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Ene cyclisations of α-(prenyl)dialkylsilyloxy aldehydes: formation and oxidative cleavage of oxasilacyclohexanols†‡

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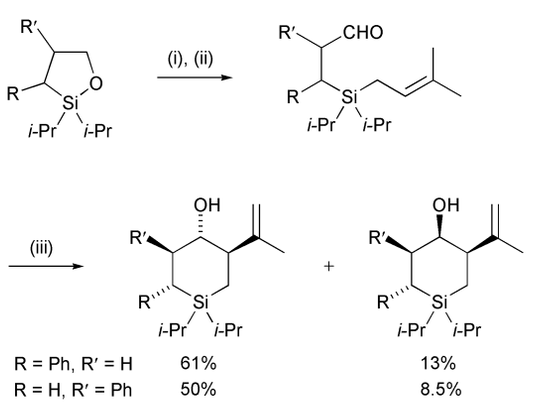
A variety of routes are described for the synthesis of α-silyloxy aldehydes in which the silicon atom bears a prenyl side chain. These compounds are shown to undergo stereoselective carbonyl ene cyclisation under mildly Lewis acidic conditions and the derived silacycles are cleaved to afford single diastereomers of functionalised triols.

Introduction

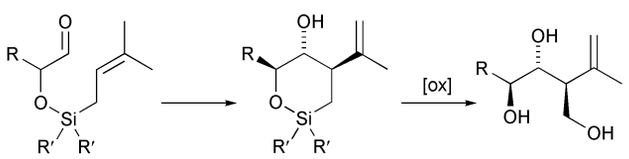
As part of our ongoing development of *de novo* syntheses of both natural and non-natural carbohydrates and polyol intermediates, we reported the first examples of silicon tethered Type I and II carbonyl ene cyclisations.[1] In these studies, both ene and enophile components were readily assembled around the silicon atom by organometallic ring-opening of oxasilacyclopentanes (Scheme 1).[2] That chemistry successfully established the viability of silicon tethered Type I carbonyl ene cyclisations but the ene products were not readily amenable to oxidative cleavage and the overall route suffered from a lack of efficiency and experimental convenience. In seeking to ease both precursor synthesis and elaboration to silicon-free polyols, ene precursors were identified in which the ene component would be tethered to the enophile (aldehyde) simply by silylation of an α-hydroxyaldehyde equivalent (Scheme 2).



Scheme 1 *Reagents:* (i) prenyllithium; (ii) PDC, MS 4 Å; (iii) Me_2AlCl.

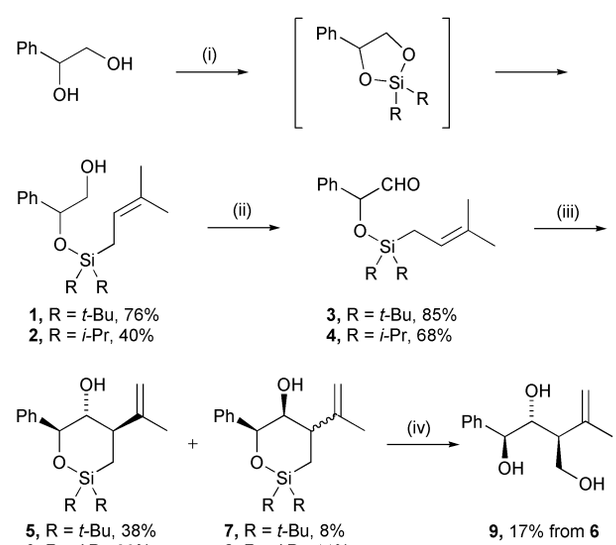
Results and discussion

At the outset of this investigation we elected to apply Kuwajima's protocol[3] for silylation of the internal hydroxyl group in terminal 1,2-diols since this would constitute a direct synthesis



Scheme 2

of the ene precursors assuming that oxidation of the residual (primary) hydroxyl could be achieved. In the event this strategy proved successful (Scheme 3); for example, when the assumed 2-siladioxolane derived from phenylethane-1,2-diol was treated with prenyllithium, a 76% yield of the product (**1**) of internal silylation was isolated. Confirmation of silylation at the 2°-hydroxyl was readily established from the ^{1}H NMR spectrum that showed the hydroxyl resonance as a triplet (δ = 1.96, J 5.6 Hz) and the benzylic methine as a clean double doublet (δ = 4.92, J 6.1, 4.9 Hz). Of the various oxidising agents screened, *o*-iodoxybenzoic acid (IBX)[4] proved to be convenient and efficient to give the somewhat unstable ene precursor **3** in 85% yield. Subjecting this material to the conditions previously optimised[1b] for *C*-linked substrates resulted in a mixture of diastereomers of the cyclised product in which the *trans*,*trans* isomer (**5**) predominated (4.75 : 1 ratio). Support for the stereochemistry of the major adduct—that was predicted on the basis



Scheme 3 *Reagents:* (i) BuLi; R_2SiHCl; prenyllithium; (ii) IBX; (iii) Me_2AlCl; (iv) KF, $KHCO_3$, H_2O_2.

† This is one of a number of contributions from the current members of the Dyson Perrins Laboratory to mark the end of almost 90 years of organic chemistry research in that building, as all its current academic staff move across South Parks Road to a new purpose-built laboratory.

‡ Electronic supplementary information (ESI) available: spectroscopic data for compounds **1**–**4**, and procedures with supporting characterisation for compounds **11**, **21**, **24**, **25**, **26** and **29**. See http://www.rsc.org/suppdata/ob/b3/b306922m/

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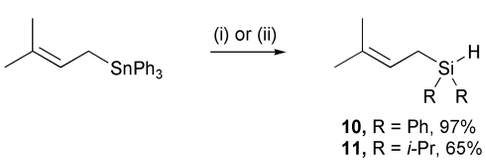
of a *trans*-decalin-like transition state—was forthcoming from coupling constant analysis of the ^{1}H NMR spectrum; notably the C*H*OH resonance appeared as a double doublet (δ = 3.33, *J* 10.5, 8.7 Hz) indicating two axial–axial couplings.

In view of the fact that terminal diols are readily prepared by asymmetric dihydroxylation,[5] this route offered promise as a reasonably efficient synthesis of enantiomerically enriched 1,2,4-triols bearing useful alkene functionality with potentially wide application. However, our plans were thwarted by the total reluctance of oxasilacyclohexane **5** to undergo oxidative cleavage, even under the forcing conditions developed by Woerpel[6] which are successful in the oxidation of similar five-membered ring analogues. Presumably, the *tert*-butyl substituents provide too great a steric impediment for successful oxidation but the use of substituents other than *tert*-butyl in Kuwajima's silylation protocol has not been reported. Changing the silylating agent to diisopropylchlorosilane led to the successful preparation of the alcohol **2**, but in reduced yield, and some product derived from overall silylation of the 1°-hydroxyl was observed, probably as a result of more rapid equilibration of the alkoxides during the silylation reaction. However, this compound (**2**) was oxidised as before and the aldehyde **4** was found to undergo ene cyclisation in comparable yield and stereoselectivity to the *tert*-butyl case. Although the major product (**6**) from the ene cyclisation was now cleavable under Tamao–Kumada conditions[7] only a low conversion to the desired triol (**9**) could be achieved.

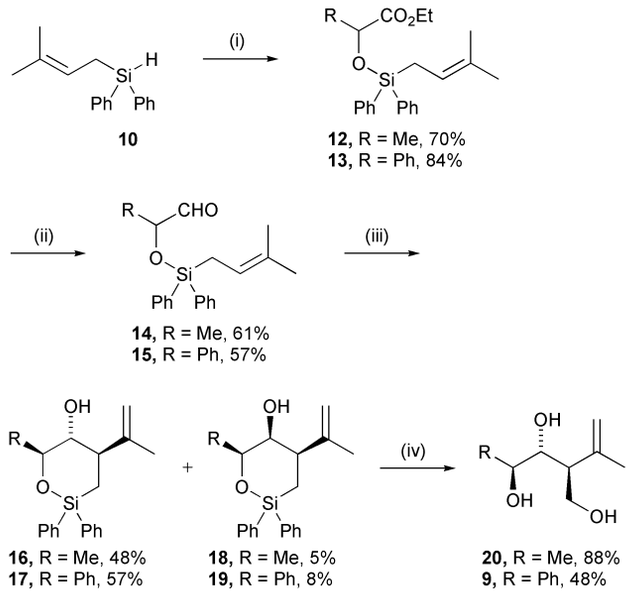
Previous experience[8] had shown that potential ene precursors in which the silicon was di*methyl*-substituted would be unlikely to survive the Lewis acidic conditions of the cyclisation in these *O*-linked cases therefore, in an effort to improve the oxidative cleavage step, phenyl substituents were selected on the basis of a balance of effective size and electronic activation of the silicon towards nucleophilic addition by hydroperoxide ion. A prediction that diphenylsilyl precursors would not be obtainable by application of the Kuwajima protocol proved disappointingly well-founded and only trace amounts of the desired internally silylated 1,2-diols were isolated. Recourse was then made to our contingency plan; *viz.*, silylation of α-hydroxy esters and reduction.

In our earlier work[1b] we had introduced dialkylprenylsilyl functionality through a sequence[9] consisting of (i) displacement of chloride from chloro(dimethylamino)dimethylsilane with prenyllithium, (ii) conversion of the dimethylamino group into chloride with acetyl chloride, and (iii) organometallic addition to the resulting chlorodimethylprenylsilane. Whilst successful in delivering substrates for testing the ene chemistry, the method was laborious and a more practical solution was sought. At this time we became aware of Piers' tris(pentafluorophenyl)borane-catalysed silylation of alcohols with simple trialkylsilanes,[10] an attractive method since the required silylating agent was easily obtainable from commercially-available chlorodiphenylsilane and prenyllithium (Scheme 4).[11] Although there was the potential problem that the Lewis acid would destroy the allylic silane, this proved not to interfere and both (*S*)-(−)-ethyl lactate and (±)-ethyl mandelate were readily silylated using this procedure (Scheme 5). In contrast to our earlier observations,[8] these prenyl substrates could be reduced successfully with DIBAL giving the aldehydes **14** and **15** in reasonable isolated yields; these aldehydes were taken on directly in the ene cyclisations which proceeded with stereoselectivity comparable to those depicted



10, R = Ph, 97%
11, R = *i*-Pr, 65%

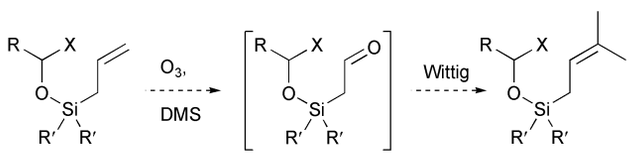
Scheme 4 *Reagents:* (i) BuLi, Ph_2SiHCl; (ii) BuLi, *i*-Pr_2SiHCl.



Scheme 5 *Reagents:* (i) RCH(OH)CO_2Et, $B(C_6F_5)_3$ cat.; (ii) DIBAL; (iii) Me_2AlCl; (iv) KF, $KHCO_3$, H_2O_2.

in Scheme 3.§ Pleasingly, the derived ene products could be oxidised to provide the triols **20** and **9** under Tamao–Kumada conditions, whose relative stereochemistry was assigned on the basis of that of the oxasilacycles **16** and **17** respectively.

