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Accurate determinations of the extent to which the S_E2' reactions of allyl-, allenyl- and propargylsilanes are stereospecifically *anti*

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Received 27th October 2003, Accepted 22nd December 2003
First published as an Advance Article on the web 9th February 2004

The allylsilanes, (*R*)-*E*- and (*R*)-*Z*-4-trimethylsilylpent-2-ene **16**, were prepared in essentially an enantiomerically and geometrically pure state (er >99.95 : 0.05, *E* : *Z* and *Z* : *E* >99.95 : 0.05) by, successively, conjugate addition of lithium dimethylcuprate to *N*-[(*E*)-3′-trimethylsilylpropenoyl]-(7*S*)-10,10-dimethyl-4-aza-5-thiatricyclo[5.2.1.$0^{3,7}$]-decane 5,5-dioxide, to give *N*-[(*E*)-(3′*R*)-3′-trimethylsilylbutanoyl]-(7*S*)-10,10-dimethyl-4-aza-5-thiatricyclo-[5.2.1.$0^{3,7}$]decane 5,5-dioxide **13**, removal of the chiral auxiliary with bromomagnesium benzyloxide, aldol reaction with acetaldehyde, and decarboxylative elimination, to give either the *Z*- or *E*-isomer. Both the *E*- and *Z*-allylsilanes **16** reacted with the adamantyl cation to give mixtures of *E*- and *Z*-4-adamantylpent-2-enes **17**. The *E*-allylsilane gave the *E*- and *Z*-products in a ratio of 40 : 60, and the *Z*-allylsilane gave the *E*- and *Z*-products in a ratio of 99.8 : 0.02. The enantiomer ratio was >99 : 1 for the reaction of the *E*-allylsilane giving the *Z*-product, 90 : 10 for the *E*-allylsilane giving the *E*-product, and 95 : 5 for the *Z*-allylsilane giving the *E*-product, showing that the reactions were stereospecific to a high degree, but not always quite completely so. The allenylsilane, 2-trimethylsilylpenta-2,3-diene **29**, was prepared enantiomerically highly enriched (er 99 : 1) by copper-catalysed reaction of methylmagnesium chloride with (*S*)-4-trimethylsilylbut-3-yn-2-yl camphor-10-sulfonate **28**. The allenylsilane **29** reacted with the adamantyl cation to give (*S*)-4-adamantylpent-2-yne (*S*)-**30** with the same level of enantiomeric purity, showing that the reaction was, as accurately as can be measured, completely stereospecific. The allenylsilane **29** also reacted with isobutanal in the presence of titanium tetrachloride to give 2,4-dimethylhept-5-yn-3-ol as a mixture of diastereoisomers, *syn* **31** and *anti* **32**, in a ratio of 95 : 5, with the major diastereoisomer present as a mixture of enantiomers (4*R*,5*R*) : (4*S*,5*S*) in a ratio of 99 : 1, showing that the reaction was, as accurately as can be measured, completely stereospecific in the *anti* sense. The corresponding propargylsilane, 4-trimethylsilylpent-2-yne **37**, reacted with the adamantyl cation to give dienes assigned the structures 2,3-diadamantyl-1,3-pentadiene **42** and 2,4-diadamantyl-1,3-pentadiene **43**, and reacted with isobutanal in the presence of titanium tetrachloride to give 2-(1-hydroxy-2-methylpropyl)-3-trimethylsilylpenta-1,3-dienes **45** and 2,4-dimethyl-5-trimethylsilylhept-5-en-3-one **46**. The enantiomerically enriched propargylsilane (*R*)-1,3-bis(trimethylsilyl)but-1-yne **62** (er >99.7 : 0.3) was prepared from the sultam **13**, by removal of the chiral auxiliary with lithium ethoxide, reduction of the ethyl ester to give (*R*)-3-trimethylsilylbutanal **60**, enol triflate formation, β-elimination and *C*-silylation. The propargylsilane **62** reacted with 2,4-dinitrobenzaldehyde in the presence of titanium tetrachloride to give the allenes, 1-(2,4-dinitrophenyl)-2-trimethylsilylpenta-2,3-dienols **63**–**66**, as two diastereoisomers in a ratio of 2 : 1, each of which was a pair of enantiomers in a ratio of approximately 3 : 1, showing that there was considerable loss of stereospecificity, but that what there was was in the *anti* sense. A similar reaction with isobutanal gave a similar set of four allenes, 2-methyl-4-trimethylsilylhepta-4,5-dien-3-ol **73**–**76**, but with a negligible degree of stereospecificity.

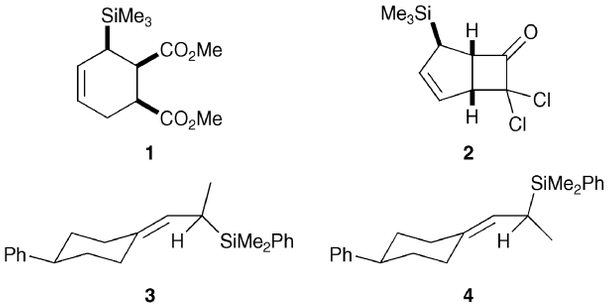
Introduction

We reported our results measuring accurately the degree of stereospecificity of the S_E2' reactions of allyl-, allenyl- and propargylsilanes in three preliminary communications.[1] This is the full paper on that work, which is the culmination of an extensive investigation on the diastereoselectivity of electrophilic attack on a double bond adjacent to a stereogenic centre carrying a silyl group.[2,3]

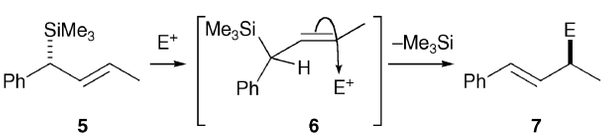
When we started our investigation of the S_E2' reactions of allylsilanes the sense and degree of the stereospecificity was unknown. Our earliest work was confined to the *diastereoselectivity* of the reactions of the chiral but racemic allylsilanes **1**, **2**, **3** and **4**, each of which had more than one stereochemical feature in the molecule, landing us with the problems of double stereo-differentiation. The stereochemical constraints in the allylsilane **1** were matched, with the preference for attack *anti* to the ester groups the same as the preference for attack *anti* to the silyl group,[4] whereas the stereochemical constraints in the allylsilane **2** were mismatched, with the *exo* attack on the bicyclic system forcing most, but not all, reactions to be *syn* to the silyl group.[5] The allylsilanes **3** and **4** were more telling, because the relatively weaker inherent preference for axial or equatorial attack provided a less demanding constraint to set against the effectiveness with which the allylsilane unit encouraged stereospecifically *anti* reactions. The allylsilane **3** was matched for those electrophiles that preferred to attack axially, and the allylsilane **4** was matched for those electrophiles that preferred to attack equatorially. In both cases the matched reactions were stereochemically clean, and in the mismatched cases the allylsilane stereochemistry overpowered, but did not remove, the effect of the inherent axial or equatorial preference.[6] Thus we were able to deduce that the S_E2' reactions of allylsilanes are powerfully and predictably, but not overwhelmingly, effective for the transfer of stereochemical information from C-1 to C-3.

At this stage, Kumada and his co-workers developed a method for the synthesis of the enantiomerically enriched allylsilane **5**, and others like it, in which the only stereogenic centre was that carrying the silyl group.[7] This enabled them to measure the extent to which allylsilanes reacted in the *anti* sense **5** ⟶ **7**, *unconstrained by the influence of any other stereochemical feature*. The major product in these reactions had the *trans* double bond and the absolute configuration **7**, with electro-

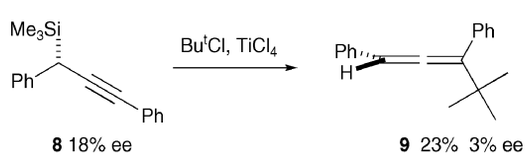
DOI: 10.1039/b313446f



philic attack having taken place *anti* to the silyl group in the most populated conformation **6**. They reported their work in a magisterial series of papers,[7,8] which showed that the S_E2' reactions were not only stereospecifically *anti*, but also that they took place with a wide variety of electrophiles with essentially complete stereospecificity, as accurately as they could measure. This work was supplemented by reports from Eschenmoser,[9] from Nakai[10] and from Kitching,[11] who also found high, but not always complete, levels of *anti* stereospecificity in the reactions of other allylsilanes. Wetter found an exception to the *anti* rule in an acylative desilylation,[12] in which there might have been a cyclic transition structure,[13] but he found later that protodesilylation of the same allyldisilane was a stereospecifically *anti* reaction.[14]



Very little was known about the stereochemistry of S_E2' reactions of allenyl- and propargylsilanes—a pair of allenylsilanes analogous to the allylsilanes **3** and **4** showed high but not complete stereospecificity in the *anti* sense for protodesilylation,[6] and Hayashi found that the propargylsilane **8**, of low enantiomeric purity, reacted with the *tert*-butyl cation to give the allene **9** with an even lower level of enantiomeric purity, and hence a low level (58 : 42) of *anti* stereospecificity.[15]



We developed two syntheses of enantiomerically enriched allylsilanes, the first of which was fairly good, but not good enough for the purpose in hand.[16] The second, adapted from a general method for the synthesis of unsymmetrical allylsilanes,[17] allowed us to make a pair of allylsilanes *E*- and *Z*-**16** that were, within experimental error, enantiomerically pure, and this in turn allowed us to measure the degree of stereospecificity in the S_E2' reaction with greater accuracy than anyone had before. We knew from Eschenmoser's and Kumada's work that it would be high, hence the need for high levels of enantiomeric purity in order to measure it accurately, but we did not know just how high it would be. Subsequently, in order to complete the picture, we found good methods for the synthesis in high enantiomeric purity of an allenylsilane **29** and of a propargylsilane **62**, and we studied their reactions as well, all of it reported in detail here.

Electrophilic attack on allylsilanes *anti* to the silyl group has also been observed in a variety of cycloadditions, and in other reactions in which the silyl group remains in the molecule, at least in the first-formed product.[18,3] Stereospecifically *anti* S_E2' reactions of allylsilanes are now well established,[19] and they have been applied to the total synthesis of several natural products,[20] conspicuously in the work of Panek.[21]

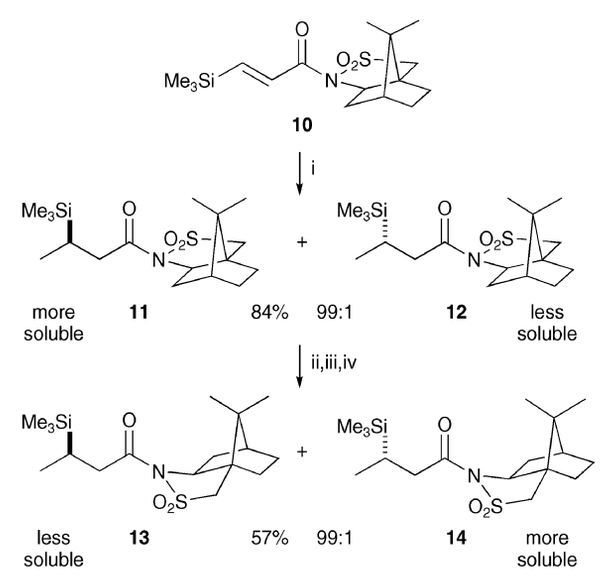
Since the work on allenylsilanes described in our preliminary communication, others have seen high levels of stereospecifically *anti* S_E2' reactions.[22] Sometimes a hydrogen atom is transferred in an ene reaction, instead of the loss of the silyl group, but these reactions also take place with electrophilic attack *anti* to the silyl group.[23] Another variant is the stereospecifically *syn* reaction with aldehydes when the silyl group is a trichlorosilyl group.[24]

More recent work on the preparation and stereospecific reactions of propargylsilanes has also been for *syn* reactions when the silyl group is a trichlorosilyl group.[25]

Results and discussion

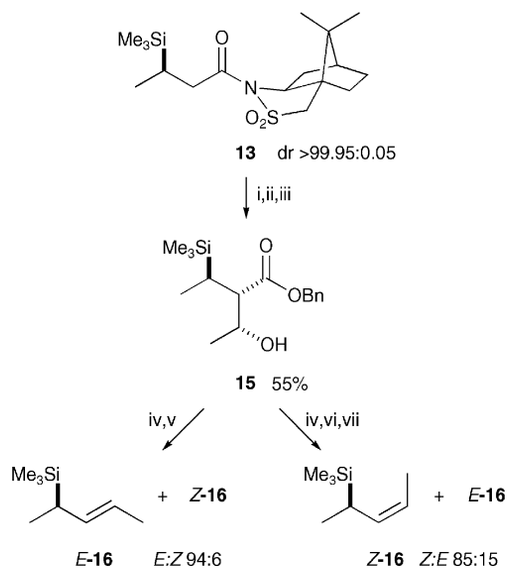
Synthesis of the allylsilanes 16 with high enantiomeric purity

The key to the synthesis of an allylsilane having a high level of enantiomeric purity was to establish the stereogenic centre in a stable intermediate **13** (Scheme 1). This allowed us to raise the enantiomeric purity to a high level, before completing the synthesis by introducing the double bond. Our method for setting up the stereogenic centre carrying the silyl group took advantage of earlier work[26] and the work of Oppolzer.[27] We obtained the highest level of stereochemical purity (99 : 1) at the silicon-bearing carbon by the conjugate addition of lithium dimethylcuprate to the silicon-containing *E*-substrate **10** based on Oppolzer's sultam derived from (+)-camphor. Unfortunately, the major product **11** was the more soluble diastereoisomer, and recrystallisation was not an efficient method for removing even the 1% of diastereoisomer **12**. We resorted therefore to a simple device that was guaranteed to work—we removed the chiral auxiliary and *replaced it with its enantiomer* derived from (−)-camphor, which was enantiomerically pure as judged by Oppolzer's test.[28] The major product **13** was now the less soluble diastereoisomer, and three recrystallisations served to remove all of the minor component **14**. This elaborate procedure would be unnecessary in synthesis, but it served us well here, because diastereoisomer purity was our primary concern, and not the overall yield. We could not detect, by careful GC analysis, any of the diastereoisomer **14**. A conservative estimate of the amount of diastereoisomer present was <0.05%, using expanded GC traces, and basing our estimate on comparisons of peak areas with those from various (and unknown but surely harmless) impurities present to the easily measurable extent of 0.6–2%.



Scheme 1 *Reagents and conditions:* i, Me_2CuLi, $EtAlCl_2$, Et_2O, −78 °C, 2 h; ii, LiOH, H_2O_2; iii, $(COCl)_2$; iv, NaH, Oppolzer's (–)-sultam.

We removed the chiral auxiliary with bromomagnesium benzyloxide (Scheme 2), and used the benzyl ester in our allylsilane synthesis, **13** ⟶ **15** ⟶ *E*-**16** or *Z*-**16**, based on the diastereoselective aldol reactions of β-silyl enolates, and stereospecific decarboxylative eliminations.[17] Since the *E*-allylsilane *E*-**16** and its *Z* isomer *Z*-**16** will give opposite enantiomers on electrophilic substitution, it was necessary to be as thorough in removing each from the other as we had been in setting up the silicon-bearing stereogenic centre in the first place. We achieved this using repeated column chromatography on silica gel heavily impregnated with silver nitrate. After this procedure, the allylsilanes *E*-**16** and *Z*-**16** were both geometrically pure, with <0.05% of the other present in each, as determined by the same careful GC analysis.

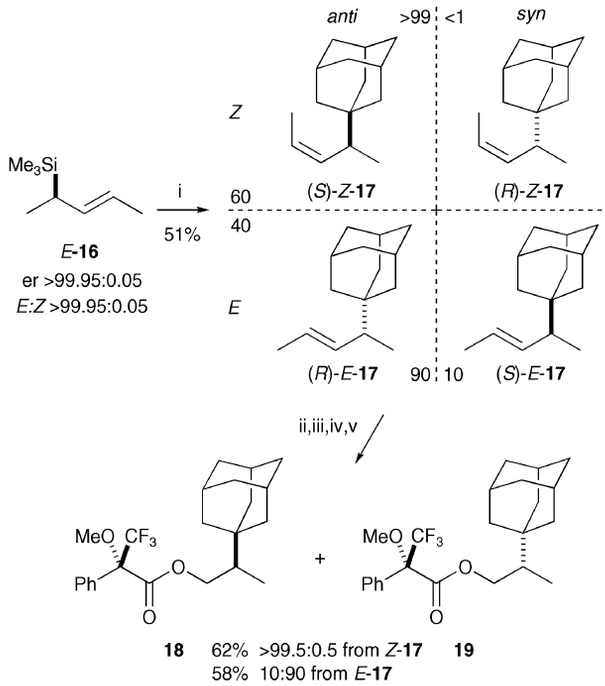


Scheme 2 *Reagents and conditions:* i, BnOMgBr, THF, rt, 20 h; ii, LDA; iii, MeCHO; iv, H_2, Pd/C; v, $(MeO)_2CHNMe_2$, $CHCl_3$, reflux, 2 h; vi, $PhSO_2Cl$, Py; vii collidine, reflux, 5 h.

Electrophilic substitution reactions of the allylsilanes 16

We carried out the reaction *E*-**16** ⟶ **17** twice, using adamantyl chloride as a representative simple electrophile[29] and a catalytic amount of titanium tetrachloride at −78 °C, with the same result each time (Scheme 3). We separated the *Z* and *E* products **17**, which were present in a ratio of 60 : 40, using the same silver nitrate-impregnated column, obtaining each free of the other (<0.05%), as determined yet again by careful GC analysis. We measured the enantiomeric purity of both alkenes by ozonolysis, followed by reduction with sodium borohydride, and derivatisation with Mosher's acid.[30] We were unable to use GC analysis at this stage, but the ^{19}F-NMR and ^{1}H-NMR spectra allowed us to measure the diastereoisomeric ratio of the final products **18** and **19** to within 0.5%. We found that the major product *Z*-**17** was enantiomerically pure (>99.5 : 0.5%). We assume that the reaction is stereospecifically *anti*, not *syn*, there being little doubt at this stage about the stereochemical sense of this type of reaction. This result helpfully confirmed that the sample of Mosher's acid was enantiomerically pure, and that there was no loss of configurational purity during the synthesis and degradation, including, most worryingly, the possibility of some racemisation of the aldehyde and during the chromatographic separations of the alkenes, where silver-coordination might, but was not expected to, constitute a danger. Clearly, for this product, the degree of stereospecificity was very high, at least 99%.

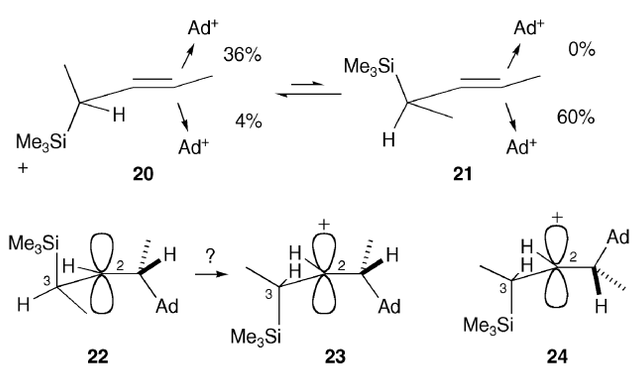
However, the minor product *E*-**17** was present as a 90 : 10 mixture of enantiomers. For this product, the degree of stereospecificity was still high, but it was also measurably incomplete, in agreement with our earlier observations described above, and



Scheme 3 *Reagents and conditions:* i, AdCl, $TiCl_4$ (0.1 eq.), CH_2Cl_2, −78 °C, 30 min; ii, separate *E* and *Z*; iii, O_3, CH_2Cl_2, MeOH −78 °C; 2 min; iv, $NaBH_4$, 0 °C, 1 h; v, (–)-Mosher's acid, DCC, DMAP, CH_2Cl_2, rt, 3 h.

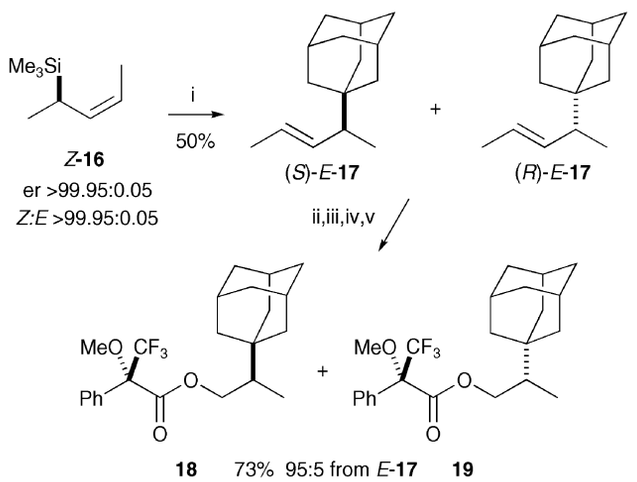
those of Kitching, that, when other stereochemical constraints are present, the extent to which the S_E2' reactions of allylsilanes are *anti* can be eroded.

We offer two simplified explanations for why the *Z* product should be formed with higher enantiomeric purity. Attack on the allylsilane *E*-**16** in a conformation close to **21** may take place on the lower surface more selectively than attack takes place on the upper surface of the alternative conformation **20**, because the lower surface of **21** is occupied by a hydrogen atom, whereas the upper surface of **20** is occupied by a methyl group. This argument assumes that *all* of the *E* product is formed by attack taking place in conformation **20**, and that *all* of the *Z* product is formed by attack taking place in conformation **21**; in other words, there is no rotation about the C2–C3 bond in the intermediate cations before the silyl group is plucked off by a nucleophile, presumably chloride ion. Alternatively, the intermediate cation **22**, produced by attack on the lower surface of the conformation **21**, may change its conformation, by rotation about the C2–C3 bond **22** ⟶ **23** before the silyl group is lost, to a greater extent than the intermediate **24**, produced by attack on the upper surface of conformation **20**, changes its conformation, because the lowering of energy is greater in the former case.



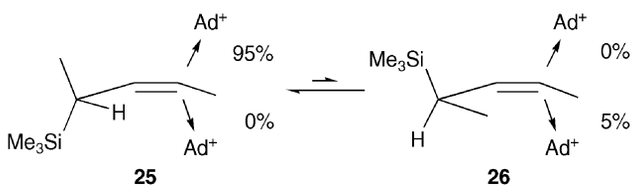
We carried out one rather inconclusive experiment to try to find out which of these explanations is the more plausible. We repeated the S_E2' reaction three times using the *Z*-allylsilane

Z-**16** in place of the *E*-allylsilane *E*-**16** (Scheme 4). In each of these reactions, we obtained largely the *E*-product. The *Z* product was just detectable as 0.2% of the mixture, too little to measure its enantiomeric purity. The major product proved on conversion to the Mosher's esters **18** and **19** to be 97 : 3, 95 : 5 and 93 : 7 mixtures of enantiomers in the three runs, averaging as a 95 : 5 mixture.



