Diastereoselectivity in the S_E2'' reaction of chiral pentadienylsilanes: a test for the relative importance of steric and electronic effects

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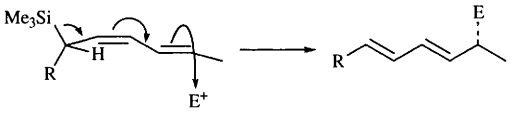
The homochiral pentadienylsilanes (3*Z*,5*E*)-(hepta-3,5-dien-2-yl)dimethyl(phenyl)silane 9, (3*Z*,5*E*)-(hepta-3,5-dien-2-yl)trimethylsilane 13, (4*Z*,6*E*)-(2-methylocta-4,6-dien-3-yl)dimethyl(phenyl)silane 14 and (4*Z*,6*E*)-(2-methylocta-4,6-dien-3-yl)trimethylsilane 17 undergo Lewis acid catalysed reactions with isobutyraldehyde and its dimethyl acetal stereospecifically *anti* with surprisingly high levels of stereoselectivity, *ca.* 90:10. The pentadienylsilanes (3*Z*)-hexa-3,5-dien-2-yldimethyl(phenyl)silane 20aa, (4*Z*)-(2-methylhepta-4,6-dien-3-yl)dimethyl(phenyl)silane 20ab, (3*Z*)-(hexa-3,5-dien-2-yl)-trimethylsilane 20ba and (2*Z*)-(1-phenylpenta-2,4-dienyl)trimethylsilane 20bc undergo dipolar cycloadditions to 2,2-dimethylpropanenitrile oxide regioselectively at the terminal double bond and stereoselectively *anti* to the silyl group to a somewhat lower extent, *ca.* 70:30. The pentadienylsilane (3*Z*,5*E*)-(6-cyclohexylhexa-3,5-dien-2-yl)trimethylsilane 25 undergoes deuteriodesilylation stereospecifically *anti* to a lower extent still, *ca.* 55:45. The pentadienylsilane (3*Z*,5*E*)-(8-methyl-8-methoxyethoxymethoxynona-3,5-dien-2-yl)trimethylsilane 34 undergoes an intramolecular reaction stereospecifically *anti* again to the extent of about 60:40, whereas the reaction of the corresponding allylsilane (3*Z*)-(6-methyl-6-methoxyethoxymethoxyhept-3-en-2-yl)trimethylsilane 32 is essentially completely *anti*. These results show that S_E2'' reactions can be highly stereoselective in the *anti* sense, that the high level is probably best accounted for by the steric effect of the silyl group, and that when the steric effect is minimised, the stereospecificity is low, but still measurable. The pentadienylsilanes were prepared by aldol reactions between β-silyl esters and the appropriate α,β-unsaturated aldehyde, followed by decarboxylative elimination. The products of the S_E2'' reactions were identified and their stereochemistry determined by comparison with authentic materials or by degradation and synthesis, using chiral auxiliaries to determine the enantiomeric purity. The products of two of the dipolar cycloadditions were identified by degradation and stereospecific vinylogous Peterson elimination, but the vinylogous Peterson elimination taking place with (1*RS*,2*Z*,4*SR*,6*SR*)-(4,6-dihydroxy-7,7-dimethyl-1-phenyloct-2-enyl)trimethylsilane 67bc and its (1*SR*) diastereoisomer 68bc was not stereospecific, giving (5*E*,7*E*)-2,2-dimethyl-8-phenylocta-5,7-dien-3-ol 73 from both isomers. The stereochemistries of all the reactions are summarised.

We,[1-3] and several others,[4,5] have established that the S_E2' reaction of allylsilanes is highly stereospecific in the *anti* sense **1** ⟶ **2**. This stereochemistry is explained by the preference for

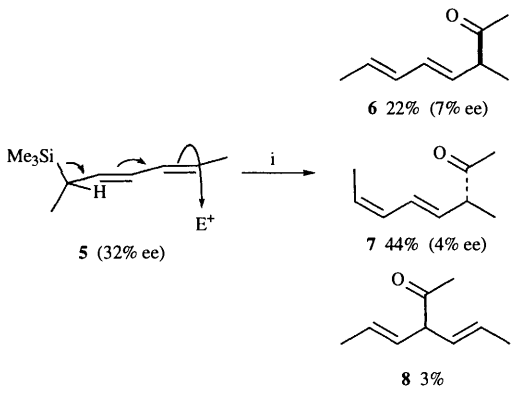
1 **2**



3 **4**

the smaller group, almost invariably hydrogen, to lie 'inside' the allylic system, to minimise $A^{1,3}$ interactions,[6] and for the electrophile to attack *anti* to the silyl group. This pattern for electrophilic attack is also found for cycloaddition to,[7,8] and hydroboration of,[9] allylsilanes and for the alkylation of enolates carrying a β-silyl group.[10] What is not clear is the extent to which the attack *anti* to the silyl group is controlled by steric or by electronic effects—both can be expected to work in the same sense, since the silyl group is unmistakably larger (although not necessarily as effective in providing steric hindrance[11]) than the carbon group R, and there is little doubt that the electropositive nature of the silyl group will encourage electrophilic attack *anti* to itself.[12] We considered that it might be possible to find out to what extent electronic factors are responsible for this selectivity by looking at the vinylogous reaction **3** ⟶ **4**, with a second double bond moving the reaction site far enough away from the silyl group to reduce any purely steric effect. When we started this work, it had the added attraction that we would also find out whether the S_E2'' reaction was inherently *anti* (as shown) or *syn*, which was not at that time known. We have published a small part of our work in one preliminary communication,[13] and two other parts in the form of lectures.[14,15] We now describe all our work in full.

Shortly before we published our first preliminary paper, Hayashi described the first stereochemically defined S_E2'' reaction (Scheme 1), in which he observed only a low level [18–22% enantiomeric excess (ee)] of stereospecificity in the *anti* sense.[16] In his reaction, the homochiral *E*,*E*-pentadienylsilane **5** was treated with acetyl chloride and aluminium chloride to give both the *E*,*E*-product **6** and the *Z*,*E*-product **7** together with the achiral product **8** of attack at C-4. These products are presumably epimerisable, and it was therefore possible that the low level of stereospecificity might have been due to some loss of stereochemical integrity in the products. Some support for this possibility can be found in some other work of Hayashi, where he observed that the S_E2' reaction with acetyl chloride was measurably less completely *anti* than the reaction with other electrophiles.[5]



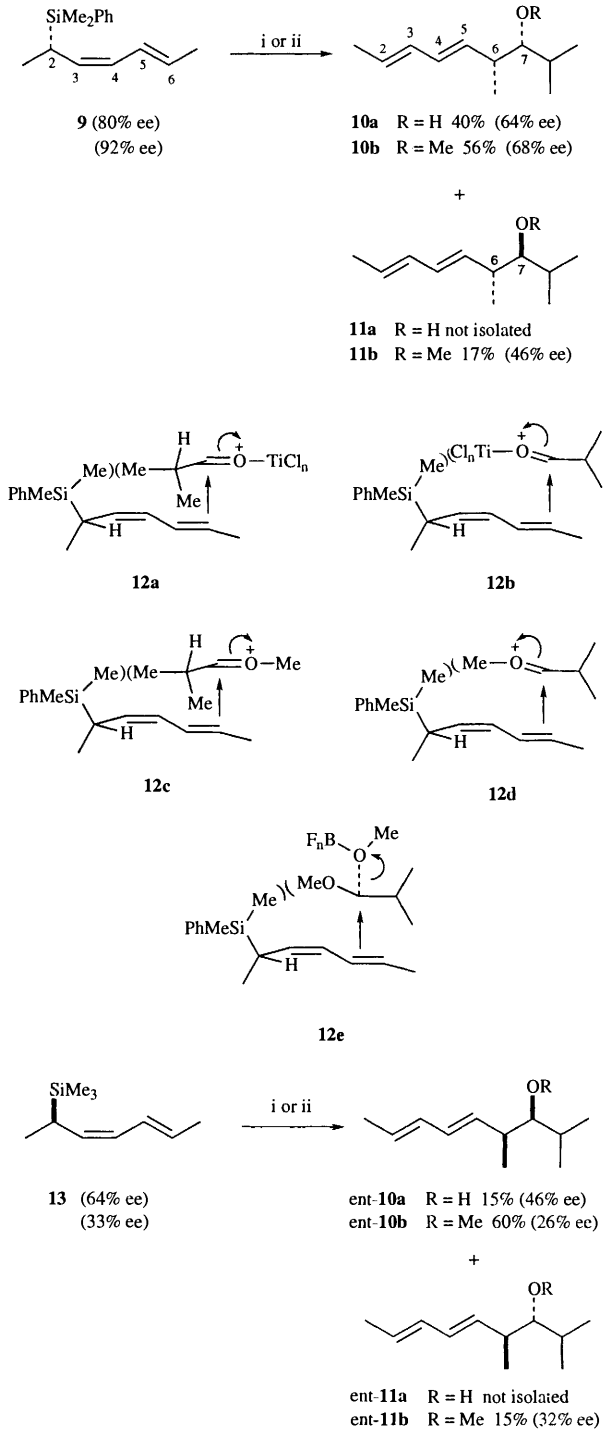
Scheme 1 *Reagents:* i, AcCl, $AlCl_3$

Results and discussion

Our work has taken several turns, as we sought to overcome the ambiguous answers each of our experiments gave to the central question: is the stereochemistry of electrophilic attack controlled to any measurable extent by electronic effects or not? We first tried the reaction of the pentadienylsilanes **9** and **13** with isobutyraldehyde. In an attempt to make the electrophile smaller, we carried out the same reactions using the corresponding dimethyl acetal instead. Using the same acetal as the electrophile, we tried increasing the size of the alkyl group on the stereogenic centre of the pentadienylsilane. We investigated 1,3-dipolar cycloadditions in place of S_E2'' reactions. We investigated the possibility of using a deuteron as the electrophile. And finally we tried two intramolecular reactions, in the hope that they would have well defined electrophiles small enough to rule out direct steric effects. We describe each of these experiments in sections 1–5, we describe the syntheses of our homochiral pentadienylsilanes in section 6, we describe the proof of structure and absolute configuration of our products in section 7, and we summarise our results and conclusions in section 8.

1. The reactions with isobutyraldehyde and its dimethyl acetal

We chose for our first reaction to use isobutyraldehyde as the electrophile and, anticipating the problems that Hayashi had, the *Z,E*-pentadienylsilane **9** as the nucleophile (Scheme 2). We chose a *cis* double bond between C-3 and C-4, because the conformation about the bond between C-2 and C-3 is more certain to have the hydrogen atom 'inside', as in **3**, and thus give only a *trans* double bond between C-2 and C-3 in the product. This expectation follows from much evidence that *cis* allylsilanes give cleaner reactions in this sense than the corresponding *trans* allylsilanes.[3,7] We chose to have a methyl group on C-6 and a *trans* double bond between C-5 and C-6, because it is known that *trans* allylsilanes in their reactions with aldehydes give products largely with the *syn* arrangement of the methyl and hydroxy substituents on the backbone, whereas the corresponding *cis* allylsilanes give quite substantial amounts of products with the methyl and hydroxy groups *anti*.[17] We chose isobutyraldehyde as the electrophile, both because aldehydes had already been combined with pentadienylsilanes, and because a branched alkyl group on the aldehyde was known to increase the proportion of the product having the methyl and hydroxy groups *syn*.[18] In the event, the homochiral (2*S*)-pentadienylsilane **9** of 80% ee gave, as the major isolated product, the *E,E*-diene **10a**, with the *syn* arrangement of the methyl and hydroxy groups, having an ee of 64%. We were able to separate this product from the minor diastereoisomer **11a**, which we did not investigate further. The major reaction therefore had taken place mainly in the *anti* sense, with a ratio of *anti* to *syn* attack of 90:10, much higher than Hayashi's ratio of 60:40. We also carried out a comparable reaction using the



Scheme 2 *Reagents:* i, Pr^iCHO, $TiCl_4$, CH_2Cl_2, −78 °C; ii, $Pr^iCH(OMe)_2$, $BF_3{\cdot}OEt_2$, CH_2Cl_2, −70 °C

dimethyl acetal of isobutyraldehyde, catalysed by boron trifluoride–diethyl ether, and using a different sample of the pentadienylsilane **9** of 92% ee. This time, although we were unable to separate the diastereoisomers **10b** and **11b**, we were able to measure the enantiomeric purity of both. For the adduct **10b**, with the *syn* relationship between C-6 and C-7, reaction took place with a ratio of *anti* to *syn* attack of 87:13, and for the diastereoisomer **11b**, with the *anti* relationship between C-6 and C-7, the ratio was 75:25. Although these ratios were measured by ^1H NMR spectroscopy, rather than the rotation of plane-polarised light, the accuracy is not high, probably no better than ± 10%, which means that all the reactions described so far have very similar ratios of *anti* to *syn* attack, close to the 90:10 mark, but probably just a little below. Whatever the explanation, *the most striking aspect of this work is the*

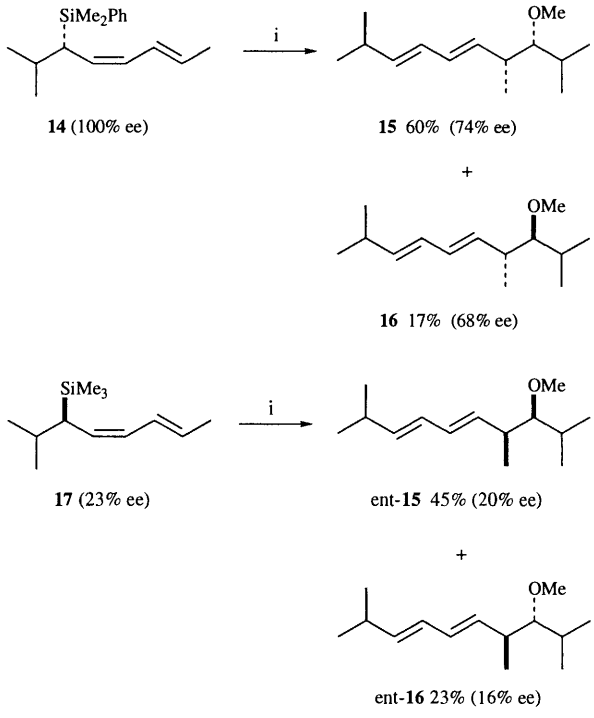
remarkably high level of stereocontrol for a reaction passing stereochemical information five atoms along a carbon chain.

There are several possible explanations for our reactions being more *anti* selective than Hayashi's. If there is a substantial electronic component to the stereoselectivity, the higher level of stereoselectivity in our work may simply be because our products **10** and **11** epimerise less than his. Alternatively, the conformational control inherent in having a *cis* double bond between C-3 and C-4 may have reduced the number of conformations undergoing reaction and hence improved the stereoselectivity. On the other hand, if steric effects are also present, it is possible in our system for the incoming electrophile to experience a substantial steric interaction with the silyl group when it attacks on the *syn* face. For attack by the aldehyde, there are two easily visualised possibilities, depending upon whether the C-5 to C-6 double bond and the carbonyl group approach one another in an antiperiplanar or synclinal arrangement. In the former, **12a**, the isopropyl group can touch the methyl group on the silicon atom, and in the latter, **12b**, the Lewis acid can occupy the same space. Either of these interactions could be severe enough to drive the electrophile onto the *anti* face, although we do not of course know that the angles of approach are such that these interactions are substantial even on the *syn* face—it is enough for the purposes of argument to know that they *could* interact in either of these ways. We have paid a penalty for having a *cis* double bond between C-3 and C-4—although our reactions gave a smaller number of products than Hayashi's, his *trans* double bond takes C-6 further away from the silyl group. Similarly for the reaction with the acetal, attack on the top face with an antiperiplanar approach **12c** gives rise to a very similar degree of steric hindrance as in the reaction **12a** with the corresponding aldehyde. Even if attack takes place with a synclinal approach, **12d**, the methoxy group of the acetal is still close enough to the methyl group on the silicon atom to be sterically repelled by it. What is clear is that the Lewis acid is most unlikely to be touching the methyl group on the silicon atom, as it could have been if the aldehyde had reacted in the sense **12b**. If the acetal reacts as an oxygen-stabilised cation,[19] as in **12c** and **12d**, the Lewis acid will have departed from the vicinity of the reaction. If on the other hand it reacts in an S_N2-like reaction,[20] it can still be relied upon to be attached to the departing methoxy group as in the illustration **12e**, and to be far away from the silyl group. Clearly changing the electrophile from a Lewis acid-complexed aldehyde to an acetal, although it may have made the electrophile smaller, has had little effect on the stereoselectivity.

The drawings **12** show the steric interaction as involving the methyl group on the silicon and not the phenyl group. We checked that the phenyl group was not responsible for our selectivity being so much higher than Hayashi's by carrying out the same reactions with the trimethylsilyl analogue **13**, which was more easily available to us in the opposite enantiomeric series and, at this stage, only with a lower degree of enantiomeric purity. The reaction with isobutyraldehyde and the pentadienylsilane **13** with an ee of 64% gave the alcohols **10** with a ratio of *anti* to *syn* attack of 86:14, insignificantly different, given the fairly large errors in the measurements of ees, from the result with the phenyldimethylsilyl group. In the reaction with the acetal the trimethylsilyl analogue **13** with an ee of 33% gave ratios of *anti* to *syn* attack of 90:10 for the *syn* adduct and an obviously rather unreliable 99:1 for the *anti* adduct. Evidently, the presence of a phenyl group in the pentadienylsilane **9** is not causing a substantially greater steric effect than the methyl group in the pentadienylsilane **13**, for we get very similar results with either.

2. The reaction of the pentadienylsilanes 14 and 17 with isobutyraldehyde dimethyl acetal

To see if we could affect the level of stereoselectivity by bulking up the substituent on the *anti* surface, we carried out the same reaction using the pentadienylsilanes **14** and **17**, having an isopropyl group on the stereogenic centre in place of the methyl group (Scheme 3). We assume that these make very similar

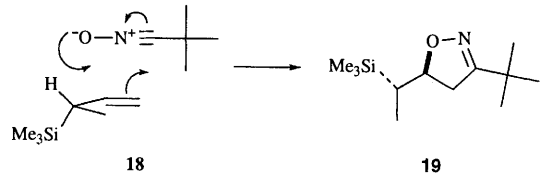


Scheme 3 *Reagents:* i, $Pr^iCH(OMe)_2$, $BF_3{\cdot}OEt_2$, CH_2Cl_2, −78 °C

contributions electronically. In the event, the stereoselectivity was little affected, if at all; the pentadienylsilane **14** gave a ratio of *anti* to *syn* attack of 87:13 for the formation of the *syn* adduct **15** and of 84:16 for the formation of the *anti* adduct **16**. The pentadienylsilane **17** was available only with a low level of enantiomeric purity, and so the results with this diene are less accurate, but the ratios were 93:7 and 85:15, respectively. Had this change in the structure made a significant difference, we could have concluded that a steric effect was indeed responsible for the high level of stereoselectivity that we have been seeing. In its absence, we conclude either that the isopropyl group is not large enough to have interfered with attack on the lower surface or that electronic effects contribute substantially to the stereoselectivity.

3. The reaction of the pentadienylsilanes 20 with 2,2-dimethylpropanenitrile oxide

Curran and Kim showed that 2,2-dimethylpropanenitrile oxide reacted with but-1-en-3-yltrimethylsilane **18** to give largely (2:1) the adduct **19**,[8] with stereoselectivity that fits Houk's calculations,[21] and that we have come to recognise is normal for cycloadditions to allylsilanes having a methyl group on the stereogenic centre and a hydrogen atom *cis* to the stereogenic centre (Scheme 4).[22] More relevant for our present purposes,



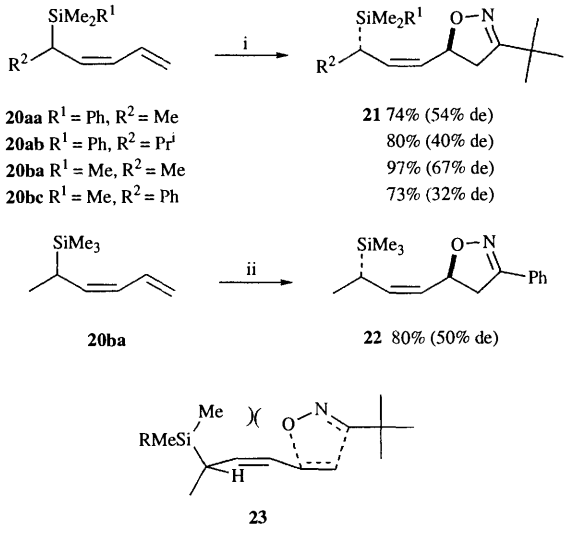
18 **19**

Scheme 4

the regioselectivity was, unsurprisingly, normal for a terminal alkene. We could hope therefore that a nitrile oxide would be significantly less sterically demanding than the electrophilic species involved in the acetal reactions, since the oxygen atom is pointing at the stereogenic centre in the most likely transition

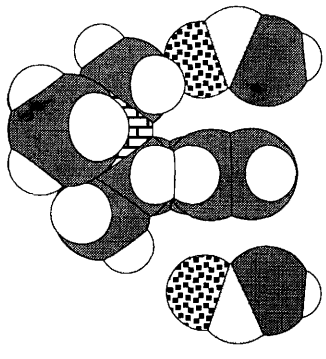
structure **23** for attack on the *syn* surface of a pentadienylsilane. Nitrile oxides are also said to be dipole-LUMO controlled in their cycloadditions,[23] which makes them electrophilic in nature, and there is some experimental support from the relative rates of the cycloadditions of benzonitrile oxide with donor-substituted styrenes.[24]

Accordingly, we carried out reactions on the racemic pentadienylsilanes **20** and measured the diastereoisomeric excesses shown in Scheme 5. The degree of diastereoselectivity



Scheme 5 *Reagents:* i, Bu^{t}CHNOH, NaOCl, CH_2Cl_2, room temp., ii, PhCHNOH, NaOCl, CH_2Cl_2, room temp.

(an average of about 75:25) was not as high as the enantioselectivities in the aldehyde and acetal reactions (an average of about 87:13), but this could be explained in two extreme ways: either a steric effect was important, and the smaller size of the nitrile oxide was revealing it, or an electronic effect was important, and the nitrile oxide was simply less electrophilic in nature. Our only attempt to resolve this issue was to carry out a similar reaction using the pentadienylsilane **20ba**, but with benzonitrile oxide, which has a significantly lower-energy LUMO,[23] in place of 2,2-dimethylpropanenitrile oxide. We observed that the diastereoselectivity in the formation of the adduct **22** was only a little lower (75:25) than that for the formation of the adduct **21ba** (80:20), implying perhaps that the electronic argument is less likely. Simple models (Chem 3D) reveal that the oxygen atom of the nitrile oxide can easily touch the edge of a methyl group on the silicon atom in a reasonable transition structure **23**.[25] Attack from above and below are illustrated in Fig. 1 with the irrelevant *tert*-butyl group replaced for simplicity by hydrogen. Although these are simple models without any minimisation of energies,



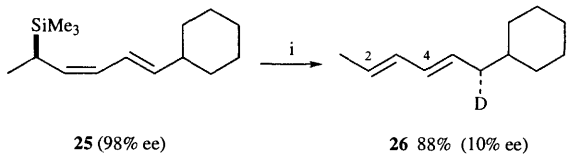
24

Fig. 1

they show clearly that we have not been able to discount the possibility that steric effects are all that we are seeing. More sophisticated calculations on the pentadienylsilane **20ba**, carried out with energy minimisation by Morokuma,[26] detect a similar steric effect, and suggest a difference in activation energy between attack on the lower and upper surfaces of 1.1 kcal mol^{-1}, corresponding to a ratio of diastereoisomers of 6:1, quite close to what we observe.

4. The reaction of the pentadienylsilane 25 with D$^+$

Our early attempts to use a solvated deuterium cation as the electrophile and the pentadienylsilane **9** as the nucleophile failed because we were unable to isolate hepta-2,4-diene, probably because of its high volatility. Accordingly, we synthesised the pentadienylsilane **25**, and treated it with deuteriated trifluoroacetic acid (Scheme 6). The products were the dienes

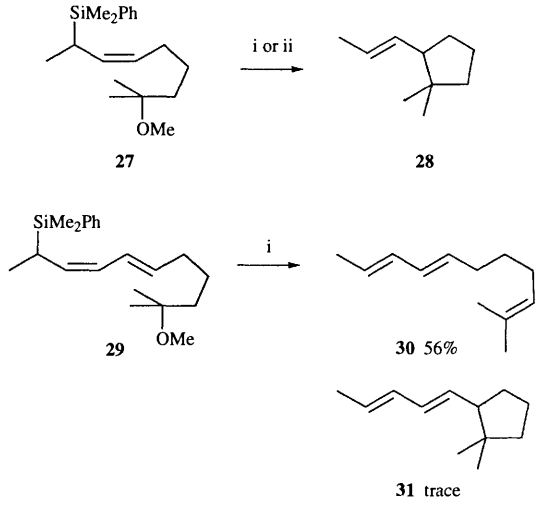


Scheme 6 *Reagents:* i, CF_3CO_2D, $CDCl_3$, 0 °C, 30 min, room temp., 10 min

26 and their 2*Z*,4*E* isomers in a ratio of 93:7. These products appeared to be present in very low enantiomeric excess (10%), even though the pentadienylsilane **25** was prepared in a state of high enantiomeric purity (97% ee). However, the measurement of the enantiomeric purity of the products was complicated (see below) by incomplete deuteriation and by the fact that we were obliged to carry through the mixture of geometric isomers, which can be expected to have opposite absolute configurations. The 10% ee could not therefore be taken with any confidence to mean that we had achieved our goal, although it was our first hint that a small electrophile, when one can find it, removes the high levels of stereoselectivity that we had seen at the beginning of this work. Very tentatively, at this stage, we deduced that the high level of stereoselectivity was largely steric in origin.

5. The intramolecular reaction of the pentadienylsilane 34

We chose the pentadienylsilane **29** as our next substrate. The racemic lower vinylogue **27** gave the cyclopentane **28**, as we had expected given that there is no 5-*endo*-trig feature to hinder cyclisation (Scheme 7). However, a great deal of work in the

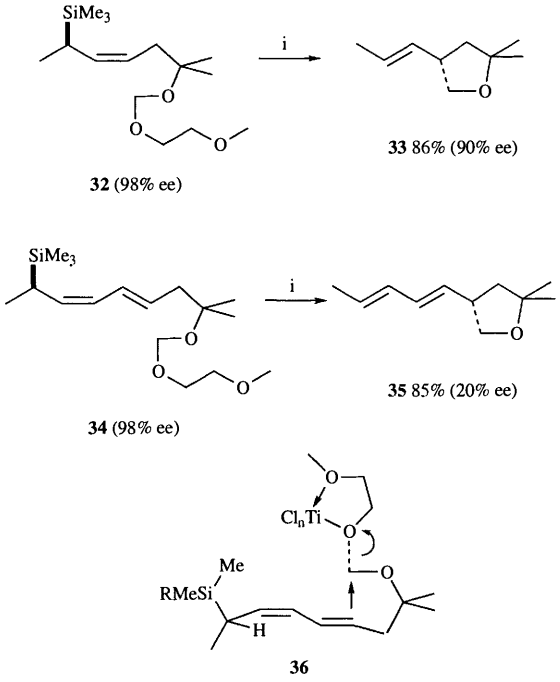


Scheme 7 *Reagents:* i, BF_3·OEt_2, $CDCl_3$, room temp.; ii, $TiCl_4$, $CDCl_3$, −60 °C, 1.5 h

racemic series, using the pentadienylsilane **29** and many different Lewis and protic acids, gave us no more than a trace of the product **31** that we sought. We prepared an authentic

sample of this diene, in order to follow its appearance during the course of the reaction, all to no avail. The only conclusion we were able to come to was that with boron trifluoride as the Lewis acid elimination took place, followed by protodesilylation to give fluorodimethylphenylsilane and probably the triene **30**.

We turned therefore to the pentadienylsilane **34**, which has a 5-*endo*-trig feature, if the mechanism involves an oxygen-stabilised cation, but also a Thorpe–Ingold effect. The choice of a methoxyethoxy acetal group was based on the observation that the methoxyethoxy group will selectively coordinate the Lewis acid, and hence be the leaving group.[27] The lower vinylogue **32** cyclised cleanly with high enantioselectivity to give the tetrahydrofuran **33** (Scheme 8). Cyclisation of the



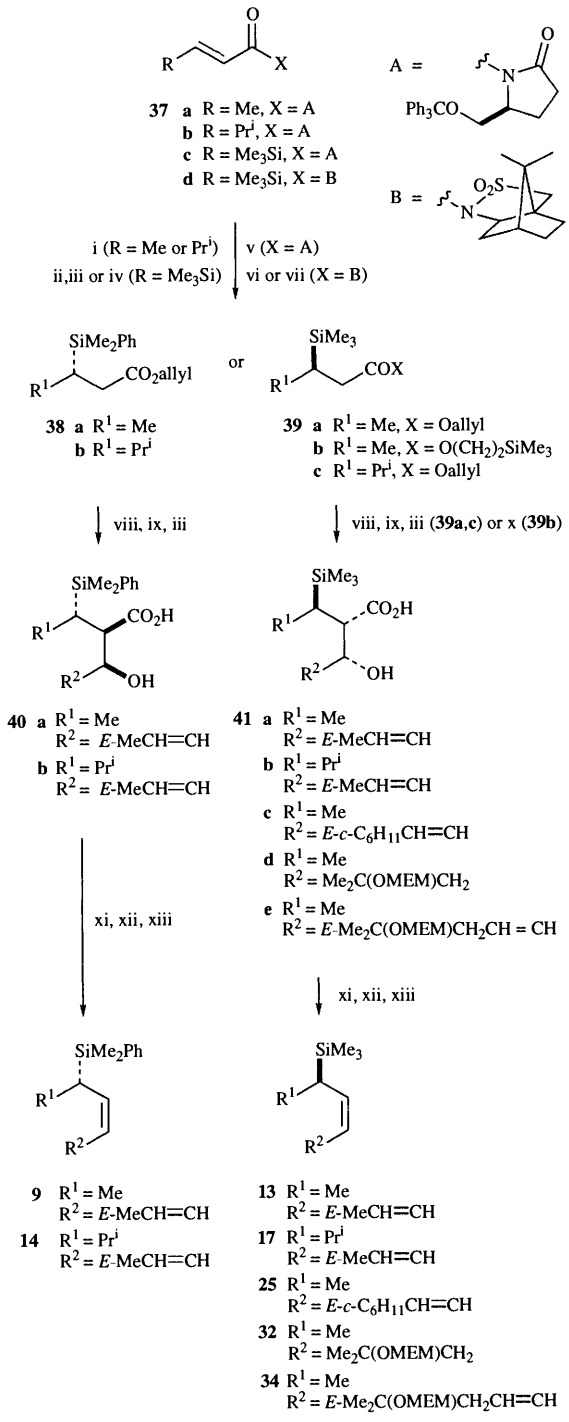
Scheme 8 *Reagents:* i, $TiCl_4$, CH_2Cl_2, −78 °C, 1 h

pentadienylsilane **34** was also straightforward in giving a high yield of the tetrahydrofuran **35**, but with a stereoselectivity of only 60:40 in favour of attack *anti* to the silyl group. Whatever the mechanism, whether by way of a carbocation or by an S_N2-like displacement of the methoxyethoxy group **36**, the electrophilic centre is small, unmistakably electrophilic in nature, and most unlikely to experience any serious steric interaction with the silyl group. This is shown for the S_N2-like version of the mechanism, using the enantiomer of the compound we actually used, to keep it in the same enantiomeric series as the drawings in Scheme 2. That the selectivity should be the same as that found by Hayashi, seems to settle at last the degree of electronic control in this type of S_E2'' reaction—the silyl group imparts a 60:40 difference in nucleophilicity to the diastereotopic faces of the diene in favour of *anti* attack.

6. The synthesis of the pentadienylsilanes

The syntheses of the homochiral pentadienylsilanes are shown in Scheme 9. They take advantage of our observations[28] and those of Oppolzer[29] on the use of chiral auxiliaries in conjugate addition reactions with silicon-containing compounds, and continue with one of our allylsilane syntheses.[30]

Conjugate addition of the phenyldimethylsilyl cuprate reagent to the enones **37a** and **37b**, carrying Koga's chiral auxiliary A, gave the corresponding β-silylimides, which we cleaved with lithium allyloxide to give the esters **38**. In the light of our later experience, this type of reaction can be carried out better by quenching the mixture at the end of the conjugate addition reaction with allyl alcohol, but at this stage in our



Scheme 9 *Reagents:* i, $(PhMe_2Si)_2CuCNLi_2$; ii, MeMgBr, CuBr·Me_2S; iii, Me_2CuLi; iv, Pr^{i}MgBr, $Cu(OAc)_2$; v, CH_2=$CHCH_2OLi$; vi, CH_2=$CHCH_2OMgBr$; vii, $BrMgO(CH_2)_2SiMe_3$; viii, LDA; ix, R^2CHO; x, TBAF; xi, $PhSO_2Cl$, Py; xii, heat, 2,4,6-trimethylpyridine; xiii, *N*-phenylmaleimide, heat

work we had not discovered this shortcut. In any case, it is necessary to isolate at least a portion of the product still carrying the chiral auxiliary, in order to measure its de. In the reaction **37a** ⟶ **38a** we obtained in separate runs products of 80% de and 92% de. We assume, and have some evidence that it is a safe assumption,[2] that the silicon-bearing centre is configurationally intact in all the subsequent steps, and that these samples of the diene **9** had 80% and 92% ee, respectively. The corresponding conjugate addition to the isopropyl-bearing substrate **37b** was, on this occasion, one of the best that we have ever seen, with no detectable (^{1}H NMR) diastereoisomer when the chiral auxiliary was still attached. We have therefore used the figure 100% ee for the diene **14** derived from this compound,

not because it will necessarily be quite that high, but because the higher the ee we claim for the pentadienylsilane, the lower is our estimate of the degree of enantiocontrol in the S_E2'' reaction. It is therefore, rather curiously, more conservative to claim a high ee for the starting material. An aldol reaction between the allyl esters **38** and *trans*-but-2-enal, followed by removal of the allyl group with lithium dimethylcuprate, gave the β-hydroxy acids **40**. Stereospecific *syn* decarboxylative elimination, using the Adam method,[31] gave the *Z*,*E*-dienes **9** and **14**, typically contaminated with only about 10% of the *E*,*E*-isomers, which we efficiently removed by heating the mixture for 48 h with an excess of *N*-phenylmaleimide in benzene. We were familiar with the Diels–Alder reactions of the *E*,*E*-dienes removed in this step, because we had already studied their stereoselectivity.[32]

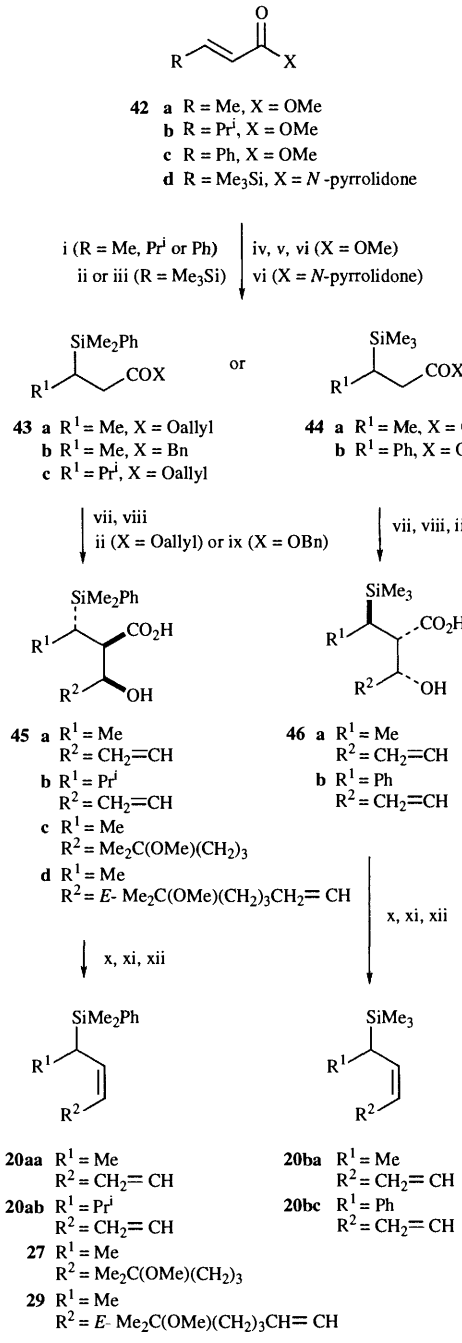
In the trimethylsilyl series, we used the copper-catalysed addition of methyl or isopropyl Grignard reagents, or of lithium dimethylcuprate, to the silicon-containing enones **37c** or **37d**. Of these reactions, the addition of the methylcuprate to the enone **37c** was not as good as the addition of the methylcuprate to the enone **37d** carrying Oppolzer's chiral auxiliary B, which was excellent, as we have reported before.[2] At first we used the inferior route for the synthesis of the ester **39a** used in the synthesis of the diene **13**, which had an ee of 64% for one reaction and only 33% for the second (Scheme 2). We used the better route, discovered later, for the synthesis of the same ester (98% ee), used for the synthesis of the diene **25**, and for the synthesis of the ester **39b** (98% ee), used in the synthesis of the allylsilane **32** and the pentadienylsilane **34**. The addition of the isopropyl Grignard to the enone **37c** was the worst that we have had to put up with, giving only 23% de in the sequence leading to the diene **17**. The remaining steps to the β-hydroxy acids **41**, and the pentadienylsilanes **13**, **17**, **25**, **32** and **34**, were similar to the steps leading to the pentadienylsilanes **9** and **14**, except that in the synthesis of the β-hydroxy acids **41d** and **41e**, the trimethylsilylethyl ester was used in place of the allyl.

