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A Suite of Novel Allenes from Australian Melolonthine Scarab Beetles. Structure, Synthesis, and Stereochemistry

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A suite of allenic hydrocarbons, previously unknown as a molecular class from insects, has been characterized from several Australian melolonthine scarab beetles. The allenes are represented by the formula $CH_3(CH_2)_nCH{=}{\bullet}{=}CH(CH_2)_7CH_3$ with n being 11−15, 17 and 19, and thus, all have $\Delta^{9,10}$-unsaturation. These structures have been confirmed by syntheses and comparisons of spectral and chromatographic properties with those of the natural components. The enantiomers of (±)-$\Delta^{9.10}$-tricosadiene and $\Delta^{9,10}$-pentacosadiene were separable on a modified β-cyclodextrin column (gas chromatography), and the natural $\Delta^{9,10}$-tricosadiene (n = 11) and $\Delta^{9,10}$-pentacosadiene (n = 13) were shown to be of >85% ee. Syntheses of nonracemic allenes of known predominating chirality were acquired using both organotin chemistry and sulfonylhydrazine intermediates, and comparisons then demonstrated that the natural allenes were predominantly (*R*)-configured.

Introduction

Larvae of melolonthine scarabs (collectively known as canegrubs) are the main pests affecting the production of sugarcane in Australia.[1] Canegrubs damage the roots of the plant and the regenerative portion of its underground stem. Nineteen species of endemic canegrubs are responsible and are representative of four genera, all within the tribe Melolonthini within the subfamily Melolonthinae: *Antitrogus* (4 species), *Dermolepida* (1 species), *Lepidiota* (13 species), and *Rhopaea* (1 species). These species exhibit diverse life cycles, distribution, and behavior. Problems associated with insecticidal breakdown and resistance have increased the interest in environmentally benign approaches within an integrated pest management (IPM) framework. In recent years, some success has been achieved with formulations utilizing sex pheromones for monitoring and control of herbivorous scarab beetles,[2] and it has been proposed that pheromones may be useful for population control within the Australian canegrub complex.[3] Although no pheromones have previously been identified from the Australian canegrub genera, chemically diverse active compounds—phenols, amino acid derivatives, terpenoid compounds—have been identified from four genera within the same Melolonthinae subfamily.[2] In developing an understanding of the chemistry of the Australian canegrub complex, we have undertaken a study of the cuticular hydrocarbon (CH) ensemble from several pest species. This enterprise was encouraged by a consideration of the known life cycle and biology of the species, with the presumption that the CHs were serving an important role in this cycle. Although the primary role of CHs is to inhibit desiccation, bioassays have demonstrated that cuticular hydrocarbons also function in the recognition systems of both social and solitary insects and that the composition of the CHs are species-specific and, in social insects, colony- and caste-specific. Other roles for insect hydrocarbons have also been suggested and include sex attractant, inhibitor, or aphrodisiac and defense and protection from microorganisms.[4] The CHs are generally straight-chained, branched, or unsaturated with the branched components often present in complex mixtures.[5]

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(3) (a) Allsopp, P. G. *Coleopterists Bull.* **1993**, *47*, 51. (b) Cribb, B. W.; Hull, C. D.; Moore, C. J.; Miller, L. J.; Yeates, D. K. *Annals Ent. Soc. Am.* **1998**, *91*, 202.
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Our examination of selected canegrub species has revealed the presence of a suite of long-chain allenic hydrocarbons (**1**−**7**) having no precedent in insect chemistry and thereby enhancing the chemical panorama of insect-derived hydrocarbons. We now wish to describe these studies in detail.[6]

$^{n}C_8H_{17}-CH=\bullet=CH-R$

(**1**) R = $^{n}C_{12}H_{25}$
(**2**) R = $^{n}C_{13}H_{27}$
(**3**) R = $^{n}C_{14}H_{29}$
(**4**) R = $^{n}C_{15}H_{31}$
(**5**) R = $^{n}C_{16}H_{33}$
(**6**) R = $^{n}C_{18}H_{37}$
(**7**) R = $^{n}C_{20}H_{41}$

Results and Discussion

A general observation made in preliminary examinations was that the cuticular hydrocarbons (CHs) from female adults of several canebeetle species were of surprisingly limited constitutional variations. This contrasts with reports of CHs from other insect species.[4,5] Hexane extracts of adults of *Antitrogus consanguineus* were examined by combined gas chromatography−mass spectrometry (GC−MS), and one component represented in excess of 50% of the cuticular components. This compound appeared to be a C25 hydrocarbon with an apparent molecular weight (MW) of 348, corresponding to $C_{25}H_{48}$. This was confirmed by GC−MS-CI measurements. An accompanying minor component was the bis-homologue $C_{27}H_{52}$, (MW 376), and thus both components incorporated two degrees of unsaturation. There were no indications that these compounds had branched carbon skeletons, and the sequential loss of 14 amu dominated the mass spectra. However, it was of interest that both components exhibited prominent ions at *m*/*z* 166, with other ions at *m*/*z* 250 in the C25 compound and *m*/*z* 278 in the C27 compound. At this stage, we did not suspect any structural novelty and believed that nonconjugated dienes were likely to be present, and indeed, this was the conclusion when what we now know to be the same C25 hydrocarbon was first observed in *A. consanguineus* larvae.[3b]

Location of Sites of Unsaturation. Methoxymercuration−demercuration has been employed to establish the position of double bonds in alkenes.[7] GC−MS analysis of the methyl ethers that result from the reaction sequence is facilitated by the directing effect of the methoxy group on the mass spectral fragmentation.[8] For internal alkenes, little regioselectivity in methoxymercuration occurs, and two methyl ethers result (Figure 1a), and from the nature of their mass spectral fragment ions (GC−MS), the location of the double bond can be deduced.[7,8] Isolated, nonterminal dienes provide a complex mixture of positional isomers of bis-methyl ethers, with each being a diastereomeric mixture, but the fragment ions reflect the double bond positions.[7] Conjugated dienic systems could experience both 1,2- and 1,4-methoxymercuration[9] that on reductive demercuration would provide bis-ethers as shown (Figure 1b).

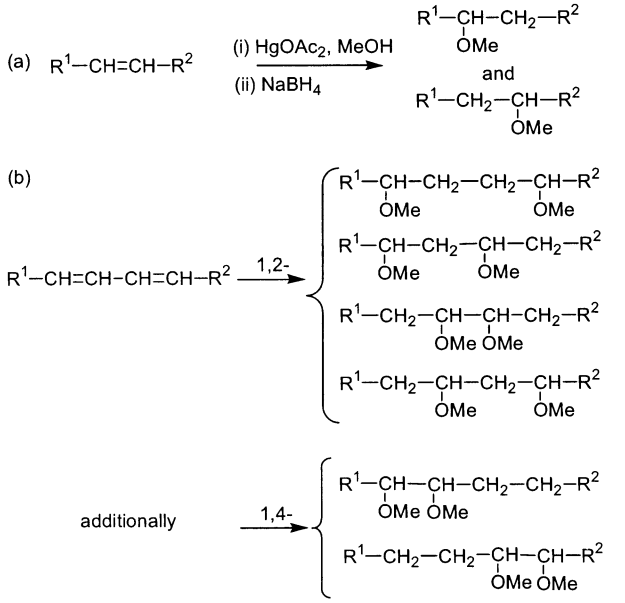

FIGURE 1. Representative methyl ethers from methoxymercuration−reduction of alkenes.

Additional complexity results if "double" addition is incomplete, as then unsaturated methyl ethers would be present. (However, these compounds are well separated from the saturated bis-methyl ethers under GC−MS conditions). Overall, then, methoxymercuration−reduction would be anticipated to yield a complex mixture of regio- and diastereomeric bis-methyl ethers.[9]

A methoxymercuration−demercuration ($NaBH_4$) procedure was conducted on the cuticular hydrocarbon extract from *A. consanguineus*. A doubly unsaturated $C_{25}H_{48}$ system should provide at least one bis-methyl ether, but two bis-methyl ether peaks were observed (GC−MS), and each appeared to be only one component with essentially *identical* mass spectra. The mass spectral fragmentations (Figure 2a) suggested that the bis-methyl ethers were diastereomers of 9,11-dimethoxypentacosane, and this, in turn, indicated the CH component was most likely to be 9,10-pentacosadiene (**3**). It is very unlikely that a conjugated diene or an isolated diene could lead to only two bis-methyl ethers displaying essentially identical mass spectra.[7,9] Strong support for the 1,2-diene (allene) structure was provided by a methoxymercuration−$NaBD_4$ demercuration procedure, as the *m*/*z* 157 and 241 ions remained unaffected, requiring both ^2H atoms to be located at the central carbon of the 1,2-propadiene unit.[10] (Other ions confirmed that *two* ^2H atoms were incorporated into the bis-methyl ether.) These outcomes are shown below in Figure 2b. Methoxymercuration−reduction of authentic $\Delta^{9,10}$-hexacosa-

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(6) Some portions of this work have been reported in preliminary form: Fletcher, M. T.; McGrath, M. J.; König, W. A.; Moore, C. J.; Cribb, B. W.; Allsopp, P. G.; Kitching, W. *Chem. Comm.* **2001**, 885.
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(8) Abley, P.; McQuillin, F. J.; Minnikin, D. E.; Kusamran, K.; Maskens, K.; Polgar, N. *Chem. Commun.* **1970**, 349.
(9) For a recent survey of the oxymercuration area, see: Kitching, W.; Glenn, M. P. In *Science of Synthesis: Houben-Weyl Methods of Molecular Transformations;* Ley, S. V., O'Neil, I., Vol. Eds.; George Thieme Verlag: Stuttgart and New York, 2002, Vol. 3, Chapter Mercury, in press.
(10) For a discussion of methoxymercuration of allenes, see: Waters, W. L.; Kiefer, E. F. *J. Am. Chem. Soc.* **1967**, *89*, 6261.

