R$ 13.75 min (87.6%); MS (70 eV, EI): *m*/*z*: 254 (<1) [$M^+$], 210 (20), 195 (8), 182 (17), 154 (15), 139 (3), 125 (8), 111 (23), 97 (33), 95 (44), 85 (64), 82 (56), 71 (41), 69 (54), 57 (100), 56 (81), 55 (58), 43 (61), 42 (56). HRMS calcd for $C_{17}H_{14}O$: 254.2610, found: 254.2606.

### 4.31. 4-Methyl-1-undecanol (47)

A solution of **45** (4.30 g, 23 mmol) in dry THF (5 mL) was added dropwise to a stirred and ice-cooled suspension of $LiAlH_4$ (600 mg, 16 mmol) in dry THF (40 mL) at 5–10 °C. After stirring for 1 h at 0–5 °C, the excess $LiAlH_4$ was destroyed by slowly adding water with stirring and ice-cooling. The mixture was acidified with dil HCl and ice, and extracted with hexane/$Et_2O$. The extract was washed successively with water, $NaHCO_3$ solution and brine, dried ($MgSO_4$), and concentrated in vacuo. The residue (8.82 g) was chromatographed over $SiO_2$ (50 g). Elution with hexane/EtOAc (10:1–2:1) gave 3.98 g (91%) of **47** as a colorless oil, $n_D^{24}$=1.4421; $\nu_{max}$ (film): 3330 (br m), 2955 (s), 2925 (s), 2855 (s), 1465 (w), 1378 (m), 1058 (m); $\delta_H$ ($CDCl_3$): 0.87 (3H, d, *J* 6.4), 0.88 (3H, t, *J* 6.4), 1.06–1.20 (2H, m), 1.20–1.38 (12H, br, peak at 1.26), 1.30–1.48 (2H, m), 1.48–1.66 (2H, m), 3.62 (2H, t, *J* 6.4); GC–MS (same conditions as those used for **12**): $t_R$ 11.08 min (97.2%); MS (70 eV, EI): *m*/*z*: 185 (<1) [$(M\text{-}1)^+$], 140 (24), 125 (31), 112 (19), 97 (27), 84 (45), 69 (100), 56 (64), 41 (55). HRMS calcd for $C_{12}H_{26}O$: 186.1984, found: 186.1975.

### 4.32. 4-Methyl-1-hexadecanol (48)

In the same manner as described for **47** in 4.31, **46** (8.50 g, 33.5 mmol) was reduced with $LiAlH_4$ (1.00 g, 26 mmol) in dry THF (110 mL) to give 7.27 g (85%) of **48** after $SiO_2$ (80 g) chromatography and elution with hexane/EtOAc (10:1–2:1). The alcohol **48** was obtained as a colorless oil, $n_D^{25}$=1.4495; $\nu_{max}$ (film): 3330 (br m), 2955 (s), 2925 (s), 2853 (s), 1466 (m), 1377 (m), 1058 (m); $\delta_H$ ($CDCl_3$): 0.86 (3H, d, *J* 6.4), 0.88 (3H, t, *J* 6.4), 1.08–1.20 (2H, m), 1.20–1.45 (23H, br, peak at 1.26), 1.45–1.65 (3H, m), 3.62 (2H, t, *J* 6.8); GC–MS (same conditions as those used for **12**): $t_R$ 14.13 min (85.2%); MS (70 eV, EI): *m*/*z*: 255 (<1) [$(M-1)^+$], 210 (27), 195 (13), 182 (16), 154 (15), 139 (5), 125 (13), 111 (28), 97 (47), 84 (37), 69 (100), 57 (65), 41 (49). HRMS calcd for $C_{17}H_{36}O$: 256.2766, found: 256.2766.

### 4.33. 4-Methylundecyl iodide (51)

In the same manner as described for **20** in 4.7, **47** (3.30 g, 18 mmol) and TsCl (4.75 g, 25 mmol) yielded 6.6 g (quant.) of **49** as a colorless oil, $\nu_{max}$ (film): 2956 (s), 2925 (s), 2855 (s), 1598 (m), 1466 (m), 1363 (s), 1189 (s), 1177 (s), 1098 (m), 966 (m), 918 (m), 814 (m), 664 (m), 574 (m), 555 (m). NaI (7 g, 39 mmol) was added to a stirred solution of **49** (6.6 g, 18 mmol) in DMF (40 mL). After the exothermic reaction, the mixture was stirred and heated at 80 °C for 1 h. It was then diluted with ice-water, and extracted with hexane. The extract was washed with dil $Na_2S_2O_3$ solution and brine, dried ($MgSO_4$), and concentrated in vacuo to give 4.54 g of an oil. This was chromatographed over $SiO_2$ (20 g). Elution with hexane gave 3.32 g (66%) of **51** as an oil, $n_D^{25}$=1.4712; $\nu_{max}$ (film): 2955 (s), 2925 (s), 2853 (s), 1463 (m), 1378 (m), 1231 (m) 1173 (m), 723 (m); $\delta_H$ ($CDCl_3$): 0.86 (3H, d, *J* 6.4), 0.88 (3H, t, *J* 6.8), 1.06–1.14 (1H, m), 1.14–1.34 (12H, br, peak at 1.26), 1.34–1.48 (2H, m), 1.70–1.90 (2H, m), 3.17 (2H, dt, *J* 3, 6.8); GC–MS (same conditions as those used for **12**): $t_R$ 13.24 min (73.5%); MS (70 eV, EI): *m*/*z*: 281 (<1) [$(M\text{-}1)^+$], 169 (17), 155 (15), 127 (6), 113 (11), 99 (17), 85 (56), 71 (81), 57 (100), 43 (40). HRMS calcd for $C_{12}H_{25}I$: 296.1001, found: 296.1021.