The syntheses of the racemic pentadienylsilanes, shown in Scheme 10, follow a similar course to the sequences in Scheme 9. We have since discovered that the allyl esters **43a** and **43c** can be prepared directly from allyl *trans*-but-2-enoate by using the silylzincate in place of the cuprate.[33] We prepared the aldehydes **47**, **49**, **50**, **52** and **53**, used in the synthesis of the silanes **25**, **32**, **34**, **27** and **29**, respectively, by the routes shown in Scheme 11, in which we took particular advantage of the method of Meyers [34] for extending an aldehyde to its vinylogue, as in the sequence **49** ⟶ **50**.

7. The proof of configuration of the products

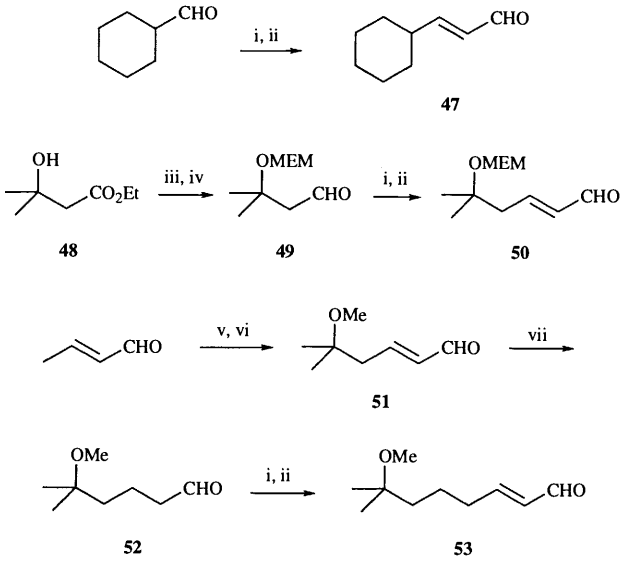
We prepared an authentic sample of the racemate of the alcohol **10** by carrying out the same reaction as in Scheme 2, but using racemic pentadienylsilane **9**, and attached Mosher's acid to the free hydroxy group to give the esters **54** and **55** with equally intense, and well resolved peaks at δ 90.81 and 90.91 in the ^{19}F NMR spectrum. We then prepared specifically the diene *ent*-**10** by the route shown in Scheme 12, starting with Evans's aldehyde **56**,[35] which was enantiomerically and diastereomerically pure, and carrying out a Wittig reaction on it to give the dienes *ent*-**10** and **57** in a ratio of 2:1. We prepared the Mosher's ester **55**, which proved to have the peak at δ 90.91, while the Mosher's ester of the *E*,*Z*-diene **57** had a peak at δ 90.79. We then prepared the mixture of Mosher's esters **54** and **55** from the alcohols produced in Scheme 2. The product, rich in the enantiomer and diastereoisomer **10**, derived from the pentadienylsilane **9**, gave a mixture of the Mosher's esters **54** and **55** with the strong signal in the ^{19}F NMR spectrum at δ 90.81 and weak signal at δ 90.91 in a ratio of 82:18, and the product, rich in *ent*-**10**, derived from the pentadienylsilane **13**, gave a strong signal at δ 90.91 and weak signal at δ 90.81 in a ratio of 73:27.

We were unable to cleave the methyl ethers **10b** and **11b**

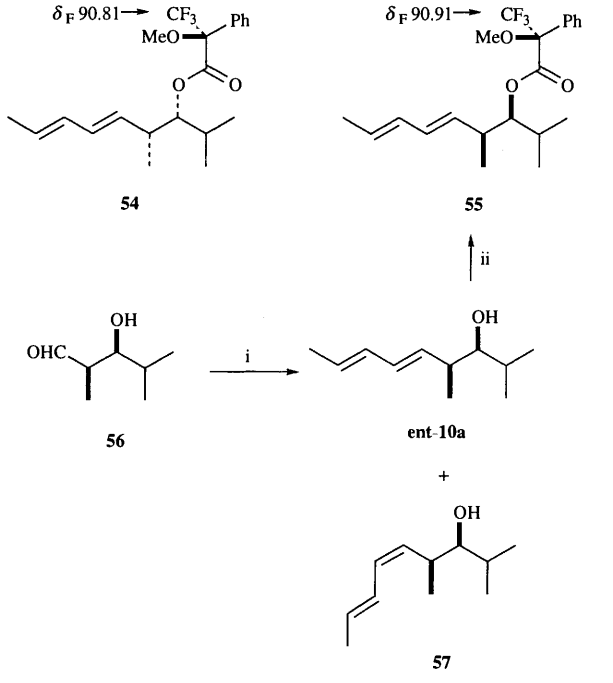


Scheme 10 *Reagents:* i, $(PhMe_2Si)_2CuCNLi_2$; ii, Me_2CuLi; iii, Ph_2CuLi; iv, LiOH; v, $(COCl)_2$; vi, $CH_2{=}CHCH_2OH$; vii, LDA; viii, R^2CHO; ix, H_2/Pd; x, $PhSO_2Cl$, Py; xi, heat, 2,4,6-trimethylpyridine; xii, *N*-phenylmaleimide, heat

produced in the reactions in Scheme 2, so we had to establish a different method for measuring their enantiomeric purity. Ozonolysis of the mixture and borohydride reduction gave a mixture of alcohols, which gave the Mosher's esters **58**, **59**, **60** and **61**, with four resolved 3'-OMe signals in the ^1H NMR spectrum at, reading from low to high field, δ 3.38, 3.335, 3.33 and 3.32. In the reaction from the racemic pentadienylsilane **9**, these four signals were present in a ratio of 9:38:41:12, respectively. The major pair of diastereoisomers appeared to be present in unequal amounts, 38 and 41%, and the minor pair also, 9 and 12%. We treated this as a measure of the likely errors in our readings, and did not correct for these differences in our calculations of the ees of the products, even though a repeat of this reaction gave the esters **58–61** in the same ratios. In the reaction from the pentadienylsilane **9**, with an ee of 92%, the



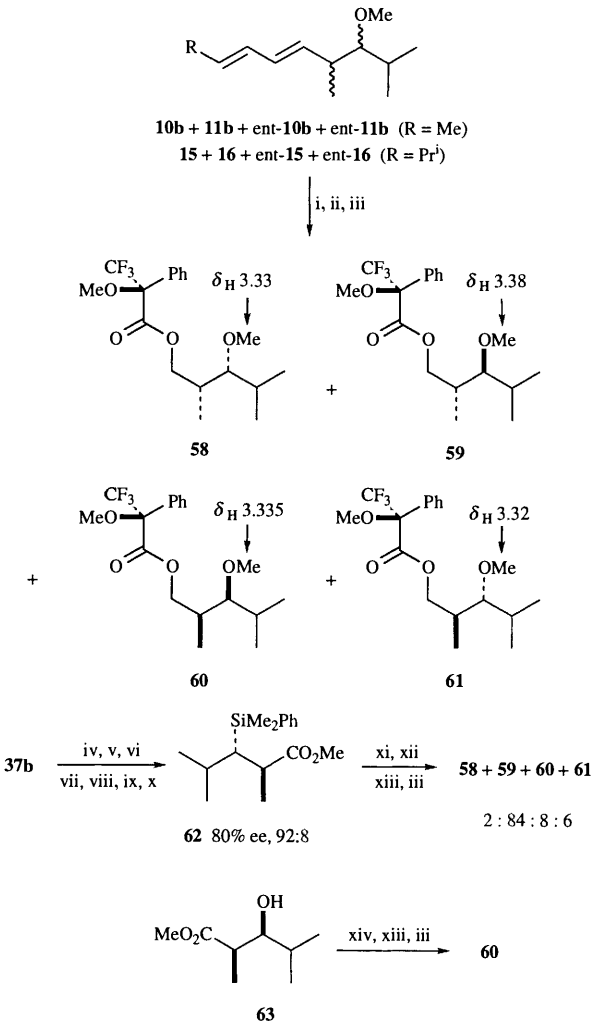
Scheme 11 *Reagents:* i, $(EtO)_2P(O)CH{=}CHNLiBu^t$; ii, $(CO_2H)_2$; iii, MEMCl, Pr^i_2NEt; iv, Bu^i_2AlH; v, Me_3SiCl, Et_3N; vi, $Me_2C(OMe)_2$, $ZnBr_2$; vii, H_2, Pd



Scheme 12 *Reagents:* i, $Ph_3P{=}CHCH{=}CHMe$; ii, (*S*)-PhC(OMe)-$(CF_3)CO_2H$, DCC, DMAP

products were present in ratios, reading from low to high field, of 16:13:65:6, and in the reaction from the pentadienylsilane **13**, with an ee of 33%, in ratios of 7:50:29:14. By assuming that the reaction is selective for the formation of the *syn* diastereoisomers **10** and *ent*-**10**, and by assuming that the S_E2'' reaction is *anti* stereospecific, we can assign these signals, as summarised on the structures of the esters **58**–**61** on Scheme 13.

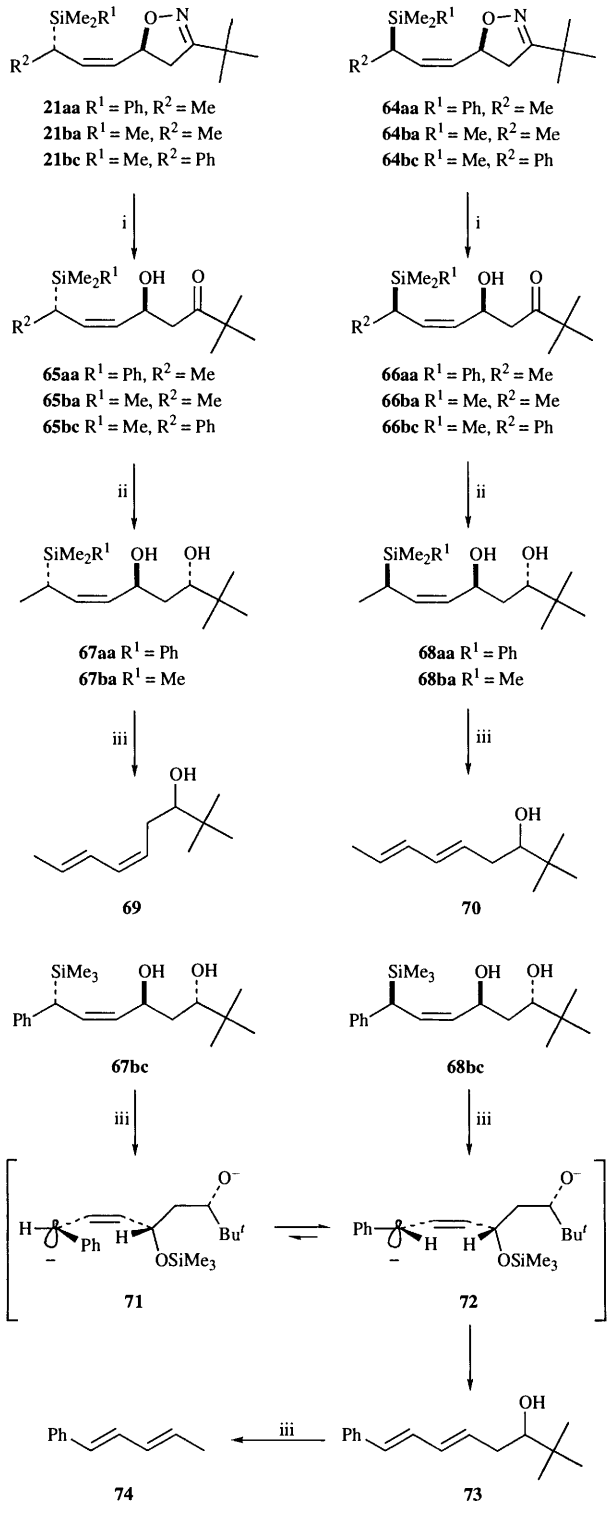
To establish reliably which OMe signal was associated with which ester, we synthesised a different mixture of the same four compounds **58**–**61** by the sequence shown in Scheme 13. Silylcupration of the imide **37b**, and methylation of the derived methyl ester gave, as the major product, the ester **62**, with absolute configuration assigned by analogy with our earlier work on the silylcupration of imides based on Koga's chiral auxiliary,[28] and relative configuration secure from our earlier work on the methylation of enolates having a β-silyl group.[10] In this case, the silylcupration reaction with **37b** was not as good as it had been in the run described in Section 6 above, and gave



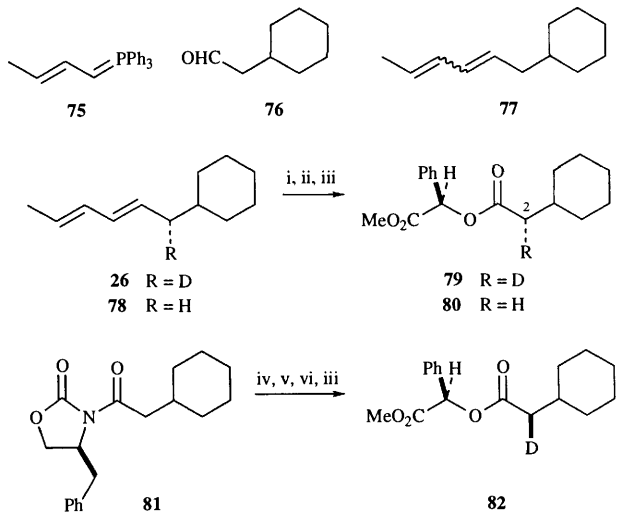
Scheme 13 *Reagents:* i, O_3; ii, $NaBH_4$; iii, (*S*)-PhC(OMe)$(CF_3)CO_2H$, DCC, DMAP; iv, $(PhMe_2Si)_2CuCNLi_2$, $MgBr_2$; v, $CH_2{=}CHCH_2OLi$; vi, Me_2CuLi; vii, $(COCl)_2$; viii, MeOH, Et_3N; ix, LDA; x, MeI; xi, $Hg(OAc)_2$, AcO_2H; xii, CH_2N_2; xiii, $LiAlH_4$; xiv, CH_2N_2, $BF_3{\cdot}OEt_2$

material of 90% de. The methylation step had previously given us the *anti* and *syn* diastereoisomers in a ratio of 85:15,[10] and gave a ratio measured as 92:8 on this occasion. We converted the silyl group in the ester **62** to a hydroxy group, methylated it, reduced the ester to the primary alcohol and made the Mosher's ester. The major product (84% of the mixture) from this sequence will have the structure **59**, and the most minor product (2% of the mixture), with the opposite absolute configuration at C-3′ and a *syn* relationship between the substituents on C-2′ and C-3′, will have the structure **58**. These structures therefore can be associated with the signals from the 3′-OMe protons in the ^1H NMR spectrum at δ 3.38 and 3.33, which were the strongest (84%) and weakest (2%) signals. The other two signals (8% and 6%) were not assignable, because of the comparable degree of incomplete stereocontrol in the silylcupration and methylation steps. We therefore made an authentic sample of one of them by converting Evans's ester **63**, which we had already used as the precursor of the aldehyde **56**, into the ester **60**. This gave rise to the signal at δ 3.335. We were thus able to assign all four isomers with confidence, especially as the assignment confirmed the assumptions made earlier. We were thus able to convert the ratios of products into ees and hence to measure the degree of stereospecificity in the reactions giving both the *syn* and the *anti* pairs of diastereoisomers, as reported in Section 2.

We were able to use the same analytical system for the products of the sequence in Scheme 3, because ozonolysis, reduction and esterification gave us the same esters **58**–**61**, in ratios, reading from low to high field, of 19:11:67:4 from the



Scheme 14 *Reagents:* i, H_2, Raney Ni, MeOH, H_2O, $B(OH)_3$; ii, $Me_4N(AcO)_3BH$, AcOH, MeOH; iii, KH, THF



Scheme 15 *Reagents:* i, O_3, MeOH; ii, H_2O_2, HCO_2H; iii, (*R*)-$PhCH(OH)CO_2Me$, DCC, DMAP; iv, (a) LDA (b) BuLi; v, $(CD_3)_2CO$; vi, LiOOH

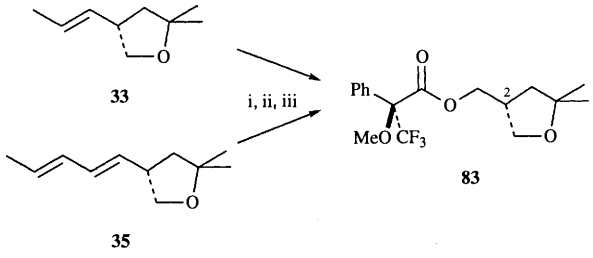
pentadienylsilane **14** with 100% ee, and 14:40:27:19 from the pentadienylsilane **17** with 23% ee.

The adducts **21** from the reactions in Scheme 5 are racemic, which required that we prove only the relative configuration between the silicon-bearing and the oxygen-bearing stereogenic centres. We separated the mixtures of adducts shown as **21aa**, **21ba** and **21bc** in Scheme 5 into the major **21** and minor **64** isomers illustrated in Scheme 14, and carried each diastereoisomer through the sequence. There was no particular need for us to use the highly stereoselective reductions **65** ⟶ **67** and **66** ⟶ **68**,[36] but it gave us cleaner products. The final step **67** ⟶ **69** and **68** ⟶ **70** identified the stereochemistry in the **aa** and **ba** series, for we had already proved that the vinylogous Peterson reaction was stereospecifically *syn*.[37] The major adducts **21aa** and **21ba** gave the *E,Z*-diene **69**, and the minor adducts **64aa** and **64ba** gave the *E,E*-diene **70**, easily identifiable by the coupling constants, 14 and 11 Hz for the diene **69** and 14 and 13 Hz for the diene **70**. However, in the corresponding elimination carried out in the **bc** series, both alcohols **67bc** and **68bc** gave the same *E,E*-diene **73**, showing that we had hit the limit of stereospecificity in the vinylogous Peterson reaction. We suggest that this observation adds further support to the idea[38] that the Peterson elimination takes place with a carbanion intermediate, which is created by the oxyanion removing the silyl group from carbon. The anion **72** produced from the isomer **68bc** with the 1,4-related silyl and hydroxy groups *syn* is set up for rapid elimination to give the *E,E*-diene. On the other hand the anion **71**, derived from the *anti* diastereoisomer **67bc**, evidently lives long enough for rotation to occur **71** ⟶ **72**, before elimination. This does not occur in a simple Peterson elimination with a benzylic silyl group; this type of system is known to be still *syn* stereospecific,[39] presumably because the rotation is slower than the elimination. The greater thermodynamic stability of the anions **71** and **72**, which are both benzylic and allylic, will give them a longer lifetime in which to rotate than that of a simple benzyl or unconjugated anion, and the extended conjugation will lower the kinetic barrier to rotation. The alcohol **73** was only obtained when we were careful to isolate the first-formed product after the minimum of time for disappearance of starting material. On further treatment with potassium hydride it easily gave the diene **74**.

In analysing the dienes produced in the reaction in Scheme 6, we first checked the stereochemistry of the double bonds, which were not in this case easily seen in the ^1H NMR spectrum to be *E,E*. Synthesis of an authentic mixture of the four possible dienes **77** (Scheme 15) gave, in order of elution from a GC column, four peaks in ratios of 40:36:12:12. A protodesilylation reaction similar to the reaction in Scheme 6 gave a mixture of dienes, rich in the *E,E* isomer **78**, with two peaks in a ratio of 97:3, coinciding with the second (major) and the third (minor) of the four peaks. Since the ylide **75** has an *E* double bond, the two major products **77** must be the *E,Z* and *E,E* isomers (reading from left to right as drawn), which we can therefore assign to the first and second peaks to be eluted. If we assume that the *Z,Z* isomer is not the minor product from the protodesilylation reaction, all four peaks can be assigned, eluting in the order *E,Z*, *E,E*, *Z,E* and *Z,Z*, and the protodesilylation reaction has as expected given very largely the

E,E isomer **78**, with 3% of the *Z,E* as a byproduct. Ozonolysis of the diene **78** from the protodesilylation reaction, and attachment of the derived acid to methyl (*R*)-mandelate [methyl (*R*)-2-hydroxy-2-phenylacetate], gave the ester **80**, which showed in its ^{1}H NMR spectrum the C-2 protons well resolved as double doublets at δ 2.21 and 2.12. Using Evans's phenylalanine-derived imide **81**, enolate deuteriation, and the same coupling with the (*R*)-mandelate, in a reaction known not to suffer significantly from racemisation,[40] we prepared a sample of the ester **82** stereospecifically deuteriated in the pro-*R* position on C-2. The ^{1}H NMR spectrum of this sample showed that the upfield signal at δ 2.12 was of reduced intensity (although, because of incomplete deuterium incorporation, it was not absent). This is in agreement with an observation by Parker that the upfield signal of mandelate esters of this type is from the pro-*R* proton.[41] Repetition of the ozonolysis sequence on the product **26** from deuteriodesilylation gave the mandelate **79**, contaminated unfortunately with the product **80** from protodesilylation, in a 50:50 ratio as determined from the mass spectrum. This made analysis of the ^{1}H NMR spectrum even less accurate than we might have hoped, but the two signals were present in a ratio of approximately 45:55, respectively, showing that the downfield signal was of reduced intensity, and that the major product **26** was that of *anti* attack.

We converted the products **33** and **35** of the successful intramolecular reactions in Scheme 8 into the Mosher's ester **83** and its epimer at C-2 (Scheme 16). The diastereoisomers were



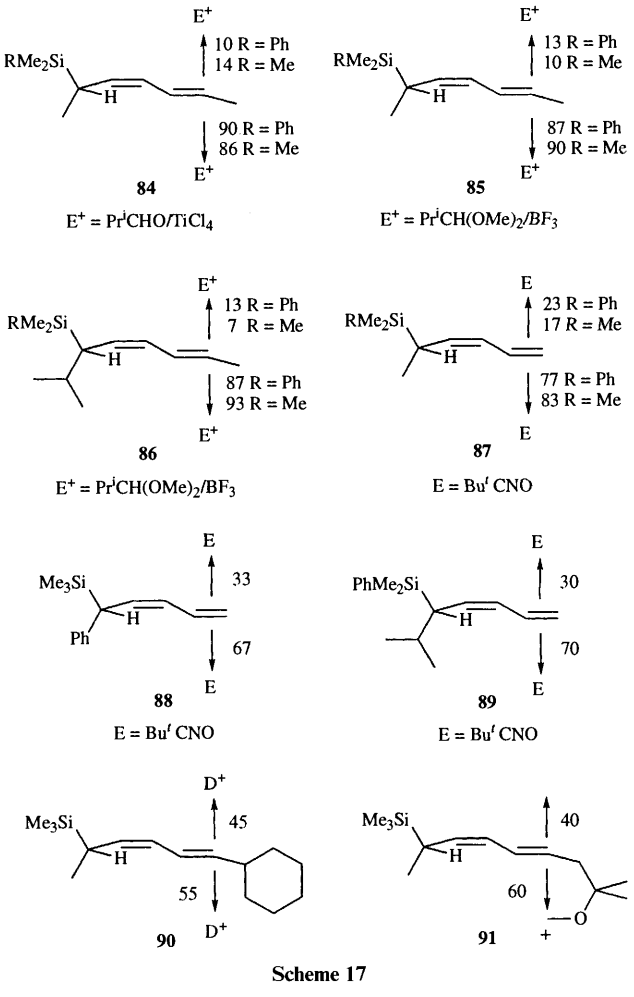
Scheme 16 *Reagents:* i, O_3, MeOH; ii, $NaBH_4$; iii, (*S*)-PhC(OMe)-$(CF_3)CO_2H$, DCC, DMAP

present in ratios of 95:5 and 60:40, respectively, as measured by integration of the ^{19}F and ^{1}H NMR spectra. We assume on the basis of much precedent [1,2,4] that the S_E2' reaction **32** ⟶ **33** was stereospecifically *anti*, and, since the major product **83** was the same, whether derived from the allylsilane **32** or the pentadienylsilane **34**, we can safely deduce that the S_E2'' reaction **34** ⟶ **35** was also *anti*.

8. Summary of results

In conclusion, large electrophiles in S_E2'' reactions of pentadienylsilanes show remarkably high levels of attack in the *anti* sense, as summarised in the drawings **84–86** (Scheme 17), which show the more reliable of our results measuring the ratios of attack on the lower and upper surfaces, all expressed in the same enantiomeric series and corrected for the incomplete enantiomeric purity of the pentadienylsilanes. The average ratio *anti*:*syn* is 89:11. The dipolar cycloadditions **87–89** are less selective, with an average ratio of 74:26, probably because the 'electrophile' is effectively smaller, but possibly also because it is less electrophilic in nature. Deuteriodesilylation **90** is less selective still, but the ratio 55:45 has a large margin for error associated with it. Finally the intramolecular reaction **91**, with an effectively small electrophilic centre, is only selective to the extent of 60:40, very similar to the results of Hayashi (Scheme 1), which are probably also free of substantial steric effects. Thus the ratio 60:40 appears to measure the extent of electronic control.

This conclusion, however, cannot be carried over to the corresponding reaction of allylsilanes, our starting point in all this work, because the extent of electronic control present in the



Scheme 17

S_E2'' reactions could be attenuated by its passing through a second double bond. Whether the high levels of *anti* selectivity seen with allylsilanes are largely steric or electronic in origin remains unknown.

Experimental

Reactions of pentadienylsilanes 9 and 13 with isobutyraldehyde

General procedure. Titanium tetrachloride (1 cm^3 of a 1 mol dm^{-3} solution in dichloromethane, 1 mmol) was added slowly with stirring to a solution of the pentadienylsilane (1 mmol) and isobutyraldehyde (1 mmol) in dichloromethane (4 cm^3) at −70 °C under nitrogen. After 3 min at −70 °C, water (1 cm^3) was added and the mixture allowed to warm to room temperature. Ether (30 cm^3)† was added and the ether layer washed with water (10 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure. Preparative TLC (SiO_2, hexane–EtOAc, 10:1) gave the products. The following compound was prepared by this method.

(5*E*,7*E*,3*R*,4*R*)-2,4-Dimethylnona-5,7-dien-3-ol 10a. As an oil (40% from **9**, 15% from **13**); R_f(hexane–EtOAc, 10:1) 0.4; ν_{max}(film)/cm^{-1} 3700–3100 (OH); δ_H($CDCl_3$; 250 MHz) 6.10–5.95 (2 H, m, MeCH=C*H*C*H*=CH), 5.7–5.55 (1 H, m, MeC*H*=CH), 5.52–5.43 (1 H, m, MeCH=CHCH=C*H*), 3.14 (1 H, t, *J* 5.8,‡ C*H*OH), 2.34 (1 H, apparent sextet, *J* 6.8, C=CHC*H*Me), 1.74 (1 H, m, C*H*Me_2), 1.73 (3 H, d, *J* 6, *Me*CH=C), 1.35 (1 H, br s, OH), 1.02 (3 H, d, *J* 6.8, C=CHCH*Me*) and 0.90 (6 H, d, *J* 6.8, Me_2CH); irradiating the multiplet at δ 2.34 gave δ 5.47 (1 H, dd, *J* 0.7 and 14.05, MeCH=CHCH=C*H*), 3.14 (1 H, d, *J* 5.8, C*H*OH), 1.02 (3 H, s, *Me*CHCH=CH) with other

† 'Ether' refers to diethyl ether.
‡ *J* Values given in Hz.

peaks unchanged; irradiating the peaks at δ 1.74 and 1.73 gave δ 5.61 (1 H, d, *J* 14.3, MeC*H*=CH), 3.14 (1 H, d, *J* 5.8, C*H*OH), 0.9 (6 H, s, CHMe_2) with other peaks unchanged.

Reactions of pentadienylsilanes with isobutyraldehyde dimethyl acetal

General procedure. Boron trifluoride–diethyl ether complex (0.24 cm^3, 2 mmol) was added slowly with stirring to a solution of the pentadienylsilane (1 mmol) and isobutyraldehyde dimethyl acetal (2 mmol) in dichloromethane (4 cm^3) at −70 °C under nitrogen. After 5 h at −70 °C, water (1 cm^3) was added and the mixture allowed to warm to room temperature. Ether (30 cm^3) was added and the ether layer washed with water (10 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure. Preparative TLC (SiO_2, hexane–EtOAc, 25:1) gave the products. The following compounds were prepared by this method.

(2*E*,4*E*,6*RS*,7*RS*)-7-Methoxy-6,8-dimethylnona-2,4-diene *10b* + *ent*-10b and (2*E*,4*E*,6*RS*,7*SR*)-7-methoxy-6,8-dimethylnona-2,4-diene 11b + *ent*-11b. As an oil (77% from the racemic pentadienylsilane **9**); R_f(hexane–EtOAc, 10:1) 0.54; ν_{max}(CH_2Cl_2)/cm^{-1} 3000–2800, 1450, 1360, 1090 and 990; δ_H($CDCl_3$) 6.03–5.91 (2 H, m, MeCH=C*H*C*H*=), 5.63–5.40 (2 H, m, MeC*H*=CH and MeCHC*H*=), 3.40 (3 H, s, OMe), 2.64 (1 H, dd, *J* 6.7 and 5, C*H*OMe), 2.33 (1 H, sextet, *J* 7, MeC*H*CH=), 1.74 (1 H, m, Me_2CH), 1.70 (3 H, d, *J* 6, *Me*CH=), 1.00 (3 H, d, *J* 6.7, *Me*CHCH=), 0.89 (3 H, d, *J* 6.9, Me_AMe_BCH) and 0.85 (3 H, d, *J* 6.7, Me_AMe_BCH); *m*/*z* 182 (0.32%, M^+), 167 (7, *M* − Me) and 87 (100, $Me_2CHCHOMe$) (Found: M^+, 182.1667. $C_{12}H_{22}O$ requires *M*, 182.1671).

(2*E*,4*E*,6*R*,7*R*)-7-Methoxy-6,8-dimethylnona-2,4-diene 10b and (2*E*,4*E*,6*R*,7*S*)-7-methoxy-6,8-dimethylnona-2,4-diene 11b. As an oil (72% from the homochiral dienylmethylsilane **9** of 92% ee).

(2*E*,4*E*,6*S*,7*S*)-7-Methoxy-6,8-dimethylnona-2,4-diene *ent*-10b and (2*E*,4*E*,6*S*,7*R*)-7-methoxy-6,8-dimethylnona-2,4-diene *ent*-11b. As an oil (75% from the homochiral dienylmethylsilane **13** of 33% ee).

(3*E*,5*E*,7*RS*,8*RS*)-8-Methoxy-2,7,9-trimethyldeca-3,5-diene 15 and *ent*-15 and (3*E*,5*E*,7*RS*,8*SR*)-8-methoxy-2,7,9-trimethyldeca-3,5-diene 16 and *ent*-16. As an oil (74% from racemic pentadienylsilane **14**); R_f(hexane–EtOAc, 25:1) 0.37; ν_{max}(film)/cm^{-1} 1450 (C=C); δ_H(250 MHz; $CDCl_3$) 6.05–5.89 (2 H, m, =CHCH=), 5.55 (1 H, dd, *J* 6.6 and 14.7, Pr^iCH), 5.50 (1 H, dd, *J* 8.6 and 14.3, C*H*CHMe), 3.43 (3 H, s, OMe), 2.67 (1 H, dd, *J* 5 and 6.6, C*H*OMe), 2.39–2.26 (2 H, m, Me_2CHCH=CH and MeC*H*CHOMe), 1.76 (1 H, d septet, *J* 4.9 and 6.7, Me_2CH), 1.03 (3 H, d, *J* 6.7, Me_AMe_BCHCH=CH), 0.99 (3 H, d, *J* 6.7, Me_AMe_BCHCH=CH), 0.99 (3 H, d, *J* 6.7, *Me*CH), 0.91 (3 H, d, *J* 6.9, Me_AMe_BCH) and 0.88 (3 H, *J* 6.7, Me_AMe_BCH); *m*/*z* 210 (0.16%, M^+) and 87 (100, MeOCHPr^i) (Found: M^+, 210.1980. $C_{14}H_{26}O$ requires *M*, 210.1984).

(3*E*,5*E*,7*R*,8*R*)-8-Methoxy-2,7,9-trimethyldeca-3,5-diene 15 and (3*E*,5*E*,7*R*,8*S*)-8-methoxy-2,7,9-trimethyldeca-3,5-diene 16. As an oil (77% from the pentadienylsilane **14** of 100% ee).

(3*E*,5*E*,7*S*,8*S*)-8-Methoxy-2,7,9-trimethyldeca-3,5-diene *ent*-15 and (3*E*,5*E*,7*S*,8*R*)-8-methoxy-2,7,9-trimethyldeca-3,5-diene *ent*-16. As an oil (68% from **17**).