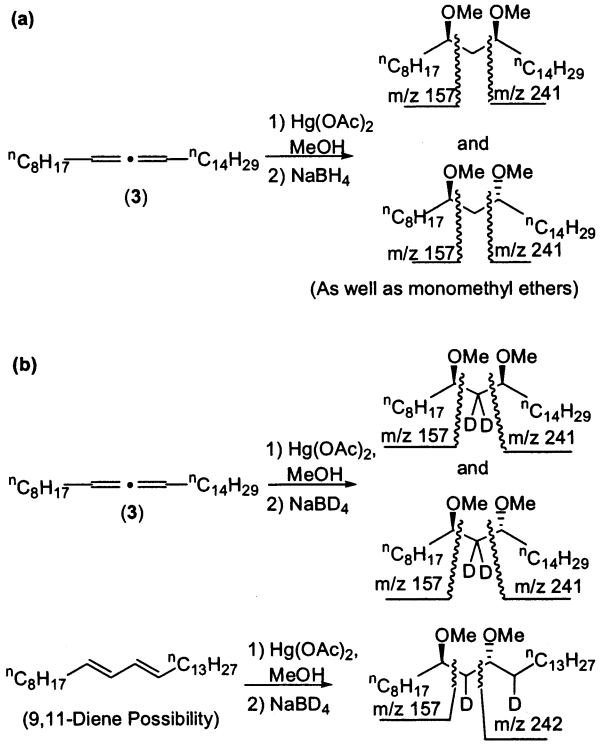

FIGURE 2. Mass spectral fragmentation of methyl ethers derived from $\Delta^{9,10}$-pentacosadiene (**3**).

diene (**4**) (for synthesis, see later text) was examined, as its bis-methyl ether should also provide an ion at *m*/*z* 157 (cleavage between C_9 and C_{10}), but cleavage between C_{10} and C_{11} should give *m*/*z* 255. The resultant mixture of unsaturated mono- and bis-methyl ethers was subjected to flash chromatography and characterized by NMR and HREIMS. A mixture of apparently diastereomeric compounds lacking unsaturation (HRMS for $M^+ - CH_3$) and exhibiting *m*/*z* 157 and 255 was formed, with $-OCH_3$ signals in ^{13}C and ^1H NMR spectra. These comparisons[11] supported the view that the insect-derived CH was $\Delta^{9,10}$-pentacosadiene (**3**).

More detailed consideration of the mass spectra of the suspected $\Delta^{9,10}$-pentacosadiene (**3**) supported this conclusion, in particular, the ions at *m*/*z* 166 and 250, which are associated with McLafferty rearrangement processes (Figure 3), previously reported[12] for simple allenes. On the basis of these processes, all unbranched allenes of the $\Delta^{9,10}$ type would be expected to exhibit an ion with *m*/*z* 166. This generalization was useful in structure elucidation of the present suite of allenes. Conversely, other locations of the propa-1,2-diene unit should provide different but still characteristic McLafferty ions. For example, authentic $\Delta^{7,8}$-pentacosadiene (**8**) was synthesized and exhibited the predicted McLafferty ions at *m*/*z* 138 and *m*/*z* 278 (Figure 3).

The natural extract was subjected to HPLC (normal phase, hexane) and a substantially pure nonpolar component, which contained the compound of interest, was isolated (~0.3 mg). The ^1H NMR spectrum (500 MHz)

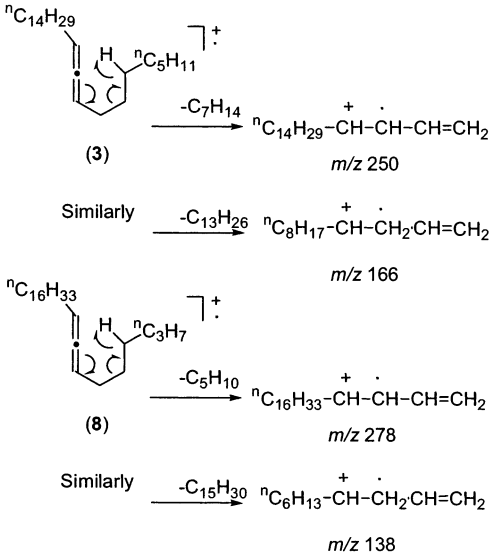

FIGURE 3. McLafferty ions derived from $\Delta^{9,10}$-pentacosadiene (**3**) and $\Delta^{7,8}$-pentacosadiene (**8**).

TABLE 1. $\Delta^{9,10}$-Alkadienes from Canebeetle Species

scarab species	$\Delta^{9,10}$-alkadienes RCH=•=CH$^nC_8H_{17}$
A. consanguineus	**2** (C-24), **3** (C-25),[a] **4** (C-26), **5** (C-27)
L. negatoria	**3** (C-25)[a]
L. crinita	**6** (C-29), **7** (C-31)[a]
L. picticollis	**1** (C-23)[a]
D. albohirtum	**1** (C-23)[a]

[a] Major allene in each species.

exhibited a multiplet (2H) at δ 5.07, a diagnostic region for internal allenes,[13] and HSQC analysis indicated coupling with the carbon resonance at δ 90.8, again appropriate[14] for the sp^2-carbon of an internal allene. Insufficient material prevented detection of the sp-C signal, which normally resonates at ca. 200 ppm.

Other Allenes from *A. consanguineus* and other Melolonthine Scarab Species. Unambiguous determination of the structure of the $C_{25}H_{48}$ cuticular hydrocarbon, deduced above to be $\Delta^{9,10}$-pentacosadiene (**3**), was achieved by synthesis and then spectroscopic and chromatographic comparisons. Minor components of the *A. consanguineus* extract were also concluded to be allenic in nature, as were components from several other canebeetle species. These are listed in Table 1 and were confirmed to be $\Delta^{9,10}$ allenes on the basis of their mass spectroscopic behavior (Table 2) and synthesis.

Synthesis of $\Delta^{9,10}$-Alkadienes, R−CH=•=CH−$^nC_8H_{17}$. The proposed allenes are chiral molecules, and with the expectation that these will be nonracemic in nature, methods of synthesis[15] capable of delivering enantioenriched allenes were sought. Consequently, we considered appropriate propargylic alcohols to be key intermediates for transformation to the allenes, as methods for

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(12) Wiersig, J. R.; Yeo, A. M. H.; Djerassi, C. *J. Am. Chem. Soc.* **1977**, *99*, 532.

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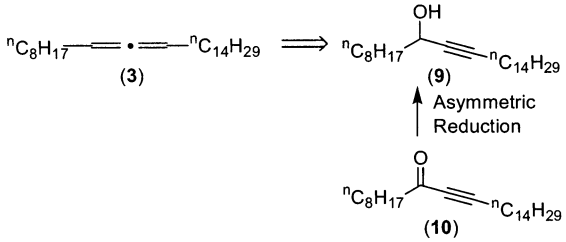
(14) Janssen, R. H. A. M.; Lousberg, R. J. J.; de Bie, M. J. A. *Recl. Trav. Chim. Pays-Bas*. **1981**, *100*, 85.

(15) For a review, see: Hopf, H. The Preparation of Allenes and Cumulenes. In *The Chemistry of Ketenes, Allenes and Related Compounds*; Patai, S., Ed.; John Wiley & Sons.: Chichester, U.K., 1980; Part 2, Vol. 20, pp 779−902.

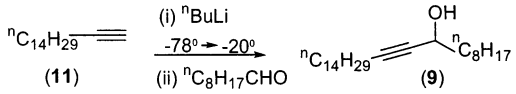
TABLE 2. Selected Mass Spectral Data for Natural $\Delta^{9,10}$-Alkadienes 1−7

$\Delta^{9,10}$-alkadiene	mol ion	McLafferty ions
1 (C-23)	320	166, 222
2 (C-24)	334	166, 236
3 (C-25)	348	166, 250
4 (C-26)	362	166, 264
5 (C-27)	376	166, 278
6 (C-29)	404	166, 306
7 (C-31)	432	166, 334

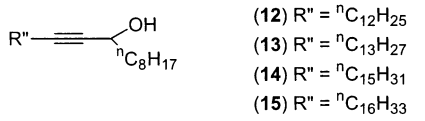
their construction were straightforward, and in addition, it appeared that asymmetric reduction of propargylic ketones would furnish the requisite chiral nonracemic propargylic alcohols.[16] These plans are summarized below for $\Delta^{9,10}$-pentacosadiene (**3**), for which propargylic alcohol (**9**) and the corresponding ketone (**10**) are suitable precursors.



Synthesis of Racemic Propargylic Alcohols. The initial approach was based on the addition of the appropriate alkynyllithium reagent to nonanal. For example, terminal alkyne (**11**) was deprotonated and the anion added to nonanal to provide pentacos-10-yn-9-ol (**9**), now ready for allene formation.

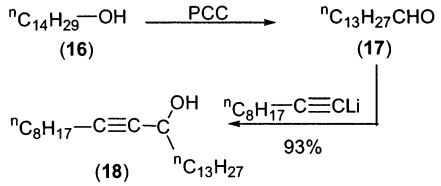


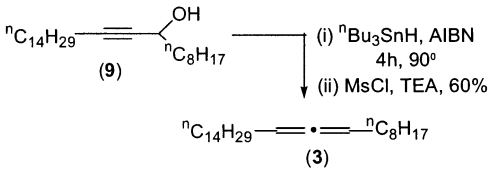
In this way, propargylic alcohols **12**−**15**, with R″ = $^nC_{12}H_{25}$, $^nC_{13}H_{27}$, $^nC_{15}H_{31}$, and $^nC_{16}H_{33}$, were also acquired. As we shall see below, these propargylic alcohols were transformed to $\Delta^{9,10}$-tricosadiene **1**, $\Delta^{9,10}$-tetracosadiene **2**, $\Delta^{9,10}$-hexacosadiene **4**, and $\Delta^{9,10}$-heptacosadiene **5**.



There are two propargylic alcohols that are possible precursors of each $\Delta^{9,10}$-allene: a 10-alkyn-9-ol and a 9-alkyn-11-ol. Reaction of 1-decynyllithium with a suitable aldehyde should afford a propargylic alcohol for further processing to a $\Delta^{9,10}$-allene. In an effort to improve the final yield of $\Delta^{9,10}$-tetracosadiene (**2**), *n*-tetradecanal (**17**) (from *n*-tetradecanol (**16**)) reacted with *n*-decynyllithium to afford the 9-yn-11-ol propargylic alcohol (**18**), cleanly and in high yield.

Conversion of (±) Propargylic Alcohols to $\Delta^{9,10}$-Alkadienes. (a) Stannylation−Deoxystannylation. In 1992, Konoike and Araki[17] described the stereoselective synthesis of allenes from propargylic alcohols via regioselective addition of $^nBu_3SnH$ to afford an α-hydroxyvinylstannane. Conversion to the mesylate was accompanied by elimination of $^nBu_3SnOMs$ to afford the allene. A stereoselective transformation was also achieved utilizing a nonracemic chiral propargylic alcohol. The conversion of propargylic alcohol (**9**) to (±)-$\Delta^{9,10}$-pentacosadiene (**3**) is shown below.

