Stereoselective Alkene Synthesis *via* Silicon-directed [2,3]-Sigmatropic Rearrangements: An Approach to Leukotrienes

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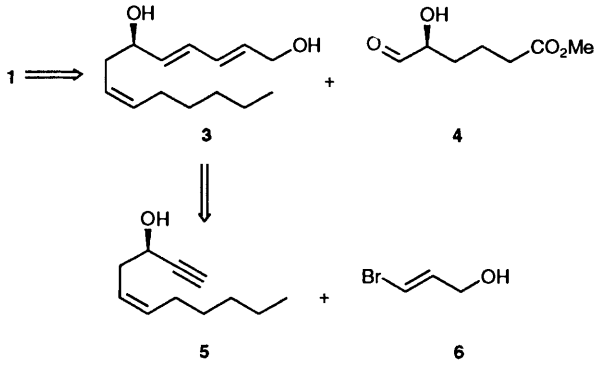
A stereoselective [2,3]-sigmatropic (Wittig) rearrangement of prop-2-ynyl 2-silyl allyl ethers **22** leading to *E*-vinyl silanes, *e.g.* **23** is described. Stereospecific protiodesilylation of **23**, *via* **26**, next produces the *Z*-alkene **27**. sp-sp and sp-sp^2 Coupling reactions between the acetylenic alcohol **5** produced from **27**, and 3-bromoprop-2-ynol or 3-bromoprop-2-enol THP ether, then leads to the key intermediates **3** and **31** in leukotriene B_4 **1** synthesis.

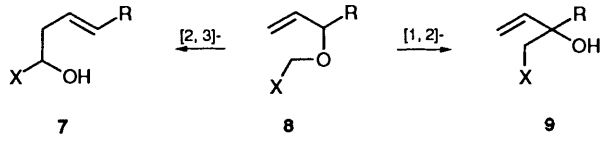
The stereocontrolled formation of *E*- and *Z*-alkenes has been a preoccupation of synthetic chemists since the early beginnings of modern organic chemistry, when the importance of alkene geometry in biological activity was first recognised. Perhaps nowhere is this feature better illustrated than in the leukotriene family of arachidonic acid derived secondary metabolites, illustrated by leukotriene B_4 **1** and leukotriene D_4 **2**.[1] Leukotriene B_4 **1** has potent chemotactic properties towards macrophages and neutrophiles, and plays a significant role as a mediator of inflammatory disorders.[2] Its biological importance and lack of availability from biological material has prompted several research groups to develop strategies for the synthesis of leukotriene B_4 in both its natural stereochemical form, *i.e.* **1**, and also in isomeric forms.[3] The general need for new, stereocontrolled syntheses of *E*- and *Z*-alkenes has now led us to examine the scope for [2,3]-sigmatropic (Wittig) rearrangements of appropriately substituted allyl ethers[4] as a route to *Z*-disubstituted double bond intermediates of use in leukotriene B_4 synthesis (Scheme 1).

Our overall synthesis design towards leukotriene B_4 **1** is summarised in retroanalytical fashion in Scheme 2. Thus, disconnection at the *Z*-disubstituted double bond in the conjugated triene segment of the molecule first leads to the trienediol **3** and the α-hydroxy aldehyde 4, which are both known intermediates in earlier described routes to LTB_4.[3] Further disconnection of the trienediol **3** then reveals the *Z*-homoallylic alcohol **5** and the vinyl bromide **6**. It was our plan to examine the scope for [2,3]-sigmatropic rearrangement from an appropriately substituted allyl ether in the controlled synthesis of the *Z*-alcohol intermediate **5**, according to Scheme 1.[5]



Scheme 2

Sigmatropic rearrangements of many types have been used in a number of ways to control stereochemical detail in a wide range of synthetic procedures; particularly poignant examples are found amongst the oxy-Cope and Ireland–Claisen rearrangements. At the outset of our studies, the anionic [2,3]-sigmatropic (Wittig) rearrangement of allylic ethers (Scheme 1) was less well described and developed.[5] What was known, however, demonstrated that the [2,3]-process favoured the formation of *E*-alkene products *viz.* **7**, and that the competing [1,2]-rearrangement, leading for example to **9**, was a significant



limitation in synthesis.[4] In more recent years, the transition state for the [2,3]-Wittig rearrangement, has been viewed as a

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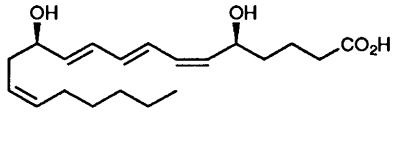

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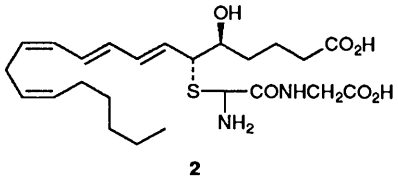

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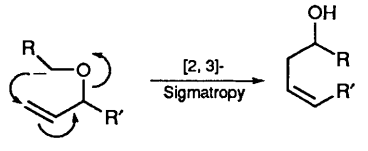
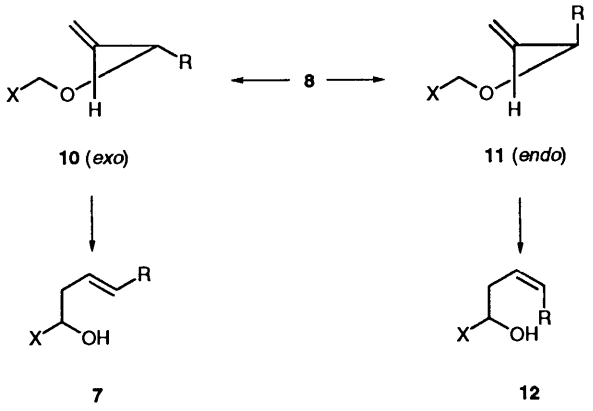
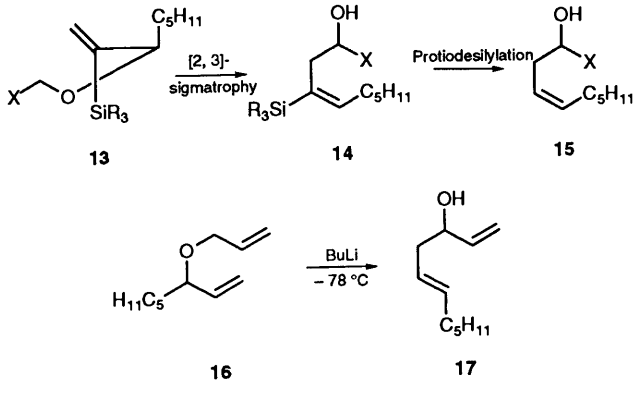


Scheme 1

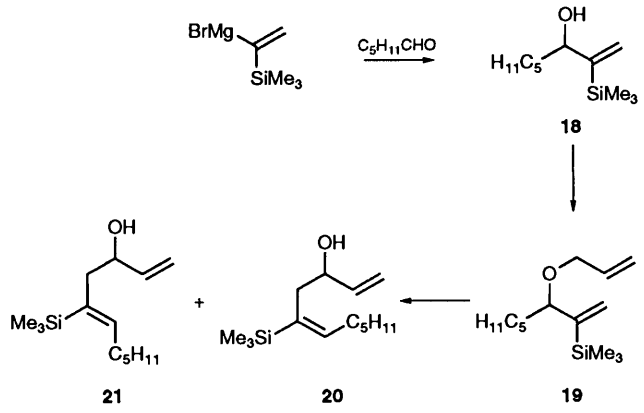
'folded envelope' with the R group in **8** occupying either an equatorial (*exo*), *viz.* **10**, or an axial (*endo*) orientation, *viz.* **11**. Clearly the *exo*-orientation **10** is favoured under normal circumstances, which not only allows for generating *E*-double bonds stereospecifically in the product, but also induces chirality transfer with chiral substrates.[4]



Our overall idea to use the [2,3]-Wittig rearrangement of allyl ethers to produce *Z*-homoallylic alcohol products specifically, required that we designed a substrate **8** which: (i) incorporated a group X capable of promoting carbanion formation at the centre to which it is attached, and which (ii) *accommodated* a bulky (and removable) substituent on the alkene group to favour a pseudo-*endo* (axial) transition state, *viz.* **11**. A clear candidate substituent became the trialkylsilyl group. This bulky group should not only ensure a transition state for the rearrangement[6] whereby a pentyl group (R = C_5H_{11}) is pseudo-axial, *viz.* **13**, thereby leading to the *E*-vinyl silane **14**, but its subsequent easy removal from **14** by protiodesilylation[7] should allow access to the desired *Z*-alkene product **15**, *i.e.* **5** (X = C=CH).

