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Silicon Tethered Alkenyl Transfer and Type I Ene Reactions

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Abstract—A range of vinyl silanes was prepared in order to investigate the possibility of effecting silicon tethered Type I ene cyclisations analogous to our previously reported Type II variant. Some of these substrates were found to undergo overall stereospecific alkenyl transfer via silacyclopentanol intermediates; in a homologous series, alkenyl transfer was accompanied by dehydration to provide 7-silylhepta-2,4-dienes in moderate yield. Formal Type I ene cyclisations were found to be successful for allysilane precursors resulting in the stereoselective formation of silacyclohexanols.

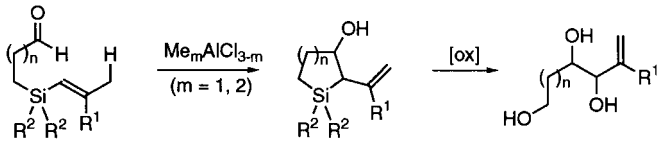
Introduction

As part of an ongoing programme to develop novel stereoselective methods for the preparation of polyhydroxylated molecules, with potential application to carbohydrate synthesis, we have shown that silicon tethered Type II carbonyl ene cyclisations successfully generate methylenesilacyclohexanols with high stereoselectivity.[1] Furthermore, these intermediates may be functionalised and converted stereospecifically into triols.[2] Whilst the vinyl silane products arising from the Type II series offer considerable synthetic potential[3] we have been keen to develop the Type I variant which would lead directly to products that could be converted in a single step[4] into triols bearing alkene functionality for further elaboration (Scheme 1). In addition, asymmetric catalysis of Type I ene cyclisations is rather more developed than that of their Type II counterparts[5] and we hoped that access to single enantiomers of the silacycles and products derived from them would ultimately be possible. This account summarises the majority of our first efforts in these directions.

Results and Discussion

Preparation and reactivity of silylpropionaldehyde precursors

Initial explorations were confined to a study of direct analogues of the successful Type II ene substrates (that formed six membered rings), i.e. vinyl silanes in which a new C–C bond would be formed α- to the silicon atom formally via a silacyclopentanol intermediate (n=1 in Scheme 1). Any build-up of positive charge would be β- to silicon in this type of cyclisation and it was of theoretical interest to investigate whether proton transfer—to complete the ene process—would compete successfully with potential desilylation pathways. Successful ene reaction would result in a product in which the silicon atom is directly connected to a stereogenic carbon atom and, with suitable silyl substituents, oxidative cleavage[4] would lead to a short stereocontrolled synthesis of trihydroxyalkenes, useful intermediates for further elaboration to carbohydrates. Whilst Type I ene cyclisations forming five-membered rings are



Scheme 1. R^1=H, Me; R^2=Me, Ph; n=1, 2.

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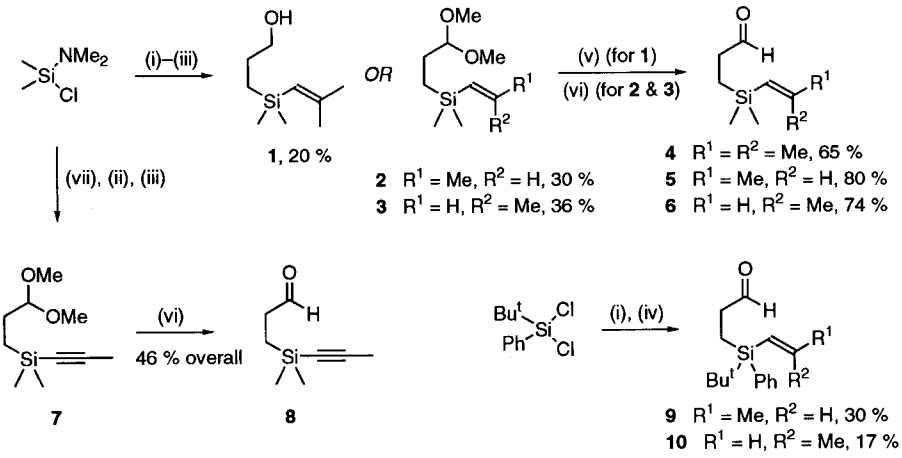


Scheme 2. *Reagents:* (i) $LiCH{=}CR^1R^2$, THF; (ii) AcCl; (iii) $ClMg(CH_2)_3OMgCl$ or $BrMg(CH_2)_2CH(OMe)_2$; (iv) *N*-allylpyrrolidine, *s*-BuLi then aq. HCl; (v) PDC, MS4 Å, CH_2Cl_2; (vi) *p*-TsOH, aq. THF; (vii) $LiC{\equiv}CMe$, THF.

less well precedented than those forming six-membered rings[6] (being less exothermic and synthetically useful only under carefully controlled conditions) our experience suggested that sila-analogues might behave differently.

A range of generic vinyl silane ene precursors **4**–**6** was prepared (Scheme 2) in which β-methyl substitution *cis*- and/or *trans*- to the silicon tether was included to allow an analysis of the stereochemical requirements of the proton transfer step in the projected ene cyclisation. In the general case sequential displacements of chloride from the requisite silicon electrophile[7] were used to prepare these precursors. The propionaldehyde chain was introduced by one of three methods: (a) with the Grignard reagent derived from 3-bromo-1,1-dimethoxypropane followed by hydrolysis;[8] (b) with the Grignard reagent derived[9] from 3-chloro-1-propanol followed by PDC oxidation; and (c) with lithiated *N*-allylpyrrolidine followed by a hydrolytic work-up.[10] The ene component was introduced in the same step with the alkenyl lithium reagent derived from the appropriate alkenyl bromide and *t*-butyllithium.[11] *Z*-Alkenyl substrate **3** was formed in combination with varying quantities of alkyne **7** but treatment of *Z*-1-bromopropene with *n*-butyllithium[12] rather than *t*-butyllithium enabled alkynyl substrate **7** to be obtained as the sole product. Later investigations used lithium metal to effect lithium–halogen exchange in generating the *Z*-alkenyl lithium reagent.[13]

Although these routes were not high yielding the primary purpose was to explore the behaviour of the substrates in the presence of Lewis acids and further optimisation studies were not attempted. An illustration of the problems associated with handling functionalised vinyl silanes of this type was discovered during the preparation of alcohol **1** en route to aldehyde **4**. An NMR sample of **1** ($CDCl_3$) left for 12 h at −10°C was completely converted into oxasilacyclopentane **11** (Fig. 1; the CH_2O protons resonating at δ 3.59 ppm in alcohol **1** and at δ 3.83 in silacycle **11**) with loss of the isobutenyl fragment as isobutene [δ 1.74 (6H, s) and 4.67 (2H, s)]; when exposed to air this silacycle underwent rapid hydrolysis giving diol **12** [δ 3.60 (CH_2O)]. This lability to acidic impurites in the solvent was in keeping with other observations of the instability of vinyl silanes possessing internal nucleophiles and provided a forewarning that unexpected behaviour might be discovered in the presence of Lewis acids.