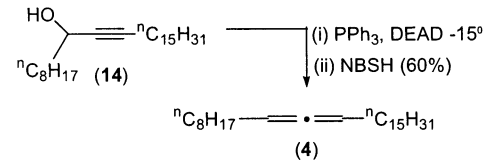


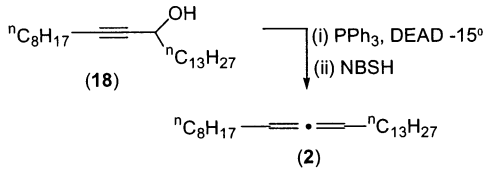


Similar treatment of other propargylic alcohols (**12**−**15**) provided $\Delta^{9,10}$-tricosadiene **1**, $\Delta^{9,10}$-tetracosadiene **2**, $\Delta^{9,10}$-hexacosadiene **4**, and $\Delta^{9,10}$-heptacosadiene **5**.

(b) Mitsunobu-Like Conversion of (±) Propargylic Alcohols to $\Delta^{9,10}$-Alkadienes. Myers[18,19] has described a very attractive procedure for transforming propargylic alcohols to allenes, using *o*-nitrobenzenesulfonylhydrazine (NBSH), triphenylphosphine, and diethylazodicarboxylate (DEAD). This Mitsunobu reaction provides the hydrazine, which experiences thermal decomposition above −15 °C to afford the allene, and details of the pathway to provide chiral nonracemic allenes are given later.

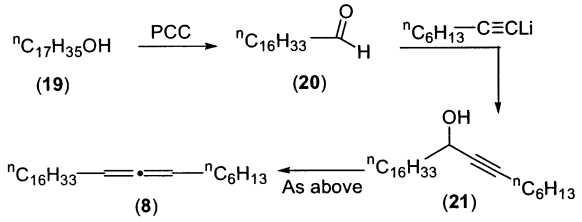
This approach was attempted on hexacos-10-yn-9-ol (**14**) and provided $\Delta^{9,10}$-hexacosadiene (**4**) in a higher yield than obtained by the stannylation−deoxystannylation protocol. Purification was also considerably simpler, and conventional flash chromatography provided pure allene. Similarly, $\Delta^{9,10}$-tetracosadiene (**2**) was obtained from tetracos-9-yn-11-ol (**18**) in good yield.



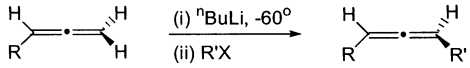


The nonnatural $\Delta^{7,8}$-pentacosadiene (**8**) was similarly obtained from heptadecanol **19**.

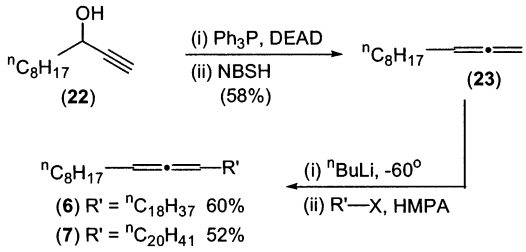
(16) Singh, V. K. *Synthesis* **1992**, *7*, 605.
(17) Konoike, T.; Araki, Y. *Tetrahedron Lett.* **1992**, *33*, 5093.
(18) Myers, A. G.; Zhang, B. *J. Am. Chem. Soc.* **1996**, *118*, 4492.
(19) Myers, A. G.; Zhang, B. *J. Org. Chem.* **1997**, *62*, 7507.



Alkylation of Allenes: Δ^{9,10}-Hentriacontadiene (7) and Δ^{9,10}-Nonacosadiene (6). Attempted synthesis of Δ^{9,10}-hentricontadiene **7** failed with the stannylation−deoxystannylation procedure with hentriacont-10-yn-9-ol. Low level formation of the allene was accompanied by predominating enyne material, and an alternative approach was required for this longer chain allene. Terminal allenes may be deprotonated with ^{n}BuLi at low temperature and then trapped with various electrophiles.[20]



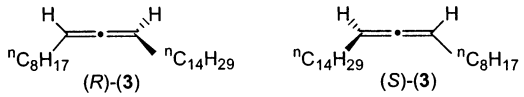
Such an approach was utilized to acquire Δ^{9,10}-hentriacontadiene **7** and Δ^{9,10}-nonacosadiene **6**. Undec-1-yn-3-ol (**22**) was converted, using the Myer's procedure,[19] to 1,2-undecadiene (**23**), which was deprotonated and alkylated with stearyl bromide to form Δ^{9,10}-nonacosadiene (**6**), as shown below. Similarly, alkylation with iodoeicosane (from reduction and halogenation of arachidonic acid) afforded Δ^{9,10}-hentriacontadiene (**7**). Purification was considerably simpler in this procedure.



Overall, the seven allenic compounds (**1**−**7**) isolated from scarab beetles have been synthesized as racemates by three separate procedures based on propargylic alcohols and involve an elimination step for final allene creation.

The synthesized allenes (**1**−**7**) were fully characterized by ^{1}H and ^{13}C NMR spectroscopy, and Δ^{9,10}-nonacosadiene (**6**) showed a diagnostic infrared absorption at 1960 cm^{-1}. In the case of Δ^{9,10}-tetracosadiene (**4**), all 24 carbon-13 NMR signals were resolved in the 187 MHz spectrum. Full details are summarized elsewhere.[11]

Allene Chiralty. 1,3-Disubstituted allenes such as those described above from canebeetles possess a chiral axis. However, the scarcity of natural material required that synthesis and enantioselective chromatography be the basis for a determination of any preferred chirality among them. König had reported[21] that the enantiomers of 1-*tert*-butyl-3-ethylallene (and higher homologues) and some cyclic allenes[22] were separated on a cyclodextrin-based phase, and we hoped that several of the predominating allenes in the canegrubs would respond to this approach. We recognized, however, that the very similar substitution patterns (H and long alkyl chain) at C-9 and C-11 and only moderate volatility could pose difficulties for practical enantiomer separation of these hydrocarbons. The enantiomers of (±)-Δ^{9,10}-pentacosadiene (**3**) failed to separate on permethylated *β*-cyclodextrin or Lipodex E [octakis(3-*O*-butyryl-2,6-di-*O*-pentyl)-*γ*-cyclodextrin] phases under a range of temperature programs and conditions. However, baseline separation was achieved with a 6-*O*-TBDMS-2,3-di-*O*-methyl-*β*-cyclodextrin stationary phase under isothermal conditions on a capillary column. This separation emphasizes the remarkable efficacy of modified cyclodextrins for enantiomer separations.[22] Examination of an extract from *A. consanguineus*, containing Δ^{9,10}-pentacosadiene (**3**), under the same conditions, established that the natural allene was nonracemic, with 89% ee, based on GC integration results. A coinjection experiment with synthetic (±)-Δ^{9,10}-pentacosadiene (**3**) confirmed that the first eluting peak was the predominant natural enantiomer. The (*R*)- and (*S*)-enantiomers of (**3**) are shown below.



The enantiomers of Δ^{9,10}-tricosadiene (**1**), from *Dermolepida albohirtum*, were also baseline separated and exhibited an ee of 86%. However, (±)-Δ^{9,10}-heptacosadiene (**5**) was not baseline separated, and examination of other higher allenes was not pursued because of poor prospects of separation and generally very low natural abundance. However, the observations of >85% ee for Δ^{9,10}-tricosadiene (**1**) and Δ^{9,10}-pentacosadiene (**3**) were of interest, and identification of the predominant enantiomer required synthesis of nonracemic samples of known predominating chirality.

Synthesis of (*R*)-(−)-Δ^{9,10}-Pentacosadiene [(*R*)-3]. On the basis of the procedures developed for acquiring the racemic allenes, the first requirement was an efficient route to the nonracemic propargylic alcohols, which would then be processed to the corresponding allenes by either the "stannylation−deoxystannylation" procedure[17] or the Myer's hydrazine method.[19] Racemic pentacos-10-yn-9-ol (**9**) was oxidized to the ketone (**10**) with TPAP/NMO, and various procedures for asymmetric reduction to the propargylic alcohols were then investigated. Treatment of pentacos-10-yn-9-one (**10**) with borane−dimethyl sulfide and (*S*)-MeCBS[23,24] afforded smooth reduction to the alcohol (*S*)-**9** of satisfactory ee, based on Mosher ester analysis.[25]

(20) Brandsma, L.; Verkruijsse, H. D. *Synthesis of Acetylenes, Allenes and Cumulenes: A Laboratory Manual*, 1st ed.; Elsevier: Amsterdam, 1981; pp 7−8 and 21−24.

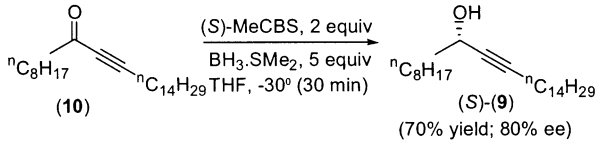
(21) Pietruszka, J.; Hochsmith, D. H.; Gehrcke, B.; Icholu, D.; Runge, T.; König, W. A. *Tetrahedron Asymmetry* **1992**, *3*, 661.

(22) König, W. A. *Gas Chromotographic Enantiomer Separation* with *Modified Cyclodextrins*; Hüthig Buch Verlag: Heidelberg, 1992; especially p 38.

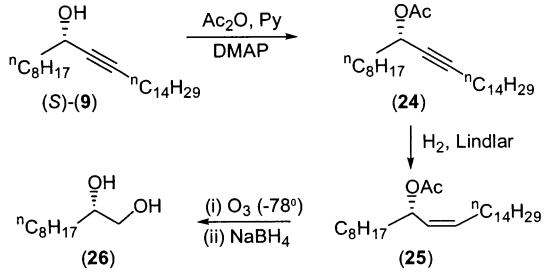
(23) (a) Corey, E. J.; Shibata, S.; Bakshi, R. K. *J. Org. Chem*. **1988**, *53*, 2861. (b) Helal, C. J.; Magriotis, P. A.; Corey, E. J. *J. Am. Chem. Soc*. **1996**, *118*, 10938. (c) Corey, E. J.; Helal, C. J. *Angew. Chem. Int. Ed*. **1998**, 1986.