Scheme 4 *Reagents and conditions:* i, AdCl, $TiCl_4$ (0.1 eq.), CH_2Cl_2, −78 °C, 30 min; ii, separate *E* and *Z*; iii, O_3, CH_2Cl_2, MeOH −78 °C; 2 min; iv, $NaBH_4$, 0 °C, 1 h; v, (–)-Mosher's acid, DCC, DMAP, CH_2Cl_2, rt, 3 h.

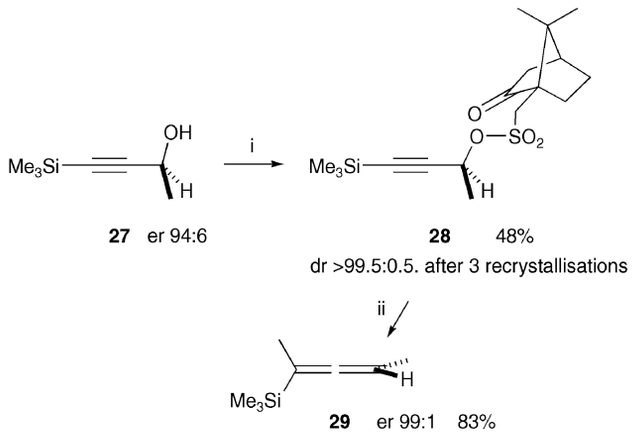
This result might mean that 95% of the electrophilic attack took place in conformation **25** and 5% in the high-energy conformation **26**, with 100% selectivity for attack *anti* to the silyl group in both cases. If the intermediate cation derived from the minor conformer, not implausibly, changed its conformation completely by rotation about the C2—C3 bond before the loss of the silyl group, it would give the 5% of the product (*R*)-*E*-**17**. It equally might mean that electrophilic attack took place only in conformation **25**, with 95% of attack from above and 5% from below. Because the 95 : 5 ratio in these experiments and the 90 : 10 ratio in the experiments on the *E*-isomer are so similar, we are unable to distinguish between these explanations, and must rest at this stage on the possibility that a combination of the two is more than likely.



Synthesis of the allenylsilane 29 of high enantiomeric purity

For the synthesis of the enantiomerically enriched allenylsilane **29**, we introduced the chirality by reduction of 4-trimethylsilylbut-3-yn-2-one with Brown's[31] and Midland's[32] "alpine" borane, giving the propargyl alcohol **27** as a 94 : 6 ratio of enantiomers (Scheme 5). More recently,[33] we have been able to make the same compound with higher enantiomeric purity using Noyori's catalytic asymmetric hydrogenation.[34] To raise the level of enantiomeric purity, we recrystallised the camphorsulfonate **28** until it was, as well as we could measure, a single diastereoisomer (>99.5 : 0.5), having first determined that the camphorsulfonate, derived from (−)-camphor, was higher melting than the diastereoisomeric camphorsulfonate derived from (+)-camphor.

The conversion of the camphorsulfonate into the allenylsilane was based on our earlier synthesis of the corresponding racemic allenylsilane.[35] We improved the earlier procedure by



Scheme 5 *Reagents and conditions:* i, (–)-camphorsulfonyl chloride, DMAP, Et_3N, CH_2Cl_2, 0 °C, 1 h; ii, MeMgCl, LiBr, CuBr, THF, −78 °C, 40 min, rt, 10 min.

treating it with the methyl Grignard reagent and copper(I) bromide in place of lithium dimethylcuprate. The latter reagent is known to racemise allenes,[36] and did indeed give us allene with considerable, and variable, loss of enantiomeric purity. The enantiomeric purity of the allene **29** was measured for us by Professor König using gas chromatography with a chiral column,[37] which gave full base-line resolution. We submitted three samples from three runs, which proved to have ratios of enantiomers of 98.7 : 1.3, 99 : 1, and 99.25 : 0.75. There must have been some minor losses of stereospecificity in the last step **28** ⟶ **29**, since we would certainly have detected the presence of 1% of the diastereoisomer of the camphorsulfonate **28**.

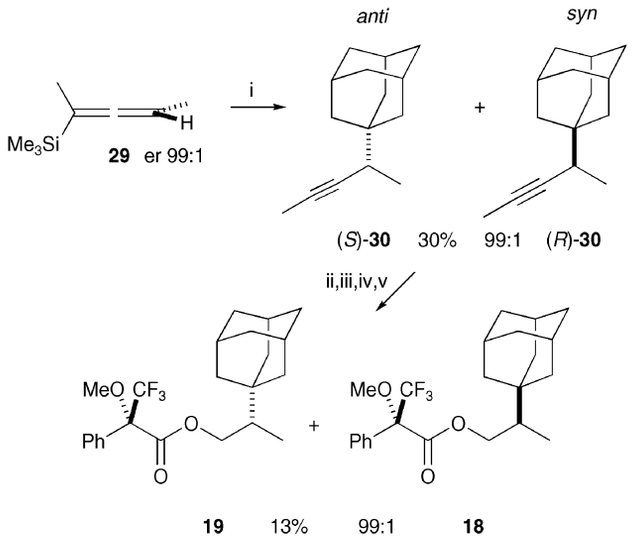
Because there was no intermediate in this synthesis in which the configuration could be securely preserved, we were unable to prepare the allenylsilane **29** with quite such a high level of enantiomeric purity as we had for the allylsilane **16**. We have, nevertheless, a synthesis of an allenylsilane of high enantiomeric purity, which we needed for our work on the synthesis of ebelactone A,[33,38] as well as for the work reported in this paper.

Electrophilic substitution reactions of the allenylsilane 29

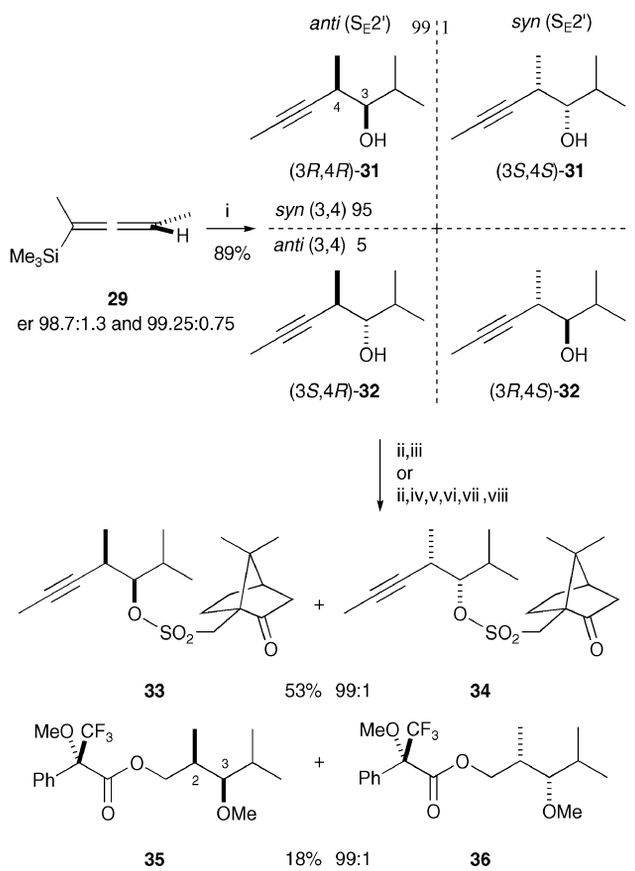
We carried out a reaction with adamantyl chloride and titanium tetrachloride, and obtained the propargyladamantanes **30** in rather low yield (Scheme 6). We measured the proportion of the enantiomers by semi-hydrogenation of the acetylenic bonds to give the mixture of *Z*-alkenes, and measured the ratio by the method described above, using the ^{19}F and ^{1}H NMR spectra of the Mosher's esters **19** and **18**. We estimate from our NMR measurements, which agree with each other, that the amount of the minor diastereoisomer present is 1%, and certainly less than 2%. Since the starting material was a mixture of enantiomers in a ratio of 99 : 1, the reaction must have been close to 100% stereospecific.

We also carried out reactions between the allenylsilane **29** and isobutyraldehyde in the presence of titanium tetrachloride, and obtained a good yield of the homopropargyl alcohols **31** and **32** in three runs (Scheme 7). This reaction, which sometimes gave us an unstable by-product in up to 20% yield,[39] is a model for a key step in our synthesis of ebelactone A, for which we want the enantiomer modelled by (3*R*,4*R*)-**31**. The diastereoisomers, *syn* and *anti* with respect to the relative configuration between C-3 and C-4, were present in a ratio **31** : **32** of 95 : 5, rather higher than that (80 : 20) for the known reaction of the corresponding allenylsilane lacking a methyl group on C-1 with cyclohexanecarboxaldehyde.[40]

As a result, there was not enough of the *anti* alcohols **32** with which to measure accurately the ratio of enantiomers, but the *syn* pair **31**, separated from the *anti* isomers by chromatography, gave the camphorsulfonates **33** and **34** (Scheme 7). The



Scheme 6 *Reagents and conditions:* i, AdCl, $TiCl_4$ (0.1 eq.), CH_2Cl_2, −78 °C, 30 min; ii, H_2, Lindlar; iii, O_3; iv, $NaBH_4$; v, (–)-Mosher's acid, DCC, DMAP, CH_2Cl_2, rt, 3 h.



Scheme 7 *Reagents and conditions:* i, Me_2CHCHO, $TiCl_4$, CH_2Cl_2, −78 °C, 1.5 h; ii, separate **31** from **32**; iii, (+)-camphorsulfonyl chloride, DMAP, Et_3N, CH_2Cl_2, reflux, 18 h; iv, H_2, Lindlar; v, NaH, DMSO, Me_2SO_4; vi, O_3; vii, $NaBH_4$; viii, (–)-Mosher's acid, DCC, DMAP.

first and second runs used the allenylsilane with a ratio of enantiomers of 98.7 : 1.3. The products **33** and **34** were present in ratios of 99.1 : 0.9 and 98.8 : 1.2, as measured by ^1H NMR spectroscopy. The third run used the allenylsilane with a ratio of enantiomers of 99.25 : 0.75, and the products were present in a ratio of 99.3 : 0.7, averaging to a ratio of 99 : 1, essentially the same for all three runs. As in the reaction with adamantyl chloride, the products and the starting material had the same degree of enantiomeric purity, indicating that the transfer of chirality had been close to 100%.

We converted the same mixture of the *syn* alcohols **31** into the Mosher's esters **35** and **36**, which were also present in a ratio of 99 : 1 (Scheme 7). All of the possible stereoisomers of these Mosher's esters were already known to us, with assigned relative and absolute configurations,[41] confirming that the S_E2' reaction of the allenylsilane is indeed stereospecifically *anti*, as well as being to a very high degree. This work confirmed that the major product **35** was the isomer with the *syn* relationship between C-2 and C-3, and hence that the reaction with the allenylsilane had given the homopropargylic alcohol (3*R*,4*R*)-**31** with the *syn* relationship between C-3 and C-4.

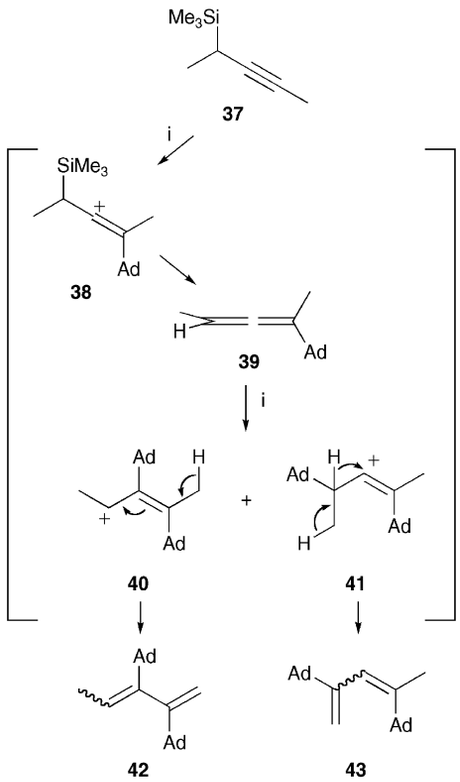
A search for a stereochemically defined electrophilic substitution reaction with a chiral propargylsilane

This left propargylsilanes to be investigated, an especially interesting case, because Hayashi and Kumada had already found that, although the one reaction they looked at **8** ⟶ **9** was stereospecifically *anti*, the degree of stereospecificity appeared to be low.[15] They found that the propargylsilane **8**, prepared as a mixture of enantiomers in a ratio of 59 : 41 (18% ee), reacted with the *tert*-butyl cation to give the allene **9** in 23% yield as a mixture of enantiomers in a ratio estimated on the basis of semi-empirical rules[42] to be 51.5 : 48.5 (3% ee). This indicated that the reaction had been stereospecific in Zimmerman's sense,[43] but the ratio of *anti* : *syn* attack was only about 58 : 42. Although there was no reason to doubt their conclusions, the proof of the absolute configuration of the product, and, less reliably, the measurements of the ratios of enantiomers were all based upon rules, and estimates, rather than upon direct physical measurements.

Although many S_E2' reactions of propargylsilanes have been reported, a high proportion of them have no other substituent on C-1 than the silyl group. These include the reactions of propargyltrimethylsilane itself,[44] and both intermolecular[45] and intramolecular reactions[46] of propargylsilanes having a substituent at the acetylenic terminus C-3, all of which produce a terminal allene. In several cases, even with these simple propargylsilanes, alternative reactions took place, including nucleophilic capture of the intermediate cation, with[47,48] or without[49] migration of the silyl group and without the loss of the silyl group, and ene reactions in which the silyl group is also retained.[50] In other cases, the allene is formed, but subsequent reactions took place, including nucleophilic attack[51] and rearrangements.[52] Only a few reactions have been reported in which the α carbon had a second substituent in addition to the silyl group, an essential feature if we are to produce a chiral allene. Furthermore, relatively few of the latter actually gave allenes,[53,54] with subsequent reaction of one kind or another taking place, apparently more easily as a consequence of the presence of the extra substituent.[55,56]

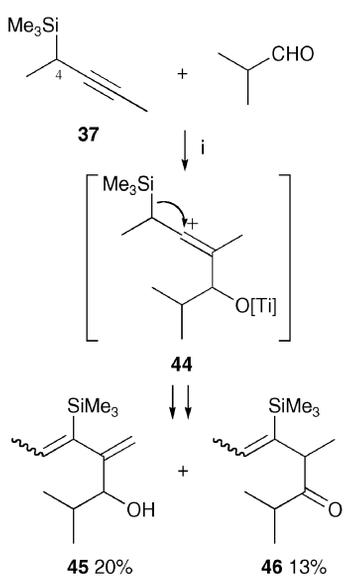
Thus we needed to find a clean reaction of this type, and ideally one using the propargylsilane **37**, in order that our results could be compared with those from the corresponding allyl- and allenylsilanes **16** and **29**. We were not successful. The chiral (but racemic) propargylsilane **37** did not give an allene with adamantyl bromide and titanium tetrachloride (Scheme 8). The products were conjugated dienes, $C_{25}H_{36}$, which have *two* adamantyl units for each C_5 unit derived from the propargylsilane. We suggest the structures **42** and **43** for these dienes. They were probably the result of electrophilic attack by a second adamantyl cation on the first-formed allene **38**, and we were unable to stop the reaction at this stage. This was perhaps no surprise, since it has been reported that even the usually well-behaved propargyltrimethylsilane does not give allenyladamantane under these conditions,[29] but Hayashi's result **8** ⟶ **9** had encouraged us to try this reaction.

In any case, we preferred a reaction in which the product was not only a chiral allene, but one in which the product had a substituent to which a chiral auxiliary could be attached, in



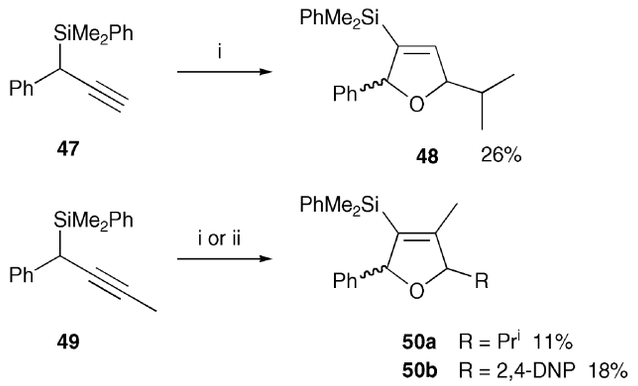
Scheme 8 *Reagents and conditions:* i, adamant-1-yl bromide, $TiCl_4$, CH_2Cl_2, −78 °C, 1 h.

order to measure the sense of electrophilic attack and the degree of enantiomeric purity without having to rely upon the rotation of polarised light. With this requirement, adamantyl bromide was of no use, because derivatisation of any allene products, even if they had been formed, would lose the chiral information. Schemes 9–11 illustrate some of the unhelpful reactions that we observed between various propargylsilanes and aldehydes or acetals.

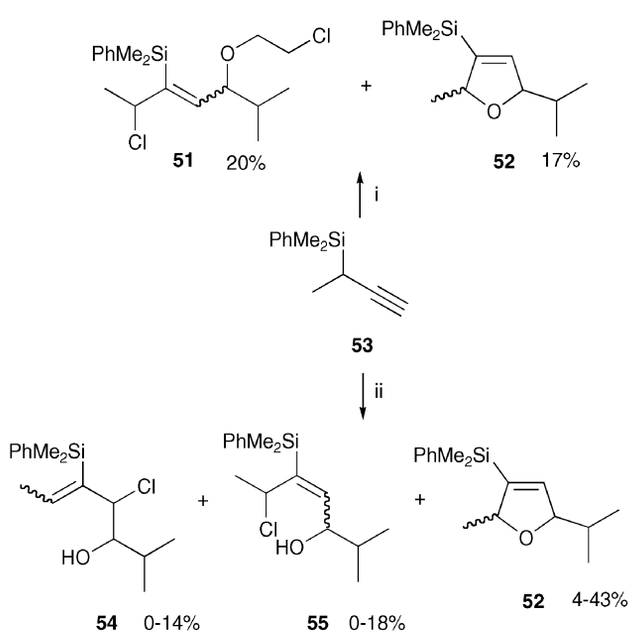


Scheme 9 *Reagents and conditions:* i, $TiCl_4$, CH_2Cl_2, −78 °C, 1 h.

Isobutyraldehyde gave the dienes **45** (*E* : *Z* 66 : 34 or 34 : 66) and the ketones **46** (*E* : *Z* 50 : 50) (Scheme 9), both of which are the result of a migration of the silyl group in the intermediate cation **44**, followed by proton loss, instead of the loss of the silyl group, and the presence of the methyl group on C-4 in the propargylsilane **37** only made the migration easier. Silyl migration was also a problem with the propargylsilanes **47** and



Scheme 10 *Reagents and conditions:* i, Me_2CHCHO, $TiCl_4$, CH_2Cl_2; ii, 2,4-$(O_2N)_2C_6H_3CHO$, $TiCl_4$, CH_2Cl_2.

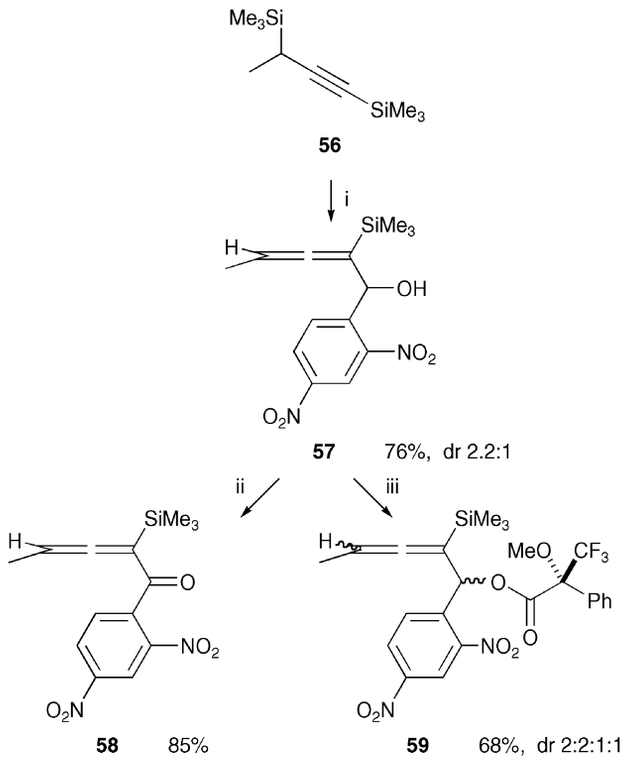


Scheme 11 *Reagents and conditions:* i, $Me_2CHCH(OCH_2CH_2Cl)_2$, $BF_3{\cdot}OEt_2$, CH_2Cl_2, −78 °C, 1 h; ii, Me_2CHCHO, various Lewis acids, CH_2Cl_2.

49, which gave the dihydrofurans **48**, **50a** and **50b** (Scheme 10). The phenyl groups no doubt were even better at stabilising the cation produced by silyl migration, but again Hayashi's result **8** ⟶ **9** had encouraged us to try this reaction. The formation of dihydrofurans as a result of the rearranged cation being trapped by the oxygen atom is well precedented.[47] We saw other unfruitful outcomes with the propargylsilane **53**, including nucleophilic capture in the formation of the allylic chlorides **51**, **54** and **55**, as well as the formation of the dihydrofuran **52** (Scheme 11).

The alkyl or aryl groups on C-1 in the propargylsilanes **37**, **47**, **49** and **52**, which were necessary adjuncts in order to make the product allenes chiral, had fatally encouraged unwelcome reactions. We reasoned that a silyl group at the acetylenic terminus would electronically stabilise, and sterically hinder, the intermediate cation, perhaps enough to prevent silyl migration, and allow the formation of an allene product. There was some evidence in the literature that this would work.[54] Happily, the racemic propargylsilane **56** with 2,4-dinitrobenzaldehyde in the presence of titanium tetrachloride gave a pair of diastereoisomeric allenyl carbinols **57** in good yield and in a ratio of 2.2 : 1 (Scheme 12). These could be oxidised to a single ketone **58**. We now had a reaction that we could use.

