ARTICLE

OBC
www.rsc.org/obc

The Ireland–Claisen rearrangement as a probe for the diastereoselectivity of nucleophilic attack on a double bond adjacent to a stereogenic centre carrying a silyl group

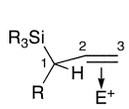
Mark S. Betson and Ian Fleming *
Department of Chemistry, Lensfield Road, Cambridge, UK CB2 1EW.
E-mail: if10000@cam.ac.uk; Fax: +44 (0)1223 336362; Tel: +44 (0)1223 336372

Received 23rd May 2003, Accepted 15th September 2003
First published as an Advance Article on the web 6th October 2003

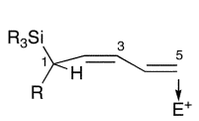
The *E*- and *Z*-silyl enol ethers **4** derived from allyl 3-R-3-dimethyl(phenyl)silylpropanoate (R = Me, Pr^i and Ph) and the *Z*-silyl enol ethers **7** derived from 4-R-4-dimethyl(phenyl)silylbut-2-enyl acetate (R = Me and Pr^i) undergo Ireland–Claisen rearrangements largely in the same stereochemical sense, with C–C bond formation taking place anti to the silyl group in the conformations **22**, **23** and **24** in which the hydrogen atom on the stereogenic centre is inside, more or less eclipsing the double bond. The *E*-silyl enol ether *E*-**7a** derived from 4-methyl-4-dimethyl(phenyl)silylbut-2-enyl acetate shows low diastereoselectivity in the alternative sense, probably because C–C bond formation takes place anti to the silyl group in the conformation **26** with the methyl group inside, but the silyl enol ether *E*-**7b** derived from 4-isopropyl-4-dimethyl(phenyl)silylbut-2-enyl acetate shows low diastereoselectivity in the normal sense. The *E*- and *Z*-silyl enol ethers **33** derived from *cis*-crotyl 3-phenyl-3-dimethyl(phenyl)silylpropanoate and the *E*-silyl enol ether **39** derived from *trans*-crotyl 3-phenyl-3-dimethyl(phenyl)silylpropanoate undergo Ireland–Claisen rearrangements largely in the same stereochemical sense as their allyl counterparts, but with moderately high levels of diastereocontrol in setting up the third stereogenic centre following from chair-like transition structures.

Introduction

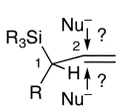
We established at length how effectively a silyl group can control the stereochemistry of electrophilic attack on a double bond in the sense **1**, anti to the silyl group, for a wide variety of reactions, some of which take place with bond formation at C-2,[1,2] some at C-3,[3,4] and some for cycloadditions taking place with bonds forming at both C-2 and C-3.[5] We have also been much exercised to determine whether the sense and the high level of control for all these reactions stems from the steric or from the electronic effect of the neighbouring Si–C bond. We have had little substantive success, managing only to show that the stereochemistry of the S_E2'' reaction **2**,[6] taking place at C-5, further away from the steric effect, was much less stereoselective with small electrophiles than the corresponding S_E2' reaction at C-3. Separating steric and electronic effects is a notorious problem, beset with pitfalls. It is clearly important for our understanding of chemical reactions, but applied to diastereoselectivity it has led so far to substantial but largely unresolved debate.[7]



1



2



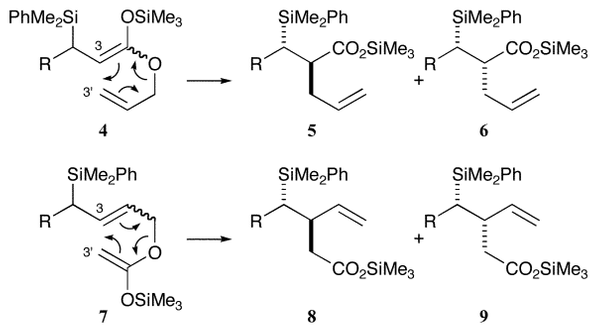
3

Our approach to the problem reported here was flawed from the start—we planned to study how changing the electronic balance from electrophilic attack to nucleophilic attack might affect the sense of the diastereoselectivity. In the meantime it has become clearer that there is no compelling reason to expect nucleophilic attack to differ fundamentally in the sense of its diastereoselectivity from the otherwise analogous electrophilic attack. Indeed, the most provocative of the theories for electronically controlled diastereoselectivity positively suggests that nucleophilic and electrophilic attack ought to take place in the same sense, anti to the best donor substituent.[8] In consequence, the results reported here do not address the problem we originally wanted to tackle, but they do shed some light on a different matter, namely on the sense of the diastereoselectivity of nucleophilic attack on a double bond adjacent to a stereogenic centre carrying a silyl group **3**.

Earlier work in this area had been largely about attack on a carbonyl group, analogous to the control exerted by the Felkin–Anh rule. For somewhat complicated but essentially steric reasons, the attack is largely anti to the silyl group in the usual Felkin–Anh conformation with the R group inside, more or less eclipsing the double bond.[9] There have also been two papers on the attack on the C=O double bond of oxenium ions derived from acetals, in which the stereogenic centre was attached to the oxygen atom.[10] For attack on a C=C double bond, there has only been our own work, described in the preceding paper, on a system in which a cuprate attacked at the β carbon of an enone having the stereogenic centre attached to the α carbon.[11] In all cases, attack takes place predominantly anti to the silyl group. In the acetal reactions, it is not clear what the conformation is at the time of reaction, and in the enone the cyclic system imposes extra rigidity. None of these cases has the attack at C-2 in the sense **3**.

The device that we chose to use was the diastereoselectivity of the Ireland–Claisen rearrangement[12] of the complementary pair of silyl enol ethers **4** and **7** (Scheme 1). We reasoned that the former, **4**, with two oxygen atoms as substituents on the double bond adjacent to the stereogenic centre, would have nucleophilic character at C-3 in the [3,3]-sigmatropic rearrangement, and hence some of the character of electrophilic attack adjacent to the stereogenic centre, symbolised by the curly arrows drawn in an anti-clockwise direction. We expected that we would see the same sense of diastereoselectivity anti to the silyl group as we had seen in the corresponding enolate alkylations,[1] just as Yamazaki found that the new bond is largely formed syn to a trifluoromethyl group for the same type of Ireland–Claisen rearrangement.[13] The more interesting case was the latter, **7**, where the [3,3]-sigmatropic rearrangement would have the nucleophilic character at C-3′ and some of the character of nucleophilic attack at C-3, symbolised by the curly arrows drawn in a clockwise direction. Would the two reactions

DOI: 10.1039/b305881f



a, R=Me; **b**, R=Pr^{i}; **c**, R=Ph

Scheme 1

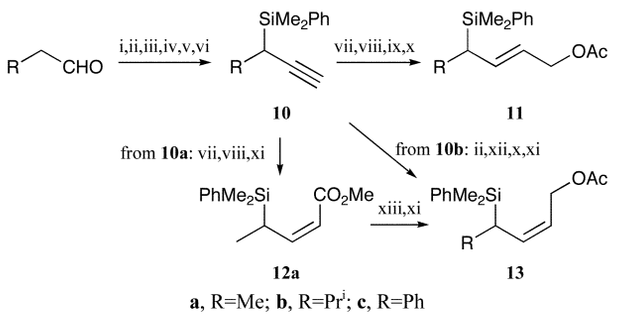
show the same sense of diastereoselectivity, and which would have the higher degree?

The idea of a complementary pair of Claisen rearrangements is not without precedent—it has been used by le Noble to probe stereoelectronic effects exocyclic to an adamantyl framework. He found that both the nucleophilic and electrophilic version took place with attack syn to a remote electron-withdrawing group, and therefore anti to the better donor substituent, and to a very similar extent.[14] There is also some support for the idea that the complementary pairs would have an opposite electronic bias of the kind that we wanted to use. The transition structure for the Ireland–Claisen rearrangement is even further above the diagonal line in a More O'Ferrall–Jencks diagram than the transition structure for an unsubstituted Claisen rearrangement,[15] implying even more bond-breaking ahead of bond-making. There is also some evidence for an unequal distribution of electron population in Claisen rearrangements, which can have a significant solvent effect, implying that the transition structure can have zwitterionic as well diradical character.[16] On the other hand, it is not reassuring to know that the transition structure for an Ireland–Claisen rearrangement appears to have four times as much bond breaking as bond making.[17]

Results and discussion

We carried out reactions using the silyl enol ethers **4** in three series, labelled **a** (R = Me), **b** (R = Pr^{i}) and **c** (R = Ph), each of which was prepared separately as an *E* and a *Z* isomer. We prepared the allyl esters used to make the silyl enol ethers from the known methyl esters[1,2] by acid-catalysed ester exchange, and the silyl enol ethers themselves using Ireland's recipes for *E* and *Z* isomers.[18] There was little doubt that the *E* isomers, made with LDA in THF at −78 °C, would be close to 94% configurationally pure, since this is a well tested and reliable method. We checked only one case, that of **4a**, which appeared to be a single isomer from its ^{1}H-NMR spectrum. In contrast, we were unable to confirm the stereochemical purity of any of the *Z* silyl enol ethers, prepared similarly, but in a mixture of HMPA and THF. The trimethylsilyl enol ethers were not isolable, because the HMPA could only be removed using an aqueous wash, during which the silyl enol ethers were hydrolysed even in the most careful workup, and the *tert*-butyldimethylsilyl enol ethers, which might have been isolable, were not formed cleanly. We reassured ourselves that we were getting mixtures rich in the *Z*-isomer, when we examined the reactions of the crotyl esters, as described below (Scheme 5).

We carried out reactions using the silyl enol ethers **7** in only two series, labelled **a** (R = Me) and **b** (R = Pr^{i}). The esters **11** and **13** used to make the silyl enol ethers **7a** and **7b** were prepared by the standard routes shown in Scheme 2. The third series **7c** (R = Ph) defeated us, because of low yields, probably because the silyl group was too easily lost from the simultaneously benzylic and propargylic carbon during the preparation of the



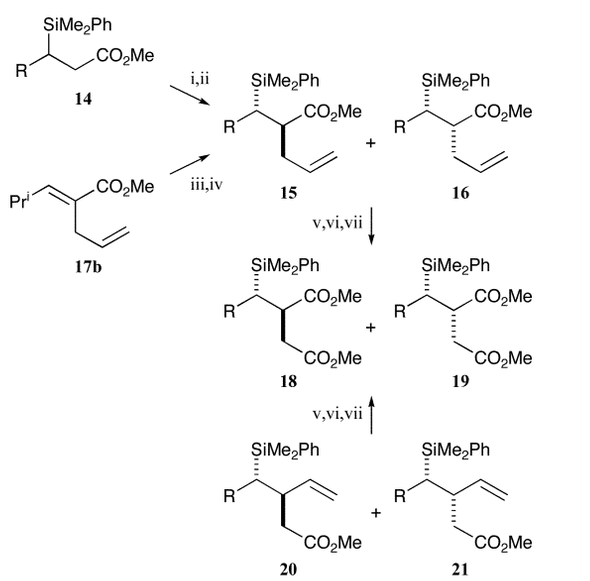
a, R=Me; **b**, R=Pr^{i}; **c**, R=Ph

Scheme 2 *Reagents and conditions:* i, CBr_4, Ph_3P, CH_2Cl_2; ii, Bu^{n}Li, THF; iii, RMe_2SiCl; iv, Bu^{t}Li, THF, TMEDA; v, $PhMe_2SiCl$; vi, $AgNO_3$, KCN, EtOH, H_2O; vii, LDA, THF; viii, $ClCO_2Me$; ix, $LiAlH_4$, Et_2O; x, Ac_2O, Et_3N, DMAP, Et_2O; xi, H_2, Pd/$BaSO_4$, MeOH xii, CH_2O; xiii, DIBAL.

intermediates analogous to those in Scheme 2 as well as in other routes that we tried.

The Ireland–Claisen rearrangements took place on refluxing the freshly-prepared solutions of the silyl enol ethers in THF for 8 hours. A brief treatment with sodium hydroxide solution converted the silyl esters into the carboxylic acids, which we analysed as their methyl esters by integration of the ^{1}H-NMR spectra of the mixtures. The overall yields from the esters used to prepare the silyl enol ethers to the methyl esters used in the analysis were in the range 43–66%. The ratios of diastereoisomers are summarised in Table 1.

We assigned relative stereochemistry to the products **5** and **6** by preparing authentic samples of the methyl esters (Scheme 3). For the **a** and **b** series, we prepared mixtures rich in the anti isomer by allylation of the enolates derived from the esters **14a** and **14b**, for which the sense of the diastereoselectivity is reliably high. In practice, the ratio **15a** : **16a** was 97 : 3, and the ratio **15b** : **16b** was 89 : 11. To identify with more confidence the NMR signals of the minor diastereoisomers **16a** and **16b**, we formed the enolates from the mixtures rich in the anti isomers using LDA, and reprotonated them with ammonium chloride solution, to give mixtures richer in the syn isomers **16a** and **16b**. This procedure gave products in the ratio **15a** : **16a** of 60 : 40 and **15b** : **16b** of 48 : 52, with clearly identifiable ^{1}H-NMR signals from the isomers that had been the minor products in the Ireland–Claisen rearrangements. Furthermore, we also carried out a conjugate addition of the silyl cuprate



a, R=Me; **b**, R=Pr^{i}; **c**, R=Ph

Scheme 3 *Reagents and conditions:* i, LDA, THF; ii, allyl bromide; iii, $(PhMe_2Si)_2CuLi$, THF; iv, NH_4Cl, H_2O; v, O_3, CH_2Cl_2; vi, H_2O_2, NaOH; vii, Me_3SiCHN_2, MeOH.

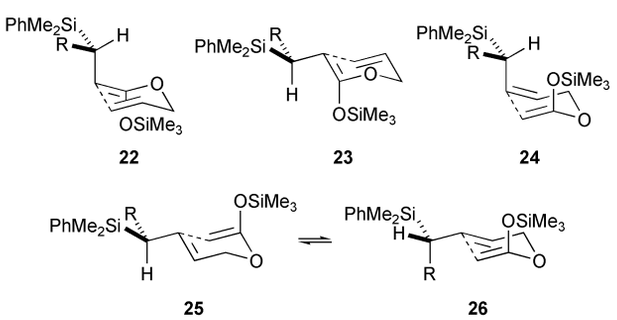
Table 1 Ratios of diastereoisomers produced by the Ireland–Claisen rearrangements in Scheme 1

	"Electrophilic attack"			"Nucleophilic attack"		
R	Starting material	*E* or *Z*	**5** : **6**	Starting material	*E* or *Z*	**8** : **9**
Me	**4a**	*E*	98 : 2	**7a**	*Z*	93 : 7
Me	**4a**	*Z*	93 : 7	**7a**	*E*	38 : 62
Pr^i	**4b**	*E*	86 : 14	**7b**	*Z*	98 : 2
Pr^i	**4b**	*Z*	69 : 31	**7b**	*E*	52 : 48
Ph	**4c**	*E*	>98 : 2	–	–	–
Ph	**4c**	*Z*	>97 : 3	–	–	–

reagent to the α,β-unsaturated ester **17b** followed by protonation of the enolate, and obtained a similar mixture of the esters **15b** and **16b** in a ratio of 45 : 55. The products **15c** and **16c**, produced in this work by allylation in the ratio 98 : 2, were already known.[1]

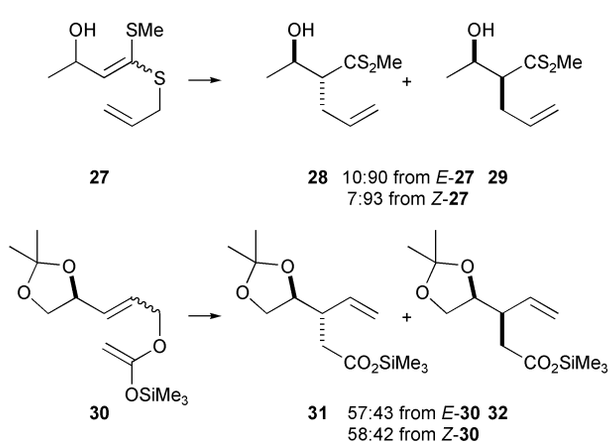
We assigned relative stereochemistry to the products **8** and **9** by ozonolysis of the mixtures of their methyl esters **20** and **21**, followed by oxidation and esterification, to give the diesters **18** and **19** (Scheme 3). We compared the ^{1}H-NMR spectra of these mixtures with the spectra of similar mixtures derived by the same sequence from the esters **15** and **16**.

