A synthesis of enantiomerically enriched propargyl silanes

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Reduction of ethyl 3-methyl-, 3-isopropyl- and 3-*n*-pentyl-3-[dimethyl(phenyl)silyl]propanoates **4** with DIBAL to the aldehydes **5**, enol trifluoromethanesulfonate (triflate) formation using trifluoromethane-sulfonic (triflic) anhydride and 2,6-di-*tert*-butylpyridine, and elimination using LDA, gives the propargyl silanes **8**. The esters **4** could also be prepared enantiomerically enriched (**11**), and the final products are the enantiomerically enriched propargyl (homochiral) silanes **14**.

Introduction

We have already measured accurately the degree to which the stereochemistry of the S_E2' reactions of open chain allyl silanes and allenyl silanes are stereospecifically *anti*. In order to carry out that work, we had to develop methods for the synthesis of allyl silanes and allenyl silanes with a high level of enantiomeric purity.[1,2] Propargyl (prop-2-ynyl) silanes are the one remaining class of three-carbon nucleophiles related to allyl and allenyl silanes that has not been properly studied. There is one report that they react stereospecifically *anti* **1**→**2** (Scheme 1), but that
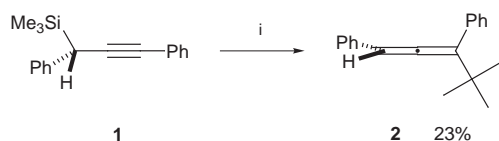
**Scheme 1** *Reagents:* i, Bu^{t}Cl, TiCl$_4$, CH$_2$Cl$_2$, 0 °C, 30 min

pioneering work could not be carried out with a high level of accuracy, because the propargyl silane **1** was only available with a low level of enantiomeric enrichment, and because the enantiomeric purity of the product allene could only be guessed at.[3] In order to complete the trio, we want to re-examine this type of reaction, but using propargyl silanes having a high level of enantiomeric purity. We now report a route to such compounds.

Results and discussion

Synthesis of racemic propargyl silanes

The standard route to propargyl silanes in which the silyl group is on a stereogenic centre is that of Zweifel,[4] where the dianion of a terminal acetylene is doubly silylated, and then the terminal silyl group removed selectively. Unfortunately, this is not suitable for making homochiral prop-2-ynyl silanes unless a chiral base or additive can be found. Not surprisingly, in view of the lack of suitable functionality like an amide or carbamate group, we find that sparteine, everyone's favourite additive, is ineffective, giving propargyl silanes with barely any sign of optical activity, when, as we later found out, the corresponding homochiral propargyl silanes have an easily measured rotation. We turned to a more reliable method, based, as with our synthesis of homochiral allyl silanes,[1] on the conjugate addition of a silyl nucleophile to an α,β-unsaturated carbonyl compound. In this route, the only question is how to convert the CH$_2$CO$_2$Et group in the ester into a triple bond. This is not a well travelled route,[5] but there is a suitable method developed by Stang based on the dehydration of a terminal aldehyde by way of an enol triflate.[6,7]

In the racemic series, we prepared the β-silylated esters **4** from the esters **3** as usual,[8] and reduced them to the aldehydes **5**
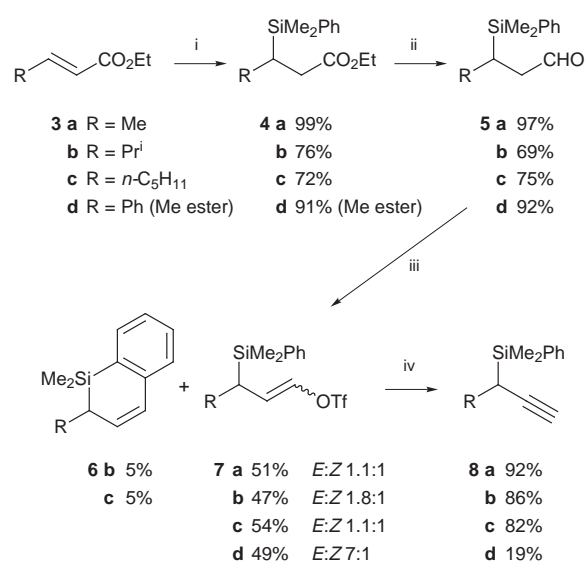
Scheme 2 *Reagents:* i, PhMe$_2$SiZnMe$_2$Li; ii, Bu$^i_2$AlH; iii, Tf$_2$O, 2,6-Bu$^t_2$Py; iv, LDA

(Scheme 2). The enol triflates **7** were best prepared, although only in moderate yield, by using hindered pyridine bases.[9] In two cases, we also isolated minor by-products to which we assign the structures **6**. These are remarkable for the attack on the phenyl ring seems to have taken place *ortho* to the silyl group rather than *ipso* to it. For the final elimination step, Stang used potassium *tert*-butoxide as the base, but we feared that this would remove the silyl group from the product. We therefore used lithium diisopropylamide (LDA), which worked well, giving the propargyl silanes **8a**–**c** in good yields. Although the enol triflates were mixtures of stereoisomers in comparable amounts, the elimination was not affected by the geometry, since it is known to take place by α-elimination and insertion into the neighbouring C–H bond.[7] The only limitation to this route, was with the propargyl silane **8d** that is also a benzyl silane, where we obtained phenylallene as the major product (43%).
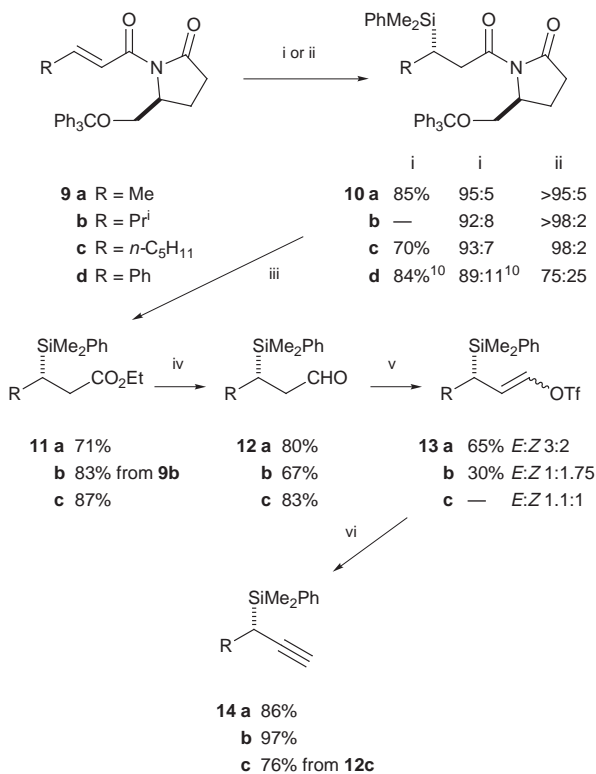
Synthesis of homochiral propargyl silanes

For the synthesis of homochiral propargyl silanes, we carried out the conjugate addition to an α,β-unsaturated carbonyl group attached to Koga's chiral auxiliary **9** to obtain the β-silylated imides **10** with reasonably high levels of diastereo-control in favour of the isomer illustrated (Scheme 3). We knew the imides **10a** and **10b** from our earlier work, and we assumed that the sense of addition in the case of **10c** was the same. We easily measured the ratio of the diastereoisomers from their ^{1}H NMR spectra.[10] The ratio was subtly dependent upon the conditions, falling as the scale of the reaction was

Table 1 Ratios of enantiomers and optical rotations

	Ratio of enantiomers[a]	$[\alpha]_D^{20}$ (c in CH₂Cl₂)		$[\alpha]_D^{20}$ (c in CH₂Cl₂)		$[\alpha]_D^{20}$ (c in CH₂Cl₂)
11a	88:12	0.31 (7.5)	**12a**	43.4 (10.2)	**14a**	6.3 (4.7)
11b	92:8	8.1 (1.8)[b]	**12b**	16.5 (2.1)	**14b**	11.8 (1.1)
11c	93:7	10.2 (2.1)	**12c**	34.0 (1.0)	**14c**	40.8 (1.0)

[a] Measured as a ratio of diastereoisomers in the imides **10**. [b] $[\alpha]_D^{28}$.

		i	i	ii
9 a	R = Me	**10 a** 85%	95:5	>95:5
b	R = Pr^i	**b** —	92:8	>98:2
c	R = n-C₅H₁₁	**c** 70%	93:7	98:2
d	R = Ph	**d** 84%[10]	89:11[10]	75:25

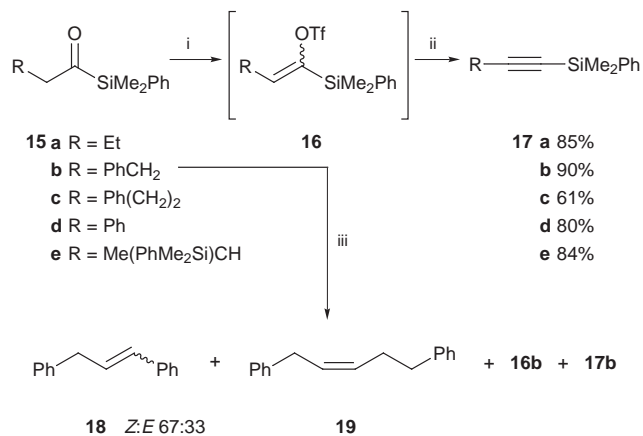| **11 a** 71%	**12 a** 80%	**13 a** 65% E:Z 3:2
b 83% from **9b**	**b** 67%	**b** 30% E:Z 1:1.75
c 87%	**c** 83%	**c** — E:Z 1.1:1

14 a 86%
  b 97%
  c 76% from **12c**

Scheme 3 *Reagents:* i, (PhMe₂Si)₂CuLi, MgBr₂; ii, PhMe₂SiZnMe₂Li; iii, LiOEt, THF; iv, Buⁱ₂AlH; v, Tf₂O, 2,6-Buᵗ₂Py; vi, LDA

increased, and with our best results recorded in Scheme 3. One new development during this work is that we found that the zincate sometimes worked better *without adding magnesium bromide*, our's and Koga's usual Lewis acid for coordinating the two carbonyl groups in the imide **9**. We obtained higher diastereoisomer ratios, from 95:5 up to no detectable (¹H NMR spectroscopy) presence of the diastereoisomer in the imide **10a**, and 98:2 for the imides **10b** and **10c**. With magnesium bromide present, these ratios were 76:24 for **10a**,[8] 92:8 for **10b** and 93:7 for **10c**. The one occasion when this change of protocol did not help, was with the imide **9d**, which gave a worse ratio (75:25) in the absence of magnesium bromide, than in its presence (96:4).[8] We converted the imides **10** into the ethyl esters **11** using lithium ethoxide. It is also possible to carry out the two steps **9**→**10**→**11** in one pot by adding one equivalent of ethanol to the conjugate addition mixture before working it up. If this method is to be used, and it is usually better, an aliquot must be removed, in order to estimate the ratio of diastereoisomers. The remaining steps **11**→**12**→**13**→**14** repeat the reactions in the racemic series with similar yields. The relationship between optical rotations and the ratio of enantiomers is summarised in Table 1, with these results not always our best. This route gives us, in principle, an opportunity to raise the enantiomeric purity of our intermediates before we set up the triple bond, just as it did when we made an allyl silane,[1] but we have not yet put this into practice.

Synthesis of ethynyl silanes
We have also developed a route to propargyl silanes that are

also ethynyl silanes (**17e**) so far only racemic, by carrying out a similar dehydration of the acyl silane **15e** by way of its enol triflate **16e** (Scheme 4). In developing this route, we first tried it

15 a R = Et	**16**	**17 a** 85%
b R = PhCH₂		**b** 90%
c R = Ph(CH₂)₂		**c** 61%
d R = Ph		**d** 80%
e R = Me(PhMe₂Si)CH		**e** 84%

18 Z:E 67:33   **19**   + **16b** + **17b**

Scheme 4 *Reagents:* i, Tf₂O, Py, −78 ⟶ 20 °C; ii, Py, 60 °C; iii, Tf₂O, CH₂Cl₂

on a few simple acyl silanes **15a**–**d** and observed that the enol triflates **16** were difficult to isolate free of the ethynyl silanes **17**, presumably formed this time with great ease by an E2 mechanism. It was easier not to try to isolate the enol triflates, but to complete the elimination, which required only warm pyridine rather than LDA. The ease of the elimination resembles our discovery that 1,1-disilylated alcohols also undergo exceptionally easy dehydration.[11] In an attempt to avoid this event, we treated the acyl silane **15b** with triflic anhydride in the absence of base, and detected unexpected by-products, which proved to be the alkenes **18** and **19**.

The signals in the ¹H NMR spectrum of the mixture were definitive for the former, and matched known values. Although the signals of the latter were almost definitive, we prepared an authentic sample of both geometries Z-**19** and E-**19**, in order to assign geometry (Scheme 5). The Z-isomer proved to have

20   **21**

22   **24**

23

Z-**19**   E-**19**
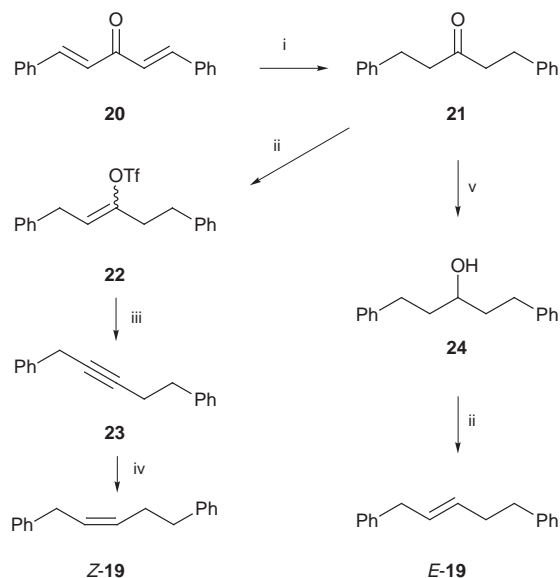
Scheme 5 *Reagents:* i, H₂, PtO₂; ii, 2,6-Buᵗ₂Py, Tf₂O; iii, Py, reflux; iv, H₂, Lindlar; v, LiAlH₄

signals identical with those seen in the ¹H NMR spectrum of the product mixture.