1,3-Dipolar cycloadditions

General procedure.[42] Sodium hypochlorite (2 cm^3 of a 1 mol dm^{-3} solution in water), the diene (0.49 mmol) and 2,2-dimethylpropanal oxime[43] (150 mg, 1.49 mmol) were kept in dichloromethane (3 cm^3) in an ultrasonic cleaning bath at room temperature for 48 h. The mixture was quenched with water (10 cm^3) and extracted with dichloromethane (2 × 30 cm^3). The organic extracts were combined, dried ($MgSO_4$) and evaporated under reduced pressure to give a mixture of the isoxazolines, in ratios measured by integration of the CHO or SiMe peaks in the ^{1}H NMR spectrum and of several peaks in the ^{13}C NMR spectrum. Separation of the isoxazolines (SiO_2, hexane–EtOAc, 40:1) gave the minor, faster-eluting isomer and the major, slower-eluting isomer. (The separated diastereoisomers **21ba** and **64ba** were resubjected to the reaction conditions for 4 d and showed no equilibration.) The following compounds were prepared by this method.

(5*RS*)-3-(1,1-Dimethylethyl)-5-[(1*Z*,3*RS*)-3-dimethyl(phenyl)-silylbut-1-enyl]-4,5-dihydroisoxazole 21aa. As an oil (57%); R_f(SiO_2, hexane–EtOAc, 9:1) 0.22; ν_{max}(film)/cm^{-1} 3070, 3010, 2960, 2860 (CH), 1640 (C=C), 1620 (C=N), 1250 (SiMe) and 1110 (SiPh); δ_H($CDCl_3$; 250 MHz) 7.49–7.44 (2 H, m, *o*-SiPh), 7.38–7.31 (3 H, m, *m*- and *p*-SiPh), 5.42 (1 H, t, *J* 10.9, SiCH-C*H*=CHCHO), 5.28 (1 H, dd, *J* 9.4 and 10.7, SiCHCH=C*H*-CHO), 4.84 (1 H, q, *J* 9.7, CHO), 2.15 (1 H, dq, *J* 11.1 and 7.1, MeC*H*), 2.06 (2 H, d, *J* 10.0, CH_2), 1.11 (3 H, d, *J* 7.1, *Me*CH), 1.09 (9 H, s, CMe_3), 0.30 (3 H, s, SiMe_AMe_B) and 0.26 (3 H, s, $SiMe_AMe_B$); *m*/*z* 315 (0.1%, M^+), 314 (0.1, M − H), 300 (0.8, M − Me), 258 (1.6, M − CMe_3), 218 (7, M − CMe_3 − C_2H_2N), 151 (5, $PhMe_2SiO$), 135 (93, $PhMe_2Si$), 107 (86, C_7H_9N), 81 (67, C_6H_9) and 57 (100, CMe_3) (Found: M^+, 315.2028. $C_{19}H_{29}NOSi$ requires *M*, 315.2018).

(5*SR*)-3-(1,1-Dimethylethyl)-5-[(1*Z*,3*RS*)-3-dimethyl(phenyl)-silylbut-1-enyl]-4,5-dihydroisoxazole 64aa. An oil (17%); R_f(SiO_2, hexane–EtOAc, 9:1) 0.27; ν_{max}(film)/cm^{-1} 3070, 3010, 2960, 2860 (CH), 1640 (C=C), 1620 (C=N), 1250 (SiMe) and 1110 (SiPh); δ_H($CDCl_3$; 250 MHz) 7.53–7.47 (2 H, m, *o*-SiPh), 7.38–7.32 (3 H, m, *m*- and *p*-SiPh), 5.46–5.32 (2 H, m, CH=CH), 5.22–5.08 (1 H, m, CHO), 3.05 (1 H, dd, *J* 9.9 and 16.6, CH_AH_B), 2.63 (1 H, dd, *J* 9.8 and 16.6, CH_AH_B), 2.10 (1 H, dq, *J* 10.9 and 7.1, MeC*H*), 1.19 (9 H, s, CMe_3), 0.99 (3 H, d, *J* 7.1, *Me*CH), 0.33 (3 H, s, SiMe_AMe_B) and 0.32 (3 H, s, $SiMe_AMe_B$); *m*/*z* 315 (0.05%, M^+), 314 (0.05, M − H), 300 (0.4, M − Me), 258 (1, M − CMe_3), 218 (5, M − CMe_3 − C_2H_2N), 151 (3, $PhMe_2SiO$), 135 (80, $PhMe_2Si$), 107 (60, C_7H_9N), 81 (42, C_6H_9) and 57 (100, CMe_3) (Found: M^+, 315.1991. $C_{19}H_{29}NOSi$ requires *M*, 315.2018).

(5*RS*)-3-(1,1-Dimethylethyl)-5-[(1*Z*,3*RS*)-3-trimethylsilyl-but-1-enyl]-4,5-dihydroisoxazole 21ba. As an oil (65%); R_f(SiO_2, hexane–EtOAc, 9:1) 0.26; ν_{max}(film)/cm^{-1} 3010, 2960, 2870 (CH), 1640 (C=C), 1605 (C=N) and 1250 (SiMe); δ_H($CDCl_3$; 250 MHz) 5.47–5.30 (2 H, m, CH=CH), 5.17 (1 H, m, CHO), 2.98 (1 H, dd, *J* 9.8 and 16.5, CH_AH_B), 2.62 (1 H, dd, *J* 9.6 and 16.5, CH_AH_B), 1.93 (1 H, dq, *J* 10.8 and 7.0, MeC*H*), 1.18 (9 H, s, CMe_3), 1.05 (3 H, d, *J* 7.0, *Me*CH) and −0.05 (9 H, s, Me_3Si); *m*/*z* 254 (0.2%, M + H), 253 (0.2, M^+), 238 (1.5, M − Me), 196 (2.4, M − Me_3C), 156 (15, M − Me_3C − C_2H_2N), 107 (40, C_7H_9N), 81 (39, C_6H_9), 73 (95, Me_3Si) and 57 (100, Me_3C) (Found: M^+, 253.1850. $C_{14}H_{27}NOSi$ requires *M*, 253.1861).

(5*SR*)-3-(1,1-Dimethylethyl)-5-[(1*Z*,3*RS*)-3-trimethylsilyl-but-1-enyl]-4,5-dihydroisoxazole 64ba. As an oil (16%); R_f(SiO_2, hexane–EtOAc, 9:1) 0.32; ν_{max}(film)/cm^{-1} 3010, 2960, 2870 (CH), 1640 (C=C), 1605 (C=N) and 1250 (SiMe); δ_H($CDCl_3$; 250 MHz) 5.47–5.30 (2 H, m, CH=CH), 5.13 (1 H, m, CHO), 3.04 (1 H, dd, *J* 9.8 and 16.5, CH_AH_B), 2.61 (1 H, dd, *J* 9.9 and 16.5, CH_AH_B), 1.88 (1 H, dq, *J* 10.8 and 7.1, MeC*H*), 1.17 (9 H, s, CMe_3), 1.01 (3 H, d, *J* 7.1, *Me*CH) and −0.01 (9 H, s, Me_3Si); *m*/*z* 254 (0.5%, M + H), 253 (0.5, M^+), 252 (0.5, M − H), 238 (2, M − Me), 196 (7, M − Me_3C), 156 (18, M − Me_3C − C_2H_2N), 107 (58, C_7H_9N), 81 (50, C_6H_9), 73 (91, Me_3Si) and 57 (100, Me_3C) (Found: M^+, 253.1844. $C_{14}H_{27}NOSi$ requires *M*, 253.1861).

(5*RS*)-3-(1,1-Dimethylethyl)-5-[(1*Z*,3*SR*)-3-trimethylsilyl-3-phenylprop-1-enyl]-4,5-dihydroisoxazole 21bc. As needles, mp 70–71 °C (from hexane) (48%); R_f(EtOAc–hexane, 10:90) 0.13; ν_{max}(Nujol)/cm^{-1} 1590 (Ph), 1240 and 830 ($SiMe_3$); δ_H(250 MHz; $CDCl_3$) 7.28–7.21 (2 H, m, *o*-ArH), 7.12–7.05 (3 H, m, *m*- and *p*-ArH), 6.05 (1 H, dd, *J* 11.0 and 12.0, SiCHC*H*), 5.52 (1 H, dd, *J* 9.6 and 11.0, SiCHCH=C*H*), 5.29 (1 H, dt, *J* 9.6 and 9.8, CHO), 3.33 (1 H, d, *J* 12.0, SiCH), 3.06 (1 H, dd, *J* 9.8 and 16.5, CH_AH_B), 2.70 (1 H, dd, *J* 9.8 and 16.5, CH_AH_B), 1.20 (9 H, s,

CMe_3) and −0.05 (9 H, s, $SiMe_3$); *m/z* 315 (9%, M^+), 73 (100, $SiMe_3$) and 57 (100, CMe_3) (Found: M^+, 315.1993. $C_{19}H_{29}NOSi$ requires *M*, 315.2021).

(5*SR*)-3-(1,1-Dimethylethyl)-5-[(1*Z*,3*SR*)-3-trimethylsilyl-3-phenylprop-1-enyl]-4,5-dihydroisoxazole 64bc. As needles, mp 89–91 °C (from hexane) (25%); R_f(EtOAc–hexane, 10:90) 0.18; ν_{max}(Nujol)/cm^{-1} 1590 (Ph) and 1240 and 830 ($SiMe_3$); δ_H(250 MHz; $CDCl_3$) 7.28–7.22 (2 H, m, *o*-ArH), 7.13–7.04 (3 H, m, *m*- and *p*-ArH), 6.07 (1 H, dd, *J* 11.0 and 12.0, SiCHC*H*), 5.54 (1 H, dd, *J* 9.5 and 11.0, SiCHCH=C*H*), 5.25 (1 H, dt, *J* 9.5 and 9.9, CHO), 3.31 (1 H, d, *J* 12.0, SiCH), 2.98 (1 H, dd, *J* 9.9 and 16.5, CH_AH_B), 2.59 (1 H, dd, *J* 9.9 and 16.5, CH_AH_B), 1.17 (9 H, s, CMe_3) and 0.00 (9 H, s, $SiMe_3$); *m/z* 315 (10%, M^+), 73 (100, $SiMe_3$) and 57 (95, CMe_3) (Found: M^+, 315.2018. $C_{19}H_{29}NOSi$ requires *M*, 315.2021).

(5*RS*)-(1,1-Dimethylethyl)-5-[(1*Z*,3*RS*)-3-dimethyl(phenyl)-silyl-4-methylpent-1-enyl]-4,5-dihydroisoxazole 21ab. As an oil (56%); R_f(hexane–EtOAc, 5:1) 0.44; δ_H(250 MHz; $CDCl_3$) 7.48–7.43 (2 H, m, *o*-Ph), 7.34–7.30 (3 H, m, *m*- and *p*-Ph), 5.58 (1 H, t, *J* 11.4, SiCHC*H*=CH), 5.43 (1 H, dd, *J* 9.0 and 11.0, SiCHCH=C*H*), 4.80 (1 H, q, *J* 9.6, CHO), 2.07 (2 H, d, *J* 10, CH_2), 2.07–1.92 (2 H, m, CHSi and Me_2CH), 1.08 (9 H, s, CMe_3), 0.92 (6 H, d, *J* 6.7, Me_2CH), 0.34 (3 H, s, Me_AMe_BSi) and 0.31 (3 H, s, Me_AMe_BSi); δ_C(63 MHz; $CDCl_3$) 166.3, 138.7, 134.1, 134.0, 132.3, 127.7, 127.1, 76.4, 39.6, 36.3, 32.9, 29.7, 27.9, 23.9, 20.3, −3.0 and −4.0; *m/z* 343 (0.6%, M^+), 231 (5%, $M - C_6H_{10}NO$) and 135 (100, $PhMe_2Si$) (Found: M^+, 343.2319. $C_{21}H_{33}NOSi$ requires *M*, 343.2331).

(5*SR*)-3-(1,1-Dimethylethyl)-5-[(1*Z*,3*RS*)-3-dimethyl(phenyl)-silyl-4-methylpent-1-enyl]-4,5-dihydroisoxazole 64ab. As an oil (24%); R_f(hexane–EtOAc, 5:1) 0.5; $\nu_{max}(CH_2Cl_2)$/cm^{-1} 1640 (C=C), 1620 (C=N), 1250 (SiMe) and 1110 (SiPh); δ_H(250 MHz; $CDCl_3$) 7.54–7.49 (2 H, m, *o*-Ph), 7.35–7.30 (3 H, m, *m*- and *p*-Ph), 5.62–5.49 (2 H, m, CH=CH), 5.14 (1 H, m, CHO), 3.02 (1 H, dd, *J* 10 and 16.5, CH_AH_B), 2.64 (1 H, dd, *J* 10 and 16.5, CH_AH_B), 2.00 (1 H, dd, *J* 5.3 and 11.4, CHSi), 1.83 (1 H, m, Me_2CH), 1.19 (9 H, s, CMe_3), 0.80 (3 H, d, *J* 6.7, Me_AMe_BCH), 0.79 (3 H, d, *J* 6.7, Me_AMe_BCH), 0.34 (3 H, s, Me_AMe_BSi) and 0.33 (3 H, s, Me_AMe_BSi); $\delta_C(CDCl_3)$ 166.0, 138.2, 134.0, 133.9, 133.5, 128.9, 127.5, 76.6, 40.6, 36.6, 33.1, 29.3, 28.7, 24.0, 20.6, −2.6 and −3.8.

(5*RS*)-3-Phenyl-5-[(1*Z*,3*RS*)-3-trimethylsilylbut-1-enyl]-4,5-dihydroisoxazole 22. As an oil (55%); R_f(hexane–EtOAc, 9:1) 0.32; δ_H(250 MHz; $CDCl_3$) 7.67–7.62 (2 H, m, *o*-Ph), 7.41–7.37 (3 H, m, *m*- and *p*-Ph), 5.56-5.35 (3 H, m, CH=CHCHO), 3.41 (1 H, dd, *J* 9.6 and 16.5, CH_AH_BC=N), 3.04 (1 H, dd, *J* 9.4 and 16.5, CH_AH_BC=N), 2.00 (1 H, dq, *J* 10.6 and 7, *Me*CHSi), 1.00 (3 H, d, *J* 7, MeC*H*Si) and 0.00 (9 H, s, $SiMe_3$); δ_C(63 MHz; $CDCl_3$) 156.6, 139.0, 129.9, 128.7, 128.3, 126.6, 123.7, 77.3, 41.0, 22.9, 14.9 and −3.5; *m/z* 273 (0.37%, M^+) and 73 (100, Me_3Si) (Found: M^+, 273.1560. $C_{16}H_{23}NOSi$ requires *M*, 273.1548).

(5*SR*)-3-Phenyl-5-[(1*Z*,3*RS*)-3-trimethylsilylbut-1-enyl]-4,5-dihydroisoxazole. As an oil (21%); R_f(hexane–EtOAc, 9:1) 0.36; $\nu_{max}(CH_2Cl_2)$/cm^{-1} 1640 (C=C), 1620 (C=N/C=C) and 1250 (SiMe); δ_H(250 MHz; $CDCl_3$) 7.67–7.62 (2 H, m, *o*-Ph), 7.39–7.37 (3 H, m, *m*- and *p*-Ph), 5.55–5.32 (3 H, m, CH=CHCHO), 3.47 (1 H, dd, *J* 9.7 and 16.4, CH_AH_BC=N), 3.03 (1 H, dd, *J* 9.3 and 16.4, CH_AH_BC=N), 1.96 (1 H, dq, *J* 10.6 and 7.1, MeC*H*Si), 1.07 (3 H, d, *J* 7.1, *Me*CHSi) and 0.04 (9 H, s, Me_3Si); δ_C(63 MHz; $CDCl_3$) 156.6, 139.9, 129.9, 129.8, 128.7, 126.6, 124.3, 76.4, 41.2, 23.0, 15.1 and −3.4.

Deuteriodesilylation of the pentadienylsilane 25

Deuteriotrifluoroacetic acid (0.77 cm^3) was added dropwise to a stirred solution of the diene **25** (118 mg, 0.5 mmol) in deuteriochloroform (3 cm^3) under argon at 0 °C. The reaction was stirred at 0 °C for 30 min and then allowed to warm to room temperature over 10 min. The reaction was quenched with saturated aqueous sodium hydrogen carbonate (5 cm^3) and the organic layer washed with sodium hydrogen carbonate (2 × 8 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure to give a mixture of (2E,4E,1S)-1-*cyclohexyl*-1-*deuteriohexa*-2,4-*diene* **26** and (2E,4E)-1-*cyclohexylhexa*-2,4-*diene* **78** (73 mg, 88%); R_f(hexane) 0.58; R_t(GLC Carlo Erba Strumentazione 4130, 24 m, BP5, 5% phenylmethylsiloxane column, 5 μm film thickness, He carrier gas, ≈0.3 m s^{-1} temperature programme) 16.243 min (*E*,*E*); $\nu_{max}(CDCl_3)$/cm^{-1} 1455 (C=C); δ_H(250 MHz; $CDCl_3$) 6.02 (1 H, ddq, *J* 10.3, 14.4 and 1.5, C*H*=CHMe), 5.95 (1 H, dd, *J* 10.3 and 10.5, C*H*CH=CHMe), 5.66–5.48 (2 H, m, C*H*=CHCH=C*H*Me), 1.96–1.89 (1.2 H, m, CD*H*CH=CH), 1.73 (9 H, m, 6 H in ring and CH*Me*) and 1.25–0.78 (5 H, m, 5 CH in ring); *m/z* 165 (19.89%, M^+), 164 (18, M − H or $C_{12}H_{20}$), 83 (67, C_6H_{11}) and 73 (100, Me_3Si impurity) (Found: M^+, 165.1613. $C_{12}H_{19}D$ requires *M*, 165.1627). Ratio in mass spectrum of 164:165:166 was 38:45:17.

Reaction of acid with the pentadienylsilane 29

Boron trifluoride–diethyl ether complex was added to a solution of the diene **29** (16 mg, 0.05 mmol) in dry deuteriochloroform (0.3 cm^3) under argon at room temperature in a dry NMR tube. The sample was placed in the NMR spectrometer and spectra were recorded at 5, 40, 75 and 120 min after the addition of the boron trifluoride–ether complex. After 135 min the reaction was quenched with a solution of saturated sodium hydrogen carbonate (0.5 cm^3) and dichloromethane (1 cm^3) added. The layers were separated and the organic layer dried ($MgSO_4$) and evaporated under reduced pressure to give the crude product (14 mg). This reaction was repeated on a larger scale (4×) and the reaction mixture purified by chromatography (SiO_2, $AgNO_3$, eluting with hexane) allowing isolation of the still impure major product to which we assigned the structure 10-*methylundeca*-2,4,8-*triene* **30** (20 mg) as a colourless oil; R_t(GLC Carlo Erba Strumentazione 4130, 24 m, BP5, 5% phenylmethylsiloxane column, 5 μm film thickness, He carrier gas, ≈0.3 m s^{-1}, 90 °C) 18.77 min; δ_H(250 MHz; $CDCl_3$) 6.02–5.97 (2 H, m, C*H*–C*H*=CHMe), 5.59–5.51 (2 H, m, C*H*=CHCH=C*H*Me), 5.09 (1 H, t, *J* 6.9, Me_2C=C*H*), 2.04–1.94 (4 H, m $CH_2CH_2CH_2$), 1.72 (3 H, d, *J* 6.4, *Me*CH=CH), 1.67 (3 H, s, Me_AMe_BC), 1.58 (3 H, s, Me_AMe_BC) and 1.39 (2 H, quintet, *J* 7.4, $CH_2CH_2CH_2$); *m/z* 163 (10%, M^+ − H) and 135 (100, $PhMe_2Si$ impurity) (Found: M^+ − H, 163.1471. $C_{12}H_{20}$ requires *M* − H, 163.1538).

1-(2,2-Dimethylcyclopentyl)propene 28

Freshly distilled titanium tetrachloride was added dropwise at −60 °C to the *Z* allylsilane **27** (135 mg, 0.44 mmol) in dry deuteriochloroform (6 cm^3) and the solution stirred for 1 h. The mixture was quenched with a saturated solution of sodium hydrogen carbonate. The organic layer was separated and washed successively with saturated aqueous sodium hydrogen carbonate and saturated brine, and dried ($MgSO_4$) to give the hydrocarbon, $\nu_{max}(CHCl_3)$ 1375 (CMe) and 920 (*trans*-CH=CH); $\delta_H(CDCl_3)$ 5.37–5.31 (2 H, m, CH=CH), 1.80–1.35 (6 H, m, 3 × CH_2), 1.66 (3 H, d, *J* 5.7, *Me*CH=CH), 0.92 (3 H, s, CMe_AMe_B) and 0.72 (3 H, s, CMe_AMe_B); *m/z* 137 (100%, M^+ − H) and 91 (13). This material was further characterised by ozonolysis, see below, without further purification.

(4*S*)-4-(Prop-1-enyl)-2,2-dimethyltetrahydrofuran 33

Titanium tetrachloride (323 mg, 1.70 mmol) was added dropwise to a stirred solution of the allylsilane **32** (400 mg, 1.39 mmol) in dichloromethane (10 cm^3) at −78 °C under argon. The mixture was stirred for 1.5 h, quenched with sodium hydroxide solution (20%, 10 cm^3) and extracted with dichloromethane (2 × 10 cm^3). The extract was dried ($MgSO_4$) and evaporated. The residue was chromatographed (SiO_2, dichloromethane) to give the *alkene* (168 mg, 86%) as a

colourless oil, R_f(EtOAc–hexane, 20:80) 0.55; ν_{max}(film)/cm^{-1} 1060 (C–O) and 970 (*trans*-CH=CH); δ_H(250 MHz; $CDCl_3$) 5.46 (1 H, ddq, *J* 0.4, 15.2 and 6.1, MeC*H*=CH), 5.31 (1 H, ddq, *J* 7.8, 15.2 and 1.3, McCH=C*H*), 3.91 (1 H, t, *J* 8.0, OCH_AH_B), 3.44 (1 H, t, *J* 8.8, OCH_AH_B), 2.91 (1 H, apparent *sextet*, *J* 8.8, C*H*CH=CH), 1.88 (1 H, dd, *J* 7.8 and 12.3, CH_AH_BCMe$_2$), 1.62 (3 H, dd, *J* 1.3 and 6.3, *Me*CH=CH), 1.48 (1 H, dd, *J* 10.0 and 12.3, CH$_A$*H*$_B$CMe$_2$), 1.26 (3 H, s, C*Me*$_A$Me$_B$) and 1.19 (3 H, s, CMe$_A$*Me*$_B$); $[\alpha]_D$ −3.7 (*c* 1.2 in $CHCl_3$) (Found: C, 76.8; H, 11.7. $C_9H_{16}O$ requires C, 77.1; H, 11.5%).

(4*S*)-4-(Penta-1,3-dienyl)-2,2-dimethyltetrahydrofuran 35

Titanium tetrachloride (33 mg, 0.17 mmol) was added dropwise to a stirred solution of the pentadienylsilane **34** (44 mg, 0.142 mmol) in dichloromethane (2 cm^3) at −78 °C under argon. The mixture was stirred for 0.5 h, quenched with sodium hydroxide solution (20%, 2 cm^3) and extracted with dichloromethane (3 × 2 cm^3). The extract was dried ($MgSO_4$) and the solvent evaporated. The residue was chromatographed (SiO_2, dichloromethane) to give the *diene* (20 mg, 85%); R_f(EtOAc–hexane, 20:80) 0.59; ν_{max}(film)/cm^{-1} 1060 (C–O) and 995 (*trans*-CH=CH); δ_H(250 MHz; $CDCl_3$) 6.10–5.91 (2 H, m, MeCH=C*H*C*H*=CH), 5.64 (1 H, dq, *J* 13.7 and 6.8, MeC*H*=CHCH=CH), 5.43 (1 H, dd, *J* 8.0 and 13.7, MeCH=CHCH=C*H*), 3.95 (1 H, t, *J* 8.0, OCH_AH_B), 3.48 (1 H, t, *J* 8.7, OCH$_A$*H*$_B$), 2.98 (1 H, br sextet, *J* 8.5, C*H*CH=CH), 1.93 (1 H, dd, *J* 7.8 and 12.3, CH_AH_BCMe$_2$), 1.72 (3 H, d, *J* 6.2, *Me*CH=CH), 1.52 (1 H, dd, *J* 9.9 and 12.3, CH$_A$*H*$_B$CMe$_2$), 1.28 (3 H, s, C*Me*$_A$Me$_B$) and 1.21 (3 H, s, CMe$_A$*Me*$_B$); *m*/*z* 166 (25%, M$^+$); $[\alpha]_D$ +0.71 (*c* 1.0 in $CHCl_3$) (Found: M$^+$, 166.1347. $C_{11}H_{18}O$ requires *M*, 166.1358).

Syntheses of the β-silyl esters and imides

The syntheses of imides **37a**[28] and **42d**,[30] and the esters **38a**,[28] **43a** and **43b**,[30] are described elsewhere.

Methyl (3*RS*)-3-dimethyl(phenyl)silyl-4-methylpentanoate. Dimethyl(phenyl)silyllithium (96 mmol) was added to copper(I) cyanide (4.32 g, 48 mmol) under argon at 0 °C. After 1 h the solution was cooled to −78 °C and methyl 4-methylpent-2-enoate[44] (4.98 g, 48 mmol) added in dry THF (25 cm^3). The solution was stirred for 3 h at −78 °C, quenched with saturated aqueous ammonium chloride (100 cm^3), and allowed to warm to room temperature. The mixture was extracted with ether (3 × 150 cm^3), the extracts combined, washed with saturated aqueous ammonium chloride (100 cm^3), dried ($MgSO_4$), and the solvent evaporated under reduced pressure. The residue was distilled [bp 113–115 °C at 0.5 mmHg (lit.,[34] 113–116 °C at 0.5 mmHg) to give the *methyl ester* (8.69 g, 84%); R_f(hexane–EtOAc, 9:1) 0.47; ν_{max}(film)/cm^{-1} 1723 (C=O), 1242 (SiMe) and 1103 (SiPh); δ_H(80 MHz; $CDCl_3$) 7.69–7.25 (5 H, m, PhMe$_2$Si), 3.57 (3 H, s, CO_2Me), 2.36 (2 H, m, CH_2CO$_2$Me), 1.97–1.84 (1 H, m, Me$_2$C*H*), 1.53 (1 H, m, CHSi), 0.93 (3 H, d, *J* 6.6, *Me*$_A$Me$_B$CH), 0.85 (3 H, d, *J* 6.6, Me$_A$*Me*$_B$CH) and 0.34 (6 H, s, Me$_2$Si).

(3*RS*)-3-Dimethyl(phenyl)silyl-4-methylpentanoic acid. The methyl ester above (6.35 g, 24 mmol) in THF (90 cm^3), water (30 cm^3) and methanol (10 cm^3) was refluxed overnight with lithium hydroxide (2.88 g, 115 mmol). The volatile solvents were evaporated under reduced pressure, and the resulting aqueous layer diluted with water (50 cm^3), and washed with ether (100 cm^3). The alkaline layer was acidified at 0 °C with dilute hydrochloric acid (3 mol dm^{-3}) and extracted with ether (4 × 100 cm^3). The extracts were combined, dried ($MgSO_4$) and evaporated under reduced pressure to give the acid (5.67 g, 95%) as an oil; R_f(hexane–EtOAc, 9:1) 0.19 (streak); ν_{max}(film)/cm^{-1} 3000 br (OH), 1705 (C=O), 1250 (SiMe) and 1110 (SiPh); δ_H(80 MHz; $CDCl_3$) 9.11 (1 H, br s, OH), 7.67–7.24 (5 H, m, PhSi), 2.38 (2 H, m, CH_2CO$_2$H), 1.94 (1 H, m, Me$_2$C*H*), 1.53 (1 H, m, CHSi), 0.96 (3 H, d, *J* 6.6, *Me*$_A$Me$_B$CH), 0.88 (3 H, d, *J* 6.6, Me$_A$*Me*$_B$CH) and 0.34 (6 H, s, Me$_2$Si), identical with the spectrum of the known enantiomerically enriched acid.[28]

Allyl (3*RS*)-3-dimethyl(phenyl)silyl-4-methylpentanoate 43c. Oxalyl chloride (4 cm^3, 45 mmol) was stirred with the acid above (6.06 g, 24 mmol) in dry dichloromethane (20 cm^3) at room temperature under argon for 2 h. The solvent was removed under reduced pressure, the residue dissolved in dry ether (20 cm^3) and the solution stirred under argon. Dry allyl alcohol (7 cm^3) was added, followed by the dropwise addition of triethylamine (7 cm^3) which produced an unstirrable suspension. After 1 h the reaction was quenched with water (20 cm^3) and the mixture extracted with ether (4 × 50 cm^3). The extracts were combined, dried ($MgSO_4$) and evaporated under reduced pressure. The residue was distilled (Kugelrohr, 160–164 °C/5 mmHg) to give the racemic *ester* (6.40 g, 91%); R_f(hexane–EtOAc, 5:1) 0.53; ν_{max}(film)/cm^{-1} 1740 (C=O), 1250 (SiMe) and 1110 (SiPh); δ_H(250 MHz; $CDCl_3$) 7.54–7.48 (2 H, m, *o*-SiPh), 7.37–7.30 (3 H, m, *m*- and *p*-SiPh), 5.87 (1 H, ddt, *J* 17.3, 10.3 and 5.8, C*H*=CH$_2$), 5.27 (1 H, dq, *J* 17.3 and 1.3, CH=C*H*$_A$H$_B$), 5.20 (1 H, dq, *J* 10.3 and 1.3, CH=CH$_A$*H*$_B$), 4.45 (2 H, dt, *J* 5.8 and 1.3, CH$_2$C=), 2.36 (1 H, dd, *J* 7.6 and 17.7, CH_AH_BCO$_2$), 2.34 (1 H, dd, *J* 6.2 and 17.7, CH$_A$*H*$_B$CO$_2$), 1.92 (1 H, m, C*H*Me$_2$), 1.53 (1 H, m, C*H*Si), 0.91 (3 H, d, *J* 6.6, *Me*$_A$Me$_B$CH), 0.84 (3 H, d, *J* 6.6, Me$_A$*Me*$_B$CH), 0.34 (3 H, s, *Me*$_A$Me$_B$Si) and 0.32 (3 H, s, Me$_A$*Me*$_B$Si); *m*/*z* 290 (0.59%, M$^+$) and 135 (100, PhMe$_2$Si) (Found: M$^+$, 290.1717. $C_{17}H_{26}O_2Si$ requires *M*, 290.1691).

Preparation of the imides 37

General procedure. Oxalyl chloride (5 cm^3) was added to a stirred solution of the acid (28.2 mmol) in dry dichloromethane (50 cm^3) at room temperature. After 2 h the solvent was evaporated under reduced pressure and the resulting acid chloride dissolved in dry THF (20 cm^3). Butyllithium (1.51 mol dm^{-3} solution in hexane; 18.5 cm^3, 28 mmol) was added to a stirred solution of the lactam (28 mmol), in dry THF (60 cm^3) at −20 °C under argon. After 20 min the solution was cooled to −78 °C and the acid chloride solution added dropwise. After stirring for 0.5 h, the solution was allowed to warm to room temperature and then quenched with saturated aqueous ammonium chloride (100 cm^3). The mixture was extracted with ether (3 × 150 cm^3), the extracts combined, dried ($MgSO_4$) and evaporated under reduced pressure to give the imide. The following compounds were prepared by this method.

(5*S*)-1-[(2*E*)-4-Methylpent-2-enoyl]-5-(triphenylmethoxymethyl)pyrrolidin-2-one 37b. As prisms, mp 118–119 °C (from hexane–EtOAc) (80–94%); $[\alpha]_D$ −73.9 (*c* 4.59 in $CHCl_3$); R_f(hexane–EtOAc, 5:1) 0.25; ν_{max}($CHCl_3$)/cm^{-1} 1725 (C=O), 1655 (C=O) and 1620 (C=C); δ_H(250 MHz; $CDCl_3$) 7.37–7.18 (16 H, m, Ph$_3$CO and Pr^{i}C*H*=CH), 7.09 (1 H, dd, *J* 6.7 and 15.5, CH=C*H*CO), 4.53 (1 H, m, CHN), 3.54 (1 H, dd, *J* 4.0 and 9.3, CH_AH_BOCPh$_3$), 3.14 (1 H, dd, *J* 2.7 and 9.3, CH$_A$C*H*$_B$OCPh$_3$), 3.03–1.9 (5 H, m, CH$_2$CH$_2$CO and Me$_2$C*H*), 1.12 (3 H, d, *J* 6.8, *Me*$_A$Me$_B$CH) and 1.10 (3 H, d, *J* 6.8, Me$_A$*Me*$_B$CH) (Found: C, 79.5; H, 6.95; N, 3.1; M$^+$, 453.2337. $C_{30}H_{31}NO_3$ requires C, 79.4; H, 6.9; N, 3.1%; *M*, 453.2303).

(5*S*)-1-[(2*E*)-3-Trimethylsilylprop-2-enoyl]-5-(triphenylmethoxymethyl)pyrrolidin-2-one 37c. From (*E*)-3-trimethylsilylpropenoic acid,[30] as prisms, mp 104–105 °C (from hexane) (68%); R_f(hexane–EtOAc, 4:1) 0.55; ν_{max}(CH_2Cl_2) 1730 (C=O), 1670 (C=O) and 1590 (C=C); δ_H(250 MHz; $CDCl_3$) 7.65 (1 H, d, *J* 18.6, Me$_3$SiC*H*), 7.37–7.17 (16 H, m, Ph$_3$C and SiCH=C*H*), 4.53 (1 H, m, CHN), 3.55 (1 H, dd, *J* 4 and 9.8, CH_AH_BOCPh$_3$), 3.16 (1 H, dd, *J* 2.7 and 9.8, CH$_A$*H*$_B$OCPh$_3$), 2.98 (1 H, dt, *J* 18 and 10.7, CH_AH_BCO), 2.59 (1 H, ddd, *J* 2.2, 9.5 and 18, CH$_A$*H*$_B$CO), 2.09–1.99 (2 H, m, CH_2CH$_2$CO) and 0.18 (9 H, s, Me$_3$Si); *m*/*z* 483 (0.91%, M$^+$), 468 (10, M − Me), 410 (10, M − Me$_3$Si), 243 (100, CPh$_3$), 240 (40), 165 (50) and 127 (45); $[\alpha]_D$ −64.35 (*c* 2.93 in $CHCl_3$) (Found: C, 74.55; H,

7.1; N, 2.8; M^+, 483.2259. $C_{30}H_{33}NO_3Si$ requires C, 74.55; H, 6.85; N, 2.9%; *M*, 483.2230).

(7*S*)-*N*-[(2*E*)-3-Trimethylsilylprop-2-enoyl]-D-2,10-camphorsultam 37d. As crystal, mp 146–148 °C (from EtOH) (84%); R_f(hexane–Et_2O, 1:1) 0.41; $[\alpha]_D$ −89 (*c* 1.1 in $CHCl_3$); $\nu_{max}(CH_2Cl_2)$/cm^{-1} 1665 (C=O), 1595 (C=C), 1330 and 1130 (SO_2N), 1220 and 850 ($SiMe_3$) and 990 (*trans*-CH=CH); δ_H(250 MHz; $CDCl_3$) 7.36 (1 H, d, *J* 18.2, CH=C*H*SiMe$_3$), 6.91 (1 H, d, *J* 18.2, C*H*=CHSiMe$_3$), 3.91 (1 H, t, *J* 6.6, CHN), 3.47 (1 H, d, *J* 13.8, C$H_AH_BSO_2$), 3.41 (1 H, d, *J* 13.8, CH$_A$*H*$_B$SO$_2$), 2.10–2.08 (2 H, m, CH_2CHN), 1.90–1.85 (3 H, m, CH and CH_2CCHN), 1.4–1.3 (2 H, m, CH_2 sultam), 1.16 (3 H, s, *Me*$_A$Me$_B$C), 0.95 (3 H, s, Me$_A$*Me*$_B$C) and 0.13 (9 H, s, Me_3Si) (Found: C, 56.3; H, 8.1; N, 3.9. $C_{16}H_{27}NO_3SSi$ requires C, 56.3; H, 8.0; N, 4.1%).

