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Stereoselective Synthesis of Silacyclohexanols by Silicon Tethered Type II Ene Cyclisation

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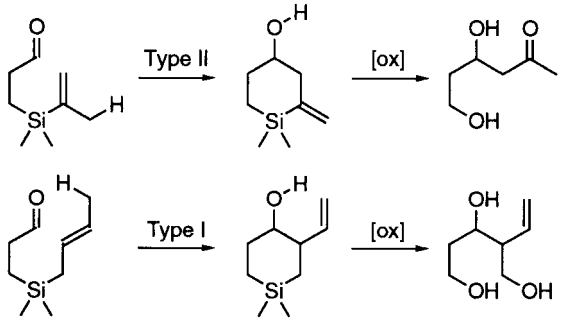
Abstract—Vinyl silane precursors for intramolecular ene reaction were prepared either by sequential organometallic substitution of appropriate silyl halides or by ring opening of oxasilacyclopentanes with 2-propenyllithium. The oxasilacyclopentane intermediates were prepared by free-radical cyclisation, intramolecular hydrosilylation, or intramolecular Diels–Alder reaction. Treatment of the ene precursors with methylaluminium dichloride resulted in the formation of silacyclohexanols with high stereoselectivity.

Introduction

The introduction in the mid 1980s of the temporary silicon connection, in the context of free-radical cyclisation[1] and hydrosilylation,[2] and of reliable procedures for the oxidative cleavage of C–Si bonds with retention of configuration,[3] has led to a proliferation of reports in which a silicon tether is used to confer the rate and selectivity advantages of intramolecularity to equivalent intermolecular processes.[4] Most commonly the tethered components are linked to the silicon atom through an oxygen or nitrogen atom giving rise to oxa- and azasilacyclic intermediates; less common are examples in which both interacting components are attached to silicon through carbon atoms.

In spite of the many examples of silicon tethered reactions that had already been documented by the time we initiated our own investigations in the area there were no reported cases of silicon tethered ene reactions.[5] We set out to explore the reactions of aldehyde enophiles which were expected to respond favourably to Lewis acid catalysis.[6] The site of attachment of the silicon tether to the ene component is open to variation so that both Type I and Type II[7] variants could be explored; coupled with oxidative cleavage of the C–Si bonds we envisaged that this method could constitute a novel stereoselective approach to polyhydroxylated molecules (Scheme 1). This paper provides full experimental details of our previously communicated[8] results that establish the methodology connected with the Type II variant. In the accompanying paper we describe the current status of our progress in identifying successful substrates for the Type I variant.



Scheme 1.

Keywords: cyclisation; ene reactions; silicon and compounds; silicon heterocycles.
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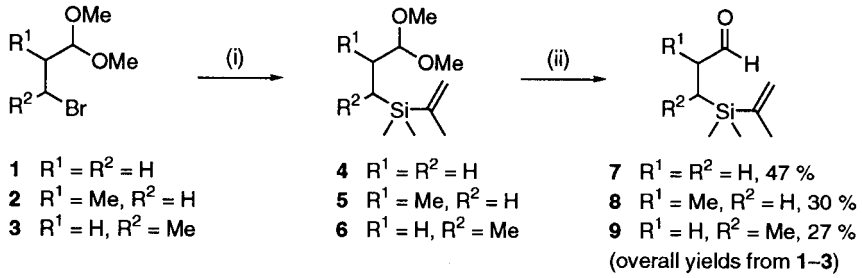


Scheme 2. *Reagents:* (i) Mg, THF then dimethyl(2-propenyl)silyl chloride; (ii) *p*-TsOH, aq. THF or HCl (aq., 1 M), acetone.

Results and Discussion

Synthesis of ene precursors

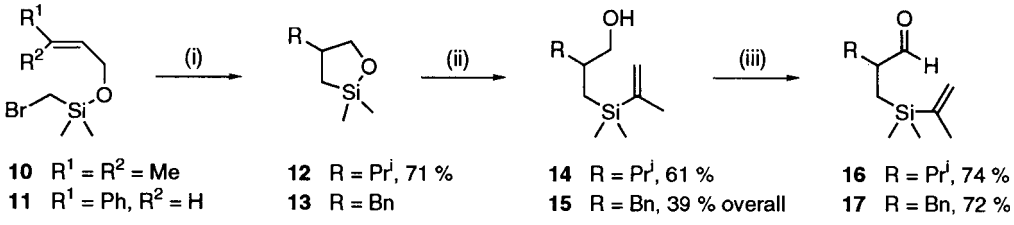
Our first route (Scheme 2) to suitable ene precursors involved displacement of chloride ion from chlorodimethyl(dimethylamino)silane[9] with 2-propenyllithium[10] followed by displacement with the Grignard reagents derived from known bromides **1**–**3**[11] after conversion of the dimethylamino substituent to chloride.[12] The so-formed acetals **4**–**6** were hydrolysed under standard conditions to give substrates **7**, **8**, and **9** in yields over the two steps of 47, 30, and 27%, respectively.

This route was effective in providing structurally simple substrates for testing purposes in only two synthetic steps but the overall yields were poor and it became clear that applications to structurally more complex molecules would be limited by the availability of appropriate organometallic nucleophiles required for the second displacement at silicon. A much more flexible approach was therefore required.

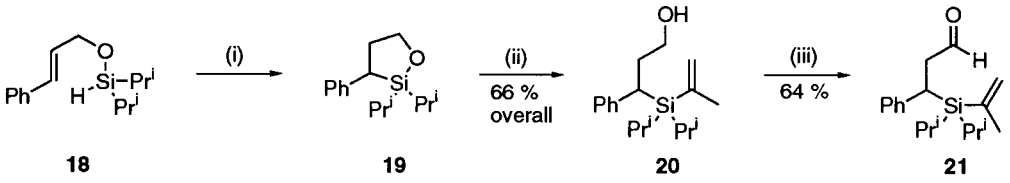
Many published silicon tethered processes afford oxasilacyclopentane derivatives, rather labile intermediates that are generally not isolated but characterised after either direct oxidation affording diols or ring-opening with methyllithium to form 3-trialkylsilylpropanol derivatives. We hoped that if this latter reaction could be routinely achieved with 2-propenyllithium (instead of methyllithium), and the product alcohols oxidised to the corresponding aldehydes, the synthesis of ene precursors would be greatly facilitated.

A survey of the literature revealed just a few examples of the ring-opening reaction of oxasilacyclopentanes with organometallic reagents other than methyllithium.[13] The most direct precedent, however, was found in the investigations of Corriu and co-workers who showed, during a study of the stereochemistry of substitution at silicon, that cyclic siloxanes were reactive to ring-opening with a diverse range of organometallics.[14] Our studies initiated with cyclic siloxanes prepared by 5-*exo*-trig free-radical cyclisation of precursors **10** and **11** (Scheme 3). The cyclisation of precursor **10** proceeded smoothly under standard conditions (tributyltin hydride, AIBN, benzene) but, on a small scale, removal of the solvent from the volatile product **12** proved to be troublesome. Fortunately, ether was an acceptable solvent for this reaction and a solvent-free sample of the oxasilacyclopentane **12** could be obtained after distillation at atmospheric pressure. Under these conditions the product was contaminated with the directly reduced material, 1-trimethylsilyloxy-3-methylbut-2-ene, which generally constituted ca. 15% of the product mixture. The cyclic siloxane **13** obtained from precursor **11**[1b] was much less volatile and could be obtained in a reasonably pure form, unaccompanied by the direct reduction product, after running the reaction in benzene. We were pleased to find that both oxasilacyclopentanes **12** and **13** were readily opened with 2-propenyllithium to generate alcohols **14** and **15** in yields of around 40% from precursors **10** and **11**; PDC oxidation gave the desired aldehydes **16** (74%) and **17** (72%).

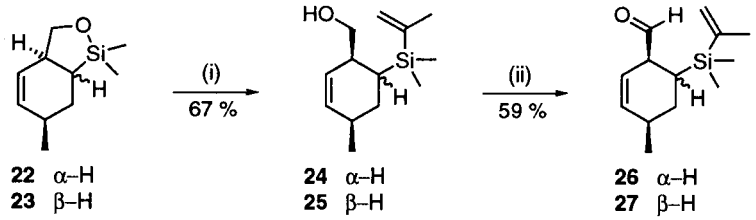
The free-radical route made available ene precursors bearing alkyl substitution α- to the aldehyde but, for substrates bearing β-substitution, intramolecular hydrosilylation of silylated allylic alcohols[2] became the method of choice (Scheme 4). In our hands dimethyl- or diphenylsilane derivatives of cinnamyl alcohol proved inconveniently labile, therefore the known diisopropylsilane derivative **18** was prepared.[15] This compound had been shown previously to cyclise in 50% yield to siloxane **19** using [Rh((*S*,*S*)-chiraphos)]$_2$(ClO$_4$)$_2$ (2 mol%) in acetone at 25°C for 48 h;[15] we found a convenient alternative procedure that employed Wilkinson's catalyst[16] [Rh(PPh$_3$)$_3$Cl, 0.2 mol%] in THF at reflux (3.5 h) to give siloxane **19** in essentially quantitative yield. This, in turn, was opened (66%) with 2-propenyllithium and the product **20** oxidised as before to give precursor **21** (64%).



Scheme 3. *Reagents:* (i) Bu_3SnH, AIBN, Et_2O or PhH; (ii) 2-propenyllithium, THF; (iii) PDC, MS4Å, CH_2Cl_2.



Scheme 4. *Reagents:* (i) $(Ph_3P)_3RhCl$ (0.2 mol%), MS4Å, THF; (ii) 2-propenyllithium, THF; (iii) PDC, MS4Å, CH_2Cl_2.



Scheme 5. *Reagents:* (i) 2-propenyllithium, THF; (ii) PDC, MS4Å, CH_2Cl_2.

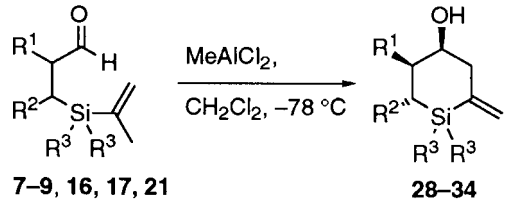
Finally we wished to consider sequences in which the oxasilacyclopentane intermediates were generated as part of a more complex conversion, an obvious example being a silicon tethered Diels–Alder reaction of a vinyl silane derivative of a dienyl alcohol.[17] In the published work, having performed the job of tethering the reaction, the silicon atom is either removed by oxidation or rendered inert by treatment with methyllithium. The idea of using the cyclic siloxane intermediates to allow subsequent carbon–carbon bond forming processes appealed to us as a way of maximising the synthetic value of silicon tethered reactions in general. Thus, in converting this proposal into practice, a mixture of Si-*endo*-(**22**) and Si-*exo*-(**23**) adducts, previously prepared by both Stork[17a] and Sieburth,[17b] and obtained by us in a 65:35 ratio (unseparated), was treated directly with 2-propenyllithium to give separable alcohols **24** and **25** in isolated yields (from the starting triene) of 40 and 27%, respectively (Scheme 5). The sequence was completed by oxidation to generate ene precursors **26** and **27** without complication.