In the event, application of conditions previously found to be optimal for Type II ene cyclisation (methylaluminium dichloride, −78°C) resulted in no products of ene cyclisation, substrates **4**, **5** and **9** merely undergoing slow decomposition. Whilst a certain amount of decomposition still took place with *Z*-alkenyl substrate **6** under the same conditions (for 1.75 h) a single product could be isolated, assigned as diol **13** (60%), in which the alkenyl group had been transferred with complete retention of configuration (CH=CH, J_{vic}=11 Hz). The *t*-butylphenyl analogue **10** afforded the oxasilacycle **18** (68%) as a single diastereoisomer tentatively assigned as that shown on the basis of NOE experiments. We have not performed further studies to try to elucidate the reaction pathway for these transformations but it is clear that cleavage of silicon from the ene component could be mediated either inter- or intramolecularly with the isolated products (diol **13** or silacycle **18**) arising during aqueous work-up; in this case the relative stability of the cyclic and acyclic forms would dictate the preferred product. It is conceivable that the oxasilacyclopentanes are the first-formed products, the dimethylsilyl

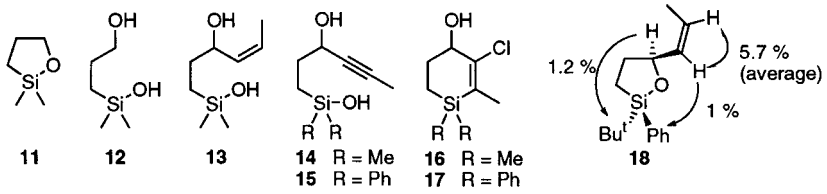
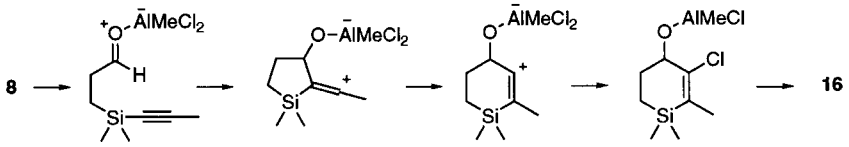


Figure 1.



Scheme 3.

compound being unstable with respect to hydrolysis, the *t*-butylphenyl analogue being much more resistant to ring-opening.

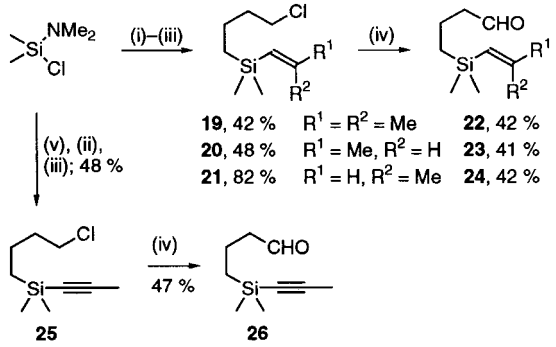
Under the same conditions the alkynyl substrate **8** afforded alkynyl transfer[14] product **14** (34%) in addition to a second component (20%) lacking an alkyne function (based on IR and ^{13}C NMR data, the latter indicating two fully substituted alkene carbons at 132.5 and 141.8 ppm) and possessing a single chlorine atom (*m/z* 210/208, $C_8H_{15}ClOSi{\cdot}NH_4^+$). These data and the large difference in chemical shift between the two alkenyl carbon resonances are consistent with the silacyclohexenol structure **16**.[15] In order for this compound to arise a 1,2-silyl migration is required after initial C–C bond formation (Scheme 3). Changing the silicon substituents from dimethyl (**8**) to diphenyl altered the balance of the reaction in favour of silyl migration giving cyclised product **17** in 46% yield and diol **15** in only 15% yield. The inhibitory effect of phenyl (compared with methyl) silyl substituents on desilylation processes has been used to minimise allyl transfer that competes with allylsilane cycloaddition; the effect is largely steric in origin.[16]

Preparation and reactivity of silylbutyraldehyde precursors

The known difficulties with Type **I** ene cyclisations forming cyclopentanols had been reflected in the reactions of substrates **4**–**6**, **9** and **10** therefore a series of substrates **22**–**24**, bearing an extra carbon atom in the aldehyde chain, was prepared (Scheme 4). Access to these precursors was most directly achieved using 1-chloro-4-lithiobutane as a 4-oxobutyl synthon. This reagent was prepared by lithium–iodine exchange,[17,18] a method that we had found was effective in generating ω-functionalised alkyl lithium reagents.[19] The so-formed chlorides **19**–**21**, obtained in 42–82% yield, were converted directly into the corresponding aldehydes using Engel's modification[20] of the Pelter procedure.[21]

These substrates did not react in a useful manner under the conditions that had been used for both the Type II cyclisations and the alkenyl transfer processes described above. For example β,β-disubstituted vinyl silane precursor **22** failed to react at an appreciable rate at −78°C in the presence of methylaluminium dichloride; raising the temperature slowly or employing other Lewis acids at a range of temperatures generally gave products of decomposition. However, when a dilute DCM solution (0.02 M) of this aldehyde was treated with dimethylaluminium chloride at room temperature immediate effervescence was observed and TLC analysis indicated complete consumption of the precursor with the formation of a single major product. After ca. 0.5 h, aqueous work-up and column chromatography yielded two dienes **27** and **28** (Fig. 2) in a combined yield of 29% and a ratio of 7.7:1, the *E*- and *Z*-isomers being clearly distinguishable on the basis of coupling constant analysis of the protons on the internal alkene. Both *E*- (**23**) and *Z*-(**24**) alkenyl substrates gave mixtures of inseparable dienes as the only isolable products under similar reaction conditions. Stereochemical analysis by proton NMR spectroscopy was somewhat complicated by overlapping signals but could be achieved by correlation of the NMR data with those published for the stereoisomers of 2,4-hexadiene.[22] Thus, precursor **23** led to a 1.8:1 ratio of *E*,*E*- and *E*,*Z*-dienes **29** and **30** in a combined yield of 48%; precursor **24** led to a mixture of all four dienes **29**–**32** in a 1.5:1.0:1.4:1.2 ratio in a combined yield of 62%. In this series the alkynyl substrate **26** failed to afford isolable products under these or any other conditions that we tested.

Whilst these room temperature conditions are rather different to those used in our previous work it is difficult to propose an entirely satisfactory explanation of this dichotomous behaviour: alkenyl transfer in the propionaldehyde series and diene formation in the butyraldehyde series. Because the two series of substrates react under mutually incompatible conditions mechanistic insight drawn from a more direct comparison is not possible.



Scheme 4. *Reagents:* (i) $LiCH{=}CR^1R^2$, THF; (ii) AcCl; (iii) $Li(CH_2)_4Cl$; (iv) NaI, $NaHCO_3$, DMSO; (v) $LiC{\equiv}CMe$, THF.

