Stereocontrol in organic synthesis using silicon-containing compounds. A formal synthesis of prostaglandins controlling the stereochemistry at C-15 using a silyl-to-hydroxy conversion following a stereochemically convergent synthesis of an allylsilane

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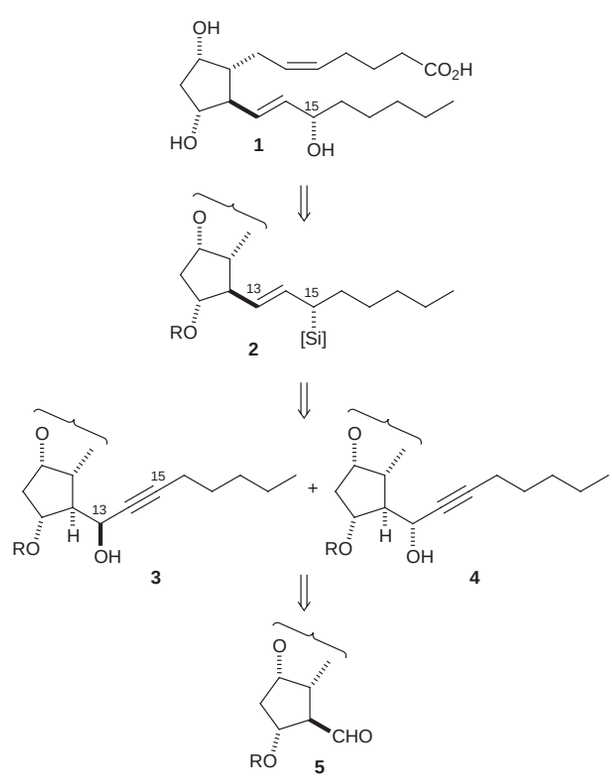
Hydrosilylation of isoprene with chloro(diphenyl)silane gave (*Z*)-chloro(2-methylbut-2-enyl)-diphenylsilane 7. The cuprate reagent derived from this chloride underwent conjugate addition to methyl cinnamate 11, 1,2-silylcupration with hex-1-yne 16 and allene 18, and allylic displacement reactions with 1-vinylcyclohexyl acetate 20 and (*Z*)-1-cyclopentyloct-2-en-1-yl acetate 22. The silyl group in each of the products was converted into a hydroxy, with the removal of the 2-methylbut-2-enyl group taking place under much milder acidic conditions than those needed to remove the phenyl group from the dimethyl(phenyl)silyl group, and making this group suitable for the conversion of an allylsilane into an allyl alcohol. A stereospecifically *anti* conjugate displacement of the allylic benzoate group in (*Z*)-(1*S*,5*R*,6*R*,7*R*,1′*S*)-7-benzoyloxy-6-(1′-benzoyloxyoct-2′-enyl)-2-oxabicyclo[3.3.0]octan-3-one 52, and a stereospecifically *syn* conjugate displacement of the carbamate group in (*Z*)-(1*S*,5*R*,6*R*,7*R*,1′*R*)-7-benzoyloxy-6-(1′-*N*-phenylcarbamoyloxyoct-2′-enyl)-2-oxabicyclo[3.3.0]octan-3-one 51, gave stereoconvergently the same allylsilane (1′*E*,2″*Z*)-(1*S*,5*R*,6*R*,7*R*,3′*S*)-7-benzoyloxy-6-[3′-(2″-methylbut-2″-enyl)-diphenylsilyloct-1′-enyl]-2-oxabicyclo[3.3.0]octan-3-one 53. Silyl-to-hydroxy conversion gave the allyl alcohol (*E*)-(1*S*,5*R*,6*R*,7*R*,3′*S*)-7-benzoyloxy-6-(3′-hydroxyoct-1′-enyl)-2-oxabicyclo[3.3.0]octan-3-one 54, having the relative and absolute stereochemistry at C-15 of the prostaglandins.

Introduction

Having developed a method for converting the phenyldimethylsilyl group into a hydroxy with retention of configuration,[1] and also a stereoselective synthesis of allylsilanes from allylic alcohols,[2] we were faced with a problem in trying to combine these two methods. We had in mind that we might be able to control the stereochemistry at C-15 in the synthesis of prostaglandin $F_{2\alpha}$ **1**, a long-standing problem, which has excited several solutions.[3,4] We had the methods for setting up a silyl group [Si] at C-15 with high levels of regio- and stereo-specificity in either sense from either or both of the diastereoisomeric propargyl (prop-2-ynyl) alcohols **3** and **4** obtained by nucleophilic attack on a C-13 aldehyde **5** (Scheme 1). Our method was not dependent upon any stereoselectivity in the formation of the mixture of propargyl alcohols **3** and **4**. It was only necessary to be able to separate the diastereoisomers, in order to achieve convergence by submitting each to a different protocol, as used already in our synthesis of the Prelog–Djerassi lactone.[5] However, there was a fundamental problem in the idea when we started the work described in this paper—we could not use our standard phenyldimethylsilyl group as [Si] in the allylsilane **2**, because the essential first step in the silyl-to-hydroxy conversion is to remove the phenyl group with an electrophile. Any attempt to attack the phenyl ring would not be able to compete with attack at C-13 of the double bond of the allylsilane. Several silyl groups have been developed to overcome this type of problem, notably Tamao and Ito's diisopropylamino-[6] and alkoxy-(dimethyl)silyl groups,[7] Chan's (dimethyl)pyrrolidinomethylsilyl group,[8] Hayashi and Hiyama's fluoro(diphenyl)silyl group,[9] Landais' phenylthiocyclopropyl(dimethyl)silyl group[10] and Roush's[11] and Kocienski's[12] various furyl(dimethyl)silyl groups, all of which allow an allylsilane to be converted into an allyl alcohol, but none of which allows the silyl group to be introduced using the powerful silylcuprate chemistry. Taber has solved the problem recently, retaining the phenyldimethylsilyl group, and hence the capacity to use its cuprate—he found that Birch reduction of the phenyl group and treatment with fluoride ion removed it, but he has not actually carried out the sequence with an allylsilane.[13] We tried unsuccessfully to remove the phenyl ring of the phenyldimethylsilyl group by converting it into its chromiumtricarbonyl complex—the complex was formed, but the allyl group remained more reactive than the phenyl.[14] Another solution to the problem has been developed by Tamao and Ito, with their diethylamino-(diphenyl)silyl group, which can be made into a cuprate reagent,[15] while we developed the (*Z*)-2-methylbut-2-



Scheme 1

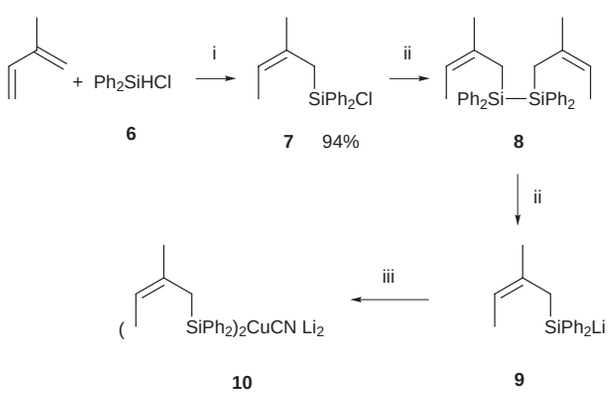
enyl(diphenyl)silyl group[16] and applied it to a prostaglandin synthesis.[17] We report all our work on this group in full here and in the following paper.

Results and discussion

The two essential features that we needed were that the silyl group should have a substituent that is attacked by an electrophile more readily than the double bond of the allylsilane **2**, and that the silyl group should also be capable of being delivered as a cuprate into the organic structure. It was the second requirement that gave us most trouble, for we found that a wide variety of aryldimethylsilyl groups, with aryl groups more susceptible to electrophilic attack than phenyl, could not be prepared as chlorides,[18] or the chlorides would only give, when they were stirred with lithium, disilanes and not silyllithium reagents.[19] It appears to be more or less essential to have at least one unsubstituted phenyl group, as Tamao and Ito found with their group, and we found with the group that we eventually succeeded with.

The (*Z*)-2-methylbut-2-enyl(diphenyl)silyl group

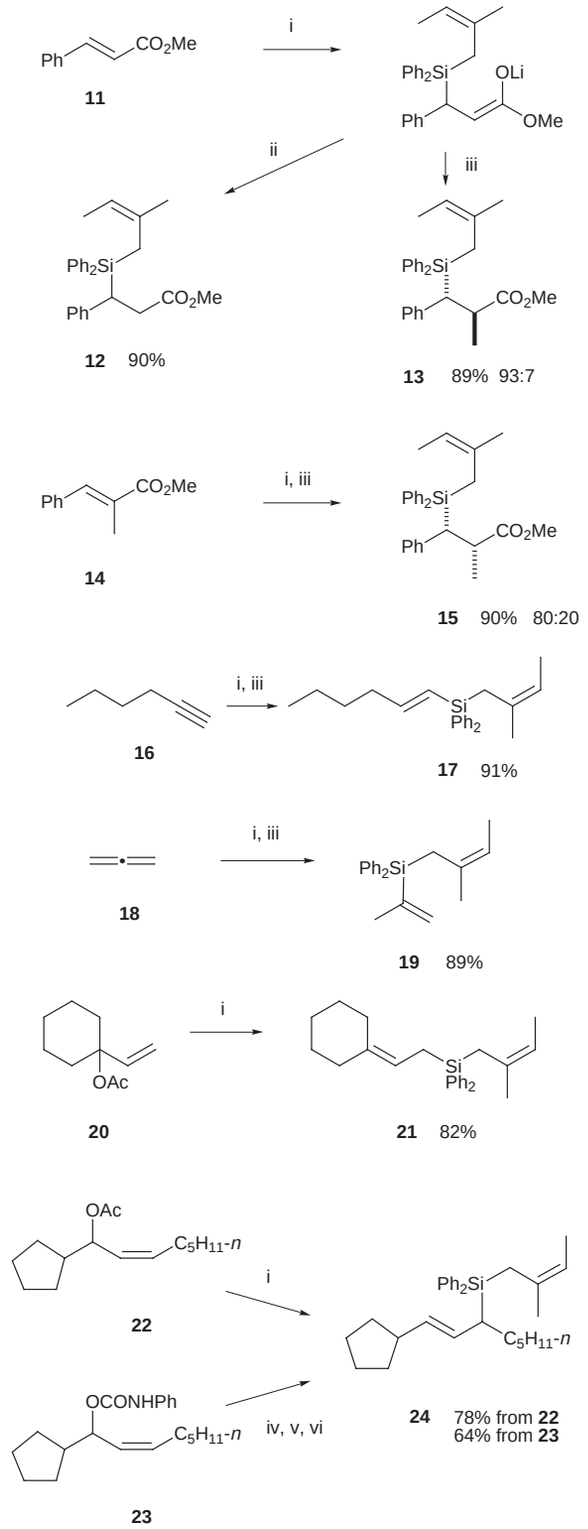
The key was provided by a report from Ojima and Kumagai of the regio- and stereo-selective hydrosilylation of isoprene with chloro(dimethyl)silane.[20] We found, similarly, that hydrosilylation of isoprene using chloro(diphenyl)silane **6** and the same catalyst in a sealed tube gave the silyl chloride **7** with high selectivity and in high yield. Although clean, this silyl chloride proved to be difficult to purify, distillation causing decomposition, but even in its slightly crude state it was easily converted into, successively, the disilane **8**, the lithium reagent **9**, and the cuprate **10** (Scheme 2). It appeared to be best not to



Scheme 2 *Reagents*: i, $PdCl_2(PhCN)_2$ cat., Ph_3P; ii, Li, THF; iii, CuCN

isolate the disilane **8**, which could be obtained in 64% yield, even though its crystallinity gave an opportunity to purify the reagent—once isolated, it needed sonication and powdered lithium to cleave it. It was better to continue stirring the silyl chloride **7** with lithium shot as usual, even though the disilane must have been an intermediate.[21] An alternative route to the silyl chloride, which does allow some purification by distillation, is described in the following paper.

We tested the cuprate reagent, to make sure that it reacted with each of the substrates that we already knew the phenyldimethylsilylcuprate reacted with, namely α,β-unsaturated esters **11** and **14**, a terminal acetylene **16**, allene **18** and the allylic acetate **20**. The reactions all worked well (Scheme 3), and were suitable for the alkylation and the protonation protocol with the esters **11** and **14**, giving the diastereoisomeric esters **13** and **15**, respectively. Moving closer to the prostaglandin problem, the silylcuprate **10** also reacted with the allylic acetate **22** to give the allylsilane **24** with the substitution pattern of the prostaglandin sidechain, and showing the expected regioselectivity for allylic displacement with an acetate having a *cis* double bond and the larger substituent at the oxygen-bearing

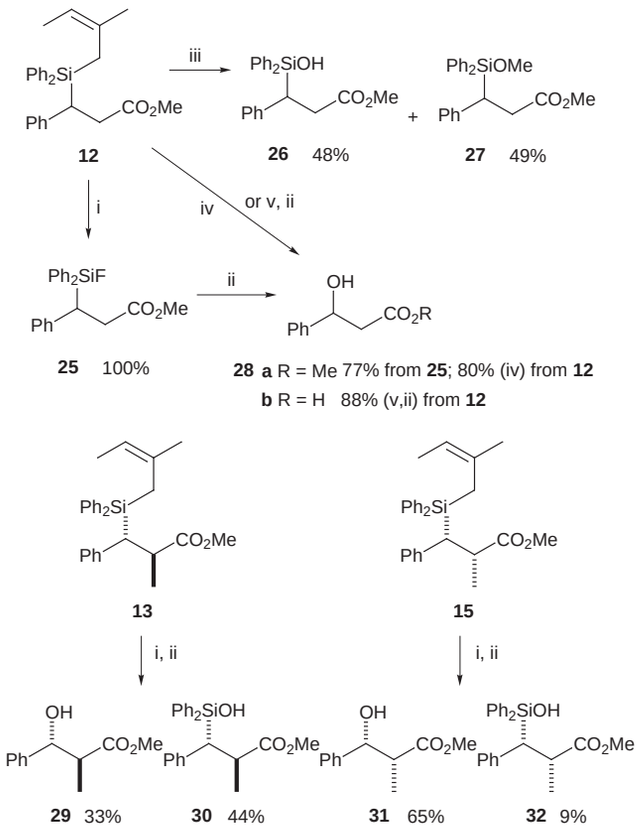


Scheme 3 *Reagents*: i, **10**; ii, NH_4Cl, H_2O; iii, MeI; iv, BuLi; v, CuI, Ph_3P; vi, **9**

end of the allylic system.[2] With a slightly different protocol, assembling the cuprate on the allylic carbamate **23**, the reagent gave the same allylsilane **24**. The reagent appeared in every way to be similar in its reactivity, regioselectivity and stereoselectivity to the corresponding phenyldimethylsilylcuprate reagent.

We used the ester **12** to test methods for converting the silyl into a hydroxy group. We had been hopeful that peracid alone, MCPBA, for example, or peracetic acid in acetic acid, would do both jobs at once—the removal of the allyl group by epoxide formation and easy loss of the silyl group, followed immediately by the silyl-to-hydroxy oxidation step. Unfortunately, we were

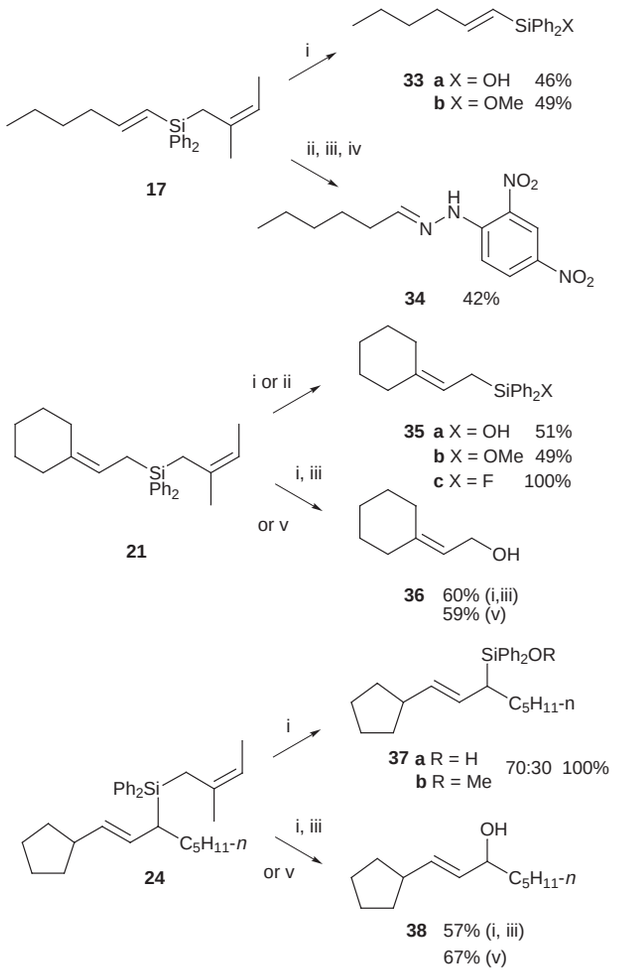
unable to find conditions that gave anything other than complex mixtures of products. We turned therefore to stepwise methods (Scheme 4). Protodesilylation was easily accomplished



Scheme 4 *Reagents*: i, BF_3·2AcOH, CH_2Cl_2; ii, H_2O_2, KF, $NaHCO_3$, MeOH, THF; iii, HCl, MeOH, H_2O; iv, KBr, AcOOH, AcOH, NaOAc; v, H_2SO_4, MeOH

under mild conditions, typically with the boron trifluoride–acetic acid complex in dichloromethane (*ca*. 0.05 M) at −10 °C for five minutes, giving the fluoride **25**, or with dilute methanolic hydrochloric acid (*ca*. 0.3 M) at room temperature for three hours. In the latter case, the product mixture was about half silanol **26** and half silyl ether **27**, even though the proportion of water present must have been only about 4%. We do not know whether this is a kinetic or a thermodynamic result, and comment only that it is known that hydroxide ion is a better nucleophile for silicon than the corresponding alkoxide ion.[22] The oxidation step could be carried out using Tamao's conditions in the usual way, to give the alcohol **28a**. Our one-pot procedure **12**→**28a** using bromine, generated *in situ* in buffered peracetic acid also worked well, as did a one-pot procedure carrying out the protodesilylation with sulfuric acid in methanol, and then basifying the mixture with sodium hydrogen carbonate and adding potassium fluoride and hydrogen peroxide, except that this gave us the acid **28b** instead of the ester. The protodesilylation–oxidation sequence applied to the alkylated esters **13**, however, did not go to completion under the standard conditions. We isolated the silanol **30** in comparable amounts to the alcohol **29**, indicating that the phenyl groups slow the oxidation down marginally. Increasing the time for the oxidation of the diastereoisomeric ester **15** from one day to three, and topping up the hydrogen peroxide each day, gave almost complete conversion to the alcohol **31**, but we still isolated a small amount of the silanol **32**. No doubt this could be remedied by even longer or stronger treatment with the oxidising agent.

We then tested the protodesilylation and oxidation conditions, in various combinations on the other allylsilanes (Scheme 5). Protodesilylations of the allylsilanes **17**, **21** and **24** in methanol gave the silanols **33a**, **35a** and **37a**, and the silyl ethers **33b**, **35b** and **37b**. Protodesilylation of the allylsilane **21** with the boron trifluoride–acetic acid complex gave the silyl fluoride **35c**. One- or two-pot oxidations gave hexanal, as its 2,4-dinitrophenylhydrazone **34**, and, most significantly, the allylic alcohols **36** and **38**. For the last of these, we also found new, essentially neutral conditions, with a combination of potassium bromide in hydrogen peroxide to create the electrophilic brominating agent, and potassium fluoride and hydrogen peroxide to carry out the oxidation step.



