A tandem radical macrocyclisation-transannular cyclisation approach towards the taxanes

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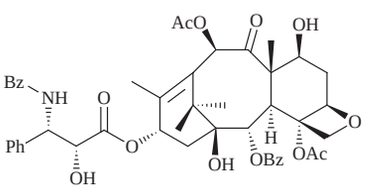
Received (in Cambridge) 7th July 1998, Accepted 24th July 1998

Separate treatment of the iodotrienedione **19** and the iododienynedione **38** with Bu_3SnH–AIBN produces the corresponding taxane ring systems **25** (25–30%) and **56** (50–60%) respectively by way of tandem radical macrocyclisation-radical transannular cyclisations. By contrast the analogous iodopolyenones **61**, **63**, **65a**, **66a**, **86a** and **87a**, together with the corresponding iodoenynones **39a** and **59** failed to undergo similar tandem radical reactions, and instead gave products resulting from direct reduction of the carbon–iodine bonds in these substrates. The structures of the taxane analogues **25** and **56** followed from analysis of their NMR spectroscopic data and comparison with similar NMR data for related taxoids described in the literature. The stereochemistry of **56** was secured from an X-ray crystal structure determination of the 1,5-diol **57** produced from reduction of **56** with DIBAL.

Taxol™ **1** together with its congeners and analogues have now been a preoccupation of medicinal and synthetic chemists for over a decade, ever since the profound anti-cancer properties of several of their members were disclosed.[1] The 'taxoids' as they have become known have as their core the novel and unusual tricyclo[9.3.1.$0^{3,8}$]pentadecane framework **2**, which has proven



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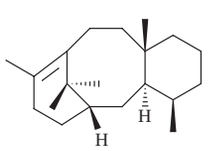

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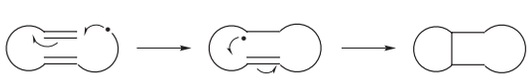
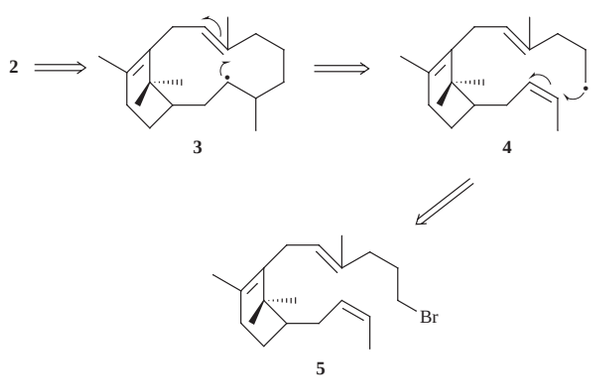
to be a significant challenge to the synthetic chemist.[2] As a consequence, a bewildering array of ingenious synthetic designs towards the taxane carbon framework have been forthcoming,[3] with four of them culminating in the total synthesis of Taxol™ **1** itself.[4] For several years our own research group has had an interest in developing the scope for an approach to polycyclic frameworks based on the principle of a cascade radical-mediated macrocyclisation-transannular cyclisation strategy from an appropriate polyene precursor.[5] The overall principle is illustrated in Scheme 1 and several examples of the scope for



Scheme 1

this strategy have now been communicated in the contemporary literature.[6] An early example of this design towards polycycles was revealed in our approach to the taxane carbon framework **2** where we planned to effect a radical cascade sequence from the substituted A-ring precursor **5** *via* the key intermediates **4** and

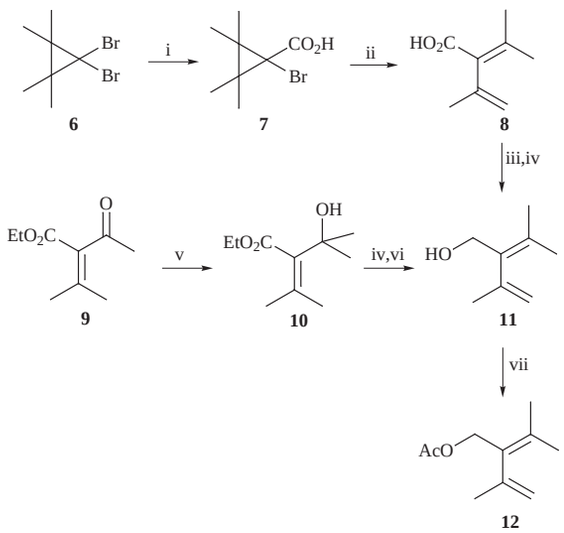


3.[7] The outcome of this idea, and the development of the proposal are now laid down in this paper.[8]

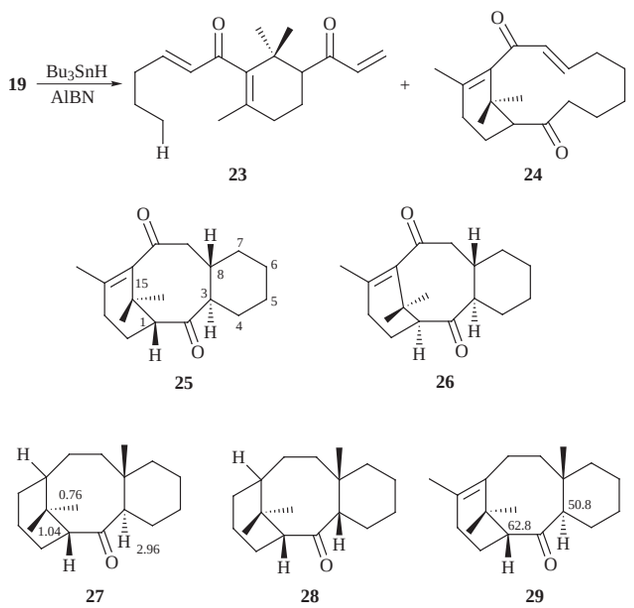
Thus, the first precursor system we examined was the iodotrienedione **19**, which incorporates two conjugated enone electrophores built into the system to facilitate the sequential 12-*endo*-trig radical macrocyclisation and 8-*endo*-trig radical transannulation reactions from the appropriate alkyl radical precursors in the desired regioselective senses. The iodotrienedione **19** was synthesised from the cyclohexene aldehyde product **13** resulting from the Diels–Alder reaction between the diene **12** and acrolein, as illustrated in Scheme 3. Thus the known acetoxy diene **12**[4b] was first prepared starting from the dibromocyclopropane **6**[9] or from the ethyl acetoacetate derivative **9** as shown in Scheme 2. A Diels–Alder reaction between the diene **12** and acrolein in the presence of boron trifluoride–diethyl ether at −78 °C then produced the cyclohexene **13** in 79% yield. Treatment of this aldehyde with two equivalents of vinylmagnesium bromide next led to the alcohol **14a** which on selective oxidation with TPAP–NMO[10] was then converted into the unstable hydroxy aldehyde **15a** in 51% yield. When the aldehyde **15a** was next treated with the vinyllithium reagent derived by tin–lithium exchange from the vinylstannane **16**,[11] it was converted into the labile bis-allylic alcohol **17a**. Oxidation of **17a** to the trienedione **18** was readily accomplished using barium manganate,[12] and treatment of the bromide **18** with sodium iodide in refluxing butan-2-one finally produced the radical precursor compound **19**. The intermediate alcohol **17a** in this sequence was found to be extremely unstable and underwent rapid and quantitative cyclisation on storage overnight

leading to the bridged bicyclic ether **20**. In order to circumvent this problem a modification to the earlier route from **13** to **19** was developed involving protection of the secondary hydroxy group in **14a** as its MOM ether **14b** and proceeding *via* the intermediates **15b**, **17b**, **21** and **22** (Scheme 3).

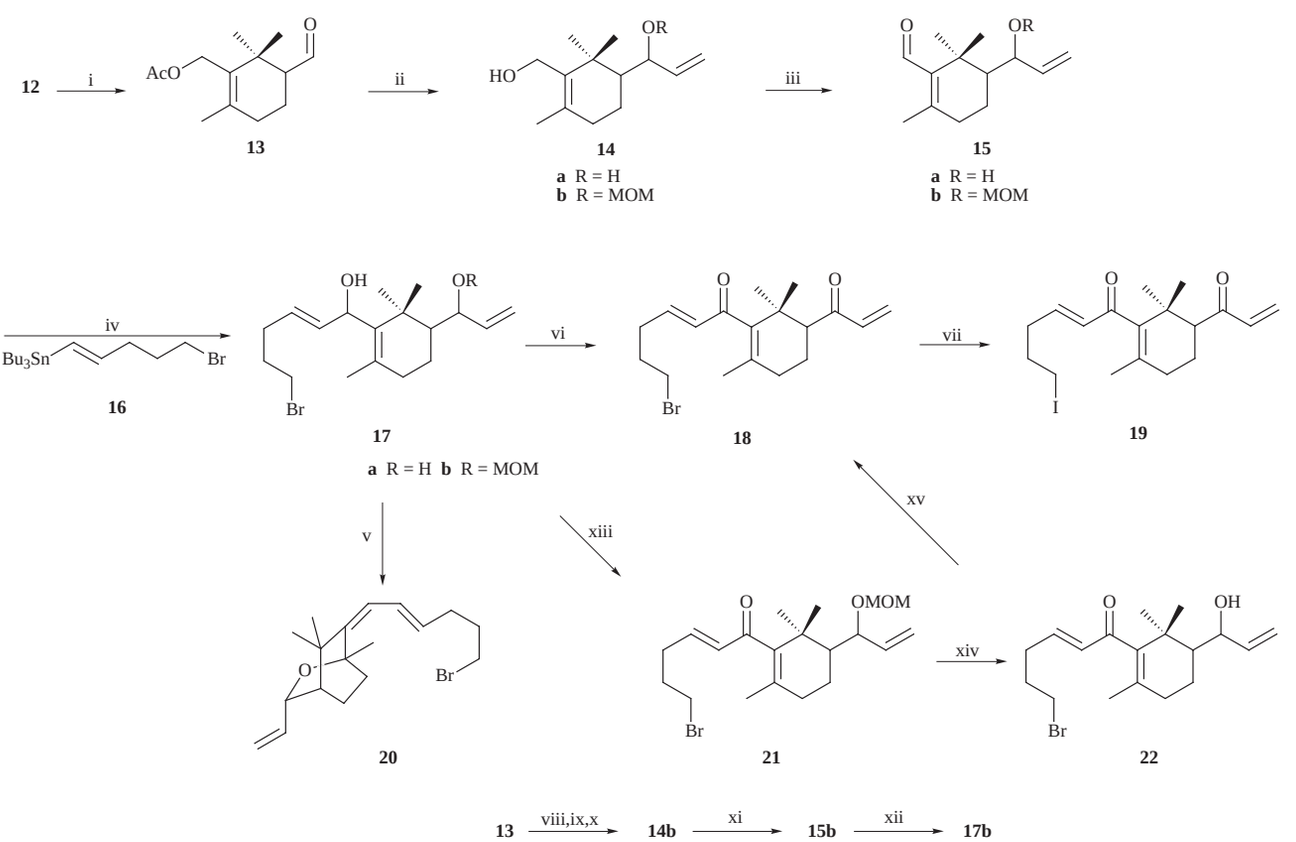
When a solution of the iodotrienedione **19** in dry, degassed benzene was heated under reflux in the presence of 1.1 equivalents of tributyltin hydride (Bu_3SnH) and catalytic azoisobutyronitrile (AIBN) for 6 h, work-up and chromatography separated: (i) the product **23** (28%) resulting from straightforward reduction of the carbon–iodine bond in **19**; (ii) the bicyclo[9.3.1]pentadecadienedione **24** (~30%), the product of 12-*endo*-trig macrocyclisation of **19** and *in situ* hydrogen atom quench, and (iii) a 3:1 mixture of C-1 epimers of the tricyclo[9.3.1.0]pentadecenedione, **25** and **26**, respectively (~25%) produced *via* the aforementioned tandem radical 12-*endo*-trig macrocyclisation-6-*exo*-trig transannulation (Scheme 4).



Scheme 2 *Reagents, conditions and yields*: i, ^nBuLi, CO_2, THF, −78 °C, 82%; ii, AgOAc, AcOH, 120 °C, 76%; iii, CH_3I, K_2CO_3, CH_3COCH_3, room temp., 73%; iv, DIBAL-H, $C_6H_5CH_3$, −60 °C, 92%; v, CH_3MgBr, THF, room temp., 98%; vi, PTSA, C_6H_6, 65 °C, 93%; vii, AcCl, DMAP, Et_3N, CH_2Cl_2, room temp., 95%.



Scheme 4



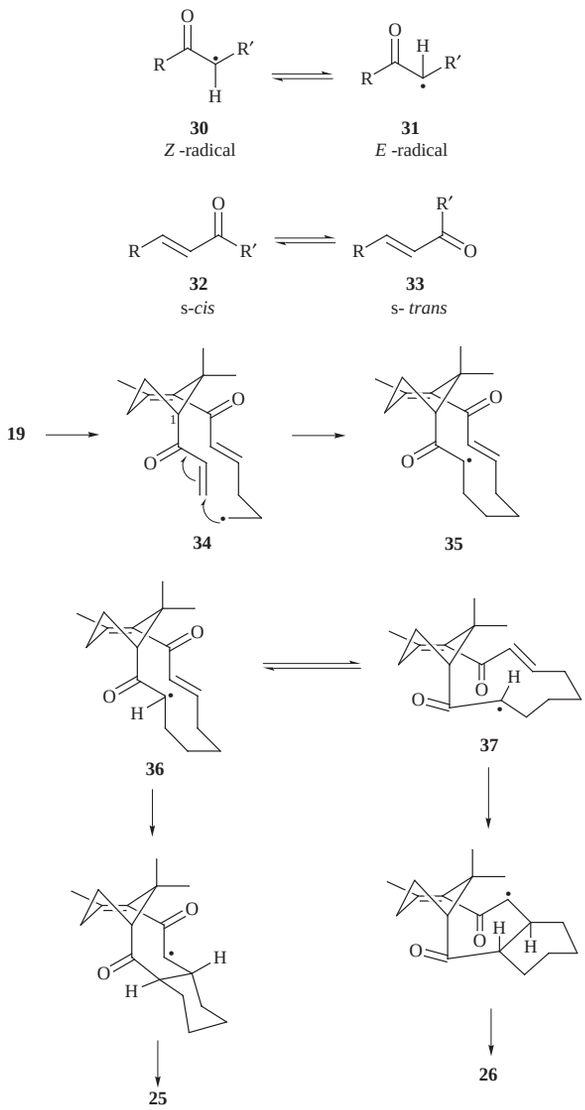
Scheme 3 *Reagents, conditions and yields*: i, H_2C=CHCHO, $BF_3{\cdot}OEt_2$, $C_6H_5CH_3$, −50 °C, 79%; ii, H_2C=CHMgBr, THF, room temp., 84%; iii, TPAP, NMO, CH_2Cl_2, room temp., 51%; iv, ^nBuLi, **16**, THF, −78 °C, 58%; v, $CDCl_3$, −5 °C, quantitative; vi, $BaMnO_4$, CH_2Cl_2, room temp., 90%; vii, NaI, butan-2-one, 80 °C, 99%; viii, H_2C=CHMgBr, THF, room temp., 72%; ix, $ClCH_2OCH_3$, Hunig's base, CH_2Cl_2, 0 °C, 91%; x, K_2CO_3, MeOH, room temp., 98%; xi, TPAP, NMO, CH_2Cl_2, room temp., 99%; xii, MeLi·LiBr, **16**, THF, −78 °C, 76%; xiii, TPAP, NMO, CH_2Cl_2, room temp., 84%; xiv, HCl, H_2O, THF, 50 °C, 90%; xv, TPAP, NMO, CH_2Cl_2, room temp., 89%.

Extensive investigations were carried out in order to optimise the yield of **25/26** at the expense of **23** and **24**, *e.g.* using high dilution techniques, the use of $(Me_3Si)_3SiH$ in place of Bu_3SnH, and atom transfer methods, but only in one instance, where AIBN was added slowly portionwise to a mixture of **19** and Bu_3SnH, were we able to secure a higher yield, *i.e.* 35% of the tricycle **25/26**.[13] Chromatography of the mixture of tricyclo-[9.3.1.0]pentadecenediones **25** and **26** produced a pure sample of the C-1 β-epimer **25**. The structures and stereochemistries of the bicyclic **24**, and tricyclic products, **25** and **26**, followed unambiguously from analysis of their NMR spectroscopic data and, in the case of the C-1 epimeric tricyclic products **25** and **26**, by comparison with similar NMR data reported earlier for related taxoids by Swindell *et al.*[14] and Jenkins *et al.*[15] Thus, in the ^{1}H NMR spectrum of the C-1 β-epimer of the tricyclic dione **25**, the C-15 β-methyl and C-15 α-methyl signals occur at δ 0.79 and 1.10 ppm respectively (*cf.* δ 0.76 and 1.04 ppm in **27**) and the C-3 α-H occurs as a double triplet [*J* 6 and 7 Hz at δ 2.85 ppm (*cf.* δ 2.96 ppm in **27**]. Methine signals characteristic of the taxane ring system were observed at δ 58.7 (C-1), 53.3 (C-3) and 37.1 (C-8) ppm in the ^{13}C NMR spectrum of **25** and at δ 67.7, 55.4 and 37.2 ppm respectively for the minor α-1 epimer **26**. Comparison of these ^{13}C NMR spectroscopic data with corresponding data for the C-3 epimeric tricyclic ketones **27** and **28** reported by Swindell *et al.*,[14] established that the molecules were not epimeric at C-3, *i.e.* the BC ring junction. This evidence, supported by further correlation with the ^{13}C NMR data reported for the taxoid **29** by Jenkins *et al.*,[15] finally led us to assign the relative configurations shown in **25** and **26** for the epimeric tricyclic (taxane) products produced when **19** was treated with Bu_3SnH–AIBN.

Explanations which rationalise the stereochemical outcome of the tandem radical cyclisation leading to the taxane ring system **25/26** from the precursor **19** are manifold. Furthermore the situation is not helped by the limited knowledge of the structures of the reacting α-keto radicals [*i.e.* (*Z*)-**30** or (*E*)-**31**] and their facial selectivities in reactions with s-*cis* and s-*trans* enone electrophores (*i.e.* **32** and **33**). Nevertheless, simply on the grounds of accessibility of reaction centres, the initial 12-*endo*-trig macrocyclisation of **19** to **35** will take place most favourably when the enone electrophore at C-1 assumes an axial orientation, *viz.* **34**. The bicyclic intermediate **35** can then adopt any number of conformations depending on whether the α-keto radical unit orientates itself (*Z*)- or (*E*)-, and whether the (*E*)-enone electrophore has an s-*trans* or s-*cis* conformation. These features will then determine the stereochemical outcomes of the resulting 6-*exo*-trig transannulations. Thus, it seems most likely that an alignment of centres presented by the conformation **36** will lead to the major C-1 β-taxane **25**, whereas the conformation reflected in structure **37** will produce the corresponding C-1 α-taxane **26** (Scheme 5).[16]

With the establishment of a new and novel radical-mediated macrocyclisation-transannulation strategy towards the taxanes, we next decided to examine a variety of alternative precursors, analogous to **19**, in order to develop and explore the limits of the method. We surmised that replacement of either of the enone electrophores in **19** by alkynones, *viz.* **38** and **39a**, would have a beneficial effect on the efficacy of the cascade macrocyclisation-transannulation process and, in addition, lead to more unsaturated taxane products thereby providing further opportunities for synthetic transformations in the tricyclic products. Thus, the iododienynedione positional isomers **38** and **39a** were both synthesised starting from the substituted ring-A precursor **13** using synthetic transformations similar to those used to convert **13** into **19** (Schemes 6 and 7).

When the 'internal' alkynone **39a** was treated with Bu_3SnH–AIBN under the same conditions that were used to convert **19** into **25** it failed to undergo any intramolecular cyclisation at all, and instead gave only the product of direct reduction of the carbon–iodine bond, *i.e.* **39b** (21%). To our satisfaction however,

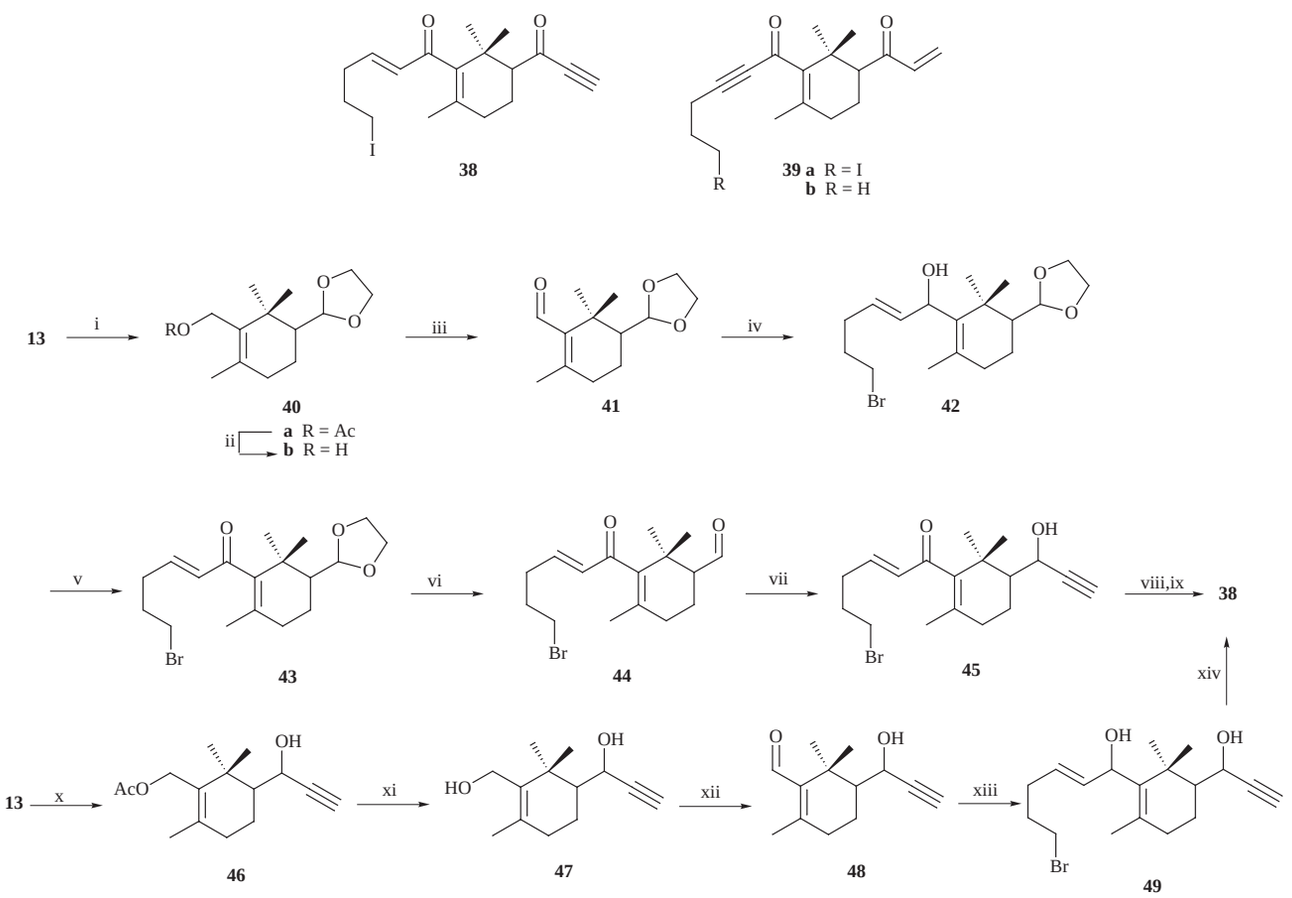


Scheme 5

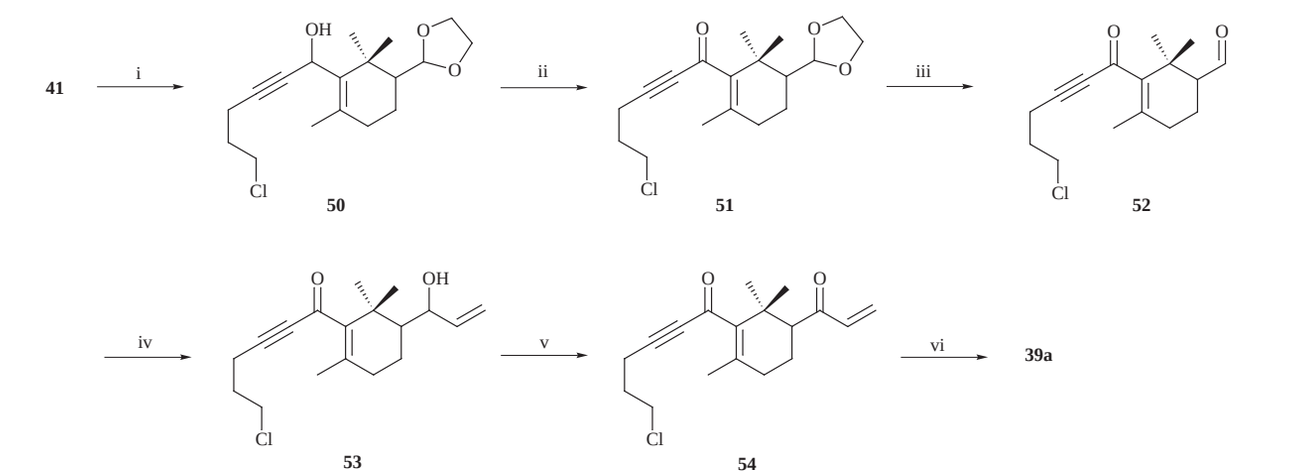
when the 'terminal' alkynone **38** was treated with Bu_3SnH–AIBN it underwent a facile cascade 12-*endo*-dig macrocyclisation (to **55**) followed by a 6-*exo*-trig transannulation producing the tricyclo[9.3.1.0^{3,8}]pentadecadienedione **56** in 45–60% yield, as a 6:1 mixture of C-1 epimers (Scheme 8). The structure of **56** followed from analysis of its NMR spectroscopic data and comparison with corresponding data recorded for the analogues **25**, **27**, **28** and **29**. Finally, the stereochemistry of **56** was secured from an X-ray crystal structure determination of the 1,5-diol **57** produced from reduction of the dione **56** with DIBAL; a view of the structure is shown in Fig. 1.

The differing outcomes of the attempted cascade cyclisations of **19**, **38** and **39a** are surely intriguing, but attempts to rationalise the results using computer modelling and energy minimisation data on little-known processes involving ill-defined reactive intermediates were unrewarding.[13] Although not unknown, at the outset of our studies with **38** and **39a**, alkynes had been used less frequently than alkenes as electrophores in radical macrocyclisations.[17] The success we enjoyed in converting **38** into **56** was not matched when we attempted an ambitious double cyclisation from the enediynedione **59** in the presence of Bu_3SnH–AIBN when only the product **60** of carbon–iodine bond reduction (~21%) was identified amongst the products (*cf.* **39a** ⟶ **39b**).

The availability of a facile radical-based cascade process allowing easy access to the functionalised taxane ring system **56** from the substituted A-ring precursor **38** encouraged us to



Scheme 6 *Reagents, conditions and yields*: i, $(CH_2OH)_2$, CSA, C_6H_6, room temp., 87%; ii, K_2CO_3, MeOH, room temp., 94%; iii, TPAP, NMO, CH_2Cl_2, room temp., 88%; iv, ^{n}BuLi, **16**, THF, −84 °C, 81%; v, TPAP, NMO, CH_2Cl_2, room temp., 81%; vi, CSA, THF, H_2O, reflux, 89%; vii, HCCMgBr, THF, room temp., 81%; viii, $BaMnO_4$, CH_2Cl_2, room temp, 59%; ix, NaI, butan-2-one, reflux, 99%; x, HCCMgBr, THF, room temp., 93%; xi, K_2CO_3, MeOH, room temp., 91%; xii, $(ClCO)_2$, DMSO, Et_3N, −60 °C, 58%; xiii, ^{n}BuLi, **16**, THF, −84 °C, 75%; xiv, $BaMnO_4$, CH_2Cl_2, room temp., 51%.



Scheme 7 *Reagents, conditions and yields*: i, $Cl(CH_2)_3CCH$, ^{n}BuLi, THF, −78 °C, 96%; ii, TPAP, NMO, CH_2Cl_2, room temp., 98%; iii, CSA, THF, H_2O, reflux, 98%; iv, H_2C=CHMgCl, THF, room temp., 98%; v, TPAP, NMO, CH_2Cl_2, room temp., 89%; vi, NaI, butan-2-one, reflux, 94%.

examine some chemistry of **56** with a view to introducing the C-8 angular methyl group and additional oxygenation in ring C in the molecule. In the event, it rapidly became apparent that we were going to have considerable problems introducing the C-8-methyl into the taxane **56**.[18] This situation made us re-think our overall strategy and we elected to overcome the problem by examining the cascade cyclisations of the vinyl methyl substituted analogues **61** and **63** of **19**, together with the *exo*-methylene-containing substrates **65a** and **66a**. The syntheses we employed to elaborate these substrates are summarised in Schemes 9 and 10, and they used closely similar methods and procedures to those we had developed earlier to prepare the molecules **19** and **38**; indeed the syntheses used some common intermediates. Much to our chagrin however each of the substrates led only to the products of direct reduction of their carbon–iodine bonds, *i.e.* **62**, **64**, **65b** and **66b** on treatment with Bu_3SnH–AIBN. Whilst this outcome, in retrospect, was perhaps not too surprising in view of the possibilities for facile 1,5-hydrogen abstraction processes by the precursor radical centres in these substrates,[19] there are clearly many additional subtle stereoelectronic/energy features associated with the ease or otherwise of cascade radical-mediated macrocyclisation-

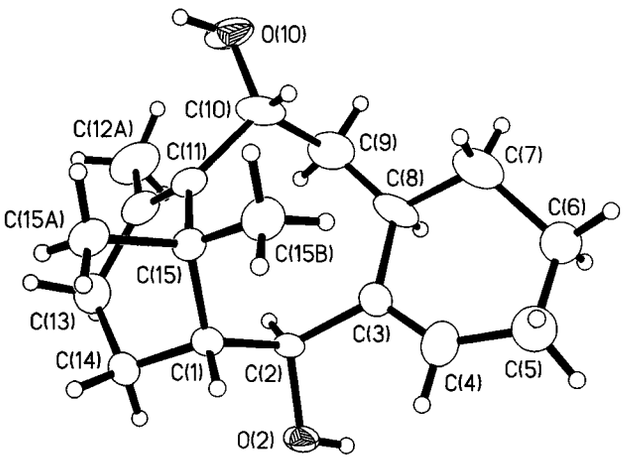
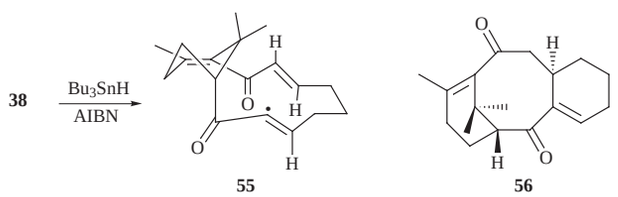
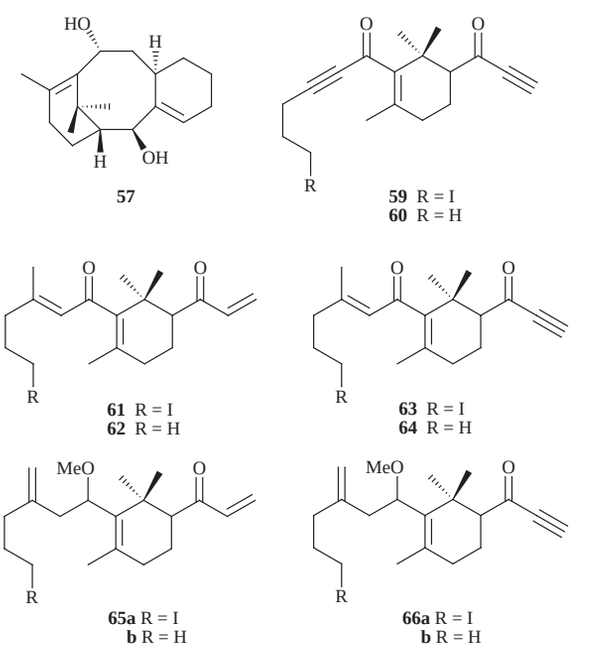


Fig. 1 X-Ray structure of compound **57**.

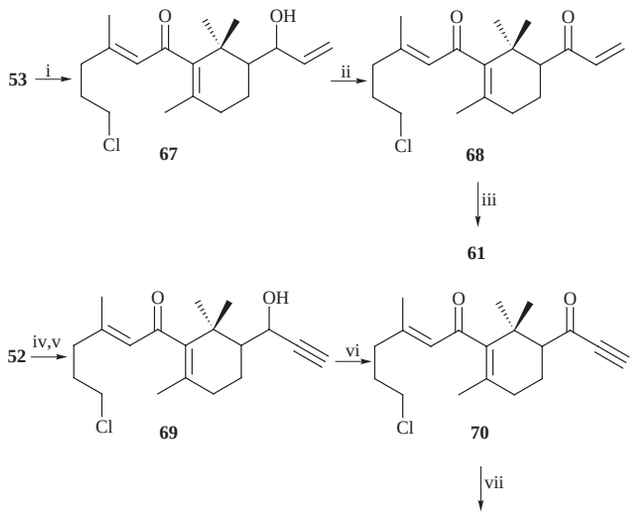


Scheme 8



transannulation processes from the precursors **19**, **38**, **39a**, **59**, **61**, **63**, **65a** and **66a**, leading to the corresponding taxane ring systems, which seem beyond our comprehension at this time.

At the outset of our studies on the radical cascade macrocyclisation-transannulation to taxanes shown by the sequences **5** ⟶ **4** ⟶ **3** ⟶ **2** we were aware that the same B/C ring juncture in **2** could be disconnected by alternative radical-mediated retro macrocyclisation-transannulation strategies including the one shown in Scheme 11. In contemporaneous studies we therefore examined the scope for this alternative strategy, and decided to synthesise specific geometrical isomers of the model compounds **86a** and **87a**. The molecules were prepared starting from the same substituted cyclohexene **89** produced by way of a Diels–Alder reaction between the diene **88** and acrolein. Thus, a Wittig reaction between **89** and the phosphonium salt **90**[20] using sodium hexamethyldisilylazide as base in THF at 0 °C first led to the (*Z*)-alkene **91**. A series of functional group manipulations next allowed the conversion of



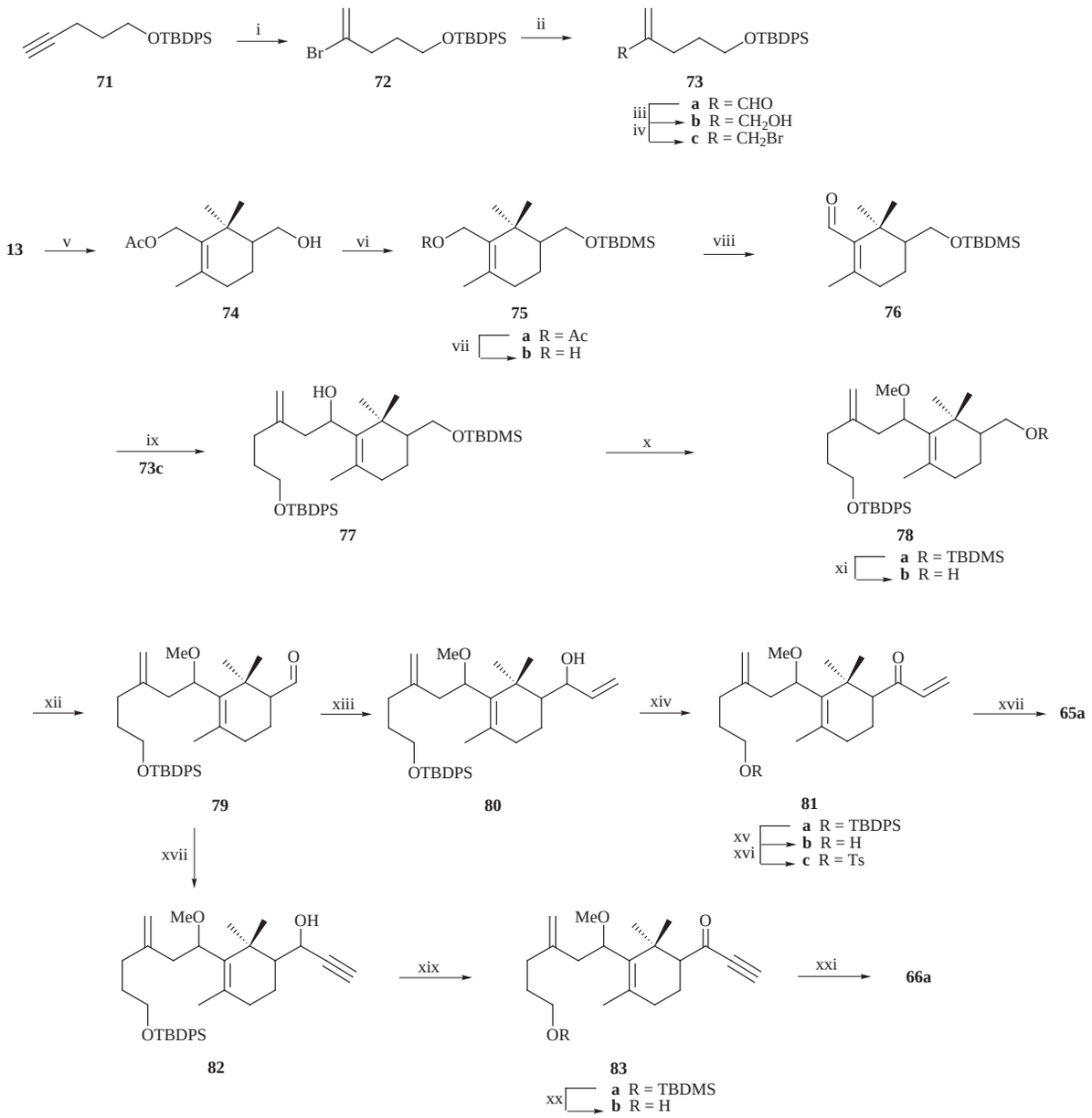
Scheme 9 *Reagents, conditions and yields*: i, MeLi·LiI, CuI, THF, 91%; ii, TPAP, NMO, CH_2Cl_2, room temp., 75%; iii, NaI, butan-2-one, reflux, 93%; iv, HCCMgBr, THF, room temp., 94%; v, MeLi·LiBr, CuI, THF, 94%; vi, $BaMnO_4$, CH_2Cl_2, room temp., 75%; vii, NaI, butan-2-one, reflux, 98%.