(24) Parker, K. A.; Ledeboer, M. W. *J. Org. Chem*. **1996**, *61*, 3214.

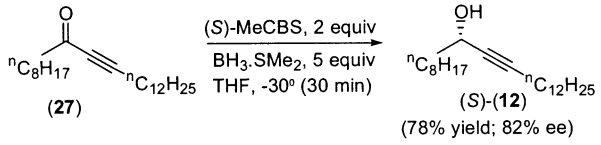
(25) Sullivan, G. R.; Dale, J. A.; Mosher, H. S. *J. Org. Chem*. *38*, 2143.



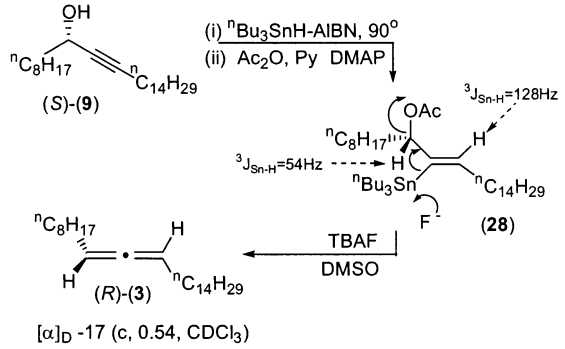
The (*R*)-alcohol (*R*)-**9**, of 85% ee, was also acquired using (*R*)-MeCBS and BH_3-Me_2S. The assigned configurations are in agreement with predictions based on the findings of Mosher and Dale.[25] Proof of the correctness of the above deductions was obtained in the following way. The pentacos-10-yn-9-ol [(*S*)-**9**], from (*S*)-MeCBS reduction, was converted to the acetate (**24**), which under Lindlar reduction conditions afforded alkene (**25**), which was ozonolyzed with reductive workup to provide (−)-decane-1,2-diol (**26**) with $[\alpha]^{23}_D$ −7 (*c*, 0.12, MeOH). Authentic (*S*)-decane-1,2-diol (**26**) has been reported[26] to exhibit $[\alpha]^{23}_D$ −11.9 (*c*, 0.43, MeOH).



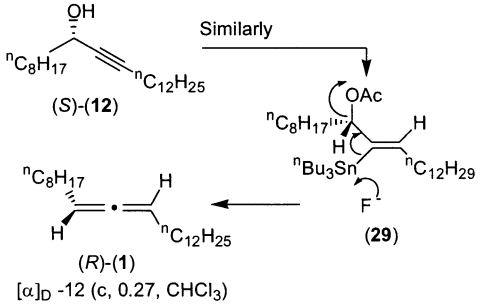
(*S*)-Tricosa-10-yn-9-ol [(*S*)-**12**], of 82% ee, was acquired similarly by (*S*)-MeCBS reduction of tricos-10-yn-9-one (**27**).



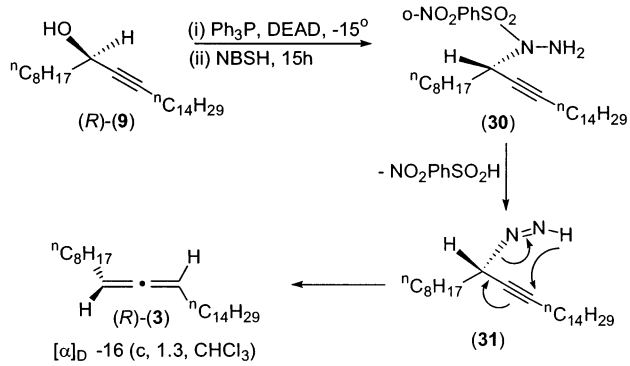
Conversion of Nonracemic Propargylic Alcohols to Allenes. Hydrostannylation with $^nBu_3SnH$ and AIBN at 90 °C of (*S*)-pentacos-10-yn-9-ol [(*S*)-**9**] produced the corresponding vinyl stannane, which was immediately converted to the acetate **28** for easier purification. This acetate exhibited a ^1H NMR spectrum confirming very predominant trans addition of $^nBu_3SnH$, to form the (*S*)-(*Z*)-α-acetoxy vinyl stannane **28**. The geometry of this stannane was critical in controlling the stereochemical outcome of the elimination, and so this was assessed by considering the $^{119}Sn-^1H$ coupling constants. A typical trans $^{119}Sn-^1H$ coupling constant ($^3J_{Sn-H}$) is ca. 130 Hz,[27] and for **28** the value was 128 Hz. The regiochemistry of the Sn−H addition was established by the magnitude of $^3J_{Sn-H}$ (54 Hz) to the methine proton. Alternate addition of $^nBu_3Sn-H$ would involve a four-bond Sn−H coupling, and for this, J = 54 Hz is unreasonably large. These parameters are shown below. Treatment of the acetoxystannane with TBAF in DMSO afforded (*R*)-$\Delta^{9,10}$-pentacosadiene [(*R*)-**3**] and under these conditions anti-elimination is very likely, as shown. Levorotation of the product allene is completely consistent with the (*R*)-configuration.[28]



$\Delta^{9,10}$-Tricosadiene formed in the same general way from (*S*)-propargylic alcohol [(*S*)-**12**] was assigned the (*R*)-configuration [(*R*)-**1**].



The above procedure of Konoike[17] furnishes (*R*)-configured allenes from (*S*)-propargylic alcohols. In contrast, the procedure of Myers,[18,19] involving a Mitsunobu inversion and a pericyclic process, provides the (*R*)-allene from the (*R*)-propargylic alcohol. (*R*)-Pentacos-10-yn-9-ol [(*R*)-**9**] was treated with triphenylphosphine and DEAD at −15 °C, and then *o*-nitrobenzenesulfonyl hydrazine (NBSH) was added. This sequence provided (*R*)-(−)-$\Delta^{9,10}$-pentacosadiene [(*R*)-**3**] in moderate yield, as summarized below.



The acquisition of (−)-$\Delta^{9,10}$-pentacosadiene [(*R*)-**3**] by two different methods from enantiomeric precursors, both

(26) Masooka, Y.; Masayuki, S.; Mori, K. *Agric. Biol. Chem.* **1982**, *46*, 2139.

(27) (a) Leusink, A. J.; Budding, A. J.; Marsman, J. W. *J. Organomet. Chem.* **1967**, *9*, 285. (b) Lautens, M.; Huboux, A. H. *Tetrahedron Lett.* **1990**, *31*, 3105.

(28) (a) Pasto, D. J.; Sugi, K. D. *J. Org. Chem.* **1991**, *56*, 4157, and references therein. (b) Alexakis, A.; Merek, I.; Mangeney, P.; Normant, J. F. *J. Am. Chem. Soc.* **1990**, *112*, 8042. (c) Runge, W.; Kreske, G. *J. Am. Chem Soc.* **1977**, *99*, 5597.

of which were predicted to provide (*R*)-configured allene, is supportive of the assignments shown.

Enantioselective Gas Chromatography and Chirality of the Natural Allenes. With the availability of the racemic and (*R*)-configured synthetic allenes, enantioselective gas chromatographic analyses were conducted to establish the absolute configuration of the natural components. Such an analysis with (±)-$\Delta^{9,10}$-pentacosadiene (**3**) provided enantiomer separation after 180 min, under isothermal conditions at 165 °C on a fused silica capillary column with heptakis(6-*O*-*tert*-butyldimethylsilyl-2,3-di-*O*-methyl)-*β*-cyclodextrin dissolved in polysiloxane OV1701 (50% w/w) and H_2 as the carrier gas. The (*R*)-enantiomer, (*R*)-**3** (76% ee), elutes first, and coelution studies with the natural samples from *A. consanguineus* show it to be (*R*)-configured with 89% ee (See Supporting Information). Similar examination with $\Delta^{9,10}$-tricosadiene (**1**) was conducted, and the synthetic sample was of 77% ee and predominantly the (*R*) enantiomer, (*R*)-**1**. The $\Delta^{9,10}$-tricosadiene from *D. albohirtum* was (*R*)-configured with 86% ee. We suggest that other allenes present in the CHs of canegrubs are also likely to be (*R*)-configured, but low natural levels or lack of separation of the enantiomers, e.g. $\Delta^{9,10}$-heptacosadiene (**5**) or $\Delta^{9,10}$-hentriacontadiene (**7**), prevented further examinations of this type.

NMR Analysis with Chiral Shift Reagents. Enantiomeric excesses of allenic compounds have been determined by ^{1}H NMR analyses with 1:1.5 mixtures of Ag(fod) and Yb(hfcd)$_3$ with $CDCl_3$ as solvent. The work of Gore[29] suggested that the allenic protons in the (*R*)-enantiomer were shifted further downfield than those in the (*S*)-antipode under these conditions. This approach was investigated for the allenic ^{1}H signals in (±)-$\Delta^{9,10}$-pentacosadiene (**3**), and the H9 and H11 signals broaden and shift to lower field. The signals for H9 and H11 within a single stereoisomer were not separated, so the two baseline separated signals represent the H9 and H11 protons of the two stereoisomers (*R*)-**3** and (*S*)-**3**. Nonracemic $\Delta^{9,10}$-pentacosadiene (**3**), prepared by the procedure of Myers,[19] [from (*R*)-pentacos-10-yn-9-ol, (*R*)-**9**] produced a 13:1 ratio of signals in the allenic region (ca. δ 5.4−6.0) when added to a solution of the chiral shift reagents, with the more intense signal at lower field (see Supporting Information). This was consistent with the predominance of the (*R*)-enantiomer (*R*)-**3**, and integration provided an ee of 80−85%, in satisfactory agreement with the enantioselective gas chromatographic analyses. This indicates that thermal- or column-induced racemization is minor under the described GC conditions.