The most reasonable pathways for the formation of the alkenes **18** and Z-**19** are shown in Scheme 6. The migration of the phenyl group from silicon to the carbonyl group of an acyl silane **25**→**26** has precedent,[12] and the remaining steps giving
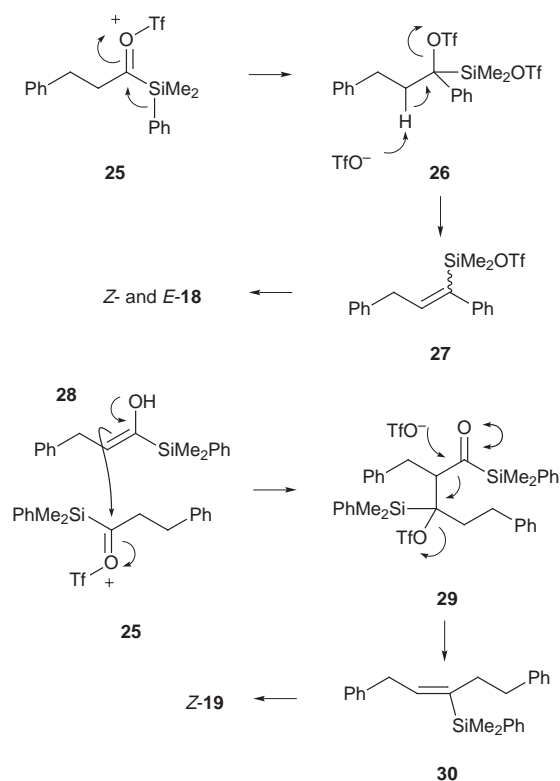
Scheme 6

the alkenes **18** from the vinyl silanes **27** are unremarkable. The formation of the alkene *Z*-**19** is more intriguing, but presumably takes place by an aldol-like reaction **28** + **25**→**29** followed by a decarbonylative elimination giving a vinyl silane **30**. If this is formed predominantly as the thermodynamically favoured *E*-isomer, protodesilylation with the usual retention of configuration explains the formation of the *cis*-alkene *Z*-**19**.

Experimental

Light petroleum refers to the fraction bp 40–60 °C and ether refers to diethyl ether. The positive and negative signs following each ^{13}C NMR value indicate the direction of the peak on the APT spectrum, the positive being on the same side as the solvent. The frequency quoted for the machine is that used for proton spectroscopy. *J* Values are given in Hz.

Preparation of α,β-unsaturated esters 3

Following Wadsworth and Emmons,[13] triethyl phosphonoacetate (23.7 g, 0.104 mol) was stirred with sodium hydride (3.72 g, 80% dispersion in oil, washed in hexane, 0.124 mol) in ether (30 cm³) under argon at 0 °C for 90 min. Freshly distilled aldehyde (0.104 mol) was added and the resulting gel left for 24 h at room temperature. The mixture was quenched with water (60 cm³), the aqueous layer was extracted with ether (3 × 50 cm³) and the combined organic extracts washed with brine (100 cm³), dried (MgSO₄), concentrated under reduced pressure and distilled. The following esters were prepared by this method.

Ethyl 4-methylpent-2-enoate[14] 3b (73%) from isobutyraldehyde. Bp 62–64 °C at 17 mmHg (lit.,[15] 77–79 °C at 20 mmHg); R_f (Et₂O–light petroleum, 3:7) 0.23; ν_{max}(film)/cm^{-1} 1724 (C=O) and 1653 (C=C); δ_H(250 MHz; CDCl₃) 6.93 (1 H, dd, *J* 15.8 and 6.6, Me₂CHC*H*=CH), 5.78 (1 H, dd, *J* 15.8 and 1.5, CH=C*H*CO), 4.18 (2 H, q, *J* 7.2, CO₂C*H*₂Me), 2.44 (1 H, octet d, *J* 6.8 and 1.5, Me₂C*H*), 1.28 (3 H, t, *J* 7.2, CO₂CH₂*Me*) and 1.06 (6 H, d, *J* 6.8, *Me*₂CH).

Ethyl oct-2-enoate[15] 3c (52%) from hexanal. Bp 67–69 °C at 15 mmHg (lit.,[16] 77–79 °C at 20 mmHg); R_f (Et₂O–light petroleum, 1:9) 0.43; ν_{max}(film)/cm^{-1} 1723 (C=O) and 1654 (C=C);

δ_H(250 MHz; CDCl₃) 6.94 (1 H, dt, *J* 15.6 and 7.0, CH₂-C*H*=CH), 5.77 (1 H, dt, *J* 15.6 and 1.5, CH₂CH=C*H*CO), 4.14 (2 H, q, *J* 7.2, OC*H*₂Me), 2.17 (2 H, qd, *J* 7.0 and 1.5, CH₂C*H*₂CH=CH), 1.65–1.2 [8 H, m, (CH₂)₄], 1.24 (3 H, t, *J* 7.1, OCH₂*Me*) and 0.85 [3 H, t, *J* 6.8, *Me*(CH₂)₄]; δ_C(250 MHz; CDCl₃) 178.6+, 149.4−, 121.2−, 60.0+, 32.1+, 31.2+, 27.6+, 22.4+, 14.2− and 13.8−.

Preparation of silylated esters 4

Following the method of Crump,[8] dimethyl(phenyl)silyllithium[16] (1.28 mol dm^{-3} in THF, 23.4 cm³, 30 mmol) was stirred with dimethylzinc (2 mol dm^{-3} in THF, 14 cm³, 28 mmol) in THF (20 cm³) at 0 °C under argon for 20 min and then cooled to −78 °C. The ester (2.33 g, 20 mmol) in THF (15 cm³) was added by cannula over 10 min and the mixture was stirred at this temperature for 2 h. The mixture was quenched at −78 °C with saturated aqueous ammonium chloride (20 cm³) and allowed to warm to room temperature. Hydrochloric acid (3 mol dm^{-3}, 80 cm³) was added and the aqueous layer extracted with ether (3 × 30 cm³). The combined organic extracts were washed with brine (80 cm³), dried (MgSO₄), evaporated under reduced pressure, and the residue chromatographed (SiO₂, Et₂O–light petroleum, 1:9). The following esters were prepared by this method.

Ethyl (3*RS*)-3-[dimethyl(phenyl)silyl]butanoate[17] 4a (92%) from ethyl crotonate 3a. R_f (Et₂O–light petroleum, 6:94) 0.27; ν_{max}(film)/cm^{-1} 1734 (C=O), 1250 (SiMe) and 1112 (SiPh); δ_H(250 MHz; CDCl₃) 7.55–7.45 (2 H, m, Ph), 7.40–7.36 (3 H, m, Ph), 4.10 (2 H, q, *J* 7.1, OC*H*₂Me), 2.36 (1 H, dd, *J* 15.2 and 4.1, C*H*ₐH_BCO), 2.05 (1 H, dd, *J* 15.2 and 11.2, CHₐ*H*_BCO), 1.45 (1 H, m, CHSi), 1.20 (3 H, t, *J* 7.1, OCH₂*Me*), 0.98 (3 H, d, *J* 7.3, *Me*CHSi) and 0.29 (6 H, s, SiMe₂); δ_C(250 MHz; CDCl₃) 174.0+, 134.4+, 133.9−, 129.1−, 127.8−, 60.2+, 36.9+, 16.5−, 14.5−, 14.3− , −5.01− and −5.31−.

Ethyl (3*RS*)-3-dimethyl(phenyl)silyl-4-methylpentanoate[17] 4b (76%) from 3b. R_f (Et₂O–light petroleum, 6:94) 0.31; ν_{max}(film)/cm^{-1} 1732 (C=O), 1250 (SiMe) and 1111 (SiPh); δ_H(250 MHz; CDCl₃) 7.5–7.48 (2 H, m, Ph), 7.38–7.35 (3 H, m, Ph), 4.0 (2 H, q, *J* 7.2, OC*H*₂Me), 2.35 (1 H, dd, *J* 15.9 and 7.7, C*H*ₐH_BCO), 2.28 (1 H, dd, *J* 15.9 and 6.2, CHₐ*H*_BCO), 1.92 (1 H, septet d, *J* 6.9 and 3.9, Me₂C*H*), 1.52 (1 H, m, CHSi), 1.20 (3 H, t, *J* 7.2, OCH₂*Me*), 0.90 (3 H, d, *J* 6.9, *Me*ₐMe_BCH), 0.82 (3 H, d, *J* 6.9, Meₐ*Me*_BCH), 0.34 (3 H, s, Si*Me*ₐMe_B) and 0.33 (3 H, s, SiMeₐ*Me*_B); δ_C(250 MHz; CDCl₃) 174.7+, 138.8+, 133.9−, 128.9−, 127.7−, 60.3+, 31.8+, 29.1−, 28.8−, 22.8−, 20.9−, 14.2−, −2.5− and −3.0−.

Ethyl (3*RS*)-3-[dimethyl(phenyl)silyl]octanoate 4c (72%) from 3c. R_f (Et₂O–light petroleum, 6:94) 0.36; ν_{max}(film)/cm^{-1} 1734 (C=O), 1589 (Ph), 1249 (SiMe) and 1112 (SiPh); δ_H(400 MHz; CDCl₃) 7.52–7.47 (2 H, m, Ph), 7.35–7.32 (3 H, m, Ph), 4.03 (2 H, q, *J* 7.1, OC*H*₂Me), 2.32 (1 H, dd, *J* 15.6 and 5.2, C*H*ₐH_BCO), 2.19 (1 H, dd, *J* 15.6 and 8.5, CHₐ*H*_BCO), 1.5–1.1 [9 H, m, CHSi and (CH₂)₄], 1.21 (3 H, t, *J* 7.1, OCH₂*Me*), 0.83 (3 H, t, *J* 7.0, *Me*CH₂), 0.280 (3 H, s, Si*Me*ₐMe_B) and 0.276 (3 H, s, SiMeₐ*Me*_B); δ_C(400 MHz; CDCl₃) 174.3+, 138.0+, 134.0−, 129.0−, 127.7−, 60.2+, 35.1+, 32.0+, 30.2+, 28.5+, 22.5+, 21.9−, 14.2−, 14.0−, −4.1− and −4.3−; *m/z* (+EI) 306 (20%, M$^+$), 291 (30, M − Me) and 135 (100, SiMe₂Ph) (Found: M$^+$, 306.2015. C₁₈H₃₀O₂Si requires *M*, 306.2050).

Methyl (3*RS*)-3-dimethyl(phenyl)silyl-3-phenylpropanoate[18] 4d (91%) from methyl cinnamate 3d. R_f (Et₂O–light petroleum, 6:94) 0.24; ν_{max}(film)/cm^{-1} 1740 (C=O), 1250 (SiMe) and 1113 (SiPh); δ_H(250 MHz; CDCl₃) 7.4–7.3 (2 H, m, Ph), 7.25–7.1 (6 H, m, Ph), 7.0–6.9 (2 H, m, Ph), 3.5 (3 H, s, OMe), 2.86 (1 H, dd, *J* 4.5 and 10.6, CHSi), 2.76 (1 H, dd, *J* 14.9 and 10.6, C*H*ₐH_BCO), 2.66 (1 H, dd, *J* 14.9 and 4.5, CHₐ*H*_BCO), 0.26 (3 H, s, Si*Me*ₐMe_B) and 0.22 (3 H, s, SiMeₐ*Me*_B); δ_C(250 MHz; CDCl₃) 173.4+, 141.8+, 136.5+, 134.1−, 129.3−, 128.1−, 127.4−, 127.5−, 125.0−, 51.5−, 34.7+, 32.2−, −4.1− and −5.5−.

Preparation of the aldehydes 5

Diisobutylaluminium hydride (1.0 mol dm^{-3} solution in hexanes, 18.0 cm^3, 18.0 mmol) in toluene (25 cm^3) was added dropwise over 40 min to a stirred solution of the ester (15 mmol) in toluene (40 cm^3) at -78 °C under argon. The mixture was stirred for 2 h, quenched with methanol (30 cm^3) and allowed to warm to room temperature. The mixture was washed with saturated aqueous potassium sodium tartrate (50 cm^3). The aqueous layer was further extracted with ether (3 × 40 cm^3) and the combined organic fractions were washed with brine (100 cm^3), dried (MgSO$_4$) and evaporated under reduced pressure. The residue was chromatographed (SiO$_2$, Et$_2$O–light petroleum, 6:94). The following aldehydes were made by this method.

(3RS)-3-[Dimethyl(phenyl)silyl]butanal [18] 5a. (95%) as an oil from 4a. R_f (Et$_2$O–light petroleum, 1:9) 0.32; ν_{max}(film)/cm^{-1} 1724 (C=O), 1250 (SiMe) and 1113 (SiPh); δ_H(250 MHz; CDCl$_3$) 9.67 (1 H, dd, J 3.2 and 1.1, CHO), 7.53–7.45 (2 H, m, Ph), 7.41–7.33 (3 H, m, Ph), 2.43 (1 H, ddd, J 16.3, 10.6 and 1.1, CH_AH_BCHO), 2.14 (1 H, ddd, J 16.3, 10.8 and 3.2, CH$_A$H$_B$-CHO), 1.5 (1 H, m, CHSi), 0.98 (3 H, d, J 7.3, MeCHSi), 0.3 (3 H, s, SiMe_AMe$_B$) and 0.29 (3 H, s, SiMe$_A$$Me_B$); δ_C(250 MHz; CDCl$_3$) 203.2−, 137.0+, 133.9−, 129.3−, 127.9−, 46.0+, 14.5−, 13.9−, −5.0− and −5.4−.