91 into **93** *via* **92** which was then oxidised to the aldehyde **94**. Addition of vinylmagnesium bromide to **94**, followed by oxidation of the resulting alcohol **95** using Dess–Martin periodinane[21] next produced the corresponding bromoenone **96** which by bromine–iodine exchange then led to the target molecule **86a** (Scheme 12). The analogous (*E*)-alkene **87a** was synthesised from the cyclohexene ring A precursor **89** using the methods and procedures collected in Scheme 13. Unfortunately, when either of the iodotrienones **86a** and **87a** were treated separately with Bu_3SnH–AIBN the only products isolated were those of direct reduction of the carbon–iodine bonds in the substrates, *i.e.* **86b** and **87b** in 92 and 63% yield respectively.

Experimental

General details

All melting points were determined on a Kofler hot-stage apparatus and are uncorrected. Ultraviolet spectra were recorded on a Philips PU 8700 spectrophotometer as solutions in spectroscopic grade ethanol. Infrared spectra were obtained using a Perkin-Elmer 1600 series FT-IR instrument either as liquid films or as dilute solutions in spectroscopic grade chloroform. Proton NMR spectra were recorded on either a Bruker WM 250 (250 MHz), a Bruker AM 400 (400 MHz) or a JEOL EX-270 (270 MHz) spectrometer as dilute solutions in deuteriochloroform. The chemical shifts are recorded relative to trimethylsilane as internal standard and the multiplicity of a signal is designated by one of the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; quin, quintet; br, broad; m, multiplet; app., apparent; obsc., obscured. All coupling constants, *J*, are reported in hertz. Carbon-13 NMR spectra were recorded on either a Bruker AM 400 (at 100.6 MHz) or a JEOL EX-270 (at 68 MHz) instrument. The spectra were recorded as dilute solutions in deuteriochloroform with chemical shifts reported relative to internal chloroform standard in a broad band decoupled mode, and the multiplicities obtained using a DEPT sequence. Where required, assignments for ^1H and ^{13}C NMR spectra were confirmed by two dimensional homonuclear (^1H–^{13}C) correlation spectroscopy. Matrix dimensions for two dimensional spectra were either 1024 points × 256 columns (homonuclear ^1H) or 2048 points × 128 columns (heteronuclear ^1H–^{13}C), and were recorded on a JEOL EX-270 instrument or a Bruker AM 400 (400 MHz). Mass spectra were



Scheme 10 *Reagents, conditions and yields*: i, 9-BrBBN, CH_2Cl_2, 0 °C; H_2O_2, 0 °C; 95%; ii, ^tBuLi, DMF, Et_2O, −110 °C, 82%; iii, $NaBH_4$, $CeCl_3 \cdot 7H_2O$, MeOH, 0 °C, 99%; iv, NBS, PPh_3, CH_2Cl_2, room temp., 99%; v, $NaBH_4$, MeOH, Et_2O, 0 °C, 98%; vi, TBDMSCl, DMAP, Et_3N, CH_2Cl_2, room temp., 94%; vii, K_2CO_3, MeOH, room temp., 95%; viii, TPAP, NMO, CH_2Cl_2, room temp., 97%; ix, $SnCl_2$, NaI, **73c**, DMF, room temp., 82%; x, KHMDS, $(MeO)_2SO_2$, −78 °C to room temp., 97%; xi, PPTS, MeOH, room temp., 88%; xii, Dess–Martin, CH_2Cl_2, room temp., 94%; xiii, $H_2C{=}CHMgCl$, THF, room temp., 94%; xiv, Dess–Martin, CH_2Cl_2, room temp., 86%; xv, TBAF, PTSA, THF, room temp., 97%; xvi, TsCl, Et_3N, CH_2Cl_2, room temp., 79%; xvii, NaI, butan-2-one, reflux, 93%; xviii, HCCMgCl, THF, room temp., 97%; xix, Dess–Martin, CH_2Cl_2, room temp., 93%; xx, TBAF, PTSA, THF, room temp., 93%; xxi, I_2, PPh_3, imidazole, room temp., 56%.

recorded on AE1 MS-902 or MM-701CF spectrometers using electron ionisation (EI) techniques. Microanalytical data were obtained on a Perkin-Elmer 240B elemental analyser.

Flash chromatography was performed on Merck silica gel 60 as the stationary phase and the solvents employed were either of analytical grade or were distilled before use. All reactions were monitored by TLC using Merck silica gel 60 F254 precoated aluminium backed plates which were visualised with ultraviolet light and then with either acidic alcoholic vanillin solution, basic potassium permanganate solution, or phosphomolybdic acid. Ether refers to diethyl ether and light petroleum to the fraction of bp 40–60 °C.

Routinely, dry organic solvents were stored under nitrogen and/or over sodium wire. Other organic solvents were dried by distillation from the following: THF (sodium benzophenone ketyl), dichloromethane (calcium hydride) and methanol (magnesium methoxide). Other organic solvents and reagents were purified by the accepted literature procedures. Solvent was removed on a Buchi rotary evaporator. Where necessary, reactions requiring anhydrous conditions were performed in a flame- or oven-dried apparatus under a nitrogen or argon atmosphere. A Buchi GKR-50 Kugelrohr apparatus was used for bulb-to-bulb distillations.

Tetra(*n*-propyl)ammonium perruthenate/4-methylmorpholine *N*-oxide oxidations. General procedure

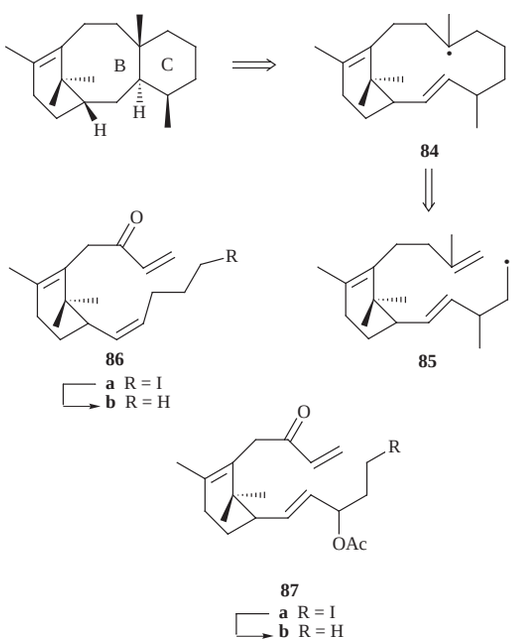
Tetra(*n*-propyl)ammonium perruthenate (0.05 equiv.) was added portionwise over 5 min to a stirred suspension of the alcohol (1 equiv.), 4-methylmorpholine *N*-oxide (1.2 equiv.) and dried powdered 4 Å molecular sieves (0.5 g per mmol) in dry dichloromethane (0.5 M) at 0 °C under nitrogen. The suspension was allowed to warm to room temperature where it was stirred for 1 h and then purified directly by chromatography on silica, eluting with 20% ether in light petroleum (bp 40–60 °C), to give the oxidation product (51–99%) as a colourless oil.

Preparation of alkyl iodides by Finkelstein exchange. General procedure

A stirred suspension of the bromide (1 equiv.), sodium iodide (3 equiv.) and butan-2-one (0.1 M) was heated at reflux for 90 min and then cooled. Water (20 ml) and ether (20 ml) were added and the organic layer was then separated, dried and evaporated *in vacuo* to leave the iodide (89–99%) as a pale yellow oil.

Reductive radical reactions of alkyl iodides. General procedure

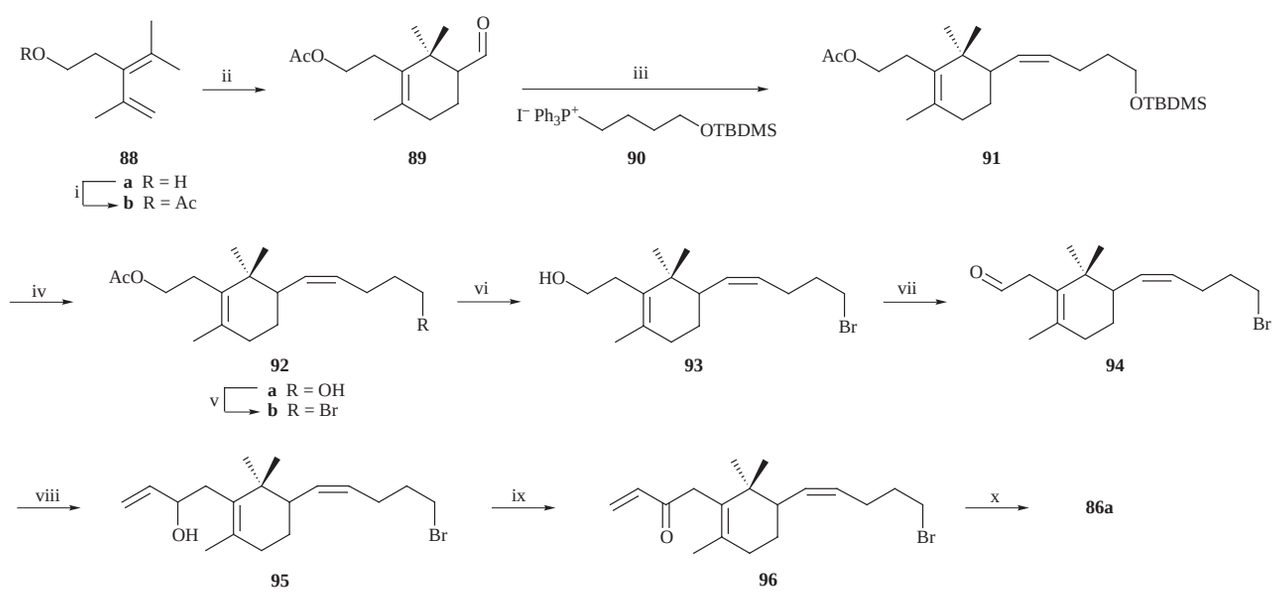
A solution of tri-*n*-butyltin hydride (1.1 equiv.), and azoisobutyronitrile (0.05 equiv.) in dry benzene (5 ml) was added dropwise over 4 h to a stirred, refluxing solution of the iodide (1 equiv.) and azoisobutyronitrile (0.02 equiv.) in dry, degassed benzene (3 mM), under argon. The mixture was held at reflux for a further 4 h and then cooled and concentrated *in vacuo.* The residue was taken up in ether (10 ml) and then stirred at room temperature for 8 h over 20% aqueous potassium fluoride (5 ml). The organic layer was separated and then dried and evaporated *in vacuo* to a yellow oil which was purified by chromatography on silica, eluting with 20% ether in light petroleum (bp 40–60 °C), to give the reduced products.



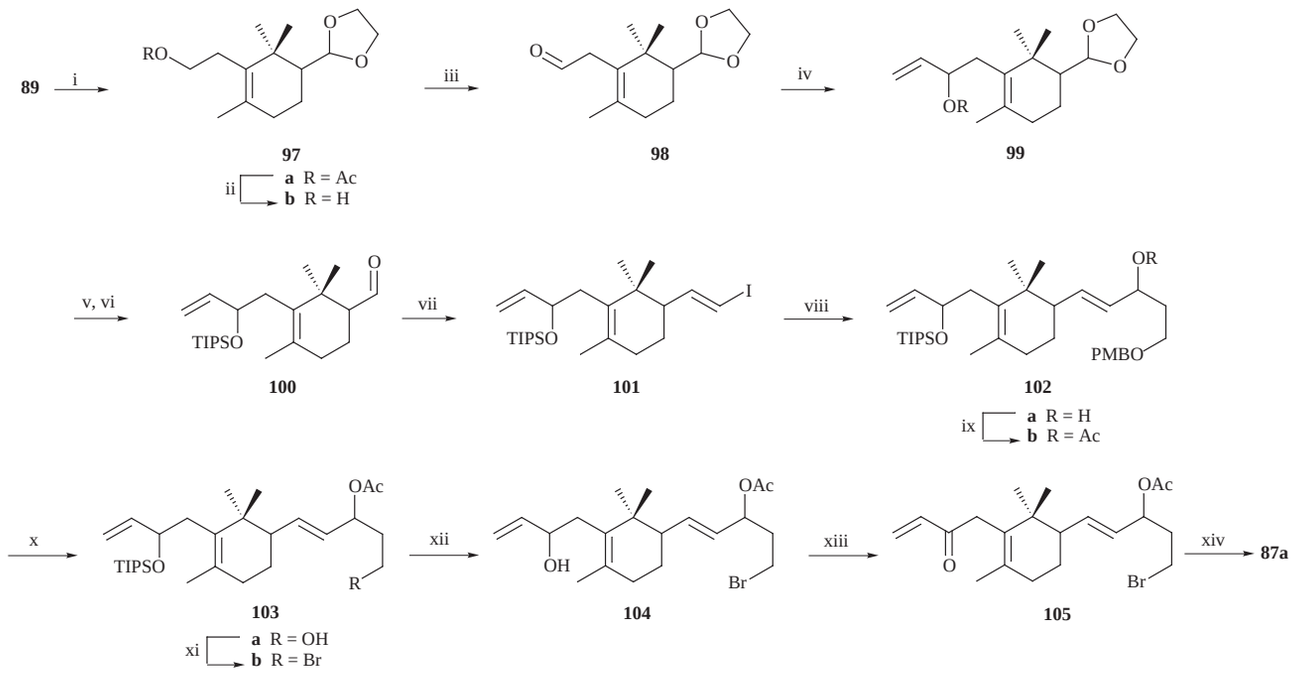
Scheme 11

1-Bromo-2,2,3,3-tetramethylcyclopropane-1-carboxylic acid 7. A solution of *n*-butyllithium (127 ml) in hexanes (1.6 M, 0.20 mol) was added dropwise over 25 min to a stirred solution of the dibromide **6**[9] (52.0 g, 0.20 mol) in THF (750 ml) at −78 °C under nitrogen and the mixture was then stirred at −78 °C for 10 min. Carbon dioxide gas was bubbled through the mixture for 3 h and the mixture was then allowed to return to room temperature. The mixture was quenched with water (15 ml) and then concentrated *in vacuo* to ~50 ml. Ether (150 ml) was added and the organic layer was separated, washed with aqueous hydrochloric acid (2 M, 50 ml) and extracted with saturated aqueous sodium hydrogen carbonate (2 × 150 ml). The combined basic extracts were acidified to pH 1 with hydrochloric acid (2 M) and extracted with dichloromethane (2 × 150 ml). The dried organic extracts were concentrated *in vacuo* to leave the *acid* (38.6 g, 82%) as a white solid, mp 162–164 °C (from pentane); $\nu_{max}(CHCl_3)/cm^{-1}$ 3180, 1716 and 957; δ_H(250 MHz) 1.19 (s, 6H, Me), 1.18 (s, 6H, Me); δ_C(67.8 MHz) 173.8 (s), 49.5 (s), 28.1 (s), 21.5 (q), 19.1 (q) (Found: $M^+ - Me$, 204.9858. $C_7H_{10}BrO_2$ requires *M*, 204.9864) (Found: C, 43.5; H, 5.9. $C_8H_{13}BrO_2$ requires C, 43.7; H, 6.1%).

3-Carboxy-2,4-dimethylpenta-2,4-diene 8. A stirred mixture of the cyclopropanecarboxylic acid **7** (14.0 g, 63.3 mmol) and silver acetate (15.9 g, 95.0 mmol) in glacial acetic acid (150 ml) was heated to 120 °C for 45 min. The cooled mixture was diluted with ether (200 ml) and then filtered through kieselguhr. The filtrate was concentrated *in vacuo* and the residue was redissolved in ether (50 ml) and extracted with saturated aqueous sodium hydrogen carbonate (2 × 50 ml). The combined basic extracts were acidified to pH 1 with aqueous hydrochloric acid (2 M) and extracted with dichloromethane (3 × 50 ml). The combined organic extracts were dried and concentrated *in vacuo* to leave the *acid* (6.7 g, 76%) as white crystals, mp 54–55 °C (from pentane); λ_{max}(EtOH)/nm 222 (ε/dm^3 mol^{-1} cm^{-1} 6 600); $\nu_{max}(CHCl_3)/cm^{-1}$ 3176, 1688, 1671, 1309 and 905; δ_H(250 MHz) 5.13 (br s, 1H, =CH*H*), 4.77 (br s, 1H, =C*H*H), 2.13 (s, 3H, Me), 1.89 (s, 3H, Me), 1.88 (s, 3H, Me); δ_C(67.8 MHz) 173.8 (s), 150.1 (s), 143.2 (s), 130.6 (s), 116.5 (t),



Scheme 12 *Reagents, conditions and yields*: i, AcCl, DMAP, Et_3N, CH_2Cl_2, room temp., 78%; ii, H_2C=CHCHO, BF_3·OEt_2, $C_6H_5CH_3$, −50 °C, 74%; iii, NaHMDS, **90**, THF, 0 °C, 74%; iv, TBAF, THF, room temp., 91%; v, CBr_4, PPh_3, CH_2Cl_2, room temp., 74%; vi, DIBAL-H, THF, −20 °C, 74%; vii, TPAP, NMO, CH_2Cl_2, room temp., 73%; viii, H_2C=CHMgBr, THF, −78 °C, 47%; ix, Dess–Martin, CH_2Cl_2, room temp., 99%; x, NaI, butan-2-one, reflux, 98%.



Scheme 13 *Reagents, conditions and yields*: i, $(CH_2OH)_2$, CSA, C_6H_6, reflux, 93%; ii, DIBAL-H, THF, −20 °C, 73%; iii, TPAP, NMO, CH_2Cl_2, room temp., 94%; iv, $CeCl_3$, H_2C=CHMgBr, THF, −78 °C, 74%; v, CSA, THF, H_2O, 60 °C; vi, TIPSCl, 2,6-lutidine, CH_2Cl_2, −20 °C, 91%; vii, CHI_3, chromous chloride, THF, room temp., 64%; viii, $PMBO(CH_2)_2CHO$; DMSO, chromous chloride, $NiCl_2$, THF, 31%; ix, Ac_2O, DMAP, Et_3N, CH_2Cl_2, 0 °C, 92%; x, DDQ, H_2O, CH_2Cl_2, room temp., 85%; xi, CBr_4, PPh_3, CH_2Cl_2, 0 °C, 96%; xii, HF, CH_3CN, room temp., 79%; xiii, Dess–Martin, CH_2Cl_2, room temp., 81%; xiv, NaI, butan-2-one, reflux, 89%.

24.6 (q), 23.6 (q), 23.0 (q) (Found: M^+, 140.0825. $C_8H_{12}O_2$ requires *M*, 140.0837) (Found: C, 68.6; H, 8.6. $C_8H_{12}O_2$ requires C, 68.5; H, 8.9%).

2,4-Dimethyl-3-(hydroxymethyl)penta-2,4-diene 11.[4b] A mixture of the diene acid **8** (10.1 g, 72 mmol), potassium carbonate (25 g, 170 mmol) and methyl iodide (102 g, 720 mmol) in dry acetone (200 ml) was stirred at room temperature for 24 h. The mixture was filtered and the filtrate was evaporated *in vacuo* and the residue redissolved in dichloromethane (100 ml). The mixture was refiltered and the filtrate was concentrated *in vacuo* to leave an oil which was distilled under vacuum to give 3-methoxycarbonyl-2,4-dimethylpenta-2,4-diene (8.0 g, 73%) as a colourless oil, bp 69–71 °C/12mm Hg; λ_{max}(EtOH)/nm 222 (ε/dm^3 mol^{-1} cm^{-1} 6 500); ν_{max}(film)/cm^{-1} 1718, 1627 and 901; δ_H(250 MHz) 5.08 (br s, 1H, CH*H*), 4.74 (br s, 1H, =C*H*H), 3.68 (s, 3H, OMe), 1.98 (s, 3H, Me), 1.80 (s, 6H, Me); δ_C(67.8 MHz) 159.3 (s), 137.3 (s), 136.1 (s), 125.1 (s), 112.2 (t), 53.9 (q), 28.6 (q), 28.6 (q), 27.6 (q) (Found: M^+, 154.1003. $C_9H_{14}O_2$ requires *M*, 154.0994).

A solution of diisobutylaluminium hydride (91.0 ml) in toluene (1 M, 91.0 mmol) was added dropwise over 20 min to a stirred solution of the diene ester from above (7.0 g, 45.5 mmol) in dry toluene (250 ml) at −60 °C under nitrogen. The mixture was stirred for 2 h and then allowed to warm to 0 °C where it was quenched with water (25 ml) and aqueous hydrochloric acid (2 M, 50 ml). The organic layer was separated, dried and concentrated *in vacuo* to leave a yellow oil. Purification by chromatography on silica, eluting with 30% ether in pentane, gave the alcohol **11** (5.2 g, 92%) as a colourless oil; λ_{max}(EtOH)/nm 225 (ε/dm^3 mol^{-1} cm^{-1} 3 400); ν_{max}(film)/cm^{-1} 3349, 1632 and 894; δ_H(250 MHz) 5.07 (br s, 1H, =CH*H*), 4.70 (br s, 1H, =C*H*H), 4.05 (s, 2H, CH_2OH), 1.82 (s, 3H, Me), 1.76 (s, 3H, Me), 1.72 (s, 3H, Me); δ_C(67.8 MHz) 144.8 (s), 135.9 (s), 129.5 (s), 114.25 (t), 60.1 (t), 22.4 (q), 21.6 (q), 19.1 (q) (Found: M^+, 126.1043. $C_8H_{14}O$ requires *M*, 126.1044). The diene alcohol was also prepared by the modified procedure published by Nicolaou *et al.*[4b]

2,4-Dimethyl-3-(acetoxymethyl)penta-2,4-diene 12.[4b] A solution of acetyl chloride (1.79 g, 22.9 mmol), triethylamine (1.54 g, 22.9 mmol), 4-dimethylaminopyridine (20 mg, 0.16 mmol) and the diene alcohol **11** (1.92 g, 15.2 mmol) in dry dichloromethane (100 ml) was stirred at room temperature for 18 h. The mixture was quenched with water (25 ml), and the organic layer was then separated and washed with saturated aqueous sodium hydrogen carbonate (25 ml) and brine (25 ml). The dried organic extracts were then concentrated *in vacuo* to leave the acetate (2.4 g, 95%) as a colourless oil; λ_{max}(EtOH)/nm 224 (ε/dm^3 mol^{-1} cm^{-1} 3 500); ν_{max}(film)/cm^{-1} 1741, 1633 and 898; δ_H(250 MHz) 5.01 (br s, 1H =CH*H*), 4.68 (br s, 3H, CH_2OAc and =C*H*H), 2.06 (s, 3H, COMe), 1.81 (s, 3H, Me), 1.80 (s, 3H, Me), 1.78 (s, 3H, Me); δ_C(67.8 MHz) 171.1 (s), 144.8 (s), 133.2 (s), 131.4 (s), 114.4 (t), 63.0 (t), 22.6 (q), 22.0 (q), 21.0 (q), 19.8 (q) (Found: M^+ − AcOH, 108.0941. C_8H_{12} requires *M*, 108.0939) (Found C, 71.4; H, 10.0. Calc. for $C_{10}H_{16}O_2$: C, 71.4; H, 9.6%); which was used without further purification. The diene acetate was also prepared according to the procedure published by Nicolaou *et al.*[4b]

Ethyl 3-methyl-2-(1-oxoethyl)but-2-enoate 9. The title enone was prepared from ethyl acetoacetate according to the procedure described by Alkonyi *et al.*[22] and showed: ν_{max}(film)/cm^{-1} 1723, 1699 and 1632; δ_H(250 MHz) 4.20 (q, 2H, *J* 7 Hz, CH_3CH_2O), 2.25 (s, 3H, CH_3C=), 2.09 (s, 3H, CH_3C=), 1.95 (s, 3H, CH_3CO), 1.25 (t, 3H, *J* 7 Hz, CH_3CH_2O); δ_C(67.8 MHz) 200.4 (s), 165.8 (s), 153.2 (s), 132.1 (s), 60.7 (t), 30.6 (q), 23.3 (q), 22.9 (q), 14.0 (q) (Found: M^+, 170.0931. $C_9H_{14}O_3$ requires *M*, 170.0943) (Found: C, 63.3; H, 8.5. Calc. for $C_9H_{14}O_3$: C, 63.5; H, 8.3%).

Ethyl 2-(1-hydroxy-1-methylethyl)-3-methylbut-2-enoate 10. The title alcohol was prepared from **9** according to the procedure published by Nicolaou *et al.*[4b] and showed: λ_{max}(EtOH)/nm 231 (ε/dm^3 mol^{-1} cm^{-1} 2 100); ν_{max}(film)/cm^{-1} 3480, 1719 and 1648; δ_H(250 MHz) 4.14 (q, *J* 7 Hz, 2H, CH_3CH_2O), 2.59 (br, 1H, O*H*), 1.85 (s, 3H, Me), 1.61 (s, 3H, Me), 1.38 (s, 6H, 2 × Me), 1.23 (t, *J* 7 Hz, 3H, CH_3CH_2O); δ_C(67.8 MHz) 171.1 (s), 137.7 (s), 133.3 (s), 71.4 (s), 60.5 (t), 30.1 (q), 24.0 (q), 20.8 (q), 14.3 (q) (Found: M^+ − H_2O, 168.1204. $C_{10}H_{16}O_2$ requires *M*, 168.1150) (Found: C, 64.1; H, 9.7; Calc. for $C_{10}H_{18}O_3$: C, 64.5; H, 9.7%).

1-Acetoxymethyl-2,6,6-trimethylcyclohex-1-ene-5-carboxaldehyde 13. Acrolein (2.0 g, 35 mmol) was added in one portion to a stirred solution of boron trifluoride–diethyl ether (5.4 g, 35 mmol) in dry toluene (150 ml) at −78 °C under nitrogen. After 5 min, a solution of the diene **12** (4.0 g, 24 mmol) in toluene (10 ml) was added dropwise over 15 min and the mixture was then stirred at −78 °C for 10 h. The mixture was quenched at −78 °C with water (50 ml) and pentane (100 ml), and was then allowed to return to room temperature. The organic layer was separated, dried and evaporated *in vacuo* to leave a yellow oil. Purification by chromatography on silica eluting with 20% ether in pentane gave the *aldehyde* (4.2 g, 79%) as a colourless liquid; ν_{max}(film)/cm^{-1} 1736, 1658 and 954; δ_H(250 MHz) 9.86 (d, *J* 3 Hz, 1H, C*H*O), 4.62 (s, 2H, CH_2OAc), 2.23 (app. dt, *J* 10, 3 Hz, 1H, C*H*CHO), 2.12 (app. t, *J* 6 Hz, 2H, =CCH_2), 2.06 (s, 3H, COMe), 1.95 (m, 2H, CH_2), 1.71 (s, 3H, Me), 1.22 (s, 3H, Me), 1.07 (s, 3H, Me); δ_C(67.8 MHz) 205.7 (d), 171.3 (s), 136.5 (s), 131.5 (s), 60.2 (t), 56.8 (d), 36.3 (t), 30.8 (q), 27.2 (s), 23.5 (q), 21.0 (q), 19.7 (q), 19.6 (t) (Found: M$^+$ − AcOH, 164.1202. $C_{11}H_{16}O$ requires *M*, 164.1201) (Found: C, 69.2; H, 9.4. $C_{13}H_{20}O_3$ requires C, 69.6; H, 9.0%).

1-Hydroxymethyl-5-(1-hydroxyprop-2-enyl)-2,6,6-trimethylcyclohex-1-ene 14a. A solution of vinylmagnesium bromide (70.8 ml) in THF (1 M, 70.8 mmol) was added dropwise over 15 min to a stirred solution of the aldehyde **13** (4.0 g, 17.7 mmol) in dry THF (250 ml) at −78 °C under nitrogen. The mixture was allowed to return to room temperature over 5 h where it was stirred for a further 2 h. The mixture was cooled to 0 °C and then quenched with saturated aqueous ammonium chloride (50 ml) and ether (200 ml). The organic layer was separated and the aqueous layer was re-extracted with ether (2 × 50 ml). The combined organic extracts were washed with brine (200 ml), dried and concentrated *in vacuo* to leave a yellow oil. Purification by chromatography on silica eluting with 25% pentane in ether gave the *diol* (3.1 g, 84%) as a colourless oil which crystallised on standing, mp 78–80 °C (from pentane); ν_{max}(film)/cm^{-1} 3392, 3084, 1642, 1367, 1092 and 986; δ_H(250 MHz) 5.90 (ddd, *J* 16, 11, 5 Hz, 1H, C*H*=CH$_2$), 5.26 (d, *J* 16 Hz, 1H, =CH*H*), 5.14 (d, *J* 11 Hz, 1H, =C*H*H), 4.48–4.45 (m, 1H, CHC*H*OH), 4.18 (d, *J* 14 Hz, 1H, CH_2OH), 4.10 (d, *J* 14 Hz, 1H, CH_2OH), 2.12 (br s, OH), 2.06 (app. t, *J* 6 Hz, 2H, =CCH_2), 1.77 (s, 3H, Me), 1.68–1.20 (m, 3H), 1.14 (s, 3H, Me), 1.08 (s, 3H, Me); δ_C(67.8 MHz) 142.1 (d), 137.9 (s), 133.9 (s), 113.4 (t), 71.1 (d), 58.7 (t), 49.5 (d), 37.6 (s), 32.5 (t), 27.1 (q), 23.1 (q), 19.8 (q), 17.5 (t) (Found: M$^+$ − H_2O, 192.1515. $C_{13}H_{20}O$ requires *M*, 192.1514) (Found: C, 74.2; H, 11.0; $C_{13}H_{22}O_2$ requires C, 74.2; H, 10.5%).

1-Formyl-5-(1-hydroxyprop-2-enyl)-2,6,6-trimethylcyclohex-1-ene 15a. Treatment of a solution of the diol **14a** (1.08 g, 5.1 mmol) in dry dichloromethane with tetra(*n*-propyl)ammonium perruthenate and 4-methylmorpholine *N*-oxide, according to the general procedure, gave the title *aldehyde* (0.55 g, 51%) as a colourless oil; ν_{max}(film)/cm^{-1} 3467, 1670, 1610 and 735; δ_H(250 MHz) 10.11 (s, 1H, C*H*O), 5.92 (ddd, *J* 17, 11, 5 Hz, 1H, C*H*=CH$_2$), 5.29 (d, *J* 17 Hz, 1H, =CH*H*), 5.16 (d, *J* 11 Hz, 1H, =C*H*H), 4.58 (br d, *J* 5 Hz, 1H, C*H*OH), 2.30–2.25 (m, 2H, =CCH_2), 2.22 (s, 3H, Me), 1.78–1.48 (m, 3H), 1.33 (s, 3H, Me), 1.32 (s, 3H, Me); δ_C(67.8 MHz) 192.1 (d), 156.3 (s), 141.7 (s), 140.6 (d), 113.6 (t), 70.2 (d), 50.3 (d), 36.6 (s), 35.7 (t), 26.5 (q), 21.8 (q), 19.5 (q), 16.8 (t) (Found: M$^+$, 208.1451. $C_{13}H_{20}O_2$ requires *M*, 208.1463); which was used immediately.

(*E*)-1-Tributylstannyl-5-bromopent-1-ene 16. A stirred mixture of pent-4-yn-1-ol (3.0 g, 36 mmol), tributyltin hydride (13.5 g, 46.4 mmol) and azoisobutyronitrile (20 mg) was heated to 80 °C for 2 h under nitrogen. The cooled mixture was purified by dry column chromatography eluting with 25% ether in pentane to give a mixture of (*E*)- and (*Z*)-isomers (6:1 ratio) of the (*E*)-1-tributylstannylpent-1-en-5-ol (11.8 g, 88%) as a colourless liquid.[11] Data for (*E*)-isomer only: ν_{max}(film)/cm^{-1} 3328, 1600 and 1070; δ_H(250 MHz) 6.53 (dt, *J* 12, 7 Hz, 1H, =C*H*CH$_2$), 6.12–5.70 (m, 1H, SnC*H*=), 3.65 (t, *J* 7 Hz, CH_2OH), 2.34–2.15 (m, 2H), 2.04–1.90 (m, 2H), 1.68–1.20 (m, 12H), 0.98–0.85 (m, 15H); δ_C(67.8 MHz) 147.0 (d), 129.8 (d), 36.0 (t), 33.0 (t), 32.8 (t), 31.8 (t), 29.2 (t), 29.1 (t), 29.0 (t), 28.9 (t), 27.3 (t), 27.2 (t), 13.7 (q) 10.2 (t) (Found: M$^+$ − C_4H_8, 321.1166. $C_{13}H_{28}OSn$ requires *M*, 320.1162).

A solution of triphenylphosphine (5.25 g, 13.3 mmol) in dry dichloromethane (10 ml) was added dropwise over 15 min to an ice-cold, stirred solution of carbon tetrabromide (6.63 g, 20.0 mmol) and the alcohol from above (5.00 g, 13.3 mmol) in dry dichloromethane (25 ml) under nitrogen. The mixture was stirred for a further 5 min and then concentrated *in vacuo* to leave a residue which was triturated with pentane. The resulting suspension was filtered and the filtrate was evaporated *in vacuo* to leave a residue which was distilled at reduced pressure to give a 6:1 mixture of (*E*)- and (*Z*)-isomers of the *bromide* (4.8 g, 82%) as a colourless oil, bp 103–105 °C/0.1mm Hg. Data for (*E*)-isomer only: ν_{max}(film)/cm^{-1} 1599 and 747; δ_H(250 MHz) 6.53 (dt, *J* 12, 7 Hz, =C*H*CH$_2$), 6.12–5.70 (m, 1H, SnC*H*=), 3.42 (t, *J* 7 Hz, 2H, CH_2Br), 2.34–2.15 (m, 2H), 2.04–1.90 (m, 2H), 1.68–1.20 (m, 12H), 0.98–0.85 (m, 15H); δ_C(67.8 MHz) 148.6 (d), 148.2 (d), 128.6 (d), 128.0 (d), 62.3 (t), 34.0 (t), 33.3 (t), 32.7 (t), 31.7 (t), 29.2 (t), 29.1 (t), 29.0 (t), 28.8 (t), 27.6 (t), 27.3 (t), 27.2 (t), 26.7 (t), 13.6 (q), 10.1 (t) and 9.3 (t) (Found: M$^+$ − C_4H_8, 381.0348. $C_{13}H_{27}BrSn$ requires *M*, 381.0348).