Biosynthetic Considerations. In natural canebeetle extracts, we noted that $\Delta^{9,10}$-pentacosadiene (**3**) and $\Delta^{9,10}$-tricosadiene (**1**) were accompanied by (*Z*)-9-pentacosene and (*Z*)-9-tricosene, respectively, each in significant amounts. The implied importance of a desaturase with Δ^9-specificity is consistent with other data on unsaturated cuticular hydrocarbons.[30] The biosynthesis of (*Z*)-9-tricosene, the female pheromone of *Musca domestica*, commences de novo from acetate, with stearic acid (C_{18}) experiencing Δ^9-desaturation, chain-elongation, and decarboxylation.[31] The more abundant odd-carbon-numbered allenes could result in a similar way, but the timing of the second desaturation with the chain elongation steps is unclear. Alkynes were not detected in the natural extracts. We also noted that 3-methyltricosane and 3-methylpentacosane accompanied the $\Delta^{9,10}$-tricosadiene (**1**) and $\Delta^{9,10}$-pentacosadiene (**3**), respectively, and these correspond with early methylmalonyl intervention in chain construction, but without desaturation.[31,32] In this general connection, the recent disclosure[33] of the presence of (*Z*)-9-docosen-1-ol (and 1-al) and (*Z*)-9-tetracosen-1-ol (and 1-al) in a hymenopteran parasitoid may be explained similarly, but with eventual reduction of the elongated fatty acyl derivative to the aldehyde or alcohol levels. Feeding experiments are being undertaken with the scarab beetles to test some of these hypotheses.

Summary and Conclusions

Insects from five canebeetle species have been demonstrated to contain unbranched, aliphatic allenic hydrocarbons, all with $\Delta^{9,10}$-unsaturation. These molecules vary in length from 23 to 31 carbon atoms, and in two cases (C23 and C25), the absolute configuration has been determined to be *R* with a high (>85%) ee by enantioselective gas chromatography. This is interesting, as the pheromone of the dried bean beetle, which contains a $\Delta^{9,10}$-alkadiene moiety, is also (*R*)-configured.[34] Both racemic and nonracemic allenes were accessed from propargylic alcohols by fluoride-ion promoted anti-deoxystannylation or Mitsunobu inversion/hydrazine elimination. (*R*)-Allenes were levorotatory, in agreement with literature reports[28] from simpler systems. Biosynthetic studies to determine the metabolic origin are required, as are field experiments to understand the biological role and possible pheromonal activity of this unprecedented family of insect hydrocarbons. The high molecular weight of these metabolities and low volatility may suggest a short-range pheromonal role, made reasonable by the structural resemblance to (*Z*)-9-tricosene from *M. domestica*.

Experimental Section

General Methods. ^{1}H NMR spectra were recorded at 400 or 200 MHz with the signal for residual $CHCl_3$ in the $CDCl_3$ solvent (δ7.24) as internal standard. ^{13}C NMR spectra were recorded at 100 or 50 MHz with either TMS (δ = 0) or the central peak of the $CDCl_3$ triplet (δ77.00) as internal standard. The ^{13}C spectrum of $\Delta^{9,10}$-tetracosadiene **2** was also recorded at 187 MHz, and resolution of all 24 signals was achieved. Flash chromatography was performed with Kieselgel S (0.032−

(29) Gore, J.; Mannschreck, A.; Burgemeister, T.; Cazes, B. *Tetrahedron* **1986**, *42*, 399.

(30) (a) Pennanec'h, M.; Bricard, L.; Kunesch, G.; Jallon, J.-M. *J. Insect Physiol.* **1997**, *43*, 111. (b) Nelson, D. R. Methyl-branched lipids in Insects. In *Insect Lipids: Chemistry, Biochemistry and Biology*; Stanley-Samuelson, D. W., Nelson D. R., Eds.; University of Nebraska Press: Lincoln, NE, 1993; pp 271−315. (c) For an overview, see: Tillman, J. A.; Seybold, S. J.; Jurenka, R. A.; Blomquist, G. J. *Insect Biochem. Mol. Biol.* **1999**, *29*, 481.

(31) Blomquist, G. J.; Dillwith, J. W.; Adams, T. S. Biosynthesis and Endocrine Regulation of Sex Pheromone Production in Diptera. In *Pheromone Biochemistry;* Prestwick, G. D., Blomquist, G. H., Eds.; Academic Press: Orlando, FL, 1987; pp 217−250.

(32) Dillwith, J. W.; Nelson, J. H.; Pomonis, J. G., Nelson, D. R.; Blomquist, G. J. *J. Biol. Chem.* **1982**, *257*, 11305.

(33) Thomas, J. A.; Knapp, J. J.; Akino, T.; Gerty, S.; Wakamura, S.; Simcox, D. J.; Wardlaw, J. C. Elmers, G. W. *Nature* **2002**, *417*, 505.

(34) (a) Landor, P. D.; Landor, S. R.; Mukasa, S. *J. Chem. Soc. D* **1971**, *24*, 1638. (b) Mori, K.; Nukada, T.; Ebata, T. *Tetrahedron* **1981**, *37*, 1343.

0.063 mm). GC−MS analyses were carried out with an EI detector, using a 30 m column, 0.25 mm i.d. with a 0.2 μm phase thickness of bonded stationary phase, with He as the carrier gas. Enantioselective gas chromatography was conducted under isothermal conditions on a fused silica capillary column with heptakis(6-*O*-*tert*-butyl-dimethylsilyl-2,3-di-*O*-methyl)-β-cyclodextrin dissolved in polysiloxane (50% w/w), with H_2 as the carrier gas.

Specimens of *A. consanguineus*, *Lepidiota negatoria*, *Lepidiota crinita*, *Lepidiota picticollis*, and *D. albohirtum* were field collected as larvae from various Queensland sugarcane fields and reared to adults under laboratory conditions at BSES Bundaberg and Ayr.

Location of Unsaturation. *A. consanguineus* cuticular extracts (hexane or DCM) were concentrated under N_2 and the resultant compounds were dissolved in a 9:1 hexane: methanol solution (1 mL). Mercuric acetate (20 mg) was added and the suspension was shaken, after which it was stored in the dark for 40 h. Acetic acid (2 drops) and either $NaBH_4$ or $NaBD_4$ (50 mg) (see text) were added. The solution was decanted from the metallic mercury, diluted with hexane, and washed with 1 M HCl. The hexane layer was then examined by GC−MS. 9-Methoxy-10-pentacosene and 11-methoxy-9-pentacosene appeared as two early eluting peaks, corresponding to the cis- and trans-isomers, with each peak being a mixture of regioisomers. GC−MS (first peak): *m/z* 380 (M^+, 0.2), 268 (4), 267 ($^nC_{14}H_{29}CH{=}CHCHOMe^+$, 20), 184 (6), 183 ($^nC_8H_{17}CH{=}CHCHOMe^+$, 53). A very similar MS was exhibited by the second peak. Two later eluting peaks with identical MS were assigned to the diastereomeric 9,11-dimethoxypentacosanes. GC−MS: *m/z* 412 (M^+, 1.1), 397 (1), 380 (10), 347 (1), 282 (1), 267 (5), 242 (6), 241 (29). Use of $NaBD_4$ in the reduction steps led to a mixture of [10-$^2H_1$]-9-methoxy-10-pentacosene and [10-$^2H_1$]-11-methoxy-9-pentacosene, which exhibited M^+ of *m/z* 381 for incorporation of one deuterium atom. Two isomers of [10,10-$^2H_2$]-9,11-dimethoxypentacosane were observed with *m/z* 399 ($M^+ - 15$, ~1), corresponding to M^+ 414.

That these interpretations were reasonable was supported by examination of authentic $\Delta^{9,10}$-hexacosadiene **4**. Processing of 10 mg of this allene as described above, followed by flash chromatography (hexane), afforded a fraction containing a mixture of mono-methyl ethers and a second containing a mixture of bis-methyl ethers. The mono-ethers were 9-methoxyhexacos-10-ene and 11-methoxyhexacos-9-ene, both as cis−trans mixtures, on the basis of GC−MS and ^1H and ^{13}C NMR spectra. The important bis-ethers [$C_{27}H_{55}O_2$ ($M^+ - CH_3$) requires 411.4202, measured 411.4197] exhibited anticipated major ions at *m/z* 255 and 157 and major and minor methoxy signals at δ 3.31 and 3.28 (^1H) and δ 56.6 (^{13}C). These mono- and bis-methyl ethers were only obtained as a mixture of stereoisomers and were not fully characterized due to insufficient material.

Synthesis of racemic $\Delta^{9,10}$-allenes was based on a procedure in which an alkynyllithium reagent was added to nonanal to afford the propargylic alcohol, which could then be processed to the $\Delta^{9,10}$-allene. This procedure is illustrated for $\Delta^{9,10}$-pentacosadiene (**3**).

Pentacos-10-yn-9-ol (9). Hexadec-1-yne (**11**) (1.0 g, 5.4 mmol) (available from Lancaster Synthesis) was dissolved in anhydrous THF (10 mL) and to the cooled solution (−78 °C), was added ^{n}BuLi (3.0 mL, 1.3 M in hexane, 3.75 mmol). After complete deprotonation (4 h) at −40 °C, a solution of nonanal (0.58 g, 4.5 mmol) was added dropwise. The reaction mixture was stirred (~12 h) and allowed to warm to room temperature. Saturated brine (20 mL) was added and the mixture extracted with ether (3 × 60 mL), The combined ether layers were dried ($MgSO_4$) and concentrated to afford the crude propargylic alcohol (**9**), which was purified by flash chromatography (hexane then 10% ether−hexane) (0.70 g, 2.3 mmol, 51%). ^1H NMR: δ 0.86 (t, J 6, 3H), 1.23 (brs, 36H), 1.54 (m, 2H), 2.21 (t of d, J 6, 2, 2H), 3.4 (brs, 1H), 4.32 (t of t, J 6.3, 1.9, 1H). ^{13}C NMR: δ 14.1, 18.7, 22.7, 25.2, 28.7, 28.8, 29.1, 29.2, 29.3, 29.4, 29.5, 31.9, 31.9, 38.2, 62.8, 81.3, 85.6 (not all signals resolved.) GC−MS: *m/z* 335 (M − 29, 1), 293 (1), 251 (4), 195 (1), 167 (15), 149 (2), 121 (13), 95 (34). Anal. Calcd for $C_{25}H_{48}O$: C, 82.4; H, 13.2. Found: C, 82.7; H, 13.4.