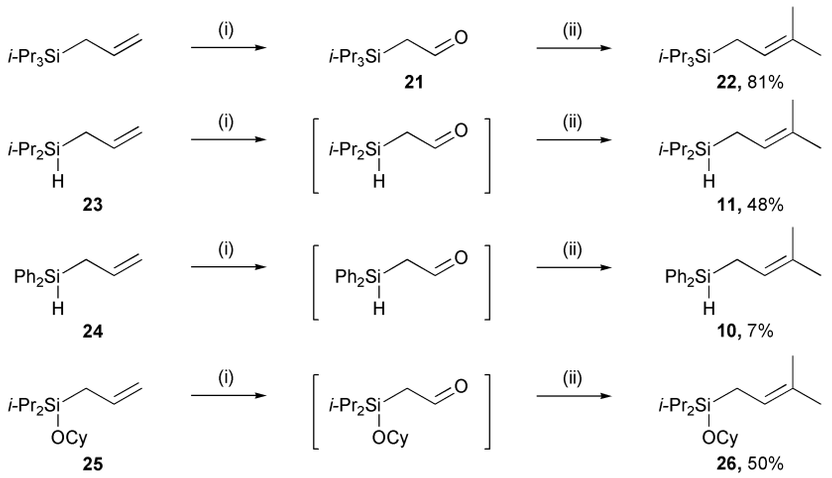
A drawback in these sequences is the need to generate prenyllithium from prenyltriphenylstannane which, in turn, derives from the reaction of prenylmagnesium chloride and triphenylstannyl chloride, reactions both attended by the usual toxicity and separation problems associated with tin-containing intermediates. In an effort to circumvent the use of tin we briefly explored the possibility of overall metathesis of the $=CH_2$ unit in simple *allyl*silyl precursors to give $=CMe_2$ by ozonolysis and immediate Wittig olefination (Scheme 6).[12]



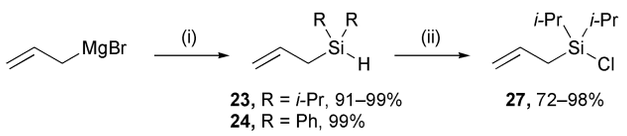
Scheme 6

This was a somewhat brave strategy since the intermediate functionalised α-(alkoxy)dialkylsilyl aldehydes were predicted to be very fragile and we therefore embarked on a short model study to explore the viability of this process. Initially allyltriisopropylsilane was selected as an unambiguous case and we were pleased to find that this could be oxidised to (triisopropylsilyl)acetaldehyde[13] (**21**, Scheme 7) very effectively and that this aldehyde could be purified by chromatography on silica.[14] Wittig olefination proceeded uneventfully to give prenyltriisopropylsilane (**22**) in good yield. Even allyldiisopropylsilane (**23**, preparation: Scheme 8) could be taken through this sequence, although the overall yield was reduced to 48%, but allyldiphenylsilane (**24**) afforded the prenyl analogue (**10**) in only 7% yield. A more exacting test was the ozonolysis and olefination *in situ* of the allyldiisopropylsilyl derivative (**25**) of cyclohexanol which was prepared from chlorodiisopropylsilane **27**[15] (Scheme 8). As expected, the overall yield for the metathesis process in this example was only moderate (50%) but was considered suffi-

§ The stereochemistry of the minor diastereomers **18** and **19** has been established, by a combination of NOE and coupling constant data, as that depicted in Scheme 5. The stereochemistry at C5 in compound **7** could not be determined but the propenyl substituent in compound **8** was shown to be *anti* to the adjacent hydroxyl group.



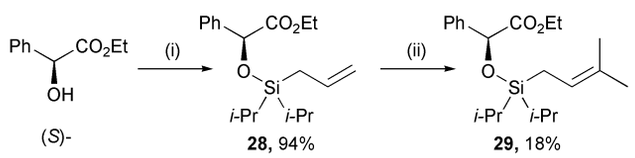
Scheme 7 *Reagents:* (i) O_3; DMS; (ii) $Ph_3P{=}CMe_2$.



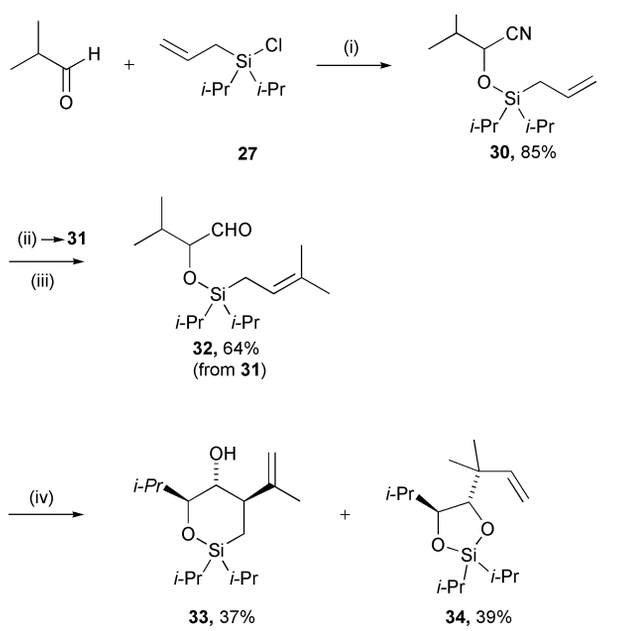
Scheme 8 *Reagents:* (i) R_2SiHCl; (ii) $CuCl_2$, CuI cat.

ciently acceptable for application in the preparation of ene precursors.

Incorporation of the allyldiisopropyl group into the ene precursors was achieved either by silylation of the requisite α-hydroxy ester (Scheme 9) or by direct conversion of aldehydes to silyl cyanohydrins (Scheme 10). Cava's method for the preparation of *O*-trialkylsilyl cyanohydrins, in which the silicon atom bears relatively bulky alkyl substituents, involves treatment of an aldehyde with a trialkylsilyl chloride in the presence



Scheme 9 *Reagents:* (i) **27**, Et_3N, DMAP; (ii) O_3; DMS then $Ph_3P{=}CMe_2$.

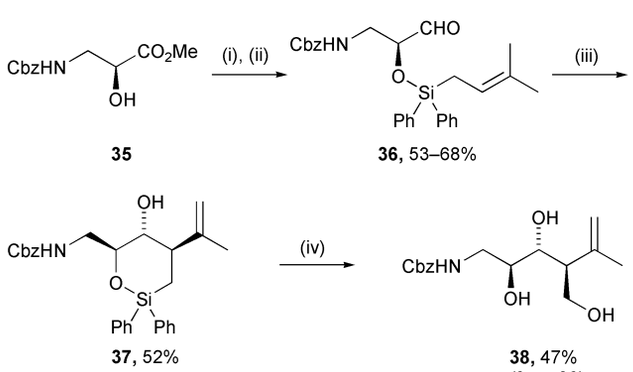


Scheme 10 *Reagents:* (i) KCN, ZnI_2; (ii) O_3; DMS then $Ph_3P{=}CMe_2$, (36%); (iii) DIBAL; (iv) Me_2AlCl.

of KCN and ZnI_2 in acetonitrile;[16] in our hands the reactions were much more effective when performed in THF as the solvent (as in Kurihara's method that uses LiCN in the absence of ZnI_2).[17] For example, isobutyraldehyde was converted into the *O*-allyldiisopropylsilyl cyanohydrin **30** in 85% yield. Sequential ozonolysis–Wittig olefination of the allylsilyl derivatives proceeded in poor yield in the case of ester **29** and in mediocre yield (36%) in the case of cyanohydrin **30**, nevertheless these routes had given us, after DIBAL reduction, an alternative access to ene precursors without recourse at any stage to organolithium additions.

Interestingly, the ene cyclisation of aldehyde **32** revealed a reaction mode for these substrates that had not been observed in the earlier studies and which could account for the moderate mass balance from some of these reactions. In this example, whilst the cyclisation proceeded to give only one isolable ene product (**33**), shown to be the *trans*,*trans* isomer, intramolecular allylic transfer competed to an almost equal extent to give the siladioxolane **34** essentially as a single diastereomer. Although we did not appreciate it at the time, this example provided an early warning of an alternative mode of reactivity that would come to dominate our subsequent studies and which will be reported separately.[18]

All of the substrates thus far had possessed inert side-chains purely for synthetic expediency, however a significant objective in pursuing this investigation was to explore its application to the synthesis of non-natural iminosugars as potential glycosidase inhibitors.[19] To this end we envisaged elaborating the protected isoserine derivative **35**[20] (Scheme 11) into aminotriol **38** which would be a useful substrate for electrophile-mediated cyclisation to a variety of iminosugars. Thus, silylation with silane **10** as before and DIBAL reduction led to ene precursor **36** in *ca.* 50–70% yield, the variation in yield originating in the



Scheme 11 *Reagents:* (i) **10**, $B(C_6F_5)_3$ cat.; (ii) DIBAL; (iii) Me_2AlCl; (iv) KF, $KHCO_3$, H_2O_2.

reduction step which proved very sensitive to the reaction conditions and to the particular batch of DIBAL employed. Although this substrate possessed a polar, protic side-chain, the ene cyclisation proceeded well under the standard conditions to yield the product apparently as a single stereoisomer (**37**, shown by NOE and ^{1}H–^{1}H coupling constant analysis to be *trans*, *trans*). Although this silacycle could be isolated in moderate yield by chromatography, it proved more efficient to take the material on crude into the oxidative cleavage to afford the aminotriol **38** in comparable overall yield.

Summary

This study has extended our previously reported silicon tethered ene cyclisations of prenyl substrates by including oxygen as a point of attachment for the silicon which eases both the assembly of the substrates and subsequent oxidation to afford triols. In the process we have developed a variety of approaches to the ene precursors that extend the scope of both Kuwajima's and Piers' silylation protocols, and we have employed silylcyanohydrin formation in a novel way to afford suitable aldehydes in two efficient synthetic operations. Furthermore, sequential ozonolysis and Wittig olefination have been applied in the conversion of easily-available allylsilanes into the required prenylsilanes. During the course of this investigation we have also observed competing allylic transfer; we will report separately on the optimisation of this reaction mode under conditions in which the reactions are both stereospecific and highly stereoselective.[18]

Experimental

General experimental details are as reported elsewhere.[21] Spectroscopic data for compounds **1**–**4**, and procedures with supporting characterisation for compounds **11**, **21**, **24**, **25**, **26** and **29** are available as Electronic Supplementary Information. ‡

Silylation procedure for compounds 1 and 2

To a solution of 1-phenyl-1,2-ethanediol (276 mg, 2 mmol) in tetrahydrofuran (8 mL) at 0 °C was added BuLi (1.4 mL, 1.6 M in pentanes, 2.2 mmol) and the requisite dialkylchlorosilane (2.2 mmol). The solution was stirred at 0 °C for 30 min and then at room temperature for 1.5 h. Meanwhile, to a solution of prenyl(tributyl)stannane[22] (862 mg, 2.4 mmol) in tetrahydrofuran (5 mL) at −78 °C was added BuLi (1.5 mL, 1.6 M in pentanes, 2.4 mmol) and the reaction mixture was stirred for 30 min. The first solution was cooled to −78 °C, TMEDA (643 μL, 4.5 mmol) and then the prenyl lithium solution were added. The reaction mixture was stirred at −78 °C for 2 h and then at −45 °C for 1 h. A saturated aqueous solution of NH_4Cl (10 mL) was added and the solution was warmed to room temperature. The mixture was extracted with ether (2 × 30 mL), the combined organic extracts were washed with brine (20 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure and the resulting oil was purified by flash column chromatography on silica gel (25 : 1, petrol : ether).

