# Synthesis of vinylsilanes by silyl-cupration of acetylenes using *tert*-butyldiphenylsilyl-cuprate reagents

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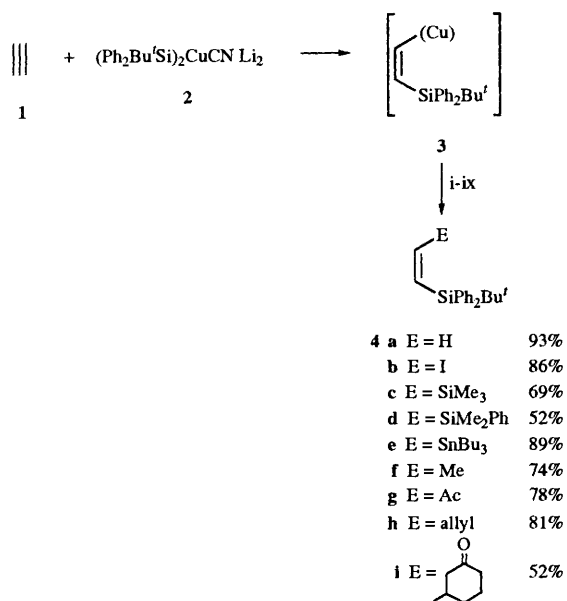
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The *tert*-butyldiphenylsilyl-cuprate **2** reacts with acetylenes **1** and **5–10** to give vinyl-cuprates **3** and **11**, which react with electrophiles to give the vinylsilanes **4** and **12–17** carrying the relatively hindered and hence unreactive *tert*-butyldiphenylsilyl group. In comparative tests, the *tert*-butyldiphenylsilyl group shows some properties that are usefully different from those of relatively unhindered silyl groups and others that are similar.

We reported some time ago that lithium dimethylphenylsilyl-cuprate reacts *syn* stereospecifically with acetylenes to place the silyl group at the C-1 terminus and the copper atom on C-2, and that the vinyl-cuprate intermediate reacts with several electrophiles regiospecifically to give a wide range of vinylsilanes.[1] We have also reported that a silyl-cuprate reagent can be prepared from *tert*-butyldiphenylsilyllithium,[2] that it reacts with enones normally[2] and with allenes with somewhat different selectivities from its smaller dimethylphenylsilyl counterpart.[3] We now report that the *tert*-butyldiphenylsilyl-cuprate reagent reacts with acetylenes in much the same way as the dimethylphenylsilyl-cuprate reagent and with comparable or better yields, making available a range of vinylsilanes carrying the large and relatively unreactive *tert*-butyldiphenylsilyl group. We also report some examples of useful differences that a hindered silyl group imparts to the chemistry of vinylsilanes.
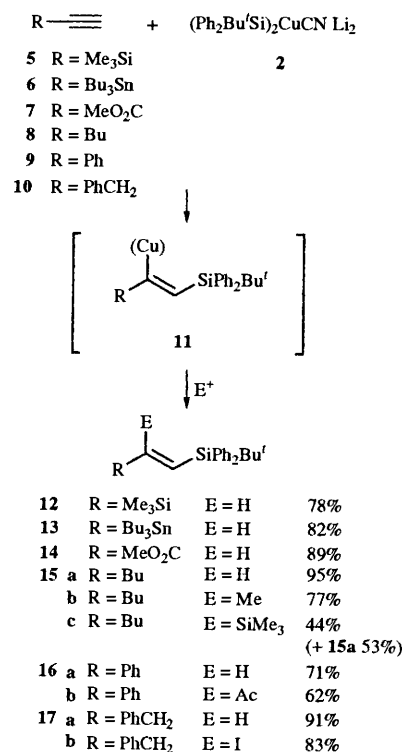
Acetylene **1** reacts with the *tert*-butyldiphenylsilyl cuprate reagent **2** to give an intermediate cuprate **3**, which reacts easily, and without the need for additives like hexamethylphosphoramide (HMPA), with electrophiles like the proton, iodine, silyl and stannyl chlorides, methyl iodide, acetyl chloride and allyl bromide, to give the vinylsilanes **4** (Scheme 1). Only in
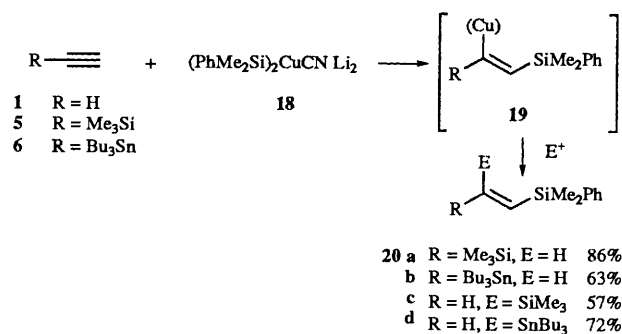
the reaction with cyclohex-2-enone did we need HMPA in order to make the conjugate addition product **4i**.

Similarly, the mono-substituted acetylenes **5–10** react with the same regiochemistry as in the earlier work to give the vinylsilanes **12–17**, in which the silyl group is placed, as usual, at the terminus (Scheme 2). We did not report in the earlier work[4]

| | | | |
|---|---|---|---|
| 5 | R = Me₃Si | | |
| 6 | R = Bu₃Sn | | |
| 7 | R = MeO₂C | | |
| 8 | R = Bu | | |
| 9 | R = Ph | | |
| 10 | R = PhCH₂ | | |

$R\!-\!\!\equiv\quad + \quad (Ph_2Bu^tSi)_2CuCN\ Li_2$

**2**

**11**

| | | | |
|---|---|---|---|
| 12 | R = Me₃Si | E = H | 78% |
| 13 | R = Bu₃Sn | E = H | 82% |
| 14 | R = MeO₂C | E = H | 89% |
| 15 a | R = Bu | E = H | 95% |
| b | R = Bu | E = Me | 77% |
| c | R = Bu | E = SiMe₃ | 44% (+ 15a 53%) |
| 16 a | R = Ph | E = H | 71% |
| b | R = Ph | E = Ac | 62% |
| 17 a | R = PhCH₂ | E = H | 91% |
| b | R = PhCH₂ | E = I | 83% |

**Scheme 2**

the reactions of the dimethylphenylsilyl-cuprate **18** with the silicon- and tin-containing acetylenes **5** and **6**, which give the vinyldisilane **20a** and the vinylstannane **20b**, and include them here (Scheme 3). The yields with the *tert*-butyldiphenylsilyl-cuprate reagent are poor only when the electrophile is trimethylsilyl chloride (44% yield of **15c**), but this was much better than we had been able to get with our usual dimethylphenylsilyl-cuprate reagent.[1] Confirming our earlier work, we repeated the reaction of hex-1-yne with the dimethylphenylsilyl-cuprate and added trimethylsilyl chloride to obtain only 5% of the corresponding disilylated product, together with *E*-1-dimethyl-

**1** + (Ph₂Bu^tSi)₂CuCN Li₂ ⟶ **2**

**3**

i-ix

**4**

| 4 a | E = H | 93% |
|---|---|---|
| b | E = I | 86% |
| c | E = SiMe₃ | 69% |
| d | E = SiMe₂Ph | 52% |
| e | E = SnBu₃ | 89% |
| f | E = Me | 74% |
| g | E = Ac | 78% |
| h | E = allyl | 81% |
| i | E = (cyclohexanone) | 52% |

**Scheme 1** *Reagents:* i, NH₄Cl; ii, I₂; iii, Me₃SiCl; iv, PhMe₂SiCl; v, Bu₃SnCl; vi, MeI; vii. AcCl; viii. allyl bromide; ix, cyclohexenone, HMPA

1  R = H
5  R = Me$_3$Si
6  R = Bu$_3$Sn

18

20 a  R = Me$_3$Si, E = H   86%
   b  R = Bu$_3$Sn, E = H   63%
   c  R = H, E = SiMe$_3$   57%
   d  R = H, E = SnBu$_3$   72%
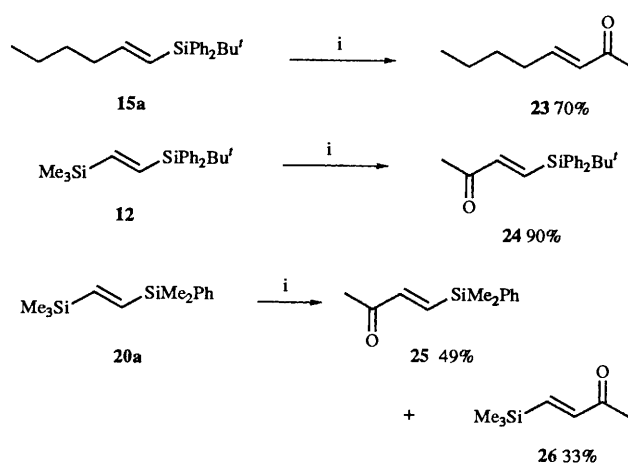
**Scheme 3**

(phenyl)silylhex-1-ene, the product of protonation, in 89% yield. In contrast, acetylene itself is anomalous: even with the dimethylphenylsilyl-cuprate reagent, trimethylsilyl chloride gave the corresponding Z-vinyldisilane **20c** in 57% yield and tributylstannyl chloride gave the vinylstannane **20d** in 72% yield (Scheme 3). Di-substituted acetylenes **21** are much less effective (Scheme 4), giving the vinylsilanes **22** in low yield.



21 a  R = Et
   b  R = Ph

2

22 a  R = Et 30%
   b  R = Ph 20%
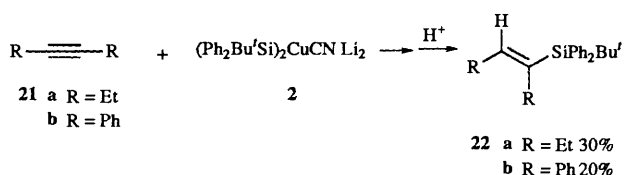
**Scheme 4**

All these reactions make available a wide range of vinylsilanes, some of which are conveniently crystalline, unlike their dimethylphenylsilyl counterparts. Also, since a trimethylsilyl or dimethylphenylsilyl group may be introduced as the electrophile (reaction **1** ⟶ **4c**) or may be the resident group (reaction **5** ⟶ **12**) it is easily possible to make either stereoisomer of differentially disilylated 1,2-disilylethylenes. It is also easy to make the differentially metallated alkenes having one silyl and one stannyl group, as in the preparation of the vinylstannanes **4e**, **13**, **20b** and **20d**.