All but one of the Ireland–Claisen rearrangements gave more of the anti isomer **5** or **8** than of the syn isomer **6** or **9** (Table 1, but note that the *E*-isomers of the silyl enol ethers **4** match the *Z*-isomers of the silyl enol ethers **7**). In the "electrophilic attack" series, the ratios match the ratios obtained in the allylation of the enolates derived from the ester **14**, with the highest ratio for R = Ph, intermediate for R = Me, and lowest for R = Pr^i, which in turn match our earlier results for the corresponding methylation reactions.[1] We can be reasonably confident that the preferred geometries in the transition structures resemble the somewhat simplified drawings **22** and **23** for the *E*- and *Z*-isomers, respectively, with the hydrogen inside and attack anti to the silyl group in all six cases.



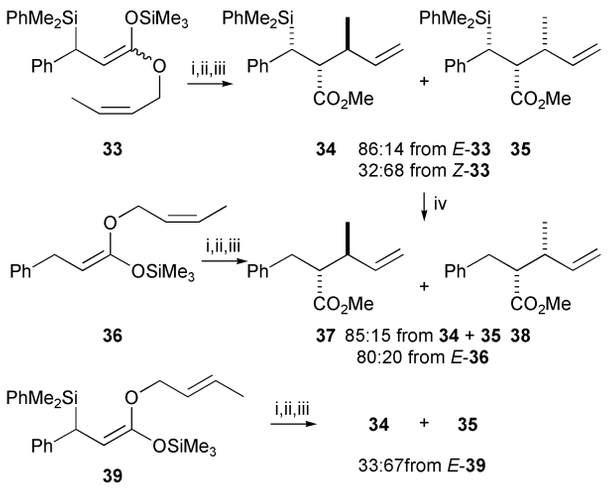
In the "nucleophilic attack" series, the *Z*-isomers *Z*-**7a** and *Z*-**7b** show remarkably high levels of diastereoselectivity, presumably because they also have a preferred transition structure **24** with the hydrogen inside and attack anti to the silyl group. The one result in which the syn isomer is the major product is with the silyl enol ether *E*-**7a**, which gives more (62 : 38) of the isomer **9a** than **8a**. The explanation is probably not related to any change in an electronic effect. The silyl enol ether *E*-**7a**, where the carbon group on the stereogenic centre is a methyl group and the substituent on the double bond cis to it is only a hydrogen atom, can have a conformation **26** (R = Me) significantly populated in which the methyl group is inside. Attack anti to the silyl group in this conformation gives the syn product **9a**, in contrast to the usual attack when the hydrogen atom is inside **25** (R = Me). As we have pointed out in our earlier work,[4,19] the diastereoselectivity in many reactions is unpredictable when the carbon substituent on the stereogenic centre is small and there is only a hydrogen atom cis to it, unless a closely analogous reaction has been investigated. The same explanation may account for the unusually low diastereoselectivity in the corresponding reaction with an isopropyl substituent *E*-**7b**. Normally a large group like this avoids being inside, but a molecular modelling calculation (MOPAC PM3) supports this explanation in this case by finding that the conformation **26** (R = Pr^i) is actually 0.84 kJ mol^{-1} lower in energy than that with the hydrogen inside **25** (R = Pr^i). As expected, similar calculations on the corresponding *Z*-isomer have the transition structure with the isopropyl inside 14.7 kJ mol^{-1} *higher* in energy than the conformation with the hydrogen atom inside **24** (R = Pr^i). It is clear from the high diastereoselectivity with both *Z*-isomers in the "nucleophilic attack" series that this translates into a highly favourable pathway leading to the products **8** by attack anti to the silyl group.

Our results in the "electrophilic attack" series **4** ⟶ **5** + **6** can be compared with those of Beslin,[20] and our results in the "nucleophilic attack" series **7** ⟶ **8** + **9** can be compared with those of Cha[21] (Scheme 4). In Beslin's and in Cha's work, the heteroatom substituent on the stereogenic centres is an electronegative element, in contrast to our electropositive element. Beslin's Claisen rearrangements of the thioenol ethers **27** were highly diastereoselective, taking place in the sense syn to the oxygen atom in the conformation with the hydrogen atom inside, making these results with an electronegative element opposite to ours with the electropositive element. In contrast, Cha's Ireland–Claisen rearrangements of the silyl enol ethers **30** showed low diastereoselectivity in favour of the anti isomer **31**, corresponding to attack anti to the oxygen atom in the conformation with the hydrogen atom inside.



Scheme 4

We also carried out a few Ireland–Claisen rearrangements with a methyl substituent at the terminus of the allyl fragment in the "electrophilic attack" series (Scheme 5). If we can rely on the preference for the chair transition structure established by Ireland's work,[22] we can expect that the double bond geometry in a crotyl ester would control a third stereocentre. This had the added advantage that it would provide some check on whether the geometry of the silyl enol ethers had been controlled to give largely the *E*- and *Z*-isomers in our earlier work. There were earlier reports of reactions controlling three contiguous stereocentres using Claisen rearrangements with electronegative substituents on the stereogenic centre, in contrast to



Scheme 5 *Reagents and conditions:* i, THF, reflux, 8 h; ii, NaOH; iii, CH_2N_2; iv, TBAF, THF.

our electropositive substituent. In one of them, a hydroxyl group sat inside in a lithium enolate providing coordination to the lithium ion, and attack was then anti to the alkyl group.[23] In another, a sulfoxide group is the stereogenic centre and a thio-Claisen rearrangement takes place anti to the lone pair.[24]

We prepared the *cis*-crotyl ester used to make the silyl enol ethers **33** from methyl 3-dimethyl(phenyl)silyl-3-phenylpropanoate, using acid-catalysed ester exchange with but-3-ynol, followed by Lindlar hydrogenation, and prepared the *E*- and *Z*-silyl enol ethers **33** using Ireland's recipes. We analysed the mixtures of silyl esters by hydrolysis and esterification in the same way as before. Four diastereoisomers must have been present, but we could detect clearly only two, to which we assign the structures **34** and **35**. The recipe expected to give largely the *E*-silyl enol ether gave the two products in a ratio of 86 : 14, whereas the recipe expected to give the *Z*-isomer gave a complementary ratio of 32 : 68, supporting our belief that we had been able to control to a reasonable extent the double bond geometry in all the silyl enol ethers. The poorer ratio from the mixture rich in the *Z*-isomer may well be a consequence of the less effective control of geometry of the silyl enol ether with that recipe. We confirmed that the two isomers differed in relative configuration between C-2 and C-3 by removing the benzylic silyl group, which give the esters **37** and **38** in a ratio close to that of the starting materials, and in a ratio unchanged by how long the treatment with TBAF was. We also prepared the same two esters in a similar ratio by carrying out the Ireland–Claisen rearrangement from the silyl enol ether *E*-**36**, supporting our assignment of which diastereoisomer was which.

Finally, we prepared the *trans*-crotyl ester used to make the silyl enol ether **39** from 3-dimethyl(phenyl)silyl-3-phenylpropanoic acid, esterifying with *trans*-but-3-enol. Ireland–Claisen rearrangement gave the same two esters as before, but now the *E*-silyl enol ether **39** gave more of the isomer **35** than of the isomer **34**. Thus the stereocontrol at the third stereocentre can be controlled either by changing the geometry of the silyl enol ether or by changing the geometry in the allyl group. The internal consistency of all these results shows that our structures are almost certainly correct.

In conclusion, the Ireland–Claisen rearrangement is quite highly controlled in the sense anti to the silyl group in a conformation with the hydrogen atom inside, whether it is carried out in the sense **4** ⟶ **5** + **6**, analogous to the allylation of an ester enolate, or in the sense **7** ⟶ **8** + **9**, provided that the double bond is *cis*, ensuring that the conformation with the hydrogen inside **24** is much the most highly populated. It appears that changing the electronic balance from a rearrangement with electrophilic character in the attack at C-3 to one with nucleophilic character does not change the sense of the diastereoselectivity, and that, in the latter case, when the conformation is well controlled, it is actually much higher.

Experimental

General

Infrared spectra were recorded on a Perkin-Elmer FT-IR 1600 spectrometer, using sodium chloride plates. NMR spectra were recorded on Bruker AC 250 and Bruker AM 400 spectrometers. Chemical shifts were measured relative to tetramethylsilane (^{1}H δ 0.0) or chloroform (^{14}C δ 77.0). Coupling constants J are expressed in Hertz are the measured values correct to one decimal place. ^{14}C-NMR spectra taken using the APT protocol are labelled + for quaternary and methylene carbons, and – for methine and methyl carbons. Flash column chromatography was carried out using Merck Kieselgel 60 (230–400 mesh). Thin layer chromatography was performed using plates coated with Kieselgel 60 PF_{254}. Ether and THF were distilled from lithium aluminium hydride immediately before use. Toluene, hexane, dichloromethane and acetonitrile were distilled from calcium hydride. Light petroleum refers to the fraction boiling between 40 °C and 60 °C. Organolithium reagents were titrated using the method of Gilman.[25]

Methyl 3-dimethyl(phenyl)silylbutanoate[26] (78%), methyl 4-methyl-3-dimethyl(phenyl)silylpentanoate[1] (80%) and methyl 3-phenyl-3-dimethyl(phenyl)silylpropanoate[1] (69%) were prepared by the methods referred to.

General method for the preparation of allyl esters

Typically, the methyl ester (8.4 mmol), allyl alcohol (15 cm^3) and concentrated sulfuric acid (1 cm^3) were refluxed overnight and allowed to cool to room temperature before being partitioned between ether (20 cm^3) and saturated aqueous sodium bicarbonate solution (20 cm^3). The aqueous layer was extracted with ether (3 × 10 cm^3) and the combined organic layers washed with saturated aqueous sodium bicarbonate solution (3 × 10 cm^3), brine (10 cm^3). The organic layer was dried ($MgSO_4$) and the solvent removed under reduced pressure. The residue was chromatographed (SiO_2, light petroleum–EtOAc, 95 : 5) to give the allyl ester.

The following esters were prepared by this method.

Allyl 3-dimethyl(phenyl)silylbutanoate[27] (63%). R_f (light petroleum–EtOAc, 97 : 3) 0.24; ν_{max} (film)/cm^{-1} 2955 (CH), 2870 (CH), 1735 (CO), 1251 (SiMe) and 1112 (SiPh); δ_H (250 MHz; $CDCl_3$) 7.50 (2 H, m, SiPh), 7.35 (3 H, m, SiPh), 5.92 (1 H, ddt, J 17.7, 10.8 and 5.7, C*H*=CH$_2$), 5.31 (1 H, d, J 17.7, CH=CH_AH$_B$), 5.22 (1 H, d, J 10.8, CH=CH$_A$$H_B$), 4.55 (2 H, d, J 5.7 OCH_2CH=CH$_2$), 2.43 (1 H, dd, J 15.2 and 4.1, CH_AH$_B$-CO$_2$), 2.10 (1 H, dd, J 15.2 and 11.1, CH$_A$$H_BCO_2$), 1.47 (1 H, ddq, J 11.1, 7.3 and 4.1, CHSi), 1.0 (3 H, d, J 7.3, CH_3CHSi) and 0.30 (6 H, s, SiMe$_2$).

Allyl 4-methyl-3-dimethyl(phenyl)silylpentanoate[6] (81%). R_f (light petroleum–EtOAc, 95 : 5) 0.30; ν_{max} (film)/cm^{-1} 3020 (C=CH), 2956 (CH), 1738 (C=O) and 1649 (C=C); δ_H (250 MHz; $CDCl_3$) 7.54 (2 H, m, SiPh), 7.35 (3 H, m, SiPh), 5.90 (1 H, dddd, J 17.3, 10.4, 9.1 and 5.8 C*H*=CH$_2$), 5.29 (1 H, dd, J 17.3 and 2.9, CH=CH_AH$_B$), 5.22 (1 H, dd, J 9.1 and 1.2, CH=CH$_A$$H_B$), 4.47 (2 H, dt, J 5.8 and 1.2 OCH_2CH=CH$_2$), 2.41 (1 H, dd, J 16.0 and 7.6, CH_AH$_B$CO$_2$), 2.35 (1 H, dd, J 16.0 and 6.2, CH$_A$$H_BCO_2$), 1.94 (1 H, d sept, J 3.9 and 6.8, C*H*Me$_2$), 1.53 (1 H, ddd, 7.5, 6.2 and 3.9, CHSi), 0.93 (3 H, d, J 6.8, CHMe_AMe$_B$), 0.85 (3 H, d, J 6.8, CHMe$_A$$Me_B$), 0.34 (3 H, s, Si$Me_AMe_B$) and 0.33 (3 H, s, SiMe$_A$$Me_B$).

Allyl 3-phenyl-3-dimethyl(phenyl)silylpropanoate[28] (70%). R_f (light petroleum–EtOAc, 97 : 3) 0.17; ν_{max} (film)/cm^{-1} 3030

(CH), 2956 (CH), 1737 (CO), 1649 (PhH), 1600 (PhH), 1493 (PhH), 1250 (SiMe) and 1114 (SiPh); δ_H (250 MHz; $CDCl_3$) 7.45–7.35 (5 H, m, Ph), 7.20 (2 H, t, *J* 7.4, *m*-PhH), 7.10 (1 H, t, *J* 7.4, *p*-PhH), 6.96 (2 H, d, *J* 7.5, *o*-PhH) 5.70 (1 H, ddt, *J* 16.1, 12.0, and 5.6, C*H*=CH_2), 5.12 (1 H, d, *J* 16.1, CH=CH_AH_B), 5.10 (1 H, d, *J* 12.2, CH=CH_AH_B), 4.37 (2 H, d, *J* 5.7, OCH_2CH=CH_2), 2.87 (1 H, dd, *J* 10.8 and 3.5, CHSi), 2.79 (1 H, dd, *J* 10.8 and 14.0, C$H_AH_BCO_2$), 2.66 (1 H, dd, *J* 14.0 and 3.4, $CH_AH_BCO_2$), 0.27 (3 H, s, Si$Me_A$$Me_B$) and 0.23 (3 H, s, $SiMe_A$$Me_B$).

1-Allyloxy-1-trimethylsilyloxy-3-dimethylphenylsilyl-4-methylpent-2-ene *E*-4b

Method A. Diisopropylamine (freshly distilled over calcium hydride under argon, 0.06 cm^3, 0.44 mmol) in dry ether (0.5 cm^3) was cooled to 0 °C under nitrogen and treated with n-butyllithium (2.0 mol dm^{-3} in hexanes, 0.22 cm^3, 0.44 mmol). The mixture was stirred at 0 °C for 15 min before being cooled to −95 °C. Triethylamine (0.1 cm^3) and trimethylsilyl chloride (0.04 cm^3, 0.3 mmol) were added, followed after 5 min by allyl 4-methyl-3-dimethyl(phenyl)silylpentanoate (0.075 g, 0.26 mmol) in dry ether (0.2 cm^3). The mixture was stirred for 1 h and then allowed to warm to room temperature over 30 min. Solvents were removed under reduced pressure and the residue dissolved in dry hexane. Insoluble materials were removed by filtration and solvents removed under reduced pressure to give the *silyl enol ether* (0.05 g) as a yellow oil; δ_H (400 MHz; $CDCl_3$) 7.52 (2 H, m, SiPh), 7.31 (3 H, m, SiPh), 5.85 (1 H, dddd, *J* 17.2, 10.4, 5.5 and 5.4, C*H*=CH_2), 5.26 (1 H, dq, *J* 17.2 and 1.7, CH=CH_AH_B), 5.13 (1 H, dq, 10.4 and 1.4, CH=CH_AH_B), 4.18 (1 H, ddt, *J* 13.0, 5.5 and 1.5, OCH_AH_B), 4.07 (1 H, ddt, 13.0, 5.4 and 1.5, OCH_AH_B), 3.62 (1 H, d, *J* 11.6, C=C*H*CHSi), 1.95 (1 H, dd, *J* 11.6 and 4.3, CHSi), 1.78 (1 H, dsept, *J* 4.3 and 6.8, C*H*Me_2), 0.83 (3 H, d, *J* 6.8, CH$Me_A$$Me_B$), 0.75 (3 H, d, *J* 6.8, CH$Me_A$$Me_B$), 0.27 (3 H, s, Si$Me_A$$Me_B$), 0.26 (3 H, s, Si$Me_A$$Me_B$) and 0.21 (9H, s, $SiMe_3$), and there was no sign of the stereoisomer. This material was used in the next step without further purification.