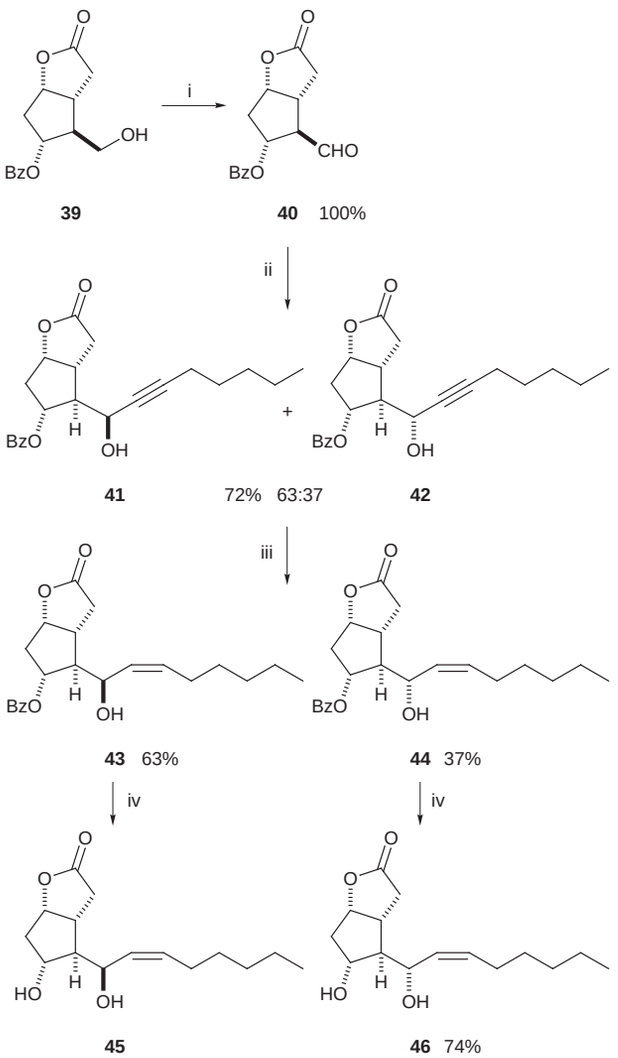
Scheme 5 *Reagents*: i, HCl, MeOH, H_2O; ii, BF_3·2AcOH, CH_2Cl_2; iii, H_2O_2, KF, $NaHCO_3$, MeOH, THF; iv, 2,4-dinitrophenylhydrazine; v, KBr, H_2O_2, KF, THF, MeOH

The prostaglandin C-15 problem

With all the exploratory work in hand, we turned to the main task: to synthesise an allylsilane of the type **2** from an aldehyde **5**. We chose the aldehyde **40** to be the aldehyde **5** that we would actually use. The protecting groups, both for the C-9 and the C-11 hydroxy groups were esters, limiting us to protocols using *cis* double bonds derived from the triple bond. Our earlier method, used in the syntheses of the Prelog–Djerassi lactone and of dihydronepetalactone, and which we shall not be able to apply here, required that we reduce the triple bond of one diastereoisomer to a *trans* double bond using lithium aluminium hydride, and the ester and lactone groups would not be compatible with this protocol. However, we had by this time developed protocols for convergence using a stereospecifically *syn* displacement for one diastereoisomer and a stereospecifically *anti* displacement for the other, with a *cis* double bond in each, avoiding the need for lithium aluminium hydride.

We prepared the aldehyde **40** in essentially quantitative yield from the alcohol **39**, already known from the work of Uskokovic[23] and Kovâcs.[24] The aldehyde was, not surprisingly,

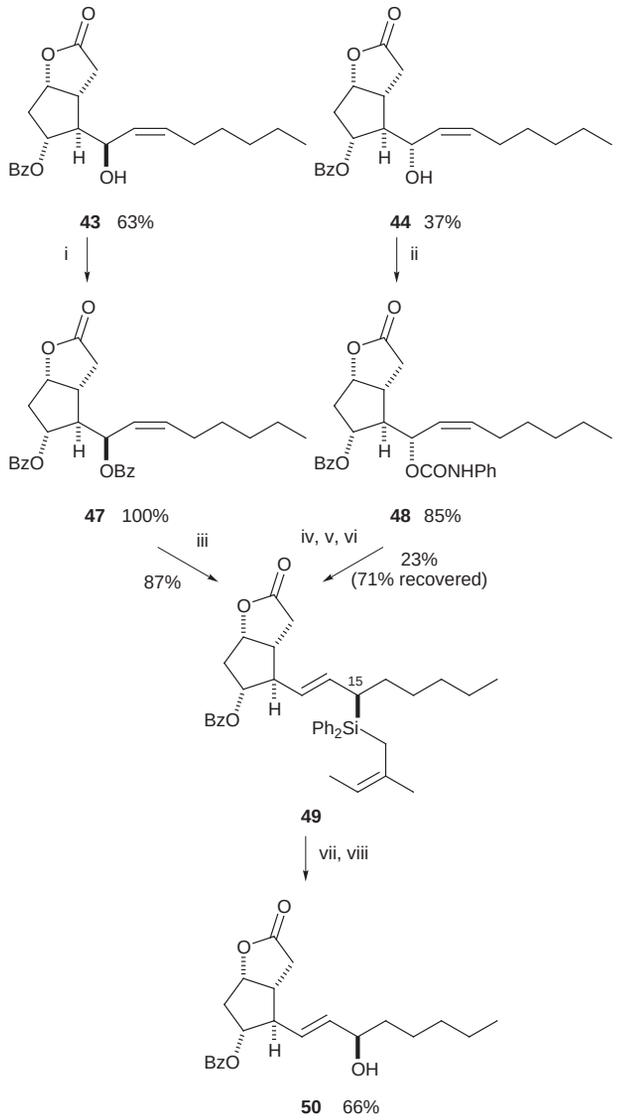
exceptionally susceptible to elimination of the β-benzoate group, so that the oxidation was rather dependent upon the virtues of the Dess–Martin periodinane. We also found that the addition of the acetylenic nucleophile gave less of the elimination product when the cerium reagent was used, and, as expected, the addition was only slightly stereoselective, giving the pair of diastereoisomers **41** and **42**, which we were not able to separate, in a ratio of 63 : 37 (Scheme 6). Thus the elegantly



Scheme 6 *Reagents*: i, Dess–Martin; ii, $C_5H_{13}C{\equiv}CCeCl_2$; iii, H_2, Pd, $MnCl_2$, quinoline, MeOH; iv, K_2CO_3, MeOH

short method in which allylic acetates are transposed in a transition metal-catalysed suprafacial 1,3 shift would not have been easy to apply here, since, like our own earlier method, it requires different double bond geometries with which to achieve convergence.[4] Fortunately, we were no longer obliged to separate the propargylic alcohols—we could delay the separation until we had the *cis*-allylic alcohols. Lindlar reduction gave the pair of alcohols **43** and **44**, which we were able to separate, and to which we were able to assign structures by converting the minor alcohol **44** into the known alcohol **46**,[4] and the mixture of the two alcohols **43** and **44** into a mixture of the alcohols **45** and **46**.

From each of the allylic alcohols **43** and **44**, we prepared the carbamates **48** and **51** and the benzoates **47** and **52** (Schemes 7 and 8). The benzoate **47** and the carbamate **48** gave the same allylsilane **49** (Scheme 7) when subjected to our standard protocols. The yield was rather low (23%) with the three-step procedure assembling the cuprate on the carbamate **48**, converting it into the allylsilane **49**, but the two procedures gave us



Scheme 7 *Reagents*: i, PhCOCl, Et_3N, DMAP; ii, PhNCO, Et_3N; iii, **10**; iv, BuLi; v, CuI; vi, **9**; vii, $BF_3{\cdot}2AcOH$; viii, H_2O_2, KF, MeOH

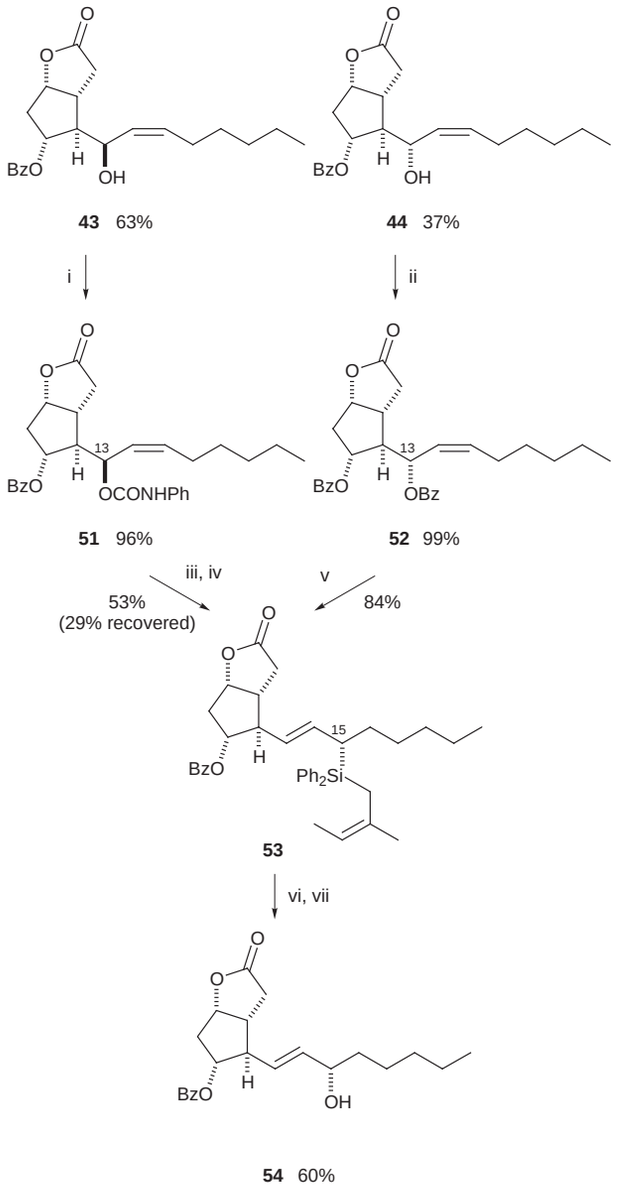
enough material to carry out the silyl-to-hydroxy conversion into the known 'unnatural' prostaglandin precursor **50**. The carbamate **51** and the benzoate **52** gave the diastereoisomeric allylsilane **53** (Scheme 8), for which we found a slightly different protocol for the conversion of the carbamate **51** into the allylsilane **53**: addition of the lithium salt of the carbamate to the 1 : 1 silylcopper reagent gave a 53% yield, with 29% of recovered carbamate, which represents a 77% yield overall. Silyl-to-hydroxy conversion gave the known 'natural' alcohol **54**, completing our long held ambition to control the stereochemistry of an allylic alcohol by taking advantage of the versatility of our convergent stereocontrolled methods for setting up allylsilanes.

Experimental

Light petroleum refers to the fraction bp 40–60 °C. Basic ammonium chloride refers to saturated aqueous ammonium chloride (9 parts) to which saturated aqueous ammonia (1 part) has been added. Ether refers to diethyl ether.

Chlorodiphenylsilane 6

Method 1.[25] Diphenylsilane (4.4 cm^3, 23.7 mmol) and chlorotriphenylmethane (6.97 g, 25.0 mmol) were refluxed in dry benzene (100 cm^3) for 24 h under argon. The mixture was cooled, filtered quickly and the residue washed with cold dry pentane.



Scheme 8 *Reagents*: i, PhNCO, Et_3N; ii, PhCOCl, Et_3N, DMAP; iii, BuLi; iv, $C_5H_9Ph_2SiCu$; v, **10**; vi, BF_3·2AcOH; vii, H_2O_2, KF, MeOH

The organic layers were combined and concentrated under reduced pressure. Kugelrohr distillation of the residue (2 distillations were necessary, 150 °C at 7 mmHg) (lit.,[25] 143 °C at 10 mmHg) gave the chlorosilane[25] (4.55 g, 88%), ν_{max}(film)/cm^{-1} 2140 (Si–H), 1580 (Ph) and 1120 (Si–Ph); δ_H(250 MHz; $CDCl_3$) 7.82 (4 H, br d, *J* 7.5, *o*-$SiPh_2$), 7.67–7.47 (6 H, m, *m*- and *p*-$SiPh_2$) and 5.91 (1 H, s, SiH).

Method 2.[26] Diphenylsilane (14.1 cm^3, 76.1 mmol) was stirred with a suspension of copper(II) chloride (20.2 g, 150 mmol, dried at 120 °C under vacuum) and copper(I) iodide (0.3 g, 1.6 mmol) in dry ether (250 cm^3) under nitrogen at room temperature for 4 d, filtered and concentrated under reduced pressure. Distillation of the residue gave the chlorosilane[25] (9.5 g, 57%), bp 95–96 °C at 0.5 mmHg; identical (IR, ^{1}H NMR) with the earlier sample. This method, although lower yielding, was the easier, and gave a cleaner product.

(*Z*)-Chloro(2-methylbut-2-enyl)diphenylsilane 7

Chlorodiphenylsilane **6** (6.58 g, 30 mmol), freshly distilled isoprene (2.18 g, 32 mmol), triphenylphosphine (0.04 g, 0.15 mmol) and bis(benzonitrile)palladium dichloride (0.025 g, 0.065 mmol) were heated in a sealed tube under argon at 70 °C for 7 h. The excess isoprene was evaporated off under reduced pressure to give the *chlorosilane* (8.1 g, 94%), which was used without further purification; ν_{max}(film)/cm^{-1} 1660 (C=C), 1600 (Ph) and 1120 (Si–Ph); δ_H(250 MHz; $CDCl_3$) 7.70 (4 H, br d, *J* 7.5, *o*-$SiPh_2$), 7.52–7.42 (6 H, m, *m*- and *p*-$SiPh_2$), 5.24 (1 H, br q, *J* 6.7, C*H*Me), 2.39 (2 H, s, $SiCH_2$), 1.63 (3 H, t, *J* 1.4, *Me*C=CH) and 1.40 (3 H, d, *J* 6.6, CH*Me*); δ_C(63 MHz; $CDCl_3$) 134.6, 133.9, 130.7, 130.3, 128.2, 119.8, 26.3, 23.1 and 14.2; *m*/*z* 288 [19%, M$^+$ (^{37}Cl)], 286 [49, M$^+$ (^{35}Cl)] and 77 (12, Ph) (Found: C, 71.3; H, 6.5; Cl, 12.5%; M$^+$, 286.0943 and 288.0912. $C_{17}H_{19}SiCl$ requires C, 71.2; H, 6.7; Cl, 12.4%; $C_{17}H_{19}Si^{35}Cl$ requires *M*, 286.0945 and $C_{17}H_{19}Si^{37}Cl$ requires *M*, 288.0915).

(*Z*)-(2-Methylbut-2-enyl)diphenylsilyllithium 9

Method 1. (*Z*)-Chloro(2-methylbut-2-enyl)diphenylsilane (0.745 g, 0.5 cm^3, 2.6 mmol) was stirred vigorously for 2 h with lithium shot (0.068 g, 9.8 mmol) in dry THF (5 cm^3) at 0 °C under argon. The deep red solution was stored overnight in a freezer at −18 °C and used within a few days. The molarity was determined by the double titration method of Gilman as modified by Whitesides.[21]

Method 2. A mixture of the disilane **8** (0.88 g, 1.75 mmol) and lithium powder (0.04 g, 6 mmol) in dry THF (5 cm^3) was sonicated for 2 h at 0 °C under argon. The resulting deep red solution of silyllithium reagent was then stored overnight in a freezer at −18 °C. Double titration indicated almost quantitative conversion.

(*Z*,*Z*)-1,2-Bis(2-methylbut-2-enyl)-1,1,2,2-tetraphenyldisilane 8

Freshly prepared silyllithium reagent **9** (0.74 mmol) was added dropwise to a stirred solution of the chlorosilane **7** (0.289 g, 1.01 mmol) in dry THF (5 cm^3) at 0 °C under argon. After stirring at this temperature for 4 h the reaction was quenched with water (10 cm^3) and the mixture filtered through Celite and extracted with light petroleum (3 × 10 cm^3). The organic layers were combined, washed with brine (10 cm^3), dried ($MgSO_4$) and concentrated under reduced pressure. The residue was chromatographed (SiO_2, EtOAc–hexane, 5:95) to give the *disilane* (0.24 g, 64%) as prisms, mp 110–111 °C (from hexane); R_f (EtOAc–hexane, 1:9) 0.49; ν_{max}(CH_2Cl_2)/cm^{-1} 1661 (C=C), 1587 (Ph) and 1103 (Si–Ph); δ_H(250 MHz; $CDCl_3$) 7.40 (8 H, br d, *J* 5.5, 2 × *o*-$SiPh_2$), 7.34–7.19 (12 H, m, 2 × *m*- and *p*-$SiPh_2$), 4.98 (2 H, br q, *J* 6.4, 2 × C=C*H*Me), 2.21 (4 H, s, 2 × $SiCH_2$), 1.40 (6 H, t, *J* 1.3, 2 × *Me*C=CH) and 1.16 (6 H, d, *J* 6.7, 2 × C=CH*Me*); δ_C(100 MHz; $CDCl_3$) 136.2, 135.4, 133.0, 129.0, 127.6, 118.2, 26.4, 18.9 and 13.7; *m*/*z* 502 (9%, M$^+$) and 433 (100, M − CH_2CMe=CHMe) (Found: C, 81.2; H, 7.6%; M$^+$, 502.2513. $C_{34}H_{38}Si_2$ requires C, 81.2; H, 7.6%; *M*, 502.2512).

Characterisation of the silyllithium reagent

(*Z*)-(2-Methylbut-2-enyl)diphenylsilane. Freshly prepared silyllithium reagent **9** (4.1 mmol) was poured into water and the mixture extracted with ether (3 × 15 cm^3). The organic layers were combined, washed with brine (10 cm^3), dried ($MgSO_4$) and concentrated under reduced pressure. The residue was chromatographed (SiO_2, EtOAc–hexane, 2:98) to give the *silane* (0.081 g, 20%); R_f (EtOAc–hexane, 2:98) 0.34; ν_{max}(film)/cm^{-1} 2140 (Si–H), 1670 (C=C) and 1600 (Ph); δ_H(250 MHz; $CDCl_3$) 7.56 (4 H, br d, *J* 7.6, *o*-$SiPh_2$), 7.43–7.31 (6 H, m, *m*- and *p*-$SiPh_2$), 5.12 (1 H, br q, *J* 6.4, C*H*Me), 4.89 (1 H, t, *J* 4.0, SiH), 2.09 (2 H, d, *J* 4.0, $SiCH_2$), 1.62 (3 H, t, *J* 1.4, *Me*C=CH) and 1.36 (3 H, d, *J* 6.7, CH*Me*); *m*/*z* 252 (19%, M$^+$), 251 (16, M − H) and 183 (100, Ph_2SiH) (Found: M$^+$, 252.1323. $C_{17}H_{20}Si$ requires *M*, 252.1334).