In order to set up an analytical system, we also prepared Mosher's esters of the carbinols. There were four products **59**, with well resolved singlets in the ^{19}F-NMR spectrum, which

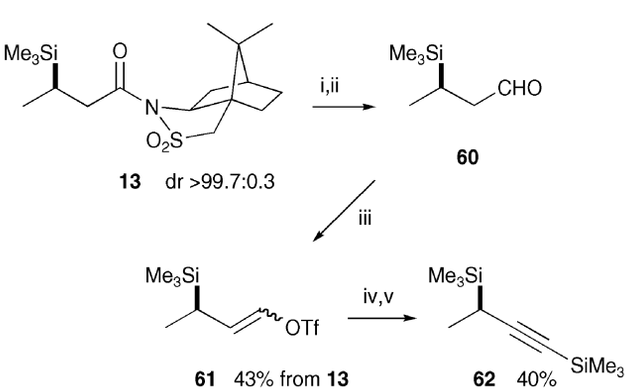


Scheme 12 *Reagents and conditions:* i, 2,4-$(O_2N)_2C_6H_3CHO$, $TiCl_4$, CH_2Cl_2, −78 °C, 15 min; ii, Dess–Martin periodinane, CH_2Cl_2, rt, 20 min; iii, (+)-Mosher's acid chloride, Et_3N, DMAP, CH_2Cl_2, rt, 1 h.

appeared at δ −70.81, −70.88, −71.03 and −70.96, to which we gave labels A, B, C and D, respectively. They were present in ratios of 2 : 2 : 1 : 1, which established that A and B were derived from one diastereoisomer, and C and D from the other.

Synthesis of the propargylsilane 62 of high enantiomeric purity

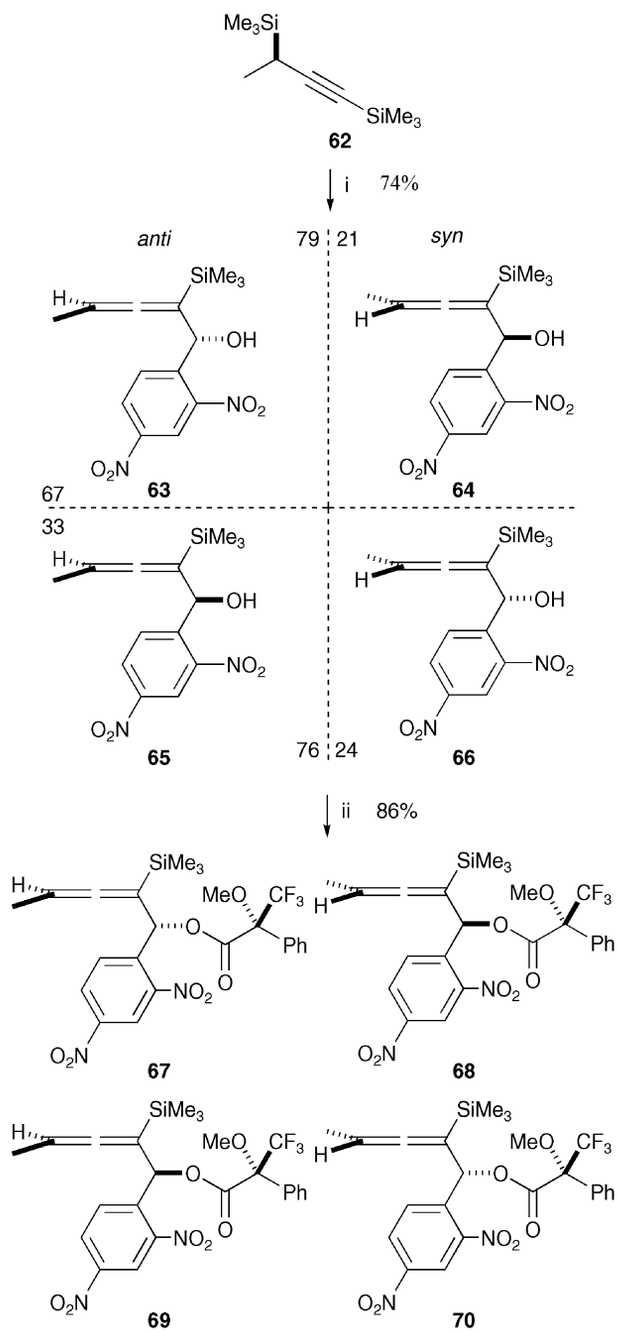
In anticipation of the work described above, we had already developed a general synthesis of chiral propargylsilanes.[57] Using this route, we prepared the enantiomerically enriched propargylsilane **62** (Scheme 13), starting with the sultam **13**, obtained this time as a mixture of diastereoisomers in a ratio better than 99.7 : 0.3. We removed the chiral auxiliary using ethoxide ion, reduced the ethyl ester to the aldehyde **60**, formed the enol triflate **61**, and carried out the elimination and silylation in one pot to give the propargylsilane **62**, which was a mixture of enantiomers presumably in a ratio of at least 99.7 : 0.3.



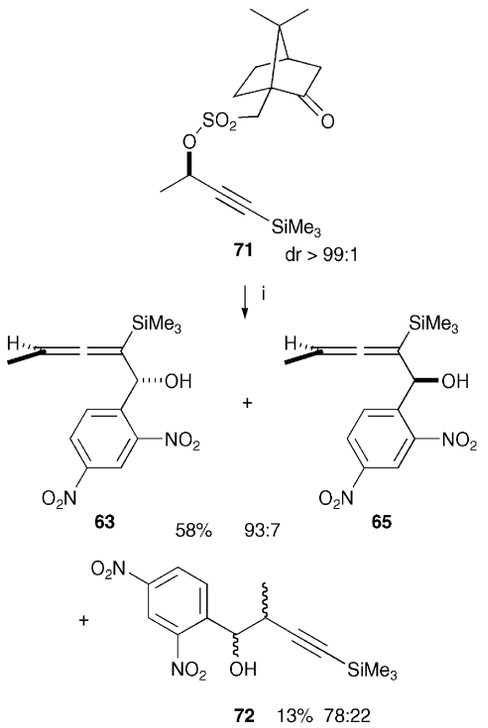
Scheme 13 *Reagents and conditions:* i, LiOEt; ii, $^{i}Bu_2AlH$; iii, Tf_2O, 2,6-$^{t}Bu_2Py$; iv LDA; v, Me_3SiCl.

Electrophilic substitution reactions using the enantiomerically enriched propargylsilane 62

We repeated the reaction with 2,4-dinitrobenzaldehyde using the enantiomerically enriched propargylsilane **62**, and obtained the mixture of four allenyl carbinols **63**–**66**, from which we prepared the Mosher's esters **67**–**70** (Scheme 14). The four isomers A, B, C and D were present in ratios of 6.3 : 1.7 : 1 : 3, respectively. We assigned relative stereochemistry at the carbinol carbon using the ^{1}H-NMR method of Kakisawa and his co-workers,[58] in which the Mosher's derivatives with the *R*- and the *S*-acid are compared. Finally, we assigned the absolute stereochemistry by synthesising authentic samples of the allenylcarbinols **63** and **65** by the method of Marshall and Adams.[25] The propargyl camphorsulfonate **71** (the enantiomer of the camphorsulfonate **28**), prepared from (+)-camphorsulfonyl chloride and the *R*-alcohol, and recrystallised to give a >99 : 1 ratio of diastereoisomers, reacted with 2,4-dinitrobenzaldehyde and trichlorosilane to give a mixture of the alcohols **63** and **65** (58%), together with a little of the corresponding homopropargylic alcohols **72** (13%) (Scheme 15). The relative and absolute configurations assigned to the major and minor



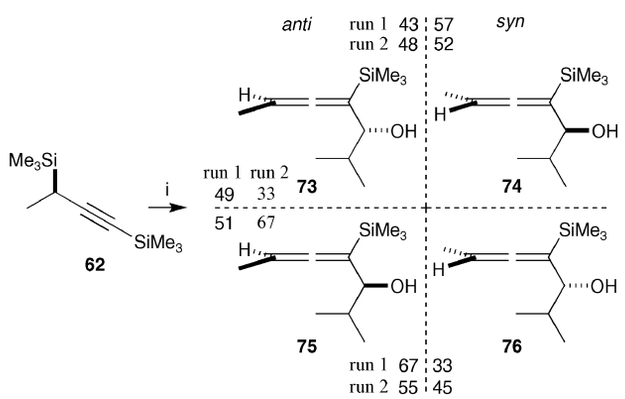
Scheme 14 *Reagents and conditions:* i, 2,4-$(O_2N)_2C_6H_3CHO$, $TiCl_4$, CH_2Cl_2, −78 °C, 15 min; ii, (+)-Mosher's acid chloride, Et_3N, DMAP, CH_2Cl_2, rt, 1 h.



Scheme 15 *Reagents and conditions:* i, 2,4-$(O_2N)_2C_6H_3CHO$, Cl_3SiH, CuCl, $^iPr_2NEt$, DMF, Et_3N.

allenes **63** and **65** are based on the stereochemistry Marshall has proved for closely similar reactions, and like his they fit the Lowe–Brewster rules. The Mosher's derivatives of these allenyl carbinols corresponded to the diastereoisomers A and D, and they were present in a ratio of 93 : 7, similar to the diastereoisomer ratios found by Marshall for other aldehydes. We were now able to assign structures to the isomers A, B, C and D as **67**, **68**, **70** and **69**, respectively, from which we calculated the ratios of diastereoisomers (67 : 33) and the ratios of the *anti* : *syn* reaction (79 : 21 and 76 : 24) shown in Scheme 14. Our proof of the relative and absolute stereochemistry is not quite as complete as we would like (none of our products crystallised), but, coupled with Marshall's extensive work with several interrelated conversions, it fits an internally consistent pattern that is compelling. Evidently, the S_E2' reaction **62** ⟶ **63**–**66** takes place predominantly in the *anti* sense, but, in contrast to the reactions of allyl- and allenylsilanes, the *anti* : *syn* ratio is only about 3 : 1.

In addition, we carried out the same series of reactions with isobutyraldehyde (Scheme 16). We assigned structures to the products **73**–**76** in the same way as for the products with 2,4-dinitrobenzaldehyde. The Mosher's derivatives from the *R*-acid showed four singlets in the ^{19}F-NMR spectrum at δ −71.42, −71.68, −71.86 and −71.75. From the racemic propargylsilane, the product mixture showed the two signals at δ −71.42 and −71.68 and the two signals at δ −71.86 and −71.75 of equal intensity within the pair, with the first pair twice as intense as the second. Comparison of the ^{1}H-NMR spectra of the derivatives of the alcohol **73** with Mosher's *R*-acid and *S*-acid identified that this diastereoisomer was *R* at the carbinol carbon. Finally, the synthesis using Marshall's method gave only the pair **73** and **75** in low yield (9%), but the Mosher's derivatives showed that they were present in a ratio of 98 : 2. The results of two runs were not completely consistent, the major pair, **75** and **76**, indicated that the reaction had been selectively *anti* (*anti* : *syn* 67 : 33 and 55 : 45), while the minor pair, **73** and **74**, indicated that it had been selectively *syn* (*anti* : *syn* 43 : 57 and 48 : 52). Combined, and averaged over the two runs, this S_E2' reaction appeared to be *anti* : *syn* in a ratio of 53 : 47, which, within experimental error, is as close to 50 : 50 as makes no matter.



Scheme 16 *Reagents and conditions:* i, Me_2CHCHO, $TiCl_4$, CH_2Cl_2, −78 °C, 30 min.

We have too little information to explain why isobutyraldehyde should be even less selective than 2,4-dinitrobenzaldehyde. The reactive species will be the aldehyde coordinated to the Lewis acid. 2,4-Dinitrobenzaldehyde may be more reactive than isobutyraldehyde, but its coordinated form will probably be present in lower concentration. As a result it is not possible to say whether its greater selectivity is a violation of the reactivity–selectivity principle. Since we do not know whether the erosion of stereospecificity is caused by rotation in the intermediate cation or by the initial attack not being *anti* to the silyl group, we can only speculate. One possibility is that the intermediate cation in the isobutyraldehyde reaction might be a little more stable than that in the 2,4-dinitrobenzaldehyde reaction, and might therefore have lived long enough to lose more of its stereochemical information. Our *anti* : *syn* ratios are close to those of Hayashi's and Kumada's, confirming the erosion of stereospecificity that they also saw. We are inclined to agree with their tentative explanation: that the intermediate cation is able to undergo rotation about the σ-bond before the loss of the silyl group. In our series, with a second silyl group stabilising the intermediate cation, we may have unwittingly exacerbated this problem. There is also the possibility that the direction of attack on a triple bond, with nearly cylindrical symmetry in the π-orbitals, is less constrained than it is on a double bond, where attack is only profitable if it is more or less directly above or below the plane of the π-bond.

Conclusions

We have developed syntheses capable of making allylsilanes, allenylsilanes and propargylsilanes in a state of high enantiomeric purity. Using these compounds, we have confirmed, with accurate measurements, that the stereochemistry of the S_E2' reactions of the allylsilanes **16** and the allenylsilane **29** are highly selective in the *anti* sense, especially the latter, which is uncomplicated by the formation of mixtures of *Z*- and *E*-alkenes. In contrast, the S_E2' reaction of the propargylsilane **62** with 2,4-dinitrobenzaldehyde is stereospecifically *anti* to a lower degree (75 : 25). Furthermore, the selectivity in the latter reaction depends upon the electrophile, being negligible with isobutyraldehyde.

Experimental

General

Melting points were taken on a Gallenkamp melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 297 infra-red grating and a Perkin-Elmer FT-IR 1600 spectrophotometer and wavenumbers were measured relative to polystyrene (1603 cm^{-1}). ^{1}H-NMR spectra were recorded on a Varian EM 390 and Bruker WM 250, AM 400, DPX250, DPX 400, DRX 400 and DRX 500 spectrometers

with chemical shifts measured relative to TMS (δ 0.0 ppm) or $CHCl_3$ (δ 7.25 ppm) as an internal standard. The coupling constant J is expressed in Hertz. ^{13}C-NMR spectra were also recorded on the Bruker WM 250, AM 400, DPX 250, DPX 400, DRX 400 and DRX 500 spectrometers. ^{19}F-NMR spectra were recorded on the Bruker WM 250 and DPX 400 spectrometers with chemical shifts measured relative to CCl_3F. In ^{13}C attached-proton test (APT) spectra, + denotes signals in the same direction as the NMR solvent. Mass spectra were recorded on AE1 MS 9 and MS 30 and on Kratos Concept (EI) and Micromass Q-TOF (ESI) spectrometers. Column chromatography was carried out using Merck Kieselgel 60 (230–400 mesh ASTM). Silver nitrate-impregnated silica was prepared by suspending Merck Kieselgel 60 in a solution of silver nitrate in acetonitrile and evaporating off the solvent.[59] Thin layer chromatography (TLC) was performed on plates coated to a thickness of 0.5 or 1.0 mm with Kieselgel 60 PF_{254}. Gas-liquid chromatography (GLC) was carried out on a Carlo Erba 4130 instrument, using a 24 m, BP5, 5% phenylmethylsiloxane capillary column (5 μm film thickness) and helium as the carrier gas (~0.3 m s^{-1}), with nitrogen "make-up" leading to a hydrogen/oxygen flame ionisation detector. The temperature programmes used accompany the data. Optical rotations were recorded on a Perkin-Elmer 241 digital polarimeter using a sodium lamp (589 nm) as the light source. Concentrations are given in units of 10^{-2} g cm^{-3}. The length of the optical rotation cell used was 10 cm. Tetrahydrofuran (THF) and diethyl ether (ether) were freshly distilled from lithium aluminium hydride under argon. All other solvents were distilled before use. Dichloromethane and toluene were freshly distilled from calcium hydride under argon. Light petroleum, unless otherwise stated, refers to the fraction boiling in the range 40–60 °C. Organolithium reagents were titrated using the method of Gilman.[60]

N-[(*E*)-3′-Trimethylsilylpropenoyl]-(7*S*)-2,10-camphorsultam 10

Using reaction conditions developed by Vandewalle and Oppolzer,[28] oxalyl chloride (4.5 cm^3) and (*E*)-3-trimethylsilylpropenoic acid[17] (7.4 g, 51 mmol) were kept in dry dichloromethane (24 cm^3) under argon at room temperature for 2 h. The solvent and excess of reagent were evaporated off under reduced pressure, and the residue dissolved in dry toluene (120 cm^3). Meanwhile sodium hydride (2.5 g of a 60% dispersion in oil) in dry hexane (20 cm^3) was stirred under argon at room temperature for 5 min. The hexane was then syringed out and a solution of (7*S*)(−)-camphorsultam[61] (9.2 g, 43 mmol, with its enantiomeric purity, which cannot be relied upon absolutely,[62] confirmed by the method of Vandewalle and Oppolzer[28]) in dry toluene (230 cm^3) was slowly added, and the mixture stirred for 1 h. The acid chloride was slowly added, and the resulting mixture stirred for a further 2 h. Water (20 cm^3) was added dropwise, the mixture diluted with more water, and extracted with toluene. The organic layer was dried ($MgSO_4$), and evaporated under reduced pressure to give the *sultam* **10** (12.2 g, 84%), mp 148–150 °C (from EtOH); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 1665 (C=O), 1595 (C=C), 1330 and 1130 (SO_2N) 1220 and 850 ($SiMe_3$) and 990 (*E* C=C); δ_H (250 MHz; $CDCl_3$) 7.36 (1 H, d, *J* 18.2, SiC*H*=CH), 6.91 (1 H, d, *J* 18.2, SiCH=C*H*), 3.91 (1 H, t, *J* 6.3, CHN), 3.48 (1 H, d, *J* 13.8, $CH_AH_BSO_2$), 3.44 (1 H, d, *J* 13.8, $CH_AH_BSO_2$), 2.09 (2 H, d, *J* 6.3, CH_2CHN), 1.9–1.8 (3 H, m, $CHCH_2CHN$ and CH_2CCHN), 1.45–1.2 (3 H, m, CH_2CH_2CCHN and CHSi), 1.16 and 0.96 (3 H each, s, Me) and 0.13 (9 H, s, $SiMe_3$); $[\alpha]_D$ −89 (*c.* 1.1 in $CHCl_3$) (Found: C, 56.3; H, 8.1; N, 3.9. $C_{16}H_{27}NO_3SiS$ requires C, 56.3; H, 8.0; N, 4.1%).

N-[(*E*)-(3′*R*)-3′-Trimethylsilylbutanoyl]-(7*S*)-2,10-camphorsultam 11

Using reaction conditions developed by Oppolzer,[27] methyllithium (1.6 mol dm^{-3} solution in Et_2O, 300 cm^3, 4.8 mmol) was slowly added to a stirred mixture of copper(I) iodide (44.1 g, 230 mmol) and tributylphosphine (73 cm^3) in ether (430 cm^3) under argon at −20 °C until a clear solution was obtained. After 20 min the solution was cooled to −78 °C and ethylaluminium dichloride (230 cm^3 of a 1 mol dm^{-3} solution in hexane, 230 mmol) was slowly added. After 20 min a solution of the sultam (8.0 g, 23 mmol) in dry ether (330 cm^3) was slowly added, and the mixture stirred for 2 h. Saturated ammonium chloride solution (250 cm^3) was added, the layers were separated, and the aqueous phase extracted with ether (3 × 150 cm^3). The combined organic layers were washed with ammonia solution (pH 8), dried ($MgSO_4$) and evaporated under reduced pressure to give a mixture of the *sultams* **11** and **12** (7.8 g, 93%) in a ratio of 99 : 1 (GLC, ^{1}H-NMR); [GLC retention times: 100 °C–20 °C/min–200 °C)/min 32.6 (**12**) and 33.8 (**11**)]; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 1695 (C=O), 1335 and 1140 (SO_2N) 1225 and 835 ($SiMe_3$); δ_H (250 MHz; $CDCl_3$) 3.85 (1 H, t, *J* 6.3, CHN), 3.45 (1 H, d, *J* 13.8, $CH_AH_BSO_2$), 3.42 (1 H, d, *J* 13.8, $CH_AH_BSO_2$), 2.60 (1 H, dd, *J* 13.6 and 2.6, CH_AH_BCO), 2.55 (1 H, dd, *J* 13.6 and 6.8, CH_AH_BCO), 2.08 (2 H, d, *J* 6.3, CH_2CHN), 1.9–1.8 (3 H, m, $CHCH_2CHN$ and CH_2CCHN), 1.45–1.2 (3 H, m, CH_2CH_2CCHN and CHSi), 1.14 and 0.94 (3 H each, s, CMe_2), 0.92 (3 H, d, *J* 7.7, *Me*CHSi) and −0.04 (9 H, s, Me_3Si); $\delta_C(CDCl_3)$ 172.7, 65.4, 53.0, 48.3, 47.7, 44.6, 38.6, 37.4, 32.8, 28.4, 20.8, 19.9, 16.7, 14.2 and −3.5; *m*/*z* (EI) 342 (30%, M − Me), 293 (20, M − SO_2) and 278 (30, M − $MeSO_2$)(Found: M^+ − Me, 342.1542. $C_{17}H_{31}NO_3SiS$ requires *M* − Me, 342.1559).

(3*R*)-3-Trimethylsilylbutanoic acid

Using reaction conditions developed by Evans,[63] hydrogen peroxide (54 cm^3 of a 30% solution in water, 480 mmol) and lithium hydroxide (9.9 g of the monohydrate, 240 mmol) and the sultam **11** (21.1 g, 59 mmol) in THF (440 cm^3) and water (150 cm^3) were stirred at room temperature for 2 h. The mixture was cooled to 0 °C and sodium sulfite solution (150 cm^3, 1.5 mol dm^{-3}) was added. The THF was evaporated under reduced pressure and the pH of the aqueous residue was adjusted to 9–10 by the addition of saturated sodium hydrogencarbonate solution, extracted with dichloromethane (4 × 150 cm^3), acidified with hydrochloric acid solution (3 mol dm^{-3}) and extracted with ethyl acetate (3 × 300 cm^3). The dichloromethane and ethyl acetate extracts were separately washed with brine, dried ($MgSO_4$) and evaporated under reduced pressure to give, respectively, Oppolzer's sultam (10.8 g, 85%) as a solid, identical (TLC, ^{1}H-NMR) to the original compound, and the *acid* (7.0 g, 74%) as an oil; R_f(hexane–Et_2O) 0.3; $\nu_{max}(CHCl_3)/cm^{-1}$ 3500–2500 (COOH), 1705 (C=O) and 835 ($SiMe_3$); δ_H(250 MHz; $CDCl_3$) 11.0 (1 H, br s, COOH), 2.43 (1 H, dd, *J* 15.2 and 4.0, CH_AH_BCOOH), 2.08 (1 H, dd, *J* 15.2 and 10.9, CH_AH_BCOOH), 1.17 (1 H, m, CHSi), 0.98 (3 H, d, *J* 7.1, *Me*CHSi) and −0.02 (9 H, s, $SiMe_3$); *m*/*z* (EI) 160 (6%, M^+), 145 (60, M – Me) and 73 (100, $SiMe_3$) (Found: M^+, 160.0908. $C_7H_{16}O_2Si$ requires *M*, 160.0915).