Method B. Dimethylphenylsilyllithium (1.3 mol dm^{-3} solution in THF, 0.7 cm^3, 0.91 mmol) was added to dimethylzinc (2 mol dm^{-3} solution in toluene, 0.46 cm^3, 0.91 mmol) at −20 °C and the mixture stirred for 5 min before being cooled to −78 °C. Allyl 4-methylpent-2-enoate (100 mg, 0.65 mmol) in THF (1 cm^3) was added over 1 min, and the mixture stirred for 15 min. Trimethylsilyl chloride (freshly distilled over calcium hydride, 0.21 cm^3, 1.63 mmol) was added, and the mixture stirred for a further 1 h before being allowed to warm to room temperature. Pentane (10 cm^3) was added and the solution filtered through celite and solvents removed under reduced pressure to give an oil. Assignable ^{1}H NMR signals were identical with those from the preparation using LDA. It appears that conjugate addition of the silylzincate gives largely the *E*-isomer, in contrast to our earlier results with the silycuprate, which gave predominantly the *Z*-silyl enol ether.[1]

1,1-Dibromobut-1-ene

Following Corey and Fuchs,[29] carbon tetrabromide (45.0 g, 136 mmol) and triphenylphosphine (74.5 g, 284 mmol) were stirred in dry dichloromethane (300 cm^3) at −10 °C (ice/acetone bath, 1 : 1) under nitrogen for 40 min, by which time the mixture had turned deep red and had deposited an orange precipitate. Propionaldehyde (freshly distilled, 4.9 cm^3, 67.5 mmol) was added dropwise, the mixture stirred for a further 2.5 h at 0 °C, allowed to warm to room temperature, and solvents removed under reduced pressure. The solid residue was extracted with light petroleum (4 × 30 cm^3), filtered through a silica plug and solvents removed under reduced pressure to give the alkene[30] as an oil (9.0 g); ν_{max} (film)/cm^{-1} 2970 CH) and 1618 (C=C); δ_H (250 MHz; $CDCl_3$) 6.37 (1 H, t, *J* 7.2, CH=CBr_2), 2.10 (2 H, qt, *J* 7.4 and 7.2, MeCH_2CH=C) and 1.02 (3 H, t, *J* 7.5, *Me*CH_2); δ_C (500 MHz, $CDCl_3$) 139.8−, 88.0+, 26.3+ and 12.0−, which was used in the next step without further purification.

1,1-Dibromo-4-methylpent-1-ene

Isovaleraldehyde (1.7 cm^3, 15 mmol) was similarly converted to the dibromoalkene,[31] which was obtained as an oil (3.1 g); δ_H (250 MHz; $CDCl_3$) 6.39 (1 H, t, *J* 7.3, CH=CBr_2), 1.99 (2 H, t, *J* 7.2, CH_2CH=CBr_2), 1.75 (1 H, nonet, *J* 6.7, C*H*Me_2) and 0.94 (6 H, d, *J* 6.7, CH*Me*$_2$), which was used in the next step without further purification.

1-Dimethyl(phenyl)silylbut-1-yne

n-Butyllithium (2.2 mol dm^{-3} in hexanes, 23.3 cm^3, 51.2 mmol) was added to a stirred solution of 1,1-dibromobut-1-ene (10.4 g, 48.7 mmol) in dry ether (100 cm^3) at −78 °C under argon. After 1 h at −78 °C, the solution was allowed to warm to 0 °C and dimethylphenylsilyl chloride (9.2 cm^3, 55 mmol) in dry ether (5 cm^3) was added. The solution was stirred at 0 °C for a further 15 min, water (20 cm^3) and ether (20 cm^3) were added, and the layers separated. The aqueous layer was washed with ether (3 × 15 cm^3) and the combined organic layers were washed with water (2 × 15 cm^3), brine (15 cm^3), and dried ($MgSO_4$). Solvents were removed under reduced pressure, and the residue was distilled to give the alkyne[3] (6.6 g, 72%) as an oil (bp 115–117 °C at 20 mm Hg, lit.[3] 116–118 °C at 17 mmHg); ν_{max} (film)/cm^{-1} 2175 (C≡C), 1249 (SiMe) and 1115 (SiPh); δ_H (250 MHz; $CDCl_3$) 7.7–7.3 (5 H, m, PhH), 2.32 (2 H, q, *J* 7.0, CH_2Me), 1.20 (3 H, t, *J* 7.0 CH_2*Me*) and 0.39 (6 H, s, $SiMe_2$).

1-Trimethylsilyl-4-methylpent-1-yne

1,1-Dibromo-4-methylpent-1-ene (5.0 g, 20.7 mmol) was similarly converted to the alkyne[32] (2.50 g, 78%) as an oil (bp 120–126 °C at 760 mm Hg); δ_H (250 MHz; $CDCl_3$) 2.08 (2 H, d, *J* 6.6, CH_2CHMe_2), 1.78 (1 H, nonet, *J* 6.6, CH_2C*H*Me_2), 0.96 (6 H, d, *J* 6.6, CH*Me*$_2$) and 0.13 (9 H, s, $SiMe_3$).

1,3-Bis[dimethyl(phenyl)silyl]butyne

tert-Butyllithium (1.9 mol dm^{-3} in hexanes, 26.3 cm^3, 50 mmol) was added to a solution of TMEDA (7.6 cm^3, 50 mmol) in dry THF (100 cm^3) at −78 °C under nitrogen. 1-Dimethyl(phenyl)lsilylbutyne (9.4 g, 50 mmol) in dry THF (10 cm^3) was added dropwise over 10 min, and the mixture stirred at −78 °C for 15 min. The mixture was allowed to warm to −40 °C and stirred for 2 h. The mixture was cooled to −78 °C and dimethyl(phenyl)silyl chloride (7.7 cm^3, 51 mmol) was added. The mixture was stirred for 15 min and then allowed to warm to room temperature over 1 h. The solution was partitioned between saturated aqueous ammonium chloride (50 cm^3) and ether (50 cm^3), and the aqueous layer was washed with ether (3 × 30 cm^3). The combined organic layers were washed with water (2 × 30 cm^3) and brine (30 cm^3). The organic layer was dried ($MgSO_4$) and solvents removed under reduced pressure. The residue was chromatographed (SiO_2, light petroleum–CH_2Cl_2, 9 : 1) to give the alkyne[33] (15.3 g, 95%) as an oil; R_f (SiO_2, light petroleum–CH_2Cl_2, 9 : 1) 0.25; ν_{max} (film)/cm^{-1} 2960 (CH), 2156 (C≡C), 1248 (SiMe) and 1114 (SiPh); δ_H (250 MHz; $CDCl_3$) 7.65–7.54 (4 H, m, SiPh), 7.43–7.31 (6 H, m, SiPh), 2.02 (1 H, q, *J* 7.2, MeC*H*), 1.18 (3 H, d, *J* 7.2, *Me*CH), 0.40 [6 H, s, $(SiMe_2Ph)_A$], and 0.39 [6 H, s, $(SiMe_2Ph)_B$].

1-Trimethylsilyl-3-dimethyl(phenyl)silyl-4-methylpent-1-yne

1-Trimethylsilyl-4-methylpent-1-yne (1.0 g, 6.5 mmol) was similarly converted to the *alkyne* (1.2 g, 60%) as an oil; R_f (SiO_2, hexane) 0.3; ν_{max} (film)/cm^{-1} 2959 (CH), 2151 (C≡C), 1249

(SiMe) and 1113 (SiPh); δ_H (250 MHz; $CDCl_3$) 7.61 (2 H, m, SiPh), 7.37 (3 H, m, SiPh), 1.95 (1 H, d, *J* 4.2, C*H*SiPhMe$_2$), 1.82 (1 H, septd, *J* 6.6 and 4.2, C*H*Me$_2$), 0.97 (3 H, d, *J* 6.6, CH*Me*$_A$Me$_B$), 0.93 (3 H, d, *J* 6.6, CHMe$_A$*Me*$_B$), 0.44 (3 H, s, Si*Me*$_A$Me$_B$Ph), 0.42 (3 H, s, SiMe$_A$*Me*$_B$Ph) and 0.17 (9 H, s, SiMe$_3$); δ_C (400 MHz, $CDCl_3$) 137.7+, 134.5−, 129.2−, 127.9−, 107.5+, 87.8+, 30.2−, 28.0−, 24.2−, 20.5−, 0.5−, −3.0− and −4.2−; *m*/*z* (EI) 288 (55%, M$^+$) and 135 (100, PhMe$_2$Si) (Found: M$^+$, 288.1723. $C_{17}H_{28}Si_2$ requires *M*, 288.1730).

3-Dimethy(phenyl)silylbutyne 10a

Following the method of Schmidt and Arens[34] and Rajagopalan and Zweifel,[35] silver nitrate (2.38 g, 14 mmol) in water (6 cm^3) and absolute ethanol (18 cm^3), was added in four equal portions, 15 min apart, to a stirred solution of 1,3-bis[dimethyl-(phenyl)silyl]butyne (2.6 g, 7.9 mmol) in ethanol (20 cm^3) at 0 °C. Fifteen minutes after the final addition a solution of potassium cyanide (4.5 g, 70 mmol) in water (8 cm^3) was added at 0 °C, producing heavy precipitation, and the mixture allowed to warm to 20 °C and stirred for 2 h. The mixture was partioned between pentane (20 cm^3) and water (20 cm^3). The aqueous layer was washed with pentane (3 × 20 cm^3), the combined organic layers were washed with water (3 × 20 cm^3), brine (20 cm^3), dried ($MgSO_4$) and solvents removed to give the alkyne[36] (1.5 g, 100%) as an oil; R_f (light petroleum–dichloromethane, 9 : 1) 0.50; ν_{max} (film)/cm^{-1} 3310 (C≡C–H), 2959 (CH), 2095 (C≡C), 1252 (SiMe) and 1117 (SiPh); δ_H (400 MHz; $CDCl_3$) 7.65–7.5 (2 H, m, SiPh), 7.45–7.3 (3 H, m, SiPh), 2.02 (1 H, d, *J*, 2.7, C≡CH), 1.90 (1 H, dq, *J* 2.7 and 7.2, MeC*H*), 1.15 (3 H, d, *J* 7.2, *Me*CH) and 0.40 (6 H, s, Si*Me*$_2$Ph).

3-Dimethyl(phenyl)silyl-4-methylpent-1-yne 10b

1-Trimethylsilyl-3-dimethyl(phenyl)silyl-4-methylpent-1-yne (0.50 g, 1.73 mmol) was similarly converted into the alkyne[36] (0.35 g, 93%), which was obtained as an oil; R_f (light petroleum–EtOAc, 90 : 10) 0.70; ν_{max} (film)/cm^{-1} 3309 (C≡C–H), 2850 (CH), 2246 (C≡C), 2096 (C≡C), 1251 (SiMe) and 1112 (SiPh); δ_H (250 MHz; $CDCl_3$) 7.62 (2 H, m, SiPh), 7.39 (3 H, m, SiPh), 2.15 (1 H, d, *J* 2.8, C≡CH), 1.93 (1 H, dd, *J* 3.9 and 2.8, SiCH), 1.83 (1 H, dsept, *J* 4.2 and 6.6, C*H*Me$_2$), 1.2 (3 H, d, *J* 6.6, CH*Me*$_A$Me$_B$), 0.97 (3 H, d, *J* 6.6, CHMe$_A$*Me*$_B$), 0.46 (3 H, s, Si*Me*$_A$Me$_B$Ph) and 0.44 (3 H, s, SiMe$_A$*Me*$_B$Ph).

Methyl 4-dimethyl(phenyl)silylpent-2-ynoate

n-Butyllithium (1.6 mol dm^{-3} solution in hexanes, 4.9 cm^3, 7.9 mmol) was added to a solution of diisopropylamine (1.1 cm^3, 7.9 mmol) in THF (15 cm^3) at 0 °C and the solution stirred for 30 min before being cooled to −78 °C. 3-Dimethyl(phenyl)-silylbutyne (**10a**) (1.5 g, 7.9 mmol) in THF (5 cm^3) was added and the solution stirred at −78 °C for 5 min before being allowed to warm to −10 °C over a period of 1 h. The solution was kept at −10 °C for 1 h before being cooled back to −78 °C. Methyl chloroformate (0.61 cm^3, 7.9 mmol) was added and the mixture stirred at −78 °C for 30 min before being allowed to warm slowly to room temperature. Water (15 cm^3) was added and the layers separated. The aqueous layer was washed with ether (3 × 10 cm^3), the combined organic layers washed with water (2 × 10 cm^3), brine (10 cm^3), dried ($MgSO_4$) and solvents removed. The residue was chromatographed (SiO_2, light petroleum–CH_2Cl_2, 9 : 1) to give the *ester* (1.1 g, 46%) as an oil together with the starting alkyne (36%); R_f (SiO_2, light petroleum–CH_2Cl_2, 95 : 5) 0.11; ν_{max} (film)/cm^{-1} 2959 (CH), 2219 (C≡C), 1712 (CO_2Me), 1254 (SiMe) and 1113 (SiPh); δ_H (400 MHz; $CDCl_3$) 7.57–7.52 (2 H, m, SiPh), 7.42–7.33 (3 H, m, SiPh), 3.73 (3 H, s, CO_2Me), 2.05 (1 H, q, *J* 7.2, MeC*H*), 1.17 (3 H, d, *J* 7.2, *Me*CH) and 0.43 (6 H, s, Si*Me*$_2$Ph); δ_C (500 MHz, $CDCl_3$) 154.5+, 135.3+, 133.9−, 129.7−, 127.9−, 94.3+, 73.2+, 52.3−, 13.9−, 13.4−, −4.6− and −5.6−; *m*/*z* (EI) 246 (45%, M) and 135 (100%, SiMe$_2$Ph)(Found: M$^+$, 246.1080. $C_{14}H_{18}O_2Si$ requires *M*, 246.1076).

Methyl 4-dimethyl(phenyl)silyl-5-methylhex-2-ynoate

3-Dimethyl(phenyl)silyl-4-methylpent-1-yne (0.65 g, 3 mmol) in dry THF (5 cm^3) was similarly converted to the *ester*, which was obtained as as a colourless oil (0.6 g, 74%) together with the starting alkyne (0.16 g, 25%); R_f (light petroleum–EtOAc, 95 : 5) 0.35; ν_{max} (film)/cm^{-1} 2960 (CH), 2321 (C≡C), (2215 (C≡C), 1712 (C=O), 1263 (SiMe) and 1113 (SiPh); δ_H (400 MHz; $CDCl_3$) 7.57 (2 H, m, SiPh), 7.38 (3 H, m, SiPh), 4.14 (3 H, s, CO_2Me), 2.04 (1 H, d, *J* 4.1, CHC≡C), 1.85 (1 H, dsept, *J* 4.1 and 6.6, Me$_2$C*H*), 0.97 (3 H, d, *J* 6.5, *Me*$_A$Me$_B$CH), 0.95 (3 H, d, 6.4, Me$_A$*Me*$_B$CH), 0.46 (3 H, s, Si*Me*$_A$Me$_B$) and 0.43 (3 H, s, SiMe$_A$*Me*$_B$); δ_C (500 MHz, $CDCl_3$) 154.5+, 136.4+, 133.9−, 129.5−, 127.9−, 91.6+, 76.2+, 52.1−, 28.7−, 27.9−, 24.2−, 20.5−, −2.9− and −4.0−; *m*/*z* (ES) 297 (100%, MNa$^+$)(Found: MNa$^+$, 297.1294. $C_{16}H_{22}O_2Si$ requires *M*+Na, 297.1289).