(*Z*)-(2-Methylbut-2-enyl)diphenylsilylmethanol. Formaldehyde gas (prepared by heating paraformaldehyde) in a stream of argon was bubbled through a solution of freshly prepared silyllithium reagent **9** (0.94 mmol) at room temperature. Mild refluxing was observed and the deep red solution changed colour to a light grey within 5 min. The mixture was poured into water and extracted with ether (3 × 15 cm^3). The organic layers

were combined, washed with brine (10 cm^3), dried ($MgSO_4$) and concentrated under reduced pressure. The residue was chromatographed (SiO_2, EtOAc–hexane, 1:4) to give the *alcohol* (0.145 g, 55%); R_f (EtOAc–hexane, 1:9) 0.16; ν_{max}(film)/cm^{-1} 3394 (br OH), 1662 (C=C), 1589 (Ph) and 1113 (SiPh); δ_H(250 MHz; $CDCl_3$) 7.66 (4 H, br d, *J* 5.5, *o*-$SiPh_2$), 7.47–7.24 (6 H, m, *m*- and *p*-$SiPh_2$), 5.21 (1 H, br q, *J* 6.7, C*H*Me), 4.65 (1 H, br s, OH), 3.98 (2 H, s, CH_2O), 2.23 (2 H, s, CH_2C), 1.61 (3 H, t, *J* 1.4, *Me*C=CH) and 1.50 (3 H, d, *J* 6.8, CH*Me*); *m*/*z* 282 (25%, M^+), 251 (19, M − CH_2OH) and 213 (100, M − CH_2-CMe=CHMe) (Found: M^+, 282.1449. $C_{18}H_{22}SiO$ requires *M*, 282.1440).

Lithium (*Z*)-bis[(2-methylbut-2-enyl)diphenylsilyl]cyanocuprate 10. Freshly prepared silyllithium reagent **9** (2.6 mmol) was added to a stirred suspension of dry copper(I) cyanide (0.096 g, 1.07 mmol) in dry THF (3 cm^3) at 0 °C under argon. The red-black mixture was stirred at this temperature for 25 min, and used immediately.

Methyl (*Z*)-3-(2-methylbut-2-enyl)diphenylsilyl-3-phenylpropanoate 12

Methyl cinnamate (0.152 g, 0.94 mmol) in THF (1 cm^3) was added dropwise to a stirred solution of freshly prepared bis-silylcuprate reagent **10** (1 mmol) at −78 °C under argon and the mixture stirred at this temperature for 1 h and then at 0 °C for a further 2 h. The mixture was quenched with basic aqueous ammonium chloride (10 cm^3), filtered through Celite and extracted with ether (3 × 10 cm^3). The combined organic layers were washed with basic aqueous ammonium chloride (5 cm^3) and brine (5 cm^3), dried ($MgSO_4$) and concentrated under reduced pressure. The residue was chromatographed (SiO_2, EtOAc–hexane, 15:85) to give the *β-silyl ester* (0.35 g, 90%) as prisms, mp 70–71 °C (from hexane); R_f (EtOAc–hexane, 15:85) 0.41; ν_{max}(film)/cm^{-1} 1738 (C=O), 1663 (C=C), 1599 (Ph) and 1100 (Si–Ph); δ_H(250 MHz; $CDCl_3$) 7.51–7.29 (10 H, m, $SiPh_2$), 7.16-7.08 (2 H, m, *m*- and *p*-CPh), 6.86 (1 H, br d, *J* 9.4, *o*-CPh), 4.90 (1 H, br q, *J* 6.4, C*H*Me), 3.46 (3 H, s, OMe), 3.36 (1 H, dd, *J* 12.3 and 3.4, PhC*H*Si), 2.82 (1 H, dd, *J* 16.1 and 3.4, CH_AH_B-CO), 2.62 (1 H, dd, *J* 16.1 and 12.3, CH_AH_BCO), 1.85 (2 H, s, $SiCH_2$), 1.41 (3 H, t, *J* 1.5, *Me*C=CH) and 1.08 (3 H, d, *J* 6.7, CH*Me*); *m*/*z* 414 (5%, M^+), 345 (100, M − CH_2CMe=CHMe) and 251 (20, M − CHPhCH$_2$CO$_2$Me) (Found: C, 78.3; H, 7.4%; M^+, 414.2010. $C_{27}H_{30}SiO_2$ requires C, 78.2; H, 7.3%; *M*, 414.2015).

Methyl (*Z*)-(2*RS*,3*RS*)-2-methyl-3-(2-methylbut-2-enyl)-diphenylsilyl-3-phenylpropanoate 13

Methyl cinnamate (0.123 g, 0.76 mmol) in THF (1 cm^3) was added dropwise to a stirred solution of freshly prepared bis-silylcuprate reagent **10** (0.95 mmol) at −78 °C under argon. The mixture was stirred at this temperature for 1 h, then at 0 °C for a further 1 h and then cooled to −78 °C. Methyl iodide (0.3 cm^3, 4.82 mmol) in THF (1 cm^3) was added dropwise and the mixture allowed to warm slowly to room temperature and stirred overnight. The mixture was quenched with basic aqueous ammonium chloride (10 cm^3), filtered through Celite and extracted with ether (3 × 10 cm^3). The organic layers were combined, washed with basic aqueous ammonium chloride (5 cm^3) and brine (5 cm^3), dried ($MgSO_4$) and concentrated under reduced pressure. The residue was chromatographed (SiO_2, EtOAc–hexane, 1:9) to give the *β-silyl ester* (0.288 g, 89%, as a 93:7 mixture with its diastereoisomer **15**); R_f (EtOAc–hexane, 1:9) 0.40; ν_{max}(film)/cm^{-1} 1745 (C=O), 1665 (C=C), 1600 (Ph) and 1115 (Si–Ph); δ_H(250 MHz; $CDCl_3$) 7.69 (2 H, br d, *J* 7.8, *o*-Si*Ph*$_A$Ph$_B$), 7.44 (2 H, br d, *J* 6.6, *o*-SiPh$_A$*Ph*$_B$), 7.42–7.36 (3 H, m, *m*- and *p*-Si*Ph*$_A$Ph$_B$), 7.33–7.23 (3 H, m, *m*- and *p*-SiPh$_A$*Ph*$_B$), 7.15–7.08 (3 H, m, *m*- and *p*-CPh), 6.84 (2 H, br d, *J* 7.9, *o*-CPh), 4.81 (1 H, br q, *J* 6.4, C=C*H*Me), 3.07 (3 H, s, OMe), 3.04 (1 H, d, *J* 10.7, PhC*H*Si), 2.96 (1 H, dq, *J* 10.8 and 6.3, CHCO), 1.76 (1 H, d, *J* 14.1, SiC*H*$_A$H$_B$), 1.73 (1 H, d, *J* 14.1, SiCH$_A$*H*$_B$), 1.28 (3 H, t, *J* 1.4, *Me*C=CH), 1.11 (3 H, d, *J* 6.7, C=CH*Me*) and 0.87 (3 H, d, *J* 6.3, *Me*CHCO); *m*/*z* 428 (37%, M^+), 413 (29, M − Me), 397 (58, M − OMe) and 359 (100, M − CH_2CMe=CHMe) (Found: M^+, 428.2168. $C_{28}H_{32}SiO_2$ requires *M*, 428.2172).

Methyl (*Z*)-(2*RS*,3*SR*)-2-methyl-3-(2-methylbut-2-enyl)-diphenylsilyl-3-phenylpropanoate 15

Methyl 2-methylcinnamate (0.158 g, 0.90 mmol) in THF (1 cm^3) was added dropwise to a stirred solution of freshly prepared bis-silylcuprate reagent **10** (0.97 mmol) at −78 °C under argon. The mixture was stirred at this temperature for 1 h, then allowed to warm slowly to 0 °C and stirred at this temperature for a further 1 h. The mixture was cooled to −78 °C, quenched with basic aqueous ammonium chloride (10 cm^3), filtered through Celite and extracted with ether (3 × 10 cm^3). The organic layers were combined, washed with basic aqueous ammonium chloride (5 cm^3) and brine (5 cm^3), dried ($MgSO_4$) and concentrated under reduced pressure. The residue, in which the diastereoisomers **15** and **13** were present in a ratio of 80:20, was chromatographed (SiO_2, EtOAc–hexane, 1:9) to give the *β-silyl ester* **15** (0.250 g, 65%) as prisms, mp 75–77 °C (from hexane); R_f (EtOAc–hexane, 1:9) 0.31; ν_{max}(film)/cm^{-1} 1740 (C=O), 1640 (C=C), 1600 (Ph) and 1110 (Si–Ph); δ_H(250 MHz; $CDCl_3$) 7.64 (2 H, br d, *J* 7.6, *o*-Si*Ph*$_A$Ph$_B$), 7.55 (2 H, br d, *J* 7.7, *o*-SiPh$_A$*Ph*$_B$), 7.48–7.37 (3 H, m, *m*- and *p*-Si*Ph*$_A$Ph$_B$), 7.36–7.27 (3 H, m, *m*- and *p*-SiPh$_A$*Ph*$_B$), 7.22–7.10 (3 H, m, *m*- and *p*-CPh), 6.98 (2 H, br d, *J* 8.3, *o*-CPh), 4.78 (1 H, br q, *J* 6.7, C=C*H*Me), 3.27 (3 H, s, OMe), 3.12 (1 H, d, *J* 11.7, PhC*H*Si), 2.86 (1 H, dq, *J* 11.7 and 6.9, CHCO), 1.67 (1 H, d, *J* 14.7, SiC*H*$_A$H$_B$), 1.52 (1 H, d, *J* 14.7, SiCH$_A$*H*$_B$), 1.28 (3 H, t, *J* 1.3, *Me*C=CH), 1.14 (3 H, d, *J* 6.9, *Me*CHCO) and 0.99 (3 H, d, *J* 6.7, C=CH*Me*); *m*/*z* 428 (23%, M^+), 413 (36, M − Me), 397 (67, M − OMe) and 359 (100, M − CH_2CMe=CHMe) (Found: M^+, 428.2206. $C_{28}H_{32}SiO_2$ requires *M*, 428.2172) (Found: C, 78.3; H, 7.5. $C_{28}H_{32}SiO_2$ requires C, 78.5; H, 7.5%), and the *β-silyl ester* **13** (0.097 g, 25%), identical (TLC, IR, ^{1}H NMR) with the ester above.

(1*E*,2′*Z*)-Hex-1-enyl(2′-methylbut-2′-enyl)diphenylsilane 17

Hex-1-yne (0.29 cm^3, 2.5 mmol) was added dropwise to a stirred solution of freshly prepared bis-silylcuprate reagent **10** (3.1 mmol) at −78 °C under argon. The mixture was stirred at this temperature for 1 h and then at room temperature overnight. The mixture was quenched with basic aqueous ammonium chloride (10 cm^3), filtered through Celite and extracted with light petroleum (3 × 10 cm^3). The organic layers were combined, washed with basic aqueous ammonium chloride (5 cm^3) and brine (5 cm^3), dried ($MgSO_4$) and concentrated under reduced pressure. The residue was chromatographed (SiO_2, hexane) to give the *vinylsilane* (0.76 g, 91%); R_f (EtOAc–hexane, 1:9) 0.58; ν_{max}(film)/cm^{-1} 1670 (C=C), 1600 (Ph) and 1120 (Si–Ph); δ_H(250 MHz; $CDCl_3$) 7.68 (4 H, br d, *J* 7.1, *o*-$SiPh_2$), 7.51–7.36 (6 H, m, *m*- and *p*-$SiPh_2$), 6.16 (1 H, dt, *J* 18.5 and 5.8, SiC=CH), 6.02 (1 H, d, *J* 18.6, SiCH=C), 5.15 (1 H, br q, *J* 6.5, C=C*H*Me), 2.25 (2 H, q, *J* 6.5, C=CCH_2), 2.18 (2 H, s, $SiCH_2$), 1.62 (3 H, t, *J* 1.4, *Me*C=CH), 1.62–1.31 (4 H, m, CH_2CH_2Me), 1.40 (3 H, d, *J* 6.6, C=CH*Me*) and 0.95 (3 H, t, *J* 7.0, CH_2*Me*); *m*/*z* 334 (56%, M^+) and 265 (100, M − CH_2-CMe=CHMe) (Found: M^+, 334.2115. $C_{23}H_{30}Si$ requires *M*, 334.2117).

(*Z*)-Propen-2-yl(2-methylbut-2-enyl)diphenylsilane 19

Condensed allene (0.04 cm^3 at −78 °C, 0.87 mmol) in dry THF (10 cm^3) was added dropwise to a stirred solution of freshly prepared bis-silylcuprate reagent **10** (2.5 mmol) at −78 °C under argon. The mixture was stirred at this temperature for 1 h and then at room temperature overnight. The mixture was quenched with basic aqueous ammonium chloride (10 cm^3), filtered through Celite and extracted with light petroleum (3 × 10 cm^3).

The organic layers were combined, washed with basic aqueous ammonium chloride (5 cm^3) and brine (5 cm^3), dried ($MgSO_4$) and concentrated under reduced pressure. The residue was chromatographed (SiO_2, hexane) to give the *vinylsilane* (0.225 g, 89%); R_f (hexane) 0.62; ν_{max}(film)/cm^{-1} 1662 (C=C), 1617 (C=C), 1588 (Ph) and 1109 (Si–Ph); δ_H(250 MHz; $CDCl_3$) 7.54 (4 H, br d, *J* 7.4, *o*-$SiPh_2$), 7.44–7.31 (6 H, m, *m*- and *p*-$SiPh_2$), 5.87 (1 H, br s, C=CH_AH_B), 5.44 (1 H, br s, C=CH_AH_B), 5.07 (1 H, br q, *J* 6.3, C=C*H*Me), 2.19 (2 H, s, $SiCH_2$), 1.91 (3 H, t, *J* 1.4, *Me*C=CH_2), 1.60 (3 H, t, *J* 1.4, *Me*C=CH) and 1.26 (3 H, dd, *J* 6.7 and 0.4, C=CH*Me*); *m*/*z* 292 (54%, M^+), 251 (32, M − MeC=CH_2) and 223 (100, M − CH_2CMe=CHMe) (Found: M^+, 292.1646. $C_{20}H_{24}Si$ requires *M*, 292.1647).

(*Z*)-(2-Cyclohexylideneethyl)(2-methylbut-2-enyl)diphenylsilane 21

1-Vinylcyclohexyl acetate[27] (0.032 g, 0.19 mmol) was added dropwise to a stirred solution of freshly prepared bis-silylcuprate reagent **10** (0.28 mmol) at −78 °C under argon. The mixture was stirred at this temperature for 1 h and then at 0 °C for 30 min. The mixture was quenched with basic aqueous ammonium chloride (10 cm^3), filtered through Celite and extracted with ether (3 × 10 cm^3). The organic layers were combined, washed with basic aqueous ammonium chloride (5 cm^3) and brine (5 cm^3), dried ($MgSO_4$) and concentrated under reduced pressure. The residue was chromatographed (SiO_2, hexane) to give the *allylsilane* (0.056 g, 82%); R_f (EtOAc–hexane, 2:98) 0.46; ν_{max}(film)/cm^{-1} 1670 (C=C), 1600 (Ph) and 1120 (Si–Ph); δ_H(250 MHz; $CDCl_3$) 7.55 (4 H, br d, *J* 5.4, *o*-$SiPh_2$), 7.41–7.29 (6 H, m, *m*- and *p*-$SiPh_2$), 5.15 (1 H, t, *J* 8.1, C=C*H*CH_2), 5.08 (1 H, br q, *J* 6.7, C*H*Me), 2.09 (2 H, s, CH_2CMe), 2.01 (2 H, d, *J* 8.2, SiCH_2CH=C), 2.01–1.99 [2 H, m, $(CH_2)_A(CH_2)_B$C=C], 1.90 [2 H, t, *J* 6.0, $(CH_2)_A(CH_2)_B$C=C], 1.52 (3 H, t, *J* 1.4, *Me*C=CH), 1.33 (3 H, d, *J* 6.7, CH*Me*) and 1.43–1.19 [6 H, m, $(CH_2)_3CH_2$C=C]; *m*/*z* 360 (53%, M^+), 290 (82, M − Me_2C=CHMe) and 183 (100, Ph_2SiH) (Found: M^+, 360.2273. $C_{25}H_{32}Si$ requires *M*, 360.2273).

1-Cyclopentyloct-2-yn-1-ol

Butyllithium (1.1 mol dm^{-3} in hexane, 2.4 cm^3, 2.6 mmol) was added dropwise to a stirred solution of hept-1-yne (0.34 cm^3, 0.88 mmol) in dry THF (20 cm^3) at −78 °C under nitrogen. After stirring at this temperature for 5 min, cyclopentanecarbaldehyde[28] (0.258 g, 2.6 mmol) in dry THF (2 cm^3) was added *via* a cannula and the solution was stirred at this temperature for a further 15 min. The mixture was poured onto saturated aqueous ammonium chloride (20 cm^3) and extracted with ethyl acetate (4 × 30 cm^3). The organic layers were combined, washed with brine (10 cm^3), dried ($MgSO_4$) and concentrated under reduced pressure. The residue was chromatographed (SiO_2, EtOAc–hexane, 15:85) to give the *propargyl alcohol* (0.422 g, 84%); R_f (EtOAc–hexane, 1:4) 0.40; ν_{max}(film)/cm^{-1} 3350 (br OH) and 2240 (C≡C); δ_H(250 MHz; $CDCl_3$) 4.21 (1 H, br d, *J* 6.9, C*H*OH), 2.18 (2 H, td, *J* 7.0 and 1.9, CH_2C≡C), 2.13 (1 H, sextet, *J* 7.5, C*H*CHOH), 1.75–1.28 [15 H, m, $(CH_2)_4$CHCHOH, $(CH_2)_3$Me and OH] and 0.88 (3 H, t, *J* 7.0, Me); *m*/*z* 194 (57%, M^+), 179 (68, M − Me), 165 (51, M − CH_2Me), 151 (33, M − CH_2CH_2Me), 138 [13, M − $(CH_2)_3$Me] and 125 (100, M − C_5H_9) (Found: M^+, 194.1722. $C_{13}H_{22}O$ requires *M*, 194.1722).

(*Z*)-1-Cyclopentyloct-2-en-1-ol

A 50 cm^3 round bottomed flask containing the propargyl alcohol (1.163 g, 6 mmol), modified Lindlar catalyst (Pd + $MnCl_2$)[29] (0.033 g) and quinoline (0.09 g) in heptane (15 cm^3), at room temperature with vigorous stirring, was alternately evacuated and then flushed with nitrogen 4 times, and the procedure repeated with hydrogen. The mixture was stirred under an atmosphere of hydrogen overnight, filtered through Celite and then washed with aqueous hydrochloric acid (10%, 10 cm^3). The washing was extracted with ether (10 cm^3), the organic layers combined, washed with brine (10 cm^3), dried (Na_2SO_4) and concentrated under reduced pressure to give the *allyl alcohol* (1.175 g, 100%); R_f (EtOAc–hexane, 1:4) 0.40; ν_{max}(film)/cm^{-1} 3360 (br OH) and 1650 (C=C); δ_H(250 MHz; $CDCl_3$) 5.49 (1 H, dt, *J* 11.1 and 7.1, C=C*H*CH_2), 5.38 (1 H, tt, *J* 11.0 and 1.3, C*H*=$CHCH_2$), 4.20 (1 H, t, *J* 8.3, CHOH), 2.23–1.25 [18 H, m, $(CH_2)_4$C*H*CHO, $(CH_2)_4$Me and OH] and 0.88 (3 H, t, *J* 6.8, Me); *m*/*z* 196 (55%, M^+), 127 (87, M − C_5H_9), 109 (83, M − C_5H_9 − H_2O) and 57 [100, Me$(CH_2)_3$] (Found: M^+, 196.1832. $C_{13}H_{24}O$ requires *M*, 196.1878).