$\Delta^{9,10}$-Pentacosadiene (3). The above pentacos-10-yn-9-ol (**9**) (38.6 mg, 0.10 mmol) and AIBN (2 mg) were added to a flame-dried 5 mL round-bottomed flask and heated to 92 °C using a thermostat-controlled oil bath. *n*-Tributyltin hydride (30.8 mg, 0.106 mmol, 1 equiv) was added via syringe and the reaction mixture was maintained, under N_2, at this temperature for a further 3 h, after which it was cooled to 0 °C. DCM (1 mL), triethylamine (0.21 g, 0.21 mmol) and methanesulfonyl chloride (18.2 mg, 0.16 mmol, 1.5 equiv) were then added. The solution was stirred at 0 °C for 15 min and then at 20 °C (30 min) before being poured into 1 M HCl (5 mL). The mixture was extracted with ether (3 × 10 mL), and the combined ether layers were dried ($MgSO_4$) and concentrated. Repeated chromatography (silica) afforded pure $\Delta^{9,10}$-pentacosadiene (**3**) (21 mg, 0.7 mmol, 60%). ^1H NMR: δ 0.86 (t, J 6.9, 6H), 1.23 (br, 36H), 2.00 (m, 4H), 5.04 (m, 2H). ^{13}C NMR: δ 14.1, 22.7, 29.0, 29.1, 29.2, 29.3, 29.4, 29.5, 29.7, 31.9, 90.9, 203.8. (Not all signals resolved.) GC−MS: *m/z* 348 (M^+, 1), 250 (6), 208 (3), 166 (15), 138 (13), 109 (19). Anal. Calcd for $C_{25}H_{48}$: C, 86.2; H, 13.8. Found: C, 85.8, H, 14.1.

Other $\Delta^{9,10}$-allenes accessed by the procedure outlined above were $\Delta^{9,10}$-tricosadiene (**1**), $\Delta^{9,10}$-tetracosadiene (**2**), $\Delta^{9,10}$-hexacosadiene (**4**), and $\Delta^{9,10}$-heptacosadiene (**5**).

Tricos-10-yn-9-ol (12). The 1-alkynyllithium reagent derived from tetradec-1-yne (available from Lancaster Synthesis) was added to nonanal as described to furnish tricos-10-yn-9-ol (**12**). ^1H NMR: δ 0.86 (t, J 6, 6H), 1.23 (brs, 32H), 1.68 (m, 2H), 2.15 (t of d, J 7, 2, 2H), 4.32 (m, 1H). ^{13}C NMR: δ 14.1, 18.7, 22.7, 25.2, 28.7, 28.8, 29.1 29.2, 29.3, 29.4, 29.5, 29.6, 29.7, 31.9 (2C), 38.2, 62.8, 81.3, 85.6. GC−MS: *m/z* 335 (1, M − 1), 307 (1), 265 (2), 223 (11), 195 (4), 167 (24), 135 (11). Anal. Calcd for $C_{23}H_{44}O$: C, 82.1; H, 13.1. Found: C, 81.8; H, 13.2.

$\Delta^{9,10}$-Tricosadiene (1). The above alcohol (**12**) was transformed to the allene in the described manner. ^1H NMR: δ 0.86 (m, 6H), 1.24 (brs, 32H), 1.94 (m, 4H), 5.04 (m, 2H). ^{13}C NMR: δ 14.1, 22.7, 29.0, 29.1, 29.2, 29.3, 29.4, 29.5 (2C), 29.7 (2C), 31.9 (2C), 31.9 (2C), 90.9, 203.8 (not all signals were resolved). GC−MS: *m/z* 320 (M^+, 2), 222 (9), 194 (4), 166 (21), 124 (20), 96 (66). Anal. Calcd for $C_{23}H_{44}$: C, 86.2 H, 13.8. Found: C, 85.9; H, 13.9.

Tetracos-10-yn-9-ol (13). The 1-alkynyllithium reagent derived from pentadec-1-yne (available from Lancaster Synthesis) was added to nonanal as described to furnish tetracos-10-yn-9-ol (**13**). ^1H NMR: δ 0.87 (m, 6H), 1.23 (m, 34H), 1.67 (m, 2H), 2.16 (m, 2H), 4.32 (m, 1H). GC−MS: *m/z* 322 (1), 293 (2), 265 (3), 237 (9), 195 (4), 167 (32). HREIMS: $C_{24}H_{46}O$ required 350.3549, measured 350.3544.

$\Delta^{9,10}$-Tetracosadiene (2). The above alcohol (**13**) was transformed to the allene in the described manner. ^1H NMR: δ 0.87 (m, 6H), 1.24 (brs, 34H), 1.97 (m, 4H), 5.07 (m, 2H). ^{13}C NMR: δ 14.1, 22.7, 26.8 (2C), 28.8, 29.0, 29.1, 29.2, 29.3, 29.4, 29.5, 29.7, 31.9, 90.9, 203.8. GC−MS: *m/z* 334 (M^+, 1), 281 (1), 253 (3), 236 (7), 207 (13), 166 (22), 138 (20), 96 (72). HREIMS: $C_{14}H_{46}$ requires 334.3600, measured 334.3599.

Hexacos-10-yn-9-ol (14). The 1-alkynyllithium reagent derived from heptadec-1-yne (available from ICN Biomedicals) was added to nonanal as described to furnish hexacos-10-yn-9-ol (**14**). ^1H NMR: δ 0.86 (m, 6H), 1.23 (m, 34H), 1.46 (m, 4H), 1.62 (m, 2H), 2.18 (m, 2H), 4.32 (m, 1H). ^{13}C NMR: δ 14.1, 18.7, 25.2, 28.6, 28.8, 29,1, 29.2, 29.3, 29.4, 29.5, 29.7, 41.9, 31.9, 38.2, 62.8, 81.3, 85.6. GC−MS: *m/z* 349 (1, M^+-29), 331 (1), 265 (5), 247 (1), 234 (1), 167 (21), 149 (6). Anal. Calcd for $C_{26}H_{50}O$: C, 82.5; H, 13.3. Found: C, 82.5; H, 13.6.

$\Delta^{9,10}$-Hexacosadiene (4). The above alcohol (**14**) was transformed to the allene in the described manner. ^1H NMR: δ 0.86 (m, 6H), 1.23 (m, 34H), 1.53 (m, 4H), 2.26 (m, 4H), 5.03 (m, 2H). ^{13}C NMR: δ 14.1, 22.7, 29.0, 29.1, 29.2, 29.3, 29.4

(2C), 29.5 (2C), 29.7, 31.9 (2C), 90.9, 203.8. GC−MS: *m/z* 362 (M^+, 8), 264 (7), 222 (3), 194 (2), 166 (15), 138 (17), 109 (23), 81 (79). HREIMS: $C_{26}H_{50}$ requires 362.3913, measured 362.3908.

Heptacos-10-yn-9-ol (15). The 1-alkynyllithium reagent derived from octadec-1-yne (available from Lancaster Synthesis) was added to nonanal as described to furnish heptacos-10-yn-9-ol (**15**). ^{1}H NMR: δ 0.86 (m, 6H), 1.23 (m, 40H), 1.59 (m, 2H), 2.17 (m, 2H), 4.39 (brs, 1H), 4.67 (m, 1H). ^{13}C NMR: δ 14.0, 18.7, 22.7, 25.2, 28.4, 28.7, 28.8, 29.1, 29.2, 29.3 (2C), 29.5, 29.7, 31.9, 38.2, 62.7, 81.3, 85.5. GC−MS: *m/z* 374 (M − H_2O, 1), 335 (2), 321 (7), 279 (18), 236 (6), 195 (7), 167 (53), 111 (53). Anal. Calcd for $C_{27}H_{52}O$: C, 82.1; H, 13.1. Found: C, 82.0; H, 13.4.

$\Delta^{9,10}$-Heptacosadiene (5). The above alcohol (**15**) was transformed to the allene in the described manner. ^{1}H NMR: δ 0.86 (t, J 6.2, 6H), 1.23 (brs, 40H), 1.94 (m, 4H), 5.04 (m, 2H). ^{13}C NMR: δ 14.1, 22.7, 29.0, 29.1, 29.2, 29.5, 29.7, 31.9, 90.9, 203.8. GC−MS: *m/z* 376 (M, 6), 278 (17), 250 (2), 236 (8), 208 (6), 166 (34), 109 (32), 82 (92), 67 (100). Anal. Calcd for $C_{27}H_{52}$: C, 86.2; H, 13.8. Found: C, 85.8, H, 14.2.

$\Delta^{9,10}$-Allenes using the Mitsunobu Protocol.[18,19] $\Delta^{9,10}$-Tetracosadiene (**2**) and $\Delta^{9,10}$-hexacosadiene (**4**), both described above, were also acquired by the Myer's variant[18,19] of the Mitsunobu reaction. The procedure is illustrated with $\Delta^{9,10}$-hexacosadiene (**4**). Triphenylphosphine (0.114 g, 0.44 mmol, 1.3 equiv) was dissolved in THF (1 mL) and to the cooled solution (−20 °C) was added DEAD (67 μL, 0.44 mmol, 1.3 equiv). After ca. 10 min, hexacos-10-yn-9-ol (**14**) (0.127 g, 0.34 mmol, 1 equiv), dissolved in THF (1 mL), was added by cannula. The resulting suspension was stirred for 10 min at −20 °C, after which time a solution of *o*-nitrobenzenesulfonylhydrazine (*o*-NBSH) (0.094 g, 0.44 mmol) in THF (1 mL) was added. After stirring at −20 °C for 30 min, the reaction mixture was further allowed to stir for ca. 12 h. Concentration under reduced pressure provided a residue that was triturated with hexane to afford a solution of the crude allene, which was then subjected to flash chromatography (hexane) to provide $\Delta^{9,10}$-hexacosadiene (**4**) (74 mg, 0.20 mmol, 60%). The full characterization of this compound is given above.