General procedure for oxidation of alcohols 1 and 2

IBX (2 eq.) was dissolved in dimethyl sulfoxide (25 mL) at room temperature and then alcohol **1** or **2** (1 mmol) was added as a solution in dimethyl sulfoxide (5 mL). The resulting solution was stirred for 16 h at room temperature and then partitioned between water (50 mL) and ether (100 mL). The aqueous layer was extracted with a further portion of ether (100 mL) and the combined organic extracts were washed with brine (100 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure and the resulting oil was purified by flash column chromatography on silica gel (20 : 1, petrol : ether).

1,1-Di(*tert*-butyl)-2-oxa-3-phenyl-5-(propen-2-yl)silinan-4-ol (5) and (7)

To a solution of aldehyde **3** (104 mg, 0.3 mmol) in dichloromethane (15 mL) at room temperature was added dimethylaluminium chloride (450 μL, 1 M in hexanes, 0.45 mmol). After 1 h a saturated aqueous solution of Na_2SO_4 (10 mL) was added and the reaction mixture was extracted with ether (2 × 30 mL). The combined organic extracts were washed with brine (20 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure and the resulting oil was purified by flash column chromatography on silica gel (25 : 1, petrol : ether) to give the major product (**5**) as a colourless oil (39 mg, 38%) and a minor product (**7**) as a colourless oil (8 mg, 8%). Data for **5**: R_f 0.39 (5 : 1 petrol : ether); ν_{max}/cm^{-1} (film) 3470m br, 3067m, 3032m, 2989s, 2964s, 2858s, 1644m, 1495w, 1471s, 1409w, 1387m, 1365m, 1205m, 1186m, 1099m, 1082s, 1067s, 1028m, 939w, 885m, 842s, 823s, 761m, 736m, 698s, 634m; δ_H (400 MHz, $CDCl_3$) 0.94–0.99 (1 H, m) and 1.04–1.06 (1 H, m, SiCH_2), 1.10 (9 H, s, C(CH_3)$_3$), 1.11 (9 H, s, C(CH_3)$_3$), 1.27 (1 H, br s, OH), 1.77 (3 H, s, C(=CH$_2$)CH_3), 2.75 (1 H, ddd, *J* 13.0, 10.5, 5.1, CH$_2$CH), 3.33 (1 H, dd, *J* 10.5, 8.7, CH(OH)), 4.69 (1 H, d, *J* 8.7, PhCH), 4.87 (1 H, s) and 4.90 (1 H, s, C=CH_2), 7.30–7.49 (5 H, m, Ph); [for **7**: δ_H (200 MHz, $CDCl_3$) 0.92–1.14 (2 H, m, SiCH_2), 1.12 (9 H, s, C(CH_3)$_3$), 1.21 (9 H, s, C(CH_3)$_3$), 1.67 (1 H, br s, OH), 1.89 (3 H, s, C(=CH$_2$)CH_3), 2.72–2.87 (1 H, m, CH$_2$CH), 3.98 (1 H, dd, *J* 7.3, 4.4, CH(OH)), 4.84 (1 H, s, C=CH_2), 4.85 (1 H, s, C=CH_2), 5.32 (1 H, d, *J* 4.4, PhCH), 7.38–7.56 (5 H, m, Ph)]; δ_C (100 MHz, $CDCl_3$) 10.7, 17.5, 20.1, 22.2, 27.6, 28.3, 50.1, 74.0, 81.3, 112.9, 127.2, 127.9, 128.2, 142.7, 148.6; *m*/*z* (CI$^+$) 364 (MNH_4^+, 41%), 347 (87), 329 (44), 289 (37), 227 (32), 176 (100), 91 (33); Accurate mass (CI$^+$): Found 364.2674, $C_{21}H_{38}NO_2Si$ (MNH_4^+) requires 364.2672.

1,1-Di(isopropyl)-2-oxa-3-phenyl-5-(propen-2-yl)silinan-4-ol (6) and (8)

To a solution of aldehyde **4** (36 mg, 0.11 mmol) in dichloromethane (5 mL) at room temperature was added dimethylaluminium chloride (175 μL, 1 M in hexanes, 0.18 mmol). After 1 h a saturated aqueous solution of Na_2SO_4 (10 mL) was added and the reaction mixture was extracted with ether (2 × 20 mL). The combined organic extracts were washed with brine (20 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure and the resulting oil was purified by flash column chromatography on silica gel (25 : 1, petrol : ether) to give the major product (**6**) as a colourless oil (14 mg, 39%) and the minor product (**8**) as a colourless oil (4 mg, 11%). Data for **6**: R_f 0.65 (1 : 1 petrol : ether); ν_{max}/cm^{-1} (film) 3477m br, 3066m, 3031m, 2941s, 2892s, 2065s, 1736w, 1644m, 1603w, 1495m, 1463s, 1382m, 1246m, 1178m, 1083s, 1061s, 1028s, 917m, 883s, 846s, 764s, 699s, 679m, 658m, 629m, 589m; δ_H (400 MHz, $CDCl_3$) 0.86 (1 H, dd, *J* 14.4, 4.0, SiCH_2(equatorial)), 1.00 (1 H, dd, *J* 14.4, 13.4, SiCH_2-(axial)), 1.04–1.14 (14 H, m, SiCH(CH_3)$_2$), 1.76 (3 H, s, CH_3), 2.67 (1 H, ddd, *J* 13.4, 10.2, 4.0, CH$_2$CH), 3.28 (1 H, dd, *J* 10.2, 8.7, CH(OH)), 4.62 (1 H, d, *J* 8.7, PhCH), 4.87 (1 H, s, C=CH_2), 4.91 (1 H, s, C=CH_2), 7.23–7.47 (5 H, m, Ph); [for **8**: δ_H (200 MHz, $CDCl_3$) 0.98–1.21 (16 H, m, SiCH_2 and Si(*iso*-Pr)$_2$), 1.83 (3 H, s, C(=CH$_2$)CH_3), 2.72 (1 H, apparent q, apparent *J* 7.1, CH$_2$CH), 3.93 (1 H, dd, *J* 5.6, 3.8, CH(OH)) 4.87 (1 H, s, C=CH_2), 4.90 (1 H, s, C=CH_2), 5.09 (1 H, d, *J* 3.8, PhCH), 7.22–7.58 (5 H, m, Ph)]; δ_C (100 MHz, $CDCl_3$) 10.9, 12.0, 12.9, 17.5, 17.6, 17.7, 17.8, 49.6, 74.5, 80.6, 112.4, 127.1, 127.9, 128.2, 128.3, 142.7, 148.4; *m*/*z* (CI$^+$) 336 (MNH_4^+, 13%), 319 (MH^+, 45), 301 (89), 275 (56), 249 (45), 211 (68), 199 (100), 171 (59), 121 (21), 105 (35); Accurate mass (CI$^+$): Found 319.2098, $C_{19}H_{31}O_2Si$ (MH^+) requires 319.2093.

3,4-*anti*-4,5-*anti*-3-(Hydroxymethyl)-2-methyl-5-phenylpent-1-ene-4,5-diol (9)

From ene adduct 6. To a solution of oxasilinane **6** (14.1 mg, 0.044 mmol) in methanol (0.5 mL) and tetrahydrofuran (0.5 mL) was added KF (3 mg, 0.05 mmol), $KHCO_3$ (5 mg, 0.05 mmol) and H_2O_2 (30 μL, 35% in water, 0.3 mmol) and the resulting mixture was heated at reflux for 16 h. The reaction mixture was allowed to cool to room temperature, a saturated solution of $NaHSO_3$ (2 mL) was added and the reaction mixture extracted with ether (4 × 10 mL). The combined organic extracts were dried over $MgSO_4$, the solvent was removed under reduced pressure and the resulting material purified by flash column chromatography on silica gel (ether) to give the product as a white powder (1.6 mg, 17%). R_f 0.42 (10 : 1 dichloromethane : methanol); ν_{max}/cm^{-1} (film) 3384s br, 2921m, 1641m, 1260s, 1024s, 798m, 701s; δ_H (200 MHz, $CDCl_3$) 1.82 (3 H, s, CH_3), 2.02 (1 H, br s, OH), 2.54 (1 H, dt, J 6.5, 6.3, CHCH$_2$), 3.12 (2 H, br s, 2 × OH), 3.64–3.72 (2 H, m, CH_2OH), 3.89 (1 H, dd, J 7.2, 6.5, CH(OH)), 4.57 (1 H, d, J 7.2, PhCH), 4.90 (1 H, s, C=CH_2), 5.02 (1 H, s, C=CH_2), 7.30–7.43 (5 H, m, Ph); δ_C (50 MHz, $CDCl_3$) 21.7, 51.7, 62.7, 74.3, 75.9, 115.2, 127.3 (two peaks), 128.2, 128.6, 141.1, 143.8; *m*/*z* (CI^+) 240 (MNH_4^+, 21%), 223 (MH^+, 100), 208 (11); mp 81–88 °C; Accurate mass (CI^+): Found 240.1593, $C_{13}H_{22}NO_3$ (MNH_4^+) requires 240.1600.

From ene adduct 17. A mixture of oxasilinane **17** (112 mg, 0.29 mmol), KF (85 mg, 1.47 mmol), $KHCO_3$ (46 mg, 0.46 mmol) and H_2O_2 (143 μL, 35% in water, 1.47 mmol) in methanol (3 mL) and tetrahydrofuran (3 mL) was stirred at room temperature for 16 h. The mixture was filtered through a glass sinter and the solvent removed under reduced pressure. The resulting material was triturated with ether (20 mL), the solvent was removed under reduced pressure and the resulting material purified by flash column chromatography on silica gel (20 : 1, dichloromethane : methanol) to give the product as a white powder (31 mg, 48%). Data as above.

(3-Methylbut-2-enyl)diphenylsilane (10)

Method A. To a stirred solution of prenyl(triphenyl)-stannane[23] (1.04 g, 2.48 mmol) in anhydrous tetrahydrofuran (25 mL) cooled to −78 °C was added BuLi (1.6 M in hexanes, 1.55 mL, 2.48 mmol) dropwise over 5 min and the mixture was stirred for 1.5 h. Diphenylchlorosilane (490 μL, 2.50 mmol) was added rapidly and the mixture was stirred at −78 °C for a further 1 h. The solution was warmed to room temperature and the solvent removed *in vacuo*. The crude residue was triturated with petrol, and the petrol extracts were filtered and the solvent removed *in vacuo*. The resulting oil was purified by flash column chromatography (petrol) to furnish the product as a colourless oil (606 mg, 97%). R_f 0.67 (10 : 1, petrol : ether); Found: C, 80.56; H, 8.34. $C_{17}H_{20}Si$ requires C, 80.89; H 7.99%; ν_{max} (film)/cm^{-1} 3086m, 3068s, 3050s, 3020s, 2999s, 2966s, 2912s, 2879s, 2855m, 2122s, 1955w, 1883w, 1818w, 1765w, 1665w, 1589m, 1486m, 1450m, 1428s, 1404w, 1376m, 1343w, 1330w, 1302w, 1264w, 1224w, 1189w, 1156s, 1117s, 1066w, 998m, 858s, 835s, 804s, 734s, 698s; δ_H (400 MHz, $CDCl_3$) 1.53 and 1.73 (2 × 3 H, 2 × s, =C(CH_3)$_2$), 2.09 (2 H, dd, J 8.4, 3.2, SiCH_2), 4.91 (1 H, t, J 3.2, SiH), 5.30 (1 H, br t, J 8.4, CH=C(CH$_3$)$_2$), 7.40–7.48 (6 H, m, Ph), 7.57–7.74 (4 H, m, Ph); δ_C (100 MHz, $CDCl_3$) 14.1, 17.6, 25.7, 118.3, 127.8, 129.6, 131.0, 134.3, 135.2; *m*/*z* (CI^+) 270 (MNH_4^+, 100%), 253 (MH^+, 29), 199 (85), 192 (36), 183 (50), 139 (22), 105 (20), 78 (16); Accurate Mass (CI^+): Found 270.1682, $C_{17}H_{24}NSi$ (MNH_4^+) requires 270.1678.