However, the tert-butyldiphenylsilyl group cannot be relied upon to impart to vinylsilanes the normal properties associated with this functional group in synthesis, because the tert-butyldiphenylsilyl group may or may not be the electrofugal group following electrophilic attack.[5] We have shown already that it can function as the electrofugal group in the epoxidation of an allylsilane and in the formation of an αβ-unsaturated ketone from a β-silyl ketone.[2] We now add that it can function normally in the electrophilic substitution of a vinylsilane **15a** ⟶ **23**, where it cleanly underwent normal desilylative acetylation (Scheme 5). We also checked that it would indeed impart regioselectivity to the desilylative acetylation of the vinyldisilane **12**, where the trimethylsilyl group was exclusively removed to give only the silyl enone **24**, readily identifiable as the trans isomer, not only by its ¹H NMR spectrum (J 19 Hz) but also because we already had the cis isomer **4g** (J 14 Hz). Furthermore, the cis isomer **4g** cleanly gave the trans isomer **24** in 99% yield on treatment with sulfuric acid in THF at reflux for 3 h, showing that the tert-butyldiphenylsilyl group can be usefully more difficult to remove than a less hindered silyl group. For comparison, we also carried out the desilylative acetylation of the vinyldisilane **20a**. As expected from our considerable experience with how similar the trimethylsilyl and the dimethylphenylsilyl groups are, this was not significantly regioselective, giving both silyl enones **25** and **26** in comparable amounts, showing again that the tert-butyldiphenylsilyl group is a silyl group imparting usefully distinct reactivity.



15a

23 70%

12

24 90%

20a

25 49%

+

26 33%

**Scheme 5**   Reagents: i, AcCl, AlCl$_3$

Having now established the range of 'electrophiles' that we can expect the tert-butyldiphenylsilyl-cuprate to react with, we investigated briefly a few other reactions where this hindered silyl group might behave differently from the more usual silyl groups. One area where a silyl group that does not leave too easily might be especially useful is in silyl epoxides (Schemes 6 and 7). We find that the epoxides **27** can easily be made from the



27 a  R = H
   b  R = Bu$^n$

28 a  75%
   b  80%

30 65%

29
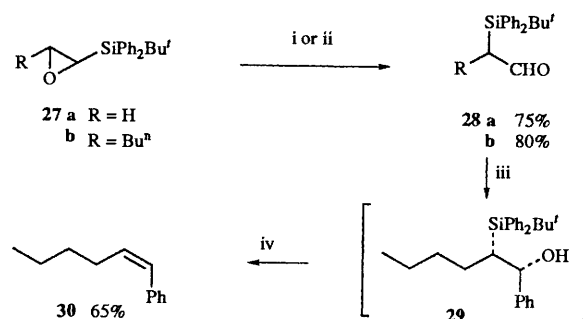
**Scheme 6**   Reagents and conditions: i, H$_2$SO$_4$; ii, BF$_3$·OEt$_2$; iii, PhMgBr, Et$_2$O, 0 °C; iv, KH, THF, 30 °C



31 93%

27a

31 43%   +

32 48%

33 50% at −25 °C
   44% at 0 °C

34 36% at 0 °C
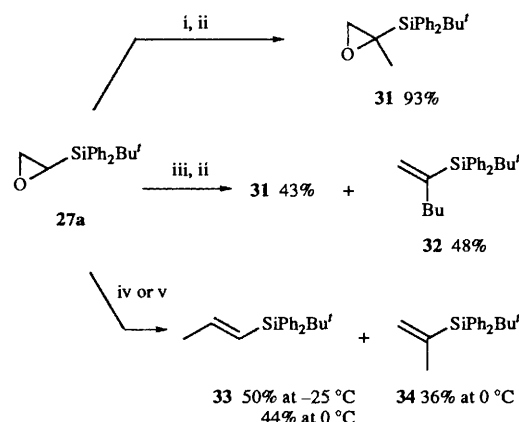
**Scheme 7**   Reagents and conditions: i, BuLi, TMEDA, THF, −50 °C; ii, MeI; iii, BuLi, 0 °C; iv, MeLi, −25 °C; v, MeLi, 0 °C

corresponding vinylsilanes, and their acid-catalysed rearrangements, with Lewis or protic acid, cleanly give the aldehydes **28** retaining the α-silyl group in a reaction similar to that observed with other epoxides having hindered silyl groups.[6] Aldehydes like **28** can be used for alkene synthesis by way of a β-silyl alcohol and a Peterson olefination, as in the reaction **28b** ⟶ **29** ⟶ **30**, where the nucleophilic attack on the aldehyde is

Cram-selective, and the *tert*-butyldiphenylsilyl group is evidently still capable of taking part in the *syn*-stereospecific elimination step.

The epoxide **27a** shows no reaction with lithium dimethylcuprate, but it does undergo metallation with butyllithium at −50 °C in the presence of *N*,*N*,*N'*,*N'*-tetramethylethylenediamine (TMEDA), and the intermediate can be methylated to give the substituted epoxide **31** (Scheme 7). Metallations of trimethylsilyl and triphenylsilyl epoxides are known.[7,8] The larger silyl group appears to make this reaction a little cleaner, but when carried out at 0 °C, it gives the same methylated epoxide **31** in lower yield together with the alkene **32** in a reaction with precedent.[7,9] The reaction with methyllithium is more puzzling as at −25 °C the alkene **33** was produced, and at 0 °C a mixture of the alkene **33** and **34**. The formation of the alkene **34** is understandable as a consequence of metallation α to the silyl group and carbene formation,[7,9] as in the formation of the alkene **32**. The formation of its regioisomer **33**, however, appears to indicate either that metallation took place, unprecedentedly β to the silyl group, or that the methyllithium acted as a nucleophile and opened the epoxide, again β to the silyl group, and that then the dehydration step was unusually easy, since all that was involved was a simple aqueous work-up.

A second area where the large silyl group might have some advantages is in the control of regio- and stereo-chemistry in the reactions of β-silyl ketones (Scheme 8). We therefore compared
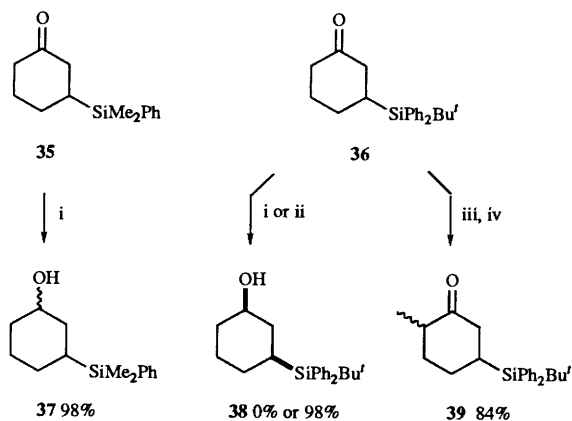


**Scheme 8** *Reagents and conditions:* i, NaBH₄, EtOH, r.t.; ii, LiAlH₄, THF, r.t.; iii, LDA, THF, −20 °C; iv, MeI

the ketones **35** and **36**. Whereas the ketone **35** unremarkably gives the alcohols **37** in a ratio of 73:27 on reduction with sodium boranuide (NaBH₄) in methanol at 0 °C in 30 min,[10] the β-silyl group in the ketone **36** hinders this reagent enough for there to be no reaction even under reflux in ethanol for several hours. This ketone is however reduced by lithium aluminium hydride to give only the equatorial alcohol **38**. Both equatorial alcohols gave 4-methylbenzenesulfonates, with the latter, **38**, taking perceptibly longer for reaction to go to completion. We already knew that the ketone **35** underwent methylation exclusively on C-6,[11] and we now find that this is equally true of the ketone **36**, which gave a 1:1.5 mixture of diastereoisomers **39**, with no evidence of any hindrance from the large silyl group in the deprotonation step.

A final point that we wished to establish was that the *tert*-butyldiphenylsilyl group would be significantly less reactive with respect to our silyl-to-hydroxy conversion than the dimethylphenylsilyl group.[12] We already have a silyl group that is more reactive in this transformation,[13] but we foresaw a need for one that was less reactive or even inert. We prepared the disilane **41** from the known[14] alcohol **40** (Scheme 9). This compound smoothly underwent the silyl-to-hydroxy conversion to give the mono-alcohol **42**, the *tert*-butyl group evidently
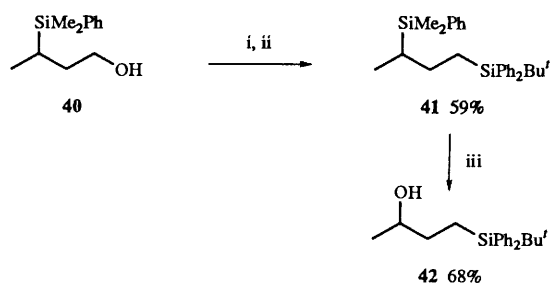


**Scheme 9** *Reagents:* i, TsCl, Et₃N; ii, Bu'Ph₂SiLi; iii, Br₂, AcOOH, AcOH

hindering the first step, the electrophilic attack on the phenyl ring, for both phenyl groups on the *tert*-butyldiphenylsilyl group were intact.

## Experimental

### Silyl-cupration of acetylenes

Typically, *tert*-butyldiphenylsilyl chloride (1.64 g, 6 mmol) was stirred with lithium shot (0.252 g, 36 mmol) under nitrogen in THF (6 cm³) for 4 h at 0 °C. Copper(I) cyanide (268 mg, 3 mmol) in THF (5 cm³) was added at 0 °C and the mixture stirred for 30 min. The acetylene (3 mmol) in THF (1 cm³) was added at 0 °C, except where otherwise stated, and the mixture stirred for 30 min. The electrophile (6 mmol usually) was then added at 0 °C, except where otherwise stated, and stirred for 1–3 h before the mixture was quenched at 0 °C with aqueous ammonium chloride. Aqueous work-up with diethyl ether, drying (MgSO₄) and chromatography gave the following vinylsilanes.

*tert*-**Butyl(diphenyl)silylethene 4a**, 93%; by quenching **3** with saturated aqueous ammonium chloride, $R_f$(hexane) 0.42; $\nu_{max}$(film)/cm⁻¹ 1600 (C=C), 1250 (SiBu') and 1115 (SiPh); $\delta_H$(80 MHz; CDCl₃) 7.64–7.55 (4 H, m, Ph), 7.34–7.28 (6 H, m, Ph), 6.81–5.54 (3 H, m, CH=CH₂) and 1.09 (9 H, s, SiCMe₃); $\delta_C$(20 MHz; CDCl₃) 136.55 (=CH₂), 136.25, 134.32, 129.14 and 127.62 (SiPh), 133.55 (=CHSi), 27.76 ($Me_3$CSi) and 18.05 (CSi); *m/z* 266 (3%, M⁺), 209 (100%, M − Bu') 183 (21), 131 (4) and 105 (20) (Found: C, 81.3; H, 8.2. C₁₈H₂₂Si requires C, 81.1; H, 8.3%).