### 4.34. 4-Methylhexadecyl iodide (52)

In the same manner as described for **51** in 4.33, **48** (7.02 g, 27 mmol) and TsCl (6.0 g, 32 mmol) in $C_5H_5N$ (30 mL) gave 10.9 g (quant.) of **50** as a colorless oil, $\nu_{max}$ (film): 2955 (s), 2925 (s), 2853 (s), 1599 (w), 1466 (m), 1365 (s), 1189 (s), 1177 (s), 1098 (m), 968 (m), 918 (m), 814 (m), 664 (m), 555 (m). Then treatment of **50** (10.9 g, 27 mmol) with NaI (10.0 g, 67 mmol) in DMF (50 mL) afforded 6.07 g (80%) of **52** as an oil, $n_D^{24}$=1.4792; $\nu_{max}$ (film): 2955 (s), 2924 (s), 2852 (s), 1465 (m), 1378 (m), 1232 (w), 1173 (m), 721 (m); $\delta_H$ ($CDCl_3$): 0.86 (3H, d, *J* 6.4), 0.88 (3H, t, *J* 6.8), 1.06–1.14 (1H, m), 1.15–1.34 (22H, br, peak at 1.26), 1.34–1.46 (2H, m), 1.72–1.90 (2H, m), 3.17 (2H, dt, *J* 3, 6.8): GC–MS (same conditions as those used for **12**): $t_R$ 15.39 min (97.8%); MS (70 eV, EI): *m*/*z*: 366 (<1) [$M^+$], 239 (21), 197 (4), 183 (5), 169 (7), 155 (18), 141 (8), 127 (12), 113 (16), 99 (25), 85 (75), 71 (92), 57 (100), 43 (53). HRMS calcd for $C_{17}H_{35}I$: 366.1783, found: 366.1795.

### 4.35. Methyl 8-methyl-3-oxoicosanoate (54)

The dianion of methyl acetoacetate (**53**) was prepared as follows. A solution of **53** (2.90 g, 25 mmol) in dry THF (10 mL) was added dropwise to a stirred and cooled (dry ice-acetone) suspension of 60% NaH (1.20 g, 30 mmol) in dry THF (40 mL) at −10 to 0 °C under argon. After the disappearance of solid NaH with evolution of $H_2$ to generate the monoanion of **53**, the stirred mixture was cooled at −60 °C and a solution of *n*-BuLi in hexane (1.6 M, 17 mL, 27 mmol) was added slowly via a syringe over 5 min (exothermic) to give a yellow solution of the dianion of **53**. The mixture was stirred for 1 h at −20 to −10 °C. Subsequently a solution of **52** (5.97 g, 17 mmol) in dry THF (10 mL) was added dropwise via a syringe to the stirred mixture over 5 min at −78 to −60 °C. The cooling bath was removed after 30 min, and the mixture was stirred for 2 h at room temperature, when solid NaI precipitated. The reaction was quenched by adding ice and dil HCl. The mixture was diluted with water, and extracted with hexane/$Et_2O$. The extract was washed with water and brine, dried ($MgSO_4$), and concentrated in vacuo. The residue (8.72 g) was chromatographed over $SiO_2$ (60 g). Elution with hexane/EtOAc (20:1) gave 4.24 g (73%) of **54** as a slightly yellow oil, $n_D^{23}$=1.4552; $\nu_{max}$ (film): 2924 (s), 2853 (s), 1752 (s), 1720 (s), 1656 (m), 1630 (m), 1450 (m), 1406 (w), 1377 (w), 1319 (m), 1236 (s), 1152 (m); $\delta_H$ ($CDCl_3$): 0.83 (3H, d, *J* 6.4), 0.88 (3H, t, *J* 6.4), 1.04–1.14 (2H, m), 1.16–1.42 (24H, br, peak at 1.26), 1.52–1.62 (3H, m), 2.53 (2H, t, *J* 7.2): 3.45 (2H, s), 3.74 (3H, s); GC–MS [column: HP-5MS, 5% phenylmethylsiloxane, 0.25 mm i.d.×30 m; carrier gas, He; Press, 52.8 kPa; temp: 50–300 °C siloxane (50 °C for 2 min, +15 °C/min, 300 °C for 60 min)]: $t_R$ 15.46 min (98.1%); MS (70 eV, EI): *m*/*z*: 355 (<1) [$(M+1)^+$], 278 (7), 236 (38), 221 (2), 208 (3), 194 (3), 180 (2), 166 (2), 152 (4), 137 (6), 123 (10), 109 (22), 99 (19), 85 (23), 82 (33), 71 (53), 58 (100), 43 (97). HRMS calcd for $C_{22}H_{42}O_3Na$: 377.3032, found: 377.3029. Further elution with hexane/EtOAc (15:1–5:1) gave 1.29 g of a solid with unknown structure.

### 4.36. 12-Methoxycarbonyl-8,18-dimethyl-13-triacontanone (55)

Iodide **51** (73.5% purity, 3.30 g, 8.2 mmol) and $K_2CO_3$ (3.45 g, 25 mmol) were added to a solution of **54** (2.72 g, 7.7 mmol) in acetone (30 mL) and DMF (2 mL) with vigorous stirring. The mixture was stirred and heated under reflux for 4 h and stirred overnight at room temperature. The powdered $K_2CO_3$ partly dissolved in the course of the reaction. The mixture was concentrated in vacuo, diluted with water, and extracted with $Et_2O$. The extract was washed with water and brine, dried ($MgSO_4$), and concentrated in vacuo to give 5.5 g of an oil. This was chromatographed over $SiO_2$ (50 g). Elution with hexane/EtOAc (30:1) gave 3.92 g (98%) of **55** as a colorless oil, $n_D^{24}$=1.4568; $\nu_{max}$ (film): 2954 (s), 2925 (s), 2854 (s), 1748 (s), 1718 (s), 1646 (w), 1617 (m), 1464 (s), 1377 (m), 1238 (m), 1198 (m), 1164 (m), 1142 (m), 722 (w); $\delta_H$ ($CDCl_3$): 0.83 (6H, d, *J* 6.4), 0.88 (6H, t, *J* 6.8), 1.00–1.15 (4H, m), 1.15–1.44 (40H, br, peak at 1.26), 1.48–1.60 (2H, m), 1.72–1.86 (2H, m), 2.42–2.60 (2H, m), 3.40–3.48 (1H, m), 3.72 (3H, s); GC–MS (same conditions as those used for **54**): $t_R$ 22.02 min (58.4%); 24.20 min (25.8%); MS (70 eV, EI) of the isomer with $t_R$ 22.02 min: *m*/*z*: 446 (9), 281 (11), 236 (54), 221 (14), 166 (100), 152 (5), 137 (12), 123 (18), 109 (39), 95 (39), 82 (33), 71 (38), 57 (48), 43 (47). MS (70 eV, EI) of the isomer with $t_R$ 24.20 min: *m*/*z*: 491 (10), 355 (59), 339 (11), 323 (5), 281 (5), 263 (6), 236 (29), 183 (7), 166 (100), 140 (23), 117 (39), 101 (12), 85 (40), 71 (55), 57 (94), 43 (75). HRMS calcd for $C_{34}H_{66}O_3Na$: 545.4910, found: 545.4892.