Ene reactions

With eight ene precursors in hand, bearing alkyl substituents α- and/or β- to the aldehyde, a study of the stereochemical features of the cyclisation could be pursued and reasonable comparisons drawn with all-carbon analogues. Conditions for the ene reaction were optimised with the unsubstituted precursor **7**. Early results were disappointing with no signs of product formation at dry-ice/acetone temperatures either with dimethylaluminium chloride[18] or titanium(IV) chloride. Higher temperatures led to complex product mixtures. Fortunately, treatment of a DCM solution of substrate **7** with the more potent Lewis acid methylaluminium dichloride[19] (1.5 equiv., −78°C, 6–7 h) resulted in clean conversion to a single compound assigned as the silacyclohexanol **28** (80% isolated yield, Table 1). In comparison with the results of Andersen,[20] in which 4,4,5-trimethylhex-5-enal was shown to cyclise within 0.5 h at −72°C (diethylaluminium chloride), the reaction of the sila-analogue **7** is significantly slower. We speculate that the longer C–Si bonds[21] and the reduced ability for silicon to stabilise adjacent positive charge[22] in an asynchronous ene reaction[23] may be contributory factors.[8a]

These cyclisation conditions were found to be general; applied to the methyl analogues **8** and **9** the stereochemical aspects of the reaction were found to parallel those found by Snider for the all-carbon analogues 2,5- and 3,5-dimethylhex-5-enal.[24] Thus, in the α-methyl case (**8**) both diastereomers of the cyclised product were formed (13:1 *cis*:*trans*) which were separable by careful chromatography. Assignment of stereochemistry was based on the assumption that the major conformer of the *cis*-adduct would be that shown (B) in Fig. 1 wherein the substituent with the smaller *A*-value[25] occupies the axial site and the destabilising *syn*-pentane interaction (in A) is avoided. The C*H*OH resonance in the ^1H NMR spectrum appears at δ 3.77 ppm (ddd, J=4.4, 2.3, 1.9 Hz) for the *cis*-isomer **29** and at δ 3.16 ppm (td, J=10.1, 3.7 Hz) for the *trans*-isomer **30** which indicate, respectively, predominantly axial and equatorial hydroxyl groups. Under the same conditions β-methyl precursor **9** cyclised with a higher stereoselectivity with only resonances corresponding to the

Table 1.



Precursor	R^1	R^2	R^3	Product(s)	Yield/% (d.r.)
7	H	H	Me	**28**	80
8	Me	H	Me	**29, 30**	80 (13:1)
9	H	Me	Me	**31**	69
16	Pr^i	H	Me	**32**	84 (21:1)
17	Bn	H	Me	**33**	79
21	H	Ph	Pr^i	**34**	76

Figure 1.

trans-product **31** being visible in the ^{1}H NMR spectrum (500 MHz) of the crude material [δ 4.01 (ca. tt, J=5.9, 2.6 Hz C*H*OH)]. Similar trends were observed for the α-isopropyl (**16**) and α-benzyl (**17**) precursors which both cyclised with high *cis*-stereoselectivity (**32**, 21:1 and **33**, >98:<2, respectively). Finally, the β-phenyl precursor **21** also cyclised successfully, the isopropyl substituents not markedly affecting the reaction rate, and, as with β-methyl substrate **9**, only the *trans*-product **34** was observed. In each case stereochemical assignment was possible either by coupling constant analysis of the C*H*OH resonance or of the allylic CH_2 resonances which typically showed small (J=<6 Hz) vicinal couplings indicating an axial hydroxyl group in adducts **29** and **31**–**34**.

These stereochemical results may be rationalised by a transition state model in which both isomers are obtained through distorted chair conformations, the favoured conformation having the alkyl substituent equatorially disposed. The less favoured transition state conformer could be either chair-like with axial alkyl substituents[23,24] or the alkyl substituents could remain in equatorial sites but the C–CO and Si–C= bonds could rotate by approximately 180° with respect to the favoured conformer to give a boat-like conformation.[26] These possibilities are sketched in Fig. 2.

Applying these considerations to the ene cyclisation of the more complex precursors **26** and **27** led to the expectation that the *cis*-isomer **26** should cyclise to give silabicycle **35** through a conformation in which the cyclohexenyl methyl substituent is pseudo-equatorial in a favourable half-chair conformation with the forming ring adopting a chair-like arrangement (Scheme 6). A boat-like arrangement would be required in order to form the hydroxyl epimer if the alternative half-chair cyclohexene conformation, having an axial methyl group, may be ruled out. In the cyclisation of the *trans*-isomer **27** the conformational possibilities are more clearly defined and the silabicycle **36** was predicted. These predictions were confirmed experimentally with 88 and 48% yields of adducts **35** and **36** being obtained under the standard conditions.

Conclusions

We have developed the silicon tethered Type II ene cyclisation to the point where we have reliable methods for the preparation of precursors bearing substitution at either or both the linking carbon atoms and have shown that the ene cyclisations follow a predictable stereochemical course. With this methodology in hand we are in a position to address synthetic applications and will report on the development of this chemistry in due course.

Experimental

General

^{1}H and ^{13}C NMR spectra were recorded on Varian Gemini 200, Bruker AC 200, or Bruker AM 500 spectrometers with ^{1}H assignments being made on the basis of a combination of chemical shift, coupling constant, COSY, and NOE data as appropriate; ^{13}C assignments were supported by DEPT experiments. Coupling constants (J) are quoted to the nearest 0.1 Hz. Infrared spectra were recorded on either Perkin–Elmer 1750 or Perkin–Elmer Paragon 1000 FT spectrometers as thin films unless stated otherwise. Mass spectra were recorded on VG Micromass ZAB 1F, Masslab 20–250, VG Platform, or VG TRIO-1 spectrometers. Accurate mass data were obtained by the EPSRC National Mass Spectrometry Service Centre. All solvents and commercially available reagents were dried and purified according to standard procedures. 'Petrol' refers to the fraction of light petroleum ether boiling in the range 30–40°C. Bromoacetals **1**–**3** were prepared essentially according to the method of Ayers[11a] but with the inclusion of dicinnamalacetone as an indicator;[11b] Diels–Alder

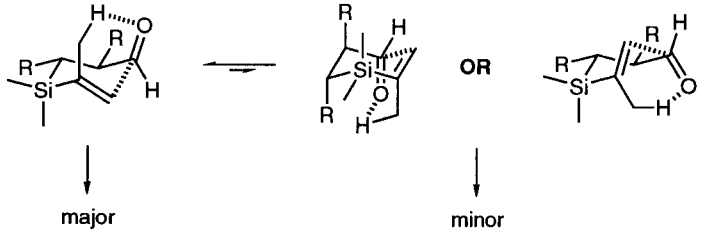
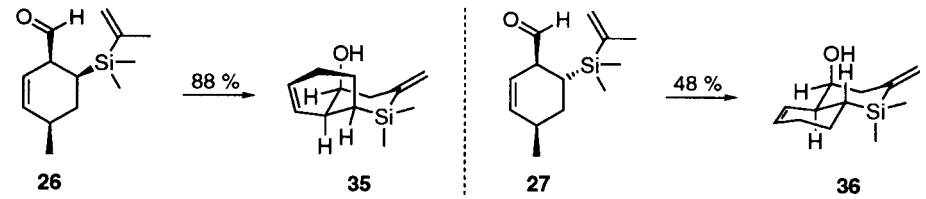


Figure 2.



Scheme 6. *Reagents:* $MeAlCl_2$, CH_2Cl_2 (allylic methyl group in products omitted for clarity).

adducts **22** and **23** were prepared by the method of Stork[17a] and Sieburth.[17b] All experiments involving air-sensitive reagents were performed under an argon atmosphere.

1,1-Dimethoxy-4,4,5-trimethyl-4-silahex-5-ene (4). To a warmed (35–40°C) suspension of Mg turnings (51 mg, 2.09 mmol) in THF (0.4 cm^3) was added dropwise a solution of bromoacetal **1**[11] (0.3 cm^3, 2.2 mmol) in THF (3 cm^3) and the mixture stirred for 1.75 h. To a cooled (−78°C) solution of *t*-butyllithium (2.7 cm^3 of a 1.7 M solution in pentane, 4.60 mmol) in THF (4 cm^3) was added dropwise 2-bromopropene (0.21 cm^3, 2.3 mmol). After 1 h chlorodimethyl(dimethylamino)silane (0.34 cm^3, 2.2 mmol) was added and the mixture stirred for 5 min at −78°C then at rt for 15 min. Acetyl chloride (0.16 cm^3, 2.2 mmol) was added dropwise and the mixture stirred for 1 h. The previously prepared Grignard reagent was added to the cooled (0°C) alkenylsilane mixture and stirred for 5 min at 0°C then at 35–40°C for 15 h. The mixture was added to a mixture of water (20 cm^3) and ether (5 cm^3) then 1 M hydrochloric acid was added dropwise until the emulsions had dispersed (ca. 0.5 cm^3). The aqueous layer was separated, extracted with ether (3×8 cm^3) and the combined organic portions were washed with brine (15 cm^3), dried (magnesium sulphate) and concentrated in vacuo. The resulting oil (which could also be carried onto the next step crude) was purified by column chromatography (34:1 petrol:ether) to yield *acetal* **4** as a colourless oil (218 mg, 52%). R_f 0.55 (3:1 petrol:ether); Accurate mass: Found 171.1205, $C_9H_{19}OSi$ (MH^+−MeOH) requires 171.12051; ν_{max}/cm^{-1} 2947s, 2829s, 1449w, 1249m, 1162m, 1125s, 1064s, 920m, 839s, 773m; δ_H (500 MHz; $CDCl_3$) 0.75 (6H, s, $SiMe_2$), 0.59–0.62 (2H, m, $SiCH_2$), 1.54–1.59 (2H, m, CH_2), 1.81 (3H, t, *J*=1.5 Hz, MeC═), 3.31 (6H, s, $HC(OMe)_2$), 4.28 (1H, t, *J*=5.7 Hz, $HC(OMe)_2$), 5.25 (1H, dq, *J*=3.3, 1.5 Hz) and 5.58 (1H, dq, *J*=3.3, 1.5 Hz, ═CH_2); δ_C (125 MHz; $CDCl_3$) −4.1, 8.9, 22.5, 26.7, 52.7, 106.3, 125.3, 146.6; *m/z* (CI) 171 (MH^+−MeOH, 15%), 156 (5), 129 (10), 106 (20), 89 (30), 75 (100).

1,1-Dimethoxy-2,4,4,5-tetramethyl-4-silahex-5-ene (5). To a cooled (−78°C) solution of *t*-butyllithium (6.3 cm^3 of a 1.7 M solution in pentane, 10.7 mmol) in THF (9 cm^3) was added dropwise 2-bromopropene (0.48 cm^3, 5.33 mmol). After 1 h chlorodimethyl(dimethylamino)silane (0.78 cm^3, 5.07 mmol) was added and the mixture stirred for 5 min at −78°C and at rt for 30 min. Acetyl chloride (0.36 cm^3, 5.07 mmol) was added dropwise and the mixture stirred for 1 h. To a suspension of powdered Mg (1.6 g, 66 mmol) in THF (8 cm^3) at rt was added dropwise 1,2-dibromoethane (0.57 cm^3, 6.6 mmol) and the mixture stirred for 30 min. A solution of bromoacetal **2** (4.3 g, 21.8 mmol) in THF (5 cm^3) was added dropwise and the mixture stirred for 1 h after which time the chlorosilane solution was added by cannula to the Grignard solution at rt. The mixture was stirred at rt for 2 h and at 35–40°C for 15 h. The mixture was added to a mixture of 1 M hydrochloric acid (50 cm^3) and ether (15 cm^3), separated and the aqueous layer extracted with ether (3×20 cm^3). The combined organic portions were washed with brine (20 cm^3), dried (magnesium sulphate) and concentrated in vacuo and the resulting oil carried onto the next step crude. An analytical sample was obtained by column chromatography (44:1 petrol:ether) to yield *acetal* **5** as a colourless oil. R_f 0.61 (3:1 petrol:ether); Accurate mass: Found 185.1362, $C_{10}H_{21}OSi$ (MH^+−MeOH) requires 185.13616; ν_{max}/cm^{-1} 2955s, 2911s, 1449m, 1249m, 1122s, 1107s, 1079s, 1059s, 920m, 834s; δ_H (500 MHz; $CDCl_3$) 0.10 and 0.11 (2×3H, 2×s, $SiMe_2$), 0.42 (1H, dd, *J*=15.0, 10.6 Hz) and 0.90 (1H, dd, *J*=15.0, 7.5 Hz, $SiCH_2$), 0.92 (3H, d, *J*=6.8 Hz, *Me*CH), 1.82–1.88 (1H, m, MeC*H*), 1.83 (3H, t, *J*=1.4 Hz, MeC═), 3.34 and 3.35 (2×3H, 2×s, $HC(OMe)_2$), 3.90 (1H, d, *J*=6.1 Hz, $HC(OMe)_2$), 5.26 (1H, dq, *J*=3.3, 1.4 Hz) and 5.57 (1H, dq, *J*=3.3, 1.4 Hz, ═CH_2); δ_C (125 MHz; $CDCl_3$) −3.0, −2.8, 16.9, 17.2, 22.5, 32.3, 54.1, 54.2, 110.4, 125.0, 147.5; *m/z* (CI) 185 (MH^+−MeOH, 10%), 169 (5), 153 (5), 143 (5), 106 (25), 89 (30), 75 (100).