(*Z*)-**1-*tert*-Butyl(diphenyl)silyl-2-iodoethene 4b**, 86%; by adding iodine at −78 °C to **3**, prepared at −78 °C, and after 15–30 min allowing the mixture to warm to 0 °C, keeping it at that temperature for 1 h before quenching; $R_f$(hexane) 0.30; $\nu_{max}$(film)/cm⁻¹ 1620 (C=C), 1260 and 1100; $\delta_H$(80 MHz; CDCl₃) 7.79–7.69 (4 H, m, Ph), 7.40–7.30 (6 H, m, Ph), 7.56 (1 H, d, *J* 8, IC*H*=CH), 7.35 (1 H, d, *J* 8, HC=C*H*Si) and 1.02 (9 H, s, SiCMe₃); *m/z* 392 (1%, M⁺), 335 (25, M − Bu') 309 (100, I–SiPh₂⁺) and 181 (20, M − HI) (Found: C, 55.0; H, 5.2. C₁₈H₂₁ISi requires C, 55.1; H, 5.4%).

(*Z*)-**1-*tert*-Butyl(diphenyl)silyl-2-trimethylsilylethene 4c**, 69%; by adding trimethylsilyl chloride to **3**, prepared at −78 °C, at −78 °C and keeping the mixture at 0 °C for 8 h, $R_f$(pentane) 0.47; $\nu_{max}$(film)/cm⁻¹ 1595 (C=C), 1250 (SiMe) and 1100 (SiPh); $\delta_H$(300 MHz; CDCl₃) 7.79–7.76 (4 H, m, Ph), 7.39–7.36 (6 H, m, Ph), 7.22 (1 H, d, *J* 20, Me₃SiC*H*=CHSiBu'Ph₂), 7.13 (1 H, *J* 20, Me₃SiCH=C*H*SiBu'Ph), 0.96 (9 H, s, SiCMe₃) and −0.39 (9 H, d, SiMe₃); $\delta_C$(20 MHz; CDCl₃) 158.44 (=CHSiBu'Ph₂), 142.85 (=CHSiMe₃), 136.42, 134.98, 129.25 and 127.47 (SiPh), 27.07 (SiC$Me_3$), 18.05 (SiCMe₃) and −0.69 (SiMe₃); *m/z* 338 (0.6%, M⁺), 323 (14, M − Me), 281 (100, M − Bu'), 207 (24), 197 (31), 183 (47), 135 (54) and 73 (41).

(*Z*)-**1-*tert*-Butyl(diphenyl)silyl-2-dimethyl(phenyl)silylethene 4d**, 52%; by adding dimethyl(phenyl)silyl chloride to **3**, prepared at −78 °C, at −78 °C and keeping the mixture at 0 °C for 8 h;

$R_f$(hexane–Et$_2$O, 20:1) 0.56; $v_{max}$(film)/cm$^{-1}$ 1580 (C=C), 1250 (SiMe) and 1100 (SiPh); $\delta_H$(80 MHz; CDCl$_3$) 7.88–7.51 (6 H, m, Ph), 7.43–7.34 (9 H, m, Ph), 7.16 (2 H, s, CH=CH), 0.97 (9 H, s, SiCMe$_3$) and 0.40 (6 H, s, SiMe$_2$); $\delta_C$(20 MHz; CDCl$_3$) 167.71 (=CHSiBu$^t$Ph$_2$), 150.44 (=CHSiMe$_2$Ph), 137.52, 136.31, 135.08, 133.88, 130.85, 129.17, 128.81 and 127.59 (SiPh), 27.79 (SiCMe$_3$), 18.29 (SiCMe$_3$) and −2.78 (SiMe$_2$); m/z 343 (61%, M − Bu$^t$), 183 (22, Ph$_2$SiH$^+$) and 135 (100, PhMe$_2$Si$^+$).

**(Z)-1-tert-Butyl(diphenyl)silyl-2-tributylstannylethene 4e**, 89%; by adding tributylstannyl chloride to **3**, prepared at −78 °C, at −78 °C and keeping the mixture at 0 °C for 3 h; $R_f$(hexane) 0.49; $v_{max}$(CCl$_4$)/cm$^{-1}$ 1610 (C=C), 1245 (Si–C) and 1100 (SiPh); $\delta_H$(80 MHz; CDCl$_3$) 7.81–7.67 (4 H, m, Ph), 7.40–7.29 (6 H, m, Ph), 7.70 (1 H, d, J 18.7, $^2J_{Sn-H}$ 94, 98, SnC$H$=CHSi), 7.40 (1 H, d, J 18.7, $^3J_{Sn\ H_{trans}}$ 165, 171, SnCH=C$H$Si), 1.25–1.00 (12 H, m, 3 × CH$_2$CH$_2$), 0.97 (9 H, s, SiCMe$_3$), 0.82 (9 H, t, J 7.3, 3 × MeCH$_2$) and 0.31 (6 H, t, J 7.5, 3 × CH$_2$Sn); $\delta_C$(20 MHz; CDCl$_3$) 160.05 (=CHSi), 145.81 (=CHSn), 136.57, 134.58, 129.16 and 127.59 (SiPh), 29.05 (CH$_2$CH$_2$), 27.28 (SiCMe$_3$), 18.14 (CSi), 13.63 (MePh$_2$) and 10.37 (SnCH$_2$); m/z 499 (52%, M − Bu$^t$), 197 (100), 183 (92) and 57 (24).

**(Z)-1-tert-Butyl(diphenyl)silylprop-1-ene 4f**, 74%; by adding methyl iodide to **3**, prepared at −23 °C, at −23 °C and keeping the mixture at 0 °C for 3 h; $R_f$(hexane) 0.41; $v_{max}$(CCl$_4$)/cm$^{-1}$ 1610 (C=C), 1250 and 1115; $\delta_H$(80 MHz; CDCl$_3$) 7.82–7.57 (4 H, m, Ph), 7.34–7.26 (6 H, m, Ph), 6.77 (1 H, dq, J 14 and 7, MeC$H$=CHSi), 5.95 (1 H, dq, J 14 and 1.5, CH=C$H$Si), 1.38 (3 H, dd, J 7 and 1.5, MeCH=CH) and 1.02 (9 H, s, SiCMe$_3$); $\delta_C$(20 MHz; CDCl$_3$) 148.12 (HC=CHSi), 135.93, 135.06, 128.98 and 127.64 (SiPh), 123.30 (HC=CHSi), 27.39 (SiCMe$_3$), 20.42 (MeC=) and 18.10 (CSi); m/z 280 (1%, M$^+$), 223 (100, M − Bu$^t$), 183 (33) and 105 (17) (Found: C, 81.6; H, 8.4. C$_{19}$H$_{24}$Si requires C, 81.4; H, 8.6%).

**(Z)-4-tert-Butyl(diphenyl)silylbut-3-en-2-one 4g**, 78%; by adding acetyl chloride to **3**, prepared at −78 °C, at −78 °C and keeping the mixture at 0 °C for 3 h; mp 50–51 °C (from hexane); $R_f$(hexane–Et$_2$O, 20:1) 0.28; $v_{max}$(CCl$_4$)/cm$^{-1}$ 1690 (C=O), 1580 (C=C), 1250 and 1110; $\delta_H$(80 MHz; CDCl$_3$) 7.72–7.46 (4 H, m, Ph), 7.38–7.20 (6 H, m, Ph), 7.22 (1 H, d, J 14, C$H$=CHSi), 6.73 (1 H, d, J 14, CH=C$H$Si), 1.84 (3 H, s, MeCO) and 1.02 (9 H, s, SiCMe$_3$); m/z (1%, M$^+$), 251 (100, M − Bu$^t$), 183 (21) and 43 (7, MeCO$^+$) (Found: C, 78.1; H, 7.9. C$_{20}$H$_{24}$OSi requires C, 77.9; H, 7.8%).

**(Z)-1-tert-Butyl(diphenyl)silylpenta-1,4-diene 4h**, 81%; by adding allyl bromide to **3**, prepared at −78 °C, at −78 °C and keeping the mixture at 0 °C for 2 h; $R_f$(hexane) 0.31; $v_{max}$(CCl$_4$)/cm$^{-1}$ 1640 and 1610 (C=C), 1250, 1110, 995 and 915 (CH=CH$_2$); $\delta_H$(80 MHz; CDCl$_3$) 7.78–7.62 (4 H, m, Ph), 7.36–7.24 (6 H, m, Ph), 6.67 (1 H, dt, J 14 and 7.2, CH$_2$C$H$=CHSi), 6.01 (1 H, br d, J 14, CH=C$H$Si), 5.49 (1 H, tdd, J 6.3, 10.3 and 16.5, CH$_2$=C$H$CH$_2$), 4.73 (1 H, dq, J 10.3 and 1.8, C$H_A$H$_B$=CHCH$_2$), 4.64 (1 H, dq, J 16.5 and 1.8, CH$_A$$H_B$=CHCH$_2$), 2.49 (2 H, dd, J 7.2 and 6.3, =CHC$H_2$CH=) and 1.03 (9 H, s, SiCMe$_3$); $\delta_C$(20 MHz; CDCl$_3$) 150.54 (HC=CHSi), 135.93, 134.84, 129.05 and 127.61 (SiPh), 123.18 (=CHSi), 115.29 (=CH$_2$), 38.70 (CH$_2$), 27.35 (SiCMe$_3$) and 18.04 (CSi); m/z 249 (100%, M − Bu$^t$), 221 (56), 183 (75, Ph$_2$SiH$^+$), 171 (65) and 105 (68).

**3-[(Z)-1-tert-Butyl(diphenyl)silylethen-2-yl]cyclohexanone 4i**, 52%; by adding cyclohex-2-enone and HMPA (1.1 cm$^3$) to **3**, prepared at −23 °C, at −23 °C and keeping the mixture at 0 °C for 2 h; mp 74–74.5 °C (from hexane); $R_f$(hexane–Et$_2$O, 7:3) 0.40; $v_{max}$(CCl$_4$)/cm$^{-1}$ 1710 (C=O), 1610 (C=C), 1250 and 1115; $\delta_H$(80 MHz; CDCl$_3$) 7.72–7.55 (4 H, m, Ph), 7.40–7.29 (6 H, m, Ph), 6.42 (1 H, dd, J 9.1 and 14, CHC$H$=CHSi), 5.94 (1 H, d, J 14, HC=C$H$Si), 2.13–2.00 (5 H, m), 1.86–1.54 (2 H, m), 1.36–1.13 (2 H, m) and 1.02 (9 H, s, SiCMe$_3$); m/z 305 (100%,

M − Bu$^t$), 227 (13), 199 (60), 183 (13, Ph$_2$SiH$^+$) and 105 (28) (Found: C, 79.4; H, 8.2. C$_{24}$H$_{30}$OSi requires C, 79.5; H, 8.3%).