N-[(*E*)-(3′*R*)-3′-Trimethylsilylbutanoyl]-(7*R*)-2,10-camphorsultam 13

This was prepared in the same way as the sultam **10** above from (3*R*)-3-trimethylsilylbutanoic acid (7.2 g, 45 mmol) and the (7*R*)(+)-sultam[61] (7.6 g, 35 mmol) to give a solid, which was recrystallised three times to give the pure *sultam* **13** (10.2 g, 63%), mp 132.5–133.5 °C (from hexane), with dr >99.95 : 0.05 (GLC); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 1685 (C=O), 1335 and 1135 (SO_2N) 1215 and 845 ($SiMe_3$); δ_H(250 MHz; $CDCl_3$) 3.87 (1 H, t, *J* 6.3, CHN), 3.45 (1 H, d, *J* 13.8, $CH_AH_BSO_2$), 3.42 (1 H, d, *J* 13.8, $CH_AH_BSO_2$), 2.81 (1 H, dd, *J* 15.7 and 4.3, CH_AH_BCO), 2.39 (1 H, dd, *J* 15.7 and 10.4, CH_AH_BCO), 2.07 (2 H, d, *J* 6.3, CH_2CHN), 1.9–1.8 (3 H, m, $CHCH_2CHN$ and CH_2CCHN), 1.45–1.2 (3 H, m, CH_2CH_2CCHN and CHSi), 1.13 and 0.95

(3 H each, s, CMe_2), 0.94 (3 H, d, *J* 7.7, *Me*CHSi) and −0.02 (9 H, s, Me_3Si); δ_C ($CDCl_3$) 172.5, 65.2, 53.0, 48.3, 47.7, 44.6, 38.6, 38.3, 32.8, 26.5, 20.8, 19.9, 16.3, 14.2 and −3.5; $[\alpha]_D$ +83 (*c.* 1.2 in $CHCl_3$) (Found: C, 57.1; H, 8.8; N, 3.8. $C_{17}H_{31}NO_3SiS$ requires C, 57.1; H, 8.7; N, 3.9%).

Benzyl (3*R*)-3-trimethylsilylbutanoate 15

Using reaction conditions developed by Evans,[64] methylmagnesium bromide (29 cm^3 of a 3.0 mol dm^{-3} solution in ether, 87 mmol) was slowly added to a stirred solution of benzyl alcohol (12 cm^3, 116 mmol) in dry THF (50 cm^3) under argon at 0 °C. After 10 min a solution of the sultam **13** (10.4 g, 29 mmol) in dry THF (100 ml) was added at 0 °C and the solution was stirred at room temperature for 20 h. Light petroleum (bp 40–60 °C) (20 cm^3) was added, followed by saturated ammonium chloride solution (20 cm^3). The layers were separated and the aqueous phase was extracted with light petroleum (bp 40–60 °C) (3 × 20 cm^3). The combined organic layers were dried ($MgSO_4$) and evaporated under reduced pressure. The residue was flash chromatographed (SiO_2, hexane–Et_2O, 9 : 1–1 : 1) to give Oppolzer's sultam (5.6 g, 89%), identical (TLC, ^{1}H-NMR) to the original compound, and the *ester* (7.0 g, 96%) as an oil, identical (TLC, ^{1}H-NMR) to the racemic ester;[17] $[\alpha]_D$ +9.2 (*c.* 1.2 in $CHCl_3$); R_f(hexane–Et_2O, 9 : 1) 0.5; (Found: C, 67.0; H, 8.8. $C_{14}H_{22}O_2Si$ requires C, 67.2; H, 8.9%).

Benzyl (2*S*,3*R*,1′*R*)-3-hydroxy-2-(1′-trimethylsilylethyl)-butanoate 15

This was prepared in the same way as the racemic ester[17] using the enantiomerically enriched ester (6.9 g, 28 mmol) to give the *ester* (6.4 g, 79%), identical (TLC, ^{1}H NMR) to the racemic material; R_f(hexane–Et_2O, 3 : 1) 0.14.

(2*S*,3*R*,1′*R*)-3-hydroxy-2-(1′-trimethylsilylethyl)butanoic acid

This was prepared in the same way as the racemic acid[17] using the ester **15** (6.0 g, 20 mmol) to give the *acid* (3.7 g, 89%) as prisms, mp 79–84 °C (from hexane), identical (TLC, ^{1}H NMR) to the racemic material.

(*E*)-(4*R*)-4-Trimethylsilylpent-2-ene (*E*)-16

This was prepared in the same way as the racemic allylsilane[17] using *N*,*N*-dimethylformamide dimethylacetal and the enantiomerically enriched acid (1.50 g, 7.3 mmol) to give a mixture of *E- and Z*-allylsilanes in a ratio of 94 : 6 (GLC). The mixture was separated by flash chromatography (SiO_2–$AgNO_3$, 4 : 1; pentane)[59] to give the pure *E-allylsilane* (0.61 g, 58%), identical (GLC, ^{1}H NMR) to the racemic material; R_f(SiO_2–$AgNO_3$, 4 : 1; hexane–Et_2O, 19 : 1) 0.5; $[\alpha]_D$ +29 (*c.* 1.2 in $CHCl_3$).

(2*S*,3*R*,1′*R*)-3-Methyl-2-(1′-trimethylsilylethyl)propan-3-olide

This was prepared in the same way as the as the racemic lactone[17] using benzenesulfonyl chloride and the enantiomerically enriched acid (1.44 g, 7.0 mmol) to give the *β-lactone* (0.62 g, 47%) as an oil, identical (TLC, ^{1}H NMR) to the racemic material, and, and like it, contaminated with 12% (^{1}H NMR) of another diastereoisomer.

(*Z*)-(4*R*)-4-Trimethylsilylpent-2-ene (*Z*)-16

This was prepared in the same way as the as the racemic allylsilane[17] using the enantiomerically enriched β-lactone (0.62 g, 3.3 mmol) to give a mixture of *Z*- and *E*-allylsilanes in a ratio of 85 : 15 (GLC). The mixture was separated by flash chromatography (SiO_2–$AgNO_3$, 4 : 1; pentane–Et_2O, 19 : 1)[59] to give the pure *Z-allylsilane* (0.25 g, 53%), identical (GLC, ^{1}H NMR) to the racemic material; $[\alpha]_D$ −79 (*c.* 1.5 in $CHCl_3$); R_f(SiO_2–$AgNO_3$, 4 : 1; hexane–Et_2O, 19 : 1) 0.35.

(*E*)-(4*R*)-4-Adamantylpent-2-ene (*E*)-17 and (*Z*)-(4*S*)-4-adamantylpent-2-ene (*Z*)-17

Using reaction conditions developed by Sasaki,[29] the allylsilane (*E*)-**16** (142 mg, 1.0 mmol) in dry dichloromethane (1 cm^3) was added to the yellow solution of titanium tetrachloride (0.070 cm^3 of a 1.0 mol dm^{-3} solution in CH_2Cl_2, 0.07 mmol) and 1-chloroadamantane (171 mg, 1.0 mmol) in dry dichloromethane (3 cm^3) under argon at −78 °C, and kept at −78 °C for 30 min. Sodium hydrogencarbonate solution (5 cm^3) and THF (1 cm^3) was added, and the mixture extracted with hexane (3 × 5 cm^3). The combined organic extracts were washed with water, dried ($MgSO_4$) and evaporated under reduced pressure. The residue was flash chromatographed (SiO_2, hexane) to give a mixture of the *E*- and *Z-alkenes* (103 mg, 51%) in a ratio of 40 : 60 (GLC). The mixture was separated by repeated flash chromatography (SiO_2–$AgNO_3$, 4 : 1; hexane)[59] optimising for geometrical purity to give a sample of the pure *E-alkene* (*E*)-**17** (17 mg); R_f(SiO_2–$AgNO_3$, 4 : 1; hexane) 0.2; (GLC retention time; 150 °C/min, 8.3); ν_{max}($CHCl_3$)/cm^{-1} 1630 (C=C) and 980 (*E* C=C); δ_H(250 MHz; $CDCl_3$) 5.4–5.3 (2 H, m, CH=CH), 2.0–1.9 (4 H, m, MeC*H* and adamantyl CHs), 1.75–1.5 (12 H, m, adamantyl CH_2s), 1.65 (3 H, d, *J* 4.7 Hz, *Me*CH=), and 0.86 (3 H, d, *J* 7.0, *Me*CHCH=); δ_C($CDCl_3$) 133.9, 124.2, 47.8, 39.8, 37.5, 34.5, 28.8, 18.0 and 14.1; *m*/*z* (EI) 204 (11%, M^+), and 135 (100, $C_{10}H_{15}$) (Found: M^+, 204.1875. $C_{15}H_{24}$ requires *M*, 204.1878); and the pure *Z-alkene* (*Z*)-**17** (36 mg); R_f(SiO_2–$AgNO_3$, 4 : 1; hexane) 0.1; (GLC retention time; 150 °C/min 8.9); δ_H(250 MHz; $CDCl_3$) 5.43 (1 H, dq, *J* 11.0 and 6.5, MeC*H*=), 5.28 (1 H, dd, *J* 11.0 and 10.2, CHC*H*=), 2.07 (1 H, dq, *J* 10.2 and 6.9, C*H*CH=), 2.0–1.9 (3 H, m, adamantyl CHs), 1.7–1.5 (12 H, m, adamantyl CH_2s), 1.58 (3 H, d, *J* 6.5, *Me*CH=), and 0.82 (3 H, d, *J* 6.9, *Me*CH); δ_C ($CDCl_3$) 133.7, 122.7, 41.3, 39.6, 37.4, 35.1, 28.8, 13.9 and 13.1; *m*/*z* (EI) 204 (25%, M^+), and 135 (100, $C_{10}H_{15}$) (Found: M^+, 204.1865. $C_{15}H_{24}$ requires *M*, 204.1878). Similarly, the *Z*-allylsilane *Z*-**16** (17 mg, 0.12 mmol) gave a mixture of the *E*- and *Z-alkenes* (20 mg, 82%) in a ratio of 99.7 : 0.3 (GLC). The mixture was separated by flash chromatography (SiO_2–$AgNO_3$, 4 : 1; hexane) to give the pure *E-alkene*, identical (GLC, ^{1}H-NMR) to the material described above; $[\alpha]_D$ −17 (*c.* 0.47 in $CHCl_3$). The structures of these compounds were confirmed by independent synthesis of racemic samples described below.

(2*RS*)-2-Adamantylpropanoic acid

Using reaction conditions developed by Reetz,[65] 1,1-bis(trimethylsilyloxy)prop-1-ene[66] (10.0 g, 46 mmol) was added dropwise with stirring to dry zinc chloride (1.88 g, 14 mmol) in dry dichloromethane (50 cm^3) under argon at room temperature. After 5 min, 1-bromoadamantane (9.86 g, 46 mmol) in dry dichloromethane (25 cm^3) was added dropwise, and the mixture kept for 5 h. The mixture was poured into cooled hydrochloric acid solution (175 cm^3, 6 mol dm^{-3}) and extracted with dichloromethane (3 × 125 cm^3). The combined organic extracts were washed with sodium hydroxide solution (3 × 125 cm^3, 10%). The combined aqueous layers were cooled, acidified with hydrochloric acid solution (3 mol dm^{-3}) and extracted with dichloromethane (3 × 200 cm^3). The combined organic extracts were dried ($MgSO_4$) and evaporated under reduced pressure to give the acid (3.0 g, 31%) as prisms, mp 155–159 °C (from hexane) (lit.,[67] 158–159 °C); ν_{max}($CHCl_3$)/cm^{-1} 3500–2500 (COOH) and 1700 (C=O); δ_H(250 MHz; $CDCl_3$) 10.2 (1 H, br s, COOH), 2.13 (1 H, q, *J* 7.1, MeC*H*), 2.05–1.95 (3 H, m, adamantyl CHs), 1.8–1.4 (12 H, m, adamantyl CH_2s) and 1.09 (3 H, d, *J* 7.1, *Me*CH).

(2*RS*)-2-Adamantylpropanal

Using reaction conditions developed by Peters and van Bekkum,[68] oxalyl chloride (0.84 cm^3) was added dropwise to a

stirred mixture of the acid (1.63 g, 7.8 mmol) in dry dichloromethane (11 cm^3) under argon at 0 °C. After 2 h the solvent and excess reagent were evaporated off under reduced pressure. The residue was dissolved in dry ethyl acetate (25 cm^3) and added to palladium on charcoal (0.39 g, 10%), ethyl acetate (25 cm^3) and ethyldiisopropylamine (2.2 cm^3) under hydrogen at room temperature. After 3 h the catalyst was filtered off, and the filtrate washed with hydrochloric acid solution (2 × 100 cm^3, 3 mol dm^{-3}), sodium hydroxide solution (2 × 100 cm^3, 10%), brine, dried ($MgSO_4$) and evaporated under reduced pressure to give the *aldehyde* (1.34 g, 89%); ν_{max}(film)/cm^{-1} 1720 (C=O); δ_H(250 MHz; $CDCl_3$) 9.85 (1 H, d, *J* 4.0, CHO), 2.2–1.9 (4 H, m, MeC*H* and adamantyl CHs), 1.8–1.4 (12 H, m, adamantyl CH_2s), and 1.09 (3 H, d, *J* 7.0, *Me*CH); *m*/*z* (EI) 192 (1.5%, M^+), 163 (45, M − CHO) and 135 (100, $C_{10}H_{15}$) (Found: M^+, 192.1504. $C_{13}H_{20}O$ requires *M*, 192.1514).

(*E*)-(4*RS*)-4-Adamantylpent-2-ene and (*Z*)-(4*RS*)-4-adamantylpent-2-ene

Using reaction conditions developed by Meyers and Collington,[69] *n*-butyllithium (5.4 cm^3 of a 1.6 mol dm^{-3} solution in hexane) was added dropwise to a stirred mixture of ethyltriphenylphosphonium bromide (2.56 g, 8.7 mmol) in dry THF (45 cm^3) under argon at room temperature. The resulting red solution was stirred for 20 min and a solution of the aldehyde (1.33 g, 6.9 mmol) in dry THF (25 cm^3) was added dropwise. The orange suspension was stirred for 30 min, poured over water (120 cm^3), extracted with ether (3 × 120 cm^3), dried ($MgSO_4$), evaporated under reduced pressure, and the residue flash chromatographed (SiO_2, hexane) to give a mixture of the *E*- and *Z*-*alkenes* (0.31 g 22%) in a ratio of 17 : 83 (GLC); R_f(hexane) 0.6; the mixture was separated by flash chromatography (SiO_2–$AgNO_3$, 4 : 1; hexane)[59] to give the pure *E*-alkene and *Z*-alkenes, identical (TLC, GLC, ^{1}H-NMR) with the enantiomerically enriched samples *E*- and *Z*-**17** described above.

(2*S*)-2-Adamantylpropanol and (2*R*)-2-adamantylpropanol

Ozone was bubbled through the pure *E*-alkene [rich in the *R*-isomer (*R*)-*E*-**17**, derived from the reaction with the (*E*)-allylsilane] (17 mg, 0.08 mmol) in a mixture of dry dichloromethane (1 cm^3) and methanol (1 cm^3) at −78 °C for 2 min. The solution was then purged with nitrogen and allowed to warm to 0 °C. Sodium borohydride (10 mg, 0.26 mmol) was added and the solution stirred for 1 h. The solvent was then evaporated off under reduced pressure and the residue dissolved in ether (10 cm^3), washed with water (10 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure to give largely the (2*S*)-*alcohol* (13 mg, 80%). Similarly, the pure *Z*-alkene [rich in the *S*-isomer (*S*)-*Z*-**17**, derived from the reaction with the (*E*)-allylsilane] (36 mg, 0.18 mmol) gave largely the (2*R*)-*alcohol* (27 mg, 79%). Similarly, the pure *E*-alkene [rich in the *S*-isomer (*S*)-*Z*-**17**, derived from the reaction with the (*Z*)-allylsilane] (13 mg, 0.06 mmol) gave largely the (2*R*)-*alcohol* (11 mg, 89%). Physical data (TLC, ^{1}H-NMR) for all three samples were identical with those determined on a racemic sample: R_f(hexane–Et_2O, 1 : 1) 0.3; ν_{max}(film)/cm^{-1} 3500–3100 (OH); δ_H(250 MHz; $CDCl_3$) 3.84 (1 H, dd, *J* 10.4 and 3.9, C$H_A$$H_B$O), 3.35 (1 H, dd, *J* 10.4 and 8.4, CH$_A$$H_B$O), 2.5 (1 H, br s, OH), 2.2–1.9 (4 H, m, MeC*H* and adamantyl CHs), 1.7–1.4 (12 H, m, adamantyl CH_2s) and 0.91 (3 H, d, *J* 6.9, *Me*CH); *m*/*z* (EI) 194 (15%, M^+), 177 (16, M − OH), 163 (37, M − CH_2OH) and 135 (100, $C_{10}H_{15}$) (Found: M^+, 194.1660. $C_{13}H_{22}O$ requires *M*, 194.1671).

(2′*R*)-2′-Adamantylpropyl (2*S*)-2-methoxy-2-phenyl-3,3,3-trifluoropropanoate 18 and (2′*S*)-2′-adamantylpropyl (2*S*)-2-methoxy-2-phenyl-3,3,3-trifluoropropanoate 19

Dicyclohexylcarbodiimide (41 mg, 0.2 mmol) in dry dichloromethane (0.1 cm^3) was added to a stirred solution of the alcohol [27 mg, 0.14 mmol, derived from the (*Z*)-alkene derived from the reaction with the (*E*)-allylsilane], dimethylaminopyridine (3.2 mg, 0.03 mmol) and (−)-Mosher's acid (45 mg, 0.19 mmol) in dry dichloromethane (0.2 cm^3) under argon at room temperature. After 3 h the mixture was filtered through silica gel eluting with dichloromethane. The solvent was removed under reduced pressure and the residue chromatographed (preparative TLC, hexane–Et_2O, 9 : 1) to give the *Mosher's ester* **18** (45 mg, 79%) free (>95.5 : 0.5, ^{19}F-NMR) of the isomer **19**; δ_H(250 MHz; $CDCl_3$) 7.5–7.3 (5 H, m, Ph), 4.46 (1 H, dd, *J* 10.7 and 3.8, C$H_A$$H_B$O), 4.07 (1 H, dd, *J* 10.7 and 8.5, CH$_A$$H_B$O), 3.54 (3 H, q, *J* 1.1, OMe), 2.0–1.9 (4 H, m, MeC*H* and adamantyl CHs), 1.7–1.4 (12 H, m, adamantyl CH_2s) and 0.85 (3 H, d, *J* 6.9, *Me*CH); δ_F($CDCl_3$; relative to CCl_3F) −72.02. Similarly, the alcohol [13 mg, 0.07 mmol, derived from the (*E*)-alkene derived from the reaction with the (*E*)-allylsilane] gave a mixture of the Mosher's esters **18** and **19** (20 mg, 73%) rich (90 : 10, ^{19}F-NMR) in the isomer **19**; δ_H(250 MHz; $CDCl_3$) 7.5–7.3 (5 H, m, Ph), 4.54 (1 H, dd, *J* 10.7 and 3.9, C$H_A$$H_B$O), 4.00 (1 H, dd, *J* 10.7 and 8.7, CH$_A$$H_B$O), 3.54 (3 H, q, *J* 1.1, OMe), 2.0–1.9 (4 H, m, MeC*H* and adamantyl CHs), 1.7–1.4 (12 H, m, adamantyl CH_2s) and 0.84 (3 H, d, *J* 6.9, *Me*CH); δ_F($CDCl_3$; relative to CCl_3F) −71.95. Similarly, the alcohol [11 mg, 0.06 mmol, derived from the (*E*)-alkene derived from the reaction with the (*Z*)-allylsilane] gave a mixture of the *Mosher's esters* **18** and **19** (19 mg, 82%) in a ratio of 95 : 5 (^{1}H-NMR, ^{19}F-NMR). A 50 : 50 mixture of the (2′*R*)- and (2′*S*)-esters, prepared from racemic alcohol, showed that there was no chiral recognition in the making of the Mosher's esters, and gave additional data: R_f(hexane–Et_2O, 9 : 1) 0.35; ν_{max}($CHCl_3$)/cm^{-1} 1740 (C=O) and 1500 (Ph); δ_C($CDCl_3$) 166.8, 132.4, 129.5, 128.4, 127.3, 68.7, 55.4, 42.4, 39.6, 37.1, 34.1, 28.6 and 11.1; *m*/*z* (EI) 410 (13%, M^+), 189 (25, $C_9H_8F_3O$), 177 (28, $C_{13}H_{21}$) and 135 (100, $C_{10}H_{15}$) (Found: M^+, 410.2032. $C_{23}H_{29}F_3O_3$ requires M, 410.2069).

(2*S*)-4-Trimethylsilylbut-3-yn-2-ol 27

Following Brown,[31] 9-BBN dimer (11.2 g, 92 mmol) and (−)-α-pinene (14.6 cm^3, 91 mmol) were stirred together and heated at 65 °C under argon for 5 h. The mixture was cooled to room temperature and 4-trimethylsilylbut-3-yn-2-one[70] (6.4 g, 46 mmol) was added. The orange mixture was stirred at room temperature for 18 h, then cooled to 0 °C. Acetaldehyde (8 cm^3, 141 mmol) was added and the mixture stirred for 15 min. The liberated α-pinene was removed by evaporation under reduced pressure with gentle heating. The mixture was then cooled back to 0 °C and ether (60 cm^3) and distilled ethanolamine (5.3 cm^3, 130 mmol) were added. A white precipitate appeared and the mixture was stirred for 15 min. The mixture was then filtered and the residue washed with cold ether (120 cm^3). The combined organic layers were washed with brine, dried ($MgSO_4$), concentrated by evaporation under reduced pressure and distilled to give the alcohol (4.0 g, 62%) as an oil, bp 71–72 °C/20 mmHg (lit.,[35] 83–85 °C/13 mmHg); ν_{max}($CHCl_3$)/cm^{-1} 3580 (OH), 2160 (C≡C) and 1250 ($SiMe_3$); δ_H(250 MHz; $CDCl_3$) 4.50 (1 H, q, *J* 6.6, C*H*Me), 1.43 (3 H, d, *J* 6.6, CH*Me*) and 0.16 (9 H, s, $SiMe_3$).