1-[(*E*)-6-Bromo-1-hydroxyhex-2-enyl]-2,6,6-trimethyl-5-(1-hydroxyprop-2-enyl)cyclohex-1-ene 17a. A solution of *n*-butyllithium (1.68 ml) in hexanes (1.6 M, 2.69 mmol) was added dropwise over 15 min to a stirred solution of the vinylstannane **16** (1.26 g, 2.88 mmol) in dry THF (10 ml) at −78 °C under nitrogen. The mixture was stirred at −78 °C for 1 h and then a solution of the freshly purified aldehyde **15a** (0.18 g, 0.85 mmol) in dry THF (2 ml) was added dropwise over 5 min. The mixture was stirred at −78 °C for a further 30 min and then quenched with water (10 ml) and ether (20 ml) and allowed to warm to room temperature. The organic layer was separated and washed with brine (25 ml). Evaporation of the dried organic extracts *in vacuo* left a yellow oil which was purified by chromatography on silica eluting with 50% ether in pentane to give a mixture of diastereoisomers of the *diol* (0.18 g, 58%) as a colourless oil. Data for one diastereoisomer: ν_{max}(film)/cm^{-1} 3431, 1709 and 969; δ_H(250 MHz) 5.90 (ddd, *J* 16, 11, 5 Hz, 1H, C*H*=CH$_2$), 5.78 (dd, *J* 16, 7 Hz, 1H, CH$_2$CH=C*H*), 5.58 (dt, *J* 16, 7 Hz, 1H, CH$_2$C*H*=CH), 5.24 (d, *J* 16 Hz, 1H, =CH*H*), 5.12 (d, *J* 11 Hz, 1H, =C*H*H), 4.80 (d, *J* 7 Hz, 1H, C*H*OH), 4.46 (br d, *J* 5 Hz, 1H, C*H*OH), 3.38 (t, *J* 7 Hz, 2H, CH_2Br), 2.20 (app. q, *J* 7 Hz, 2H, CH_2CH=), 2.02–1.86 (m, 2H, =CCH_2), 1.78 (s, 3H, Me), 1.75–1.26 (m, 5H), 1.22 (s, 3H, Me), 1.02 (s, 3H, Me); δ_C(67.8 MHz) 141.8 (d), 139.4 (s), 134.3 (d), 133.5 (s), 128.1 (d), 113.5 (t), 71.4 (d), 70.6 (d), 49.8 (d), 38.4 (s), 33.5 (t), 33.2 (t), 32.0 (t), 30.5 (t), 27.2 (q), 22.7 (q), 21.3 (q), 17.5 (t) (Found: M$^+$ − H_2O, 340.1266. $C_{18}H_{27}BrO$ requires *M*, 340.1262).

6-(6-Bromo-hex-2-enylidene)-3-ethenyl-2-oxa-1,5,5-trimethylbicyclo[2.2.2]octane 20. A solution of the diol **17a** in deuterated chloroform was evaporated, and the residue was kept at −5 °C for 12 h to afford the *bicyclic ether* as a colourless oil; δ_H(250 MHz) 7.36 (dd, *J* 16, 11 Hz, 1H, CH=C*H*CH), 6.70 (ddd, *J* 16, 11, 6 Hz, 1H, C*H*=CH$_2$), 6.64 (d, *J* 11 Hz, 1H, C*H*=C), 6.56 (dt, *J* 16, 7 Hz, 1H, CH$_2$C*H*=CH), 6.16 (d, *J* 16 Hz, 1H, =C*H*H), 5.94 (d, *J* 11 Hz, 1H, =CH*H*), 4.60 (br s, 1H, C*H*OR), 3.44 (t, *J* 7 Hz, 2H, CH_2Br), 2.30 (q, *J* 7 Hz, 2H, CH_2CH=), 2.00–1.50 (m, 5H), 1.47 (s, 3H, Me), 1.40 (s, 3H, Me), 1.26 (s, 3H, Me); δ_C(67.8 MHz) 149.6 (s), 140.1 (d), 132.6 (d), 128.7 (d), 120.6 (d), 114.4 (t), 73.9 (d), 73.2 (s), 44.9 (d), 37.3 (s), 33.2 (t), 33.0 (t), 32.0 (t), 31.2 (t), 28.4 (q), 27.6 (q), 24.3 (q) and 15.7 (t) (Found: M$^+$, 338.1266. $C_{18}H_{27}BrO$ requires *M*, 340.1262).

1-[(*E*)-6-Bromo-1-oxohex-2-enyl]-2,6,6-trimethyl-5-(1-oxoprop-2-enyl)cyclohex-1-ene 18. A mixture of the diol **17a** (38 mg, 0.11 mmol) and barium manganate (0.27 g, 1.1 mmol) in dry dichloromethane (10 ml) was stirred at room temperature

for 24 h. The mixture was filtered through kieselguhr and the filtrate was evaporated *in vacuo* to leave the *enone* (34 mg, 90%) as a colourless oil; λ_{max}(EtOH)/nm 235 (ε/dm^3 mol^{-1} cm^{-1} 13 000); ν_{max}(film)/cm^{-1} 1675, 1645 and 985; δ_H(250 MHz) 6.96 (dt, *J* 16, 7 Hz, 1H, CH_2CH=CH), 6.42 (dd, *J* 16, 11 Hz, 1H, CH=CH_2), 6.22 (d, *J* 16 Hz, 1H, =CH*H*), 6.35 (d, *J* 16 Hz, 1H, CH=C*H*CO), 5.74 (d, *J* 11 Hz, 1H, =C*H*H), 3.41 (t, *J* 7 Hz, 2H, CH_2Br), 2.86 (app. t, *J* 7 Hz, 1H, C*H*CO), 2.43 (app. q, *J* 7 Hz, 2H, CH_2CH=), 2.22–1.80 (m, 6H), 1.52 (s, 3H, Me), 1.14 (s, 3H, Me), 1.02 (s, 3H, Me); δ_C(67.8 MHz) 200.5 (s), 199.5 (s), 147.8 (d), 137.0 (s), 134.9 (d), 132.0 (d), 128.0 (s), 125.7 (t), 51.7 (d), 33.7 (s), 30.5 (t), 28.8 (t), 28.7 (t), 27.2 (q), 26.9 (t), 22.0 (q), 19.2 (t), and 19.2 (q) (Found: M$^+$, 352.0912. $C_{18}H_{25}BrO_2$ requires *M*, 352.0924).

The title ketone was also prepared from the alcohol **22** by treatment of the alcohol in dry dichloromethane with tetra-(*n*-propyl)ammonium perruthenate and 4-methylmorpholine *N*-oxide, according to the general procedure (89%).

1-[(*E*)-6-Iodo-1-oxohex-2-enyl]-2,6,6-trimethyl-5-(1-oxoprop-2-enyl)cyclohex-1-ene 19. Treatment of a solution of the bromide **18** (35 mg, 0.10 mmol) in butan-2-one with sodium iodide, according to the general procedure, gave the title *iodide* (39 mg, 99%) as a colourless oil; λ_{max}(EtOH)/nm 235 (ε/dm^3 mol^{-1} cm^{-1} 13 000); ν_{max}(film)/cm^{-1} 1675, 1645 and 986; δ_H(250 MHz) 6.96 (dt, *J* 16, 7 Hz, 1H, CH_2CH=CH), 6.42 (dd, *J* 16, 11 Hz, 1H, CH=CH_2), 6.22 (d, *J* 16 Hz, 1H, =CH*H*), 6.35 (d, *J* 16 Hz, 1H, CH=C*H*CO), 5.74 (d, *J* 11 Hz, 1H, =C*H*H), 3.22 (t, *J* 7 Hz, 2H, CH_2I), 2.86 (app. t, *J* 7 Hz, 1H, C*H*CO), 2.43 (app. q, *J* 7 Hz, 2H, CH_2CH=), 2.22–1.80 (m, 6H), 1.52 (s, 3H, Me), 1.14 (s, 3H, Me), 1.02 (s, 3H, Me); δ_C(67.8 MHz) 202.3 (s), 201.6 (s), 149.3 (d), 139.1 (s), 137.0 (d), 134.0 (d), 130.0 (s), 127.8 (t), 53.9 (d), 35.8 (t), 33.2 (t), 31.5 (q), 29.3 (q), 29.0 (t), 24.1 (q), 21.3 (q), 21.3 (t), 5.4 (t) (Found: M$^+$ 400.0892. $C_{18}H_{25}IO_2$ requires *M*, 400.0899).

1-Hydroxymethyl-5-[1-(methoxymethoxy)prop-2-enyl]-2,6,6-trimethylcyclohex-1-ene 14b. A solution of vinylmagnesium bromide (6.69 ml) in THF (1 M, 6.69 mmol) was added dropwise over 10 min to a stirred solution of the aldehyde **13** (1.5 g, 6.69 mmol) in dry THF (50 ml) at −78 °C under an atmosphere of nitrogen. The solution was stirred at −78 °C for 1 h and then allowed to warm to room temperature where it was stirred for a further 1 h. The solution was cooled to 0 °C and then quenched with water (10 ml), saturated aqueous ammonium chloride (25 ml) and ether (50 ml). The organic layer was separated and the aqueous layer was then extracted with ether (2 × 50 ml). The combined organic extracts were washed with saturated aqueous sodium hydrogen carbonate (50 ml) and brine (50 ml), and then dried and evaporated to dryness *in vacuo* to leave a viscous yellow oil. Purification by chromatography on silica eluting with 35% ether in light petroleum (bp 40–60 °C) gave firstly recovered starting material (0.15 g, 10%). Further elution then gave two diastereoisomers of 1-acetoxymethyl-5-(1-hydroxyprop-2-enyl)-2,6,6-trimethylcyclohex-1-ene (1.2 g, 72%) as a colourless oil; (data for one diastereoisomer): ν_{max}(film)/cm^{-1} 3499, 1733, 991, 953 and 918; δ_H(250 MHz) 5.89 (ddd, *J* 17, 10, 5 Hz, 1H, CHC*H*=CH_2), 5.25 (app. dt, *J* 17, 2 Hz, 1H, CHCH=C*H*H), 5.13 (app. dt, *J* 10, 2 Hz, 1H, CHCH=CH*H*), 4.59 (s, 2H, AcOCH_2), 4.50–4.45 (m, 1H, HOC*H*CH=), 2.10–2.04 (m, 2H, =CCH_2CH_2), 2.04 (obsc. s, 3H, CH_3CO), 1.67 (s, 3H, =CCH_3), 1.63–1.38 (m, 3H), 1.06 (s, 3H, Me), 1.05 (s, 3H, Me); δ_C(67.8 MHz) 171.9 (s), 142.2 (d), 137.1 (s), 132.8 (s), 113.8 (t), 71.5 (d), 61.5 (t), 49.6 (d), 37.9 (s), 33.0 (t), 27.1 (q), 23.4 (q), 21.5 (q), 20.2 (q), 17.7 (t) (Found: M$^+$ − AcOH, 192.1511. $C_{13}H_{20}O$ requires *M*, 192.1514).

Chloromethyl methyl ether (3.6 ml, 47.8 mmol) was added dropwise over 5 min to a stirred solution of the above alcohol (6.0 g, 23.9 mmol) and Hunig's base (8.3 ml, 47.8 mmol) in dry dichloromethane (100 ml) at 0 °C under an atmosphere of nitrogen. The solution was allowed to warm to room temperature where it was stirred for 14 h. The mixture was diluted with dichloromethane (50 ml) and then washed with water (100 ml). The aqueous layer was extracted with dichloromethane (2 × 50 ml) and then the combined organic layers were washed with saturated aqueous ammonium chloride (100 ml) and water (100 ml), dried ($MgSO_4$), and evaporated to dryness *in vacuo* to leave a yellow oil. Purification by chromatography on silica eluting with 25% ether in light petroleum (bp 40–60 °C) gave two diastereoisomers of the corresponding *MOM ether* (6.5 g, 91%) as a pale yellow oil; (data for one diastereoisomer): ν_{max}(film)/cm^{-1} 1736, 953, 920 and 733; δ_H(250 MHz) 5.81 (ddd, *J* 17, 10, 7 Hz, 1H, CHOMOMC*H*=CH_2), 5.20–5.14 (m, 2H, CH=CH_2), 4.67 (d, *J* 7 Hz, 1H, OC*H*HOCH$_3$), 4.58 (s, 2H, AcOCH_2), 4.50 (d, *J* 7 Hz, 1H, OCH*H*OCH$_3$), 4.24 (d, *J* 7 Hz, 1H, C*H*O-MOM), 3.37 (s, 3H, OCH_3), 2.12–1.97 (m, 2H), 2.05 (obsc. s, 3H, CH_3CO), 1.79–1.38 (m, 3H), 1.66 (obsc. s, 3H, =CCH_3), 1.06 (s, 3H, Me), 1.01 (s, 3H, Me); δ_C(67.8 MHz) 171.4 (s), 138.9 (d), 136.3 (s), 132.6 (s), 115.8 (t), 94.6 (t), 77.5 (d), 61.2 (t), 56.4 (q), 50.0 (d), 37.7 (s), 33.0 (t), 26.4 (q), 22.4 (q), 21.1 (q), 19.8 (q), 18.6 (t) (Found: M$^+$ − AcOH − MOMOH, 174.1414. $C_{13}H_{18}$ requires *M*, 174.1404).

Potassium carbonate (6.8 g, 49.2 mmol) was added in one portion to a stirred solution of the above MOM ether acetate (4.9 g, 16.4 mmol) in methanol (100 ml) at room temperature. The solution was stirred at room temperature for 14 h and then concentrated *in vacuo*. The residue was dissolved in ether (100 ml) and water (100 ml). The organic layer was separated and the aqueous layer was re-extracted with ether (2 × 50 ml). The combined organic extracts were washed with saturated aqueous ammonium chloride (100 ml) and brine (100 ml) and then dried and concentrated *in vacuo* to leave a colourless oil. Purification by chromatography on silica eluting with 50% ether in light petroleum (bp 40–60 °C) gave two diastereoisomers of the *MOM ether* (4.1 g, 98%) as a pale yellow oil. Data for one diastereoisomer: ν_{max}(film)/cm^{-1} 3424, 1716, 919 and 734; δ_H(250 MHz) 5.82 (ddd, *J* 17, 10, 7 Hz, 1H, C*H*=CH_2), 5.17–5.12 (m, 2H, CH=CH_2), 4.68 (d, *J* 7 Hz, 1H, OC*H*HOCH$_3$), 4.51 (d, *J* 7 Hz, 1H, OCH*H*OCH$_3$), 4.24 (d, *J* 7 Hz, 1H, C*H*O-MOM), 4.19 (d, *J* 11 Hz, 1H, HOC*H*H), 4.10 (d, *J* 11 Hz, 1H, HOCH*H*), 3.38 (s, 3H, OCH_3), 2.05–2.00 (m, 2H, =CCH_2), 1.76 (obsc. s, 3H, =CCH_3), 1.78–1.52 (m, 2H, =CCH$_2$CH_2), 1.41–1.37 (dt, *J* 2, 12 Hz, 1H, C*H*CHOMOM), 1.06 (s, 3H, Me), 1.01 (s, 3H, Me); δ_C(67.8 MHz) 138.9 (d), 138.3 (s), 133.7 (s), 115.9 (t), 94.6 (t), 77.1 (d), 59.0 (t), 56.4 (q), 50.2 (d), 37.7 (s), 32.9 (t), 28.9 (q), 22.5 (q), 19.7 (q), 18.7 (t) (Found: M$^+$ − H_2O − MOMO, 175.1441. $C_{13}H_{19}$ requires *M*, 175.1487).

1-Formyl-5-[1-(methoxymethoxy)prop-2-enyl]-2,6,6-trimethylcyclohex-1-ene 15b. Treatment of a solution of the alcohol **14b** (0.25 g, 0.98 mmol) in dry dichloromethane with tetra-(*n*-propyl)ammonium perruthenate and 4-methylmorpholine *N*-oxide, according to the general procedure, gave the title *aldehyde* (0.24 g, 99%) as a colourless oil; λ_{max}(EtOH)/nm 247 (ε/dm^3 mol^{-1} cm^{-1} 15 100); ν_{max}(film)/cm^{-1} 1672, 1613 and 920; δ_H(250 MHz) 10.10 (s, 1H, C*H*O), 5.81 (ddd, *J* 17, 10, 7 Hz, 1H, C*H*=CH_2), 5.22–5.14 (m, 2H, CH=CH_2), 4.67 (d, *J* 7 Hz, 1H, OC*H*HOCH$_3$), 4.50 (d, *J* 7 Hz, 1H, OCH*H*OCH$_3$), 4.29 (d, *J* 7 Hz, 1H, C*H*OMOM), 3.36 (s, 3H, OCH_3), 2.27–2.20 (m, 2H, =CCH_2), 2.09 (s, 3H, =CCH_3), 1.84–1.51 (m, 2H, =CCH$_2$CH_2), 1.35 (dt, *J* 12, 2 Hz, 1H, C*H*CHOMOM), 1.30 (s, 3H, CH_3), 1.25 (s, 3H, CH_3); δ_C(67.8 MHz) 192.5 (d), 155.9 (s), 140.8 (s), 138.7 (d), 116.0 (t), 94.6 (t), 76.3 (d), 56.4 (q), 50.8 (d), 36.7 (s), 35.9 (t), 26.7 (q), 21.5 (q), 19.4 (q), 18.0 (t).

1-[(*E*)-6-Bromo-1-hydroxyhex-2-enyl]-5-[1-(methoxymethoxy)prop-2-enyl]-2,6,6-trimethylcyclohex-1-ene 17b. A solution of methyllithium–lithium bromide complex (4.43 ml) in ether (1.5 M, 6.64 mmol) was added dropwise over 5 min to a stirred solution of the stannane **16** (2.9 g) in dry THF (35 ml) at −78 °C under an atmosphere of nitrogen. The mixture was allowed to warm to 0 °C for 30 min and then recooled to −78 °C. A solution of the aldehyde **15b** (0.42 g, 1.66 mmol) in dry THF (15 ml) was added portionwise over 5 min and the

mixture was then stirred at −78 °C for 1 h. The mixture was then allowed to warm to room temperature where it was quenched with water (50 ml) and ether (50 ml). The organic layer was separated and the aqueous layer was extracted with ether (2 × 50 ml). The combined organic extracts were washed with saturated aqueous ammonium chloride (75 ml) and brine (75 ml), and then dried and concentrated *in vacuo* to leave a yellow oil. Purification by chromatography on silica eluting with 35% ether in light petroleum (bp 40–60 °C) gave a mixture of diastereoisomers of the *alcohol* (0.51 g, 76%) as a pale yellow oil. Data for one diastereoisomer: ν_{max}(film)/cm^{-1} 3456, 1641, 969 and 921; δ_H(270 MHz) 5.65–5.35 (m, 3H), 5.12–5.00 (m, 2H, CH=CH_2), 4.60 (s, 1H, =CC*H*OHCH=), 4.49 (d, *J* 7 Hz, 1H, OC*H*HOCH$_3$), 4.32 (d, *J* 7 Hz, 1H, OCH*H*OCH$_3$), 4.05 (d, *J* 7 Hz, 1H, C*H*OMOM), 3.22 (t, *J* 7 Hz, 2H, CH_2Br), 3.19 (s, 3H, OCH$_2$OCH_3), 2.02 (app. q, *J* 7 Hz, 2H, CH=CHCH_2), 1.81–1.70 (m, 4H), 1.58 (s, 3H, =CCH_3), 1.52–1.17 (m, 3H), 1.03 (s, 3H, Me), 0.80 (s, 3H, Me); δ_C(67.8 MHz) 139.3 (s), 138.7 (d), 134.4 (d), 133.1 (s), 127.6 (d), 115.8 (t), 94.4 (t), 77.1 (d), 70.4 (d), 56.3 (q), 50.5 (d), 38.4 (s), 33.8 (t), 33.1 (t), 32.1 (t), 30.5 (t), 26.8 (q), 22.0 (q), 21.2 (q), 18.7 (t) (Found: M$^+$ − MOMOH, 338.1241. $C_{18}H_{27}OBr$ requires 338.1245).

1-[(*E*)-6-Bromo-1-oxohex-2-enyl]-5-[1-(methoxymethoxy)-prop-2-enyl]-2,6,6-trimethylcyclohex-1-ene 21. Treatment of a solution of the alcohol **17b** (0.34 g, 0.84 mmol) in dry dichloromethane with tetra(*n*-propyl)ammonium perruthenate and 4-methylmorpholine *N*-oxide, according to the general procedure, gave the *ketone* (0.28 g, 84%) as a colourless oil; λ_{max}(EtOH)/nm 227 (ε/dm^3 mol^{-1} cm^{-1} 14 000); ν_{max}(film)/cm^{-1} 1675, 1644, 1616 and 920; δ_H(400 MHz) 6.65 (dt, *J* 16, 7 Hz, 1H, CH=C*H*CH$_2$), 6.14 (d, *J* 16 Hz, 1H, C*H*=CHCH$_2$), 5.84–5.75 (m, 1H, C*H*=CH$_2$), 5.17–5.13 (m, 2H, CH=CH_2), 4.64 (d, *J* 7 Hz, 1H, OC*H*HOCH$_3$), 4.48 (d, *J* 7 Hz, 1H, OCH*H*OCH$_3$), 4.21 (d, *J* 6 Hz, 1H, C*H*OMOM), 3.38 (t, *J* 7 Hz, 2H, CH_2Br), 3.34 (s, 3H, OCH$_2$OCH_3), 2.38 (app. q, *J* 7 Hz, 2H, =CHCH_2), 2.04–1.97 (m, 4H, CH=CCH_2, CH_2CH$_2$Br), 1.83–1.68 (m, 2H, =CCH$_2$-CH_2), 1.48 (s, 3H, =CCH_3), 1.44–1.41 (m, 1H, C*H*CHOMOM), 1.12 (s, 3H, Me), 1.01 (s, 3H, Me); δ_C(67.8 MHz) 202.0 (s), 147.9 (d), 141.0 (s), 138.9 (d), 134.3 (d), 130.7 (s), 116.4 (t), 94.7 (t), 76.7 (d), 56.7 (q), 49.6 (d), 37.1 (s), 32.8 (t), 31.8 (t), 31.1 (t), 30.9 (t), 28.0 (q), 23.4 (q), 21.5 (q), 18.7 (t) (Found: M$^+$, 398.1445. $C_{20}H_{31}BrO_3$ requires *M*, 398.1457).

1-[(*E*)-6-Bromo-1-oxohex-2-enyl]-5-(1-hydroxyprop-2-enyl)-2,6,6-trimethylcyclohex-1-ene 22. A mixture of the MOM ether **21** (0.11 g, 0.266 mmol) and hydrochloric acid (6 M, 4.5 ml) in THF (2 ml) and water (2 ml) was heated at 50–60 °C for 2 h and then allowed to cool to room temperature. The mixture was diluted with ether (10 ml) and brine (10 ml) and the organic layer was separated. The aqueous layer was extracted with ether (2 × 10 ml) and the combined organic extracts were washed successively with saturated aqueous sodium hydrogen carbonate (10 ml), water (10 ml), and brine (10 ml), then dried and concentrated *in vacuo* to leave an orange oil. Purification by chromatography on silica eluting with 40% ether in light petroleum (bp 40–60 °C) gave the *alcohol* (85 mg, 90%) as a colourless oil; λ_{max}(EtOH)/nm 227 (ε/dm^3 mol^{-1} cm^{-1} 11 200); ν_{max}(film)/cm^{-1} 3453, 1643, 1616, 918, 732 and 647; δ_H(270 MHz) 6.73 (dt, *J* 16, 7 Hz, 1H, CH=C*H*CH$_2$), 6.20 (dt, *J* 16, 1 Hz, 1H, C*H*=CHCH$_2$), 5.94 (ddd, *J* 17, 11, 5 Hz, 1H, C*H*=CH$_2$), 5.29 (app. dt, *J* 17, 2 Hz, 1H, CH=C*H*H), 5.17 (app. dt, *J* 11, 2 Hz, 1H, CH=CH*H*), 4.52 (br s, 1H, C*H*OH), 3.38 (t, *J* 7 Hz, 2H, CH_2Br), 2.44 (app. q, *J* 7 Hz, 2H, CH=CHCH_2), 2.11–2.00 (m, 4H), 1.91 (d, 1H, *J* 5 Hz, O*H*), 1.75–1.66 (m, 2H), 1.54 (s, 3H, =CCH_3), 1.46–1.41 (m, 1H), 1.19 (s, 3H, Me), 1.08 (s, 3H, Me); δ_C(67.8 MHz) 201.7 (s), 147.9 (d), 141.6 (d), 140.3 (s), 133.8 (d), 130.5 (s), 113.5 (t), 70.5 (d), 48.5 (d), 36.5 (s), 32.4 (t), 31.1 (t), 30.64 (t), 30.57 (t), 27.8 (q), 23.6 (q), 21.1 (q), 17.1 (t) (Found: M$^+$ − C_3H_5O − HBr, 215.1395. $C_{15}H_{19}O$ requires 215.1436).

2,10-Dioxo-12,15,15-trimethyltricyclo[9.3.1.0^{3,8}]pentadec-11-ene 25. Treatment of a solution of the iodide **19** (100 mg, 0.25 mmol) in benzene with tri-*n*-butyltin hydride and azoisobutyronitrile according to the general procedure gave (i) the reduced product **23** (19 mg, 28%) (eluted first) as a colourless oil; λ_{max}(EtOH)/nm 237 (ε/dm^3 mol^{-1} cm^{-1} 13 000); ν_{max}(film)/cm^{-1} 2930, 1677, 1645, 1404, 1279 and 980; δ_H(250 MHz) 6.94 (dt, *J* 16, 7 Hz, 1H, COC*H*=CH), 6.44 (dd, *J* 16, 12 Hz, 1H, C*H*=CH$_2$), 6.23 (dd, *J* 16, 1 Hz, 1H, COC*H*=CH), 6.12 (dd, *J* 16, 1 Hz, 1H, =CH*H*), 5.74 (dd, *J* 12, 1 Hz, 1H, =C*H*H), 2.86 (dd, *J* 7, 4 Hz, 1H, C*H*CO), 2.24 (app. dq. *J* 7, 1 Hz, 2H, CH_2CH=), 2.15–1.15 (m, 6H), 1.50 (s, 3H, Me), 1.12 (s, 3H, Me), 1.04 (s, 3H, Me), 0.94 (t, *J* 7 Hz, 3H, Me); δ_C(67.8 MHz) 202.4 (s), 201.9 (s), 152.2 (d), 139.2 (s), 133.2 (d), 129.9 (d), 128.4 (s), 127.7 (t), 53.9 (d), 35.9 (t), 34.6 (t), 29.7 (q), 29.2 (q), 29.1 (t), 24.0 (q), 21.3 (t), 21.2 (q), 13.7 (q) (Found: M$^+$, 274.1901. $C_{18}H_{26}O_2$ requires *M*, 274.1933); and (ii) an inseparable mixture of the bicyclic diketone **24** (~30%) and a 3 : 1 mixture of β- and α-epimers of the title *tricyclic diketone* (19 mg, 25%) (eluted second) as a colourless oil; λ_{max}(EtOH)/nm 237; ν_{max}(film)/cm^{-1} 2928, 1691, 1666, 1619, 1415 and 1240; δ_H(400 MHz) 6.57 (ddd, *J* 16, 8, 6 Hz, 1H, COCH=C*H*), 5.92 (d, *J* 16 Hz, 1H, COC*H*=CH), 2.85 (app. dt, *J* 6, 6 Hz, 1H, C*H*CO), 2.62–1.28 (m), 1.51 (s, 3H, Me), 1.49 (s, 3H, Me), 1.19 (s, 3H, Me) 1.13 (s, 3H, Me), 1.10 (s, 3H, Me), 1.06 (s, 3H, Me), 0.81 (s, 3H, Me), 0.79 (s, 3H, Me); ^{13}C signals assigned to **24**; δ_C(67.8 MHz) 212.9 (s), 201.9 (s), 154.2 (d), 136.2 (s), 131.3 (d), 129.7 (s), 56.2 (t), 39.6 (t), 32.0 (q), 30.8 (t), 26.1 (t), 25.9 (q), 25.8 (t), 23.3 (t), 22.6 (t), 20.1 (q) and 19.3 (t); ^{13}C signals assigned to **26** (minor isomer); δ_C(67.8 MHz) 219.5 (s), 211.9 (s), 146.8 (s), 67.7 (d), 55.4 (d), 46.1 (t), 37.2 (d), 35.3 (t), 30.1 (q), 28.1 (t), 26.3 (t), 24.7 (q), 24.6 (t), 20.4 (t), 19.9 (q), 18.2 (t); a pure sample of the C-1 β-epimer **25** was separated by reversed-phase HPLC and showed: δ_C(67.8 MHz) 213.12 (s), 206.0 (s), 141.7 (s), 137.5 (s), 58.7 (d), 54.3 (t), 53.3 (d), 37.1 (d), 35.4 (t), 30.2 (t), 29.3 (q), 27.6 (t), 27.5 (q), 24.3 (t), 23.9 (t), 19.7 (q) and 19.6 (t) (Found: M$^+$, 274.1874. $C_{18}H_{26}O_2$ requires *M*, 274.1933).

1-Acetoxymethyl-5-(1,3-dioxolan-2-yl)-2,6,6-trimethylcyclohex-1-ene 40a. A mixture of the aldehyde **13** (5.0 g, 20.0 mmol), ethylene glycol (25 ml), (±)-camphor-10-sulfonic acid (0.36 g, 1.4 mmol) and dry benzene (170 ml) was stirred vigorously at room temperature for 14 h under nitrogen. The mixture was then diluted with ether (200 ml) and the organic solution was extracted with saturated brine (2 × 200 ml). The organic fraction was then dried and evaporated *in vacuo* to a yellow oil which was purified by chromatography on silica, eluting with 30% ether in light petroleum (bp 40–60 °C) to give the *acetal* (5.2 g, 87%) as a colourless oil; ν_{max}(film)/cm^{-1} 1734 and 949; δ_H(250 MHz) 4.94 (d, *J* 3 Hz, 1H, OC*H*O), 4.60 (s, 2H, CH_2OAc), 3.97–3.94 (m, 2H, OCH$_2$CH_2O), 3.87–3.82 (m, 2H, OCH_2CH$_2$O), 2.13–2.04 [obsc. m, 2H, =C(Me)CH_2], 2.06 (s, 3H, Me), 1.78–1.49 (obsc. m, 3H, C*H*CH_2), 1.68 (s, 3H, Me), 1.12 (s, 3H, Me), 0.99 (s, 3H, Me); δ_C(67.8 MHz) 171.1 (s), 136.3 (s), 132.1 (s), 104.3 (d), 64.8 (t), 64.2 (t), 60.6 (t), 47.9 (d), 36.2 (s), 32.0 (t), 26.4 (q), 23.3 (q), 22.5 (q), 20.8 (q), 18.4 (t) (Found: M$^+$, 268.1626. $C_{15}H_{24}O_4$ requires *M*, 268.1675) (Found: C, 67.3; H, 9.4. $C_{15}H_{24}O_4$ requires C, 67.1; H, 9.0%).

5-(1,3-Dioxolan-2-yl)-1-hydroxymethyl-2,6,6-trimethylcyclohex-1-ene 40b. A suspension of the acetate **40a** (2.0 g, 7.5 mmol), potassium carbonate (3.3 g, 22.5 mmol) and methanol (75 ml) was stirred vigorously at room temperature for 24 h under nitrogen. The suspension was diluted with ether (120 ml) and water (100 ml) and the organic layer was separated. The aqueous layer was re-extracted with ether (2 × 100 ml) and the combined organic fractions were dried and evaporated *in vacuo* to a colourless oil, which was purified by chromatography on silica, eluting with 50% ether in light petroleum (bp 40–60 °C) to give the *hydroxy acetal* (1.6 g, 94%) as a colourless oil; ν_{max}(film)/cm^{-1} 3404 and 979; δ_H(250 MHz) 4.94 (d, *J* 3 Hz, 1H, OC*H*O), 4.21 (app. dd, *J* 10, 4 Hz, 1H, CH*H*OH), 4.11 (app. dd, *J* 10, 4 Hz, 1H, C*H*HOH), 3.98–3.94 (m, 2H, OCH$_2$CH_2O), 3.87–3.82 (m, 2H, OCH_2CH$_2$O), 2.10–1.99 [m, 2H, =C(Me)-

CH_2], 1.78 (s, 3H, Me), 1.77–1.42 (m, 3H, $CHCH_2$), 1.20 (s, 3H, Me), 1.01 (s, 3H, Me); δ_C(67.8 MHz) 137.5 (s), 133.4 (s), 104.3 (d), 64.8 (t), 64.2 (t), 58.2 (t), 48.0 (d), 36.0 (s), 31.8 (t), 26.7 (q), 22.6 (q), 19.5 (q), 18.5 (t) (Found: M^+, 226.1532. $C_{13}H_{22}O_3$ requires *M*, 226.1569) (Found: C, 68.7; H, 10.2. $C_{13}H_{22}O_3$ requires C, 68.9; H, 9.8%).

1-Formyl-5-(1,3-dioxolan-2-yl)-2,6,6-trimethylcyclohex-1-ene 41. Treatment of a solution of the alcohol **40b** (3.90 g, 17.2 mmol) in dry dichloromethane with tetra(*n*-propyl)ammonium perruthenate and 4-methylmorpholine *N*-oxide, according to the general procedure, gave the title aldehyde (3.4 g, 88%) as an unstable colourless oil; λ_{max}/nm 247 (ε/dm^3 mol^{-1} cm^{-1} 12 600); ν_{max}(film)/cm^{-1} 1677 and 944; δ_H(250 MHz) 10.11 (s, 1H, C*H*O), 4.98 (d, *J* 2 Hz, 1H, OC*H*O), 3.97–3.93 (m, 2H, OCH_2CH_2O), 3.88–3.82 (m, 2H, OCH_2CH_2O), 2.27–2.23 [m, 2H, =C(Me)CH_2], 2.11 (s, 3H, Me), 1.78–1.49 (m, 3H, $CHCH_2$), 1.35 (s, 3H, Me), 1.22 (s, 3H, Me); δ_C(67.8 MHz) 192.3 (d), 156.2 (s), 140.9 (s), 103.8 (d), 65.2 (t), 64.4 (t), 48.9 (d), 35.4 (s), 35.2 (t), 26.7 (q), 21.8 (q), 19.5 (q), 17.8 (t), which was used immediately.

5-(1,3-Dioxolan-2-yl)-1-(6-bromo-1-hydroxyhex-2-enyl)-2,6,6-trimethylcyclohex-1-ene 42. A solution of *n*-butyllithium (4.88 ml) in hexanes (1.6 M, 7.80 mmol) was added dropwise over 10 min to a stirred solution of the stannane **16** (3.64 g, 8.32 mmol) in dry THF (80 ml) at −84 °C under nitrogen, and the yellow solution then stirred at −84 °C for 1 h. The aldehyde **41** (0.57 g, 2.60 mmol) was taken up in dry THF (10 ml) and then added dropwise over 10 min, and the resulting mixture allowed to warm to room temperature over 2 h. Water (100 ml) and ether (100 ml) were added and the organic layer was separated. The aqueous layer was re-extracted with ether (2 × 100 ml) and the combined organic fractions were dried and evaporated *in vacuo* to a yellow oil which was purified by chromatography on silica, eluting with 30% ether in light petroleum (bp 40–60 °C) to give two diastereoisomers (5:1 ratio) of the *hydroxy acetal* (0.90 mg, 81%) as a colourless oil; (data for major diastereoisomer): ν_{max}(film)/cm^{-1} 3455, 1652 and 970; δ_H(250 MHz) 5.78 (dd, *J* 15, 5 Hz, 1H, =C*H*CHOH), 5.62–5.54 (m, 1H, =C*H*CH_2), 4.92 (d, *J* 3 Hz, 1H, OC*H*O), 4.80 (br d, *J* 5 Hz, 1H, C*H*OH), 3.98–3.93 (m, 2H, OCH_2CH_2O), 3.87–3.83 (m, 2H, OCH_2CH_2O), 3.40 (t, *J* 7 Hz, 2H, CH_2Br), 2.20 (app. q, *J* 7 Hz, 2H, =CHCH_2), 2.04–1.88 [m, 4H, =C(Me)CH_2CH_2], 1.78 (s, 3H, Me), 1.72–1.30 (m, 3H, CH_2CH_2Br, $CHCH_2$), 1.27 (s, 3H, Me), 0.94 (s, 3H, Me); δ_C(67.8 MHz) 138.8 (s), 134.2 (d), 133.0 (s), 127.5 (d), 104.4 (d), 69.9 (d), 64.8 (t), 64.2 (t), 48.4 (d), 36.7 (s), 33.0 (t), 32.7 (t), 32.0 (t), 30.3 (t), 26.8 (q), 22.2 (q), 21.1 (q), 18.6 (t) (Found: $M^+ - H_2O$, 354.1210. $C_{18}H_{27}O_2Br$ requires *M*, 354.1194).