**(E)-1-tert-Butyl(diphenyl)silyl-2-trimethylsilylethene 12**, 78%; by adding trimethylsilylacetylene **5** to **2** at 0 °C and quenching the vinylcopper intermediate **11** with ammonium chloride solution; $R_f$(hexane) 0.39; $v_{max}$(film)/cm$^{-1}$ 1590 (C=C), 1250 (SiMe), 1110 (SiPh) and 1010 (trans-CH=CH); $\delta_H$(300 MHz; CDCl$_3$) 7.66–7.54 (4 H, m, Ph), 7.32–7.20 (6 H, m, Ph), 7.08 (1 H, d, J 22.6, Me$_3$SiC$H$=CHSiPh$_2$Bu$^t$), 6.75 (1 H, d, J 22.6, Me$_3$SiCH=C$H$SiPh$_2$Bu$^t$), 1.09 (9 H, s, SiCMe$_3$) and 0.10 (9 H, s, SiMe$_3$); $\delta_C$(20 MHz; CDCl$_3$) 157.49 (=CHSiPh$_2$Bu$^t$), 143.67 (=CHSiMe$_3$), 135.77, 134.62, 129.14 and 127.64 (SiPh), 27.96 (SiCMe$_3$), 18.29 (SiCMe$_3$) and −1.43 (SiMe$_3$); m/z 338 (1%, M$^+$), 323 (1, M − Me), 281 (100%, M − Bu$^t$), 207 (64), 197 (81), 183 (96), 135 (98) and 73 (91).

**(E)-1-tert-Butyl(diphenyl)silyl-2-tributylstannylethene 13**, 82%; by adding tributylstannylacetylene **6** to **2** at −78 °C for 30 min and quenching the intermediate **11** at 0 °C with aqueous ammonium chloride, $R_f$(hexane) 0.41; $v_{max}$(CCl$_4$)/cm$^{-1}$ 1600 (C=C), 1250, 1110 and 1000 (trans-CH=CH); $\delta_H$(80 MHz; CDCl$_3$) 7.67–7.59 (4 H, m, Ph), 7.40–7.30 (6 H, m, Ph), 7.21 (1 H, d, J 22.8, $^2J_{Sn\ H_{gem}}$ 95, 101, SnC$H$=CHSi), 6.92 (1 H, d, J 22.8, $^3J_{Sn-H_{cis}}$ 96, 101, SnCH=C$H$Si), 1.55–1.17 (12 H, m, 3 × CH$_2$CH$_2$), 1.08 (9 H, s, SiCMe$_3$) 0.92 (6 H, t, J 7, 3 × CH$_2$Sn) and 0.88 (9 H, t, J 6.5, 3 × CH$_3$CH$_2$); $\delta_C$(20 MHz; CDCl$_3$) 157.50 (=CHSi), 147.39 (=CHSn), 136.34, 134.80, 128.98 and 127.49 (SiPh), 29.11 and 27.25 (CH$_2$CH$_2$), 27.80 (SiCMe$_3$), 18.23 (SiC), 13.77 (Me) and 9.70 (CH$_2$Sn); m/z 499 (31%, M − Bu$^t$), 179 (65), 135 (100) and 57 (26).

**Methyl (E)-3-tert-butyl(diphenyl)silylacrylate 14**, 89%; by adding methyl propiolate **7** to **2** at −78 °C for 30 min and quenching at 0 °C with aqueous ammonium chloride; mp 58–59 °C (from MeOH); $R_f$(hexane–EtOAc, 20:1) 0.31; $v_{max}$(CCl$_4$)/cm$^{-1}$ 1730 (C=O), 1610 (C=C), 1250, 1110 and 990 (trans-CH=CH); $\delta_H$(80 MHz; CDCl$_3$) 7.74 (1 H, d, J 18.8, HC=C$H$Si), 7.60–7.52 (4 H, m, Ph), 7.38–7.26 (6 H, m, Ph), 6.28 (1 H, d, J 18.8, MeO$_2$CC$H$=CHSi), 3.67 (3 H, s, CO$_2$Me), 1.11 (9 H, s, SiCMe$_3$); $\delta_C$(20 MHz; CDCl$_3$) 165.51 (CO$_2$Me), 143.68 (=CHCO$_2$Me), 138.15 (=CHSi), 135.94, 132.67, 129.98 and 127.71 (SiPh), 51.36 (MeOCO), 27.52 (SiCMe$_3$) and 18.08 (CSi); m/z 324 (1%, M$^+$), 293 (1, M − OMe), 267 (100, M − Bu$^t$), 183 (25) and 105 (34) (Found: C, 74.2; H, 7.5. C$_{20}$H$_{24}$O$_2$Si requires C, 74.0; H, 7.4%).

**(E)-1-tert-Butyl(diphenyl)silylhex-1-ene 15a**, 95%; by adding hex-1-yne **8** to **2** at 0 °C and quenching at 0 °C with aqueous ammonium chloride; $R_f$(hexane) 0.54; $v_{max}$(CCl$_4$)/cm$^{-1}$ 1610 (C=C), 1250, 1110 and 990 (trans-CH=CH); $\delta_H$(80 MHz; CDCl$_3$) 7.70–7.54 (4 H, m, Ph), 7.30–7.20 (6 H, m, Ph), 6.05 (1 H, s, HC=C$H$Si), 6.05 (1 H, t, J 3.5, CH$_2$C$H$=CHSi), 2.18–2.05 (2 H, m, C$H_2$CH=CHSi), 1.45–1.12 (4 H, m, CH$_2$CH$_2$), 1.06 (9 H, s, SiCMe$_3$) and 0.98 (3 H, t, J 7, CH$_2$Me); $\delta_C$(20 MHz; CDCl$_3$) 153.11 (HC=CHSi), 136.27, 135.14, 129.39 and 127.83 (SiPh), 122.91 (HC=CHSi), 36.91 (CH$_2$), 30.89 (CH$_2$), 27.84 (SiCMe$_3$), 22.29 (CH$_2$), 18.16 (CSi) and 13.98 (Me); m/z 322 (0.2%, M$^+$), 265 (100, M − Bu$^t$), 183 (63) and 105 (24) (Found: C, 82.1; H, 9.2. C$_{22}$H$_{30}$Si requires C, 81.9; H, 9.4%).

**(E)-1-tert-Butyl(diphenyl)silyl-2-methylhex-1-ene 15b**, 77%; using hex-1-yne and methyl iodide; $R_f$(hexane) 0.51; $v_{max}$(film)/cm$^{-1}$ 1610 (C=C), 1250 and 1115; $\delta_H$(80 MHz; CDCl$_3$) 7.87–7.60 (4 H, m, Ph), 7.40–7.25 (6 H, m, Ph), 5.64 (1 H, s, C=CHSi), 2.23 (2 H, t, J 7, CH$_2$C=C), 1.39 (3 H, s, MeC=C), 1.63–1.15 (4 H, m, CH$_2$CH$_2$), 1.00 (9 H, s, SiCMe$_3$) and 0.95 (3 H, t, J 7, CH$_2$Me); $\delta_C$(20 MHz; CDCl$_3$) 160.54 (C=CHSi), 135.96, 135.35, 129.35, 128.79 and 127.52 (SiPh), 115.95 (=CHSi), 42.83 (CH$_2$), 30.37 (CH$_2$), 27.44 (SiCMe$_3$), 23.11 (MeC=), 22.45 (CH$_2$), 18.12 (CSi) and 14.03 (CH$_2$Me); m/z 336 (1%, M$^+$), 279 (100, M − Bu$^t$) and 183 (27).

(Z)-1-tert-Butyl(diphenyl)silyl-2-trimethylsilylhex-1-ene 15c, 44%; by adding hex-1-yne to 2 at 0 °C and quenching with trimethylsilyl chloride at 0 °C; $R_f$(hexane) 0.52; $\nu_{max}$(film)/cm$^{-1}$ 1590 (C=C), 1250 (SiMe) and 1110 (SiPh); $\delta_H$(80 MHz; CDCl$_3$) 7.75–7.59 (6 H, m, Ph), 7.42–7.31 (4 H, m, Ph), 6.38 (1 H, s, C=CHSiPh$_2$Bu$^t$), 2.28 (2 H, t, J 7, CH$_2$C=C), 1.58–1.29 (4 H, m, CH$_2$CH$_2$), 1.14 (9 H, s, SiCMe$_3$), 0.88 (3 H, t, J 7, MeCH$_2$) and 0.18 (9 H, s, SiMe$_3$); $\delta_C$(20 MHz; CDCl$_3$) 159.58 (=CSi), 147.57 (=CHSi), 136.27, 133.89, 129.38 and 127.83 (SiPh), 37.86 (CH$_2$), 33.08 (CH$_2$), 26.83 (SiCMe$_3$), 19.57 (CH$_2$), 18.13 (SiCMe$_3$), 13.59 (Me) and 0.66 (SiMe$_3$); m/z 394 (0.5%, M$^+$), 379 (1, M $-$ Me), 337 (56, M $-$ Bu$^t$), 197 (80), 135 (100) and 73 (85, Me$_3$Si$^+$).

(E)-1-tert-Butyl(diphenyl)silyl-2-phenylethene 16a, 71%; by adding phenylacetylene 9 to 2 and quenching with aqueous ammonium chloride; mp 62–63 °C (from hexane), $R_f$(hexane) 0.37; $\nu_{max}$(CCl$_4$)/cm$^{-1}$ 1605 (C=C), 1600, 1580 (Ph), 1250, 1110 and 990 (trans-CH=CH); $\delta_H$(80 MHz; CDCl$_3$) 7.72–7.60 (4 H, m, Ph). 7.41–7.22 (11 H, m, Ph), 6.89 (2 H, s, PhCH=CHSi) and 1.06 (9 H, s, SiMe$_3$); $\delta_C$(20 MHz; CDCl$_3$) 148.80 (=CHPh), 138.30, 136.30, 134.56, 129.17, 128.51, 128.29, 127.63 and 126.57 (Ph), 122.75 (=CHSi), 22.82 (SiCMe$_3$) and 18.41 (CSi); m/z 342 (4%, M$^+$), 285 (100, M $-$ Bu$^t$), 207 (62), 183 (44) and 105 (33).