(4*S*)-4-Benzyl-3-(2-cyclohexylethanoyl)oxazolidin-2-one 81. As plates, mp 83.5–85 °C (from hexane) (91%); R_f(hexane–EtOAc; 4:1) 0.27; $\nu_{max}(CDCl_3)$/cm^{-1} 1785 (C=O) and 1700 (C=O); δ_H(400 MHz; $CDCl_3$) 7.36 (5 H, m, Ph), 4.66 (1 H, m, CHN), 4.20–4.13 (2 H, m, CH_2O), 3.29 (1 H, dd, *J* 3.2 and 13.2, CH_AH$_B$Ph), 2.87 (1 H, dd, *J* 6.6 and 16.0, CH_AH$_B$CO), 2.77 (1 H, dd, *J* 7.0 and 16.0, CH$_A$*H*$_B$CO), 2.74 (1 H, dd, *J* 9.7 and 13.2, CH$_A$*H*$_B$Ph), 1.89 (1 H, m, C*H*CH$_2$CON) and 1.78–0.88 (10 H, m, 5 × CH_2); *m*/*z* 301 (3.4%, M^+), 125 (100, $C_6H_{11}CH_2CO$) and 91 (85, $C_6H_{11}CH_2$) (Found: M^+, 301.1688. $C_{18}H_{23}NO_3$ requires *M*, 301.1677).

Conjugate addition reactions to imides

(5*S*)-1-[(3*R*)-3-Trimethylsilylbutanoyl]-5-(triphenylmethoxymethyl)pyrrolidin-2-one and (5*S*)-1-[(3*S*)-3-trimethylsilylbutanoyl]-5-(triphenylmethoxymethyl)-pyrrolidin-2-one. Methylmagnesium bromide (3 mol dm^{-3} solution in Et_2O; 27.7 cm^3, 83 mmol) was added to a stirred solution of copper(I) bromide–dimethyl sulfide complex (freshly recrystallised[45]) (8.5 g, 41.5 mmol) in dry THF (165 cm^3) and dry dimethyl sulfide (82.5 cm^3) at −40 °C under nitrogen. After 30 min the solution was cooled to −78 °C and a solution of the imide **37c** (8.3 g, 17.2 mmol) and anhydrous magnesium bromide (5.2 g, 28 mmol) in dry THF (30 cm^3) added dropwise over 30 min. After 1 h the solution was allowed to warm to −10 °C over 3 h. Saturated aqueous ammonium chloride (30 cm^3) was added slowly and the mixture was extracted with ether (4 × 50 cm^3). The combined organic extracts were dried ($MgSO_4$) and evaporated. Chromatography (SiO_2, EtOAc–hexane, 1:7) gave the inseparable *imides* in a ratio of 82:18 (by integration of the Me doublet peaks) (7.74 g, 90%); R_f(EtOAc–hexane, 1:4) 0.6; $\nu_{max}(CH_2Cl_2)$ 1730 (C=O), 1680 (C=O), 1600 and 1490 (Ph); δ_H(250 MHz; $CDCl_3$) for 3*R* compound (major): 7.4–7.2 (15 H, m, 3 × Ph), 4.45 (1 H, m, CHN), 3.57 (1 H, dd, *J* 3.8 and 9.7, CH_AH$_B$OCPh$_3$), 3.14 (1 H, dd, *J* 2.65 and 9.7, CH$_A$*H*$_B$OCPh$_3$), 3.08 (1 H, dd, *J* 3.55 and 16.35, SiCHCH_AH$_B$CO), 2.93 (1 H, ddd, *J* 1.25, 9.9 and 17.8, CH$_2$CH_AH$_B$CO), 2.63 (1 H, dd, *J* 10.9 and 16.35, SiCHCH$_A$*H*$_B$CO), 2.46 (1 H, ddd, *J* 1.7, 9.4 and 17.8, CH$_2$CH$_A$*H*$_B$CO), 2.3–1.85 (2 H, m, CH_2CH$_2$CO), 1.22 (1 H, m, SiC*H*CH$_2$CO), 0.94 (3 H, d, *J* 7.3, *Me*CH) and 0.01 (9 H, s, $SiMe_3$), and for 3*S* compound (minor): 7.4–7.19 (15 H, m, 3 × Ph), 4.45 (1 H, m, CHN), 3.50 (1 H, dd, *J* 4.05 and 9.7, CH_AH$_B$OCPh$_3$), 3.17 (1 H, dd, *J* 2.8 and 9.7, CH$_A$*H*$_B$OCPh$_3$), 3.00 (1 H, m, SiCHCH_AH$_B$CO), 2.93 (1 H, ddd, *J* 1.25, 9.9 and 17.8, CH$_2$CH_AH$_B$CO), 2.61 (1 H, dd, *J* 11.3 and 15.8, SiCHCH$_A$*H*$_B$CO), 2.46 (1 H, ddd, *J* 1.7, 9.4 and 17.8, CH$_2$CH$_A$*H*$_B$CO), 2.3–1.85 (2 H, m, CH_2CH$_2$CO), 1.22 (1 H, m, SiC*H*CH$_2$CO), 0.89 (3 H, d, *J* 7.3, *Me*CH) and 0.02 (9 H, s, $SiMe_3$); *m*/*z* 499 (0.37%, M^+), 484 (20, M − Me), 256 (15, M − Ph_3C), 244 (20, $Me_3SiCHMeCH_2CO$), 243 (100, Ph_3C), 186 (30) and 165 (50) (Found: M^+, 499.2578. $C_{31}H_{37}NO_3Si$ requires *M*, 499.2543).

(7*S*)-*N*-[(3*R*)-Trimethylsilylbutanoyl]-D-2,10-camphorsultam. Following Oppolzer,[29] methyllithium (1.6 mol dm^{-3}; 225.6 cm^3, 0.361 mol) was added dropwise to a stirred suspension of copper(I) iodide (41.5 g, 0.218 mol) in dry ether (400 cm^3) under argon at −20 °C. After stirring for 20 min the solution was cooled to −78 °C and ethylaluminium dichloride (1 mol dm^{-3} in hexane; 218 cm^3, 0.218 mol) was added dropwise. After 20 min a solution of the sultam **37d** [7.54 g, 22.1 mmol, derived from D-(+)-camphor] in dry ether (316 cm^3) was added slowly and the mixture stirred for a further 2 h. The reaction was quenched with saturated aqueous ammonium chloride (300 cm^3) and the aqueous layer extracted with ether (3 × 200 cm^3). The organic extracts were combined, washed with brine, dried ($MgSO_4$) and evaporated under reduced pressure to give the *sultam* (7.33 g, 93%), as needles, mp 124–126 °C (from hexane); GLC (Carlo Erba 4130 instrument, using a 24 m, BP5, 5% phenylmethylsiloxane capillary column, 5 μm film thickness, He carrier gas, ~0.3 m s^{-1}, 100 °C, 20 °C min^{-1} to 200 °C) 34.4 min (3′*S*,7*S*), 35.9 min (3′*R*,7*S*) in a ratio of 1.2:98.8; R_f(hexane–Et_2O, 1:1) 0.4; δ_H(250 MHz; $CDCl_3$) 3.87 (1 H, t, *J* 6.2, CHN), 3.49 (1 H, d, *J* 13.8, CH_AH$_B$SO$_2$), 3.41 (1 H, d, *J* 13.8, CH$_A$*H*$_B$SO$_2$), 2.65 (1 H, dd, *J* 5.3 and 15.9, CH_AH$_B$CON), 2.56 (1 H, dd, *J* 9.4 and 15.9, CH$_A$*H*$_B$CON), 2.11–2.08 (2 H, m, CH_2CHN), 1.96–1.86 (3 H, m, CH$_2$C*H*CH$_2$), 1.44–1.21 (3 H, m, CHSi and CH_2CCHN), 1.56 (3 H, s, *Me*$_A$Me$_B$C), 0.96 (3 H, s, Me$_A$*Me*$_B$C), 0.95 (3 H, d, *J* 7.6, *Me*CH) and −0.02 (9 H, s, Me_3Si).

(5*S*)-1-[(3*R*)-3-Dimethyl(phenyl)silyl-4-methylpentanoyl]-5-(triphenylmethoxymethyl)pyrrolidin-2-one. Dimethyl(phenyl)-silyllithium (143 mmol) was added to a stirred solution of anhydrous magnesium bromide (27.79 g, 151 mmol) in dry THF (100 cm^3) at 0 °C under argon. After 20 min the solution was transferred by cannula to a stirred suspension of recrystallised copper(I) bromide–dimethyl sulfide complex (15.5 g, 75.5 mmol) in dry THF (100 cm^3) at −50 °C. After 30 min, the solution was cooled to −78 °C and a premixed solution of the pyrrolidinone **37b** (15.3 g, 33.6 mmol) and anhydrous magnesium bromide (6.17 g, 33.6 mmol) in dry THF (100 cm^3) was added by cannula over 30 min. After 2 h the reaction was quenched with saturated aqueous ammonium chloride (200 cm^3), the mixture extracted with ether (3 × 300 cm^3), the extracts combined, dried ($MgSO_4$), and evaporated under reduced pressure. The residue was chromatographed (SiO_2, hexane–EtOAc, 9:1) to give the *pyrrolidinone* (15.78 g, 79%); R_f(hexane–EtOAc, 9:1) 0.35; $\nu_{max}(CCl_4)$/cm^{-1} 1735 (C=O), 1687 (C=C), 1245 (SiMe) and 1108 (SiPh); δ_H(250 MHz; $CDCl_3$) 7.52–7.49 (2 H, m, *o*-SiPh), 7.34–7.16 (18 H, m, other Ph), 4.25 (1 H, m, CHN), 3.41 (1 H, dd, *J* 4.3 and 9.6, CH_AH$_B$O), 3.21 (1 H, dd, *J* 7.7 and 17.3, CH_AH$_B$CON), 3.09 (1 H, dd, *J* 2.7 and 9.6, CH$_A$*H*$_B$O), 2.78 (1 H, m, CH$_2$C*H*$_A$H$_B$CO), 2.75 (1 H, dd, *J* 5.6 and 17.3, CH$_A$C*H*$_B$CON), 2.40 (1 H, ddd, *J* 2.3, 9.2 and 17.8, CH$_2$CH$_A$*H*$_B$CO), 1.93–1.83 (3 H, m, CH_2CH$_2$CO and Me$_2$C*H*), 1.65 (1 H, m, CHSi), 0.89 (3 H, d, *J* 6.8, *Me*$_A$Me$_B$C), 0.84 (3 H, d, *J* 6.8, Me$_A$*Me*$_B$C) and 0.32 (6 H, s, Me_2Si); *m*/*z* 589 (1.8%, M^+), 574 (40, M − Me), 346 (25, M − Ph_3C), 243 (100, Ph_3C) and 135 (62, $SiMe_2Ph$) (Found: M^+, 589.3052. $C_{38}H_{43}NO_3Si$ requires *M*, 589.3012). There was no trace of any signals for the diastereoisomer.

(5*S*)-1-[(3*S*)-3-Trimethylsilyl-4-methylpentanoyl]-5-(triphenylmethoxymethyl)pyrrolidin-2-one. 2-Bromopropane (5.96 cm^3, 63.5 mmol) was added dropwise to a stirred suspension of magnesium turnings (1.54 g, 63.5 mmol) in dry ether (125 cm^3) under argon and the solution heated gently until it began to reflux. The heat source was removed and the remaining 2-bromopropane added at an appropriate rate in order to maintain the reflux. The mixture was refluxed for a further 1 h, cooled to room temperature and added to a stirred suspension of copper(II) acetate (2.3 g, 12.7 mmol), magnesium bromide (7.06 g, 38.1 mmol) and the pyrrolidinone **37c** (6.17 g, 12.7 mmol) in dry THF (125 cm^3) at −78 °C under argon. The solution was stirred for 2 h at −78 °C, allowed to warm to 0 °C, quenched with saturated aqueous ammonium chloride (250 cm^3) and extracted with ether (3 × 200 cm^3). The extracts were combined, dried ($MgSO_4$), evaporated under reduced pressure

and the residue chromatographed (SiO_2, hexane–EtOAc, 9:1) to give the *pyrrolidinone* (6.5 g, 97%) of 23% de (from the ratio, 61.5:38.5, of the Me_3Si peaks in the ^1H NMR spectrum); R_f(hexane–EtOAc, 5:1) 0.40; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 1735 (C=O), 1670 (C=C) and 1250 (SiMe); δ_H(250 MHz; $CDCl_3$) for the major isomer 7.38–7.19 (15 H, m, Ph_3C), 4.45 (1 H, m, CHN), 3.58 (1 H, dd, *J* 3.9 and 9.6, $CH_AH_BOCPh_3$), 3.15 (1 H, dd, *J* 2.6 and 9.6, $CH_AH_BOCPh_3$), 3.09–2.86 (3 H, m, CH_2CON and $CH_2CH_AH_BCO$), 2.46 (1 H, ddd, *J* 1.6, 9.6 and 17.8, $CH_2CH_AH_BCO$), 2.08–1.8 (3 H, m, CH_2CH_2CO and Me_2CH), 1.43–1.33 (1 H, m, CHSi), 0.95 (3 H, d, *J* 6.7, Me_AMe_BCH), 0.93 (3 H, d, *J* 6.7, Me_AMe_BCH) and 0.03 (9 H, s, Me_3Si); *m/z* 527 (0.3%, M^+), 284 (19, M − Ph_3C), 243 (100, Ph_3C) and 73 (57, Me_3Si) (Found: M^+, 527.2855. $C_{33}H_{41}NO_3Si$ requires *M*, 527.2855).

Preparation of esters from imides

General procedures. *Method A.* Butyllithium (1.3 mol dm^{-3} solution in hexane; 23 cm^3, 30 mmol) was added dropwise to a stirred solution of dry allyl alcohol[46] (5 cm^3, 74 mmol) in dry THF (30 cm^3) at 0 °C under nitrogen. After 10 min the imide (12 mmol) in dry THF (15 cm^3) was added and the solution stirred at room temperature for 24 h. Saturated aqueous ammonium chloride (10 cm^3) was added and the mixture extracted with diethyl ether (4 × 50 cm^3). The combined organic extracts were dried ($MgSO_4$), concentrated and the residue chromatographed (SiO_2) eluting first with ethyl acetate–hexane (1:5) to give the ester, and then with ethyl acetate to give the lactam **A**-H.

Method B. Methylmagnesium bromide (1.45 mol dm^{-3} solution in ether; 12 cm^3, 17.4 mmol) was added to a stirred solution of dry allyl alcohol (3 cm^3) in dry THF (25 cm^3) under argon at 0 °C, and kept for 10 min. The sultam (4.3 g, 12.1 mmol) was added in dry THF (50 cm^3) and the solution stirred for 15 h at room temperature. The reaction mixture was quenched with saturated aqueous sodium hydrogen carbonate and the aqueous layer extracted with ether (3 × 100 cm^3). The combined organic extracts were washed with saturated aqueous sodium hydrogen carbonate (100 cm^3) and brine, dried ($MgSO_4$) and evaporated under reduced pressure. The residue was chromatographed (a small silica plug, hexane–EtOAc, 9:1) to give the ester **39a** (2.27 g, 93%) identical (TLC and ^1H NMR) to the earlier sample. The sodium hydrogen carbonate extracts were combined and acidified with hydrochloric acid (3 mol dm^{-3}) to pH 1. The solution was then extracted with dichloromethane (3 × 50 cm^3), the organic extracts combined, washed with brine, dried ($MgSO_4$) and evaporated under reduced pressure to give the sultam **B**-H (2.44 g, 93%).

Method C (racemic). Methyllithium (or phenyllithium for **44b**) (70 cm^3 of a 1.7 mol dm^{-3} solution in Et_2O, 120 mmol) was added dropwise at 0 °C under nitrogen to a stirred slurry of copper(I) iodide (11.4 g, 60 mmol) in ether (90 cm^3), stopping the addition just before complete dissolution of the solid. The mixture was stirred for 10 min, cooled to −78 °C and ethylaluminium dichloride (1 mol dm^{-3} solution in hexane; 60 cm^3, 60 mmol) was added dropwise, stirring for a further 20 min. A solution of (*E*)-*N*-[3-trimethylsilylpropenoyl]pyrrolidin-2-one (6.33 g, 30 mmol) in ether (90 cm^3) was added dropwise. The mixture was kept at room temperature for 2 h, allyl alcohol (15 cm^3, excess) was added and the mixture stirred for 26 h. The resulting mixture was filtered, washing the residue with ether, and water (100 cm^3) added to the combined ether layers. The ether layer was dried ($MgSO_4$), filtered and evaporated, and the residue distilled to give the ester (5.75 g, 82%), bp 92–95 °C at 16 mmHg, identical (TLC and ^1H NMR) to the earlier sample.

The following compounds were prepared by one of these methods.

Allyl (3*R*)-3-dimethyl(phenyl)silyl-4-methylpentanoate 38b. As an oil by Method A (91%, 100% ee), identical (TLC, ^1H NMR) with the racemic ester **43c** described above, together with the lactam **A**-H (75%).

Allyl (3*R*)-3-trimethylsilylbutanoate 39a. As an oil from the imide **37c** and methylmagnesium bromide–copper(I) bromide (83%); R_f(EtOAc–hexane, 1:5) 0.8; ν_{max}(film)/cm^{-1} 3090 (CH_2=), 1735 (C=O), 1250 (SiMe) and 985 (CH_2=CH); δ_H(250 MHz; $CDCl_3$) 5.90 (1 H, ddt, *J* 10.3, 17.2 and 5.7, CH_2CH=CH_2), 5.31 (1 H, dq, *J* 17.2 and 1.5, CH=CH_AH_B), 5.23 (1 H, dq, *J* 10.3 and 1.3, CH=CH_AH_B), 4.57 (2 H, dt, *J* 5.7 and 1.3, CH_2CH=CH_2), 2.41 (1 H, dd, *J* 4.15 and 15.1, CH_AH_BCO), 2.08 (1 H, dd, *J* 11.1 and 15.1, CH_AH_BCO), 1.2 (1 H, m, $CHCH_2CO$), 0.95 (3 H, d, *J* 7.15, *Me*CH) and −0.025 (9 H, s, $SiMe_3$); $[\alpha]_D$ −2.0 (*c* 0.25 in $CHCl_3$); *m/z* 200 (0.1%, M^+), 199 (0.1, M − 1), 185 (7, M − Me), 157 (2, M − Me − CO), 145 (2, M − Me − H_2C=C=CH_2), 143 (2, M − C_3H_5O), 129 (3, M + H − C_3H_5O − Me), 117 (6, M − Me − C_3H_4 − CO), 115 (18, M − C_3H_5O − CO), 101 (3, M − Me − C_3H_4 − CO_2), 99 (3, $Me_3SiC_3H_5$), 85 (5, C_3H_5OC=O) and 73 (100, Me_3Si) (Found: M^+, 200.1243. $C_{10}H_{20}O_2Si$ requires *M*, 200.1233), together with the lactam **A**-H (70% after recrystallisation).

Allyl (3*S*)-4-methyl-3-trimethylsilylpentanoate 39c. As an oil by Method A (52%); $\nu_{max}(CCl_4)/cm^{-1}$ 1730 (C=O), 1640 (C=O) and 1250 (SiMe); δ_H(250 MHz; $CDCl_3$) 5.92 (1 H, ddt, *J* 15.8, 10.5 and 6.1, CH=CH_2), 5.31 (1 H, dq, *J* 15.8 and 1.5, CH=CH_AH_B), 5.22 (1 H, dq, *J* 10.5 and 1.2, CH=CH_AH_B), 2.31 (2 H, dt, *J* 1.3 and 5.8, CH_2CH=CH_2), 2.37 (1 H, dd, *J* 7.7 and 15.9, $CH_AH_BCO_2$), 2.28 (1 H, dd, *J* 6.1 and 15.9, $CH_AH_BCO_2$), 1.91 (1 H, d septet, *J* 3.9 and 6.8, Me_2CH), 1.23 (1 H, m, CHSi), 0.92 (3 H, d, *J* 6.8, Me_AMe_BCH), 0.89 (3 H, d, *J* 6.8, Me_AMe_BCH) and 0.02 (9 H, s, Me_3Si); *m/z* 213 (5.5%, M^+ − Me), 73 (100, Me_3Si) (Found: M^+ − Me, 213.1381. $C_{11}H_{21}O_2Si$ requires *M* − Me, 213.1310), together with the pyrrolidinone **A**-H (41%).

Allyl (3*RS*)-3-trimethylsilyl-3-phenylpropanoate 44b. As an oil by adding 1.1 molar equivalents of allyl alcohol to the reaction mixture immediately following the conjugate addition (74%); R_f(EtOAc–hexane, 1:9) 0.28; ν_{max}(film)/cm^{-1} 1737 (C=O), 1648 (CH=CH_2), 1600 (Ph), 1250 and 840 ($SiMe_3$); δ_H(250 MHz; $CDCl_3$) 7.26–7.20 (2 H, m, *o*-SiPh), 7.12–7.03 (3 H, m, *m*- and *p*-SiPh), 5.74 (1 H, ddt, *J* 17.1, 10.5 and 5.6, CH=CH_2), 5.14 (2 H, m, CH=CH_2), 4.44 (2 H, ddd, *J* 5.6, 1.4 and 1, OCH_2), 2.91–2.61 (3 H, m, $CH_2CHSiMe_3$) and −0.03 (9 H, s, Me_3Si); *m/z* 262 (20%, M^+), 247 (68, M − Me), 205 (90, M − OC_3H_5) and 73 (100, $SiMe_3$) (Found: M^+, 262.1399. $C_{15}H_{22}O_2Si$ requires *M*, 262.1389).

2-Trimethylsilylethyl (3*R*)-3-trimethylsilylbutanoate 39b. As an oil by Method B using 2-trimethylsilylethanol (96%); R_f(EtOAc–hexane, 20:80) 0.66; ν_{max}(film)/cm^{-1} 1735 (C=O) and 1250 and 835 ($SiMe_3$); δ_H(250 MHz; $CDCl_3$) 4.19–4.12 (2 H, m, OCH_2), 2.35 (1 H, dd, *J* 4.1 and 15.0, CH_AH_BCHSi), 2.01 (1 H, dd, *J* 11.0 and 15.0, CH_AH_BCHSi), 1.24–1.11 (1 H, m, CHSi), 1.03–0.93 (2 H, m, $SiCH_2$), 0.93 (3 H, d, *J* 6.6, *Me*CH), 0.19 (9 H, s, $SiMe_{3A}$) and −0.03 (9 H, s, $SiMe_{3B}$); $[\alpha]_D$ +5.3 (*c* 1.3 in $CHCl_3$) (Found: C, 55.3; H, 10.7. $C_{12}H_{28}O_2$ requires C, 55.3; H, 10.8%).

Syntheses of aldehydes and their precursors

(*E*)-5-Methoxy-5-methylhex-2-enal 51. Dry powdered zinc bromide (0.41 g, 1.79 mmol), 1-trimethylsilyloxybuta-1,3-diene[47] (4.1 g, 28.9 mmol) and 2,2-dimethoxypropane (3.88 cm^3, 31.0 mmol) were stirred at room temperature for 2 h in dry dichloromethane (100 cm^3), quenched with saturated aqueous sodium hydrogen carbonate and extracted with dichloromethane. The extract was washed with brine, dried ($MgSO_4$) and evaporated (at 20 °C) to give the crude *aldehyde* (4.1 g, *ca.* 100%). An analytical sample was obtained by chromatography on silica gel (hexane–EtOAc, 9:1); R_f(hexane–EtOAc, 7:3) 0.3; $\nu_{max}(CHCl_3)/cm^{-1}$ 2820 (OMe), 1680 (C=O), 1155 (C–O–C) and 975 (C=C); δ_H(250 MHz; $CDCl_3$) 9.32 (1 H, d, *J* 8, CHO), 6.88

(1 H, dt, *J* 7.4 and 14.9, C*H*=CHCHO), 6.13 (1 H, ddt, *J* 1.2, 7.9 and 15.7, CH=C*H*CHO), 3.20 (3 H, s, OMe), 2.48 (2 H, dd, *J* 1.2 and 7.4, CH_2) and 1.19 (6 H, s, Me_2C); *m/z* 127 (2%, M^+ – Me), 95 (2.5) and 73 (100, C_4H_9O) (Found: M^+ – Me, 127.0754. $C_8H_{14}O_2$ requires *M* – Me, 127.0759).

5-Methoxy-5-methylhexanal 52. The unsaturated aldehyde **51** (1.04 g, 7.3 mmol) was stirred with a suspension of palladium black[48] (40 mg, 0.37 mmol) in cyclohexane (25 cm^3) under hydrogen for 3 h. The catalyst was removed by filtration, the solvent was evaporated at 20 °C and the residue distilled (Kugelrohr, bp 105 °C at 1 mmHg) to give the *aldehyde* (0.9 g, 85%); R_f(hexane–EtOAc, 7:3) 0.31; ν_{max}($CHCl_3$)/cm^{-1} 2800 (C–H), 1695 (C=O) and 1135 (C–O); δ_H(250 MHz; $CDCl_3$) 9.75 (1 H, t, *J* 1.7, CHO), 3.16 (3 H, s, OMe), 2.43 (2 H, dt, *J* 1.7 and 7.1, CH_2CHO), 1.72–1.45 (4 H, m, CH_2CH_2CHO and CH_2CMe_2OMe) and 1.14 (6 H, s, Me_2C); *m/z* 129 (2%, M – Me), 97 (2), 95 (5), 85 (10) and 73 (100, C_4H_9O) (Found: M^+ – Me, 129.0924. $C_8H_{16}O_2$ requires *M* – Me, 129.0916).

Ethyl 3-(2-methoxyethoxy)methoxy-3-methylbutanoate. (2-Methoxyethoxy)methyl chloride (14.8 cm^3, 15.9 g, 130 mmol) was added dropwise to a stirred solution of the alcohol **48** (11.5 g, 79 mmol) and diisopropylethylamine (18.9 cm^3, 16.8 g, 130 mmol) in dichloromethane (200 cm^3) at room temperature under argon. The mixture was stirred for 48 h, quenched with ether (500 cm^3), washed with dilute hydrochloric acid (5%, 2 × 100 cm^3), saturated aqueous sodium hydrogen carbonate (100 cm^3) and brine (100 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure. The residue was chromatographed (SiO_2, EtOAc–hexane, 20:80) to give the *ester* (12.9 g, 70%) as a colourless oil, R_f(EtOAc–hexane, 20:80) 0.17; ν_{max}(film)/cm^{-1} 1730 (C=O); δ_H(250 MHz; $CDCl_3$) 4.82 (2 H, s, OCH_2O), 4.11 (2 H, q, *J* 7.1, $MeCH_2O$), 3.73–3.68 (2 H, m, $MeOCH_2CH_2$), 3.57–3.52 (2 H, m, $MeOCH_2CH_2$), 3.37 (3 H, s, MeO), 2.53 (2 H, s, CH_2C=O), 1.36 (6 H, s, CMe_2) and 1.24 (3 H, t, *J* 7.1, $MeCH_2$); *m/z* 219 (8%, M^+ – Me), 189 (28, M – EtO), 159 (85, M – $MeOC_2H_4O$) and 129 (100, M – $MeOC_2H_4O$-CH_2O) (Found: M^+ – Me, 219.1231. $C_{11}H_{22}O_5$ requires *M* – Me, 219.1233).

3-(2-Methoxyethoxy)methoxy-3-methylbutanal 49. Diisobutylaluminium hydride (1 mol dm^{-3} in hexanes; 1.4 cm^3, 1.4 mmol) was added dropwise to a stirred solution of the ester above (300 mg, 1.28 mmol) in dry dichloromethane (10 cm^3) at −78 °C under argon. The mixture was stirred at this temperature for 1.5 h, quenched with methanol (10 cm^3) and saturated aqueous sodium potassium tartrate (20 cm^3), allowed to warm and extracted with dichloromethane (2 × 25 cm^3). The extract was washed with brine (50 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure. The residue was chromatographed (SiO_2, EtOAc–hexane, 50:50) to give the *aldehyde* (199 mg, 82%) as a colourless oil, R_f(ether) 0.51; ν_{max}(film)/cm^{-1} 2730 (aldehyde CH) and 1720 (C=O); δ_H(250 MHz; $CDCl_3$) 9.84 (1 H, t, *J* 2.9, CHO), 4.84 (2 H, s, OCH_2O), 3.75–3.67 (2 H, m, $MeOCH_2CH_2$), 3.56–3.50 (2 H, m, $MeOCH_2CH_2$), 3.37 (3 H, s, MeO), 2.53 (2 H, d, *J* 2.9, CH_2C=O) and 1.36 (6 H, s, CMe_2); *m/z* 189 (2%, M^+ – H), 159 (60, M – MeO), 131 (85, M – $MeOC_2H_4$), 115 (55, M – $MeOC_2H_4O$), 101 (45, M – $MeOC_2H_4OCH_2$), 85 (40, M – $MeOC_2H_4OCH_2O$) and 59 (100, $MeOC_2H_4$) (Found: M^+ – H, 189.1127. $C_9H_{18}O_4$ requires *M* – H, 189.1127).

General procedure. Butyllithium (1.6 mol dm^{-3} solution in hexane; 56 cm^3, 89.6 mmol) was added to a stirred solution of diisopropylamine (14 cm^3, 0.1 mol) in THF (120 cm^3) under argon at −20 °C. After 20 min the solution was cooled to −78 °C, the *tert*-butyl imine[34] (5.6 g, 41.6 mmol) was added dropwise and the reaction stirred for 30 min. Diethyl chlorophosphate (6.1 cm^3, 41.6 mmol) was then added and the mixture allowed to warm to −10 °C over 3 h. The mixture was cooled to −78 °C and the aldehyde (27.8 mmol) in dry THF (25 cm^3) was added, the mixture allowed to warm to room temperature and stirred for 15 h. A mixture of oxalic acid (8 g, 89 mmol), water (200 cm^3) and benzene (200 cm^3) was added and the resulting mixture stirred vigorously for 15 h at room temperature. The organic layer was decanted and the aqueous layer extracted with ether (3 × 200 cm^3). The organic layers were combined, washed with brine, dried ($MgSO_4$) and evaporated under reduced pressure. The residue was chromatographed (SiO_2, hexane) to give the aldehyde. The following α,β-unsaturated aldehydes were prepared by this method.

(*E*)-3-Cyclohexylpropenal 47.[49] As an oil (100%); R_f(hexane–EtOAc, 9:1) 0.32; ν_{max}(film)/cm^{-1} 1690 (C=O), 1635 (C=C) and 1450; δ_H(250 MHz; $CDCl_3$) 9.46 (1 H, d, *J* 7.8, CHO), 6.74 (1 H, dd, *J* 6.5 and 15.7, C*H*=CHCHO), 6.03 (1 H, ddd, *J* 1.4, 7.8 and 15.7, CH=C*H*CHO), 2.22 (1 H, m, C*H*CH=CH), 2.00–1.58 (5 H, m, 5 × CH) and 1.40–0.85 (5 H, m, 5 × CH); *m/z* 138 (7%, M^+), 82 (90, C_6H_{10}) and 67 (100, C_4H_3O) (Found: M^+, 138.1053. $C_9H_{14}O$ requires *M*, 138.1045).

(*E*)-7-Methoxy-7-methyloct-2-enal 53. As an oil (75%); R_f(hexane–EtOAc, 7:3) 0.11; ν_{max}($CHCl_3$)/cm^{-1} 2820 (OMe), 1670 and 1630 (C=O); δ_H(250 MHz; $CDCl_3$) 9.49 (1 H, d, *J* 7.9, CHO), 6.83 (1 H, dt, *J* 15.6 and 6.7, C*H*=CHCHO), 6.11 (1 H, ddt, *J* 7.9, 15.6 and 1.5, CH=C*H*CHO), 3.15 (3 H, s, OMe), 2.33 (2 H, q, *J* 6.7, CH_2CH=CH), 1.57–1.55 (4 H, m, CH_2CH_2) and 1.14 (6 H, s, Me_2C); *m/z* 171 (6%, M^+ + H), 109 (6, *M* – C_3H_9O), 85 (12) and 73 (100, C_4H_9O) (Found: M^+ – OMe, 139.0767. $C_{10}H_{18}O_2$ requires *M* – OMe, 139.0759).

(*E*)-5-(2-Methoxyethoxy)methoxy-5-methylhex-2-enal 50. As an oil (83%); R_f(Et_2O) 0.68; ν_{max}(film)/cm^{-1} 2750 (aldehyde CH), 1690 (C=O) and 1640 (C=C); δ_H(250 MHz; $CDCl_3$) 9.52 (1 H, d, *J* 7.9, CHO), 6.93 (1 H, dt, *J* 15.7 and 7.4, CH_2CH=CH), 6.12 (1 H, ddt, *J* 7.9, 15.7 and 1.3, C=CHC=O), 4.83 (2 H, s, OCH_2O), 3.73–3.65 (2 H, m, $MeOCH_2CH_2$), 3.56–3.50 (2 H, m, $MeOCH_2CH_2$), 3.37 (3 H, s, MeO), 2.54 (2 H, dd, *J* 1.2 and 7.4, CH_2C=C) and 1.27 (6 H, s, CMe_2); *m/z* 216 (2%, M^+), 215 (20, M – H), 185 (40, M – MeO), 157 (40, M – $MeOC_2H_4$), 127 (60, M – $MeOC_2H_4OCH_2$), 89 (100, $MeOC_2H_4OCH_2$) and 59 (90, $MeOC_2H_4$) (Found: M^+, 216.1340. $C_{11}H_{20}O_4$ requires *M*, 216.1362).

Aldol reactions

General procedure. Butyllithium (1.2 mol dm^{-3} solution in hexane; 14.75 cm^3, 17.7 mmol) was added dropwise to a stirred solution of dry diisopropylamine (1.9 g, 19 mmol) in dry THF (35 cm^3) at −20 °C and under nitrogen. After 30 min the solution was cooled to −78 °C and the ester (16.1 mmol) in dry THF (6 cm^3) added dropwise over 15 min. After 20 min the freshly distilled aldehyde (48 mmol) was added. After 1 h saturated aqueous ammonium chloride (10 cm^3) was added. The solution was allowed to warm to room temperature and extracted with ether (4 × 30 cm^3). The combined organic extracts were dried ($MgSO_4$) and evaporated under reduced pressure. Chromatography (SiO_2, EtOAc–hexane, 1:10) gave the hydroxy ester. The following compounds were prepared by this method.