Method B. A solution of (prop-2-enyl)diphenylsilane (**24**, 492 mg, 2.19 mmol) and Sudan Red 7B indicator (10 μL, 0.05% solution in dichloromethane) in anhydrous dichloromethane (44 mL) was cooled to −78 °C. Ozone was passed through the solution until the magenta colouration dispersed; excess ozone was purged from the system with argon. Dimethyl sulfide (193 μL, 2.63 mmol) was added and the mixture stirred at −78 °C for 1 h and then warmed to room temperature over 30 min. Meanwhile, to a solution of isopropyltriphenylphosphonium iodide (1.89 g, 4.37 mmol) in anhydrous tetrahydrofuran (18 mL) cooled to −45 °C was added BuLi (1.6 M in hexanes, 2.3 mL, 3.7 mmol). The blood red solution was stirred for 1 h at −45 °C then warmed to room temperature over 2 h. Both solutions were cooled to −45 °C and the ylide added *via* cannula to the solution of silylacetaldehyde. The solution was stirred at −45 °C for 30 min and then warmed to room temperature over 2 h. The reaction mixture was partitioned between water (100 mL) and dichloromethane (50 mL). The aqueous phase was extracted with dichloromethane (3 × 25 mL), the combined organic layers washed with saturated aqueous NaCl solution (2 × 50 mL), dried ($MgSO_4$) and solvents removed *in vacuo*. The crude residue was triturated with ether, the ether extracts were filtered through Celite®, and the solvent was removed *in vacuo*. The resulting yellow oil was purified by flash column chromatography (petrol) to furnish silane **10** as a colourless oil (39.6 mg, 7%). Data as above.

(*S*)-Ethyl 2-[(3-methylbut-2-enyl)diphenylsilanyloxy]propanoate (12)

To a stirred solution of silane **10** (794 mg, 3.15 mmol) and (*S*)-(−)-ethyl lactate (357 μL, 3.15 mmol) in anhydrous dichloromethane (10 mL) was added tris(pentafluorophenyl)-borane (80.6 mg, 0.16 mmol) and the reaction mixture heated at reflux for 15 h. The solution was allowed to cool to room temperature and then partitioned between water (25 mL) and ether (25 mL), the aqueous layer was separated and extracted with ether (2 × 25 mL). The combined organic extracts were washed with saturated aqueous NaCl solution (50 mL), dried ($MgSO_4$) and solvents removed *in vacuo*. The resulting oil was purified by flash column chromatography (10 : 1, petrol : ether) to furnish the product (**12**) as a colourless oil (807 mg, 70%). R_f 0.64 (2 : 1, petrol : ether); $[\alpha]_D^{22}$ −36.1 (*c* 0.79, $CHCl_3$); ν_{max} (film)/cm^{-1} 3070m, 3050m, 2981m, 2912m, 1751s, 1590w, 1446m, 1429s, 1375m, 1272w, 1198m, 1118s, 1061m, 1023m, 976m, 817m, 735s, 701s; δ_H (400 MHz, $CDCl_3$) 1.21 (3 H, t, J 7.2, $CO_2CH_2CH_3$), 1.41 and 1.65 (2 × 3 H, 2 × d, J 1.2, =C(CH_3)$_2$), 1.43 (3 H, d, J 6.8, OCHCH_3), 2.12 (2 H, br apparent d, apparent J 8.0, SiCH_2), 4.05–4.13 (2 H, m, $CO_2CH_2CH_3$), 4.38 (1 H, q, J 6.8, OCHCH$_3$), 5.24 (1 H, tsept, J 8.0, 1.2, CH=C(CH$_3$)$_2$), 7.36–7.47 (6 H, m, Ph), 7.62–7.71 (4 H, m, Ph); δ_C (100 MHz, $CDCl_3$) 14.0, 16.2, 17.6, 21.2, 25.8, 60.7, 68.8, 117.2, 127.7, 127.8, 129.9, 130.1, 131.3, 134.4, 134.5, 134.8, 134.9, 135.5, 173.6; *m*/*z* (ES^+) 391 (MNa^+, 100%), 300 (11); Accurate mass (CI^+): Found 386.2157, $C_{22}H_{32}NO_3Si$ (MNH_4^+) requires 386.2151.

Ethyl [(3-methylbut-2-enyl)diphenylsilanyloxy]phenylacetate (13)

To a solution of silane **10** (1.01 g, 4 mmol) and ethyl mandelate (720 mg, 4 mmol) in dichloromethane (20 mL), was added tris(pentafluorophenyl)borane (80 mg, 0.16 mmol) and the reaction mixture was heated at reflux for 16 h. The solution was allowed to cool to room temperature and then partitioned between water (10 mL) and ether (10 mL). The aqueous layer was extracted with ether (2 × 10 mL) and the combined organic extracts were washed with brine (10 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure and the resulting oil was purified by flash column chromatography on silica gel (25 : 1, petrol : ether) to give the product as a colourless oil (1.46 g, 84%). R_f 0.35 (10 : 1 petrol : ether); Found: C, 75.15; H 7.29. $C_{27}H_{30}O_3Si$ requires C, 75.31, H, 7.02%; ν_{max}/cm^{-1} (film) 3070s, 2978s, 2912s, 1960w, 1891w,

1823w, 1753s, 1590m, 1494m, 1454s, 1429s, 1371s, 1263s, 1177s br, 1119s br, 1072s, 1028s, 882s, 838s, 816s, 729s, 699s; δ_H (200 MHz, $CDCl_3$) 1.14 (3 H, t, *J* 7.1, CH_2CH_3), 1.37 (3 H, s, CH_3), 1.62 (3 H, s, CH_3), 2.12 (2 H, apparent d, apparent *J* 8.2, $SiCH_2$), 3.90–4.10 (2 H, m, OCH_2), 5.20 (1 H, br t, *J* 8.2, C*H*=C), 5.28 (1 H, s, PhC*H*), 7.33–7.70 (15 H, m, Ph); δ_C (50 MHz, $CDCl_3$) 14.0, 16.2, 17.6, 25.8, 61.0, 74.7, 117.1, 126.6, 127.8, 128.2, 128.8, 130.0, 131.5, 134.1, 135.0, 138.8, 171.7; *m*/*z* (CI^+) 448 (MNH_4^+, 5%), 361 (100), 333 (12), 244 (9), 216 (10), 167 (14).

(*S*)-2-[(3-Methylbut-2-enyl)diphenylsilanyloxy]propionaldehyde (14)

To a stirred solution of ester **12** (530 mg, 1.44 mmol) in anhydrous dichloromethane (15 mL) cooled to −78 °C was added di(isobutyl)aluminium hydride (1.0 M in dichloromethane, 2.16 mL, 2.16 mmol) dropwise and the solution stirred at −78 °C for 45 min. The reaction was quenched by the addition of a saturated solution of tartaric acid in methanol (2 mL). The mixture was warmed to room temperature and partitioned between aqueous tartaric acid solution (30% w/v, 20 mL) and ether (25 mL). The aqueous layer was extracted with ether (2 × 25 mL) and the combined organic extracts washed with saturated aqueous NaCl solution (40 mL), dried ($MgSO_4$) and solvents removed *in vacuo*. The crude product was purified by flash column chromatography (30 : 1, petrol : ether) to furnish aldehyde **14** as a colourless oil (285 mg, 61%). R_f 0.26 (10 : 1, petrol : ether, [streaks]); $[\alpha]_D^{22}$ −14.7 (*c* 1.10, $CHCl_3$); ν_{max} (film)/cm^{-1} 3070m, 3050m, 3024m, 2975m, 2913m, 2856m, 2803w, 1960w, 1889w, 1822w, 1739s, 1590w, 1429s, 1376m, 1160m, 1118s, 1011m, 998m, 967w, 859w, 816m, 734s, 701s; δ_H (400 MHz, $CDCl_3$) 1.29 (3 H, d, *J* 6.8, $OCHCH_3$), 1.43 and 1.66 (2 × 3 H, 2 × d, *J* 1.2, $=C(CH_3)_2$), 2.12 (2 H, br apparent d, apparent *J* 8.0, $SiCH_2$), 4.19 (1 H, qd, *J* 6.8, 1.2, $OCHCH_3$), 5.23 (1 H, tsept, *J* 8.0, 1.2, $CH=C(CH_3)_2$), 7.38–7.48 (6 H, m, Ph), 7.61–7.68 (4 H, m, Ph), 9.46 (1 H, d, *J* 1.2, C*H*O); δ_C (100 MHz, $CDCl_3$) 16.1, 17.6, 18.4, 25.7, 74.3, 116.9, 127.9, 128.0, 130.0, 130.2, 130.4, 131.7, 134.2, 134.3, 134.7, 134.8, 135.4, 203.5; *m*/*z* (CI^+) 342 (MNH_4^+, 39%), 325 (MH^+, 34), 255 (100), 243 (20), 216 (82), 78 (19); Accurate mass (CI^+): Found 342.1891, $C_{20}H_{28}NO_2Si$ (MNH_4^+) requires 342.1889.

[(3-Methylbut-2-enyl)diphenylsilanyloxy]phenylacetaldehyde (15)

Ester **13** (836 mg, 1.93 mmol) was dissolved in a mixture of dichloromethane (4 mL) and heptane (6 mL) and cooled to −78 °C. Di(isobutyl)aluminium hydride (1.94 mL, 1.0 M in hexanes, 1.94 mmol) was added dropwise and the solution was stirred at −78 °C for 1 h. Water (5 mL) was added, the solution was warmed to room temperature and then partitioned between ether (10 mL) and saturated aqueous Na_2SO_4 solution (10 mL). The aqueous layer was extracted with ether (20 mL), the combined organic extracts were washed with brine (20 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure and the resulting oil was purified by flash column chromatography on silica gel (25 : 1, petrol : ether) to give the product as a colourless oil (425 mg, 57%). R_f 0.46 (4 : 1 petrol : ether); ν_{max}/cm^{-1} (film) 3070m, 3027m, 2966m, 2913m, 1737s, 1590w, 1490w, 1452m, 1429s, 1376w, 1118s br, 1073m, 923w, 857w, 733m, 699s; δ_H (200 MHz, $CDCl_3$) 1.37 (3 H, s, CH_3), 1.62 (3 H, s, CH_3), 2.11 (2 H, apparent d, apparent *J* 8.1, $SiCH_2$), 5.11 (1 H, d, *J* 1.8, PhC*H*), 5.17 (1 H, br t, *J* 8.1, C*H*=C), 7.22–7.52 (11 H, m, Ph), 7.56–7.67 (4 H, m, Ph), 9.64 (1 H, *J* 1.8, C*H*O); δ_C (50 MHz, $CDCl_3$) 16.2, 17.6, 25.7, 80.4, 116.8, 126.7, 127.9, 128.7, 130.2, 131.8, 133.9, 134.8, 136.1, 198.9; *m*/*z* (EI^+) 319 ($M^+ - C_5H_9$, 32%), 199 (84), 139 (33), 105 (100), 77 (89); Accurate mass (CI^+): Found 404.2051, $C_{25}H_{30}NO_2Si$ (MNH_4^+) requires 404.2046.