(Z)-4-tert-Butyl(diphenyl)silyl-3-phenylbut-3-en-2-one 16b, 62%; by adding phenylacetylene to 2 and quenching with acetyl chloride; mp 124–125 °C (from hexane); $R_f$(hexane–Et$_2$O, 20:1) 0.18; $\nu_{max}$(CCl$_4$)/cm$^{-1}$ 1690 (C=O), 1585 (C=C), 1570 and 1490 (Ph), 1250 and 1110; $\delta_H$(80 MHz; CDCl$_3$) 7.73–7.61 (4 H, m, SiPh), 7.41–7.30 (6 H, m, SiPh), 7.37 (5 H, s, Ph), 6.55 (1 H, s, =CHSi), 1.57 (3 H, s, MeCO) and 1.09 (9 H, s, SiCMe$_3$); $\delta_C$(20 MHz; CDCl$_3$) 203.58 (C=O), 161.40 (=CHSi), 139.15 (=CPhCO), 136.25, 133.81, 129.21, 128.67, 128.14, 127.46 and 126.87 (Ph), 29.50 (COMe), 27.80 (SiCMe$_3$) and 18.62 (CSi); m/z 384 (11%, M$^+$), 327 (100, M $-$ Bu$^t$), 249 (69), 181 (22), 105 (44) and 43 (18, MeCO$^+$) (Found: C, 81.0; H, 7.2. C$_{26}$H$_{28}$OSi requires C, 81.2; H, 7.3%).

(E)-1-tert-Butyl(diphenyl)silyl-3-phenylprop-1-ene 17a, 91%; by adding benzylacetylene 10 to 2 and quenching with aqueous ammonium chloride; $R_f$(hexane) 0.60; $\nu_{max}$(film)/cm$^{-1}$ 1610 (C=C), 1250, 1110 and 990 (trans-CH=CH); $\delta_H$(80 MHz; CDCl$_3$) 7.72–7.53 (4 H, m, Ph), 7.37–7.07 (11 H, m, Ph), 6.18 (1 H, t, J 4.4, CH$_2$CH=CHSi), 6.16 (1 H, s, HC=CHSi), 3.53 (2 H, d, J 4.4, PhCH$_2$CH=) and 1.06 (9 H, s, SiCMe$_3$); $\delta_C$(20 MHz; CDCl$_3$) 150.58 (HC=CHSi), 136.82, 135.70, 134.81, 133.93, 129.05, 128.67 and 127.55 (Ph), 125.03 (=CHSi), 43.58 (CH$_2$), 27.76 (SiCMe$_3$) and 18.18 (CSi); m/z 356 (1%, M$^+$), 299 (100, M $-$ Bu$^t$), 221 (10), 183 (43) and 105 (15).

(Z)-1-tert-Butyl(diphenyl)silyl-2-iodo-3-phenylprop-1-ene 17b, 83%; by adding benzylacetylene to 2 and quenching with iodine; $R_f$(hexane) 0.44; $\nu_{max}$(film)/cm$^{-1}$ 1600 (C=C), 1245 and 1105; $\delta_H$(80 MHz; CDCl$_3$) 7.79–7.66 (4 H, m, Ph), 7.44–7.20 (11 H, m, Ph), 6.82 (1 H, t, J 1.1, CH$_2$CI=CHSi), 4.08 (2 H, d, J 1.1, CH$_2$CI=CHSi) and 0.96 (9 H, s, SiCMe$_3$); $\delta_C$(20 MHz; CDCl$_3$) 138.26 (=CI), 132.28 (=CHSi), 136.34, 129.16, 128.54, 127.59, 126.93 and 126.36 (Ph), 57.96 (CH$_2$), 27.38 (SiCMe$_3$) and 18.39 (CSi); m/z 425 (27%, M $-$ Bu$^t$), 309 (100, Ph$_2$ISi$^+$), 297 (53) (Found: C, 62.4; H, 5.7. C$_{25}$H$_{27}$ISi requires C, 62.2; H, 5.6%).

(E)-1-Dimethyl(phenyl)silyl-2-trimethylsilylethene[4] 20a, 86%; by adding the acetylene 5 to the dimethyl(phenyl)silylcuprate 18; $R_f$(hexane) 0.43; $\nu_{max}$(film)/cm$^{-1}$ 1590 (C=C), 1250 (SiMe), 1112 (SiPh) and 1010 (trans-CH=CH); $\delta_H$(80 MHz; CDCl$_3$) 7.60–7.53 (2 H, m, Ph), 7.41–7.32 (3 H, m, Ph), 6.81 (2 H, s, Me$_3$SiCH=CHSiMe$_2$Ph). 0.43 (6 H, s, SiMe$_2$Ph) and 0.17 (9 H, s, SiMe$_3$); $\delta_C$(20 MHz; CDCl$_3$) 153.02 (=CHSiMe$_2$Ph), 148.23 (=CHSiMe$_3$), 138.70, 133.94, 128.97 and 127.84 (SiPh), $-$1.45 (SiMe$_3$) and $-$2.72 (SiMe$_2$Ph); m/z 234 (0.5%, M$^+$), 219 (1,

M $-$ Me), 161 (12, M $-$ SiMe$_3$), 135 (58, Me$_2$PhSi$^+$) and 73 (100, Me$_3$Si$^+$).

(E)-1-Dimethyl(phenyl)silyl-2-tributylstannylethene 20b, 63%; by adding the acetylene 6 to the dimethyl(phenyl)silylcuprate 18; $R_f$(hexane) 0.44; $\nu_{max}$(CCl$_4$)/cm$^{-1}$ 1600 (C=C), 1250 (SiMe), 1110 (SiPh) and 995 (trans-CH=CH); $\delta_H$(80 MHz; CDCl$_3$) 7.57–7.42 (2 H, m, Ph), 7.39–7.19 (3 H, m, Ph), 7.24 (1 H, d, J 22.6, $^2J_{Sn-H_{gem}}$ 97, 101, SnCH=CHSi), 6.68 (1 H, d, J 22.6, $^3J_{Sn-H_{cis}}$ 96, 101, SnCH=CHSi), 1.53–1.09 (12 H, m, 3 × CH$_2$CH$_2$), 0.95 (15 H, t, J 7, 3 × MeCH$_2$ and 3 × CH$_2$Sn) and 0.32 (6 H, s, SiMe$_2$Ph); $\delta_C$(20 MHz; CDCl$_3$) 152.72 (=CHSi), 152.32 (=CHSn), 133.91, 131.86, 128.78 and 127.69 (SiPh), 29.12 (CH$_2$), 27.25 (CH$_2$), 13.61 (CH$_2$Me), 9.51 (CH$_2$Sn) and $-$2.78 (SiMe$_2$Ph); m/z 395 (100%, M $-$ Bu), 339 (42), 283 (30), 135 (Me$_2$PhSi$^+$) and 121 (16).

(E)-3-tert-Butyl(diphenyl)silylhex-3-ene 22a, 30%; by adding hex-3-yne 21a to 2 and quenching with aqueous ammonium chloride; $R_f$(pentane) 0.45; $\nu_{max}$(CCl$_4$)/cm$^{-1}$ 1610 (C=C), 1250 and 1110; $\delta_H$(80 MHz; CDCl$_3$) 7.72–7.55 (4 H, m, Ph), 7.40–7.29 (6 H, m, Ph), 6.07 (1 H, t, J 7, CH$_2$CH=CSi), 2.23 (4 H, m, CH$_2$CH=CCH$_2$), 1.07 (9 H, s, SiCMe$_3$), 0.83 and 0.74 (3 H, each, t, J 7.5, 2 × MeCH$_2$); m/z 322 (0.16%, M$^+$), 265 (98, M $-$ Bu$^t$), 183 (100, M $-$ SiPh$_2$Bu$^t$) and 105 (32).

(E)-1-tert-Butyl(diphenyl)silyl-1,2-diphenylethene 22b, 20%; by adding diphenylacetylene 21b to 2 and quenching with aqueous ammonium chloride; $R_f$(hexane) 0.32; $\nu_{max}$(CCl$_4$)/cm$^{-1}$ 1600 (C=C and Ph), 1575 and 1500 (Ph), 1250 and 1110; $\delta_H$(80 MHz; CDCl$_3$) 7.81–6.83 (21 H, m, 4 × Ph and =CH) and 0.96 (9 H, s, SiCMe$_3$); m/z 418 (1%, M$^+$), 361 (85, M $-$ Bu$^t$), 283 (40), 183 (100, Ph$_2$SiH$^+$) and 105 (26).

(Z)-1-Dimethyl(phenyl)silyl-2-trimethylsilylethene 20c, 57%; by reaction of (PhMe$_2$Si)$_2$CuCNLi$_2$ 18 with acetylene 1 at $-$78 °C, quenching with trimethylsilyl chloride at $-$78 °C and keeping at 0 °C for 8 h; $R_f$ (hexane) 0.43; $\nu_{max}$(film)/cm$^{-1}$ 1600 (C=C), 1250 (SiMe) and 1115 (SiPh); $\delta_H$(80 MHz; CDCl$_3$) 7.68–7.54 (2 H, m, Ph), 7.49–7.25 (3 H, m, Ph), 7.01 (2 H, s, Me$_3$SiCH=CHMe$_2$Ph), 0.49 (6 H, s, SiMe$_2$Ph) and 0.13 (9 H, s, SiMe$_3$); $\delta_C$(20 MHz; CDCl$_3$) 154.23 (=CHSiMe$_2$Ph), 149.23 (=CHSiMe$_3$), 139.87, 134.04, 128.94 and 127.74 (SiPh), 0.06 (SiMe$_3$) and $-$0.60 (SiMe$_2$Ph); m/z 234 (5%, M), 219 (6, M $-$ Me), 161 (36, M $-$ SiMe$_3$), 135 (100, PhMe$_2$Si$^+$) and 73 (71, Me$_3$Si$^+$).

(Z)-1-Dimethyl(phenyl)silyl-2-tributylstannylethene 20d, 72%; by reaction of (PhMe$_2$Si)$_2$CuCNLi$_2$ 18 with acetylene 1 at $-$78 °C and quenching at $-$78 °C with tributylstannyl chloride; $R_f$(hexane) 0.44; $\nu_{max}$(CCl$_4$)/cm$^{-1}$ 1610 (C=C), 1245 and 1110; $\delta_H$(80 MHz; CDCl$_3$) 7.61–7.49 (2 H, m, Ph), 7.41–7.30 (3 H, m, Ph), 7.38 (1 H, d, J 14.7, $^2J_{Sn-H_{gem}}$ 85, 91, SiCH=CHSn), 7.18 (1 H, d, J 14.7, $^3J_{Sn-H_{trans}}$ 165, 171, SiCH=CHSn), 1.62–1.22 (12 H, m, 3 × CH$_2$CH$_2$), 0.99–0.71 (15 H, m, 3 × MeCH$_2$ and CH$_2$Sn) and 0.34 (6 H, s, SiMe$_2$Ph); $\delta_C$(20 MHz; CDCl$_3$) 153.74 (=CHSi), 151.27 (=CHSn), 138.97, 134.04, 128.91 and 127.75 (SiPh), 29.66 and 27.32 (CH$_2$CH$_2$), 13.67 (MeCH$_2$), 10.90 (CH$_2$Sn) and $-$1.47 (Me$_2$Si); m/z 395 (15, M $-$ Bu), 177 (25), 135 (100, PhMe$_2$Si$^+$) and 121 (48).