Allyl (4*E*,2*R*,3*S*)-2-[(1*S*)-1-dimethyl(phenyl)silylethyl]-3-hydroxyhex-4-enoate. As an oil (44%) from the ester **38a** (80% ee) and *trans*-but-2-enal; R_f(EtOAc–hexane, 1:5) 0.3; ν_{max}(film)/cm^{-1} 3460 (OH), 1720 (C=O), 1240 (SiMe) and 1105 (SiPh); δ_H($CDCl_3$; 250 MHz) 7.55–7.50 (2 H, m, *o*-SiPh), 7.34–7.30 (3 H, m, *m*- and *p*- SiPh), 5.84 (1 H, m, CH_2CH=CH_2), 5.59 (2 H, m, CHOHC*H*=C*H*Me), 5.28 (1 H, dd, *J* 1.1 and 17.2, CH_AH_B=CHCH$_2$O), 5.20 (1 H, dd, *J* 1.1 and 10.4, CH_AH_B=CHCH$_2$O), 4.36 (2 H, m, CH_2=CHCH_2O), 4.24 (1 H, t, *J* 6.7, C*H*OH), 2.66 (1 H, t, *J* 7.3, $CHCO_2$), 1.65 (3 H, d, *J* 5.1, *Me*CH=CH), 1.48 (1 H, quintet, *J* 7.5, MeC*H*Si), 1.00 (3 H, d, *J* 7.5, *Me*CHSi), 0.31 (3 H, s, Si$Me_A$$Me_B$) and 0.29 (3 H, s, Si$Me_A$$Me_B$); *m/z* 317 (1.5%, M^+ – Me), 261 (17, *M* – C_4H_7O) and 135 (100, $SiMe_2Ph$) (Found: M^+ – Me, 317.1557. $C_{19}H_{28}O_3Si$ requires *M* – Me, 317.1572). The ^1H NMR spectrum showed several minor peaks, amounting to about

10%, probably from other diastereoisomers. The racemic compound was prepared similarly in 46% yield.

Allyl (4*E*,2*R*,3*S*)-2-[(1*S*)-1-dimethyl(phenyl)silyl-2-methylpropyl]-3-hydroxyhex-4-enoate. As an oil (33%, +7% of **38b**) from the ester **38b** and *trans*-but-2-enal; R_f(hexane–EtOAc, 5:1) 0.3; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3600 (OH), 1725 (C=O) and 1110 (SiPh); δ_H(250 MHz; $CDCl_3$), 7.62–7.58 (2 H, m, *o*-SiPh), 7.52 (1 H, br s, OH), 7.35–7.28 (3 H, m, *m*- and *p*-SiPh), 5.85 (1 H, ddt, *J* 10.3, 17.3 and 5.9, C*H*=CH_2), 5.48–5.32 (2 H, m, MeC*H*=CH), 5.26 (1 H, dq, *J* 17.3 and 1.3, CH=CH_AH_B), 5.20 (1 H, dq, *J* 10.3 and 1.3, CH=CH_AH_B), 4.46 (2 H, dt, *J* 5.8 and 1.3, CH_2), 3.98 (1 H, dd, *J* 6.5 and 8.8, C*H*OH), 2.77 (1 H, dd, *J* 8.6 and 2.6, $CHCO_2$), 2.04–1.98 (1 H, m, Me_2CH), 1.63 (3 H, d, *J* 4.9, *Me*CH=CH), 1.60–1.41 (1 H, m, CHSi), 0.90 (3 H, d, *J* 6.7, C*Me*$_A$Me$_B$), 0.84 (3 H, d, *J* 6.7, CMe$_A$*Me*$_B$), 0.43 (3 H, s, Si*Me*$_A$Me$_B$) and 0.39 (3 H, s, SiMe$_A$*Me*$_B$); *m*/*z* 345 (1.52%, M^+ – Me) and 135 (100, $PhMe_2Si$) (Found: M^+ – Me, 345.1878. $C_{21}H_{32}O_3Si$ requires *M* – Me, 345.1885).

Allyl (4*E*,2*S*,3*R*)-3-hydroxy-2-[(1*R*)-1-trimethylsilylethyl]-hex-4-enoate. As an oil (50%) from **39a** (64% ee) and *trans*-but-2-enal; R_f(EtOAc–hexane, 1:5) 0.35; ν_{max}(film)/cm^{-1} 3700–3100 (OH), 3090 (CH_2=), 1730 (C=O), 1250 (SiMe) and 985 (CH_2=CH); δ_H(250 MHz; $CDCl_3$) 6.0–5.9 (1 H, m, CH_2CH=CH_AH_B), 5.74 (1 H, dq, *J* 15.3 and 5.4, MeC*H*=CH), 5.62 (1 H, dd, *J* 6.3 and 15.3, MeCH=C*H*), 5.32 (1 H, dq, *J* 17.2 and 1.55, CH_2CH=CH_AH_B), 5.23 (1 H, dq, *J* 10.3 and 1.3, CH_2CH=CH_AH_B), 4.54 (2 H, dt, *J* 5.5 and 1.3, CH_2CH=CH_AH_B), 4.38–4.32 (1 H, m, C*H*OH), 2.65 (1 H, t, *J* 7.3, $CHCO_2$), 1.79 (3 H, d, *J* 5.4, *Me*CH=CH), 1.68–1.54 (1 H, br s, OH), 1.22 (1 H, m, Me_3SiCH), 1.00 (3 H, d, *J* 7.4, *Me*CHSi) and 0.00 (9 H, s, $SiMe_3$); *m*/*z* 199 (12%, $M^+ - C_4H_7O$), 143 (40), 95 (45), 75 (55), 73 (100, $SiMe_3$) and 69 (75) (Found: $M^+ - C_4H_7O$, 199.1160. $C_{14}H_{26}O_3Si$ requires *M* – C_4H_7O, 199.1154).

Allyl (4*E*,2*S*,3*R*)-2-[(1*R*)-1-trimethylsilyl-2-methylpropyl]-3-hydroxyhex-4-enoate. As an oil (29%, 58% based on starting material not recovered) from **39c** and *trans*-but-2-enal; R_f(hexane–EtOAc, 4:1) 0.44; ν_{max}(film)/cm^{-1} 3400 (OH), 1730 (C=O) and 1250 (SiMe); δ_H(250 MHz; $CDCl_3$) 5.93 (1 H, ddt, *J* 17.2, 10.3 and 5.9, C*H*=CH_2), 5.79–5.54 (2 H, m, C*H*=C*H*Me), 5.38 (1 H, dq, *J* 17.2 and 1.1, CH=CH_AH_B), 5.28 (1 H, dq, *J* 10.3 and 1.1, CH=CH_AH_B), 4.57 (2 H, dt, *J* 5.9 and 1.1, CH_2CH=CH_2), 4.23 (1 H, t, *J* 7.6, C*H*OH), 2.81 (1 H, dd, *J* 2.6 and 8.2, $CHCO_2$), 2.11 (1 H, m, Me_2CH), 1.73 (3 H, d, *J* 5.5, *Me*CH=CH), 1.33–1.24 (1 H, m, CHSi), 0.99 (3 H, d, *J* 7.1, C*Me*$_A$Me$_B$), 0.92 (3 H, d, *J* 7.1, CMe$_A$*Me*$_B$) and 0.16 (9 H, s, $SiMe_3$); *m*/*z* 283 (6%, M – Me) and 73 (100%, Me_3Si) (Found: M^+ – Me, 283.1720. $C_{16}H_{30}O_3Si$ requires *M* – Me, 283.1729).

Allyl (4*E*,2*S*,3*R*)-5-cyclohexyl-2-[(1*R*)-1-trimethylsilylethyl]-3-hydroxypent-4-enoate. As an oil (52%) from **39a** and the aldehyde **47**; R_f(hexane–EtOAc, 9:1) 0.24; $\nu_{max}(CDCl_3)/cm^{-1}$ 3460 (OH), 1735 (C=O), 1450 (C=C) and 1250 (SiMe); δ_H(250 MHz; $CDCl_3$) 5.86 (1 H, ddt, *J* 10.4, 17.1 and 5.8, C*H*=CH_2), 5.61 (1 H, dd, *J* 6 and 15.5, C*H*=CHCHOH), 5.51 (1 H, dd, *J* 7 and 15.5, CH=C*H*CHOH), 5.29 (1 H, dd, *J* 1.5 and 17.1, CH=CH_AH_B), 5.19 (1 H, dd, *J* 1.5 and 10.4, CH=CH_AH_B), 4.53 (2 H, d, *J* 5.8, CH_2O), 4.33 (1 H, t, *J* 6.9, C*H*OH), 2.65 (1 H, t, *J* 7.2, $CHCO_2$), 1.97–1.64 (6 H, m, 6 × CH ring), 1.29–0.81 (6 H, m, 5 × CH ring and MeC*H*Si), 0.98 (3 H, d, *J* 7.5, *Me*CHSi) and –0.2 (9 H, s, $SiMe_3$); *m*/*z* 323 (7%, M^+ – Me), 200 [100, $MeCH(Me_3Si)CH_2CO_2allyl$], 199 [90, $MeCH(Me_3Si)CHCO_2allyl$] and 143 [60, $MeCH(Me_3Si)$-CHCHO] (Found: M^+ – Me, 323.2060. $C_{19}H_{34}O_3Si$ requires *M* – Me, 323.2042).

2-Trimethylsilylethyl (2*S*,3*R*)-2-[(1*R*)-1-trimethylsilylethyl]-3-hydroxy-5-methyl-5-(2-methoxyethoxy)methoxyhexanoate. As an oil (72%) from the ester **39b** and the aldehyde **49**; R_f(EtOAc–hexane, 20:80) 0.29; ν_{max}(film)/cm^{-1} 3500 (OH), 1725 (C=O) and 1250 and 840 ($SiMe_3$); δ_H(250 MHz; $CDCl_3$) 4.83 (1 H, d, *J* 7.6, OCH_AH_BO), 4.79 (1 H, d, *J* 7.6, OCH$_A$$H_B$O), 4.23 (1 H, br t, *J* 8.7, C*H*OH), 4.18–4.06 (2 H, m, CO_2CH_2), 3.88 (1 H, br s, OH), 3.75–3.66 (2 H, m, OCH_2OCH_2), 3.55–3.47 (2 H, m, CH_2OMe), 3.37 (3 H, s, OMe), 2.50 (1 H, dd, *J* 6.1 and 8.4, CHC=O), 1.74 (1 H, dd, *J* 10.1 and 14.6, CH_AH_BCMe$_2$), 1.49 (1 H, dd, *J* 1.0 and 14.6, CH$_A$$H_BCMe_2$), 1.30–0.90 (1 H, m, CHSi), 1.34 (3 H, s, C*Me*$_A$Me$_B$), 1.28 (3 H, s, CMe$_A$*Me*$_B$), 0.99 (3 H, d, *J* 7.7, *Me*CH), 1.00–0.90 (2 H, m, CH_2Si), 0.03 (9 H, s, $SiMe_{3A}$) and 0.00 (9 H, s, $SiMe_{3B}$); *m*/*z* 451 (40%, M + H^+), 435 (40, M – Me), 419 (35, M – MeO), 405 (10, M – $MeOCH_2$), 89 (30, $MeOC_2H_4OCH_2$), 73 (70, $SiMe_3$) and 59 (30, $MeOC_2H_4$); $[\alpha]_D$ –15.2 (*c* 1.5 in $CHCl_3$) (Found: M + H^+, 451.2913. $C_{21}H_{46}O_6Si_2$ requires *M* + H, 451.2911).

2-Trimethylsilylethyl (4*E*,2*S*,3*R*)-2-[(1*R*)-1-trimethylsilylethyl]-3-hydroxy-7-methyl-7-(2-methoxyethoxy)methoxyoct-4-enoate. As an oil (77%) from the ester **39b** and the aldehyde **50**; R_f(EtOAc–hexane, 40:60) 0.30; ν_{max}(film)/cm^{-1} 3475 (OH), 1725 (C=O) and 1250 and 840 ($SiMe_3$); δ_H(250 MHz; $CDCl_3$) 5.75 (1 H, dt, *J* 15.4 and 6.5, C*H*=CHC=O), 5.64 (1 H, dd, *J* 6.5 and 15.4, CH=C*H*C=O), 4.79 (2 H, s, OCH_2O), 4.40–4.32 (1 H, m, C*H*OH), 4.16–4.07 (2 H, m, CO_2CH_2), 3.72–3.67 (2 H, m, OCH_2OCH_2), 3.56–3.51 (2 H, m, CH_2OMe), 3.38 (3 H, s, OMe), 2.59 (1 H, t, *J* 7.2, CHC=O), 2.27 (1 H, dd, *J* 6.4 and 14.6, CH_AH_BCMe$_2$), 2.23 (1 H, dd, *J* 6.2 and 14.6, CH$_A$$H_BCMe_2$), 1.93 (1 H, d, *J* 4.6, OH), 1.30–0.90 (1 H, m, CHSi), 1.19 (6 H, s, CMe_2), 0.99 (3 H, d, *J* 7.2, *Me*CH), 1.01–0.91 (2 H, m, CH_2Si), 0.03 (9 H, s, $SiMe_{3A}$) and 0.00 (9 H, s, $SiMe_{3B}$); *m*/*z* 461 (8%, M^+ – Me), 445 (10, M – MeO), 431 (40, M – $MeOCH_2$), 89 (95, $MeOC_2H_4OCH_2$), 73 (100, $SiMe_3$) and 59 (90, $MeOC_2H_4$); $[\alpha]_D$ –20.3 (*c* 1.5 in $CHCl_3$) (Found: M^+ – Me, 461.2767. $C_{23}H_{48}O_6Si_2$ requires *M* – Me, 461.2755).

Allyl (2*SR*,3*RS*)-[(1*RS*)-1-dimethyl(phenyl)silylethyl]-3-hydroxypent-4-enoate. As an oil (32%), very largely one diastereoisomer, from the ester **43a** and acrolein (acrylaldehyde); R_f(SiO_2, hexane–EtOAc, 9:1) 0.20; ν_{max}(film)/cm^{-1} 3380 (broad OH), 3070, 2960, 2870 (CH), 1720 (C=O), 1640 (C=C), 1250 (CO) and 1110 (SiPh); δ_H(250 MHz; $CDCl_3$) 7.6–7.4 (2 H, m, *o*-SiPh), 7.4–7.3 (3 H, m, *m*- and *p*-SiPh), 5.95 (1 H, ddd, *J* 6.6, 10.4 and 17.0, CHOHC*H*=CH_2), 5.85 (1 H, ddt, *J* 10.4, 17.1 and 5.8, OCH_2CH=CH_2), 5.29 (1 H, dq, *J* 17 and 1.5, OCH_2CH=CH_AH_B), 5.23 (1 H, d, *J* 17, CHOHCH=CH_AH_B), 5.21 (1 H, dq, *J* 10 and 1.2, OCH_2CH=CH$_A$$H_B$), 5.14 (1 H, dt, *J* 10.4 and 1.2, CHOHCH=CH$_A$$H_B$), 4.37 (2 H, ddd, 1.3, 2.7 and 5.8, OCH_2CH=CH_2), 4.32 (1 H, br t, *J* 6.8, C*H*OHCH=CH_2), 2.69 (1 H, t, *J* 7.3, C*H*C=O), 1.54 (1 H, quintet, *J* 7.5, SiC*H*Me), 1.05 (3 H, d, *J* 7.6, SiCH*Me*), 0.33 (3 H, s, Si*Me*$_A$Me$_B$) and 0.31 (3 H, s, SiMe$_A$*Me*$_B$); *m*/*z* 303 (1.5%, M – Me), 261 (25, M – C_3H_5O), 241 (8, M – Ph), 183 (7, M – C_3H_4 – Ph – H_2O), 143 (100, M – Me_2SiPh – C_3H_4) and 135 (94, Me_2SiPh) (Found: M^+ – Me, 303.1401. $C_{18}H_{26}O_3Si$ requires *M* – Me, 303.1417).

Allyl (2*SR*,3*RS*)-2-[(1*RS*)-1-dimethyl(phenyl)silyl-2-methylpropyl]-3-hydroxypent-4-enoate. As an oil (31%) from the ester **43c** and acrolein; R_f(hexane–EtOAc, 5:1) 0.31; $\nu_{max}(CH_2Cl_2)$/cm^{-1} 3500 (OH), 1740 (C=O), 1250 (SiMe) and 1110 (SiPh); δ_H(250 MHz; $CDCl_3$) 7.62–7.56 (2 H, m, *o*-Ph), 7.34–7.31 (3 H, m, *m*- and *p*-Ph), 5.86 (1 H, ddt, *J* 10.4, 17.2 and 5.8, OCH_2CH=CH_2), 5.81 (1 H, ddd, *J* 6.9, 10.4 and 17.1, CHOHC*H*=CH_2), 5.31 (1 H, dq, *J* 17.1 and 1.4, OCH_2CH=CH_AH_B), 5.22 (1 H, dq, *J* 10.4 and 1.2, OCH_2CH=CH$_A$$H_B$), 5.10 (1 H, dd, *J* 1.4 and 17.1, CHOHCH=CH_AH_B), 5.08 (1 H, dd, *J* 1.2 and 10.4, CHOHCH=CH$_A$$H_B$), 4.47 (2 H, td, *J* 1.2 and 5.8, CH_2), 4.07 (1 H, t, *J* 7.5, C*H*OH), 2.78 (1 H, dd, *J* 2.7 and 8.4, CHC=O), 2.03 (1 H, d septet, *J* 3 and 6.8, Me_2CH), 1.61–1.59 (2 H, m, OH and CHSi), 0.91 (3 H, d, *J* 6.8, C*Me*$_A$Me$_B$), 0.84 (3 H, d, *J* 6.8, CMe$_A$*Me*$_B$), 0.43 (3 H, s, Si*Me*$_A$Me$_B$) and 0.39 (3 H, s, SiMe$_A$*Me*$_B$); *m*/*z* 289 (22%, M^+ – CHOHCH=CH_2) and 135 (100, $PhMe_2Si$) (Found: M^+ – CHOHCH=CH_2, 289.1625. $C_{20}H_{30}O_3Si$, requires *M* – CHOHCH=CH_2, 289.1623).

Allyl (2*SR*,3*RS*)-2-[(1*RS*)-1-dimethyl(phenyl)silylethyl]-3-hydroxy-7-methoxy-7-methyloctanoate. As an oil (74%) from the ester **43a** and the aldehyde **52**; $\nu_{max}(CHCl_3)/cm^{-1}$ 1725 (C=O), 1255 (SiMe) and 1110 (SiPh); $\delta_H(CDCl_3)$ 7.55–7.45 (2 H, m, *o*-SiPh), 7.35–7.33 (3 H, m, *m*- and *p*-SiPh), 5.85 (1 H, m, CH_2CH=CH_2), 5.34–5.20 (2 H, m, CH_2CH=CH_2), 4.41 (2 H, m, CH_2CH=CH_2), 3.75 (1 H, m, CHOH), 3.13 (3 H, s, OMe), 2.59 (1 H, dd, *J* 6.9 and 7.4, CHCO), 1.72–1.15 (7 H, m, 3 × CH_2 and CHSi), 1.10 (6 H, s, Me_2C), 0.99 (3 H, d, *J* 7.6, *Me*CH), 0.31 (3 H, s, $SiMe_AMe_B$) and 0.29 (3 H, s, $SiMe_AMe_B$).

Allyl (4*E*,2*SR*,3*RS*)-2-[(1*RS*)-1-dimethyl(phenyl)silylethyl]-3-hydroxy-9-methoxy-9-methyldec-4-enoate. As an oil (61%) from the ester **43a** and the aldehyde **53**; major diastereoisomer: R_f(hexane–EtOAc, 7:3) 0.54; $\nu_{max}(CHCl_3)/cm^{-1}$ 3460 (OH), 1725 (C=O), 1250 (SiMe) and 1110 (SiPh); δ_H(250 MHz; $CDCl_3$) 7.54–7.46 (2 H, m, *o*-SiPh), 7.36–7.31 (3 H, m, *m*- and *p*-SiPh), 5.84 (1 H, ddt, *J* 10.4, 17.2 and 6.8, CH=CH_2), 5.62–5.57 (2 H, m, CH=CH), 5.28 (1 H, dt, *J* 17.2 and 1.4, CH=CH_AH_B), 5.20 (1 H, dd, *J* 1.3 and 10.4, CH=CH_AH_B), 4.36 (2 H, dt, *J* 6.8 and 1.4, CH_2O), 4.25 (1 H, t, *J* 6.7, CHOH), 3.14 (3 H, s, OMe), 2.67 (1 H, t, *J* 7.3, CHCO), 1.99 (2 H, m, CH_2CH=CH), 1.72–0.85 (5 H, m, CH_2CH_2COMe and CHSi), 1.10 (6 H, s, Me_2C), 1.01 (3 H, d, *J* 7.5, *Me*CHSi), 0.31 (3 H, s, $SiMe_AMe_B$) and 0.29 (3 H, s, $SiMe_AMe_B$); *m*/*z* 417 (0.3%, M − Me), 355 (2, M − C_6H_5), 305 (3), 261 (21), 143 (84), 135 (75, $SiMe_2Ph$) and 73 (100, C_4H_9O) (Found: M^+ − Me, 417.2470. $C_{25}H_{40}O_4Si$ requires *M* − Me, 417.2461).

Allyl (2*SR*,3*RS*)-[(1*RS*)-1-trimethylsilylethyl]-3-hydroxypent-4-enoate. As an oil (41%) from the ester **44a** and acrolein; $R_f(SiO_2$, hexane–EtOAc, 9:1) 0.15; ν_{max}(film)/cm^{-1} 3480 (br, OH), 3080, 2960, 2870 (CH), 1720 (C=O), 1640 (C=C) and 1250 (SiMe); δ_H(250 MHz; $CDCl_3$) 5.98 (1 H, ddd, *J* 6.6, 10.5 and 17.2, HOCHCH=CH_2), 5.89 (1 H, ddt, *J* 10.4, 17.1 and 5.8, CHCH=CH_2), 5.32 (1 H, dq, *J* 17.1 and 1.5, CH_2CH=CH_AH_B), 5.28 (1 H, dt, *J* 17.2 and 1.4, CHCH=CH_AH_B), 5.21 (1 H, dq, *J* 10.4 and 1.3, CH_2CH=CH_AH_B), 5.16 (1 H, dt, *J* 10.5 and 1.3, CHCH=CH_AH_B), 4.53 (1 H, dt, *J* 5.8 and 1.3, CH_2CH=CH_2), 4.40 (1 H, br t, *J* 6, CHCH=CH_2), 2.65 (1 H, t, *J* 7.2, CHCO), 2.04 (1 H, br s, OH), 1.23 (1 H, dq, *J* 10.2 and 7.4, MeCH), 1.01 (3 H, d, *J* 7.4, *Me*CH) and −0.01 (9 H, s, Me_3Si); *m*/*z* 241 (1%, M − Me), 223 (0.3, M − H_2O − Me), 199 (30, M − C_3H_5O), 183 (4, M − C_3H_4 − Me − H_2O or M − Me_3Si), 143 (5, M − C_3H_4 − Me_3Si), 99 (6, $Me_3SiC_3H_5$) and 73 (100, Me_3Si) (Found: M − Me, 241.1244. $C_{13}H_{24}O_3Si$ requires *M* − Me, 241.1260).

Allyl (2*SR*,3*RS*)-2-[(α*SR*)-α-trimethylsilylbenzyl]-3-hydroxypent-4-enoate. As crystals, mp 63–65 °C (49%) from the ester **44b** and acrolein; R_f(EtOAc–hexane, 1:4) 0.18; ν_{max}(film)/cm^{-1} 3475 (OH), 1733 (C=O), 1598 (Ph), 1249 and 841 ($SiMe_3$); δ_H(250 MHz; $CDCl_3$) 7.23–7.17 (2 H, m, *o*-SiPh), 7.13–7.07 (1 H, m, *p*-SiPh), 7.02–6.99 (2 H, m, *m*-SiPh), 5.95 (2 H, m, CH_2=CHCHOH, CH_2=$CHCH_2O$), 5.39 (1 H, dd, *J* 17.1 and 1.4, CH_2CH=CH_AH_B), 5.27 (1 H, dd, *J* 10.4 and 1.2, CH_2CH=CH_AH_B), 5.17 (1 H, dd, *J* 10.4 and 1.2, CHOHCH=CH_AH_B), 4.86 (1 H, dd, *J* 17.1 and 1.4, CHOHCH=CH_AH_B), 4.64 (2 H, dd, *J* 4.6 and 1.2, OCH_2), 4.12 (1 H, m, CHOH), 3.39 (1 H, dd, *J* 12.5 and 4.8, CHCO), 2.44 (1 H, d, *J* 12.5, $CHSiMe_3$), 1.89 (1 H, br s, CHO*H*) and −0.11 (9 H, s, Me_3Si); *m*/*z* 261 (62%, M^+ − C_3H_5O) and 73 (100, $SiMe_3$) (Found: M^+ − C_3H_5O, 261.1288. $C_{18}H_{26}O_3Si$ requires *M* − C_3H_5O, 261.1311).

Removal of allyl group from the esters

General procedure. Methyllithium (1.5 mol dm^{-3} solution in Et_2O; 27 cm^3, 40.5 mmol) was added dropwise to a stirred suspension of copper(I) iodide (4.0 g, 21 mmol) in ether (30 cm^3) at −10 °C under nitrogen. After 15 min the solution was cooled to −20 °C and the allyl ester (7.1 mmol) in ether (10 cm^3) added dropwise over 10 min. After 1 h the solution was allowed to warm to 0 °C. Dilute hydrochloric acid (2 mol dm^{-3} solution; 30 cm^3) was added and the mixture extracted with ether (4 × 50 cm^3). The combined organic extracts were evaporated to a smaller volume (25 cm^3) and extracted with aqueous potassium hydroxide (1 mol dm^{-3} solution; 2 × 25 cm^3). The combined alkaline extracts were acidified to pH 1 with hydrochloric acid (1 mol dm^{-3}) and extracted with ether (4 × 30 cm^3). The combined organic extracts were dried ($MgSO_4$), passed through a short column (SiO_2, Et_2O) and evaporated under reduced pressure to give the acid. The following acids were prepared by this method.

(4*E*,2*R*,3*S*)-2-[(1*S*)-1-Dimethyl(phenyl)silylethyl]-3-hydroxyhex-4-enoic acid 40a. As an oil (67%) (80% ee); R_f(EtOAc–hexane, 1:3) 0.1; $\nu_{max}(CCl_4)/cm^{-1}$ 3100 (OH), 1695 (C=O), 1245 (SiMe) and 1105 (SiPh); δ_H(250 MHz; $CDCl_3$) 7.55–7.50 (2 H, m, *o*-SiPh), 7.35–7.30 (3 H, m, *m*- and *p*-SiPh), 5.70–5.53 (2 H, m, CHOHCH=CHMe), 4.25 (1 H, t, *J* 6.8, CHOH), 2.67 (1 H, t, *J* 7.0, CHCO), 1.66 (3 H, d, *J* 4.9, *Me*CH=CH), 1.48 (1 H, quintet, *J* 7.3, CHSi), 1.00 (3 H, d, *J* 7.6, *Me*CHSi), 0.33 (3 H, s, $SiMe_AMe_B$) and 0.32 (3 H, s, $SiMe_AMe_B$); *m*/*z* 259 (1%, M^+ − Me − H_2O), 143 (59) and 135 (100, $PhMe_2Si$) (Found: M^+ − Me − H_2O, 259.1138. $C_{16}H_{24}O_3Si$ requires *M* − Me − H_2O, 259.1155).

(3*R*)-3-Dimethyl(phenyl)silyl-4-methylpentanoic acid. As an oil (90%), identical to the sample prepared previously by a different route.[28]

(4*E*,2*R*,3*S*)-2-[(1*S*)-1-Dimethyl(phenyl)silyl-2-methylpropyl]-3-hydroxyhex-4-enoic acid 40b. As an oil (59%); R_f(hexane–EtOAc, 3:1) 0.89; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3150 (OH), 1700 (C=O) and 1110 (SiPh); δ_H(250 MHz; $CDCl_3$), 7.59–7.49 (2 H, m, *o*-SiPh), 7.35–7.30 (3 H, m, *m*- and *p*-SiPh), 5.56 (1 H, dq, *J* 15.2 and 5.2, MeCH=CH), 5.47 (1 H, dd, *J* 6.2 and 15.3, MeCH=CH), 4.03 (1 H, t, *J* 6.9, CHOH), 2.77 (1 H, dd, *J* 2.4 and 8, CHCO), 2.04 (1 H, d septet, *J* 3 and 6.7, Me_2CH), 1.65 (3 H, d, *J* 5.2, *Me*CH=CH), 1.66–1.58 (1 H, m, CHSi), 0.90 (3 H, d, *J* 6.7, CMe_AMe_B), 0.88 (3 H, d, *J* 6.7, CMe_AMe_B) and 0.39 (6 H, s, Me_2Si). This sample failed to give a satisfactory mass spectrum.

(4*E*,2*S*,3*R*)-3-Hydroxy-2-[(1*R*)-1-trimethylsilylethyl]hex-4-enoic acid 41a. As an oil (70%) (64% ee); R_f(EtOAc–hexane, 1:3) 0.1; ν_{max}(film)/cm^{-1} 3700–2200 (2OH), 1700 (C=O), 1245 (SiMe) and 970 (*trans*-CH=CH); δ_H(250 MHz; $CDCl_3$) 5.80–5.60 (2 H, m, MeCH=CH), 4.36 (1 H, t, *J* 6.85, CHOH), 2.65 (1 H, t, *J* 7.2, CHCO), 1.70 (3 H, d, *J* 5.45, *Me*CH=CH), 1.18 (1 H, m, MeCHSi), 1.01 (3 H, d, *J* 7.5, *Me*CHSi) and 0.02 (9 H, s, $SiMe_3$); *m*/*z* 160 (1.04%, M^+ − C_4H_6O), 143 (10) and 73 (100, $SiMe_3$) (Found: M^+ − C_4H_6O, 160.0917. $C_{11}H_{22}O_3Si$ requires *M* − C_4H_6O, 160.0920).

(4*E*,2*S*,3*R*)-2-[(1*R*)-1-Trimethylsilyl-2-methylpropyl]-3-hydroxyhex-4-enoic acid 41b. As an oil (52%); ν_{max}(film)/cm^{-1} 3400 (OH), 3300–2500 (CO_2H), 1710 (C=O) and 1250 (SiMe); δ_H(250 MHz; $CDCl_3$) 5.75–5.65 (2 H, m, MeCH=CH), 4.26 (1 H, t, *J* 8.2, CHOH), 2.67 (1 H, dd, *J* 3.3 and 8.2, CHCO), 2.05 (1 H, m, Me_2CH), 1.70 (3 H, d, *J* 8.2, *Me*CH=CH), 1.19 (1 H, m, CHSi), 0.97 (3 H, d, *J* 7.1, CMe_AMe_B) and 0.88 (3 H, d, *J* 7.1, CMe_AMe_B) and 0.06 (9 H, s, Me_3Si).

(4*E*,2*S*,3*R*)-5-Cyclohexyl-2-[(1*R*)-1-trimethylsilylethyl]-3-hydroxypent-4-enoic acid 41c. As an oil (54%); $R_f(CHCl_3$–MeOH, 40:1) 0.11; δ_H(250 MHz; $CDCl_3$) 5.68 (1 H, dd, *J* 6.2 and 15.5, CH=CHCHOH), 5.56 (1 H, dd, *J* 7.0 and 15.5, CH=CHCHOH), 4.35 (1 H, t, *J* 7, CHOH), 2.66 (1 H, t, *J* 7, CHCO), 1.95–1.66 (8 H, m, OH, CO_2H and 6 × ring CH), 1.26–0.98 (6 H, m, MeCHSi and 5 × ring CH), 1.00 (3 H, d, *J* 7.5, *Me*CHSi) and 0.02 (9 H, s, Me_3Si); *m*/*z* 265 (8.4%, M^+ − H_2O − Me) and 73 (100, Me_3Si) (Found: M^+ − H_2O − Me, 265.1633. $C_{16}H_{30}O_3Si$ requires *M* − H_2O − Me, 265.1624).

(2*SR*,3*RS*)-[(1*RS*)-Dimethyl(phenyl)silylethyl]-3-hydroxypent-4-enoic acid 45a. As an oil (77%); ν_{max}(film)/cm^{-1} 3500–2500 (br CO_2H and OH), 1690 (C=O), 1250 (SiMe) and 1110 (SiPh); δ_H(250 MHz; $CDCl_3$), 7.57–7.50 (2 H, m, *o*-SiPh), 7.38–7.32 (3 H, m, *m*- and *p*-SiPh), 5.97 (1 H, ddd, *J* 6.7, 10.4 and 17.1, CH_2=CHCH), 5.25 (1 H, d, *J* 17.2, CH=CH_AH_B), 5.17

(1 H, d, J 10.4, CH=CH$_A$H$_B$), 4.33 (1 H, t, J 7.0, CHOH), 2.68 (1 H, t, J 7.1, CHCO), 1.52 (1 H, quintet, J 7.4, SiCHMe), 1.04 (3 H, d, J 7.6, SiCHMe), 0.35 (3 H, s, SiMe$_A$Me$_B$) and 0.34 (3 H, s, SiMe$_A$Me$_B$); m/z 263 (0.3%, M$^+$ − Me), 245 (2, M − Me − H$_2$O), 201 (6, M − Ph), 183 (7, M − Ph − H$_2$O), 143 (75, M − Me$_2$SiPh) and 135 (100, Me$_2$SiPh) (Found: M$^+$ − Me, 263.1101. $C_{15}H_{22}O_3Si$ requires M − Me, 263.1104).

(2*SR*,3*RS*)-2-[(1*RS*)-1-Dimethyl(phenyl)silyl-2-methylpropyl]-3-hydroxypent-4-enoic acid 45b. As an oil (59%); ν_{max}(CH$_2$Cl$_2$)/cm^{-1} 3000 (OH), 1690 (C=O), 1250 (SiMe) and 1110 (SiPh); δ_H(250 MHz; CDCl$_3$) 7.56–7.49 (2 H, m, *o*-SiPh), 7.35–7.31 (3 H, m, *m*- and *p*-SiPh), 5.93 (1 H, ddd, J 6.6, 10.3 and 17.1, CH=CH$_2$), 5.27 (1 H, dd, J 1.2 and 17.1, CH=CH$_A$H$_B$), 5.18 (1 H, dd, J 1.2 and 10.3, CH=CH$_A$H$_B$), 4.22 (1 H, t, J 6.7, CHOH), 2.75 (1 H, dd, J 2.8 and 7.6, CHCO), 2.05 (1 H, m, Me$_2$CH), 1.22 (1 H, t, J 2.8, SiCH), 0.98 (3 H, d, J 6.8, CMe$_A$Me$_B$), 0.93 (3 H, d, J 6.8, CMe$_A$Me$_B$), 0.44 (3 H, s, SiMe$_A$Me$_B$) and 0.39 (3 H, s, SiMe$_A$Me$_B$). This sample failed to give a satisfactory mass spectrum.

(2*SR*,3*RS*)-2-[(1*RS*)-1-Dimethyl(phenyl)silylethyl]-3-hydroxy-7-methoxy-7-methyloctanoic acid 45c. As an oil (44%); ν_{max}(CHCl$_3$) 1700 (C=O), 1250 (SiMe) and 1110 (SiPh); δ_H(CDCl$_3$) 7.56–7.49 (2 H, m, *o*-SiPh), 7.35–7.32 (3 H, m, *m*- and *p*-SiPh), 3.77 (1 H, m, CHOH), 3.14 (3 H, s, OMe), 2.60 (1 H, t, J 7, CHCO), 1.65–1.15 (7 H, m, 3 × CH$_2$ and CHSi), 1.11 (6 H, s, Me$_2$C), 1.02 (3 H, d, J 7.7, MeCH), 0.33 (3 H, s, SiMe$_A$Me$_B$) and 0.32 (3 H, s, SiMe$_A$Me$_B$).