(*Z*)-1-Cyclopentyloct-2-en-1-yl acetate 22

Acetic anhydride (0.04 cm^3, 0.42 mmol), (*Z*)-1-cyclopentyloct-2-en-1-yl (0.063 g, 0.32 mmol) and 4-dimethylaminopyridine (0.044 g, 0.36 mmol) were stirred in dry dichloromethane (5 cm^3) under nitrogen at room temperature overnight. Ether (5 cm^3) and hydrochloric acid (1 mol dm^{-3} in H_2O, 5 cm^3) were added, and the organic layer washed with aqueous sodium hydroxide (1 mol dm^{-3}, 5 cm^3) and brine (5 cm^3), dried ($MgSO_4$) and concentrated under reduced pressure. The residue was chromatographed (SiO_2, EtOAc–hexane, 5:95) to give the *acetate* (0.064 g, 85%); R_f (EtOAc–hexane, 1:9) 0.47; ν_{max}(film)/cm^{-1} 1740 (C=O); δ_H(250 MHz; $CDCl_3$) 5.53 (1 H, dt, *J* 10.7 and 7.4, C=C*H*CH_2), 5.41 (1 H, dd, *J* 9.3 and 8.3, C*H*OAc), 5.27 (1 H, ddt, *J* 10.8, 9.3 and 1.5, C*H*=$CHCH_2$), 2.21–2.04 (3 H, m, C*H*CHOAc and C=CHCH_2), 2.02 (3 H, s, OMe), 1.75–1.43 [6 H, m, $(CH_2)_3$Me], 1.41–1.12 [8 H, m, $(CH_2)_4$CHCHOAc)] and 0.87 (3 H, t, *J* 6.7, CH_2*Me*); *m*/*z* 238 (10%, M^+), 196 (40, M − CH_2CO), 179 (33, M − OAc) and 127 (100, M − CH_2CO − C_5H_9) (Found: M^+, 238.1939. $C_{15}H_{26}O_2$ requires *M*, 238.1933).

(*Z*)-1-Cyclopentyloct-2-en-1-yl *N*-phenylcarbamate 23

Phenyl isocyanate (0.2 cm^3, 1.8 mmol), the allyl alcohol (0.193 g, 0.985 mmol) and triethylamine (0.2 cm^3, 1.4 mmol) were stirred in dry dichloromethane (2 cm^3) under nitrogen at room temperature for 2.5 h. The mixture was quenched with water (5 cm^3) and extracted with dichloromethane (5 × 5 cm^3). The organic layers were combined, washed with aqueous hydrochloric acid (0.1 mol dm^{-3}, 3 cm^3) and brine (3 cm^3), dried ($MgSO_4$) and concentrated under reduced pressure. The residue was chromatographed (SiO_2, EtOAc–hexane, 1:4) to give the *carbamate* (0.278 g, 82%); R_f (EtOAc–hexane, 1:4) 0.58; ν_{max}(film)/cm^{-1} 3321 (br NH), 1704 (C=O) and 1601 (Ph); δ_H(250 MHz; $CDCl_3$) 7.37 (2 H, d, *J* 7.5, *o*-Ph), 7.32–7.25 (2 H, m, *m*-Ph), 7.01 (1 H, br t, *J* 7.2, *p*-Ph), 6.52 (1 H, br s, NH), 5.57 (1 H, dt, *J* 10.4 and 7.4, C=C*H*CH_2), 5.42 (1 H, dd, *J* 9.4 and 7.4, CHO), 5.33 (1 H, ddt, *J* 10.4, 9.4 and 1.5, C*H*=$CHCH_2$), 2.21 (2 H, br q, *J* 7.2, CH_2C=C), 2.09 (1 H, sextet, *J* 7.7, C*H*CHO), 1.81–1.18 [14 H, m, $(CH_2)_4$CHCHO) and $(CH_2)_3$Me] and 0.87 (3 H, t, *J* 6.5, Me); *m*/*z* 315 (9%, M^+), 271 (19, M − CO_2) and 179 (69, M − OCONHPh) (Found: M^+, 315.2197. $C_{20}H_{29}NO_2$ requires *M*, 315.2198).

(1*E*,2′*Z*)-1-Cyclopentyloct-1-en-3-yl-2′-methylbut-2′-enyl-(diphenyl)silane 24

Method 1. Butyllithium (1.43 mol dm^{-3} in hexane, 0.28 cm^3, 0.40 mmol) was added dropwise to a stirred solution of the carbamate **23** (0.114 g, 0.36 mmol) in dry THF (2 cm^3) at 0 °C under nitrogen. After stirring at this temperature for 2 min the solution was added *via* a cannula to a vigorously stirred slurry of dry copper(I) iodide (0.069 g, 0.362 mmol) and triphenylphosphine (0.191 g, 0.73 mmol) in dry ether (3 cm^3) at 0 °C under nitrogen. The mixture was stirred at this temperature for a further 45 min forming a yellow slurry. The silyllithium reagent **9** (0.40 mmol) was added dropwise to the slurry and the mixture stirred at 0 °C for 3 h and then at room temperature for a further 12 h. The mixture was quenched with basic aqueous

ammonium chloride (10 cm^3), filtered through Celite and extracted with light petroleum (3 × 10 cm^3). The organic layers were combined, washed with basic aqueous ammonium chloride (5 cm^3) and brine (5 cm^3), dried ($MgSO_4$) and concentrated under reduced pressure. The residue was chromatographed (SiO_2, hexane) to give the *allylsilane* (0.098 g, 64%); R_f (EtOAc–hexane, 1:9) 0.40; ν_{max}(film)/cm^{-1} 1660 (C=C) and 1110 (Si–Ph); δ_H(250 MHz; $CDCl_3$) 7.57–7.47 (4 H, m, *o*-$SiPh_2$), 7.41–7.27 (6 H, m, *m*- and *p*-$SiPh_2$), 5.24 (1 H, dd, *J* 15.3 and 7.0, C*H*=CHCHSi), 5.13 (1 H, dd, *J* 15.3 and 9.1, CH=C*H*CHSi), 4.95 (1 H, br q, *J* 6.5, C=C*H*Me), 2.35 (1 H, sextet, *J* 7.4, C*H*CH=CHCHSi), 2.13–2.02 (1 H, m, C=CHC*H*Si), 2.08 (1 H, d, *J* 13.8, $SiCH_AH_B$), 2.02 (1 H, d, *J* 13.7, $SiCH_AH_B$), 1.72–1.37 [8 H, m, $(CH_2)_4$CHCH=CHCHSi], 1.48 (3 H, t, *J* 1.4, *Me*C=CH), 1.24–1.09 [8 H, m, $(CH_2)_4$Me], 1.17 (3 H, d, *J* 6.7, C=CH*Me*) and 0.82 (3 H, t, *J* 6.7, CH_2Me); δ_C(100 MHz; $CDCl_3$) 135.7, 135.0, 134.7, 134.6, 132.7, 128.9, 127.7, 127.2, 117.5, 43.5, 33.2, 31.3, 30.3, 28.8, 28.5, 26.3, 24.9, 22.5, 17.9 and 14.0; *m*/*z* 361 (20%, M − C_5H_9) and 183 (100, Ph_2SiH) (Found: $M^+ - C_5H_9$, 361.2347. $C_{25}H_{33}Si$ requires *M*, 361.2351), and the recovered carbamate **23** (0.021 g, 18%).

Method 2. Freshly prepared silyllithium reagent **9** (0.27 mmol) was added dropwise to stirred slurry of dry copper(I) iodide (0.044 g, 0.23 mmol) in dry ether (1.5 cm^3) and triphenylphosphine (0.120 g, 0.46 mmol) at 0 °C under argon. The mixture was stirred at this temperature for 20 min. Butyllithium (1.34 mol dm^{-3} in hexane, 0.17 cm^3, 0.23 mmol) was added dropwise to a stirred solution of the carbamate **23** (0.072 g, 0.23 mmol) in dry THF (1 cm^3) at 0 °C under argon. After stirring at this temperature for 2 min the solution was added *via* a cannula to the silylcopper reagent at 0 °C. The mixture was stirred at this temperature for a further 4 h. The reaction was quenched with basic aqueous ammonium chloride (1 cm^3) and the mixture filtered through Celite and extracted with light petroleum (3 × 5 cm^3). The organic layers were combined, washed with basic aqueous ammonium chloride (3 cm^3) and brine (3 cm^3), dried ($MgSO_4$) and concentrated under reduced pressure. The residue was chromatographed (SiO_2, light petroleum) to give the allylsilane (0.068 g, 69%), identical (TLC, IR, ^1H NMR) with the earlier sample, and the recovered carbamate **23** (0.014 g, 19%).

Method 3. The allylic acetate **22** (0.048 g, 0.2 mmol) in dry ether–pentane (1:1, 2 cm^3) was added dropwise to a mixture of the silylcuprate reagent **10** (0.2 mmol) and triphenylphosphine (0.053 g, 0.2 mmol) and the mixture stirred at 0 °C for a further 45 min. The mixture was quenched with basic aqueous ammonium chloride (1 cm^3), filtered through Celite and extracted with light petroleum (3 × 3 cm^3). The organic layers were combined, washed with basic aqueous ammonium chloride (2 cm^3) and brine (2 cm^3), dried ($MgSO_4$) and concentrated under reduced pressure. The residue was chromatographed (SiO_2, hexane) to give a mixture of the allylsilane and another isomer (0.067 g, 78%, 4:1).

Methyl 3-(fluorodiphenylsilyl)-3-phenylpropanoate 25

Boron trifluoride–acetic acid complex (0.05 cm^3, 0.2 mmol) was added dropwise to a stirred solution of the allylsilane **12** (0.057 g, 0.14 mmol) in dichloromethane (5 cm^3) at 0 °C under argon. TLC indicated that the reaction was complete almost immediately. The mixture was poured into water and extracted with dichloromethane (2 × 15 cm^3). The organic layers were combined and washed with saturated aqueous sodium hydrogen carbonate (10 cm^3), dried ($MgSO_4$) and concentrated under reduced pressure to give the *fluorosilane* (crude yield 0.050 g, 100%); R_f (EtOAc–hexane, 1:4) 0.34; ν_{max}(film)/cm^{-1} 1745 (C=O), 1600 (Ph), 1130 (Si–Ph) and 850 (Si–F); δ_H(250 MHz; $CDCl_3$) 7.57 (2 H, br d, *J* 5.7, *o*-$SiPh_APh_B$), 7.48–7.27 (8 H, m, *m*-, *p*-$SiPh_2$ and *o*-$SiPh_APh_B$), 7.18–7.11 (3 H, m, *m*- and *p*-CPh), 7.04 (2 H, br d, *J* 6.4, *o*-CPh), 3.49 (3 H, s, OMe), 3.35 (1 H, q, *J* 7.5, PhC*H*Si) and 2.88 (2 H, d, *J* 7.6, CH_2CO); *m*/*z* 364 (25%, M^+), 345 (62, M − F) and 201 (100, Ph_2SiF) (Found: M^+, 364.1296. $C_{22}H_{21}SiO_2F$ requires *M*, 364.1291).

Methyl 3-(hydroxydiphenylsilyl)-3-phenylpropanoate 26 and methyl 3-(methoxydiphenylsilyl)-3-phenylpropanoate 27

Hydrochloric acid (10 mol dm^{-3}, 5 drops) and the allylsilane **12** (0.05 g, 0.12 mmol) were refluxed in methanol (5 cm^3) for 1 h. The solvent was evaporated under reduced pressure and the residue taken up in ether (10 cm^3), washed with aqueous sodium hydrogen carbonate (2 cm^3) and brine (2 cm^3), dried ($MgSO_4$) and concentrated under reduced pressure. The residue was chromatographed (SiO_2, EtOAc–hexane, 1:4) to give successively the *methoxysilane* **27** (0.022 g, 49%); R_f (EtOAc–hexane, 1:9) 0.44; ν_{max}(film)/cm^{-1} 1738 (C=O) and 1113 (Si–Ph); δ_H(250 MHz; $CDCl_3$) 7.54 (2 H, br d, *J* 5.5, *o*-$SiPh_APh_B$), 7.48–7.20 (8 H, m, *m*-, *p*-$SiPh_2$ and *o*-$SiPh_APh_B$), 7.16–7.04 (3 H, m, *m*- and *p*-CPh), 6.95 (2 H, br d, *J* 8.0, *o*-CPh), 3.47 (3 H, s, OMe), 3.46 (3 H, s, OMe), 3.31 (1 H, dd, *J* 11.1 and 4.7, PhC*H*Si), 2.87 (1 H, dd, *J* 16.2 and 4.7, CH_AH_BCO) and 2.77 (1 H, dd, *J* 16.2 and 11.1, CH_AH_BCO); *m*/*z* 376 (64%, M^+) and 213 (100, Ph_2SiOMe) (Found: M^+, 376.1530. $C_{23}H_{24}SiO_3$ requires *M*, 376.1495), and the *silanol* **26** (0.021 g, 48%), R_f (EtOAc–hexane, 1:9) 0.13; ν_{max}(film)/cm^{-1} 3440 (br OH), 1715 (C=O), 1600 (Ph) and 1116 (Si–Ph); δ_H(250 MHz; $CDCl_3$) 7.57 (2 H, br d, *J* 7.5, *o*-$SiPh_APh_B$), 7.45–7.28 (8 H, m, *m*-, *p*-$SiPh_2$ and *o*-$SiPh_APh_B$), 7.19–7.06 (3 H, m, *m*- and *p*-CPh), 6.98 (2 H, br d, *J* 6.5, *o*-CPh), 3.50 (3 H, s, OMe), 3.21 (1 H, dd, *J* 8.6 and 6.5, PhC*H*Si), 2.87 (1 H, dd, *J* 16.4 and 6.6, CH_AH_BCO) and 2.84 (1 H, dd, *J* 16.4 and 8.7, CH_AH_BCO); *m*/*z* 362 (26%, M^+) and 199 (100, Ph_2SiOH) (Found: M^+, 362.1312. $C_{22}H_{22}SiO_3$ requires *M*, 362.1318).

Methyl 3-hydroxy-3-phenylpropanoate 28a

Method 1. Boron trifluoride–acetic acid complex (0.04 cm^3, 0.16 mmol) was added dropwise to a stirred solution of the allylsilane **12** (0.051 g, 0.12 mmol) in dichloromethane (5 cm^3) at room temperature under argon. After 30 seconds the mixture was quenched with sodium hydrogen carbonate (0.175 g, 2.1 mmol) and the solvent evaporated under reduced pressure. THF (4 cm^3), methanol (4 cm^3), potassium fluoride (0.03 g, 0.5 mmol) and hydrogen peroxide (30%, 1 cm^3, 8.7 mmol) were added and the mixture was stirred for 3 d at room temperature, with further hydrogen peroxide (30%, 1 cm^3) added each day. The mixture was poured into water and extracted with dichloromethane (5 × 10 cm^3). The organic layers were combined, washed with brine (5 cm^3), dried ($MgSO_4$) and concentrated under reduced pressure. The residue was chromatographed (SiO_2, EtOAc–hexane, 1:4) to give the alcohol[30] (0.017 g, 77%); R_f (EtOAc–hexane, 1:4) 0.17; ν_{max}($CDCl_3$)/cm^{-1} 3601 (OH), 3510 (br OH), 1726 (C=O) and 1605 (Ph); δ_H(250 MHz; $CDCl_3$) 7.37–7.25 (5 H, m, Ph), 5.14 (1 H, ddd, *J* 8.0, 4.3 and 3.5, C*H*OH), 3.72 (3 H, s, OMe), 3.23 (1 H, d, *J* 3.4, OH), 2.76 (1 H, dd, *J* 16.4 and 8.4, CH_AH_BCO) and 2.72 (1 H, dd, *J* 16.4 and 4.5, CH_AH_BCO).

Method 2. Peracetic acid (36–40% in AcOH, 0.7 cm^3, 3.5 mmol) was added dropwise to a stirred mixture of the allylsilane **12** (0.287 g, 0.69 mmol), potassium bromide (0.099 g, 0.83 mmol) and sodium acetate (0.17 g, 2 mmol) in acetic acid (3.5 cm^3) at 0 °C. The mixture was allowed to warm to room temperature and more peracetic acid (2.1 cm^3, 10.5 mmol) and sodium acetate (0.5 g, 6 mmol) were added and the mixture stirred overnight. The mixture was quenched with aqueous sodium thiosulfate solution (25%), the aqueous layer saturated with salt and the mixture extracted with ethyl acetate (5 × 10 cm^3). The combined organic layers were washed with saturated aqueous sodium hydrogen carbonate (5 cm^3) and brine (5 cm^3), dried (Na_2SO_4) and concentrated under reduced pressure. The residue was chromatographed (SiO_2, EtOAc–hexane, 1:4) to give the alcohol (0.099 g, 80%), identical (TLC, ^1H NMR) with the earlier sample.

Methyl (2*RS*,3*RS*)-2-methyl-3-hydroxy-3-phenylpropanoate 29 and methyl (2*RS*,3*RS*)-2-methyl-3-(hydroxydiphenylsilyl)-3-phenylpropanoate 30

Boron trifluoride–acetic acid complex (0.07 cm^3, 0.25 mmol) was added dropwise to a stirred solution of the allylsilane **13** (0.214 g, 0.5 mmol) in dichloromethane (5 cm^3) at room temperature under argon. After 5 min the reaction was quenched with sodium hydrogen carbonate (0.2 g, 2.4 mmol) and the solvent evaporated under reduced pressure. THF (4 cm^3), methanol (4 cm^3), potassium fluoride (0.03 g, 0.5 mmol) and hydrogen peroxide (30%, 1 cm^3, 8.7 mmol) were added and the mixture was stirred for 24 h at room temperature. The mixture was poured into water (5 cm^3) and extracted with dichloromethane (5 × 10 cm^3). The organic layers were combined, washed with brine (5 cm^3), dried ($MgSO_4$) and concentrated under reduced pressure. The residue was chromatographed (SiO_2, EtOAc–hexane, 1:9) to give the alcohol[31] **29** (0.032 g, 33%); R_f (EtOAc–hexane, 1:9) 0.07; $\nu_{max}(CDCl_3)/cm^{-1}$ 3603 (OH), 3510 (br OH), 1736 (C=O), 1604 (Ph) and 1587 (Ph); δ_H(250 MHz; $CDCl_3$) 7.38–7.26 (5 H, m, Ph), 4.73 (1 H, d, *J* 8.6, C*H*OH), 3.72 (3 H, s, OMe), 2.95 (1 H, br s, OH), 2.81 (1 H, qn, *J* 7.2, C*H*Me) and 0.99 (3 H, d, *J* 7.2, CH*Me*) and the *silanol* **30** (0.082 g, 44%); R_f (EtOAc–hexane, 1:9) 0.14; $\nu_{max}(CDCl_3)/cm^{-1}$ 3649 (OH), 3530 (br OH), 1720 (C=O), 1599 (Ph) and 1590 (Ph); δ_H(250 MHz; $CDCl_3$) 7.58 (2 H, br d, *J* 7.7, *o*-Si*Ph*$_A$Ph$_B$), 7.44 (2 H, br d, *J* 7.5, *o*-SiPh$_A$*Ph*$_B$), 7.40–7.31 (3 H, m, *m*- and *p*-Si*Ph*$_A$Ph$_B$), 7.28–7.22 (3 H, m, *m*- and *p*-SiPh$_A$*Ph*$_B$), 7.16–7.11 (3 H, m, *m*- and *p*-CPh), 6.97 (2 H, br d, *J* 6.5, *o*-CPh), 3.28 (3 H, s, OMe), 3.12 (1 H, dq, *J* 11.0 and 6.6, C*H*Me), 2.96 (1 H, d, *J* 11.0, SiCH) and 1.04 (3 H, d, *J* 6.7, CH*Me*).