(*E*)-Pent-4-dimethyl(phenyl)silylpent-2-en-1-ol

Lithium aluminium hydride (0.20 g, 5.0 mmol) was suspended in dry THF under a nitrogen atmosphere and the mixture cooled to −78 °C. Methyl 4-dimethyl(phenyl)silylpent-2-ynoate (0.50 g, 2.0 mmol) in THF (2 cm^3) was added and the mixture stirred at −78 °C for 30 min before being allowed to warm to room temperature. The mixture was then refluxed for 9 h before being allowed to cool to room temperature. The mixture was poured onto ice and left for 10 min. Dilute aqueous hydrochloric acid (5 cm^3) and ether (2 cm^3) were added, and the layers separated. The aqueous layer was washed with ether (3 × 2 cm^3) and the combined organic layers washed with water (2 × 2 cm^3) and brine (2 cm^3). The organic layer was dried ($MgSO_4$) and solvents removed under reduced pressure. The residue was chromatographed (SiO_2, light petroleum–EtOAc, 8 : 2) to give the *alcohol* as an oil (0.19 g, 43%); R_f (light petroleum–EtOAc, 8 : 2) 0.17; ν_{max} (film)/cm^{-1} 3332 (OH), 2955 (CH), 1654 (C=C), 1248 (SiMe), 1112 (SiPh) and 971 (*trans*-H–C=C–H); δ_H (400 MHz; $CDCl_3$) 7.51–7.45 (2 H, m, SiPh), 7.39–7.30 (3 H, m, SiPh), 5.70 (1 H, dd, *J* 15.3 and 7.6, *H*C=CHCH$_2$), 5.40 (1 H, dt, *J* 15.3 and 6.3, HC=C*H*CH$_2$), 4.05 (2 H, d, *J* 6.3, C*H*$_2$OH), 1.83 (1 H, dq, *J* 7.6 and 7.7, SiC*H*Me), 1.06 (3 H, d, *J* 7.7, CH*Me*) and 0.27 (6 H, s, SiMe$_2$); δ_C (500 MHz, $CDCl_3$) 137.5+, 136.5−, 133.9−, 129.0−, 127.6−, 125.5−, 64.3+, 25.7−, 13.5−, −5.0− and −5.3−; *m*/*z* (ESI) 243.1 (85%, MNa$^+$)(Found: MNa$^+$, 243.1185. $C_{13}H_{20}OSi$ requires *M*+Na, 243.1181).

(*E*)-5-Methyl-4-dimethyl(phenyl)silylhex-2-en-1-ol and 5-methyl-4-dimethyl(phenyl)silylhexa-1,2-diene

Methyl 4-dimethyl(phenyl)silyl-5-methylhex-2-ynoate (0.19 g, 0.7 mmol) was similarly converted into the *alcohol* which was obtained as an oil (0.13 g, 75%); R_f (light petroleum–EtOAc, 8 : 2) 0.17; ν_{max} (film)/cm^{-1} 3356 (OH), 2956 (CH), 1655 (C=C), 1248 (SiMe) and 1112 (SiPh); δ_H (250 MHz; $CDCl_3$) 7.50 (2 H, m, SiPh), 7.35 (3 H, m, SiPh), 5.59 (1 H, dd, *J* 15.1 and 10.7, SiCHC*H*=CH), 5.42 (1 H, dt, *J* 15.1 and 6.02, SiCHCH=C*H*), 4.05 (2 H, d, *J* 6.1, C*H*$_2$OH), 1.87 (1 H, dsept, *J* 5.3 and 6.7, Me$_2$C*H*), 1.67 (1 H, dd, *J* 10.7 and 5.2, SiC*H*CH=C), 0.97 (3 H, d, *J* 6.7, *Me*$_A$Me$_B$CH), 0.90 (3 H, d, *J* 6.8, Me$_A$*Me*$_B$CH), 0.33 (3 H, s, Si*Me*$_A$Me$_B$) and 0.30 (3 H, s, SiMe$_A$*Me*$_B$); δ_C (500 MHz, $CDCl_3$) 138.7+, 133.9−, 132.3−, 128.9−, 128.8−, 127.6−, 64.1+, 40.9−, 28.3−, 23.8−, 20.9−, −3.3− and −3.4−; *m*/*z* (ES) 271 (100%, MNa$^+$)(Found: MNa$^+$, 271.1481. $C_{15}H_{24}OSi$ requires *M*+Na, 271.1494), together with the *allene* (34 mg, 21%); R_f (light petroleum–EtOAc, 8 : 2) 0.65; ν_{max} (film)/cm^{-1} 3050 (CH), 2957 (CH), 1950 (C=C=C), 1249 (SiMe) and 1111 (SiPh); δ_H (250 MHz; $CDCl_3$) 7.55 (2 H, m, SiPh), 7.35 (3 H, m,

SiPh), 5.02 (1 H, dt, *J* 10.7 and 6.5, C*H*=C=CH$_2$), 4.62 (1 H, dd, 16.5 and 6.8, CH=C=C*H*$_A$H$_B$), 4.56 (1 H, dd, *J* 16.6 and 6.5, CH=C=CH$_A$*H*$_B$), 1.87 (1 H, dsept, *J* 5.3 and 6.8, Me$_2$C*H*),1.60 (1 H, dd, *J* 10.8 and 5.3, SiC*H*CHMe$_2$), 0.92 (3 H, d, *J* 6.7, *Me*$_A$Me$_B$CH), 0.87 (3 H, d, *J* 6.8, Me$_A$*Me*$_B$CH), 0.35 (3 H,s, Si*Me*$_A$Me$_B$) and 0.33 (3 H, s, SiMe$_A$*Me*$_B$); δ_C (500 MHz, $CDCl_3$) 209.1+, 138.8+, 134.1−, 128.7−, 127.6−, 88.3−, 73.4+, 36.3−, 28.7−, 23.7−, 20.8−, −2.9− and −3.5−.

(*E*)-4-Dimethyl(phenyl)silylpent-2-enyl acetate 11a

(*E*)-5-Methyl-4-dimethyl(phenyl)silylhex-3-en-1-ol (0.17 g, 0.77 mmol), DMAP (0.01 g, 0.1 mmol), acetic anhydride (0.15 cm^3, 1.2 mmol) and triethylamine (0.23 cm^3, 1.5 mmol) were stirred in ether (3 cm^3) at room temperature for 9 h. Water (5 cm^3) was added and the layers separated. The aqueous layer was washed with ether (3 × 2 cm^3) and the combined organic layers washed with water (2 × 2 cm^3), brine (2 cm^3), dried ($MgSO_4$) and solvents removed under reduced pressure. The residue was chromatographed (SiO_2, light petroleum–EtOAc, 9 : 1) to give the *acetate* as an oil (0.19 g, 93%); R_f (light petroleum–EtOAc, 9 : 1) 0.60; ν_{max} (film)/cm^{-1} 3048 (CH), 2955 (CH), 1740 (C=O), 1655 (C=C), 1248 (SiMe), 1112 (SiPh) and 970 (*trans*-CH=CH); δ_H (400 MHz; $CDCl_3$) 7.57–7.45 (2 H, m, SiPh), 7.38–7.30 (3 H, m, SiPh), 5.80 (1 H, dd, *J* 15.4 and 7.6, *H*C=CHCH$_2$), 5.35 (1 H, dt, *J* 15.4 and 6.7, HC=C*H*CH$_2$), 4.49 (2 H, d, *J* 6.7, C*H*$_2$OH), 2.03 (3 H, s, COMe), 1.85 (1 H, dq, *J* 7.6 and 7.2, SiC*H*Me), 1.05 (3 H, d, *J* 7.2, SiCH*Me*) and 0.27 (6 H, s, SiMe$_2$); δ_C (500 MHz, $CDCl_3$) 170.9+, 139.6−, 137.3+, 134.0 −, 129.1−, 127.6−, 120.1−, 65.7+, 26.0−, 21.1−, 13.3−, −5.1− and −5.4−; *m*/*z* (ESI) 158.1 (100%, PhMe$_2$SiNa) 285.1 (85%, MNa)(Found: M$^+$, 285.1279. $C_{15}H_{22}O_2Si$ requires *M*+Na, 285.1287).

(*E*)-4-Dimethyl(phenyl)silyl-5-methylhex-2-enyl acetate 11b

(*E*)-5-Methyl-4-dimethyl(phenyl)silylhex-3-en-1-ol (0.125 g, 0.50 mmol) was similarly converted into the *acetate*, which was obtained as an oil (80 mg, 54%); R_f (light petroleum–EtOAc, 9 : 1) 0.57; ν_{max} (film)/cm^{-1} 2955 (CH) 1740 (C=O), 1112 (SiPh), and 970 (*trans*-CH=CH); δ_H (250 MHz; $CDCl_3$) 7.44 (2 H, m, SiPh), 7.35 (3 H, m, SiPh), 5.68 (1 H, dd, *J* 15.2 and 10.9, SiCHC*H*=CH), 5.36 (1 H, dt, *J* 15.1 and 6.7, SiCHCH=C*H*), 4.51 (2 H, d, *J* 6.7, C*H*$_2$CO$_2$Me), 2.0 (3 H, s, COMe), 1.87 (1 H, dsept, *J* 5.2 and 6.7, C*H*Me$_2$), 1.68 (1 H, dd, *J* 10.9 and 5.2, SiC*H*CHMe$_2$), 0.85 (6 H, d, *J* 6.7, *Me*$_2$CH), 0.30 (3 H, s, Si*Me*$_A$-Me$_B$) and 0.27 (3 H, s, SiMe$_A$*Me*$_B$); δ_C (500 MHz, $CDCl_3$) 170.8+, 138.4+, 135.5−, 133.9−, 128.8−, 127.6−, 123.5−, 65.5+, 41.1−, 29.0−, 23.8−, 21.0−, 20.7−, −3.1− and −3.6−; *m*/*z* (ES) 313 (68%, MNa$^+$)(Found: MNa$^+$, 313.1610. $C_{17}H_{26}O_2Si$ requires *M*+Na, 313.1600).

4-Dimethyl(phenyl)silyl-5-methylhex-2-yn-1-ol

n-Butyllithium (1.7 mol dm^{-3} solution in hexanes, 0.9 cm^3, 1.4 mmol) was added dropwise to a solution of 3-dimethyl-(phenyl)silyl-4-methylpent-1-yne (**10b**) (0.2 g, 0.9 mmol) in THF (10 cm^3) at −78 °C under argon. The mixture was allowed to warm to −20 °C over a period of 1 h before being cooled to −78 °C. Formaldehyde [cracked from paraformaldehyde (dried over phosphorous pentoxide) at 160 °C] was bubbled through the reaction mixture in a stream of argon for 15 min. The mixture was allowed to warm to room temperature and saturated aqueous ammonium chloride (10 cm^3) and ether (10 cm^3) were added. The layers were separated, and the aqueous layer washed with ether (3 × 10 cm^3). The combined organic phases were washed with water (2 × 10 cm^3), brine (10 cm^3), dried ($MgSO_4$) and the solvents removed. The residue was chromatographed (SiO_2, light petroleum–EtOAc, 90 : 10) to give starting material (0.087 g, 0.4 mmol) and the *alcohol* as an oil (0.072 g, 58% based on unrecovered starting material); R_f (light petroleum–EtOAc, 90 : 10) 0.10; ν_{max} (film)/cm^{-1} 3415 (OH), 2960 (CH), 2249 (C≡C), 1251 (SiMe), 1112 (SiPh); δ_H (250 MHz; $CDCl_3$) 7.61 (2 H, m, SiPh), 7.37 (3 H, m, SiPh), 4.29 (2 H, d, *J* 2.2, C*H*$_2$OH), 1.93 (1 H, dt, *J* 4.3 and 2.3, SiCH), 1.83 (1 H, dsept, *J* 4.3 and 6.6, C*H*Me$_2$), 0.97 (3 H, d, *J* 6.6, CH*Me*$_A$Me$_B$), 0.94 (3 H, d, *J* 6.6, CHMe$_A$*Me*$_B$), 0.43 (3 H, s, Si*Me*$_A$Me$_B$Ph) and 0.42 (3 H, s, SiMe$_A$*Me*$_B$Ph); δ_C (400 MHz, $CDCl_3$) 137.7+, 133.9−, 129.3−, 127.9−,86.5+,81.5+, 51.5+, 28.1−, 28.0−, 24.2−, 20.3−, −3.0− and −3.8−; *m*/*z* (EI) 246 (9%, M$^+$) and 135 (100%, SiMe$_2$Ph)(Found: M$^+$, 246.1432. $C_{15}H_{22}OSi$ requires *M*, 246.1440).

4-Dimethyl(phenyl)silyl-5-methylhex-2-ynyl acetate

4-Dimethyl(phenyl)silyl-5-methylhex-2-yn-1-ol (0.055 g, 0.22 mmol), DMAP (0.007 g, 0.055 mmol), acetic anhydride (0.036 g, 0.35 mmol) and triethylamine (freshly distilled, 0.06 cm^3, 0.4 mmol) were stirred in dry ether (5 cm^3) under argon at room temperature for 16 h. Saturated aqueous sodium bicarbonate solution (5 cm^3) was added and the layers separated. The aqueous layer was washed with ether (2 × 5 cm^3) and the combined organic layers washed with saturated aqueous sodium bicarbonate solution (2 × 5 cm^3), brine (5 cm^3), dried ($MgSO_4$) and solvents removed under reduced pressure. The residue was chromatographed (SiO_2, light petroleum–EtOAc, 90 : 10) to give the *ester* (0.05 g, 80%) as an oil; R_f (light petroleum–EtOAc, 90 : 10) 0.35; ν_{max} (film)/cm^{-1} 2960 (CH), 2350 (C≡C), 2262 (C≡C), 1736 (C=O), 1250 (SiMe) and 1112 (SiPh); δ_H (400 MHz; $CDCl_3$) 7.57 (2 H, m, SiPh), 7.36 (3 H, m, SiPh), 4.72 (2 H, d, *J* 2.4, C*H*$_2$OH), 2.08 (3 H, s, COMe), 1.92 (1 H, dt, *J* 4.1 and 2.3, SiCH), 1.80 (1 H, dsept, *J* 4.3 and 6.6, C*H*Me$_2$), 0.95 (3 H, d, *J* 6.6, CH*Me*$_A$Me$_B$), 0.91 (3 H, d, *J* 6.7, CHMe$_A$*Me*$_B$), 0.41 (3 H, s, Si*Me*$_A$Me$_B$Ph) and 0.39 (3 H, s, SiMe$_A$*Me*$_B$Ph); δ_C (400 MHz, $CDCl_3$) 170.5+, 137.5+, 134.0−, 129.0−, 127.5−, 87.5+, 77.1+, 53.2+, 28.2−, 28.0−, 24.1−, 20.4−, 20.2−, −3.0− and −3.8−; *m*/*z* (EI) 288.0 (30%, M$^+$) and 135 (100%, SiMe$_2$Ph)(Found: M$^+$, 288.1546. $C_{17}H_{24}O_2Si$ requires *M*, 288.1545).