### 4.37. 8,18-Dimethyl-13-triacontanone (56)

A solution of KOH (1.20 g, 21 mmol) in water (10 mL) was added to a solution of **55** (3.82 g, 7.3 mmol) in 99% EtOH (40 mL). The mixture was stirred and heated under reflux for 2 h. After cooling, it was diluted with water and extracted with hexane/$Et_2O$. The extract was washed with water and brine, dried ($MgSO_4$), and concentrated in vacuo to give an oil (3.14 g), which was chromatograpahed over $SiO_2$ (50 g). Elution with hexane/EtOAc (30:1) gave 2.90 g (86%) of **56** as a colorless oil, $n_D^{24}$=1.4560; $\nu_{max}$ (film): 2954 (s), 2925 (s), 2854 (s), 1717 (s), 1464 (m), 1411 (w), 1377 (m), 1140 (w), 722 (w); $\delta_H$ ($CDCl_3$): 0.83 (6H, d, *J* 6.4 Hz), 0.90 (6H, t, *J* 6.8), 1.00–1.14 (4H, m), 1.14–1.40 (40H, br, peak at 1.26), 1.46–1.60 (4H, m), 2.39 (4H, t, *J* 7.2); GC–MS (same conditions as those used for **54**): $t_R$ 22.09 min (93.8%); MS (70 eV, EI): *m*/*z*: 465 (<1) [$(M+H)^+$], 446 (11), 323 (3), 297 (5), 281 (17), 236 (63), 229 (13), 211 (16), 166 (100), 152 (5), 137 (13), 123 (18), 109 (37), 95 (35), 83 (27), 71 (29), 57 (35), 43 (33). HRMS calcd for $C_{32}H_{64}O$: 464.4957, found: 464.4954.

### 4.38. 8,18-Dimethyltriacontane (5) by Wolff-Kishner reduction of 56

A solution of KOH (2.0 g, 36 mmol) in $H_2O$ (2 mL) and $N_2H_4 \cdot H_2O$ (3 mL) were added to a mixture of **56** (1.50 g, 5 mmol) in diethylene glycol (20 mL). The mixture was stirred and heated under reflux for 30 min. Then water and excess $N_2H_4 \cdot H_2O$ were distilled off from the mixture, and the bath temperature was gradually raised to 210 °C and kept there for 2 h. After cooling, the mixture was diluted with water and extracted with hexane. The hexane extract was washed with water and brine, dried ($MgSO_4$), and concentrated in vacuo to give an oil (1.5 g), which was chromatographed over $SiO_2$ (20 g). Elution with hexane afforded 247 mg (18%) of **5** as a colorless oil, which solidified in a deep freezer, $n_D^{24}$=1.4530; $\nu_{max}$ (film): 2955 (s), 2926 (s), 2853 (s), 1466 (m), 1377 (m), 1304 (w), 1154 (w), 1076 (w), 890 (w), 721 (m); $\delta_H$ ($CDCl_3$): 0.835 (6H, d, *J* 6.4), 0.881 (6H, t, *J* 6.8), 1.01–1.14 (4H, m), 1.18–1.40 (50H, br, peak at 1.259); $\delta_C$ ($CDCl_3$): 14.13, 19.74, 22.71, 27.11, 29.39, 29.42, 29.73, 30.05, 31.95, 32.76, 37.11; GC–MS (same conditions as those used for **54**): $t_R$ 20.55 min (91.6%); MS (70 eV, EI): *m*/*z*: 451 (<1) [$(M+H)^+$], 435 (7), 421 (5), 351 (17), 281 (18), 196 (32), 181 (6), 170 (6), 155 (9), 141 (13), 126 (38), 111 (18), 99 (26), 97 (24), 85 (81), 71 (100), 57 (96), 43 (47). HRMS calcd for $C_{32}H_{66}$: 450.5165, found: 450.5152.

### 4.39. 8,18-Dimethyl-13-triacontanol (57)

A solution of **56** (1.40 g, 3 mmol) in dry THF (10 mL) was added dropwise to a stirred and ice-cooled suspension of $LiAlH_4$ (300 mg, 8 mmol) in dry THF (5 mL) at 5–10 °C. After stirring for 1 h at 0–5 °C, water was added dropwise to the stirred and ice-cooled mixture to destroy the excess $LiAlH_4$. The mixture was then acidified with ice and dil HCl, and extracted with hexane/$Et_2O$. The extract was washed successively with $NaHCO_3$ solution and brine, dried ($MgSO_4$), and concentrated in vacuo to give 1.27 g (91%) of **57** as a colorless oil, $n_D^{24}$=1.4584; $\nu_{max}$ (film): 3433 (br m), 2955 (s), 2926 (s), 2854 (s), 1465 (m), 1377 (m), 1305 (w), 1133 (w), 1059 (w), 722 (w); $\delta_H$ ($CDCl_3$): 0.82 (6H, d, *J* 7), 0.88 (6H, t, *J* 6),1.04–1.16 (4H, m), 1.18–1.50 (49H, br, peak at 1.26), 3.90 (1H, m); GC–MS (same conditions as those used for **54**): $t_R$ 22.26 min (96.5%); MS (70 eV, EI): *m*/*z*: 466 (<1) [$M^+$], 449 (5), 348 (4), 283 (50), 213 (43), 195 (13), 181 (3), 167 (5), 153 (6), 139 (17), 125 (53), 111 (70), 97 (100), 83 (78), 68 (67), 57 (85), 43 (50). HRMS calcd for $C_{32}H_{66}ONa$: 489.5011, found: 489.5044.