Methyl (2*RS*,3*SR*)-2-methyl-3-hydroxy-3-phenylpropanoate 31 and methyl (2*RS*,3*SR*)-2-methyl-3-(hydroxydiphenylsilyl)-3-phenylpropanoate 32

Boron trifluoride–acetic acid complex (0.04 cm^3, 0.14 mmol) was added dropwise to a stirred solution of the allylsilane **15** (0.051 g, 0.12 mmol) in dichloromethane (5 cm^3) at room temperature under argon. After 30 seconds the reaction was quenched with sodium hydrogen carbonate (0.175 g, 2.1 mmol) and the solvent evaporated under reduced pressure. THF (4 cm^3), methanol (4 cm^3), potassium fluoride (0.03 g, 0.5 mmol) and hydrogen peroxide (30%, 1 cm^3, 8.7 mmol) were added and the mixture was stirred for 3 d at room temperature, with further hydrogen peroxide (30%, 1 cm^3) added each day. The mixture was poured into water (5 cm^3) and extracted with dichloromethane (5 × 10 cm^3). The organic layers were combined, washed with brine (5 cm^3), dried ($MgSO_4$) and concentrated under reduced pressure. The residue was chromatographed (SiO_2, EtOAc–hexane, 1:4) to give, successively, the alcohol[31] **31** (0.015 g, 65%); R_f (EtOAc–hexane, 1:4) 0.21; $\nu_{max}(CDCl_3)/cm^{-1}$ 3607 (OH), 3530 (br OH), 1719 (C=O) and 1605 (Ph); δ_H(250 MHz; $CDCl_3$) 7.38–7.26 (5 H, m, Ph), 5.11 (1 H, d, *J* 4.0, C*H*OH), 3.67 (3 H, s, OMe), 2.95 (1 H, br s, OH), 2.79 (1 H, dq, *J* 7.1 and 4.1, C*H*Me) and 0.99 (3 H, d, *J* 7.2, CH*Me*) and the *silanol* **32** (0.004 g, 9%), R_f (EtOAc–hexane, 1:4) 0.30; $\nu_{max}(CDCl_3)/cm^{-1}$ 3650 (OH), 3480 (br OH), 1732 (C=O), 1598 (Ph) and 1590 (Ph); δ_H(250 MHz; $CDCl_3$) 7.67 (2 H, br d, *J* 6.9, *o*-Si*Ph*$_A$Ph$_B$), 7.45–7.11 (11 H, m, *m*-, *p*-SiPh$_2$, *m*-, *p*-CPh and *o*-SiPh$_A$*Ph*$_B$), 7.04 (2 H, br d, *J* 7.5, *o*-CPh), 3.61 (1 H, br s, OH), 3.46 (3 H, s, OMe), 3.15 (1 H, qn, *J* 7.1, PhC*H*Si), 2.95 (1 H, d, *J* 7.3, SiCH) and 1.17 (3 H, d, *J* 7.0, CH*Me*).

3-Hydroxy-3-phenylpropanoic acid 28b

Sulfuric acid (98%, 5 drops) was stirred with the allylsilane **12** (0.088 g, 0.21 mmol) in methanol (5 cm^3) at room temperature for 3 h. The reaction was quenched with sodium hydrogen carbonate (0.175 g, 2.1 mmol). THF (5 cm^3), potassium fluoride (0.03 g, 0.5 mmol) and hydrogen peroxide (30%, 1 cm^3, 8.7 mmol) were added and the mixture was refluxed overnight. Aqueous sodium thiosulfate (25%) was added to consume the excess hydrogen peroxide and the mixture acidified with aqueous hydrochloric acid (1 mol dm^{-3}). The mixture was poured into water (5 cm^3) and extracted with ether (5 × 10 cm^3). The organic layers were combined, washed with brine (5 cm^3), dried ($MgSO_4$) and concentrated under reduced pressure. The residue was chromatographed (SiO_2, EtOAc–hexane, 1:1) to give the acid[30] (0.031 g, 88%); R_f (MeOH–CH_2Cl_2, 1:9) 0.26; δ_H(250 MHz; $CDCl_3$) 7.38–7.25 (5 H, m, Ph), 5.15 (1 H, dd, *J* 8.8 and 4.1, C*H*OH), 5.72 (2 H, br s, OH), 2.83 (1 H, dd, *J* 16.6 and 8.8, CH_AH$_B$CO) and 2.76 (1 H, dd, *J* 16.7 and 4.1, CH$_A$*H*$_B$CO).

(*E*)-Hydroxy(hex-1-enyl)diphenylsilane 33a and (*E*)-methoxy-(hex-1-enyl)diphenylsilane 33b

Hydrochloric acid (10 mol dm^{-3}, 2 drops) was stirred with the allylsilane **17** (0.023 g, 0.069 mmol) in methanol (3 cm^3) at room temperature for 2 h. The reaction was quenched with sodium hydrogen carbonate and the solvent evaporated under reduced pressure. The residue was taken up in ether (5 cm^3), dried ($MgSO_4$) and concentrated under reduced pressure. Preparative TLC (EtOAc–hexane, 1:4) gave, successively, the *methoxysilane* **33b** (0.010 g, 49%); R_f (EtOAc–hexane, 1:4) 0.69; ν_{max}(film)/cm^{-1} 1620 (C=C) and 1120 (Si–Ph); δ_H(250 MHz; $CDCl_3$) 7.65–7.51 (4 H, m, *o*-SiPh$_2$), 7.49–7.28 (6 H, m, *m*- and *p*-SiPh$_2$), 6.30 (1 H, dt, *J* 18.7 and 6.2, C=C*H*CH$_2$), 5.97 (1 H, dt, *J* 18.7 and 1.4, SiCH=C), 3.57 (3 H, s, OMe), 2.22 (2 H, br q, *J* 6.5, C=CHC*H*$_2$), 1.62–1.01 (4 H, m, C*H*$_2$C*H*$_2$Me) and 0.92 (3 H, t, *J* 7.3, CH*Me*); *m*/*z* 296 (14%, M^+), 239 (32, M − C_4H_9) and 213 (100, Ph_2SiOMe) (Found: M^+, 296.1603. $C_{19}H_{24}SiO$ requires *M*, 296.1596) and the *silanol* **33a** (0.009 g, 46%), R_f (EtOAc–hexane, 1:4) 0.31; ν_{max}(film)/cm^{-1} 3620 (br OH), 1600 (Ph) and 1120 (Si–Ph); δ_H(250 MHz; $CDCl_3$) 7.63–7.57 (4 H, m, *o*-SiPh$_2$), 7.45–7.33 (6 H, m, *m*- and *p*-SiPh$_2$), 6.32 (1 H, dt, *J* 18.7 and 6.2, C=C*H*CH$_2$), 5.97 (1 H, dt, *J* 18.7 and 1.4, SiCH=C), 2.20 (2 H, br q, *J* 6.5, C=CHC*H*$_2$), 1.55–1.11 (5 H, m, C*H*$_2$C*H*$_2$Me and OH) and 0.92 (3 H, t, *J* 6.7, Me); *m*/*z* 282 (13%, M^+), 225 (51, M − C_4H_9) and 199 (100, Ph_2SiOH) (Found: M^+, 282.1441. $C_{18}H_{22}SiO$ requires *M*, 282.1440).

Hexanal 2,4-dinitrophenylhydrazone 34

Boron trifluoride–acetic acid complex (0.2 cm^3, 0.8 mmol) was added dropwise to a stirred solution of the allylsilane **17** (0.207 g, 0.62 mmol) in dichloromethane (15 cm^3) at −10 °C under argon. After 5 min the reaction was quenched with sodium hydrogen carbonate (0.29 g, 3.5 mmol) and the solvent evaporated under reduced pressure. THF (6 cm^3), methanol (6 cm^3), potassium fluoride (0.15 g, 2.5 mmol) and hydrogen peroxide (30%, 2 cm^3, 17.4 mmol) were added and the mixture was stirred at room temperature overnight. A solution of 2,4-dinitrophenylhydrazine (0.25 g, 1.3 mmol) and sulfuric acid (98%, 0.5 cm^3) in methanol (5 cm^3) was added dropwise and the mixture stirred for a further 1 h at room temperature. The solvents were evaporated under reduced pressure and the residue taken up in ether (10 cm^3), washed with aqueous sodium hydroxide (1 mol dm^{-3}, 2 cm^3), and brine (2 cm^3), dried ($MgSO_4$) and concentrated under reduced pressure to give the hydrazone (0.073 g, 42%) as yellow prisms, mp 107–108 °C (from EtOH) (lit.,[32] 108 °C); $\nu_{max}(CDCl_3)/cm^{-1}$ 3307 (NH), 1619 (C=N), 1594 (Ar), 1520 (NO_2) and 1336 (NO_2); δ_H(250 MHz; $CDCl_3$) 11.01 (1 H, s, NH), 9.13 (1 H, d, *J* 2.5, 3-ArH), 8.29 (1 H, dd, *J* 9.5 and 2.5, 5-ArH), 7.92 (1 H, d, *J* 9.6, 6-ArH), 7.53 (1 H, t, *J* 5.4, CH=N), 2.33–2.22 (2 H, m, CH_2C=N), 1.71–1.55 (2 H, m, C*H*$_2$CH$_2$C=N), 1.43-1.28 (4 H, m, C*H*$_2$C*H*$_2$Me) and 1.00–0.83 (3 H, m, Me).

Hydroxy(2-cyclohexylideneethyl)diphenylsilane 35a and methoxy(2-cyclohexylideneethyl)diphenylsilane 35b

Hydrochloric acid (10 mol dm^{-3}, 2 drops) was stirred with the allylsilane **21** (0.031 g, 0.086 mmol) in methanol (3 cm^3) at room

temperature for 3 h. The reaction was quenched with sodium hydrogen carbonate and the solvent evaporated under reduced pressure. The residue was taken up in ether (5 cm^3), dried ($MgSO_4$) and concentrated under reduced pressure. Preparative TLC (EtOAc–hexane, 1:4) gave, successively, the *methoxysilane* **35b** (0.013 g, 49%); R_f (EtOAc–hexane, 1:4) 0.63; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 1580 (Ph) and 1100 (Si–Ph); δ_H(250 MHz; $CDCl_3$) 7.59 (4 H, br d, *J* 7.3, *o*-$SiPh_2$), 7.45–7.31 (6 H, m, *m*- and *p*-$SiPh_2$), 5.15 (1 H, t, *J* 8.2, C=CH), 3.54 (3 H, s, Me), 2.06 (2 H, d, *J* 8.2, $SiCH_2$), 2.05–1.91 [2 H, m, $(CH_2)_A(CH_2)_BC{=}C$], 1.93 [2 H, t, *J* 5.9, $(CH_2)_A(CH_2)_BC{=}C$], 1.43–1.33 (4 H, m, 2 × CH_2CH_2-C=C) and 1.30–1.12 (2 H, m, $CH_2CH_2CH_2C{=}C$); *m*/*z* 322 (76%, M^+), 291 (9, M − OMe) and 213 (100, Ph_2SiOMe) (Found: M^+, 322.1767. $C_{21}H_{26}SiO$ requires *M*, 322.1753) and the *silanol* **35a** (0.014 g, 51%), R_f (EtOAc–hexane, 1:4) 0.33; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3610 (br OH); δ_H(250 MHz; $CDCl_3$) 7.64 (4 H, br d, *J* 7.4, *o*-$SiPh_2$), 7.48–7.33 (6 H, m, *m*- and *p*-$SiPh_2$), 5.20 (1 H, t, *J* 8.3, C=CH), 2.50 (1 H, br s, OH), 2.09–1.99 (6 H, m, 3 × $CH_2C{=}C$), 1.55–1.47 (4 H, m, 2 × $CH_2CH_2C{=}C$) and 1.38–1.22 (2 H, m, $CH_2CH_2CH_2C{=}C$); *m*/*z* 308 (59%, M^+) and 199 (100, Ph_2SiOH) (Found: M^+, 308.1590. $C_{20}H_{24}SiO$ requires *M*, 308.1596).

Fluoro(2-cyclohexylideneethyl)diphenylsilane 35c

Boron trifluoride–acetic acid complex (0.04 cm^3, 0.16 mmol) was added dropwise to a stirred solution of the allylsilane **21** (0.058 g, 0.16 mmol) in dichloromethane (5 cm^3) at −10 °C under argon. After 5 min the reaction was quenched with sodium hydrogen carbonate (0.17 g, 2.0 mmol) and the mixture washed with water (5 cm^3) and extracted with dichloromethane (2 × 15 cm^3). The organic layers were combined, washed with brine (5 cm^3), dried ($MgSO_4$) and concentrated under reduced pressure to give the crude *fluorosilane* (0.050 g, 100%); R_f (EtOAc–hexane, 1:4) 0.46; δ_H(250 MHz; $CDCl_3$) 7.78–7.60 (4 H, m, *o*-$SiPh_2$), 7.59–7.25 (6 H, m, *m*- and *p*-$SiPh_2$), 5.17 (1 H, t, *J* 8.2, C=CH), 2.36–2.03 (6 H, m, 3 × $CH_2C{=}C$) and 1.75–1.19 [6 H, m, $(CH_2)_3CH_2C{=}C$].

2-Cyclohexylideneethanol 36

Method 1. Hydrochloric acid (10 mol dm^{-3}, 9 drops) was stirred with the allylsilane **21** (0.104 g, 0.28 mmol) in a THF–methanol mixture (1:1, 8 cm^3) at room temperature for 3 h. The reaction was quenched with sodium hydrogen carbonate (0.350 g, 4.2 mmol). Potassium fluoride (0.060 g, 1.0 mmol) and hydrogen peroxide (30%, 1 cm^3, 8.7 mmol) were added and the mixture was refluxed for 3 h. The mixture was poured into water (5 cm^3) and extracted with dichloromethane (5 × 10 cm^3). The organic layers were combined, washed with brine (5 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure. The residue was chromatographed (SiO_2, EtOAc–hexane, 1:4) to give the alcohol[33] (0.022 g, 60%); R_f (EtOAc–hexane, 1:4) 0.27; $\nu_{max}(CDCl_3)/cm^{-1}$ 3330 (br OH) and 1667 (C=C); δ_H(250 MHz; $CDCl_3$) 5.34 (1 H, br t, *J* 7.1, C=CH), 4.12 (2 H, d, *J* 7.1, CH_2O), 2.17 [2 H, br s, $(CH_2)_A(CH_2)_BC{=}C$], 2.09 [2 H, br s, $(CH_2)_A(CH_2)_BC{=}C$], 1.54 [6 H, br s, $(CH_2)_3CH_2C{=}C$] and 1.23 (1 H, v br s, OH).

Method 2. The allylsilane **21** (0.18 g, 0.5 mmol), sodium hydrogen carbonate (0.25 g, 3 mmol), potassium fluoride (0.058 g, 1 mmol), potassium bromide (0.12 g, 1 mmol) and hydrogen peroxide (30%, 2 cm^3, 17.4 mmol) were refluxed in a THF–methanol mixture (1:1, 10 cm^3) overnight. Water (5 cm^3) was added and the mixture extracted with ethyl acetate (2 × 20 cm^3). The combined organic layers were washed with brine (5 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure. The residue was chromatographed (SiO_2, EtOAc–hexane, 1:4) to give the alcohol (0.037 g, 59%) identical (TLC, ^1H NMR) with the earlier sample.

(*E*)-Hydroxy(1-cyclopentyloct-1-en-3-yl)diphenylsilane 37a and (*E*)-methoxy(1-cyclopentyloct-1-en-3-yl)diphenylsilane 37b

Hydrochloric acid (10 mol dm^{-3}, 6 drops) and the allylsilane **24** (0.013 g, 0.03 mmol) were stirred in a mixture of THF and methanol (1:1, 4 cm^3) at room temperature for 3 h. The reaction was quenched with sodium hydrogen carbonate and the solvent evaporated under reduced pressure. The residue was taken up in ether (10 cm^3), washed with water (2 cm^3) and brine (2 cm^3), dried ($MgSO_4$) and concentrated under reduced pressure to give a 5:2 mixture of the *silanol* **37a** and the *methoxysilane* **37b** (0.014 g); δ_H(250 MHz; $CDCl_3$) 7.64–7.49 (4 H, m, *o*-$SiPh_2$), 7.41–7.31 (6 H, m, *m*- and *p*-$SiPh_2$), 5.27–5.16 (2 H, m, CH=CH), 3.05 (3 H, s, OMe **37b**), 2.36 (1 H, sextet, *J* 7.4, C*H*CH=CHCHO), 2.20–2.03 (1 H, m, Si*CH*CH_2), 1.72–1.06 [16 H, m, 2 × $(CH_2)_4$] and 0.83 (3 H, t, *J* 6.7, CH_2Me).

(*E*)-1-Cyclopentyloct-1-en-3-ol 38

Method 1. Hydrochloric acid (10 mol dm^{-3}, 4 drops) and the allylsilane **24** (0.105 g, 0.24 mmol) were stirred in a mixture of THF and methanol (1:1, 8 cm^3) at room temperature overnight. The reaction was quenched with sodium hydrogen carbonate (0.145 g, 1.73 mmol). Potassium fluoride (0.030 g, 0.5 mmol) and hydrogen peroxide (30%, 1 cm^3, 8.7 mmol) were added and the mixture was stirred at room temperature for 12 h. Additional hydrogen peroxide (1 cm^3) was added and the mixture was refluxed for 6 h. The excess hydrogen peroxide was quenched with sodium sulfite and the mixture acidified with aqueous hydrochloric acid (1 mol dm^{-3}). The organic solvents were evaporated off under reduced pressure. The aqueous residue was extracted with ether (4 × 5 cm^3) and the organic layers combined, washed with brine (2 cm^3), dried ($MgSO_4$), and concentrated under reduced pressure. The residue was chromatographed (SiO_2, EtOAc–hexane, 7:93) to give the alcohol[34] (0.022 g, 57%); R_f (EtOAc–hexane, 1:4) 0.38; $\nu_{max}(CDCl_3)/cm^{-1}$ 3605 (OH) and 1667 (C=C); δ_H(250 MHz; $CDCl_3$) 5.60 (1 H, dd, *J* 15.4 and 7.3, C=C*H*CHOH), 5.41 (1 H, dd, *J* 15.3 and 7.5, C*H*=CHCHOH), 4.01 (1 H, q, *J* 6.5, C*H*OH), 2.43 (1 H, sextet, *J* 7.8, C*H*CH=CHCHOH), 1.79–1.20 [17 H, m, 2 × $(CH_2)_4$ and OH] and 0.87 (3 H, t, *J* 6.6, CH_2Me).

Method 2. Hydrogen peroxide (30%, 2 cm^3, 17.4 mmol), sodium hydrogen carbonate (0.163 g, 1.94 mmol), potassium fluoride (0.045 g, 0.78 mmol), potassium bromide (0.092 g, 0.77 mmol) and the allylsilane **24** (0.105 g, 0.24 mmol) were refluxed in a mixture of THF and methanol (1:1, 8 cm^3) for 12 h. The excess hydrogen peroxide was quenched with sodium sulfite. The mixture was acidified with aqueous hydrochloric acid (1 mol dm^{-3}) and the organic solvents evaporated off under reduced pressure. The aqueous residue was extracted with ether (4 × 5 cm^3) and the organic layers combined, washed with brine (2 cm^3), dried ($MgSO_4$), and concentrated under reduced pressure. The residue was chromatographed (SiO_2, EtOAc–hexane, 7:93) to give the alcohol (0.051 g, 67%), identical (TLC, IR, ^1H NMR) to the earlier sample.