(3RS)-3-Dimethyl(phenyl)silyl-4-methylpentanal [18] 5b. (74%) from 4b. R_f (Et$_2$O–light petroleum, 6:94) 0.26; ν_{max}(film)/cm^{-1} 1722 (C=O), 1250 (SiMe) and 1110 (SiPh); δ_H(250 MHz; CDCl$_3$) 9.62 (1 H, dd, J 2.5 and 1.8, CHO), 7.52–7.47 (2 H, m, Ph), 7.38–7.32 (3 H, m, Ph), 2.45 (1 H, ddd, J 17.2, 7.7 and 2.5, CH_AH_BCHO), 2.33 (1 H, ddd, J 17.2, 5.4 and 1.8, CH$_A$H$_B$-CHO), 1.92 (1 H, septet d, J 6.9 and 3.9, Me$_2$$CH$), 1.54 (1 H, ddd, J 7.7, 5.4 and 3.9, CHSi), 0.89 (3 H, d, J 6.8, Me_AMe$_B$CH), 0.82 (3 H, d, J 6.9, Me$_A$$Me_B$CH), 0.34 (3 H, s, Si$Me_AMe_B$) and 0.32 (3 H, s, SiMe$_A$$Me_B$); δ_C(250 MHz; CDCl$_3$) 203.4−, 138.3+, 133.8−, 129.1−, 127.9−, 41.4+, 28.7−, 27.0−, 23.4−, 20.9−, −2.6− and −3.2−.

(3RS)-3-Dimethyl(phenyl)silyl-3-phenylpropanal [18] 5d. (92%) from 4d. R_f (Et$_2$O–light petroleum, 1:9) 0.25; ν_{max}(film)/cm^{-1} 1722 (C=O), 1250 (SiMe) and 1113 (SiPh); δ_H(400 MHz; CDCl$_3$) 9.54 (1 H, br s, CHO), 7.43–6.90 (10 H, m, Ph), 2.90–2.78 (2 H, m, CHSi and CH_AH_BCHO), 2.67–2.56 (1 H, m, CH$_A$H$_B$CHO), 0.26 (3 H, s, SiMe_AMe$_B$) and 0.23 (3 H, s, SiMe$_A$$Me_B$); δ_C(400 MHz; CDCl$_3$) 202.6−, 141.2+, 136.2+, 134.1−, 129.5−, 128.1−, 127.9−, 127.7−, 125.2−, 43.5+, 30.1−, −4.2− and −5.5−.

(3RS)-3-[Dimethyl(phenyl)silyl]octanal 5c. (75%) from 4c. R_f (Et$_2$O–light petroleum, 6:94) 0.30; ν_{max}(film)/cm^{-1} 1723 (C=O), 1250 (SiMe) and 1112 (SiPh); δ_H(400 MHz; CDCl$_3$) 9.65 (1 H, dd, J 2.7 and 1.6, CHO), 7.51–7.44 (2 H, m, Ph), 7.38–7.32 (3 H, m, Ph), 2.39 (1 H, ddd, J 17.0, 4.7 and 1.6, CH_AH_BCHO), 2.28 (1 H, ddd, J 17.0, 8.2 and 2.7, CH$_A$H$_B$CHO), 1.53–1.10 [9 H, m, CH_2CHSi and (CH$_2$)$_3$], 0.85 (3 H, t, J 7.0, MeCH$_2$), 0.30 (3 H, s, SiMe_AMe$_B$) and 0.29 (3 H, s, SiMe$_A$$Me_B$); δ_C(400 MHz; CDCl$_3$) 203.4−, 137.7+, 133.9−, 129.2−, 127.9−, 44.7+, 31.9+, 30.3+, 29.0+, 22.5+, 19.6−, 14.0−, −4.0− and −4.4−; m/z (+CI) 263 (40%, M + 1), 247 (20, M − 15) and 135 (100, SiMe$_2$Ph) (Found: M$^+$, 262.1757. C$_{16}$H$_{26}$OSi requires M, 262.1753). The chromatography also gave (3RS)-3-[dimethyl(phenyl)silyl]octanol (10%); R_f (Et$_2$O–light petroleum, 4:6) 0.30; ν_{max}(film)/cm^{-1} 3320 (OH), 1588 (Ph), 1248 (SiMe) and 1111 (SiPh); δ_H(400 MHz; CDCl$_3$) 7.53–7.47 (2 H, m, Ph), 7.36–7.31 (3 H, m, Ph), 3.61–3.46 (2 H, m, CH_2OH), 1.68 (1 H, m, CH_AH_BCH$_2$OH), 1.55 (1 H, m, CH$_A$H$_B$-CH$_2$OH), 1.44 (1 H, m, CHSi), 1.35–1.08 [8 H, m, (CH$_2$)$_4$], 0.85 (3 H, t, J 7.0, MeCH$_2$), 0.28 (3 H, s, SiMe_AMe$_B$) and 0.27 (3 H, s, SiMe$_A$$Me_B$); δ_C(400 MHz; CDCl$_3$) 138.9+, 133.8−, 128.9−, 127.8−, 62.6+, 33.1+, 32.2+, 29.9+, 29.1+, 22.6+, 21.4−, 14.1−, −3.8− and −4.2−; m/z (+CI) 287 (100%, M + Na) (Found: M$^+$, 264.1911. C$_{16}$H$_{28}$OSi requires M, 264.1909).

(3RS)-3-[Dimethyl(phenyl)silyl]but-1-enyl trifluoromethanesulfonate 7a

Following Stang,[9] the aldehyde **5a** (1.154 g, 5.6 mmol) in dichloromethane (20 cm^3) was added via syringe with the tip immersed in the solution over 23 min to a refluxing solution of 2,6-di-tert-butylpyridine (1.7 cm^3, 1.448 g, 7.33 mmol) and trifluoromethanesulfonic (triflic) anhydride (0.82 mol dm^{-3} in CH$_2$Cl$_2$, 8.2 cm^3, 6.70 mmol) in dichloromethane (8 cm^3) under argon. The solution was refluxed for 19 h, and concentrated under reduced pressure. The residue was washed with light petroleum (3 × 40 cm^3) to precipitate the pyridinium salts. The combined organic extracts were washed with brine (100 cm^3) and dried (MgSO$_4$). The solvent was evaporated under reduced pressure. The residue was chromatographed (SiO$_2$, CH$_2$Cl$_2$–light petroleum 1:9) to give the enol triflate (0.938 g, 50%) (cis:trans 1.1:1); R_f (CH$_2$Cl$_2$–light petroleum, 1:9) 0.25; ν_{max}(film)/cm^{-1} 1651 (C=C), 1589 (Ph), 1247 (SiMe), 1210 (OTf) and 1114 (SiPh); δ_H(250 MHz; CDCl$_3$) Z-**7a**: 7.5–7.3 (5 H, m, Ph), 6.5 (1 H, d, J 5.58, CHOTf), 5.02 (1 H, dd, J 11.6 and 5.6, CH=CHOTf), 2.30 (1 H, dqd, J 11.6, 7.1 and 0.8, CHSi), 1.06 (3 H, d, J 7.1, MeCHSi), 0.31 (3 H, s, SiMe_AMe$_B$) and 0.30 (3 H, s, SiMe$_A$$Me_B$); E-**7a**: 7.5–7.3 (5 H, m, Ph), 6.25 (1 H, dd, J 11.7 and 1.2, CHOTf), 5.80 (1 H, dd, J 11.7 and 8.3, CH=CHOTf), 1.80 (1 H, dqd, J 8.3, 7.1 and 1.5, CHSi), 1.08 (3 H, d, 7.1, MeCHSi), 0.31 (3 H, s, SiMe_AMe$_B$) and 0.30 (3 H, s, SiMe$_A$-Me_B); δ_C(400 MHz; CDCl$_3$) Z + E 136.0+, 135.96+, 134.0−, 133.9−, 133.6−, 132.8−, 129.5−, 129.45−, 127.94−, 127.87−, 127.0−, 123.8−, 119.0+ (q, J 321.7, CF$_3$), 21.5−, 19.8−, 14.5−, 13.4−, −4.9−, −5.3−, −5.47 and −5.52−; m/z (+EI) 338 (<1%, M$^+$), 323 (60, M − Me), 261 (50, M − Ph), 189 (90, M − OTf) and 135 (100, SiMe$_2$Ph) (Found: M$^+$. 338.0600. C$_{13}$H$_{17}$F$_3$O$_3$SSi requires M, 338.0620). The pyridinium salts obtained after the hexane washings, were washed with saturated aqueous sodium hydrogen carbonate (100 cm^3) to regenerate the 2,6-di-tert-butylpyridine.

(3RS)-3-Dimethyl(phenyl)silyl-4-methylpent-1-enyl trifluoromethanesulfonate 7b

Following Stang,[9] triflic anhydride (0.88 cm^3, 4.49 mmol) was added to 2,6-di-tert-butyl-4-methylpyridine (1.13 g, 5.39 mmol) in 1,2-dichloroethane (8 cm^3) under argon, and the mixture warmed to 70 °C. The aldehyde **5b** (0.98 g, 3.74 mmol) in 1,2-dichloroethane (20 cm^3) was added slowly to the reaction mixture, and stirred for 18 h. The solvent was evaporated under reduced pressure, and the residue was washed with light petroleum (3 × 40 cm^3). The combined organic extracts were vigorously shaken with hydrochloric acid (1 mol dm^{-3}, 90 cm^3), washed with brine (80 cm^3), dried (MgSO$_4$) and evaporated under reduced pressure. The residue was chromatographed (SiO$_2$, CH$_2$Cl$_2$–light petroleum, 6:94) to give the enol triflate (0.77 g, 47%) (cis:trans ratio 1.75:1); R_f (CH$_2$Cl$_2$–light petroleum 6:94) 0.28; ν_{max}(film)/cm^{-1} 1649 (C=C), 1422 (OTf), 1213 (OTf), 1247 (SiMe) and 1112 (SiPh); δ_H(400 MHz; CDCl$_3$) Z-**7b**: 7.51–7.45 (2 H, m, Ph), 7.4–7.32 (3 H, m, Ph), 6.64 (1 H, d, J 5.6, CHOTf), 5.15 (1 H, dd, J 12.4 and 5.6, CH=CHOTf), 2.24 (1 H, dd, J 12.4 and 5.2, CHSi), 1.9 (1 H, m, Me$_2$$CH$), 0.87 (3 H, d, J 6.7, Me_AMe$_B$CH), 0.82 (3 H, d, J 6.8, Me$_A$$Me_B$CH), 0.34 (3 H, s, Si$Me_AMe_B$) and 0.335 (3 H, s, SiMe$_A$$Me_B$); E-**7b**: 7.5 (2 H, m, Ph), 7.4–7.3 (3 H, m, Ph), 6.28 (1 H, d, J 11.7, CHOTf), 5.75 (1 H, dd, J 12.4 and 11.7, CH=CHOTf), 1.9 (1 H, m, Me$_2$$CH$), 1.65 (1 H, dd, J 12.5 and 4.5, CHSi), 0.86 (3 H, d, J 6.75, Me_AMe$_B$CH), 0.83 (3 H, d, J 6.81, Me$_A$$Me_B$CH), 0.35 (3 H, s, Si$Me_AMe_B$) and 0.32 (3 H, s, SiMe$_A$$Me_B$); δ_C(400 MHz; CDCl$_3$) Z + E 137.2+, 137.0+, 134.6−, 134.2−, 133.9−, 129.4−, 129.3−, 127.93−, 127.89−, 122.4−, 119.3−, 118.0+, (q, J 320.8, CF$_3$), 35.1−, 33.5−, 24.0−, 23.8−, 20.5−, 20.1−, −3.2−, −3.4−, −3.7− and −3.8−; m/z (+CI) 389 (100%, M + Na) (Found: M$^+$, 366.0923. C$_{15}$H$_{21}$F$_3$O$_3$SSi requires M, 366.0933) and 1,1-dimethyl-2-(prop-2-yl)-1-sila-1,2-dihydronaphthalene **6b** (0.040 g, 5%); R_f (light petroleum) 0.41;

ν_{max}(film)/cm^{-1} 1631 (C=C) and 1248 (SiMe); δ_H(400 MHz; CDCl$_3$) 7.42 (1 H, dd, J 7.1 and 0.9, Ph-H), 7.28 (1 H, td, J 7.5 and 1.4, Ph-H), 7.16 (1 H, dt, J 1.0 and 7.3, Ph-H), 7.05 (1 H, d, J 7.8, Ph-H), 6.41 (1 H, dd, J 10.8 and 2.5, CH=CHPh), 5.94 (1 H, dd, J 10.8 and 4.4, CHSiCH=CH), 2.0 (1 H, m, CHMe$_2$), 1.65 (1 H, m, CHSi), 1.02 (3 H, d, J 6.8, Me_AMe$_B$CH), 0.95 (3 H, d, J 6.8, Me$_A$$Me_B$CH), 0.31 (3 H, s, Si$Me_AMe_B$) and 0.24 (3 H, s, SiMe$_A$$Me_B$); δ_C(400 MHz; CDCl$_3$) 141.8+, 134.1+, 132.5−, 131.6−, 130.1−, 129.5−, 127.5−, 126.4−, 32.5−, 30.0−, 22.8−, 21.5−, −1.8− and −4.0−; m/z (+CI) 217 (4%, M + 1) (Found: M$^+$, 216.1334. C$_{14}$H$_{16}$Si requires M, 216.1334).