(*Z*)-4-Dimethyl(phenyl)silyl-5-methylhex-2-enyl acetate 13b

Quinoline (freshly distilled, 1 drop) was added to a suspension of 5% palladium on barium sulfate in dry methanol (10 cm^3) and the mixture stirred under hydrogen for 5 min. 4-Dimethyl-(phenyl)silyl-5-methylhex-2-ynyl acetate (0.05 g, 0.17 mmol) in methanol (5 cm^3) was added and the mixture stirred under hydrogen at room temperature for 72 h, during which time the reaction was monitored by TLC. Dilute hydrochloric acid (3 mol dm^{-3}, 5 cm^3) was added and the layers separated. The aqueous layer was washed with ether (3 × 5 cm^3) and the combined organic layers washed with dilute aqueous hydrochloric acid (3 × 5 cm^3), brine (5 cm^3), dried ($MgSO_4$) and solvents removed under reduced pressure. The residue was chromatographed (SiO_2, light petroleum–EtOAc, 95 : 5) to give the *alkene* as an oil (0.03 g, 68%); R_f (light petroleum–EtOAc, 95 : 5) 0.31; ν_{max} (film)/cm^{-1} 2958 (CH), 1728 (C=O), 1250 (SiMe) and 1100 (SiPh); δ_H (250 MHz; $CDCl_3$) 7.51 (2 H, m, SiPh), 7.29 (3 H, m, SiPh), 5.58 (2 H, m, C*H*=C*H*), 4.52 (1 H, dd, *J* 6.3 and 12.5, C*H*$_A$H$_B$O), 4.24 (1 H, dd, *J* 4.9 and 12.6, CH$_A$*H*$_B$O), 2.02 (3 H, s, COMe), 2.02 (1 H, m, SiCH), 1.88 (1 H, dsept, *J* 5.3 and 6.7, C*H*Me$_2$), 0.95 (6 H, d, *J* 6.7, CH*Me*$_2$), 0.33 (3 H, s, Si*Me*$_A$Me$_B$) and 0.31 (3 H, s, SiMe$_A$*Me*$_B$); δ_C (400 MHz, $CDCl_3$) 171.0+, 138.2+, 133.9−, 133.7−, 129.0−, 127.7−, 122.6−, 60.6+, 36.5−, 28.7−, 23.9−, 20.5−, 15.3−, −3.2− and −3.6−; *m*/*z* (ES) 313 (100%, MNa$^+$)(Found: MNa$^+$, 313.1597. $C_{17}H_{26}O_2Si$ requires *M*+Na, 313.1600).

(*Z*)-Methyl 4-dimethyl(phenyl)silylpent-2-enoate 12a

Methyl 4-dimethyl(phenyl)silylpent-2-ynoate (0.60 g, 2.4 mmol) was similarly converted into the *alkene*, which was obtained as a

colourless oil (0.35 g, 59%); R_f (light petroleum–EtOAc, 95 : 5) 0.29; ν_{max} (film)/cm^{-1} 2951 (CH), 1715 (CO_2Me), 1622 (C=CCO_2Me), 1250 (SiMe), 1112 and (SiPh); δ_H (250 MHz; $CDCl_3$) 7.55–7.47 (2 H, m, SiPh), 7.38–7.32 (3 H, m, SiPh), 6.05 (1 H, t, *J* 11.5, CHC*H*=CH), 5.63 (1 H, d, *J* 11.5, CH=C*H*CO_2Me), 3.66 (3 H, s, CO_2Me), 3.55 (1 H, dq, 11.5 and 6.9, SiC*H*Me), 1.07 (3 H, d, *J* 6.9, SiCH*Me*) and 0.31(6 H, s, $SiMe_2$); δ_C (500 MHz, $CDCl_3$) 167.1+, 155.1−, 136.5+, 133.8−, 128.9−, 127.4−, 114.9−, 50.5−, 25.2−, 14.5−, −4.8− and −5.9−; *m*/*z* (ESI) 271.1 (100%, MNa^+)(Found: MNa^+, 271.1140. $C_{14}H_{20}O_2Si$ requires *M*+Na, 271.1130).

(*Z*)-4-Dimethyl(phenyl)silylpent-2-en-1-ol

DIBAL (1.0 mmol dm^{-3} solution in hexane, 1.4 cm^3, 1.4 mmol) was added to a solution of (*Z*)-methyl 4-dimethyl(phenyl)-silylpent-2-enoate **12a** (0.18 g, 0.72 mmol) in hexane (1.5 cm^3) at −78 °C and the mixture stirred for 1 h at −78 °C and 2 h at room temperature. The mixture was poured onto ice and left for 5 minutes. Ether (5 cm^3) was added and the layers separated. The aqueous layer was washed with ether (2 × 2 cm^3) and the combined organic layers were washed with dilute aqueous hydrochloric acid (3 cm^3), water (3 cm^3), brine (3 cm^3), dried ($MgSO_4$) and solvents removed under reduced pressure to give the *alcohol* as a colourless oil (0.16 g, 97%); ν_{max} (film)/cm^{-1} 3332 (OH), 3068 (CH), 2956 (CH), 1640 (C=C), 1249 (SiMe) and 1112 (SiPh); δ_H (400 MHz; $CDCl_3$) 7.55–7.46 (2 H, m, SiPh), 7.40–7.33, (3 H, m, SiPh), 5.42 (1 H, dt, *J* 11.0 and 6.7, C*H*CH_2OH), 5.35 (1 H, t, *J*, 11.0, SiCHC*H*=CH), 3.96 (1 H, dd, *J* 12.4 and 6.9, C$H_A$$CH_B$OH), 3.75 (1 H, dd, *J* 12.4 and 6.5, CH_ACH_BOH), 2.08 (1 H, dq, *J* 11.0 and 7.1, SiC*H*Me), 1.06 (3 H, d, *J* 6.9, SiCH*Me*), 0.30 (3 H, s, Si$Me_A$$Me_B$) and 0.25 (3 H, s, $SiMe_A$$Me_B$); δ_C (500 MHz, $CDCl_3$) 137.4+, 135.8−, 134.0−, 129.2−, 127.7−, 125.3−, 58.7+, 22.6−, 15.2−, −5.2− and −5.8−; *m*/*z* (EI) 220.1 (35%, M), 135.0 (50%, $PhMe_2Si$) and 68 (100%, C_5H_8)(Found: M^+, 220.1291. $C_{13}H_{20}OSi$ requires *M*, 220.1283).

(*Z*)-4-Dimethyl(phenyl)silylpent-2-enyl acetate 13a

(*Z*)-4-Dimethyl(phenyl)silyl-pent-2-en-1-ol (0.16 g, 0.72 mmol), acetic anhydride (0.15 cm^3, 1.2 mmol), DMAP (0.01 g, 0.1 mmol) and triethylamine (0.23 cm^3, 1.5 mmol) were stirred in ether (3 cm^3) at room temperature for 9 h. Water (5 cm^3) was added and the layers separated. The aqueous layer was washed with ether (3 × 2 cm^3) and the combined organic layers washed with water (2 × 2 cm^3), brine (2 cm^3), dried ($MgSO_4$) and the solvents removed under reduced pressure. The residue was chromatographed (SiO_2, light petroleum–EtOAc, 9 : 1) to give the *acetate* as a colourless oil (0.145 g, 77%); R_f (light petroleum–EtOAc, 9 : 1) 0.56; ν_{max} (film)/cm^{-1} 3069 (CH), 2957 (CH), 1739 (C=O) and 1112 (SiPh); δ_H (250 MHz; $CDCl_3$) 7.50–7.45 (2 H, m, SiPh), 7.37–7.30 (3 H, m, SiPh), 5.44 (1 H, t, *J* 10.8, C*H*=CHCH_2OAc), 5.40 (1 H, ddd, *J* 11.1, 7.7 and 5.6, CH=C*H*CH_2OAc), 4.54 (1 H, dd, *J* 12.6 and 7.0, C$H_A$$CH_B$OAc), 4.24 (1 H, dd, *J* 12.6 and 5.4, CH_ACH_BOAc), 2.10 (1 H, dq, *J* 10.7 and 7.1, SiC*H*Me), 2.05 (3 H, s, COMe), 1.03 (3 H, d, *J* 7.1, SiCH*Me*), 0.27 (3 H, s, Si$Me_A$$Me_B$) and 0.25 93 H, s, (3 H, s, $SiMe_A$$Me_B$); δ_C (500 MHz, $CDCl_3$) 171.0+, 138.2−, 137.0+, 134.0−, 129.2−, 127.7−, 120.0−, 60.5+, 22.7−, 15.1−, −5.1− and −5.5−; *m*/*z* (ESI) 285.1 (100%, M^+)(Found: 285.1282. $C_{15}H_{22}O_2Si$ requires *M*Na^+ 285.1287).

Methyl 4-methyl-2-prop-2′-enylpent-2-enoate 17b

Diisopropylamine (freshly distilled over calcium hydride under an argon atmosphere, 0.41 cm^3, 2.9 mmol) in THF (3 cm^3) was cooled to 0 °C under argon and treated with n-butyllithium (1.6 mol dm^{-3} solution in hexane, 1.6 cm^3, 2.9 mmol). The solution was stirred at that temperature for 20 min and then cooled to −78 °C. Methyl pent-4-enoate (0.30 g, 2.6 mmol) in THF (3 cm^3) was added and the mixture stirred at −78 °C for a further 1 h. Isobutyraldehde (0.26 cm^3, 2.9 mmol) was added and the mixture allowed to warm to −10 °C over 2 h. Saturated aqueous ammonium chloride solution (5 cm^3) was added and the layers separated. The aqueous layer was washed with ether (3 × 3 cm^3) and the combined organic layers were washed with water (2 × 3 cm^3) and brine (3 cm^3), dried ($MgSO_4$) and the solvents removed. The residue was chromatographed (SiO_2, light petroleum–EtOAc, 9 : 1) to give *methyl* 4-*methyl*-3-*hydroxy*-2-*prop*-2′-*enylpentanoate* as an oil (0.32 g, 66%) and as a mixture of diastereoisomers; R_f (light petroleum–EtOAc, 9 : 1) 0.09; ν_{max} (film)/cm^{-1} 3499 (OH), 2960 (CH) and 1714 (C=O); δ_H (250 MHz; $CDCl_3$) 5.75 (1 H, dddd, *J* 4.1, 7.1, 10.1 and 13.9, C*H*=CH_2), 5.05 (2 H, m, CH=CH_2), 3.68 (1.5 H, s, OMe), 3.65 (1.5 H, s, OMe), 3.55 (1 H, dd, *J* 11.1 and 4.7, C*H*OH) 2.75–2.32 (3 H, m, CH(OH)C*H*CH_2), 1.65 (1 H, dsept, *J* 4.7 and 6.7, Me_2C*H*), 0.97 (3 H, d, *J* 6.7 CH$Me_A$$Me_B$) and 0.90 (3 H, d, *J* 6.7, CH$Me_A$$Me_B$); δ_C (400 MHz, $CDCl_3$) 175.7+, 175.4+, 135.8−, 134.9−, 117.2+, 116.6+, 77.0−, 76.7−, 48.6−, 47.8−, 34.3+, 32.1−, 31.6+, 31.0−, 17.6− and 14.2−; *m*/*z* (ESI) 209.1 (100%, M)(Found: MNa^+, 209.1162. $C_{10}H_{18}O_3$ requires *M*+Na, 209.1154). Triethylamine (1.4 cm^3, 10 mmol) was added dropwise to a stirred solution of methyl 4-methyl-3-hydroxy-2-prop-2′-enylpentanoate (0.50 g, 2.7 mmol) and methanesulfonyl chloride (0.32 cm^3, 4.1 mmol) in THF (20 cm^3) at 0 °C under a argon. The cloudy mixture was stirred at 0 °C for 1 h and then allowed to warm to room temperature before being concentrated *in vacuo*. The residue was dissolved in ethyl acetate (20 cm^3) and washed with saturated aqueous ammonium chloride solution (10 cm^3), water (10 cm^3) and brine (10 cm^3). The organic layer was dried ($MgSO_4$), the solvents were removed under reduced pressure, and the residue was chromatographed (SiO_2, light petroleum–ethyl acetate, 8 : 2) to give *methyl* 4-*methyl*-3-*hydroxymethanesulfonyl*-2-*prop*-2′-*enyl-pentanoate* as an oil (0.44 g, 67%) and as a mixture of separable diastereoisomers (50 : 50); isomer A: R_f (light petroleum–EtOAc, 8 : 2) 0.25; ν_{max} (film)/cm^{-1} 2968 (CH) and 1732 (C=O); δ_H (250 MHz; $CDCl_3$) 5.73 (1 H, ddt, *J* 17.0, 7.0 and 6.7, C*H*=CH_2), 5.05 (2 H, m, CH=CH_2), 4.80 (1 H, t, *J* 5.8, C*H*OSO_2Me), 3.68 (3 H, s, SO_2Me), 3.05 (3 H, s, CO_2Me), 2.80 (1 H, quintet, *J* 5.8, C*H*CO_2Me), 2.30 (2 H, m, CH_2CH=CH_2), 1.95 (1 H, octet, *J* 6.5, C*H*Me_2)1.03 (3 H, d, *J* 6.8, CH$Me_A$$Me_B$) and 1.0 (3 H, d, *J* 6.7, CH$Me_A$$Me_B$); isomer B: R_f (light petroleum–EtOAc, 8 : 2) 0.25; δ_H (250 MHz; $CDCl_3$) 5.73 (1 H, ddt, *J* 17.0, 10.1 and 6.7, C*H*=CH_2), 5.10 (2 H, m, CH=CH_2), 4.80 (1 H, dd, *J* 7.4 and 4.5, C*H*OSO_2Me), 3.70 (3 H, s, SO_2Me), 3.05 (3 H, s, CO_2Me), 2.90 (1 H, ddd, *J* 9.5, 7.4 and 5.2, C*H*CO_2Me), 2.36 (2 H, m, CH_2CH=CH_2), 2.01 (1 H, m, C*H*Me_2)1.07 (3 H, d, *J* 6.9, CH$Me_A$$Me_B$) and 0.98 (3 H, d, *J* 6.7, CH$Me_A$$Me_B$). The mixture of mesylates (0.34 g, 1.3 mmol) and DBU (0.95 cm^3, 6.4 mmol) were refluxed in toluene (5 cm^3) for 2 h, and then allowed to cool to room temperature. Saturated aqueous ammonium chloride solution (5 cm^3) was added and the layers separated. The aqueous layer was washed with ether (3 × 3 cm^3) and the combined organic layers washed with saturated aqueous ammonium chloride solution (3 cm^3), water (3 cm^3) and brine (3 cm^3), dried ($MgSO_4$) and solvents removed under reduced pressure to give the *alkene* (0.19 g, 87%); R_f (light petroleum–EtOAc, 90 : 10) 0.42; ν_{max} (film)/cm^{-1} 3080 (CH), 2962 (CH) and 1718 (C=O); δ_H (400 MHz; $CDCl_3$) 6.63 (1 H, d, *J* 10.0, Me_2CHC*H*), 5.80 (1 H, ddt, *J* 16.0, 11.6 and 5.9, C*H*=CH_2), 4.92–5.02 (2 H, m, CH=CH_2), 3.70 (3 H, s, CO_2Me), 3.05 (2 H, d, *J* 6.0, CH_2CH=CH_2), 2.65 (1 H, dsept, *J* 10.0 and 6.1, Me_2C*H*) and 1.0 (6 H, d, *J* 6.0, *Me*$_2$CH); δ_C (400 MHz, $CDCl_3$) 168.3+, 150.4−, 135.9−, 127.3+, 114.9+, 51.7−, 30.8+, 27.9− and 22.1+; *m*/*z* (EI) 168.1 (100%, M^+) 153.0 (18%, M–CH_3) and 109.0 (52%, M–CO_2Me)(Found: M^+, 168.1139. $C_{10}H_{16}O_2$ requires *M*, 304.1150).

Preprations of the mixtures of esters 15 and 16, 20 and 21, 34 and 35 and 37 and 38

Method A, by enolate allylation. Typically, diisopropylamine (freshly distilled over calcium hydride under an argon atmosphere, 1.5 eq.) in THF (2 cm^3) was cooled to 0 °C under argon and treated with n-butyllithium (1.5 eq). The solution was stirred at that temperature for 20 min and then cooled to −78 °C. Ester (1 eq.) in THF (1 cm^3) was added dropwise and the mixture stirred for 30 min at −78 °C before being allowed to warm to −20 °C and stirred at that temperature for 30 min. The mixture was cooled to −78 °C and allyl bromide (1.5 eq.) in THF (0.5 cm^3) added. The mixture was allowed to warm to room temperature over 2 h and saturated aqueous ammonium chloride solution (5 cm^3) added. The layers were separated and the aqueous layer washed with ether (3 × 2 cm^3). The combined organic layers were washed with water (2 × 2 cm^3) and brine (2 cm^3). The organic layer was dried ($MgSO_4$), and solvents removed under reduced pressure. The residue was chromatographed (SiO_2, light petroleum–EtOAc, 95 : 5) to give the authentic mixture of esters.