(1*S*,5*R*,6*R*,7*R*)-7-Benzoyloxy-6-formyl-2-oxabicyclo[3.3.0]-octan-3-one 40

(1*S*,5*R*,6*R*,7*R*)-7-Benzoyloxy-6-hydroxymethyl-2-oxabicyclo-[3.3.0]octan-3-one **39**[23,24,35–37] [mp 116–117 °C (lit.,[37] 115–116 °C) (Found: C, 65.3; H, 5.8. $C_{15}H_{16}O_5$ requires C, 65.2; H, 5.8%)] (0.559 g, 2 mmol) in dry dichloromethane (4 cm^3) was added *via* a cannula to a solution of Dess–Martin periodinane[38] (1 g, 2.4 mmol) in dry dichloromethane (8 cm^3) at 0 °C under argon. The reaction was allowed to warm to room temperature for 1 h, after which a white precipitate had formed. Ether (20 cm^3) was added and the mixture was cooled to 0 °C. Sodium thiosulfate (4 g) and saturated aqueous sodium hydrogen carbonate (20 cm^3) were added and the mixture warmed to room temperature and stirred for a further 10 min after which the precipitate had gone. The mixture was extracted with ether (3 × 10 cm^3) and the organic layers combined, washed with saturated aqueous sodium hydrogen carbonate (5 cm^3) and brine (5 cm^3), dried (Na_2SO_4) and concentrated under reduced pressure to give the aldehyde[37] (0.555 g, 100%), which was used

immediately without further purification; R_f (Et_2O) 0.10; δ_H(250 MHz; $CDCl_3$) 9.81 (1 H, s, CH=O), 7.97 (2 H, br d, *J* 7.1, *o*-Ph), 7.55 (1 H, br t, *J* 7.2, *p*-Ph), 7.43 (2 H, br t, *J* 7.5, *m*-Ph), 5.74 (1 H, br d, *J* 5.4, CHOBz), 5.13 (1 H, br t, *J* 6.3, C*H*OCOCH$_2$), 3.57–3.46 (1 H, m, C*H*CH$_2$CO), 3.19 (1 H, br s, C*H*CH=O), 2.97 (1 H, dd, *J* 18.5 and 10.9, CH_AH$_B$CO$_2$), 2.53–2.43 (1 H, m, CH_AH$_B$COBz), 2.47 (1 H, dd, *J* 18.5 and 2.5, CH$_A$$H_BCO_2$) and 2.04 (1 H, dt, *J* 16.0 and 5.7, CH$_A$$H_B$COBz).

(1*S*,5*R*,6*R*,7*R*,1′*S*)-7-Benzoyloxy-6-(1′-hydroxyoct-2′-ynyl)-2-oxabicyclo[3.3.0]octan-3-one 41 and (1*S*,5*R*,6*R*,7*R*,1′*R*)-7-benzoyloxy-6-(1′-hydroxyoct-2′-ynyl)-2-oxabicyclo[3.3.0]octan-3-one 42

n-Butyllithium (1.43 mol dm^{-3} in hexane, 2.8 cm^3, 4 mmol) was added dropwise to a stirred solution of hept-1-yne (0.52 cm^3, 4 mmol) in dry THF (25 cm^3) at −78 °C under argon. After stirring at this temperature for 10 min, the solution was added *via* a cannula to a slurry of cerium trichloride (dried at 140 °C at 0.1 mmHg for 4 h) in dry THF (2 cm^3) also at −78 °C under argon. The mixture was stirred at this temperature for 1 h and then at 0 °C for 30 min forming a yellow coloured slurry. The aldehyde **40** (0.555 g, 2 mmol) in dry THF (7 cm^3) was added slowly *via* a cannula to this slurry at −78 °C, and the mixture stirred for 30 min. The reaction was quenched with saturated aqueous ammonium chloride (10 cm^3) and the mixture extracted with ether (3 × 20 cm^3). The organic layers were combined, washed with brine (10 cm^3), dried ($MgSO_4$) and concentrated under reduced pressure. The residue was chromatographed (SiO_2, EtOAc–light petroleum, 1:1) to give the *propargyl alcohols* **41** and **42** (0.537 g, 72%) in a 5:3 ratio, which were inseparable by chromatography; R_f (Et_2O) 0.44; ν_{max}(film)/cm^{-1} 3452 (br OH), 2360 (C≡C), 1770 (C=O), 1715 (C=O), 1602 (Ph) and 1584 (Ph); δ_H(250 MHz; $CDCl_3$) 8.00 (2 H, br d, *J* 7.6, *o*-Ph), 7.55 (1 H, br t, *J* 7.4, *p*-Ph), 7.43 (2 H, br t, *J* 7.5, *m*-Ph), 5.46 (1 H, dt, *J* 6.7 and 3.5, C*H*OBz), 5.05 (1 H, br t, *J* 5.6, C*H*OCOCH$_2$), 4.64–4.58 (1 H, m, C*H*OH major), 4.58-4.51 (1 H, m, C*H*OH minor), 3.14–3.01 (1 H, m, C*H*CH$_2$CO$_2$), 2.93 (1 H, dd, *J* 17.9 and 9.8, CH_AH$_B$CO$_2$), 2.63 (1 H, dd, *J* 18.0 and 2.0, CH$_A$$H_BCO_2$), 2.54 (1 H, dt, *J* 16.9 and 6.2, CH_AH$_B$COBz), 2.45–2.30 (2 H, m, CH$_A$$H_B$COBz and C*H*CHCOH), 2.18 (2 H, td, *J* 7.0 and 2.0, C≡CCH$_2$ major), 2.13 (2 H, td, *J* 7.1 and 2.0, C≡CCH$_2$ minor), 1.53–1.35 (2 H, m, C≡CCH$_2$C*H*$_2$), 1.35–1.23 (4 H, m, CH$_2$CH$_2$-Me) and 0.92–0.82 (3 H, m, Me); δ_C(100 MHz; $CDCl_3$) 176.6, 171.2, 166.5, 133.5, 133.4, 133.3, 129.7, 129.6, 128.6, 128.5, 88.0, 87.4, 85.0, 84.8, 84.7, 78.8, 78.5, 77.7, 77.2, 66.7, 63.0, 62.2, 60.4, 59.2, 59.0, 40.4, 39.6, 39.1, 38.9, 38.5, 38.3, 36.6, 36.4, 35.8, 31.1, 28.20, 28.15, 27.2, 22.1, 21.1, 19.1, 18.6, 14.2 and 13.9; *m*/*z* 248 (80%, M − BzOH), 230 (24, M − BzOH − H_2O) and 105 (100, PhCO$^+$) (Found: M$^+$ − BzOH, 248.1432. $C_{22}H_{26}O_5$ − BzOH requires *M*, 248.1412).

(*Z*)-(1*S*,5*R*,6*R*,7*R*,1′*R*)-7-Benzoyloxy-6-(1′-hydroxyoct-2′-enyl)-2-oxabicyclo[3.3.0]octan-3-one 43 and (*Z*)-(1*S*,5*R*,6*R*,7*R*,1′*S*)-7-benzoyloxy-6-(1′-hydroxyoct-2′-enyl)-2-oxabicyclo-[3.3.0]octan-3-one 44

The propargyl alcohols **41** and **42** (0.521 g, 1.41 mmol), the modified Lindlar catalyst (Pd + $MnCl_2$)[29] (0.020 g) and quinoline (0.030 g) in dry methanol (15 cm^3) were alternately evacuated and flushed with argon (4 ×) and the procedure repeated with hydrogen, at room temperature with vigorous stirring. The mixture was stirred under hydrogen overnight, filtered through Celite and concentrated under reduced pressure. The residue was taken up in ether (20 cm^3), washed with aqueous hydrochloric acid (0.1 mol dm^{-3}, 5 cm^3), brine (5 cm^3), dried ($MgSO_4$) and concentrated under reduced pressure. The residue was chromatographed (SiO_2, EtOAc–light petroleum, 3:7) to give the (1′R)-*allyl alcohol* **43** (0.325 g, 63%), mp 66–67 °C (from EtOAc–light petroleum); R_f (Et_2O) 0.34; $[\alpha]_D$ −139.5 (*c* 1.1, $CHCl_3$); ν_{max}(film)/cm^{-1} 3492 (br OH), 1747 (C=O), 1714 (C=O), 1602 (Ph) and 1584 (Ph); δ_H(400 MHz; $CDCl_3$) 7.99 (2 H, d, *J* 7.7, *o*-Ph), 7.55 (1 H, br t, *J* 7.5, *p*-Ph), 7.43 (2 H, br t, *J* 7.7, *m*-Ph), 5.57 (1 H, dt, *J* 11.0 and 7.3, C=C*H*CH$_2$), 5.46 (1 H, dd, *J* 10.9 and 8.7, C*H*=CHCH$_2$), 5.36 (1 H, dt, *J* 6.1 and 3.4, C*H*OBz), 5.08 (1 H, t, *J* 6.4, C*H*OCOCH$_2$), 4.55 (1 H, ddd, *J* 8.6, 5.3 and 3.3, C*H*OH), 3.17–3.09 (1 H, m, C*H*CH$_2$CO$_2$), 2.93 (1 H, dd, *J* 18.2 and 10.3, CH_AH$_B$CO$_2$), 2.55 (1 H, dd, *J* 18.3 and 2.3, CH$_A$$H_BCO_2$), 2.45 (1 H, dt, *J* 15.6 and 6.0, CH_AH$_B$COBz), 2.35 (1 H, br d, *J* 15.6, CH$_A$$H_B$COBz), 2.18 (1 H, br q, *J* 4.6, C*H*CHOBz), 2.15–1.96 (2 H, m, CH$_2$C=C), 1.36 (2 H, quintet, *J* 7.7, C=CHCH$_2$C*H*$_2$), 1.33–1.22 (4 H, m, C*H*$_2$C*H*$_2$Me) and 0.86 (3 H, t, *J* 6.8, Me); δ_C(100 MHz; $CDCl_3$) 176.9, 166.3, 134.3, 133.3, 129.7, 129.6, 128.5, 85.0, 78.3, 67.4, 59.0, 38.7, 38.6, 36.7, 31.5, 29.2, 27.8, 22.4 and 14.0 (Found: C, 70.9; H, 7.5. $C_{25}H_{28}O_5$ requires C, 70.9; H, 7.6%), and the (1′S)-*allyl alcohol* **44** (0.192 g, 37%); R_f (Et_2O) 0.37; $[\alpha]_D$ −38.8 (*c* 1.4, $CHCl_3$); ν_{max}(film)/cm^{-1} 3450 (br OH), 1772 (C=O), 1719 (C=O) and 1601 (Ph); δ_H(400 MHz; $CDCl_3$) 7.97 (2 H, d, *J* 7.1, *o*-Ph), 7.53 (1 H, br t, *J* 7.4, *p*-Ph), 7.42 (2 H, br t, *J* 7.7, *m*-Ph), 5.59 (1 H, dt, *J* 11.0 and 7.4, C=C*H*CH$_2$), 5.53 (1 H, dt, *J* 5.6 and 2.7, C*H*OBz), 5.42 (1 H, dd, *J* 10.9 and 9.2, C*H*=CHCH$_2$), 5.04 (1 H, t, *J* 5.8, C*H*OCOCH$_2$), 4.41 (1 H, dd, *J* 8.8 and 7.2, C*H*OH), 2.89 (1 H, dd, *J* 17.5 and 10.2, CH_AH$_B$CO$_2$), 2.88–2.78 (1 H, m, C*H*CH$_2$CO$_2$), 2.54 (1 H, dd, *J* 17.5 and 1.4, CH$_A$$H_B$-CO$_2$), 2.44 (1 H, dt, *J* 15.8 and 5.7, CH_AH$_B$COBz), 2.38 (1 H, br d, *J* 15.8, CH$_A$$H_B$COBz), 2.28–2.24 (1 H, m, C*H*CHOBz), 2.17–1.97 (2 H, m, CH$_2$C=C), 1.36 (2 H, quintet, *J* 7.2, C=CHCH$_2$-C*H*$_2$), 1.33–1.20 (4 H, m, C*H*$_2$C*H*$_2$Me) and 0.85 (3 H, t, *J* 6.8, Me); δ_C(100 MHz; $CDCl_3$) 176.8, 166.2, 134.9, 133.3, 129.72, 129.67, 129.2, 128.5, 85.1, 77.6, 67.8, 59.3, 40.6, 38.7, 36.7, 31.5, 29.2, 27.8, 22.5 and 14.0; *m*/*z* 372 (16%, M$^+$), 355 (41, M − OH), 354 (34, M − H_2O), 301 [23, M − (CH$_2$)$_4$Me], 275 [66, M − CH=CH(CH$_2$)$_4$Me], 250 (36, M − BzOH), 232 (60, M − BzOH − H_2O) and 105 (100, PhCO$^+$) (Found: M$^+$, 372.1915. $C_{22}H_{28}O_5$ requires *M*, 372.1937).

(*Z*)-(1*S*,5*R*,6*R*,7*R*,1′*S*)-7-Hydroxy-6-(1′-hydroxyoct-2′-enyl)-2-oxabicyclo[3.3.0]octan-3-one 46

Potassium carbonate (0.037 g, 0.27 mmol) was added to a stirred solution of the benzoate **44** (0.069 g, 0.185 mmol) in methanol (1 cm^3). The mixture was stirred at room temperature overnight and then acidified with aqueous hydrochloric acid (3 mol dm^{-3}). The solvent was evaporated under reduced pressure and the residue taken up in ether (5 cm^3), dried ($MgSO_4$), and concentrated under reduced pressure. The residue was chromatographed (SiO_2, EtOAc) to give the diol[4] (0.035 g, 74%); R_f (EtOAc) 0.38; $[\alpha]_D$ +28.9 (*c* 1.0, $CHCl_3$); ν_{max}($CDCl_3$)/cm^{-1} 3608 (OH), 3450 (br OH), 1765 (C=O) and 1655 (C=C); δ_H(250 MHz; $CDCl_3$) 5.57 (1 H, dt, *J* 11.1 and 7.4, C=C*H*CH$_2$), 5.36 (1 H, br t, *J* 10.3, C*H*=CHCH$_2$), 4.84 (1 H, dt, *J* 7.2 and 4.0, C*H*OCOCH$_2$), 4.38 (1 H, t, *J* 9.0, C=CC*H*OH), 4.20 (1 H, q, *J* 7.3, CH$_2$C*H*OH), 2.66 (1 H, dd, *J* 18.5 and 9.8, CH_AH$_B$CO$_2$), 2.57–2.35 (3 H, m, CH$_A$$H_BCO_2$, C*H*CH$_2CO_2$ and CH_AH$_B$COH), 2.19–1.79 (4 H, m, CH$_2$C=C, CH$_A$$H_B$COH and CHC*H*COH), 1.37–1.23 [6 H, m, (C*H*$_2$)$_3$Me] and 0.86 (3 H, t, *J* 6.7, Me); δ_C(100 MHz; $CDCl_3$) 176.8, 134.5, 129.8, 82.5, 76.0, 71.4, 57.7, 40.3, 39.6, 35.2, 31.5, 29.3, 27.9, 22.5 and 14.0; *m*/*z* 268 (13%, M$^+$), 250 (39, M − H_2O), 232 (25, M − 2H_2O), 197 [81, M − (CH$_2$)$_4$Me], 179 [51, M − (CH$_2$)$_4$Me − H_2O] and 161 [15, M − (CH$_2$)$_4$Me − 2H_2O] (Found: M$^+$, 268.1674. $C_{15}H_{24}O_4$ requires *M*, 268.1675).

(*Z*)-(1*S*,5*R*,6*R*,7*R*,1′*R*)-7-Hydroxy-6-(1′-hydroxyoct-2′-enyl)-2-oxabicyclo[3.3.0]octan-3-one 45 and (*Z*)-(1*S*,5*R*,6*R*,7*R*,1′*S*)-7-hydroxy-6-(1′-hydroxyoct-2′-enyl)-2-oxabicyclo[3.3.0]octan-3-one 46

These were prepared by the same method using a mixture of the benzoates **43** and **44** (0.029 g, 0.08 mmol, ratio 1:2), potassium carbonate (0.015 g, 0.1 mmol) and methanol (0.5 cm^3) to give an inseparable mixture of the diols[4] **45** and **46** (0.015 g, 72%) in a 1:2 ratio, identical (TLC, IR) with the diol above; δ_H(250

MHz; $CDCl_3$) 5.57 (1 H, dt, *J* 11.0 and 7.5, C=C*H*CH_2), 5.36 (1 H, br t, *J* 10.2, C*H*=$CHCH_2$), 4.84 (1 H, dt, *J* 7.2 and 3.9, C*H*$OCOCH_2$), 4.37 (1 H, t, *J* 9.1, C=CC*H*OH), 4.20 (1 H, q, *J* 7.2, CH_2CHOH), 2.66 (1 H, dd, *J* 18.5 and 9.9, $CH_AH_BCO_2$), 2.57–2.34 (3 H, m, $CH_AH_BCO_2$, C*H*CH_2CO_2 and CH_AH_B-COH), 2.20–1.78 (4 H, m, CH_2C=C, CH_AH_BCOH and CHC*H*COH), 1.40–1.18 [6 H, m, $(CH_2)_3$Me] and 0.88 (3 H, t, *J* 6.7, Me); δ_C(100 MHz; $CDCl_3$) 177.2 (minor), 176.8 (major), 134.5 (major), 134.4 (minor), 129.8 (major), 129.6 (minor), 83.6 (minor), 82.5 (major), 76.0 (major), 74.3 (minor), 71.4 (major), 67.8 (minor), 59.1 (minor), 57.7 (major), 40.8 (minor), 40.3 (major), 39.6 (major), 38.9 (minor), 35.9 (minor), 35.2 (major), 31.5, 29.3, 27.9, 22.5 and 14.0.