1,1-Dimethoxy-3,4,4,5-tetramethyl-4-silahex-5-ene (6). To a cooled (−78°C) solution of *t*-butyllithium (1.3 cm^3 of a 1.7 M solution in pentane, 2.26 mmol) in THF (3 cm^3) was added dropwise 2-bromopropene (0.1 cm^3, 1.13 mmol). After 1 h chlorodimethyl(dimethylamino)silane (0.17 cm^3, 1.08 mmol) was added and the mixture stirred for 5 min at −78°C and at rt for 25 min. Acetyl chloride (77 μL, 1.08 mmol) was added dropwise and the mixture stirred for 1.25 h. To a suspension of powdered Mg (87 mg, 3.56 mmol) in THF (1 cm^3) at rt was added dropwise 1,2-dibromoethane (28 μL, 0.32 mmol) and the mixture stirred for 50 min. A solution of acetal **3** (0.5 cm^3, 3.24 mmol) in THF (2 cm^3) was added dropwise and the mixture stirred for 2.5 h after which time the chlorosilane solution was added by cannula to the Grignard solution at rt then stirred for 15 h. The reaction mixture was added to a mixture of 1 M hydrochloric acid (15 cm^3) and ether (10 cm^3), extracted with ether (3×10 cm^3) and the combined organic portions washed with brine (20 cm^3), dried (magnesium sulphate) and concentrated in vacuo. The resulting oil was purified by column chromatography (39:1 petrol:ether) to yield *acetal* **6** as a colourless oil (69 mg, 30%). R_f 0.46 (3:1 petrol:ether); Accurate mass: Found 185.1362, $C_{10}H_{21}OSi$ (MH^+−MeOH) requires 185.13616; ν_{max}/cm^{-1} 2952s, 1450m, 1376m, 1250m, 1196m, 1124s, 1079m, 1055s, 961m, 921m, 834s, 816s, 770m; δ_H (500 MHz; $CDCl_3$) 0.06 (6H, s, $SiMe_2$), 0.89–0.94 (1H, m, MeC*H*), 0.97 (3H, d, *J*=6.9 Hz, *Me*CH), 1.32 (1H, ddd, *J*=14.3, 10.8, 4.1 Hz) and 1.74–1.79 (1H, ddd, *J*=14.3, 7.7, 3.3 Hz, CH_2), 1.82 (3H, t, *J*=1.5 Hz, MeC═), 3.29 and 3.33 (2×3H, 2×s, $HC(OMe)_2$), 4.50 (1H, dd, *J*=7.7, 4.1 Hz, $HC(OMe)_2$), 5.26 (1H, dq, *J*=3.3, 1.5 Hz) and 5.62 (1H, dq, *J*=3.3, 1.5 Hz, ═CH_2); δ_C (125 MHz; $CDCl_3$) −5.9, −5.7, 13.7, 14.1, 23.0, 34.0, 51.6, 53.3, 103.4, 126.0, 145.8; *m/z* (CI) 202 (MNH_4^+−MeOH, 5%), 185 (40), 169 (15), 153 (15), 143 (30), 125 (10), 106 (35), 95 (15), 89 (50), 86 (20), 81 (20), 75 (100).

4,4,5-Trimethyl-4-silahex-5-enal (7). A mixture of crude acetal **4** (1.13 g, 5.59 mmol), isopropanol (1 cm^3), water (5 cm^3) and PTSA (105 mg, 0.55 mmol) in THF (12 cm^3) was heated at reflux for 1.5 h. The reaction mixture was added to a mixture of water (10 cm^3), saturated sodium hydrogen carbonate solution (10 cm^3) and ether (10 cm^3) and the separated aqueous layer was extracted with ether

(3×10 cm^3). The combined organic portions were washed with brine (10 cm^3), dried (magnesium sulphate) and concentrated in vacuo. The resulting oil was purified by column chromatography (39:1 petrol:ether) to yield *aldehyde* **7** as a colourless oil (410 mg, 47% based on Mg). R_f 0.49 (3:1 petrol:ether); Accurate mass: Found 174.1314, $C_8H_{20}NOSi$ (MNH_4^+) requires 174.13141; ν_{max}/cm^{-1} 3048w, 2955m, 2901m, 2811m, 2716w, 1726s, 1449m, 1413m, 1251m, 1178m, 1035w, 938m, 923m, 880m, 838s, 690w, 675w, 624w; δ_H (500 MHz; $CDCl_3$) 0.10 (6H, s, $SiMe_2$), 0.83–0.87 (2H, m, $SiCH_2$), 1.81 (3H, t, J=1.5 Hz, MeC=), 2.35–2.39 (2H, m, CH_2), 5.26 (1H, dq, J=3.1, 1.5 Hz) and 5.62 (1H, dq, J=3.1, 1.5 Hz, $=CH_2$), 9.75 (1H, t, J=1.8 Hz, CHO); δ_C (125 MHz; $CDCl_3$) −4.2, 6.2, 22.4, 38.3, 125.9, 145.8, 202.9; *m/z* (CI) 174 (MNH_4^+, 15%), 157 (MH^+, 10), 141 (55), 115 (100), 99 (25), 90 (25), 76 (40), 74 (40), 73 (35), 59 (25).

2,4,4,5-Tetramethyl-4-silahex-5-enal (8). A mixture of crude acetal **5** (1.1 g, 5.09 mmol) and 1 M hydrochloric acid (7.6 cm^3) in acetone (10 cm^3) was stirred at rt for 2 h. The reaction mixture was added to saturated sodium hydrogen carbonate solution (40 cm^3) and extracted with ether (3×20 cm^3). The combined organic portions were washed with brine (25 cm^3), dried (magnesium sulphate) and concentrated in vacuo. The resulting oil was purified by column chromatography (49:1 petrol:ether) to yield *aldehyde* **8** as a colourless oil (260 mg, 30% from chlorodimethyl(dimethylamino)silane). R_f 0.61 (3:1 petrol:ether); Accurate mass: Found 171.1205, $C_9H_{19}OSi$ (MH^+) requires 171.12051; ν_{max}/cm^{-1} 2958s, 1727s, 1450m, 1257m, 1058m, 923m, 836s; δ_H (500 MHz; $CDCl_3$) 0.13 (6H, s, $SiMe_2$), 0.57 (1H, dd, J=14.9, 8.9 Hz) and 1.06 (1H, dd, J=14.9, 5.4 Hz, $SiCH_2$), 1.11 (3H, d, J=7.0 Hz, *Me*CH), 1.82 (3H, t, J=1.5 Hz, MeC=), 2.35–2.40 (1H, m, MeC*H*), 5.28 (1H, dq, J=3.3, 1.5 Hz) and 5.61 (1H, dq, J=3.3, 1.5 Hz, $=CH_2$), 9.55 (1H, d, J=1.8 Hz, C*H*O); δ_C (125 MHz; $CDCl_3$) −3.1, 15.6, 16.1, 22.4, 42.5, 125.9, 146.3, 204.7; *m/z* (CI) 188 (MNH_4^+, 10%), 171 (MH^+, 15), 155 (30), 129 (100), 116 (20), 99 (15), 95 (20), 91 (20), 74 (30), 58 (30).

3,4,4,5-Tetramethyl-4-silahex-5-enal (9). A mixture of pure acetal **6** (34 mg, 0.16 mmol) and 1 M hydrochloric acid (0.24 cm^3) in acetone (1 cm^3) was stirred at rt for 2.5 h. The mixture was added to saturated sodium hydrogen carbonate solution (10 cm^3) and extracted with ether (3×5 cm^3). The combined organic portions were washed with brine (10 cm^3), dried (magnesium sulphate) and concentrated in vacuo. The resulting oil was purified by column chromatography (44:1 petrol:ether) to yield *aldehyde* **9** as a colourless oil (24 mg, 89%). R_f 0.45 (3:1 petrol:ether); Accurate mass: Found 171.1205, $C_9H_{19}OSi$ (MH^+) requires 171.12051; ν_{max}/cm^{-1} 3049w, 2957s, 2710m, 1728s, 1451m, 1412w, 1254s, 1059m, 938m, 924m, 835s, 817s, 775m, 688w; δ_H (500 MHz; $CDCl_3$) 0.08 and 0.09 (2×3H, 2×s, $SiMe_2$), 0.98 (3H, d, J=7.4 Hz, *Me*CH), 1.34–1.42 (1H, m, MeC*H*), 1.82 (3H, t, J=1.5 Hz, MeC=), 2.16 (1H, ddd, J=16.3, 10.9, 3.3 Hz) and 2.44 (1H, ddd, J=16.3, 3.6, 1.1 Hz, CH_2), 5.27 (1H, dq, J=3.2, 1.5 Hz) and 5.65 (1H, dq, J=3.2, 1.5 Hz, $=CH_2$), 9.73 (1H, dd, J=3.3, 1.1 Hz, C*H*O); δ_C (125 MHz; $CDCl_3$) −5.9, −5.7, 12.7, 14.5, 22.9, 46.0, 126.7, 145.0, 203.0; *m/z* (CI) 171 (MH^+, 90%), 155 (35), 148 (50), 129 (100), 116 (55), 99 (35), 95 (75), 91 (65), 85 (65), 74 (45), 58 (25).

1-(Bromomethyl)dimethylsilyloxy-3-methylbut-2-ene (10). To a cooled (0°C) solution of DMAP (61 mg, 0.5 mmol), triethylamine (1.3 cm^3, 9 mmol), and (bromomethyl)chlorodimethylsilane (1.2 cm^3, 9 mmol) in DCM (12 cm^3) was added dropwise 3-methyl-2-butenol (1.0 cm^3, 10 mmol). The mixture was allowed to warm up to rt then stirred for 18 h. The solvent was removed in vacuo and the resultant paste triturated with petrol (4×10 cm^3) then the combined extracts were filtered through Celite®. The solvent was removed in vacuo and the residual oil purified by distillation (Kugelrohr, bath temperature 50°C, 2 mm Hg) to give *silane* **10** as a colourless oil (1.69 g, 80%). R_f 0.71 (1:1 petrol:ether); Accurate mass: Found 254.0576, $C_8H_{21}BrNOSi$ (MNH_4^+) requires 254.05762; ν_{max}/cm^{-1} 2970m, 2933m, 1676w, 1447w, 1382w, 1254m, 1120m, 1067s, 838s; δ_H (500 MHz; $CDCl_3$) 0.28 (6H, s, $SiMe_2$), 1.67 and 1.74 (2×3H, 2×s, Me_2C=), 2.49 (2H, s, CH_2Br), 4.21 (2H, d, J=6.9 Hz, CH_2O), 5.33 (1H, ca. tsept, J=6.9, 1.4 Hz, =C*H*); δ_C (125 MHz; $CDCl_3$) −3.1, 16.1, 17.9, 25.8, 60.1, 123.3, 135.5; *m/z* (CI) 256 ($M(^{81}Br)NH_4^+$, 5%), 254 ($M(^{79}Br)NH_4^+$, 5), 223 (32), 221 (30), 170 (19), 168 (17), 92 (21), 86 (100), 69 (11).