Method B, by Ireland–Claisen rearrangement using LDA in THF. Typically, diisopropylamine (freshly distilled over calcium hydride under an argon atmosphere, (1.5 eq.) in THF (5 cm^3) was cooled to 0 °C under argon and treated with n-butyllithium (1.5 eq.). The solution was stirred at that temperature for 20 min and then cooled to −78 °C. The allyl ester (1 eq.) in THF (1 cm^3) was added dropwise and the solution stirred at −78 °C for 1 h before the addition of trimethylsilyl chloride (freshly distilled, 1.6 eq.). The mixture was stirred at −78 °C for 2 h before being allowed to warm to room temperature. The mixture was then refluxed for 8 h before being allowed to cool to room temperature. Aqueous sodium hydroxide (10%, 3 cm^3) was added and the solution stirred for 15 min. THF was removed under reduced pressure, and the basic layer extracted with pentane (3 × 2 cm^3). The basic aqueous phase was carefully acidified with aqueous hydrochloric acid (3 mol dm^{-3}), extracted with ether (4 × 1 cm^3), dried ($MgSO_4$) and solvents removed under reduced pressure. The residue was taken into dry ether (1.5 cm^3), or dry methanol (when trimethylsilyldiazomethane was used for esterification). An ethanolic solution of diazomethane or trimethylsilyldiazomethane (2.0 mol dm^{-3} solution in hexanes) was added dropwise to the stirred solution at room temperature until there was a permanent yellow colour. The mixture was stirred for a further 30 min. Glacial acetic acid was added dropwise until the evolution of nitrogen had ceased, followed by saturated aqueous sodium bicarbonate solution. The layers were separated and the aqueous phase washed with ether (3 × 2 cm^3). The combined organic layers were washed with water (2 cm^3), dried ($MgSO_4$) and solvents removed under reduced pressure. The residue was chromatographed (SiO_2, light petroleum–EtOAc, 95 : 5) to give the mixtures of esters.

Method C, by Ireland–Claisen rearrangement using LDA in HMPA and THF. Typically, diisopropylamine (freshly distilled over calcium hydride under an argon atmosphere, 0.85 eq.) in THF (5 cm^3) was cooled to 0 °C under argon and treated with n-butyllithium (0.85 eq.). The solution was stirred at that temperature for 20 min and then cooled to −78 °C. HMPA (freshly distilled under nitrogen at reduced pressure, 1.6 cm^3) was added and the mixture stirred for 5 min. The allyl ester (1 eq.) in THF (5 cm^3) was added and the reaction and workup conducted in the same way as in method B, to give the mixtures of esters.

Method D, by enolate protonation. Diisopropylamine (freshly distilled over calcium hydride under an argon atmosphere, 0.48 cm^3, 3.2 mmol) in THF (2 cm^3) and n-butyllithium (1.7 mol dm^{-3} in hexanes, 2.1 cm^3, 3.2 mmol) were kept at 0 °C under argon for 25 min. The esters rich in the isomers **15a** and **15b** (0.58 g, 2.1 mmol) in THF (2 cm^3) were added, and the mixture stirred at 0 °C for 2.5 h before being cooled to −78 °C. Saturated aqueous ammonium chloride solution (3 cm^3) was added and the mixture allowed to warm to room temperature. The layers were separated, the aqueous layer washed with ether (3 × 2 cm^3) and the combined organic layers washed with water (2 × 2 cm^3) and brine (2 cm^3), dried ($MgSO_4$) and the solvents removed under reduced pressure. The residue was chromatographed (SiO_2, hexane–EtOAc, 95 : 5) to give the mixtures of esters.

The following esters were prepared using these methods.

Methyl 3-dimethyl(phenyl)silyl-2-prop-2′-enylbutanoate 15a + 16a. By method A, the mixture of *esters* (0.165 g, 71%, **15a** : **16a**, 97 : 3,) was obtained as an oil; ν_{max} (film)/cm^{-1} 3070 (CH), 1735 (CO), 1250 (SiMe) and 1112 (SiPh); δ_H (250 MHz; $CDCl_3$) (**15a**, major isomer) 7.53 (2 H, m, SiPh), 7.36 (3 H, m, SiPh), 5.67 (1 H, ddt, *J* 17.1, 10.3 and 6.9, $CH_2CH{=}CH_2$), 4.98 (1 H, dd, *J* 17.3 and 1.4, $CH{=}CH_AH_B$), 4.95 (1 H, d, *J* 10.0, $CH{=}CH_AH_B$), 3.53 (3 H, s, OMe), 2.50 (1 H, ddd, *J* 10.9, 5.8 and 3.5, $CHCO_2Me$), 2.35 (1 H, ddd, *J* 14.0, 10.9 and 1.0, $CH_ACH_BCH{=}CH_2$), 2.10 (1 H, dddd, *J* 14.0, 5.0, 3.5 and 1.5, $CH_ACH_BCH{=}CH_2$), 1.39 (1 H, dq, *J* 7.6 and 5.9, MeCHSi), 0.99 (3 H, d, *J* 7.6, *Me*CHSi), 0.34 (3 H, s, $SiMe_AMe_B$) and 0.33 (3 H, s, $SiMe_AMe_B$); (**16a**, minor isomer, where different from the major isomer) 3.56 (3 H, s, OMe) and 0.97 (3 H, d, *J* 7.5, *Me*CHSi); δ_C (500 MHz, $CDCl_3$) 175.4+, 137.7+, 136.0−, 133.7−, 128.8−, 127.5−, 115.9+, 50.9−, 46.4−, 33.4+, 26.7−, 22.2−, 11.2−, −4.1− and −4.3−; *m*/*z* (ESI) 299.1 (100%, MNa^+)-(Found: MNa^+, 299.1446. $C_{16}H_{24}O_2Si$ requires $M{+}Na^+$ 299.1443). Method B gave the mixture of esters (56 mg, 53%, **15a** : **16a**, 98 : 2). Method C gave the mixture of esters (45 mg, 43%, **15a** : **16a**, 93 : 7), together with methyl 3-dimethyl(phenyl)silylbutanoate (13 mg, 15%). Method D gave the mixture of esters (0.55 g, 95%, **15a** : **16a**, 48 : 52).

Methyl 4-methyl-3-dimethyl(phenyl)silyl-2-prop-2′-enylpentanoate 15b + 16b. By method A, the mixture of *esters* (0.11 g, 95%, **15b** : **16b**, 89 : 11) was obtained as an oil; R_f (light petroleum–EtOAc, 95 : 5) 0.23; ν_{max} (film)/cm^{-1} 2958 (CH), 2253 (C=C), 1727 (C=O), 1251 (SiMe) and 1109 (SiPh); δ_H (250 MHz; $CDCl_3$) (**15b**, major isomer) 7.57 (2 H, m, SiPh), 7.30 (3 H, m, SiPh), 5.70 (1 H, dddd, *J* 16.0, 9.5, 7.3 and 6.5 $CH{=}CH_2$), 5.00 (2 H, m, $CH{=}CH_2$), 3.59 (3 H, s, CO_2Me), 2.70 (1 H, ddd, *J* 9.0, 5.7 and 3.2, $CHCO_2Me$), 2.47 (1 H, dt, *J* 14.0 and 7.8, $CH_2{=}CHCH_ACH_B$), 2.13 (1 H, dt, *J* 14.1 and 7.1, $CH_2{=}CHCH_ACH_B$), 2.00 (1 H, dsept, *J* 4.1 and 6.8, $CHMe_2$), 1.33 (1 H, dd, *J* 3.9 and 3.3, SiCH), 0.92 (3 H, d, *J* 6.8, $CHMe_AMe_B$), 0.85 (3 H, d, *J* 6.9, $CHMe_AMe_B$), 0.43 (3 H, s, $SiMe_AMe_B$) and 0.42 (3 H, s, $SiMe_AMe_B$); δ_H (250 MHz; $CDCl_3$) (**16b**, minor isomer, where different from the major isomer) 3.62 (3 H, s, CO_2Me), 0.39 (3 H, s, $SiMe_AMe_B$) and 0.37 (3 H, s, $SiMe_AMe_B$); δ_C (400 MHz, $CDCl_3$) 177.7+, 140.5+, 137.0−, 134.0−, 128.5−, 127.5−, 116.5+, 51.2−, 44.2−, 36.3+, 36.0−, 28.0−, 23.8−, 21.5−, −0.7− and −1.7−; *m*/*z* (ESI) 327.18 (100%, MNa^+)(Found: MNa^+, 327.1756. $C_{18}H_{28}O_2Si$ requires $M{+}Na$, 327.1858). Method B gave the mixture of esters (63 mg, 60%, **15b** : **16b**, 84 : 16). Method C gave the mixture of esters (0.045 g, 43%, **15b** : **16b**, 69 : 31). Method D gave the mixture of esters (0.07 g, 85%, **15b** : **16b**, 60 : 40).

Methyl 3-phenyl-3-dimethyl(phenyl)silyl-2-prop-2′-enylpropanoate 15c + 16c. By method A, the mixture of esters[1] (1.65 g, 98%, with the known minor isomer undetectable in the ^{1}H-NMR spectrum) was obtained as an oil; R_f (light petroleum–EtOAc, 95 : 5) 0.23; ν_{max} (film)/cm^{-1} 3070 CH), 1736 (CO), 1640 (PhH), 1598 (PhH), 1492 (PhH), 1249 (SiMe) and 1113 (SiPh); δ_H (400 MHz; $CDCl_3$) 7.40–7.27 (5 H, m, SiPh), 7.18 (2 H, t, *J* 7.2, *m*-PhH), 7.10 (1 H, t, *J* 7.4, *p*-PhH), 6.90

(2 H, d, *J* 7.8, *o*-PhH), 5.58 (1 H, dddd, *J* 14.3, 10.2, 8.0 and 6.2, CH_2CH=CH_2), 4.87 (1 H, d, *J* 10.2, CH=CH_AH_B), 4.83 (1 H, d, *J* 14.2, CH=CH$_A$$H_B$), 3.31 (3 H, s, OMe), 2.95 (1 H, ddd, *J* 12.0, 10.4 and 3.9, C$H$$CO_2$Me), 2.62 (1 H, d, *J* 12.0, PhCH), 2.15–1.95 (2 H, m, CH_2CH=CH_2), 0.26 (3 H, s, SiMe_AMe$_B$) and 0.07 (3 H, s, SiMe$_A$$Me_B$). Method B gave the mixture of esters (51 mg, 49%, >98 : 2, with the minor isomer undetectable in the ^{1}H-NMR spectrum). Method C gave the mixture of esters (67 mg, 66%, >97 : 3, with the minor isomer undetectable in the ^{1}H-NMR spectrum).

Methyl 4-dimethyl(phenyl)silyl-3-ethenyl-pentanoate 20a and 21a. By method B, (*Z*)-4-dimethyl(phenyl)silylpent-2-enyl acetate (**13a**) (100 mg, 0.38 mmol) gave the mixture of *esters* (53 mg, 53%, **20a** : **21a**, 93 : 7) as an oil; R_f (light petroleum–EtOAc, 95 : 5) 0.27; ν_{max} (film)/cm^{-1} 2998 (CH), 1738 (C=O), 1251 (SiMe) and 1113 (SiPh); δ_H (400 MHz; $CDCl_3$) (major isomer, **20a**) 7.54–7.47 (2 H, m, SiPh), 7.36–7.33 (3 H, m, SiPh), 5.70 (1 H, ddd, *J* 16.7, 10.7 and 8.3, CH=CH_2), 4.95 (1 H, d, *J* 16.7, CH=CH_AH_B), 4.93 (1 H, d, *J* 10.7, CH=CH$_A$$H_B$), 3.61 (3 H, s, OMe), 2.68 (1 H, dddd, *J* 12.4, 10.2, 8.5 and 4.1, CHCH=CH_2), 2.35 (1 H, dd, *J* 14.7 and 4.2, C$H_AH_B$$CO_2$Me), 2.20 (1 H, dd, *J* 14.7 and 10.2, CH$_A$$H_B$$CO_2$Me), 1.07 (1 H, dq, *J* 12.2 and 7.4, CHSi), 0.95 (3 H, d, *J* 7.4, *Me*CHSi), 0.34 (3 H, s, SiMe_AMe$_B$) and 0.32 (3 H, s, SiMe$_A$$Me_B$); δ_C (500 MHz, $CDCl_3$) 173.3+, 141.1−, 138.7+, 133.−, 128.8−, 127.7−, 114.6+, 51.4−, 42.6−, 37.7+, 24.8−, −2.9− and −3.7−; *m*/*z* (ESI) 299.1 (55%, MNa$^+$)(Found: M$^+$, 299.1457. $C_{16}H_{24}O_2Si$ requires *M*+Na, 299.1443). Method B starting with (*E*)-4-dimethyl(phenyl)silylpent-2-enyl acetate (**11a**)(100 mg, 0.38 mmol) gave the mixture of *esters* (73 mg, 68%, **20a** : **21a**, 38 : 62); δ_H (400 MHz; $CDCl_3$) signals from the minor isomer **20a** (identical to the major isomer in the previous experiment) and (major isomer, **21a**) 7.54–7.45 (2 H, m, SiPh), 7.35–7.30 (3 H, m, SiPh), 5.68 (1 H, dt, *J* 18.4 and 9.5, CH=CH_2), 5.0–4.9 (2 H, m, CH=CH_AH_B), 3.59 (3 H, s, OMe), 2.82 (1 H, ddt, *J* 15.7, 9.5 and 4.0, CHCH=CH_2), 2.38 (2 H, m, C$H_2$$CO_2$Me), 1.07 (1 H, dq, *J* 15.1 and 7.4, CHSi), 0.93 (3 H, d, *J* 7.4, *Me*CHSi), 0.32 (3 H, s, SiMe_AMe$_B$) and 0.27 (3 H, s, SiMe$_A$$Me_B$).

Methyl 5-Methyl-4-dimethyl(phenyl)silyl-3-ethenyl-hexanoate 20b and 21b. By method B, (*Z*)-4-dimethyl(phenyl)silyl-5-methylhex-2-enyl acetate (**13b**) (100 mg, 0.34 mmol) gave the mixture of *esters* (0.045 g, 44%, **20b** : **21b**, 98 : 2) as an oil; R_f (light petroleum–EtOAc, 95 : 5) 0.35; ν_{max} (film)/cm^{-1} 3070 (CH), 2954 (CH), 1740 (CH), 1251 (SiMe) and 1110 (SiPh); δ_H (400 MHz; $CDCl_3$) (major isomer **20b**) 7.55–7.50 (2 H, m, SiPh), 7.35–7.32 (3 H, m, SiPh), 5.82 (1 H, ddd, *J* 17.8, 10.0 and 8.1, CH=CH_2), 4.97 (1 H, d, 17.8, CH=CH_AH_B), 4.95 (1 H, d, *J* 10.0, CH=CH$_A$$H_B$), 3.62 (3 H, s, OMe), 2.96 (1 H, dddd, *J* 9.5, 8.2, 6.5 and 3.0, CHCH=CH_2), 2.33 (1 H, dd, *J* 14.5 and 6.6, CH_ACH$_B$$CO_2$Me), 2.31 (1 H, dd, *J* 14.5 and 8.5, CH$_A$CH_B-CO_2Me), 1.97 (1 H, dsept, 3.7 and 6.9, Me$_A$Me$_B$CH), 1.02 (1 H, t, *J* 3.4, SiCH), 0.96 (3 H, d, *J* 6.9, *Me*$_A$Me$_B$CH), 0.93 (3 H, d, *J* 6.9, Me$_A$*Me*$_B$CH), 0.40 (3 H, s, SiMe_AMe$_B$) and 0.38 (3 H, s, SiMe$_A$$Me_B$); δ_C (400 MHz, $CDCl_3$) 172.8+, 141.7−, 140.1+, 133.7−, 128.4−, 127.4−, 114.3+, 51.1−, 39.8+, 39.4−, 38.2−, 28.1−, 23.6−, 22.3−, −0.61− and −1.1−; *m*/*z* (EI) 304.2 (3%, M$^+$) and 135.1 (100%, PhMe$_2$Si)(Found: M$^+$, 304.1871. $C_{18}H_{28}O_2Si$ requires *M*, 304.1858). Method B, starting with (*E*)-4-dimethyl(phenyl)silyl-5-methylhex-2-enyl acetate (**11b**) (55 mg, 0.24 mmol) gave the mixture of *esters* (20 mg, 29%, **20b** : **21b**, 52 : 48), together with recovered starting material **11b** (21 mg, 29%); δ_H (400 MHz; $CDCl_3$) signals from the major isomer **20b** (identical to the major isomer in the previous experiment) and (minor isomer **21b**, where different from the major isomer **20b**) 7.55–7.50 (2 H, m, SiPh), 7.35–7.30 (3 H, m, SiPh), 5.75 (1 H, m, CH=CH_2), 4.95 (2 H, m, CH=CH_2), 3.57 (3 H, s, OMe), 2.94 (1 H, dddd, *J* 13.8, 12.7, 5.0 and 3.9, CHCH=CH2), 2.45 (1 H, dd, *J* 14.5 and 5.5, C$H_AH_B$$CO_2$Me) 1.06 (1 H, dd, *J* 4.2 and 3.2, Me$_2$CH), 0.39 (3 H, s, SiMe_AMe$_B$) and 0.37 (3 H, s, SiMe$_A$$Me_B$).