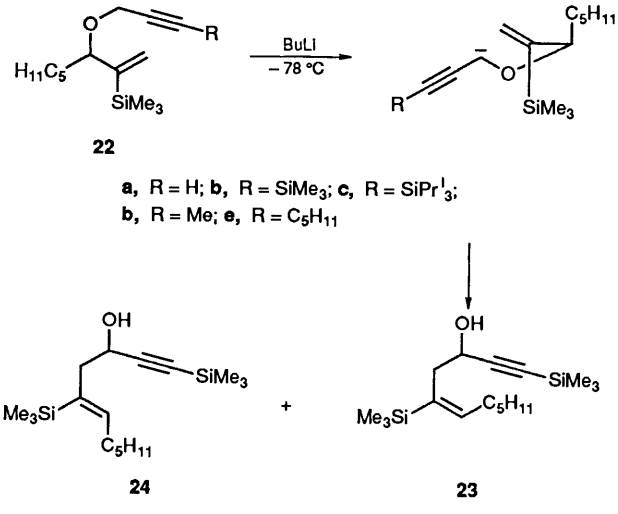


We first examined the proposed 'silicon-directed' [2,3]-Wittig rearrangement using the allyl ether **19** derived from the trimethylsilyl substituted allyl alcohol **18**. Wittig rearrangement of the corresponding bisallylic ether **16**, using butyllithium at −78 °C, had been shown to produce exclusively the *E*-alkene **17** in 86% yield. When the vinylsilyl ether **19** was treated similarly with butyllithium at −78 °C, it underwent smooth [2,3]-rearrangement leading to a 1:2 mixture of the *E*- and *Z*-isomers, **20** and **21** respectively, of the expected allylic alcohols in 60% yield. The *E*- and *Z*-vinylsilanes, **20** and **21**, respectively, can be readily distinguished on analysis of their NMR spectroscopic data. Thus, in their ^{1}H NMR spectra the *Z*-isomer **21** shows a vinylsilane olefinic hydrogen signal at δ 6.06 (triplet, *J* 7 Hz), which is significantly deshielded compared to the corresponding signal, δ 5.96, in the *E*-isomer **20**. In addition, in their ^{13}C NMR spectra, the vinyl methylene carbon in the *E*-



isomer **20** is shielded (δ ~32.2) in comparison with the same signal (δ ~47.6) in the *Z*-isomer ('γ-effect').

Remarkably, when the silicon protected prop-2-ynyl ether **22b**, corresponding to **19**, was treated in a similar manner with butyllithium, the stereoselectivity of the Wittig rearrangement was turned round, leading to the *E*- and *Z*-alkene products **23** and **24** in a 4:1 ratio, in 80% yield. The difference between the

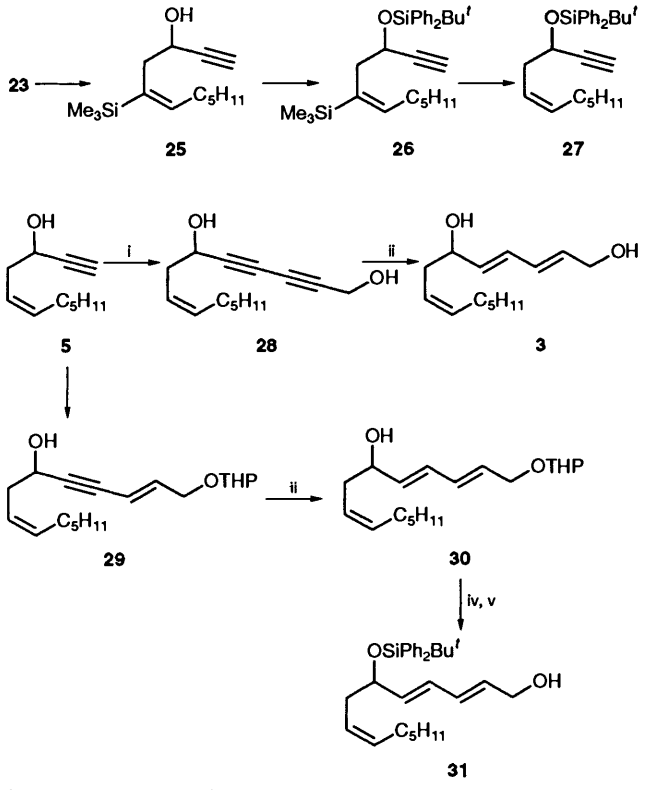


allyl and prop-2-ynyl ether systems **19** and **22b** in these silicon-directed Wittig rearrangements is intriguing and the effect was briefly investigated further. Thus, replacement of the Me_3Si group on the acetylene residue in **22b** for the more bulky Pr^i_3Si group, *i.e.* **22c**, did not alter the ratio of *E*- and *Z*-alkene products, and replacement of the same $SiMe_3$ group with alkyl groups (*i.e.* CH_3 **22d** and C_5H_{11} **22e**) led to 2:1 ratios of *E*:*Z* alkene products. Other researchers have also noted the special directing effects of the acetylenic moiety in related sigmatropic processes.[8]

With the development of a stereoselective synthesis of the *E*-vinylsilane **23**, based on [2,3]-sigmatropic rearrangement of the prop-2-ynyl ether **22b**, we now required to demonstrate that **23** could be converted into the *Z*-alkene precursor **27** to leukotriene B_4 **1**, by protiodesilylation. Thus, deprotection of the acetylene residue in **23b**, followed by protection of the secondary hydroxy group in the product **25** as the TBDPS ether, first led to **26**. When the vinylsilane **26** was treated with aqueous hydriodic acid overnight, it underwent smooth protiodesilylation with complete retention of stereochemistry[7] producing the *Z*-alkene product **27** in 95% yield. Subsequent deprotection of **27** then gave the *Z*-enynol **5**. The *Z*-stereochemistries assigned to the alkene double bonds in **27** and **5** followed from inspection of their NMR spectroscopic data. Thus, in the ^{1}H NMR spectrum, their olefinic hydrogen atoms

each appeared as double triplets (δ 5.47 and 5.64) with an olefinic coupling (J 11 Hz) which is diagnostic for a Z-disubstituted double bond. In their ^{13}C NMR spectra, the vinylic carbon atoms resonated at δ < 136 which is also characteristic for a Z-disubstituted double bond ('γ-effect').