(*E*)-1-(Bromomethyl)dimethylsilyloxy-3-phenylprop-2-ene (11).[1b] To a cooled (0°C) solution of DMAP (61 mg, 0.5 mmol), triethylamine (1.3 cm^3, 9 mmol), and (bromomethyl)chlorodimethylsilane (1.3 cm^3, 9 mmol) in DCM (12 cm^3) was added dropwise a solution of cinnamyl alcohol (1.34 g, 10 mmol) in DCM (2 cm^3). The mixture was allowed to warm to rt and stirred for 18 h. The solvent was removed in vacuo and the resultant paste triturated with petrol (4×10 cm^3). The extracts were combined and filtered through Celite® then concentrated in vacuo and the residual oil distilled (Kugelrohr, bath temperature 170°C, 2 mm Hg) to give silyl ether **11**[1b] as a colourless oil (2.21 g, 86%). R_f 0.69 (1:1 petrol:ether); ν_{max}/cm^{-1} 3083w, 3060m, 3027m, 2961m, 2936m, 2859m, 1599w, 1495m, 1450m, 1380m, 1255s, 1116s, 1059s, 966s, 840s, 733s, 692s; δ_H (200 MHz; $CDCl_3$) 0.32 (6H, s, Me_2Si), 2.52 (2H, s, CH_2Br), 4.40 (2H, dd, J=5.5 Hz, 1.5 Hz, CH_2O). 6.29 (1H, dt, J=16.0, 5.5 Hz, PhCH=C*H*), 6.60 (1H, dt, J=16.0, 1.5 Hz, PhC*H*=CH), 7.24–7.41 (5H, m, Ph); *m/z* (CI) 286 (3%), 284 (3), 134 (26), 117 (100).

1,1-Dimethyl-4-isopropyl-2-oxa-1-silacyclopentane (12). To a solution of silyl allyl ether **10** (1.19 g, 5 mmol) and AIBN (82 mg, 0.5 mmol) in degassed ether (120 cm^3) heated at reflux was added a solution of tributyltin hydride (2.0 cm^3, 7.5 mmol) and AIBN (82 mg, 0.5 mmol) in ether (18 cm^3) over a period of 48 h (syringe pump). Heating was maintained for a further 2 h then the ether was removed by distillation at atmospheric pressure. The residue was distilled (Kugelrohr, bath temperature 150°C, 220 mm Hg) to give an oil (560 mg, 71%) consisting of the hydrolytically labile *oxasilacyclopentane* **12** and the direct reduction product, 3-methyl-1-(trimethylsilyloxy)but-2-ene, in a ratio of 6.6:1. Data for **12**: δ_H (200 MHz; $CDCl_3$) 0.18 and 0.24 (2×3H, 2×s, $SiMe_2$), 0.36 (1H, dd, J=14.0, 11.5 Hz) and 0.90–1.05 (1H, m, CH_2Si), 0.88 and 0.95 (2×3H, 2×d, J=6.5 Hz, Me_2C), 1.42 (1H, apparent oct,

J=6.5 Hz, Me_2CH), 1.66–1.89 (1H, m, Pr^iCH), 3.36 (1H, dd, J=10.0, 8.5 Hz) and 4.08 (1H, dd, J=10.0, 6.5 Hz, CH_2O); m/z (CI) 159 (MH^+, 100%), 141 (32).

5-Hydroxymethyl-2,3,3,6-tetramethyl-3-silahept-1-ene (14). To a cooled (−78°C) solution of *t*-butyllithium (4.8 cm^3 of a 1.7 M solution in pentane, 8.16 mmol) in THF (6.5 cm^3) was added dropwise 2-bromopropene (0.36 cm^3, 4.1 mmol) and the mixture was stirred for 1 h. A solution of impure oxasilacyclopentane **12** (308 mg, 1.95 mmol) in THF (3 cm^3) was added dropwise; the mixture was stirred for 3 h at −78°C then allowed to warm up to rt and stirred for a further 2.5 h. Water (20 cm^3) was added and the product extracted with ether (3×20 cm^3). The combined organic portions were washed with brine (20 cm^3) then dried (magnesium sulphate) and the solvent removed in vacuo. The yellow oil was purified by column chromatography (8:1 petrol:ether) to afford the *alcohol* **14** as a colourless oil (190 mg, 61% based on the purity of **12**). R_f 0.47 (1:1 petrol:ether); Accurate mass: Found 159.1202, $C_8H_{19}OSi$ (MH^+−propene) requires 159.12051; Found: C, 65.64; H, 12.51; $C_{11}H_{24}OSi$ requires C, 65.93; H, 12.07%; ν_{max}/cm^{-1} 3334m, 3048m, 2956s, 1466m, 1447m, 1386m, 1368m, 1248s, 1045s, 920s, 836s; δ_H (500 MHz; $CDCl_3$) 0.10 and 0.11 (2×3H, 2×s, $SiMe_2$), 0.43 (1H, dd, J=15.0, 9.3 Hz) and 0.60 (1H, dd, J=15.0, 4.1 Hz, CH_2Si), 0.85 and 0.88 (2×3H, 2×d, J=6.9 Hz, Me_2C), 1.34 (1H, br s, OH), 1.51–1.57 (1H, m, Pr^iCH), 1.83 (3H, t, J=1.5 Hz, MeC=), 1.85 (1H, septd, J=6.9, 4.0 Hz, Me_2CH), 3.47 (1H, dd, J=10.9, 4 Hz) and 3.50 (1H, dd, J=10.9, 4.9 Hz, CH_2OH), 5.27 (1H, dq, J=3.3, 1.5 Hz) and 5.59 (1H, dq, J=3.3, 1.5 Hz, $=CH_2$); δ_C (125 MHz; $CDCl_3$) −3.2, −3.0, 12.0, 17.9, 19.7, 22.6, 29.2, 42.6, 65.4, 125.3, 147.5; m/z (CI) 218 (MNH_4^+, 9%), 201 (MH^+, 9), 185 (15), 176 (11), 159 (100), 141 (15), 118 (54), 101 (56), 99 (60), 92 (72), 75 (86), 59 (31).

2-Benzyl-4,4,5-trimethyl-4-silahex-5-en-1-ol (15). To a solution of silyl ether **11** (1.0 g, 3.51 mmol) and AIBN (29 mg, 0.18 mmol) in degassed benzene (65 cm^3) heated at reflux was added a solution of tributyltin hydride (1.42 cm^3, 5.26 mmol) and AIBN (29 mg, 0.18 mmol) in benzene (5 cm^3) over 2 h (syringe pump). Heating was maintained for a further 2.5 h then the solvent was removed in vacuo to give a pale brown oil that was distilled (Kugelrohr, bath temperature 150°C, 20 mm Hg) to give the hydrolytically labile *oxasilacyclopentane* **13** as a colourless oil (1.16 g, impure) that was used directly in the next reaction. δ_H (200 MHz; $CDCl_3$) 0.16 and 0.25 (2×3H, 2×s, Me_2Si), 0.47 (1H, dd, J=14.5, 10.2 Hz, C*H*HSi; second CH*H*Si proton obscured by tin residues), 2.25–2.42 (1H, m, BnC*H*), 2.57 (1H, dd, J=13.3, 7.5 Hz) and 2.70 (1H, dd, J=13.3, 7.0 Hz, PhCH_2), 3.46 (1H, apparent t, J=9.3 Hz) and 3.95 (1H, dd, J=9.3, 6.0 Hz, CH_2O), 7.12–7.37 (5H, m, Ph). 2-Bromopropene (0.45 cm^3, 5.09 mmol) was added dropwise to a cooled (−78°C) solution of *t*-butyllithium (6 cm^3 of a 1.7 M solution in pentane, 10.2 mmol) in THF (8 cm^3) and the mixture was stirred for 1 h. A solution of the impure oxasilacyclopentane **13** (500 mg) in THF (1 cm^3) was added dropwise and the mixture allowed to warm to rt over 16 h. Water (20 cm^3) was added and the product extracted with ether (3×20 cm^3). The combined organic portions were washed with brine (25 cm^3) then dried (magnesium sulphate) and the solvent removed in vacuo. Purification by column chromatography (9:1 petrol:ether) afforded the *alcohol* **15** as a colourless oil (148 mg, 39% based on silyl ether **11**). R_f 0.44 (1:1 petrol:ether); Accurate mass: found 266.1944, $C_{15}H_{28}NOSi$ (MNH_4^+) requires 266.19401; ν_{max}/cm^{-1} 3350s, 3085m, 3047m, 3027m, 2952s, 1604m, 1496s, 1453s, 1248s, 1051s, 1030s, 920s, 835s, 787s, 700s; δ_H (500 MHz; $CDCl_3$) 0.13 and 0.14 (2×3H, 2×s, Me_2Si), 0.68 (1H, dd, J=14.9, 6.5 Hz) and 0.74 (1H, dd, J=14.9, 7.2 Hz, CH_2Si), 1.38 (1H, br s, OH), 1.83 (3H, t, J=1.4 Hz, MeC=), 1.95–1.98 (1H, m, BnC*H*), 2.64 (1H, dd, J=13.5, 6.3 Hz) and 2.70 (1H, dd, J=13.5, 8.0 Hz, PhCH_2), 3.46–3.48 (2H, m, CH_2OH), 5.31 (1H, dq, J=3.2, 1.4 Hz) and 5.62 (1H, dq, J=3.2, 1.4 Hz, $=CH_2$), 7.19–7.23 (3H, m) and 7.28–7.32 (2H, m, Ph); δ_C (125 MHz; $CDCl_3$) −3.1, −2.9, 16.5, 22.5, 39.2, 40.6, 66.8, 125.4, 125.9, 128.3, 129.2, 140.7, 147.3; m/z (CI) 266 (MNH_4^+, 100%), 207 (58), 189 (28), 116 (57), 91 (69), 74 (42).