## Friedel–Crafts reactions on the vinylsilanes

Typically the vinylsilane (1 mmol), acetyl chloride (0.14 cm$^3$, 2 mmol) and aluminium trichloride (266 mg, 2 mmol) were kept in dichloromethane (20 cm$^3$) at 0 °C for 30 min. The mixture was diluted with dichloromethane, washed with aqueous sodium hydrogencarbonate and dried (MgSO$_4$), and the product chromatographed (SiO$_2$, hexane–CH$_2$Cl$_2$, 3:2). The following compounds were prepared by this method.

(E)-Oct-3-en-2-one 23,[15] 70%; $R_f$(hexane–Et$_2$O, 4:1) 0.20; $\nu_{max}$(film)/cm$^{-1}$ 1680 (C=O) and 1630 (C=C); $\delta_H$(80 MHz; CDCl$_3$) 6.73 (1 H, dt, J 15.9 and 6.7, CH$_2$CH=CH), 6.05 (1 H, dt, J 15.9 and 1.3, CH$_2$CH=CHCO), 2.36–2.01 (2 H,

m, C$H_2$CH=CH), 2.24 (3 H, s, COMe), 1.65–1.12 (4 H, m, CH$_2$CH$_2$) and 0.91 (3 H, t, $J$ 6.3, CH$_2$$Me$); $m/z$ 126 (5%, M$^+$), 111 (27, M – Me), 83 (4, M – COMe), 55 (100, CH$_2$=CHCO$^+$) and 43 (75, MeCO$^+$).

($E$)-4-*tert*-Butyl(diphenyl)silylbut-3-en-2-one     24,     90%; $R_f$(hexane)–Et$_2$O, 4:1) 0.43; $v_{max}$(film)/cm$^{-1}$ 1680 (C=O), 1590 (C=C), 1110 and 990 (*trans*-CH=CH); $\delta_H$(80 MHz; CDCl$_3$) 7.63–7.49 (4 H, m, Ph), 7.42–7.31 (6 H, m, Ph), 7.51 (1 H, d, $J$ 19.1, =CHSi), 6.49 (1 H, d, $J$ 19.1, =CHCO), 2.28 (3 H, s, COMe) and 1.12 (9 H, s, SiCMe$_3$); $m/z$ 308 (1%, M), 251 (100, M – Bu$^t$), 183 (Ph$_3$SiH$^+$), 105 (36) and 43 (4, MeCO$^+$).

($E$)-4-Dimethyl(phenyl)silylbut-3-en-2-one 25, and ($E$)-4-tri-methylsilylbut-3-en-2-one[16] 26. 25, 49%; $R_f$(hexane–Et$_2$O, 4:1) 0.50; $v_{max}$(film)/cm$^{-1}$ 1680 (C=O), 1600 (C=C), 1250, 1115 and 990 (*trans*-CH=CH); $\delta_H$(80 MHz; CDCl$_3$) 7.53–7.38 (5 H, m, Ph), 7.13 (1 H, d, $J$ 19.3, =CHSi), 6.46 (1 H, d, $J$ 19.3, =CHCO), 2.24 (3 H, s, COMe) and 0.42 (6 H, s, Si$Me_2$Ph); $m/z$ 205 (54%, M$^+$ + 1), 189 (37, M – Me), 127 (100, M – Ph); 26, 33%; $R_f$(hexane–Et$_2$O, 4:1) 0.60; $v_{max}$(film)/cm$^{-1}$ 1680 (C=O), 1590 (C=C), 1250 and 990 (*trans*-CH=CH); $\delta_H$(80 MHz; CDCl$_3$) 7.04 (1 H, d, $J$ 19.3, =CHSi), 6.42 (1 H, d, $J$ 19.3, =CHCO), 2.24 (3 H, s, COMe) and 0.14 (9 H, s, SiMe$_3$); $m/z$ 143 (100%, M$^+$ + 1), 127 (58, M – Me) and 103 (26).

## Equilibration of the β-silyl enones 4g and 24

($Z$)-4-*tert*-Butyl(diphenyl)silylbut-3-en-2-one 4g (0.10 g, 0.3 mmol) and sulfuric acid (1.5 cm$^3$) were refluxed in THF (15 cm$^3$) for 3 h. The mixture was diluted with water, washed with aqueous sodium hydrogen carbonate, dried (MgSO$_4$) and concentrated to give ($E$)-4-*tert*-butyl(diphenyl)silylbut-3-en-2-one 24 (99%), identical (TLC, $^1$H NMR) with the sample described above.

## Epoxidation of vinylsilanes

Typically, a solution of *m*-chloroperoxybenzoic acid (85%; 0.59 g, 2.7 mmol) was stirred with the vinylsilane (2 mmol) and sodium hydrogen carbonate (0.36 g, 4 mmol) in chloroform (20 cm$^3$) at reflux until complete reaction (20–24 h). The mixture was washed with saturated aqueous sodium bisulfite, saturated aqueous hydrogen carbonate and brine, dried (MgSO$_4$), concentrated, and chromatographed (hexane–Et$_2$O). The following compounds were made by this method.

1-*tert*-Butyl(diphenyl)silyl-1,2-epoxyethane 27a, 90%; $R_f$-(hexane–Et$_2$O, 10:1) 0.47; $v_{max}$(film)/cm$^{-1}$ 1110 (SiPh); $\delta_H$(300 MHz; CDCl$_3$) 7.65 (4 H, m, Ph), 7.42 (6 H, m, Ph), 3.00 (1 H, t, $J$ 5.6), 2.84 (1 H, dd, $J$ 5.6 and 4.0), 2.45 (1 H, dd, $J$ 5.6 and 4.0), and 1.21 (9 H, s, Bu$^t$); $\delta_C$(75 MHz; CDCl$_3$) 136.01, 131.78, 129.54 and 127.60 (SiPh), 44.31 (CH$_2$O), 41.20 (SiCHO), 27.77 ($Me_3$CSi) and 18.59 (CSi); $m/z$ 225 (54%, M – Bu$^t$), 183 (100, Ph$_2$SiH$^+$) and 105 (63).

($E$)-1-*tert*-Butyl(diphenyl)silyl-1,2-epoxyhexane 27b, 97%; $R_f$-(hexane–Et$_2$O, 20:1) 0.24; $v_{max}$(film)/cm$^{-1}$ 1110 (SiPh); $\delta_H$(300 MHz; CDCl$_3$), 7.65 (4 H, m, Ph), 7.44–7.34 (6 H, m, Ph), 2.69 (1 H, dt, $J$ 3.4 and 5.5, OC$H$CH$_2$), 2.60 (1 H, d, $J$ 3.4, OCHSi), 1.63 (2 H, m, OCHC$H_2$), 1.45–1.25 (m, 4 H, CH$_2$CH$_2$), 1.19 (9 H, s, SiBu$^t$) and 0.90 (3 H, t, $J$ 7.1, $Me$CH$_2$); $\delta_C$(75 MHz; CDCl$_3$) 136.02, 132.34, 129.57 and 127.78 (SiPh), 55.93 (CHO), 48.69 (SiCHO), 33.68 (CH$_2$), 28.44 (CH$_2$), 27.78 (SiC$Me_3$), 22.64 (CH$_2$), 18.59 (CSi) and 13.96 (Me); $m/z$ 281 (20%, M – Bu$^t$), 199 (100, HOSiPh$_2$$^+$), 183 (98) and 105 (89).

## Reaction of epoxysilanes with acid

Typically, the epoxide 27a or 27b (1.8 mmol) in THF (20 cm$^3$) was added to acid (1 cm$^3$ of H$_2$SO$_4$, or 2 mmol of BF$_3$·Et$_2$O) and heated at 65 °C for 5 h. The reaction mixture was quenched with aqueous sodium hydrogen carbonate. The organic phase was washed with aqueous sodium chloride (3 × 10 cm$^3$), dried (MgSO$_4$) and evaporated under reduced pressure. Column

chromatography (hexane–Et$_2$O, 10:1) gave the following α-silylaldehydes.

*tert*-Butyl(diphenyl)silylacetaldehyde 28a (75 and 71%, respectively); $R_f$(hexane–Et$_2$O, 10:1) 0.28; $v_{max}$(film)/cm$^{-1}$ 1700 (C=O), 1110 (SiPh); $\delta_H$(300 MHz; CDCl$_3$) 9.58 (1 H, t, $J$ 4.1, CHO), 7.73–7.61 (4 H, m, Ph), 7.48–7.28 (6 H, m, Ph), 2.83 (2 H, d, $J$ 4.1, CH$_2$) and 1.11 (9 H, s, Bu$^t$); $m/z$ 282 (5.5%, M$^+$), 225 (100, M – Bu$^t$), 183 (66) and 105 (37) (Found: C, 76.3; H, 7.7. C$_{18}$H$_{22}$OSi requires C, 76.5; H, 7.8%).

2-*tert*-Butyl(diphenyl)silylhexanal 28b (80 and 77%, respectively); $R_f$ (hexane–Et$_2$O, 10:1) 0.31; $v_{max}$(film)/cm$^{-1}$ 1700 (C=O), 1115 (SiPh); $\delta_H$(300 MHz; CDCl$_3$) 9.81 (1 H, d, $J$ 3.5, CHO), 7.73–7.60 (4 H, m, Ph), 7.45–7.30 (6 H, m, Ph), 2.97 (1 H, ddd, $J$ 11.0, 3.5 and 1.8, HCSi), 1.63 (2 H, m, CH$_2$), 1.52–1.15 (4 H, m, CH$_2$CH$_2$), 1.11 (9 H, s, Bu$^t$) and 0.77 (3 H, t, $J$ 6.9, CH$_2$$Me$); $\delta_C$(CDCl$_3$) 203.3 (CHO), 136.2, 132.5, 129.6, 127.8 (SiPh), 47.0 (CH), 33.2 (CH$_2$), 28.4 (SiC$Me_3$), 25.0 (CH$_2$), 22.3 (CH$_2$), 19.4 (SiCMe$_3$) and 13.8 (Me); $m/z$ 339 (58%, M$^+$ + 1), 281 (20, M – Bu$^t$) and 261 (100, M – Ph).