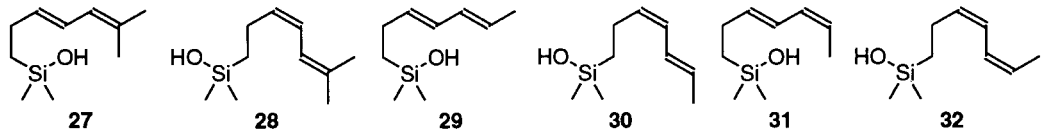


Figure 2.

Preparation and reactivity of prenylsilane ene precursors

Our investigations to this point had shown that, under the conditions we had explored, Type I carbonyl ene cyclisation of vinyl silane precursors was not a viable process, desilylative alkenyl transfer being the preferred reaction mode. Even bulky silicon substituents did not facilitate ene pathways[2] and we therefore focused on the reactions of *prenyl* silyl derivatives such as aldehyde **33** (Scheme 5) in processes mirroring the archetypal Type I ene process, the cyclisation of citronellal to isopulegol. In light of the divergent reactivity of silane ene precursors compared with all-carbon analogues it was less than obvious that such substrates would react successfully and we wished to establish some bounds to the chemistry.

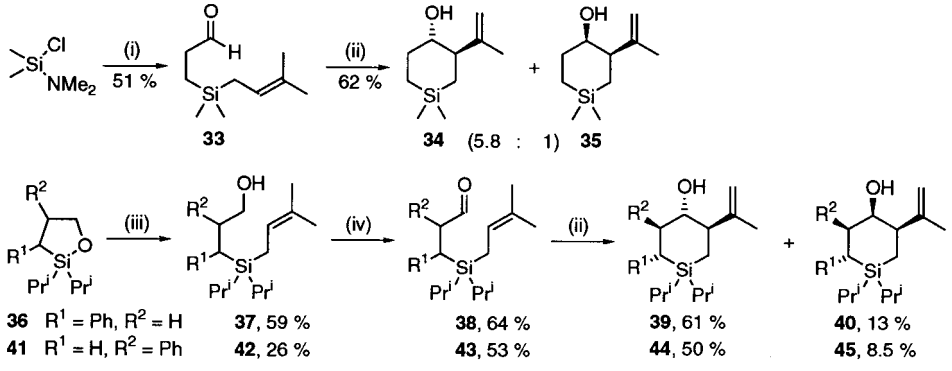
At the outset we perceived the potential reaction modes that could render ene cyclisation unsuccessful; for example Reetz had shown in early work that intramolecular allyl transfer represented a useful method for controlled delivery of an allyl function to aldehydes[23] and later reports by Hioki[24] demonstrated similar additions to iminium electrophiles. Recently, support for a non-desilylative pathway was provided by Linderman[25] who showed that a prenyl silane could cyclise onto an oxonium electrophile in a process whereby any positive charge development would be γ- to the silicon atom.

Fortunately the idea was easily tested since the precursor **33** was readily available using the methodology developed for the preparation of precursors **9** and **10**. Sequential treatment of chlorodimethyl(dimethylamino)silane with prenyllithium,[26] acetyl chloride, and 1-(*N*-pyrrolidinyl)allyllithium[10] followed by hydrolytic work-up afforded the aldehyde **33** in an acceptable 51% yield. This substrate was found to be unresponsive to Lewis acid mediation at low temperatures but, as with the earlier silylbutyraldehyde substrates **22**–**24**, success was achieved under the dimethylaluminium chloride/ambient temperature conditions and a 5.8:1 ratio of *trans*-/*cis*-ene products **34** and **35** was obtained in 62% isolated yield. Stereochemical assignment was based on coupling constant analysis [for the C*H*OH proton in **34**: δ 3.32 (td, *J*=10.6, 3.4 Hz); in **35**: δ 3.98 (br s)] assuming an equatorial isopropenyl substituent in the predominant conformer.

To provide stereochemical comparisons with the Type II series two further substrates were prepared using previously developed oxasilacyclopentane ring-opening methodology.[1a] Thus silacycle **36** was cleaved with prenyllithium and the resulting alcohol **37** oxidised to precursor **38** in moderate yield. Similarly silacycle **41**, prepared by silylation and intramolecular hydrosilylation of 2-phenyl-2-propenol,[27] was cleaved and oxidised to provide the regioisomeric precursor **43**. These substrates behaved similarly to produce the 1,2-*trans*- and 1,2-*cis*-adducts **39**, **44** and **40**, **45**, respectively in good yield. The observed relative stereochemistry can be rationalised on the basis of a *trans*-decalin-like transition state conformation giving the 1,2-*trans*-adducts (**34**, **39** and **44**) and a *cis*-decalin-like arrangement affording the 1,2-*cis*-isomers (**35**, **40** and **45**), in both cases with the phenyl substituent adopting an equatorial site during cyclisation.

Summary

Under the conditions that we have explored, silicon tethered Type I carbonyl ene cyclisations of vinyl silane precursors are not effective, the C–C bond forming step being accompanied by cleavage of the silicon atom from the alkenyl or alkynyl ene component. In some cases this process is stereospecific and reasonably efficient to provide novel silylated allylic alcohols or dienes in short sequences. Only in the case of alkynyl substrates did the silicon atom remain bound to the ene component although, even in these cases, products arising from silyl migration were obtained.



Scheme 5. *Reagents:* (i) prenyllithium, THF; AcCl; *N*-allylpyrrolidine, *s*-BuLi; aq. HCl; (ii) Me_2AlCl, CH_2Cl_2; (iii) prenyllithium, THF; (iv) PDC, MS4 Å, CH_2Cl_2.

Allylsilanes offer more promise; the prenyl systems we have tested so far are sterically and electronically biased to cyclise β- to silicon thus preventing Si–C cleavage modes. It will be of interest to compare the reactions of *E*- and *Z*-crotyl ene precursors: (a) to see if ene cyclisation remains the preferred mode; and (b) to investigate the stereospecificity of ene cyclisation.[28]

This and the preceding paper have described the majority of our studies on the methodology associated with both Type II and Type I silicon tethered ene cyclisations to produce silacyclohexanol derivatives. Our current work is centred on exploiting the combination of vinyl silane, hydroxyl and alkene functionality present in these ene adducts as part of novel syntheses of carbohydrates and natural product fragments.

Experimental

For general experimental procedures see the preceding paper in this issue.