(3*S*,4*R*,5*R*)-2-Oxa-1,1-diphenyl-3-methyl-5-(propen-2-yl)-silinan-4-ol (16) and (3*S*,4*S*,5*R*)-2-oxa-1,1-diphenyl-3-methyl-5-(propen-2-yl)silinan-4-ol (18)

To a stirred solution of aldehyde **14** (228 mg, 0.70 mmol) in anhydrous dichloromethane (7 mL) at room temperature was added dimethylaluminium chloride (1.0 M in hexanes, 634 μL, 0.63 mmol). After 20 min the reaction was quenched by the addition of saturated aqueous Na_2SO_4 solution (5 mL) and the mixture partitioned between water (20 mL) and ether (20 mL). The aqueous layer was extracted with ether (3 × 10 mL); the combined organic layers washed with saturated aqueous NaCl solution (40 mL), dried (Na_2SO_4) and solvents removed *in vacuo*. The resulting oil was purified by flash column chromatography (30 : 1, petrol : ether) to furnish the major product (**16**) as colourless needles (109 mg, 48%) and a minor product (**18**) as a colourless syrup (11 mg, 5%). Data for **16**: R_f 0.38 (2 : 1, petrol : ether); mp 82–85 °C (from ether); $[\alpha]_D^{22}$ −25.0 (*c* 0.62 in $CHCl_3$); ν_{max} (KBr)/cm^{-1} 3521m, 3071m, 2970m, 2878m, 1635w, 1590w, 1489w, 1430s, 1371m, 1334w, 1307w, 1264w, 1180w, 1157m, 1120s, 1072s, 1037m, 1018s, 997m, 978s, 941w, 910m, 892w, 824w, 804m, 772m, 743s, 712s, 701s; δ_H (400 MHz, $CDCl_3$) 1.32–1.36 (2 H, m, $SiCH_2$), 1.47 (3 H, d, *J* 6.0, $CHCH_3$), 1.80 (3 H, br s, $C(CH_3)=$), 2.51 (1 H, td, *J* 10.0, 6.8, $SiCH_2CH$), 3.25 (1 H, dd, *J* 10.0, 8.4, C*H*(OH)), 3.88 (1 H, qd, *J* 8.4, 6.0, $CHCH_3$), 4.88 and 4.94 (2 × 1 H, 2 × br s, $C(CH_3)=CH_2$), 7.33–7.50 (6 H, m, Ph), 7.54–7.57 (2 H, m, Ph), 7.67–7.71 (2 H, m, Ph); δ_C (100 MHz, $CDCl_3$) 15.0, 17.7, 21.8, 49.8, 74.4, 74.5, 113.8, 127.9, 128.2, 130.1, 130.3, 133.9, 134.3, 134.8, 147.5; *m*/*z* (CI^+) 342 (MNH_4^+, 16%), 325 (MH^+, 45), 307 (21), 281 (20), 255 (75), 247 (95), 233 (26), 216 (57), 203 (100), 181 (14), 156 (24), 138 (14), 109 (24); Accurate mass (CI^+): Found 342.1879, $C_{20}H_{28}NO_2Si$ (MNH_4^+) requires 342.1889. Data for **18**: R_f 0.33 (2 : 1, petrol : ether); $[\alpha]_D^{22}$ −44.4 (*c* 0.50, $CHCl_3$); ν_{max} (film)/cm^{-1} 3455s, 3069m, 2973m, 2930m, 1643m, 1428s, 1375w, 1261w, 1118s, 1070m, 997m, 957m, 914w, 852w, 821w, 782m, 737s, 699s; δ_H (400 MHz, $CDCl_3$) 1.11 (1 H, dd, *J* 14.4, 3.2, $SiCH_{eq}H$), 1.43 (3 H, d, *J* 6.8, $CHCH_3$), 1.49 (1 H, t, *J* 14.4, $SiCH_{ax}H$), 1.70 (1 H, br s, CH(O*H*)), 1.84 (3 H, br s, $C(CH_3)=$), 2.46 (1 H, br d, *J* 14.4, $SiCH_2CH$), 3.66 (1 H, apparent s, C*H*(OH)), 4.14 (1 H, qd, *J* 6.8, 1.2, $CHCH_3$), 4.96–4.99 (2 H, m, $C(CH_3)=CH_2$), 7.33–7.49 (6 H, m, Ph), 7.57–7.61 (2 H, m, Ph), 7.68–7.71 (2 H, m, Ph); δ_C (100 MHz, $CDCl_3$) 8.2, 20.8, 22.0, 46.3, 71.9, 73.2, 111.1, 127.9, 128.2, 130.1, 130.3, 134.3, 134.4, 148.5; *m*/*z* (CI^+) 342 (MNH_4^+, 87%), 325 (MH^+, 20), 299 (85), 291 (44), 279 (50), 247 (61), 226 (19), 217 (65), 209 (88), 172 (100), 150 (71); Accurate mass (CI^+): Found 342.1878, $C_{20}H_{28}NO_2Si$ (MNH_4^+) requires 342.1889.

2-Oxa-1,1,3-triphenyl-5-(propen-2-yl)silinan-4-ol (17) and (19)

To a solution of aldehyde **15** (264 mg, 0.68 mmol) in dichloromethane (10 mL) at room temperature was added dimethylaluminium chloride (690 μL, 1 M in hexanes, 0.69 mmol). After 30 min a saturated aqueous Na_2SO_4 solution (10 mL) was added and the mixture was extracted with ether (2 × 30 mL). The combined organic extracts were washed with brine (20 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure and the resulting oil was purified by flash column chromatography on silica gel (15 : 1, petrol : ether) to give the major product (**17**) as a colourless oil (151 mg, 57%) and the minor product (**19**) as a colourless oil (21 mg, 8%). Data for **17**: R_f 0.23 (10 : 1 petrol : ether); ν_{max}/cm^{-1} (film) 3458m br, 3069m, 2974s, 2926m, 2874s, 1958w, 1888w, 1823w, 1644w, 1590w, 1453m, 1429s, 1380m, 1305w, 1261w, 1174m, 1117s, 1058s, 1026s, 998m, 944w, 861s, 770m, 737s, 699s; δ_H (400 MHz, $CDCl_3$) 1.43–1.51 (2 H, m, $SiCH_2$), 1.79 (3 H, s, CH_3), 2.75 (1 H, ddd, *J* 10.4, 8.6, 6.8, $CHCH_2$), 3.53 (1 H, dd, *J* 10.4, 8.7, C*H*(OH)), 4.72 (1 H, d, *J* 8.7, PhC*H*), 4.90 (2 H, s, $C=CH_2$), 7.36–7.74 (15 H, m, Ph); [For **19**: δ_H (400 MHz, $CDCl_3$) 1.11–1.32 (2 H, m, $SiCH_2$), 1.86 (3 H, s, CH_3), 2.70

(1 H, br d, *J* 13.9, C*H*CH_2), 3.98 (1 H, apparent s, C*H*(OH)), 4.94 (1 H, s, C=CH_2), 4.98 (1 H, s, C=CH_2), 5.13 (1 H, s, PhC*H*), 7.30–7.79 (15 H, m, Ph)]; δ_C (100 MHz, $CDCl_3$) 15.5, 17.6, 49.6, 74.3, 80.2, 112.9, 127.2, 127.6, 127.9, 128.0, 128.3, 130.0, 130.3, 134.3, 134.4, 134.7, 141.9, 147.8; *m*/*z* (CI^+) 404 (MNH_4^+, 10%), 387 (MH^+, 100), 396 (28), 267 (15); Accurate mass (CI^+): Found 387.1780, $C_{25}H_{27}O_2Si$ (MH^+) requires 387.1770.

(2*S*,3*R*,4*S*)-4-(Hydroxymethyl)-5-methylhex-5-ene-2,3-diol (20)

To a solution of oxasilinane **16** (88.1 mg, 0.27 mmol) in methanol (5 mL) and tetrahydrofuran (5 mL) was added KF (47.3 mg, 0.81 mmol), $KHCO_3$ (54.4 mg, 0.54 mmol) and H_2O_2 (35% in water, 130 μL, 1.36 mmol). The mixture was stirred for 16 h at room temperature, filtered through Celite® and the solvent removed *in vacuo*. The residue was triturated with ether (20 mL), the extracts were filtered and the solvent removed *in vacuo*. The resulting material was purified by flash column chromatography (1 : 2, petrol : ether) to furnish triol **20** as a colourless syrup (38.3 mg, 88%). R_f 0.18 (ethyl acetate); $[a]_D^{22}$ +1.67 (*c* 0.60 in $CHCl_3$); ν_{max} (film)/cm^{-1} 3368s, 3078w, 2970m, 2929m, 1644m, 1450m, 1376m, 1282w, 1134w, 1073s, 1040s, 983m, 897m; δ_H (400 MHz, DMSO-d_6) 1.07 (3 H, d, *J* 6.0, CH(OH)CH_3), 1.70 (3 H, s, C(CH_3)=), 2.44 (1 H, dt, *J* 7.2, 4.4, C*H*CH_2OH), 3.35 (1 H, ddd, *J* 7.2, 5.6, 4.4, C*H*(OH)-CH(OH)CH_3) overlaying 3.40–3.54 (3 H, m, C*H*(OH)CH_3 and CH_2OH), 4.25 (1 H, d, *J* 5.6, CH(O*H*)CH(OH)CH_3), 4.27 (1 H, d, *J* 5.6, CH(O*H*)CH_3), 4.33 (1 H, t, *J* 5.2, CH_2O*H*), 4.73 and 4.75 (2 H, 2 × br s, C(CH_3)=CH_2); δ_C (100 MHz, DMSO-d_6) 20.9, 23.2, 51.1, 62.7, 68.0, 75.2, 113.7, 145.7; *m*/*z* (ES^-) 159 ($M - H^+$, 100%), 157 (10); Accurate mass (ES^-): Found 159.1029, $C_8H_{15}O_3$ ($M - H^+$) requires 159.1021.