## ($Z$)-1-Phenylhex-1-ene 30

Phenylmagnesium bromide (3 mol dm$^{-3}$ in Et$_2$O; 0.14 cm$^3$, 0.432 mmol) was added to the aldehyde 28b (73 mg, 0.216 mmol) in diethyl ether (2 cm$^3$) at 0 °C and the mixture stirred for 1 h. Standard aqueous work-up gave the crude alcohol 29, $R_f$ (EtOAc–hexane, 1:10) 0.25, which was treated with potassium hydride (90 mg) in THF (1.5 cm$^3$) first at 0 °C and then at 30 °C for 1.5 h. Aqueous work-up using diethyl ether, and chromatography gave the alkene (22 mg, 65%); $\delta_H$(300 MHz; CDCl$_3$) 6.41 (1 H, dt, $J$ 11.6 and 0.5, PhC$H$), 5.66 (1 H, dt, $J$ 11.6 and 7.2, =CHCH$_2$), 2.37 (2 H, br q, $J$ 7.2, =CHC$H_2$), essentially identical with that reported.[17]

## 1-*tert*-Butyl(diphenyl)silyl-1-methylepoxyethane 31

The epoxysilane 27a (0.21 g, 0.75 mmol) in THF (5 cm$^3$) at – 50 °C, under nitrogen, was treated with butyllithium (1.6 mol dm$^{-3}$ in hexane; 0.94 cm$^3$, 1.5 mmol) and TMEDA (0.22 cm$^3$, 1.5 mmol). The resulting orange solution was stirred at – 50 °C for 15 min. Methyl iodide (0.30 cm$^3$, 5 mmol) was added and the mixture stirred at – 50 °C for 2 h. The mixture was quenched with methanol, warmed to room temperature and saturated aqueous ammonium chloride was added. The mixture was extracted with diethyl ether, and the extract dried (MgSO$_4$) and concentrated to give the epoxide 31 (93%); $R_f$(hexane–Et$_2$O, 20:1) 0.25; $v_{max}$(CCl$_4$)/cm$^{-1}$ 1110 (SiPh); $\delta_H$(300 MHz; CDCl$_3$) 7.69 (2 H, m, Ph), 7.56 (2 H, m, Ph), 7.47–7.27 (6 H, m, Ph), 2.61 (1 H, d, $J$ 5.4, CH$_A$H$_B$O), 2.56 (1 H, d, $J$ 5.4, CH$_A$H$_B$O), 1.47 (3 H, s, Me) and 1.20 (9 H, s, Bu$^t$); $\delta_C$(75 MHz; CDCl$_3$) 136.06, 135.97, 129.48, 129.34, 127.85 and 127.54 (SiPh$_2$), 52.31 (CH$_2$O), 28.65 ($Me_3$CSi), 23.52 (Me) and 18.81 (CSi); $m/z$ 296 (6%, M$^+$), 239 (100, M – Bu$^t$, 183 (55) and 105 (15) (Found: C, 76.8; H, 8.0. C$_{19}$H$_{24}$OSi requires C, 77.0; H, 8.1%). When the reaction was repeated at 0 °C, a mixture was obtained consisting of the epoxide 31 (43%) and 2-*tert*-butyl(diphenyl)-silylhex-1-ene 32 (48%); $R_f$(hexane) 0.54; $v_{max}$(film)/cm$^{-1}$ 1610 (C=C), 1115 (SiPh) and 890 (CH$_2$=); $\delta_H$(300 MHz; CDCl$_3$) 7.63–7.58 (4 H, m, Ph), 7.40–7.32 (6 H, m, Ph), 5.98 (1 H, dt, $J$ 3.6 and 1.7, CH$_A$H$_B$=), 5.62 (1 H, dt, $J$ 3.6 and 1.1, CH$_A$H$_B$=), 2.17 (2 H, t, $J$ 7.5, CH$_2$C=C), 1.36 (2 H, m, CH$_2$), 1.24 (2 H, m, CH$_2$), 1.16 (9 H, s, Bu$^t$) and 0.80 (3 H, t, $J$ 7.2, CH$_2$$Me$); $\delta_C$(75 MHz; CDCl$_3$) 146.79 (=CSi), 136.30, 134.93, 128.96, 127.51 (SiPh), 129.29 (=CH$_2$), 36.56 (CH$_2$C=), 30.69 (CH$_2$), 28.76 (SiC$Me_3$), 22.55 (C$H_2$Me), 18.51 (CSi) and 13.97 ($Me$CH$_2$); $m/z$ 322 (1%, M$^+$), 265 (100, M – Bu$^t$), 183 (81, HSiPh$_2$) and 105 (29) (Found: C, 81.7; H, 9.5. C$_{22}$H$_{30}$Si requires C, 81.9; H, 9.4%).

## ($E$)-1-*tert*-Butyl(diphenyl)silylprop-1-ene 33

The epoxysilane 27a (0.282 g, 1 mmol) in THF (5

cm$^3$) was stirred under nitrogen with methyllithium (1.2 cm$^3$, 1.67 mol dm$^{-3}$ in Et$_2$O, 2 mmol) at $-25\,°C$ for 1.5 h. The mixture was quenched with methanol and saturated aqueous ammonium chloride, extracted with diethyl ether, and the extract dried (MgSO$_4$) and concentrated to give the vinylsilane **33** (50%); $R_f$(hexane) 0.42; $\nu_{max}$(film)/cm$^{-1}$ 1610 (C=C), 1110 (SiPh) and 940 (*trans*-CH=CH); $\delta_H$(300 MHz; CDCl$_3$) 7.66–7.58 (4 H, m, Ph), 7.44–7.28 (6 H, m, Ph), 6.08 (2 H, m, =CHMe), 1.92 (3 H, d, $J$ 4.4, =CHMe) and 1.08 (9 H, s, Bu$^t$); $\delta_C$(75 MHz; CDCl$_3$) 147.75 (=CHMe), 136.23, 135.90, 129.00 and 127.75 (SiPh), 124.54 (=CHSi), 27.71 (SiC*Me*$_3$), 23.05 (*Me*C=) and 18.09 (CSi); $m/z$ 280 (2%, M$^+$), 223 (100, M $-$ Bu$^t$), 183 (47) and 105 (25) (Found: C, 81.2; H, 8.8. C$_{19}$H$_{24}$Si requires C, 81.4; H, 8.6%). When the reaction was conducted at 0 °C a mixture was obtained consisting of the vinylsilane **33** (44%) and 2-*tert*-butyl(diphenyl)silylprop-1-ene **34** (36%); $R_f$(hexane) 0.41; $\nu_{max}$(film)/cm$^{-1}$ 1615 (C=C), 1110 (SiPh) and 895 (=CH$_2$); $\delta_H$(300 MHz; CDCl$_3$) 7.65–7.54 (4 H, m, Ph), 7.42–7.30 (6 H, m, Ph), 5.94 (1 H, d, $J$ 3.2, =CH), 5.46 (1 H, d, $J$ 3.2, =CH), 1.97 (3 H, s, *Me*CSi=) and 1.05 (9 H, s, Bu$^t$); $\delta_C$(75 MHz; CDCl$_3$) 136.17, 135.34, 129.10 and 127.44 (SiPh), 131.54 (CH$_2$=), 27.46 (SiC*Me*$_3$), 25.22 (*Me*C=) and 18.29 (CSi); $m/z$ 280 (1%, M$^+$), 223 (100, M $-$ Bu$^t$), 183 (39) and 105 (22).

## cis-3-tert-Butyl(diphenyl)silylcyclohexan-1-ol 38

3-*tert*-Butyl(diphenyl)silylcyclohexanone$^2$ **36** (1.68 g, 5 mmol) was stirred with lithium aluminium hydride (0.38 g, 10 mmol) in THF (10 cm$^3$) overnight at room temperature. The mixture was quenched with ammonium chloride solution, extracted with diethyl ether, and the extract dried (MgSO$_4$) and concentrated to give the alcohol **38** (98%); $R_f$(hexane–EtOAc 3:1) 0.43; $\nu_{max}$(film)/cm$^{-1}$ 3340 (OH) and 1110 (SiPh); $\delta_H$(300 MHz; CDCl$_3$) 7.63–7.59 (4 H, m, Ph), 7.42–7.32 (6 H, m, Ph), 3.56 (1 H, tt, $J$ 4.3 and 10.7, HOCH$_{ax}$), 2.15 (1 H, m, CH), 1.97 (1 H, m, CH), 1.81 (2 H, m, 2 × CH), 1.56 (1 H, br s, OH), 1.46 (2 H, m, 2 × CH), 1.31 (2 H, m, 2 × CH), 1.17 (1 H, m, CH) and 1.10 (9 H, s, Bu$^t$); $\delta_C$(75 MHz; CDCl$_3$) 136.42, 134.18, 128.88 and 127.41 (SiPh), 72.00 (CHOH), 37.55 (CH$_2$), 35.83 (CH$_2$), 28.84 (SiC*Me*$_3$), 27.26 (CH$_2$), 26.71 (CH$_2$), 21.82 (CHSi) and 18.83 (CSi); $m/z$ 337 (1%, M $-$ 1), 321 (5, M $-$ OH), 281 (2, M $-$ Bu$^t$), 261 (3, M $-$ Ph), 239 (70) and 179 (100) (Found: C, 77.8; H, 9.1. C$_{22}$H$_{30}$OSi requires C, 78.0; H, 8.9%).

## Synthesis of 4-methylbenzenesulfonates

The alcohol **37** or **38** (7.8 mmol) was stirred with tosyl chloride (1.90 g, 10 mmol) and triethylamine (1.01 g, 10 mmol) in dichloromethane (15 cm$^3$) at 0 °C for 12 h. Hexane (5 cm$^3$) was added to precipitate the excess of tosyl chloride and the solution filtered, concentrated and chromatographed (hexane–EtOAc, 20:1) to give the following 4-methylbenzenesulfonates.