4,4,6-Trimethyl-4-silahept-5-en-1-ol (1). To a cooled (−30°C) solution of 3-chloropropan-1-ol (210 μL, 2.50 mmol) in THF (2.5 cm^3) was added dropwise methylmagnesium chloride (880 μL of a 3 M solution in THF, 2.64 mmol) and the mixture was stirred at rt for 20 min. Magnesium turnings (91 mg, 3.75 mmol) and 1,2-dibromoethane (7 μL, 50.0 μmol) were added and the mixture heated to reflux. After 1 h 1,2-dibromoethane (7 μL, 50.0 μmol) was added and the mixture heated for a further 2.75 h. To a cooled (−78°C) solution of *t*-butyllithium (3.2 cm^3 of a 1.7 M solution in pentane, 5.44 mmol) in THF (4.5 cm^3) was added dropwise 1-bromo-2-methylpropene (280 μL, 2.75 mmol). After 1 h chlorodimethyl(dimethylamino)silane (400 μL, 2.63 mmol) was added and the mixture stirred at −78°C for 5 min then at rt for 20 min. Acetyl chloride (190 μL, 2.63 mmol) was added dropwise and the mixture was stirred for 1.5 h. This solution was then cooled (−78°C) and the Grignard reagent added; the mixture was stirred at −78°C for 45 min then at reflux for 1.75 h after which time it was added to 1 M hydrochloric acid (5 cm^3) and ether (10 cm^3). The aqueous layer was separated, extracted with ether (3×5 cm^3) and the combined organic portions washed with brine (20 cm^3), dried (magnesium sulfate) and concentrated in vacuo. The resulting oil (which could also be carried onto the next step crude) was purified by chromatography (3:1 petrol/ether) to yield *alcohol* **1** as a colourless oil (88 mg, 20%). R_f 0.35 (1:1 petrol/ether); Accurate mass: Found 117.0736, $C_5H_{13}OSi$ (MH^+−isobutene) requires 117.07357; ν_{max}/cm^{-1} 3333br s, 2954s, 1622m, 1446m, 1249s, 1177w, 1149m, 1054s, 1013m, 862s, 836s 819s, 696m; δ_H (500 MHz; C_6D_6) 0.13 (6H, s, $SiMe_2$), 0.50–0.53 (2H, m, $SiCH_2$), 0.86 (1H, br s, OH), 1.43–1.49 (2H, m, CH_2), 1.65 and 1.74 (2×3H, 2×s, Me_2C=), 3.37 (2H, t, J=6.7 Hz, CH_2OH), 5.27 (1H, s, =CH); δ_C (125 MHz; C_6D_6) −1.6, 12.6, 23.3, 29.4, 27.7, 65.6, 123.4, 152.2; *m/z* (CI) 166 (10%), 149 (10), 117 (100), 110 (25), 92 (15), 74 (25).

(*E*)-1,1-Dimethoxy-4,4-dimethyl-4-silahept-5-ene (2). To a warmed (35–40°C) suspension of magnesium turnings (136 mg, 5.58 mmol) in THF (1 cm^3) was added dropwise a solution of 3-bromo-1,1-dimethoxypropane (800 μL, 5.86 mmol) in THF (8 cm^3) and the mixture was stirred for 2.25 h. To a cooled (−78°C) solution of *t*-butyllithium (7.2 cm^3 of a 1.7 M solution in pentane, 12.2 mmol) in THF (10 cm^3) was added dropwise (*E*)-1-bromopropene (530 μL, 6.14 mmol). After 1 h chlorodimethyl(dimethylamino)silane (890 μL, 5.86 mmol) was added and the mixture stirred at −78°C for 10 min then at rt for 10 min. Acetyl chloride (420 μL, 5.86 mmol) was added dropwise and the mixture stirred for 1 h. The previously prepared Grignard solution was added to the alkenylsilane at rt and the mixture was stirred for 16 h then added to a mixture of water (15 cm^3), 1 M hydrochloric acid (5 cm^3) and ether (5 cm^3); the aqueous layer was separated, extracted with ether (3×10 cm^3) and the combined organic portions washed with brine (20 cm^3), dried (magnesium sulfate) and concentrated in vacuo. The resulting oil (which could also be carried directly onto the next step) was purified by chromatography (39:1 petrol/ether) to yield the *acetal* **2** as a colourless oil (334 mg, 30%). R_f 0.54 (3:1 petrol/ether); Accurate mass: Found 129.0736, $C_6H_{13}OSi$ (MH^+−propene−MeOH) requires 129.07357; ν_{max}/cm^{-1} 2988m, 2945s, 2829m, 1620m, 1440m, 1362m, 1249m, 1125s, 1065s, 985m, 840s, 782m, 710w; δ_H (500 MHz; $CDCl_3$) 0.03 (6H, s, $SiMe_2$), 0.53–0.56 (2H, m, $SiCH_2$), 1.54–1.58 (2H, m, CH_2), 1.80 (3H, dd, J=6.2, 1.6 Hz, MeC=), 3.31 (6H, s, 2×OMe), 4.28 (1H, t, J=5.7 Hz, $CH(OMe)_2$), 5.62 (1H, dq, J=18.4, 1.6 Hz, =CHSi), 6.06 (1H, dq, J=18.4, 6.2 Hz, MeC*H*=); δ_C (125 MHz; $CDCl_3$) −3.2, 10.1, 22.6, 26.7, 52.7, 106.4, 129.7, 142.9; *m/z* (CI) 155 (10%), 129 (15), 106 (40), 99 (10), 89 (40), 75 (100), 59 (10).

(*Z*)-1,1-Dimethoxy-4,4-dimethyl-4-silahept-5-ene (3). By a procedure analagous to that used for the preparation of *E*-isomer **2** the *title compound* **3** was obtained, after chromatography (39:1 petrol/ether), as a colourless oil (420 mg, 36%) from 3-bromo-1,1-dimethoxypropane (800 μL, 5.86 mmol), (*Z*)-1-bromopropene (530 μL, 6.14 mmol), and chlorodimethyl(dimethylamino)silane (890 μL, 5.86 mmol). R_f 0.56 (3:1 petrol/ether); Accurate mass: Found 220.1733, $C_{10}H_{26}NO_2Si$, (MNH_4^+) requires 220.17328; ν_{max}/cm^{-1} 2947s, 2829m, 1610m, 1439m, 1380m, 1361m, 1250s, 1163m, 1125s, 1064s, 962m, 840s, 776s; δ_H (500 MHz; $CDCl_3$) 0.12 (6H, s, $SiMe_2$), 0.60–0.64 (2H, m, $SiCH_2$), 1.57–1.61 (2H, m, CH_2), 1.77 (3H, dd, J=6.9, 1.5 Hz, MeC=), 3.31 (6H, s, 2×OMe), 4.29 (1H, t, J=5.7 Hz, $CH(OMe)_2$), 5.46 (1H, dq, J=14.0, 1.5 Hz, =CHSi), 6.42 (1H, dq, J=14.0, 6.9 Hz, MeC*H*=); δ_C (125 MHz; $CDCl_3$) −1.8, 10.9, 19.2, 26.8, 52.6, 106.4, 128.3, 143.9; *m/z* (CI) 171 (5%), 155 (10), 129 (20), 106 (45), 99 (10), 89 (50), 75 (100), 59 (10). Also isolated was *1,1-dimethoxy-4,4-dimethyl-4-silahept-5-yne (7)* (120 mg, 11%). R_f 0.42 (3:1 petrol/ether); Accurate mass: Found 169.1049, $C_9H_{17}OSi$ (MH^+−MeOH) requires 169.10487; ν_{max}/cm^{-1} 2947s, 2830m, 2183s, 1439w, 1379w, 1363w, 1251m, 1162m, 1125s, 1063s, 1028s, 962w, 842s, 778m; δ_H (500 MHz; $CDCl_3$) 0.14 (6H, s, $SiMe_2$), 0.60–0.63 (2H, m, $SiCH_2$), 1.64–1.69 (2H, m, CH_2), 1.88 (3H, s, MeC≡C), 3.34 (6H, s, 2×OMe), 4.33 (1H, t, J=5.7 Hz, $CH(OMe)_2$); δ_C (125 MHz; $CDCl_3$) −1.8, 4.7, 10.7, 26.6, 52.6, 82.3, 103.6, 106.1; *m/z* (CI) 169 (35%), 156 (10), 153 (15), 139 (25), 129 (35), 114 (20), 106 (100).