### 4.40. 13-Mesyloxy-8,18-dimetyltriacontane (58)

A solution of MsCl (1.0 g, 8.7 mmol) in dry $CH_2Cl_2$ (5 mL) was added dropwise to a stirred and ice-cooled solution of **57** (1.2 g, 2.6 mmol) in dry $C_5H_5N$ (6 mL) at 0–5 °C. The mixture was stirred at 0–5 °C for 1 h and then left to stand in a refrigerator for 2 d. It was diluted with ice-water and extracted with $Et_2O$. The extract was washed successively with dil HCl, $NaHCO_3$ solution and brine, dried ($MgSO_4$), and concentrated in vacuo to give 1.02 g (73%) of **58** as a colorless oil, $\nu_{max}$ (film): 2955 (s), 2925 (s), 2854 (s), 1465 (m), 1358 (m), 1176 (s), 906 (s), 529 (m). This was employed in the next step without further purification.

### 4.41. 8,18-Dimethyltriacontane (5) by $LiAlH_4$ reduction of 58

In the same manner as described for **35** in 4.17, **58** (1.02 g, 1.9 mmol) was reduced with $LiAlH_4$ (300 mg, 8 mmol) in THF (10 mL) to give 663 mg (79%) of **5** after $SiO_2$ (20 g) chromatography (elution with hexane) as a colorless oil, $n_D^{26}$=1.4520; GC–MS (same conditions as those used for **54**): $t_R$ 20.54 min (92.6%). Its IR, $^1H$ and $^{13}C$ NMR and MS spectra were identical with those reported in 4.38. HRMS calcd for $C_{32}H_{66}$: 450.5165, found: 450.5171.

### 4.42. 3-Methylpentyl tosylate (60)

TsCl (17.6 g, 93 mmol) and DMAP (50 mg) were added to a stirred and ice-cooled solution of **59** (TCI, 8.60 g, 84 mmol) in dry $C_5H_5N$ (40 mL). The mixture was stirred for 2 h at 0–5 °C, and then worked up to give 23.1 g (quant.) of **60** as a colorless oil, $\nu_{max}$, (film): 2962 (m), 2929 (m), 2875 (m), 1599 (w), 1462 (m), 1362 (s), 1189 (s), 1177 (s), 942 (s), 644 (s), 555 (s). This was employed in the next step without further purification.

### 4.43. 3-Methylpentyl bromide (61)

LiBr (16.0 g, 183 mmol) was added to a solution of **60** (23.1 g, 93 mmol) in DMF (70 mL). After the exothermic reaction, the mixture was stirred and heated at 70 °C for 1 h. It was then cooled (solid NaOTs precipitated.), diluted with ice-water, and extracted with pentane. The pentane solution was washed with water and brine, dried ($MgSO_4$), and concentrated in vacuo. The residue was distilled to give 10.6 g (76%) of **61** as a colorless oil, bp 68–69 °C/58 Torr; $n_D^{25}$=1.4488; $\nu_{max}$ (film): 2963 (s), 2928 (s), 2875 (m), 1462 (m), 1380 (m), 1254 (m), 1215 (m), 965 (w), 877 (w), 678 (w), 644 (m), 568 (w); $\delta_H$ ($CDCl_3$): 0.87 (3H, d, *J* 8), 0.87 (3H, t, *J* 7.2), 1.12–1.24 (1H, m), 1.31–1.42 (1H, m), 1.50–1.60 (1H, m), 1.62–1.72 (1H, m), 1.84–1.94 (1H, m), 3.36–3.50 (2H, m); GC–MS (same conditions as those used for **12**): $t_R$ 3.47 min (98.5%); MS (70 eV, EI): *m*/*z*: 166 (4) [$M^+$], 164 (4) [$M^+$], 137 (3), 135 (3), 109 (4), 107 (4), 85 (88), 84 (33), 69 (33), 57 (100), 55 (67), 41 (58). HRMS calcd for $C_6H_{13}Br$: 164.0201, found: 164.0183.

### 4.44. Triphenyl-2-methylpentylphosphoniun bromide (62)

A solution of **61** (10.5 g, 64 mmol) and $Ph_3P$ (10.2 g, 77 mmol) in xylene (20 mL) was stirred and heated at 125 °C (bath temp) for 18 h. The mixture was cooled, concentrated in vacuo, and tritulated with $C_6H_6$ to give 18.3 g (67%) of **62** as prisms, mp 192–193 °C; $\nu_{max}$, (Nujol): 3052 (w), 2791 (w), 1856 (w), 1114 (s), 749 (s), 724 (s), 692 (s). HRMS [ESI MS (positive ion mode, direct injection)] calcd for $C_{24}H_{28}P$: 347.1929, found: 347.1925. calcd for $C_{48}H_{56}BrP_2^+$: 773.3035, found: 773.3040.