(4*E*,2*SR*,3*RS*)-2-[(1*RS*)-1-Dimethyl(phenyl)silylethyl]-3-hydroxy-9-methoxy-9-methyldec-4-enoic acid 45d. As an oil (26%); δ_H(250 MHz; CDCl$_3$) 7.56–7.41 (2 H, m, *o*-SiPh), 7.36–7.31 (3 H, m, *m*- and *p*-SiPh), 5.60 (1 H, td, J 5.6 and 15.4, CH=CHCHOH), 5.56 (1 H, dd, J 6.3 and 15.4, CH=CHCHOH), 4.26 (1 H, t, J 6.6, CHOH), 3.14 (3 H, s, OMe), 2.67 (1 H, t, J 6.9, CHCO), 2.05–1.92 (2 H, m, CH$_2$CH=CH), 1.57–1.16 (5 H, m, CH$_2$CH$_2$CMe$_2$ and CHSi), 1.11 (6 H, s, Me$_2$C), 1.01 (3 H, d, J 7.2, MeCHSi), 0.33 (3 H, s, SiMe$_A$Me$_B$) and 0.32 (3 H, s, SiMe$_A$Me$_B$).

(2*SR*,3*RS*)-[(1*RS*)-1-Trimethylsilylethyl]-3-hydroxypent-4-enoic acid 46a. As an oil (86%); ν_{max}(film)/cm^{-1} 3500–2500 (br CO$_2$H, OH and CH), 1700 (C=O), 1640 (C=C) and 1250 (SiMe); δ_H(250 MHz; CDCl$_3$) 6.01 (1 H, ddd, J 6.7, 10.4 and 17.1, CHCH=CH$_2$), 5.31 (1 H, td, J 1.2 and 17.1, CHCH=CH$_A$H$_B$), 5.19 (1 H, td, J 1.2 and 10.4, CHCH=CH$_A$H$_B$), 4.42 (1 H, t, J 6.8, CHCH=CH$_2$), 2.64 (1 H, t, J 7.2, CHCO), 1.25–1.06 (1 H, m, MeCH), 1.02 (3 H, d, J 7.4, MeCH) and 0.01 (9 H, s, Me$_3$Si); m/z 199 (0.2%, M$^+$ − OH), 183 (7, M − Me − H$_2$O), 159 (6, M − C$_3$H$_5$O), 143 (20, M − Me$_3$Si), 81 (27, CH$_2$=CHCH=CHC=O) and 73 (100, Me$_3$Si) (Found: M$^+$ − OH, 199.1152. $C_{10}H_{20}O_3Si$ requires M − OH, 199.1154).

(2*SR*,3*RS*)-2-[(α*SR*)-α-Trimethylsilylbenzyl]-3-hydroxypent-4-enoic acid 46b. As fine needles, mp 135–136 °C (81%); ν_{max}(CH$_2$Cl$_2$)/cm^{-1} 3596 (OH), 1708 (C=O), 1251 and 846 (SiMe$_3$); δ_H(250 MHz; CDCl$_3$) 7.24 (2 H, m, *o*-SiPh), 7.12 (1 H, m, *p*-SiPh), 7.02 (2 H, m, *m*-SiPh), 5.96 (1 H, ddd, J 17.1, 10.5 and 7.1, CH=CH$_2$), 5.14 (1 H, d, J 10.5, CH=CH$_A$H$_B$), 4.91 (1 H, d, J 17.1, CH=CH$_A$H$_B$), 4.18 (1 H, dd, J 7.1 and 4.7, CHOH), 3.41 (1 H, dd, J 12.5 and 4.7, CHCO), 2.42 (1 H, d, J 12.5, CHSi) and −0.06 (9 H, s, Me$_3$Si) (Found: C, 64.8%; H, 8.1; M$^+$ − C$_3$H$_5$O, 221.1015. $C_{15}H_{22}O_3Si$ requires C, 64.7; H, 7.95; M − C$_3$H$_5$O, 221.0998).

Removal of silylethyl group from the esters

General procedure. Tetrabutylammonium fluoride (1.1 mol dm^{-3} in THF; 12.5 cm^3, 13.8 mmol) was added dropwise to a stirred solution of the ester (3.44 mmol) in THF (25 cm^3) under argon at room temperature. The resulting green solution was stirred for 2 h, quenched with ether (50 cm^3) and water (50 cm^3), stirred for 5 min and extracted with ether (3 × 50 cm^3). The combined organic layers were extracted with potassium hydroxide solution (1 mol dm^{-3}; 4 × 50 cm^3). The aqueous phases were acidified with hydrochloric acid (3 mol dm^{-3}) and extracted with ether (4 × 50 cm^3). The organic extract was dried (MgSO$_4$) and evaporated under reduced pressure to give the acid. The following acids were prepared by this method.

(2*S*,3*R*)-2-[(1*R*)-1-Trimethylsilylethyl]-3-hydroxy-5-methyl-5-(2-methoxyethoxy)methoxyhexanoic acid 41d. As an oil (98%) from the hydroxyester prepared from **39b** and **49**; R_f(EtOAc–hexane, 50:50) 0.26; [α]$_D$ −9.9 (c 1.4 in CHCl$_3$); ν_{max}(film)/cm^{-1} 3500 (OH), 3500–2500 (acid OH), 1710 (C=O) and 1245 and 835 (SiMe$_3$); δ_H(250 MHz; CDCl$_3$) 4.84 (1 H, d, J 7.6, OCH$_A$H$_B$O), 4.81 (1 H, d, J 7.6, OCH$_A$H$_B$O), 4.29 (1 H, br dd, J 7.2 and 9.3, CHOH), 3.71–3.66 (2 H, m, OCH$_2$OCH$_2$), 3.55–3.50 (2 H, m, CH$_2$OMe), 3.37 (3 H, s, OMe), 2.59 (1 H, t, J 7.3, CHC=O), 1.77 (1 H, dd, J 10.3 and 14.7, CH$_A$H$_B$CMe$_2$), 1.55 (1 H, br d, J 14.7, CH$_A$H$_B$CMe$_2$), 1.30–0.90 (1 H, m, CHSi), 1.35 (3 H, s, CMe$_A$Me$_B$), 1.30 (3 H, s, CMe$_A$Me$_B$), 0.99 (3 H, d, J 7.6, MeCH) and 0.02 (9 H, s, SiMe$_3$); m/z 351 (10%, M + H$^+$), 333 (30, M − OH), 275 (40, M − MeOCH$_2$CH$_2$O), 245 (20, M − MeOCH$_2$CH$_2$OCH$_2$O), 89 (95, MeOC$_2$H$_4$OCH$_2$), 73 (100, SiMe$_3$) and 59 (95, MeOC$_2$H$_4$) (Found: M + H$^+$, 351.2185. $C_{16}H_{34}O_6Si$ requires M + H$^+$, 351.2203).

(4*E*,2*S*,3*R*)-2-[(1*R*)-Trimethylsilylethyl]-3-hydroxy-7-methyl-7-(2-methoxyethoxy)methoxyoct-4-enoic acid 41e. As an oil (98%); R_f(Et$_2$O) 0.26; [α]$_D$ −22.1 (c 1.1 in CHCl$_3$); ν_{max}(film)/cm^{-1} 3475 (OH), 3500–2500 (acid OH), 1710 (C=O) and 1250 and 840 (SiMe$_3$); δ_H(250 MHz; CDCl$_3$) 5.82 (1 H, dt, J 15.4 and 7.2, CH=CHCO), 5.61 (1 H, dd, J 7.0 and 15.4, CH=CHCO), 4.78 (1 H, d, J 7.6, OCH$_A$H$_B$O), 4.76 (1 H, d, J 7.6, OCH$_A$H$_B$O), 4.40 (1 H, br t, J 7.2, CHOH), 3.76–3.64 (2 H, m, OCH$_2$OCH$_2$), 3.62–3.55 (2 H, m, CH$_2$OMe), 3.39 (3 H, s, OMe), 2.64 (1 H, t, J 7.1, CHC=O), 2.27 (1 H, dd, J 7.1 and 14.0, CH$_A$H$_B$CMe$_2$), 2.19 (1 H, dd, J 7.1 and 14.0, CH$_A$H$_B$CMe$_2$), 1.30–0.90 (1 H, m, CHSi), 1.19 (6 H, s, CMe$_2$), 1.03 (3 H, d, J 7.5, MeCH) and 0.02 (9 H, s, SiMe$_3$); m/z 376 (20%, M$^+$) (Found: M$^+$, 376.2276. $C_{18}H_{36}O_6Si$ requires M, 376.2281).

Removal of a benzyl group from an ester

2-[1-Dimethyl(phenyl)silylethyl]-3-hydroxy-7-methoxy-7-methyloctanoic acid 45c. The aldol product derived from the benzyl ester **43b** and the aldehyde **52** (0.41 g, 0.93 mmol) in methanol (15 cm^3) was stirred with palladium (50 mg, 10% on C) in a low-pressure hydrogenator under hydrogen for 7 h. The mixture was filtered and the solvent was evaporated. The residue was taken up in ether (25 cm^3) and extracted with sodium hydroxide solution (5%; 2 × 10 cm^3). The combined aqueous layers were acidified with dilute hydrochloric acid and extracted with ethyl acetate. The extract was washed with brine, dried (MgSO$_4$) and evaporated at reduced pressure to give the diastereoisomeric mixture of acids (0.244 g, 75%), identical (IR, ^{1}H NMR) with the material prepared from the corresponding allyl ester.

Synthesis of allylsilanes and pentadienylsilanes by decarboxylative eliminations and removal of *E*,*E* isomers

General procedure. Benzenesulfonyl chloride (0.9 cm^3, 7 mmol) was added to a solution of the hydroxy acid (2.4 mmol) in dry pyridine (14 cm^3) at 0 °C and under nitrogen, and the solution kept in a refrigerator at 4 °C for 18 h. Ice–water (15 cm^3) was added and the mixture extracted with ether (4 × 30 cm^3). The combined organic extracts were dried (MgSO$_4$) and evaporated under reduced pressure, and the residue chromatographed (SiO$_2$, hexane) to give an inseparable mixture of allylsilanes or pentadienylsilanes (typically 50%), with the pentadienylsilanes in a ratio Z,E:E,E typically of 90:10 (^{1}H NMR). In the case of the pentadienylsilanes, the mixture (1.1 mmol) was dissolved in dry benzene (10 cm^3) and stirred with *N*-phenylmaleimide (0.35 g, 2 mmol) and hydroquinone (1 mg) at 60 °C for 2 d. The solvent was removed under reduced pressure and the residue chromatographed (SiO$_2$, hexane) to give the 3Z,5E-dienylsilane. The following allylsilanes and

pentadienylsilanes were prepared by this method, in some cases with isolation of the intermediate β-lactone.

(3*Z*,5*E*,2*S*)-Dimethyl(hepta-3,5-dien-2-yl)phenylsilane 9. As an oil (42%) from the acid **40a** (80% ee); R_f(hexane) 0.6; $[\alpha]_D$ +62.65 (*c* 3.5 in $CHCl_3$); ν_{max}(film)/cm^{-1} 1250 (SiMe), 1105 (SiPh) and 970 (*trans*-CH=CH); δ_H(250 MHz; $CDCl_3$) 7.5–7.3 (5 H, m, Ph), 6.17 (1 H, dd, *J* 11.0 and 14.7, MeCH=C*H*), 5.85 (1 H, t, *J* 11.0, MeCH=CHC*H*=), 5.58 (1 H, dq, *J* 14.7 and 6.1, MeC*H*=CH), 5.06 (1 H, t, *J* 11, SiCHC*H*=C), 2.24 (1 H, dq, *J* 11 and 7.3, MeC*H*Si), 1.72 (3 H, dd, *J* 1.2 and 6.1, *Me*CH=CH), 1.00 (3 H, d, *J* 7.3, *Me*CHSi) and 0.26 (6 H, s, $SiMe_2$); *m*/*z* 230 (1.37%, M^+) and 135 (100, $PhMe_2Si$) (Found: M^+, 230.1509. $C_{15}H_{22}Si$ requires *M*, 230.1490).

(3*Z*,5*E*,2*R*)-Hepta-3,5-dien-2-yl(trimethyl)silane 13. As an oil (32%) from **41a** (64% ee); R_f(hexane) 0.8; $[\alpha]_D$ −51.4 (*c* 1.67 in $CDCl_3$); ν_{max}(film)/cm^{-1} 1245 (SiMe) and 945 (*trans*-CH=CH); δ_H(250 MHz; $CDCl_3$) 6.28–6.18 (1 H, m, MeCH=C*H*), 5.84 (1 H, t, *J* 10.7, C*H*=CHCHSi), 5.60 (1 H, dq, *J* 15.0 and 6.7, MeC*H*=CH), 5.09 (1 H, t, *J* 10.7, CH=C*H*CHSi), 2.03 (1 H, dq, *J* 10.7 and 7.05, CHSi), 1.74 (3 H, dd, *J* 1.3 and 6.7, *Me*CH=CH), 1.03 (3 H, d, *J* 7.05, *Me*CHSi) and −0.04 (9 H, s, $SiMe_3$); *m*/*z* 168 (8.4%, M^+) and 73 (100, $SiMe_3$) (Found: M^+, 168.1326. $C_{10}H_{20}Si$ requires *M*, 168.1334). The ratio of *Z*,*E* to *E*,*E* isomers in the crude reaction mixture was 5:1 (determined by integration of the *Me*CH=CH peaks in the 250 MHz ^{1}H NMR spectrum). The *E*,*E* isomer had δ_H(250 MHz; $CDCl_3$; assignable peaks) 6.11–5.95 (1 H, m, MeCH=C*H*), 5.7–5.4 (1 H, m, MeC*H*=CH), 1.71 (3 H, dd, *J* 1.3 and 8.2, *Me*CH=CH), 1.04 (3 H, d, *J* 7.1, *Me*CHSi) and −0.04 (9 H, s, $SiMe_3$).

(4*Z*,6*E*,3*S*)-(2-Methylocta-4,6-dien-3-yl)dimethyl(phenyl)-silane 14. As an oil (43%); R_f(hexane–EtOAc, 25:1) 0.63; ν_{max}($CHCl_3$)/cm^{-1} 1250 (SiMe), 1100 (PhSi) and 970 (*trans*-CH=CH); δ_H(250 MHz; $CDCl_3$) 7.56–7.49 (2 H, m, *o*-SiPh), 7.39–7.27 (3 H, m, *m*- and *p*-SiPh), 6.11 (1 H, ddq, *J* 11.7, 14.9 and 1.2, MeCH=C*H*), 6.00 (1 H, dd, *J* 10.8 and 11.7, SiCHCH=C*H*), 5.25 (1 H, dq, *J* 14.9 and 6.5, MeC*H*), 5.23 (1 H, dd, *J* 10.8 and 12.7, SiCHC*H*=CH), 2.15 (1 H, dd, *J* 2.5 and 12.7, CHSi), 1.91–1.78 (1 H, m, C*H*Me_2), 1.72 (3 H, dd, *J* 1.2 and 6.5, *Me*CH=CH), 0.83 (3 H, d, *J* 6.7, C*Me*$_A$$Me_B$), 0.82 (3 H, d, *J* 6.7, CMe_A*Me*$_B$), 0.30 (3 H, s, Si*Me*$_A$$Me_B$) and 0.27 (3 H, s, $SiMe_A$*Me*$_B$); *m*/*z* 258 (3.32%, M^+) and 135 (100, $PhMe_2Si$) (Found: M^+, 258.1811. $C_{17}H_{26}Si$ requires *M*, 258.1803).

(4*Z*,6*E*,3*R*)-(2-Methylocta-4,6-dien-3-yl)trimethylsilane 17. As an oil (31%); R_f(hexane–EtOAc, 25:1) 0.65; ν_{max}(film)/cm^{-1} 1600 (C=C) and 1250 (SiMe); δ_H(250 MHz; $CDCl_3$) 6.20 (1 H, dd, *J* 11 and 14.7, C*H*=CHMe), 5.98 (1 H, t, *J* 10.9, SiCHCH=C*H*), 5.62 (1 H, dq, 14.7 and 6.7, CH=C*H*Me), 5.21 (1 H, t, *J* 11, SiCHC*H*=CH), 1.94–1.84 (2 H, m, CHSi and Me_2C*H*), 1.75 (3 H, dd, *J* 1.4 and 6.6, CH=CH*Me*), 0.92 (3 H, d, *J* 6.4, C*Me*$_A$$Me_B$), 0.90 (3 H, d, *J* 6.4, CMe_A*Me*$_B$) and 0.00 (9 H, s, Me_3Si); *m*/*z* 198 (5.5%, M^+), 122 (28, M − $PhMe_2SiH$) and 73 (100, $PhMe_2Si$) (Found: M^+, 196.1664. $C_{12}H_{24}Si$ requires *M*, 196.1647).

(2*SR*,3*RS*)-[(1*RS*)-1-Dimethyl(phenyl)silylethyl]-3-ethenyl-propano-3-lactone. As an oil (69%); R_f(hexane–EtOAc, 9:1) 0.38; ν_{max}($CDCl_3$) 3060, 2950, 2870 (CH), 1800 (C=O), 1720 (C=C), 1250 (SiMe) and 1110 (SiPh); δ_H(250 MHz; $CDCl_3$) 7.59–7.53 (2 H, m, *o*-SiPh), 7.39–7.34 (3 H, m, *m*- and *p*-SiPh), 6.00 (1 H, ddd, *J* 7.0, 10.4 and 17.2, CH_2=C*H*), 5.50 (1 H, d, *J* 17.2, CH=C*H*$_A$H$_B$), 5.46 (1 H, d, *J* 10.6, CH=CH$_A$*H*$_B$), 4.88 (1 H, t, *J* 6.7, CHO), 3.52 (1 H, dd, *J* 6.3 and 12.3, CHCO), 1.44 (3 H, dq, *J* 12.3 and 7.2, SiC*H*Me), 0.82 (3 H, d, *J* 7.2, SiCH*Me*), 0.46 (3 H, s, Si*Me*$_A$$Me_B$) and 0.40 (3 H, s, $SiMe_A$*Me*$_B$), with signals due to traces of each of the minor diastereoisomers also observed, notably those for the methyl doublet, at 1.20 (*J* 7.3), 1.19 (*J* 7.3) and 1.10 (*J* 7.4), the approximate relative ratios, for all four diastereoisomers, in order of decreasing chemical shift, were 2:4:6:88; *m*/*z* 245 (0.5%, M^+ − Me), 216 (3, M − CO_2) and 135 (100, Me_2SiPh) (Found: M^+ − Me, 245.0987. $C_{15}H_{20}O_2Si$ requires *M* − Me, 245.0998).

(3*Z*)-Hexa-3,5-dien-2-yldimethyl(phenyl)silane 20aa. As an oil by refluxing the lactone above (0.43 g, 1.65 mmol) in 2,4,6-trimethylpyridine (10 cm^3) (redistilled from calcium hydride) for 3.75 h to give the mixture of *dienes* (0.31 g, 87%), which were separated in the usual way to give the pure *Z* diene; R_f(hexane) 0.62; ν_{max}(film)/cm^{-1} 3070, 3000, 2950, 2860 (CH), 1630, 1580 (diene), 1250 (SiMe) and 1110 (SiPh); δ_H(250 MHz; $CDCl_3$) 7.56–7.49 (2 H, m, *o*-SiPh), 7.41–7.35 (3 H, m, *m*- and *p*-SiPh), 6.56 (1 H, ddt, *J* 1.0, 16.8 and 10.6, CH_2=C*H*), 5.96 (1 H, dt, *J* 0.6 and 11.0, CH_2=CHC*H*), 5.28 (1 H, t, *J* 11.4, CH_2=CHCH=C*H*), 5.15 (1 H, dd, *J* 2.2 and 16.8, CH=C*H*$_A$H$_B$), 5.02 (1 H, d, *J* 10.0, CH=CH$_A$*H*$_B$), 2.33 (1 H, ddq, *J* 0.9, 11.3 and 7.1, SiC*H*Me), 1.07 (3 H, d, *J* 7.1, SiCH*Me*), 0.311 (3 H, s, Si*Me*$_A$Me$_B$) and 0.307 (3 H, s, $SiMe_A$*Me*$_B$); *m*/*z* 216 (6%, M^+), 201 (1, M − Me) and 135 (100, Me_2SiPh) (Found: M^+, 216.1338. $C_{14}H_{20}Si$ requires *M*, 216.1334). The *E* isomer gave ^{1}H NMR signals at δ 6.35 (1 H, dt, *J* 17.0 and 10.2, CH_2=C*H*), 5.94 (1 H, dd, *J* 9.9 and 15.0, CH_2=CHC*H*), 5.78 (1 H, dd, *J* 7.3 and 15.0, CH_2=CHCH=C*H*), 5.05 (1 H, dd, *J* 2.2 and 17.0, CH=C*H*$_A$H$_B$), 4.91 (1 H, dd, *J* 2.2 and 10.6, CH=CH$_A$*H*$_B$) and 1.10 (3 H, d, *J* 7.2, SiCH*Me*). The ratio of *Z*- to *E*-diene was 11:2.

(4*Z*)-(2-Methylhepta-4,6-dien-3-yl)dimethyl(phenyl)silane 20ab. As an oil (86%); R_f(hexane–EtOAc, 5:1) 0.78; ν_{max}(CH_2Cl_2)/cm^{-1} 1630 (C=C), 1580 (C=C), 1250 (SiMe) and 1110 (SiPh); δ_H(250 MHz; $CDCl_3$) 7.61–7.51 (2 H, m, *o*-SiPh), 7.42–7.38 (3 H, m, *m*- and *p*-SiPh), 6.60 (1 H, dt, *J* 16.8 and 10.8, C*H*=CH_2), 6.17 (1 H, t, *J* 10.9, SiCHCH=C*H*), 5.50 (1 H, t, *J* 11.7, SiCHC*H*=CH), 5.21 (1 H, d, *J* 16.8, CH=C*H*$_A$H$_B$), 5.07 (1 H, d, *J* 10.8, CH=CH$_A$*H*$_B$), 2.29 (1 H, dd, *J* 5.1 and 12.3, SiCH), 1.95 (1 H, d septet, *J* 5.1 and 5.8, Me_2C*H*), 0.92 (6 H, d, *J* 6.8, *Me*$_2$CH), 0.39 (3 H, s, Si*Me*$_A$Me$_B$) and 0.36 (3 H, s, $SiMe_A$*Me*$_B$); *m*/*z* 244 (3%, M^+) and 135 (100, $PhMe_2Si$) (Found: M^+, 244.1658. $C_{16}H_{24}Si$ requires *M*, 244.1647).

(2*SR*,3*RS*)-[(1*RS*)-Trimethylsilylethyl]-3-ethenylpropano-3-lactone. As an oil (65%); R_f(hexane–EtOAc, 9:1) 0.33; ν_{max}(film)/cm^{-1} 3100, 2960, 2910, 2870 (CH), 1820 (C=O) and 1250 (SiMe); δ_H(250 MHz; $CDCl_3$) 6.02 (1 H, ddd, *J* 6.9, 10.5 and 17.2, C*H*=CH_2), 5.53 (1 H, td, *J* 1.2 and 17.2, CH=C*H*$_A$H$_B$), 5.47 (1 H, td, *J* 1.0 and 10.5, CH=CH$_A$*H*$_B$), 4.95 (1 H, br t, *J* 7.4, CH_2=CHC*H*OCO), 3.62 (1 H, dd, *J* 6.3 and 12.4, SiCHC*H*COO), 1.22 (1 H, dq, *J* 12.4 and 7.2, MeC*H*), 0.85 (3 H, d, *J* 7.2, *Me*CH) and 0.08 (9 H, s, Me_3Si); *m*/*z* 183 (10%, M^+ − Me), 154 (1, M − CO_2) and 73 (100, Me_3Si) (Found: M^+ − Me, 183.0826. $C_{10}H_{18}O_2Si$ requires *M* − Me, 183.0841).

(3*Z*)-(Hexa-3,5-dien-2-yl)trimethylsilane 20ba. Heating the lactone above (1.23 g, 6.2 mmol) in a Kugelrohr apparatus at atmospheric pressure for 2 h, while the temperature was gradually increased from 170 °C to 200 °C, gave a mixture of dienes (*ca.* 0.9 g), which were separated in the usual way to give the pure *Z diene* as an oil (0.70 g, 73%); R_f(hexane–EtOAc, 9:1) 0.71; ν_{max}($CDCl_3$)/cm^{-1} 3070, 2950, 2920, 2870 (CH), 1630, 1580 (C=CC=C) and 1250 (SiMe); δ_H(250 MHz; $CDCl_3$) 6.58 (1 H, ddt, *J* 0.9, 16.8 and 10.6, CH_2=C*H*CH=CH), 5.93 (1 H, t, *J* 11.0, CH_2=CHC*H*=CH), 5.29 (1 H, t, *J* 11.1, CH_2=CHCH=C*H*), 5.15 (1 H, dd, *J* 2.1 and 16.8, CH=CHCH=C*H*$_A$H$_B$), 5.02 (1 H, d, *J* 10.1, CH=CHCH=CH$_A$*H*$_B$), 2.10 (1 H, dq, *J* 11.3 and 7.0, MeC*H*), 1.08 (3 H, d, *J* 7.0, *Me*CH) and 0.00 (9 H, s, Me_3Si); *m*/*z* 154 (34%, M^+) and 73 (100, Me_3Si) (Found: M^+, 154.1185. $C_9H_{18}Si$ requires *M*, 154.1178). The *E* isomer gave ^{1}H NMR signals at δ_H(250 MHz; $CDCl_3$) 6.35 (1 H, dt, *J* 10.6 and 16.8, CH_2=C*H*CH=CH) and 5.76 (1 H, dd, *J* 9 and 16, CH_2=CHC*H*=CH).

(2*Z*)-(1-Phenylpenta-2,4-dienyl)trimethylsilane 20bc. Refluxing the crude lactone in 2,4,6-trimethylpyridine for 3 h, and separating in the usual way gave the pure *Z* diene as an oil (50%); R_f(EtOAc–hexane, 10:90) 0.62; ν_{max}(film)/cm^{-1} 1235 and 825 ($SiMe_3$); δ_H(250 MHz; $CDCl_3$) 7.28–7.22 (2 H, m, *o*-SiPh), 7.12–7.06 (3 H, m, *m*- and *p*-SiPh), 6.66 (1 H, dt,

J 16.9, 10.2, C*H*=CH_AH_B), 6.05 (1 H, dd, *J* 11.0 and 10.2, PhCHCH=C*H*), 5.88 (1 H, dd, *J* 11.5 and 11.0, PhCHC*H*), 5.19 (1 H, dd, *J* 16.9 and 1.8, CH=CH_AH_B), 5.08 (1 H, dd, *J* 10.2 and 1.8, CH=CH_AH_B), 3.46 (1 H, d, *J* 11.5, CHSi) and −0.04 (9 H, s, Me_3Si); *m/z* 216 (9%, M^+) and 73 (100, $SiMe_3$) (Found: M^+, 216.1332. $C_{14}H_{20}Si$ requires *M*, 216.1334).

(2*S*,3*Z*,5*E*)-(6-Cyclohexylhexa-3,5-dien-2-yl)trimethylsilane 25. As an oil (83%); R_f(hexane) 0.51; ν_{max}(film)/cm^{-1} 1450 (C=C) and 1250 (MeSi); δ_H(250 MHz; $CDCl_3$) 6.7 (1 H, dd, *J* 10.9 and 15.2, CHCH=C*H*), 5.84 (1 H, t, *J* 10.9, SiCHCH=C*H*), 5.55 (1 H, dd, *J* 6.8 and 15.2, CHC*H*=CH), 5.11 (1 H, t, *J* 10.9, SiCHC*H*=CH), 2.09–1.96 (2 H, m, C*H*CH=CH and MeC*H*Si), 1.73–1.61 (5 H, m, 5 × ring CH), 1.29–1.02 (5 H, m, 5 × ring CH), 1.03 (3 H, d, *J* 6.8, *Me*CHSi) and −0.42 (9 H, s, Me_3Si); *m/z* 236 (7.7%, M^+), 162 (23, M − Me_3SiH) and 73 (100, Me_3Si) (Found: M^+, 236.1953. $C_{15}H_{28}Si$ requires *M*, 236.1960).

2-[1-Dimethyl(phenyl)silylethyl]-3-(4-methoxy-4-methylpentyl)propano-3-lactone. As an oil (61%) as a mixture of diastereoisomers, of which the major lactone had the following properties; ν_{max}($CHCl_3$) 1805 (C=O), 1250 (SiMe) and 1110 (SiPh); δ_H($CDCl_3$) 7.58–7.34 (5 H, m, Ph), 4.46 (1 H, m, CHO), 3.43 (1 H, dd, *J* 6.3 and 12.0, CHCO), 3.15 (3 H, s, OMe), 1.73–1.21 (7 H, m, 3 × CH_2 and CHSi), 1.13 (6 H, s, Me_2C), 0.86 (3 H, d, *J* 7.2, *Me*CH), 0.45 (3 H, s, Si$Me_A$$Me_B$) and 0.40 (3 H, s, $SiMe_A$$Me_B$); *m/z* 333 (1%, M^+ − Me), 301 (6), 216 (6), 189 (7), 135 (100, $SiMe_2Ph$) and 73 (67, C_4H_9O) (Found: M^+ − Me, 333.1904. $C_{20}H_{32}O_3Si$ requires *M* − Me, 333.1885).

(3*Z*)-2-Dimethyl(phenyl)silyl-8-methoxy-8-methylnon-3-ene 27. By refluxing the lactones above (0.2 g, 0.57 mmol) in 2,4,6-trimethylpyridine (5 cm^3) for 5 h under argon to give a 2:1 mixture of the *Z*- and *E*-*allylsilanes* (46%); major (*Z*) isomer, obtained geometrically pure (>95:5) on one occasion: ν_{max}($CHCl_3$) 1250 (SiMe) and 1105 (SiPh); δ_H($CDCl_3$) 7.51–7.46 (2 H, m, *o*-SiPh), 7.34–7.32 (3 H, m, *m*- and *p*-SiPh), 5.23–5.15 (2 H, m, CH=CH), 3.15 (3 H, s, OMe), 2.08–1.24 (7 H, m, 3 × CH_2 and CHSi), 1.11 (6 H, s, Me_2C), 0.98 (3 H, d, *J* 7.2, *Me*CH), 0.25 (3 H, s, Si$Me_A$$Me_B$) and 0.24 (3 H, s, $SiMe_A$$Me_B$); *m/z* 272 (0.8%), 216 (2), 167 (32), 151 (5), 135 (100, $SiMe_2Ph$), 82 (12) and 73 (20) (Found: M^+, 304.2241. $C_{19}H_{32}OSi$ requires *M*, 304.2223); minor (*E*) isomer: δ_H($CDCl_3$) 7.50–7.46 (2 H, m, *o*-SiPh), 7.36–7.31 (3 H, m, *m*- and *p*-SiPh), 5.40 (1 H, ddt, *J* 15.3, 7.6 and 1.0, C*H*=CHCH_2), 5.19 (1 H, m, CH=C*H*CH_2), 3.16 (3 H, s, OMe), 1.97 (2 H, m, CH=CHCH_2), 1.74 (1 H, m, CHSi), 1.45–1.28 (4 H, m, 2 × CH_2), 1.12 (6 H, s, Me_2C), 1.00 (3 H, d, *J* 7.2, *Me*CH) and 0.24 (6 H, s, $SiMe_2$).

(3*Z*,5*E*)-10-Methoxy-10-methyl-2-dimethyl(phenyl)silylundeca-3,5-diene 29. As an oil (54%), R_f(hexane–EtOAc, 9:1) 0.34; δ_H(250 MHz; $CDCl_3$) 7.54–7.45 (2 H, m, *o*-SiPh), 7.38–7.31 (3 H, m, *m*- and *p*-SiPh), 6.15 (1 H, dd, *J* 10.3 and 14.9, C*H*=CHCH_2), 5.85 (1 H, t, *J* 10.3, C*H*=CHCHSi), 5.57 (1 H, td, *J* 7.1 and 14.9, CH=C*H*CH_2), 5.08 (1 H, t, *J* 10.7, CH=C*H*CHSi), 3.16 (3 H, s, OMe), 2.28–2.21 (1 H, m, CHSi), 2.09–1.99 (2 H, m, CH_2CH=CH), 1.66–1.15 (4 H, m, CH_2CH_2-CMe_2), 1.13 (6 H, s, Me_2C), 1.01 (3 H, d, *J* 7.0, *Me*CHSi) and 0.26 (6 H, s, Me_2Si).

(2*S*,3*R*)-2-[(1*R*)-1-Trimethylsilylethyl]-3-[2-methyl-2-(2-methoxyethoxy)methoxypropyl]propano-3-lactone. As an oil (69%); R_f(EtOAc–hexane, 20:80) 0.21; ν_{max}(film)/cm^{-1} 1815 (C=O) and 1250 and 840 ($SiMe_3$); δ_H(400 MHz; $CDCl_3$) 4.86 (1 H, dd, *J* 6.4 and 8.7, CHO), 4.85 (1 H, d, *J* 7.7, OC$H_A$$H_B$O), 4.78 (1 H, d, *J* 7.6, OC$H_A$$H_B$O), 3.76–3.65 (2 H, m, OCH_2OCH_2), 3.56 (1 H, dd, *J* 6.5 and 12.1, CHC=O), 3.54–3.49 (2 H, m, CH_2OMe), 3.37 (3 H, s, OMe), 2.05 (1 H, d, *J* 15.1, C$H_A$$H_BCMe_2$), 1.79 (1 H, dd, *J* 10.2 and 15.1, C$H_A$$H_BCMe_2$), 1.30 (6 H, s, C$Me_2$), 1.28–1.12 (1 H, m, CHSi), 0.91 (3 H, d, *J* 7.2, *Me*CH) and 0.09 (9 H, s, $SiMe_3$); *m/z* 333 (50%, M + H^+), 89 (100, $MeOC_2H_4OCH_2$), 73 (70, $SiMe_3$) and 59 (60, $MeOC_2H_4$); [α]$_D$ +26.6 (*c* 1.1 in $CHCl_3$) (Found: M + H^+, 333.2100. $C_{16}H_{32}O_5Si$ requires *M* + H^+, 333.2098).

(2*R*,3*Z*)-6-Methyl-6-(2-methoxyethoxy)methoxyhept-3-en-2-yltrimethylsilane 32. By refluxing the lactone above (855 mg, 2.58 mmol) in 2,4,6-trimethylpyridine (8 cm^3) to give an oil (70%); R_f(EtOAc–hexane, 20:80) 0.33; ν_{max}(film)/cm^{-1} 1630 (C=C) and 1245 and 835 ($SiMe_3$); δ_H(250 MHz; $CDCl_3$) 5.35–5.20 (2 H, m, CH=CH), 4.82 (2 H, s, OCH_2O), 3.74–3.69 (2 H, m, OCH_2OCH_2), 3.56–3.52 (2 H, m, CH_2OMe), 3.38 (3 H, s, OMe), 2.24 (1 H, dd, *J* 7.4 and 14.5, C$H_A$$H_BCMe_2$), 2.09 (1 H, dd, *J* 3.5 and 14.5, C$H_A$$H_BCMe_2$), 1.85–1.78 (1 H, m, CHSi), 1.22 (3 H, s, C$Me_A$$Me_B$), 1.21 (3 H, s, C$Me_A$$Me_B$), 0.99 (3 H, d, *J* 7.1, *Me*CH) and −0.05 (9 H, s, $SiMe_3$); *m/z* 288 (15%, M^+), 89 (8, $MeOC_2H_4OCH_2$), 73 (15, $SiMe_3$) and 59 (8, $MeOC_2H_4$); [α]$_D$ −69.2 (*c* 1.7 in $CHCl_3$) (Found: M^+, 288.2107. $C_{15}H_{32}O_3Si$ requires *M*, 288.2121).