5-Formyl-2,3,3,6-tetramethyl-3-silahept-1-ene (16). To a cooled mixture of alcohol **14** (290 mg, 1.45 mmol) and 4 Å molecular sieves (1.45 g) in DCM (7 cm^3) was added PDC (817 mg, 2.17 mmol). The mixture was allowed to warm to rt and stirring continued for 16 h. After dilution with ether (15 cm^3) the mixture was filtered through Celite®, washing through with ether (2×20 cm^3), and the filtrate concentrated in vacuo. Purification by column chromatography (8:1 petrol:ether) afforded the *aldehyde* **16** as a colourless oil (213 mg, 74%). R_f 0.71 (1:1 petrol:ether); Accurate mass: Found 199.1518, $C_{11}H_{23}OSi$ (MH^+) requires 199.15181; ν_{max}/cm^{-1} 3049w, 2960s, 2875m, 1727s, 1464w, 1370w, 1250m, 922m, 838s; δ_H (500 MHz; $CDCl_3$) 0.07 and 0.08 (2×3H, 2×s, Me_2Si), 0.65 (1H, dd, J=14.9, 3.1 Hz) and 0.96 (1H, dd, J=14.9, 10.1 Hz, CH_2Si), 0.92 and 0.96 (2×3H, 2×d, J=6.8 Hz, Me_2C), 1.81 (3H, t, J=1.5 Hz, MeC=), 2.00 (1H, septd, J=6.8, 5.0 Hz, Me_2CH), 2.22 (1H, apparent ddt, J=10.1, 5.0, 3.1 Hz, C*H*CHO), 5.25 (1H, dq, J=3.2, 1.5 Hz) and 5.59 (1H, dq, J=3.2, 1.5 Hz, $=CH_2$), 9.60 (1H, d, J=3.1 Hz, CHO); δ_C (125 MHz; $CDCl_3$) −3.5, −3.2, 9.7, 19.0, 19.8, 22.4, 30.2, 53.9, 125.8, 146.4, 205.2; m/z (CI) 216 (MNH_4^+, 100%), 199 (MH^+, 17), 198 (23), 183 (80), 157 (100), 141 (21), 116 (78), 99 (94), 91 (41), 74 (46), 59 (28).

2-Benzyl-4,4,5-trimethyl-4-silahex-5-enal (17). To a cooled (0°C) mixture of alcohol **15** (178 mg, 0.72 mmol) and 4 Å molecular sieves (720 mg) in DCM (5 cm^3) was added PDC (403 mg, 1.07 mmol); the mixture was allowed to warm to rt then stirring was continued for 16 h. Ether (10 cm^3) was added, the mixture filtered through Celite®, washing through with ether (2×10 cm^3), and the combined filtrate concentrated in vacuo to give a brown-orange oil. Purification by column chromatography afforded *aldehyde* **17** as a colourless oil (128 mg, 72%). R_f 0.66 (1:1 petrol:ether); Accurate mass: Found 264.1784, $C_{15}H_{26}NOSi$ (MNH_4^+) requires 264.17836; ν_{max}/cm^{-1} 3029m, 2954s, 2716m, 1728s, 1604m, 1497m, 1455s, 1413m, 1250s, 938m, 923m, 836s, 746m, 700s; δ_H (500 MHz; $CDCl_3$) 0.12 (6H, s, Me_2Si), 0.73 (1H, dd, J=14.9, 5.7 Hz) and 0.99 (1H, dd, J=14.9, 7.7 Hz, CH_2Si), 1.79 (3H, t, J=1.5 Hz, MeC=), 2.70 (1H, ca. dddd, J=7.7, 6.2, 5.7, 2.5 Hz, C*H*CHO), 2.73 (1H, dd, J=13.2, 6.2 Hz) and 2.99 (1H, dd, J=13.2, 7.7 Hz, PhCH_2), 5.27 (1H, dq, J=3.0,

1.5 Hz) and 5.63 (1H, dq, J=3.0, 1.5 Hz, =CH_2), 7.17 (2H, ca. dt, J=7.3, 1.4 Hz), 7.22 (1H, tt, J=7.3, 1.4 Hz) and 7.30 (2H, ca. tt, J=7.3, 1.4 Hz, Ph), 9.62 (1H, d, J=2.5 Hz, CHO); δ_C (125 MHz; $CDCl_3$) −3.3, −3.1, 13.7, 22.3, 38.1, 49.6, 126.1, 126.4, 128.5, 129.0, 138.8, 146.1, 203.9; *m/z* (CI) 264 (MNH_4^+, 100%), 247 (MH^+, 11), 231 (34), 205 (46), 155 (13), 116 (22), 99 (24), 91 (85), 73 (22), 59 (12).

(*E*)-1-Diisopropylsilyloxy-3-phenylprop-2-ene (18).[15] A mixture of DMAP (18 mg, 0.15 mmol), triethylamine (63 μl, 0.45 mmol) and cinnamyl alcohol (50 mg, 0.37 mmol) in hexane (2 cm^3) was stirred at rt for 10 min then chlorodiisopropylsilane (83 μl, 0.48 mmol) was added dropwise. The mixture was stirred for 4.5 h then filtered through Celite®, the filtrate being concentrated in vacuo to give an oil that was purified by column chromatography (99:1 petrol:ether). Hydrosilane **18**[15] was obtained as a colourless oil (82 mg, 89%). R_f 0.71 (1:1 petrol:ether); ν_{max}/cm^{-1} 3028m, 2944s, 2865s, 2094s, 1496m, 1463s, 1382m, 1244m, 1126s, 1059s, 1001s, 964s, 881s, 832s, 731s, 691s; δ_H (500 MHz; $CDCl_3$) 0.93–1.34 (14H, m, Pr^i_2Si), 4.30 (1H, s, folded SiH), 4.48 (2H, dd, J=5.3, 1.6 Hz, CH_2O), 6.35 (1H, dt, J=15.8, 5.3 Hz, PhCH=C*H*), 6.67 (1H, dt, J=15.8, 1.6 Hz, PhC*H*=CH), 7.27 (1H, ca. tt, J=7.3, 1.4 Hz), 7.36 (2H, ca. tt, J=7.3, 1.4 Hz), 7.43 (2H, ca. dt, J=7.3, 1.4 Hz, Ph); δ_C (125 MHz; $CDCl_3$) 12.5, 17.3, 17.4, 66.2, 126.4, 127.4, 128.5, 130.0, 137.0; *m/z* (CI) 249 (MH^+, 11%), 222 (32), 205 (36), 117 (100), 115 (21), 91 (15).

1,1-Diisopropyl-2-oxa-5-phenyl-1-silacyclopentane (19). To a mixture of Wilkinson's catalyst (5.5 mg, 0.2 mol%) and 4 Å molecular sieves (61 mg) in THF (4.5 cm^3) at rt was added dropwise a solution of hydrosilane **18** (630 mg, 2.54 mmol) in THF (2 cm^3) and the mixture brought to reflux. Heating was continued for 3.5 h then the THF was removed in vacuo to give a brown oily residue (641 mg) containing oxasilacyclopentane **19** which was sufficiently pure to be used directly in the next reaction. R_f 0.50 and 0.62 (1:1 petrol:ether—hydrolysis); ν_{max}/cm^{-1} 2943s, 2866s, 1601m, 1464s, 1384w, 1245w, 1055s, 1032s, 999m, 883s, 825s, 786s, 698s; δ_H (200 MHz; $CDCl_3$) 0.75 and 0.79 (2×3H, 2×d, J=6.5 Hz) and 0.85–1.28 (8H, m, Pr^i_2Si), 2.24–2.40 (2H, m, PhCHCH_2), 2.79 (1H, dd, J= 10.5, 8.5 Hz, PhC*H*), 3.90 (1H, apparent dt, J=9.5, 6.0 Hz) and 4.25 (1H, apparent dt, J=6.0, 3.0 Hz, CH_2O), 7.08–7.32 (5H, m, Ph); δ_C (50.3 MHz; $CDCl_3$) 12.1, 12.4, 16.7, 16.9, 17.4, 17.6, 30.1, 32.2, 67.2, 124.6, 126.8, 128.5, 142.6; *m/z* (CI) 266 (MNH_4^+, 6%), 249 (MH^+, 98), 248 (47), 222 (83), 205 (100), 177 (28), 117 (83), 91 (37).

4,4-Diisopropyl-5-methyl-3-phenyl-4-silahex-5-en-1-ol (20). 2-Bromopropene (0.39 cm^3, 4.43 mmol) was added dropwise to a cooled (−78°C) solution of *t*-butyllithium (5.9 cm^3 of a 1.5 M solution in pentane, 8.85 mmol) in THF (7 cm^3) and the mixture was stirred for 1 h. A solution of the crude oxasilacyclopentane **19** (524 mg, 2.11 mmol) in THF (2 cm^3) was added dropwise then the mixture was allowed to warm to rt and stirred for 18 h. Water (20 cm^3) was added and the product extracted with ether (3×20 cm^3). The combined organic extracts were washed with brine (25 cm^3), dried (magnesium sulphate) and the solvent removed in vacuo. Purification by column chromatography (9:1 petrol:ether) gave the *alcohol* **20** as a colourless oil (402 mg, 66%). R_f 0.39 (1:1 petrol:ether); Found: C, 74.50; H, 10.88; $C_{18}H_{30}OSi$ requires C, 74.42; H, 10.41%; ν_{max}/cm^{-1} 3306s, 3025m, 2944s, 1599s, 1492s, 1458s, 1389m, 1247m, 1144m, 1032s, 922m, 883m, 803m, 775m, 759m; δ_H (500 MHz; $CDCl_3$) 0.99–1.09 (13H, m) and 1.17 (1H, sept, J=7.3 Hz, Pr^i_2Si), 1.32 (1H, br s, OH), 1.82 (3H, t, J=1.3 Hz, MeC=), 2.03–2.15 (2H, m, PhCHCH_2), 2.55 (1H, dd, J=12.2, 3.1 Hz, PhC*H*), 3.42 (1H, apparent dt, J=10.4, 7.4 Hz) and 3.55 (1H, ddd, J=10.4, 7.3, 4.5 Hz, CH_2OH), 5.29 (1H, dq, J=3.1, 1.3 Hz) and 5.79 (1H, dq, J=3.1, 1.3 Hz, =CH_2), 7.10 (1H, tt, J=7.2, 1.5 Hz), 7.16 (2H, ca. dt, J=7.2, 1.5 Hz), and 7.23 (2H, tt, J=7.2, 1.5 Hz, Ph); δ_C (125 MHz; $CDCl_3$) 10.7, 11.2, 18.2, 18.5, 18.6, 28.7, 24.7, 28.8, 33.5, 62.2, 124.8, 128.1, 128.5, 128.9, 142.3, 142.8; *m/z*(CI) 308 (MNH_4^+, 100%), 291 (MH^+, 6), 264 (7), 249 (10), 247 (11), 172 (12), 146 (12), 130 (11), 118 (34), 91 (10).

4,4-Diisopropyl-5-methyl-3-phenyl-4-silahex-5-enal (21). To a cooled (0°C) mixture of alcohol **20** (100 mg, 0.34 mmol) and 4 Å molecular sieves (344 mg) in DCM (2 cm^3) was added PDC (194 mg, 0.52 mmol). The mixture was allowed to warm to rt then stirred for 4 h. Ether (10 cm^3) was added, the mixture filtered through Celite®, washing through with ether (4×10 cm^3), and the combined filtrates were concentrated in vacuo to give an orange oil. Purification by column chromatography (40:1 petrol:ether) afforded *aldehyde* **21** as a colourless oil (63 mg, 64%). R_f 0.67 (1:1 petrol:ether); Accurate mass: Found 306.2253, $C_{18}H_{32}NOSi$ (MNH_4^+) requires 306.22530; ν_{max}/cm^{-1} 3428w, 3026m, 2946s, 2868s, 2717m, 1728s, 1600s, 1494s, 1451s, 1384s, 1371m, 1247m, 1188m, 1079m, 1018s, 924s, 883s, 776m, 701s; δ_H (500 MHz; $CDCl_3$) 0.98, 1.05, 1.07 and 1.13 (4×3H, 4×d, J=7.0 Hz), 1.03–1.12 (1H, m) and 1.17 (1H, septd, J=7.0 Hz, 1.0, Pr^i_2Si), 1.80 (3H, t, J=1.4 Hz, MeC=), 2.72 (1H, d, J=12.7 Hz, PhC*H*), 3.04 (1H, td, J=12.7, 2.6 Hz) and 3.09 (1H, d, J=12.7 Hz, CH_2CHO), 5.31 (1H, dq, J=3.0, 1.4 Hz) and 5.83 (1H, dq, J=3.0, 1.4 Hz, =CH_2), 7.11 (1H, tt, J=7.3, 1.6 Hz), 7.18 (2H, ca. dt, J=7.3, 1.6 Hz) and 7.23 (2H, tt, J=7.3, 1.6 Hz, Ph), 9.60 (1H, d, J=2.6 Hz, CHO); δ_C (125 MHz; $CDCl_3$) 10.5, 11.0, 18.1, 18.4 (2), 18.6, 24.5, 26.0, 44.5, 125.2, 128.2, 128.3, 129.5, 141.5, 141.7, 202.7; *m/z* (CI) 306 (MNH_4^+, 100%), 289 (MH^+, 4), 271 (3), 262 (6), 245 (24).