### 4.45. 3,7,11-Trimethyl-5,7-nonacosadiene (63)

A solution of *n*-BuLi in hexane (1.6 M, 11.2 mL, 18 mmol) was added to a stirred and cooled suspension of **62** (7.70 g, 18 mmol) in dry THF (45 mL) at −70 to −60 °C under argon. The cooling bath (dry ice/acetone) was then removed, and the temperature of the mixture was allowed to rise upto 0 °C to give a red solution of the ylide. The stirred mixture was cooled again to −70 °C. A solution of **38** (3.40 g, 9 mmol) in dry THF (10 mL) was added dropwise at −70 to −60 °C, and the mixture was stirred at −70 °C for 30 min and then at room temperature (22 °C) for 1 h. The reaction was quenched by pouring the mixture into ice-water. The mixture was extracted with hexane/$Et_2O$. The extract was washed with water and brine, dried ($MgSO_4$), and concentrated in vacuo in the presence of chromatographic $SiO_2$ (15 g). The resulting powder was placed on the top of a column of $SiO_2$ (50 g) in hexane. Elution with hexane afforded 2.04 g (47%) of **63** as a colorless oil, $n_D^{25}$=1.4698; $\nu_{max}$ (film): 2957 (s), 2925 (s), 2853 (s), 1647 (w), 1463 (m), 1377 (m), 1306 (w), 1154 (w), 963 (m), 862 (w), 721 (m); $\delta_H$ ($CDCl_3$): 0.81–0.94 (12H, m), 1.06–1.20 (3H, m), 1.20–1.35 (31H, br, peak at 1.26), 1.35–1.46 (4H), 1.73 (2H, s) and 1.75 (1H, s), 1.86–1.96 (1H, m), 2.00–2.28 (3H, m), 5.24–5.44 (1.4H, m) and 5.48–5.58 (0.6H, m), 5.84 (0.3H, d, *J* 12) and 6.03 (0.7H, d, *J* 15.6); $\delta_C$ ($CDCl_3$): 11.52, 12.46, 14.14, 16.75, 19.16, 19.61, 22.72, 25.64, 25.71, 27.05, 27.10, 29.17, 29.40, 29.74, 30.05, 31.96, 32.47,32.50, 35.19, 35.48, 35.66, 36.94, 36.97, 37.01, 40.06, 126.04, 128.33, 130.87, 132.40, 133.30, 133.49, 135.91; GC–MS (same conditions as those used for **24**): $t_R$ 20.44 (29.1%), 21.09 min (62.4%) (total 91.5%. These are the *E*/*Z* isomers at C-5). MS (70 eV, EI) of **63** with $t_R$ 20.44 min: *m*/*z*: 446 (42) [$M^+$], 417 (13), 361 (4), 347 (6), 281 (7), 253 (4), 207 (13), 193 (5), 165 (7), 137 (18), 123 (100), 109 (47), 95 (91), 81 (68), 70 (38), 57 (45), 55 (38), 43 (42); MS (70 eV, EI) of **63** with $t_R$ 21.09 min: *m*/*z*: 446 (13) [$M^+$], 361 (11), 347 (4), 306 (7), 207 (4), 193 (13), 165 (21), 152 (7), 138 (15), 123 (38), 109 (43), 95 (63), 81 (100), 70 (29), 57 (36), 43 (29). HRMS calcd for $C_{32}H_{62}$: 446.4852, found: 446.4871.

### 4.46. 3,7,11-Trimethylnonacosane (6)

10% Pd–C (150 mg) was added to a solution of **63** (1.83 g, 4.8 mmol) in hexane (10 mL). The mixture was stirred under $H_2$ (balloon) at room temperature for 2.5 h. The suspension was filtered through $SiO_2$ (15 g) in hexane, and the $SiO_2$ column was washed with hexane. Concentration in vacuo of the hexane solution gave 1.83 g (99%) of **6** as a colorless oil, $n_D^{25}$=1.4521; $\nu_{max}$ (film): 2957 (s), 2925 (s), 2853 (s), 1464 (m), 1377 (m), 1304 (w), 1151 (w), 965 (w), 721 (m); $\delta_H$ ($CDCl_3$): 0.80–0.92 (15H, m), 1.00–1.16 (6H, m), 1.16–1.45 (45H, br, peak at 1.26); $\delta_C$ ($CDCl_3$): 11.47, 14.18, 19.26, 19.32, 19.75, 19.79, 19.82, 22.78, 24.56, 24.59, 27.20, 29.48, 29.55, 29.65, 29.81, 30.14, 32.03, 32.86, 34.50, 37.04, 37.09, 37.16, 37.26, 37.47, 37.53, 37.59; GC–MS (same conditions as those used for **24**): $t_R$ 20.30 min (87.6%); MS (70 eV, EI): *m*/*z*: 435 (4) [$(M-CH_3)^+$], 421 (7), 351 (23), 323 (4), 281 (11), 280 (13), 267 (2), 253 (3), 239 (2), 225 (2), 211 (3), 197 (23), 183 (4), 169 (7), 155 (8), 141 (14), 127 (35), 113 (23), 99 (29), 97 (27), 85 (79), 71 (96), 57 (100), 43 (45). HRMS calcd for $C_{32}H_{66}$: 450.5165, found: 450.5125.

### 4.47. 2-Methylbutyl iodide (66)

As reported in Ref. 9 for the preparation of (*R*)-**66**, racemic 2-methyl-1-butanol (**64**, 20.0 g, 227 mmol) was treated with TsCl (47.5 g, 250 mmol) in $C_5H_5N$ (50 mL) to give 56.6 g (quant.) of **65**, which was heated with NaI (60 g, 400 mmol) in DMF (150 mL) to give 34.4 g (78%) of **66** as a colorless oil, bp 144–146 °C; $\nu_{max}$ (film): 2961 (s), 2927 (s), 2874 (s), 1456 (m), 1379 (m), 1194 (m), 602 (w).