4,4,6-Trimethyl-4-silahept-5-enal (4). To a solution of crude alcohol **1** (1.61 g, 9.34 mmol) in DCM (30 cm^3) was added powdered molecular sieves (7 g, 4 Å) and PDC (5.27 g, 14.0 mmol) and the mixture was stirred at rt for 4 h. The mixture was added to ether (300 cm^3), filtered through a pad of Celite® and concentrated in vacuo. The resulting oil was purified by chromatography (44:1 petrol/ether) to yield *aldehyde* **4** as a colourless oil (186 mg, 13% over two steps). R_f 0.49 (6:1 petrol/ether); Accurate mass: Found 115.0579, $C_5H_{11}OSi$ (MH^+−isobutene) requires 115.05792; ν_{max}/cm^{-1} 2956m, 2910m, 1727s, 1622m, 1446m, 1372w, 1250m, 1178w, 1037m, 862s, 837s, 696w; δ_H (500 MHz; $CDCl_3$) 0.11 (6H, s, $SiMe_2$), 0.82–0.85 (2H, m, $SiCH_2$), 1.78 and 1.85 (2×3H, 2×s, Me_2C═), 2.38 (2H, ca. td, J=8.4, 1.9 Hz, CH_2), 5.14 (1H, s, ═CH), 9.75 (1H, t, J=1.9 Hz, CHO); δ_C (125 MHz; $CDCl_3$) −1.8, 8.3, 23.3, 29.4, 38.6, 121.7, 153.4, 203.2; *m/z* (CI) 171 (MH^+, 5%), 155 (10), 115 (100), 113 (5), 92 (15), 74 (10).

(*E*)-4,4-Dimethyl-4-silahept-5-enal (5). A mixture of acetal **2** (330 mg, 1.63 mmol), isopropanol (0.3 cm^3), water (1.5 cm^3), and *p*-TsOH (31 mg, 0.163 mmol) in THF (4 cm^3) was heated at reflux for 1.5 h. The reaction mixture was added to a mixture of water (10 cm^3), saturated aqueous $NaHCO_3$ (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 (15 cm^3), dried (magnesium sulfate) and concentrated in vacuo. The resulting oil was purified by chromatography (39:1 petrol/ether) to give the *aldehyde* **5** as a colourless oil (205 mg, 80%). R_f 0.54 (3:1 petrol/ether); Accurate mass: Found 156.1209, $C_8H_{18}NSi$ ($MNH_4^+-H_2O$) requires 156.12085; ν_{max}/cm^{-1} 2955m, 2912m, 2810w, 2715w, 1726s, 1620m, 1442w, 1416w, 1250s, 1177w, 1036w, 986m, 841s, 712m; δ_H (500 MHz; $CDCl_3$) 0.06 (6H, s, $SiMe_2$), 0.77–0.81 (2H, m, $SiCH_2$), 1.81 (3H, dd, J=6.2, 1.6 Hz, MeC═), 2.37 (2H, ca. td, J=8.2, 1.8 Hz, CH_2), 5.59 (1H, dq, J=18.5, 1.6 Hz, ═CHSi), 6.08 (1H, dq, J=18.5, 6.2 Hz, MeC*H*═), 9.74 (1H, t, J=1.8 Hz, CHO); δ_C (125 MHz; $CDCl_3$) −3.3, 7.4, 22.6, 38.4, 129.0, 143.7, 203.2; *m/z* (CI) 174 (MNH_4^+, 10%), 157 (MH^+, 5), 148 (10), 141 (75), 116 (30), 99 (65), 92 (10), 85 (10), 75 (35), 74 (30), 59 (50).

(*Z*)-4,4-Dimethyl-4-silahept-5-enal (6). By a procedure analogous to that used for the preparation of aldehyde **5** the *aldehyde* **6** was obtained, after purification by chromatography (39:1 petrol/ether), as a colourless oil (178 mg, 74%) from acetal **3** (311 mg, 1.54 mmol). R_f 0.54 (3:1 petrol/ether); Accurate mass: Found 174.1314, $C_8H_{20}NOSi$ (MNH_4^+) requires 174.13142; ν_{max}/cm^{-1} 2957m, 2811w, 2714w, 1726s, 1610m, 1413w, 1251m, 1179w, 1035w, 839s, 655m; δ_H (500 MHz; $CDCl_3$) 0.15 (6H, s, $SiMe_2$), 0.85–0.89 (2H, m, $SiCH_2$), 1.77 (3H, dd, J=6.9, 1.5 Hz, MeC═), 2.40 (2H, ca. td, J=8.2, 1.8 Hz, CH_2), 5.44 (1H, dq, J=14.0, 1.5 Hz, ═CH), 6.45 (1H, dq, J=14.0, 6.9 Hz, MeC*H*), 9.75 (1H, t, J=1.8 Hz, CHO); δ_C (125 MHz; $CDCl_3$) −1.8, 8.1, 19.2, 38.5, 127.4, 144.7, 203.1; *m/z* (CI) 174 (MNH_4^+, 20%), 141 (65), 115 (100), 99 (30), 92 (20), 76 (15), 59 (10).

1,1-Dimethoxy-4,4-dimethyl-4-silahept-5-yne (7). To a warmed (35–40°C) suspension of magnesium turnings (136 mg, 5.58 mmol) in THF (1 cm^3) was added dropwise a solution of 3-bromo-1,1-dimethoxypropane (800 μL, 5.86 mmol) in THF (8 cm^3) and the mixture was stirred for 1.5 h. To a cooled (−78°C) solution of (*Z*)-1-bromopropene (350 μL, 4.09 mmol) in THF (2.5 cm^3) was added dropwise *n*-butyllithium (3.6 cm^3 of a 1.6 M solution in hexanes, 5.73 mmol). After 2 h chlorodimethyl(dimethylamino)silane (570 μL, 3.72 mmol) was added and the mixture stirred for 10 min at −78°C and at rt for 1 h. To the cooled (0°C) silane mixture was added dropwise acetyl chloride (265 μL, 3.72 mmol) and the mixture stirred at 0°C for 10 min and at rt for 1 h. The previously prepared Grignard solution was transferred by cannula to the alkynylsilane at 0°C and the mixture was allowed to warm up to rt over 13 h. The reaction mixture was added to a mixture of water (25 cm^3), 1 M hydrochloric acid (1 cm^3) and ether (15 cm^3); the aqueous layer was separated, extracted with ether (3×15 cm^3) and the combined organic portions washed with brine (20 cm^3), dried (magnesium sulfate) and concentrated in vacuo. The resulting oil was carried onto the next step crude (746 mg, > quantitative). Data for *alkynylsilane* **7** are reported above (in the preparation of alkenylsilane **3**).