1-Phenyl-1-dimethyl(phenyl)silyl-2-methoxycarbonyl-3-methylpent-5-ene 34 and 35. By method B, (*Z*)-but-2-enyl 3-phenyl-3-dimethyl(phenyl)silylpropanoate (80 mg, 0.25 mmol) gave the mixture of esters (58 mg, 66%, **34** : **35**, 86 : 14) as an oil; R_f (light petroleum–EtOAc, 95 : 5) 0.33; ν_{max} (film)/cm^{-1} 2957 (CH), 2959 (CH), 1732 (C=O), 1248 (SiMe) and 1112 (SiPh); δ_H (400 MHz; $CDCl_3$) (major isomer **34**) 7.38–7.25 (5 H, m, SiPh), 7.17 (2 H, t, *J* 7.6, *m*-PhH), 7.07 (1 H, t, *J* 7.4, *p*-PhH), 6.82 (2 H, d, *J* 7.7, *o*-PhH), 5.75 (1 H, ddd, *J* 17.2, 10.2 and 8.6, CH=CH_2), 4.88 (1 H, d, *J* 10.3, CH=CH_AH_B), 4.49 (1 H, d, *J* 17.2, CH=CH$_A$$H_B$), 3.37 (3 H, s, CO_2Me), 3.00 (1 H, dd, *J* 12.7 and 4.0, C$H$$CO_2$Me), 2.75 (1 H, d, *J* 12.7, PhCH), 2.32 (1 H, ddq, 8.6, 4.2 and 7.3, MeCH), 0.89 (3 H, d, *J* 7.1, CH*Me*), 0.20 (3 H, s, SiMe_AMe$_B$) and 0.10 (3 H, s, SiMe$_A$$Me_B$), (minor isomer **35**, where different from **34**) 6.90 (2 H, d, *J* 7.01, *o*-PhH), 5.70 (1 H, ddd, *J* 17.2, 10.5 and 6.7, CH=CH_2), 4.91 (1 H, d, *J* 10.7, CH=CH_AH_B), 4.87 (1 H, d, *J* 17.2, CH=CH$_A$$H_B$), 3.37 (3 H, s, CO_2Me), 3.10 (1 H, dd, *J* 12.4 and 4.2, C$H$$CO_2$Me), 2.82 (1 H, d, *J* 12.4, PhCH), 2.32 (1 H, ddq, 6.7, 4.2 and 6.9, MeCH), 0.86 (3 H, d, *J* 6.9, CH*Me*), 0.23 (3 H, s, SiMe_AMe$_B$) and 0.12 (3 H, s, SiMe$_A$$Me_B$); δ_C (400 MHz, $CDCl_3$) 173.6+, 139.9+, 138.4−, 136.8+, 134.2−, 128.9−, 128.7−, 127.6−, 124.8−, 124.7−, 115.3+, 50.5−, 50.3−, 37.5−, 36.4−, 18.7−, −3.0− and −4.6−; *m*/*z* (ESI) 375.2 (100%, MNa$^+$), 316.2 (15%, MNa$^+$ − CO_2Me)(Found: MNa$^+$, 375.1740. $C_{22}H_{28}O_2Si$ requires *M*+Na, 352.1859). Method C, starting from (*Z*)-but-2-enyl 3-phenyl-3-dimethyl(phenyl)silylpropanoate (93 mg, 0.27 mmol), gave the mixture of esters (70 mg, 87%, **34** : **35**, 32 : 68). Method B, starting from (*E*)-but-2-enyl 3-phenyl-3-dimethyl(phenyl)-silylpropanoate (110 mg, 0.324 mmol), gave the mixture of esters (70 mg, 61%, **34** : **35**, 33 : 67).

1-Phenyl-2-methoxycabonyl-3-methylpent-5-ene 37 and 38. Method B, starting from (*Z*)-but-2-enyl 3-phenylpropanoate (100 mg, 0.5 mmol) gave the mixture of esters **37** and **38** (63 mg, 58%, **37** : **38**, 80 : 20) as an oil, with the same signals (^{1}H NMR) as in the mixture produced by the experiment using TBAF, described below.

Preparation of the mixtures of diesters 18a + 19a and 18b + 19b

Typically, ozone was bubbled through a solution the mixtures of esters **15** + **16** or **20** + **21** (0.45 mmol) in dry dichloromethane (5 cm^3) at −78 °C, until there was a permanent blue colour (approximately 5 min). The mixture was allowed to warm to 0 °C. Aqueous hydrogen peroxide (30%, 5 cm^3) was added and the mixture stirred at room temperature for 16 h at room temperature. Dilute aqueous hydrochloric acid (3 mol dm^{-3}, 2 cm^3) was added and the layers separated. The aqueous layer was washed with dichloromethane (3 × 2 cm^3) and the combined organic layers washed with brine (3 cm^3), dried ($MgSO_4$) and solvents removed under reduced pressure. The residue was dissolved in dry methanol (1 cm^3) and trimethylsilyldiazomethane (2.0 mol dm^{-3}) added dropwise until the mixture was a permanent yellow colour. The mixture was stirred for a further 30 min and glacial acetic acid added until nitrogen evolution had ceased. Ether (3 cm^3) was added and the mixture was neutralised with aqueous sodium bicarbonate solution (3 cm^3). The layers were separated and the aqueous layer washed with ether (3 × 3 cm^3). The combined organic layers were washed with water (3 cm^3), aqueous sodium bicarbonate solution (3 cm^3), dried ($MgSO_4$) and solvents removed under reduced pressure. The residue was chromatographed (SiO_2, light petroleum–EtOAc, 95 : 5) to give the mixtures of *diesters*.

The following diesters were prepared using these methods.

Methyl 4-dimethyl(phenyl)silyl-3-methoxycarbonylpentanoate 18a + 19a. The mixture of esters **15a** + **16a** gave the mixture of *diesters* (0.10 g, 72%, **18a** : **19a**, 98 : 2) as an oil; R_f (light petroleum–EtOAc, 95 : 5) 0.11; ν_{max} (film)/cm^{-1} 2951 (CH), 1732 (CO), 1252 (SiMe) and 1112 (SiPh); δ_H (400 MHz; $CDCl_3$) (major isomer) 7.55–7.47 (2 H, m, SiPh), 7.40–7.42 (3 H, m, SiPh), 3.64 [3 H, s, $(CO_2Me)_A$], 3.62 [3 H, s, $(CO_2Me)_B$], 3.02 [1 H, dt, *J* 11.5 and 3.5, $CH_2CH(CO_2Me)_A$], 2.70 [1 H, dd, *J* 16.8 and 11.5, $CH_AH_B(CO_2Me)_B$], 2.15 [1 H, dd, *J* 16.8 and 3.2, $CH_AH_B(CO_2Me)_B$], 1.47 (1 H, dq, *J* 7.6 and 3.8, CHSi), 0.94 (3 H, d, *J* 7.6, *Me*CH) and 0.34 (6 H, s, $SiMe_2$) (minor isomer, where different from major isomer) 3.08 [1 H, dt, 10.0 and 3.5, $CH_2CH(CO_2Me)_A$]; δ_C (400 MHz, $CDCl_3$) 175.2+, 172.6+, 137.0+, 133.6−, 129.1−, 129.0−, 51.6−, 51.4−, 41.8−, 32.8+, 22.1−, 10.7−, −4.2− and −4.3−; *m*/*z* (ESI) 331.1 (100%, M^+)(Found: MNa^+, 331.1345. $C_{16}H_{24}O_4Si$ requires *M*+Na 331.1342). The mixture of esters **20a** + **21a** (98 : 2) derived from the silylenol ether *Z*-**7a** gave the mixture of diesters (27 mg, 50%), in which only the isomer **18a** was detectable in the ^{1}H-NMR spectrum.

Methyl 4-dimethyl(phenyl)silyl-3-methoxycarbonyl-5-methylhexanoate 18b + 19b. The mixture of esters **15b** + **16b** gave the mixture of *diesters* (67 mg, 79%, 94 : 6) as an oil; R_f (light petroleum–EtOAc, 95 : 5) 0.17; ν_{max} (film)/cm^{-1} 2954 (CH), 1736 (C=O), 1253 (SiMe) and 1110 (SiPh); δ_H (250 MHz; $CDCl_3$) (major isomer) 7.50–7.57 (2 H, m, SiPh), 7.30–7.36 (3 H, m, SiPh), 3.67 [3 H, s, $(CO_2Me)_A$], 3.65 [3 H, s, $(CO_2Me)_B$], 3.17 [1 H, ddd, *J* 10.7, 3.5 and 2.5, $CH(CO_2Me)_A$], 2.80 [1 H, dd, *J* 16.4 and 10.7, $CH_AH_B(CO_2Me)_B$], 2.27 [1 H, dd, *J* 16.4 and 3.7, $CH_AH_B(CO_2Me)_B$], 1.88 (1 H, octet, *J* 6.7 $CHMe_2$), 1.50 (1 H, dd, *J* 6.1 and 2.5, CHSi), 0.92 (3 H, d, *J* 6.8, $CHMe_AMe_B$), 0.85 (3 H, d, *J* 6.8, $CHMe_AMe_B$), 0.42 (3 H, s, $SiMe_AMe_B$) and 0.40 (3 H, s, $SiMe_AMe_B$) (minor isomer, where different from the major isomer) 3.67 [3 H, s, $(CO_2Me)_A$], 3.59 [3 H, s, $(CO_2Me)_B$] and 3.30 [1 H, dt, *J* 7.1 and 3.5, $CH(CO_2Me)_A$]; δ_C (400 MHz, $CDCl_3$) 176.3−, 172.6−, 139.2+, 133.8−, 128.9−, 127.7−, 51.7−, 51.6−, 40.7−, 36.0−, 34.6+, 28.1−, 24.0−, 22.8−, −1.2− and −1.8−; *m*/*z* (EI) 336.2 (10%, M^+) 135.1 (100%, $SiMe_2Ph$)(Found: M^+, 336.1746. $C_{18}H_{28}O_4Si$ requires *M* 336.1757). The mixture of esters **20b** + **21b** (>98 : 2) derived from the silylenol ether *Z*-**7b** gave the mixture of diesters (20 mg, 45%), in which only the isomer **18b** was detectable in the ^{1}H-NMR spectrum.

But-2-ynyl 3-phenyl-3-dimethyl(phenyl)silylpropanoate

Methyl 4-phenyl-3-dimethyl(phenyl)silylpentanoate (1.50 g, 5.0 mmol), but-2-yn-1-ol (20 cm^3) and concentrated sulfuric acid (0.5 cm^3) were refluxed overnight and allowed to cool to room temperature before being partitioned between ether (25 cm^3) and saturated aqueous sodium bicarbonate solution (25 cm^3). The aqueous layer was extracted with ether (3 × 20 cm^3) and the combined organic layers washed with saturated aqueous sodium bicarbonate solution (3 × 20 cm^3) and brine (20 cm^3). The organic layer was dried ($MgSO_4$) and solvent removed under reduced pressure. The residue was chromatographed (SiO_2, light petroleum–EtOAc, 97 : 3) to give the *ester* (0.64 g, 33%) as an oil; R_f (light petroleum–EtOAc, 95 : 5) 0.29; ν_{max} (film)/cm^{-1} 2995 (CH), 2241 (C≡C), 1740 (C=O), 1250 (SiMe) and 1114 (SiPh); δ_H (400 MHz; $CDCl_3$) 7.35 (5 H, m, Ph), 7.18 (2 H, t, *J* 6.5, *m*-PhH), 7.07 (1 H, t, *J* 7.4, *p*-PhH), 6.94 (2 H, d, *J* 7.8, *o*-PhH) 4.45 (1 H, dq, *J* 15.3 and 2.4 CH_AH_B≡CMe), 4.37 (1 H, dq, *J* 15.2 and 2.4, CH_AH_B≡CMe), 2.85 (1 H, dd, *J* 11.2 and 3.9, $CH_AH_BCO_2$), 2.77 (1 H, dd, *J* 15.1 and 11.2, CHSi), 2.66 (1 H, dd, *J*, 15.0 and 3.9, $CH_AH_BCO_2$), 1.79 (3 H, t, *J* 2.4, C≡CMe), 0.23 (3 H, s, $SiMe_AMe_B$) and 0.21 (3 H, s, $SiMe_AMe_B$); δ_C (400 MHz, $CDCl_3$) 172.5+, 141.5+, 136.5+, 134.0 −, 129.5−, 128.0−, 127.8−, 127.5−, 125.0−, 83.0+, 73.0+, 52.5+, 34.8+, 32.0 −, 3.0 −, −4.0− and −6.0−; *m*/*z* (ESI) 359.14 (100%, MNa^+)(Found: MNa^+, 359.1426. $C_{21}H_{24}O_2Si$ requires *M*+Na, 359.1443).

But-2-ynyl 3-phenylpropanoate

DCC (7.3 g, 36.3 mmol) in dichloromethane (5 cm^3) was added to hydrocinnamic acid (5 g, 33 mmol), but-2-yn-1-ol (3.5 g, 50 mmol) and DMAP (0.35 g, 3 mmol) in dry dichloromethane (50 cm^3) at 0 °C, and the cloudy mixture stirred for 1 h before being allowed to warm to room temperature. The mixture was stirred for a further 2 h, and the precipitate filtered off. The mixture was washed with saturated aqueous sodium bicarbonate solution (15 cm^3) and saturated aqueous ammonium chloride solution (15 cm^3). The combined aqueous layers were washed with dichloromethane (3 × 10 cm^3) and the combined organic layers washed with water (2 × 10 cm^3) and brine (15 cm^3). The orgnaic layer was dried ($MgSO_4$) and solvents removed under reduced pressure. The residue was filtered through a silica pad (light petroleum–EtOAc, 95 : 5) to give the *ester* (5.5 g, 82%) as an oil; R_f (light petroleum–EtOAc, 95 : 5) 0.36; ν_{max} (film)/cm^{-1} 2933 (CH), 2240 (C≡C), 1740 (C=O), 1604 (Ph) and 1496 (Ph); δ_H (400 MHz; $CDCl_3$) 7.32–7.25 (2 H, m, Ph), 7.23–7.17 (3 H, m, Ph), 4.64 (2 H, q, *J* 2.4, OCH_2), 2.95 (2 H, t, *J* 7.6, $PhCH_2CH_2$), 2.65 (2 H, t, *J*, 7.6, $PhCH_2CH_2$) and 1.84 (3 H, t, *J* 2.4, C≡CMe); δ_C (500 MHz, $CDCl_3$) 172.1+, 140.1+, 128.2−, 128.0−, 126.0−, 82.9+, 72.9+, 52.7+, 35.4+, 30.6+ and 3.3 −; *m*/*z* (ESI) 225.09 (100%, MNa^+) (Found: MNa^+, 225.0882. $C_{13}H_{14}O_2$ requires *M*+Na, 225.0891).