### 4.48. 3,7,11-Trimethyl-10-dodecen-5-ol (67)

As reported in Ref. 9 for the preparation of (3*R*,5*RS*,7*S*)-**67**, racemic **66** (11.08 g, 56 mmol) in dry $Et_2O$ (110 mL) was treated with *t*-BuLi in pentane (1.9 M, 59 mL, 112 mmol) at -78-0 °C under argon to generate 2-methylbutyllithium. A solution of **30** (7.20 g, 46.7 mmol) in dry $Et_2O$ (20 mL) was added to the mixture at −78 °C. Subsequent work-up gave 9.70 g (92%) of **67** as a colorless oil, bp 132–133 °C/6 Torr; $n_D^{22}$=1.4568; $\nu_{max}$ (film): 3343 (m), 2961 (s), 2925 (s), 2874 (m), 2854 (m), 1461 (m), 1378 (m), 1025 (w), 840 (w); $\delta_H$ ($CDCl_3$): 0.86–0.93 (9H, m), 1.06–1.50 (8H, m), 1.50–1.70 (3H, m), 1.61 (3H, s), 1.69 (3H, s), 1.90–2.10 (2H, m), 3.79 (1H, m), 5.10 (1H, t-like, *J* 7.6); GC–MS [column: HP-5MS, 5% phenylmethylsiloxane, 0.25 mm i.d.×30 m; carrier gas, He; press, 69 kPa; temp: 70–230 °C (+10 °C/min)]: $t_R$ 12.75 min (50.5%); 12.87 min (46.8%). These two stereoisomers showed the same MS (70 eV, EI): *m*/*z*: 226 (<1) [$M^+$], 208 (2), 197 (5), 152 (7), 141 (42), 123 (21), 109 (59), 95 (46), 82 (100), 81 (57), 69 (55), 55 (34), 41 (50). HRMS calcd for $C_{15}H_{30}O$: 226.2297, found: 226.2309 (short $t_R$), 226.2312 (long $t_R$).

### 4.49. 5-Mesyloxy-3,7,11-trimethyl-10-dodecene (68)

As reported in Ref. 9 for the preparation of (3*R*,5*RS*,7*S*)-**68**, a solution of MsCl (6.90 g, 60 mmol) in dry $CH_2Cl_2$ (20 mL) was added to a stirred and ice-cooled solution of **67** (9.70 g, 43 mmol) in dry $C_5H_5N$ (40 mL). Subsequent work-up gave 13.57 g (quant.) of **68** as a colorless oil, $\nu_{max}$ (film): 2962 (s), 2927 (s), 2875 (m), 1462 (m), 1336 (s), 1175 (s), 899 (s). This was employed in the next step without further characterization.

### 4.50. 2,6,10-Trimethyl-2-dodecene (69)

As reported in Ref. 9 for the preparation of (6*R*,10*R*)-**69**, a solution of **68** (13.55 g, 43 mmol) in dry THF (20 mL) was added dropwise to a stirred and ice-cooled suspension of $LiAlH_4$ (2.35 g, 62 mmol) in dry THF (100 mL). Subsequent work-up afforded 7.39 g (82%) of **69** as a colorless oil, bp 109–110 °C/8 Torr; $n_D^{21}$=1.4454; $\nu_{max}$ (film): 2962 (s), 2926 (s), 2872 (m), 1461 (m), 1377 (m), 969 (w), 825 (w); $\delta_H$ ($CDCl_3$): 0.80–0.90 (9H, m), 1.00–1.20 (4H, m), 1.20–1.50 (7H, m), 1.60 (3H, s), 1.68 (3H, s), 1.88–2.08 (2H, m), 5.11 (1H, *t*-like, *J* 7); GC–MS (same conditions as those used for **67**): $t_R$ 10.79 min (75.2%); MS (70 eV, EI): 210 (30) [$M^+$], 140 (6) 126 (15), 125 (14), 111 (26), 97 (18), 83 (31), 70 (70), 69 (100), 57 (49), 56 (42), 55 (41), 41 (58). HRMS calcd for $C_{15}H_{30}$: 210.2348, found: 210.2357.

### 4.51. 2,6,10-Trimethyldodecane-2,3-diol (70)

As described in 4.3. for the preparation of **11**, **69** (7.30 g, 35 mmol) was oxidized with a solution of $OsO_4$ in *t*-BuOH (140 mg in 14 mL) and aqueous NMO (50%, 27 g, ca. 110 mmol) in a mixture of *t*-BuOH (70 mL), acetone (60 mL) and water (40 mL) for 3 d at room temperature. Subsequent work-up followed by $SiO_2$ chromatography [70 g $SiO_2$, elution with hexane/EtOAc (4:1)] gave 7.05 g (83%) of **70** as a slightly yellow oil, $n_D^{19}$=1.4490; $\nu_{max}$ (film): 3406 (br. m), 2959 (s), 2927 (s), 2872 (m), 1463 (m), 1378 (m), 1165 (w), 1073 (m), 963 (w); $\delta_H$ ($CDCl_3$): 0.82–0.92 (9H, m), 1.02–1.20 (3H, m), 1.16 (3H, s), 1.24 (3H, s), 1.20–1.66 (11H, m), 2.19 (1H), 2.33 (1H), 3.32 (1H, m). HRMS calcd for $C_{15}H_{32}O_2$: 244.2402, found: 244.2397.

### 4.52. 4,8-Dimethyldecanal (71)

As described in 4.4. for the preparation of **12**, $HIO_4 \cdot 2H_2O$ (7.98 g, 35 mmol) was added portionwise to a stirred and ice-cooled solution of **70** (7.00 g, 29 mmol) in THF (70 mL). The mixture was stirred at 0–5 °C for 20 min, diluted with ice-water, and extracted with hexane. Further work-up gave an oil (6.67 g). This was chromatographed over $SiO_2$ (65 g), and elution with hexane/EtOAc (30:1) gave crude **71** (5.64 g), which was distilled to furnish 3.86 g (73%) of **71** as a colorless oil, bp 95–96 °C/4 Torr; $n_D^{24}$=1.4344; $\nu_{max}$ (film): 2959 (s), 2927 (s), 2873 (s), 2714 (m), 1728 (s), 1463 (m), 1412 (w), 1379 (m), 1015 (w); $\delta_H$ ($CDCl_3$): 0.80–0.93 (9H, m), 1.00–1.18 (3H, m), 1.18–1.38 (6H, m), 1.38–1.50 (2H, m), 1.61–1.72 (1H, m), 2.35–2.50 (2H, m), 9.78 (1H, *t*-like), GC–MS (same conditions as those used for **67**): $t_R$ 9.79 min (93.0%); MS (70 eV, EI): *m*/*z*: 184 (<1) [$M^+$], 140 (19), 137 (14), 125 (12), 111 (34), 95 (53), 85 (58), 81 (51), 71 (59), 70 (90), 69 (73), 57 (100), 56 (63), 55 (75), 43 (62), 41 (84). HRMS calcd for $C_{12}H_{24}O$: 184.1827, found: 184.1818.