(1*SR*, 2*SR*, 5*RS*)-2-Hydroxymethyl-5-methyl-1-[dimethyl-(propen-2-yl)silyl]cyclohex-3-ene (24) and (1*RS*, 2*SR*, 5*RS*)-2-hydroxymethyl-5-methyl-1-[dimethyl(propen-2-yl)silyl]cyclohex-3-ene (25). A solution of the dimethyl-(vinyl)silyl ether of sorbyl alcohol[17] (275 mg, 1.51 mmol) in benzene (20 cm^3) was heated at 170°C (sealed tube) for 13 h. The solution was cooled and concentrated in vacuo and the resulting oil dissolved in THF (5 cm^3). To a cooled (−78°C) solution of *t*-butyllithium (4.7 cm^3 of a 1.6 M solution in pentane, 7.52 mmol) in THF (6.5 cm^3) was added dropwise 2-bromopropene (0.34 cm^3, 3.79 mmol). After 1.5 h the THF solution of the Diels–Alder adduct was added by cannula and the mixture was allowed to warm up to 0°C then stirred for 6 h at 0°C and at rt for 12 h. The mixture was added to a mixture of water (25 cm^3) and 1 M hydrochloric acid (5 cm^3) and extracted with ether

(3×5 cm^3). The combined organic portions were washed with brine (20 cm^3), dried (magnesium sulphate) and concentrated in vacuo and the resulting oil purified by column chromatography (14:1 petrol:ether) to yield *alcohols* **24** (135 mg, 40%) and **25** (91 mg, 27%). Data for **24**: R_f 0.53 (1:1 petrol:ether); Accurate mass: Found 242.1940, $C_{13}H_{28}NOSi$ (MNH_4^+) requires 242.19401; ν_{max}/cm^{-1} 3340m, 3048m, 3015m, 2954s, 2909s, 2870s, 1648w, 1456m, 1370m, 1250s, 1126w, 1035s, 1003m, 938m, 921s, 860s, 833s, 819s, 783s, 762m, 732s, 689m, 674m; δ_H (500 MHz; $CDCl_3$) 0.16 and 0.18 (2×3H, 2×s, $SiMe_2$), 1.00 (3H, d, *J*=7.1 Hz, *Me*CH), 1.15–1.25 (2H, m, CHSi and ring-C*H*H), 1.68 (1H, br s, OH), 1.72 (1H, dd, *J*=10.4, 4.8 Hz, ring-CH*H*), 1.88 (3H, br s, MeC=), 2.14–2.19 (1H, br m, MeC*H*), 2.37–2.39 (1H, br m, C*H*CH_2OH), 3.57 (1H, dt, *J*=10.5, 5.5 Hz) and 3.71 (1H, dt, *J*=10.5, 5.5 Hz, C*H*$_2$OH), 5.34 (1H, dq, *J*=3.0, 1.5 Hz) and 5.66 (1H, dq, *J*=3.0, 1.5 Hz, =CH_2), 5.74 (1H, dd, *J*=10.2, 1.2 Hz, =C*H*CHMe), 5.80 (1H, ddd, *J*=10.2, 4.7, 2.4 Hz, =C*H*CHCH$_2$OH); δ_C (125 MHz; $CDCl_3$) −4.5, −4.3, 21.7, 23.0 24.0, 29.3, 32.4, 38.1, 65.5, 125.9, 128.5, 136.2, 146.9; *m*/*z* (CI) 242 (MNH_4^+, 75%), 209 (10), 200 (20), 183 (70), 165 (15), 116 (30), 108 (80), 99 (50), 93 (80), 75 (100), 59 (30). Data for **25**: R_f 0.47 (1:1 petrol:ether); Accurate mass: Found 242.1940, $C_{13}H_{28}NOSi$ (MNH_4^+) requires 242.19401; ν_{max}/cm^{-1} 3320s, 3048m, 3012m, 2954s, 2928s, 2870s, 1456s, 1410m, 1370m, 1248s, 1055s, 1026s, 1002m, 938m, 920s, 855s, 834s, 814s, 776s, 726s, 696m; δ_H (500 MHz; $CDCl_3$) 0.13 (6H, s, $SiMe_2$), 0.99 (3H, d, *J*=7.0 Hz, *Me*CH), 1.23 (1H, dt, *J*=6.0, 4.5 Hz, CHSi), 1.45 (1H, ddd, *J*=13.3, 8.1, 4.5 Hz, ring-C*H*H), 1.71 (1H, s, OH), 1.73 (1H, dd, *J*=13.3, 6.0 Hz, ring-CH*H*), 1.88 (3H, t, *J*=1.3 Hz, MeC=), 2.16–2.20 (1H, br m, MeC*H*), 2.25–2.27 (1H, br m, C*H*CH_2OH), 3.56 (2H, 'd'—only inner peaks resolved, *J*=5.9 Hz, C*H*$_2$OH), 5.31 (1H, dq, *J*=3.2, 1.3 Hz) and 5.64 (1H, dq, *J*=3.2, 1.3 Hz, =CH_2), 5.63 (1H, ddd, *J*=10.1, 3.7, 2.2 Hz, =C*H*CHMe), 5.75 (1H, dt, *J*=10.1, 2.2 Hz, =C*H*CHCH$_2$OH); δ_C (125 MHz; $CDCl_3$) −4.5, −4.2, 18.5, 21.4, 22.9, 28.9, 29.4, 38.2, 66.5, 125.8, 127.7, 136.2, 146.6; *m*/*z* (CI) 242 (MNH_4^+, 20%), 207 (10), 200 (10), 193 (20), 183 (55), 165 (10), 148 (10), 134 (10), 118 (20), 116 (100), 107 (25), 99 (95), 93 (40), 91 (30), 75 (50), 73 (70), 59 (25).

(1*SR*,2*SR*,5*RS*)-2-Formyl-5-methyl-1-[dimethyl(propen-2-yl)silyl]cyclohex-3-ene (26). To a cooled (0°C) solution of alcohol **24** (125 mg, 0.56 mmol) in DCM (4 cm^3) was added powdered 4 Å molecular sieves (0.42 g) and PDC (0.32 g, 0.84 mmol) and the mixture was allowed to warm up to rt over 14 h. Petrol:ether (10 cm^3, 3:1) was added to the mixture that was then filtered through a pad of silica, washed through with petrol:ether (100 cm^3, 3:1), and the filtrate concentrated in vacuo. The resulting oil was purified by column chromatography (150:1→10:1 petrol:ether) to yield *aldehyde* **26** as a colourless oil (73 mg, 59%). R_f 0.60 (3:1 petrol:ether); Accurate mass: Found 240.1784, $C_{13}H_{26}NOSi$ (MNH_4^+) requires 240.17836; ν_{max}/cm^{-1} 3017m, 2956s, 2854s, 2719m, 1716s, 1455m, 1370w, 1251s, 1191w, 1126w, 1069w, 922m, 819s, 785s, 730m, 691m; δ_H (500 MHz; $CDCl_3$) 0.14 and 0.15 (2×3H, 2×s, $SiMe_2$), 1.02 (3H, d, *J*=7.1 Hz, *Me*CH), 1.23–1.30 (2H, m) and 1.79–1.82 (1H, m, CHSi and ring-CH_2), 1.84 (3H, t, *J*=1.5 Hz, MeC=), 2.20–2.22 (1H, br m, MeC*H*), 2.99–3.00 (1H, br m, C*H*CHO), 5.29 (1H, dq, *J*=3.0, 1.5 Hz) and 5.66 (1H, dq, *J*=3.0, 1.5 Hz, =CH_2), 5.58 (1H, ddd, *J*=9.9, 5.2, 2.6 Hz, =C*H*CHMe), 5.89 (1H, d, *J*=9.9 Hz, =C*H*CHCHO), 9.62 (1H, d, *J*= 3.3 Hz, CHO); δ_C (125 MHz; $CDCl_3$) −4.6, −4.5, 21.4, 22.7, 22.9, 29.5, 31.9, 49.9, 122.1, 126.8, 138.9, 145.4, 201.5; *m*/*z* (CI) 240 (MNH_4^+, 100%), 223 (MH^+, 15), 207 (20), 181 (65), 147 (25), 116 (20), 107 (60), 73 (35), 59 (20).

(1*RS*,2*SR*,5*RS*)-2-Formyl-5-methyl-1-[dimethyl(propen-2-yl)silyl]cyclohex-3-ene (27). To a cooled (0°C) solution of alcohol **25** (81 mg, 0.36 mmol) in DCM (3 cm^3) was added powdered 4 Å molecular sieves (0.27 g) and PDC (0.21 g, 0.54 mmol) and the mixture was allowed to warm up to rt over 14 h. Petrol:ether (10 cm^3, 3:1) was added to the mixture that was then filtered through a pad of silica, washed through with petrol:ether (100 cm^3, 3:1) and the filtrate concentrated in vacuo. The resulting oil was purified by column chromatography (90:1→15:1 petrol:ether) to yield *aldehyde* **27** as a colourless oil (47 mg, 59%). R_f 0.61 (3:1 petrol:ether); Accurate mass: Found 240.1784, $C_{13}H_{26}NOSi$ (MNH_4^+) requires 240.17836; ν_{max}/cm^{-1} 3018w, 2957s, 2872m, 1725s, 1454w, 1370w, 1251m, 1164w, 1019w, 922m, 835m, 816s, 779m, 737w; δ_H (500 MHz; $CDCl_3$) 0.14 and 0.15 (2×3H, 2×s, $SiMe_2$), 1.03 (3H, d, *J*=7.1 Hz, *Me*CH), 1.43 (1H, ddd, *J*=13.1, 7.4, 4.4 Hz, ring-C*H*H), 1.62 (1H, dt, *J*=7.0, 4.4 Hz, CHSi), 1.75 (1H, ddd, *J*=13.1, 7, 5.7 Hz, ring-CH*H*), 1.86 (3H, t, *J*=1.4 Hz, MeC=), 2.21–2.27 (1H, m, MeC*H*), 2.92 (1H, dq, *J*=4.4, 2.5 Hz, C*H*CHO), 5.32 (1H, dq, *J*=3.1, 1.4 Hz) and 5.68 (1H, dq, *J*=3.1, 1.4 Hz, =CH_2), 5.64 (1H, ddd, *J*=10.0, 4.1, 2.5 Hz, =C*H*CHMe), 5.93 (1H, dt, *J*=10.0, 2.5 Hz, =C*H*CHCHO), 9.54 (1H, d, *J*=2.5 Hz, CHO); δ_C (125 MHz; $CDCl_3$) −4.2, −4.8, 16.4, 21.0, 22.8, 28.5, 29.2, 49.4, 120.8, 126.7, 138.3, 145.4, 201.5; *m*/*z* (CI) 240 (MNH_4^+, 45%), 223 (MH^+, 15), 205 (15), 193 (15), 181 (35), 147 (25), 116 (65), 107 (100), 99 (50), 91 (25), 73 (30), 59 (10).