$\Delta^{9,10}$-Tetracosadiene (2) from Tetracos-9-yn-11-ol (18). ^{n}BuLi (6.5 mL, 1.2 M in hexane, 7.8 mmol) was added to a stirred solution of dec-1-yne (1.1 g, 8.0 mmol) in THF (10 mL) at −78 °C, and a solution of tetradecanal (**17**) (1.7 g, 8 mmol) [PCC oxidation of tetradecanol (**16**)] in THF (10 mL) was added, and the reaction mixture was extracted with hexane (3 × 100 mL). The combined organic layers were dried ($MgSO_4$) and concentrated to afford crude alcohol (**18**) (2.7 g, 7.4 mmol, 93%), which was purified by flash chromatography. ^{1}H NMR: δ 0.86 (m, 6H), 1.23−1.61 (m, 34H), 2.15 (m, 2H), 2.33 (m, 1H), 2.46 (m, 1H), 2.64 (brs, 1H), 4.29 (m, 1H). ^{13}C NMR: δ 14.0 (2C), 18.6, 22.6 (2C), 28.7, 28.8, 29.1, 29.2, 29.3 (2C), 29.6 (3C), 29.7, 31.8, 31.9, 38.1, 62.7, 81.4, 85.3. (Not all signals resolved). GC−MS: *m/z* 350 (M^+, 1), 294 (1), 265 (2), 237 (14), 209 (2), 167 (19), 149 (4). Anal. Calcd for $C_{24}H_{46}O$: C, 82.3; H, 13.1. Found: C, 82.1; H, 12.9. Treatment of this alcohol (**18**) (0.35 g, 1.0 mmol) as described above, with triphenyl phosphine, DEAD, and *o*-nitrobenzenesulfonylhydrazine provided $\Delta^{9,10}$-tetracosadiene (**2**) (0.145 g, 0.4 mmol, 44%). The spectroscopic data matched those listed above for this compound, and a fully resolved ^{13}C NMR spectra for this compound is included in the Supporting Information.

$\Delta^{7,8}$-Pentacosadiene (8). Heptadecanal (**20**) (0.8 g, 3.1 mmol) [oxidation of heptadecanol (**19**)] was added to a solution of octynyllithium in THF to afford pentacos-7-yn-9-ol (**21**), which was purified in the manner described above for other propargylic alcohols (0.75 g, 2.0 mmol, 65%). ^{1}H NMR: δ 0.86 (m, 6H), 1.25 (m, 36H), 1.43 (m, 2H), 2.0 (brs, 1H), 2.20 (m, 2H), 4.30 (m, 1H). ^{13}C NMR: δ 14.0, 14.1, 18.6, 22.5, 22.7, 25.2, 28.5, 29.2, 29.3 (2C), 29.6, 29.7, 31.3, 31.9, 38.2, 62,7, 81.3, 85.4 (not all signals were resolved). Anal. Calcd for $C_{25}H_{48}O$: C, 82.4; H, 13.2. Found: C, 81.9; H, 13.6. This alcohol (**21**) (0.26 g, 0.71 mmol) was processed in the described fashion to afford $\Delta^{7,8}$-pentacosadiene (**8**) (0.11 g, 0.32 mmol, 46%). ^{1}H NMR: δ 0.86 (m, 6H), 1.23 (m, 32H), 1.48 (m, 4H), 1.94 (M, 4H), 5.04 (m, 2H). ^{13}C NMR: δ 14.1, 22.7, 28.8, 29.0, 29.1. 29.2, 29.4, 29.5, 29.7, 31.7, 31.9, 90.9, 203.0. GC−MS: *m/z* 348 (M^+,1), 320 (1), 278 (5), 263 (1), 236 (3), 208 (1), 180 (2), 152 (1), 138 (55), 123 (9), HREIMS: $C_{25}H_{48}$ requires 348.3756, measured 348.3766.

$\Delta^{9,10}$-Hentriacontadiene (7). Triphenylphosphine (1.8 g, 6.9 mmol, 1.3 equiv) was dissolved in THF (20 mL) and to the cooled solution (−15 °C) was added DEAD (1.06 g, 6.9 mmol, 1.3 equiv) via syringe. The resulting orange solution was stirred for 10 min at −15 °C, and then 1-undecyn-3-ol (**22**) (0.89 g, 5.3 mmol, 1 equiv) (from addition of trimethylsilyl-protected ethynyllithium to nonanal[35]) was added as a THF solution (5 mL). After 10 min, a solution of *o*-NBSH (1.5 g, 6.9 mmol, 1.3 equiv) in THF (2 mL) was added via cannula, and the solution was allowed to warm to 20 °C over 2 h. The solution was concentrated and the residue purified by flash chromatography (hexane) to afford $\Delta^{1,2}$-undecadiene (**23**) (0.47 g, 3.1 mmol, 58%). ^{1}H NMR: δ 0.86 (t, J 6.8, 3H), 1.23−1.40 (m, 12H), 1.90−2.02 (m, 12H), 4.64 (m, 2H), 5.10 (m, 1H). ^{13}C NMR: δ 14.1, 22.7, 28.3, 28.4, 29.1 (2C), 29.3, 31.9, 74.5, 90.1, 208.5. These spectra matched those reported.[36] The $\Delta^{1,2}$-undecadiene (**23**) (100 mg, 0.66 mmol, 3 equiv) was dissolved in THF (2 mL) and to the cooled solution (−78 °C) was added ^{n}BuLi (1 equiv) dropwise, and after 30 min, a solution of 1-iodoeicosane ($^nC_{20}H_{41}I$) (87 mg, 0.21 mmol, 1 equiv) in 1:1 THF/HMPA (3 mL) was added. The deep red solution was stirred for a further hour at −78 °C and GC−MS analysis indicated complete consumption of the iodide. The reaction was worked up in the standard way, and the crude oil was purified by flash chromatography (hexane) to afford Δ9,10-hentriacontadiene (**7**) (47.9 mg, 52%). ^{1}H NMR: δ 0.86 (m, 6H), 1.23 (m, 48H), 1.89−1.97 (m, 4H), 5.06 (m, 2H). ^{13}C NMR: δ 14.1, 22.7, 29.0, 29.2, 29.3, 29.4, 29.5, 29.7, (2C), 31.9, 32.0, 90.9, 203.8. GC−MS: *m/z* 432 (M^+, 1), 363 (1), 334 (4), 292 (2), 166 (31), 152 (3), 124 (29), 110 (30). HREIMS: $C_{31}H_{60}$ requires 432.4695, measured 432.4688.

$\Delta^{9,10}$-Nonacosadiene (6). Similar deprotonation of $\Delta^{1,2}$-undecadiene (**23**) with ^{n}BuLi and alkylation with stearyl bromide (100 mg, 0.3 mmol) afforded Δ9,10-nonacosadiene (**6**) (78 mg, 65%). ^{1}H NMR: δ 0.86 (m, 6H), 1.23 (brm, 44H), 1.89−1.97 (m, 4H), 5.06 (m, 2H). ^{13}C NMR: δ 14.1, 22.7, 29.0, 29.2, 29.3, 29.4, 29.5, 29.7 (2C), 31.9, 32.0, 90.9, 203.8. (Not all signals resolved). GC−MS: *m/z* 404 (M^+, 1), 306 (13), 278 (2), 264 (3), 236 (1), 208 (1), 194 (1), 180 (1), 166 (45). IR 1960 cm^{-1}. Anal. Calcd for $C_{29}H_{56}$: C, 86.1; H, 13.9. Found: C, 85.7; H, 14.2. HREIMS: $C_{29}H_{56}$ requires 404.4382, measured 404.4391.

Pentacos-10-yn-9-one (10). A solution of *N*-methylmorpholine *N*-oxide (0.53 g, 4.5 mmol, 1.5 equiv) in DCM (50 mL) containing dry 4 Å sieves (3 g) was cooled (0 °C) and TPAP (40 mg) was added in one portion. The dark green solution was stirred under a nitrogen atmosphere for 5 min, after which a DCM solution (5 mL) of pentacos-10-yn-9-ol (**9**) (1.1 g, 3.02 mmol) was added by cannula. After 4 h, the suspension was filtered through Celite, concentrated, and chromatographed (silica, 20% ether/hexane) to provide pentacos-10-yn-9-one (**10**) (0.89 g, 2.5 mmol, 89%). ^{1}H NMR: δ 0.86 (m, 6H), 1.23 (brs, 32H), 1.58 (m, 4H), 2.26 (m, 2H), 2.33 (t, J 6.8, 1H), 2.49 (t, J 7.2, 1H). ^{13}C NMR: δ 14.1 (2C), 18.9, 22.6, 22.7, 24.2, 27.7, 28.9, 29.0 (2C), 29.1, 29.3 (2C), 29.4, 29.6, 29.7, 31.8, 31.9, 33.4, 45.5, 80.9, 94.3, 188.7. GC−MS: *m/z* 362 (M^+, 2), 305 (9), 291, (26), 249 (15), 207 (3), 193, (4). Anal. Calcd for $C_{25}H_{46}O$: C, 82.9, H, 12.7. Found: C. 83.1, H, 12.8.

(*S*)-(−)-Pentacos-10-yn-9-ol [(*S*)-9]. The above ynone (**10**) (0.212 g, 0.586 mmol) was dissolved in THF (2 mL) containing three molecular sieves (4 Å). After standing for 2 h under N_2, a toluene solution of (*S*)-Me-CBS catalyst (1.2 mL, 1 M, 1.2

(35) Katsuhira, T.; Harada, T.; Oku, A. *J. Org. Chem.* **1994**, *59*, 4010.
(36) Tsuji, J.; Sugiura, T.; Minamu, I. *Synthesis* **1987**, 603.

mmol, 2 equiv) was added via syringe. The resulting solution was cooled to −30 °C (dry ice−CCl_4 bath) and borane−dimethyl sulfide complex (0.35 mL, 10 M, 3.5 mmol, 6 equiv) was added dropwise with stirring. The reaction was monitored by TLC until no starting material remained, and then excess borane was destroyed by the addition of distilled MeOH (0.5 mL) at −30 °C. On reaching 20 °C, 1 M HCl (3 mL) was added, and the reaction mixture was extracted with ether (3 × 10 mL), washed with brine (2 mL), dried ($MgSO_4$), and concentrated to provide the crude alcohol. Flash chromatography afforded (*S*)-pentacos-10-yn-9-ol, (*S*)-(**9**) (0.148 g, 0.086 mmol, 70%). Mosher ester analysis indicated 80% ee, and according to the arguments of Mosher and Dale,[25] the compound was (*S*)-configured. The ^{1}H NMR spectrum agreed with that of the racemate listed above. Anal. Calcd for $C_{25}H_{48}O$: C, 82.4; H, 13.2. Found: C, 82.2; H, 13.2. $[\alpha]^{22}_D$ −0.63 (*c* = 1.34, $CHCl_3$). **[(*R*)-(+)-pentacos-10-yn-9-ol [(*R*)-9]** of 88% ee was acquired by use of (*R*)-Me-CBS catalyst, and it exhibited $[\alpha]^{22}_D$ +0.72 (*c*, 2.2, $CHCl_3$).]