(*Z*)-(1*S*,5*R*,6*R*,7*R*,1′*R*)-7-Benzoyloxy-6-(1′-benzoyloxyoct-2′-enyl)-2-oxabicyclo[3.3.0]octan-3-one 47

Benzoyl chloride (0.06 cm^3, 0.5 mmol), the alcohol **43** (0.119 g, 0.32 mmol), triethylamine (0.07 cm^3, 0.5 mmol) and 4-dimethylaminopyridine (0.005 g, 0.04 mmol) were stirred in dry dichloromethane (2 cm^3) under argon at room temperature overnight. The mixture was diluted with ether (10 cm^3) and quenched with hydrochloric acid (1 mol dm^{-3}, 2 cm^3). The mixture was extracted with ether (3 × 1 cm^3) and the organic layers combined, washed with saturated aqueous sodium hydrogen carbonate (1 cm^3) and brine (1 cm^3), dried ($MgSO_4$) and concentrated under reduced pressure. The residue was chromatographed (SiO_2, EtOAc–light petroleum, 1:1) to give the *dibenzoate* (0.152 g, 100%); R_f (Et_2O) 0.63; $[\alpha]_D$ −36.8 (*c* 1.36, $CHCl_3$); ν_{max}(film)/cm^{-1} 1770 (C=O), 1714 (C=O), 1602 (Ph) and 1584 (Ph); δ_H(400 MHz; $CDCl_3$) 7.98 (4 H, d, *J* 7.7, 2 × *o*-Ph), 7.55 (2 H, br t, *J* 6.9, 2 × *p*-Ph), 7.43 (2 H, br t, *J* 6.4, *m*-Ph_A), 7.41 (2 H, br t, *J* 7.5, *m*-Ph_B), 5.86 (1 H, br t, *J* 8.2, C=CHC*H*OBz), 5.70 (1 H, dt, *J* 10.7 and 7.5, C=C*H*CH_2), 5.50 (1 H, br t, *J* 10.1, C*H*=$CHCH_2$), 5.40 (1 H, dt, *J* 6.0 and 3.6, CH_2C*H*OBz), 5.12 (1 H, t, *J* 5.8, C*H*$OCOCH_2$), 3.07–2.98 (1 H, m, C*H*CH_2CO_2), 2.92 (1 H, dd, *J* 18.0 and 10.0, $CH_AH_BCO_2$), 2.62 (1 H, dd, *J* 17.9 and 1.7, $CH_AH_BCO_2$), 2.58 (1 H, br q, *J* 5.8, C*H*CHOBz), 2.48 (1 H, dt, *J* 15.8 and 6.2, CH_AH_B-COBz), 2.36 (1 H, br d, *J* 15.7, CH_AH_BCOBz), 2.27 (1 H, dq, *J* 14.5 and 7.7, CH_AH_BC=C), 2.19 (1 H, dq, *J* 14.4 and 7.0, CH_AH_BC=C), 1.46–1.33 (2 H, m, C=CHCH_2CH_2), 1.33-1.22 (4 H, m, CH_2CH_2Me) and 0.85 (3 H, t, *J* 6.7, Me); δ_C(100 MHz; $CDCl_3$) 176.3, 165.8, 165.5, 136.9, 133.3, 129.9, 129.7, 129.6, 128.5, 125.0, 84.3, 70.7, 56.9, 40.0, 38.8, 36.3, 31.5, 29.1, 28.1, 22.5 and 14.0; *m*/*z* 354 (29%, M − BzOH) and 105 (100, PhCO) (Found: M^+ − BzOH, 354.1825. $C_{29}H_{32}O_6$ − BzOH requires *M*, 354.1831).

(*Z*)-(1*S*,5*R*,6*R*,7*R*,1′*S*)-7-Benzoyloxy-6-(1′-benzoyloxyoct-2′-enyl)-2-oxabicyclo[3.3.0]octan-3-one 52

A similar benzoylation using the alcohol **44** (0.052 g, 0.14 mmol) gave the *dibenzoate* (0.066 g, 99%); R_f (Et_2O) 0.65; ν_{max}($CDCl_3$)/cm^{-1} 1771 (C=O), 1717 (C=O) and 1602 (Ph); $[\alpha]_D$ −106.9 (*c* 0.7, $CHCl_3$); δ_H(400 MHz; $CDCl_3$) 8.02–7.95 (4 H, m, 2 × *o*-Ph), 7.55 (2 H, br t, *J* 7.4, 2 × *p*-Ph), 7.45–7.38 (4 H, m, 2 × *m*-Ph), 5.85 (1 H, dd, *J* 9.2 and 7.1, C=CHC*H*OBz), 5.73 (1 H, dt, *J* 10.9 and 7.5, C=C*H*CH_2), 5.54–5.43 (2 H, m, C*H*=$CHCH_2$ and CH_2C*H*OBz), 5.07 (1 H, br t, *J* 5.7, C*H*$OCOCH_2$), 3.04–2.86 (2 H, m, C*H*C$H_AH_BCO_2$), 2.75–2.55 (3 H, m, $CH_AH_BCO_2$, CH_AH_BCOBz and C*H*CHOBz), 2.35 (1 H, br d, *J* 15.8, CH_AH_BCOBz), 2.32–2.11 (2 H, m, CH_2C=C), 1.45–1.20 [6 H, m, $(CH_2)_3$Me] and 0.84 (3 H, t, *J* 7.0, Me); δ_C(100 MHz; $CDCl_3$) 176.3, 165.7, 165.6, 137.4, 133.28, 133.26, 129.8, 129.7, 129.64, 129.57, 128.5, 124.5, 84.2, 76.9, 56.7, 40.1, 38.7, 36.3, 31.5, 29.0, 28.2, 22.5 and 14.0; *m*/*z* 354 (49%, M^+) and 105 (100, PhCO) (Found: M^+ − BzOH, 354.1830. $C_{29}H_{32}O_6$ − BzOH requires *M*, 354.1831).

(*Z*)-(1*S*,5*R*,6*R*,7*R*,1′*S*)-7-Benzoyloxy-6-(1′-*N*-phenylcarbamoyloxyoct-2′-enyl)-2-oxabicyclo[3.3.0]octan-3-one 48

Phenyl isocyanate (0.025 cm^3, 0.19 mmol), the alcohol **44** (0.069 g, 0.185 mmol) and triethylamine (0.03 cm^3, 0.21 mmol) were stirred in dry dichloromethane (1 cm^3) under argon at room temperature overnight. The mixture was diluted with ether (10 cm^3) and the organic layer washed with water (1 cm^3), aqueous hydrochloric acid (1 mol dm^{-3}, 1 cm^3), saturated aqueous sodium hydrogen carbonate (1 cm^3) and brine (1 cm^3), dried ($MgSO_4$) and concentrated under reduced pressure. The residue was chromatographed (SiO_2, EtOAc–light petroleum, 1:5 and then 1:1) to give the *carbamate* (0.077 g, 85%); R_f (Et_2O) 0.70; ν_{max}($CHCl_3$)/cm^{-1} 3431 (NH), 1771 (C=O), 1718 (C=O) and 1602 (Ph); $[\alpha]_D$ −94.6 (*c* 1.07 $CHCl_3$); δ_H(400 MHz; $CDCl_3$) 7.99 (2 H, d, *J* 7.2, *o*-Bz), 7.55 (1 H, t, *J* 7.4, *p*-Bz), 7.43 (2 H, t, *J* 7.7, *m*-Bz), 7.38–7.25 (4 H, m, *o*- and *m*-PhN), 7.05 (1 H, t, *J* 7.2, *p*-PhN), 6.69 (1 H, br s, NH), 5.71 (1 H, dt, *J* 10.8 and 7.5, C=C*H*CH_2), 5.56 (1 H, t, *J* 8.9, CHOCON), 5.49 (1 H, dt, *J* 5.9 and 3.1, C*H*OBz), 5.38 (1 H, dd, *J* 10.8 and 9.5, C*H*=$CHCH_2$), 5.06 (1 H, t, *J* 6.0, C*H*$OCOCH_2$), 2.92 (1 H, dd, *J* 17.8 and 10.4, $CH_AH_BCO_2$), 2.88–2.79 (1 H, m, C*H*CH_2CO_2), 2.58 (1 H, dd, *J* 17.8 and 1.3, $CH_AH_BCO_2$), 2.56–2.42 (2 H, m, CH_AH_BCOBz and C*H*CHC=C), 2.35 (1 H, d, *J* 15.7, CH_AH_BCOBz), 2.30–2.05 (2 H, m, CH_2C=C), 1.52–1.21 (6 H, m, $CH_2CH_2CH_2$) and 0.86 (3 H, t, *J* 6.9, Me); δ_C(100 MHz; $CDCl_3$) 176.4, 165.8, 152.6, 137.5, 137.2, 133.3, 129.7, 129.2, 129.1, 128.6, 124.9, 84.4, 77.0, 70.3, 57.0, 40.1, 38.5, 36.3, 31.5, 29.1, 28.1, 22.5 and 14.0; *m*/*z* 491 (23%, M^+), 354 (28, M − PhNHCO_2H), 233 (87, M − PhNHCO_2H − BzOH) and 105 (100, PhCO) (Found: M^+, 491.2267. $C_{29}H_{33}NO_6$ requires *M*, 491.2308).

(*Z*)-(1*S*,5*R*,6*R*,7*R*,1′*R*)-7-Benzoyloxy-6-(1′-*N*-phenylcarbamoyloxyoct-2′-enyl)-2-oxabicyclo[3.3.0]octan-3-one 51

A similar preparation from the alcohol **43** (0.053 g, 0.14 mmol) gave the *carbamate* (0.067 g, 96%); R_f (Et_2O) 0.82; $[\alpha]_D$ −39.1 (*c* 0.57, $CHCl_3$); ν_{max}($CHCl_3$)/cm^{-1} 3434 (NH), 1772 (C=O), 1729 (C=O) and 1602 (Ph); δ_H(400 MHz; $CDCl_3$) 7.98 (2 H, br d, *J* 7.2, *o*-Bz), 7.54 (1 H, br t, *J* 7.4, *p*-Bz), 7.42 (2 H, br t, *J* 7.7, *m*-Bz), 7.34 (2 H, br d, *J* 7.8, *o*-PhN), 7.28 (2 H, br t, *J* 7.4, *m*-PhN), 7.06 (1 H, br t, *J* 7.2, *p*-PhN), 6.77 (1 H, br s, NH), 5.68 (1 H, dt, *J* 10.9 and 7.5, C=C*H*CH_2), 5.56 (1 H, dd, *J* 9.1 and 7.8, CHOCON), 5.39 (1 H, dd, *J* 10.8 and 9.6, C*H*=$CHCH_2$), 5.36 (1 H, q, *J* 3.5, C*H*OBz), 5.07 (1 H, br t, *J* 5.1, C*H*$OCOCH_2$), 3.00–2.87 (2 H, m, C*H*C$H_AH_BCO_2$), 2.57 (1 H, d, *J* 16.2, $CH_AH_BCO_2$), 2.43 (1 H, dt, *J* 7.1 and 4.0, C*H*CHC=C), 2.40–2.30 (1 H, m, CH_AH_BCOBz), 2.35 (1 H, br d, *J* 15.9, CH_AH_BCOBz), 2.29–2.09 (2 H, m, CH_2C=C), 1.45–1.22 [6 H, m, $(CH_2)_3$Me] and 0.86 (3 H, t, *J* 6.9, Me); δ_C(100 MHz; $CDCl_3$) 176.5, 165.8, 152.5, 137.5, 136.9, 133.3, 129.65, 129.56, 129.1, 128.5, 125.1, 84.5, 77.3, 70.3, 57.0, 39.9, 38.7, 36.3, 31.5, 29.1, 28.1, 22.5 and 14.0; *m*/*z* 491 (1%, M^+), 119 (91, PhNCO) and 105 (100, PhCO) (Found: M^+, 491.2319. $C_{29}H_{33}NO_6$ requires *M*, 491.2308).

(1′*E*,2″*Z*)-(1*S*,5*R*,6*R*,7*R*,3′*R*)-7-Benzoyloxy-6-[3′-(2″-methylbut-2″-enyl)diphenylsilyloct-1′-enyl]-2-oxabicyclo[3.3.0]-octan-3-one 49

Method 1. The dibenzoate **47** (0.152 g, 0.32 mmol) in ether (2 cm^3) was added dropwise to a stirred solution of freshly prepared silylcuprate reagent **10** (0.35 mmol) and triphenylphosphine (0.183 g, 0.7 mmol) at −78 °C under argon. The solution was stirred at this temperature for 1 h and allowed to warm to 0 °C over 2 h. The reaction was quenched with basic aqueous ammonium chloride (2 cm^3) and the mixture extracted with ether (3 × 5 cm^3). The organic layers were combined, washed with basic aqueous ammonium chloride (1 cm^3) and brine (1 cm^3), dried ($MgSO_4$) and concentrated under reduced pressure. The residue was chromatographed (SiO_2, EtOAc–light petroleum, 1:9) to give the *allylsilane* (0.169 g, 87%); R_f (Et_2O) 0.69; $[\alpha]_D$ −45.5 (*c* 1.03, $CHCl_3$); ν_{max}(film)/cm^{-1} 1770 (C=O), 1714 (C=O), 1662 (C=C), 1602 (Ph), 1586 (Ph) and 1112 (Si–Ph); δ_H(400 MHz; $CDCl_3$) 7.96 (2 H, br d, *J* 7.9, *o*-Bz), 7.56–7.43 (5 H, m, *p*-Bz and *o*-$SiPh_2$), 7.43–7.28 (8 H, m, *m*-Bz,

m- and *p*-$SiPh_2$), 5.34 (1 H, dd, *J* 15.2 and 10.1, C*H*=CHCHSi), 5.13–5.04 (2 H, m, CHOBz and C=C*H*CHSi), 4.99 (1 H, br q, *J* 6.6, C=C*H*Me), 4.88 (1 H, dt, *J* 6.8 and 2.2, C*H*OCOCH$_2$), 2.63 (1 H, dd, *J* 18.2 and 8.5, CH_AH$_B$CO$_2$), 2.59–2.41 (3 H, m, CH_AH$_B$COBz, C*H*CH$_2$CO$_2$ and C*H*CH=CHCHSi), 2.24 (1 H, dd, *J* 18.2 and 1.8, CH$_A$$H_BCO_2$), 2.18 (1 H, br t, *J* 10.8, C=CCHSi), 2.06 (1 H, d, *J* 13.8, CH_AH$_B$Si), 2.05–1.97 (1 H, m, CH$_A$$H_B$COBz), 2.03 (1 H, d, *J* 13.4, CH$_A$$H_B$Si), 1.47 (3 H, t, *J* 1.3, *Me*C=CH), 1.30–0.98 [8 H, m, (CH_2)$_4$Me], 1.21 (3 H, d, *J* 6.6, C=CH*Me*) and 0.73 (3 H, t, *J* 6.9, CH$_2$*Me*); δ_C(100 MHz; $CDCl_3$) 176.5, 166.0, 135.7, 135.6, 134.7, 134.2, 133.9, 133.2, 132.2, 129.7, 129.6, 129.5, 129.4, 128.4, 127.6, 127.5, 127.4, 118.1, 82.8, 78.7, 54.3, 42.4, 37.4, 34.3, 31.4, 28.9, 28.8, 26.4, 22.4, 17.9, 14.0 and 13.7; *m*/*z*(CI) 624 (48%, M^+ + NH_4), 537 (80, M − CH_2MeC=CHMe) and 105 (100, PhCO) (Found: M^+ + NH_4, 624.3507. $C_{39}H_{46}O_4Si$ + NH_4 requires *M*, 624.3509).

Method 2. Butyllithium (1.3 mol dm^{-3} in hexane, 0.02 cm^3, 0.026 mmol) was added dropwise to a stirred solution of the carbamate **48** (0.014 g, 0.029 mmol) in dry THF (1 cm^3) at −78 °C under argon. After stirring at this temperature for 15 min the solution was added *via* a cannula to a vigorously stirred slurry of copper(I) bromide–dimethyl sulfide complex (0.006 g, 0.03 mmol) in dry ether (1.5 cm^3) at 0 °C under argon. The mixture was stirred at this temperature for a further 45 min. The silyllithium reagent **9** (0.45 mol dm^{-3} in THF, 0.06 cm^3, 0.027 mmol) was added dropwise to the slurry and the mixture stirred at 0 °C for 3 h. The reaction was quenched with basic aqueous ammonium chloride (2 cm^3) and the mixture extracted with ether (3 × 5 cm^3). The organic layers were combined, washed with basic aqueous ammonium chloride (1 cm^3) and brine (1 cm^3), dried ($MgSO_4$) and concentrated under reduced pressure. The residue was chromatographed (SiO_2, EtOAc–light petroleum, 1:9) to give the allylsilane (0.004 g, 23%), identical (TLC, IR, ^{1}H NMR) with the earlier sample, and the recovered carbamate (0.010 g, 71%).

(1′*E*,2″*Z*)-(1*S*,5*R*,6*R*,7*R*,3′*S*)-7-Benzoyloxy-6-[3′-(2″-methylbut-2″-enyl)diphenylsilyloct-1′-enyl]-2-oxabicyclo[3.3.0]octan-3-one 53

Method 1. A similar preparation to Method 1 above, converted the dibenzoate **52** (0.058 g, 0.12 mmol) into the *allylsilane* (0.062 g, 84%); R_f (Et_2O) 0.69; $[a]_D$ −36.2 (*c* 1.0, $CHCl_3$); ν_{max}($CDCl_3$)/cm^{-1} 1771 (C=O), 1716 (C=O), 1602 (Ph) and 1112 (Si–Ph); δ_H(400 MHz; $CDCl_3$) 7.95 (2 H, br d, *J* 7.8, *o*-Bz), 7.54 (1 H, br t, *J* 5.4, *p*-Bz), 7.47–7.21 (12 H, m, *m*-Bz and $SiPh_2$), 5.36 (1 H, dd, *J* 15.3 and 9.8, C*H*=CHCHSi), 5.08 (1 H, dd, *J* 15.2 and 7.5, C=C*H*CHSi), 5.05 (1 H, q, *J* 6.1, C=CH*Me*), 4.93 (1 H, br t, *J* 6.7, C*H*OCOCH$_2$), 4.92 (1 H, td, *J* 6.7 and 1.8, C*H*OBz), 2.76 (1 H, dd, *J* 18.3 and 9.4, CH_AH$_B$CO$_2$), 2.66–2.54 (2 H, m, C*H*CH$_2$CO$_2$ and C*H*CH=CHCHSi), 2.49 (1 H, dt, *J* 15.5 and 6.8, CH_AH$_B$COBz), 2.41 (1 H, dd, *J* 18.3 and 1.8, CH$_A$$H_BCO_2$), 2.16 (1 H, br t, *J* 10.6, C=CCHSi), 2.07 (1 H, ddd, *J* 15.4, 5.5 and 1.8, CH$_A$$H_B$COBz), 1.97 (2 H, s, $SiCH_2$), 1.40 (3 H, t, *J* 1.4, *Me*C=CH), 1.38–1.12 [8 H, m, (CH_2)$_4$Me], 1.12 (3 H, d, *J* 6.5, C=CH*Me*) and 0.82 (3 H, t, *J* 7.0, CH$_2$*Me*); δ_C(100 MHz; $CDCl_3$) 176.6, 165.9, 135.6, 134.7, 134.1, 133.9, 133.2, 132.2, 129.7, 129.6, 129.4, 129.3, 128.4, 127.6, 127.5, 127.3, 118.0, 83.1, 79.1, 54.3, 43.0, 37.5, 34.6, 31.4, 31.2, 28.9, 28.7, 26.4, 22.6, 17.8, 14.1 and 13.6; *m*/*z*(FAB) 606 (11%, M^+) and 537 (89, M − CH_2MeC=CHMe) (Found: M^+, 624.3201. $C_{39}H_{46}O_4Si$ requires *M*, 624.3165).

Method 2. A similar preparation to Method 2 above, converted the carbamate **51** (0.031 g, 0.063 mmol) into the allylsilane (0.009 g, 24%), identical (TLC, ^{1}H NMR) with the earlier sample, and the recovered carbamate **51** (0.022 g, 71%).