1-(6-Bromo-1-oxohex-2-enyl)-5-(1,3-dioxolan-2-yl)-2,6,6-trimethylcyclohex-1-ene 43. Treatment of a solution of the alcohol **42** (0.90 g, 0.24 mmol) in dry dichloromethane with tetra(*n*-propyl)ammonium perruthenate and 4-methylmorpholine *N*-oxide, according to the general procedure, gave the title ketone (0.73 g, 81%) as a colourless oil; λ_{max}(EtOH)/nm 227 (ε/dm^3 mol^{-1} cm^{-1} 10 700); ν_{max}(film)/cm^{-1} 1643 and 1060; δ_H(250 MHz) 6.68 (dt, *J* 16, 7 Hz, 1H, =C*H*CH_2), 6.17 (dt, *J* 16, 1 Hz, 1H, =C*H*CO), 4.92 (d, *J* 3 Hz, 1H, OC*H*O), 3.97–3.90 (m, 2H, OCH_2CH_2O), 3.85–3.81 (m, 2H, OCH_2CH_2O), 3.40, (t, *J* 7 Hz, 2H, CH_2Br), 2.40 (app. q, *J* 7 Hz, 2H, =CHCH_2), 2.09–2.00 [m, 4H, =C(Me)CH_2, CH_2CH_2Br], 1.81–1.68 (m, 3H, $CHCH_2$), 1.51 (s, 3H, Me), 1.09 (s, 6H, 2 × Me) (Found: M^+, 370.1181. $C_{18}H_{27}BrO_3$ requires *M*, 370.1144).

1-(6-Bromo-1-oxohex-2-enyl)-5-formyl-2,6,6-trimethylcyclohex-1-ene 44. A solution of the acetal **43** (0.72 g, 1.95 mmol), (±)-camphor-10-sulfonic acid (0.23 g, 0.98 mmol) in water (20 ml) and THF (20 ml) was held at reflux for 14 h. The cooled solution was diluted with water (20 ml) and ether (50 ml) and the organic layer was separated. The aqueous layer was re-extracted with ether (2 × 50 ml) and the combined organic fractions were dried and evaporated *in vacuo* to a yellow oil which was purified by chromatography on silica, eluting with 30% ether in light petroleum (bp 40–60 °C) to afford the *aldehyde* (0.57 g, 89%) as a colourless oil; λ_{max}(EtOH)/nm 228 (ε/dm^3 mol^{-1} cm$^-$ 12 300); ν_{max}(film)/cm^{-1} 1716, 1643 and 1237; δ_H 9.87 (d, *J* 3 Hz, 1H, C*H*O), 6.73 (dt, *J* 16, 7 Hz, 1H, =C*H*CH_2), 6.20 (dt, *J* 16, 1 Hz, 1H, =C*H*CO), 3.42 (t, 2H, *J* 7 Hz, 2H, CH_2Br), 2.44 (app. q, *J* 7 Hz, 2H, =CHCH_2), 2.29 (ddd, *J* 7, 7, 1 Hz, 1H, C*H*CHO), 2.14–1.87 [m, 6H, =C(Me)CH_2CH_2, CH_2CH_2Br], 1.56 (s, 3H, Me), 1.22 (s, 3H, Me), 1.16 (s, 3H, Me); δ_C(67.8 MHz) 204.5 (d), 200.3 (s), 148,3 (d), 138.9 (s), 133.5 (d), 130.7 (s), 56.0 (d), 35.2 (s), 32.3 (t), 30.5 (t), 29.1 (t), 28.9 (t), 28.1 (q), 23.8 (q), 20.9 (q), 18.8 (t) (Found: M^+, 326.0909. $C_{16}H_{23}BrO_2$ requires *M*, 326.0881).

1-(6-Bromo-1-oxohex-2-enyl)-5-(1-hydroxyprop-2-ynyl)-2,6,6-trimethylcyclohex-1-ene 45. A solution of ethynylmagnesium bromide (4.1 ml) in THF (0.5 M, 2.0 mmol) was added dropwise over 10 min to a stirred solution of the aldehyde **44** (0.56 g, 1.70 mmol) in dry THF (20 ml) at −78 °C under nitrogen. The yellow solution was allowed to warm to room temperature over a period of 12 h and was then quenched with water (40 ml) and ether (40 ml). The organic layer was separated and the aqueous layer was re-extracted with ether (3 × 40 ml). The combined organic fractions were dried and evaporated *in vacuo* to a yellow oil which was purified by chromatography on silica, eluting with 50% ether in light petroleum (bp 40–60 °C) to give two diastereoisomers (1:1 ratio) of the *propargylic alcohol* (0.49 g, 81%) as a colourless oil; (data for one diastereoisomer): λ_{max}/nm 228 (ε/dm^3 mol^{-1} cm^{-1} 17 800); ν_{max}(film)/cm^{-1} 3301, 2210, 1639 and 756; δ_H(250 MHz) 6.70 (dt, *J* 16, 7 Hz, =C*H*CH_2), 6.18 (dt, *J* 16, 1 Hz, 1H, =C*H*CO), 4.73 (m, 1H, C*H*OH), 3.41 (t, *J* 7 Hz, 2H, CH_2Br), 2.48 (d, *J* 2 Hz, 1H, alkyne-H), 2.40 (app. q, *J* 7 Hz, 2H, =CHCH_2), 2.14 [dd, *J* 8, 5 Hz, 2H, =C(Me)CH_2], 2.08–1.87 (m, 4H, $CHCH_2$, CH_2CH_2Br), 1.69–1.63 (m, 1H, C*H*CHOH), 1.52 (s, 3H, Me), 1.13 (s, 3H, Me), 1.09 (s, 3H, Me); δ_C(67.8 MHz) 201.7 (s), 148.2 (d), 139.9 (s), 133.9 (d), 130.7 (s), 85.6 (d), 72.6 (s), 61.8 (d), 50.0 (d), 36.4 (s), 32.5 (t), 30.8 (t), 30.7 (t), 30.7 (t), 28.2 (q), 23.8 (q), 21.2 (q), 18.5 (t) (Found: M^+, 352.1027. $C_{18}H_{25}BrO_2$ requires *M*, 352.1038).

5-(1-Oxoprop-2-ynyl)-1-(6-iodo-1-oxohex-2-enyl)-2,6,6-trimethylcyclohex-1-ene 38. (a) A suspension of the alcohol **45** (0.24 g, 0.67 mmol), barium manganate (0.92 g, 3.35 mmol) and dry dichloromethane (7 ml) was agitated, on a Decon FS100 ultrasonic bath, at room temperature for 7 h under nitrogen. The suspension was filtered through a plug of celite and the residue was then washed with dichloromethane (100 ml). The combined filtrate was evaporated *in vacuo* to a yellow oil which was purified by chromatography on silica, eluting with 30% ether in light petroleum (bp 40–60 °C) to give 1-(6-bromo-1-oxohex-2-enyl)-5-(1-oxoprop-2-ynyl)-2,6,6-trimethylcyclohex-1-ene (0.14 g, 59%) as a colourless oil; λ_{max}(EtOH)/nm 224 (ε/dm^3 mol^{-1} cm^{-1} 15 900); ν_{max}(film)/cm^{-1} 3246, 2088, 1667, 1643 and 1041; δ_H(400 MHz) 6.86 (dt, *J* 16, 7 Hz, 1H, =C*H*CH_2), 6.16 (dt, *J* 16, 1 Hz, 1H, =C*H*CO), 3.41 (t, *J* 7 Hz, 2H, CH_2Br), 3.29 (s, 1H, alkyne-H), 2.73–2.68 (m, 1H, C*H*CO), 2.42 (app. q, *J* 7 Hz, 2H, =CHCH_2), 2.08–2.01 [m, 6H, =C(Me)CH_2CH_2, CH_2CH_2Br], 1.52 (s, 3H, Me), 1.18 (s, 3H, Me), 1.11 (s, 3H, Me); δ_C 201.1 (s), 189.4 (s), 149.4 (d), 139.2 (s), 133.9 (d), 130.1 (s), 82.4 (s), 78.9 (d), 58.7 (d), 36.1 (s), 32.5 (t), 30.9 (t), 30.8 (t), 29.0 (t), 28.8 (q), 23.9 (q), 21.2 (q), 21.0 (t) (Found: M^+, 350.0884. $C_{18}H_{23}BrO_2$ requires *M*, 350.0881). The same bromide was also produced when a suspension of the diol **49** (129 mg, 0.36 mmol), barium manganate (922 mg, 3.60 mmol) and dry dichloromethane (5 ml) was agitated, on a Decon FS100 ultrasonic bath, at room temperature for 4 h under nitrogen, followed by work-up and chromatography (66 mg, 51%).

(b) Treatment of a solution of the bromide from above (95 g, 0.27 mmol) in butan-2-one with sodium iodide, according to the general procedure, gave the title *iodide* (106 mg, 99%) as a pale yellow oil; δ_H(270 MHz) 6.70 (dt, *J* 16, 7 Hz, 1H,

=C*H*CH$_2$), 6.18 (dt, *J* 16, 1 Hz, 1H, =C*H*CO), 4.73 (dd, *J* 2, 2 Hz, 1H, C*H*OH), 3.16 (t, *J* 7 Hz, 2H, C*H*$_2$I), 2.46 (d, *J* 2 Hz, 1H, alkyne-H), 2.35 (app. q, *J* 7 Hz, 2H, =CHC*H*$_2$), 2.11 [app. t, *J* 6 Hz, 2H, =C(Me)C*H*$_2$], 1.98–1.74 (m, 4H, C*H*$_2$CH$_2$I, CHC*H*$_2$), 1.65 (dt, *J* 10, 3 Hz, 1H, C*H*CHOH), 1.50 (s, 3H, Me), 1.11 (s, 3H, Me), 1.07 (s, 3H, Me); δ_C(67.8 MHz) 201.7 (s), 148.0 (d), 139.9 (s), 133.9 (d), 130.7 (s), 85.6 (d), 72.6 (s), 61.7 (d), 50.0 (d), 36.4 (s), 32.9 (t), 31.3 (t), 30.8 (t), 28.2 (q), 23.8 (q), 21.2 (q), 18.5 (t), 5.3 (t); which was used without further purification.

1-Acetoxymethyl-5-(1-hydroxyprop-2-ynyl)-2,6,6-trimethylcyclohex-1-ene 46. A solution of ethynylmagnesium bromide (50.0 ml) in THF (0.5 M, 24.9 mmol) was added dropwise over 30 min to a stirred solution of the aldehyde **13** (3.50 g, 15.6 mmol) in dry THF (60 ml) at −78 °C under nitrogen. The yellow solution was stirred at −78 °C for 40 min and then allowed to warm to room temperature over 3 h. The reaction was quenched by the addition of water (100 ml) and ether (100 ml) and the organic layer was separated. The aqueous layer was re-extracted with ether (2 × 100 ml) and the combined organic fractions were dried and evaporated *in vacuo* to a yellow oil. Purification by chromatography on silica eluting with 40% ether in light petroleum (bp 40–60 °C) gave the *acetoxy alcohol* (3.6 g, 93%) as a colourless oil; ν_{max}(film)/cm^{-1} 3435, 3242, 2109, 1709 and 951; δ_H(250 MHz) 4.75–4.71 (m, 1H, C*H*OH), 4.60 (s, 2H, C*H*$_2$OAc), 2.46 (d, *J* 2 Hz, 1H, alkyne-H), 2.16–2.14 [m, 2H, =C(Me)C*H*$_2$], 2.06 (s, 3H, COC*H*$_3$), 1.94–1.92 (m, 1H, CH$_2$C*H*), 1.70 (s, 3H, Me), 1.74–1.60 (m, 2H, CHC*H*$_2$), 1.10 (s, 3H, Me), 1.03 (s, 3H, Me); δ_C(67.8 MHz) 172.0 (s), 136.7 (s), 132.1 (s), 85.8 (d), 72.5 (s), 62.2 (d), 60.9 (t), 50.8 (d), 37.3 (s), 32.3 (t), 26.9 (q), 23.0 (q), 21.1 (q), 19.8 (q), 18.6 (t) (Found: M$^+$ − AcOH, 190.1366. $C_{13}H_{18}O$ requires *M*, 190.1315) (Found: C, 72.0; H, 9.1. $C_{15}H_{22}O_3$ requires C, 72.0; H, 8.9%).

1-Hydroxymethyl-5-(1-hydroxyprop-2-ynyl)-2,6,6-trimethylcyclohex-1-ene 47. A suspension of the acetate **46** (3.43 g, 13.7 mmol), potassium carbonate (8.00 g, 54.8 mmol) and methanol (100 ml) was stirred vigorously at room temperature for 2 h. The suspension was diluted with ether (150 ml) and water (100 ml) and the organic layer was separated. The aqueous layer was re-extracted with ether (2 × 100 ml) and the combined organic fractions were dried and evaporated *in vacuo* to a colourless oil which was purified by chromatography on silica eluting with 50% ether in light petroleum (bp 40–60 °C) to give the *diol* (2.6 g, 91%) as a colourless solid, mp 119–20 °C (from pentane); ν_{max}(film)/cm^{-1} 3306, 2110 and 987; δ_H(250 MHz) 4.73–4.71 (m, 1H, C*H*OH), 4.18 (d, *J* 11.6 Hz, 1H, C*H*HOH), 4.10 (d, *J* 12 Hz, 1H, CH*H*OH), 2.46 (d, *J* 2 Hz, 1H, alkyne-H), 2.16–2.06 (m, 2H, =C(Me)C*H*$_2$), 1.99–1.89 (m, 1H, C*H*CH$_2$), 1.77 (s, 3H, Me), 1.75–1.58 (m, 2H, CHC*H*$_2$), 1.18 (s, 3H, Me), 1.06 (s, 3H, Me); δ_C(67.8 MHz) 137.3 (s), 134.0 (s), 85.9 (d), 72.4 (s), 62.3 (d), 58.8 (t), 51.0 (d), 37.3 (s), 32.2 (t), 27.3 (q), 23.1 (q), 19.7 (q), 18.7 (t) (Found: M$^+$ − H$_2$O, 190.1359. $C_{13}H_{18}O$ requires *M*, 190.1358) (Found: C, 75.0; H, 9.8. $C_{13}H_{20}O_2$ requires C, 75.0; H, 9.9%).

1-Formyl-5-(1-hydroxyprop-2-ynyl)-2,6,6-trimethylcyclohex-1-ene 48. A solution of dimethyl sulfoxide (68 μl, 0.96 mmol) in dry dichloromethane (0.2 ml) was added dropwise over 2 min to a solution of oxalyl chloride (50 μl, 0.57 mmol) in dry dichloromethane (1.5 ml) at −60 °C under nitrogen. The solution was stirred at −60 °C for 2 min and then a solution of the diol **47** (100 mg, 0.48 mmol) in dry dichloromethane (0.5 ml) was added dropwise over 2 min. The solution was stirred at −60 °C for a further 15 min and then triethylamine (333 μl, 2.4 mmol) was added dropwise over 2 min and the resulting cloudy suspension was allowed to warm to room temperature. The suspension was diluted with dichloromethane (3 ml) and water (5 ml) and the organic layer was separated. The aqueous layer was re-extracted with dichloromethane (2 × 5 ml) and the combined organic fractions were dried and evaporated *in vacuo* to a colourless solid which was purified by chromatography on silica, eluting with 50% ether in light petroleum (bp 40–60 °C) to give the *hydroxy aldehyde* (57 mg, 58%) as a colourless solid, mp 85–87 °C (from pentane); λ_{max}(EtOH)/nm 247 (ε/dm^3 mol^{-1} cm^{-1} 11 900); ν_{max}(film)/cm^{-1} 3420, 3305, 1668 and 1121; δ_H(250 MHz) 9.39 (s, 1H, C*H*O), 4.77 (br s, 1H, C*H*OH), 2.46 (d, *J* 2 Hz, 1H, alkyne-H), 2.37–2.32 [m, 2H, =C(Me)C*H*$_2$], 2.12 (s, 3H, Me), 2.02–1.92 (m, 1H, C*H*CH$_2$), 1.81–1.55 (m, 2H, CHC*H*$_2$), 1.34 (s, 3H, Me), 1.25 (s, 3H, Me); δ_C(67.8 MHz) 192.3 (d), 156.3 (s), 140.2 (s), 85.8 (d), 72.4 (s), 61.3 (d), 51.8 (d), 36.4 (s), 35.3 (t), 26.7 (q), 21.9 (q), 19.4 (q), 18.1 (t) (Found: M$^+$, 206.1316. $C_{13}H_{18}O_2$ requires *M*, 206.1307).

1-(6-Bromo-1-hydroxyhex-2-enyl)-5-(1-hydroxyprop-2-ynyl)-2,6,6-trimethylcyclohex-1-ene 49. A solution of *n*-butyllithium (1.2 ml) in hexanes (1.6 M, 1.92 mmol) was added dropwise over 5 min to a stirred solution of the stannane **16** (0.88 g, 2.02 mmol) in dry THF (20 ml) at −84 °C under nitrogen and the yellow solution then stirred at −84 °C for 1 h. The aldehyde **48** (100 mg, 0.48 mmol) was taken up in dry THF (2 ml) and then added dropwise over 5 min, and the resulting pale yellow solution allowed to warm to room temperature over 2 h. Water (20 ml) and ether (20 ml) were then added and the organic layer was separated. The aqueous layer was re-extracted with ether (2 × 20 ml) and the combined organic fractions were dried and evaporated *in vacuo* to a yellow oil which was purified by chromatography on silica, eluting with 20% ether in light petroleum (bp 40–60 °C) to give two diastereoisomers (5:1 ratio) of the *diol* (130 mg, 75%) as a colourless oil; (data for major diastereoisomer): ν_{max}(film)/cm^{-1} 3416, 3303 and 909; δ_H(250 MHz) 5.77 (dd, *J* 15, 5 Hz, 1H, =C*H*CHOH), 5.65–5.51 (m, 1H, =C*H*CH$_2$), 4.80 (br s, 1H, C*H*OH), 4.69 (br s, 1H, C*H*OH), 3.41 (t, *J* 7 Hz, 2H, C*H*$_2$Br), 2.47 (d, *J* 2 Hz, 1H, alkyne-H), 2.21 (app. q, *J* 7 Hz, 2H, =CHC*H*$_2$), 2.10–2.06 (m, 1H, C*H*CHOH), 2.00–1.82 [m, 2H, =C(Me)C*H*$_2$], 1.80 (s, 3H, Me), 1.72–1.54 (m, 4H, CHC*H*$_2$, C*H*$_2$CH$_2$Br), 1.25 (s, 3H, Me), 0.99 (s, 3H, Me); δ_C(67.8 MHz) 139.0 (s), 134.1 (d), 132.5 (s), 128.2 (d), 85.9 (s), 72.4 (d), 70.5 (d), 62.4 (d), 51.5 (d), 38.1 (s), 33.3 (t), 33.2 (t), 32.1 (t), 30.5 (t), 27.4 (q), 22.7 (q), 21.2 (q), 18.9 (t) (Found: M$^+$ − H$_2$O, 336.1099. $C_{18}H_{25}BrO$ requires *M*, 336.1089).

12,15,15-Trimethyltricyclo[9.3.1.0^{3,8}]pentadeca-3,11-diene-2,10-dione 56. Treatment of a solution of the iodide **38** (169 mg, 0.42 mmol) in benzene with tri-*n*-butyltin hydride and azoisobutyronitrile according to the general procedure gave (i) 1-(1-oxohex-2-enyl)-5-(1-oxoprop-2-ynyl)-2,6,6-trimethylcyclohex-1-ene (19 mg, 17%) (eluted first) as a colourless oil; λ_{max}(EtOH)/nm 223 (ε/dm^3 mol^{-1} cm^{-1} 9 500); ν_{max}(film)/cm^{-1} 3241, 2087, 1669, 1641 and 1095; δ_H(250 MHz) 6.86 (dt, *J* 16, 7 Hz, 1H, =C*H*CH$_2$), 6.11 (d, *J* 16 Hz, 1H, =C*H*CO), 3.29 (s, 1H, alkyne-H), 2.72–2.49 (m, 1H, C*H*CO), 2.23 (app. q, *J* 7 Hz, 2H, =CHC*H*$_2$), 2.10–1.89 (m, 4H, =C(Me)C*H*$_2$C*H*$_2$), 1.69–1.50 (m, 2H, C*H*$_2$CH$_3$), 1.52 (s, 3H, Me), 1.17 (s, 3H, Me), 1.13 (s, 3H, Me), 0.93 (t, *J* 7 Hz, 3H, CH$_2$C*H*$_3$); δ_C(67.8 MHz) 201.4 (s), 189.6 (s), 152.1 (d), 139.0 (s), 133.1 (d), 129.9 (s), 82.4 (s), 79.1 (d), 58.7 (d), 36.2 (s), 34.5 (t), 29.1 (t), 28.4 (q), 23.9 (q), 21.3 (q), 21.2 (t), 21.1 (t), 13.6 (q) (Found M$^+$, 272.1756. $C_{18}H_{24}O_2$ requires *M*, 272.1776); and (ii) the title compound as a 6:1 mixture of C-1 epimers (50.2 mg, 43%) (eluted second) as a colourless oil; (data for major diastereoisomer): λ_{max}(EtOH)/nm 228 (ε/dm^3 mol^{-1} cm^{-1} 4 500); ν_{max}(film)/cm^{-1} 1731, 1681 and 703; δ_H(250 MHz) 5.61 (t, *J* 4 Hz, 1H, H-4), 2.79 (dd, *J* 19, 13 Hz, 1H, 1 × H-9), 2.48–2.29 (m, 4H, H-1, H-8, 1 × H-9, 1 × H-13), 2.13–1.92 (m, 5H, 2 × H-5, 2 × H-6, 1 × H-13), 1.72–1.50 (m, 3H, 1 × H-7, 2 × H-14), 1.38–1.14 (m, 1H, 1 × H-7), 1.47 (s, 3H, Me), 1.40 (s, 3H, Me), 1.07 (s, 3H, Me); δ_C(67.8 MHz) 210.3 (s), 210.2 (s), 146.7 (s), 143.4 (s), 134.3 (s), 128.2 (d), 57.9 (d), 51.4 (t), 33.7 (s), 33.1 (d), 30.3 (q), 30.1 (t), 27.4 (q), 26.9 (t), 24.7 (t), 22.0 (t), 21.3 (q), 16.8 (t) (Found: M$^+$, 272.1753. $C_{18}H_{24}O_2$ requires *M*, 272.1776), which crystallised on standing at 0 °C.

2β,10α-Dihydroxy-12,15,15-trimethyltricyclo[9.3.1.0^{3,8}]-pentadeca-3,11-diene 57. A solution of diisobutylaluminium

hydride (42 μl) in toluene (1.5 M, 0.065 mmol) was added dropwise over 2 min to a stirred solution of the dione **56** (4.0 mg, 0.026 mmol) in dry dichloromethane (260 μl) at −78 °C under nitrogen. The mixture was stirred at −78 °C for 30 min and then quenched with dichloromethane (0.5 ml) and water (0.5 ml). The mixture was then allowed to warm to room temperature and the organic layer was separated. The aqueous layer was re-extracted with dichloromethane (2 × 0.5 ml) and the combined organic fractions were dried and evaporated *in vacuo* to a yellow oil. Purification by chromatography on silica eluting with 30% ether in light petroleum (40–60 °C) gave (i) the *anti*-diol diastereoisomer **57** (2.4 mg, 60%) (eluted first) as a white crystals, mp 86–88 °C (from pentane); $\nu_{max}(CHCl_3)/cm^{-1}$ 3372, 1652 and 1456; δ_H(500 MHz) 5.83 (t, *J* 4 Hz, 1H, H-4), 4.69 (dd, *J* 5, 5 Hz, 1H, H-10), 3.59 (d, *J* 7 Hz, 1H, H-2), 2.42–2.28 (m, 3H, H-8, 1 × H-13, 1 × H-9), 2.16–2.11 (m, 1H, 1 × H-5), 2.10–2.00 (obs. m, 4H, 1 × H-5, 1 × H-7, 1 × H-9, 1 × H-13), 2.00 (obs. s, 3H, Me), 1.99–1.94 (m, 1H, 1 × H-7), 1.73–1.56 (m, 4H, 2 × H-6, 2 × H-14), 1.49–1.44 (m, 1H, H-1), 1.22 (s, 3H, Me), 1.01 (s, 3H, Me); δ_C(125.8 MHz) 147.5 (s), 139.7 (s), 130.0 (s), 124.3 (d), 78.9 (d), 69.0 (d), 55.6 (d), 44.5 (t), 36.5 (s), 36.2 (d), 32.2 (t), 30.2 (t), 30.0 (q), 27.9 (q), 24.5 (t), 23.5 (t), 21.4 (q), 19.0 (t) (Found: M^+, 276.2087. $C_{18}H_{28}O_2$ requires *M*, 276.2089); and (ii) a minor diastereoisomer (0.4 mg, 10%) (eluted second) as a colourless oil; δ_H (500 MHz) 5.88 (t, *J* 4 Hz, 1H, H-4), 4.77 (dd, *J* 3, 1 Hz, 1H, H-10), 4.41 (dd, *J* 1, 1 Hz, 1H, H-2), 2.30–2.17 (m, 3H, H-8, 1 × H-13, 1 × H-9), 1.89 (obs. s, 3H, Me), 2.05–1.38 (obs. m, 11H, H-1, 2 × H-6, 2 × H-14, 2 × H-7, 2 × H-5, 1 × H-9, 1 × H-13), 1.31 (s, 3H, Me), 1.10 (s, 3H, Me).

X-ray crystal structure determination of diol 57 †

A colourless cuboid was mounted on a glass fibre and transferred to the diffractometer.

Crystal data. $C_{18}H_{28}O_2 \cdot \frac{1}{2}CH_2Cl_2$, $M = 318.86$. Tetragonal, $a = 20.095(4)$, $c = 8.598(4)$ Å, $V = 3472(2)$ Å^3 [from 2θ values of 32 reflections measured at $\pm\omega$ ($22 \leqslant 2\theta \leqslant 31°$, $\lambda = 0.710\ 73$ Å, $T = 260$ K)], space group *P*4/*n* (No. 85), $Z = 8$, $D_x = 1.216$ g cm^{-3}, colourless cuboidal crystal $0.77 \times 0.62 \times 0.50$ mm, μ(Mo-Kα) = 0.224 mm^{-1}.

Data collection and processing. Stoe Stadi-4 four-circle diffractometer, ω/θ scans with ω scan width $(1.1 + 0.35\tan\theta)°$, graphite-monochromated Mo-Kα *X*-radiation; 3366 reflections measured ($5 \leqslant 2\theta \leqslant 50°$, $\pm h$, $\pm k$, l), 3042 unique [merging $R = 0.011$], giving 1969 with $F \geqslant 4\sigma(F)$ and 3019 which were retained in all calculations. No crystal decay was observed and no corrections were applied for absorption.

Structure solution and refinement. Automatic direct methods[23] (all non-H atoms). Full-matrix least squares refinement[24] with all ordered non-H atoms anisotropic; H atoms were located from a ΔF synthesis (OH) or introduced at geometrically calculated positions (all others) and thereafter refined as rigid rotating groups or riding on their parent C atoms, respectively, with $U_{iso}(H) = xU_{eq}(C)$ [$x = 1.5$ for OH and 1.2 for others]. Disorder was identified in the C(3)–C(8) ring and was modelled by allowing equal occupations of alternative positions for C(5), C(6) and their H atoms. However, the disorder appears to be more extensive and could not be modelled further, contributing to the rather high residuals. The weighting scheme $w^{-1} = [\sigma^2(F_o^2) + (0.178P)^2 + 5.73P]$, $P = \frac{1}{3}[\mathrm{MAX}(F_o^2,0) + 2F_c^2]$, gave satisfactory agreement analyses. Final R_1 [$F \geqslant 4\sigma(F)$] = 0.101, wR_2 [all data] = 0.340, $S[F^2] = 1.11$ for 208 refined parameters. The highest peak of 1.09 e Å^{-3} in the final ΔF synthesis was located 1.4 Å from both C(9) and C(10). The Figure was produced using SHELXTL/PC.[25]

1-(6-Chloro-1-hydroxyhex-2-ynyl)-5-(1,3-dioxolan-2-yl)-2,6,6-trimethylcyclohex-1-ene 50. A solution of *n*-butyllithium (1.6 ml) in hexane (2.5 M, 3.99 mmol) was added dropwise over 5 min to a stirred solution of 5-chloropent-1-yne (0.41 g, 3.99 mmol) in dry THF (40 ml) at 0 °C under an atmosphere of nitrogen. The solution was stirred at 0 °C for 15 min and then cooled to −78 °C. A solution of the aldehyde **41** (0.51 g, 2.28 mmol) in dry THF (25 ml) was added dropwise over 5 min to the stirred solution at −78 °C. The solution was stirred at −78 °C for a further 30 min and then allowed to warm to 0 °C where it was quenched with water (100 ml) and ether (50 ml). The organic layer was separated and the aqueous layer was extracted with ether (3 × 50 ml). The combined organic extracts were washed with saturated aqueous ammonium chloride (50 ml) and brine (2 × 50 ml), then dried and concentrated *in vacuo* to leave a yellow oil. Purification by chromatography on silica, eluting with 60% ether in light petroleum (bp 40–60 °C), gave the *alcohol* (0.72 g, 96%) as a colourless oil; ν_{max}(film)/cm^{-1} 3442 and 979; δ_H(270 MHz) 5.03 (m, 1H, C*H*OH), 4.91 (d, *J* 3 Hz, 1H, OC*H*O), 4.00–3.80 (m, 4H, OCH_2CH_2O), 3.62 (t, *J* 7 Hz, 2H, CH_2Cl), 2.40 (dt, *J* 7, 2 Hz, 2H, alkyne-CH_2), 2.11–1.98 (m, 4H), 1.97 (obsc. s, 3H, =CCH_3), 1.76 (d, *J* 4 Hz, O*H*), 1.72–1.40 (m, 3H), 1.23 (s, 3H, Me), 0.99 (s, 3H, Me); δ_C(67.8 MHz) 138.2 (s), 134.5 (s), 104.5 (d), 82.7 (s), 82.4 (s), 64.9 (t), 64.4 (t), 59.5 (d), 48.3 (d), 43.6 (t), 36.8 (s), 32.6 (t), 31.3 (t), 26.5 (q), 22.6 (q), 21.1 (q), 18.7 (t), 16.2 (t) (Found: M^+, 326.1653. $C_{18}H_{27}ClO_3$ requires *M*, 326.1649).

1-(6-Chloro-1-oxohex-2-ynyl)-5-(1,3-dioxolan-2-yl)-2,6,6-trimethylcyclohex-1-ene 51. Treatment of a solution of the alcohol **50** (0.59 g, 1.81 mmol) in dry dichloromethane with tetra-(*n*-propyl)ammonium perruthenate and 4-methylmorpholine *N*-oxide, according to the general procedure, gave the title aldehyde (0.58 g, 98%) as a colourless oil; λ_{max}(EtOH)/nm 226 (ε/dm^3 mol^{-1} cm^{-1} 7 600), 231 (7 600); ν_{max}(film)/cm^{-1} 2207, 1648 and 888; δ_H(250 MHz) 4.86 (d, *J* 3 Hz, 1H, OC*H*O), 3.92–3.75 (m, 4H, OCH_2CH_2O), 3.59 (t, *J* 6 Hz, 2H, CH_2Cl), 2.56 (t, *J* 7 Hz, 2H, alkyne-CH_2), 2.05–1.94 (m, 4H), 1.74–1.57 (m, 3H), 1.67 (obsc. s, 3H, =CCH_3), 1.18 (s, 3H, Me), 1.15 (s, 3H, Me); δ_C(67.8 MHz) 186.7 (s), 142.2 (s), 133.3 (s), 103.8 (d), 93.1 (s), 83.7 (s), 64.8 (t), 64.4 (t), 47.4 (d), 43.1 (t), 35.9 (s), 31.1 (t), 30.3 (t), 27.4 (q), 23.2 (q), 20.5 (q), 18.3 (t), 16.5 (t) (Found: M^+, 324.1468. $C_{18}H_{25}ClO_3$ requires *M*, 324.1492).

5-Formyl-1-(6-chloro-1-oxohex-2-ynyl)-2,6,6-trimethylcyclohex-1-ene 52. A stirred mixture of the acetal **51** (0.11 g, 0.344 mmol), (±)-camphor-10-sulfonic acid (0.04 g, 0.172 mmol) and water (1.7 ml) in THF (1.7 ml) was heated to reflux for 14 h and then cooled to room temperature. The mixture was diluted with ether (5 ml) and saturated aqueous sodium hydrogen carbonate (5 ml) and the organic layer was separated. The aqueous layer was extracted with ether (3 × 5 ml) and the combined organic extracts were washed with brine (5 ml) and then dried and concentrated *in vacuo* to leave a yellow oil. Purification by chromatography on silica, eluting with 25% ether in light petroleum (bp 40–60 °C), gave the *aldehyde* (95 mg, 98%) as a colourless oil; λ_{max}(EtOH)/nm 224 (ε/dm^3 mol^{-1} cm^{-1} 9 600), 230 (9 300), ν_{max}(film)/cm^{-1} 2207, 1717, 1841 and 668; δ_H(400 MHz) 9.83 (d, *J* 3 Hz, 1H, *H*CO), 3.61 (t, *J* 6 Hz, 2H, CH_2Cl), 2.58 (t, *J* 7 Hz, 2H, alkyne-CH_2), 2.21 (ddd, *J* 10, 3, 3 Hz, 1H, C*H*CHO), 2.10 (dd, *J* 8, 6 Hz, 2H, =CCH_2), 2.02 (app. quintet., *J* 7 Hz, 2H, alkyne-CH$_2$CH_2), 1.91–1.77 (m, 2H, =CCH$_2$CH_2), 1.72 (s, 3H, =CCH_3), 1.30 (s, 3H, Me), 1.22 (s, 3H, Me); δ_C(67.8 MHz) 204.8 (d), 185.4 (s), 141.1 (s), 134.3 (s), 93.8 (s), 83.6 (s), 56.3 (d), 43.2 (t), 35.8 (s), 30.3 (t), 29.9 (t), 27.7 (q), 23.9 (q), 20.6 (q), 19.0 (t), 16.6 (t).