A number of alternative synthetic routes to the key Z,E,E-trienediol **3** and its differentially protected forms, *e.g.* **30** and **31** which have been used earlier in the sysnthesis of leukotriene B_4,[3] starting with the Z-enynol **5** were now investigated. These routes, which are summarised in Scheme 3, depended for their



Scheme 3 *Reagents:* i, $BrC{\equiv}CCH_2OH$, CuCl, EtOH; ii, $LiAlH_4$; iii, (*E*)-BrCH=CHCH$_2$OTHP, $[Pd(PPh_3)_4]$, CuI, Et_2NH; iv, TBDPSiCl, DMAP; v, AcOH

success on either copper-catalysed sp-sp or palladium(0)–copper(I) catalysed sp-sp^2 coupling reactions between **5** and acetylenic or vinylic substrates, followed by stereoselective reductions using lithium aluminium hydride. The Z,E,E-geometries of the trienes **3**, **30** and **31** followed unambiguously from analysis of chemical shift and coupling data in their high field ^1H NMR and ^{13}C NMR spectra. The overall yields for the conversions of **5** into **3** and **31** were 21 and 14% respectively.

Experimental

^1H and ^{13}C NMR spectra were recorded on a Bruker WM250 at 250 MHz or a Bruker AM400 at 400 MHz, as dilute solutions in deuteriochloroform unless stated otherwise. The chemical shifts in the ^1H NMR spectra were recorded relative to internal tetramethylsilane, and the multiplicity of a signal is a singlet unless otherwise stated, when the following abbreviations are used: d = doublet, t = triplet, q = quartet, m = multiplet and dt = doublet of triplets. The chemical shifts in the ^{13}C NMR spectra are reported relative to internal tetramethylsilane in a broad band decoupled mode. The multiplicities were obtained using either a DEPT program or from an off-resonance spectrum. J-Values are recorded in Hz.

Column chromatography was carried out using Merck-Kieselgel 60, Art. 9385 silica, and light petroleum (b.p. 40–60 °C) was redistilled before use. Analytical TLC plates were visualised with basic aqueous potassium permanganate or acidic ethanolic vanillin. Preparative HPLC work was carried out using a Waters Associates Prep LC/System 500 machine.

Routinely, dry organic solvents were stored under nitrogen over freshly activated molecular sieves. Concentration of organic solutions refers to solvent removal using a Büchi rotary evaporator under water aspirator pressure (12 mmHg). All reactions where necessary were carried out under a nitrogen or argon atmosphere.

Allyl Oct-1-en-3-yl Ether **16**.—Freshly distilled hexanal (9.10 g, 1 equiv.) was added dropwise during 20 min to a stirred solution of vinylmagnesium bromide (1 mol dm^{-3} solution in THF; 100 cm^3, 1.1 equiv.) in dry THF (200 cm^3) under a nitrogen atmosphere. The mixture was stirred at room temperature for 3 h after which it was poured onto crushed ice (75 g) and the resulting aqueous solution extracted with ether (3 × 100 cm^3). The combined organic extracts were dried and then concentrated under reduced pressure to leave a yellow oil, vacuum distillation of which gave oct-1-en-3-ol (4.86 g, 46%) as a clear oil, b.p. 72–75 °C at 18 mmHg (lit.,[9] b.p. 173–175 °C); $\nu_{max}(CCl_4)$/cm^{-1} 3600 and 1680; $\delta_H(CDCl_3)$, 0.85 (t, J 7, CH_3), 1.35 (m, 4 × CH_2), 2.15 (OH), 3.86 (m, C*H*OH), 5.20 (m, CH=C*H*$_2$) and 5.80 (m, C*H*=CH$_2$) (Found: m/z 128.1191; $C_8H_{16}O$ requires M, 128.1197) (Found: C, 75.15; H, 12.9. Calc. for $C_8H_{16}O$: C, 74.9; H, 12.6%).

Sodium hydride (200 mg, 2 equiv.) was added to a solution of oct-1-en-3-ol (460 mg, 1 equiv.) in dry THF (10 cm^3) at 0 °C under a nitrogen atmosphere and the mixture was then stirred at 0 °C for 15 min. Allyl bromide (518 mg, 1.2 equiv.) was then added dropwise to it during 20 min after which it was stirred at room temperature for 20 h. The mixture was diluted with ether (20 cm^3) and the solution was then washed with dilute HCl (0.1 mol dm^{-3}; 10 cm^3). The organic layer was dried and then concentrated under reduced pressure to leave a yellow oil, chromatography of which using light petroleum (b.p. 40–60 °C)–ether (19:1) as eluent gave the *diallyl ether* **16** (420 mg, 70%) as a clear oil; $\nu_{max}(CCl_4)$/cm^{-1} 1650, 995 and 920; $\delta_H(CDCl_3)$, 0.88 (5, J ~7, CH_3), 1.40 (m, 4 × CH_2), 3.82 (m, $CHOCH_2$) and 5.0–6.18 (m, 2 × CH=C*H*$_2$) (Found: m/z 168.1512. $C_{11}H_{20}O$ requires M, 168.1509) (Found: C, 78.3; H, 12.3. $C_{11}H_{20}O$ requires C, 78.5; H, 11.9%).

(E)-*Undeca-1,5-dien-3-ol* **17**.—Butyllithium (2 cm^3, 1.5 equiv.) was added dropwise during 10 min, to a stirred solution of the allyl ether **16** (140 mg, 1 equiv.) in dry THF (20 cm^3) maintained at −78 °C under nitrogen. The mixture was stirred at −78 °C under a nitrogen atmosphere for a further 1 h and then allowed to warm to room temperature. The solution was diluted with ether (20 cm^3) and dilute HCl (2 mol dm^3; 15 cm^3), and then stirred for 10 min. The organic layer was separated, dried and then concentrated under reduced pressure to leave a golden oil, chromatography of which on silica using light petroleum (b.p. 40–60 °C)–ether (19:1) as eluent gave the *undecadienol* (120 mg, 86%) as a clear oil; $\nu_{max}(CCl_4)$/cm^{-1} 3550, 1643, 968 and 920; $\delta_H(CDCl_3)$, 0.88 (t, J 7, CH_3), 1.0–1.3 (m, 3 × CH_2), 1.85 (OH), 2.01 (m, CH_2), 2.27 (m, CH_2), 4.11 (m, C*H*OH), 5.11 (dd, J 10 and 1, C*H*H), 5.24 (dd, J 16 and 1, CH*H*), 5.38 (dt, J 6.5 and 15, C*H*=CH), 5.56 (dt, J 5.8 and 15, CH=C*H*) and 5.87 (ddd, J 16, 10 and 7, H_2C=C*H*); δ_C-($CDCl_3$), 14.04 (q), 22.59 (t), 29.21 (t), 31.46 (t), 32.68 (t), 40.66 (t), 72.29 (d), 114.39 (t), 125.36 (d), 134.46 (d) and 140.79 (d) [Found: m/z 169.1550. $C_{11}H_{20}O$ (M + 1) requires 169.1592] (Found: C, 78.6; H, 12.3. $C_{11}H_{21}O$ requires C, 78.5; H, 12.0%).

2-*Trimethylsilyoct-1-en-3-ol* **18**.—A solution of commercially available α-bromovinyltrimethylsilane (10 g, 1 equiv.) in

dry THF (20 cm^3) was added dropwise to a suspension of magnesium turnings (1.32 g, 1 equiv.) in dry THF (5 cm^3) under a nitrogen atmosphere. The reaction was initiated by the addition of a few drops of 1,2-dibromoethane and the α-bromovinyltrimethylsilane solution was added at such a rate so as to maintain gentle reflux. The reaction was heated under reflux for a further hour, and then allowed to cool to room temperature. Freshly distilled hexanal (5.6 g, 1 equiv.) was added during 20 min to the stirred reaction mixture, and the resulting solution was then heated under reflux for 2 h. After cooling to room temperature, the mixture was acidified with cold dilute sulfuric acid (2 mol dm^{-3} solution; 3 cm^3). The organic layer was separated, and the aqueous layer was then extracted with ether (2 × 20 cm^3). The combined organic extracts were dried ($MgSO_4$) and concentrated under reduced pressure to leave a golden oil. Chromatography using light petroleum (b.p. 40–60 °C)–ether (5:1) as eluent gave the silyl alcohol (6.7 g, 51%) as a pale yellow oil, $\nu_{max}(CCl_4)/cm^{-1}$ 3600, 3475 and 1640; $\delta_H(CDCl_3)$ 0.14 ($SiMe_3$), 0.90 (t, *J* 7, CH_3) 1.1–1.5 (m, 4 × CH_2), 1.76 (OH), 4.23 (m, C*H*OH), 5.40 (br, =C*H*H) and 5.76 (br, =CH*H*); $\delta_C(CDCl_3)$–0.66 (q), 13.91 (q), 22.54 (t), 25.41 (t), 31.68 (t), 37.27 (t), 76.19 (d), 123.54 (t) and 155.47 (t) (Found: *m/z* 200.1565. $C_{11}H_{24}OSi$ requires *M*, 200.1596).