### 4.53. 4,8-Dimethyl-1-decanol (72)

As reported in Ref. 9 for the preparation of (4*R*,8*R*)-**72**, **71** (3.80 g, 20.6 mmol) in dry $Et_2O$ (20 mL) was reduced with $LiAlH_4$ (0.80 g, 21 mmol) to give 3.49 g (91%) of **72** as a colorless oil, bp 115–116 °C/6 Torr; $n_D^{23}$=1.4428; $\nu_{max}$ (film): 3328 (br. m), 2958 (s), 2928 (s), 2871 (s), 1462 (m), 1378 (m), 1059 (m), 900 (w); $\delta_H$ ($CDCl_3$): 0.82–0.90 (9H, m), 1.02–1.20 (4H, m), 1.20–1.46 (8H, m), 1.46–1.66 (3H, m), 3.63 (2H, t, *J* 6.8), GC–MS (same conditions as those used for **67**): $t_R$ 10.63 min (94.0%); MS (70 eV, EI): *m*/*z*: 185 (<1) [$M^+$-1], 140 (23), 125 (16), 111 (25), 97 (28), 84 (42), 83 (40), 70 (75), 69 (100), 57 (50), 56 (41), 55 (60), 43 (35), 41 (57). HRMS calcd for $C_{12}H_{26}O$: 186.1984, found: 186.1971.

### 4.54. 4,8-Dimethyldecyl tosylate (73)

As reported in Ref. 9 for the preparation of (*R*)-**66**, **72** (3.49 g, 19 mmol) in dry $C_5H_5N$ (15 mL) was treated with TsCl (4.10 g, 22 mmol) at 0–5 °C. Subsequent work-up gave 6.16 g (quant.) of **73** as a colorless oil, $\nu_{max}$ (film): 2958 (s), 2926 (s), 2871 (m), 1599 (m), 1463 (m), 1363 (s), 1189 (s), 1177 (s), 966 (m), 918 (m), 814 (m), 664 (m), 555 (m). This oil was employed in the next step without further purification.

### 4.55. 4,8-Dimethyldecyl iodide (74)

As described in 4.33. for the preparation of **51**, a mixture of **73** (6.16 g, 19 mmol) and NaI (7.50 g, 50 mmol) in DMF (40 mL) was stirred and heated at 60 °C for 30 min. Subsequent work-up gave 4.38 g (86%) of **74** as a colorless oil, bp 122–124 °C/5 Torr; $n_D^{21}$=1.4814; $\nu_{max}$ (film): 2958 (s), 2926 (s), 2871 (m), 1462 (m), 1378 (m), 1234 (w), 1173 (m); $\delta_H$ ($CDCl_3$): 0.845 (3H, d, *J* 7.2), 0.857 (3H, t, *J* 7.2), 0.866 (3H, d, *J* 7.2), 1.00–1.16 (3H, m), 1.16–1.36 (7H, m), 1.36–1.46 (2H, m), 1.74–1.92 (2H, m), 3.17 (2H, dt, *J* 2.8, 7.2); GC–MS (same conditions as those used for **67**): $t_R$ 12.80 min (87.2%); MS (70 eV, EI): *m*/*z*: 155 (14) [$(M-I)^+$], 113 (14), 99 (21), 85 (54), 73 (69), 57 (100), 43 (47), 41 (39). HRMS calcd for $C_{12}H_{25}I$: 296.1001, found: 296.1001.

### 4.56. 1-Methoxycarbonyl-3,7,17-trimethyl-12-nonacosanone (75)

In the same manner as described in 4.36. for the preparation of **55**, iodide **74** (4.01 g, 14 mmol) and $K_2CO_3$ (5.10 g, 37 mmol) were added to a stirred solution of β-keto ester **54** (4.01 g, 11.3 mmol) in acetone (45 mL) and DMF (6 mL). The mixture was stirred and heated under reflux for 3 h. Subsequent work-up gave a colorless oil (7.39 g), which was chromatographed over $SiO_2$ (80 g). Elution with hexane gave 1.70 g of non-polar materials (recovered **74**, etc.) as fraction 1. Further elution with hexane/EtOAc (20:1) gave 2.06 g of **75** as fraction 2, and 2.90 g of **75** as fraction 3. The combined yield of **75** as a colorless oil was 4.96 g (83%), $n_D^{21}$=1.4586; $\nu_{max}$ (film): 2954 (s), 2925 (s), 2854 (s), 1749 (m), 1718 (m), 1646 (w), 1617 (w), 1463 (m), 1377 (m), 1236 (m), 1164 (m), 722 (w); $\delta_H$ ($CDCl_3$): 0.80–0.92 (15H, m), 1.02–1.16 (5H, m), 1.16–1.42 (37H, a peak at 1.26), 1.50–1.60 (2H, m), 1.74–1.86 (1H, m), 2.44–2.56 (2H, m), 3.45 (1H, t-like), 3.72 (3H, plural singlets due to the isomers); GC–MS (same conditions as those used for **54**): $t_R$ 21.76 min (44.9%) and 23.83 min (43.4%); MS of **75** with $t_R$=21.76 min (70 eV, EI): *m*/*z*: 446 (1), 281 (17), 236 (88), 166 (72), 137 (41), 123 (43), 109 (77), 83 (65), 57 (100); MS of **75** with $t_R$=23.83 min (70 eV, EI): *m*/*z*: 491 (7), 353 (50), 236 (25), 166 (38), 140 (27), 116 (22), 85 (39), 57 (100). HRMS calcd for $C_{34}H_{66}O_3$: 522.5012, found: 522.4996.