4,4-Dimethyl-3-methylene-4-silacyclohexanol (28). To a cooled (−78°C) solution of aldehyde **7** (326 mg, 2.09 mmol) in DCM (7 cm^3) was added dropwise methylaluminium dichloride (3.1 cm^3 of a 1 M solution in hexane, 3.1 mmol). After 6 h saturated sodium hydrogen carbonate solution (3 cm^3) was added dropwise and the mixture was allowed to warm up to rt then added to a mixture of ether (10 cm^3), saturated sodium hydrogen carbonate solution (5 cm^3), water (5 cm^3) and saturated potassium sodium tartrate solution (5 cm^3, which dissolved the white precipitate on shaking). The separated aqueous layer was extracted with ether (3×10 cm^3) and the combined organic portions washed with brine (20 cm^3), dried (magnesium sulphate) and concentrated in vacuo. The resulting oil was purified by column chromatography (5:1 petrol:ether) to yield the *silacycle* **28** as a colourless oil (258 mg, 80%). R_f 0.32 (1:1 petrol:ether); Accurate mass: Found 174.1314, $C_8H_{20}NOSi$ (MNH_4^+) requires 174.13141; ν_{max}/cm^{-1} 3350s, 2953s, 2916s, 1438m, 1411m, 1249s, 1037s, 924m, 874m, 839s, 821s, 781s, 721m, 689m, 644m; δ_H (500 MHz; $CDCl_3$) 0.12 and 0.13 (2×3H, 2×s, $SiMe_2$), 0.57 (1H, ddd, *J*=14.7, 10.1, 4.4 Hz) and 0.82 (1H, ddd, *J*=14.7, 8.4, 4.2 Hz, $SiCH_2$), 1.64 (1H, br s, OH), 1.82 (1H, dtd, *J*=18.1, 8.4, 4.4 Hz) and 1.96–2.02 (1H, m, CH_2), 2.42 (1H, dd, *J*=13.3,

8.4 Hz) and 2.64 (1H, ddd, J=13.3, 3, 1.3 Hz, CH_2C=), 3.72 (1H, tt, J=8.4, 3 Hz, C*H*OH), 5.28 (1H, d, J=3.4 Hz) and 5.57 (1H, dd, J=3.4, 1.3 Hz, =CH_2); δ_C (125 MHz; $CDCl_3$) −4.6, −4.2, 10.0, 32.0, 47.3, 71.9, 124.5, 148.1; *m/z* (CI) 174 (MNH_4^+, 75%), 158 (20), 157 (MH^+, 10), 156 (45), 141 (80), 139 (80), 123 (15), 115 (30), 91 (70), 74 (100).

(*cis*)-5-Methylene-2,4,4-trimethyl-4-silacyclohexanol (29) and (*trans*)-5-methylene-2,4,4-trimethyl-4-silacyclohexanol (30). To a cooled (−78°C) solution of aldehyde **8** (91 mg, 0.53 mmol) in DCM (2.5 cm^3) was added dropwise methylaluminium dichloride (0.91 cm^3 of a 1 M solution in hexane, 0.91 mmol). After 3 h water (2 cm^3) was added dropwise and the mixture allowed to warm up to rt then added to a mixture of ether (10 cm^3), saturated sodium hydrogen carbonate solution (5 cm^3) and saturated potassium sodium tartrate solution (6 cm^3, which dissolved the white precipitate on shaking). The separated aqueous layer was extracted with ether (3×8 cm^3) and the combined organic portions washed with brine (15 cm^3), dried (magnesium sulphate) and concentrated in vacuo. The resulting oil was purified by column chromatography (3:1 petrol: ether) to yield a mixture of *silacycles* **29** and **30** in a ratio of 13:1 (*cis*:*trans*) as a colourless oil (73 mg, 80%). Separation of the isomers was possible by further chromatography (19:1 petrol:ether). Data for **29**: R_f 0.51 (1:1 petrol:ether); Accurate mass: Found 188.1471, $C_9H_{22}NOSi$ (MNH_4^+) requires 188.14706; ν_{max}/cm^{-1} 3429m, 2955s, 2903s, 1452m, 1434m, 1411m, 1250s, 1184w, 1145w, 1024m, 984m, 921m, 874m, 844s, 802s, 758w, 659m; δ_H (500 MHz; $CDCl_3$) 0.11 and 0.15 (2×3H, 2×s, $SiMe_2$), 0.56–0.63 (2H, m, $SiCH_2$), 1.09 (3H, d, J=6.8 Hz, *Me*CH), 1.28 (1H, br s, OH), 1.90 (1H, dqdd, J=14.0, 6.8, 2.6, 1.9 Hz, MeC*H*), 2.56 (1H, dd, J=14.0, 4.4 Hz) and 2.61 (1H, dq, J=14.0, 2.3 Hz, CH_2C=), 3.77 (1H, ddd, J=4.4, 2.3, 1.9 Hz, C*H*OH), 5.37 (1H, dd, J=3.1, 2.3 Hz) and 5.61 (1H, dd, J=3.1, 2.3 Hz, =CH_2); δ_C (125 MHz; $CDCl_3$) −4.2, −3.9, 17.4, 23.2, 35.1, 45.6, 73.7, 126.0, 146.8; *m/z* (CI) 188 (MNH_4^+, 75%), 171 (MH^+, 10), 170 (15), 155 (70), 153 (100), 137 (10), 129 (30), 91 (40), 74 (65), 60 (15). Data for **30**: R_f 0.43 (1:1 petrol:ether); Accurate mass: Found 188.1471, $C_9H_{22}NOSi$ (MNH_4^+) requires 188.14706; ν_{max}/cm^{-1} 3371s, 2955s, 2903s, 2876s, 1442m, 1412w, 1252m, 1093m, 1075m, 1029m, 923w, 819m, 784m, 842m; δ_H (200 MHz; $CDCl_3$) 0.12 and 0.14 (2×3H, 2×s, $SiMe_2$), 0.36 (1H, dd, J=14.6, 11.7 Hz) and 0.85 (1H, dd, J=14.6, 3.7 Hz, $SiCH_2$), 1.13 (3H, d, J=6.5 Hz, *Me*CH), 1.56 (1H, br s, OH), 1.71–1.81 (1H, m, MeC*H*), 2.41 (1H, ddt, J=13.2, 10.1, 1.9 Hz) and 2.68 (1H, dd J=13.2, 3.7 Hz, CH_2C=), 3.16 (1H, td, J=10.1, 3.7 Hz, C*H*OH), 5.24 (1H, dd, J=3.3, 1.5 Hz) and 5.57 (1H, ca. t, J=2.6 Hz, =CH_2); *m/z* (CI) 188 (MNH_4^+, 25%), 171 (MH^+, 10), 170 (30), 155 (60), 153 (100), 137 (10), 129 (20), 113 (10), 100 (10), 91 (40), 74 (65), 60 (15).

(*trans*)-3-Methylene-4,4,5-trimethyl-4-silacyclohexanol (31). To a cooled (−78°C) solution of aldehyde **9** (58 mg, 0.34 mmol) in DCM (1.5 cm^3) was added dropwise methylaluminium dichloride (0.51 cm^3 of a 1 M solution in hexane, 0.51 mmol). After 3 h water (2 cm^3) was added dropwise and the mixture allowed to warm up to rt then added to a mixture of ether (5 cm^3), saturated sodium hydrogen carbonate solution (5 cm^3), water (5 cm^3) and saturated potassium sodium tartrate solution (5 cm^3, which dissolved the white precipitate on shaking). The separated aqueous layer was extracted with ether (3×5 cm^3) and the combined organic portions washed with brine (15 cm^3), dried (magnesium sulphate) and concentrated in vacuo. The resulting oil was purified by column chromatography (44:1→3:1 petrol:ether) to yield *silacycle* **31** as a colourless oil (40 mg, 69%). R_f 0.34 (1:1 petrol:ether); Accurate mass: Found 188.1471, $C_9H_{22}NOSi$ (MNH_4^+) requires 188.14706; ν_{max}/cm^{-1} 3353s, 2951s, 2905s, 2865s, 1457m, 1377m, 1353m, 1250s, 1195m, 1035s, 991m, 959m, 922s, 839s, 814s, 776s, 694s, 617m; δ_H (500 MHz; $CDCl_3$) 0.04 and 0.15 (2×3H, 2×s, $SiMe_2$), 0.96 (3H, d, J=7.1 Hz, *Me*CH), 1.01–1.07 (1H, m, MeC*H*), 1.55 (1H, br s, OH), 1.61 (1H, ddd, J=13.8, 11.1, 2.2 Hz) and 1.97 (1H, dddd, J=13.8, 5.9, 4.7, 1.6 Hz, CH_2), 2.46 (1H, dd, J=13.6, 5.9 Hz) and 2.60 (1H, br dq, J=13.6, 1.6 Hz, CH_2C=), 4.01 (1H, ca. tt, J=5.9, 2.6 Hz, C*H*OH), 5.34 (1H, d, J=3.0 Hz) and 5.61 (1H, dt, J=3.0, 1.2 Hz, =CH_2); δ_C (125 MHz; $CDCl_3$) −8.7, −6.8, 13.6, 14.4, 39.5, 45.1, 67.9, 124.6, 146.3; *m/z* (CI) 188 (MNH_4^+, 5%), 171 (MH^+, 5), 170 (20), 153 (100), 137 (25), 109 (15), 95 (15), 91 (30), 74 (55), 59 (30).

(*cis*)-4,4-Dimethyl-5-methylene-2-(2-propyl)-4-silacyclohexanol (32). To a cooled (−78°C) solution of aldehyde **16** (50 mg, 0.25 mmol) in DCM (1.5 cm^3) was added dropwise methylaluminium dichloride (0.53 cm^3 of a 1 M solution in hexane, 0.53 mmol) and the mixture stirred for 6 h. Water (1 cm^3) was added and the mixture was allowed to warm to rt whereupon more water (10 cm^3) was added and the product was extracted with ether (3×10 cm^3). The combined extracts were washed with brine (20 cm^3) then dried (magnesium sulphate) and the solvent removed in vacuo. Purification by column chromatography (30:1 petrol:ether) gave the *silacycle* **32** as a colourless oil (42 mg, 84%). R_f 0.39 (3:1 petrol:ether); Accurate mass: Found 216.1789, $C_{11}H_{26}NOSi$ (MNH_4^+) requires 216.17836; ν_{max}/cm^{-1} 3469m, 3041m, 2956s, 2899s, 2872s, 1475m, 1432m, 1384m, 1250s, 1144m, 1030m, 923m, 843s, 765s, 664m; δ_H (500 MHz; $CDCl_3$) 0.10 and 0.17 (2×3H, 2×s, Me_2Si), 0.51 (1H, apparent t, J=14.0 Hz) and 0.75 (1H, dd, J=14.0, 3.4 Hz, CH_2Si), 0.94 and 0.97 (2×3H, 2×d, J=6.7 Hz, Me_2C), 1.22 (1H, d, J=7.7 Hz, OH), 1.35 (1H, dddd, J=14.0, 6.7, 3.4, 1.1 Hz, Pr^iCH), 1.65 (1H, apparent oct, J=6.7 Hz, Me_2CH), 2.53–2.60 (2H, m, CH_2CHOH), 4.11 (1H, br s, C*H*OH), 5.38 (1H, d, J=2.9 Hz) and 5.60 (1H, ca. t, J=2.9 Hz, =CH_2); δ_C (125 MHz; $CDCl_3$) −4.3, −3.9, 12.0, 20.6, 21.2, 33.1, 46.3, 46.6, 70.4, 126.0, 147.5; *m/z* (CI) 216 (MNH_4^+, 64%), 183 (100), 181 (86), 157 (46), 155 (64), 141 (73), 137 (48), 127 (73), 113 (61), 99 (64), 92 (95).