4,4-Dimethyl-4-silahept-5-ynal (8). A mixture of crude acetal **7** (746 mg, contains ≤3.72 mmol), isopropanol (0.72 cm^3), water (3.6 cm^3) and *p*-TsOH (70 mg, 0.372 mmol) in THF (7.5 cm^3) was heated at reflux for 1.5 h. The reaction mixture was added to a mixture of water (5 cm^3), saturated aqueous sodium hydrogen carbonate solution (20 cm^3) and ether (15 cm^3) and the separated aqueous layer was extracted with ether (3×5 cm^3). The combined organic portions were washed with brine (20 cm^3), dried (magnesium sulfate) and concentrated in vacuo. The resulting oil was purified by chromatography (25:1 petrol/ether) to yield the *aldehyde* **8** as a colourless oil (265 mg, 46% over two steps). R_f 0.43 (3:1 petrol/ether); Accurate mass: Found 155.0892, $C_8H_{15}OSi$ (MH^+) requires 155.08922; ν_{max}/cm^{-1} 2960m, 2920m, 2815w, 2720w, 2182s, 1725s, 1413m, 1253s, 1179w, 1028s, 841s; δ_H (500 MHz; $CDCl_3$) 0.14 (6H, s, $SiMe_2$), 0.82–0.85 (2H, m, $SiCH_2$), 1.87 (3H, s, MeC≡), 2.49 (2H, ca. td, J=8.2, 1.6 Hz, CH_2), 9.77 (1H, t, J=1.6 Hz, CHO); δ_C (125 MHz; $CDCl_3$) −1.8, 4.8, 8.0, 38.4, 81.7, 104.4, 202.9; *m/z* (CI) 155 (MH^+, 5%), 154 (10), 148 (10), 139 (80), 116 (20), 115 (100), 114 (20), 99 (25), 97 (55), 75 (20), 74 (20), 67 (10).

(*E*)-4-*t*-Butyl-4-phenyl-4-silahept-5-enal (9). To a cooled (−78°C) solution of *t*-butyllithium (670 μL of a 1.7 M solution in pentane, 1.14 mmol) in THF (1.5 cm^3) was added dropwise (*E*)-1-bromopropene (50 μL, 0.572 mmol). After 1 h *t*-butyldichlorophenylsilane (127 μL, 0.44 mmol) was added and the mixture was stirred for 3 h then allowed to warm up to rt over 18 h. To a cooled (−78°C) solution of *N*-allylpyrrolidine (130 μL, 0.97 mmol) in THF (2 cm^3) was added dropwise *s*-butyllithium (1.5 cm^3 of a 1.3 M solution in cyclohexane, 1.94 mmol) and the solution was allowed to warm up to −10°C over 1.5 h then stirred at −10°C for 2 h. To this cooled (−78°C) mixture was added the previously prepared chlorosilane solution and the mixture was stirred at −78°C for 2 h then allowed to warm up to rt over 19 h. The reaction mixture was added to 1 M hydrochloric acid (20 cm^3) and ether (10 cm^3); the aqueous layer was

separated, extracted with ether (3?×10 cm^3) and the combined organic portions were washed with brine (20 cm^3), dried (magnesium sulfate) and concentrated in vacuo. The resulting oil was purified by chromatography (49:1 petrol/ether) to yield the *aldehyde* **9** as a colourless oil (35 mg, 30%). R_f 0.47 (3:1 petrol/ether); Accurate mass: Found 278.1940, $C_{16}H_{28}NOSi$ (MNH_4^+) requires 278.19402; ν_{max}/cm^{-1} 2954s, 2928s, 2856s, 1724s, 1618m, 1471m, 1428m, 1107m, 988m, 821m, 738m, 702s; δ_H (500 MHz; $CDCl_3$) 0.93 (9H, s, Bu^{t}Si), 1.15 (1H, ddd, *J*=15.0, 11.5, 5.4 Hz) and 1.27 (1H, ddd, *J*=15.0, 11.5, 5.2 Hz, $SiCH_2$), 1.93 (3H, dd, *J*=6.2, 1.7 Hz, MeC=), 2.38 (1H, dddd, *J*=17.1, 11.5, 5.2, 1.4 Hz) and 2.42 (1H, dddd, *J*=17.1, 11.5, 5.4, 1.4 Hz, CH_2), 5.85 (1H, dq, *J*=18.7, 1.7 Hz, =CHSi), 6.24 (1H, dq, *J*=18.7, 6.2 Hz, MeC*H*=), 7.37–7.39 (3H, m) and 7.52 (2H, dd, *J*=7.4, 1.9 Hz, Ph), 9.76 (1H, t, *J*=1.4 Hz, CHO); δ_C (125 MHz; $CDCl_3$) 0.8, 17.4, 23.1, 26.8, 38.8, 123.3, 127.6, 129.1, 134.0, 135.3, 146.9, 203.0; *m/z* (CI) 278 (MNH_4^+, 55%), 275 (100), 261 (MH^+, 20), 245 (30), 220 (40), 219 (40), 218 (40), 203 (80), 196 (40), 175 (30), 160 (15), 122 (15), 105 (15), 78 (15).