(2*S*)-4-Trimethylsilylbut-3-yn-2-yl (1*R*)-camphorsulfonate 28

(−)-Camphorsulfonyl chloride[71] (8.4 g, 33 mmol) in dry dichloromethane (30 cm^3) was added to a stirred mixture of the alcohol **27** (4.0 g, 28 mmol), 4-dimethylaminopyridine (0.68 g, 6 mmol) and triethylamine (4.7 cm^3, 33 mmol) in dry dichloromethane (18 cm^3) under argon at −5 °C. A white precipitate appeared and the mixture was stirred at 0 °C for 1 h, then poured onto a mixture of ice and water and extracted with dichloromethane (3 × 150 cm^3). The combined organic layers

were washed with hydrochloric acid solution (2 × 150 cm^3, 3 mol dm^{-3}) and sodium hydrogencarbonate solution (2 × 150 cm^3), dried ($MgSO_4$), evaporated under reduced pressure, and the residue flash chromatographed (SiO_2, hexane–Et_2O, 4 : 1) to give a mixture of the sulfonate esters (9.0 g, 90%) in a ratio of 94 : 6 (^{1}H-NMR); R_f(hexane–Et_2O, 4 : 1) 0.2. The mixture was recrystallised three times from hexane to give the pure sulfonate ester (4.6 g, 51%) as plates, diastereomerically pure (>99.5 : 0.5, ^{1}H-NMR), mp 67–68.5 °C; ν_{max}($CHCl_3$)/cm^{-1} 2150 (C≡C), 1745 (C=O), 1350 and 1165 (SO_2) and 835 ($SiMe_3$); δ_H(250 MHz; $CDCl_3$) 5.31 (1 H, q, *J* 6.7, C*H*Me), 3.82 (1 H, d, *J* 15.0, C$H_AH_BSO_2$), 3.09 (1 H, d, *J* 15.0, C$H_AH_BSO_2$), 2.6–1.4 (7 H), 1.61 (3 H, d, *J* 6.7, CH*Me*) 1.14 (3 H, s, CMe_AMe_B) and 0.88 (3 H, s, CMe_AMe_B) and 0.16 (9 H, s, $SiMe_3$); $[a]_D$ −69 (*c.* 1.1 in $CHCl_3$)(Found: C, 57.4; H, 8.0. $C_{17}H_{28}O_4SiS$ requires C, 57.3; H, 7.9%). The *RR* diastereoisomer gave recognisable signals in the ^{1}H-NMR spectrum at: δ_H(250 MHz; $CDCl_3$) 5.28 (1 H, q, *J* 6.7, C*H*Me), 3.70 (1 H, d, *J* 15.2, C$H_AH_BSO_2$), 3.23 (1 H, d, *J* 15.2, C$H_AH_BSO_2$), 2.6–1.4 (7 H), 1.61 (3 H, d, *J* 6.7, CH*Me*), 1.15 (3 H, s, CMe_AMe_B) and 0.90 (3 H, s, CMe_AMe_B) and 0.17 (9 H, s, $SiMe_3$).

(*S*)-2-Trimethylsilylpenta-2,3-diene 29

Using reaction conditions developed by Danheiser,[72] methylmagnesium chloride (1.0 cm^3 of a 3.0 mol dm^{-3} solution in THF, 3 mmol) was added to a stirred solution of dry copper(I) bromide[73] (0.45 g, 3.15 mmol) and dry lithium bromide (0.27 g, 3.15 mmol) in dry THF (4.8 cm^3) under argon at 0 °C. The resulting yellow paste was stirred for 20 min, and then cooled to −78 °C. A solution of the sulfonate ester (1.07 g, 3 mmol) in dry THF (4.8 cm^3) was slowly added, and the resulting yellow-green mixture was stirred at −78 °C for 40 min, warmed to room temperature and stirred for a further 10 min. The mixture was then poured into a mixture of pentane (45 cm^3), water (12 cm^3) and saturated ammonium chloride solution (12 cm^3). The organic layer was separated, washed with saturated ammonium chloride solution (2 × 15 cm^3), water (10 × 30 cm^3) and brine, dried ($MgSO_4$), and the solvent removed by fractional distillation. The residue was flash chromatographed (SiO_2, pentane) and the solvent removed by fractional distillation, followed by careful evaporation under reduced pressure (water pump) at −20 °C to give the allene[35] (0.35 g, 83%) as an oil with enantiomer ratios measured as 98.7 : 1.3, 99 : 1 and 99.25 : 0.75 in three runs [chiral GLC using heptakis(6-*O*-methyl-2,3-di-*O*-*n*-pentyl)-β-cyclodextrin, with retention times of 14.9 (*S*) and 16.0 (*R*)];[37] R_f(hexane) 0.65; ν_{max}($CHCl_3$)/cm^{-1} 1935 (C=C=C), 1240 and 840 ($SiMe_3$); δ_H(250 MHz; $CDCl_3$) 4.68 (1 H, qq, *J* 6.9 and 2.8, MeC*H*=), 1.65 (3 H, d, *J* 2.8, MeSiC=), 1.43 (3 H, d, *J* 6.9, *Me*CH=) and 0.06 (9 H, s, $SiMe_3$); $[a]_D$ +79 (*c.* 1.4 in $CHCl_3$).

(4*R*)-4-Adamantylpent-2-yne (*S*)-30

A solution of titanium tetrachloride in dichloromethane (0.11 cm^3 of a 1.0 mol dm^{-3} solution, 0.11 mmol) was added to a stirred solution of 1-chloroadamantane (122 mg, 0.70 mmol) in dry dichloromethane (2 cm^3) under argon at −78 °C. After 10 min, the allene (100 mg, 0.70 mmol) in dry dichloromethane (1 cm^3) was added, and the mixture stirred under argon at −78 °C for 30 min. Cold sodium hydrogencarbonate solution (5 cm^3) was added, and the mixture extracted with hexane (3 × 5 cm^3). The combined organic extracts were washed with water, dried ($MgSO_4$), evaporated under reduced pressure and flash chromatographed (SiO_2, hexane) to give the *alkyne* (~40 mg, 30%) as an oil, contaminated with 1-chloroadamantane; R_f(hexane) 0.4; δ_H(250 MHz; $CDCl_3$) 2.0–1.95 (4 H, m, R_3CH), 1.80 (3 H, d, *J* 2.5, MeC≡), 1.7–1.5 (12 H, m, R_2CH_2) and 1.02 (3 H, d, *J* 7.1, *Me*CH); *m*/*z* (EI) 202 (32%, M^+) and 135 (100, $C_{10}H_{15}$) (Found: M^+, 202.1724. $C_{15}H_{22}$ requires *M*, 202.1716).

(*Z*)-(4*R*)-4-Adamantylpent-2-ene (*R*)-(*Z*)-17

The alkyne **30** (30 mg, 0.15 mmol), Lindlar catalyst (10 mg) and quinoline (20 mg) in hexane (3 cm^3) were stirred under hydrogen at room temperature for 5 h. The mixture was filtered through Celite, the solvent evaporated under reduced pressure and the residue flash chromatographed (SiO_2, hexane) to give the *Z-alkene Z*-**17** (8 mg, 26%), identical (TLC, ^{1}H-NMR) with the earlier sample.

(2*S*)-2-Adamantylpropanol

This was prepared in the same way as the alcohol above using the alkene (10 mg, 0.05 mmol) to give the *alcohol* (5 mg, 53%), identical (TLC, ^{1}H-NMR) with the earlier sample.

(2′*S*)-2′-Adamantylpropyl (2*S*)-2-methoxy-2-phenyl-3,3,3-trifluoropropanoate 19

This was prepared in the same way as the mixture of esters above using the alcohol (5 mg, 0.03 mmol) to give a mixture of the *Mosher's esters* **18** and **19** (10.5 mg, 100%) in a ratio of 1 : 99 (^{1}H-NMR, ^{19}F-NMR), identical (TLC, ^{1}H NMR) to the earlier samples.

(3*R*,4*R*)-2,4-Dimethylhept-5-yn-3-ol (3*R*,4*R*)-31 and 2,4-Dimethylhept-5-yn-3-ol 32

Using reaction conditions developed by Danheiser,[40] isobutyraldehyde (0.023 cm^3, 0.25 mmol) was added to titanium tetrachloride (0.28 cm^3 of a 1 mol dm^{-3} solution in dichloromethane, 0.28 mmol) under argon at −78 °C and the mixture stirred for 5 min. The allene (28 mg, 0.20 mmol) in dry dichloromethane (0.2 cm^3) was added dropwise and the resulting brown mixture was stirred at −78 °C for 1.5 h. Sodium hydrogencarbonate solution (2.5 cm^3) was added and the aqueous phase was extracted with dichloromethane (3 × 5 cm^3). The combined organic layers were washed with sodium hydrogencarbonate solution, dried ($MgSO_4$) and concentrated by evaporation under reduced pressure (with ice-bath cooling) to give a mixture of the alcohols **31** and **32** (24 mg, 89%) in a ratio of 95 : 5 (^{1}H-NMR) as an oil. The mixture was separated by flash chromatography (SiO_2, pentane–Et_2O, 19 : 1) to give the *syn alcohol* **31**; R_f(hexane–Et_2O, 4 : 1) 0.25; ν_{max}($CHCl_3$)/cm^{-1} 3600–3400 (OH); δ_H(250 MHz; $CDCl_3$) 3.25 (1 H, t, *J* 5.9, C*H*OH), 2.55 (1 H, m, CHC≡), 1.91 (1 H, octet, *J* 6.8, C*H*Me_2), 1.78 (3 H, d, *J* 2.4, MeC≡), 1.70 (1 H, br s, OH), 1.13 (3 H, d, *J* 6.9, *Me*CHC≡), 0.94 and 0.89 (3 H each, d, *J* 6.7, CH*Me*$_2$); *m*/*z* (EI) 140 (3%, M^+), 123 (23, M – OH), 73 (27, C_4H_9O) and 68 (100, C_5H_8)(Found: M^+, 140.1266. $C_9H_{16}O$ requires *M*, 140.1197), and the *anti alcohol* **32**; R_f(hexane–Et_2O, 4 : 1) 0.20; δ_H(250 MHz; $CDCl_3$) 2.97 (1 H, m, C*H*OH), 2.65 (1 H, m, CHC≡), 1.9–1.6 (2 H, m, C*H*Me_2 and OH), 1.80 (3 H, d, *J* 2.4, MeC≡), 1.18 (3 H, d, *J* 7.0, *Me*CHC≡), (3 H, d, *J* 6.9, CH*Me*$_A$Me$_B$) and 0.92 (3 H, d, *J* 6.7, CHMe$_A$*Me*$_B$).

(3*R*,4*R*)-2,4-Dimethylhept-5-yn-3-yl (1*S*)-camphorsulfonate 33 and (3*S*,4*S*)-2,4-Dimethylhept-5-yn-3-yl (1*S*)-camphorsulfonate 34

(+)-Camphorsulfonyl chloride (42 mg, 0.17 mmol) in dry dichloromethane (0.2 cm^3) was added to a stirred mixture rich in the (3*R*,4*R*)-alcohol **31** (10 mg, 0.07 mmol), 4-dimethylaminopyridine (3.4 mg, 0.03 mmol) and triethylamine (0.025 cm^3, 0.17 mmol) in dry dichloromethane (0.4 cm^3) under argon at room temperature. The mixture was refluxed for 16 h, then cooled to 0 °C. Ice-cold water was added and the mixture extracted with dichloromethane (3 × 5 cm^3). The combined organic layers were washed with hydrochloric acid solution (2 × 5 cm^3, 3 mol dm^{-3}) and sodium hydrogencarbonate solution (2 × 5 cm^3), dried ($MgSO_4$), evaporated under reduced

pressure, and the residue flash chromatographed (SiO_2, hexane–Et_2O, 9 : 1) to give a mixture of the *sulfonate esters* (13.5 mg, 53%) in a ratio of 99 : 1 (^{1}H-NMR) rich in the *R*,*R*,*S*-isomer **33**; δ_H(250 MHz; $CDCl_3$) 4.54 (1 H, dd, *J* 6.5 and 5.1, $CHOSO_2$), 3.82 (1 H, d, *J* 15.0, $CH_AH_BSO_2$), 3.09 (0.5 H, d, *J* 15.0, $CH_AH_BSO_2$), 2.77 (1 H, m, CHC≡), 2.6–1.9 (5 H), 1.78 (3 H, d, *J* 2.4, MeC≡), 1.7–1.3 (2 H), 1.24 (3 H, d, *J* 6.9, *Me*CHC≡), 1.14 (3 H, s, CMe_AMe_B), 0.89 (3 H, s, CMe_AMe_B) and 1.00 (3 H, d, *J* 6.8, $CHMe_2$). A similar preparation from racemic alcohol (9 mg, 0.06 mmol) gave a 50 : 50 mixture of the camphorsulfonates **33** and **34** (19 mg, 84%); R_f(hexane–Et_2O, 4 : 1) 0.20; ν_{max}($CHCl_3$)/cm^{-1} 2230 (C≡C), 1730 (C=O), 1330 and 1150 (OSO_2); δ_H(250 MHz; $CDCl_3$) as above for the isomer **33** together with the following different signals from the *S*,*S*,*S*-isomer: 4.53 (1 H, dd, *J* 6.8 and 4.7, $CHOSO_2$), 3.69 (1 H, d, *J* 15.0, $CH_AH_BSO_2$), 3.17 (1 H, d, *J* 15.0, $CH_AH_BSO_2$), 1.77 (3 H, d, *J* 2.7, MeC≡), 1.02 (3 H, d, *J* 5.2, $CHMe_AMe_B$) and 0.99 (3 H, d, *J* 5.0, $CHMe_AMe_B$); δ_C($CDCl_3$) 214.5, 90.7, 80.0, 78.4, 58.1, 48.5, 47.7, 42.8, 42.5, 30.3, 29.0, 26.8, 25.0, 20.0, 19.9, 19.7, 17.2, 17.1 and 3.5 (*R,R,S* dias.), 214.6, 90.6, 79.9, 78.3, 58.2, 48.6, 47.6, 42.9, 42.5, 30.3, 29.1, 26.8, 25.0, 20.0, 19.9, 19.7, 17.2, 17.1 and 3.5 (*S,S,S* dias.); *m*/*z* (EI) 287 (34%, $M^+ - C_5H_7$) and 215 (100, $C_{10}H_{15}O_3S$) (Found: $M^+ - C_5H_7$, 287.1330. $C_{19}H_{30}O_4S - C_5H_7$ requires *M*, 287.1317).

(3*S*,4*R*)-2,4-Dimethylhept-5-yn-3-yl (1*S*)-camphorsulfonate

This was prepared in the same way as the sulfonate esters **33** and **34** using the alcohol **32** (1 mg, 0.01 mmol) to give the *sulfonate ester* (1.5 mg, 60%) with a ratio of diastereoisomers >95 : 5 (^{1}H-NMR), presumably in favour of the 3*S*,4*R*-isomer; δ_H(250 MHz; $CDCl_3$) 4.43 (1 H, t, *J* 5.6, $CHOSO_2$), 3.73 (1 H, d, *J* 15.1, $CH_AH_BSO_2$), 3.20 (1 H, d, *J* 15.1, $CH_AH_BSO_2$), 2.81 (1 H, m, CHC≡), 2.65–1.9 (5 H), 1.78 (3 H, d, *J* 2.4, MeC≡), 1.7–1.3 (2 H), 1.23 (3 H, d, *J* 7.0, *Me*CHC≡), 1.17 (3 H, s, CMe_AMe_B), 1.03 (3 H, d, *J* 7.1, $CHMe_AMe_B$), 1.00 (3 H, d, *J* 7.1, $CHMe_AMe_B$) and 0.90 (3 H, s, CMe_AMe_B).

(*Z*)-(3*R*,4*R*)-2,4-Dimethylhept-5-en-3-ol

The *syn* alcohol **31** (60 mg, 0.43 mmol), Lindlar catalyst (21 mg) and quinoline (43 mg) in hexane (3 cm^3) were stirred under hydrogen at room temperature for 5 h. The mixture was then filtered through Celite, the solvent evaporated under reduced pressure (water pump) with ice-bath cooling and the residue flash chromatographed (SiO_2, pentane–Et_2O, 9 : 1) to give the *alcohol* (42 mg, 69%); R_f(hexane–Et_2O, 4 : 1) 0.25; ν_{max}($CHCl_3$)/cm^{-1} 3630 (OH) and 1600 (C=C); δ_H(250 MHz; $CDCl_3$) 5.42 (1 H, ddq, *J* 10.9, 0.8 and 6.7, MeC*H*=), 5.22 (1 H, ddq, *J* 10.9, 9.6 and 1.6, CHMeC*H*=), 3.14 (1 H, dd, *J* 7.1 and 4.4, C*H*OH), 2.60 (1 H, dquintet, *J* 9.6 and 7.0, C*H*MeCH=), 1.76 (1 H, m, C*H*Me_2), 1.62 (3 H, dd, *J* 6.7 and 1.6, *Me*CH=), 1.33 (1 H, br s, OH), 0.99 (3 H, d, *J* 6.7, CH*Me*CH=), 0.93 (3 H, d, *J* 6.9, $CHMe_AMe_B$) and 0.85 (3 H, d, *J* 6.7, $CHMe_AMe_B$).

(*Z*)-(4*R*,5*R*)-5-Methoxy-4,6-dimethylhept-2-ene

Using reaction conditions developed by Sjöberg,[74] sodium methylsulfinylmethanide[75] was added to the alcohol (42 mg, 0.30 mmol) and a trace of triphenylmethane in dry DMSO (0.3 cm^3) until a deep red colour was produced. Distilled dimethyl sulfate (0.15 cm^3, 1.58 mmol) was then added and the solution stirred at room temperature for 1 h. Pentane (2 cm^3) and water (2 cm^3) were added and the aqueous layer was extracted with pentane (3 × 5 cm^3). The combined organic layers were washed with water, dried ($MgSO_4$), evaporated under reduced pressure (water pump) with ice-bath cooling and flash chromatographed (SiO_2, pentane–Et_2O, 19 : 1) to give the *methyl ether* (22 mg, 48%) as an oil; R_f(hexane–Et_2O, 9 : 1) 0.5; ν_{max}($CHCl_3$)/cm^{-1} 1600 (C=C); δ_H(250 MHz; $CDCl_3$) 5.38 (1 H, dq, *J* 10.9 and 6.7, MeC*H*=), 5.23 (1 H, m, CHMeC*H*=), 3.45 (3 H, s, OMe), 2.65 (2 H, m, C*H*MeC*H*OMe), 1.74 (1 H, m, C*H*Me_2), 1.61 (3 H, dd, *J* 6.7 and 1.5, *Me*CH=), 0.98 (3 H, d, *J* 6.3, CH*Me*CH=), 0.94 (3 H, d, *J* 6.9, $CHMe_AMe_B$) and 0.86 (3 H, d, *J* 6.7, $CHMe_AMe_B$).

(2*R*,3*R*)-3-Methoxy-2,4-dimethylpentanol

Ozone was bubbled through a solution of the methyl ether (22 mg, 0.14 mmol) in methanol (3 cm^3) at −78 °C for 1 min. The solution was then purged with nitrogen and allowed to warm to 0 °C. Sodium borohydride (21 mg, 0.28 mmol) was then added and the solution, and the mixture stirred for 1 h. The solvent was evaporated under reduced pressure and the residue dissolved in ether (5 cm^3), washed with water (2 × 5 cm^3), dried ($MgSO_4$), evaporated under reduced pressure (water pump) with ice-bath cooling and flash chromatographed (SiO_2, pentane–Et_2O, 1 : 1) to give the *alcohol* (22 mg, 100%); R_f(hexane–Et_2O, 1 : 1) 0.2; δ_H(250 MHz; $CDCl_3$) 3.64 (1 H, dd, *J* 10.4 and 6.8, CH_AH_BOH), 3.60 (1 H, dd, *J* 10.4 and 5.6, CH_AH_BOH), 3.45 (3 H, s, OMe), 2.94 (1 H, dd, *J* 7.8 and 3.2, C*H*OMe), 2.0–1.7 (2 H, m, C*H*Me and C*H*Me_2), 1.67 (1 H, br s, OH), 0.99 (3 H, d, *J* 6.6, $CHMe_AMe_B$), 0.89 (3 H, d, *J* 7.0, CH*Me*) and 0.87 (3 H, d, *J* 6.8, $CHMe_AMe_B$). A similar preparation from racemic alkene (33 mg, 0.21 mmol) gave racemic alcohol (10 mg, 32%), identical (^{1}H-NMR) to the enantiomerically enriched product; ν_{max}($CHCl_3$)/cm^{-1} 3610 (OH); *m*/*z* (EI) 103 (63%, $M^+ - CHMe_2$) and 87 (100, M − $CHMeCH_2OH$) (Found: $M^+ - CHMe_2$, 103.0760. $C_8H_{18}O_2 - CHMe_2$ requires *M*, 103.0759).

(2′*R*,3′*R*)-3′-Methoxy-2′,4′-dimethylpentyl (2*S*)-2-methoxy-2-phenyl-3,3,3-trifluoropropanoate 35 and (2′*S*,3′*S*)-3′-Methoxy-2′,4′-dimethylpentyl (2*S*)-2-methoxy-2-phenyl-3,3,3-trifluoropropanoate 36

Dicyclohexylcarbodiimide (20 mg, 0.10 mmol) in dry dichloromethane (0.2 cm^3) was added to a stirred solution of the alcohol (10 mg, 0.07 mmol), (−)-Mosher's acid (22 mg, 0.09 mmol) and 4-dimethylaminopyridine (1.5 mg, 0.01 mmol) in dry dichloromethane (0.2 cm^3) under argon at room temperature. After 3 h the solution was filtered through silica gel, eluting with dichloromethane. The filtrate was evaporated under reduced pressure and the residue flash chromatographed (SiO_2, hexane–Et_2O, 9 : 1) to give a mixture of the known Mosher's esters[41] **35** and **36** (14 mg, 56%) in a ratio of 99 : 1 (^{1}H-NMR) as an oil; δ_H(250 MHz; $CDCl_3$) 7.53–7.50 (2 H, m, *o*-ArH), 7.43–7.35 (3 H, m, *m*- and *p*-ArH), 4.25 (1 H, dd, *J* 10.6 and 7.6, CH_AH_BO), 4.21 (1 H, dd, *J* 10.6 and 6.4, CH_AH_BO), 3.54 (3 H, s, PhCO*Me*), 3.33 (3 H, s, CHO*Me*), 2.70 (1 H, dd, *J* 8.0 and 3.2, C*H*OMe), 2.01 (1 H, dsextet, *J* 3.3 and 7.0, C*H*Me), 1.75 (1 H, octet, *J* 6.7, C*H*Me_2), 0.93 (3 H, d, *J* 6.6, $CHMe_AMe_B$), 0.88 (3 H, d, *J* 6.9, CH*Me*) and 0.80 (3 H, d, *J* 6.8, $CHMe_AMe_B$). A similar preparation from racemic alcohol (10 mg, 0.07 mmol) gave a 50 : 50 mixture of the Mosher's esters **35** and **36** (18 mg, 73%); δ_H(250 MHz; $CDCl_3$) as above for the isomer **35** together with the following different signals: δ_H(250 MHz; $CDCl_3$) 4.33 (1 H, dd, *J* 10.6 and 6.1, CH_AH_BO), 4.14 (1 H, dd, *J* 10.6 and 7.8, CH_AH_BO), 3.34 (3 H, s, CHO*Me*), 2.65 (1 H, dd, *J* 8.0 and 3.4, C*H*OMe), 0.92 (3 H, d, *J* 6.6, $CHMe_AMe_B$), 0.87 (3 H, d, *J* 6.9, CH*Me*) and 0.78 (3 H, d, *J* 6.7, $CHMe_AMe_B$); R_f(hexane–Et_2O, 9 : 1) 0.2; ν_{max}($CHCl_3$)/cm^{-1} 1745 (C=O); *m*/*z* (EI) 331 (19%, M^+ − OMe), 319 (41, M − $CHMe_2$), 189 (50, $PhCCF_3OMe$), 87 (97, $CHOMeCHMe_2$) and 85 (100, $CH_2CHMeCHOMe$) (Found: M^+ − OMe, 331.1515. $C_{18}H_{25}O_4F_3$ − OMe requires *M*, 331.1521).