Allyl 2-Trimethylsilyloct-1-en-3-yl Ether **19**.—Sodium hydride (410 mg, 2 equiv.) was added to a solution of the silyloctenol **18** (1.70 g, 1 equiv.) in dry THF (70 cm^3) at 0 °C and the mixture was then stirred at 0 °C for 1 h. Allyl bromide (1.5 cm^3, 1.1 equiv.) was added dropwise during 5 min to the mixture which was then stirred at room temperature under a nitrogen atmosphere for 2 days. After this the solution was diluted with ether (50 cm^3) and washed with dilute HCl (2 mol dm^{-3}; 30 cm^3). The separated organic layer was dried and concentrated under reduced pressure to leave a pale yellow oil which was chromatographed on silica using light petroleum (b.p. 40–60 °C) as eluent to give the *silyl allyl ether* (1.98 g, 88%) as a clear oil; $\nu_{max}(CCl_4)/cm^{-1}$ 1642, 990, 930 and 920; $\delta_H(CDCl_3)$, 0.12 ($SiMe_3$), 0.89 (t, *J* ~7, CH_3), 1.1–1.5 (m, 4 × CH_2), 3.78 (m, $CHOCH_2$), 5.17 (br, $Me_3SiC{=}CH_2$), 5.47 (br, =C*H*H), 5.73 (m, =CH*H*) and 5.95 (m, 3-H); $\delta_C(CDCl_3)$ −0.54 (q), 13.97 (q), 22.58 (t), 25.68 (t), 31.77 (t), 36.22 (t), 69.27 (t), 84.89 (d), 115.99 (t), 126.06 (t), 135.41 (d) and 152.85 [Found: *m/z* 241.1992. $C_{11}H_{29}OSi$ (M + 1) requires 241.1987].

(E)-5-*Trimethylsilylundeca*-1,5-*dien*-3-*ol* **20** *and* (Z)-5-*Trimethylsilylundeca*-1,5-*dien*-3-*ol* **21**.—Butyllithium (2.5 cm^3, equiv.) was added dropwise during 10 min to a stirred solution of the silyl allyl ether **19** (220 mg, 1 equiv.) in dry THF (20 cm^3) cooled to −78 °C under a nitrogen atmosphere. The mixture was stirred at −78 °C for 5 h and then diluted with ether (15 cm^3). The solution was washed with water (10 cm^3) and the separated organic layer was then dried and concentrated under reduced pressure to leave a golden oil. Chromatography of this on silica using light petroleum (b.p. 40–60 °C)–ether (19:1) as eluent gave the undecadienol (120 mg, 60%) as a 1:2 mixture of *E*- and *Z*-isomers; $\nu_{max}(CCl_4)/cm^{-1}$ 3560, 1640, 1600, 980 and 920, *E*-isomer **20**; $\delta_H(CDCl_3)$ 0.10 ($SiMe_3$), 0.90 (t, *J* ~7, CH_3), 1.1–1.5 (m, 3 × CH_2), 1.74 (OH), 2.15 (m, CH_2), 2.3–2.6 (m, CH_2), 4.12 (m, C*H*OH), 5.09 (dd, *J* 10 and 2, =C*H*H), 5.24 (dd, *J* 15 and 2, =CH*H*), 5.86 (ddd, *J* 15, 10 and 7, C*H*=CH_2) and 5.96 (t, *J* 7, $Me_3SiC{=}CH$); $\delta_C(CDCl_3)$ −0.78 (q), 14.01 (q), 22.64 (t), 29.17 (t), 31.66 (t), 32.35 (t), 37.89 (t), 72.20 (d), 114.32 (t), 136.47, 140.83 (d) and 144.82 (d). *Z*-Isomer **21**; $\delta_H(CDCl_3)$ 0.17 ($SiMe_3$), 0.90 (t, *J* 7, CH_3), 1.1–1.5 (m, 3 × CH_2), 1.90 (OH), 2.15 (m, CH_2), 2.38 (m, CH_2), 4.01 (m, C*H*OH), 5.09 (m, =C*H*H), 5.24 (m, –CH*H*), 5.86 (m, C*H*=CH_2) and 6.06 (t, *J* 7, $Me_3SiC{=}CH$); $\delta_C(CDCl_3)$ 0.41 (q), 14.01 (q), 22.64 (t), 29.78 (t), 31.66 (t), 32.32 (t), 46.60 (t), 71.68 (d), 114.32 (t), 135.46, 140.49 (d) and 147.85 (d) [Found: *m/z* 241.2012. $C_{14}H_{29}OSi$ (M + 1) requires 241.1987].

3-*Trimethylsilylprop*-2-*ynyl* 2-*Trimethylsilyloct*-1-*en*-3-*ol Ether* **22b**.—2-Trimethylsilyl-1-octen-3-ol (3.0 g, 1 equiv.) was added to aqueous sodium hydroxide (50% w/v; 200 cm^3) containing tetrabutylammonium hydrogen sulfate (250 mg, 0.05 equiv.). Prop-2-ynyl bromide (80% solution in toluene; 8.3 cm^3, 5 equiv.) was added to the mixture which was then stirred at room temperature for 16 h. After dilution of the mixture with water (100 cm^3) it was extracted with ether (5 × 75 cm^3) and the combined extracts were dried ($MgSO_4$) and concentrated under reduced pressure to leave a dark brown oil. Chromatography of this using light petroleum (b.p. 40–60 °C)–ether (9:1) as eluent gave the corresponding prop-2-ynyl ether **22a** (3.0 g, 84%) as a yellow oil, $\nu_{max}(CCl_4)/cm^{-1}$ 3300 and 2125; $\delta_H(CDCl_3)$ 0.13 ($SiMe_3$), 0.8–1.0 (m, CH_3), 1.1–1.5 (m, 4 × CH_2), 2.35 (t, *J* 2, C≡CH), 4.03 (dd, *J* 6 and 8, $CHOCH_2$), 5.56 (d, *J* 3, =C*H*H), 5.83 (d, *J* 3, =CH*H*) [Found: *m/z* 239.1836. $C_{14}H_{27}OSi$ (M + 1) requires 239.1831].

Trimethylsilyl chloride (6.42 cm^3, 4 equiv.) was added to a solution of the prop-2-ynyl ether **22a** (3.0 g, 1 equiv.) in dry THF (100 cm^3) at −78 °C under a nitrogen atmosphere. Butyllithium (9 cm^3, 1.1 equiv.) was added dropwise over 10 min to the mixture which was then stirred at −78 °C for a further 1 h. The mixture was allowed to warm to room temperature and then diluted with ether (50 cm^3) and water (75 cm^3). The mixture was stirred for 5 min and then the organic layer separated, dried ($MgSO_4$) and concentrated under reduced pressure to leave the silyl-protected propynyl ether (3.87 g, 99%) as a pale yellow oil, $\nu_{max}(CCl_4)/cm^{-1}$ 2190, 995 and 950; $\delta_H(CDCl_3)$ 0.1 ($SiMe_3$), 0.15 ($SiMe_3$), 0.8–1.0 (m, CH_3), 1.32 (m, 4 × CH_2), 3.93 (dd, *J* 6 and 8, $CHOCH_2$), 5.48 (d, *J* 3, =CH*H*) and 5.75 (d, *J* 3, =C*H*H), which was used without further purification.