Tri(isopropyl)-3-methylbut-2-enylsilane (22)[24]

A solution of allyltri(isopropyl)silane (482 μL, 2.0 mmol) in anhydrous dichloromethane (40 mL) was cooled to −78 °C. Ozone was passed through the solution until a blue colouration persisted; excess ozone was purged from the system with argon. Dimethyl sulfide (176 μL, 2.4 mmol) was added and the reaction mixture was stirred at −78 °C for 1 h and then warmed to room temperature over 3.5 h. Meanwhile, to a solution of isopropyltriphenylphosphonium iodide (3.46 g, 8.0 mmol) in anhydrous tetrahydrofuran (35 mL) cooled to −78 °C was added BuLi (1.6 M in hexanes, 4.4 mL, 7.0 mmol). The blood red solution was stirred for 1.5 h at −78 °C then warmed to room temperature over 1.5 h. Both solutions were cooled to −45 °C and the ylide added *via* cannula to the solution of silylacetaldehyde. The solution was stirred at −45 °C for 30 min and then warmed to room temperature over 3 h. The reaction mixture was partitioned between water (50 mL) and dichloromethane (50 mL). The aqueous phase was extracted with dichloromethane (3 × 25 mL), the combined organic layers were washed with saturated aqueous NaCl solution (50 mL), dried (Na_2SO_4) and solvents removed *in vacuo*. The crude residue was triturated with ether and petrol, the combined extracts were filtered through Celite®, and the solvents removed *in vacuo*. The resulting yellow oil was purified by flash column chromatography (petrol ⟶ 9 : 1, petrol : ether) to furnish silane **22** as a colourless oil (366 mg, 81%) as well as a small quantity of aldehyde **21** (9.0 mg, 2%). Data for **22**: R_f 0.63 (petrol); ν_{max} (film)/cm^{-1} 2942s, 2867s, 1463m, 1404w, 1383m, 1346w, 1244w, 1158m, 1099m, 1070w, 999w, 918w, 883s, 845w, 812w, 738s, 712s; δ_H (400 MHz, $CDCl_3$) 0.90–1.09 (21 H, m, 3 × SiC*H*(CH_3)$_2$), 1.50 (2 H, d, *J* 8.4, SiCH_2), 1.63 and 1.69 (2 × 3 H, 2 × s, =C(CH_3)$_2$), 5.22 (1 H, br t, *J* 8.4, C*H*=C(CH_3)$_2$); δ_C (100 MHz, $CDCl_3$) 10.8, 11.1, 17.6, 18.6, 25.8, 120.9, 128.0; *m*/*z* (EI) 226 (M^+, 9%), 157 (50), 115 (49), 99 (24), 87 (60), 73 (61), 59 (100). Data for **21** see Electronic Supplementary Information.‡

Di(isopropyl)prop-2-enylsilane (23)

To a stirred solution of di(isopropyl)chlorosilane (854 μL, 5.0 mmol) in anhydrous tetrahydrofuran (5 mL) cooled to 0 °C was added dropwise allylmagnesium bromide (1.0 M in ether, 5.3 mL, 5.3 mmol) over 5 min; the cloudy suspension was warmed to 40 °C for 2 h. The reaction was cooled to room temperature and quenched by the addition of ice and saturated aqueous NH_4Cl solution (20 mL). The mixture was extracted with ether (3 × 25 mL) and the combined organic phases washed with saturated aqueous NaCl solution (2 × 50 mL), dried ($MgSO_4$) and solvents removed *in vacuo* to furnish a pale yellow oil. Purification by flash column chromatography (petrol) gave silane **23** as a colourless oil (775 mg, 99%). R_f 0.76 (petrol); ν_{max} (film)/cm^{-1} 2942s, 2891s, 2865s, 2100s, 1632s, 1463s, 1420w, 1385m, 1366w, 1242w, 1193w, 1160m, 1068w, 1045w, 1003s, 931m, 918m, 895s, 806s, 732m, 710m, 693m; δ_H (400 MHz, $CDCl_3$) 0.95–1.08 (14 H, m, 2 × SiC*H*(CH_3)$_2$), 1.67 (2 H, ddt, *J* 8.0, 3.2, 1.2, SiCH_2), 3.47 (1 H, br s, Si*H*), 4.85 (1 H, ddt, *J* 10.0, 2.0, 1.2, CH=CHH_E), 4.94 (1 H, ddt, *J* 16.8, 2.0, 1.2, CH=CH_ZH), 5.87 (1 H, ddt, *J* 16.8, 10.0, 8.0, C*H*=CH_2); δ_C (100 MHz, $CDCl_3$) 10.4, 16.3, 18.6, 18.9, 113.1, 135.7; *m*/*z* (CI^+) 174 (MNH_4^+, 100%), 157 (MH^+, 29), 132 (30), 90 (18), 76 (23), 60 (14); Accurate mass (EI^+): Found 156.1338, $C_9H_{20}Si$ (M^+) requires 156.1334.

Chlorodi(isopropyl)prop-2-enylsilane (27)

A flame-dried two-necked flask (100 mL) was charged with anhydrous $CuCl_2$ (6.10 g, 45.4 mmol) and anhydrous CuI (108 mg, 0.57 mmol). The flask was equipped with a flame-dried Schlenk filter attached to a second round bottomed flask (100 mL). All joints were sealed with PTFE tape and the apparatus purged several times with argon. Anhydrous tetrahydrofuran (45 mL) was added followed by allyldi(isopropyl)silane (3.55 g, 22.7 mmol) and the orange suspension stirred for 21 h at room temperature. The apparatus was inverted and the inorganics filtered off by suction under argon; tetrahydrofuran was removed from the filtrate *in vacuo* to give a crude product that was distilled under reduced pressure into a flask cooled to −78 °C, to furnish chlorosilane **27** as a colourless oil (4.24 g, 98%). R_f 0.50 (2 : 1, petrol : ether); bp 38–40 °C (0.2 mmHg); ν_{max} (film)/cm^{-1} 3081m, 2984s, 2870s, 1632s, 1465s, 1419w, 1387m, 1368w, 1247w, 1191w, 1166m, 1070m, 993s, 901s, 883s, 768m, 734m; δ_H (500 MHz, $CDCl_3$) 1.10–1.14 (12 H, m, 2 × SiCH(CH_3)$_2$), 1.16–1.25 (2 H, m, 2 × SiC*H*(CH_3)$_2$), 1.88 (2 H, dt, *J* 8.0, 1.5, SiCH_2), 4.96 (1 H, ddt, *J* 10.0, 2.0, 1.5, CH=CHH_E), 5.02 (1 H, ddt, *J* 17.0, 2.0, 1.5, CH=CH_ZH), 5.84 (1 H, ddt, *J* 17.0, 10.0, 8.0, C*H*=CH_2); δ_C (125 MHz, $CDCl_3$) 13.8, 17.0, 20.6, 115.0, 132.6; *m*/*z* (CI^+) 208 (MNH_4^+, 22%), 191 (MH^+, 25), 166 (100), 148 (11), 138 (31), 93 (22), 74 (41), 63 (19), 60 (15); Accurate mass (CI^+): Found 191.1027, $C_9H_{20}SiCl$ (MH^+) requires 191.1023.

(*S*)-Ethyl [(prop-2-enyl)di(isopropyl)silanyloxy]phenylacetate (28)

To a stirred solution of (*S*)-(−)-ethyl mandelate (265 mg, 1.47 mmol), 4-dimethylaminopyridine (11 mg, 0.09 mmol) and triethylamine (205 μL, 1.47 mmol) in anhydrous dimethylformamide (6 mL) was added chlorosilane **27** (350 mg, 1.83 mmol). The solution was warmed to 80 °C for 16 h, then cooled to room temperature and partitioned between water (25 mL) and ether (25 mL). The aqueous phase was extracted with ether (2 × 15 mL) and the combined organic fractions washed with saturated aqueous NaCl solution (50 mL), dried ($MgSO_4$) and solvents removed *in vacuo*. The resulting yellow oil was purified by flash column chromatography (39 : 1, petrol : ether) to give ester **28** as a colourless oil (459 mg, 94%). R_f 0.38 (2 : 1, petrol : ether); $[a]_D^{22}$ +43.8 (*c* 1.04 in $CHCl_3$); ν_{max} (film)/cm^{-1} 3076w, 3032w, 2944s, 2867s, 1760s, 1734s, 1630m, 1495w, 1464m,

1419w, 1388w, 1368w, 1262m, 1132s, 1071m, 1029m, 995w, 884s; δ_H (400 MHz, $CDCl_3$) 0.97–1.12 (14 H, m, 2 × SiC*H*(CH_3)$_2$), 1.22 (3 H, t, *J* 7.2, OCH_2CH_3), 1.75 (2 H, dt, *J* 8.0, 1.2, $SiCH_2$), 4.08–4.21 (2 H, m, OCH_2CH_3), 4.85 (1 H, ddt, *J* 10.4, 2.0, 1.2, CH=CHH_E), 4.93 (1 H, ddt, *J* 16.8, 2.0, 1.2, CH=CHH_ZH), 5.32 (1 H, s, C*H*Ph), 5.82 (1 H, ddt, *J* 16.8, 10.4, 8.0, C*H*=CH_2), 7.26–7.34 (3 H, m, Ph), 7.47–7.49 (2 H, m, Ph); δ_C (100 MHz, $CDCl_3$) 12.5, 12.6, 14.0, 17.3, 17.4, 18.9, 61.0, 74.4, 114.1, 126.3, 128.0, 128.2, 134.0, 139.3, 172.0; *m*/*z* (CI^+) 335 (MH^+, 17%), 293 (100), 265 (13); Accurate mass (CI^+): Found 335.2036, $C_{19}H_{31}O_3Si$ (MH^+) requires 335.2042.

3-Methyl-2-[(prop-2-enyl)di(isopropyl)silanyloxy]butyronitrile (30)

To a stirred mixture of isobutyraldehyde (400 μL, 4.40 mmol), KCN (1.15 g, 17.6 mmol) and ZnI_2 (28.7 mg, 0.09 mmol) in anhydrous tetrahydrofuran (20 mL) was added chlorosilane **27** (1.01 g, 5.29 mmol). The reaction vessel was placed in an ultrasonic cleaning bath, sonicated for 1 h, then stirred at 25 °C for 50 h. Tetrahydrofuran was removed *in vacuo*, the crude residue triturated with ether and the extracts filtered through Celite®. The filtrate was washed successively with water (3 × 20 mL), saturated aqueous NaCl solution (50 mL), then dried (Na_2SO_4) and solvents removed *in vacuo* to furnish a pale yellow oil. Purification by flash column chromatography (19 : 1, petrol : ether) gave silylcyanohydrin **30** as a colourless oil (945 mg, 85%). R_f 0.83 (2 : 1, petrol : ether); ν_{max} (film)/cm^{-1} 3079w, 2964s, 2869s, 1631m, 1464m, 1390m, 1371w, 1249w, 1110s, 1066m, 994m, 883m, 826m, 804m, 752m; δ_H (400 MHz, $CDCl_3$) 1.00–1.20 (20 H, m, 2 × SiC*H*(CH_3)$_2$ and CH(CH_3)$_2$), 1.80 (2 H, dt, *J* 8.0, 1.2, $SiCH_2$), 1.99 (1 H, septd, *J* 6.8, 5.2, C*H*(CH_3)$_2$), 4.40 (1 H, d, *J* 5.2, C*H*CN), 4.92 (1 H, ddt, *J* 10.0, 2.0, 1.2 CH=CHH_E), 5.02 (1 H, ddt, *J* 16.8, 2.0, 1.2, CH=CH_ZH), 5.87 (1 H, ddt, *J* 16.8, 10.0, 8.0, C*H*=CH_2); δ_C (100 MHz, $CDCl_3$) 12.4, 16.9, 17.3, 17.5, 18.5, 34.1, 68.0, 114.7, 119.0, 133.4; *m*/*z* (CI^+) 271 (MNH_4^+, 20%), 254 (MH^+, 13), 229 (100), 212 (35), 202 (27), 185 (14); Accurate mass (CI^+): Found 271.2202, $C_{14}H_{31}N_2OSi$ (MNH_4^+) requires 271.2206.