Ethyl (3*RS*)-3-trimethylsilylbutanoate

n-Butyllithium (1.1 mol dm^{-3} in hexanes, 172 cm^3, 189.0 mmol) was added dropwise to a stirred solution of absolute ethanol

(17.6 g, 22.0 cm^3, 382.0 mmol) in dry THF (144 cm^3) under argon at −10 °C. After 10 min, 1-(3-trimethylsilylbutanoyl)-2-pyrrolidone[17] (13.1 g, 57.6 mmol) in dry THF (140 cm^3) was added. The mixture was stirred at −10 °C for 2 h and allowed to warm to room temperature. The mixture was then stirred at room temperature overnight. Water (300 cm^3) was added and the mixture was extracted with light petroleum (3 × 100 cm^3). The combined organic extracts were washed with brine (50 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure to give the ester[76] (10.8 g, 100%) as an oil; R_f(light petroleum–Et_2O, 9 : 1) 0.43; ν_{max}(film)/cm^{-1} 1738 (C=O), 1250 (SiMe) and 836 (SiMe); δ_H(400 MHz; $CDCl_3$) 4.15 (2 H, q, *J* 7.1, OCH_2Me), 2.40 (1 H, dd, *J* 15.0 and 4.3, COCH_AH$_B$), 2.07 (1 H, dd, *J* 15.0 and 11.0, COCH$_A$$H_B$), 1.28 (3 H, t, *J* 7.1, OCH$_2$*Me*), 1.25–1.15 (1 H, m, MeC*H*Si), 0.98 (3 H, d, *J* 7.3, *Me*CHSi) and 0.00 (9 H, s, $SiMe_3$); δ_C(400 MHz; $CDCl_3$) 174.1+, 60.1+, 36.9+, 16.8−, 14.3−, 14.2− and −3.4−; *m*/*z* (EI) 188 (23%, M$^+$), 173 (15, M − Me) and 143 (12, M − OEt) (Found: M$^+$, 188.1237. $C_9H_{20}O_2Si$ requires *M*, 188.1233).

(3*RS*)-3-Trimethylsilylbutanal

Using conditions reported by Zakharkin,[77] diisobutylaluminium hydride (1.0 mol dm^{-3} in hexanes, 65.0 cm^3, 65.0 mmol) in hexane (94 cm^3) was added dropwise over 10 min to a stirred solution of racemic ethyl 3-trimethylsilylbutanoate (10.9 g, 57.6 mmol) in hexane (160 cm^3) at −78 °C under argon. The mixture was stirred for 2 h, quenched with methanol (117 cm^3) and allowed to warm to room temperature. The mixture was washed with saturated aqueous potassium sodium tartrate (60 cm^3). The aqueous layer was further extracted with ether (3 × 60 cm^3) and the combined organic fractions were washed with brine (120 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure to give the aldehyde[78] (8.31 g, 100%) as an oil; R_f(light petroleum–Et_2O, 9 : 1) 0.36; ν_{max}(film)/cm^{-1} 1725 (C=O), 1250 (SiMe) and 837 (SiMe); δ_H(400 MHz; $CDCl_3$) 9.73 (1 H, dd, *J* 3.3 and 1.4, CHO), 2.43 (1 H, ddd, *J* 16.1, 3.8 and 1.4, COCH_AH$_B$), 2.15 (1 H, ddd, *J* 16.1, 10.7 and 3.3, COCH$_A$$H_B$), 1.27–1.17 (1 H, m, MeC*H*Si), 0.96 (3 H, d, *J* 7.3, *Me*CHSi) and 0.00 (9 H, s, $SiMe_3$); δ_C(400 MHz; $CDCl_3$) 203.5+, 46.0+, 14.4−, 14.1− and −3.5−; *m*/*z* (EI) 144 (100%, M$^+$), 129 (57, M − Me) and 115 (26, M − CHO) (Found: M$^+$, 144.0968. $C_7H_{16}OSi$ requires *M*, 144.0970).

(3*RS*)-3-Trimethylsilylbut-1-enyl trifluoromethanesulfonate

Using conditions developed by Mwaniki,[57] the aldehyde (8.31 g, 57.6 mmol) in dichloromethane (195 cm^3) was added over 20 min by syringe with the tip immersed in the solution to a refluxing solution of 2,6-di-*tert*-butylpyridine (14.87 g, 77.7 mmol, 17.5 cm^3) and trifluoromethanesulfonic anhydride (20.0 g, 70.9 mmol, 14.9 cm^3) in dichloromethane (195 cm^3) under argon, and the solution refluxed for 19 h. The mixture was concentrated under reduced pressure. The combined organic extracts were washed with light petroleum (3 × 380 cm^3) to precipitate the pyridinium salts. The combined organic extracts were washed with dilute aqueous hydrochloric acid (3 mol dm^{-3}, 4 × 400 cm^3), brine (500 cm^3) and dried ($MgSO_4$). The solvent was evaporated under reduced pressure and the residue chromatographed (SiO_2, light petroleum–Et_2O, 95 : 5) to give the *enol triflates* (8.70 g, 55% over 3 steps) (*Z* : *E*, 6.6 : 1); R_f(light petroleum–Et_2O, 8 : 2) 0.65; ν_{max}(film)/cm^{-1} 1656 (C=C), 1250 (SiMe), 1210 (OTf) and 840 (SiMe); δ_H(400 MHz; $CDCl_3$) *Z* isomer: 6.50 (1 H, d, *J* 5.6, C*H*OTf), 5.06 (1 H, dd, *J* 11.6 and 5.6, C*H*=CHOTf), 2.07 (1 H, dqd, *J* 11.6, 7.2 and 0.8, CHSi), 1.08 (3 H, d, *J* 7.2, *Me*CHSi), 0.01 (9 H, s, $SiMe_3$); *E* isomer: 6.30 (1 H, dd, *J* 11.6 and 1.2, C*H*OTf), 5.85 (1 H, dd, *J* 11.6 and 8.6, C*H*=CHOTf), 2.30–2.21 (1 H, m, CHSi), 1.09 (3 H, d, *J* 7.1, *Me*CHSi), 0.01 (9 H, s, $SiMe_3$); δ_C(400 MHz; $CDCl_3$) 133.3−, 132.5−, 127.4−, 124.3−, 120.2+. 117.0+, 21.7−, 19.9−, 14.3−, 13.2−, −3.4− and −3.7−.

(4*RS*)-4-Trimethylsilylpent-2-yne 37

A solution of LDA (72.1 mmol) was added dropwise to the racemic enol triflates (8.30 g, 30.0 mmol) in dry THF (200 cm^3) and the mixture was allowed to stir at 0 °C for 2 h. Methyl iodide (75.9 g, 33.3 cm^3, 534 mmol) was added and the mixture was stirred at room temperature for 1 h. The mixture was washed with dilute aqueous hydrochloric acid (3 mol dm^{-3}, 330 cm^3), water (2 × 330 cm^3), brine (500 cm^3), dried ($MgSO_4$) and the solvent evaporated under reduced pressure. Distillation give the alkyne[79] (2.19 g, 52%), bp 55 °C at 130 mmHg; R_f(light petroleum) 0.37; ν_{max}(film)/cm^{-1} 2360 (C≡C) and 1249 (SiMe); δ_H(400 MHz; $CDCl_3$) 1.79 (3 H, d, *J* 2.7, C≡CMe), 1.62–1.53 (1 H, m, MeC*H*Si), 1.11 (3 H, d, *J* 7.3, *Me*CHSi) and 0.04 (9 H, s, $SiMe_3$); δ_C(400 MHz; $CDCl_3$) 82.4+, 74.5+, 15.0−, 13.0−, 3.6− and −3.6−; *m*/*z* (EI) 140 (80%, M$^+$), 125 (10, M − Me) and 97 (100, M − C_3H_7)(Found: M$^+$, 140.1018. $C_8H_{16}Si$ requires *M*, 140.1021).

2,3-Diadamantyl-1,3-pentadiene 42 and 2,4-diadamantyl-1,3-pentadiene 43

Titanium tetrachloride (1.0 mol dm^{-3} in CH_2Cl_2, 1.44 cm^3, 1.44 mmol) was added to a stirred solution of 1-bromoadamantane (0.308 g, 1.44 mmol) in dry dichloromethane (4 cm^3) under argon at −78 °C. After 10 min, (4*RS*)-trimethylsilylpent-2-yne **37** (0.20 g, 1.44 mmol) in dry dichloromethane (4 cm^3) was added to the yellow solution, and the mixture stirred under argon at −78 °C for 1 h. Saturated aqueous sodium hydrogencarbonate (20 cm^3) was added and the mixture extracted with hexane (3 × 20 cm^3). The combined organic extracts were washed with water (2 × 10 cm^3), brine (50 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure. The residue was chromatographed (SiO_2, light petroleum) to give the *dienes* **42** and **43** (27 mg, 6%) (major : minor: 1.5 : 1, ^{1}H NMR); R_f(light petroleum) 0.70; δ_H(500 MHz; $CDCl_3$) major isomer **42**: 5.45 (1 H, q, *J* 6.8, MeC*H*=C), 5.16 (1 H, d, *J* 1.8, C=CH_AH$_B$), 4.65 (1 H, d, *J* 1.8, C=CH$_A$$H_B$), 2.01–1.63 (30 H, m, 2 × adamantyl) and 1.55 (3 H, d, *J* 6.8, *Me*CH=C); minor isomer **43**: 5.79 (1 H, br s, C*H*=C), 4.92 (1 H, d, *J* 2.1, C=CH_AH$_B$), 4.58 (1 H, dd, *J* 2.1 and 1.8, C=CH$_A$$H_B$) and 2.01–1.63 (33 H, m, 2 × adamantyl, MeC=C); *m*/*z* (EI) 336 (70%, M$^+$), 201 (55, M − Ad) and 135 (100, Ad) (Found: M$^+$, 336.2816. $C_{25}H_{36}$ requires *M*, 336.2817).

2-(1-Hydroxy-2-methylpropyl)-3-trimethylsilylpenta-1,3-dienes 45 and 2,4-dimethyl-5-trimethylsilylhept-5-en-3-ones 46

Titanium tetrachloride (1.0 mol dm^{-3} in CH_2Cl_2, 0.36 cm^3, 0.36 mmol) was stirred at −78 °C under argon for 10 min before addition of isobutyraldehyde (51 mg, 0.71 mmol) in dichloromethane (1 cm^3). The mixture was stirred at −78 °C for 1 h. A solution of propargylsilane **37** (100 mg, 0.71 mmol) in dichloromethane was added by cannula, and the mixture stirred at −78 °C for 1.5 h. The mixture was quenched with saturated aqueous ammonium chloride solution (5 cm^3) and allowed to stir at room temperature for 30 min. The aqueous layer was extracted with dichloromethane (3 × 10 cm^3). The combined organic extracts were washed with dilute aqueous hydrochloric acid (3 mol dm^{-3}, 10 cm^3), water (2 × 10 cm^3), brine (20 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure. The residue was chromatographed (SiO_2, light petroleum–Et_2O, 95 : 5) to give the *diene* **45** (30 mg, 20%) as a mixture of geometrical isomers (1.9 : 1, ^{1}H NMR); R_f(light petroleum–Et_2O, 9 : 1) 0.23; ν_{max}(film)/cm^{-1} 3400 (OH), 2998 (C=CH), 1243 (SiMe) and 841 (SiMe); δ_H(500 MHz; $CDCl_3$) major isomer: 6.07 (1 H, q, *J* 7.0, MeC*H*=C), 4.91 (1 H, s, C=CH_AH$_B$), 4.70 (1 H, d, *J* 0.7, C=CH$_A$$H_B$), 3.92 (1 H, s, C*H*OH), 1.85–1.75 (1 H, m, C*H*Me$_2$), 1.80 (3 H, d, *J* 7.0, *Me*CH=C), 0.99 (3 H, d, *J* 6.8, CH*Me*$_A$Me$_B$), 0.81 (3 H, d, *J* 6.8, CHMe$_A$*Me*$_B$) and 0.17 (9 H, s, $SiMe_3$); minor isomer: 5.96 (1 H, q, *J* 6.6, MeC*H*=C), 5.15 (1 H, s, C=CH_AH$_B$), 4.68 (1 H, s, C=CH$_A$$H_B$), 3.97 (1 H, s, C*H*OH),

1.85–1.75 (1 H, m, C*H*Me$_2$), 1.73 (3 H, d, *J* 6.6, *Me*CH=C), 1.02 (3 H, d, *J* 6.9, CH*Me*$_A$Me$_B$), 0.87 (3 H, d, *J* 6.9, CHMe$_A$*Me*$_B$) and 0.08 (9 H, s, SiMe$_3$); δ_C(500 MHz; $CDCl_3$) 151.7+, 139.6+, 138.9−, 136.6−, 109.1+, 77.7−, 49.4−, 39.2−, 20.6−, 19.6−, 18.4−, 17.8−, 16.1−, 14.8−, −0.4− and −0.6−. *m/z* (EI) 212 (10%, M^+), 197 (40, M − Me) and 73 (100, SiMe) (Found: M^+, 212.1601. $C_{12}H_{24}OSi$ requires *M*, 212.1596), and the *ketone* **46** (20 mg, 13%) as a mixture of geometrical isomers (1 : 1, ^{1}H NMR); R_f(light petroleum–Et_2O, 95 : 5) 0.56; ν_{max}(film)/cm^{-1} 1703 (C=O), 1603 (C=C), 1250 (SiMe) and 839 (SiMe); δ_H(500 MHz; $CDCl_3$) isomer A: 5.97 (1 H, q, *J* 6.8, MeC*H*=C), 3.34 (1 H, q, *J* 6.8, MeCH=CC*H*), 2.73 (1 H, sep, *J* 6.8, C*H*Me$_2$), 1.67 (3 H, d, *J* 6.8, *Me*CH=C), 1.06 (3 H, d, *J* 6.8, C=CCH*Me*), 1.00 (6 H, d, *J* 6.8, CH*Me*$_2$) and 0.08 (9 H, s, SiMe$_3$); isomer B: 5.93 (1 H, q, *J* 7.0, MeC*H*=C), 3.57 (1 H, q, *J* 6.9, MeCH=CC*H*), 2.61 (1 H, sep, *J* 6.9, C*H*Me$_2$), 1.75 (3 H, d, *J* 7.0, *Me*CH=C), 1.14 (3 H, d, *J* 6.9, C=CCH*Me*), 1.00 (6 H, d, *J* 6.9, CH*Me*$_2$) and 0.06 (9 H, s, SiMe$_3$); δ_C(500 MHz; $CDCl_3$) 216.3+, 215.4+, 141.6+, 139.6+, 138.9−, 137.4−, 49.4−, 46.2−, 39.2−, 38.1−, 20.0−, 19.6−, 18.1−, 17.8−, 15.3−, 14.0−, −0.3− and −0.6−; *m/z* (EI) 212 (5%, M^+), 197 (22, M − Me) and 73 (100, SiMe) (Found: M^+, 212.1602).

5-(2-Methylpropyl)-2-phenyl-3-dimethyl(phenyl)silyl-2,5-dihydrofuran 48

Titanium tetrachloride (1.0 mol dm^{-3} in CH_2Cl_2, 0.14 cm^3, 0.14 mmol) was added to a solution of isobutyraldehyde (20 mg, 0.025 cm^3, 0.28 mmol) in dry dichloromethane (1 cm^3) at −78 °C under argon. The mixture was stirred at −78 °C for 5 min and a solution of the propargylsilane[57] **47** (70 mg, 0.28 mmol) in dry dichloromethane (0.75 cm^3) was added, and the mixture stirred at −78 °C for 15 min, warmed to 0 °C and stirred for 1.5 h, warmed to room temperature and stirred overnight. The mixture was quenched with saturated aqueous sodium hydrogencarbonate (5 cm^3), and the aqueous layer was extracted with dichloromethane (3 × 5 cm^3). The combined organic extracts were washed with brine (20 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure. The crude product was chromatographed (SiO_2, light petroleum–CH_2Cl_2, 8 : 2) to give the *dihydrofuran* 47 (23 mg, 26%) as a mixture of diastereoisomers (1.8 : 1, ^{1}H NMR); R_f(light petroleum–Et_2O, 9 : 1) 0.38; ν_{max}(film)/cm^{-1} 1646 (C=C), 1252 (SiMe), 1111 (SiPh) and 1088 (C-O); δ_H(500 MHz; $CDCl_3$) major isomer: 7.35–7.10 (10 H, m, 2 × Ph), 6.16 (1 H, dd, *J* 2.3 and 1.3, C=CH), 5.64 (1 H, dd, *J* 4.8 and 2.3, PhC*H*O), 4.54–4.52 (1 H, m, OC*H*CH), 1.88–1.75 (1 H, m, C*H*Me$_2$), 1.02–0.92 (6 H, m, CH*Me*$_2$), 0.12 (3 H, s, Si*Me*$_A$Me$_B$) and −0.02 (3 H, s, SiMe$_A$-*Me*$_B$); Minor isomer: 7.35–7.10 (10 H, m, 2 × Ph), 6.10 (1 H, dd, *J* 2.1 and 1.4, C=CH), 5.72 (1 H, dd, *J* 5.8 and 2.1, PhC*H*O), 4.93–4.90 (1 H, m, OC*H*CH), 1.88–1.75 (1 H, m, C*H*Me$_2$), 1.02–0.92 (6 H, m, CH*Me*$_2$), 0.14 (3 H, s, Si*Me*$_A$Me$_B$) and −0.01 (3 H, s, SiMe$_A$*Me*$_B$); δ_C(500 MHz; $CDCl_3$) 143.3+, 143.2+, 142.2+, 141.8+, 140.7−, 139.7−, 137.2+, 137.1+, 133.8−, 133.7−, 129.1−, 129.0−, 128.3−, 128.2−, 128.1−, 127.9−, 127.8−, 127.7−, 127.3−, 92.9−, 92.8−, 92.7−, 92.2−, 33.8−, 33.6−, 19.3−, 19.2−, 18.9−, 18.8−, −2.6−, −2.7−, −3.1− and −3.2−; *m/z* (EI) 322 (36%, M^+), 307 (15, M − Me), 279 (77, M − C_3H_7) and 135 (100, SiMe$_2$Ph) (Found: M^+, 322.1752. $C_{21}H_{26}OSi$ requires *M*, 322.1753).

(1*RS*)-1-Dimethyl(phenyl)silyl-1-phenylbut-2-yne 49

A solution of LDA (15.6 mmol) was added dropwise to (3*RS*)-3-dimethyl(phenyl)silyl-3-phenylprop-1-enyl trifluoromethanesulfonate[57] (2.60 g, 6.49 mmol) in dry THF (65 cm^3) and the mixture was allowed to stir at 0 °C for 2 h. Methyl iodide (18.5 g, 8.1 cm^3, 0.13 mol) was added and the mixture was stirred at room temperature for 30 min. The mixture was washed with dilute aqueous hydrochloric acid (3 mol dm^{-3}, 80 cm^3), water (2 × 80 cm^3), brine (110 cm^3), dried ($MgSO_4$) and the solvent evaporated under reduced pressure. The crude product was chromatographed (SiO_2, light petroleum–CH_2Cl_2, 95 : 5) to give the *alkyne* (318 mg, 19%); R_f(light petroleum–CH_2Cl_2, 9 : 1) 0.16; ν_{max}(film)/cm^{-1} 2153 (C≡C), 1597 (Ph), 1248 (SiMe) and 1115 (SiPh); δ_H(250 MHz; $CDCl_3$) 7.70–7.02 (10 H, m, 2 × Ph), 3.28 (1 H, q, *J* 2.6, CHSi), 1.90 (3 H, d, *J* 2.6, C≡CMe), 0.39 (3 H, s, Si*Me*$_A$Me$_B$) and 0.29 (3 H, s, SiMe$_A$*Me*$_B$); δ_C(500 MHz; $CDCl_3$) 142.1+, 139.4+, 135.0−, 134.3−, 133.7−, 127.9−, 127.4−, 127.2−, 85.7+, 78.5+, 29.1−, 22.0−, −4.9− and −5.0−; *m/z* (EI) 264 (12%, M^+), 249 (32, M – Me) and 135 (83, SiMe$_2$Ph) (Found: M^+, 264.1328. $C_{18}H_{20}Si$ requires *M*, 264.1334), together with *(4RS)-4-dimethyl(phenyl)silyl-4-phenylpent-2-yne* (398 mg, 22%); R_f(light petroleum–CH_2Cl_2, 9 : 1) 0.28; ν_{max}(film)/cm^{-1} 2193 (C≡C), 1597 (Ph), 1248 (SiMe) and 1112 (SiPh); δ_H(250 MHz; $CDCl_3$) 7.68–7.04 (10 H, m, 2 × Ph), 1.96 (3 H, s, C≡CMe), 1.58 (3 H, s, SiCMe), 0.37 (3 H, s, Si*Me*$_A$Me$_B$) and 0.28 (3 H, s, SiMe$_A$*Me*$_B$); δ_C(500 MHz; $CDCl_3$) 143.4+, 135.7+, 135.0−, 129.2−, 127.5−, 127.2−, 126.6−, 124.9−, 83.7+, 79.2+, 29.9+, 22.4−, 3.8−, −5.5− and −5.8−; *m/z* (EI) 278 (20%, M^+), 263 (10, M − Me) and 135 (70, SiMe$_2$Ph) (Found: M^+, 278.1481. $C_{19}H_{22}Si$ requires *M*, 278.1491), and *4-dimethyl(phenyl)silyl-4-phenylbuta-2,3-diene* (144 mg, 8.4%); R_f(light petroleum–CH_2Cl_2, 9 : 1) 0.38; ν_{max}(film)/cm^{-1} 1926 (C=C=C), 1596 (Ph), 1249 (SiMe) and 1112 (SiPh); δ_H(250 MHz; $CDCl_3$) 7.65–7.17 (10 H, m, 2 × Ph), 5.22 (1 H, q, *J* 7.0, C=C=C*H*Me), 1.78 (3 H, d, *J* 7.0, C=C=CH*Me*) and 0.49 (6 H, s, SiMe$_2$); δ_C(500 MHz; $CDCl_3$) 210.7+, 138.7+, 137.6+, 133.9−, 133.0−, 129.1−, 128.3−, 127.9−, 126.0−, 97.9+, 82.2−, 13.5−, −1.6− and −1.8−; *m/z* (EI) 264 (25%, M^+) and 135 (64, SiMe$_2$Ph) (Found: M^+, 264.1337. $C_{18}H_{20}Si$ requires *M*, 264.1334).