1-(6-Chloro-1-oxohex-2-ynyl)-5-(1-hydroxyprop-2-enyl)-2,6,6-trimethylcyclohex-1-ene 53. A solution of vinylmagnesium

† Full crystallographic details, excluding structure factor tables, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see 'Instructions for authors', *J. Chem. Soc.*, *Perkin Trans. 1*, available *via* the RSC Web page (http://www.rsc.org/authors). Any request to the CCDC for this material should quote the full literature citation and the reference number 207/249.

chloride (0.24 ml) in THF (1.7 M, 0.40 mmol) was added dropwise over 10 min to a stirred solution of the aldehyde **52** (0.113 g, 0.40 mmol) in dry THF (4 ml) at −78 °C under an atmosphere of nitrogen. The solution was stirred at −78 °C for 2 h and then quenched with water (2 ml), saturated aqueous ammonium chloride (2 ml) and ether (5 ml). The mixture was allowed to warm to room temperature and the organic layer was separated. The aqueous layer was extracted with ether (2 × 5 ml) and the combined organic extracts were washed with saturated aqueous ammonium chloride (5 ml) and brine (5 ml), and then dried and concentrated *in vacuo* to leave a slightly yellow oil. Purification by chromatography on silica, eluting with 40% ether in light petroleum (bp 40–60 °C) gave the *alcohol* (0.12 g, 98%) as a colourless oil; λ_{max}(EtOH)/nm 224 (ε/dm^3 mol^{-1} cm^{-1} 8 000), 229 (7 800); ν_{max}(film)/cm^{-1} 3478, 2208, 1940 and 660; δ_H(250 MHz) 5.91 (ddd, *J* 17, 10, 5 Hz, 1H, C*H*=CH$_2$), 5.28 (app. dt, *J* 17, 2 Hz, 2H, CH=C*H*H), 5.16 (app. dt, *J* 10, 2 Hz, 1H, CH=CH*H*), 4.52 (m, 1H, C*H*OH), 3.65 (t, *J* 6 Hz, 2H, C*H*$_2$Cl), 2.61 (t, *J* 7 Hz, 2H, alkyne-C*H*$_2$), 2.10–1.96 (m, 4H), 1.79–1.36 (m, 3H), 1.72 (obsc. s, 3H, =CC*H*$_3$), 1.28 (s, 3H, Me), 1.19 (s, 3H, Me); δ_C(67.8 MHz) 186.7 (s), 142.3 (s), 141.5 (d), 133.4 (s), 113.5 (t), 93.2 (s), 83.6 (s), 70.3 (d), 48.5 (d), 43.1 (t), 36.9 (s), 31.6 (t), 30.2 (t), 27.1 (q), 23.4 (q), 20.5 (q), 16.9 (t), 16.4 (t) (Found: M$^+$, 308.1554. $C_{18}H_{25}ClO_2$ requires *M*, 308.1543).

1-(6-Chloro-1-oxohex-2-ynyl)-5-(1-oxoprop-2-enyl)-2,6,6-trimethylcyclohex-1-ene 54. Treatment of a solution of the alcohol **53** (0.18 g, 0.58 mmol) in dry dichloromethane with tetra(*n*-propyl)ammonium perruthenate and 4-methylmorpholine *N*-oxide, according to the general procedure, gave the title ketone (0.16 g, 89%) as a colourless oil; ν_{max}(film)/cm^{-1} 2209, 1690, 1642, 1609, 764 and 658; δ_H(400 MHz) 6.46 (dd, *J* 17, 11 Hz, 1H, C*H*=CH$_2$), 6.25 (d, *J* 17 Hz, 1H, CH=C*H*H), 5.74 (d, *J* 11 Hz, 1H, CH=CH*H*), 3.66 (t, *J* 6 Hz, 2H, C*H*$_2$Cl), 2.84 (dd, *J* 11, 3 Hz, 1H, C*H*COCH=), 2.62 (t, *J* 7 Hz, 2H, alkyne-C*H*$_2$), 2.13–1.72 (m, 6H), 1.75 (obsc. s, 3H, =CC*H*$_3$), 1.22 (s, 3H, Me), 1.20 (s, 3H, Me); δ_C(67.8 MHz) 202.3 (s), 185.6 (s), 141.6 (s), 137.1 (d), 133.3 (s), 127.7 (t), 93.6 (s), 83.5 (d), 53.6 (d), 43.2 (t), 36.5 (s), 30.5 (t), 30.2 (t), 27.8 (q), 23.5 (q), 21.2 (t), 20.4 (q), 16.5 (t).

1-(6-Iodo-1-oxohex-2-ynyl)-5-(1-oxoprop-2-enyl)-2,6,6-trimethylcyclohex-1-ene 39a. A stirred mixture of the chloride **54** (50 mg, 0.16 mmol) and sodium iodide (37 mg, 0.24 mmol) in butan-2-one (2 ml) was heated under reflux for 18 hr. The cooled mixture was diluted with ether (5 ml) and water (2 ml) and the organic layer was separated. The aqueous layer was extracted with ether (2 × 5 ml) and the combined organic extracts were washed with 10% aqueous sodium thiosulfate (5 ml) and brine (5 ml), and then dried and concentrated *in vacuo* to give the *iodide* (61 mg, 94%) as a colourless oil; δ_H(250 MHz) 6.46 (dd, *J* 17, 10 Hz, 1H, C*H*=CH$_2$), 6.24 (d, *J* 17 Hz, 1H, CH=C*H*H), 5.74 (d, *J* 10 Hz, 1H, CH=CH*H*), 3.29 (t, *J* 7 Hz, 2H, C*H*$_2$I), 2.84 (dd, *J* 11, 3 Hz, 1H, C*H*COCH=), 2.57 (t, *J* 7 Hz, 2H, alkyne-C*H*$_2$), 2.09–1.54 (m, 6H), 1.73 (obsc. s, 3H, =CCH$_3$), 1.21 (s, 3H, Me), 1.18 (s, 3H, Me); which was used directly without any further purification.

1-(1-Oxohex-2-ynyl)-5-(1-oxoprop-2-enyl)-2,6,6-trimethylcyclohex-1-ene 39b. Treatment of a solution of the alkyl iodide **39a** (50 mg, 0.12 mmol) in benzene with tri-*n*-butyltin hydride and azoisobutyronitrile, according to the general procedure, gave the title cyclohexene (15 mg, 43%) as a colourless oil; λ_{max}(EtOH)/nm 225 (ε/dm^3 mol^{-1} cm^{-1} 6 500); ν_{max}(film)/cm^{-1} 2203, 1704, 1643, 914, 733 and 648; δ_H(270 MHz) 6.39 (dd, *J* 17, 10 Hz, 1H, C*H*=CH$_2$), 6.17 (dd, *J* 17, 1 Hz, 1H, CH=C*H*H), 5.67 (dd, *J* 10, 1 Hz, 1H, CH=CH*H*), 2.78 (dd, *J* 11, 3 Hz, 1H, C*H*CO), 2.31 (t, *J* 7 Hz, 2H, alkyne-C*H*$_2$), 2.03–1.51 (m, 6H), 1.67 (obsc. s, 3H, =CC*H*$_3$), 1.15 (s, 3H, Me), 1.12 (s, 3H, Me), 0.95 (t, *J* 7 Hz, 3H, CH$_2$C*H*$_3$); δ_C(67.8 MHz) 202.6 (s), 185.9 (s), 141.6 (s), 137.2 (d), 133.3 (s), 127.8 (t), 96.3 (s), 83.3 (d), 53.8 (d), 36.6 (s), 30.6 (t), 27.8 (q), 23.6 (q), 21.3 (t), 21.2 (t), 21.1 (t), 20.5 (q), 13.4 (q) (Found: M$^+$, 272.1784. $C_{18}H_{24}O_2$ requires *M*, 272.1776).

1-(*E*,*Z*-6-Chloro-3-methyl-1-oxohex-2-enyl)-5-(1-hydroxyprop-2-enyl)-2,6,6-trimethylcyclohex-1-ene 67. A solution of methyllithium–lithium iodide complex (1.74 ml) in ether (1 M, 1.7 mmol) was added dropwise over 5 min to a stirred suspension of copper(I) iodide (0.16 g, 0.87 mmol) in dry THF (8 ml) at 0 °C under an atmosphere of nitrogen. The solution was stirred at 0 °C for 10 min until the solution became colourless and all solids were dissolved. The stirred solution was cooled to −78 °C and a solution of the enone **53** (0.122 g, 0.40 mmol) in dry THF (4 ml) was added portionwise over 5 min. The solution was stirred at −78 °C for 30 min and then allowed to warm to 0 °C, where it was quenched with saturated aqueous ammonium chloride (10 ml) and ether (15 ml). The organic layer was separated and the aqueous layer was extracted with ether (2 × 15 ml). The combined ether extracts were washed with saturated aqueous ammonium chloride (20 ml), water (20 ml) and brine (20 ml), and then dried and evaporated *in vacuo* to leave a yellow oil. Purification by chromatography on silica eluting with 15% ether in light petroluem (bp 40–60 °C) gave a mixture of (*E*)- and (*Z*)-isomers (1 : 1 ratio) of the *alcohol* (0.12 g, 91%) as a colourless oil; [data for (*E*)-isomer]: λ_{max}(EtOH)/nm 244 (ε/dm^3 mol^{-1} cm^{-1} 6 300); ν_{max}(film)/cm^{-1} 3442, 1665, 1601 and 919; δ_H(400 MHz) 6.10 [d, *J* 1 Hz, 1H, C*H*=C(CH$_3$)], 5.87 (ddd, *J* 17, 10, 5 Hz, 1H, C*H*=CH$_2$), 5.23 (app. dt, *J* 17, 2 Hz, 1H, CH=C*H*H), 5.11 (app. dt, *J* 10, 2 Hz, 1H, CH=CH*H*), 4.46 (s, 1H, C*H*OH), 3.58 (t, *J* 7 Hz, 2H, C*H*$_2$Cl), 2.70 [t, *J* 7 Hz, 2H, CH=C(CH$_3$)C*H*$_2$], 2.00–1.92 (m, 4H), 1.88 (d, *J* 1.2 Hz, 3H, CH=CC*H*$_3$), 1.63–1.57 (m, 2H), 1.52 (s, 3H, C=CC*H*$_3$), 1.36–1.32 (m, 1H), 1.16 (s, 3H, Me), 1.06 (s, 3H, Me); δ_C(67.8 MHz) 200.6 (s), 156.7 (s), 144.0 (s), 141.6 (d), 128.8 (s), 127.7 (d), 113.5 (t), 70.6 (d), 48.7 (d), 44.9 (t), 36.9 (s), 31.4 (t), 31.2 (t), 31.1 (t), 27.4 (q), 25.6 (q), 23.4 (q), 20.3 (q), 17.2 (t).

1-(*E*,*Z*-6-Chloro-3-methyl-1-oxohex-2-enyl)-5-(1-oxoprop-2-enyl)-2,6,6-trimethylcyclohex-1-ene 68. Treatment of a solution of the alcohol **67** (0.59 g, 1.81 mmol) in dry dichloromethane with tetra(*n*-propyl)ammonium perruthenate and 4-methylmorpholine *N*-oxide, according to the general procedure, gave a mixture of (*E*)- and (*Z*)-isomers (1 : 1 ratio) of the title ketone (0.44 g, 75%) as a colourless oil; (data for (*E*)-isomer): λ_{max}(EtOH)/nm 243 (ε/dm^3 mol^{-1} cm^{-1} 14 300); ν_{max}(film)/cm^{-1} 1666, 1604 and 966; δ_H(250 MHz) 6.45 (dd, *J* 17, 10 Hz, 1H, C*H*=CH$_2$), 6.23 (dd, *J* 17, 1 Hz, 1H, CH=C*H*H), 6.18 (d, *J* 1 Hz, 1H, C*H*=CCH$_3$), 5.72 (dd, *J* 10, 1 Hz, 1H, CH=CH*H*), 3.60 (t, *J* 7 Hz, 2H, C*H*$_2$Cl), 2.82 (dd, *J* 10, 3 Hz, 2H, C*H*COCH=), 2.73 [d, *J* 8 Hz, 1H, CH=C(CH$_3$)CH*H*], 2.70 [d, *J* 8 Hz, 1H, CH=C(CH$_3$)CH*H*], 2.02–1.61 (m, 6H), 1.92 (obsc. d, *J* 1 Hz, 3H, CH=CC*H*$_3$), 1.56 (s, 3H, =CC*H*$_3$), 1.10 [s, 6H, C(C*H*$_3$)$_2$]; δ_C(67.8 MHz) 202.7 (s), 200.0 (s), 157.3 (s), 143.1 (s), 137.1 (d), 128.2 (s), 127.6 (t), 127.5 (d), 54.1 (d), 44.9 (t), 36.4 (s), 31.5 (t), 31.1 (t), 29.8 (t), 28.3 (q), 25.6 (q), 23.6 (q), 21.4 (t), 20.3 (q).

1-(*E*,*Z*-6-Iodo-3-methyl-1-oxohex-2-enyl)-5-(1-oxoprop-2-enyl)-2,6,6-trimethylcyclohex-1-ene 61. A stirred mixture of the chloride **68** (67 mg, 0.21 mmol) and sodium iodide (93 mg, 0.63 mmol) in butan-2-one (2 ml) was heated to reflux for 18 h. The mixture was allowed to cool to room temperature and then diluted with ether (5 ml) and water (2 ml). The organic layer was separated and the aqueous layer was extracted with ether (2 × 5 ml). The combined ether extracts were washed with 10% aqueous sodium thiosulfate (5 ml) and brine (5 ml) and then dried and evaporated *in vacuo* to give a mixture of (*E*)- and (*Z*)-isomers of the the *iodide* (80 mg, 93%) as a colourless oil; (data for both isomers): δ_H(250 MHz) 6.46 (dd, *J* 17, 10 Hz, 1H, C*H*=CH$_2$), 6.45 (dd, *J* 17, 10 Hz, 1H, C*H*=CH$_2$), 6.27–6.18 (m, 4H, CH=C*H*H, C*H*=CCH$_3$), 5.73 (d, *J* 10 Hz, 1H, CHCH*H*), 5.72 (d, *J* 10 Hz, 1H, CH=CH*H*), 3.26 (t, *J* 7 Hz, 2H, C*H*$_2$I), 3.17 (t, *J* 7 Hz, 2H, C*H*$_2$I), 2.86–2.81 (m, 2H, C*H*CO), 2.69 [dd, *J* 8, 7 Hz, 2H, CH=C(CH$_3$)C*H*$_2$], 2.27 [dd, *J* 8, 7 Hz, 2H, CH=C(CH$_3$)C*H*$_2$], 2.17 (d, *J* 1 Hz, 3H, CH=CC*H*$_3$), 2.10–1.90

(m, 8H), 1.92 (obsc. d, *J* 1 Hz, 3H, CH=CCH_3), 1.88–1.65 (m, 4H), 1.58 (s, 3H, =CCH_3), 1.57 (s, 3H, =CCH_3), 1.12 [s, 6H, C(CH_3)$_2$], 1.11 [s, 6H, C(CH_3)$_2$], which was used directly without any further purification.

5-(1-Oxoprop-2-enyl)-2,6,6-trimethyl-1-(*E*,*Z*-3-methyl-1-oxohex-2-enyl)cyclohex-1-ene 62. Treatment of a solution of the alkyl iodide **61** (0.25 g, 0.562 mmol) in benzene with tri-*n*-butyltin hydride and azoisobutyronitrile, according to the general procedure, gave a mixture of (*E*)- and (*Z*)-isomers (1 : 1 ratio) of the title cyclohexene (0.12 g, 67%) as a colourless oil; (data for both isomers): ν_{max}(film)/cm^{-1} 1705, 1666 and 838; δ_H(250 MHz) 6.45 (dd, *J* 17, 10 Hz, 2H, C*H*=CH$_2$), 6.23 (dd, *J* 17 Hz, 2H, CH=C*H*H), 6.12 (s, 2H, C*H*=CCH$_3$), 5.71 (d, *J* 10 Hz, 2H, CH=CH*H*), 2.82 (dd, *J* 11, 2 Hz, 2H, C*H*CO), 2.62 [t, *J* 8 Hz, 2H, (*E*)-CH=C(CH$_3$)CH_2], 2.16 [s, 3H, (*Z*)-CH=CCH_3], 2.12 [t, *J* 8 Hz, 2H, (*Z*)-CH=C(CH$_3$)CH_2], 2.03–1.62 (m, 6H), 1.88 (obsc. s, 3H, (*E*)-CH=CCH_3), 1.92 (obsc. d, *J* 1 Hz, 3H, CH=CCH_3), 1.58 (s, 6H, =CCH_3), 1.55–1.17 (m, 4H, CH_2CH$_3$), 1.12 [s, 6H, C(CH_3)$_2$], 1.11 [s, 6H, C(CH_3)$_2$], 0.97 [t, *J* 7 Hz, 3H, (*E*)-CH$_2$CH_3], 0.91 [t, *J* 7 Hz, 3H, (*Z*)-CH$_2$CH_3]; δ_C(67.8 MHz) 202.8 (s), 200.5 (s), 199.8 (s), 159.3 (s), 158.0 (s), 143.4 (s), 137.2 (d), 127.9 (t), 127.8 (s), 127.5 (t), 127.0 (d), 126.7 (d), 54.2 (d), 43.2 (t), 36.5 (s), 35.6 (t), 29.9 (t), 28.25 (q), 28.2 (q), 25.5 (q), 23.6 (q), 21.5 (t), 21.3 (t), 20.7 (t), 20.3 (q), 19.2 (q), 14.2 (q), 13.6 (q) (Found: M$^+$, 288.2079. $C_{19}H_{28}O_2$ requires *M*, 288.2089).

1-(*E*,*Z*-6-Chloro-3-methyl-1-oxohex-2-enyl)-5-(1-hydroxyprop-2-ynyl)-2,6,6-trimethylcyclohex-1-ene 69. A solution of ethynylmagnesium bromide (1.94 ml) in THF (0.5 M, 0.97 mmol) was added dropwise over 10 min to a stirred solution of the aldehyde **52** (0.25 g, 0.88 mmol) in dry THF (10 ml) at −78 °C under nitrogen. The solution was stirred at −78 °C for 2 h and then quenched with water (5 ml), saturated aqueous ammonium chloride (10 ml) and ether (10 ml). The mixture was allowed to warm to room temperature and the organic layer was separated. The aqueous layer was extracted with ether (2 × 10 ml) and the combined organic extracts were washed with saturated aqueous ammonium chloride (10 ml) and brine (10 ml) and then dried and evaporated *in vacuo* to a yellow oil. Purification by chromatography on silica, eluting with 40% ether in light petroleum (bp 40–60 °C), gave 1-(6-chloro-1-oxohex-2-ynyl)-5-(1-hydroxyprop-2-ynyl)-2,6,6-trimethylcyclohex-1-ene (0.26 g, 94%) as a colourless oil; λ_{max}(EtOH)/nm 230 (ε/dm^3 mol^{-1} cm^{-1} 7 200); ν_{max}(film)/cm^{-1} 3452, 3297, 2208, 1640 and 733; δ_H(250 MHz) 4.72–4.70 (m, 1H, C*H*OH), 3.64 (t, *J* 6 Hz, 2H, CH_2Cl), 2.60 (t, *J* 7 Hz, 2H, alkyne-CH_2), 2.47 (d, *J* 2 Hz, 1H, alkyne-H), 2.15 (dd, *J* 8, 5 Hz, 2H, =CCH_2), 2.04 (app. quintet, *J* 7 Hz, 2H, CH_2CH$_2$Cl), 2.00–1.76 (m, 3H), 1.72 (obsc. s, 3H, =CCH_3), 1.64 (dt, *J* 11, 3 Hz, 1H, C*H*CHOH), 1.23 (s, 3H, Me), 1.22 (s, 3H, Me); δ_C(67.8 MHz) 186.6 (s), 141.8 (s), 133.5 (s), 93.5 (s), 85.6 (s), 83.6 (s), 72.5 (d), 61.3 (d), 50.0 (d), 43.1 (t), 36.7 (s), 31.3 (t), 30.4 (t), 27.4 (q), 23.7 (q), 20.5 (q), 18.2 (t), 16.4 (t) (Found: M$^+$, 306.1386. $C_{18}H_{23}ClO_2$ requires *M*, 306.1387).

A solution of methyllithium–lithium bromide complex (1.38 ml) in ether (1.5 M, 2.1 mmol) was added dropwise over 5 min to a stirred suspension of copper(I) iodide (0.20 g, 1.0 mmol) in dry THF (5 ml), at 0 °C under nitrogen. The solution was stirred at 0 °C for 10 min until the solution became colourless and all solids had dissolved. The stirred solution was cooled to −78 °C and a solution of the ynone from above (0.127 g, 0.413 mmol) in dry THF (4 ml) was added portionwise over 5 min. The solution was stirred at −78 °C for 30 min and then allowed to warm to 0 °C where it was quenched with saturated aqueous ammonium chloride (5 ml) and ether (10 ml). The organic layer was separated and the aqueous layer was extracted with ether (2 × 10 ml). The combined organic extracts were washed with saturated aqueous ammonium chloride (10 ml), water (10 ml) and brine (10 ml), and then dried and evaporated *in vacuo* to a yellow oil. Purification by chromatography on silica, eluting with 15% ether in light petroleum (bp 40–60 °C), gave a mixture of (*E*)- and (*Z*)-isomers (1 : 1 ratio) of the 1-(6-chloro-3-methyl-1-oxohex-2-ynyl)-5-(1-hydroxyprop-2-ynyl)-2,6,6-trimethylcyclohex-1-ene (0.12 g, 94%) as a colourless oil; [data for (*E*)-isomer]: λ_{max}(EtOH)/nm 244 (ε/dm^3 mol^{-1} cm^{-1} 13 800); ν_{max}(film)/cm^{-1} 3440, 3297, 1662, 1599 and 835; δ_H(400 MHz) 6.12 [s, 1H, C*H*=C(CH$_3$)], 4.71 (s, 1H, C*H*OH), 3.62 (t, *J* 7 Hz, 2H, CH_2Cl), 2.74 [app. t, *J* 8 Hz, 2H, CH=C(CH$_3$)CH_2], 2.47 (d, *J* 2 Hz, 1H, alkyne-H), 2.11 (d, *J* 5 Hz, 1H, C=CC*H*H), 2.09 (d, *J* 5 Hz, 1H, C=CCH*H*), 2.02–1.94 (m, 3H), 1.92 (d, *J* 1 Hz, 3H, CH=CCH_3), 1.86–1.78 (m, 1H), 1.63 (dt, *J* 11, 3 Hz, 1H, C*H*CHOH), 1.57 (s, 3H, C=CCH_3), 1.16 (s, 3H, Me), 1.13 (s, 3H, Me); δ_C(67.8 MHz) 201.1 (s), 157.7 (s), 144.2 (s), 129.5 (s), 128.3 (d), 86.3 (s), 73.2 (d), 62.5 (d), 50.8 (d), 45.6 (t), 37.2 (s), 32.1 (t), 31.8 (t), 31.6 (t), 28.4 (q), 26.3 (q), 24.3 (q), 21.0 (q), 19.2 (t) (Found: M$^+$, 322.1696. $C_{19}H_{27}ClO_2$ requires *M*, 322.1670).

1-(*E*,*Z*-6-Chloro-3-methyl-1-oxohex-2-enyl)-5-(1-oxoprop-2-ynyl)-2,6,6-trimethylcyclohex-1-ene 70. Barium manganate (0.16 g, 0.61 mmol) was added in one portion to a stirred solution of the propargylic alcohol **69** (39 mg, 0.12 mmol) in dry dichloromethane (5 ml) at room temperature. The mixture was stirred at room temperature for 30 min and then a further portion of barium manganate (0.16 g, 0.12 mmol) was added. The mixture was stirred at room temperature for a further 30 min and then filtered through a short plug of Celite. The Celite plug was washed exhaustively with dichloromethane (100 ml) and then the combined filtrate was evaporated to dryness *in vacuo* to leave a pale yellow oil. Purification by chromatography on silica eluting with 20% ether in light petroleum (bp 40–60 °C) gave a mixture of (*E*)- and (*Z*)-isomers (1 : 1 ratio) of the *ketone* (30 mg, 75%) as a colourless oil; [data for (*E*)-isomer]: λ_{max}(EtOH)/nm 245 (ε/dm^3 mol^{-1} cm^{-1} 12 200); ν_{max}(film)/cm^{-1} 3249, 1665, 1601 and 762; δ_H(250 MHz) 6.15 (d, *J* 1 Hz, 1H, C*H*=CCH$_3$), 3.60 (t, *J* 7 Hz, 2H, CH_2Cl), 3.31 (s, 1H, alkyne-H), 2.72 [m, 2H, CH=C(CH$_3$)CH_2], 2.62 (m, 1H, C*H*CO-alkyne), 2.05–1.89 (m, 6H), 1.92 (obsc. d, *J* 1 Hz, 3H, CH=CCH_3), 1.56 (s, 3H, =CCH_3), 1.19 (s, 3H, Me), 1.18 (s, 3H, Me); δ_C(67.8 MHz) 199.5 (s), 189.9 (s), 157.5 (s), 142.7 (s), 128.3 (s), 127.4 (d), 82.5 (s), 79.4 (s), 58.6 (d), 44.9 (t), 36.7 (s), 31.5 (t), 31.1 (t), 29.7 (t), 27.7 (q), 25.7 (q), 23.6 (q), 21.2 (t), 20.3 (q).

1-(*E*,*Z*-6-Iodo-3-methyl-1-oxohex-2-enyl)-5-(1-oxoprop-2-ynyl)-2,6,6-trimethylcyclohex-1-ene 63. A stirred mixture of the chloride **70** (50 mg, 0.16 mmol) and sodium iodide (35 mg, 0.23 mmol) in butan-2-one (2 ml) was heated to reflux for 18 h and then cooled. The mixture was diluted with ether (5 ml) and water (2 ml) and the organic layer was separated. The aqueous layer was extracted with ether (2 × 5 ml) and the combined organic extracts were washed with 10% aqueous sodium thiosulfate (5 ml) and brine (5 ml), and then dried and concentrated *in vacuo* to give a mixture of (*E*)- and (*Z*)-isomers (1 : 1 ratio) of the *iodide* (63 mg, 98%) as a colourless oil; (data for both isomers): δ_H(250 MHz) 6.14 (br s, 2H, C*H*=CCH$_3$), 3.30 (s, 2H, alkyne-H), 3.26 (t, *J* 7 Hz, 2H, CH_2I), 3.17 (t, *J* 7 Hz, 2H, CH_2I), 2.72 [m, 2H, CH=C(CH$_3$)CH_2], 2.65–2.60 (m, 2H, C*H*CO), 2.30 [m, 2H, CH=C(CH$_3$)CH_2], 2.16 (d, *J* 1 Hz, 3H, CH=CCH_3), 2.05–1.88 (m, 12H), 1.92 (obsc. d, *J* 1 Hz, 3H, CH=CCH_3), 1.56 (s, 6H, =CCH_3), 1.19 [s, 6H, C(CH_3)$_2$], 1.18 [s, 6H, C(CH_3)$_2$], which was used directly without any further purification.

1-(*E*,*Z*-3-Methyl-1-oxohex-2-enyl)-5-(1-oxoprop-2-ynyl)-2,6,6-trimethylcyclohex-1-ene 64. Treatment of a solution of the iodide **63** (64 mg, 0.16 mmol) in benzene with tri-*n*-butyltin hydride and azoisobutyronitrile, according to the general procedure, gave a mixture of (*E*)- and (*Z*)-isomers (1 : 1 ratio) of the title cyclohexane (18 mg, 41%) as a colourless oil; (data for both isomers): λ_{max}(EtOH)/nm 225 (ε/dm^3 mol^{-1} cm^{-1} 900), 246 (1 500); ν_{max}(film)/cm^{-1} 3244, 2088, 1720, 1666 and 764; δ_H(270 MHz) 6.03 (s, 2H, C*H*=CCH$_3$), 3.24 (s, 2H, alkyne-H), 2.56–

2.52 [m, 4H, C*H*CO, (*E*)-CH=C(CH$_3$)C*H*$_2$], 2.09 [s, 3H, (*Z*)-CH=CC*H*$_3$], 2.08–1.84 (m, 10H), 1.82 [s, 3H, (*E*)-CH=CC*H*$_3$], 1.53–1.39 (m, 4H, C*H*$_2$CH$_3$), 1.51 (obsc. s, 6H, =CC*H*$_3$), 1.13 [s, 12H, C(C*H*$_3$)$_2$], 0.90 [t, *J* 7 Hz, 3H, (*E*)-CH$_2$C*H*$_3$], 0.84 [t, *J* 7 Hz, 3H, (*Z*)-CH$_2$C*H*$_3$]; δ_C(67.8 MHz) 200.2 (s), 199.5 (s), 190.1 (s), 159.6 (s), 158.5 (s), 143.0 (s), 142.9 (s), 128.0 (s), 127.9 (s), 126.9 (d), 126.6 (d), 82.5 (s), 79.4 (d), 58.7 (d), 43.2 (t), 36.7 (t), 35.7 (s), 29.7 (t), 27.6 (q), 27.5 (q), 25.6 (q), 23.6 (q), 21.3 (t), 21.2 (t), 20.7 (t), 20.3 (q), 19.2 (q), 14.2 (q), 13.6 (q) (Found: M$^+$, 286.1955. $C_{19}H_{26}O_2$ requires *M*, 286.1933).

1-(*tert*-Butyldiphenylsiloxy)-pent-4-yne 71. *tert*-Butyldiphenylsilyl chloride (7.4 ml, 28.8 mmol) was added dropwise over 10 min to a stirred solution of pent-4-yn-1-ol (2.0 g, 24.0 mmol), 4-dimethylaminopyridine (0.29 g, 2.4 mmol) and triethylamine (4.0 ml, 28.8 mmol) in dry dichloromethane (80 ml) at 0 °C under nitrogen. The mixture was stirred at 0 °C for 1 h and then allowed to warm to room temperature where it was stirred for a further 14 h. The mixture was diluted with dichloromethane (80 ml) and then washed with saturated aqueous ammonium chloride (100 ml). The organic layer was separated and the aqueous layer was re-extracted with dichloromethane (2 × 80 ml). The combined organic extracts were washed with brine (80 ml) and then dried and evaporated *in vacuo* to a colourless oil, which was purified by chromatography on silica, eluting with 10% ether in light petroleum (bp 40–60 °C), to give the *silyl ether* (7.75 g, 99%) as a colourless oil; λ_{max}(EtOH)/nm 254 (ε/dm^3 mol^{-1} cm^{-1} 500), 260 (700), 264 (800), 270 (600); ν_{max}(film)/cm^{-1} 3306, 2118, 1958, 1888, 1823 and 702; δ_H(250 MHz) 7.73–7.69 (m, 4H, Ar-H), 7.46–7.41 (m, 6H, Ar-H), 3.79 (t, *J* 6 Hz, 2H, C*H*$_2$OTBDPS), 2.38 (dt, *J* 2, 7 Hz, 2H, C*H*$_2$CH$_2$CH$_2$OTBDPS), 1.95 (t, *J* 2 Hz, 1H, alkyne-H), 1.85–1.75 (m, 2H, C*H*$_2$CH$_2$OTBDPS), 1.09 [s, 9H, C(C*H*$_3$)$_3$]; δ_C(67.8 MHz) 135.5 (d), 133.8 (s), 129.6 (d), 127.6 (d), 84.2 (s), 68.3 (d), 62.6 (t), 31.4 (t), 26.8 (q), 19.2 (s), 15.0 (t) (Found: M$^+$ − ^{t}Bu, 265.1036. $C_{17}H_{17}OSi$ requires *M*, 265.1049).

4-Bromo-1-(*tert*-butyldiphenylsiloxy)pent-4-ene 72. A solution of 9-bromoborabicyclo[3.3.1]nonane (56.0 ml) in dichloromethane (1.0 M, 56.0 mmol) was added dropwise over 10 min to a stirred solution of the alkyne **71** in dry dichloromethane (290 ml) at 0 °C under nitrogen. The solution was allowed to warm to room temperature over 14 h and was then cooled to 0 °C. Dilute acetic acid (19.0 ml) was added dropwise over 5 min and the mixture was allowed to warm to room temperature where it was stirred vigourously for 1hr. The mixture was cooled to 0 °C and then aqueous sodium hydroxide (112 ml, 5 N) was added dropwise over 30 min. The mixture was stirred at 0 °C for 1 h and then a solution of hydrogen peroxide (30%) in water (31.0 m) was added dropwise over 30 min. The mixture was stirred at 0 °C for 2 h and then diluted with water (200 ml) and dichloromethane (100 ml). The organic layer was separated and the aqueous layer was re-extracted with dichloromethane (2 × 200 ml). The combined organic extracts were washed with saturated aqueous ammonium chloride (100 ml) and brine (100 ml) and then dried and evaporated *in vacuo* to a yellow oil, which was purified by chromatography on silica, eluting with 10% ether in light petroleum (bp 40–60 °C), to give the *bromide* (10.7 g, 95%) as a colourless oil; λ_{max}(EtOH)/nm 254 (ε/dm^3 mol^{-1} cm^{-1} 500), 260 (700), 264 (700), 270 (500); ν_{max}(film)/cm^{-1} 1958, 1888, 1822, 1770, 1628 and 701; δ_H(250 MHz) 7.68–7.66 (m, 4H, Ar-H), 7.44–7.37 (m, 6H, Ar-H), 5.56 (d, *J* 2 Hz, 1H, =CH*H*), 5.39 (d, *J* 2 Hz, 1H, =C*H*H), 3.70 (t, *J* 6 Hz, 2H, C*H*$_2$OTBDPS), 2.58 (t, *J* 7 Hz, 2H, C*H*$_2$CH$_2$CH$_2$-OTBDPS), 1.85–1.75 (m, 2H, C*H*$_2$CH$_2$OTBDPS), 1.06 [s, 9H, C(C*H*$_3$)$_3$]; δ_C(67.8 MHz) 135.6 (d), 133.9 (s), 134.4 (s), 129.7 (d), 127.7 (d), 116.8 (t), 62.4 (t), 38.0 (t), 31.0 (t), 26.9 (q), 19.3 (s) (Found: M$^+$ − ^{t}Bu, 345.0285. $C_{17}H_{18}OBrSi$ requires *M*, 345.0310).

1-*tert*-Butyldiphenylsiloxy-4-formylpent-4-ene 73a. A solution of *t*-butyllithium (50.0 ml) in THF (1.7 M, 85.0 mmol) was added dropwise over 30 min to a stirred solution of the bromide **72** (13.7 g, 34.0 mmol) in dry ether (300 ml) at −110 °C under argon. The solution was stirred at −110 °C for 1 h and then dimethylformamide (26.0 ml, 340 mmol) was added dropwise over 20 min. The solution was allowed to warm to room temperature over 1 h and was then diluted with ether (200 ml) and water (300 ml). The organic layer was separated and the aqueous layer was re-extracted with ether (2 × 200 ml). The combined organic extracts were dried and concentrated *in vacuo* to an orange oil which was purified by chromatography on silica, eluting with 20% ether in light petroleum (bp 40–60 °C), to give the *aldehyde* (9.8 g, 82%) as a colourless oil; λ_{max}(EtOH)/nm 264 (ε/dm^3 mol^{-1} cm^{-1} 800); ν_{max}(film)/cm^{-1} 1695 and 702; δ_H(250 MHz) 9.54 (s, 1H, C*H*O), 7.70–7.67 (m, 4H, Ar-H), 7.45–7.37 (m, 6H, Ar-H), 6.22 (s, 1H, =CH*H*), 5.98 (s, 1H, =C*H*H), 3.68 (t, *J* 6 Hz, 2H, C*H*$_2$OTBDPS), 2.37 (t, *J* 8 Hz, 2H, C*H*$_2$CH$_2$CH$_2$OTBDPS), 1.80–1.68 (m, 2H, C*H*$_2$CH$_2$-OTBDPS), 1.07 [s, 9H, C(C*H*$_3$)$_3$]; δ_C(67.8 MHz) 194.6 (d), 149.9 (s), 135.6 (d), 134.1 (t), 133.9 (s), 129.6 (d), 127.7 (d), 63.1 (t), 30.5 (t), 26.9 (q), 24.3 (t), 19.3 (s) (Found: M$^+$ − ^{t}Bu, 297.1363. $C_{18}H_{21}O_2Si$ requires *M*, 297.1311).