*cis*-3-Dimethyl(phenyl)silylcyclohexyl 4-methylbenzenesulfonate (2.23 g, 74%); $R_f$(hexane–EtOAc, 20:1) 0.22; $\nu_{max}$(film)/cm$^{-1}$ 1370 and 1170 (OSO$_2$), 1250 (SiMe) and 1110 (SiPh); $\delta_H$(300 MHz; CDCl$_3$) 7.77 (2 H, d, $J$ 8.2, Ts), 7.30 (2 H, d, $J$ 8.2, Ts), 7.50–7.33 (5 H, m, Ph), 4.41 (1 H, tt, $J$ 4.5 and 15.4, *H*COTs), 2.44 (3 H, s, *Me*Ar), 1.89–1.75 (4 H, m, 4 × CH), 1.40–1.15 (3 H, m, 3 × CH), 0.96–0.75 (2 H, m, 2 × CH) and 0.22 (6 H, s, SiMe$_2$); $\delta_C$(75 MHz; CDCl$_3$) 144.24, 137.01, 134.83, 133.77, 129.62, 129.01, 127.69 and 127.48 (Ar), 83.56 (HCOSO$_2$), 33.43 (CH$_2$), 32.80 (CH$_2$), 26.53 (CH$_2$), 25.49 (CH$_2$), 24.18 (CHSi), 21.58 (Me), $-$5.30 (SiMe$_A$Me$_B$) and $-$5.44(SiMe$_A$Me$_B$); $m/z$ 389 (0.5%, M $+$ 1), 373 (3, M $-$ Me), 201 (7, M $-$ MeC$_6$H$_4$SO$_3$H $-$ Me) and 187 (100) (Found: C, 65.1; H, 7.2. C$_{21}$H$_{28}$O$_3$SSi requires C, 64.9; H, 7.3%).

*cis*-3-*tert*-Butyl(diphenyl)silylcyclohexyl 4-methylbenzenesulfonate (65%), as prisms, mp 115–116 °C (from hexane); $R_f$(hexane–EtOAc, 3:1) 0.54; $\nu_{max}$(CCl$_4$)/cm$^{-1}$ 1360 and 1170

(OSO$_2$) and 1110 (SiPh); $\delta_H$(300 MHz; CDCl$_3$) 7.72 (2 H, d, $J$ 8.3, Ts), 7.70–7.46 (4 H, m, Ph), 7.43–7.29 (6 H, m, Ph), 7.26 (2 H, d, $J$ 8.3, Ts), 4.43 (1 H, tt, $J$ 4.6 and 15.3, HCO), 2.43 (3 H, s, *Me*Ar), 2.03–1.97 (2 H, m, 2 × CH), 1.81–1.71 (3 H, m, 3 × CH), 1.40–1.20 (4 H, m, 4 × CH) and 0.99 (9 H, s, Bu$^t$); $\delta_C$(75 MHz; CDCl$_3$) 144.16, 136.30, 133.55, 133.36, 129.65, 129.03 and 127.47 (Ar), 83.54 (COTs), 34.27 (CH$_2$), 32.82 (CH$_2$), 28.66 (SiC*Me*$_3$), 26.67 (CH$_2$), 26.58 (CH$_2$), 21.72 (Me), 21.60 (CSi) and 18.69 (SiC*Me*$_3$); $m/z$ 492 (1%, M$^+$), 353 (100, M $-$ C$_7$H$_7$SO), 263 (27, M $-$ C$_7$H$_7$SO$_3$ $-$ Bu$^t$), 183 (62, HSiPh$_2$) and 91 (72) (Found: C, 70.9; H, 7.5. C$_{29}$H$_{36}$O$_3$SSi requires C, 70.7; H, 7.4%).

**3-Dimethyl(phenyl)silylbutyl 4-methylbenzenesulfonate** (95%), from the alcohol **40**;$^{14}$ $R_f$(hexane–EtOAc 3:1) 0.34; $\nu_{max}$(film)/cm$^{-1}$ 1360 and 1170 (OSO$_2$), 1250 (SiMe) and 1105 (SiPh); $\delta_H$(300 MHz; CDCl$_3$) 7.76 (2 H, d, $J$ 8.4, Ts), 7.47–7.44 (2 H, m, Ph), 7.37–7.31 (3 H, m, Ph), 7.32 (2 H, d, $J$ 8.4, Ts), 4.03 (2 H, m, CH$_2$OTs), 2.44 (3 H, s, *Me*C$_6$H$_4$SO$_3$), 1.85 and 1.36 (2 H, m, CH$_2$CH), 0.96 (1 H, m, CHSi), 0.86 (3 H, d, $J$ 6.7, MeCH) and 0.24 (6 H, s, SiMe$_2$); $\delta_C$(75 MHz; CDCl$_3$) 144.54, 137.75, 133.25, 133.00, 129.69, 128.93, 127.72 and 127.65 (Ar), 69.42 (CH$_2$Ts), 30.44 (CH$_2$), 21.51 (*Me*C$_6$H$_4$SO$_3$), 14.92 (CH), 13.18 (*Me*-CHSi), $-$5.18 (Si*Me*$_A$Me$_B$) and $-$5.43 (SiMe$_A$*Me*$_B$); $m/z$ 347 (3%, M $-$ Me), 291 (40, PhMeSiOTs), 229 (100), 135 (68, PhMe$_2$Si$^+$) and 91 (73).

## 2-Methyl-5-tert-butyl(diphenyl)silylcyclohexanone 39

Butyllithium (1.6 mol dm$^{-3}$ in hexane; 1.34 cm$^3$, 2.14 mmol) was added under nitrogen to diisopropylamine (0.30 cm$^3$, 2.14 mmol) in THF (5 cm$^3$) at $-20\,°C$ for 15 min, followed by the ketone **36** (0.20 g, 0.6 mmol) in THF (4 cm$^3$). The mixture was stirred for 30 min at $-20\,°C$ and methyl iodide (0.372 cm$^3$, 6 mmol) added. After 1 h, the mixture was quenched with saturated aqueous ammonium chloride, extracted with diethyl ether, and the extract dried (MgSO$_4$) and concentrated to give the ketone **39** (84%) as a *ca.* 1:1.5 mixture of *cis*- and *trans*-isomers; $R_f$(hexane–Et$_2$O, 3:1) 0.45; $\nu_{max}$(CCl$_4$)/cm$^{-1}$ 1710 (C=O) and 1100 (SiPh); $\delta_H$(300 MHz; CDCl$_3$) 7.61–7.58 (4 H, m, Ph), 7.42–7.34 (6 H, m, Ph), 2.55 (1 H, m), 2.34 (2 H, m), 2.20–1.40 (5 H, m), 1.10 and 1.09 (9 H, s, Bu$^t$), 0.98 (3 H, d, $J$ 7.2, Me *cis* or *trans*) and 0.97 (3 H, d, $J$ 6.4, Me *trans* or *cis*); $m/z$ 293 (86%, M $-$ Bu$^t$), 199 (70), 135 (68) and 105 (100) (Found: C, 78.6; H, 8.8. C$_{23}$H$_{30}$OSi requires C, 78.8; H, 8.6%). The 2-methyl-3-*tert*-butyl(diphenyl)silylcyclohexan-1-one$^2$ (Me doublet at $\delta$ 0.8) was absent.

## 1-tert-Butyl(diphenyl)silyl-3-dimethyl(phenyl)silylbutane 41

3-Dimethyl(phenyl)silylbutyl 4-methylbenzenesulfonate (0.756 g, 2.08 mmol) was added under nitrogen to *tert*-butyl(diphenyl)-silyllithium$^2$ (2.08 mmol) in THF (5 cm$^3$) at 0 °C and stirred for 10 h. Aqueous ammonium chloride was added, and the mixture worked up and chromatographed to give the disilane **41** (0.556 g, 62%) as an oil; $R_f$(hexane) 0.48; $\nu_{max}$(film)/cm$^{-1}$ 1250 (SiMe) and 1105 (SiPh); $\delta_H$(300 MHz; CDCl$_3$) 7.64–7.35 (15 H, m, Ph), 1.64 (2 H, m, C*H*$_2$CH), 1.41 (2 H, m, C*H*$_2$SiPh$_2$Bu$^t$), 1.07 (9 H, s, SiBu$^t$), 1.05 (3 H, d, $J$ 8.1, *Me*CH), 0.93 (1 H, m, C*H*SiMe$_2$Ph), 0.26 (3 H, s, Si*Me*$_A$Me$_B$) and 0.24 (3 H, s, SiMe$_A$*Me*$_B$); $\delta_C$(75 MHz; CDCl$_3$) 138.83, 136.16, 135.83, 133.80, 129.37, 128.79, 127.78 and 127.45 (SiPh), 27.87 (SiC*Me*$_3$), 26.52 (CH$_2$CH), 23.29 (CHSi), 18.09 (CSi), 13.98 (*Me*CH), 9.70 (CH$_2$Si), $-$4.53 (Si*Me*$_A$Me$_B$) and $-$4.91 (SiMe$_A$*Me*$_B$); $m/z$ 373 (33, M $-$ Bu$^t$), 237 (20, M $-$ Bu$^t$ $-$ HSiPhMe$_2$), 197 (100, MeSiPh$_2$) and 135 (85, PhMe$_2$Si).

## 4-tert-Butyl(diphenyl)silylbutan-2-ol 42

Potassium bromide (0.18 g, 1.53 mmol) and anhydrous sodium acetate (0.324 g, 3.95 mmol) were stirred with the disilane **41** (0.54 g, 1.27 mmol) in glacial acetic acid (3.24 cm$^3$). Peracetic

acid (3.24 cm$^3$ of a 15% solution in acetic acid) was added dropwise with ice-cooling to moderate the exothermic production of bromine. More sodium acetate (0.972 g, 11.86 mmol) and peracetic acid (9.72 cm$^3$, 23.33 mmol) were added, and the resulting turbid mixture was stirred at a room temperature for 12 h. Diethyl ether (130 cm$^3$) and powdered sodium thiosulfate (13 g) were added, and the resulting suspension was stirred vigorously for 0.5 h, filtered through Celite and evaporated under reduced pressure. The residue was taken up in diethyl ether (25 cm$^3$), and the solution washed with aqueous sodium hydrogen carbonate and brine, dried (MgSO$_4$) and evaporated and the residue chromatographed (SiO$_2$, hexane–EtOAc, 3:1) to give alcohol **42** (0.27 g, 68%); $R_f$(hexane–EtOAc, 3:1) 0.21; $\nu_{max}$(CCl$_4$)/cm$^{-1}$ 3650s and 3400br (OH) and 1105 (SiPh); $\delta_H$(300 MHz; CDCl$_3$) 7.65–7.61 (4 H, m, Ph), 7.43–7.34 (6 H, m, Ph), 3.70 (1 H, sextet, $J$ 6.1, CHOH), 2.01 (1 H, br s, OH), 1.41 (2 H, m, C$H_2$CH), 1.20 (2 H, m, CH$_2$Si), 1.15 (3 H, d, $J$ 6.1, $Me$CH) and 1.06 (9 H, s, Bu$^t$); $m/z$ 255 (1%, M − Bu$^t$), 199 (4, HOPh$_2$Si$^+$), 105 (7) and 71 (100, Me(OH)C$^+$CH=CH$_2$) (Found: C, 77.1; H, 9.2. C$_{20}$H$_{28}$OSi requires C, 76.9; H, 9.0%).

## Acknowledgements

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