4-Methyl-2-phenyl-5-(2-methylethyl)-3-dimethyl(phenyl)silyl-2,5-dihydrofuran 50a

Titanium tetrachloride (1.0 mol dm^{-3} in CH_2Cl_2, 0.19 cm^3, 0.19 mmol) was added to isobutyraldehyde (27 mg, 0.03 cm^3, 0.38 mmol) in dry dichloromethane (1.5 cm^3) at −78 °C under argon. The mixture was stirred at −78 °C for 5 min and a solution of the propargylsilane **49** (100 mg, 0.38 mmol) in dry dichloromethane (1 cm^3) was added. The mixture was stirred at −78 °C for 1 h, warmed to 0 °C and stirred for 2 h, and warmed to room temperature and stirred for 30 min. The reaction was quenched with saturated aqueous sodium hydrogencarbonate (5 cm^3) and the aqueous layer was extracted with dichloromethane (3 × 5 cm^3). The combined organic extracts were washed with brine (20 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure. The crude product was chromatographed (SiO_2, light petroleum–Et_2O, 9 : 1) to give the *dihydrofuran* (14 mg, 11%) as an oil; R_f(light petroleum–Et_2O, 8 : 2) 0.47; ν_{max}(film)/cm^{-1} 1623 (C=C), 1258 (SiMe), 1109 (SiPh) and 1090 (C-O); δ_H(400 MHz; $CDCl_3$) 7.39 (10 H, m, 2 Ph), 5.65 (1 H, dq, *J* 4.8 and 2.1, PhCHO), 4.85–4.57 (1 H, m, OC*H*CH), 1.95 (1 H, sepd, *J* 6.9 and 2.4, C*H*Me$_2$), 1.68–1.67 (3 H, m, C=CMe), 1.02 (3 H, d, *J* 6.9, CH*Me*$_A$Me$_B$), 0.86 (3 H, d, *J* 6.9, CHMe$_A$*Me*$_B$), 0.16 (3 H, s, Si*Me*$_A$Me$_B$) and 0.02 (3 H, s, SiMe$_A$-*Me*$_B$); δ_C(500 MHz; $CDCl_3$) 151.0+, 142.0+, 138.4+, 133.7−, 132.6+, 129.0−, 128.8−, 128.0−, 127.9−, 127.7−, 93.6−, 92.1−, 30.2−, 20.1−, 15.9−, 13.5−, −1.7− and −1.8−; *m/z* (ESI) 359 (68%, MNa^+) and 316 (100, MNa − C_3H_7) (Found: M + Na^+, 359.1797. $C_{22}H_{28}OSi$ requires *M* + Na, 359.1807).

4-Methyl-2-phenyl-5-(2,4-dinitrophenyl)-3-dimethyl(phenyl)silyl-2,5-dihydrofuran 50b

Similarly, 2,4-dinitrobenzaldehyde (74 mg, 0.38 mmol) and the propargylsilane **49** (60 mg, 0.23 mmol) gave the *dihydrofuran* (19 mg, 18%) as a mixture of diastereoisomers (9.3 : 1, ^{1}H NMR); R_f(light petroleum–Et_2O, 8 : 2) 0.37; ν_{max}($CDCl_3$)/cm^{-1} 1606 (Ph), 1538 and 1348 ($ArNO_2$), 1259 (SiMe) and 1112 (SiPh); δ_H(500 MHz; $CDCl_3$) major isomer: 8.76 (1 H, d, *J* 2.0,

ArH), 8.37 (1 H, dd, *J* 8.7 and 2.0, ArH), 7.90 (1 H, d, *J* 8.7, ArH), 7.37–7.18 (10 H, m, 2 × Ph), 6.42 (1 H, d, *J* 4.0, PhCHO), 5.88 (1 H, br s, ArCHO), 1.61 (3 H, br s, C=CMe), 0.25 (3 H, s, Si*Me*$_A$Me$_B$) and 0.14 (3 H, s, SiMe$_A$*Me*$_B$); minor isomer: 8.73 (1 H, d, *J* 2.0, ArH), 8.47 (1 H, dd, *J* 8.7 and 2.0, ArH), 7.84 (1 H, d, *J* 8.7, ArH), 7.37–7.18 (10 H, m, 2 × Ph), 6.52 (1 H, d, *J* 5.0, PhCHO), 6.06 (1 H, br s, ArCHO), 1.65 (3 H, br s, C=CMe), 0.32 (3 H, s, Si*Me*$_A$Me$_B$) and 0.17 (3 H, s, SiMe$_A$*Me*$_B$); δ_C(500 MHz; $CDCl_3$) 149.3+, 148.5+, 147.0+, 143.0+, 140.5+, 136.9+, 134.7+, 133.7−, 131.7−, 129.3−, 128.8−, 128.7−, 127.9−, 127.3−, 119.8−, 95.7−, 93.9−, 86.2−, 85.4−, 13.9−, 13.4−, −1.9−, −2.1−, −2.2− and −2.3−; *m*/*z* (ESI) 483 (100%, MNa^+) (Found: M + Na^+, 483.1351. $C_{25}H_{24}N_2O_5Si$ requires *M* + Na, 483.1352).

2-Chloro-5-(2-Chloroethoxy)-6-methyl-3-dimethyl(phenyl)-silylhept-3-ene 51 and 2-methyl-3-dimethyl(phenyl)silyl-5-(2-methylpropyl)-2,5-dihydrofuran 52

Boron trifluoride-diethyletherate (0.01 cm^3, 0.13 mmol) was added to isobutyraldehyde di-(2-chloroethyl) acetal[80] (54 mg, 0.25 mmol) in dry dichloromethane (1 cm^3) at −78 °C under argon. The mixture was stirred at −78 °C for 5 min and a solution of (3*RS*)-3-dimethyl(phenyl)silylbutyne[57] **53** (47 mg, 0.25 mmol) in dichloromethane (0.5 cm^3) was added. The mixture was stirred at −78 °C for 10 min, warmed to 0 °C and stirred for 1 h. Saturated aqueous sodium hydrogencarbonate (3 cm^3) was added and the mixture was stirred at room temperature for 30 min. The aqueous layer was extracted with dichloromethane (3 × 3 cm^3) and the combined organic extracts were washed with brine (10 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure. Chromatography (SiO_2, light petroleum–Et_2O, 99 : 1) gave the *dihydrofuran* **52** (11 mg, 17%) as a single diastereoisomer; R_f(light petroleum–Et_2O, 9 : 1) 0.44; ν_{max}($CDCl_3$)/cm^{-1} 1600 (Ph), 1252 (SiMe), 1112 (SiPh) and 833 (SiMe); δ_H(400 MHz; $CDCl_3$) 7.53–7.50 (2 H, m, Ph), 7.39–7.33 (3 H, m, Ph), 5.97 (1 H, br s, SiC=CH), 4.94 (1 H, qdd, *J* 6.4, 4.1 and 2.2, MeC*H*O), 4.55 (1 H, ddd, *J* 5.4, 4.1 and 1.4, OC*H*CH), 1.73 (1 H, sepd, *J* 6.8 and 5.4, C*H*Me$_2$), 1.17 (3 H, d, *J* 6.4, *Me*CHO), 0.92 (3 H, d, *J* 6.8, CH*Me*$_A$Me$_B$), 0.90 (3 H, d, *J* 6.8, CHMe$_A$*Me*$_B$), 0.41 (3 H, s, Si*Me*$_A$Me$_B$) and 0.39 (3 H, s, SiMe$_A$-*Me*$_B$); δ_C(500 MHz; $CDCl_3$) 143.5+, 139.9−, 137.5+, 133.8−, 129.2−, 127.8−, 91.9−, 86.0−, 33.1−, 23.0−, 18.4−, 18.3−, −2.2− and −2.7−, and the *ether* **51** (18 mg, 20%) as a mixture of diastereoisomers (1.8 : 1, ^{1}H NMR); R_f(light petroleum–Et_2O, 98 : 2) 0.21; ν_{max}(film)/cm^{-1} 1603 (Ph), 1251 (SiMe) and 1111 (SiPh); δ_H(500 MHz; $CDCl_3$) 7.58–7.48 (4 H, m, Ph), 7.35–7.34 (6 H, m, Ph), 5.64 (2 H, d, *J* 9.0, 2 × SiC=CH), 5.16–5.10 (2 H, m, 2 × MeC*H*Cl), 3.92 (1 H, dd, *J* 9.0 and 6.9, C*H*OR major), 3.92–3.87 (1 H, m, C*H*OR), 3.70–3.48 (8 H, m, 2 × OCH_2CH_2Cl), 1.78–1.62 (2 H, m, 2 × C*H*Me$_2$), 1.53 (3 H, d, *J* 6.9, *Me*CHCl major), 1.51 (3 H, d, *J* 6.9, *Me*CHCl minor), 0.96 (3 H, d, *J* 6.7, CH*Me*$_A$Me$_B$ major), 0.95 (3 H, d, *J* 6.6, CH*Me*$_A$Me$_B$ minor), 0.86 (3 H, d, *J* 6.9, CHMe$_A$*Me*$_B$ major), 0.80 (3 H, d, *J* 6.9, CHMe$_A$*Me*$_B$ minor), 0.55 (3 H, s, Si*Me*$_A$Me$_B$ minor), 0.54 (3 H, s, Si*Me*$_A$Me$_B$ major) and 0.49 (6 H, s, 2 × SiMe$_A$*Me*$_B$); δ_C(500 MHz; $CDCl_3$) 145.6+, 145.5+, 143.8−, 143.6−, 138.7+, 138.6+, 134.0−, 133.9−, 129.1−, 127.8−, 80.7−, 80.3−, 69.0+, 68.9+, 56.6−, 56.5−, 43.2+, 43.0+, 32.9−, 32.8−, 26.0−, 25.5−, 18.6−, 18.5−, 18.4−, 18.3−, −0.4−, −0.5−, −0.6− and −0.7−; *m*/*z* (ESI) 385 (5%, MNa^+), 383 (9, MNa^+), 381 (10, MNa^+), 345 (100, M – Cl) and 316 (26, M – C_2H_4Cl) (Found: M + Na^+, 381.1177. $C_{18}H_{28}Cl_2OSi$ requires *M* + Na, 381.1184).

4-Chloro-6-methyl-3-dimethyl(phenyl)silylhept-2-en-5-ol 54 and 2-chloro-6-methyl-3-dimethyl(phenyl)silylhept-3-en-5-ol 55

Isobutyraldehyde (38 mg, 0.05 cm^3, 0.53 mmol) in dry dichloromethane (1.25 cm^3) under argon was cooled to −78 °C. Titanium tetrachloride (1.0 mol dm^{-3} in CH_2Cl_2, 0.27 cm^3, 0.27 mmol) was added and the mixture was stirred at −78 °C for 5 min. A solution of propargylsilane[57] **53** (100 mg, 0.53 mmol) in dry dichloromethane (0.5 cm^3) was added. The mixture was stirred at −78 °C for 2 h, warmed to −20 °C and stirred at −20 °C for 18 h. Saturated aqueous sodium hydrogen carbonate (5 cm^3) was added and the mixture was stirred at room temperature for 30 min. The aqueous phase was extracted with ether (3 × 5 cm^3) and the combined organic extracts were dried ($MgSO_4$) and evaporated under reduced pressure. Column chromatography (SiO_2, light petroleum–Et_2O, 9 : 1) gave the *dihydrofuran* **52** (12 mg, 9%) as a mixture of diastereoisomers (1.3 : 1) the major one of which was identical (^{1}H NMR) with the earlier sample, and the minor gave the following data: δ_H(500 MHz; $CDCl_3$) 7.52–7.48 (4 H, m, 2 × Ph), 7.37–7.32 (6 H, m, 2 × Ph), 5.97–5.95 (2 H, m, 2 × SiC=CH), 5.00–4.95 (1 H, m, MeC*H*O), 4.67 (1 H, td, *J* 5.3 and 1.4, OC*H*CH), 1.78–1.69 (2 H, m, 2 × C*H*Me$_2$), 1.15 (3 H, d, *J* 6.4, *Me*CHO), 0.88 (6 H, d, *J* 6.8, CH*Me*$_2$), 0.40 (6 H, s, 2 × Si*Me*$_A$-Me$_B$) and 0.39 (6 H, s, 2 × SiMe$_A$*Me*$_B$), the *alcohol* **55** (28 mg, 18%) as a single diastereoisomer; R_f(light petroleum–Et_2O, 9 : 1) 0.13; ν_{max}($CDCl_3$)/cm^{-1} 3604 (OH), 1602 (Ph), 1252 (SiMe), 1111 (SiPh) and 836 (SiMe); δ_H(500 MHz; $CDCl_3$) 7.55–7.51 (2 H, m, Ph), 7.36–7.33 (3 H, m, Ph), 5.78 (1 H, dd, *J* 8.9 and 0.5, SiC=CH), 5.16 (1 H, q, *J* 6.9, MeC*H*Cl), 4.31 (1 H, dd, *J* 8.9 and 6.8, C*H*OH), 1.67 (1 H, oct, *J* 6.8, C*H*Me$_2$), 1.51 (3 H, d, *J* 6.9, *Me*CHCl), 0.95 (3 H, d, *J* 6.8, CH*Me*$_A$Me$_B$), 0.85 (3 H, d, *J* 6.8, CHMe$_A$*Me*$_B$), 0.54 (3 H, s, Si*Me*$_A$Me$_B$) and 0.49 (3 H, s, SiMe$_A$*Me*$_B$); δ_C(500 MHz; $CDCl_3$) 145.2−, 143.7+, 138.5+, 134.0−, 129.0−, 127.8−, 72.2−, 56.6−, 34.0−, 25.8−, 18.4−, 17.9−, −0.8− and −0.9−; *m*/*z* (EI) 296 (5%, M^+) and 135 (100, $SiMe_2Ph$) (Found: M^+, 296.1360. $C_{16}H_{25}ClOSi$ requires *M*, 296.1363), and the *alcohol* **54** (22 mg, 14%) as a single diastereoisomer; R_f(light petroleum–Et_2O, 9 : 1) 0.30; ν_{max}($CDCl_3$)/cm^{-1} 3582 (OH), 1601 (Ph), 1260 (SiMe), 1110 (SiPh) and 835 (SiMe); δ_H(500 MHz; $CDCl_3$) 7.55–7.51 (2 H, m, Ph), 7.36–7.32 (3 H, m, Ph), 6.10 (1 H, qd, *J* 6.9 and 0.6, Me*H*C=C), 5.07 (1 H, dd, *J* 8.7 and 0.6, CHCl), 3.53 (1 H, dt, *J* 8.7 and 3.1, C*H*OH), 2.19 (1 H, dd, *J* 3.5 and 0.9, OH), 1.82 (3 H, d, *J* 6.8, *Me*HC=C), 1.60–1.53 (1 H, m, C*H*Me$_2$), 0.78 (3 H, d, *J* 6.8, CH*Me*$_A$Me$_B$), 0.77 (3 H, d, *J* 6.9, CHMe$_A$*Me*$_B$), 0.48 (3 H, s, Si*Me*$_A$Me$_B$) and 0.45 (3 H, s, SiMe$_A$*Me*$_B$); δ_C(500 MHz; $CDCl_3$) 142.1−, 138.8+, 138.5+, 134.1−, 129.0−, 127.7−, 77.2−, 67.6−, 29.9−, 20.5−, 15.3−, 14.8−, −0.3− and −0.4−; *m*/*z* (EI) 253 (10%, M − C_3H_7), 135 (45, $SiMe_2Ph$) and 118 (32, M − $C_{11}H_{18}Si$) (Found: (M − C_3H_7)$^+$, 253.0800. $C_{13}H_{18}ClOSi$ requires *M* − C_3H_7, 253.0815). Other Lewis acids gave similar mixtures of one or more of these three products with titanium tetrachloride giving largely (43%) the dihydrofuran **52**, as a mixture of diastereoisomers (1.2 : 1) having identical signals (^{1}H NMR) with the earlier samples (Found: M^+, 260.1607. $C_{16}H_{24}OSi$ requires *M*, 260.1596).

1-(2,4-dinitrophenyl)-2-trimethylsilylpenta-2,3-dienol 57

2,4-Dinitrobenzaldehyde (0.50 g, 2.52 mmol) in dry dichloromethane (9 cm^3) under argon was cooled to −78 °C. Titanium tetrachloride (1.0 mol dm^{-3} in CH_2Cl_2, 1.25 cm^3, 1.25 mmol) was added and the mixture was stirred at −78 °C for 5 min. A solution of racemic 1,3-bis(trimethylsilyl)butyne[81] **56** (0.50 g, 2.52 mmol) in dry dichloromethane (5 cm^3) was added. The mixture was stirred at −78 °C for 15 min and saturated aqueous sodium hydrogencarbonate (25 cm^3) was added. The mixture was stirred at room temperature for 30 min. The aqueous phase was extracted with ether (3 × 15 cm^3) and the combined organic extracts were dried ($MgSO_4$) and concentrated under reduced pressure. Flash column chromatography (SiO_2, light petroleum–Et_2O, 8 : 2) gave the *allene* (0.61 g, 76%) as a mixture of diastereoisomers (2.2 : 1, ^{1}H NMR); R_f(light petroleum–Et_2O, 9 : 1) 0.05; ν_{max}(film)/cm^{-1} 3422 (OH), 1938 (C=C=C), 1535 and 1346 (Ar–NO_2), 1248 (SiMe) and 841 (SiMe); δ_H(500 MHz;

$CDCl_3$) major isomer: 8.75 (1 H, d, *J* 2.3, ArH), 8.44 (1 H, dd, *J* 8.8 and 2.3, ArH), 8.05 (1 H, d, *J* 8.8, ArH), 6.11 (1 H, br s, C*H*OH), 4.70 (1 H, qd, *J* 7.1 and 2.0, Me*H*C=C=C), 2.29 (1 H, br s, CHO*H*), 1.34 (3 H, d, *J* 7.1, *Me*HC=C=C) and 0.17 (9 H, s, $SiMe_3$); minor isomer: 8.72 (1 H, d, *J* 2.3, ArH), 8.42 (1 H, dd, *J* 8.7 and 2.3, ArH), 8.03 (1 H, d, *J* 8.7, ArH), 6.01 (1 H, br s, C*H*OH), 4.77 (1 H, qd, *J* 7.1 and 2.2, Me*H*C=C=C), 2.39 (1 H, br s, CHO*H*), 1.43 (3 H, d, *J* 7.1, *Me*HC=C=C) and 0.14 (9 H, s, $SiMe_3$); δ_C(500 MHz; $CDCl_3$) 207.2+, 207.1+, 147.7+, 147.4+, 146.9+, 146.7+, 146.3+, 145.8+, 130.0−, 129.9−, 126.9−, 126.7−, 119.9−, 119.7−, 101.0+, 100.9+, 84.1−, 84.0−, 70.0−, 69.7−, 13.0−, 12.7−, −0.8− and −0.9−; *m/z* (ESI) 345 (89%, M + Na^+) (Found: M + Na^+, 345.0894. $C_{14}H_{18}N_2O_5Si$ requires *M* + Na, 345.0883).

1-(2,4-Dinitrophenyl)-2-trimethylsilylpenta-2,3-dienone 58

Following the precedent of Marshall,[82] 1,1,1-triacetoxy-1,1-dihydro-1,2-benziodoxol-3(1*H*)-one (Dess–Martin periodinane) (53 mg, 0.126 mmol) was added to the allenyl alcohols **57** (27 mg, 0.08 mmol) in dry dichloromethane (0.5 cm^3) at room temperature under argon. After 20 min, the mixture was filtered through a pad of silica gel and eluted with dichloromethane (10 cm^3). The organic solvents were evaporated under reduced pressure and the crude product was chromatographed (SiO_2, light petroleum) to give the *ketone* (22 mg, 85%) as an oil; R_f(light petroleum–Et_2O, 9 : 1) 0.18; ν_{max}(film)/cm^{-1} 1928 (C=C=C), 1665 (C=O), 1535 and 1347 ($ArNO_2$), 1248 (SiMe) and 846 (SiMe); δ_H(500 MHz; $CDCl_3$) 8.90 (1 H, d, *J* 2.2, ArH), 8.50 (1 H, dd, *J* 8.4 and 2.2, ArH), 7.56 (1 H, d, *J* 8.4, ArH), 5.01 (1 H, q, *J* 7.4, Me*H*C=C=C), 1.48 (3 H, d, *J* 7.4, *Me*HC=C=C) and 0.27 (9 H, s, $SiMe_3$); δ_C(500 MHz; $CDCl_3$) 218.3+, 193.3+, 147.8+, 146.3+, 142.6+, 129.7−, 128.0−, 119.3−, 104.4+, 84.9−, 12.2− and −1.5−; *m/z* (EI) 320 (92%, M^+), 305 (33, M − Me) and 73 (100, $SiMe_3$) (Found: M^+, 320.0819. $C_{14}H_{16}N_2O_5Si$ requires *M*, 320.0828).