1-tert-Butyldiphenylsiloxy-4-hydroxymethylpent-4-ene 73b. Sodium borohydride (1.17 g, 30.8 mmol) was added portionwise over 20 min to a stirred solution of the aldehyde **73a** (9.83 g, 28.0 mmol) and cerium trichloride heptahydrate (11.48 g, 30.8 mmol) in methanol (70 ml) at 0 °C under nitrogen. The solution was stirred at 0 °C for 20 min and then diluted with water (1000 ml) and ether (100 ml). The organic layer was separated and the aqueous layer was re-extracted with ether (2 × 100 ml). The combined organic extracts were dried and then concentrated *in vacuo* to a colourless oil which was purified by chromatography on silica, eluting with 30% ether in light petroleum (bp 40–60 °C), to give the *alcohol* (9.8 g, 99%) as a colourless oil; λ_{max}(EtOH)/nm 254 (600), 259 (700), 264 (700), 271 (600); ν_{max}(film)/cm^{-1} 3353, 1959, 1889 and 702; δ_H(250 MHz) 7.71–7.67 (m, 4H, Ar-H), 7.48–7.36 (m, 6H, Ar-H), 5.02 (s, 1H, =CH*H*), 4.87 (s, 1H, =C*H*H), 4.08–4.02 (m, 2H, C*H*$_2$OH), 3.70 (t, *J* 6 Hz, 2H, C*H*$_2$OTBDPS), 2.17 (t, *J* 8 Hz, 2H, C*H*$_2$CH$_2$CH$_2$OTBDPS), 1.80–1.68 (m, 2H, C*H*$_2$CH$_2$OTB-DPS), 1.07 [s, 9H, C(C*H*$_3$)$_3$]; δ_C(67.8 MHz) 148.7 (s), 135.6 (d), 134.0 (s), 129.6 (d), 127.7 (d), 109.3 (t), 65.9 (t), 63.5 (t), 30.7 (t), 29.2 (t), 26.9 (q), 19.3 (s) (Found: M$^+$ − ^{t}Bu, 297.1351. $C_{18}H_{21}O_2Si$ requires *M*, 297.1311).

4-Bromomethyl-1-*tert*-butyldiphenylsiloxypent-4-ene 73c. *N*-Bromosuccinimide (1.6 g, 9.1 mmol) was added in one portion to a stirred solution of the alcohol **73b** (2.2 g, 6.1 mmol) and triphenylphosphine (2.4 g, 9.1 mmol) in dry dichloromethane (60 ml) at 0 °C under nitrogen. The solution was allowed to warm to room temperature over 20 min and then diluted with ether (100 ml) and water (100 ml). The organic layer was separated and the aqueous layer was re-extracted with ether (2 × 100 ml). The combined organic fractions were washed with saturated aqueous sodium hydrogen carbonate (100 ml) and saturated brine (100 ml) and then dried and concentrated *in vacuo* to a volume of *ca*. 10 ml. The resulting orange suspension was poured into light petroleum (bp 40–60 °C) (100 ml) and the white precipitate was removed by filtration. The filtrate was evaporated *in vacuo* to a yellow oil which was purified by chromatography on silica, eluting with 10% ether in light petroleum (bp 40–60 °C) to give the *bromide* (2.3 g, 99%) as a colourless oil; λ_{max}(EtOH)/nm 254 (ε/dm^3 mol^{-1} cm^{-1} 400), 260 (513), 264 (600), 270 (400); ν_{max}(film)/cm^{-1} 1959, 1889, 1822 and 701; δ_H(250 MHz) 7.71–7.68 (m, 4H, Ar-H), 7.48–7.37 (m, 6H, Ar-H), 5.17 (s, 1H, =CH*H*), 4.96 (s, 1H, =C*H*H), 3.96 (s, 2H, C*H*$_2$Br), 3.71 (t, *J* 6 Hz, 2H, C*H*$_2$-OTBDPS), 2.34 (t, *J* 8 Hz, 2H, C*H*$_2$CH$_2$CH$_2$OTBDPS), 1.77–1.69 (m, 2H, C*H*$_2$CH$_2$OTBDPS), 1.08 [s, 9H, C(C*H*$_3$)$_3$]; δ_C(67.8 MHz) 145.1 (s), 135.5 (d), 133.8 (s), 129.5 (d), 127.6 (d), 114.9 (t), 63.1 (t), 36.6 (t), 30.3 (t), 29.6 (t), 26.8 (q), 19.2 (s) (Found: M$^+$ − ^{t}Bu, 349.0259. $C_{17}H_{18}BrOSi$ requires *M*, 349.0310).

1-Acetoxymethyl-5-hydroxymethyl-2,6,6-trimethylcyclohex-1-ene 74. Methanol (7.61 ml, 188 mmol) was added dropwise over 10 min to a stirred solution of the aldehyde **13** (4.22 g, 18.8 mmol) and sodium borohydride (0.78 g, 20.7 mmol) in dry ether (94 ml) at 0 °C under nitrogen. The solution was stirred at 0 °C for 30 min and then warmed to room temperature over 20 min. The solution was quenched with water (100 ml) and the organic layer was separated. The aqueous layer was re-extracted with ether (2 × 100 ml) and the combined organic extracts were dried and evaporated *in vacuo* to a yellow oil, which was purified by chromatography on silica, eluting with 50% ether in light petroleum (bp 40–60 °C), to give the *alcohol* (4.21 g, 98%) as a colourless oil; ν_{max}(film)/cm^{-1} 3429, 1735 and 733; δ_H(250 MHz) 4.55 (s, 2H, CH_2OAc), 3.83 (dd, *J* 10, 3 Hz, 1H, CH*H*OH), 3.37 (dd, *J* 10, 9 Hz, 1H, C*H*HOH), 2.62 (br s, 1H, O*H*), 2.02 (s, 3H, COCH_3), 2.10–1.81 [m, 3H, CHCH*H*, =C(Me)CH_2], 1.65 (s, 3H, Me), 1.49–1.42 (m, 2H, C*HCH*H), 1.05 (s, 3H, Me), 0.82 (s, 3H, Me); δ_C(67.8 MHz) 171.5 (s), 136.5 (s), 131.9 (s), 63.4 (t), 60.9 (t), 47.0 (d), 36.2 (s), 31.5 (t), 26.6 (q), 22.2 (q), 21.4 (t), 21.0 (q), 19.8 (q) (Found: M$^+$ − AcOH, 166.1312. $C_{11}H_{18}O$ requires *M*, 166.1358) (Found: C, 68.6; H, 9.9. $C_{13}H_{22}O_3$ requires C, 69.0; H, 9.8%).

1-Acetoxymethyl-5-*tert*-butyldimethylsilyloxymethyl-2,6,6-trimethylcyclohex-1-ene 75a. Triethylamine (1.67 ml, 11.9 mmol) was added portionwise over 5 min to a stirred solution of the alcohol **74** (2.24 g, 9.91 mmol), *tert*-butyldimethylsilyl chloride (1.80 g, 11.9 mmol) and 4-dimethylaminopyridine (122 mg, 0.99 mmol) in dry dichloromethane (30 ml) at 0 °C under nitrogen. The mixture was allowed to warm to room temperature over a period of 12 h and then diluted with dichloromethane (30 ml) and saturated aqueous ammonium chloride (100 ml). The organic layer was separated and the aqueous layer was re-extracted with dichloromethane (2 × 60 ml). The combined organic extracts were dried and evaporated *in vacuo* to a yellow oil which was purified by chromatography on silica, eluting with 30% ether in light petroleum (bp 40–60 °C), to give the *silyl ether* (3.16 g, 94%) as a colourless oil; ν_{max}(film)/cm^{-1} 1738, 1471 and 774; δ_H(400 MHz) 4.57 (s, 2H, CH_2OAc), 3.83 (dd, *J* 10, 4 Hz, 1H, CH*H*OTBDMS), 3.37 (dd, *J* 10, 10 Hz, 1H, C*H*HOTBDMS), 2.04 (s, 3H, COCH_3), 2.06–1.95 [obs. m, 2H, =C(Me)CH_2], 1.88–1.82 (m, 1H, CHCH*H*), 1.67 (s, 3H, Me), 1.51–1.37 (m, 2H, C*HCH*H), 1.07 (s, 3H, Me), 0.89 [s, 9H, SiC(CH_3)$_3$], 0.84 (s, 3H, Me), 0.05 [s, 6H, Si(CH_3)$_2$]; δ_C(67.8 MHz) 171.4 (s), 136.5 (s), 132.2 (s), 63.2 (t), 61.0 (t), 46.9 (d), 36.4 (s), 31.2 (t), 26.6 (q), 26.0 (q), 22.3 (q), 21.3 (t), 21.1 (q), 19.9 (q), 18.3 (s), −5.3 (q) (Found: M$^+$ − AcOH, 280.2185. $C_{17}H_{32}OSi$ requires *M*, 280.2222).

5-*tert*-Butyldimethylsilyloxymethyl-1-hydroxymethyl-2,6,6-trimethylcyclohex-1-ene 75b. Potassium carbonate (3.99 g, 27.3 mmol) was added in one portion to a stirred solution of the acetate **75a** (3.16 g, 9.1 mmol) in methanol (91 ml) at room temperature under nitrogen. The solution was stirred at room temperature for 14 h and then diluted with ether (200 ml) and water (200 ml). The organic layer was separated and the aqueous layer was re-extracted with ether (2 × 100 ml). The combined organic extracts were dried and evaporated *in vacuo* to give a white solid which was purified by chromatography on silica, eluting with 50% ether in light petroleum (bp 40–60 °C), to give the *alcohol* (2.64 g, 95%) as a white crystalline solid, mp 50–51 °C (from pentane); ν_{max}(film)/cm^{-1} 3344, 1471 and 774; δ_H(400 MHz) 4.12 (app. q, *J* 12 Hz, 2H, CH_2OH), 3.78 (dd, *J* 10, 4 Hz, 1H, CH*H*OTBDMS), 3.37 (dd, *J* 10, 10 Hz, 1H, C*H*HOTBDMS), 2.00–1.97 [m, 2H, =C(Me)CH_2], 1.84–1.79 (m, 1H, CHCH*H*), 1.76 (s, 3H, Me), 1.47–1.36 (m, 2H, C*HCH*H), 1.14 (s, 3H, Me), 0.89 [s, 9H, SiC(CH_3)$_3$], 0.87 (s, 3H, Me), 0.05 [s, 6H, Si(CH_3)$_2$]; δ_C(67.8 MHz) 137.7 (s), 133.9 (s), 63.7 (t) 58.7 (t), 46.9 (d), 36.3 (s), 31.5 (t), 27.1 (q), 25.9 (q), 22.3 (q), 21.5 (t), 19.7 (q), 18.2 (s), −5.4 (q) (Found: M$^+$ − ^{t}Bu − H_2O, 223.1502. $C_{13}H_{23}OSi$ requires *M*, 223.1518) (Found: C, 68.4; H, 11.9. $C_{17}H_{34}O_2Si$ requires C, 68.5; H, 11.5%).

5-*tert*-Butyldimethylsilyloxymethyl-1-formyl-2,6,6-trimethylcyclohex-1-ene 76. Treatment of a solution of the alcohol **75b** (1.12 g, 3.76 mmol) in dry dichloromethane with tetra(*n*-propyl)-ammonium perruthenate and 4-methylmorpholine *N*-oxide, according to the general procedure, gave the title aldehyde (1.1 g, 97%) as an unstable colourless oil; λ_{max}(EtOH)/nm 247 (ε/dm^3 mol^{-1} cm^{-1} 15 000); ν_{max}(film)/cm^{-1} 1674, 1613 and 775; δ_H(400 MHz) 10.11 (s, 1H, C*H*O), 3.82 (dd, *J* 10, 4 Hz, 1H, CH*H*O-TBDMS), 3.37 (dd, *J* 10, 9 Hz, 1H, C*H*HOTBDMS), 2.24–2.21 [m, 2H, =C(Me)CH_2], 2.10 (s, 3H, Me), 1.91–1.88 (m, 1H, CHCH*H*), 1.46–1.41 (m, 2H, C*HCH*H), 1.31 (s, 3H, Me), 1.08 (s, 3H, Me), 0.90 [s, 9H, SiC(CH_3)$_3$], 0.06 [s, 6H, Si(CH_3)$_2$]; δ_C(67.8 MHz) 192.2 (d), 156.1 (s), 140.4 (s), 62.9 (t), 47.7 (d), 35.3 (s), 34.5 (t), 26.7 (q), 25.6 (q), 21.4 (q), 20.6 (t), 19.4 (q), 18.2 (s), −5.4 (q); which was used immediately.

5-*tert*-Butyldimethylsilyloxymethyl-1-(6-*tert*-butyldiphenylsilyloxy-1-hydroxy-3-methylenehexyl)-2,6,6-trimethylcyclohex-1-ene 77. Sodium iodide (0.66 g, 4.39 mmol) and tin(II) chloride dihydrate (0.99 g, 4.39 mmol) were added in one portion to a stirred solution of the aldehyde **76** (1.24 g, 4.18 mmol) and the bromide **73c** (2.10 g, 5.02 mmol) in dry dimethylformamide (42 ml) at room temperature under nitrogen. The mixture was stirred at room temperature for 4 h and then diluted with ether (400 ml) and water (5 ml). The suspension was dried with magnesium sulfate and then filtered through a short plug of Celite. The filtrate was diluted with water (200 ml) and the organic layer was separated. The aqueous layer was re-extracted with ether (2 × 200 ml) and the combined organic extracts were dried and evaporated *in vacuo* to an orange oil, which was purified by chromatogaphy on silica, eluting with 5% ether in light petroleum (bp 40–60 °C), to give two diastereoisomers (5:4 ratio) of the *alcohol* (2.2 g, 82%) as a colourless oil; (data for major diastereoisomer): λ_{max}(EtOH)/nm 217 (ε/dm^3 mol^{-1} cm^{-1} 16 800), 252 (800); ν_{max}(film)/cm^{-1} 1956, 1888, 1821, 1674, 1642 and 702; δ_H(400 MHz) 7.75–7.69 (m, 4H, Ar-H), 7.46–7.33 (m, 6H, Ar-H), 4.91 (s, 2H, C=CH_2), 4.38 (br d, *J* 11 Hz, 1H, C*H*OH), 3.81–3.76 (m, 1H, CH*H*OTBDMS), 3.71 (t, *J* 6 Hz, 2H, CH_2OTBDPS), 3.41–3.31 (m, 1H, C*H*HOTBDMS), 2.71–2.60 [m, 1H, CH(OH)CH*H*], 2.29–2.11 [m, 3H, =C(Me)CH_2, CH(OH)C*H*H], 2.01–1.97 (m, 2H, CH_2CH$_2$CH$_2$OTBDPS), 1.90 (s, 3H, Me), 1.87–1.65 (m, 3H, CHCH*H*, CH_2CH$_2$OTB-DPS), 1.52–1.39 (m, 2H, C*HCH*H), 1.23 (s, 3H, Me), 1.09 (obs. s, 3H, Me), 1.08 [s, 9H, SiC(CH_3)$_3$], 0.93 [s, 9H, SiC(CH_3)$_3$], 0.08 [s, 6H, Si(CH_3)$_2$]; δ_C(67.8 MHz) 147.2 (s), 138.6 (s), 135.5 (d), 133.9 (s), 132.3 (s), 129.5 (d), 127.5 (d), 112.1 (t), 67.9 (d), 63.6 (t), 63.4 (t), 47.2 (d), 43.6 (t), 37.1 (s), 32.4 (t), 31.9 (t), 30.7 (t), 27.4 (q), 26.8 (q), 25.9 (q), 21.4 (t), 21.2 (q), 19.2 (s), 18.2 (s), 15.2 (q), −5.3 (q).

5-*tert*-Butyldimethylsilyloxymethyl-1-(6-*tert*-butyldiphenylsilyloxy-1-methoxy-3-methylenehexyl)-2,6,6-trimethylcyclohex-1-ene 78a. Potassium hexamethyldisilazide (0.47 g, 2.36 mmol) was added portionwise over 5 min to a stirred solution of the alcohol **77** (0.75 g, 1.18 mmol) in dry THF (24 ml) at −78 °C under nitrogen. The solution was stirred at −78 °C for 7 min and then dimethyl sulfate (0.56 ml, 17.7 mmol) was added dropwise over 5 min. The mixture was warmed to room temperature over 30 min and then diluted with ether (50 ml) and water (50 ml). The organic layer was separated and the aqueous layer was re-extracted with ether (2 × 50 ml). The combined organic extracts were dried and evaporated *in vacuo* to a colourless oil, which was purified by chromatography on silica, eluting with 10% ether in light petroleum (bp 40–60 °C), to give two diastereoisomers (5:4 ratio) of the *methyl ether* (0.75 g, 97%) as a colourless oil; (data for major diastereoisomer): λ_{max}/nm 248 (ε/dm^3 mol^{-1} cm^{-1} 400), 254 (500), 260 (600), 264 (600), 271 (400); ν_{max}(film)/cm^{-1} 1956, 1888, 1821, 1462, 836 and 701; δ_H(270 MHz) 7.75–7.69 (m, 4H, Ar-H), 7.46–7.33 (m, 6H, Ar-H), 4.85 (s, 2H, C=CH_2), 4.02–3.96 (m, 1H, C*H*OMe), 3.87–

3.79 (m, 1H, CH*H*OTBDMS), 3.74 (t, *J* 6 Hz, 2H, CH_2OTBDPS), 3.47–3.39 (m, 1H, C*H*HOTBDMS), 3.23 (s, 3H, OCH_3), 2.65–2.55 [m, 1H, CH(OMe)CH*H*], 2.29–2.20 [m, 3H, =C(Me)CH_2, CH(OMe)C*H*H], 2.04–1.97 (m, 2H, CH_2CH_2CH$_2$OTBDPS), 1.85 (s, 3H, Me), 1.89–1.72 (m, 3H, CHCH*H*, CH_2CH$_2$OTBDPS), 1.68–1.40 (m, 2H, C*H*CH*H*), 1.24 (s, 3H, Me), 1.10 [s, 9H, SiC(CH_3)$_3$], 1.08 (s, 3H, Me), 0.94 [s, 9H, SiC(CH_3)$_3$], 0.10 [s, 6H, Si(CH_3)$_2$]; δ_C(67.8 MHz) 147.6 (s), 135.5 (s), 135.5 (d), 134.0 (s), 131.8 (s), 129.5 (d), 127.6 (d), 110.2 (t), 78.0 (d), 63.6 (t), 63.0 (t), 56.0 (q), 47.8 (d), 42.8 (t), 36.4 (s), 32.1 (t), 31.4 (t), 30.8 (t), 28.9 (q), 26.8 (q), 25.9 (q), 23.4 (q), 20.9 (t), 20.4 (q), 19.2 (s), 18.2 (s), −5.3 (q).

1-(6-*tert*-Butyldiphenylsilyloxy-1-methoxy-3-methylenehexyl)-5-hydroxymethyl-2,6,6-trimethylcyclohex-1-ene 78b. Pyridinium toluene-*p*-sulfonate (2.21 g, 8.80 mmol) was added in one portion to a solution of the silyl ether **78a** (1.14 g, 1.76 mmol) in methanol (18 ml) at room temperature under nitrogen. The solution was stirred at room temperature for 4.5 h and then diluted with ether (50 ml) and water (50 ml). The organic layer was separated and the aqueous layer was re-extracted with ether (2 × 50 ml). The combined organic extracts were dried and evaporated *in vacuo* to a colourless oil which was purified by chromatography on silica, eluting with a gradient of 5 to 70% ether in light petroleum (bp 40–60 °C), to give two diastereoisomers (5:4 ratio) of the *alcohol* (0.83 g, 88%) as a colourless oil; (data for major diastereoisomer): λ_{max}(EtOH)/nm 248 (ε/dm^3 mol^{-1} cm^{-1} 700), 253 (800), 259 (800), 264 (700), 270 (500); ν_{max}(film)/cm^{-1} 3416, 1890, 1824, 1644, 1471 and 702; δ_H(400 MHz) 7.70–7.66 (m, 4H, Ar-H), 7.44–7.36 (m, 6H, Ar-H), 4.81 (s, 2H, C=CH_2), 4.00–3.91 (m, 1H, C*H*OMe), 3.91–3.79 (m, 1H, CH*H*OH), 3.70 (t, *J* 6 Hz, 2H, CH_2OTBDPS), 3.52–3.39 (m, 1H, C*H*HOH), 3.20 (s, 3H, OCH_3), 2.67–2.51 [m, 1H, CH(OMe)CH*H*], 2.29–2.13 [m, 3H, =C(Me)CH_2, CH(OMe)C*H*H], 2.08–1.98 (m, 2H, CH_2CH$_2$CH$_2$OTBDPS), 1.82 (s, 3H, Me), 1.95–1.70 (m, 3H, CHCH*H*, CH_2CH$_2$OTBDPS), 1.62–1.41 (m, 2H, C*H*CH*H*), 1.21 (s, 3H, Me), 1.06 [s, 9H, SiC(CH_3)$_3$], 0.89 (s, 3H, Me); δ_C(67.8 MHz) 147.4 (s), 135.5 (s), 135.1 (d), 133.9 (s), 131.7 (s), 129.4 (d), 127.5 (d), 110.3 (t), 78.0 (d), 63.6 (t), 63.0 (t), 56.0 (q), 48.2 (d), 42.8 (t), 36.4 (s), 32.1 (t), 31.3 (t), 30.8 (t), 28.8 (q), 26.8 (q), 23.4 (q), 20.9 (t), 20.4 (q), 19.2 (s).

1-(6-*tert*-Butyldiphenylsilyloxy-1-methoxy-3-methylenehexyl)-5-formyl-2,6,6-trimethylcyclohex-1-ene 79. Dess–Martin periodinane (1.59 g, 3.37 mmol) was added in one portion to the alcohol **78b** (1.00 g, 1.87 mmol) in dry dichloromethane (20 ml) at 0 °C under nitrogen. The mixture was warmed to room temperature and the whole stirred for 3 h. The mixture was then diluted with dichloromethane (20 ml) and quenched with 5% aqueous sodium thiosulfate (10 ml). The mixture was stirred vigorously at room temperature for 20 min and then neutralised with potassium carbonate and diluted with water (20 ml). The organic layer was separated and the aqueous layer was re-extracted with dichloromethane (2 × 30 ml). The combined organic extracts were washed with saturated brine (30 ml) and then dried and concentrated *in vacuo* to a yellow oil. Purification by chromatography on silica, eluting with 30% ether in light petroleum (bp 40–60 °C), gave two diastereoisomers (5:4 ratio) of the *aldehyde* (0.93 g, 94%) as a colourless oil; (data for major diastereoisomer): λ_{max}(EtOH)/nm 254 (ε/dm^3 mol^{-1} cm^{-1} 700), 260 (900), 265 (900), 270 (700); ν_{max}(film)/cm^{-1} 3070, 2929, 1959, 1889, 1823, 1719, 1644, 1471, 1428, 1109, 823, 703; δ_H(250 MHz) 9.85 (d, *J* 3 Hz, 1H, C*H*O), 7.70–7.66 (m, 4H, Ar-H), 7.44–7.35 (m, 6H, Ar-H), 4.83 (s, 2H, C=CH_2), 4.09–3.95 (m, 1H, C*H*OMe), 3.71 (t, *J* 6 Hz, 2H, CH_2OTBDPS), 3.22 (s, 3H, OCH_3), 2.58 [d, *J* 10 Hz, 1H, CH(OMe)CH*H*], 2.29–2.14 [m, 4H, C*H*CHO, =C(Me)CH_2, CH(OMe)C*H*H], 2.13–2.06 (m, 2H, CH_2CH$_2$CH$_2$OTBDPS), 1.94–1.71 (m, 4H, CHCH_2, CH_2CH$_2$OTBDPS), 1.85 (s, 3H, Me), 1.30 (s, 3H, Me), 1.08 (s, 3H, Me), 1.07 [s, 9H, SiC(CH_3)$_3$]; δ_C(67.8 MHz) 205.8 (d), 146.8 (s), 135.0 (d), 134.5 (s), 133.4 (s), 130.9 (s), 129.0 (d), 127.0 (d), 110.0 (t), 77.5 (d), 63.1 (t), 57.5 (d), 55.6 (q), 42.3 (t), 35.4 (s), 31.6 (t), 30.5 (t), 30.3 (t), 28.2 (q), 26.3 (q), 23.9 (q), 19.8 (q), 19.7 (s), 18.8 (t) (Found: [M + NH$_4$]$^+$, 550.3720. $C_{34}H_{52}NO_3Si$ requires *M*, 550.3716).

1-(6-*tert*-Butyldiphenylsilyloxy-1-methoxy-3-methylenehexyl)-5-(1-hydroxyprop-2-enyl)-2,6,6-trimethylcyclohex-1-ene 80. A solution of vinylmagnesium chloride (1.60 ml) in THF (1.7 M, 2.68 mmol) was added dropwise over 10 min to a stirred solution of the aldehyde **79** (0.71 g, 1.34 mmol) in dry THF (14 ml) at −78 °C under nitrogen. The solution was stirred at −78 °C for 1 h and then warmed to room temperature over 1 h. The mixture was then quenched with water (30 ml) and diluted with ether (30 ml). The organic layer was separated and the aqueous layer was re-extracted with ether (2 × 30 ml). The combined organic extracts were dried and evaporated *in vacuo* to a yellow oil which was purified by chromatography on silica, eluting with a gradient of 30 to 50% ether in light petroleum (bp 40–60 °C), to give two diastereoisomers (5:4 ratio) of the *alcohol* (0.71 g, 95%) as a colourless oil; (data for major diastereoisomer): λ_{max}(EtOH)/nm 254 (ε/dm^3 mol^{-1} cm^{-1} 800), 259 (900), 264 (1000), 271 (800); ν_{max}(film)/cm^{-1} 3478, 1644 and 702; δ_H(250 MHz) 7.70–7.66 (m, 4H, Ar-H), 7.44–7.35 (m, 6H, Ar-H), 5.92 (ddd, *J* 17, 10 Hz, 5 Hz, 1H, C*H*=CH$_2$), 5.32 (ddd, *J* 17, 2, 2 Hz, 1H, CH=CH*H*), 5.17 (ddd, *J* 10, 2, 2 Hz, 1H, CH=C*H*H), 4.86 (s, 2H, C=CH_2), 4.56 (br s, 1H, C*H*OH), 4.11–4.03 (m, 1H, C*H*OMe), 3.74 (t, *J* 6 Hz, 2H, CH_2OTBDPS), 3.24 (s, 3H, OCH_3), 2.61 [dd, *J* 15, 10 Hz, 1H, CH(OMe)CH*H*], 2.31–2.21 [m, 3H, =C(Me)CH_2, CH(OMe)C*H*H], 2.09–2.02 (m, 2H, CH_2CH$_2$CH$_2$OTBDPS), 1.87 (s, 3H, Me), 1.82–1.55 (m, 4H, CHCH_2, CH_2CH$_2$OTBDPS), 1.46–1.39 (m, 1H, C*H*CH$_2$), 1.25 (s, 3H, Me), 1.13 (s, 3H, Me), 1.10 [s, 9H, SiC(CH_3)$_3$]; δ_C(67.8 MHz) 147.4 (s), 141.3 (d), 136.6 (s), 135.5 (d), 133.9 (s), 132.7 (s), 129.4 (d), 127.5 (d), 113.3 (t), 110.4 (t), 78.2 (d), 71.9 (d), 63.6 (t), 56.0 (q), 49.4 (d), 42.8 (t), 37.4 (s), 33.1 (t), 32.1 (t), 30.7 (t), 28.7 (q), 26.8 (q), 23.5 (q), 20.4 (q), 19.2 (s), 17.9 (t) (Found: [M + NH$_4$]$^+$, 578.4030. $C_{36}H_{56}NO_3Si$ requires *M*, 578.4029).

1-(6-*tert*-Butyldiphenylsilyloxy-1-methoxy-3-methylenehexyl)-5-(1-oxoprop-2-enyl)-2,6,6-trimethylcyclohex-1-ene 81a. Dess–Martin periodinane (1.07 g, 2.52 mmol) was added in one portion to the alcohol **80** (0.71 g, 1.26 mmol) in dry dichloromethane (13 ml) at 0 °C under nitrogen. The mixture was warmed to room temperature and the whole stirred for 3 h. The mixture was then diluted with dichloromethane (13 ml) and quenched with 5% aqueous sodium thiosulfate (8 ml). The mixture was stirred vigorously at room temperature for 20 min and then neutralised with potassium carbonate and diluted with water (20 ml). The organic layer was separated and the aqueous layer was re-extracted with dichloromethane (2 × 30 ml). The combined organic extracts were washed with saturated brine (30 ml) and then dried and concentrated *in vacuo* to a yellow oil. Purification by chromatography on silica, eluting with 30% ether in light petroleum (bp 40–60 °C) gave two diastereoisomers (5:4 ratio) of the *ketone* (0.61 g, 86%) as a colourless oil; (data for major diastereoisomer): λ_{max}(EtOH)/nm 254 (ε/dm^3 mol^{-1} cm^{-1} 100), 260 (300), 265 (300), 270 (100); ν_{max}(film)/cm^{-1} 1958, 1889, 1823, 1691, 1644, 1608 and 702; δ_H(400 MHz) 7.70–7.66 (m, 4H, Ar-H), 7.44–7.35 (m, 6H, Ar-H), 6.48 (dd, *J* 17, 10 Hz, 1H, C*H*=CH$_2$), 6.26 (dd, *J* 17, 1 Hz, 1H, CH=CH*H*), 5.72 (dd, *J* 10, 1 Hz, 1H, CH=C*H*H), 4.83 (s, 2H, C=CH_2), 3.95 (br d, *J* 10 Hz, 1H, C*H*OMe), 3.71 (t, *J* 6 Hz, 2H, CH_2OTBDPS), 3.19 (s, 3H, OCH_3), 2.81 (dd, *J* 12, 3 Hz, 1H, C*H*CO), 2.60 [dd, *J* 16, 10 Hz, 1H, CH(OMe)CH*H*], 2.28–2.17 [m, 3H, =C(Me)CH_2, CH(OMe)C*H*H], 2.10–2.05 (m, 2H, CH_2CH$_2$CH$_2$OTBDPS), 1.82 (obs s, 3H, Me), 1.98–1.63 (m, 4H, CHCH_2, CH_2CH$_2$OTBDPS), 1.14 (s, 3H, Me), 1.08 (s, 3H, Me), 1.07 [s, 9H, SiC(CH_3)$_3$]; δ_C(67.8 MHz) 203.4 (s), 147.5 (s), 137.3 (d), 135.4 (d), 135.4 (s), 133.9 (s), 130.7 (s), 129.4 (d), 127.5 (d), 127.1 (t), 110.2 (t), 77.9 (d), 63.5 (t), 55.9

(d), 55.6 (q), 42.7 (t), 37.4 (s), 32.1 (t), 31.5 (t), 30.7 (t), 29.1 (q), 26.8 (q), 23.8 (q), 21.7 (t), 20.1 (q), 19.1 (s).

1-(6-Hydroxy-1-methoxy-3-methylenehexyl)-5-(1-oxoprop-2-enyl)-2,6,6-trimethylcyclohex-1-ene 81b. Tetrabutylammonium fluoride (0.34 g, 1.08 mmol) was added in one portion to a stirred solution of the silyl ether **81a** (0.10 g, 0.18 mmol) and toluene-*p*-sulfonic acid (0.07 g, 0.54 mmol) in THF (11 ml) at 0 °C under nitrogen. The solution was allowed to warm to room temperature where it was stirred for 60 h. The mixture was then diluted with ether (20 ml) and water (20 ml) and the organic layer was separated. The aqueous layer was re-extracted with ether (2 × 20 ml) and the combined organic extracts were dried and evaporated *in vacuo* to a yellow oil which was purified by chromatography on silica, eluting with 70% ether in light petroleum (bp 40–60 °C), to give two diastereoisomers (5:4 ratio) of the *alcohol* (0.06 g, 97%) as a colourless oil; (data for major diastereoisomer): ν_{max}(film)/cm^{-1} 3424, 1684, 1644, 1608 and 891; δ_H(270 MHz) 6.36 (dd, *J* 17, 10, 1H, C*H*=CH$_2$), 6.16 (dd, *J* 17, 1, 1H, CH=CH*H*), 5.63 (dd, *J* 10, 1, 1H, CH=C*H*H), 4.76 (s, 2H, C=CH_2), 3.92 (br d, *J* 10, 1H, C*H*OMe), 3.56 (t, *J* 6, 2H, CH_2OH), 3.14 (s, 3H, OCH_3), 2.74–2.70 (m, 1H, C*H*CO), 2.57–2.47 [m, 1H, CH(OMe)CH*H*], 2.24–2.18 [m, 1H, CH(OMe)C*H*H], 2.11–2.06 [m, 2H, =C(Me)CH_2], 1.72 (obs. s, 3H, Me), 2.00–1.60 (m, 6H, CHCH_2, CH_2CH_2CH$_2$OH), 1.16 (s, 3H, Me), 1.05 (s, 3H, Me); δ_C(67.8 MHz) 203.7 (s), 147.2 (s), 137.1 (d), 135.1 (s), 130.5 (s), 127.4 (t), 110.3 (t), 78.0 (d), 62.1 (t), 55.8 (d), 55.5 (q), 42.2 (t), 37.2 (s), 32.1 (t), 31.3 (t), 30.4 (t), 29.0 (q), 23.7 (q), 21.5 (t), 20.0 (q) (Found: M$^+$ − MeOH, 288.2088. $C_{19}H_{28}O_2$ requires *M*, 288.2089).

1-(1-Methoxy-3-methylene-6-*p*-tolylsulfonylhexyl)-5-(1-oxoprop-2-enyl)-2,6,6-trimethylcyclohex-1-ene 81c. Toluene-*p*-sulfonyl chloride (65 mg, 0.34 mmol) was added in one portion to a stirred solution of the alcohol **81b** (55 mg, 0.17 mmol) and triethylamine (120 μl, 1.36 mmol) in dry dichloromethane (3.4 ml) at room temperature under nitrogen. The mixture was stirred at room temperature for 24 h and then concentrated *in vacuo* to a yellow oil which was purified by chromatography on silica, eluting with 10% ether in light petroleum (bp 40–60 °C), to give two diastereoisomers (5:4 ratio) of the *tosylate* (0.064 g, 79%) as a colourless oil; (data for major diastereoisomer): λ_{max}(EtOH)/nm 254 (ε/dm^3 mol^{-1} cm^{-1} 800), 262 (800), 266 (800), 273 (700); ν_{max}(film)/cm^{-1} 1805, 1682, 1599 and 814; δ_H(400 MHz) 7.80 (d, *J* 8, 2H, Ar-H), 7.35 (d, *J* 8, 2H, Ar-H), 6.47 (dd, *J* 17, 10, 1H, C*H*=CH$_2$), 6.24 (dd, *J* 17, 1, 1H, CH=CH*H*), 5.73 (dd, *J* 10, 1, 1H, CH=C*H*H), 4.81 (s, 2H, C=CH_2), 4.05 (t, *J* 6, 2H, CH_2OTos), 3.90 (br d, *J* 10, 1H, C*H*OMe), 3.19 (s, 3H, OCH_3), 2.81–2.77 (m, 1H, C*H*CO), 2.59–2.48 [m, 1H, CH(OMe)CH*H*], 2.45 (s, 3H, ArCH_3), 2.24–2.18 [m, 1H, CH(OMe)C*H*H], 2.16–2.10 [m, 2H, =C(Me)CH_2], 1.79 (obs. s, 3H, Me), 2.06–1.70 (m, 6H, CHCH_2, CH_2CH_2-CH$_2$OTos), 1.21 (s, 3H, Me), 1.13 (s, 3H, Me); δ_C(67.8 MHz) 203.4 (s), 145.9 (s), 144.4 (s), 137.1 (d), 134.4 (s), 132.9 (s), 130.5 (s), 129.6 (d), 127.6 (d), 127.2 (t), 110.9 (t), 78.1 (d), 69.9 (t), 55.5 (d), 55.5 (q), 42.1 (t), 37.1 (s), 31.5 (t), 31.4 (t), 29.0 (q), 26.6 (t), 23.7 (q), 21.5 (t), 21.4 (q), 19.9 (q) (Found: M$^+$ − MeOH, 422.2180. $C_{26}H_{34}O_4S$ requires 422.2178).