(2*R*,3*Z*,5*E*)-8-Methyl-8-(2-methoxyethoxy)methoxynona-3,5-dien-2-yltrimethylsilane 34. As an oil (42%); R_f(EtOAc–hexane, 20:80) 0.39; ν_{max}(film)/cm^{-1} 1250 and 840 ($SiMe_3$); δ_H(250 MHz; $CDCl_3$) 6.23 (1 H, ddd, *J* 1.0, 10.9 and 15.0, CH_2CH=C*H*CH=CH), 5.86 (1 H, t, *J* 10.9, CH_2CH=CH-C*H*=CH), 5.60 (1 H, dt, *J* 15.0 and 7.5, CH_2C*H*=CHCH=CH), 5.14 (1 H, t, *J* 11.0, CH_2CH=CHCH=C*H*), 4.82 (2 H, s, OCH_2O), 3.73–3.68 (2 H, m, OCH_2OCH_2), 3.56–3.51 (2 H, m, CH_2OMe), 3.38 (3 H, s, OMe), 2.31 (1 H, dd, *J* 7.3 and 14.1, C$H_A$$H_BCMe_2$), 2.27 (1 H, dd, *J* 7.2 and 14.1, C$H_A$$H_BCMe_2$), 2.03 (1 H, dq, *J* 11.3 and 7.1, CHSi), 1.20 (6 H, s, CMe_2), 1.04 (3 H, d, *J* 7.1, *Me*CH) and −0.05 (9 H, s, $SiMe_3$); *m/z* 314 (5%, M^+), 89 (100, $MeOC_2H_4OCH_2$), 73 (90, $SiMe_3$) and 59 (65, $MeOC_2H_4$); [α]$_D$ −72.3 (*c* 1.0 in $CHCl_3$) (Found: M^+, 314.2260. $C_{17}H_{34}O_3Si$ requires *M*, 314.2278).

Proofs of configurations

Preparation of Mosher's esters 54 and 55. *N*,*N*-Dicyclohexylcarbodiimide (DCC) (2 mol dm^{-3} solution in CH_2Cl_2; 0.16 cm^3, 0.32 mmol), the alcohols **10a** and *ent*-**10a** (0.04 g, 0.24 mmol), (2*S*)-2-methoxy-2-phenyl-3,3,3-trifluoropropanoic acid [(−)-MTPA] (0.07 g, 0.3 mmol) and 4-dimethylaminopyridine (DMAP) (0.005 g, 0.04 mmol) were kept in dry dichloromethane (0.2 cm^3) at room temperature under nitrogen for 3 h. The solution was diluted with dichloromethane (5 cm^3) and passed through a short column of silica, eluting with dichloromethane. The solvent was evaporated under reduced pressure and the residue chromatographed (PLC, SiO_2, EtOAc–hexane, 1:10) to give an inseparable mixture of the diastereoisomers (5E,7E,3R,4R)-2,4-*dimethylnona*-5,7-*dien*-3-*yl* (2S)-2-*methoxy*-2-*phenyl*-3,3,3-*trifluoropropanoate* **54** and (5E,7E,3S,4S)-2,4-*dimethylnona*-5,7-*dien*-3-*yl* (2S)-2-*methoxy*-2-*phenyl*-3,3,3-*trifluoropropanoate* **55** (0.07 g, 0.18 mmol, 75%) contaminated with four minor products; R_f(EtOAc–hexane, 1:10) 0.6; ν_{max}(film)/cm^{-1} 2850 (OMe) and 1745 (C=O); δ_H(250 MHz; $CDCl_3$) for **54**: 4.91 (1 H, dd, *J* 4.77 and 7.24, CHOC=O), 3.52 (3 H, s, OMe) and 1.72 (3 H, d, *J* 6.0, *Me*CH=CH); for **55**: 4.95–4.89 (1 H, m, CHOC=O), 3.51 (3 H, s, OMe) and 1.73 (3 H, d, *J* 5.9, *Me*CH=CH); peaks common to both compounds: 7.6–7.5 (2 H, m, *o*-ArH), 7.40–7.35 (3 H, m, *m*- and *p*-ArH), 6.04–5.90 (2 H, m, MeCH=C*H*C*H*=C), 5.66–5.52 (1 H, m, MeC*H*=CHC=CH), 5.46–5.29 (1 H, m, MeCH=CHCH=C*H*), 2.51 (1 H, sextet, *J* 7.15, CH=CHC*H*Me), 2.06–1.88 (1 H, m, C*H*Me_2) and 1.05–0.75 (9 H, m, CHMe_2 and CH=CHCH*Me*); δ_F(235 MHz; $CDCl_3$) 90.91 (3 F, s, CF_3 of **55**), 90.81 (3 F, s, CF_3 of **54**), with other peaks at 90.72 (A), 90.70 (B), 90.64 (C) and 90.42 (D). Integral ratios **55**:**54**: A:B:C:D, 14:64:9:6:2:5; *m/z*, 271 (10), 189 (100), 150 (80), 135 (20) and 95 (85). Thus the ratio of **54** to **55** was 82:18.

Authentic sample of methyl (2*R*,3*S*)-3-hydroxy-2-methylpentanoate 63. Following Evans,[50] butyllithium (1.5 mol dm^{-3} solution in hexane; 10.5 mmol) was added at −20 °C with stirring to dry methanol (3 cm^3) in THF (25 cm^3) followed, after 15 min, by (4*R*,5*S*)-4-methyl-3-[(2*S*,3*R*)-3-hydroxy-2-methylpentanoyl]-5-phenyl-1,3-oxazolidin-2-one[35] (2 g, 6.55 mmol) in THF (25 cm^3), and stirring continued for 1 h. The

solution was then quenched with water (5 cm^3) and the organic phase separated, dried ($MgSO_4$) and evaporated under reduced pressure. Chromatography gave the ester[51] (0.84 g, 80%); $\delta_H(CDCl_3)$ 3.69 (3 H, s, CO_2Me), 3.55 (1 H, dd, *J* 8 and 3.6, C*H*OH), 2.66 (1 H, dq, *J* 3.6 and 7.2, CHCO), 2.45 (1 H, br s, OH), 1.67 (1 H, d septet, *J* 8 and 6.7, C*H*Me_2), 1.17 (3 H, d, *J* 7.2, *Me*CHCO), 1.00 (3 H, d, *J* 6.7, C*Me*$_A$$Me_B$) and 1.21 (3 H, d, *J* 6.7, CMe_A*Me*$_B$).

(5*E*,7*E*,3*S*,4*S*)-2,4-Dimethylnona-5,7-dien-3-ol *ent*-10a and (5*Z*,7*E*,3*S*,4*S*)-2,4-dimethylnona-5,7-dien-3-ol 57. Diisobutylaluminium hydride (1 mol dm^{-3} solution in hexane; 3.6 cm^3) and the ester **63** (240 mg, 1.5 mmol) in toluene (5 cm^3) were kept at −90 °C (internal temperature) for 2 h. The mixture was quenched with methanol (2 cm^3) and stirring continued for a further 10 min at −90 °C. The solution was then warmed to room temperature. Saturated aqueous potassium sodium tartrate (10 cm^3) was added and the mixture extracted with ethyl acetate (4 × 15 cm^3). The combined extracts were washed with brine (10 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure to give the crude aldehyde **56** (0.2 g). Butyllithium (1.5 mol dm^{-3} solution in hexane; 3 mmol) and (*E*)-but-2-enyltriphenylphosphonium bromide[52] (1.2 g, 3 mmol) were stirred in dry ether (5 cm^3) at room temperature for 3 h, and the solution cooled to 0 °C. The crude aldehyde (0.2 g) in ether (2 cm^3) was added and the mixture stirred for 2 h, warmed to room temperature, and kept for 15 h. The yellow precipitate was filtered off and washed with ether. The filtrate was washed with dilute sulfuric acid (5 cm^3) and water (5 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure. The residue was chromatographed (PLC) to give the *dienyl alcohols* (75 mg, 30%) as an *E*,*E*: *E*,*Z* mixture (2:1) [determined by high field ^1H and ^{19}F NMR of the Mosher's esters of **10** (**55**) and **57**]. The *E*,*E*-isomer was identical (^1H NMR) to the earlier sample **10a**, and the *E*,*Z*-isomer **57** showed the following signals: $\delta_H(CDCl_3)$ 6.42–5.96 (4 H, m, olefinic Hs), 3.16 (1 H, t, *J* 6, C*H*OH), 2.40 (1 H, sextet, *J* 6.9, MeC*H*CH=), 1.76 (1 H, m, C*H*Me_2), 1.74 (3 H, d, *J* 6.9, *Me*CH=), 1.4 (1 H, br s, OH), 1.05 (3 H, d, *J* 7, *Me*CHCH=), 0.92 (3 H, d, *J* 6.8, C*Me*$_A$$Me_B$) and 0.91 (3 H, d, *J* 6.8, CMe_A*Me*$_B$). The formation of more *E* than *Z* double bond in this Wittig reaction is somewhat unusual, but not unprecedented.[53]

(5*E*,7*E*,3*S*,4*S*)-2,4-Dimethylnona-5,7-dien-3-yl (2*S*)-2-methoxy-2-phenyl-3,3,3-trifluoropropanoate 55 and (5*Z*,7*E*,3*S*,4*S*)-2,4-dimethylnona-5,7-dien-3-yl (2*S*)-2-methoxy-2-phenyl-3,3,3-trifluoropropanoate. Following Mosher,[54] the alcohols *ent*-**10a** and **57** (42 mg, 0.25 mmol), DCC (80 mg, 0.4 mmol), DMAP (5 mg, 0.04 mmol) and (−)-MTPA (70 mg, 0.3 mmol) were kept in dichloromethane (0.5 cm^3) at room temperature under nitrogen for 3 h. The suspension was filtered through silica, washing with dichloromethane (10 cm^3), and the solvent evaporated under reduced pressure. The residue was chromatographed (SiO_2, hexane–EtOAc, 10:1) to give an inseparable mixture of the esters (77 mg, 80%); the *E*,*E*-isomer showed the same signals as those of the ester **55** derived from the minor product of the pentadienylsilane reaction, and the *E*,*Z*-isomer showed the following signals: $\delta_H(CDCl_3)$ 7.58–7.35 (5 H, m, Ph), 6.45–5.3 (4 H, m, olefinic Hs), 4.9 (1 H, dd, *J* 6.8 and 5.2, CHOCO), 3.51 (3 H, s, OMe), 2.6 (1 H, sextet, *J* 6.8, MeC*H*CH=), 1.95 (1 H, m, C*H*Me_2), 1.73 (3 H, d, *J* 7, *Me*CH=), 0.99 (3 H, d, *J* 6.8, *Me*CHCH=), 0.88 (3 H, d, *J* 6.7, C*Me*$_A$$Me_B$) and 0.84 (3 H, d, *J* 6.7, CMe_A*Me*$_B$).

Preparation of the mixtures of Mosher's esters 58–61 by ozonolysis, reduction and esterification. Typically, ozonised oxygen was passed through a solution of the mixture of **10b** and **11b** and their enantiomers (100 mg, 0.55 mmol) in methanol (5 cm^3) at −78 °C for 4 h. The solution was then purged with nitrogen and sodium borohydride (110 mg, 3 mmol) added in three portions. The solution was stirred at 0 °C for 1 h, and the methanol removed under reduced pressure. The residue was diluted with ether (15 cm^3), washed with water (2 × 5 cm^3), dried ($MgSO_4$), evaporated under reduced pressure and chromatographed, in such a way (SiO_2, CH_2Cl_2) as to cause no change in the proportions, to give a mixture the alcohols (66 mg, 83%). Typically, the mixture of alcohols (30 mg, 0.2 mmol), (−)-MTPA (70 mg, 0.3 mmol), DCC (100 mg, 0.5 mmol) and DMAP (6 mg) were kept in dichloromethane (1 cm^3) at room temperature for 2 h to give the mixture of esters (66 mg, 92%). The proportions of the four diastereoisomers were measured using the OMe signals in the ^1H NMR spectra. Using this procedure, the mixture derived from racemic pentadienylsilane **9** gave ratios **58**:**59**:**60**:**61** of 41:9:38:12; the mixture derived from the pentadienylsilane **9** (92% ee) gave ratios **58**:**59**:**60**:**61** of 65:16:13:6; the mixture derived from the pentadienylsilane **13** (33% ee) gave ratios **58**:**59**:**60**:**61** of 29:7:50:14; the mixture derived from racemic pentadienylsilane **14** gave ratios **58**:**59**:**60**:**61** of 41:9:38:12; the mixture derived from the pentadienylsilane **14** (100% ee) gave ratios **58**:**59**:**60**:**61** of 67:19:11:4; and the mixture derived from the pentadienylsilane **17** (23% ee) gave ratios **58**:**59**:**60**:**61** of 27:14:40:19.

Methyl (2*RS*,3*RS*)-3-hydroxy-2,4-dimethylpentanoate. Racemic methyl (2*RS*,3*SR*)-2,4-dimethyl-3-dimethyl(phenyl)silylpentanoate **62**[10] (0.14 g, 0.5 mmol), mercury(II) acetate (0.2 g, 0.62 mmol) and peracetic acid (15%) in acetic acid (5 cm^3) were kept at 35 °C for 2 h. Sodium thiosulfate (1 g) and ether (20 cm^3) were added and the mixture stirred for 1 h and then filtered through Celite. The solvent was evaporated off and the residue chromatographed (PLC, EtOAc–hexane, 2:1) to give the racemic *anti* hydroxy ester[51] (36 mg, 45%); $\delta_H(CDCl_3)$ 3.68 (3 H, s, CO_2Me), 3.36 (1 H, dd, *J* 6.3 and 5.6, C*H*OH), 2.64 (1 H, quintet, *J* 6.9, C*H*CO), 1.68 (1 H, m, C*H*Me_2), 1.17 (3 H, d, *J* 7.2, *Me*CH), 0.93 (3 H, d, *J* 6.7, C*Me*$_A$$Me_B$) and 0.89 (3 H, d, *J* 6.7, CMe_A*Me*$_B$).

Methyl (2*RS*,3*RS*)-3-methoxy-2,4-dimethylpentanoate. Following Johnson,[55] the racemic ester above (30 mg, 0.18 mmol), boron trifluoride–diethyl ether complex (0.25 cm^3, 0.2 mmol) and excess diazomethane in ether at 0 °C gave the racemic *anti* methoxy ester[56] (22 mg, 70%); R_f(hexane–EtOAc, 5:1) 0.42; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 1720; $\delta_H(CDCl_3)$ 3.67 (3 H, s, CO_2Me), 3.37 (3 H, s, OMe), 3.17 (1 H, dd, *J* 4 and 8.1, C*H*OMe), 2.64 (1 H, dq, *J* 8.1 and 7, CHCO), 1.79 (1 H, m, C*H*Me_2), 1.07 (3 H, d, *J* 7, *Me*CH), 0.95 (3 H, d, *J* 6.8, C*Me*$_A$$Me_B$) and 0.86 (3 H, d, *J* 6.8, CMe_A*Me*$_B$).

Methyl (2*R*,3*S*)-3-methoxy-2,4-dimethylpentanoate. Similarly, the ester **63** (160 mg, 1 mmol) gave the *syn* methoxy ester[56] (116 mg, 67%); R_f(hexane–EtOAc, 5:1) 0.42; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 1722 (C=O); $\delta_H(CDCl_3)$ 3.67 (3 H, s, CO_2Me), 3.38 (3 H, s, OMe), 3.21 (1 H, dd, *J* 5.2 and 5.6, C*H*OMe), 2.62 (1 H, dq, *J* 5.6 and 7, $CHCO_2$), 1.70 (1 H, m, C*H*Me_2), 1.16 (3 H, d, *J* 7, *Me*CH), 0.93 (3 H, d, *J* 6.6, C*Me*$_A$$Me_B$) and 0.90 (3 H, d, *J* 6.6, CMe_A*Me*$_B$).

(2*SR*,3*RS*)-3-Methoxy-2,4-dimethylpentanol and its Mosher's ester. Methyl (2*RS*,3*RS*)-3-methoxy-2,4-dimethylpentanoate and lithium aluminium hydride (2 equiv.) in ether at 0 °C for 1 h gave the anti *alcohol* (95%); ν_{max}(film)/cm^{-1} 3400 (OH); $\delta_H(CDCl_3)$ 3.69 (1 H, dd, *J* 10.8 and 5.7, C$H_A$$H_B$OH), 3.58 (1 H, dd, *J* 10.8 and 5.7, CH_AH_BOH), 3.47 (3 H, s, OMe), 2.84 (1 H, dd, *J* 6.3 and 5.2, C*H*OMe), 2.37 (1 H, br s, OH), 1.93–1.77 (2 H, m, C*H*Me_2 and C*H*Me), 0.96 (3 H, d, *J* 6.8, *Me*$_A$CH), 0.94 (3 H, d, *J* 6.8, *Me*$_B$CH) and 0.92 (3 H, d, *J* 6.8, *Me*$_C$CH). Mosher's ester formation, as described above, gave ratios **58**:**59**:**60**:**61** of 7:43.5:5.5:44.

(2*S*,3*S*)-3-Methoxy-2,4-dimethylpentanol and its Mosher's ester 60. Similarly, methyl (2*R*,3*S*)-3-methoxy-2,4-dimethylpentanoate gave the enantiomerically enriched syn *alcohol* (92%); R_f(hexane–EtOAc, 2:1) 0.34; ν_{max}(film)/cm ^{1} 3380 (OH); $\delta_H(CDCl_3)$ 3.60 (2 H, dd, *J* 6 and 3, CH_2OH), 3.44 (3 H, s, OMe), 2.92 (1 H, dd, *J* 7.8 and 3.2, C*H*OMe), 2.02 (1 H, br s, OH), 1.93–1.74 (2 H, m, Me_2C*H* and MeC*H*), 0.97 (3 H, d, *J* 6.7, C*Me*$_A$$Me_B$), 0.88 (3 H, d, *J* 7, *Me*CH) and 0.86 (3 H, d, *J* 6.8, CMe_A*Me*$_B$); *m*/*z* 117 (2.25%, M^+ − Et), 103 (48, M −

$CHMe_2$) and 87 (100, M − $MeCHCH_2OH$) (Found: M^+ − Et, 117.0918. $C_8H_{18}O_2$ requires *M* − Et, 117.0916). Mosher's ester formation, as described above, gave (2S,3S)-3-*methoxy*-2,4-*dimethylpentyl* (2S)-2-*methoxy*-2-*phenyl*-3,3,3-*trifluoropropanoate* **60** (92%); R_f(hexane–EtOAc, 10:1) 0.28; ν_{max}(film)/cm^{-1} 1745 (C=O); δ_H($CDCl_3$) 7.54–7.50 (2 H, m, *o*-ArH), 7.42–7.37 (3 H, m, *m*- and *p*-ArH), 4.43 (1 H, dd, *J* 10.6 and 6, CH_AH_BO), 4.14 (1 H, dd, *J* 10.6 and 7.8, CH_AH_BO), 3.54 (3 H, s, OMe_A), 3.35 (3 H, s, OMe_B), 2.65 (1 H, dd, *J* 8 and 3.4, *CH*OMe), 2.07 (1 H, m, *CH*Me), 1.73 (1 H, m, *CH*Me_2), 0.92 (3 H, d, *J* 6.7, CMe_AMe_B), 0.87 (3 H, d, *J* 7, *Me*CH) and 0.78 (3 H, d, *J* 6.7, CMe_A*Me*$_B$); δ_F($CDCl_3$) 90.58; *m*/*z* 319 (8.8%, M^+ − Me_2CH), 189 (18, $PhCCF_3OMe$), 87 (95, $Me_2CHCHOMe$), 86 (24, $Me_2CHCOMe$) and 85 (100, $CH_2CHMeCHOMe$) (Found: M^+ − Me_2CH, 319.1157. $C_{18}H_{25}F_3O_4$ requires *M* − Me_2CH, 319.1157).

Methyl (3*R*)-3-dimethyl(phenyl)silyl-4-methylpentanoate. (3*R*)-3-Dimethyl(phenyl)silyl-4-methylpentanoic acid (80% ee) (0.35 g, 1.4 mmol) and oxalyl chloride (0.2 g, 1.6 mmol) were kept in dichloromethane (10 cm^3) at room temperature under nitrogen for 2 h. The solvent and excess oxalyl chloride were evaporated under reduced pressure to give the acid chloride. Dry methanol (1 cm^3) and triethylamine (1.5 mmol) in ether (10 cm^3) were added at −20 °C, under nitrogen, and the mixture kept at room temperature for 2 h, diluted with ether (10 cm^3), washed with water (5 cm^3), dried ($MgSO_4$), evaporated under reduced pressure and filtered through silica, eluting with dichloromethane to give the *ester* (0.35 g, 96%), identical (^{1}H NMR) with the racemic ester prepared earlier;[57] R_f(hexane–EtOAc, 9:1) 0.35; ν_{max}(film)/cm^{-1} 1723 (C=O), 1242 (SiMe) and 1103 (SiPh); δ_H($CDCl_3$) 7.58–7.26 (5 H, m, Ph), 3.55 (3 H, s, CO_2Me), 2.33 (2 H, d, *J* 6.9, CH_2CO_2), 2.15–1.75 (1 H, m, *CH*Me_2), 1.49 (1 H, ddd, *J* 3.8, 6.8 and 7.5, CHSi), 0.87 (6 H, t, *J* 6.5, *Me*$_2$CH), 0.33 (3 H, s, Si*Me*$_A$$Me_B$) and 0.32 (3 H, s, $SiMe_A$*Me*$_B$); *m*/*z* 264 (1.25%, M^+), 249 (9, M − Me) and 135 (100, $SiMe_2Ph$) (Found: M^+, 264.1568. $C_{15}H_{24}O_2Si$ requires *M*, 264.1545).

Methyl (2*R*,3*S*)-2,4-dimethyl-3-dimethyl(phenyl)silylpentanoate 62. Methyl (3*R*)-3-dimethyl(phenyl)silyl-4-methylpentanoate (2.64 g, 10 mmol) and LDA (12 mmol) were kept in THF (40 cm^3) at −78 °C for 30 min, and methyl iodide (15 mmol) was added dropwise. The solution was kept at −78 °C for 10 min before warming to room temperature. Saturated aqueous ammonium chloride was added, and the usual work-up and chromatography (SiO_2, hexane–EtOAc, 10:1) gave the ester (2.55 g, 92%) as a mixture of *anti* and *syn* diastereoisomers (87.5:12.5), identical (TLC, ^{1}H NMR) with the racemic ester.[10]

(2*R*,3*S*) 3-Methoxy-2,4-dimethylpentanol and its Mosher's ester 59. The silyl group in the mixture rich in ester **62** was oxidised, the resultant alcohol methylated, the ester reduced and the Mosher's ester prepared in the same way and in comparable yields as for the racemic ester to give (2R,3S)-3-*methoxy*-2,4-*dimethylpentyl* (2S)-2-*methoxy*-2-*phenyl*-3,3,3-*trifluoropropanoate* **59**; δ_H($CDCl_3$) 7.54–7.50 (2 H, m, *o*-ArH), 7.42–7.36 (3 H, m, *m*- and *p*-ArH), 4.51 (1 H, dd, *J* 10.7 and 3.7, CH_AH_B), 4.20 (1 H, dd, *J* 10.7 and 6.5, CH_AH_B), 3.54 (3 H, br s, OMe_A), 3.38 (3 H, s, OMe_B), 2.73 (1 H, dd, *J* 7.5 and 4.4, *CH*OMe), 1.99 (1 H, m, *CH*Me), 1.77 (1 H, m, *CH*Me_2), 0.95 (3 H, d, *J* 6.9, CH*Me*$_A$), 0.90 (3 H, d, *J* 6.9, CH*Me*$_B$) and 0.86 (3 H, d, *J* 6.9, CH*Me*$_C$). The ratio of the isomers **58**:**59**:**60**:**61** was 2:84:8:6.

The following signals can be assigned by difference to (2R,3R)-3-*methoxy*-2,4-*dimethylpentyl* (2S)-*methoxy*-2-*phenyl*-3,3,3-*trifluoropropanoate* **58**: δ_H(400 MHz; $CDCl_3$) 7.55–7.50 (2 H, m, *o*-ArH), 7.42–7.37 (3 H, m, *m*- and *p*-ArH), 4.24 (1 H, dd, *J* 6.6 and 9.6, CH_AH_BO), 4.21 (1 H, dd, *J* 5.1 and 9.6, CH_AH_BO), 3.53 (3 H, s, OMe), 3.33 (3 H, s, CHO*Me*), 2.69 (1 H, dd, *J* 3.2 and 8.0, *CH*OMe), 2.07 (1 H, m, *CH*Me), 1.74 (1 H, m, *CH*Me_2), 0.93 (3 H, d, *J* 6.7, CMe_AMe_B), 0.87 (3 H, d, *J* 6.9, *Me*CH) and 0.80 (3 H, d, *J* 6.7, CMe_A*Me*$_B$).

Reduction of 4,5-dihydroisoxazoles

General procedure. Following Curran and Kim,[8] Raney nickel (W2)[58] (*ca.* 20 mg, in propan-2-ol), boric acid (124 mg, 2 mmol) and the dihydroisoxazole (0.39 mmol) were stirred in methanol (1 cm^3) and water (0.2 cm^3) at room temperature under an atmosphere of hydrogen for 2.5 h. The mixture was filtered through Celite, washing with dichloromethane (20 cm^3). Water (10 cm^3) was added and the layers were separated, the aqueous layer extracted with dichloromethane (2 × 10 cm^3) and the combined organic layers washed with brine (50 cm^3), dried (K_2CO_3), filtered and evaporated to give the hydroxy ketone. The following β-hydroxy ketones were prepared by this method.

(5*RS*,8*RS*,6*Z*)-2,2-Dimethyl-5-hydroxy-8-dimethyl(phenyl)-silylnon-6-en-3-one 65aa. As an oil (100%); R_f(hexane–EtOAc, 9:1) 0.09; ν_{max}(film)/cm^{-1} 3450 (br OH), 3060, 2960, 2880 (CH), 1700 (C=O), 1650 (C=C), 1250 (SiMe) and 1110 (SiPh); δ_H(250 MHz; $CDCl_3$) 7.50–7.42 (2 H, m, *o*-SiPh), 7.34–7.28 (3 H, m, *m*-and *p*-SiPh), 5.34 (1 H, t, *J* 10.8, SiCHC*H*=CH), 5.24 (1 H, dd, *J* 8.5 and 10.8, SiCHCH=C*H*), 4.63 (1 H, dt, *J* 2.4 and 8.8, CH=CHC*H*OH), 2.97 (1 H, br s, OH), 2.41 (1 H, dd, *J* 9.1 and 18.0, CH_AH_B), 2.18 (1 H, dq, *J* 10.8 and 7.1, MeC*H*), 1.97 (1 H, dd, *J* 2.4 and 18.0, CH_AH_B), 1.07 (3 H, d, *J* 7.1, *Me*CH), 1.05 (9 H, s, CMe_3), 0.27 (3 H, s, Si*Me*$_A$$Me_B$) and 0.24 (3 H, s, $SiMe_A$*Me*$_B$); *m*/*z* 300 (1%, M^+ − H_2O), 219 (1, M − Me_3CCOCH_2), 218 (2, M − Me_3CCOCH_3), 166 (2, M − $PhMe_2SiOH$), 135 (60, Me_2SiPh), 85 (45, Me_3CCO) and 57 (100, Me_3C) (Found: M^+ − H_2O, 300.1913. $C_{19}H_{30}O_2Si$ requires *M* − H_2O, 300.1909).

(5*RS*,8*SR*,6*Z*)-2,2-Dimethyl-5-hydroxy-8-dimethyl(phenyl)-silylnon-6-en-3-one 66aa. As an oil (47%); R_f(hexane–EtOAc, 9:1) 0.12; ν_{max}($CDCl_3$)/cm^{-1} 3560 (br OH), 3060, 2960, 2870 (CH), 1690 (C=O), 1650 (C=C), 1250 (SiMe) and 1110 (SiPh); δ_H(250 MHz; $CDCl_3$) 7.54–7.46 (2 H, m, *o*-SiPh), 7.40–7.32 (3 H, m, *m*- and *p*-SiPh), 5.30–5.14 (2 H, m, CH=CH), 4.58 (1 H, m, CH=CHC*H*OH), 2.5 (1 H, br s, OH), 2.66 (1 H, dd, *J* 7.6 and 17.4, CH_AH_B), 2.52 (1 H, dd, *J* 4.7 and 17.4, CH_AH_B), 2.12 (1 H, dq, *J* 10.5 and 7.1, MeC*H*), 1.09 (9 H, s, CMe_3), 1.02 (3 H, d, *J* 7.1, *Me*CH), 0.32 (3 H, s, Si*Me*$_A$$Me_B$) and 0.29 (3 H, s, $SiMe_A$*Me*$_B$); *m*/*z* 300 (1%, M^+ − H_2O), 219 (1, M − Me_3CCOCH_2), 218 (4, M − Me_3CCOCH_3), 166 (2, M − $PhMe_2SiOH$), 135 (70, Me_2SiPh), 85 (40, Me_3CCO) and 57 (100, Me_3C) (Found: M^+ − H_2O, 300.1936. $C_{19}H_{30}O_2Si$ requires *M* − H_2O, 300.1909).

(5*RS*,8*RS*,6*Z*)-2,2-Dimethyl-5-hydroxy-8-trimethylsilylnon-6-en-3-one 65ba. As an oil (79%); R_f(hexane–EtOAc, 9:1) 0.16; ν_{max}($CDCl_3$)/cm^{-1} 3520 (br OH), 2960, 2870 (CH), 1690 (C=O), 1650 (C=C) and 1250 (SiMe); δ_H(250 MHz; $CDCl_3$) 5.37–5.22 (2 H, m, CH=CH), 4.78 (1 H, dt, *J* 3.7 and 7.8, *CH*OH), 2.7 (1 H, br s, CHO*H*), 2.73–2.54 (2 H, m, CH_2), 1.92 (1 H, dq, *J* 10.7 and 7.0, MeC*H*), 1.11 (9 H, s, Me_3C), 1.02 (3 H, d, *J* 7.0, *Me*CH) and −0.07 (9 H, s, Me_3Si); *m*/*z* 241 (0.1%, M^+ − Me), 239 (0.1, M − OH), 238 (0.3, M − H_2O), 223 (0.8, M − H_2O − Me), 166 (5, M − Me_3SiOH), 157 (25, M − Me_3CCOCH_2), 85 (60, Me_3CCO), 73 (70, Me_3Si) and 57 (100, Me_3C) (Found: M^+ − H_2O, 238.1751. $C_{14}H_{28}O_2Si$ requires *M* − H_2O, 238.1753).

(5*RS*,8*SR*,6*Z*)-2,2-Dimethyl-5-hydroxy-8-trimethylsilylnon-6-en-3-one 66ba. As an oil (69%); R_f(hexane–EtOAc, 9:1) 0.20; ν_{max}($CDCl_3$)/cm^{-1} 3520 (br OH), 2960, 2870 (CH), 1690 (C=O), 1650 (C=C) and 1250 (SiMe); δ_H(250 MHz; $CDCl_3$) 5.29–5.16 (2 H, m, CH=CH), 4.74 (1 H, dt, *J* 3.6 and 7.8, *CH*OH), 2.9 (1 H, br s, CHO*H*), 2.69 (1 H, dd, *J* 8.1 and 17.6, CH_AH_B), 2.56 (1 H, dd, *J* 3.6 and 17.6, CH_AH_B), 1.80 (1 H, dq, *J* 10.6 and 7.1, MeC*H*), 1.09 (9 H, s, Me_3C), 0.97 (3 H, d, *J* 7.1, *Me*CH) and −0.05 (9 H, s, Me_3Si); *m*/*z* 238 (1.1%, M^+ − H_2O), 223 (0.5, M − H_2O − Me), 166 (2.2, M − Me_3SiOH), 157 (6, M − Me_3CCOCH_2), 156 (7, M − Me_3CCOMe), 85 (23, Me_3CCO), 73 (50, Me_3Si) and 57 (100, Me_3C) (Found: M^+ − H_2O, 238.1775. $C_{14}H_{28}O_2Si$ requires *M* − H_2O, 238.1753).

(5*RS*,8*SR*,6*Z*)-2,2-Dimethyl-5-hydroxy-8-phenyl-8-trimethylsiloct-6-en-3-one 65bc. As an oil (63%); R_f(EtOAc–hexane, 20:80) 0.28; ν_{max}(film)/cm^{-1} 3450 (OH), 1700 (C=O) and 1250 and 840 ($SiMe_3$); δ_H(250 MHz; $CDCl_3$) 7.25–7.16 (2 H, m, *o*-Ph), 7.11–6.98 (3 H, m, *m*- and *p*-Ph), 5.96 (1 H, dd, *J* 10.7 and 12.1, SiCHC*H*), 5.47 (1 H, dd, *J* 9.3 and 10.7, SiCHCH=C*H*), 4.94 (1 H, dt, *J* 2.9 and 8.8, C*H*OH), 3.38 (1 H, d, *J* 12.1, SiCH), 2.77 (1 H, dd, *J* 8.6 and 17.8, CH_AH_B), 2.63 (1 H, dd, *J* 3.0 and 17.8, CH_AH_B), 1.15 (9 H, s, CMe_3) and −0.04 (9 H, s, $SiMe_3$); *m*/*z* 300 (12%, $M^+ - H_2O$), 73 (95, $SiMe_3$) and 57 (100, CMe_3) (Found: $M^+ - H_2O$, 300.1897. $C_{19}H_{30}O_2Si$ requires $M - H_2O$, 300.1909).

(5*RS*,8*RS*,6*Z*)-2,2-Dimethyl-5-hydroxy-8-trimethylsilyl-8-phenyloct-6-en-3-one 66bc. As an oil (50%); R_f(EtOAc–hexane, 20:80) 0.33; ν_{max}(film)/cm^{-1} 3450 (OH), 1700 (C=O) and 1250 and 840 ($SiMe_3$); δ_H(250 MHz; $CDCl_3$) 7.25–7.18 (2 H, m, *o*-Ph), 7.11–6.98 (3 H, m, *m*- and *p*-Ph), 5.89 (1 H, dd, *J* 10.8 and 11.8, SiCHC*H*), 5.48 (1 H, dd, *J* 8.5 and 10.8, SiCHCH=C*H*), 4.88 (1 H, dt, *J* 2.9 and 8.0, C*H*OH), 3.18 (1 H, d, *J* 11.8, SiCH), 2.58 (1 H, dd, *J* 8.2 and 18.0, CH_AH_B), 2.49 (1 H, dd, *J* 3.3 and 18.0, CH_AH_B), 1.04 (9 H, s, CMe_3) and −0.02 (9 H, s, $SiMe_3$); *m*/*z* 300 (10%, $M^+ - H_2O$), 73 (75, $SiMe_3$) and 57 (100, CMe_3) (Found: $M^+ - H_2O$, 300.1903. $C_{19}H_{30}O_2Si$ requires $M - H_2O$, 300.1909).