2-*Trimethylsilyloct*-1-*en*-3-*yl* 3-(*Triisopropylsilyl*)*prop*-2-*ynyl Ether* **22c**.—Triisopropylsilyl chloride (0.54 cm^3, 1.2 equiv.) was added to a solution of the corresponding propynyl ether **22a** (500 mg, 1 equiv.) in dry THF (15 cm^3) at −78 °C under a nitrogen atmosphere. Butyllithium (1.9 cm^3, 1 equiv.) was added during 5 min to the mixture and the resulting solution was stirred at −78 °C for 1 h and then allowed to warm to room temperature. The mixture was diluted with ether (15 cm^3) and water (5 cm^3) and was then stirred for 10 min. The organic layer was separated, dried ($MgSO_4$) and concentrated under reduced pressure to leave a yellow oil. Chromatography of this using light petroleum (b.p. 40–60 °C)–ether (19:1) as the eluent gave the triisopropylsilyl-protected prop-2-ynyl ether (600 mg, 72%) as a clear oil, $\nu_{max}(CCl_4)/cm^{-1}$ 2180; $\delta_H(CDCl_3)$ 0.13 ($SiMe_3$), 0.90 (t, *J* ~7, CH_3), 1.10 [$(CHMe_2)_3$], 1.30 (m, 4 × CH_2), 4.03 (dd, *J* 6 and 8, $CHOCH_2$), 5.53 (d, *J* 3, C=CH*H*) and 5.80 (d, *J* 3, C=CH*H*) [Found: *m/z* 395.3204. $C_{23}H_{47}OSi_2$ (M + 1) requires 395.3166].

(Z)-1-*Triisopropylsilyl*-5-*trimethylsilylundec*-5-*en*-1-*yn*-3-*ol and* (E)-1-*Triisopropylsilyl*-5-*trimethylsilylundec*-5-*en*-1-*yn*-3-*ol*.—Butyllithium (0.9 cm^3, 2.5 equiv.) was added dropwise during 5 min to a stirred solution of the prop-2-ynyl ether **22c** (200 mg, 1 equiv.) in dry THF (20 cm^3) and the solution cooled to −78 °C under a nitrogen atmosphere. The mixture was stirred at −78 °C for 1 h and then allowed to warm to room temperature. The solution was diluted with ether (20 cm^3) and water (10 cm^3) and the mixture was then stirred for 10 min. The organic layer was dried and concentrated under reduced pressure to leave the ynol (140 mg) as a 3:1 mixture of *E*- and *Z*-isomers. Chromatography on silica using light petroleum (b.p.

40–60 °C)–ether (19:1) as eluent afforded the separated isomers, $\nu_{max}(CCl_4)/cm^{-1}$ 3640, 2200 and 1610; *E*-isomer, $\delta_H(CDCl_3)$ 0.09 ($SiMe_3$), 0.90 (t, *J* ~7, CH_3), 1.08 [$(CHMe_2)_3$], 1.32 (m, 3 × CH_2), 1.6 (OH), 2.18 (m, CH_2), 2.57 (m, CH_2), 4.30 (m, C*H*OH) and 5.90 (t, *J* 7, $Me_3SiC{=}CH$); $\delta_C(CDCl_3)$, 0.73 (q), 11.33 (d), 14.12 (q), 18.70 (q), 22.69 (t), 29.28 (t), 31.78 (t), 38.66 (t), 62.77 (d), 85.49, 108.96, 135.75 and 145.14 (d); *Z*-isomer, $\delta_H(CDCl_3)$ 0.16 ($SiMe_3$), 0.90 (t, *J* ~7, CH_3), 1.08 [$(CHMe_2)_3$], 1.32 (m, 3 × CH_2), 1.62 (OH), 2.18 (m, CH_2), 2.57 (m, CH_2), 4.30 (m, C*H*OH) and 6.11 (t, *J* 7, $Me_3SiC{=}CH$); $\delta_C(CDCl_3)$ 0.44 (q), 11.33 (d), 14.12 (q), 18.70 (q), 22.69 (t), 29.80 (t), 31.78 (t), 32.43 (t), 46.95 (t), 62.87 (d), 85.49, 108.96, 134.08 and 148.17 (d).

But-2-*ynyl 2-Trimethylsilyloct*-1-*en*-3-*yl Ether* **22d**.—Methyl iodide (0.3 cm^3, 9 equiv.) was added during 5 min to a solution of the prop-2-ynyl ether **22a** (100 mg, 1 equiv.) in dry THF (6 cm^3) at −78 °C under a nitrogen atmosphere. After butyllithium (0.45 cm^3, 1.2 equiv.) followed by HMPA (0.08 cm^3, 1 equiv.) had been added to the mixture it was stirred at room temperature for 20 h. The solution was diluted with ether (15 cm^3) and dilute HCl (2 mol dm^{-3}; 5 cm^3), and then stirred for 10 min. The organic layer was separated, washed with water, dried ($MgSO_4$) and concentrated under reduced pressure to leave the title ether **22d** (80 mg, 76%) as a clear oil, $\nu_{max}(CCl_4)/cm^{-1}$ 2222 and 940; $\delta_H(CDCl_3)$, 0.10 ($SiMe_3$), 0.90 (m, CH_3), 1.32 (m, 4 × CH_2), 1.82 (t, *J* 1.5, $C{\equiv}CCH_3$), 3.88 (m, $CHOCH_2$), 5.47 (d, *J* 3, C=C*H*H) and 5.72 (d, *J* H, C=CH*H*) (Found: *m*/*z* 252.1887. $C_{15}H_{28}OSi$ requires 252.1909).

(E)- *and* (Z)-6-*Trimethylsilyldodec*-6-*en*-2-*yn*-4-*ol*.—Butyllithium (1.8 cm^3, 2.5 equiv.) was added dropwise during 10 min to a solution of the prop-2-ynyl ether **22d** (160 mg, 1 equiv.) in dry THF (20 cm^3) cooled to −78 °C for 1 h and then allowed to warm to room temperature. The mixture was diluted with ether (20 cm^3) and water (10 cm^3), and then stirred for a further 10 min. The separated organic layer was dried and then concentrated under reduced pressure to leave a pale yellow oil. Chromatography using light petroleum (b.p. 40–60 °C)–ether (19:1) as eluent gave the methylated undecenynols (90 mg, 56%) as a 2:1 mixture of *E*- and *Z*-isomers, $\nu_{max}(CCl_4)/cm^{-1}$ 3640, 2260 and 1620; *E*-isomers, $\delta_H(CDCl_3)$, 0.09 ($SiMe_3$), 0.89 (t, *J* ~7, CH_3), 1.29 (m, CH_2), 1.84 (d, *J* 2, $C{=}CCH_3$), 1.91 (OH), 2.16 (m, CH_2), 2.54 (m, CH_2), 4.32 (m, C*H*OH) and 5.96 (t, *J* 7, Me_3SiCH); $\delta_C(CDCl_3)$ 0.83 (q), 3.63 (q), 14.06 (q), 22.63 (t), 29.21 (t), 31.69 (t), 32.37 (t), 38.52 (t), 62.24 (d), 80.59, 80.83, 135.65 and 145.37 (d); *Z*-isomer, $\delta_H(CDCl_3)$ 0.17 ($SiMe_3$), 0.89 (t, *J* ~7, CH_3), 1.29 (m, 3 × CH_2), 1.84 (d, *J* 2, $C{\equiv}CCH_3$), 1.91 (OH), 2.16 (m, CH_2), 2.54 (m, CH_2), 4.24 (m, C*H*OH) and 6.11 (t, *J* 7, $Me_3SiC{=}CH$); $\delta_C(CDCl_3)$ 0.38 (q), 3.63 (q), 14.06 (q), 22.63 (t), 29.73 (t), 31.68 (t), 32.37 (t), 46.41 (t), 62.42 (d), 80.41, 81.05, 134.42 and 148.42 (d) [Found: *m*/*z* 253.2003. $C_{15}H_{29}OSi$ (M + 1) requires 253.1986].