1-(6-Iodo-1-methoxy-3-methylenehexyl)-5-(1-oxoprop-2-enyl)-2,6,6-trimethylcyclohex-1-ene 65a. A stirred suspension of sodium iodide (78 mg, 0.51 mmol), butan-2-one (9 ml) and the tosylate **81c** (83 mg, 0.18 mmol) was heated at reflux for 90 min and then cooled. Water (15 ml) and ether (15 ml) were then added and the organic layer was separated. The aqueous layer was re-extracted with ether (2 × 10 ml) and the combined organics were washed with 5% aqueous sodium thiosulfate (15 ml) and then dried and evaporated *in vacuo* to give two diastereoisomers (5:4 ratio) of the *iodide* (70 mg, 93%) as a colourless oil; (data for major diastereoisomer): ν_{max}(film)/cm^{-1} 1689, 1644, 1608 and 892; δ_H(270 MHz) 6.44 (dd, *J* 17, 10, 1H, C*H*=CH$_2$), 6.24 (dd, *J* 17, 1 Hz, 1H, CH=CH*H*), 5.72 (dd, *J* 10, 1, 1H, CH=C*H*H), 4.84 (s, 2H, C=CH_2), 4.01–3.88 (m, 1H, C*H*OMe), 3.22 (s, 3H, OCH_3), 3.20 (obs. t, *J* 6, 2H, CH_2I), 2.81–2.76 (m, 1H, C*H*CO), 2.64–2.51 [m, 1H, CH(OMe)CH*H*], 2.28–2.14 [m, 3H, CH(OMe)C*H*H, CH_2CH$_2$CH$_2$I], 2.06–1.81 [m, 5H, =C(Me)CH_2CH*H*, CH_2CH$_2$I], 1.80 (s, 3H, Me), 1.68–1.56 (m, 1H, CHC*H*H), 1.23 (s, 3H, Me), 1.12 (s, 3H, Me); δ_C(67.8 MHz) 203.6 (s), 145.9 (s), 137.3 (d), 135.3 (s), 130.7 (s), 127.3 (t), 111.4 (t), 78.0 (d), 55.8 (d), 55.6 (q), 42.3 (t), 37.4 (s), 36.5 (t), 31.4 (t), 31.3 (t), 29.2 (q), 23.9 (q), 21.7 (t), 20.1 (q), 6.8 (t); which was used without further purification.

1-(1-Methoxy-3-methylenehexyl)-5-(1-oxoprop-2-enyl)-2,6,6-trimethylcyclohex-1-ene 65b. Treatment of a solution of the iodide **65a** (55 mg, 0.13 mmol) in benzene with tri-*n*-butyltin hydride and azoisobutyronitrile, according to the general procedure, gave two diastereoisomers (5:4 ratio) of the title cyclohexene (12 mg, 31%) as a colourless oil; (data for major diastereoisomer): ν_{max}(film)/cm^{-1} 1689, 1644, 1609 and 891; δ_H(250 MHz) 6.44 (dd, *J* 17, 10, 1H, C*H*=CH$_2$), 6.21 (dd, *J* 17, 1, 1H, CH=CH*H*), 5.68 (dd, *J* 10, 1, 1H, CH=C*H*H), 4.80 (s, 2H, C=CH_2), 4.03–3.93 (m, 1H, C*H*OMe), 3.21 (s, 3H, OCH_3), 2.82–2.74 (m, 1H, C*H*CO), 2.27–2.14 [m, 1H, CH(OMe)-CH*H*], 2.14–2.01 [m, 1H, CH(OMe)C*H*H], 2.09–1.72 [m, 4H, =C(Me)CH_2, CH_2CH$_2$CH$_3$], 1.79 (obs. s, 3H, Me), 1.70–1.52 (m, 4H, CHCH_2, CH_2CH$_3$), 1.24 (s, 3H, Me), 1.22 (s, 3H, Me), 0.89 (t, *J* 7, 3H, CH$_2$CH_3); δ_C(67.8 MHz) 204.0 (s), 147.7 (s), 137.4 (d), 135.7 (s), 130.8 (s), 127.5 (t), 110.1 (t), 77.8 (d), 55.8 (d), 55.8 (q), 42.4 (t), 38.2 (t), 37.5 (s), 31.6 (t), 29.2 (q), 23.8 (q), 21.8 (t), 20.9 (t), 20.2 (q), 13.9 (q) (Found: M$^+$, 304.2404. $C_{20}H_{32}O_2$ requires *M*, 304.2402).

1-(6-*tert*-Butyldiphenylsilyloxy-1-methoxy-3-methylenehexyl)-5-(1-hydroxyprop-2-ynyl)-2,6,6-trimethylcyclohex-1-ene 82. A solution of ethynylmagnesium chloride (4.0 ml) in THF (0.5 M, 1.98 mmol) was added dropwise over 10 min to a stirred solution of the aldehyde **79** (0.88 g, 1.65 mmol) in dry THF (16 ml) at −78 °C under nitrogen. The solution was stirred at −78 °C for 1 h and then warmed to −30 °C over 1 h. The mixture was then quenched with water (30 ml) and diluted with ether (30 ml). The organic layer was separated and the aqueous layer was re-extracted with ether (2 × 30 ml). The combined organic extracts were dried and evaporated *in vacuo* to a yellow oil which was purified by chromatography on silica, eluting with 30% ether in light petroleum (bp 40–60 °C), to give two diastereoisomers (5:4 ratio) of the *alcohol* (0.90 g, 97%) as a colourless oil; (data for major diastereoisomer): λ_{max}(EtOH)/nm 254 (ε/dm^3 mol^{-1} cm^{-1} 900), 259 (1100), 264 (1100), 27 (800); ν_{max}(film)/cm^{-1} 3428, 3306, 2089, 1956, 1890, 1823 and 702; δ_H(250 MHz) 7.70–7.63 (m, 4H, Ar-H), 7.45–7.38 (m, 6H, Ar-H), 4.82 (s, 2H, C=CH_2), 4.75–4.70 (m, 1H, C*H*OH), 4.03–3.99 (m, 1H, C*H*OMe), 3.70 (t, *J* 6, 2H, CH_2OTBDPS), 3.22 (s, 3H, OCH_3), 2.57 [dd, *J* 15, 10, 1H, CH(OMe)CH*H*], 2.49 (d, *J* 2, 1H, alkyne-H), 2.21–2.07 [m, 5H, CH_2CH$_2$CH$_2$OTBDPS, =C(Me)CH_2, CH(OMe)C*H*H], 1.86 (obs. s, 3H, Me), 1.95–1.69 (m, 4H, CHCH_2, CH_2CH$_2$OTBDPS), 1.66–1.59 (m, 1H, C*H*CHOH), 1.58 (s, 1H, O*H*), 1.23 (s, 3H, Me), 1.08 (obs. s, 3H, Me), 1.08 [obs. s, 9H, SiC(CH_3)$_3$]; δ_C(67.8 MHz) 147.9 (s), 136.6 (s), 136.0 (d), 134.5 (s), 133.1 (s), 129.9 (d), 128.0 (d), 110.9 (t), 86.0 (s), 78.6 (d), 73.2 (d), 64.1 (t), 63.6 (d), 56.6 (q), 51.1 (d), 43.3 (t), 37.7 (s), 33.2 (t), 32.6 (t), 31.2 (t), 29.4 (q), 27.3 (q), 24.1 (q), 20.8 (q), 19.7 (t), 19.7 (s) (Found: M$^+$ − ^{t}Bu − MeOH, 469.2596. $C_{31}H_{37}O_2Si$ requires *M*, 469.2563).

1-(6-*tert*-Butyldiphenylsilyloxy-1-methoxy-3-methylenehexyl)-5-(1-oxoprop-2-ynyl)-2,6,6-trimethylcyclohex-1-ene 83a. Dess–Martin periodinane (1.21 g, 2.86 mmol) was added in one portion to the alcohol **82** (0.80 g, 1.43 mmol) in dry dichloromethane (14 ml) at 0 °C under nitrogen. The mixture was warmed to room temperature and the whole stirred for 3 h. The mixture was then diluted with dichloromethane (14 ml) and quenched with 5% aqueous sodium thiosulfate (8 ml). The mixture was stirred vigorously at room temperature for 20 min and then neutralised with potassium carbonate and diluted with water (20 ml). The organic layer was separated and the aqueous

layer was re-extracted with dichloromethane (2 × 30 ml). The combined organic extracts were washed with saturated brine (30 ml) and then dried and concentrated *in vacuo* to a yellow oil. Purification by chromatography on silica, eluting with 30% ether in light petroleum (bp 40–60 °C), gave two diastereoisomers (5:4 ratio) of the *ketone* (0.74 g, 93%) as a colourless oil; (data for the major diastereoisomer): λ_{max}(EtOH)/nm 247 (ε/dm^3 mol^{-1} cm^{-1} 800), 253 (900), 260 (1000), 264 (1000), 271 (800); ν_{max}(film)/cm^{-1} 3268, 2090, 1958, 1889, 1824 and 702; δ_H(270 MHz) 7.70–7.63 (m, 4H, Ar-H), 7.45–7.38 (m, 6H, Ar-H), 4.83 (s, 2H, C=CH_2), 4.03–3.98 (m, 1H, C*H*OMe), 3.71 (t, *J* 6, 2H, CH_2OTBDPS), 3.25 (s, 1H, alkyne-H), 3.22 (s, 3H, OCH_3), 2.68–2.55 [m, 2H, CH(OMe)CH*H*, C*H*CO], 2.29–2.16 [m, 3H, CH_2CH$_2$CH$_2$OTBDPS, CH(OMe)C*H*H], 2.07–2.01 [m, 2H, =C(Me)CH_2], 1.99–1.92 (m, 2H, CHCH_2), 1.84 (s, 3H, Me), 1.80–1.70 (m, 2H, CH_2CH$_2$OTBDPS), 1.31 (s, 3H, Me), 1.07 (obs. s, 3H, Me), 1.07 [obs. s, 9H, SiC(CH_3)$_3$]; δ_C(67.8 MHz) 190.2 (s), 147.5 (s), 135.5 (d), 134.9 (s), 134.0 (s), 131.3 (s), 129.5 (d), 127.6 (d), 110.4 (t), 82.5 (s), 78.6 (d), 78.0 (d), 63.6 (t), 60.2 (d), 56.2 (q), 42.6 (t), 37.1 (s), 32.1 (t), 31.5 (t), 30.8 (t), 28.5 (q), 26.8 (q), 23.8 (q), 21.6 (t), 20.2 (q), 19.2 (s).

1-(6-Hydroxy-1-methoxy-3-methylenehexyl)-5-(1-oxoprop-2-ynyl)-2,6,6-trimethylcyclohex-1-ene 83b. Tetrabutylammonium fluoride (1.53 g, 4.86 mmol) was added in one portion to a stirred solution of the silyl ether **83a** (0.45 g, 0.81 mmol) and toluene-*p*-sulfonic acid (0.46 g, 2.43 mmol) in THF (48 ml) at 0 °C under nitrogen. The solution was allowed to warm to room temperature where it was stirred for 72 h. The mixture was then diluted with ether (100 ml) and water (100 ml) and the organic layer was separated. The aqueous layer was re-extracted with ether (2 × 100 ml) and the combined organic extracts were dried and evaporated *in vacuo* to a yellow oil which was purified by chromatography on silica, eluting with 70% ether in light petroleum (bp 40–60 °C), to give two diastereoisomers (5:4 ratio) of the *alcohol* (0.24 g, 93%) as a colourless oil; (data for major diastereoisomer): ν_{max}(film)/cm^{-1} 3406, 3252, 2088, 1666 and 892; δ_H(270 MHz) 5.03 (s, 2H, C=CH_2), 3.91 (br d, *J* 9, 1H, C*H*OMe), 3.65 (t, *J* 6, 2H, CH_2OH), 3.32 (s, 1H, alkyne-H), 3.16 (s, 3H, OCH_3), 2.64–2.53 [m, 2H, CH(OMe)CH*H*, C*H*CO], 2.26–2.10 [m, 3H, CH(OMe)C*H*H, CH_2CH$_2$CH$_2$OH], 2.07–1.96 [m, 2H, =C(Me)CH_2], 1.96–1.86 (m, 2H, CHCH_2), 1.78 (s, 3H, Me), 1.77–1.68 (m, 2H, CH_2CH$_2$OH), 1.16 (s, 3H, Me), 1.15 (s, 3H, Me); δ_C(67.8 MHz) 191.0 (s), 147.3 (s), 134.9 (s), 130.9 (s), 110.5 (t), 82.6 (s), 79.6 (d), 78.0 (d), 62.5 (t), 60.0 (d), 55.6 (q), 42.3 (t), 37.6 (s), 32.4 (t), 32.2 (t), 30.6 (t), 28.6 (q), 22.8 (q), 21.5 (t), 20.2 (q) (Found: M$^+$ − MeOH, 286.1931. $C_{19}H_{26}O_2$ requires *M*, 286.1933).

1-(6-Iodo-1-methoxy-3-methylenehexyl)-5-(1-oxoprop-2-ynyl)-2,6,6-trimethylcyclohex-1-ene 66a. Imidazole (0.05 g, 0.74 mmol) was added in one portion to a solution of triphenylphosphine (0.20 g, 0.74 mmol) in dry dichloromethane (4.0 ml) at 0 °C under nitrogen. The mixture was stirred at 0 °C for 10 min, until the imidazole had dissolved, and then iodine (0.19 g, 0.74 mmol) was added in one portion. The mixture was stirred at 0 °C for 5 min and then a solution of the alcohol **83b** (0.20 g, 0.62 mmol) in dry dichloromethane (2.2 ml) was added dropwise over 2 min. The mixture was warmed to room temperature, stirred for 30 min, and then concentrated *in vacuo* to a yellow oil. Purification by chromatography on silica, eluting with 5% ether in light petroleum (bp 40–60 °C), gave two diastereoisomers (5:4 ratio) of the *iodide* (0.18 g, 68%) as a colourless oil; (data for major diastereoisomer): ν_{max}(film)/cm^{-1} 3257, 2089, 1666, 1574 and 733; δ_H(270 MHz) 4.86 (s, 2H, C=CH_2), 3.91 (br d, *J* 10, 1H, C*H*OMe), 3.25 (s, 1H, alkyne-H), 3.21 (obs. t, *J* 6, 2H, CH_2I), 3.20 (s, 3H, OCH_3), 2.66–2.47 [m, 2H, CH(OMe)CH*H*, C*H*CO], 2.26–2.14 [m, 3H, CH(OMe)C*H*H, CH_2CH$_2$CH$_2$I], 2.10–1.90 (m, 6H, CHCH_2CH_2, CH_2CH$_2$I), 1.79 (s, 3H, Me), 1.18 (s, 3H, Me), 1.16 (s, 3H, Me); δ_C(67.8 MHz) 190.9 (s), 145.8 (s), 135.0 (s), 130.9 (s), 111.4 (t), 82.4 (s), 78.6 (d), 78.0 (d), 60.1 (d), 55.8 (q), 42.3 (t), 37.6 (s), 36.5 (t), 31.4 (t), 31.3 (t), 28.6 (q), 23.8 (q), 21.6 (t), 20.1 (q), 6.8 (t).

1-(1-Methoxy-3-methylenehexyl)-5-(1-oxoprop-2-ynyl)-2,6,6-trimethylcyclohex-1-ene 66b. Treatment of a solution of the iodide **66a** (180 mg, 0.42 mmol) in benzene with tri-*n*-butyltin hydride and azoisobutyronitrile, according to the general procedure, gave two diastereoisomers (5:4 ratio) of the title cyclohexene (61 mg, 48%) as a colourless oil; (data for major diastereoisomer): ν_{max}(film)/cm^{-1} 3252, 2089, 1668 and 892; δ_H(400 MHz) 4.82 (s, 2H, C=CH_2), 3.93 (br d, *J* 10, 1H, C*H*OMe), 3.24 (s, 1H, alkyne-H), 3.19 (s, 3H, OCH_3), 2.66–2.54 [m, 2H, CH(OMe)CH*H*, C*H*CO], 2.26–2.17 [m, 1H, CH(OMe)C*H*H], 2.14–2.04 [m, 4H, =C(Me)CH_2, CH_2CH$_2$-CH$_3$], 2.03–1.96 (m, 2H, CHCH_2), 1.81 (s, 3H, Me), 1.56–1.44 (m, 2H, CH_2CH$_3$), 1.20 (s, 3H, Me), 1.18 (s, 3H, Me), 0.92 (t, *J* 7, 3H, CH$_2$CH_3); δ_C(67.8 MHz) 191.0 (s), 147.6 (s), 135.3 (s), 130.8 (s), 110.0 (t), 82.7 (s), 78.6 (d), 77.8 (d), 60.1 (d), 55.8 (q), 42.4 (t), 38.2 (t), 37.7 (s), 31.5 (t), 28.6 (q), 22.8 (q), 21.6 (t), 20.8 (t), 20.3 (q), 13.9 (q) (Found: M$^+$, 302.2233. $C_{20}H_{36}O_2$ requires *M*, 302.2246).

2,4-Dimethyl-3-(2-hydroxyethyl)penta-2,4-diene 88a. A solution of t-butyllithium (6.72 ml) in pentane (1.7 M, 11.4 mmol) was added dropwise over 10 min to a stirred solution of 3-bromo-2,4-dimethylpenta-2,4-diene[26] (1.04 g, 5.7 mmol) in dry THF (40 ml) at −78 °C under nitrogen. The mixture was stirred for 30 min at −78 °C, and then excess ethylene oxide was bubbled through the yellow solution for 5 min. The mixture was stirred at −78 °C for 30 min, and then warmed to −40 °C over 45 min. The solution was quenched with water (10 ml), and the organic layer was then separated, dried and concentrated *in vacuo* to leave a yellow residue. The residue was purified by chromatography on silica eluting with 35% ether in hexane to give the *alcohol* (0.56 g, 70%) as a colourless oil; ν_{max}(film)/cm^{-1} 3402, 1642 and 886; δ_H(250 MHz) 4.97 (s, 1H, =CH_2), 4.59 (s, 1H, =CH_2), 3.60 (t, *J* 7, 2H, CH_2OH), 2.42 (t, *J* 7, 2H, CH_2CH$_2$OH), 1.78 (s, 3H, Me), 1.72 (s, 3H, Me), 1.69 (s, 3H, Me); δ_C(67.8 MHz) 146.8 (s), 134.2 (s), 128.1 (s), 113.7 (t), 61.0 (t), 34.2 (t), 23.1 (q), 22.8 (q), 19.7 (q) (Found: M$^+$, 140.1204. $C_9H_{16}O$ requires *M*, 140.1201) (Found: C, 76.7; H, 11.3. $C_9H_{16}O$ requires C, 77.1; H, 11.5%).

3-(2-Acetoxyethyl)-2,4-dimethylpenta-2,4-diene 88b. A solution of acetyl chloride (3.27 ml, 46.0 mmol), triethylamine (6.40 ml, 46.0 mmol), 4-dimethylaminopyridine (28 mg, 2.3 mmol) and the diene alcohol 88a (4.30 g, 31.0 mmol) in dry dichloromethane (50 ml) was stirred at room temperature for 4 h. The yellow mixture was quenched with water (40 ml) and the organic layer was then separated and washed with saturated aqueous sodium hydrogen bicarbonate (2 × 25 ml) and brine (20 ml). Evaporation of the dried organic extracts left a yellow oil which was purified by chromatography eluting with 15% ether in hexane to give the *acetate* (4.4 g, 78%) as a colourless oil; ν_{max}(film)/cm^{-1} 1742, 1666, 1632 and 1031; δ_H(250 MHz) 4.93 (s, 1H, =CH_2), 4.58 (s, 1H, =CH_2), 4.03 (t, *J* 8, 2H, CH_2OAc), 2.42 (t, *J* 8, 2H, CH_2CH$_2$OAc), 2.06 (s, 3H, OCOMe), 1.77 (s, 3H, Me), 1.69 (s, 3H, Me), 1.62 (s, 3H, Me); δ_C(67.8 MHz) 171.4 (s), 146.1 (s), 132.8 (s), 128.8 (s), 114.2 (t), 63.3 (t), 30.4 (t), 23.4 (q), 22.8 (q), 21.6 (q), 19.8 (q) (Found: M$^+$, 182.1317. $C_{11}H_{18}O_2$ requires *M*, 182.1307) (Found: C, 72.8; H, 10.1. $C_{11}H_{18}O_2$ requires C, 72.4; H, 9.9%).

1-(2-Acetoxyethyl)-2,6,6-trimethylcyclohex-1-ene-5-carboxaldehyde 89. Acrolein (4.40 ml, 67.0 mmol) was added in one portion to a stirred solution of boron trifluoride–diethyl ether (8.24 ml, 67.0 mmol) in dry toluene (180 ml) at −60 °C under nitrogen. The mixture was stirred at −60 °C for 15 min and then a solution of the diene **88b** (8.09 g, 44.5 mmol) in toluene (20 ml) was added dropwise over 15 min. The yellow solution was stirred at −60 °C for 10 h and then cooled to −78 °C and quenched with water (150 ml) and pentane (150 ml). The mixture was allowed to warm to room temperature overnight and then the organic layer was separated, dried and evaporated

in vacuo to leave a yellow oil. Purification by chromatography on silica gel eluting with 20% diethyl ether in hexane gave the *aldehyde* (7.7 g, 74%) as a colourless oil, which crystallised on standing at 0 °C to a white solid, mp 43–45 °C (from hexane); ν_{max}(film)/cm^{-1} 1740, 1720 and 1031; δ_H(400 MHz) 9.84 (d, *J* 3, 1H, C*H*O), 4.01 (t, *J* 9, 2H, CH_2OAc), 2.41 (br t, *J* 9, 2H, CH_2CH$_2$OAc), 2.17 (app. dt, *J* 10, 3, 1H, C*H*CHO), 2.08 (s, 3H, OCOMe), 2.04 (app. t, *J* 6, 2H, =CCH_2), 1.87–1.76 (m, 2H), 1.68 (s, 3H, Me), 1.24 (s, 3H, Me), 1.09 (s, 3H, Me); δ_C(67.8 MHz) 205.6 (d), 170.7 (s), 131.5 (s), 130.4 (s), 63.4 (t), 57.2 (d), 36.6 (s), 30.4 (t), 27.6 (q), 27.3 (t), 23.2 (q), 20.7 (q), 19.8 (q), 19.3 (t) (Found: M$^+$, 238.1572. $C_{14}H_{22}O_3$ requires *M*, 238.1569) (Found: C, 70.7; H, 9.3. $C_{14}H_{22}O_3$ requires C, 70.6; H, 9.3%).

1-(2-Acetoxyethyl)-2,6,6-trimethyl-5-[(*Z*-5-*tert*-butyldimethylsiloxypent-1-enyl)]cyclohex-1-ene 91. A solution of sodium hexamethyldisilazide (14.5 ml) in THF (1 M, 14.0 mmol) was added dropwise over 5 min to a stirred solution of phosphonium salt **90** (8.04 g, 14.0 mmol) in dry THF (75 ml) at 0 °C under nitrogen. The deep orange solution was stirred at 0 °C for 15 min and then a solution of the aldehyde **89** (3.00 g, 13.0 mmol) in THF (7 ml) was added dropwise over 10 min. The resulting yellow solution was allowed to warm slowly to room temperature over 7 h. The solvent was evaporated *in vacuo* to leave a pale yellow residue which was triturated with pentane (6 × 10 ml). The pentane extracts were evaporated *in vacuo* to leave a clear oil which was purified by column chromatography on silica, eluting with 25% ether in hexane to give a mixture of (*E*)- and (*Z*)-isomers (1 : 18 ratio) of the *olefin* (3.6 g, 74%) as a colourless oil; [data for (*Z*)-isomer only]: ν_{max}(film)/cm^{-1} 1742 and 874; δ_H(400 MHz) 5.41–5.29 (m, 2H, *H*C=C*H*), 4.00 (t, *J* 9, 2H, CH_2OAc), 3.58 (t, *J* 7, 2H, CH_2OSi), 2.44–2.29 (m, 2H, CH_2CH$_2$OAc), 2.07 (s, 3H, OCOMe), 2.19–2.01 (m, 2H), 1.97–1.79 (m, 3H), 1.58 (s, 3H, Me), 1.69–1.43 (m, 4H), 0.91 (s, 9H, ^{t}Bu), 0.89 (s, 3H, Me), 0.86 (s, 3H, Me), 0.02 (s, 6H, Me$_2$Si); δ_C(67.8 MHz) 171.1 (s), 133.4 (d), 132.1 (s), 129.6 (s), 128.3 (d), 64.1 (t), 62.9 (t), 43.0 (d), 37.8 (s), 32.3 (t), 31.0 (t), 28.1 (t), 27.0 (q), 25.8 (t), 25.6 (t), 22.9 (q), 22.4 (q), 20.8 (q), 19.7 (q), 14.3 (s) (Found: M$^+$, 408.3066. $C_{24}H_{44}O_3Si$ requires *M*, 408.3060).

1-(2-Acetoxyethyl)-2,6,6-trimethyl-5-[(*Z*)-5-hydroxypent-1-enyl]cyclohex-1-ene 92a. A solution of tetrabutylammonium fluoride (3.95 ml) in THF (1.0 M, 3.95 mmol) was added in one portion to a solution of the silyl ether **91** (1.50 g, 3.8 mmol) in THF (12 ml) at room temperature. The pale yellow solution was stirred at room temperature for 40 min and then quenched with water (5 ml). The organic layer was separated, washed with brine (2 × 10 ml) and then dried and evaporated *in vacuo* to leave the *alcohol* as a clear oil (0.97 g, 91%); ν_{max}(film)/cm^{-1} 3426, 1741, 1654 and 738; δ_H(400 MHz) 5.46–5.34 (m, 2H, *H*C=C*H*), 4.03 (t, *J* 8, 2H, CH_2OAc), 3.70–3.62 (br. m, 2H, CH_2OH), 2.43–2.32 (m, 2H, CH_2CH$_2$OAc), 2.18–2.10 (m, 1H), 2.06 (s, 3H, OCOMe), 2.01 (app. t, *J* 7, 2H, =CCH_2), 1.97–1.90 (m, 2H, =CCH_2), 1.67 (s, 3H, Me), 1.70–1.60 (m, 2H), 1.58–1.48 (m, 2H), 1.06 (s, 3H, Me), 0.89 (s, 3H, Me); δ_C(67.8 MHz) 170.7 (s), 132.6 (d), 132.2 (s), 129.7 (s), 128.7 (d), 63.8 (t), 62.4 (t), 43.0 (d), 37.7 (s), 32.5 (t), 31.2 (t), 27.6 (t), 27.1 (q), 25.3 (t), 24.2 (t), 22.6 (q), 22.3 (q), 19.6 (q) (Found: M$^+$, 294.2191. $C_{18}H_{30}O_3$ requires *M*, 294.2195), which was used without further purification.

1-(2-Acetoxyethyl)-2,6,6-trimethyl-5-[(*Z*)-5-bromopent-1-enyl]cyclohex-1-ene 92b. A solution of the alcohol **92a** (1.60 g, 5.7 mmol) and carbon tetrabromide (2.83 g, 8.5 mmol) in dry dichloromethane (15 ml) was stirred at 0 °C under nitrogen. Triphenylphosphine (1.64 g, 6.3 mmol) was added in one portion and the yellow solution was then stirred at room temperature for 1 h. The solvent was evaporated *in vacuo* to leave a pale yellow residue which was preadsorbed onto silica and chromatographed, eluting with 15% ether in hexane to give the *bromide* (1.5 g, 74%) as a clear oil; ν_{max}(film)/cm^{-1} 1736, 1654, 1029 and 666; δ_H(400 MHz) 5.46–5.31 (m, 2H, *H*C=C*H*), 4.01 (t, *J* 8, 2H, CH_2OAc), 3.39 (t, *J* 7, 2H, CH_2Br), 2.38 (br t, *J* 8, 2H, CH_2CH$_2$OAc), 2.07 (s, 3H, OCOMe), 2.31–2.01 (m, 3H), 1.92 (app. t, *J* 7, 2H, =CCH_2), 1.71–1.63 (m, 2H), 1.68 (s, 3H, Me), 1.55–1.49 (m, 2H), 1.01 (s, 3H, Me), 0.89 (s, 3H, Me); δ_C(67.8 MHz) 170.8 (s), 133.5 (d), 132.0 (s), 129.6 (s), 128.2 (d), 63.6 (t), 43.0 (d), 37.6 (s), 33.0 (t), 32.3 (t), 31.0 (t), 27.6 (t), 27.0 (q), 25.6 (t), 25.3 (t), 27.3 (q), 20.7 (q), 19.7 (q) (Found: M$^+$, 356.1355. $C_{18}H_{29}BrO_2$ requires *M*, 356.1351).

1-(2-Hydroxyethyl)-2,6,6-trimethyl-5-[(*Z*)-5-bromopent-1-enyl]cyclohex-1-ene 93. A solution of diisobutylaluminium hydride (2.61 ml) in hexanes (1.0 M, 2.6 mmol) was added dropwise to a stirred solution of the bromoacetate **92b** (0.60 g, 1.7 mmol) in dry THF (10 ml) at −20 °C under nitrogen. The mixture was stirred at −20 °C for 30 min and then quenched with water (5 ml). The resulting emulsion was filtered through a glass sinter and the organic layer was separated, washed with brine (2 × 15 ml) and dried. The solvent was removed *in vacuo* to leave the *bromo alcohol* (0.39 g, 74%), as a clear oil; λ_{max}(EtOH)/nm 223 (ε/dm^3 mol^{-1} cm^{-1} 10 300); ν_{max}(film)/cm^{-1} 3490, 1719, 1686, 1631 and 981; δ_H(250 MHz) 5.50–5.34 (m, 2H, *H*C=C*H*), 3.73 (t, *J* 8, 2H, CH_2OH), 3.49 (t, *J* 7, 2H, CH_2Br), 2.43 (br t, *J* 8, 2H, CH_2CH$_2$OH), 2.36–2.19 (m, 2H), 2.11–1.97 (m, 3H), 1.61 (s, 3H, Me), 1.81–1.57 (m, 2H), 1.54–1.30 (m, 2H), 1.09 (s, 3H, Me), 0.97 (s, 3H, Me); δ_C(67.8 MHz) 133.9 (d), 132.3 (s), 128.9 (s), 127.4 (d), 62.8 (t), 43.8 (t), 43.4 (d), 37.9 (s), 33.4 (t), 32.3 (t), 31.4 (t), 27.1 (q), 25.8 (t), 24.2 (t), 22.8 (q), 20.2 (q) (Found: C, 61.4; H, 8.1. Calc. for $C_{16}H_{27}BrO$: C, 61.0; H, 8.6%) (Found: M$^+$, 314.1253. $C_{16}H_{27}BrO$ requires *M*, 314.1245); which was used without further purification.

1-Formylmethyl-2,6,6-trimethyl-5-[(*Z*)-5-bromopent-1-enyl]cyclohex-1-ene 94. Treatment of a solution of the alcohol **93** (0.90 g, 0.24 mmol) in dry dichloromethane with tetra(*n*-propyl)ammonium perruthenate and 4-methylmorpholine *N*-oxide, according to the general procedure, gave the title aldehyde (0.65 g, 73%) as a colourless oil; ν_{max}(film)/cm^{-1} 1721, 1673, 915 and 739; δ_H(250 MHz) 9.52 (t, *J* 2, 1H, CHO), 5.46–5.31 (m, 2H, C=CH), 3.41 (t, *J* 7, 2H, CH$_2$Br), 3.12 (br s, 2H, CH$_2$CHO), 2.49–2.01 (m, 3H), 1.92 (app. q, *J* 7, 2H, =CCH$_2$), 1.72–1.59 (m, 2H), 1.51 (s, 3H, Me), 1.53–1.47 (m, 2H), 0.90 (s, 3H, Me), 0.82 (s, 3H, Me); δ_C(67.8 MHz) 201.0 (d), 133.4 (d), 132.2 (s), 128.6 (s), 127.7 (d), 43.7 (t), 43.0 (d), 37.6 (s), 33.3 (t), 32.4 (t), 31.5 (t), 27.4 (q), 26.6 (t), 25.7 (t), 22.5 (q), 20.1 (q) (Found: M$^+$, 312.1087. $C_{16}H_{25}BrO$ requires *M*, 312.1089) (Found: C, 61.6; H, 7.7. $C_{16}H_{25}BrO$ requires C, 61.3; H, 8.1%).

1-(2-Hydroxybut-3-enyl)-2,6,6-trimethyl-5-[(*Z*)-5-bromopent-1-enyl]cyclohex-1-ene 95. A solution of vinylmagnesium bromide (1.80 ml) in dry THF (1.0 M, 1.8 mmol) was added dropwise over 5 min to a stirred solution of the aldehyde **94** (0.36 g, 1.2 mol) in dry THF (7 ml) at −78 °C under nitrogen. The mixture was stirred at −78 °C for 30 min and then quenched with saturated aqueous ammonium chloride (6 ml) and allowed to warm to room temperature over 30 min. The organic layer was separated, washed with brine (15 ml) and then evaporated *in vacuo* to leave a yellow oil which was purified by chromatography on silica, eluting with 35% diethyl ether in hexane to give two diastereoisomers of the *alcohol* (0.18 g, 47%) as a colourless oil; (data for both diastereoisomers): ν_{max}(film)/cm^{-1} 3422, 1719, 1654 and 991; δ_H(400 MHz) 5.90 (ddd, *J* 17, 10, 6, 1H, *H*C=CH$_2$), 5.49–5.31 (m, 2H, *H*C=C*H*), 5.26 (dd, *J* 17, 2, 1H, HC=CH_2), 5.09 (dd, *J* 10, 2, 1H, HC=CH_2), 4.28 (br m, 1H, C*H*OH), 3.41 (t, *J* 7, 2H, CH_2Br), 2.42–1.97 (m, 3H), 1.92 (app. q, *J* 7, 2H, =CCH_2), 1.74–1.63 (m, 4H), 1.61–1.56 (m, 2H), 1.56 (s, 3H, Me), 1.04 (s, 3H, Me), 0.94 (s, 3H, Me); δ_C(67.8 MHz) 140.9 (d), 133.5/133.6 (d), 132.7/132.8 (s), 131.0/131.1 (s), 127.3/127.4 (d), 113.7/113.8 (t), 72.3 (t), 43.1/43.2 (d), 37.5/37.8 (s), 36.1/36.2 (t), 33.1/33.2 (t), 30.9/31.2 (t), 27.8/28.1 (d), 25.7/25.8 (t), 25.2/25.3 (t), 23.7 (q), 22.9 (q), 20.9 (q) (Found: M$^+$, 340.1405. $C_{18}H_{29}BrO$ requires *M*, 340.1402).

1-(2-Oxobut-3-enyl)-2,6,6-trimethyl-5-[(*Z*)-5-bromopent-1-enyl]cyclohex-1-ene 96. A mixture of the alcohol **95** (36 mg, 0.1

mmol) and Dess–Martin periodinane (186 mg, 0.4 mmol) in dry dichloromethane (2 ml) was stirred at room temperature for 2 h. A 1:1 solution of hexane–diethyl ether (6 ml) was added, followed immediately by 10% aqueous sodium metabisulfite (12 drops). The cloudy mixture was stirred at room temperature for 45 min, during which time two layers separated out. The biphasic solution was loaded directly onto a silica gel column and chromatographed, eluting with 30% diethyl ether in hexane to yield the desired *enone* (35 mg, 99%) as a colourless oil; ν_{max}(film)/cm^{-1} 1687, 1464 and 981; δ_H(250 MHz) 6.45 (dd, *J* 18, 10, 1H, *H*C=CH$_2$), 6.27 (dd, *J* 18, 2, 1H, HC=C*H*$_2$), 5.75 (dd, *J* 10, 2, 1H, HC=C*H*$_2$), 5.48–5.29 (m, 2H, *H*C=C*H*), 3.40 (t, *J* 7, 2H, C*H*$_2$Br), 3.32 (app. s, 2H, C*H*$_2$CO), 2.41 (app. dt, *J* 10, 7, 1H, *H*CC=C), 2.32–2.01 (m, 4H), 1.93–1.86 (app. q, *J* 7, 2H, =CC*H*$_2$), 1.62–1.49 (m, 2H), 1.48 (s, 3H, Me), 0.91 (s, 3H, Me), 0.86 (s, 3H, Me); δ_C(67.8 MHz) 198.6 (s), 135.8 (d), 133.8 (d), 131.0 (s), 130.7 (s), 127.7 (t), 127.0 (d), 43.2 (d), 40.7 (t), 37.7 (s), 36.2 (t), 33.6 (t), 31.7 (t), 28.3 (t), 27.2 (q), 26.3 (t), 22.5 (q), 20.6 (q) (Found: M$^+$, 338.1248. $C_{18}H_{27}BrO$ requires *M*, 338.1245).