Method 3. Freshly prepared silyllithium reagent **9** (0.11 mmol) was added dropwise to stirred slurry of dry copper(I) iodide (0.018 g, 0.09 mmol) in dry ether (1 cm^3) and triphenylphosphine (0.049 g, 0.19 mmol) at 0 °C under argon. The mixture was stirred at this temperature for 20 min. Butyllithium (1.34 mol dm^{-3} in hexane, 0.07 cm^3, 0.1 mmol) was added dropwise to a stirred solution of the carbamate **51** (0.046 g, 0.09 mmol) in dry THF (0.8 cm^3) at −78 °C under argon. After stirring at this temperature for 5 min the solution was added *via* a cannula to the silylcopper reagent at 0 °C, and the mixture was stirred at this temperature for a further 4 h. The mixture was quenched with basic aqueous ammonium chloride (1 cm^3), filtered through Celite and extracted with light petroleum (3 × 5 cm^3). The organic layers were combined, washed with basic aqueous ammonium chloride (3 cm^3) and brine (3 cm^3), dried ($MgSO_4$) and concentrated under reduced pressure. The residue was chromatographed (SiO_2, EtOAc–light petroleum, 1:9) to give the allylsilane (0.030 g, 55%), identical (TLC, ^{1}H NMR) with the earlier sample, and the recovered carbamate **51** (0.013 g, 29%).

(*E*)-(1*S*,5*R*,6*R*,7*R*,3′*R*)-7-Benzoyloxy-6-(3′-hydroxyoct-1′-enyl)-2-oxabicyclo[3.3.0]octan-3-one 50

Boron trifluoride–acetic acid complex (0.02 cm^3, 0.08 mmol) was added dropwise to the allylsilane **49** (0.049 g, 0.08 mmol) in dichloromethane (1 cm^3) at −10 °C under argon. After 5 min the reaction was quenched with sodium hydrogen carbonate (0.04 g, 0.4 mmol) and the solvent evaporated under reduced pressure. Methanol (1 cm^3), THF (1 cm^3), potassium fluoride (0.01 g, 0.17 mmol) and hydrogen peroxide (30%, 0.4 cm^3, 3.5 mmol) were added to the residue and the mixture stirred at room temperature overnight and then refluxed for 2 h. The excess hydrogen peroxide was quenched with sodium sulfite and the mixture acidified with hydrochloric acid (1 mol dm^{-3}). The organic solvents were evaporated off under reduced pressure and the aqueous residue extracted with ether (4 × 5 cm^3). The organic layers were combined, washed with brine (2 cm^3), dried ($MgSO_4$), and concentrated under reduced pressure. The residue was chromatographed (SiO_2, EtOAc–light petroleum, 1:4 and then EtOAc) to give the alcohol (0.020 g, 66%); R_f (EtOAc) 0.52; $[a]_D$ −96.5 (*c* 1.4, $CHCl_3$) [lit.,[37] (for enantiomer) +98 (*c* 0.78, $CHCl_3$)]; ν_{max}(CH_2Cl_2)/cm^{-1} 3599 (OH), 3393 (br OH), 1773 (C=O), 1718 (C=O) and 1602 (Ph); δ_H(400 MHz; CH_2Cl_2) 7.99 (2 H, br d, *J* 7.9, *o*-Ph), 7.56 (1 H, br t, *J* 7.4, *p*-Ph), 7.43 (2 H, br t, *J* 7.7, *m*-Ph), 5.64 (1 H, dd, *J* 15.5 and 6.0, C= C*H*CHOH), 5.55 (1 H, dd, *J* 15.6 and 7.5, C*H*=CHCHOH), 5.22 (1 H, q, *J* 6.0, C*H*OBz), 5.05 (1 H, td, *J* 6.6 and 1.6, C*H*OCOCH$_2$), 4.08 (1 H, q, *J* 6.1, C*H*OH), 2.84 (1 H, dd, *J* 17.3 and 9.6, CH_AH$_B$CO$_2$), 2.82–2.76 (1 H, m, C*H*CH$_2$CO$_2$), 2.73 (1 H, br q, *J* 6.6, C*H*CH=CHCHOH), 2.61 (1 H, dt, *J* 15.4 and 6.7, CH_AH$_B$CHOBz), 2.51 (1 H, d, *J* 16.4, CH$_A$$H_BCO_2$), 2.22 (1 H, ddd, *J* 15.4, 5.2 and 1.7, CH$_A$$H_B$CHOBz), 1.60 (1 H, br s, OH), 1.55–1.39 (2 H, m, CH_2CHOH), 1.36–1.16 [6 H, m, (CH_2)$_3$Me] and 0.82 (3 H, t, *J* 6.4, Me); δ_C(100 MHz; $CDCl_3$) 176.4, 166.0, 136.5, 133.3, 129.65, 129.55, 128.5, 128.4, 83.2, 79.0, 72.4, 54.0, 42.7, 37.6, 37.3, 34.8, 31.7, 25.0, 22.5 and 14.0; *m*/*z* 354 (9%, M − H_2O), 301 [84, M − (CH$_2$)$_4$Me], 250 (60%, M − BzOH), 179 [69, M − BzOH − (CH$_2$)$_4$Me], 105 (100, $SiPh^+$) and 77 (76, Ph) (Found: M^+ − H_2O, 354.1825. $C_{22}H_{28}O_3$ − H_2O requires *M*, 354.1831).

(*E*)-(1*S*,5*R*,6*R*,7*R*,3′*S*)-7-Benzoyloxy-6-(3′-hydroxyoct-1′-enyl)-2-oxabicyclo[3.3.0]octan-3-one 54

A similar preparation from the allylsilane **53** (0.036 g, 0.06 mmol) gave the alcohol (0.013 g, 60%); R_f (EtOAc) 0.59; $[a]_D$ −95.1 (*c* 1.0, $CHCl_3$) [lit.,[37] (for enantiomer) +77 (*c* 1.04, $CHCl_3$)]; ν_{max}($CHCl_3$)/cm^{-1} 3602 (OH), 1772 (C=O), 1716 (C=O) and 1602 (Ph); δ_H(400 MHz; $CDCl_3$) 7.98 (2 H, br d, *J* 7.9, *o*-Ph), 7.56 (1 H, br t, *J* 7.4, *p*-Ph), 7.44 (2 H, br t, *J* 7.7, *m*-Ph), 5.64 (1 H, dd, *J* 15.5 and 5.5, C=C*H*CHOH), 5.58 (1 H, dd, *J* 15.5 and 6.9, C*H*=CHCHOH), 5.24 (1 H, q, *J* 5.9, C*H*OBz), 5.05 (1 H, td, *J* 6.6 and 1.9, C*H*OCOCH$_2$), 4.08 (1 H, q, *J* 6.0, C*H*OH), 2.84 (1 H, dd, *J* 17.0 and 9.6, CH_AH$_B$CO$_2$), 2.82–2.77 (1 H, m, C*H*CH$_2$CO$_2$), 2.73 (1 H, br q, *J* 6.4,

C*H*CH=CHCHOH), 2.60 (1 H, dt, *J* 15.4 and 6.7, C*H*$_A$H$_B$-CHOBz), 2.51 (1 H, d, *J* 16.4, CH$_A$*H*$_B$CO$_2$), 2.22 (1 H, ddd, *J* 15.4, 5.1 and 1.7, CH$_A$*H*$_B$CHOBz), 1.60 (1 H, br s, OH), 1.56–1.39 (2 H, m, C*H*$_2$CHOH), 1.38–1.19 [6 H, m, (C*H*$_2$)$_3$Me] and 0.85 (3 H, t, *J* 6.7, Me); δ_C(100 MHz; $CDCl_3$) 176.4, 166.1, 136.4, 133.3, 129.7, 129.6, 128.5, 128.3, 83.2, 79.0, 72.2, 54.0, 42.7, 37.6, 37.2, 34.9, 31.7, 25.0, 22.5 and 14.0; *m*/*z* 250 (37%, M − BzOH), 179 [55, M − BzOH − $(CH_2)_4$Me] and 77 (100, Ph) (Found: M^+ − BzOH, 250.1563. $C_{22}H_{28}O_5$ − BzOH requires *M*, 250.1565).

Hydrolysis of the benzoates 50 and 54 for further characterisation

(*E*)-(1*S*,5*R*,6*R*,7*R*,3′*R*)-7-Hydroxy-6-(3′-hydroxyoct-1′-enyl)-2-oxabicyclo[3.3.0]octan-3-one. Potassium carbonate (0.006 g, 0.04 mmol) was stirred with the benzoate **50** (0.011 g, 0.03 mmol) in methanol (0.5 cm^3) at room temperature for 30 min and then acidified with aqueous hydrochloric acid (1 mol dm^{-3}). The solvent was evaporated off under reduced pressure and the residue taken up in ether (5 cm^3), dried ($MgSO_4$), and concentrated under reduced pressure. The residue was chromatographed (SiO_2, EtOAc) to give the diol[37,39] (0.006 g, 76%); R_f (EtOAc) 0.28; $\nu_{max}(CDCl_3)/cm^{-1}$ 3690 (OH), 3602 (OH), 3393 (br OH), 1768 (C=O) and 1602 (C=C); δ_H(400 MHz; $CDCl_3$) 5.64 (1 H, ddd, *J* 15.4, 5.9 and 0.5, C=C*H*CHOH), 5.50 (1 H, ddd, *J* 15.4, 8.4 and 0.9, C*H*=CHCHOH), 4.91 (1 H, td, *J* 7.0 and 2.9, C*H*OCOCH$_2$), 4.11 (1 H, q, *J* 6.1, C=CHC*H*OH), 4.00 (1 H, q, *J* 7.0, C=CHCHC*H*OH), 2.74 (1 H, dd, *J* 18.1 and 9.7, C*H*$_A$H$_B$CO$_2$), 2.63 (1 H, br q, *J* 8.4, C*H*CH$_2$CO$_2$), 2.49 (1 H, dt, *J* 14.8 and 6.9, C*H*$_A$H$_B$CHOBz), 2.48 (1 H, dd, *J* 18.1 and 1.9, CH$_A$*H*$_B$CO$_2$), 2.34 (1 H, q, *J* 7.8, C*H*CH=CHCHOH), 1.97 (1 H, ddd, *J* 14.8, 7.2 and 2.9, CH$_A$*H*$_B$CHOBz), 1.64–1.47 (2 H, m, C*H*$_2$CHOH), 1.42–1.23 [6 H, m, (C*H*$_2$)$_3$Me] and 0.88 (3 H, t, *J* 6.8, Me).

(*E*)-(1*S*,5*R*,6*R*,7*R*,3′*S*)-7-Hydroxy-6-(3′-hydroxyoct-1′-enyl)-2-oxabicyclo[3.3.0]octan-3-one. A similar hydrolysis of the benzoate **54** (0.008 g, 0.02 mmol) gave the diol[37,39] (0.004 g, 70%), R_f (EtOAc) 0.25; $[a]_D$ −7.2 (*c* 0.3, $CHCl_3$) [lit.,[37] (for enantiomer) +10 (*c* 2.51, $CHCl_3$)]; $\nu_{max}(CDCl_3)/cm^{-1}$ 3690 (OH), 3602 (OH), 3395 (br OH), 1768 (C=O) and 1602 (C=C); δ_H(400 MHz; $CDCl_3$) 5.61 (1 H, dd, *J* 15.4 and 6.6, C=C*H*CHOH), 5.56 (1 H, dd, *J* 15.4 and 8.4, C*H*=CHCHOH), 4.89 (1 H, td, *J* 7.0 and 3.0, C*H*OCOCH$_2$), 4.07 (1 H, q, *J* 6.5, C=CHC*H*OH), 3.96 (1 H, q, *J* 7.3, C=CHCHC*H*OH), 2.72 (1 H, dd, *J* 18.0 and 9.6, C*H*$_A$H$_B$CO$_2$), 2.62–2.46 (2 H, m, C*H*CH$_2$CO$_2$ and C*H*$_A$H$_B$CHOBz), 2.43 (1 H, dd, *J* 18.0 and 1.8, CH$_A$*H*$_B$CO$_2$), 2.28 (1 H, q, *J* 8.2, C*H*CH=CHCHOH), 1.94 (1 H, ddd, *J* 14.8, 7.6 and 3.0, CH$_A$*H*$_B$CHOBz), 1.63 (1 H, br s, OH), 1.60–1.42 (2 H, m, C*H*$_2$CHOH), 1.40–1.21 [6 H, m, (C*H*$_2$)$_3$Me] and 0.88 (3 H, t, *J* 6.7, Me); δ_C(100 MHz; $CDCl_3$) 176.7, 136.8, 129.5, 82.4, 72.6, 56.3, 42.6, 39.9, 37.4, 34.2, 31.7, 25.1, 22.6 and 14.0.

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References

1 I. Fleming, R. Henning, D. C. Parker, H. E. Plaut and P. E. J. Sanderson, *J. Chem. Soc.*, *Perkin Trans. 1*, 1995, 317.
2 I. Fleming, D. Higgins, N. J. Lawrence and A. P. Thomas, *J. Chem. Soc.*, *Perkin Trans. 1*, 1992, 3331.
3 J. S. Bindra and R. Bindra, *Prostaglandin Synthesis*, Academic Press, London, 1977; A. Mitra, *The Synthesis of Prostaglandins*, Wiley, New York, 1977; S. M. Roberts and R. F. Newton, *Prostaglandins and Thromboxanes*, Butterworths, London, 1982; *New Synthetic Routes to Prostaglandins and Thromboxanes*, eds. S. M. Roberts and F. Scheinmann, Academic Press, London, 1982; E. J. Corey and X.-M. Cheng, *The Logic of Chemical Synthesis*, Wiley, New York, 1989; P. W. Collins and S. W. Djuric, *Chem. Rev.*, 1993, **93**, 1533; R. Noyori, I. Tomino and M. Nishizawa, *J. Am. Chem. Soc.*, 1979, **101**, 5843; P. A. Grieco, T. Takigawa, S. L. Bongers and H. Tanaka, *J. Am. Chem. Soc.*, 1980, **102**, 7587; S. Iguchi, H. Nakai, M. Hayashi, H. Yamamato and K. Maruoka, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 3033; S. J. Danishefsky, M. P. Cabal and K. Chow, *J. Am. Chem. Soc.*, 1989, **111**, 3456.
4 R. Mahrwald, H. Schick, K. K. Pivnitsky and S. Schwarz, *J. Prakt. Chem.*, 1990, **332**, 403; H. Schick, J. Spanig, R. Mahrwald, M. Bohle, T. Reiher and K. K. Pivnitsky, *Tetrahedron*, 1992, **48**, 5579.
5 I. Fleming and H.-F. Chow, *J. Chem. Soc.*, *Perkin Trans. 1*, 1998, 2651.
6 K. Tamao, E. Nakajo and Y. Ito, *J. Org. Chem.*, 1987, **52**, 957.
7 K. Tamao, N. Ishida and M. Kumada, *J. Org. Chem.*, 1983, **48**, 2120; K. Tamao, T. Iwahara, R. Kanatani and M. Kumada, *Tetrahedron Lett.*, 1984, **25**, 1909; H.-J. Gais and G. Bülow, *Tetrahedron Lett.*, 1992, **33**, 461 and 465; W. R. Roush and P. T. Grover, *Tetrahedron*, 1992, **48**, 1981.
8 S. Lamothe, K. L. Cook and T. H. Chan, *Can. J. Chem.*, 1992, **70**, 1733.
9 T. Hayashi, S. Hengrasmee and Y. Matsumoto, *Chem. Lett.*, 1990, 1377; Y. Hatanaka, K. Goda, F. Yamashita and T. Hiyama, *Tetrahedron Lett.*, 1994, **35**, 7981.
10 R. Angelaud, Y. Landais and C. Maignan, *Tetrahedron Lett.*, 1995, **36**, 3861.
11 J. A. Hunt and W. R. Roush, *J. Org. Chem.*, 1997, **62**, 1112.
12 M. C. Norley, P. J. Kocienski and A. Faller, *Synlett*, 1994, 77.
13 D. F. Taber, L. Yet and R. S. Bhamidipati, *Tetrahedron Lett.*, 1995, **36**, 351; D. F. Taber, R. S. Bhamidipati and L. Yet, *J. Org. Chem.* 1995, **60**, 5537.
14 I. Fleming, P. E. J. Sanderson and F. Zammattio, *J. Chem. Res.* (*S*), 1994, 159; *J. Chem. Res.* (*M*), 1994, 1020.
15 K. Tamao, A. Kawachi, Y. Tanaka, H. Ohtani and Y. Ito, *Tetrahedron*, 1996, **52**, 5765; A. Kawachi and K. Tamao, *Bull. Chem. Soc. Jpn.*, 1997, **70**, 945.
16 I. Fleming and S. B. D. Winter, *Tetrahedron Lett.*, 1993, **34**, 7287.
17 I. Fleming and S. B. D. Winter, *Tetrahedron Lett.*, 1995, **36**, 1733.
18 N. Abd.Rahman, PhD Thesis, Cambridge, 1990.
19 N. Abd.Rahman, I. Fleming and A. B. Zwicky, *J. Chem. Res.* (*S*), 1992, 292; *J. Chem. Res.* (*M*), 1992, 2401.
20 I. Ojima and M. Kumagai, *J. Organomet. Chem.*, 1978, **157**, 359.
21 I. Fleming, R. S. Roberts and S. C. Smith, *J. Chem. Soc.*, *Perkin Trans. 1*, 1998, 1209.
22 C. Eaborn and S. H. Parker, *J. Chem. Soc.*, 1955, 126.
23 J. J. Partridge, N. K. Chadha and M. S. Uskokovic, *J. Am. Chem. Soc.*, 1973, **95**, 7171.
24 I. Tömösközi, L. Gruber, G. Kovâcs, I. Székely and V. Simonidesz, *Tetrahedron Lett.*, 1976, **17**, 4639.
25 J. Y. Corey and R. West, *J. Am. Chem. Soc.*, 1963, **85**, 2430.
26 A. Kunai, T. Kawakami, E. Toyoda and M. Ishikawa, *Organometallics*, 1992, **11**, 2708.
27 C. R. Johnson, C. J. Cheer and D. J. Goldsmith, *J. Org. Chem.*, 1964, **29**, 3320; G. Höfle and W. Steglich, *Synthesis*, 1972, 619.
28 V. Dev, *J. Chem. Educ.*, 1970, **47**, 476.
29 J. Rajaram, A. P. S. Narula, H. P. S. Chawla and S. Dev, *Tetrahedron*, 1983, **39**, 2315.
30 S. G. Davies, I. M. Dorder-Hedgecock, P. Warner, R. H. Jones and K. Prout, *J. Organomet. Chem.*, 1985, **285**, 213.
31 T. Matsumoto, I. Tanaka and K. Fukui, *Bull. Chem. Soc. Jpn.*, 1971, **44**, 3378.
32 *Vogel's Textbook of Practical Organic Chemistry*, Longman, Harlow, England, 1989, p. 1332.
33 G. H. Kulkarni and A. A. Arbale, *Synth. Commun.*, 1988, **18**, 2147.
34 J. Nakayama and A. Hirashima, *J. Am. Chem. Soc.*, 1990, **112**, 7648.
35 E. J. Corey and R. Noyori, *Tetrahedron Lett.*, 1970, **21**, 311.
36 I. Tömösközi, L. Gruber and E. Baitz-Gács, *Tetrahedron*, 1992, **48**, 10 345.
37 E. L. Cooper and E. W. Yankee, *J. Am. Chem. Soc.*, 1974, **96**, 5876.
38 D. B. Dess and J. C. Martin, *J. Org. Chem.*, 1983, **48**, 4155; D. B. Dess and J. C. Martin, *J. Am. Chem. Soc.*, 1991, **113**, 7277; R. E. Ireland and L. Liu, *J. Org. Chem.*, 1993, **58**, 2899.
39 R. F. Newton, D. P. Reynolds, C. F. Webb, S. N. Young, Z. Grudzinski and S. M. Roberts, *J. Chem. Soc.*, *Perkin Trans. 1*, 1979, 2789; J. P. Marino, R. Fernández de la Pradilla and E. Laborde, *J. Org. Chem.*, 1987, **52**, 4898.

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