Reduction of β-hydroxy ketones

General procedure. Following Evans and Chapman,[59] dry acetic acid (1 cm^3) was added to tetramethylammonium triacetoxyborohydride (0.33 g, 1.25 mmol) in acetonitrile (1 cm^3) at −40 °C under nitrogen and the resulting mixture was added to the hydroxy ketone (0.24 mmol) in acetonitrile (0.25 cm^3). The mixture was kept overnight at −20 °C, quenched with aqueous sodium potassium tartrate (0.5 mol dm^{-3}; 4 cm^3) and stirred for 0.5 h. The mixture was diluted with dichloromethane (20 cm^3) and saturated aqueous sodium hydrogen carbonate (20 cm^3) and extracted with dichloromethane (7 × 20 cm^3). The extract was washed with saturated aqueous sodium hydrogen carbonate (50 cm^3) and the washing was extracted with dichloromethane (7 × 20 cm^3). The combined extracts were dried (Na_2SO_4) and evaporated under reduced pressure. The residue was flash chromatographed (SiO_2, hexane–EtOAc, 9:1) to give the diol. The following diols were prepared by this method.

(3*RS*,5*RS*,8*RS*,6*Z*)-2,2-Dimethyl-3,5-dihydroxy-8-dimethyl(phenyl)silylnon-6-ene 67aa. As an oil (61 mg, 78%); R_f(hexane–EtOAc, 4:1) 0.14; ν_{max}(film)/cm^{-1} 3380 (br OH), 3060, 2950, 2860 (CH), 1640 (C=C), 1250 (SiMe) and 1110 (SiPh); δ_H(250 MHz; $CDCl_3$), 7.50–7.46 (2 H, m, *o*-SiPh), 7.36–7.32 (3 H, m, *m*- and *p*-SiPh), 5.42 (1 H, dd, *J* 8.7 and 11.0, CH=C*H*CHOH), 5.31 (1 H, t, *J* 11.0, SiCHC*H*=CH), 4.54 (1 H, dt, *J* 3.5 and 7.9, CH=CHC*H*OH), 3.50 (1 H, dd, *J* 2.4 and 10.4, C*H*CMe_3), 2.3–2.0 (2 H, br s, 2 × OH), 2.18 (1 H, dq, *J* 11.0 and 7.1, MeC*H*), 1.36 (1 H, ddd, *J* 2.4, 7.2 and 14.3, CH_AH_B), 1.23 (1 H, ddd, *J* 3.5, 10.4 and 14.3, CH_AH_B), 1.06 (3 H, d, *J* 7.1, C*H*Me), 0.84 (9 H, s, CMe_3), 0.28 (3 H, s, $SiMe_AMe_B$) and 0.26 (3 H, s, $SiMe_AMe_B$); *m*/*z* 305 (0.4%, M^+ − Me), 302 (0.5, $M - H_2O$), 287 (0.3, $M - H_2O$ − Me), 269 (1.6, $M - 2H_2O$ − Me), 245 (2.2, $M - H_2O - CMe_3$), 243 (1.5, M − Ph), 135 (100, $PhMe_2Si$), 87 (33, $Me_3CCH{=}OH$) and 57 (19, CMe_3) (Found: $M^+ - H_2O$, 302.2047. $C_{19}H_{32}O_2Si$ requires $M - H_2O$, 302.2066).

(3*RS*,5*RS*,8*SR*,6*Z*)-2,2-Dimethyl-3,5-dihydroxy-8-dimethyl(phenyl)silylnon-6-ene 68aa. As an oil (63%); R_f(hexane–EtOAc, 4:1) 0.18; ν_{max}($CDCl_3$)/cm^{-1} 3560 (br OH), 3060, 2960, 2860 (CH), 1640 (C=C), 1250 (SiMe) and 1110 (SiPh); δ_H(400 MHz; $CDCl_3$), 7.55–7.43 (2 H, m, *o*-SiPh), 7.39–7.29 (3 H, m, *m*- and *p*-SiPh), 5.33–5.23 (2 H, m, CH=CH), 4.26 (1 H, dt, *J* 4.2 and 7.4, CH=CHC*H*OH), 3.45 (1 H, dd, *J* 1.8 and 10.5, C*H*CMe_3), 2.09 (1 H, dq, *J* 10.6 and 7.1, MeC*H*), 1.51 (1 H, ddd, *J* 2.1, 7.2 and 14.3, CH_AH_B), 1.39 (1 H, ddd, *J* 4.1, 10.5 and 14.3, CH_AH_B), 1.25 (2 H, br s, 2 × OH), 1.07 (3 H, d, *J* 7.1, CH*Me*), 0.84 (9 H, s, CMe_3), 0.33 (3 H, s, $SiMe_AMe_B$) and 0.29 (3 H, s, $SiMe_AMe_B$); *m*/*z* 287 (0.6%, $M^+ - H_2O$ − Me), 276 (1.3, $M - C_2H_4O$), 255 (0.2, M − 2Me − H_2O − OH), 245 (1.3, $M - H_2O - CMe_3$), 153 (3, *M* − Me − $PhMe_2SiOH$), 135 (78, $PhMe_2Si$) and 87 (41, $Me_3CCH{=}OH$) (Found: M^+ − H_2O − Me, 287.1811. $C_{19}H_{32}O_2Si$ requires $M - H_2O$ − Me, 287.1831). The saturated diol (3SR,5RS,8RS)-2,2-*dimethyl*-8-*dimethyl*(*phenyl*)*silylnonane*-3,5-*diol* was also isolated (1.6 mg) as needles, mp 105–108 °C (from hexane–EtOAc, 9:1); R_f(hexane–EtOAc, 4:1) 0.12; ν_{max}($CDCl_3$)/cm^{-1} 3500 (br OH), 2960, 2880 (CH), 1250 (SiMe) and 1110 (SiPh); δ_H(400 MHz; $CDCl_3$) 7.50–7.47 (2 H, m, *o*-SiPh), 7.34–7.31 (3 H, m, *m*- and *p*-SiPh), 3.73 [1 H, m, $(CH_2)_2CHOH$], 3.52 (1 H, dd, *J* 4.7 and 8.1, Me_3CHOH), 1.67 (2 H, br s, 2 × OH), 1.49 [2 H, t, *J* 5.1, $CH_2(CHOH)_2$, symmetry of CH_2 is evidence for *anti* reduction], 1.36–1.20 (5 H, m, $SiCHCH_2CH_2CHOH$), 0.95 (3 H, d, *J* 7.0, *Me*CH), 0.86 (9 H, s, Me_3C) and 0.25 (6 *H*, s, $SiMe_2$); *m*/*z* 290 (0.2%, M^+ − MeOH), 289 (0.6, $M - H_2O$ − Me), 263 (0.2, M − Me − CH_2CHOH), 247 (3, $M - Me_3C - H_2O$), 245 (0.5, M − Ph), 221 (9, $M - Me_3CCHOHCH_2$), 187 (3, $M - PhMe_2Si$), 169 (2, $M - PhMe_2Si - H_2O$), 153 (6, $PhMe_2SiOH_2$), 152 (5, $PhMe_2SiOH$) and 135 (100, $PhMe_2Si$) (Found: $M^+ - H_2O$ − Me, 289.1986. $C_{19}H_{34}O_2Si$ requires $M - H_2O$ − Me, 289.1987).

(3*RS*,5*RS*,8*RS*,6*Z*)-3,5-Dihydroxy-2,2-dimethyl-8-trimethylsilylnon-6-ene 67ba. As an oil (95%); R_f(hexane–EtOAc, 4:1) 0.19; ν_{max}(film)/cm^{-1} 3400 (br OH), 2960, 2920, 2880 (CH), 1640 (C=C) and 1250 (SiMe); δ_H(400 MHz; $CDCl_3$) 5.44 (1 H, dd, *J* 9.1 and 10.8, CH=C*H*CHOH), 5.30 (1 H, t, *J* 11.3, C*H*=CHCHOH), 4.72 (1 H, dt, *J* 9.0 and 5.3, CH=CHC*H*OH), 3.61 (1 H, dd, *J* 5.7 and 7.4, Me_3CCHOH), 2.3 (2 H, br s, 2 × OH), 1.92 (1 H, dq, *J* 11.7 and 7.0, MeC*H*), 1.58 (2 H, dd, *J* 4.0 and 7.1, CH_2) (symmetry of CH_2 is evidence for *anti* reduction), 1.02 (3 H, d, *J* 7.0, *Me*CH), 0.87 (9 H, s, Me_3C) and −0.06 (9 H, s, Me_3Si); *m*/*z* 240 (5%, $M^+ - H_2O$), 225 (3, $M - H_2O$ − Me), 201 (3, $M - Me_3C$), 183 (6, $M - Me_3C - H_2O$), 159 (38, $M - Me_3CCOCH_2$), 87 (48, $Me_3CCH{=}OH$), 73 (100, Me_3Si) and 57 (39, Me_3C) (Found: $M^+ - H_2O$, 240.1914. $C_{14}H_{30}O_2Si$ requires $M - H_2O$, 240.1909).

(3*RS*,5*RS*,8*SR*,6*Z*)-3,5-Dihydroxy-2,2-dimethyl-8-trimethylsilylnon-6-ene 68ba. As a waxy solid, mp 85–92 °C (76%); R_f(hexane–EtOAc, 4:1) 0.20; ν_{max}($CDCl_3$)/cm^{-1} 3620, 3520 (OH), 2960, 2880 (CH), 1640 (C=C) and 1250 (SiMe); δ_H(250 MHz; $CDCl_3$) 5.41 (1 H, dd, *J* 8.3 and 11.0, CH=C*H*CHOH), 5.27 (1 H, dt, *J* 0.7 and 11.0, C*H*=CHCHOH), 4.65 (1 H, ddd, *J* 4.0, 6.9 and 8.3, CH=CHC*H*OH), 3.58 (1 H, dd, *J* 2.4 and 10.2, Me_3CCHOH), 2.2 (2 H, br s, 2 × OH), 1.85 (1 H, dq, *J* 11.4 and 7.1, MeC*H*), 1.66 (1 H, ddd, *J* 2.4, 6.9 and 14.2, CH_AH_B), 1.54 (1 H, ddd, *J* 4.0, 10.2 and 14.2, CH_AH_B), 1.01 (3 H, d, *J* 7.1, *Me*CH), 0.88 (9 H, s, Me_3C) and −0.02 (9 H, s, Me_3Si); *m*/*z* 225 (0.5%, $M^+ - H_2O$ − Me), 214 (2, $M - C_2H_4O$), 201 (0.4, $M - Me_3C$), 183 (2, $M - Me_3C - H_2O$), 168 (1, $M - Me_3SiOH$, or $M - Me_3C - H_2O$ − Me), 87 (60, $Me_3CCH{=}OH$) and 73 (78, Me_3Si) (Found: M^+ − H_2O − Me, 225.1656. $C_{14}H_{30}O_2Si$ requires $M - H_2O$ − Me, 225.1674).

(1*RS*,2*Z*,4*SR*,6*SR*)-(4,6-Dihydroxy-7,7-dimethyl-1-phenyloct-2-enyl)trimethylsilane 67bc. As needles, mp 102–104 °C (from hexane) (78%); R_f(EtOAc–hexane, 20:80) 0.15; ν_{max}(Nujol)/cm^{-1} 3330 (OH), 1590 (Ph) and 1235 and 820 ($SiMe_3$); δ_H(250 MHz; $CDCl_3$) 7.25–7.18 (2 H, m, *o*-ArH), 7.11–7.04 (3 H, m, *m*-and *p*-ArH), 5.96 (1 H, dd, *J* 10.9 and 12.1, SiCHC*H*), 5.61 (1 H, dd, *J* 9.4 and 10.9, SiCHCH=C*H*), 4.95–4.87 (1 H, m, CH=CHC*H*OH), 3.64 (1 H, dd, *J* 4.3 and 8.5, C*H*OHCMe_3), 3.35 (1 H, d, *J* 12.1, SiCH), 1.68–1.60 (2 H, m, CH_2), 0.90 (9 H, s, CMe_3) and −0.05 (9 H, s, $SiMe_3$) (Found: C, 71.5; H, 10.2. $C_{19}H_{32}SiO_2$ requires C, 71.2; H, 10.1%).

(1*SR*,2*Z*,4*SR*,6*SR*)-(4,6-Dihydroxy-7,7-dimethyl-1-phenyloct-2-enyl)trimethylsilane 68bc. As needles, mp 111–112 °C (from hexane) (82%); R_f(EtOAc–hexane, 20:80) 0.14; ν_{max}(Nujol)/cm^{-1} 3330 (OH), 1590 (Ph) and 1235 and 820 ($SiMe_3$); δ_H(250 MHz; $CDCl_3$) 7.25–7.19 (2 H, m, *o*-ArH), 7.11–7.00 (3 H, m, *m*-and *p*-ArH), 5.90 (1 H, dd, *J* 10.9 and 11.7, SiCHC*H*), 5.60 (1 H, dd, *J* 8.4 and 10.9, SiCHCH=C*H*), 4.83–4.74 (1 H, m, CH=CHC*H*OH), 3.49 (1 H, dd, *J* 2.6 and 10.2, C*H*OHCMe$_3$), 3.22 (1 H, d, *J* 11.7, SiCH), 1.56 (1 H, ddd, *J* 2.6, 7.0 and 14.3, CH_AH$_B$), 1.47 (1 H, ddd, *J* 3.8, 10.2 and 14.3, CH$_A$$H_B$), 0.78 (9 H, s, CMe$_3$) and −0.02 (9 H, s, $SiMe_3$) (Found: C, 71.0; H, 10.2. $C_{19}H_{32}SiO_2$ requires C, 71.2; H, 10.1%).

Vinylogous Peterson reactions

General procedure. Potassium hydride (20% suspension in oil; 114 mg, 0.57 mmol) was washed under nitrogen with pentane (4 × 2 cm^3) and then stirred in THF (2 cm^3) with the diol (143 μmol) for 2 h. *TLC* showed that reaction was complete and ether (3 cm^3) and water (3 cm^3) were added, the layers separated and the aqueous layer extracted with ether (3 cm^3). The combined extracts were washed with brine (3 cm^3), dried (K_2CO_3), filtered, evaporated and flash chromatographed (hexane–EtOAc, 19:1) to give the diene. The following dienes were prepared by this method.

(5*Z*,7*E*)-2,2-Dimethylnona-5,7-dien-3-ol 69. As an oil (15 mg, 62%); R_t(GLC, Carlo Erba Strumentazione 4130, 25 m, BP5, 5% phenylmethylsiloxane column, 5 μm film thickness, He carrier gas, *ca.* 0.3 m s^{-1}, 90 °C) 15.58 (*Z*,*E* diene, 84% PAR), 17.76 (*E*,*E* diene, 12% PAR) and 18.36 min (presumed *E*,*Z* diene, 4% PAR); R_f(hexane–EtOAc, 9:1) 0.23; ν_{max}($CDCl_3$)/cm^{-1} 3580 (br OH), 3020, 2960 and 2870 (CH); δ_H(400 MHz; $CDCl_3$) 6.30 (1 H, dd, *J* 11.0 and 14.5, MeCH=C*H*-CH=CH), 6.12 (1 H, t, *J* 11.0, MeCH=CHC*H*=CH), 5.72 (1 H, dq, *J* 14.5 and 6.8, MeC*H*=CHCH=CH), 5.36 (1 H, ddd, *J* 11.9 and 6.6, MeCH=CHCH=C*H*CH$_2$), 3.23 (1 H, dd, *J* 2.7 and 10.3, C*H*OH), 2.32 (1 H, ddd, *J* 1.7, 6.6 and 14.1, CH_AH$_B$), 2.24 (1 H, td, *J* 9.0 and 14.1, CH$_A$$H_B$), 1.77 (3 H, d, *J* 6.8, *Me*CH), 1.60 (1 H, br s, OH) and 0.93 (9 H, s, CMe$_3$); *m*/*z* 150 (1%, M$^+$ − H_2O), 135 (100, M − H_2O − Me), 87 (29, Me_3CCH=OH), 67 (16, M − $CH_2CHOHCMe_3$) and 57 (40, CMe$_3$) (Found: M$^+$ − H_2O − Me, 135.1161. $C_{11}H_{20}O$ requires *M* − H_2O − Me, 135.1173). The yield from the trimethylsilyl analogue **67ba** was 28%; R_t(GLC) 15.58 (20.5% PAR) and 17.76 min (9.6% PAR) and several other peaks, one obscuring the region where the presumed *E*,*Z* diene peak appears in other samples.

(5*E*,7*E*)-2,2-Dimethylnona-5,7-dien-3-ol 70. As an oil (17% from **68aa**, 21% from **68ba**); R_t(GLC) 17.76 min (98% PAR) and 18.36 min (2% PAR) from **68aa** and from **68ba**; R_f(hexane–EtOAc, 4:1) 0.47; ν_{max}($CDCl_3$)/cm^{-1} 3580 (br OH), 3020, 2960 and 2870(CH); δ_H(400 MHz; $CDCl_3$) 6.10 (1 H, ddd, *J* 0.9, 10.0 and 13.2, MeCH=CHC*H*=CH), 6.04 (1 H, ddq, *J* 14.4, 10.0 and 1.4, MeCH=C*H*CH=CH), 5.62 (1 H, dq, *J* 14.4 and 7.2, MeC*H*=CHCH=CH), 5.57 (1 H, ddd, *J* 6.6, 8.8 and 13.2, MeCH=CHCH=C*H*), 3.22 (1 H, dd, *J* 2.2 and 10.3, C*H*OH), 2.35 (1 H, ddd, *J* 2.2, 6.6 and 14.4, CH_AH$_B$), 1.96 (1 H, dt, *J* 14.4 and 9.4, CH$_A$$H_B$), 1.73 (3 H, d, *J* 7.2, *Me*CH), 1.25 (1 H, br s, OH) and 0.90 (9 H, s, CMe$_3$); *m*/*z* 149 (27%, M$^+$ − H_3O), 111 (27, M − CMe$_3$), 87 (40, Me_3CCH=OH) and 57 (Me$_3$C) (Found: M$^+$ − H_3O, 149.1324. $C_{11}H_{20}O$ requires *M* − H_3O, 149.1330).

(5*E*,7*E*)-2,2-Dimethyl-8-phenylocta-5,7-dien-3-ol 73. By stirring at 0 °C for 5 min, as an oil (67% from **67bc**, 76% from **68bc**); R_f(EtOAc–hexane, 20:80) 0.46; ν_{max}(film)/cm^{-1} 3400 (OH) and 1595 (Ph); δ_H(250 MHz; $CDCl_3$) 7.40–7.18 (5 H, m, Ph), 6.77 (1 H, dd, *J* 10.4 and 15.6, PhCH=C*H*), 6.48 (1 H, d, *J* 15.6, PhC*H*), 6.31 (1 H, dd, *J* 10.4 and 15.2, PhCH=CHC*H*), 5.86 (1 H, ddd, *J* 6.2, 8.5 and 15.2, PhCH=CHCH=C*H*), 3.30 (1 H, d, *J* 10.4, C*H*OH), 2.43 (1 H, dd, *J* 6.2 and 14.4, CH_AH$_B$), 2.09 (1 H, ddd, *J* 8.9, 10.4 and 14.5, CH$_A$$H_B$) and 0.94 (9 H, s, CMe$_3$); *m*/*z* 230 (70%, M$^+$), 144 (95, M − CHOCMe$_3$), 77 (40, Ph) and 57 (80, CMe$_3$) (Found: M$^+$, 230.1669. $C_{16}H_{22}O$ requires *M*, 230.1671).

(1*E*,3*E*)-1-Phenylpenta-1,3-diene[60] 74. By stirring at 0 °C for 1 h, as an oil (67% from **67bc**, 60% from **68bc** and 93% from **73**); R_f(EtOAc–hexane, 20:80) 0.64; δ_H(250 MHz; $CDCl_3$) 7.38–7.16 (5 H, m, Ph), 6.74 (1 H, dd, *J* 10.3 and 15.6, PhCH=C*H*), 6.41 (1 H, d, *J* 15.6, PhCH), 6.21 (1 H, dd, *J* 10.3 and 15.0, PhCH=CHC*H*), 5.84 (1 H, dq, *J* 15.0 and 6.8, C*H*Me) and 1.82 (3 H, d, *J* 6.8, Me).

1-Cyclohexylhexa-2,4-dienes 77

Diisobutylaluminium hydride (1 mol dm^{-3} solution in hexane; 19.1 cm^3) and methyl cyclohexylacetate (1.25 g, 8 mmol) were kept in dry toluene (25 cm^3) at −90 °C for 2 h. Dry methanol (10 cm^3) was then added and the solution allowed to warm to room temperature. Saturated aqueous potassium sodium tartrate (50 cm^3) was added and the mixture extracted with ethyl acetate (3 × 50 cm^3). The combined organic extracts were washed with brine, dried ($MgSO_4$) and evaporated under reduced pressure to give the crude aldehyde **76** (0.9 g, 89%) as a pale yellow oil; R_f(hexane–EtOAc, 4:1) 0.49; ν_{max}(film)/cm^{-1} 1735 (C=O); δ_H(250 MHz; $CDCl_3$) 9.61 (1 H, t, *J* 2.3, CHO), 2.16 (2 H, dd, *J* 2.3 and 6.8, CH_2CHO), 1.76 (1 H, m, C*H*CH$_2$), 1.68–1.51 (5 H, m, 5 × CH ring) and 1.39–0.72 (5 H, m, 5 × CH ring), which was used immediately in the next step. Butyllithium (1.6 mol dm^{-3} solution in hexane; 7.13 cm^3) was added dropwise to a stirred suspension of but-2-enyltriphenylphosphonium bromide[52] (4.5 g, 11.4 mmol) in dry ether (18 cm^3) under argon at room temperature and the resulting red solution stirred for 3 h. The solution was cooled to 0 °C and the aldehyde **76** (0.9 g, 7.1 mmol) added in dry ether (18 cm^3). The resulting solution was stirred for 1 h at 0 °C and then for 15 h at room temperature. The suspension was then filtered through Celite, washing with ether, and the filtrate washed with sulfuric acid (3 mol dm^{-3}; 30 cm^3) and water (30 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure. The residue was chromatographed (SiO_2, hexane) to give a mixture of the *dienes* (0.7 g, 60%); R_t(GLC, 100 °C) 15.937 min (*Z*,***E***), 16.243 min (*E*,***E***), 16.673 min (*E*,*Z*), 17.37 min (*Z*,*Z*) in a ratio of 40:36:12:12); R_f(hexane) 0.58; ν_{max}($CDCl_3$)/cm^{-1} 1610 (C=C); δ_H(250 MHz; $CDCl_3$) 6.10–5.40 (4 H, m, C*H*=C*H*C*H*=C*H*Me), 1.96–1.89 (2 H, m, CH_2CH=CH), 1.73 (9 H, m, 6 H ring and CH*Me*) and 1.25–0.78 (5 H, m, 5 CH ring).

2-Cyclohexylethanoic acid

Following Bailey,[61] ozone was bubbled through a solution of the diene **77** (100 mg, 0.61 mmol) in dry methanol (3 cm^3) at −78 °C for 2 h. The system was then purged with argon, allowed to warm to room temperature and the solvent evaporated under reduced pressure. The residue was dissolved in formic acid (0.5 cm^3, 98%) and hydrogen peroxide (0.25 cm^3, 30%) added, and the solution was warmed gently. When the evolution of gas had ceased, the mixture was refluxed for 15 min and then allowed to cool to room temperature. Hydrochloric acid (3 mol dm^{-3}; 8 cm^3) was added and the aqueous layer extracted with a mixture of ethyl acetate and ether (3 × 20 cm^3, 1:1). The combined organic extracts were then washed with saturated aqueous sodium hydrogen carbonate (3 × 20 cm^3). The aqueous extracts were combined and acidified with hydrochloric acid (3 mol dm^{-3}) to pH 1, and the solution was then extracted with dichloromethane (3 × 20 cm^3). These organic extracts were combined, washed with brine, dried ($MgSO_4$) and evaporated under reduced pressure to give the acid (80 mg, 92%) identical with a commercial sample; ν_{max}(CH_2Cl_2)/cm^{-1} 3700–2300 (OH) and 1710 (C=O); δ_H(250 MHz; $CDCl_3$) 10.81 (1 H, s, CO_2H), 2.20 (2 H, d, *J* 6.7, CH_2CO_2), 1.84–1.66 (6 H, m, 6 × CH ring) and 1.44–0.80 (5 H, m, 5 × CH ring).

Methyl (*R*)-2-(2-cyclohexylethanoyloxy)-2-phenylethanoate 80

Following Parker,[41] the acid above (56 mg, 0.4 mmol), DMAP (spatula tip), methyl (*R*)-mandelate (methyl 2-hydroxy-2-phen-

ylacetate) (66 mg, 0.4 mmol) and DCC (82.4 mg, 0.4 mmol) were kept in dry dichloromethane (2 cm^3) under argon at −10 °C for 2 h and then filtered through a cotton wool plug with the aid of dichloromethane (5 cm^3). The solution was evaporated under reduced pressure and the residue chromatographed (PLC, SiO_2, hexane–EtOAc, 5:1) to give the *ester* (0.11 g, 95%); R_f(hexane–EtOAc, 3:1) 0.5; ν_{max}(film)/cm^{-1} 1750 (C=O); δ_H(400 MHz; C_6D_6) 7.47–7.45 (2 H, m, *o*-Ph), 7.10–7.03 (3 H, m, *m*- and *p*-Ph), 6.07 (1 H, s, C*H*Ph), 3.18 (3 H, s, CO_2Me), 2.21 (1 H, dd, *J* 7 and 14.9, CH_AH_BCO), 2.12 (1 H, dd, *J* 7 and 14.9, CH_AH_BCO), 1.86 (1 H, m, $CHCH_2CO_2$), 1.75–1.46 (5 H, m, 5 × CH ring) and 1.34–0.80 (5 H, m, 5 × CH ring); *m/z* 293 (12%, M^+ + H), 313 (20, M + Na) and 149 (100, PhCH-CO_2Me) (Found: M^+ + H, 291.1595. $C_{17}H_{22}O_4$ requires *M* + H, 291.1596).

Methyl (*R*)-2-[(2*S*)-2-cyclohexyl-2-deuterioethanoyloxy]-2-phenylethanoate 79, methyl (*R*)-2-[(2*R*)-2-cyclohexyl-2-deuterioethanoyloxy]-2-phenylethanoate and methyl (*R*)-2-[2-cyclohexylethanoyloxy]-2-phenylethanoate 80

Ozonolysis of the mixture of dienes **26** and **78** as described above for the non-deuteriated diene gave a mixture of the deuteriated acids and the protonated acid (20 mg, 26%) as plates. This crude product was converted as described above into the mandelate esters (43 mg, 67%); R_f(3:1 hexane–EtOAc) 0.5; δ_H(400 MHz; C_6D_6) 7.47–7.45 (2 H, m, *o*-Ph), 7.10–7.03 (3 H, m, *m*- and *p*-Ph), 6.07 (1 H, s, C*H*Ph), 3.18 (3 H, s, CO_2Me), 2.21 (0.5 H, d, *J* 6.9, CH_ADCO), 2.12 (0.5 H, d, *J* 6.9, CDH_BCO), 1.90–1.79 (1 H, m, $CHCH_2CO_2$), 1.75–1.46 (5 H, m, 5 CH ring) and 1.34–0.80 (5 H, m, CH ring). Unfortunately the CDHCO peaks were complicated by the double doublets of the protonated ester **80**. An impurity, which was probably cyclohexanecarboxylate mandelate ester gave a nearby signal at δ 2.3. Cutting out and weighing of the appropriate signals suggested a selectivity of 45:55 *R* ester to *S* ester. The most important errors are the low incorporation of deuterium and the possible 3% racemisation that is known to take place during the DCC–DMAP coupling reaction with methyl *R*-mandelate.

(4*S*)-4-Benzyl-3-[(2*R*)-2-cyclohexyl-2-deuterioethanoyloxy]-1,3-oxazolidin-2-one

Following Evans,[62] the oxazolidinone **81** (0.252 g, 0.83 mmol) in dry THF (1.5 cm^3) was added dropwise to a stirred solution of LDA (0.83 mmol) in dry THF (3 cm^3) under argon at −78 °C. After stirring for 1 h at −78 °C, butyllithium (1.6 mol dm^{-3} in hexanes; 0.52 cm^3, 0.84 mmol) was added dropwise and the mixture stirred for a further 30 min. The reaction was then quenched with hexadeuterioacetone (1 cm^3) and the mixture allowed to warm to 0 °C. Saturated aqueous ammonium chloride (5 cm^3) was then added, and the aqueous layer extracted with ether (2 × 10 cm^3). The organic extracts were combined, washed with brine, dried ($MgSO_4$) and evaporated under reduced pressure to give the *deuteriated oxazolidinone* (2.4 g, 95%) as plates, mp 83.5–85 °C (from hexane), identical (mp, IR, ^1H NMR) with the undeuteriated sample **81** except that the signal at δ 2.87 was a weak unresolved multiplet, and that its integration along with that at δ 2.77 was not reliable; *m/z* 302 (9.8%, M^+), 220 (29, M − C_6H_{11}) and 126 (100, $C_6H_{11}CHDCO$) (Found: M^+, 302.1728. $C_{18}H_{22}NO_3D$ requires *M*, 302.1740). In the mass spectrum the ratios of 301:302:303 were 23:64:13, respectively.

(3*S*)-3-Hydroxymethyl-5,5-dimethyltetrahydrofuran

Ozone was bubbled through a solution of the alkene **33** (134 mg, 0.96 mmol) in methanol (15 cm^3) until a bubbler filled with potassium iodide solution connected to the exhaust showed a discolouration due to liberated iodine. The flask was purged with nitrogen for 10 min and allowed to warm to 0 °C. Sodium borohydride (144 mg, 3.8 mmol) was added and the mixture stirred for 1.5 h. The solvent was removed under reduced pressure, the residue taken up in ether (30 cm^3) and washed with water (10 cm^3). The aqueous phase was extracted with ether (10 × 5 cm^3). The combined extracts were dried ($MgSO_4$) and evaporated under reduced pressure to give the *alcohol* (78 mg, 63%); $R_f(Et_2O)$ 0.26; ν_{max}(film)/cm^{-1} 3400 (OH) and 1060 (C–O); δ_H(250 MHz; $CDCl_3$) 3.96 (1 H, dd, *J* 7.4 and 8.9, $CMe_2OCH_AH_B$), 3.64 (1 H, dd, *J* 6.4 and 8.9, $CMe_2OCH_AH_B$), 3.65–3.55 (2 H, m, CH_2OH), 2.56 (1 H, br septet, *J* 7.3, $CHCH_2OH$), 1.88 (1 H, dd, *J* 8.5 and 12.4, $CH_AH_BCMe_2$), 1.41 (1 H, dd, *J* 7.8 and 12.4, $CH_AH_BCMe_2$), 1.29 (3 H, s, CMe_AMe_B) and 1.20 (3 H, s, CMe_AMe_B); *m/z* 130 (1%, M^+), 115 (100, M − Me) and 97 (75, M − Me − H_2O); $[\alpha]_D$ +27.7 (*c* 1.0 in $CHCl_3$) (Found: M^+, 130.0997. $C_7H_{14}O_2$ requires *M*, 130.0994). The same (TLC, IR and ^1H NMR) compound (8 mg, 57%) was prepared similarly from the diene **35** (18 mg, 0.108 mmol); $[\alpha]_D$ +5.0 (*c* 0.8 in $CHCl_3$).

(3*R*)-5,5-Dimethyltetrahydro-3-furylmethyl (2*S*)-2-methoxy-2-phenyl-3,3,3-trifluoropropanoate and (3*S*)-5,5-dimethyltetrahydro-3-furylmethyl (2*S*)-2-methoxy-2-phenyl-3,3,3-trifluoropropanoate 83

DCC (23 mg, 0.11 mmol), 3-hydroxymethyl-5,5-dimethyltetrahydrofuran (11 mg, 0.085 mmol, prepared from the alkene **33**), (−)-MTPA (26 mg, 0.11 mmol) and DMAP (3 mg, 0.02 mmol) were kept in dry dichloromethane (0.4 cm^3) at room temperature under argon for 2.5 h, filtered through Celite and evaporated under reduced pressure. The residue was chromatographed (SiO_2, EtOAc–hexane, 10:90) to give an inseparable mixture of the *esters* **83** (29 mg, 99%) in a ratio of 95:5 (as determined by integration of ^1H and ^{19}F NMR signals); $R_f(Et_2O)$ 0.67; ν_{max}(film)/cm^{-1} 1750 (C=O); δ_H(400 MHz; $CDCl_3$) 7.51–7.48 (2 H, m, *o*-ArH), 7.43–7.36 (3 H, m, *m*- and *p*-ArH), 4.35 (1 H, dd, *J* 6.3 and 10.8, $CO_2CH_AH_B$, *RS* isomer), 4.28 (1 H, dd, *J* 6.7 and 10.9, $CO_2CH_AH_B$, *SS* isomer), 4.25 (1 H, dd, *J* 7.7 and 10.9, $CO_2CH_AH_B$, *SS* isomer), 4.19 (1 H, dd, *J* 8.3 and 10.8, $CO_2CH_AH_B$, *RS* isomer), 3.89 (1 H, dd, *J* 7.3 and 9.0, $CMe_2OCH_AH_B$, *RS* isomer), 3.88 (1 H, dd, *J* 7.2 and 9.1, $CMe_2OCH_AH_B$, *SS* isomer), 3.56 (1 H, dd, *J* 5.0 and 6.6, $CMe_2OCH_AH_B$, *RS* isomer), 3.54 (1 H, dd, *J* 4.9 and 6.6, $CMe_2OCH_AH_B$, *SS* isomer), 3.52 (3 H, s, OMe), 2.72 (1 H, br septet, *J* 7.5, $CHCH_2O$, *RS* isomer), 2.71 (1 H, br septet, *J* 7.5, $CHCH_2O$, *SS* isomer), 1.88 (1 H, dd, *J* 8.5 and 12.5, $CH_AH_BCMe_2$, *RS* isomer), 1.87 (1 H, dd, *J* 8.5 and 12.5, $CH_AH_BCMe_2$, *SS* isomer), 1.40 (1 H, dd, *J* 7.9 and 12.5, $CH_AH_BCMe_2$), 1.26 (3 H, s, CMe_AMe_B, *RS* isomer), 1.25 (3 H, s, CMe_AMe_B, *SS* isomer), 1.18 (3 H, s, CMe_AMe_B, *RS* isomer) and 1.17 (3 H, s, CMe_AMe_B, *SS* isomer); δ_F(235 MHz; $CDCl_3$; relative to CCl_3F) −72.05 (*RS* isomer) and −72.08 (*SS* isomer); *m/z* 346 (8%, M^+), 331 (75, M − Me) and 189 (100, $PhCOMeCF_3$) (Found: M^+, 346.1382. $C_{17}H_{21}O_4F_3$ requires *M*, 346.1392). The same (TLC, IR and ^1H NMR) compounds (15 mg, 80%) in a ratio of 60:40 (by integration of ^1H and ^{19}F NMR signals) were prepared similarly from the alcohol (7 mg, 0.054 mmol) derived from the diene **35**.

Acknowledgements

We thank the SERC for maintenance awards (G. R. J., N. D. K., C. P. L. and I. T. M.), the EEC for a Fellowship (Y. L.) and the Government of Bengal for a scholarship (A. K. S.).

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Paper 5/06836C
Received 16*th October* 1995
Accepted 22*nd January* 1996