1′-(2,4-Dinitrophenyl)-2′-trimethylsilylpenta-2′,3′-dienyl (2*R*)-2-methoxy-2-phenyl-3,3,3-trifluoropropanoate 59

Following a recipe of Ward's,[83] oxalyl chloride (206 mg, 0.14 cm^3, 1.62 mmol) was added to (*R*)-(+)-Mosher's acid (80 mg, 0.34 mmol) and *N*,*N*-dimethylformamide (DMF) (25 mg, 0.03 cm^3, 0.34 mmol) in hexane (14 cm^3) at room temperature. After 1 h, the mixture was filtered and concentrated. The alcohol **57** (64 mg, 0.22 mmol), triethylamine (103 mg, 0.14 cm^3, 1.02 mmol) and 4-dimethylaminopyridine (42 mg, 0.34 mmol) in dry dichloromethane (2 cm^3) were added, and after 1 h the mixture was filtered through a silica pad, eluting with dichloromethane. The solvent was removed under reduced pressure, and the residue flash column chromatographed (SiO_2, light petroleum–Et_2O, 8 : 2) to give the mixture of four *esters* **59** (99 mg, 84%) in a ratio A : B : C : D of 2 : 2 : 1 : 1; R_f(light petroleum–Et_2O, 8 : 2) 0.45; ν_{max}($CDCl_3$)/cm^{-1} 1940 (C=C=C), 1750 (C=O), 1606 (Ar), 1540 and 1347 ($ArNO_2$), 1262 (SiMe) and 844 (SiMe); δ_C(500 MHz; $CDCl_3$) 211.0+, 210.7+, 165.7+, 165.6+, 165.5+, 147.3+, 147.1+, 147.0+, 146.9+, 141.8+, 141.7+, 131.2+, 131.1+, 129.9−, 129.8−, 129.7+, 129.5−, 128.6−, 128.5−, 127.5−, 127.4−, 126.9−, 126.8−, 126.7−, 120.0−, 119.9−, 97.3+, 97.2+, 97.0+, 84.6−, 84.4−, 72.7−, 72.5−, 55.5−, 55.4−, 12.6−, 12.5−, 12.3−, −1.1−, −1.2−, −1.3− and −1.4−; δ_F(400 MHz; $CDCl_3$) A −70.81, B −70.88, C −70.96 and D −71.03; *m/z* (EI) 538 (10%, M^+), 321 (10, M − $C_{10}H_8F_3O_2$) and 73 (89, $SiMe_3$)(Found: M^+, 538.1383. $C_{24}H_{25}F_3N_2O_7Si$ requires *M*, 538.1383); chromatography allowed the separation of a mixture rich in isomers A and C (2 : 1), which we guessed had the same relative configuration between the carbinol carbon and the stereogenic centre in the Mosher's acid fragment, as later proved to be true, and another rich in the isomers B and D (2 : 1); δ_H(500 MHz; $CDCl_3$) A + C: 8.83 (1 H, d, *J* 2.3, ArH isomer A), 8.82 (1 H, d, *J* 2.3, ArH isomer C), 8.25 (1 H, dd, *J* 8.7 and 2.3, ArH isomer A), 8.24 (1 H, dd, *J* 8.7 and 2.3, ArH isomer C), 7.48–7.36 (12 H, m, ArH and Ph), 7.12 (1 H, d, *J* 1.8, CHO isomer A), 7.08 (1 H, d, *J* 1.8, CHO isomer C), 4.83–4.78 (1 H, m, Me*H*C=C=C isomer C), 4.81 (1 H, qd, *J* 7.1 and 1.8, Me*H*C=C=C isomer A), 3.52 (3 H, s, OMe), 3.51 (3 H, s, OMe), 1.47 (3 H, d, *J* 7.1, *Me*HC=C=C isomer C), 1.29 (3 H, d, *J* 7.1, *Me*HC=C=C isomer A), 0.12 (9 H, s, $SiMe_3$ isomer A) and 0.06 (9 H, s, $SiMe_3$ isomer C); B + D: 8.83 (2 H, d, *J* 2.3, ArH), 8.34 (2 H, dd, *J* 8.7 and 2.3, ArH), 7.61 (1 H, d, *J* 8.7, ArH isomer D), 7.60 (1 H, d, *J* 8.7, ArH isomer B), 7.48–7.36 (10 H, m, 2 × Ph), 7.10 (1 H, d, *J* 1.8, CHO isomer B), 7.06 (1 H, d, *J* 1.8, CHO isomer D), 4.80–4.75 (1 H, m, Me*H*C=C=C isomer D), 4.77 (1 H, qd, *J* 7.1 and 1.8, Me*H*C=C=C isomer B), 3.50 (6 H, s, 2 × OMe), 1.45 (3 H, d, *J* 7.1, *Me*HC=C=C isomer D), 1.30 (3 H, d, *J* 7.1, *Me*HC=C=C isomer B), 0.10 (9 H, s, $SiMe_3$ isomer D) and 0.07 (9 H, s, $SiMe_3$ isomer B).

Ethyl (3*R*)-3-trimethylsilylbutanoate

This was prepared in the same way as the racemic ester using the sultam **13** (5.70 g, 15.9 mmol) to give the enantiomerically enriched ester, which was used in the next reaction without purification; $[a]_D$ +5.5 (*c.* 1.47 in $CHCl_3$).

(3*R*)-3-Trimethylsilylbutanal (*R*)-60

This was prepared in the same way as the racemic aldehyde using the enantiomerically enriched ester (derived from 5.70 g of sultam **13**, 15.9 mmol) to give the enantiomerically enriched aldehyde (*R*)-**60**, which was used in the next step without purification; $[a]_D$ −34 (*c.* 1.28 in $CHCl_3$).

(3*R*)-3-Trimethylsilylbut-1-enyl trifluoromethanesulfonates (*R*)-61

This was prepared in the same way as the racemic enol triflates using the enantiomerically enriched aldehyde (*R*)-**60** to give the enantiomerically enriched *enol triflates* (1.90 g, 43% over 3 steps) (*Z* : *E*, 5.5 : 1); $[a]_D$ −65 (*c.* 1.15 in $CHCl_3$).

(3*R*)-1,3-Bis(trimethylsilyl)butyne (*R*)-62

This was prepared in the same way as the racemic propargylsilane **56** from the enol triflates (*R*)-**60** (1.20 g, 4.34 mmol) giving the alkyne (*R*)-**62** (0.34 g, 40%), identical (TLC, IR, ^{1}H NMR) to the racemic sample; $[a]_D$ −6.2 (*c.* 1.06 in $CHCl_3$).

1-(2,4-Dinitrophenyl)-2-trimethylsilylpenta-2,3-dienols 63–66

These were prepared in the same way as the allenyl alcohol **57** using the enantiomerically enriched propargylsilane (*R*)-**62** (0.20 g, 1.00 mmol) and 2,4-dinitrobenzaldehyde (198 mg, 1.00 mmol) to give the *allenyl alcohols* (0.25 g, 74%) as a mixture of diastereoisomers (2 : 1), identical (TLC, IR, ^{1}H NMR) to the earlier sample; $[a]_D$ −89.3 (*c.* 1.1 in $CHCl_3$).

1′-(2,4-Dinitrophenyl)-2′-trimethylsilylpenta-2′,3′-dienyl (2*R*)-2-methoxy-2-phenyl-3,3,3-trifluoropropanoate 67–70

These were prepared in the same way as the esters **59** using the mixture of allenyl alcohols **63**–**65** to give the *esters* **66**–**70** as a mixture of diastereoisomers A : B : C : D in the ratios 6.3 : 1.7 : 1 : 3, identical (TLC, IR) to the earlier sample, and with appropriate signals in the ^{1}H NMR spectrum.

(2*R*)-4-Trimethylsilylbut-3-yn-2-ol

Following Marshall,[84] (*R*)-Chirald® (16.7 g, 59.2 mmol) in ether (130 cm^3) was added dropwise to a suspension of lithium aluminium hydride (1.01 g, 26.6 mmol) in ether (650 cm^3) at 0 °C under argon. The mixture was cooled to −78 °C and a solution of 4-trimethylsilylbut-3-en-2-one (3.13 g, 22.3 mmol)

in ether (130 cm^3) was added over 2 h. The mixture was stirred at −78 °C for 5 h and quenched with dilute aqueous hydrochloric acid (3 mol dm^{-3}, 430 cm^3). The aqueous layer was extracted with ether (3 × 170 cm^3) and the combined organic extracts were washed with saturated aqueous sodium hydrogencarbonate (500 cm^3), brine (500 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure. Column chromatography (SiO_2, light petroleum–Et_2O, 8 : 2) gave the (*R*)-alcohol (2.73 g, 86%) as an oil identical (TLC, IR, ^1H NMR) with the earlier sample.

(2*R*)-4-Trimethylsilylbut-3-yn-2-yl (1*S*)-camphorsulfonate 71

This was prepared in the same way as its enantiomer **28** from the (*R*)-alcohol (2.00 g, 14.1 mmol) giving the sulfonate (2.61 g, 52%) diastereomerically pure (>99 : 1, ^1H-NMR); mp 67.5 °C; $[a]_D$ +98 (*c.* 1.06 in $CHCl_3$); ν_{max}(Nujol)/cm^{-1} 2178 (C≡C), 1745 (C=O), 1364 (SO_2), 1251 ($SiMe_3$), 1176 (SO_2) and 846 ($SiMe_3$); δ_H(250 MHz; $CDCl_3$) 5.32 (1 H, q, *J* 6.7, C*H*Me), 3.83 (1 H, d, *J* 15.0, $CH_AH_BSO_2$), 3.10 (1 H, d, *J* 15.0, $CH_AH_BSO_2$), 2.60–1.40 (7 H, m), 1.64 (3 H, d, *J* 6.7, *Me*CH), 1.16 (3 H, s, CMe_AMe_B), 0.90 (3 H, s, CMe_AMe_B) and 0.19 (9 H, s, $SiMe_3$).

(1*R*,3*M*)-1-(2,4-Dinitrophenyl)-2-trimethylsilylpenta-2,3-dienol 63

Using the method developed by Marshall,[25] copper(I) chloride (20 mg, 0.20 mmol), trichlorosilane (0.12 cm^3, 1.24 mmol) and diisopropylethylamine (0.22 cm^3, 1.24 mmol) were added successively to the sulfonate ester (0.36 g, 1.00 mmol) in THF (3 cm^3) at room temperature, and the mixture stirred at room temperature for 1 h. THF, DMF and acetonitrile (2 : 1 : 1, 40 cm^3) were added, and the mixture cooled to 0 °C. 2,4-Dinitrobenzaldehyde (0.49 g, 2.50 mmol) in a mixture of THF, DMF and acetonitrile (2 : 1 : 1, 6 cm^3) was added. The mixture was stirred at 0 °C for 5 h and kept at 10 °C overnight. The mixture was quenched with cold water (40 cm^3) and extracted with ether (2 × 40 cm^3). The combined organic extracts were washed with brine (100 cm^3), dried ($MgSO_4$) and concentrated under reduced pressure. Flash column chromatography (SiO_2, light petroleum–Et_2O, 8 : 2) gave the *alkyne* **72** (43 mg, 13%) as a mixture of diastereoisomers (3.5 : 1); R_f(light petroleum–Et_2O, 1 : 1) 0.40; ν_{max}($CDCl_3$)/cm^{-1} 3604 (OH), 2164 (C≡C), 1606 (Ar), 1537 and 1347 ($ArNO_2$), 1251 (SiMe) and 845 (SiMe); δ_H(500 MHz; $CDCl_3$) major isomer: 8.78 (1 H, d, *J* 2.3, ArH), 8.46 (1 H, dd, *J* 8.7 and 2.3, ArH), 8.10 (1 H, d, *J* 8.7, ArH), 5.53 (1 H, d, *J* 6.3, C*H*OH), 2.94 (1 H, qd, *J* 6.9 and 6.3, MeC*H*), 2.68 (1 H, br s, OH), 1.19 (3 H, d, *J* 6.9, *Me*CH) and 0.08 (9 H, s, $SiMe_3$); minor isomer: 8.84 (1 H, d, *J* 2.3, ArH), 8.46–8.43 (1 H, m, ArH), 8.08 (1 H, d, *J* 8.8, ArH), 5.34 (1 H, dd, *J* 6.3 and 3.0, C*H*OH), 3.02 (1 H, qd, *J* 7.1 and 3.0, MeC*H*), 2.72 (1 H, d, *J* 6.3, OH), 1.42 (3 H, d, *J* 7.1, *Me*CH) and 0.14 (9 H, s, $SiMe_3$); δ_C(500 MHz; $CDCl_3$) 148.2+, 147.1+, 143.5+, 130.9−, 130.7−,126.9−, 126.8−, 120.0−, 119.7−, 105.8+, 88.8+, 71.2−, 35.7−, 34.6−, 18.5−, 16.1−, −0.1− and −0.2−; *m*/*z* (EI) 307 (12%, M − Me), 197 (20, M − $C_7H_{13}Si$), 126 (50, $C_7H_{14}Si$) and 73 (93, $SiMe_3$) (Found: (M − Me)$^+$, 307.0749. $C_{13}H_{15}N_2O_5Si$ requires *M* − Me, 307.0750), and the *allenyl alcohols* **63** and **65** (187 mg, 58%) as a mixture of diastereoisomers (93 : 7), identical (TLC, IR) to the earlier mixture of all four diastereoisomers, and with identical signals (^1H NMR) to the isomers hitherto given the labels major and minor, respectively; $[a]_D$ −203 (*c.* 1.13 in $CHCl_3$).

(1′*R*,3′*M*)-1′-(2,4-Dinitrophenyl)-2′-trimethylsilylpenta-2′,3′-dienyl (2*R*)-2-methoxy-2-phenyl-3,3,3-trifluoropropanoate 67

This was prepared in the same way as before, using the allenyl alcohol **63** to give the *esters* **67** and **69** (93 : 7), identical (TLC, IR) to the earlier mixture of all four diastereoisomers, and with identical signals (^1H NMR, ^{19}F NMR) to the isomers hitherto given the labels A and D, respectively.

(1′*R*,3′*M*)-1′-(2,4-Dinitrophenyl)-2′-trimethylsilylpenta-2′,3′-dienyl (2*S*)-2-methoxy-2-phenyl-3,3,3-trifluoropropanoate

This was prepared in the same way as the ester above using the allenyl alcohol **63** (50 mg, 0.16 mmol) and (*S*)-Mosher's acid chloride to give the *ester* (62 mg, 93%) as a mixture of diastereoisomers (93 : 7), identical (TLC, IR) to the earlier mixture of all four diastereoisomers, and with identical signals (^1H NMR) to the isomers hitherto given the labels B and C, respectively.

2-Methyl-4-trimethylsilylhepta-4,5-dien-3-ol

Isobutyraldehyde (0.98 g, 1.2 cm^3, 13.6 mmol) in dry dichloromethane (34 cm^3) under argon was cooled to −78 °C. Titanium tetrachloride (1.0 mol dm^{-3} in CH_2Cl_2, 6.8 cm^3, 6.80 mmol) was added and the mixture was stirred at −78 °C for 5 min. A solution of racemic propargylsilane **56** (2.70 g, 13.6 mmol) in dry dichloromethane (13.6 cm^3) was added. The mixture was stirred at −78 °C for 30 min and saturated aqueous sodium hydrogencarbonate (65 cm^3) was added. The mixture was stirred at room temperature for 30 min. The aqueous phase was extracted with ether (3 × 15 cm^3) and the combined organic extracts were dried ($MgSO_4$) and concentrated under reduced pressure. Flash column chromatography (SiO_2, light petroleum–Et_2O, 94 : 6) gave the *allenes* (1.35 g, 50%) as a mixture of diastereoisomers (2 : 1); R_f(light petroleum–Et_2O, 9 : 1) 0.28; ν_{max}(film)/cm^{-1} 3469 (OH), 1935 (C=C=C), 1248 (SiMe) and 840 (SiMe); δ_H(500 MHz; $CDCl_3$) major isomer: 5.03 (1 H, qd, *J* 7.0 and 2.3, MeC*H*C=C=C), 3.88–3.85 (1 H, m, C*H*OH), 1.80–1.70 (1 H, m, C*H*Me_2), 1.64 (3 H, d, *J* 7.0, *Me*HC=C=C), 0.97 (3 H, d, *J* 6.9, CHMe_AMe_B), 0.88 (3 H, d, *J* 6.7, CHMe_AMe_B) and 0.11 (9 H, s, $SiMe_3$); minor isomer: 4.96 (1 H, qd, *J* 7.0 and 2.2, MeC*H*C=C=C), 3.93–3.88 (1 H, m, C*H*OH), 1.80–1.70 (1 H, m, C*H*Me_2), 1.63 (3 H, d, *J* 7.0, *Me*HC=C=C), 0.96 (3 H, d, *J* 6.8, CHMe_AMe_B), 0.87 (3 H, d, *J* 6.8, CHMe_AMe_B) and 0.11 (9 H, s, $SiMe_3$); δ_C(500 MHz; $CDCl_3$) 205.0+, 204.8+, 101.4+, 101.3+, 83.6−, 83.2−, 75.8−, 75.1−, 33.5−, 33.4−, 20.1−, 19.6−, 15.9−, 15.7−, 13.6−, 13.5−, −0.7− and −0.9−; *m*/*z* (EI) 181 (80%, M − OH) (Found: (M − OH)$^+$, 181.1413. $C_{11}H_{21}Si$ requires *M* − OH, 181.1413).

2′-Methyl-4′-trimethylsilylhepta-4′,5′-dien-3′-yl (2*R*)-2-methoxy-2-phenyl-3,3,3-trifluoropropanoate

These were prepared by the same method as for the esters **59** using (*R*)-(+)-Mosher's acid (36 mg, 0.15 mmol) and the mixture of alcohols (26 mg, 0.13 mmol), and chromatography (SiO_2, light petroleum–Et_2O, 95 : 5) to give the *esters* (37 mg, 68%) as a mixture of diastereoisomers, labelled as A, B, C and D, and correlated later as derived from the alcohols **73**, **76**, **74** and **75**, respectively, in a ratio of 2 : 1 : 2 : 1; R_f(light petroleum–Et_2O, 9 : 1) 0.58; ν_{max}($CDCl_3$)/cm^{-1} 1937 (C=C=C), 1740 (C=O), 1601 (Ph), 1250 (SiMe) and 842 (SiMe); δ_H(500 MHz; $CDCl_3$) A: 7.60–7.34 (5 H, m, Ph), 5.11 (1 H, dd, *J* 6.3 and 1.4, CHO), 4.88 (1 H, qd, *J* 7.1 and 1.4, MeC*H*C=C=C), 3.55 (3 H, s, OMe), 1.91 (1 H, oct, *J* 6.6, C*H*Me_2), 1.61 (3 H, d, *J* 7.1, *Me*HC=C=C), 0.89 (3 H, d, *J* 6.9, CHMe_AMe_B), 0.86 (3 H, d, *J* 6.7, CHMe_AMe_B) and 0.06 (9 H, s, $SiMe_3$); B: 7.60–7.34 (5 H, m, Ph), 5.14 (1 H, dd, *J* 6.1 and 1.3, CHO), 4.94 (1 H, qd, *J* 7.1 and 1.3, MeC*H*C=C=C), 3.57 (3 H, s, OMe), 1.97–1.85 (1 H, m, C*H*Me_2), 1.54 (3 H, d, *J* 7.1, *Me*HC=C=C), 0.88 (3 H, d, *J* 6.7, CHMe_AMe_B), 0.86 (3 H, d, *J* 6.7, CHMe_AMe_B) and 0.10 (9 H, s, $SiMe_3$); C: 7.60–7.34 (5 H, m, Ph), 5.07 (1 H, dd, *J* 6.2 and 1.5, CHO), 4.64 (1 H, qd, *J* 7.1 and 1.5, MeC*H*C=C=C), 3.54 (3 H, s, OMe), 1.92 (1 H, oct, *J* 6.5, C*H*Me_2), 1.54 (3 H, d, *J* 7.1, *Me*HC=C=C), 0.96 (3 H, d, *J* 6.9, CHMe_AMe_B), 0.95 (3 H, d,

J 6.7, $CHMe_AMe_B$) and 0.11 (9 H, s, $SiMe_3$); and D: 7.60–7.34 (5 H, m, Ph), 5.13 (1 H, dd, *J* 6.3 and 1.2, CHO), 4.89 (1 H, qd, *J* 7.1 and 1.2, Me*H*C=C=C), 3.52 (3 H, s, OMe), 1.97–1.85 (1 H, m, C*H*Me_2), 1.44 (3 H, d, *J* 7.1, *Me*HC=C=C), 0.93 (6 H, d, *J* 6.6, CH*Me*$_2$) and 0.08 (9 H, s, $SiMe_3$); δ_C(500 MHz; $CDCl_3$) 208.5+, 208.3+, 165.8+, 132.6+, 132.4+, 129.4−, 129.3−, 128.4−, 128.2−, 128.1−, 128.0−, 127.8−, 127.6−, 96.6+, 96.3+, 84.7+, 84.5+, 84.4+, 84.2+, 82.6−, 82.5−, 80.9−, 80.8−, 55.5−, 55.3−, 32.7−, 32.6−, 32.5−, 32.4−, 19.5−, 19.4−, 17.4−, 17.3−, 13.1−, 13.0−, 1.0−, −0.9− and −1.0−; δ_F(400 MHz; $CDCl_3$) A −71.42, B −71.68, C −71.75, and D −71.86; *m*/*z* (ESI) 437 (100%, MNa^+), 393 (14, MNa − C_3H_8) and 333 (22, MNa − $C_4H_{12}OSi$) (Found: MNa^+, 437.1749. $C_{21}H_{29}F_3O_3SiNa$ requires *MNa*, 437.1736).

2-Methyl-4-trimethylsilylhepta-4,5-dien-3-ol 73–76

These were prepared in two runs in the same way as in the preparation from the racemic propargylsilane, but using the enantiomerically enriched propargylsilane (*R*)-**62** (0.20 g, 1.00 mmol) and isobutyraldehyde (72 mg, 0.09 cm^3, 1.00 mmol) to give the *allenyl alcohols* (102 mg, 51%) as a mixture of diastereoisomers (1.6 : 1), identical (TLC, IR, ^{1}H NMR) to the earlier sample.

2′-Methyl-4′-trimethylsilylhepta-4′,5′-dien-3′-yl (2*R*)-2-methoxy-2-phenyl-3,3,3-trifluoropropanoate

These were prepared in the same way as the esters derived from the racemic propargylsilane, but using the mixture of allenyl alcohols **73**–**76** to give the *esters* as a mixture of diastereoisomers A : B : C : D, 1.2 : 1 : 1.6 : 2.8 from the first run and 1 : 1.9 : 1.1 : 2.3 from the second run, identical (TLC, IR) with the earlier sample, and with matching signals (^{1}H NMR and ^{19}F NMR).

(3*R*,5*M*)-2-Methyl-4-trimethylsilylhepta-4,5-dien-3-ol 73

This was prepared in the same way as the ester **63** from the sulfonate ester **71** (0.36 g, 1.00 mmol) and isobutyraldehyde (0.36 g, 0.45 cm^3, 5.00 mmol) with chromatography (SiO_2, light petroleum, 7 : 3) giving a mixture rich (98 : 2) in the *allenyl alcohol* **73** (18 mg, 9%), identical (TLC, IR, ^{1}H NMR) to the major isomer in the racemic sample.

(3′*R*,5′*M*)-2′-Methyl-4′-trimethylsilylhepta-4′,5′-dien-3′-yl (2*R*)-2-methoxy-2-phenyl-3,3,3-trifluoropropanoate

This was prepared in the same way as the racemic esters using the allenyl alcohol **73** to give the *ester* as a mixture of diastereoisomers, which matched (TLC, IR, ^{1}H NMR and ^{19}F NMR) those labelled A and D (98 : 2).

Acknowledgements

We thank Professor Albert Eschenmoser for several fruitful discussions before we began the work reported here. We thank the Conselleria de Cultura Educació i Ciencia of the Generalitat Valenciana for a grant (SG), the SERC for a maintenance award (MJCB) and Nathalie Maugein for assistance with some of the preparative work. We thank Professor König (Hamburg) for his generous help in measuring the enantiomeric purity of our allenylsilane, Jérôme Bazin for preliminary work on the synthesis of the enantiomerically enriched allenylsilane, Professor Rick Danheiser for steering us towards the successful recipe for that synthesis, and Ken Takaki, Anne Ware and Sarah Archibald for exploratory work on the reaction between the allenylsilane and isobutyraldehyde. We thank the Economic Development Board of Singapore and GlaxoSmithKline for a grant (KLCP) and Dr Valentin Martinez-Barrasa for some exploratory work in the propargylsilane series.

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