(3RS)-3-[Dimethyl(phenyl)silyl]oct-1-enyl trifluoromethanesulfonate 7c

A similar procedure to that used for the enol triflate **7b** but using the aldehyde **5c** (0.98 g, 3.74 mmol) and heating for 2.5 h, gave the *enol triflate* (0.77 g, 54%) (*cis* : *trans* 1.1 : 1); R_f (CH$_2$Cl$_2$–light petroleum, 6 : 94) 0.35; ν_{max}(film)/cm^{-1} 1652 (C=C), 1590 (Ph), 1425, 1212 (OTf), 1246 (SiMe) and 1114 (SiPh); δ_H(400 MHz; CDCl$_3$) *Z*-**7c**: 7.58–7.33 (5 H, m, Ph), 6.58 (1 H, d, J 5.6, CHOTf), 4.95 (1 H, dd, J 11.7 and 5.6, CH=CHOTf), 2.83 (1 H, td, J 11.6 and 2.8, CHSi), 1.55–1.04 [8 H, m, Me(CH_2)$_4$], 0.83 (3 H, t, J 6.8, MeCH$_2$), 0.32 (3 H, s, SiMe_AMe$_B$) and 0.31 (3 H, s, SiMe$_A$$Me_B$); *E*-**7c**: 7.58–7.33 (5 H, m, Ph), 6.3 (1 H, d, J 11.7, CHOTf), 5.56 (1 H, t, J 11.4, CH=CHOTf), 1.64 (1 H, td, J 11.3 and 3.1, CHSi), 1.55–1.04 [8 H, m, Me(CH_2)$_4$], 0.84 (3 H, t, J 7.0, MeCH$_2$), 0.31 (3 H, s, SiMe_AMe$_B$) and 0.30 (3 H, s, SiMe$_A$-Me_B); δ_C(400 MHz; CDCl$_3$) $Z + E$ 136.3+, 136.2+, 134.0−, 133.9−, 133.8−, 133.1−, 129.5−, 129.4−, 127.91−, 127.85−, 125.5−, 122.3−, 119.0+ (q, J 320.8, CF$_3$), 31.4+, 29.4+, 29.2+, 28.9+, 28.4+, 27.6−, 26.4−, 22.5+, 14.0−, −4.6−, −4.7− and −5.2−; m/z (+CI) 417 (100%, M + Na) (Found: M$^+$, 394.1230. C$_{17}$H$_{25}$F$_3$O$_3$SSi requires M, 394.1246) and 1,1-*dimethyl*-2-*pentyl*-1-*sila*-1,2-*dihydronaphthalene* **6c** (0.050 g, 5%); R_f (light petroleum) 0.44; ν_{max}(film)/cm^{-1} 1600 (C=C), 1590 (Ph) and 1246 (SiMe); δ_H(400 MHz; CDCl$_3$) 7.45 (1 H, dd, J 7.2 and 1.2, Ph–H), 7.30 (1 H, td, J 7.5 and 1.4, Ph–H), 7.17 (1 H, td, J 7.3 and 1.0, Ph–H), 7.05 (1 H, d, J 7.6, Ph–H), 6.33 (1 H, dd, J 10.7 and 2.6, CH=CHPh), 5.90 (1 H, dd, J 10.7 and 3.8, CH=CHPh), 1.75–1.65 (1 H, m, CHSi), 1.59–1.42 (2 H, m, CH_2CHSi), 1.33–1.25 [6 H, m, Me(CH_2)$_3$], 0.89 (3 H, td, J 6.7 and 1.7, MeCH$_2$), 0.32 (3 H, s, SiMe_AMe$_B$) and 0.15 (3 H, s, SiMe$_A$$Me_B$); δ_C(400 MHz; CDCl$_3$) 141.9+, 133.8−, 133.5+, 133.0−, 129.6−, 129.1−, 127.6−, 126.4−, 32.0+, 30.5+, 28.8+, 24.2−, 22.6+, 14.2−, −3.2− and −5.4−; m/z (+CI) 244 (15%, M$^+$) and 229 (80, M − 15) (Found: M$^+$, 244.1638. C$_{16}$H$_{24}$Si requires M, 244.1647).

(3RS)-3-Dimethyl(phenyl)silyl-3-phenylprop-1-enyl trifluoromethanesulfonate 7d

A similar procedure to that used for the enol triflate **7a** but starting with the aldehyde **5d** (1.722 g, 6.78 mmol) and refluxing for 27 h, gave the *enol triflate* (1.724 g, 49%) (*cis* : *trans* 7 : 1); R_f (CH$_2$Cl$_2$–light petroleum, 1 : 9) 0.31; ν_{max}(film)/cm^{-1} 1654 (C=C), 1426 and 1215 (OTf), 1247 (SiMe) and 1117 (SiPh); δ_H(250 MHz; CDCl$_3$) *Z*-**7b**: 7.42–6.81 (10 H, m, Ph), 6.57 (1 H, d, J 5.7, CHOTf), 5.55 (1 H, dd, J 12.0 and 5.7, CH=CHOTf), 3.63 (1 H, d, J 12.0, CHSi), 0.31 (3 H, s, SiMe_AMe$_B$) and 0.27 (3 H, s, SiMe$_A$$Me_B$); *E*-**7b**: 7.41–6.84 (10 H, m, Ph), 6.58 (1 H, d, J 11.6, CHOTf), 6.11 (1 H, dd, J 11.6 and 10.7, CH=CHOTf), 3.05 (1 H, d, J 10.7, CHSi), 0.30 (3 H, s, SiMe_AMe$_B$) and 0.26 (3 H, s, SiMe$_A$$Me_B$); δ_C(400 MHz; CDCl$_3$) $E + Z$ 139.3+, 135.1+, 134.6+, 134.3−, 134.2+, 132.7+, 129.73−, 129.66−, 128.6−, 128.4−, 127.9−, 127.7−, 127.3−, 127.1−, 125.6−, 125.4−, 123.3−, 119.9−, 118.7+ (q, J 320.8, CF$_3$), 36.6−, 35.2−, −4.4−, −4.5−, −4.9− and −5.1−; m/z (+EI) 385 (<1%, M − Me), 267 (M − OTf), 251 (5, M − OTf), 135 (100, SiMe$_2$Ph) and 77 (20, Ph) (Found: M$^+$, 400.0770. C$_{18}$H$_{19}$F$_3$O$_3$-SSi requires M, 400.0776).

Preparation of prop-2-ynyl silanes 8

The enol triflate (1.5 mmol) in THF (10 cm^3) was added dropwise to the LDA solution (3.3 mmol) and the mixture was stirred for 10 min before being quenched dropwise with water (20 cm^3), and allowed to warm to room temperature. The aqueous layer was extracted with ether (2 × 20 cm^3), dried (MgSO$_4$), the solvent evaporated under reduced pressure, and the residue chromatographed (SiO$_2$, CH$_2$Cl$_2$–light petroleum, 1 : 9). The following alkynes were prepared by this method.

(3RS)-3-[Dimethyl(phenyl)silyl]butyne 8a. (92%) from **7a**. R_f (CH$_2$Cl$_2$–light petroleum, 1 : 9) 0.35; ν_{max}(film)/cm^{-1} 3311 (C≡CH), 2096 (C≡C), 1250 (SiMe) and 1113 (SiPh); δ_H(250 MHz; CDCl$_3$) 7.6–7.5 (2 H, m, Ph), 7.4–7.3 (3 H, m, Ph), 2.0 (1 H, d, J 2.8, C≡CH), 1.9 (1 H, qd, J 7.2 and 2.8, MeCHSi), 1.19 (3 H, d, J 7.2, MeCHSi) and 0.39 (6 H, s, SiMe$_2$); δ_C(400 MHz; CDCl$_3$) 136.5+, 134.1−, 129.4−, 127.8−, 88.0+, 68.0+, 14.9−, 12.6−, −4.8− and −5.62−; m/z (EI)[19] 188 (20%, M$^+$), 173 (10, M − Me) and 135 (100, SiMe$_2$Ph) (Found:[19] M$^+$, 188.1014. C$_{12}$H$_{16}$Si requires M, 188.1022).

(3RS)-3-Dimethyl(phenyl)silyl-4-methylpentyne 8b. (86%) from 7b. R_f (light petroleum) 0.26; ν_{max}(film)/cm^{-1} 3311 (C≡CH), 2098 (C≡C), 1590 (Ph), 1250 (SiMe) and 1113 (SiPh); δ_H(250 MHz; CDCl$_3$) 7.63–7.53 (2 H, m, Ph), 7.40–7.33 (3 H, m, Ph), 2.08 (1 H, d, J 2.8, C≡CH), 1.91 (1 H, dd, J 4.0 and 2.9, CHSi), 1.8 (1 H, septet d, J 6.6 and 4.1, Me$_2$CH), 0.98 (3 H, d, J 6.6, Me_AMe$_B$CH), 0.93 (3 H, d, J 6.7, Me$_A$$Me_B$CH), 0.44 (3 H, s, Si$Me_AMe_B$) and 0.43 (3 H, s, SiMe$_A$$Me_B$); δ_C(250 MHz; CDCl$_3$) 137.6+, 133.9−, 129.2−, 127.7−, 84.3+, 70.9+, 27.9−, 27.7−, 24.0−, 20.2−, −3.1− and −4.1−; m/z (+EI) 201 (80%, M − Me) and 135 (100, SiMe$_2$Ph) (Found: M$^+$, 216.1313. C$_{14}$H$_{20}$Si requires M, 216.1334).

(3RS)-3-[Dimethyl(phenyl)silyl]octyne 8c. (82%) from 7c. R_f (light petroleum) 0.29; ν_{max}(film)/cm^{-1} 3312 (≡CH), 2099 (CH), 1590 (Ph), 1250 (SiMe) and 1113 (SiPh); δ_H(250 MHz; CDCl$_3$) 7.61–7.52 (2 H, m, Ph), 7.41–7.33 (3 H, m, Ph), 2.01 (1 H, d, J 2.8, C≡CH), 1.86 (1 H, td, J 6.5 and 2.8, CHSi), 1.68–1.08 [8 H, m, (CH_2)$_4$CHSi], 0.86 (3 H, td, J 6.8 and 1.2, MeCH$_2$) and 0.38 (6 H, s, SiMe$_2$); δ_C(250 MHz; CDCl$_3$) 136.8+, 134.0−, 129.3−, 127.7−, 86.5+, 69.0+, 31.4+, 29.1+, 29.0+, 22.5+, 19.3−, 14.0−, −4.4− and −5.2−; m/z (+EI) 244 (20%, M$^+$), 229 (30, M − Me), 215 (40, M − C$_2$H$_5$), 201 (16, M − C$_3$H$_7$), 187 (20, M − C$_4$H$_9$) and 135 (100, SiMe$_2$Ph) (Found: M$^+$, 244.1644. C$_{16}$H$_{24}$Si requires M, 244.1647).

(3RS)-3-Dimethyl(phenyl)silyl-3-phenylpropyne 8d. (19%) from 7d. R_f (light petroleum) 0.31; ν_{max}(film)/cm^{-1} 3308 (≡CH), 2104 (C≡C), 1597 (Ph), 1250 (SiMe) and 1114 (SiPh); δ_H(400 MHz; CDCl$_3$) 7.42–6.96 (10 H, m, Ph), 3.34 (1 H, d, J 2.8, C≡CH), 2.28 (1 H, d, J 2.8, CHSi), 0.40 (3 H, s, SiMe_AMe$_B$) and 0.29 (3 H, s, SiMe$_A$$Me_B$); δ_C(400 MHz; CDCl$_3$) 138.1+, 135.7+, 134.3−, 129.5−, 128.0−, 127.7−, 127.6−, 125.3−, 84.3+, 71.1+, 29.0−, −5.0− and −5.1−; m/z (+EI) 250 (30%, M$^+$), 235 (15, M − Me) and 135 (100, SiMe$_2$Ph) (Found: M$^+$, 250.1174. C$_{17}$H$_{18}$Si requires M, 250.1178) and 1-phenylpropa-1,2-diene[20] (0.083 g, 43%); R_f (light petroleum) 0.55; ν_{max}(film)/cm^{-1} 1942 (C=C=C) and 1597 (Ph); δ_H(250 MHz; CDCl$_3$) 7.6–7.1 (5 H, m, Ph), 6.2 (1 H, t, J 6.8, PhCH=C=CH$_2$), 5.13 (2 H, d, J 6.8, CH=C=CH_2); δ_C(400 MHz; CDCl$_3$) 209.8+, 134.0+, 128.4−, 127.4−, 127.1−, 94.0− and 78.8+.

(5S)-1-Crotonoyl-5-(triphenylmethoxymethyl)pyrrolidin-2-one 9a

This was prepared by the method of Kindon.[10] Recrystallisation from hexane gave the imide (2.76 g, 68%) as prisms (mp 133–134 °C) (lit.,[10] 115–116; lit.,[21] 116–117 °C); R_f (EtOAc–light petroleum, 1 : 3) 0.31; ν_{max}(CH$_2$Cl$_2$)/cm^{-1} 1725 (C=O), 1670 (C=O) and 1630 (C=C); δ_H(250 MHz; CDCl$_3$) 7.4–7.0 (17 H, m, 3 Ph and MeCH_A=CH_B), 4.50 (1 H, m, CHN), 3.55 (1 H, dd, J 9.7 and 3.9, CH_AH$_B$OCPh$_3$), 3.15 (1 H, dd, J 9.7 and 2.6, CH$_A$$H_B$OCPh$_3$), 3.0 (1 H, ddd, J 17.9, 10.0 and 1.0, CH_AH$_B$CO), 2.55 (1 H, ddd, J 17.9, 9.6 and 2.1 CH$_A$$H_B$CO),

2.15–1.9 (2 H, m, CH$_2$CH$_2$CO) and 2.0 (3 H, dd, J 8.4 and 1.5, *Me*CH=CH); δ_C(400 MHz; CDCl$_3$) 176.5+, 165,8+, 145.7−, 143.7+, 128.6−, 127.9−, 127.2−, 124.0−, 87.0+, 64.2+, 56.8−, 33.4+, 21.5+ and 18.6−; *m/z* (+FAB) 426 (50%, M + 1) (Found: M$^+$, 425.1991. C$_{28}$H$_{28}$NO$_3$ requires *M*, 425.1991). The ^{1}H NMR data matched the spectra obtained earlier,[10] and reported by Koga,[21] but since the mp was significantly higher than that reported earlier, we characterised it anew.