(*cis*)-2-Benzyl-4,4-dimethyl-5-methylene-4-silacyclohexanol (33). To a cooled (−78°C) solution of aldehyde **17** (252 mg, 1.02 mmol) in DCM (6 cm^3) was added dropwise methylaluminium dichloride (1.53 cm^3 of a 1 M solution in hexane, 1.53 mmol) and the mixture stirred for 7 h. Water (5 cm^3) was added, the mixture was allowed to warm to rt, more water (30 cm^3) was added and the product extracted with ether (3×30 cm^3). The combined organic extracts were dried (magnesium sulphate) and the solvent removed in vacuo. Purification by column chromatography

(30:1→18:1 petrol:ether) gave *silacycle* **33** as a colourless oil (199 mg, 79%). R_f 0.26 (3:1 petrol:ether); Accurate mass: Found 229.1413, $C_{15}H_{21}Si$ (MH^+-H_2O) requires 229.14125; ν_{max}/cm^{-1} 3566m, 3466s, 3027s, 2951s, 2909s, 1602m, 1496s, 1454s, 1435m, 1410s, 1249s, 1165s, 1074s, 1031m, 993m, 930s, 844s, 798s, 779s, 740s, 700s, 663s; δ_H (500 MHz; $CDCl_3$) 0.10 and 0.18 (2×3H, 2×s, Me_2Si), 0.62 (1H, dd, J=14.6, 12.3 Hz) and 0.67 (1H, dd, J=14.6, 4.6 Hz, CH_2Si), 1.38 (1H, br s, OH), 1.98 (1H, dtdd, J=12.3, 7.5, 4.6, 1.4 Hz, BnC*H*), 2.54 (1H, dd, J=14.1, 4.4 Hz) and 2.59 (1H, dd, J=14.1, 2.1 Hz, CH_2CHOH), 2.64 (1H, dd, J=13.3, 7.5 Hz) and 2.87 (1H, dd, J=13.3, 7.5 Hz, PhCH_2), 3.86 (1H, br s, C*H*OH), 5.41 (1H, dd, J=3.1, 1.1 Hz) and 5.64 (1H, ca. t, J=2.6, =CH_2), 7.20–7.23 (3H, m) and 7.31 (2H, ca. t, J=7.5 Hz, Ph); δ_C (125 MHz; $CDCl_3$) −4.4, −4.0, 15.3, 42.3, 43.6, 45.7, 70.7, 125.7, 126.2, 128.2, 129.3, 141.1, 146.9; *m/z* (CI) 264 (MNH_4^+, 9%), 248 (15), 246 (24), 231 (46), 229 (97), 228 (46), 156 (23), 139 (72), 91 (100), 74 (86), 59 (61).

(*trans*)-4,4-Diisopropyl-5-methylene-3-phenyl-4-silacyclohexanol (34). To a cooled (−78°C) solution of aldehyde **21** (63 mg, 0.22 mmol) in DCM (1.5 cm^3) was added dropwise methylaluminium dichloride (0.33 cm^3 of a 1 M solution in hexane, 0.33 mmol) and the mixture was stirred for 7 h. Water (3 cm^3) was added, the mixture warmed to rt, and more water (10 cm^3) added. The product was extracted into ether (3×15 cm^3) and the combined extracts were washed with brine (20 cm^3) then dried (magnesium sulphate) and concentrated in vacuo. The oil was purified by column chromatography (9:1 petrol:ether) to afford *silacycle* **34** (48 mg, 76%) as a white solid. R_f 0.35 (1:1 petrol:ether); mp 61–62°C; Accurate mass: Found 306.2253, $C_{18}H_{32}NOSi$ (MNH_4^+) requires 306.22530; ν_{max}/cm^{-1} 3254s, 3024w, 2945s, 2866s, 1599m, 1496m, 1464m, 1448m, 1313m, 1219m, 1087m, 1040m, 928m, 854m, 769s, 700s, 662s; δ_H (500 MHz; $CDCl_3$) 0.76, 1.03 and 1.04 (3×3H, 3×d, J=7.2 Hz), 1.10 (1H, ca. sept, J=7.2 Hz), and 1.16–1.24 (4H, m, Pr^i_2Si), 1.58 (1H, br s, OH), 2.28–2.31 (2H, m, PhCHCH_2), 2.60 (1H, dd, J=14.6, 4.6 Hz) and 2.71 (1H, dq, J=14.6, 2.5 Hz, CH_2C=), 2.87 (1H, ca. t, J=9.0 Hz, PhC*H*), 4.27 (1H, br s, C*H*OH), 5.48 (1H, t, J=2.5 Hz) and 5.81 (1H, t, J=2.5 Hz, =CH_2), 7.12 (1H, tt, J=7.3, 1.4 Hz), 7.19 (2H, ca. dt, J=7.3, 1.4 Hz) and 7.26 (2H, tt, J=7.3, 1.4 Hz, Ph); δ_C (125 MHz; $CDCl_3$) 9.5, 9.7, 17.5, 17.6, 18.2, 19.3, 25.3, 38.1, 47.2, 68.3, 124.6, 127.7, 128.2, 128.3, 142.6, 144.4; *m/z* (CI) 306 (MNH_4^+, 100%), 288 (9), 271 (30), 262 (10), 245 (24), 91 (11).

(1*SR*,5*SR*,6*SR*,9*RS*)-5-Hydroxy-3-methylene-2,2,9-trimethyl-2-silabicyclo[4.4.0]dec-7-ene (35). To a cooled (−78°C) solution of aldehyde **26** (68 mg, 0.31 mmol) in DCM (5 cm^3) was added dropwise methylaluminium dichloride (0.46 cm^3 of a 1 M solution in hexane, 0.46 mmol). After 6 h water (5 cm^3) and ether (5 cm^3) were added and the mixture was stirred vigorously and allowed to warm up to rt. The mixture was added to water (5 cm^3), extracted with ether (3×8 cm^3) and the combined organic portions were washed with brine (10 cm^3), dried (magnesium sulphate) and concentrated in vacuo. The resulting oil was purified by column chromatography (20:1→10:1 petrol:ether) to yield *silabicycle* **35** as a colourless oil (60 mg, 88%). R_f 0.60 (1:1 petrol:ether); Accurate mass: Found 240.1784, $C_{13}H_{26}NOSi$ (MNH_4^+) requires 240.17836; ν_{max}/cm^{-1} 3566m, 3480m, 3005m, 2953s, 2919s, 2868s, 1456m, 1436m, 1386m, 1304m, 1246s, 1172m, 1126w, 1068m, 1036m, 1006m, 942m, 922m, 864s, 827s, 800s, 783s, 768s, 722w, 676m, 643m, 607s; δ_H (500 MHz; $CDCl_3$) 0.16 and 0.22 (2×3H, 2×s, $SiMe_2$), 1.00 (3H, d, J=7.1 Hz, *Me*CH), 1.20 (1H, ddd, J=14.4, 5.0, 2.9 Hz, CHSi), 1.39 (1H, td, J=14.4, 10.5 Hz) and 1.64 (1H, ddd, J=14.4, 5.9, 2.9 Hz, CH_2), 1.58 (1H, br d, J=2.1, OH), 2.14–2.19 (1H, m, MeC*H*), 2.42 (1H, td, J=5.0, 2.5 Hz, C*H*CHOH), 2.64 (1H, br d, J=14.2 Hz) and 2.73 (1H, dd, J=14.2, 4.1 Hz, CH_2C=), 3.95 (1H, br s, C*H*OH), 5.41 (1H, apparent dd, J=3.1, 2.0 Hz) and 5.71 (1H, apparent dd, J=3.1, 2.7 Hz, =CH_2), 5.68 (1H, ddd, J=10.1, 5.0, 2.5 Hz, =C*H*CHMe), 5.91 (1H, br d, J=10.1 Hz, =C*H*CHCHOH); δ_C (125 MHz; $CDCl_3$) −6.7, −2.9, 21.7, 22.5, 30.6, 31.1, 39.8, 43.6, 71.8, 125.6, 128.9, 137.9, 145.6; *m/z* (CI) 240 (MNH_4^+, 15%), 223 (MH^+, 5), 205 (35), 146 (20), 127 (100), 113 (20), 107 (30), 94 (35), 91 (30), 75 (75), 74 (50), 59 (10).

(1*RS*,5*SR*,6*SR*,9*RS*)-5-Hydroxy-3-methylene-2,2,9-trimethyl-2-silabicyclo[4.4.0]dec-7-ene (36). To a cooled (−78°C) solution of aldehyde **27** (40 mg, 0.18 mmol) in DCM (3 cm^3) was added dropwise methylaluminium dichloride (0.27 cm^3 of a 1 M solution in hexane, 0.27 mmol). After 7 h water (5 cm^3) and ether (5 cm^3) were added and the mixture was stirred vigorously and allowed to warm up to rt. The mixture was added to water (5 cm^3), extracted with ether (38 cm^3) and the combined organic portions were washed with brine (10 cm^3), dried (magnesium sulphate) and concentrated in vacuo. The resulting oil was purified by column chromatography (20:1→10:1 petrol:ether) to yield *silabicycle* **36** as a colourless oil (19 mg, 48%). R_f 0.24 (3:1 petrol:ether); Accurate mass: Found 240.1784, $C_{13}H_{26}NOSi$ (MNH_4^+) requires 240.17836; ν_{max}/cm^{-1} 3447m, 3042m, 3008s, 2955s, 2903s, 2868s, 1456m, 1432m, 1394m, 1368m, 1247s, 1196m, 1161m, 1126w, 1091m, 1075m, 1055m, 1043m, 1021m, 1003m, 924s, 852s, 834s, 822s, 785s, 759s, 704s, 667m, 642m, 616s; δ_H (500 MHz; $CDCl_3$) 0.19 and 0.22 (2×3H, 2×s, $SiMe_2$), 1.04 (3H, d, J=7.1 Hz, *Me*CH), 1.10 (1H, ddd J=13.6, 12.2, 2.2 Hz, CHSi), 1.43 (1H, d, J=5.5 Hz, OH), 1.53 (1H, br d, J=13.6 Hz) and 1.75 (1H, td, J=13.6, 6 Hz, CH_2), 2.24–2.28 (1H, m, MeC*H*), 2.31 (1H, br d, J=12.2 Hz, C*H*CHOH), 2.64 (1H, dd, J=14.3, 3.8 Hz) and 2.67 (1H, dq, J=14.3, 2.4, CH_2C=), 4.01–4.02 (1H, br s, J=2.2 Hz, C*H*OH), 5.42 (1H, apparent dd, J=3.0, 1.6 Hz) and 5.67 (1H, apparent d, J=3.0 Hz, =CH_2), 5.65 (1H, dt, J=10.0, 1.5 Hz, =C*H*CHCHOH), 5.82 (1H, br d, J=10.0 Hz, =C*H*CHMe); δ_C (125 MHz; $CDCl_3$) −7.3, −6.9, 15.4, 21.0, 28.2, 29.2, 43.6, 45.0, 73.0, 125.7, 130.9, 135.7, 147.2; *m/z* (CI) 240 (MNH_4^+, 80%), 222 (10), 207 (15), 206 (20), 205 (100), 189 (10), 180 (10), 146 (25), 127 (30), 107 (20), 92 (20), 91 (35), 75 (90), 74 (60), 59 (10).

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