(Z)-1,5-*Bis*(*trimethylsilyl*)*undec*-5-*en*-1-*yn*-3-*ol* **24** *and* (E)-1,5-*Bistrimethylsilylundec*-5-*en*-1-*yn*-3-*ol* **23**.—Butyllithium (2.52 cm^3, 2.5 equiv.) was added dropwise to a solution of the prop-2-ynyl ether **22b** (500 mg, 1 equiv.) in dry THF (30 cm^3) at −78 °C for 1 h and then the solution was allowed to warm to room temperature. The solution was diluted with ether (25 cm^3) and water (15 cm^3) and then stirred at 25 °C for 5 min. The organic layer was separated, dried and concentrated under reduced pressure to leave a 4:1 mixture (80%) of *E*- and *Z*-products as a deep red oil. Chromatography using light petroleum (b.p. 40–60 °C)–ether (19:1) gave the *E*- (225 mg, 45%) and *Z*-isomers (75 mg, 15%) of the undecenynol as pale yellow oils, $\nu_{max}(CCl_4)/cm^{-1}$ 3630, 2200 and 1615; $\delta_H(CDCl_3)$ (*E* isomer) 0.09 ($SiMe_3$), 0.16 ($SiMe_3$), 0.8–1.0 (m, CH_3), 1.3–1.6 (m, 3 × CH_2), 1.92 (OH), 2.1–2.3 (m, CH_2), 2.59 (app. d, *J* 7, CH_2), 4.35 (t, *J* 7, C*H*OH), 5.96 (t, *J* 7, $Me_3SiC{=}CH$); (*Z*-isomer) 0.16 ($SiMe_3$), 0.17 ($SiMe_3$), 0.8–1.0 (m, CH_3), 1.3–1.6 (m, 3 × CH_2), 1.92 (OH), 2.1–2.3 (m, CH_2), 2.5 (app. d, *J* 7, CH_2), 4.27 (t, *J*, C*H*OH) and 6.12 (t, *J* 7.5, $Me_3SiC{=}CH$) (Found: C, 66.3; H, 11.1. $C_{17}H_{34}OSi_2$ requires: C, 65.8; H, 11.0%).

(E)-5-*Trimethylsilylundec*-5-*en*-1-*yn*-3-*ol* **25**.—Sodium hydride (150 mg, 4 equiv.) was added to a solution of **23** (470 mg, 1 equiv.) in dry DMF (12 cm^3), and the mixture was then stirred at room temperature under nitrogen for 20 h. The mixture was diluted with ether (50 cm^3) and the solution was then washed with water (3 × 100 cm^3). The organic layer was separated, dried and then concentrated under reduced pressure to leave a dark brown oil (550 mg). Chromatography of this using light petroleum (b.p. 40–60 °C)–ether (9:1) as eluent gave the *acetylene* (300 mg, 83%) as a yellow oil, $\nu_{max}(CCl_4)/cm^{-1}$ 3600 and 3300; $\delta_H(CDCl_3)$ 0.09 ($SiMe_3$), 0.7–1.0 (m, CH_3), 1.1–1.5 (m, 3 × CH_2), 1.95 (OH), 2.0–2.3 (m, CH_2), 2.45 (d, *J* 2, C≡CH); 2.63 (app. d, *J* 7, CH_2), 4.37 (m, C*H*OH) and 5.98 (t, *J* 7, C=CH); $\delta_C(CDCl_3)$, −0.77 (q), 14.08 (q), 22.65 (t), 29.25 (t), 31.70 (t), 38.13 (t), 61.98 (d), 72.85, 85.07 (d), 135.27 and 145.79 (d) (Found: *m*/*z* 238.1744. $C_{14}H_{26}OSi$ requires 238.1752).

(E)-3-(tert-*Butyldiphenylsilyloxy*)-5-*trimethylsilylundec*-5-*en*-1-*yne* **26**.—Dimethylaminopyridine (128 mg, 1 equiv.) and *tert*-butyldiphenylsilyl chloride (347 mg, 1.2 equiv.) were added to a solution of (*E*)-5-trimethylsilylundec-5-en-1-yn-3-ol **25** (250 mg, 1 equiv.) in dry dichloromethane (25 cm^3), and the mixture was then stirred at room temperature under a nitrogen atmosphere for 20 h. It was then concentrated under reduced pressure and the residue was taken up in ether. The solution was washed with dilute HCl and brine, dried and evaporated to leave a yellow oil which was chromatographed using light petroleum (b.p. 40–60 °C)–ether (19:1) as eluent to give the silyl ether (465 mg, 93%) as a clear oil, $\nu_{max}(CCl_4)/cm^{-1}$ 3320, 2120, 1601; $\delta_H(CDCl_3)$ 0.12 ($SiMe_3$), 0.7–1.0 (m, CH_3) 1.22 (Bu^t), 1.36 (m, 3 × CH_2), 2.09 (m, CH_2), 2.32 (d, *J* 2, C≡CH), 2.79 (app. d, *J* 7, CH_2), 4.45 (m, C*H*O$SiPh_2Bu^t$), 5.92 (t, *J* 6.5, $Me_3SiC{=}CH$), 7.44 (2 H, $SiPh_2$), 7.50 (4 H, $SiPh_2$) and 7.83 (4 H, $SiPh_2$); $\delta_C(CDCl_3)$ −0.84 (q), 14.14 (q), 19.37 (t), 22.70 (t), 27.13 (q), 29.23 (t), 31.70 (t), 38.73 (t), 63.87 (d), 72.91 (d), 85.36 (d), 127.55 (d), 127.72 (d), 127.78 (d), 133.66, 133.78, 134.95, 136.06 (d), 136.24 (d) and 144.97 (d) (Found: *m*/*z* 476.2939. $C_{30}H_{44}OSi_2$ requires 476.2929).

(Z)-3-(tert-*Butyldiphenylsilyloxy*)*undec*-5-*en*-1-*yne* **27**.—Hydriodic acid (55% aqueous solution; 0.20 cm^3, 1 equiv.) was added to a solution of **26** (400 mg, 1 equiv.) in benzene (10 cm^3) and the mixture was then stirred at room temperature for 20 h. The mixture was diluted with ether (40 cm^3) and the separated organic layer was washed with saturated aqueous sodium hydrogencarbonate (2 × 10 cm^3), dried and concentrated under reduced pressure to leave a dark brown oil. Chromatography of this using light petroleum (b.p. 40–60 °C)–ether (9:1) as eluent gave the *O*-silyl undecenynol (324 mg, 95%) as a clear oil, $\nu_{max}(CCl_4)/cm^{-1}$ 3320 and 2110; $\delta_H(CDCl_3)$ 0.88 (t, *J* ~7, CH_3), 1.07 (Bu^t), 1.2–1.5 (m, 3 × CH_2), 1.9–2.1 (m, CH_2), 2.13 (d, *J* 2, C≡CH), 2.36 (app. t, *J* ~7, CH_2), 4.26 (dt, *J* 2 and 7, C*H*O$SiPh_2Bu^t$), 5.37 (m, HC=CH), 7.25 (m, 6 H, $SiPh_2$) and 7.62 (m, 4 H, $SiPh_2$); $\delta_C(CDCl_3)$, 14.17 (q), 19.42 (t), 22.65 (t), 27.06 (q), 27.47 (t), 29.36 (t), 31.57 (t), 36.44 (t), 63.77 (d), 72.84, 84.95 (d), 123.98 (d), 127.55 (d), 127.71 (d), 129.33 (d), 133.01 (d), 133.55, 133.73, 135.98 (d) and 136.16 (d) [Found: *m*/*z* 404.2530. $C_{27}H_{36}OSi$ requires 404.2535].