### 4.57. 3,7,17-Trimethyl-12-nonacosanone (76)

In the same manner as described for **56** in 4.37, a solution of KOH (2.24 g, 40 mmol) in water (10 mL) was added to a solution of **75** (4.94 g, 9.5 mmol) in 99% EtOH (40 mL). The mixture was stirred and heated under reflux for 1.5 h. Subsequent work-up gave 4.28 g of crude **76**, which was chromatographed over $SiO_2$ (50 g). Elution with hexane/EtOAc first gave 2.19 g of 92.8% pure (GC) **76** and then afforded 1.67 g of 67.4% pure (GC) **76**. The total yield of **76** was calcd as 3.16 g (71%). The purer fraction (2.19 g) showed the following properties: a colorless oil, $n_D^{23}$=1.4552; $\nu_{max}$ (film): 2955 (s), 2925 (s), 2854 (s), 1717 (m), 1463 (m), 1410 (w), 1377 (m), 1138 (w), 722 (w); $\delta_H$ ($CDCl_3$): 0.80–0.91 (15H, m), 1.00–1.16 (6H, m), 1.16–1.44 (35H, br, peak at 1.26), 1.48–1.60 (4H, m), 2.39 (4H, t, *J* 7.6); GC–MS (same conditions as those used for **54**): $t_R$ 21.81 min (92.8%) MS (70 eV, EI): *m*/*z*: 464 (<1) [$M^+$], 446 (17), 323 (4), 302 (9), 281 (27), 236 (100), 227 (19), 211 (18), 166 (73), 137 (41), 123 (40), 109 (69), 96 (48), 94 (55), 83 (52), 71 (56), 69 (42), 57 (73), 55 (47); HRMS calcd for $C_{32}H_{64}O$: 464.4957, found: 464.4947.

### 4.58. 3,7,17-Trimethyl-12-nonacosanol (77)

In the same manner as described in 4.39. for the preparation of **57**, a solution of **76** (2.10 g, 4.6 mmol) in dry THF (10 mL) was added dropwise to a stirred and ice-cooled suspension of $LiAlH_4$ (400 mg, 10.5 mmol) in dry THF (10 mL) at 5–10 °C. After stirring for 1 h at 0–5 °C, the reaction was quenched by adding water with stirring and ice-cooling. Subsequent work-up gave 2.09 g (99%) of **77** as a colorless oil, $n_D^{25}$=1.4578; $\nu_{max}$ (film): 3344 (br. m), 2956 (m), 2925 (s), 2854 (m), 1464 (m), 1377 (m), 1060 (w), 981 (w), 722 (w); $\delta_H$ ($CDCl_3$): 0.82–0.91 (15H, m), 1.02–1.16 (6H, m), 1.18–1.50 (44H, m, peak at 1.26), 3.55–3.65 (1H, br); GC–MS (same conditions as those used for **54**): $t_R$ 22.00 min (94.5%) MS (70 eV, EI): *m*/*z*: 448 (6) [$(M-H_2O)^+$], 283 (49), 213 (36), 199 (12), 182 (5), 167 (6), 153 (8), 139 (18), 125 (50), 111 (73), 97 (96), 85 (66), 83 (80), 71 (66), 69 (73), 57 (100), 55 (54). HRMS calcd for $C_{32}H_{66}ONa$: 489.5011, found: 489.5012.

### 4.59. 12-Mesyloxy-3,7,17-trimethylnonacosane (78)

In the same manner as described for **58** in 4.40, a solution of MsCl (1.50 g, 13 mmol) in dry $CH_2Cl_2$ (10 mL) was added dropwise to a stirred and ice-cooled solution of **77** (2.00 g, 4.3 mmol) in dry $C_5H_5N$ (10 mL) at 0–5 °C. The mixture was stirred at 0–5 °C for 1 h and then left to stand overnight in a refrigerator. Subsequent work-up gave 2.41 g (quant.) of **78** as a colorless oil, $\nu_{max}$ (film): 2925 (s), 2854 (s), 1464 (m), 1376 (m), 1358 (m), 1176 (s), 970 (m), 906 (s). This was employed in the next step without further purification.

### 4.60. 3,7,17-Trimethylnonacosane (7)

In the same manner as described for **35** in 4.17, **78** (2.41 g, 4.3 mmol) was reduced with $LiAlH_4$ (500 mg, 13 mmol) in dry THF (10 mL) to give 1.77 g of crude **7**. This was purified by chromatography over $SiO_2$ (30 g). Elution with hexane gave 1.57 g (81%) of **7** as a colorless oil, $n_D^{23}$=1.4516; $\nu_{max}$ (film): 2927 (s), 2957 (s), 2853 (s), 1464 (m), 1377 (m), 1304 (w), 1153 (w), 966 (w), 769 (w), 721 (m); $\delta_H$ ($CDCl_3$): 0.81–0.90 (15H, m), 1.02–1.14 (6H, m), 1.16–1.42 (45H, br, peak at 1.26); $\delta_C$ ($CDCl_3$): 11.43, 11.45, 14.14, 19.22, 19.28, 19.71, 19.74, 19.77, 22.73, 24.52, 27.12, 29.41, 29.50, 29.51, 29.70, 29.75, 29.77, 30.07, 31.97, 32.78, 34.44, 36.97, 37.02, 37.12, 37.19, 37.42, 37.47; GC–MS (same conditions as those used for **54)**: $t_R$ 20.39 min (89.2%) MS (70 eV, EI): *m*/*z*: 393 (3), 351 (15), 323 (3), 281 (12), 253 (4), 239 (3), 225 (4), 211 (5), 196 (25), 155 (10), 127 (35), 113 (19), 111 (12), 99 (26), 97 (27), 85 (77), 71 (96), 57 (100). HRMS calcd for $C_{32}H_{66}$: 450.5165, found: 450.5155.

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