The following compounds were prepared similarly.

(5*S*)-1-[(2*E*)-4-Methylpent-2-enoyl]-5-(triphenylmethoxymethyl)pyrrolidin-2-one[11] 9b (72%). Isolated as needles, mp 117–119 °C (from EtOAc–light petroleum, 1:5) (lit.,[11] 118–119 °C); δ_C(400 MHz; CDCl$_3$) 176.4+, 166.2+, 156.7−, 143.7+, 128.6−, 127.9−, 127.1−, 120.0−, 87.0+, 64.2+, 56.8−, 33.4+, 31.5−, 21.497−, 21.472− and 21.1+.

(5*S*)-1-[(2*E*)-Oct-2-enoyl]-5-(triphenylmethoxymethyl)pyrrolidin-2-one 9c (76%). R_f (EtOAc–light petroleum, 15:85) 0.29; v_{max}(film)/cm^{-1} 1732, 1680 (C=O), 1631 C=C) and 1597 (Ph); δ_H(400 MHz; CDCl$_3$) 7.38–7.18 (16 H, m, Ph and CH=C*H*CO), 7.09 (1 H, dd, J 15.3 and 7.0, C*H*=CHCO), 4.54 (1 H, m, CHN), 3.56 (1 H, dd, J 9.7 and 4.0, C*H*$_A$H$_B$OCPh$_3$), 3.14 (1 H, dd, J 9.7 and 2.3, CH$_A$*H*$_B$OCPh$_3$), 2.96 (1 H, dt, J 17.9 and 10.2, C*H*$_A$H$_B$CO), 2.49 (1 H, dd, J 17.9 and 1.7, CH$_A$*H*$_B$CO), 2.29 (2 H, q, J 6.9, C*H*$_2$CH=CH), 2.12–1.92 (2 H, m, C*H*$_2$CH$_2$CO), 1.55–1.47 (2 H, m, C*H*$_2$CH$_2$CH=CH), 1.37–1.28 [4 H, m, Me(C*H*$_2$)$_2$] and 0.89 (3 H, t, J 6.8, *Me*CH$_2$); δ_C(400 MHz; CDCl$_3$) 176.5+, 166.0+, 150.8−, 143.7−, 128.6−, 127.9−, 127.1−, 122.5−, 87.0−, 64.2+, 56.8−, 33.4+, 32.7+, 31.4−, 28.0+, 22.5+, 21.1+ and 14.0−; $[a]_D^{20}$ −79.90 (*c* 23.05 in CH$_2$Cl$_2$); *m/z* (+FAB) 504.5 (40%, M + Na) and 480.5 (45, M − 1) (Found: M$^+$, 481.2632. C$_{32}$H$_{35}$NO$_3$ requires *M*, 481.2617).

Conjugate additions to the imides 9

Method A. Typically, following Kindon,[10] but using copper(I) iodide in place of copper(I) bromide, dimethyl(phenyl)silyllithium (0.92 mol dm^{-3} in THF, 10.5 cm^3, 9.6 mmol) was added to magnesium bromide (2.54 g, 13.8 mmol) in THF (30 cm^3) at 0 °C under argon. The mixture was stirred for 20 min, transferred with stirring to copper(I) iodide (0.914 g, 4.8 mmol) in THF (30 cm^3) at −40 °C, stirred for 30 min and then cooled to −78 °C. The imide (3 mmol) and magnesium bromide (0.773 g, 4.2 mmol) in THF (40 cm^3) were added over 12 min and the mixture stirred for 1 h at −78 °C. Saturated ammonium chloride solution (35 cm^3) was added. The aqueous layer was extracted with ether (3 × 50 cm^3), washed with basic ammonium chloride solution (60 cm^3), brine (80 cm^3) and dried (MgSO$_4$). The solvent was evaporated under reduced pressure and the residue chromatographed (SiO$_2$, EtOAc–light petroleum, 15:85).

The following compounds were prepared by this method.

(5*S*)-1-{(3*S*)-3-[Dimethyl(phenyl)silyl]butanoyl}-5-(triphenylmethoxymethyl)pyrrolidin-2-one[10] 10a (85%). R_f (EtOAc–light petroleum, 15:85) 0.27; v_{max}(film)/cm^{-1} 1740 (C=O), 1680 (C=O), 1597 (Ph) and 1112 (SiPh); δ_H(250 MHz; CDCl$_3$) 7.6–7.2 (20 H, m, 4 Ph), 4.45 (1 H, m, CHN), 3.49 (1 H, dd, J 9.8 and 3.8, C*H*$_A$H$_B$OCPh$_3$), 3.17 (1 H, J 9.8 and 2.6, CH$_A$*H*$_B$-OCPh$_3$), 2.97 (1 H, dd, J 16.2 and 3.4, MeCHC*H*$_A$H$_B$CO), 2.92 (1 H, dd, J 17.8 and 8.9, CH$_2$C*H*$_A$H$_B$CO), 2.77 (1 H, dd, J 16.2 and 11.3, MeCHCH$_A$*H*$_B$CO), 2.43 (1 H, ddd, J 17.8, 9.3 and 2.0, CH$_2$CH$_A$*H*$_B$CO), 2.1–1.9 (2 H, m, C*H*$_2$CH$_A$H$_B$CO), 1.5 (1 H, m, MeC*H*CH$_A$H$_B$CO), 0.88 (3 H, d, J 7.4, *Me*CH-CH$_2$CO), 0.37 (3 H, s, Si*Me*$_A$Me$_B$) and 0.36 (3 H, s, SiMe$_A$*Me*$_B$); δ_C(400 MHz; CDCl$_3$) 176.2+, 173.9+, 143.6+, 137.8+, 129.0−, 128.6−, 127.9−, 127.8− 127.3−, 127.2−, 87.0+, 64.1+, 56.7−, 39.0+, 333.2+, 21.3+, 15.3−, 14.5− and −4.9− and −5.1−. The ratio of diastereoisomers was 95:5 measured by integration of the methyl doublets at δ 0.88 (major) and 0.95 (minor).

(5*S*)-1-{(3*R*)-3-[Dimethyl(phenyl)silyl]-4-methylpentanoyl}-5-(triphenylmethoxymethyl)pyrrolidin-2-one[11] 10b. R_f (EtOAc–light petroleum 1:4) 0.44; v_{max}(film)/cm^{-1} 1735, 1687 (C=O), 1245 (SiMe) and 1108 (SiPh); δ_H(400 MHz; CDCl$_3$) 7.54–7.15 (20 H, m, Ph), 4.24 (1 H, m, CHN), 3.43 (1 H, dd, J 9.6 and 4.3, C*H*$_A$H$_B$OCPh$_3$), 3.22 (1 H, dd, J 17.4 and 7.8, CH$_2$C*H*$_A$H$_B$CO), 3.07 (1 H, dd, J 9.6 and 2.7, CH$_A$*H*$_B$OCPh$_3$), 2.82 (1 H, ddd, J 17.8, 10.0 and 1.0, CHSiC*H*$_A$H$_B$CO), 2.76 (1 H, dd, J 17.4 and 5.7, CH$_2$CH$_A$*H*$_B$CO), 2.4 (1 H, ddd, J 17.8, 9.6 and 1.7, CHSiCH$_A$*H*$_B$CO), 1.98–1.88 (3 H, m, C*H*$_2$CH$_2$CO and Me$_2$C*H*), 1.64 (1 H, m, CHSi), 0.89 (3 H, d, J 6.8, *Me*$_A$Me$_B$-CH), 0.83 (3 H, d, J 6.9, Me$_A$*Me*$_B$CH), 0.321 (3 H, s, Si*Me*$_A$-Me$_B$) and 0.319 (3 H, s, SiMe$_A$*Me*$_B$); δ_C(400 MHz; CDCl$_3$) 176.1+, 174.6+, 143.7+, 139.5+, 134.0−, 128.6−, 127.9−, 127.86−, 127.6−, 127.1−, 87.0+, 63.9+, 56.9−, 34.5+, 33.1+, 29.0−, 27.8−, 22.7−, 21.5−, 21.2+, −2.0− and −2.8−. The ratio of diastereoisomers was in the range 100:0 to 92:8 measured by integration of the double doublets at δ 3.49 (minor) and 3.43 (major). When a run was carried out without magnesium bromide, the ratio was 63:37, and characteristic signals for the minor diastereoisomer could now be identified at δ 4.19 (m, CHN), 3.49 (dd, J 9.6 and 4.0, C*H*$_A$H$_B$OCPh$_3$), 3.03 (t, J 8.5), 2.30 (t, J 8.1), 2.14 (m) and 0.92 (d, J 6.5, *Me*$_A$Me$_B$CH).

(5*S*)-1-{(3*S*)-3-[Dimethyl(phenyl)silyl]octanoyl}-5-(triphenylmethoxymethyl)pyrrolidin-2-one 10c. (70%). R_f (EtOAc–light petroleum 15:85) 0.35; v_{max}(film)/cm^{-1} 1731 (C=O), 1692 (C=O) and 1597 (Ph); δ_H(400 MHz; CDCl$_3$) 7.53–7.49 (2 H, Ph), 7.36–7.17 (18 H, m, Ph), 4.35 (1 H, m, CHN), 3.42 (1 H, dd, J 9.7 and 4.4, C*H*$_A$H$_B$OCPh$_3$), 3.15 (1 H, dd, J 9.7 and 2.3, CH$_A$*H*$_B$-OCPh$_3$), 3.04 (1 H, dd, J 17.2 and 8.8, C*H*$_A$H$_B$CO), 2.84 (2 H, m, CH$_A$*H*$_B$CO and CH$_2$C*H*$_A$H$_B$CO), 2.42 (1 H, ddd, J 17.9, 9.8 and 1.7, CH$_2$CH$_A$*H*$_B$CO), 2.04–1.84 (2 H, m, C*H*$_2$CO), 1.54 (1 H, m, CHSi), 1.42–1.06 [8 H, m, (CH$_2$)$_4$], 0.80 (3 H, t, J 6.7, *Me*CH$_2$), 0.294 (3 H, s, Si*Me*$_A$Me$_B$) and 0.291 (3 H, s, SiMe$_A$-*Me*$_B$); δ_C(400 MHz; CDCl$_3$) 176.1+, 174.3+, 143.7+, 138.6+, 134.0−, 128.9−, 128.6−, 127.9−, 127.7−, 127.5−, 127.1−, 87.0+, 63.9+, 56.8, 37.5+, 33.1+, 32.1+, 30.5+, 28.7+, 22.5+, 21.1+, 20.6−, 14.1−, −3.7− and −4.0−; *m/z* (+FAB) 630 (8%, M + Na), 616 (50, M − 1) and 602 (100, M − Me) (Found: M$^+$, 617.3325. C$_{40}$H$_{47}$NO$_3$Si requires *M*, 617.3325). The ratio of diastereoisomers was 93:7 measured by integration of the double doublets at δ 3.04 (major) and 2.68 (minor).

Method B. Dimethyl(phenyl)silyllithium (0.90 mol dm^{-3} in THF, 14.3 cm^3, 12.9 mmol) was added to dimethylzinc (2 mol dm^{-3} in toluene, 6 cm^3, 12 mmol) in THF (30 cm^3) at 0 °C under argon. The imide (8 mmol) was added over 30 min at −78 °C, and the mixture stirred for 2 h before being quenched with ammonium chloride (30 cm^3) at −78 °C. The mixture was washed with hydrochloric acid (3 mol dm^{-3}, 80 cm^3), the aqueous layer was extracted with ether (3 × 40 cm^3), the combined organic extracts were washed with brine (80 cm^3) and dried (MgSO$_4$). The solvent was evaporated under reduced pressure to give the crude product, which was analysed using ^{1}H NMR spectroscopy. The following imides, identical (TLC, ^{1}H NMR spectroscopy) with the earlier samples, were prepared by this method.

(5*S*)-1-{(3*S*)-3-[Dimethyl(phenyl)silyl]butanoyl}-5-(triphenylmethoxymethyl)pyrrolidin-2-one[10] 10a. The ratio of diastereoisomers was in the range 100:0 to 95:5 by integration of the double doublets at δ 3.66 (minor) and 3.49 (major). An impurity formed from the conjugate addition of the methyl group (from the dimethylzinc) to the imide **9a** had a double doublet in the region (δ 0.91–0.98) preventing us from using the signals from the methyl doublets used in the cuprate addition for diagnostic purposes.

(5*S*)-1-[(3*R*)-3-Dimethyl(phenyl)silyl-4-methylpentanoyl]-5-(triphenylmethoxymethyl)pyrrolidin-2-one[11] 10b. The ratio of diastereoisomers was slightly above 98:2 by cutting and weighing the double doublets at δ 3.49 (minor) and 3.43 (major).

(5S)-N-{(3S)-3-[Dimethyl(phenyl)silyl]octanoyl}-5-(tri-phenylmethoxymethyl)pyrrolidin-2-one 10c. The ratio of diastereoisomers was 98:2 by integration of the double doublets at δ 3.04 (major) and 2.68 (minor).