3-Methyl-2-[(3-methylbut-2-enyl)di(isopropyl)silanyloxy]-butyronitrile (31)

A solution of silylcyanohydrin **30** (536 mg, 2.12 mmol) and Sudan Red 7B indicator (10 μL, 0.05% solution in dichloromethane) in anhydrous dichloromethane (40 mL) was cooled to −78 °C. Ozone was passed through the solution until the magenta colouration dispersed; excess ozone was purged from the system with argon. Dimethyl sulfide (186 μL, 2.54 mmol) was added and the reaction stirred at −78 °C for 30 min and then warmed to room temperature over 1 h. Meanwhile, to a suspension of isopropyl-triphenylphosphonium iodide (1.83 g, 4.23 mmol) in anhydrous tetrahydrofuran (16 mL) cooled to −45 °C was added BuLi (1.6 M in hexanes, 2.38 mL, 3.81 mmol). The blood red solution was stirred for 30 min at −45 °C then warmed to room temperature over 1 h. Both solutions were cooled to −45 °C and the ylide added *via* cannula to the solution of silylacetaldehyde. The solution was stirred at −45 °C for 30 min and then warmed to room temperature over 3 h. The mixture was partitioned between water (100 mL) and dichloromethane (50 mL). The aqueous phase was extracted with dichloromethane (3 × 25 mL), the combined organic layers were washed with saturated aqueous NaCl solution (2 × 50 mL), dried ($MgSO_4$) and solvents removed *in vacuo*. The crude residue was triturated with ether and petrol, the extracts filtered through Celite® and the solvents removed *in vacuo*. The resulting yellow oil was purified by flash column chromatography (petrol) to furnish silylcyanohydrin **31** as a colourless oil (213 mg, 36%). R_f 0.80 (2 : 1, petrol : ether); ν_{max} (film)/cm^{-1} 3052w, 2964s, 2893s, 2868s, 2240w, 1464s, 1388m, 1372m, 1351w, 1247w, 1224w, 1185m, 1161m, 1110s, 1061s, 997m, 958w, 920w, 883s, 827s, 800m, 746m, 724m; δ_H (500 MHz, $CDCl_3$) 0.98–1.15 (20 H, m, 2 × SiC*H*(CH_3)$_2$ and CH(CH_3)$_2$), 1.64 and 1.70 (2 × 3 H, 2 × s, =C(CH_3)$_2$), 1.65 (2 H, apparent d, apparent *J* 8.5, $SiCH_2$), 1.98 (1 H, septd, *J* 6.5, 5.0, C*H*(CH_3)$_2$), 4.35 (1 H, d, *J* 5.0, C*H*CN), 5.19 (1 H, br t, *J* 8.5, C*H*=C(CH_3)$_2$); δ_C (125 MHz, $CDCl_3$) 12.2, 12.4, 12.5, 16.8, 17.1, 17.5, 17.6, 25.7, 34.1, 67.9, 117.9, 118.9, 130.3; *m*/*z* (CI^+) 299 (MNH_4^+, 100%), 282 (MH^+, 36), 255 (42), 229 (80), 212 (47), 185 (28), 147 (25), 130 (35); Accurate mass (CI^+): Found 299.2518, $C_{16}H_{35}N_2OSi$ (MNH_4^+) requires 299.2519.

3-Methyl-2-[(3-methylbut-2-enyl)di(isopropyl)silanyloxy]-butyraldehyde (32)

To a stirred solution of silylcyanohydrin **31** (68.6 mg, 0.24 mmol) in anhydrous heptane (2 mL) cooled to −78 °C was added di(isobutyl)aluminium hydride (1.0 M in heptane, 268 μL, 0.27 mmol) dropwise and the solution stirred at −78 °C for 45 min. The mixture was diluted with ethyl acetate (1.2 mL), quenched by the addition of aqueous tartaric acid solution (60% w/v, 600 μL), warmed to room temperature, and partitioned between aqueous tartaric acid solution (30% w/v, 10 mL) and ethyl acetate (10 mL). The aqueous layer was extracted with ethyl acetate (2 × 15 mL) and the combined organic extracts washed with saturated aqueous NaCl solution (25 mL), dried (Na_2SO_4) and solvents removed *in vacuo*. The crude product was purified by flash column chromatography (49 : 1, petrol : ether) to furnish aldehyde **32** as a colourless oil (44.4 mg, 64%). R_f 0.83 (2 : 1, petrol : ether); ν_{max} (film)/cm^{-1} 2965s, 2944s, 2893s, 2868s, 1736s, 1464m, 1387w, 1246w, 1162w, 1099m, 1066m, 996w, 883m, 837w, 814w, 789w, 746m, 722m; δ_H (500 MHz, $CDCl_3$) 0.96 and 1.00 (2 × 3 H, 2 × d, *J* 7.0, CH(CH_3)$_2$), 1.03–1.07 (14 H, m, 2 × SiC*H*(CH_3)$_2$), 1.57 (2 H, br d, *J* 8.0, $SiCH_2$) 1.60 (3 H, apparent s) and 1.67 (3 H, d, *J* 1.5, =C(CH_3)$_2$), 2.02 (1 H, septd, *J* 7.0, 5.0, C*H*(CH_3)$_2$), 3.83 (1 H, dd, *J* 5.0, 2.5, C*H*CHO), 5.15 (1 H, tsept, *J* 8.0, 1.5, C*H*=C(CH_3)$_2$), 9.60 (1 H, d, *J* 2.5, C*H*O); δ_C (125 MHz, $CDCl_3$) 12.7, 12.8, 16.8, 17.4, 17.6, 18.1, 25.7, 32.4, 81.9, 118.5, 129.8, 205.1; *m*/*z* (CI^+) 285 (MH^+, 27%), 241 (30), 229 (35), 215 (76), 203 (95), 148 (100), 137 (17); Accurate mass (CI^+): Found 285.2256, $C_{16}H_{33}O_2Si$ (MH^+) requires 285.2250.

trans,*trans*-1,1,3-Tri(isopropyl)-2-oxa-5-(propen-2-yl)silinan-4-ol (33) and *trans*-3-(1,1-dimethylprop-2-enyl)-2,5-dioxa-1,1,4-tri(isopropyl)silolane (34)

To a stirred solution of aldehyde **32** (41.2 mg, 0.15 mmol) in anhydrous dichloromethane (1.5 mL) at room temperature was added dimethylaluminium chloride (1.0 M in hexanes, 131 μL, 0.13 mmol). After 30 min the reaction was quenched by the addition of saturated aqueous Na_2SO_4 solution (2.5 mL) and the mixture partitioned between water (5 mL) and ether (10 mL). The aqueous layer was extracted with ether (3 × 10 mL); the combined organic layers were washed with saturated aqueous NaCl solution (2 × 10 mL), dried (Na_2SO_4) and solvents removed *in vacuo*. The resulting oil was purified by flash column chromatography (18 : 1, petrol : ether) to furnish the ene product **33** as a colourless oil (15.4 mg, 37%) and the allyl transfer product **34** as a colourless oil (16 mg, 39%). Data for **33**: R_f 0.41 (9 : 1, petrol : ether); ν_{max} (film)/cm^{-1} 3554m, 2957s, 2866s, 1642w, 1464m, 1383w, 1246w, 1180w, 1152w, 1101w, 1044s, 882m, 841w, 794w, 747w; δ_H (400 MHz, $CDCl_3$) 0.72 (1 H, dd, *J* 14.8, 4.4, $SiCH_{eq}H$), 0.80 (1 H, dd, *J* 14.8, 13.2, $SiCH_{ax}H$), 0.88 and 0.99 (6 H, 2 × d, *J* 6.8, CH(CH_3)$_2$), 0.93–1.08 (14 H, m, 2 × SiC*H*(CH_3)$_2$), 1.61 (1 H, d, *J* 1.6, O*H*), 1.76 (3 H, br s, C(CH_3)=), 2.14 (1 H, septd, *J* 6.8, 1.6, C*H*(CH_3)$_2$), 2.43 (1 H, ddd, *J* 13.2, 10.4, 4.4, $SiCH_2CH$), 3.16 (1 H, ddd, *J* 10.4, 8.8, 1.6, C*H*(OH)), 3.48 (1 H, dd, *J* 8.8, 1.6, C*H*CH(CH_3)$_2$), 4.88 and 4.91 (2 × 1 H, 2 × br s, C(CH_3)=CH_2); δ_C (100 MHz, $CDCl_3$) 10.6, 12.0, 12.6, 14.0, 17.1, 17.2, 17.5, 17.6, 17.7, 20.0, 29.3, 50.6, 70.1, 81.1, 113.2, 148.3; *m*/*z* (CI^+) 302 (MNH_4^+, 4%),

285 (MH^+, 100), 267 (26), 241 (43), 215 (41), 213 (39), 203 (17), 173 (25), 169 (41), 148 (53), 137 (20), 121 (13), 104 (15), 81 (18); Accurate mass (CI^+): Found 285.2253, $C_{16}H_{33}O_2Si$ (MH^+) requires 285.2250. Data for **34**: R_f 0.76 (9 : 1, petrol : ether); ν_{max} (film)/cm^{-1} 2961s, 2869s, 1465m, 1385w, 1024s, 1006s, 916w, 884m, 844m; δ_H (400 MHz, $CDCl_3$; starred resonances form a strongly second order spectrum and the *apparent* shifts/multiplicities are given) 0.91 and 1.01 (2 × 3 H, 2 × d, *J* 6.8, $CH(CH_3)_2$), 0.90–1.16 (18 H, m, 2 × $SiCH(CH_3)_2$ and $C(CH_3)_2$), 1.53–1.65 (2 H, m, 2 × $SiCH(CH_3)_2$), 1.68 (1 H, septd, *J* 6.8, 3.2, $CH(CH_3)_2$), 3.56 (1 H, d, *J* 7.2, $CHC(CH_3)_2$), 3.63 (1 H, dd, *J* 7.2, 3.2, $CHCH(CH_3)_2$), 5.00* (1 H, dd, *J* 16.8, 1.6, $CH=CH_ZH$), 5.01* (1 H, s, $CH=CH_EH$), 5.88* (1 H, "dd", *J* 16.8, 10.8, $CH=CH_2$); δ_C (100 MHz, $CDCl_3$) 13.3, 15.6, 17.1, 17.3, 18.2, 20.9, 22.4, 24.6, 32.3, 40.9, 80.5, 83.5, 112.2, 144.9; *m*/*z* (CI^+) 285 (MH^+, 27%), 241 (31), 229 (33), 215 (84), 203 (100), 148 (92), 137 (16); Accurate mass (CI^+): Found 284.2176, $C_{16}H_{32}O_2Si$ (M^+) requires 284.2172.