1-(2-Oxobut-3-enyl)-2,6,6-trimethyl-5-[(*Z*)-5-iodopent-1-enyl]cyclohex-1-ene 86a. Treatment of a solution of the bromide **96** (210 mg, 0.60 mmol) in butan-2-one with sodium iodide, according to the general procedure, gave the title iodide (232 mg, 97%) as a pale yellow oil; ν_{max}(film)/cm^{-1} 1706, 1687, 1614, 984 and 746; δ_H(250 MHz) 6.45 (dd, *J* 18, 10, 1H, *H*C=CH$_2$), 6.27 (dd, *J* 18, 2, 1H, HC=C*H*$_2$), 5.75 (dd, *J* 10, 2, 1H, HC=C*H*$_2$), 5.46–5.29 (m, 2H, *H*C=C*H*), 3.34 (app. s, 2H, C*H*$_2$CO), 3.19 (t, *J* 7, 2H, C*H*$_2$I), 2.43 (app. dt, *J* 10, 7, 1H, *H*CC=C), 2.28–2.01 (m, 4H), 1.90–1.83 (app. q, *J* 7, 2H, =CC*H*$_2$), 1.62–1.52 (m, 2H), 1.53 (s, 3H, Me), 0.89 (s, 3H, Me), 0.83 (s, 3H, Me); δ_C(67.8 MHz) 198.6 (s), 135.8 (d), 133.8 (d), 131.0 (s), 130.7 (s), 127.5 (t), 127.4 (d), 43.2 (d), 40.7 (t), 37.7 (s), 33.6 (t), 31.3 (t), 28.3 (t), 27.1 (q), 25.7 (t), 22.5 (q), 20.6 (q), 6.6 (t) (Found: M$^+$, 386.1113. $C_{18}H_{27}IO$ requires *M*, 386.1107); which was used without further purification.

1-(2-Oxobut-3-enyl)-2,6,6-trimethyl-5-[(*Z*)-pent-1-enyl)]-cyclohex-1-ene 86b. Treatment of a solution of the iodide **86a** (110 mg, 0.3 mmol) in benzene with tri-*n*-butyltin hydride and azoisobutyronitrile according to the general procedure gave the title cyclohexene (68 mg, 92%) as a yellow oil; ν_{max}(film)/cm^{-1} 1706, 1686, 1614 and 986; δ_H(250 MHz) 6.45 (dd, *J* 18, 10, 1H, *H*C=CH$_2$), 6.27 (dd, *J* 18, 2, 1H, HC=C*H*$_2$), 5.74 (dd, *J* 10, 2, 1H, HC=C*H*$_2$), 5.46–5.29 (m, 2H, *H*C=C*H*), 3.34 (app. s, 2H, C*H*$_2$CO), 2.42 (app. dt, *J* 10, 7, 1H, *H*CC=C), 2.17–1.93 (m, 4H), 1.63–1.52 (m, 2H), 1.52 (s, 3H, Me), 1.42–1.31 (m, 2H), 0.93–0.86 (m, 6H), 0.83 (s, 3H, Me); δ_C(67.8 MHz) 198.4 (s), 135.7 (d), 132.0 (d), 130.9 (s), 130.6 (s), 129.8 (d), 127.5 (t), 42.9 (d), 40.6 (t), 37.8 (s), 31.4 (t), 29.6 (t), 26.8 (q), 25.6 (t), 22.9 (t), 22.3 (q), 20.5 (q), 13.9 (q) (Found: M$^+$, 260.2143. $C_{18}H_{28}O$ requires *M*, 260.2140).

1-(2-Acetoxyethyl)-2,6,6-trimethyl-5-(1,3-dioxolan-2-yl)-cyclohex-1-ene 97a. A stirred solution of the aldehyde **89** (0.87 g, 3.6 mmol), (±)-camphor-10-sulfonic acid (41 mg, 0.2 mmol), ethylene glycol (2.03 ml, 36.4 mmol) and benzene (10 ml) was heated to reflux for 30 min. The cooled solution was diluted with water (4 ml) and ether (20 ml) and the organic layer was separated, washed with brine (2 × 15 ml) and then dried and evaporated *in vacuo* to leave the *acetal* (0.97 g, 93%) as a clear oil, which crystallised on standing at −10 °C to give white crystals, mp 54–56 °C (from pentane); ν_{max}(film)/cm^{-1} 1746, 1499 and 979; δ_H(250 MHz) 4.89 [d, *J* 3, 1H, HC(O)$_2$], 4.07–3.73 (m, 6H, 2 × C*H*$_2$O and C*H*$_2$OAc), 2.35 (br t, *J* 9, 2H, C*H*$_2$CH$_2$OAc), 2.07 (s, 3H, OCOMe), 1.93–1.37 (m, 5H), 1.65 (s, 3H, Me), 1.12 (s, 3H, Me), 0.97 (s, 3H, Me); δ_C(67.8 MHz) 170.8 (s), 132.4 (s), 130.3 (s), 104.6 (d), 64.9 (t), 64.3 (t), 63.9 (t), 48.4 (d), 37.0 (s), 32.0 (t), 27.6 (t), 27.0 (q), 22.3 (q), 20.8 (q), 20.1 (q), 18.7 (t) (Found: M$^+$, 282.1834. $C_{16}H_{26}O_4$ requires *M*, 282.1831) (Found: C, 67.8; H, 9.4. $C_{16}H_{26}O_4$ requires C, 68.1; H, 9.3%).

1-(2-Hydroxyethyl)-2,6,6-trimethyl-5-(1,3-dioxolan-2-yl)-cyclohex-1-ene 97b. A solution of diisobutylaluminium hydride (10.9 ml) in hexanes (1 M, 10.9 mmol) was added dropwise over 5 min to a stirred solution of the acetate **97a** (2.56 g, 0.1 mmol) in dry THF (26 ml) at −20 °C under argon. The mixture was stirred at −20 °C for 30 min and then quenched with saturated aqueous ammonium chloride (8 ml). The organic layer was separated, washed with brine (50 ml) and then dried and evaporated *in vacuo* to leave a clear oil which was purified by column chromatography on silica gel eluting with 30% diethyl ether in hexane to give the *hydroxy acetal* (1.8 g, 73%) as a colourless oil; ν_{max}(film)/cm^{-1} 3410, 1513 and 1061; δ_H(250 MHz) 4.90 [d, *J* 3, 1H, HC(O)$_2$], 4.00–3.79 (m, 4H, 2 × C*H*$_2$O), 3.61 (t, *J* 9, 2H, C*H*$_2$OH), 2.34 (br t, *J* 9, C*H*$_2$CH$_2$OH), 1.63 (s, 3H, Me), 2.10–1.85 (m, 5H), 1.12 (s, 3H, Me), 0.97 (s, 3H, Me); δ_C(67.8 MHz) 132.8 (s), 129.8 (s), 104.7 (d), 65.0 (t), 64.4 (t), 62.5 (t), 48.4 (d), 37.0 (s), 32.1 (t), 32.0 (t), 27.3 (q), 22.6 (q), 20.3 (q), 18.7 (t) (Found: M$^+$, 240.1726. $C_{14}H_{24}O_3$ requires *M*, 240.1725) (Found: C, 69.8; H, 10.4. $C_{14}H_{24}O_3$ requires C, 70.0; H, 10.1%).

1-Formylmethyl-2,6,6-trimethyl-5-(1,3-dioxolan-2-yl)-cyclohex-1-ene 98. Treatment of a solution of the alcohol **97b** (1.10 g, 5.4 mmol) in dry dichloromethane with tetra(*n*-propyl)-ammonium perruthenate and 4-methylmorpholine *N*-oxide, according to the general procedure, gave the title aldehyde (1.0 g, 94%) as a colourless oil; ν_{max}(film)/cm^{-1} 1721 and 949; δ_H(250 MHz) 9.48 (app. s, 1H, C*H*O), 4.89 [d, *J* 3, 1H, *H*C(O)$_2$], 3.94–3.77 (m, 4H, C*H*$_2$O), 3.07 (app. s, 2H, C*H*$_2$CHO), 1.59 (s, 3H, Me), 2.14–1.62 (m, 5H), 1.06 (s, 3H, Me), 0.93 (s, 3H, Me); δ_C(67.8 MHz) 201.1 (d), 132.6 (s), 128.8 (s), 104.6 (d), 64.9 (t), 64.4 (t), 48.1 (d), 43.5 (t), 36.8 (s), 32.1 (t), 26.8 (q), 22.0 (q), 20.3 (q), 18.8 (t) (Found: M$^+$ − CH$_2$CHO, 195.1269. $C_{12}H_{19}O_2$ requires *M*, 195.1385).

1-(2-Hydroxybut-3-enyl)-2,6,6-trimethyl-5-(1,3-dioxolan-2-yl)cyclohex-1-ene 99. Cerium trichloride heptahydrate (1.21 g, 4.9 mmol) was dried by stirring at 140 °C and 0.1 Torr for 3 h. The reaction vessel was vented to argon and dry THF (8 ml) was then added, and the white slurry stirred at room temperature overnight. The slurry was cooled to −78 °C and a solution of vinylmagnesium bromide (4.8 ml) in dry THF (1 M, 4.8 mmol) was then added dropwise over 5 min, and the resulting dark tan suspension stirred at −78 °C for 1 h. To this suspension was then added the aldehyde **98** (0.96 g, 3.9 mmol) in dry THF (4 ml), and the cream coloured mixture was stirred at −78 °C for 1 h, then allowed to warm to room temperature over 2 h. The solution was quenched with saturated aqueous ammonium chloride (3 ml) and the organic layer was separated. The aqueous fraction was extracted with ether (3 × 10 ml) and then washed with brine (5 ml). The combined organics were dried and evaporated *in vacuo* to leave two diastereoisomers of the *alcohol* (0.79 g, 74%) as a colourless oil; (data for both diastereoisomers): ν_{max}(film)/cm^{-1} 3447, 1642 and 920; δ_H(250 MHz) 5.83 (ddd, *J* 17, 10, 6, 1H, *H*C=CH$_2$), 5.14 (dd, *J* 17, 1, 1H, HC=C*H*$_2$), 4.96 (dd, *J* 10, 1, 1H, HC=C*H*$_2$), 4.81 [d, *J* 2, 1H, *H*C(O)$_2$], 4.31–4.12 (br m, 1H, C*H*OH), 3.94–3.71 (m, 4H, 2 × C*H*$_2$O), 2.40–2.11 (m, 3H), 1.99–1.86 (m, 2H), 1.78–1.46 (m, 2H), 1.49 (s, 3H, Me), 0.93 (s, 3H, Me), 0.82 (s, 3H, Me); δ_C(67.8 MHz) 141.1 (d), 132.2/132.5 (s), 131.6/131.3 (s), 113.6/113.5 (t), 104.8/104.4 (d), 72.4/72.3 (d), 64.8 (t), 64.7/64.3 (t), 48.2/47.9 (d), 36.9/36.7 (s), 36.0/35.8 (t), 31.9/31.7 (t), 28.6/27.9 (q), 23.8/23.3 (q), 21.3/21.2 (q), 18.6/18.5 (t) (Found: M$^+$, 266.1857. $C_{16}H_{26}O_3$ requires *M*, 266.1882) (Found: C, 71.9; H, 10.0. $C_{16}H_{26}O_3$ requires C, 72.1; H, 9.9%).

1-(2-Triisopropylsiloxybut-3-enyl)-2,6,6-trimethyl-5-formyl-cyclohex-1-ene 100. A solution of the acetal **99** (0.79 g, 2.9 mmol) and (±)-camphor-10-sulfonic acid (0.32 g, 1.4 mmol) in THF (6 ml) and water (6 ml) was heated to 60 °C for 3 h. The cooled mixture was diluted with ether (8 ml) and the organic layer was then separated. The aqueous layer was re-extracted with ether (3 × 6 ml) and the combined organic extracts were dried and evaporated *in vacuo* to a clear oil (0.70 g, 3.2 mmol)

which was then taken up in dry dichloromethane (8 ml) and cooled to −20 °C under argon. 2,6-Lutidine (670 μl, 5.7 mmol) was then added dropwise, followed immediately by triisopropylsilyl trifluoromethanesulfonate (1.02 ml, 3.8 mmol), and the clear solution stirred at −20 °C for 20 min. The reaction was quenched with water (2 ml), and the organic layer was separated and then dried. The solvent was evaporated *in vacuo* to leave a pale yellow oil which was purified by chromatography on silica gel, eluting with 20% ether in hexane to give two diastereoisomers of the *silyl ether* (0.80 g, 91%) as a clear oil; (data for both diastereoisomers): ν_{max}(film)/cm^{-1} 1721, 883 and 740; δ_H(250 MHz) 9.82 (d, *J* 1, 1H, C*H*O), 5.82 (ddd, *J* 17, 10, 6, 1H, *H*C=CH$_2$), 5.07 (dd, *J* 17, 1, 1H, HC=C*H*$_2$), 4.96 (dd, *J* 10, 1, 1H, HC=C*H*$_2$), 4.47–4.37 (m, 1H, C*H*OSi), 2.48–2.39 (m, 1H), 2.36–2.12 (m, 2H), 2.06–1.99 (app. t, *J* 7, 2H, C*H*$_2$), 1.91–1.72 (m, 2H), 1.58 (s, 3H, Me), 1.17 (s, 3H, Me), 1.12 (s, 3H, Me), 1.12–0.99 (m, 3H, 3 × C*H*Me$_2$), 1.04 (d, *J* 7, 18H, 3 × Me$_2$); δ_C(67.8 MHz) 206.5 (d), 141.8/141.7 (d), 132.5/132.6 (s), 130.2/130.1 (s), 113.4/113.3 (t), 74.9/74.7 (d), 57.8/57.6 (d), 37.6 (s), 37.4/37.1 (t), 30.6/30.5 (t), 28.6/28.3 (q), 24.5/24.3 (q), 21.6/21.5 (q), 19.8/19.9 (t), 17.7/18.0 (q), 11.9/12.2 (d) (Found: M$^+$ − ^{i}Pr, 335.2448. $C_{20}H_{35}O_2Si$ requires *M*, 335.2406).

1-(2-Triisopropylsiloxybut-3-enyl)-2,6,6-trimethyl-5-[(*E*)-2-iodoethenyl]cyclohex-1-ene 101. A solution of the aldehyde **100** (0.20 g, 0.5 mmol) and iodoform (314 mg, 0.6 mmol) in dry THF was added dropwise to a stirred suspension of chromous chloride (0.52 g, 3.0 mmol) in dry THF (3 ml) at room temperature under nitrogen. The brown solution was stirred at room temperature for 3 h and then quenched with water (6 ml) and ether (6 ml). The organic layer was separated, washed with saturated aqueous sodium metabisulfite (3 ml) and brine (6 ml), then dried and evaporated *in vacuo* to leave a pale yellow oil. Purification by chromatography on silica eluting with dichloromethane gave two diastereoisomers of the *iodide* (0.17 g, 64%) as a colourless oil; (data for both diastereoisomers): ν_{max}(film)/cm^{-1} 1658, 1646 and 883; δ_H(250 MHz) 6.52 (dd, *J* 14, 9, 1H, *H*C=CHI), 5.96 (d, *J* 14, 1H, I*H*C=CH), 5.81 (ddd, *J* 17, 10, 6, 1H, *H*C=CH$_2$), 5.07 (dd, *J* 17, 1, 1H, HC=C*H*$_2$), 4.95 (dd, *J* 10, 1, 1H, HC=C*H*$_2$), 4.44–4.37 (m, 1H, C*H*OSi), 2.47–2.34 (m, 1H), 2.31–2.04 (m, 2H), 2.02–1.91 (app. t, *J* 7, 2H, C*H*$_2$), 1.72–1.42 (m, 2H), 1.60 (s, 3H, Me), 1.04 (d, *J* 7, 18H, 3 × Me$_2$), 1.02 (s, 3H, Me), 0.94–0.89 (m, 3H, 3 × C*H*Me$_2$), 0.89 (s, 3H, Me); δ_C(67.8 MHz) 149.2/149.1 (d), 142.3/141.9 (d), 132.7 (s), 129.5/129.3 (s), 113.2/113.1 (t), 74.7/74.6 (d), 74.5/74.2 (d), 53.5/53.2 (d), 37.9 (s), 37.8 (t), 31.0/30.9 (t), 28.5/28.2 (q), 24.5 (t), 24.3 (q), 21.5 (q), 17.8/17.7 (q), 12.4/12.2 (d) (Found: M$^+$ − ^{i}Pr, 459.1514. $C_{21}H_{36}OISi$ requires *M*, 459.1580).

1-(2-Triisopropylsiloxybut-3-enyl)-2,6,6-trimethyl-5-[(*E*)-3-hydroxy-5-(4-methoxybenzyloxy)pent-1-enyl]cyclohex-1-ene 102a. A solution of 3-(4-methoxybenzyloxy)propanal (0.13 g, 0.7 mmol) and the vinyl iodide **101** (0.45 g, 0.9 mmol) in toluene (3 ml) was azeotroped for 2 h and then concentrated *in vacuo* and dried under high vacuum for 1 h. The reaction vessel was vented to argon and then dimethyl sulfoxide (5 ml) and THF (2 ml) were added and the resulting pale yellow solution was stirred at room temperature for 5 min. Chromous chloride (0.58 g, 4.7 mmol), containing 0.1% nickel(II) chloride (0.6 mg, 0.07 mmol), was then added in one portion and the green suspension was stirred at room temperature for 20 h. Saturated aqueous ammonium chloride (4 ml) and ethyl acetate (4 ml) were added and the mixture was then stirred at room temperature for 30 min. The organic layer was separated and the aqueous fraction was extracted with ethyl acetate (3 × 10 ml). The combined organic extracts were washed with brine (10 ml) and then dried and evaporated *in vacuo* to a pale green oil, which was purified by chromatography on silica gel eluting with 25% ether in hexane to give (i) two diastereoisomers of the *allylic alcohol* (0.11 g, 31%) (eluted first) as a colourless oil; (data for both diastereoisomers): λ_{max}(EtOH)/nm 226 (ε/dm^3 mol^{-1} cm^{-1} 12 500); ν_{max}(film)/cm^{-1} 3425, 1612 and 911; δ_H(250 MHz) 7.22 (d, *J* 9, 2H, Ar), 6.85 (d, *J* 9, 2H, Ar), 5.82 (ddd, *J* 18, 10, 6, 1H, C=CH$_2$), 5.71–5.59 (m, 1H, HC=C*H*), 5.43 (dd, *J* 15, 6, 1H, *H*C=CH), 5.09 (dd, *J* 18, 1, 1H, HC=CH*H*), 4.97 (dd, *J* 10, 1, 1H, HC=C*H*H), 4.44 (s, 2H, OC*H*$_2$Ar), 4.42–4.39 (m, 1H, C*H*OH), 4.37–4.23 (br m, 1H, C*H*OSi), 3.79 (s, 3H, OMe), 3.74–3.54 (m, 2H, C*H*$_2$OPMB), 2.72–2.64 (m, 1H), 2.42 (dd, *J* 14, 6, 1H, C*H*CHOSi), 2.34–2.14 (m, 1H), 2.06–1.90 (m, 2H), 1.89–1.74 (m, 2H), 1.72–1.53 (m, 2H), 1.60 (s, 3H, Me), 1.09–0.92 (m, 24H, 2 × Me and 3 × Me$_2$), 0.89 (m, 3H, 3 × C*H*Me$_2$); δ_C(67.8 MHz) 158.6/158.9 (s), 142.0/142.1 (d), 133.2/133.3 (d), 132.8/132.9 (d), 132.6/132.7 (s), 132.2/132.4 (s), 129.9/130.2 (s), 129.7/129.8 (d), 113.4/113.5 (d), 112.7 (t), 82.5 (d), 74.3/74.5 (d), 72.6/73.9 (t), 68.1/68.4 (t), 64.0/64.5 (t), 54.7 (q), 48.6/48.8 (d), 39.3/39.4 (t), 37.3/37.4 (t), 34.3 (s), 31.1/31.2 (t), 25.0/25.1 (q), 21.2/21.3 (q), 17.8/17.9 (q), 13.9/14.9 (q), 11.6/11.8 (d) (Found (FAB-MS): M$^+$, 571. $C_{35}H_{58}O_4Si$ requires *M*, 571); and (ii) the recovered vinyl iodide **101** (168 mg) (eluted second) as a colourless oil.

1-(2-Triisopropylsiloxybut-3-enyl)-2,6,6-trimethyl-5-[(*E*)-3-acetoxy-5-(4-methoxybenzyloxy)pent-1-enyl]cyclohex-1-ene 102b. Acetic anhydride (29 μl, 0.40 mmol) was added dropwise over 5 min to a stirred solution of the alcohol **102a** (0.15 g, 0.27 mmol), 4-dimethylaminopyridine (1.6 mg, 0.013 mmol) and triethylamine (56 μl, 0.40 mmol) in dry dichloromethane (2 ml) at 0 °C under nitrogen and the clear solution was then stirred at 0 °C for 2 h. The solution was diluted with water (2 ml) and the organic layer was separated. The aqueous layer was extracted with dichloromethane (3 × 10 ml) and the combined dichloromethane extracts were dried and concentrated *in vacuo* to leave a pale yellow oil. Purification by column chromatography on silica eluting with 20% ether in light petroleum gave two diastereoisomers of the *acetate* (0.14 g, 92%) as a clear oil; (data for both diastereoisomers): λ_{max}(EtOH)/nm 217 (ε/dm^3 mol^{-1} cm^{-1} 58 200); ν_{max}(film)/cm^{-1} 1738, 1614 and 821; δ_H(250 MHz) 7.21 (d, *J* 9, 2H, Ar), 6.84 (d, *J* 9, 2H, Ar), 5.82 (ddd, *J* 18, 10, 6, 1H, *H*C=CH$_2$), 5.79–5.66 (m, 1H, *H*C=CH), 5.52–5.39 (m, 2H, C*H*OAc and HC=C*H*), 5.07 (dd, *J* 18, 1, 1H, HC=C*H*$_2$), 4.96 (dd, *J* 10, 1, 1H, HC=C*H*$_2$), 4.45 (s, 2H, OC*H*$_2$Ar), 4.41–4.30 (br m, 1H, C*H*OSi), 3.80 (s, 3H, OMe), 3.69–3.50 (m, 2H, C*H*$_2$-OPMB), 2.67–2.60 (m, 1H), 2.37 (dd, *J* 14, 6, 1H, C*H*CHOSi), 2.29–2.12 (m, 3H), 2.04 (s, 3H, OCOMe), 1.82–1.43 (m, 4H), 1.56 (s, 3H, Me), 1.09–0.92 (m, 24H, 2 × Me and 3 × Me$_2$), 0.92 (m, 3H, C*H*Me$_2$); δ_C(67.8 MHz) 170.1/170.8 (s), 159.0 (s), 143.1/143.2 (d), 131.6/132.1 (d), 131.3/131.4 (d), 130.7/131.1 (s), 130.5/130.6 (s), 129.8/130.1 (s), 129.1/129.4 (d), 113.1/113.4 (d), 112.1 (t), 82.3/82.5 (d), 74.4/74.9 (d), 72.4/73.7 (t), 69.1/69.7 (t), 64.3/64.7 (t), 54.6 (q), 48.5/48.7 (d), 39.1/39.2 (t), 36.4/36.7 (t), 34.1 (s), 30.7/31.0 (t), 24.5/24.8 (q), 21.6 (q), 20.8/21.0 (q), 17.8/17.9 (q), 13.3/13.6 (q), 11.7/11.8 (d) (Found: M$^+$ − AcOH, 552.3983. $C_{35}H_{56}O_3Si$ requires *M*, 552.3999).

1-(2-Triisopropylsiloxybut-3-enyl)-2,6,6-trimethyl-5-[(*E*)-3-acetoxy-5-hydroxypent-1-enyl]cyclohex-1-ene 103a. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (0.29 g, 1.26 mmol) was added in one portion to a stirred solution of the *p*-methoxybenzyl ether **102b** (0.25 g, 0.42 mmol) and water (0.5 ml) in dichloromethane (8.8 ml) at room temperature. The brown suspension was stirred at room temperature for 3 h and then saturated aqueous sodium metabisulfite (3 ml) was added dropwise over a period of 20 min. The mixture was diluted with water (10 ml) and dichloromethane (12 ml) and the organic layer was separated. The aqueous layer was re-extracted with dichloromethane (× 2) and the combined organic extracts were washed with saturated aqueous sodium hydrogen carbonate (6 ml), then dried and evaporated *in vacuo* to leave a clear oil. Purification by column chromatography on silica eluting with 30% ether in light petroleum gave two diastereoisomers of the *alcohol* (0.16 g, 85%) as a colourless oil; (data for both diastereoisomers): ν_{max}(film)/cm^{-1} 3445, 1723 and 910; δ_H(250 MHz) 5.83 (ddd, *J* 18, 10, 6, 1H, *H*C=CH$_2$), 5.79–5.66 (m, 1H, *H*C=CH), 5.52–5.39 (m, 2H, C*H*OAc and HC=C*H*), 5.09 (dd,

J 18, 1, 1H, HC=CH_2), 4.95 (dd, *J* 10, 1, 1H, HC=CH_2), 4.48–4.39 (m, 1H, C*H*OSi), 3.69–3.59 (m, 2H, CH_2OH), 2.49–2.38 (m, 1H), 2.31–2.17 (m, 2H), 2.04 (s, 3H, OCOMe), 2.01–1.82 (m, 4H), 1.78–1.63 (m, 2H), 1.61 (s, 3H, Me), 1.09–1.01 (m, 24H, 2 × Me and 3 × Me_2), 0.97 (m, 3H, C*H*Me_2); δ_C(67.8 MHz) 171.0/172.4 (s), 141.9/142.4 (d), 136.8/136.9 (d), 132.9/133.0 (s), 129.5 (s), 128.2/128.3 (d), 113.0 (t), 74.1/74.6 (d), 72.4 (d), 58.7 (t), 49.1/49.0 (d), 37.6/37.8 (t), 34.0 (s), 32.2 (t), 31.4/32.1 (t), 25.1/25.8 (q), 23.8/24.0 (t), 21.5/21.6 (q), 20.9/21.3 (q), 18.0/18.1 (q), 17.9 (q), 11.9/12.4 (d) [Found (FAB-MS): M^+, 492. $C_{29}H_{52}O_4Si$ requires *M*, 492].

1-(2-Triisopropylsiloxybut-3-enyl)-2,6,6-trimethyl-5-[(*E*)-3-acetoxy-5-bromopent-1-enyl]cyclohex-1-ene 103b. Triphenylphosphine (0.11 g, 0.43 mmol) was added portionwise over 30 min to a stirred solution of the alcohol **103a** (0.16 g, 0.36 mmol) and carbon tetrabromide (0.24 g, 0.71 mmol) in dry dichloromethane (4 ml) at 0 °C under nitrogen and the mixture then stirred at 0 °C for 3 h. The solution was warmed to room temperature and then the solvent was evaporated *in vacuo* to afford a pale yellow gum. Purification by column chromatography eluting with 20% ether in light petroleum gave two diastereoisomers of the *bromide* (0.18 g, 96%) as a clear oil; (data for both diastereoisomers): ν_{max}(film)/cm^{-1} 1734, 1464 and 741; δ_H(250 MHz) 5.92–5.71 (m, 2H, *H*C=CH and *H*C=CH_2), 5.46–5.31 (m, 2H, C*H*OAc and HC=C*H*), 5.09 (dd, *J* 18, 1, 1H, HC=CH_2), 4.95 (dd, *J* 10, 1, 1H, HC=CH_2) , 4.50–4.39 (m, 1H, C*H*OSi), 3.45–3.34 (m, 2H, CH_2Br), 2.43–2.14 (m, 3H), 2.07 (s, 3H, OCOMe), 2.04–1.91 (m, 4H), 1.63–1.56 (m, 2H), 1.62 (s, 3H, Me), 1.09–1.01 (m, 24H, 2 × Me and 3 × Me_2), 0.97 (m, 3H, 3 × C*H*Me_2); δ_C(67.8 MHz) 169.7/170.9 (s), 140.6/141.1 (d), 136.7/136.8 (d), 130.9/131.7 (s), 129.6 (s), 127.5/128.1 (d), 112.6 (t), 74.0/74.4 (d), 70.9 (d), 57.8 (t), 48.7/48.9 (d), 37.4/37.9 (t), 34.0 (s), 33.0 (t), 31.9/32.3 (t), 25.0/25.6 (q), 23.4/24.0 (t), 21.4/21.5 (q), 20.9/21.3 (q), 17.7/18.0 (q), 17.1 (q), 12.1/12.3 (d).

1-(2-Hydroxybut-3-enyl)-2,6,6-trimethyl-5-[(*E*)-3-acetoxy-5-bromopent-1-enyl]cyclohex-1-ene 104. A solution of HF (3 M) in dry acetonitrile (2 ml) was added dropwise over 5 min to a stirred solution of the silyl ether **103b** (35 mg, 0.067 mmol) in acetonitrile (1 ml), in a teflon Eppendorf tube, at room temperature and the resulting pale yellow solution was then stirred at room temperature for 6 h. Saturated aqueous sodium hydrogen carbonate (3 ml) was added dropwise over 10 min, and the mixture was then stirred at room temperature for a further 1 h. The organic layer was separated and the aqueous fraction was extracted with ether (3 × 8 ml). The combined organic layers were dried and evaporated *in vacuo* to leave two diastereoisomers of the *alcohol* (16 mg, 79%) as a clear oil; (data for both diastereoisomers): ν_{max}(film)/cm^{-1} 3456, 1737, 1644 and 738; δ_H(250 MHz) 5.82 (ddd, *J* 17, 10, 6, 1H, *H*C=CH_2), 5.78–5.67 (m, 1H, HC=C*H*), 5.37–5.21 (m, 2H, C*H*OAc and *H*C=CH), 5.17 (dd, *J* 17, 2, 1H, H_2C=CH), 5.03 (dd, *J* 10, 2, 1H, H_2C=CH), 4.20–4.14 (br m, 1H, C*H*OH), 3.33–3.26 (m, 2H, CH_2Br), 2.42–1.99 (m, 5H), 1.98 (s, 3H, OCOMe), 1.76–1.43 (m, 4H), 1.61 (s, 3H, Me), 0.95 (s, 3H, Me), 0.83 (s, 3H, Me); δ_C(67.8 MHz) 170.4 (s), 141.1 (d), 137.8/138.1 (d), 132.8 (s), 130.4/130.9 (s), 127.4/127.5 (d), 113.9/114.1 (t), 73.4 (d), 72.6/72.7 (d), 49.0/49.1 (d), 37.7 (s), 37.3/37.6 (t), 36.2/36.3 (t), 31.2/31.4 (t), 28.2/28.4 (t), 27.8/28.1 (q), 24.9/25.0 (t), 23.5 (q), 21.2 (q), 21.0 (q) (Found: M^+ − AcOH − C_3H_4OH, 281.0893. $C_{15}H_{22}Br$ requires *M*, 281.0905); which was used without further purification.

1-(2-Oxobut-3-enyl)-2,6,6-trimethyl-5-[(*E*)-3-acetoxy-5-bromopent-1-enyl]cyclohex-1-ene 105. Dess–Martin periodinane reagent (270 mg, 0.63 mmol) was added in one portion to a stirred solution of the alcohol **104** (84 mg, 0.21 mmol) in dry dichloromethane (3 ml) at room temperature under nitrogen, and the resulting solution stirred at room temperature for 1 h. The solution was diluted with hexane (2 ml), ethyl acetate (2 ml) and 30 drops of saturated aqueous sodium metabisulfite and then stirred at room temperature for 30 min. The mixture was purified directly by chromatography on silica, eluting with 30% ether in light petroleum, to give two diastereoisomers of the *ketone* (67 mg, 81%) as a clear oil; (data for both distereoisomers): ν_{max}(film)/cm^{-1} 1737, 1689, 1613, 912 and 734; δ_H(250 MHz) 6.39 (dd, *J* 18, 10, 1H, H_2C=C*H*), 6.20 (dd, *J* 18, 2, 1H, H_2C=CH) , 5.81–5.68 (m, 1H, *H*C=C*H*), 5.71 (dd, *J* 10, 2, 1H, H_2C=CH), 5.32–5.26 (m, 2H, *H*C=C*H* and C*H*OAc), 3.32 (app. t, *J* 7, 2H, CH_2Br), 3.25 (app. s, 2H, CH_2CO), 2.18–1.99 (m, 3H), 2.08 (s, 3H, OCOMe), 1.53 (s, 3H, Me), 1.65–1.36 (m, 4H), 0.93 (s, 3H, Me), 0.89 (s, 3H, Me); δ_C(67.8 MHz) 198.5 (s), 170.1 (s), 141.6 (s), 137.7/137.9 (d), 135.7 (d), 130.9/131.0 (s), 128.0 (t), 127.7 (d), 73.4 (d), 48.4/48.6 (d), 40.5 (t), 37.4/37.5 (t), 33.2 (s), 31.2/31.3 (t), 29.7 (t), 26.6/26.7 (q), 24.9 (t), 22.5/22.6 (q), 20.5 (q), 20.4 (q) (Found: M^+ − AcOH, 336.1094. $C_{18}H_{25}BrO$ requires *M*, 336.1089).

1-(2-Oxobut-3-enyl)-2,6,6-trimethyl-5-[(*E*)-3-acetoxy-5-iodopent-1-enyl]cyclohex-1-ene 87a. Treatment of a solution of the bromide **105** (65 mg, 0.16 mmol) in butan-2-one with sodium iodide, according to the general procedure, gave the title iodide (65 mg, 89%) as a pale yellow oil; (data for both diastereoisomers): ν_{max}(film)/cm^{-1} 1735, 1690, 1620 and 984; δ_H 6.44 (dd, *J* 18, 10, 1H, H_2C=C*H*), 6.26 (dd, *J* 18, 2, 1H, H_2C=CH), 5.83–5.76 (m, 1H, HC=C*H*), 5.76 (dd, *J* 10, 2, 1H, H_2C=CH), 5.40–5.23 (m, 2H, *H*C=C*H* and C*H*OAc), 3.31 (app. s, 2H, CH_2CO), 3.10 (app. t, *J* 7, 2H, CH_2I), 2.26–2.05 (m, 3H), 2.04 (s, 3H, OCOMe), 1.59–1.51 (m, 4H), 1.56 (s, 3H, Me), 0.93 (s, 3H, Me), 0.89 (s, 3H, Me); δ_C(67.8 MHz) 198.7 (s), 170.4 (s), 140.9 (s), 137.7/137.9 (d), 135.1 (d), 130.7/130.9 (s), 127.8 (t), 127.4 (d), 73.7 (d), 48.2/48.6 (d), 40.9 (t), 31.6 (s), 31.0/31.3 (t), 28.7 (t), 26.4/26.7 (q), 23.8 (t), 22.5/22.6 (q), 20.5 (q), 20.0 (q), 8.6 (t) (Found: M^+ − AcOH, 384.0943. $C_{18}H_{25}IO$ requires *M*, 384.0950); which was used immediately without further purification.

1-(2-Oxobut-3-enyl)-2,6,6-trimethyl-5-[(*E*)-3-acetoxypent-1-enyl]cyclohex-1-ene 87b. Treatment of a solution of the iodide **87a** (65 mg, 0.15 mmol) in benzene with tri-*n*-butyltin hydride and azoisobutyronitrile, according to the general procedure, gave the title cyclohexene (29 mg, 63%) as a yellow oil; δ_H(250 MHz) 6.38 (dd, *J* 17, 10, 1H, H_2C=C*H*), 6.24 (dd, *J* 17, 2, 1H, H_2C=CH), 5.79–5.66 (m, 1H, HC=C*H*), 5.69 (dd, *J* 10, 2, 1H, H_2C=CH), 5.33–5.24 (m, 2H, HC=C*H* and C*H*OAc), 3.29 (app. s, 2H, CH_2CO), 2.32–1.94 (m, 3H), 2.09 (s, 3H, OCOMe), 1.51 (s, 3H, Me), 1.61–1.31 (m, 4H), 0.91–0.93 (m, 3H, Me), 0.89 (s, 3H, Me), 0.87 (s, 3H, Me) (Found: M^+ − AcOH, 257.1981. $C_{18}H_{26}O$ requires *M*, 258.1984).

Acknowledgements

We thank the EPSRC (studentships to S. A. H., D. C. P. and N. M. T.) and Astra Charnwood (studentship to S. J. H.) for support of this work. We also thank Dr J. Bateson (SmithKline Beecham), Drs M. F. Jones and P. J. Meyers (Glaxo Wellcome) for their interest in this work, and Drs D. C. Harrowven and A. D. Green for their contributions to our studies in this area.

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Paper 8/05268I