(*Z*)-4-*t*-Butyl-4-phenyl-4-silahept-5-enal (10). To a cooled (−20°C) suspension of lithium shot (20 mg, 2.88 mmol) in ether (3.5 cm^3) was added dropwise (*Z*)-1-bromopropene (125 μL, 1.44 mmol). After the lithium had dissolved (ca 1 h) *t*-butyldichlorophenylsilane (275 μL, 1.20 mmol) was added and the mixture was allowed to warm up to rt over 19 h. From this point the procedure followed that described for aldehyde **9** [using *N*-allylpyrrolidine (345 μL, 2.64 mmol) and *s*-butyllithium (4.1 cm^3 of a 1.3 M solution in cyclohexane, 5.28 mmol)] to produce the *aldehyde* **10** as a colourless oil (52 mg, 17%) after purification by chromatography (5:1 petrol/ether). R_f 0.51 (3:1 petrol/ether); Accurate mass: Found 278.1940, $C_{16}H_{28}NOSi$ (MNH_4^+) requires 278.19402; ν_{max}/cm^{-1} 3070m, 3050m, 2956s, 2928s, 2857s, 2713m, 1724s, 1607s, 1472s, 1420s, 1391m, 1362s, 1177s, 1108s, 1035m, 1008m, 880m, 822s, 738s, 702s, 664s, 619s; δ_H (500 MHz; $CDCl_3$) 0.94 (9H, s, Bu^{t}Si), 1.26 (1H, ddd, *J*=15.0, 9.6, 7.7 Hz) and 1.34 (1H, ddd, *J*=15.0, 9.6, 7.5 Hz, $SiCH_2$), 1.62 (3H, dd, *J*=6.9, 1.5 Hz, MeC=), 2.45–2.49 (2H, m, CH_2), 5.76 (1H, dq, *J*=14.2, 1.5 Hz, =CHSi), 6.73 (1H, dq, *J*=14.2, 6.9 Hz, MeC*H*=), 7.34–7.38 (3H, m) and 7.53–7.55 (2H, m, Ph), 9.78 (1H, t, *J*=1.4 Hz, CHO); δ_C (125 MHz; $CDCl_3$) 2.4, 17.5, 20.5, 26.8, 39.0, 122.0, 127.6, 129.0, 134.8, 135.0, 147.6, 202.9; *m/z* (CI) 278 (MNH_4^+, 20%), 261 (MH^+, 5), 219 (20), 203 (100), 196 (20), 192 (10), 175 (35), 161 (25), 125 (10), 105 (15).

(*Z*)-2-Methyl-2-silaoct-6-en-2,5-diol (13). To a cooled (−78°C) solution of aldehyde **6** (73 mg, 0.47 mmol) in DCM (1.6 cm^3) was added dropwise methylaluminium dichloride (0.7 cm^3 of a 1.0 M solution in hexanes, 0.7 mmol). After 1.75 h, water (1 cm^3) was added and the mixture allowed to warm up to rt then added to a mixture of ether (10 cm^3) and water (5 cm^3). The separated aqueous layer was extracted with ether (3×8 cm^3) and the combined organic portions washed with brine (10 cm^3), dried (magnesium sulfate) and concentrated in vacuo. The resulting oil was purified by chromatography (9:1→1:1 petrol/ether) to yield the *title compound* **13** as a colourless oil (49 mg, 60%). R_f 0.13 (1:1 petrol/ether); Accurate mass: Found 157.1049, $C_8H_{17}OSi$ (MH^+-H_2O) requires 157.10487; ν_{max}/cm^{-1} 3352br s, 3014s, 2926s, 1660w, 1446m, 1415m, 1254s, 1179s, 1056s, 1007s, 843s, 785s; δ_H (500 MHz; $CDCl_3$) 0.05 (6H, s, $SiMe_2$), 0.46 (1H, ddd, *J*=14.4, 12.9, 4.8 Hz) and 0.54 (1H, ddd, *J*=14.4, 12.9, 4.8 Hz, $SiCH_2$), 1.44 (1H, ddt, *J*=12.9, 5.5, 4.8 Hz) and 1.59 (1H, qd, *J*=12.9, 5.5 Hz, CH_2), 1.67 (3H, dd, *J*=6.9, 1.7 Hz, MeC=), 1.88 (1H, br s, OH), 4.37 (1H, apparent q, *J*=6.6 Hz, C*H*OH), 5.36 (1H, ddq, *J*=11.0, 7.1, 1.7 Hz, MeCH=C*H*), 5.59 (1H, dq, *J*=11.0, 6.9 Hz, MeC*H*=); δ_C (125 MHz; $CDCl_3$) 0.2, 13.4, 13.5, 30.9, 69.5, 126.4, 133.3; *m/z* (CI) 174 (5%), 166 (15), 157 (50), 156 (30), 141 (45), 128 (15), 113 (40), 92 (100), 75 (15).

Treatment of aldehyde (8) with methylaluminium dichloride. To a cooled (−78°C) solution of aldehyde **8** (145 mg, 0.94 mmol) in DCM (13 cm^3) was added dropwise methylaluminium dichloride (1.4 cm^3 of a 1.0 M solution in hexanes, 1.4 mmol). After 2.75 h, water (10 cm^3) was added, the mixture allowed to warm up to rt, and the separated aqueous layer extracted with ether (2×15 cm^3). The combined organic portions were washed with brine (20 cm^3), dried (magnesium sulfate), concentrated in vacuo and the resulting oil purified by chromatography (20:1→1:1 petrol/ether) to yield *alkyne* **14** (54 mg, 34%) and *silacycle* **16** (35 mg, 20%) as colourless oils. Data for *2-methyl-2-silaoct-6-yn-2,5-diol (**14**):* R_f 0.18 (1:1 petrol/ether); Accurate mass: Found 172.1158, $C_8H_{16}NOSi$ ($MNH_4^+-H_2O$) requires 172.11577; ν_{max}/cm^{-1} 3352br s, 2955s, 2922s, 2232w, 1418m, 1339w, 1254s, 1182m, 1057s, 1013s, 928w, 843s, 792s, 706m; δ_H (500 MHz; $CDCl_3$) 0.07 (6H, s, $SiMe_2$), 0.62–0.65 (2H, m, $SiCH_2$), 1.63–1.69 (2H, m, CH_2), 1.84 (3H, d, *J*=1.3 Hz, MeC≡), 2.22 (1H, br s, OH), 4.26 (1H, br t, *J*=6.0 Hz, C*H*OH); δ_C (125 MHz; $CDCl_3$) 0.2, 3.5, 13.3, 31.9, 64.7, 80.3, 80.9; *m/z* (CI) 172 (25%), 155 (70), 154 (75), 148 (20), 139 (65), 126 (65), 115 (30), 114 (55), 97 (85), 92 (95), 75 (100), 74 (95), 60 (15). Data for *2-Chloro-3,4,4-trimethyl-4-silacyclohex-2-enol (**16**):* R_f 0.51 (1:1 petrol/ether); Accurate mass: Found 208.0924, $C_8H_{19}ClNOSi$ (MNH_4^+) requires 208.09244; ν_{max}/cm^{-1} 3372br s, 2955s, 2918s, 2856m, 1609s, 1443m, 1410m, 1250s, 1154s, 1095m, 1050s, 1001s, 959s, 913m, 845s, 799s, 768s, 678s, 615s; δ_H (500 MHz; $CDCl_3$) 0.15 and 0.19 (2×3H, 2×s, $SiMe_2$), 0.68 (1H, ddd, *J*=14.5, 8.4, 3.3 Hz) and 1.00 (1H, ddd, *J*=14.5, 11.7, 3.6 Hz, $SiCH_2$), 1.87 (3H, s, MeC=), 2.05–2.16 (2H, m, CH_2), 2.48 (1H, br s, OH), 4.31 (1H, br s, C*H*OH); δ_C (125 MHz; $CDCl_3$) −3.8, −3.4, 5.8, 17.1, 28.7, 73.4, 132.5, 141.8; *m/z* (CI) 208 ($M(^{35}Cl)NH_4^+$, 10%), 192 (15), 190 (35), 175 (10), 173 (25), 172 (20), 155 (40), 154 (35), 139 (45), 115 (100), 97 (30), 92 (25), 75 (45), 74 (40).