(Z)-*Undec*-5-*en*-1-*yn*-3-*ol* **5**.—Tetrabutylammonium fluoride (1 mol dm^{-3} solution in THF; 2.60 cm^3, 1.1 equiv.) was added to

a solution of **27** (960 mg, 1 equiv.) in dry THF (30 cm^3), and the resulting mixture was then stirred at room temperature under a nitrogen atmosphere for 1 h. The solution was diluted with ether (50 cm^3) and water (20 cm^3), and the mixture was then stirred at 25 °C for 10 min. The organic layer was separated, dried and then concentrated under reduced pressure to leave a yellow oil. Chromatography of this using light petroleum (b.p. 40–60 °C)–ether (5:1) as eluent gave the alcohol (371 mg, 94%) as a clear oil,[3] $\nu_{max}(CCl_4)/cm^{-1}$ 3640 and 3340; $\delta_H(CDCl_3)$ 0.89 (t, *J* 7, CH_3), 1.2–1.5 (m, 3 × CH_2), 1.98 (OH), 2.0–2.15 (m, CH_2), 2.47 (d, *J* 2, C≡CH), 2.51 (app. t, *J* ~7, CH_2), 4.40 (m, C*H*OH), 5.47 (dt, *J* 11 and 7, C*H*=CH–) and 5.64 (dt, *J* 11 and 7, CH=C*H*); $\delta_C(CDCl_3)$, 14.05 (q), 22.59 (t), 27.54 (t), 29.33 (t), 31.56 (t), 35.64 (t), 61.95 (d), 72.98, 84.66 (d), 123.05 (d) and 134.62 (d) (Found: *m/z* 166.1348. $C_{11}H_{18}O$ requires 166.1353).

(8Z)-*Tetradec*-8-*ene*-2,4-*diyne*-1,6-*diol* **28**.—A solution of the undecenynol **5** (350 mg, 1 equiv.) in ethanol (3 cm^3) was added to a suspension of hydroxylamine hydrochloride (145 mg, 1 equiv.), butylamine (0.38 cm^3, 1.8 equiv.) and cuprous chloride (4 mg, 0.02 equiv.) in water (10 cm^3). The mixture was stirred for 5 min and then a solution of 3-bromopropynol[10] (312 mg, 1.1 equiv.) in ethanol (1 cm^3) was added dropwise to it during 5 min. The mixture was stirred at 60 °C for 5 h and then allowed to cool to room temperature when it was saturated with sodium chloride and extracted with ether. The combined organic fractions were dried and concentrated under reduced pressure to leave a dark oil. Chromatography of this using ether as eluent gave the diynediol (241 mg, 52%) as a clear oil; $\nu_{max}(CCl_4)/cm^{-1}$ 3620; $\delta_H(CDCl_3)$ 0.90 (t, *J* ~7, CH_3), 1.2–1.5 (m, 3 × CH_2), 2.1–2.4 (m, 2 × CH_2), 2.55 (OH), 4.30 (C*H*$_2$OH), 4.41 (app. t, *J* 5, C*H*OH), 5.38 (dt, *J* 11 and 7, CH=C*H*–) and 5.72 (dt, *J* 11 and 7, C*H*=CH) (Found: *m/z* 220.1471. $C_{14}H_{20}O_2$ requires 220.1463).

(2E,4E,8Z)-*Tetradeca*-2,4,8-*triene*-1,6-*diol* **3**.—Lithium aluminium hydride (120 mg, 4 equiv.) was added cautiously to a solution of the diynediol **28** (230 mg, 1 equiv.) in dry THF (30 cm^3), and the resulting suspension was then heated under reflux in a nitrogen atmosphere for 4 h. The mixture was cooled to room temperature and then water (0.12 cm^3) followed by aqueous sodium hydroxide (15% w/w; 0.12 cm^3) and more water (0.36 cm^3) were added to it. The suspension was stirred for 15 min and then filtered. The filtrate was concentrated under reduced pressure to leave a yellow oil. Chromatography of this using ether as eluent gave the trienediol (73 mg, 40%) as a clear oil, $\nu_{max}(CCl_4)/cm^{-1}$ 3600, 1640 and 980; $\delta_H(CDCl_3)$, 0.88 (t, *J* ~7, CH_3), 1.1–1.4 (m, 3 × CH_2), 1.76 (2 × OH), 2.08 (m, CH_2), 2.30 (m, CH_2), 4.20 (m, C*H*OH and C*H*$_2$OH), 5.37 (dt, *J* 11 and 7, CH=C*H*), 5.54 (dt, *J* 11 and 7, C*H*=CH), 5.73 (dd, *J* 6 and 15, CH(OH)C*H*), 5.84 (dt, *J* 15 and 6, CH=C*H*CH$_2$OH) and 6.1–6.35 (m, CH=C*H*C*H*=CH); $\delta_C(CDCl_3)$ 14.05 (q), 22.55 (t), 27.4 (t), 29.26 (t), 31.49 (t), 35.29 (t), 63.24, (t), 71.82 (d), 124.07 (d), 129.56 (d), 130.59 (d), 132.32 (d) and 137.87 (d) (Found: *m/z* 224.1782. $C_{14}H_{24}O_2$ requires 224.1776).

(2E,8Z)-1-*Tetrahydropyranyloxytetradeca*-2,8-*dien*-4-*yn*-6-*ol* **29**.—The THP ether derived from 3-bromopropenol[11] (300 mg, 1 equiv.) was added to a suspension of tetrakis(triphenylphosphine)palladium(0) (80 mg, 0.05 equiv.) in degassed diethylamine (3 cm^3), and the mixture was then stirred at room temperature under a nitrogen atmosphere for 5 min. Cuprous iodide (13 mg, 0.05 equiv.) was added followed by the undecenynol **5** (225 mg, 1 equiv.) during 10 min and the mixture was then stirred at room temperature for 16 h.[12] The solution was diluted with ether (20 cm^3) and stirred for 10 min. The separated ether solution was washed with water (2 × 10 cm^3) and the organic layer was then dried and concentrated under reduced pressure to leave a golden oil. Chromatography of this using light petroleum (b.p. 40–60 °C)–ether (2:1) as eluent gave the mono THP dienynediol (244 mg, 59%) as a pale yellow oil, ν_{max}/cm^{-1} 3600, 3400 and 1040; λ_{max}(EtOH)/nm 228.1; $\delta_H(CDCl_3)$, 0.89 (t, *J* 7, CH_3), 1.2–1.4 (3 × CH_2), 1.70 (m, 3 × CH_2 in THP), 2.0–2.2 (m, CH_2), 2.50 (app. t, *J* ~7, CH_2), 3.53 (m, OCH in THP), 3.84 (dt, *J* 3 and 10, OCH_2 in THP), 4.03 (dd, *J* 1.5 and 16, C*H*$_2$OTHP), 4.50 (m, C*H*OH), 4.64 (t, *J* 3, OCHO), 5.47 (dt, *J* 11 and 7, CH=C*H*), 5.62 (dt, *J* 11 and 7, C*H*=CH), 5.78 (dt, *J* 16 and 1, C*H*=CHCH$_2$OTHP), 6.20 (dt, *J* 16 and 3, CH=C*H*CH$_2$OTHP); $\delta_C(CDCl_3)$, 14.10 (q), 19.33 (t), 22.62 (t), 25.49 (t), 25.57 (t), 29.37 (t), 30.57 (t), 31.59 (t), 35.83 (t), 62.16 (t), 62.56 (d), 66.59 (t), 83.04, 90.41, 97.99 (d), 110.74 (d), 123.37 (d), 134.43 (d) and 140.04 (d) [Found: *m/z* 221.1557. $C_{14}H_{21}O_2$ (M − THP) requires 221.1542].