(*S*)-(−)-Pentacos-10-yn-9-yl acetate (24) was obtained from the above (*S*)-ynol [(*S*)-(**9**)] (88 mg, 0.24 mmol) by treatment of the DCM solution (5 mL) with pyridine (1 mL), DMAP (20 mg), and Ac_2O (49.6 mg, 0.48 mmol, 2 equiv). After 12 h, the solution was washed with saturated aqueous $CuSO_4$ (2 × 10 mL) and brine (10 mL) and then separated and concentrated. The crude acetate (**24**) was purified by flash chromatography (10% ether/hexane) (42 mg, 10.6 mmol, 44%). ^{1}H NMR: δ 0.86 (t, J 6.7, 6H), 1.24 (brs, ∼34 H), 1.72 (m, 2H), 2.05 (s, 3H), 2.26 (m, 4H), 5.33 (t of t, J 6.6, 1.9, 1H). ^{13}C NMR: δ 14.1, 18.7, 22.7 (2), 25.0, 28.8, 29.1, 29.2, 29.4, 29.5, 29.6 (2), 29.7, 31.8, 31.9, 35.1, 64.7, 86.2, 170.1. GC−MS: *m*/*z* 406 (M^+, 1), 364 (1), 307 (4), 293 (2), 223 (18), 209 (4), 167 (5), 121 (7). Anal. Calcd for $C_{27}H_{50}O_2$: C, 79.8; H, 12.3. Found: C, 80.3; H, 12.5. $[\alpha]^{22}_D$ −23 (*c*, 4.2, $CHCl_3$).

(*S*)-(*Z*)-(+)-Pentacos-10-en-9-yl acetate (25) was obtained from the above ynyl acetate (**24**) (40 mg, 0.01 mmol) by hydrogenation in hexane (6 mL) using Lindlar catalyst (20 mg). After 2 h, the reaction mixture was filtered through a plug of silica to yield the enyl acetate (**25**) (22 mg, 0.054 mmol, 55%). ^{1}H NMR: δ 0.86 (t, J 6.7, 6 H), 1.23 (brs, 34H), 1.57 (m, 4H), 2.09 (s, 3H), 2.20 (m, 2H), 5.26 (m, 1H), 5.51 (m, 2H). ^{13}C NMR: δ 14.1 (2), 21.4, 22.6, 22.7, 27.9, 29.2, 29.3, 29.4 (2), 29.5 (2), 29.7 (2), 31.9, 70.5, 128.1, 134.1, 170.4. GC−MS: *m*/*z* 408 (M^+, 1), 366 (4), 309 (1), 268 (1), 253 (13), 208 (1), 169 (15). Anal. Calcd for $C_{27}H_{55}O_2$: C, 79.4; H, 12.8. Found: C, 79.7; H, 13.1.

(*S*)-(−)-Decane-1,2-diol (26). The above enyl acetate (**25**) (22 mg, 0.053 mmol) was dissolved in MeOH/DCM 1:1 (4 mL), cooled to −78 °C, and treated with ozone until a faint blue color persisted. At this stage, $NaBH_4$ (20 mg, 10 equiv) was added at once, and after stirring at −78 °C for 15 min, acetaldehyde (∼1 mL) was added to destroy excess hydride. The solution was concentrated and purified by chromatography to provide (*S*)-decan-1,2-diol (**26**) (2.2 mg, 0.1 mmol, 23%). The spectral data were in agreement with those of Mori,[26] and the sample exhibited $[\alpha]^{22}_D$ −7 (*c*, 0.22, MeOH). (lit. $[\alpha]_D$ −11.9 (*c*, 0.42, MeOH)).[26]

(*S*)-(*Z*)-10-(Tributylstannyl)pentacos-10-en-9-yl Acetate (28). The above (*S*)-pentacos-10-yn-9-ol [(*S*)-(**9**)] (0.104 g, 0.29 mmol) and AIBN (20 mg) were mixed in a dry round-bottomed flask under N_2 and then heated in an oil bath to 93 °C. Tributyltin hydride (0.124 g, 0.43 mmol, 1.5 equiv) was added via syringe, and the resulting solution was stirred at 90 °C for 4 h before being cooled in ice. At 0 °C, DCM (2 mL), Ac_2O (87.5 mg, 0.86 mmol, 3 equiv), pyridine (225 mg, 10 equiv), and DMAP (2 mg) were added. After 12 h, the reaction was diluted with ether (10 mL) and quenched with brine (5 mL). Extraction with ether (2 × 10 mL) followed by drying and concentration afforded the crude acetate (**28**), which was purified by chromatography (hexane/ether, 100:1) (14 mg, 8%), together with some stannyl alcohol (18 mg, 9%). ^{1}H NMR: δ 0.86 (m, 15H), 1.23 (brm, ∼56 H), 1.98 (s, 3H), 2.25 (m, 2H), 5.19 (t, J 6.5, J_{Sn-H} 54), 6.15 (t, J 7.3, J_{Sn-H} 128). ^{13}C NMR: δ 11.0, 13.7, 14.1 (2), 22.7 (2), 27.4, 29.2 (2), 29.4, 29.5, 29.6, 29.7, 31.9 (2), 82.7, 142.6, 143.4, 170.1. Anal. Calcd for $C_{39}H_{78}O_2Sn$: C, 67.0; H, 11.2. Found: C, 67.2; H, 11.6. $[\alpha]^{22}_D$ −14 (*c*, 0.14, $CDCl_3$).

(*R*)-(−)-$\Delta^{9,10}$-Pentacosadiene [(*R*)-3]. The above acetate (**28**) (14 mg, 0.02 mmol) was added to dry DMSO (2 mL) and a THF solution of TBAF (0.06 mL, 1M, 3 equiv) was added by syringe. The reaction mixture was refluxed under N_2 until TLC indicated complete conversion (2 h) to the allene. The solution was diluted with brine and extracted with ether (3 × 10 mL). The combined organic layers were dried ($MgSO_4$) and concentrated to yield the allene, which was purified by chromatography (silica) to provide (*R*)-(−)-$\Delta^{9,10}$-pentacosadiene [(*R*)-(**3**)] (5.4 mg, 0.017 mmol, 77%) of 77% ee based on enantioselective gas chromatography. GC−MS: *m*/*z* 348 (M^+,1), 250 (6), 208 (3), 166 (15), 138 (13). [α] −17 (*c*, 0.54, $CDCl_3$). The ^{1}H and ^{13}C NMR spectra matched those for the racemate. (*R*)-(−)-$\Delta^{9,10}$-pentacosadiene [(*R*)-(**3**)] was also acquired from (*R*)-pentacos-10-yn-9-ol [(*R*)-(**9**)] using the Myers procedure.[18,19] Thus from the ynol (*R*)-**9** (60 mg, 0.16 mmol) was obtained the allene (*R*)-**3** (21 mg, 6.1 mol, 38%) after flash chromatography ($[\alpha]^{22}_D$ −15.6 (*c* 1.3, $CHCl_3$)), with 80−85% ee based on NMR experiments with 1:1.5 Ag(fod) and Yb(hfcd)$_3$ in $CDCl_3$.

(*S*)-(−)-Tricos-10-yn-9-ol [(*S*)-12] was obtained from tricosa-10-yn-9-one (**27**) (0.41 g, 1.2 mmol) by reduction using (*S*)-Me-CBS catalyst, in 78% yield (0.32 g, 0.95 mmol) and 82% ee (Mosher ester). ^{1}H NMR: δ 0.86 (t, J 6, 6H), 1.23 (brs, 32H), 1.68 (m, 2H), 2.15 (t of d, J 7, 2, 2H), 4.32 (m, 1H). Anal. Calcd for $C_{23}H_{44}O$: C, 82.1; H, 13.1. Found: C, 82.5; H, 13.3. $[\alpha]^{22}_D$ −0.65 (*c*, 1.0, $CHCl_3$).

(*S*)-(*Z*)-(Tributylstannyl)tricosa-10-en-9-yl acetate (29) was prepared from (*S*)-(−)tricos-10-yn-9-ol [(*S*)-**12**] (86 mg) (by the same method as described above for **28**) in 68% yield (109 mg of the acetate). ^{1}H NMR: δ 0.88 (m, 21H), 1.23 (brm, 46 H), 1.98 (s, 3H), 2.26 (m, 2H), 5.20 (t, J 7.2, J_{Sn-H} 58, 1H), 6.16 (t, J 7.2, J_{Sn-H} 121.6, 1H). ^{13}C NMR: δ 8.0, 11.0, 13.7, 14.1 (2), 21.5, 22.7 (2), 25.5, 27.4, 29.0, 29.2 (2), 29.4, 29.5 (2), 29.6, 29.7 (2), 29.9, 31.9 (2), 34.2, 35.5, 82.7, 142.6, 143.4, 170.0. HREIMS: $C_{35}H_{69}{}^{119}SnO_2$ (M − Et) requires 641.41, measured 641.43. $[\alpha]^{22}_D$ −13 (*c*, 1.45, $CHCl_3$).

(*R*)-(−)-$\Delta^{9,10}$-Tricosadiene [(*R*)-1]. The title compound was acquired from the above stannane in the manner already described for formation of *R*-(−)-$\Delta^{9,10}$-pentacosadiene. In this way the stannyl acetate (82 mg, 0.13 mmol) gave the allene (*R*)-**1** (28 mg, 0.09 mmol, 67%) of 76% ee based on enantioselective gas chromatography. The ^{1}H and ^{13}C NMR spectra matched those of the racemic compound. GC−MS: *m*/*z* 320 (M^+, 7), 222 (9), 180 (5), 166 (23), 124 (28), 96 (82). HREIMS: $C_{23}H_{44}$ requires 320.3436, measured 320.3447. $[\alpha]^{22}_D$ −12 (*c*, 0.27, $CHCl_3$).

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Supporting Information Available: Gas chromatographic trace of an extract of *A. consanguineus*, EIMS of natural and synthetic $\Delta^{9,10}$-pentacosadiene (**3**), enantioselective GC traces for natural and synthetic samples of $\Delta^{9,10}$-pentacosadiene (**3**) and the chromatographic conditions, copies of the ^{1}H NMR spectra of racemic and (*R*)-(−)-$\Delta^{9,10}$-pentacosadiene (**3**) in the presence of chiral shift reagents, and NMR spectra are also provided for compounds **2** (including fully resolved 187-MHz ^{13}C NMR), **7**, **8**, **13**, and **29**. This material is available free of charge via the Internet at http://pubs.acs.org.

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