(5S)-1-[(3R)-3-Dimethyl(phenyl)silyl-3-phenylpropanoyl]-5-(triphenylmethoxymethyl)pyrrolidin-2-one[10] 10d. The ratio of diastereoisomers was 75:25 by integration of the silyl methyl singlets at δ 0.32 and 0.21 (major) and 0.28 and 0.26 (minor).

Preparation of the esters 11

Method A. Dimethyl(phenyl)silyllithium (1.12 mol dm^{-3} in THF, 13.40 cm^3, 15.0 mmol) was added with stirring to magnesium bromide (3.98 g, 21.62 mmol) in THF (40 cm^3) at 0 °C under argon. After 20 min the mixture was transferred by cannula to copper(I) iodide (1.429 g, 7.52 mmol) in THF (30 cm^3) at −40 °C, the mixture stirred for 30 min, and cooled to −78 °C. A mixture of the imide **9** (4.70 mmol) and magnesium bromide (1.212 g, 6.58 mmol) in THF (60 cm^3) was added over 50 min and the mixture stirred for 2 h at −78 °C. Ethanol (0.432 g, 9.4 mmol) in THF (10 cm^3) was then added dropwise, and the mixture was then stirred for 24 h. Saturated aqueous ammonium chloride (50 cm^3) was added, the aqueous layer was extracted with ether (3 × 40 cm^3), the combined organic extracts were washed with basic ammonium chloride (60 cm^3), brine (100 cm^3) and dried (MgSO$_4$). The solvent was evaporated under reduced pressure to give the residue. The pyrrolidine crystallised and was washed with hexane (4 × 30 cm^3) to give the recovered auxiliary (1.262 g, 76%). The extracts from the hexane washings were combined, concentrated under reduced pressure and chromatographed (SiO$_2$, Et$_2$O–light petroleum, 6:94). The following esters were prepared in this way.

Ethyl (3S)-3-[dimethyl(phenyl)silyl]butanoate 11a. (86% based on 9a). $[\alpha]_D^{20}$ +0.31 (c 7.5 in CH$_2$Cl$_2$) From the imide with a diastereoisomer ratio of 88:12; identical (TLC, IR and ^{1}H NMR) with the racemic ester **4a**. This sample was carried through the rest of the synthetic sequence.

Ethyl (3S)-3-[dimethyl(phenyl)silyl]octanoate 11c. (43% based on 9c). Identical (TLC, IR and ^{1}H NMR) with the racemic ester **4c**, but in this run we also isolated the open chain amide *ethyl* (4S)-4-{(3'S)-3-[*dimethyl(phenyl)silyl*]*octanamido*}-5-(*triphenylmethoxy*)*pentanoate* (45%); R_f (EtOAc–light petroleum, 1:5) 0.31; v_{max}(film)/cm^{-1} 3320 (NH), 1729 (C=O), 1650 (C=O), 1596 (Ph), 1244 (SiMe) and 1111 (SiPh); δ_H(250 MHz; CDCl$_3$) 7.5–7.1 (20 H, m, Ph), 5.5 (1 H, m, CHN), 4.13–3.98 (4 H, m, OCH$_2$Me and CH$_2$OCPh$_3$), 3.16 (1 H, dd, J 9.4 and 3.6, CH$_A$-H$_B$CONH), 3.06 (1 H, dd, J 9.4 and 4.3, CH$_A$H$_B$CONH), 2.28–2.2 (2 H, m, CHNHCH$_2$CH$_2$CO), 2.15–1.80 (3 H, m, CHNCH$_2$-CH$_2$ and CHSi), 1.46–1.04 [8 H, m, CH$_2$CH$_2$CHSi and Me(CH$_2$)$_3$], 1.20 (3 H, t, J 7.1, OCH$_2$Me), 0.8 [3 H, t, J 7.2, Me(CH$_2$)$_4$] and 0.24 (6 H, s, SiMe$_2$); δ_C(250 MHz; CDCl$_3$) 173.5+, 172.8+, 143.7+, 138.2+, 133.9−, 128.9−, 128.6−, 127.9−, 127.8−, 127.1−, 86.5+, 64.9+, 60.4+, 48.9−, 37.5+, 32.2+, 31.1+, 30.4+, 28.8+, 27.4+, 22.5+, 21.9−, 14.2−, 14.0−, −3.9−, −4.1−; m/z (+FAB) 687 (30%, M + Na), 663 (10, M − 1) and 649 (15, M − Me) (Found: M$^+$, 663.3744. C$_{42}$H$_{53}$NO$_4$Si requires M, 663.3744). This compound could be converted into the ester **11c** by treatment with ethoxide in ethanol, see below.

Method B. Following Kindon,[10] *n*-butyllithium (1.2 mol dm^{-3} in hexanes, 8.98 cm^3, 10.78 mmol) was added to ethanol (0.638 g, 13.86 mmol) at 0 °C under argon. After 15 min the imide **10** (3.08 mmol) in THF (20 cm^3) was added slowly by cannula, and the mixture stirred for 23 h. Saturated aqueous ammonium chloride (20 cm^3) was added and the aqueous layer was extracted with ether (3 × 40 cm^3). The combined organic extracts were washed with brine (80 cm^3), dried (MgSO$_4$) and the solvent evaporated under reduced pressure. A mixture of ethyl acetate and light petroleum (1:9) was added to precipate the lactam (73%). The solution was concentrated under reduced pressure and the residue chromatographed (SiO$_2$, EtOAc–light petrol-

eum, 6:94). The following esters were prepared by this method.

Ethyl (3S)-3-[dimethyl(phenyl)silyl]butanoate 11a (71% based on 10a). Identical (TLC, IR and ^{1}H NMR) with the racemic ester; $[\alpha]_D^{20}$ +0.37 (c 6.18 in CH$_2$Cl$_2$) from the imide with a diastereoisomer ratio of 95:5.

Ethyl (3S)-3-dimethyl(phenyl)silyl-4-methylpentanoate 11b (83% based on 9b). Identical (TLC, IR and ^{1}H NMR) with the racemic ester; $[\alpha]_D^{28}$ +8.1 (c 1.8 in CH$_2$Cl$_2$) from the imide with a diastereoisomer ratio of 92:8. This sample was carried through the rest of the synthetic sequence.

Ethyl (3S)-3-[dimethyl(phenyl)silyl]octanoate 11c (87% based on 10c). Identical (TLC, IR and ^{1}H NMR) with the racemic ester; $[\alpha]_D^{20}$ +10.2 (c 2.1 in CH$_2$Cl$_2$) from the imide with a diastereoisomer ratio of 93:7. This sample was carried through the rest of the synthetic sequence.

Preparation of the ester 11c from the open chain amide

n-Butyllithium (1.4 mol dm^{-3} in hexanes, 4.1 cm^3, 5.71 mmol) was added to ethanol (0.43, 7.34 mmol) in THF (20 cm^3) at 0 °C under argon and *ethyl* (4S)-4-{(3S)-3-[*dimethyl(phenyl)-silyl*]*octanamido*}-5-*triphenylmethoxypentanoate* (1.078 g, 1.63 mmol) in THF (20 cm^3) was added dropwise. The mixture was stirred at room temperature for 27 h, and then quenched with saturated aqueous ammonium chloride (20 cm^3). The usual work-up gave the chiral auxiliary (0.358 g, 62%) and the ester **11c** (0.431 g, 83%); $[\alpha]_D^{20}$ +10.84 (c 3.562 in CH$_2$Cl$_2$) from imide **10c** (with a diastereoisomer ratio of 96:4); identical (TLC, IR and ^{1}H NMR) with the racemic ester.

Preparation of aldehydes 12

The following compounds were prepared by the method used in the racemic series.

(3S)-3-[Dimethyl(phenyl)silyl]butanal 12a (81%). $[\alpha]_D^{20}$ +43.4 (c 10.2 in CH$_2$Cl$_2$) (prepared from the ester **11a** prepared by Method A; this rotation corresponds to an enantiomer ratio of 88:12); identical (TLC, IR and ^{1}H NMR) with the racemic aldehyde. $[\alpha]_D^{20}$ +51.3 (c 2.56 in CH$_2$Cl$_2$) (80%) (prepared from the ester **11a** prepared by Method B from imide **10a** having a diastereoisomer ratio of 95:5).

(3S)-3-Dimethyl(phenyl)silyl-4-methylpentanal 12b (81%). $[\alpha]_D^{20}$ +16.5 (c 2.10 in CH$_2$Cl$_2$) from the imide with a diastereoisomer ratio of 92:8; identical (TLC, IR and ^{1}H NMR) with the racemic aldehyde.

(3S)-3-[Dimethyl(phenyl)silyl]octanal 12c (83%). $[\alpha]_D^{20}$ +34.0 (c 1.04 in CH$_2$Cl$_2$) from the imide with a diastereoisomer ratio of 93:7; identical (TLC, IR and ^{1}H NMR) with the racemic aldehyde.

Preparation of enol triflates 13

The following compounds were prepared using 2,6-di-*tert*-butylpyridine, as in the preparation of the enol triflate **7a** in the racemic series.

(3S)-3-[Dimethyl(phenyl)silyl]but-1-enyl trifluoromethanesulfonate 13a (65%). (*cis*:*trans* ratio 3:2); identical (TLC, IR and ^{1}H NMR) with the racemic enol triflate.

(3S)-3-Dimethyl(phenyl)silyl-4-methylpent-1-enyl trifluoromethanesulfonate 13b (ClCH$_2$CH$_2$Cl, 70 °C, 18 h, 47%) (*cis*:*trans* 1:1.75); identical (TLC, IR and ^{1}H NMR) with the racemic enol triflate.

The following compound was prepared using 2,6-di-*tert*-butyl-4-methylpyridine, as in the preparation of the enol triflate **7b** in the racemic series.

(3S)-3-[Dimethyl(phenyl)silyl]oct-1-ene trifluoromethanesulfonate 13c (0.68 g, from **12c**, 0.495 g, 1.89 mmol) (*cis*:*trans* ratio = 1.1:1); identical (TLC, IR and ^{1}H NMR) with the racemic enol triflate, and used without purification in the next reaction.

Preparation of prop-2-ynyl silanes 14

The following compounds were prepared by the method developed in the racemic series.

(3S)-3-[Dimethyl(phenyl)silyl]butyne 14a (86%). $[\alpha]_D^{20}$ +6.31 (c 4.7 in CH$_2$Cl$_2$) from the imide with a diastereoisomer ratio of 88:12; identical (TLC, IR and ^{1}H NMR) with the racemic prop-2-ynyl silane.

(3S)-3-Dimethyl(phenyl)silyl-4-methylpentyne 14b (99%). $[\alpha]_D^{20}$ +11.8 (c 1.07 in CH$_2$Cl$_2$) from the imide with a diastereoisomer ratio of 92:8; identical (TLC, IR and ^{1}H NMR) with racemic prop-2-ynyl silane.

(3S)-3-[Dimethyl(phenyl)silyl]octyne 14c (76% yield over 2 steps). $[\alpha]_D^{20}$ +40.8 (c 1.02 in CH$_2$Cl$_2$) from the imide with a diastereoisomer ratio of 93:7; identical (TLC, IR and ^{1}H NMR) with the racemic prop-2-ynyl silane.

Sparteine reactions

1,3-Bis[dimethyl(phenyl)silyl]octyne. Modifying the route of Zweifel,[4] 1-dimethyl(phenyl)silyl]octyne (0.488 g, 2 mmol) in THF (15 cm^3) was added dropwise to a mixture of *tert*-butyllithium (1.7 mol dm^{-3} in hexane, 1.41 cm^3, 2.4 mmol) and (−)-sparteine (0.563 g, 2.4 mmol) in THF (20 cm^3) at −78 °C. The mixture was warmed to 0 °C, stirred for a further 90 min, and cooled again to −78 °C. Dimethyl(phenyl)silyl chloride (0.44 cm^3, 2.6 mmol) was added dropwise and the mixture allowed to warm to room temperature. The usual work-up gave the ethynyl silane (0.376 g, 50%); R_f (CH$_2$Cl$_2$–light petroleum, 6:94) 0.27; ν_{max}(film)/cm^{-1} 2154 (C≡C), 1589 (Ph), 1248 (SiMe) and 1114 (SiPh); δ_H(250 MHz; CDCl$_3$) 7.65–7.53 (4 H, m, Ph), 7.4–7.28 (6 H, m, Ph), 1.95 (1 H, m, CHSi), 1.71–1.12 [8 H, m, (CH$_2$)$_4$], 0.86 (3 H, m, MeCH$_2$), 0.39 (6 H, s, SiMe$_2$) and 0.37 (6 H, s, SiMe$_2$); δ_C(250 MHz; CDCl$_3$) 138.3+, 136.8+, 134.1−, 133.7−, 133.0−, 129.2−, 129.0−, 127.7−, 111.7+, 83.0+, 31.3+, 29.1+, 29.0+, 22.5+, 21.3−, 14.0−, −0.41−, −4.42− and −5.0−; $[\alpha]_D^{20}$ −0.2 (c 1.52 in CH$_2$Cl$_2$); m/z (+FAB) 378 (30%, M$^+$), 363 (55, M − Me) and 135 (100, SiMe$_2$Ph) (Found: M$^+$, 378.2170. C$_{24}$H$_{34}$Si$_2$ requires M, 378.2199).

3-[Dimethyl(phenyl)silyl]octyne 8c. Following the route of Zweifel,[4] the ethynyl silane (0.376 g, 0.993 mmol) in ethanol (15 cm^3) was added with stirring to silver nitrate (0.253 g, 1.49 mmol) in ethanol (18 cm^3) and water (6 cm^3) at 0 °C in four equal portions 15 min apart and the mixture stirred for a further 15 min. Potassium cyanide (0.484 g, 7.45 mmol) in water (5 cm^3) was added, the mixture warmed to room temperature, and stirred for a further 30 min. The usual work-up gave the essentially racemic prop-2-ynyl silane (0.238 g, 98%); $[\alpha]_D^{20}$ −0.113 (c 1.76 in CH$_2$Cl$_2$); identical (TLC, IR, ^{1}H NMR) with the earlier sample.