(*S*)-Methyl *N*-(benzyloxycarbonyl)-*O*-[(3-methylbut-2-enyl)-diphenylsilanyl]isoserinate

To a stirred solution of silane **10** (1.42 g, 5.64 mmol) and methyl (*S*)-*N*-(benzyloxycarbonyl)isoserinate **35**[20] (1.43 g, 5.64 mmol) in anhydrous dichloromethane (6 mL) was added tris(pentafluorophenyl)borane (144 mg, 0.28 mmol) and the reaction mixture heated at reflux for 19 h. The solution was allowed to cool to room temperature and then partitioned between water (50 mL) and ether (50 mL); the aqueous layer was separated and extracted with ether (2 × 25 mL). The combined organic extracts were washed with saturated aqueous NaCl solution (50 mL), dried ($MgSO_4$) and solvents removed *in vacuo*. The resulting oil was purified by flash column chromatography (4 : 1, petrol : ether) to furnish the product as a colourless syrup (2.22 g, 78%). R_f 0.41 (1 : 1, petrol : ether); $[\alpha]_D^{22}$ −14.0 (*c* 1.03 in $CHCl_3$); ν_{max} (film)/cm^{-1} 3442m br, 3070m, 3049m, 3027m, 2953m, 2926m, 2855m, 1754s, 1727s, 1590w, 1515s, 1454m, 1429s, 1402w, 1376m, 1221s, 1120s, 997m, 839w, 817m, 735s, 700s; δ_H (400 MHz, $CDCl_3$) 1.39 and 1.62 (2 × 3 H, 2 × s, $=C(CH_3)_2$), 2.11 (2 H, d, *J* 8.0, $SiCH_2$), 3.54 (2 H, apparent t, apparent *J* 5.2, $NHCH_2$), 3.58 (3 H, s, CO_2CH_3), 4.37 (1 H, t, *J* 5.2, OC*H*), 5.08 (2 H, br s, CH_2Ph), 5.12 (1 H, t, *J* 5.2, N*H*), 5.19 (1 H, t, *J* 8.0, $CH=C(CH_3)_2$), 7.33–7.64 (15 H, m, Ph); δ_C (100 MHz, $CDCl_3$) 15.9, 17.6, 25.7, 44.8, 52.0, 66.8, 71.4, 116.8, 127.8, 127.9, 128.1, 130.1, 130.2, 131.8, 133.8, 134.9, 136.4, 156.2, 171.5; *m*/*z* (CI^+) 521 (MNH_4^+, 5%), 434 (11), 413 (52), 230 (13), 163 (100), 108 (21); Accurate mass (CI^+): Found 521.2467, $C_{29}H_{37}N_2O_5Si$ (MNH_4^+) requires 521.2472.

(*S*)-*N*-(Benzyloxycarbonyl)-*O*-[(3-methylbut-2-enyl)diphenylsilanyl]isoserinal (36)

To a stirred solution of the silyl isoserinate (1.11 g, 2.20 mmol) in anhydrous dichloromethane (22 mL) cooled to −78 °C was added di(isobutyl)aluminium hydride (1.0 M in dichloromethane, 3.30 mL, 3.30 mmol) dropwise and the solution stirred at −78 °C for 2 h. The reaction was quenched by the addition of a saturated solution of tartaric acid in methanol (5 mL). The mixture was warmed to room temperature and partitioned between aqueous tartaric acid solution (30% w/v, 40 mL) and ether (20 mL). The aqueous layer was extracted with ether (3 × 25 mL) and the combined organic extracts washed with saturated aqueous NaCl solution (50 mL), dried (Na_2SO_4) and solvents removed *in vacuo*. The crude product was purified by flash column chromatography (3 : 1, petrol : ether) to furnish aldehyde **36** as a colourless syrup (708 mg, 68%). R_f 0.30 (1 : 1, petrol : ether, [streaks]); $[\alpha]_D^{22}$ −1.00 (*c* 1.03 in $CHCl_3$); ν_{max} (film)/cm^{-1} 3442m, (br, NH), 3069w, 3049w, 2965m, 2925m, 1724s (C=O), 1590w, 1517m, 1454w, 1429m, 1377w, 1331w, 1258m, 1154m, 1119s, 998w, 817w, 734s, 700s; δ_H (500 MHz, $CDCl_3$) 1.39 and 1.64 (2 × 3 H, 2 × s, $=C(CH_3)_2$), 2.14 (2 H, d, *J* 8.0, $SiCH_2$), 3.46 and 3.57 (2 × 1 H, 2 × dt, *J* 14.0, 4.5, $NHCH_2$), 4.23 (1 H, t, *J* 4.5, OC*H*), 5.02 (1 H, br s, N*H*), 5.06 and 5.10 (2 × 1 H, 2 × d, *J* 12.2, CH_2Ph), 5.21 (1 H, t, *J* 8.0, $CH=C(CH_3)_2$), 7.32–7.64 (15 H, m, Ph), 9.58 (1 H, s, C*H*O); δ_C (125 MHz, $CDCl_3$) 15.8, 17.6, 25.6, 42.6, 66.8, 77.1, 116.6, 127.7, 127.9, 128.0, 128.1, 128.4, 130.3, 132.1, 133.4, 133.5, 134.1, 134.7, 136.2, 156.1, 201.1; *m*/*z* (CI^+) 474 (MH^+, 10%), 430 (13), 360 (36), 343 (31), 253 (48), 192 (100), 149 (17), 120 (98), 106 (11); Accurate mass (CI^+): Found 474.2102, $C_{28}H_{32}NO_4Si$ (MH^+) requires 474.2100.

(3*S*,4*R*,5*R*)-3-{[(Benzyloxycarbonyl)amino]methyl}-2-oxa-1,1-diphenyl-5-(propen-2-yl)silinan-4-ol (37)

To a stirred solution of aldehyde **36** (230 mg, 0.49 mmol) in anhydrous dichloromethane (5 mL) at room temperature was added dimethylaluminium chloride (1.0 M in hexanes, 540 µL, 0.54 mmol). After 30 min the reaction was quenched by the addition of saturated aqueous Na_2SO_4 solution (5 mL) and the mixture partitioned between water (10 mL) and ether (20 mL). The aqueous layer was extracted with ether (3 × 15 mL); the combined organic layers washed with saturated aqueous NaCl solution (40 mL), dried (Na_2SO_4) and solvents removed *in vacuo*. The resulting syrup was purified by flash column chromatography (3 : 1, petrol : ether) to furnish silacycle **37** as a colourless foam (118 mg, 52%). R_f 0.32 (1 : 1, petrol : ether [streaks]); $[\alpha]_D^{22}$ +7.0 (*c* 1.00 in $CHCl_3$); ν_{max} (film)/cm^{-1} 3427m br, 3069m, 2926m, 1703s, 1590w, 1518s, 1455m, 1429s, 1374w, 1261s, 1118s, 1070s, 1038m, 987m, 909w, 802w, 768w, 737s, 699s; δ_H (500 MHz, $CDCl_3$) 1.38 (1 H, t, *J* 15.0, $SiCH_{ax}H$), 1.43 (1 H, dd, *J* 15.0, 4.5, $SiCH_{eq}H$), 1.85 (3 H, s, $C(CH_3)=$), 2.67 (1 H, ddd, *J* 15.0, 11.5, 4.5, $SiCH_2CH$), 3.23 (1 H, br s, CH(O*H*)), 3.44 (1 H, apparent br t, apparent *J* 9.5, C*H*(OH)), 3.58 (1 H, ~dt, *J* 14.0, 4.5, NHC*H*H), 3.81 (1 H, ddd, *J* 14.0, 8.0, 4.5, NHCH*H*), 3.89 (1 H, ~td, *J* 8.0, 4.5, $NHCH_2CH$), 4.92 and 4.95 (2 × 1 H, 2 × br s, $C(CH_3)=CH_2$), 5.22 and 5.2 (2 × 1 H, 2 × d, *J* 12.0, CH_2Ph), 5.35 (1 H, t, *J* 4.5, N*H*), 7.41–7.76 (15 H, m, Ph); δ_C (100 MHz, $CDCl_3$) 15.4, 17.7, 44.6, 48.7, 67.0, 70.4, 77.3, 112.6, 127.8–136.6 (this region contains many overlapping resonances), 147.9, 157.6; *m*/*z* (CI^+) 474 (MH^+, 91%), 430 (59), 366 (36), 340 (49), 322 (23), 253 (30), 240 (100), 198 (23), 192 (62), 120 (75), 107 (31); Accurate mass (CI^+): Found 474.2101, $C_{28}H_{32}NO_4Si$ (MH^+) requires 474.2100.

(2*S*,3*R*,4*S*)-1-[(Benzyloxycarbonyl)amino]-4-hydroxymethyl-5-methylhex-5-ene-2,3-diol (38)

To a solution of crude oxasilinane **37** (prepared as above from 1.26 mmol of aldehyde **36**) in methanol (6.5 mL) and tetrahydrofuran (6.5 mL) was added KF (220 mg, 3.79 mmol), $KHCO_3$ (253 mg, 2.53 mmol) and H_2O_2 (35% in water, 620 µL, 6.32 mmol). The mixture was stirred for 16 h at room temperature, filtered through Celite® and the solvent removed *in vacuo*. The residue was triturated with ether (20 mL), the extracts filtered and the solvent removed *in vacuo*. The resulting material was purified by flash column chromatography (1 : 2, petrol : ether) to give aminotriol **38** as a colourless glassy solid (182 mg, 47%). The product was then recrystallised from methanol to furnish colourless needles. R_f 0.24 (ethyl acetate); mp 65–67 °C (from methanol); $[\alpha]_D^{22}$ +8.57 (*c* 1.02 in $CHCl_3$); ν_{max} (KBr)/cm^{-1} 3319s br, 3091w, 3067w, 3039w, 2954m, 2920m, 2887m, 1694s, 1642w, 1541s, 1462m, 1434w, 1326w, 1275s, 1238w, 1151m, 1103m, 1070m, 1046m, 1027m, 970m, 893m; δ_H (500 MHz, DMSO-d_6) 1.71 (3 H, s, $C(CH_3)=$), 2.42–2.51 (1 H, m, $CHC(CH_3)=$), 2.97 (1 H, dt, *J* 12.5, 6.0, NHC*H*H), 3.34–3.43 (2 H, m, CH_2CH(OH) and NHCH*H*), 3.46–3.58 (3 H, m, $CH_2CH(OH)CH$(OH) and CH_2OH), 4.36 (1 H, t, *J* 5.0, CH_2OH), 4.53 (1 H, d, *J* 5.5, $CH_2CH(OH)CH(OH)$), 4.55 (1 H, d, *J* 6.0, $CH_2CH(OH)$), 4.77 (2 H, br s, $C(CH_3)=CH_2$), 5.02 (2 H, s, CH_2Ph), 6.92 (1 H, t, *J* 6.0, N*H*), 7.30–7.37 (5 H, m, Ph); δ_C (125 MHz, DMSO-d_6) 23.4, 45.5, 50.5, 62.5,

66.1, 71.4, 72.2, 114.2, 128.6 (two peaks), 129.2, 138.1, 145.3, 157.4; *m*/*z* (CI^+) 310 (MH^+, 14%), 266 (39), 158 (100), 128 (18); Accurate mass (CI^+): Found 310.1658, $C_{16}H_{24}NO_5$ (MH^+) requires 310.1654.

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