(*E*)-But-2-enyl 3-phenyl-3-dimethyl(phenyl)silylpropanoate

3-Phenyl-3-dimethyl(phenyl)silylpropanoic acid (0.34 g, 1.2 mmol) and *E*-but-2-enol (0.18 g, 2.4 mmol) were similarly converted into the *ester* (0.35 g, 72%), which was obtained as an oil; R_f (light petroleum–EtOAc, 95 : 5) 0.35; ν_{max} (film)/cm^{-1} 3023 (CH), 2957 (CH, 1736 (C=O), 1250 (SiMe), 1113 (SiPh) and 966 (HC=CH); δ_H (250 MHz; $CDCl_3$) 7.44–7.30 (5 H, m, SiPh), 7.18 (2 H, t, *J* 7.9, Ph) *m*-PhH), 7.10 (1 H, t, *J* 7.3, *p*-PhH), 6.95 (2 H, d, *J* 7.7, *o*-PhH), 5.60 (1 H, dq, *J* 15.3 and 6.4, OCH_2CH=CH), 5.35 (1 H, dt, *J* 15.3 and 6.4, OCH_2CH=CH), 4.30 (2 H, d, *J* 6.4, OCH_2), 2.86 (1 H, dd, *J* 10.8 and 4.2, $SiCHCH_ACH_B$), 2.75 (1 H, dd, *J* 14.8 and 10.8, $SiCHCH_ACH_B$), 2.65 (1 H, dd, *J* 14.7 and 4.2, $SiCHCH_ACH_B$), 1.64 (3 H, d, *J* 6.4, C=C*Me*), 0.25 (3 H, s, $SiMe_AMe_B$) and 0.22 (3 H, s, $SiMe_AMe_B$); δ_C (500 MHz, $CDCl_3$) 172.7+, 141.7+, 136.4+, 133.9−, 130.7−, 129.0−, 128.2−, 128.0−, 127.8−, 126.0−, 124.7−, 65.2+, 34.7+, 32.0−, 17.4−, −4.4− and −5.7−; *m*/*z* (ESI) 361.16 (100%, MNa^+) (Found: MNa^+, 361.1613. $C_{21}H_{26}O_2Si$ requires *M*+Na, 361.1600).

(*Z*)-But-2-enyl 3-phenyl-3-dimethyl(phenyl)silylpropanoate

Quinoline (freshly distilled, 0.5 cm^3) was added to a suspension of 5% palladium on barium sulfate (4 mg) in dry methanol (20 cm^3) and the mixture stirred under hydrogen for 30 min, after which time the catalyst had turned black. But-2-ynyl 3-phenyl-3-dimethyl(phenyl)silylpropanoate (0.35 g, 1.0 mmol) in methanol (5 cm^3) was added and the mixture stirred under hydrogen at room temperature for 3 h, when TLC showed the reaction to have gone to completion. The catalyst was removed by filtration and solvent removed by evaporation. The residue was taken into ether (5 cm^3) and extracted with hydrochloric acid solution (3 mol dm^{-3}, 5 cm^3). The aqueous layer was washed with ether (3 × 5cm^3) and the combined organic layers washed with dilute aqueous hydrochloric acid (3 × 5 cm^3) and brine (5 cm^3). The organic layer was dried ($MgSO_4$) and solvents removed under reduced pressure. The residue was chromatographed (SiO_2, light petroleum–EtOAc, 95 : 5) to give the *alkene* (0.30 g, 89%) as an oil; R_f (light petroleum–EtOAc, 95 : 5) 0.22; ν_{max} (film)/cm^{-1} 3025 (CH), 2958 (CH), 1738 (C=O), 1250 (SiMe) and 1114 (SiPh); δ_H (250 MHz; $CDCl_3$) 7.35 (5 H,

m, Ph), 7.17 (2 H, t, *J* 7.0, *m*-PhH), 7.07 (1 H, t, *J* 7.3, *p*-PhH), 6.94 (2 H, d, *J* 7.8, *o*-PhH), 5.61 (1 H, dq, *J* 10.9 and 7.0, CH=C*H*Me), 5.34 (1 H, dt, *J* 10.9 and 7.0, OCH_2CH), 4.44 (1 H, dd, *J* 12.6 and 7.0, OCH_AH_B), 4.38 (1 H, dd, *J* 12.6 and 6.9, OCH_AH_B), 2.85 (1 H, dd, *J* 10.7 and 4.5, $CH_AH_BCO_2$), 2.75 (1 H, 14.8 and 10.7, CHSi), 2.63 (1 H, dd, *J* 14.8 and 4.3, $CH_AH_BCO_2$), 1.57 (1 H, d, *J* 7.0, C=CHCH_3), 0.25 (3 H, s, $SiMe_AMe_B$) and 0.22 (3 H, s, $SiMe_AMe_B$); δ_C (500 MHz, $CDCl_3$) 172.7+, 141.5+, 136.2+, 130.7−, 129.5−, 129.0−, 128.0−, 127.8−, 127.5−, 125.0−, 123.9−, 59.7+, 34.5+, 32.0−, 13.3, −4.4− and −5.5−; *m*/*z* (ESI) 361.16 (100%, MNa^+)(Found: MNa^+, 361.1598. $C_{21}H_{26}O_2Si$ requires *M*+Na, 361.1600).

(*Z*)-But-2-enyl 3-phenylpropanoate

But-2-ynyl 3-phenylpropanoate (3.0 g, 14.8 mmol) was similarly converted into the *alkene* (2.8 g, 92%), which was obtained as an oil; R_f (light petroleum–EtOAc, 95 : 5) 0.22; ν_{max} (film)/cm^{-1} 3028 (CH), 2934 (CH), 1733 (CO), 1604 (PhH), 1496 (PhH) and 1454 (PhH); δ_H (400 MHz; $CDCl_3$) 7.35–7.25 (2 H, m, Ph), 7.23–7.18 (3 H, m, Ph), 5.74 (1 H, m, OCH_2CH), 5.55 (1 H, m, C=C*H*CH_3), 4.66 (2 H, d, *J* 6.9, OCH_2), 3.07 (2 H, t, *J* 7.6, $PhCH_2$), 2.65 (2 H, t, *J* 7.6, $PhCH_2CH_2$) and 1.71 (3 H, d, *J* 6.9, C=CCH_3).

1-Phenyl-2-methoxycabonyl-3-methylpent-5-ene 37 and 38

1-Phenyl-1-dimethyl(phenyl)silyl-2-methoxycarbonyl-3-methylpent-5-ene (an 81 : 19 mixture of the diastereoisomers **34** and **35**, 46 mg, 0.128 mmol) and TBAF (1.0 mol dm^{-3} in hexane, 0.26 cm^3, 0.26 mmol) were stirred in THF (0.5 cm^3) room temperature for 12 h. Ether (2 cm^3) and water (2 cm^3) were added, and the aqueous layer was washed with ether (2 × 2 cm^3). The organic layers were combined and washed with water (2 cm^3) and brine (1 cm^3), the organic layer dried ($MgSO_4$), and the solvents removed under reduced pressure. The residue was chromatographed (SiO_2, light petroleum–EtOAc, 98 : 2) to give the *esters* (21 mg, 75%, **37** : **38**, 85 : 15) as an oil; R_f (light petroleum–EtOAc, 95 : 5) 0.30; ν_{max} (film)/cm^{-1} 3028 (CH), 2959 (CH), 1737 (C=O), 1257 (SiMe) and 1119 (SiPh); δ_H (400 MHz; $CDCl_3$) (major isomer **37**) 7.30–7.22 (2 H, m, Ph), 7.20–7.04 (3 H, m, Ph), 5.71 (1 H, ddd, *J* 17.1, 10.2 and 9.0, *H*C=CH_2), 5.10 (1 H, d, *J* 17.1, HC=CH_AH_B), 5.08 (1 H, d, *J* 10.3, HC=CH_AH_B), 3.53 (3 H, s, CO_2Me), 2.88 (1 H, dd, *J* 13.7 and 4.5, $PhCH_ACH_B$), 2.77 (1 H, dd, *J* 13.6 and 10.5, $PhCH_ACH_B$), 2.54 (1 H, ddd, *J* 10.5, 8.4 and 4.4, C*H*CO_2Me), 2.47 (1 H, sext, *J* 7.5, MeC*H*) and 1.04 (3 H, d, *J* 6.6, CH*Me*); (minor isomer **38**, where different from the major isomer) 5.81 (1 H, ddd, *J* 16.9, 10.2 and 8.0, *H*C=CH_2), 5.05 (1 H, d, *J* 10.2, HC=CH_AH_B), 5.02 (1 H, d, *J* 17.0, HC=CH_AH_B), 2.87 (1 H, dd, *J* 13.7 and 10.2, $PhCH_ACH_B$), 2.79 (1 H, dd, *J* 13.7 and 4.8, $PhCH_ACH_B$), 2.64 (1 H, ddd, *J* 10.3, 6.5 and 4.9, C*H*CO_2Me) and 1.12 (3 H, d, *J* 6.9, CH*Me*); δ_C (400 MHz, $CDCl_3$) (major isomer) 174.8+, 141.1−, 139.4+, 128.5−, 128.4−, 128.1−, 125.9−, 115.1+, 53.3−, 50.9−, 40.7−, 36.4+ and 18.1−; (minor isomer) 174.3+, 140.5−, 139.4+. 128.5−, 128.4−, 128.1−, 125.9−, 114.7+, 53.0−, 50.9−, 40.0−, 35.2+ and 17.4+; *m*/*z* (EI) 218.1 (25, M^+), 162.1 (48%, M − C_4H_8) 131.0 [45%, M − (C_4H_8) − OMe] and 57.0 [100%, $(CO_2CH)^{2+}$] (Found: M^+, 218.1305. $C_{18}H_{28}SiO_4$ requires *M*, 218.1307).

Acknowledgements

We acknowledge the early work on this project by the late Professor John Hill, who established the intriguingly high level of diastereoselectivity in the reaction **7b** ⟶ **8b** (Scheme 1), but left us with the problem of finding out in what stereochemical sense the reaction had taken place. We thank the EPSRC for a maintenance award (MSB) and Dr David Fox for help with the modelling calculations.

References

1 R. A. N. C. Crump, I. Fleming, J. H. M. Hill, D. Parker, N. L. Reddy and D. Waterson, *J. Chem. Soc., Perkin Trans. 1*, 1992, 3277.
2 I. Fleming and J. D. Kilburn, *J. Chem. Soc., Perkin Trans. 1*, 1992, 3295.
3 I. Fleming and N. J. Lawrence, *J. Chem. Soc., Perkin Trans. 1*, 1992, 3309.
4 M. J. C. Buckle, I. Fleming and S. Gil, *Tetrahedron Lett.*, 1992, **33**, 4479; M. J. C. Buckle and I. Fleming, *Tetrahedron Lett.*, 1993, **34**, 2383.
5 I. Fleming, N. J. Lawrence, A. K. Sarkar and A. P. Thomas, *J. Chem. Soc., Perkin Trans. 1*, 1992, 3303.
6 I. Fleming, G. R. Jones, N. D. Kindon, Y. Landais, C. P. Leslie, I. T. Morgan, S. Peukert and A. K. Sarkar, *J. Chem. Soc., Perkin Trans. 1*, 1996, 1171 See also ref. 25.
7 Fourteen papers in the May issue of, *Chem. Rev.*, 1999, **99**, p. 1067.
8 A. S. Cieplak, *J. Am. Chem. Soc.*, 1981, **103**, 4540.
9 I. Fleming, D. Hrovat and W. T. Borden, *J. Chem. Soc., Perkin Trans. 2*, 2001, 331 and references therein.
10 R. J. Linderman and T. V. Anklekar, *J. Org. Chem.*, 1992, **57**, 5078; J. Cossrow and S. D. Rychnovsky, *Org. Lett.*, 2002, **4**, 147.
11 I. Fleming, P. Maiti and C. Ramarao, *Org. Biomol. Chem.*, **1**, 10.1039/b305880h preceding paper I. Fleming and C. Ramarao, *Chem. Commun.*, 2000, 2185.
12 R. E. Ireland and R. H. Mueller, *J. Am. Chem. Soc.*, 1972, **94**, 5897; For a review, see Y. Chai, S. Hong, H. A. Lindsay, C. M. McFarland and M. C. McIntosh, *Tetrahedron*, 2002, **58**, 2905.
13 T. Yamazaki, N. Shinohara, T. Kitazume and S. Sato, *J. Org. Chem.*, 1995, **60**, 8140 See also T. Yamazaki, S. Takei, S. Kawashita, T. Kitazume and T. Kubota, *Org. Lett.*, 2001, **3**, 2915.
14 A. Mukherjee, Q. Wu and W. J. le Noble, *J. Org. Chem.*, 1994, **59**, 3270.
15 J. J. Gajewski and J. Emrani, *J. Am. Chem. Soc.*, 1984, **106**, 5733.
16 R. M. Coates, B. D. Rogers, S. J. Hobbs, D. R. Peck and D. P. Curran, *J. Am. Chem. Soc.*, 1987, **109**, 1160.
17 L. Kupczyk-Subotkowska, W. H. Saunders, Jr., H. J. Shine and W. Subotkowski, *J. Am. Chem. Soc.*, 1994, **116**, 7088.
18 R. E. Ireland, P. Wipf and J. D. Armstrong, III, *J. Org. Chem.*, 1991, **56**, 650.
19 I. Fleming, A. Barbero and D. Walter, *Chem. Rev.*, 1997, **97**, 2063.
20 P. Beslin and S. Perrio, *Tetrahedron*, 1991, **47**, 6275.
21 J. K. Cha and S. C. Lewis, *Tetrahedron Lett.*, 1984, **25**, 5263.
22 R. E. Ireland, R. H. Mueller and A. K. Willard, *J. Am. Chem. Soc.*, 1976, **98**, 2868.
23 M. J. Kurth and C.-M. Yu, *J. Org. Chem.*, 1985, **50**, 1840.
24 S. Nowaczyk, C. Alayrac, V. Reboul, P. Metzner and M.-T. Averbuch-Pouchot, *J. Org. Chem.*, 2001, **66**, 7841.
25 M. V. George, D. J. Peterson and H. Gilman, *J. Am. Chem. Soc.*, 1960, **82**, 403.
26 I. Fleming and J. D. Kilburn, *J. Chem. Soc., Perkin Trans. 1*, 1992, 3295.
27 I. Fleming, A. K. Sarkar, M. J. Doyle and P. R. Raithby, *J. Chem. Soc., Perkin Trans. 1*, 1989, 2023.
28 R. A. N. C. Crump, I. Fleming and C. J. Urch, *J. Chem. Soc., Perkin Trans. 1*, 1994, 701.
29 E. J. Corey and P. L. Fuchs, *Tetrahedron Lett.*, 1972, **36**, 3769.
30 G. B. Bachman, *J. Am. Chem. Soc.*, 1933, **55**, 4279.
31 E. Piers and A. V. Gavai, *J. Org. Chem.*, 1990, **55**, 2374.
32 M. Marakami, M. Hayashi and Y. Ito, *J. Org. Chem.*, 1994, **25**, 7910.
33 I. Fleming, I. T. Morgan and A. K. Sarkar, *J. Chem. Soc., Perkin Trans. 1*, 1998, 2749.
34 H. M. Schmidt and J. F. Arens, *Recl. Trav. Chim. Pays-Bas.*, 1967, **86**, 1138.
35 S. Rajagopalan and G. Zweifel, *Synth. Commun.*, 1984, 111.
36 I. Fleming and J. M. Mwaniki, *J. Chem. Soc., Perkin Trans. 1*, 1998, 1237.