N,N-Dimethyl-3-[dimethyl(phenyl)silyl]butanamide

Following Ager[16] and Crump,[8] N,N-dimethylcrotonamide[22] (1 mmol) in THF (10 cm^3) was added dropwise to a mixture of dimethyl(phenyl)silyllithium (1 mmol dm^{-3} in THF, 4 cm^3, 4 mmol) and dimethylzinc (2 mol dm^{-3} in toluene, 2 cm^3, 4 mmol) in THF (20 cm^3) at −78 °C under argon, and the mixture was stirred for 90 min. The mixture was quenched with saturated aqueous ammonium chloride (20 cm^3). The mixture was allowed to warm to room temperature. Dilute hydrochloric acid (80 cm^3) was added and the aqueous layer extracted with ether (3 × 30 cm^3). The combined organic extracts were dried (MgSO$_4$), the solvent evaporated under reduced pressure and the residue chromatographed (SiO$_2$, EtOAc–light petroleum, 1:1) to give the silylated *amide* (71%); R_f (EtOAc–light petroleum, 1:1) 0.31; ν_{max}(film)/cm^{-1} 1648 (C=O), 1248 (SiMe) and 1112 (SiPh); δ_H(250 MHz; CDCl$_3$) 7.55–7.46 (2 H, m, Ph), 7.38–7.31 (3 H, m, Ph), 2.91 (3 H, s, NMe$_A$Me$_B$), 2.89 (3 H, s, NMe$_A$Me$_B$), 2.32 (1 H, dd, J 15.0 and 3.7, CH$_A$H$_B$CO), 2.06 (1 H, dd, J 15.0 and 10.9, CH$_A$H$_B$CO), 1.50 (1 H, m, CHSi), 0.97 (3 H, d, J 7.3, MeCHSi) and 0.28 (6 H, s, SiMe$_2$); δ_C(400 MHz; CDCl$_3$) 173.0+, 137.8+, 134.0−, 129.0−, 127.8−, 37.3−, 35.5−, 35.2+, 16.2−, 14.7−, −4.7− and −5.3−; m/z (+EI) 248 (10%, M − 1), 234 (100, M − Me) and 135 (95, SiMe$_2$Ph)

(Found: M$^+$, 249.1554. C$_{18}$H$_{22}$NOSi requires M, 249.1549). This compound failed to give the acyl silane 15e using the method described below.

Synthesis of acyl silanes 15a–15d

Acyl silanes are unstable in light and were prepared with the flasks covered with aluminium foil. Following Ghosh,[12] dimethyl(phenyl)silyllithium (1 mol dm^{-3} in THF, 2.4 cm^3) was added dropwise to a stirred solution of the amide (2 mmol) in dry THF (3 cm^3) under argon at −78 °C and the mixture kept at this temperature for 1.5 h. Saturated aqueous ammonium chloride (10 cm^3) was added at this temperature, and the mixture was extracted with ether (3 × 30 cm^3). The combined organic extracts were washed with brine and dried (MgSO$_4$), The solvent was evaporated under reduced pressure and the residue was chromatographed (SiO$_2$, Et$_2$O–hexane). The following acyl silanes were prepared by this method.

(Butanoyl)dimethyl(phenyl)silane 15a (55%). R_f (hexane–Et$_2$O, 94:6) 0.35; ν_{max}(film)/cm^{-1} 1641 (C=O), 1249 (SiMe) and 1110 (SiPh); δ_H(250 MHz; CDCl$_3$) 7.6–7.2 (5 H, m, Ph), 2.5 (2 H, t, J 7.3, CH$_2$CO), 1.50 (2 H, sextet, J 7.3, CH$_2$CH$_2$CO), 0.8 (3 H, t, J 7.3, MeCH$_2$) and 0.5 (6 H, s, SiMe$_2$); δ_C(400 MHz; CDCl$_3$) 246.7+, 134.7+, 134.0−, 129.9−, 127.9−, 50.8+, 15.7+, 13.8− and −4.5−; m/z (+EI) 205 (10%, M − 1) and 163 (50, M − C$_3$H$_7$) (Found: M$^+$, 206.1137. C$_{12}$H$_{18}$OSi requires M, 206.1127).

(3-Phenylpropionyl)dimethyl(phenyl)silane[13] 15b (68%). R_f (hexane–Et$_2$O 94:6) 0.29; ν_{max}(film)/cm^{-1} 1643 (C=O), 1249 (SiMe) and 1110 (SiPh); δ_H(250 MHz; CDCl$_3$) 7.6–7.0 (10 H, m, Ph), 2.90 (2 H, m, CH$_2$Ph), 2.76 (2 H, m, CH$_2$CO) and 0.46 (6 H, s, SiMe$_2$); δ_C(400 MHz; CDCl$_3$) 245.2+, 141.5+, 134.3+, 134.0−, 130,0−, 128.4−, 128.3−, 128.2−, 125.9−, 50.4+, 28.3+ and −4.8−.

(4-Phenylbutanoyl)dimethyl(phenyl)silane 15c (61%). R_f (hexane–Et$_2$O 94:6) 0.29; ν_{max}(film)/cm^{-1} 1642 (C=O), 1249 (SiMe) and 1110 (SiPh); δ_H(400 MHz; CDCl$_3$) 7.56–7.51 (2 H, m, Ph), 7.45–7.36 (3 H, m, Ph), 7.27–7.12 (3 H, m, Ph), 7.09–7.03 (2 H, d, J 7.4, Ph), 2.59 (2 H, t, J 7.3, CH$_2$Ph), 2.5 (2 H, t, J 7.3, CH$_2$CO), 1.75 (2 H, quintet, J 7.3, CH$_2$CH$_2$CO) and 0.475 (3 H, s, SiMe$_A$Me$_B$) and 0.474 (3 H, s, SiMe$_A$Me$_B$); δ_C(400 MHz; CDCl$_3$) 246.1+, 141.8+, 134.5+, 134.0−, 130.0−, 128.4−, 128.3−, 128.2−, 125.8−, 47.9+, 35.1+, 23.8+, −4.5− and −4.7−; m/z (+CI) 281 (35%, M − 1), 267 (10, M − Me) and 135 (100, SiMe$_2$Ph) (Found: M$^+$, 282.1458. C$_{18}$H$_{22}$OSi requires M, 282.1440).

(Phenylacetyl)dimethyl(phenyl)silane[23] 15d (44%). R_f (hexane–Et$_2$O, 94:6) 0.28; ν_{max}(film)/cm^{-1} 1650 (C=O), 1249 (SiMe) and 1111 (SiPh); δ_H(250 MHz; CDCl$_3$) 7.5–7.2 (8 H, m, Ph), 7.0–6.9 (2 H, m, Ph), 3.8 (2 H, s, CH$_2$Ph) and 0.39 (6 H, s, SiMe$_2$); δ_C(400 MHz; CDCl$_3$) 242.5+, 134.4+, 134.1−, 132.1+, 130.0−, 129.9−, 128.5−, 128.1−, 126.8−, 55.6+ and −4.5−.

1,1,3-Tris[dimethyl(phenyl)silyl]butanol

Following Ghosh,[13] dimethyl(phenyl)silyllithium (1.1 mol dm^{-3} in THF, 17.45 cm^3, 19.2 mmol) was stirred with the ester 4a (2.0 g, 8.0 mmol) in THF (20 cm^3) under argon at −78 °C for 3 h, and the mixture was quenched with saturated aqueous ammonium chloride (30 cm^3). The aqueous layer was extracted with ether (3 × 50 cm^3) and the combined organic extracts were dried (MgSO$_4$) and the solvent evaporated under reduced pressure. Chromatography (SiO$_2$, Et$_2$O–light petroleum, 6:94) gave the disilyl alcohol (82%); R_f (Et$_2$O–light petroleum, 1:9) 0.43; ν_{max}(film)/cm^{-1} 3544 (OH), 1251 (SiMe) and 1110 (SiPh); δ_H(400 MHz; CDCl$_3$) 7.52–7.23 (15 H, m, Ph), 1.97 (1 H, dd, J 15.1 and 2.31, CH$_A$H$_B$CHSi), 1.51 (1 H, dd, J 15.1 and 10.4, CH$_A$H$_B$CHSi), 1.07 (1 H, m, CHSi), 0.77 (3 H, d, J 7.2, MeCHSi), 0.19 (3 H, s, SiMe$_A$Me$_B$), 0.17 (3 H, s, SiMe$_A$Me$_B$), 0.14 (3 H, s, SiMe$_C$Me$_D$), 0.13 (3 H, ss, SiMe$_C$Me$_D$), 0.12 (3 H, s,

CSi$Me_E$$Me_F$) and 0.1 (3 H, s, SiMe$_E$$Me_F$); δ_C(400 MHz; CDCl$_3$) 138.7+, 138.1+, 137.9+, 134.7−, 134.3−, 129.0−, 128.9−, 127.7−, 127.6−, 66.7+, 17.8−, 16.6−, −2.7, −3.2−, −3.7−, −4.0−, −5.2− and −5.4−; m/z (+FAB) 475 (10%, M − 1), 403 (30, M − SiMe$_2$Ph) and 135 (100, SiMe$_2$Ph) (Found: M$^+$, 476.2401. C$_{28}$H$_{40}$Si$_3$O requires M, 476.2387).

1,3-Bis[dimethyl(phenyl)silyl]butanone 15e

Following Ghosh's second recipe,[13] pyridinium dichromate (4.77 g, 12.6 mmol) was stirred with 1,1,3-tris[dimethyl(phenyl)-silyl]butanol (3.33 g, 7 mmol) in dichloromethane (10 cm^3) at room temperature for 74 h. The solvent was evaporated, ether (20 cm^3) was added to dissolve the organic extracts, the crude mixture was filtered through a sintered funnel and the solvent evaporated. The residue was chromatographed (SiO$_2$, Et$_2$O–light petroleum, 1:9) to give the *acyl silane* (1.52 g, 64%) as a yellow oil; R_f (Et$_2$O–light petroleum, 1:9) 0.41; ν_{max}(film)/cm^{-1} 1643 (C=O), 1249 (SiMe) and 1111 (SiPh); δ_H(250 MHz; CDCl$_3$) 7.6–7.3 (10 H, m, Ph), 2.66 (1 H, dd, J 16.2 and 3.6, CH_AH$_B$CO), 2.32 (1 H, dd, J 16.2 and 10.4, CH$_A$$H_B$CO), 1.50 (1 H, m, CHSi), 0.78 (3 H, d, J 7.3, MeCHSi), 0.47 (3 H, s, SiMe_AMe$_B$), 0.46 (3 H, s, SiMe$_A$$Me_B$), 0.21 (3 H, s, Si$Me_CMe_D$) and 0.20 (3 H, s, SiMe$_C$$Me_D$); δ_C(250 MHz; CDCl$_3$) 246.1+, 137.1+, 134.7+, 134.0−, 133.9−, 129.8−, 129.0−, 128.5−, 127.3−, 50.9+, 14.6−, 13.3−, −4.6−, −5.0− and −5.2−; m/z (+FAB) 341 (10%, M + 1), 325 (50, M − Me) and 135 (100, SiMe$_2$Ph) (Found: M$^+$, 340.1679. C$_{20}$H$_{28}$OSi$_2$ requires M, 340.1679).

Dehydration of acyl silanes

Method A. Following Comins and Dehgani,[24] the acyl silane (1 mmol) in THF (3 cm^3) was stirred in a solution of LDA (2 mmol) in THF at −78 °C under argon for 6 h. 2-[*N,N*-Bis(trifluromethanesulfonyl)amino]-5-chloropyridine (4 mmol) in THF (2 cm^3) was added dropwise and stirring continued for 4 h. The reaction was quenched with saturated aqueous ammonium chloride (10 cm^3), the mixture extracted with ether (3 × 30 cm^3), the organic layer dried (K$_2$CO$_3$), evaporated under reduced pressure and the residue chromatographed (SiO$_2$, hexane–Et$_2$O, 90:10).

Method B. Following Stang,[9] triflic anhydride (1.5 mmol), the acyl silane (1.0 mmol) and 2,6-di-*tert*-butyl-4-methyl-pyridine (1.5 mmol) were stirred in dry dichloromethane (10 cm^3) under argon at room temperature for 17 h. The solvent was evaporated under reduced pressure and the residue combined with hexane (60 cm^3). The solid pyridinium triflate was filtered off and washed with additional hexane (20 cm^3). The hexane solution was washed with hydrochloric acid (1 mol dm^{-3}, 50 cm^3), brine (50 cm^3) and dried (K$_2$CO$_3$). The mixture was filtered, evaporated under reduced pressure and the residue chromatographed (SiO$_2$, CH$_2$Cl$_2$–hexane, 5:95) to give a mixture of enol triflates and alkynes. The mixture was heated in pyridine at 60 °C for 1 h to complete the elimination, and worked up with ether (30 cm^3), washing with hydrochloric acid (3 mol dm^{-3}, 40 cm^3) and brine (50 cm^3) and then dried (MgSO$_4$).

Method C. The acyl silane (2.0 mmol), triflic anhydride (2.95 mmol) and pyridine (0.24 cm^3, 3 mmol) were mixed at −78 °C in dichloromethane (10 cm^3) and stirred at room temperature for 21 h. The solvent was evaporated off under reduced pressure, pyridine (10 cm^3) was added to the crude triflate mixture and the mixture stirred at 60 °C for 1 h. Ether (30 cm^3) was added, and the organic layer was washed with hydrochloric acid (1 mol dm^{-3}, 3 × 20 cm^3), dried (MgSO$_4$), and the solvent was evaporated off.