(2E,4E,8Z)-1-*Tetrahydropyranyloxytetradeca*-2,4,8-*trien*-6-*ol* **30**.—A solution of the mono THP dienyne diol **29** (120 mg, 1 equiv.) in dry THF (2 cm^3) was added dropwise during 15 min to a suspension of lithium aluminium hydride (55 mg, 2 equiv.) in dry THF (10 cm^3) and the mixture was then stirred and heated under reflux in a nitrogen atmosphere for 1 h. Water (0.06 cm^3) was added to it followed by aqueous sodium hydroxide (15% w/v; 0.06 cm^3) and then more water (0.18 cm^3) was added. The mixture was stirred for 15 min and then the white precipitate was filtered off. The filtrate was dried and concentrated under reduced pressure to leave a dark green oil. Chromatography of this using light petroleum (b.p. 40–60 °C)–ether (2:1) as the eluent gave the mono THP trienediol (154 mg, 70%) as a yellow oil, ν_{max}/cm^{-1} 3600, 3400 and 1130; λ_{max}/nm 230.1; $\delta_H(CDCl_3)$ 0.82 (t, *J* 7, CH_3), 1.1–1.4 (m, 3 × CH_2), 1.4–1.6 (m, 3 × CH_2), 1.96 (m, CH_2), 2.25 (m, CH_2), 3.46 (m, CH_2 in THP), 3.80 (m, OCH_2 in THP), 3.95 (dd, *J* 5 and 7.5, C*H*$_2$OTHP), 4.12 (m, C*H*OH), 4.21 (dd, *J* 5 and 7.5, C*H*$_2$OTHP), 4.58 (t, *J* 4, OCHO), 5.3 (dt, *J* 11 and 7, CH=C*H*), 5.48 (dt, *J* 11 and 7, C*H*=CH), 5.70 (m, CH=C*H*C*H*=CH) and 6.19 (m, C*H*=CHCH=C*H*); $\delta_C(CDCl_3)$ 14.13 (q), 19.54 (t), 22.64 (t), 25.56 (t), 22.52 (t), 67.27 (t), 71.99 (d), 97.97 (d), 124.25 (d), 129.89 (d), 130.00 (d), 131.85 (d), 133.89 (d) and 135.77 (d) [Found: *m/z* 223.1705. $C_{14}H_{23}O_2$ (M − THP) requires 223.1698].

(2E,4E,8Z)-6-(tert-*Butyldiphenylsiloxy*)*tetradeca*-2,4,8-*trien*-1-*ol* **31**.—Dimethylaminopyridine (48 mg, 1 equiv.) and *tert*-butyldiphenylsilyl chloride (129 mg, 1 equiv.) were added to a solution of the mono-THP trienediol **30** (120 mg, 1 equiv.) in dry dichloromethane (5 cm^3) and the mixture was then stirred at room temperature under a nitrogen atmosphere for 40 h. The solution was concentrated under reduced pressure and the residue was then taken up in ether (20 cm^3). The separated ether solution was washed with dilute HCl (2 mol dm^{-3}; 10 cm^3) and brine (10 cm^3) and then dried and concentrated under reduced pressure to leave a yellow oil. Chromatography of this using light petroleum (b.p. 40–60 °C)–ether (3:1) as eluent gave (2*E*,4*E*,8*Z*)-6-*tert*-butyldiphenylsiloxy-1- tetrahydropyranyloxytetradeca-2,4,8-triene (152 mg, 71%) as a clear oil, ν_{max}/cm^{-1} 3050, 1450 and 1130; λ_{max}/nm 230.1; $\delta_H(CDCl_3)$, 0.82 (t, *J* 7, CH_3), 1.1–1.3 (m, 3 × CH_2), 1.4–1.6 (m, 3 × CH_2), 1.96 (m, CH_2), 2.25 (m, CH_2), 3.46 (m, OCH_2 in THP), 3.80 (m, OCH_2 in THP), 3.95 (dd, *J* 5 and 7.5, C*H*$_2$OTHP), 4.58 (t, *J* 4, OCHO), 5.3 (dt, *J* 11 and 7, CH=C*H*), 5.48 (dt, *J* 11 and 7, C*H*=CH), 5.6–5.85 (m, CH=C*H*–C*H*=CH) and 6.19 (m, C*H*=CH–CH=C*H*); $\delta_C(CDCl_3)$ 14.13 (q), 19.54 (t), 22.64 (t), 25.56 (t), 27.52 (t), 29.37 (t), 30.72 (t), 31.60 (t), 35.43 (t), 62.27 (t), 67.27 (d), 97.97 (d), 142.25 (d), 129.98 (d), 130.00 (d), 131.85 (d), 133.89 (d) and 135.77 (d) [Found: *m/z* 404.2166. $C_{26}H_{32}SiO_2$ (M − Bu^t − THP) requires 404.2172].

Acetic acid (2 cm^3) and water (0.5 cm^3) were added to a

solution of the bis-protected trienediol (25 mg) in THF (1 cm^3), and the mixture was then stirred at 45 °C for 5 h. Ether (4 cm^3) was added to the mixture which was then stirred for 10 min. The solution was neutralised with saturated aqueous potassium carbonate and then extracted with ether (3 × 10 cm^3). The combined organic extracts were dried and then concentrated under reduced pressure to leave a yellow oil. Chromatography of this using light petroleum (b.p. 40–60 °C)–ether (2:1) as eluent gave the mono TBDPS trienediol (10 mg, 47%) as a clear oil, ν_{max}/cm^{-1} 3600, 3050, 1450 and 1100; $\delta_H(CDCl_3)$ 0.86 (t, $J \sim 7$, CH_3), 1.06 (Bu^t), 1.1–1.4 (m, 3 × CH_2), 1.54 (OH), 1.80 (m, CH_2), 2.22 (m, CH_2), 4.15 (d, J 6, CH_2OH), 4.19 (m, CHOTBDPS), 5.26 (dt, J 11 and 7, CH=CH), 5.34 (dt, J 11 and 7, CH=CH), 5.65 (dd, J 6.5 and 15, CH=CHCH), 5.69 (dt, J 15 and 6, CH–CHCH$_2$OH), 5.94 (dd, J 10 and 15, CH=CHCH=CH), 6.14 (dd, J 10 and 15, CH=CHCH=CH), 7.36 (m, 6 H, $SiPh_2$) and 7.65 (m, 4 H, $SiPh_2$); $\delta_C(CDCl_3)$, 14.07 (q), 19.37, 22.58 (t), 27.06 (3 × q), 27.31 (t), 29.22 (t), 31.49 (t), 35.98 (t), 63.44 (t), 73.69 (d), 124.48 (d), 127.43 (2 × d), 127.49 (2 × d), 129.13 (d), 129.50 (d), 129.57 (d), 131.15 (d), 131.40 (d), 132.12 (d), 134.12, 134.38, 1359.95 (2 × d), 135.99 (2 × d) and 136.42 (d) [Found: m/z 405.2280. $C_{26}H_{33}O_2Si$ (M − Bu^t) requires 405.2312].

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