Method D. Similar to Method C except that the mixture of acyl silane and pyridine was cooled to −22 °C before the addition of triflic anhydride.

Method E. Triflic anhydride (1.74 mmol) was added dropwise with stirring to the acyl silane (1 mmol) and pyridine (0.2 cm^3,

2.48 mmol) in dichloromethane (25 cm^3) under argon at −25 °C and the mixture stirred at room temperature for 23 h. The solvent was removed under reduced pressure, pyridine (5 cm^3) was added, and the mixture was heated at 60 °C for 1 h. Dichloromethane (30 cm^3) was added and the mixture shaken vigorously with hydrochloric acid (3 mol dm^{-3}, 3 × 20 cm^3). The organic layer was dried (MgSO$_4$), the solvent was evaporated under reduced pressure, and the residue was chromatographed (SiO$_2$, light petroleum).

The following alkynyl silanes were prepared by one or more of these methods.

Dimethyl(phenyl)(but-1-ynyl)silane[25] 17a. As a yellow liquid (49%, Method B; 85%, Method D); R_f (hexane–CH$_2$Cl$_2$, 95:5) 0.31; ν_{max}(film)/cm^{-1} 2175 (C≡C), 1589 (Ph), 1249 (SiMe) and 1115 (SiPh); δ_H(250 MHz; CDCl$_3$) 7.6–7.0 (10 H, m, Ph), 2.29 (2 H, q, J 7.5, MeCH_2), 1.17 (3 H, t, J 7.5, MeCH$_2$) and 0.39 (6 H, s, SiMe$_2$), δ_C(400 MHz; CDCl$_3$) 137.7+, 133.7−, 129.3−, 127.8−, 110.9+, 81.5+, 13.8− , 13.7+ and −0.6−.

Dimethyl(phenyl)(3-phenylprop-1-ynyl)silane[26] 17b. As a yellow liquid (33% Method A; 90% Method C); R_f (hexane–CH$_2$Cl$_2$ 95:5) 0.23; ν_{max}(film)/cm^{-1} 2176 (C≡C), 1250 (SiMe) and 1114 (SiPh); δ_H(250 MHz; CDCl$_3$) 7.75–7.65 (2 H, m, Ph), 7.45–7.2 (8 H, m, Ph), 3.73 (2 H, s, CH$_2$) and 0.4 (6 H, s, SiMe$_2$); δ_C(250 MHz; CDCl$_3$) 137.4+, 136.2+, 133.7−, 129.4−, 128.5−, 127.93−, 127.88−, 126.7−, 106.2+, 85.0+, 26.3+ and −0.65.

Dimethyl(phenyl)(4-phenylbut-1-ynyl)silane 17c. As a yellow liquid (61% Method B); R_f (hexane–CH$_2$Cl$_2$ 95:5) 0.25; ν_{max}(film)/cm^{-1} 2174 (C≡C), 1602 (Ph), 1249 (SiMe) and 1115 (SiPh); δ_H(250 MHz; CDCl$_3$) 7.63–7.55 (2 H, m, Ph), 7.42–7.21 (8 H, m, Ph), 2.87 (2 H, t, J 7.5, CH$_2$Ph), 2.6 (2 H, m, CH$_2$C≡C) and 0.383 (6 H, s, SiMe$_2$); δ_C(250 MHz; CDCl$_3$) 140.5+, 137.5+, 133.7−, 129.2−, 128.5−, 128.3−, 127.8−, 126.3−, 108.5+, 83.3+, 35.0−, 22.2+ and −0.72−; m/z (+EI) 264 (40%, M$^+$), 249 (100, M − Me) and 135 (10, SiMe$_2$Ph) (Found: M$^+$, 264.1350. C$_{18}$H$_{22}$Si requires M, 264.1334).

Dimethyl(phenyl)(2-phenylethynyl)silane[27] 17d. As a yellow liquid (44% by method B, 80% Method E). R_f (hexane–CH$_2$Cl$_2$, 90:10) 0.33; ν_{max}(film)/cm^{-1} 2158 (C≡C), 1250 (SiMe) and 1118 (SiPh); δ_H(250 MHz; CDCl$_3$) 7.76–7.29 (10 H, m, Ph) and 0.51 (6 H, s, SiMe$_2$); δ_C(400 MHz; CDCl$_3$) 139.9+, 137.1+, 133.8−, 132.1−, 129.5−, 128.8−, 128.3−, 128.8−, 128.0−, 106.8+, 92.1+ and −0.74−.

1,3-Bis[dimethyl(phenyl)silyl]butyne 17e. As a yellow oil (84% Method B, but using 2,6-di-*tert*-butylpyridine); R_f (Et$_2$O–light petroleum, 3:97) 0.43; ν_{max}(film)/cm^{-1} 2156 (C≡C), 1589 (Ph), 1249 (SiMe) and 1114 (SiPh); δ_H(250 MHz; CDCl$_3$) 7.63–7.56 (4 H, m, Ph), 7.43–7.29 (6 H, m, Ph), 2.0 (1 H, q, J 7.3, CHSi), 1.16 (3 H, d, J 7.3, MeCHSi), 0.39 (3 H, s, SiMe_AMe$_B$) and 0.37 (3 H, s, SiMe$_A$$Me_B$); δ_C(400 MHz; CDCl$_3$) 138.1+, 136.5+, 134.2−, 133.7−, 129.4−, 129.1−, 127.8−, 127.7−, 113.1+, 81.9+, 14.8−, 14.5−, −0.42−, −4.8− and −5.4−; m/z (EI)[28] 322 (12%, M$^+$), 307 (1, M − Me), 172 (35, M − Me − PhSiMe$_2$) and 135 (100, PhSiMe$_2$) (Found: M$^+$, 322.1566 (ref. 20); 322.1590 (ref. 29). C$_{20}$H$_{26}$Si$_2$ requires M, 322.1573).

Reaction giving the alkenes 18 and 19

The acyl silane **15b** (0.53 g, 2 mmol) and triflic anhydride (3.47 mmol) were stirred in dichloromethane (35 cm^3) under argon at room temperature for 3.5 h and quenched with water (20 cm^3). The aqueous layer was extracted with dichloromethane (3 × 30 cm^3) and the combined organic extracts shaken with saturated aqueous sodium hydrogen carbonate (20 cm^3) and dried (MgSO$_4$). The solvent was evaporated under reduced pressure. The residue was chromatographed (SiO$_2$, light petroleum) to give an inseparable mixture of 1,3-diphenylpropenes[29] **18** (Z:E typically 2:1, but varying according to the time given to the

reaction), and (Z)-1,5-diphenylpent-2-ene Z-**19** (0.070 g) and a mixture of the triflate **16b** and the alkyne **17b**. The triflate–alkyne mixture was heated in pyridine at 60 °C for 1 h, cooled to room temperature and washed with dilute hydrochloric acid (40 cm³). The usual work-up gave the alkyne **17b** (0.12 g, 24%). The alkenes **18** were identified by definitive signals in the ¹H NMR spectrum; δ_H(250 MHz; CDCl₃) Z: 7.4–7.0 (10 H, m, Ph), 6.62 (1 H, dt, J 11.5 and 1.5, PhCH), 5.88 (1 H, dd, J 11.5 and 7.5, CHCH₂Ph), 3.70 (2 H, dd, J 7.5 and 1.5, CH₂Ph); E: 7.4–7.0 (10 H, m, Ph), 6.4 (1 H, d, J 15.9, PhCH), 6.35 (1 H, dt, J 15.9 and 6.0, CHCH₂Ph) and 3.57 (2 H, d, J 6, CH₂Ph), matching the literature values.[30]

1,5-Diphenylpent-2-en-3-yl trifluoromethanesulfonate 22 †

Triflic anhydride (1.7 mol dm⁻³ in CH₂Cl₂, 3 cm³, 5.1 mmol) was added dropwise to a mixture of 1,5-diphenylpentan-3-one **21**[30,31] (1 g, 4.2 mmol) and 2,6-di-*tert*-butylpyridine (0.92 g, 4.7 mmol) in dichloromethane (20 cm³), and the mixture stirred at room temperature for 92 h. The solvent was removed under reduced pressure and the residue taken up in hexane, poured into dilute hydrochloric acid, and separated. The aqueous layer was extracted with dichloromethane (2 × 50 cm³), the combined organic phases were washed with aqueous sodium hydrogen carbonate, dried (MgSO₄) and evaporated under reduced pressure. The residue was chromatographed (SiO₂, Et₂O–light petroleum, 1 : 9] to give the *enol triflate* (1.28 g, 74%) (cis:trans, 22:78); R_f (Et₂O–light petroleum, 1 : 9) 0.46 ν_{max}(film)/cm⁻¹ 1603 (Ph), 1413 (OTf) and 1210 (OTf); δ_H(500 MHz; CDCl₃) cis: 7.35–6.95 (10 H, m, Ph), 5.74 (1 H, t, J 7.9, PhCH₂CHC=C), 3.22 (2 H, d, J 7.9, PhCH₂CHC=C), 2.93 (2 H, t, J 7.3, PhCH₂CH₂), 2.80 (2 H, t, J 7.3, PhCH₂CH₂); trans: 7.35–6.95 (10 H, m, Ph), 5.38 (1 H, t, J 7.3, PhCH₂CHC=C), 3.53 (2 H, d, J 7.3, PhCH₂CHC=C), 2.90 (2 H, t, J 7.5, PhCH₂CH₂), 2.73 (2 H, t, J 7.5, PhCH₂CH₂); m/z (+EI) 370 (4.5, M⁺), 220.1 (16, M − OTf), 105 (15, PhCH₂CH₂) and 91 (100, PhCH₂) (Found: M⁺, 370.0854. C₁₈H₁₇F₃O₃S requires M, 370.0850).

1,5-diphenylpent-2-yne 23 †

Following Hargrove and Stang,[32] the vinyl triflates **22** (0.5 g, 2.55 mmol) were refluxed in pyridine (20 cm³) for 4 h, the mixture was cooled to room temperature, and stirring continued for a further 48 h. The mixture was poured into dilute hydrochloric acid solution, separated, and extracted with dichloromethane (2 × 50 cm³). The solvent was removed under reduced pressure from the combined organic phases, and the residue chromatographed (SiO₂, Et₂O–light petroleum, 1 : 9) to give the *alkyne*[23] (0.35 g, 62%); R_f (Et₂O–light petroleum, 1 : 9) 0.51; ν_{max}(film)/cm⁻¹ 2248 (C≡C) and 1602 (Ph); δ_H(250 MHz; CDCl₃) 7.4–7.2 (10 H, m, Ph), 3.6 (2 H, s, PhCH₂C≡C), 2.9 (2 H, t, J 7.5, PhCH₂CH₂) and 2.55 (2 H, m, PhCH₂CH₂C≡C); m/z (+EI) 220 (24, M⁺), 129 (35, M − PhCH₂) and 91 (100, PhCH₂) (Found: M⁺, 220.1249. C₁₇H₁₆ requires M, 220.1252).

(Z)-1,5-Diphenylpent-2-ene Z-19 †

Following Raunio and Bonner,[29] the alkyne **23** (0.250 g, 1.14 mmol) was hydrogenated over Lindlar's catalyst (0.1 g) in hexane (10 cm³) under argon for 90 min, when no alkyne remained (TLC). The residue was filtered, washed with ether (3 × 50 cm³) and the ether layers combined. The solvent was removed under reduced pressure, and the residue chromatographed (SiO₂, Et₂O–light petroleum, 1 : 9) to give the cis-*alkene* (0.230 g, 91%); R_f (Et₂O–light petroleum, 1 : 9) 0.64; ν_{max}(film)/cm⁻¹ 1602 (Ph); δ_H(250 MHz; CDCl₃) 7.35–7.1 (10 H, m, Ph), 5.6 (1 H, dt, J 11.5 and 5.7, PhCH₂CH=CH), 5.55 (1 H, dt, J 11.5 and 5.9, PhCH₂CH₂CH), 3.34 (2 H, J 5.7, PhCH₂CH), 2.73 (2 H, t, J 7.3, PhCH₂CH₂), 2.49 (2 H, m, PhCH₂CH₂); m/z (+EI) 222 (40%,

M⁺), 131 (62, M − PhCH₂) and 91 (100, PhCH₂) (Found: M⁺, 222.1408. C₁₇H₁₈ requires M, 222.1408).

(E)-1,5-Diphenylpent-2-ene E-19 †

Following Fleet and Shing,[33] triflic anhydride (1.7 mol dm⁻³ in CH₂Cl₂, 1.5 cm³, 2.55 mmol) was added dropwise to a mixture of 2,6-di-*tert*-butylpyridine (0.98 g, 5.9 mmol) and 1,5-diphenylpentan-3-ol[32] (0.60 g, 2.5 mmol) in dichloromethane (20 cm³) under argon, and the mixture stirred at room temperature for 24 h. The solvent was removed under reduced pressure, and the residue combined with hexane, and added to dilute hydrochloric acid. The aqueous layer was extracted with dichloromethane (3 × 20 cm³), the combined organic phases were washed with saturated aqueous sodium hydrogen carbonate, dried (MgSO₄) and the solvent removed under reduced pressure, to give the *alkene* (0.490 g, 88%); R_f (Et₂O–light petroleum, 1 : 9) 0.63; δ_H(250 MHz; CDCl₃) 7.4–7.1 (10 H, m, Ph–H), 5.65 (1 H, dt, J 15.1 and 4.8, PhCH₂CH), 5.56 (1 H, dt, 15.1 and 5.4, PhCH₂CH₂CH), 3.37 (2 H, d, J 4.9, PhCH₂CH), 2.73 (2 H, t, J 7.7, PhCH₂CH₂) and 2.45–2.36 (2 H, m, PhCH₂CH₂CH).

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