Treatment of 4,4-diphenyl-4-silahept-5-ynal[2] with methylaluminium dichloride. To a cooled (−78°C) solution of 4,4-diphenyl-4-silahept-5-ynal (135 mg, 0.49 mmol) in DCM (3 cm^3) was added dropwise methylaluminium dichloride (730 μL of a 1.0 M solution in hexanes, 0.73 mmol). After 7.5 h water (25 cm^3) was added and the mixture allowed to warm up to rt over 1 h. The separated aqueous layer was extracted with ether (3×8 cm^3) and the combined organic portions were washed with brine (15 cm^3), dried (magnesium sulfate) and concentrated in

vacuo. The resulting oil was purified by chromatography (34:1→3:1 petrol/ether) to yield *silacycle* **17** (70 mg, 46%) and *alkyne* **15** (23 mg, 15%) as colourless viscous oils. Data for *2-chloro-3-methyl-4,4-diphenyl-4-silacyclohex-2-enol (**17**):* R_f 0.02 (3:1 petrol/ether); Accurate mass: Found 296.0788, $C_{18}H_{17}ClSi$ (M^+-H_2O) requires 296.07880; ν_{max}/cm^{-1} 3401br w, 3069w, 3049w, 2917m, 1606m, 1428s, 1152m, 1112s, 1049w, 998m, 959w, 909w, 829s, 725s, 699s; δ_H (500 MHz; $CDCl_3$) 1.14 (1H, ddd, J=15.0, 7.6, 4.0 Hz) and 1.54 (1H, ddd, J=15.0, 9.4, 5.9 Hz, $SiCH_2$), 1.90 (3H, s, MeC=), 2.18–2.22 (2H, m, CH_2), 2.64 (1H, br s, OH), 4.47 (1H, br s, C*H*OH), 7.40–7.49 (6H, m) and 7.57–7.61 (4H, m, 2×Ph); δ_C (125 MHz; $CDCl_3$) 4.7, 18.5, 28.4, 73.4, 128.0, 128.1, 129.4, 130.0, 133.1, 135.2, 135.3, 144.9 {some overlap in aromatic region}; *m/z* (EI) 298 (15%), 296 (40), 261 (100), 219 (30), 217 (65), 180 (30), 155 (20), 141 (15), 78 (10), 63 (20), 51 (20). Data for *1,1-diphenyl-1-silahept-5-yn-1,4-diol (**15**):* R_f 0.47 (1:1 petrol/EtOAc); Accurate mass: Found 279.1205, $C_{18}H_{19}OSi$ (MH^+-H_2O) requires 279.12052; ν_{max}/cm^{-1} 3370br m, 3069m, 2919w, 2231w, 1428s, 1174w, 1119s, 1068w, 1010m, 998m, 972w, 866m, 737s, 700s; δ_H (500 MHz; $CDCl_3$) 1.21–1.38 (4H, m, C_2H_4), 1.84 (3H, s, MeC≡), 3.13 (1H, br s, OH), 4.37 (1H, br s, C*H*OH), 7.38–7.41 (6H, m) and 7.61–7.64 (4H, m, 2×Ph); δ_C (125 MHz; $CDCl_3$) 3.5, 10.5, 31.5, 64.4, 80.0, 81.5, 127.9, 129.8, 134.2, 134.4; *m/z* (CI) 296 (30%), 279 (100), 267 (85), 250 (95), 239 (25), 221 (60), 216 (30), 199 (20), 178 (20), 155 (15), 138 (10), 105 (25), 77 (10).

***cis*-1-*t*-Butyl-2-oxa-1-phenyl-3-[(*Z*)-propen-1-yl]-1-silacyclopentane (18).** To a cooled (−78°C) solution of aldehyde **10** (22 mg, 84.5 μmol) in DCM (1.5 cm^3) was added dropwise methylaluminium dichloride (130 μL of a 1.0 M solution in hexanes, 0.13 mmol). After 3 h water (1 cm^3) was added, the mixture allowed to warm up to rt, and then added to a mixture of ether (10 cm^3) and water (5 cm^3). The separated aqueous layer was extracted with ether (3×8 cm^3) and the combined organic portions were washed with brine (10 cm^3), dried (magnesium sulfate) and concentrated in vacuo. The resulting oil was purified by chromatography (100:0→100:1 petrol/ether) to yield the *title compound* **18** as a colourless oil (15 mg, 68%). R_f 0.64 (3:1 petrol/ether); Accurate mass: Found 261.1675, $C_{16}H_{25}OSi$ (MH^+) requires 261.16746; ν_{max}/cm^{-1} 3020m, 2956s, 2930s, 2858s, 1472s, 1428m, 1362m, 1114s, 1002s, 959s, 866s, 831s, 817s, 772m, 721s, 701s, 610s; δ_H (500 MHz; C_6D_6) 0.91 (1H, d, J=7.6 Hz) and 0.92 (1H, dd, J=14.9, 7.7 Hz, $SiCH_2$), 1.02 (9H, s, Bu^{t}Si), 1.39–1.47 (1H, m) and 1.95 (1H, ddd, J=17, 7.7, 4.6 Hz, CH_2), 1.51 (3H, dd, J=6.9, 1.7 Hz, MeC=), 4.82 (1H, td, J=8.4, 4.6 Hz, CHOSi), 5.37 (1H, dq, J=11, 6.9 Hz, MeC*H*=), 5.56 (1H, ddq, J=11, 8.4, 1.7 Hz, MeCH=C*H*), 7.17–7.22 (3H, m) and 7.66–7.68 (2H, m, Ph); δ_C (125 MHz; $CDCl_3$) 7.3, 13.2, 18.4, 26.0, 31.9, 75.0, 125.3, 127.5, 129.4, 133.5, 134.0, 135.6; *m/z* (CI) 278 (MNH_4^+, 45%), 261 (MH^+, 100), 220 (20), 203 (10), 196 (20), 175 (25), 155 (10).

1-Chloro-5,5,7-trimethyl-5-silaoct-6-ene (19). To a cooled (−78°C) solution of *t*-butyllithium (6.8 cm^3 of a 1.7 M solution in pentane, 11.6 mmol) in ether (9 cm^3) was added dropwise 1-bromo-2-methylpropene (595 μL, 5.78 mmol) and the mixture stirred for 1 h. Chlorodimethyl(dimethylamino)silane (0.8 cm^3, 5.26 mmol) was added and the mixture was allowed to warm up to rt over 35 min. To the cooled (0°C) silane mixture was added dropwise acetyl chloride (375 μL, 5.26 mmol) and the mixture stirred at rt for 1.5 h. To a cooled (−78°C) solution of 4-chloro-1-iodobutane (960 μL, 7.86 mmol) in ether (16 cm^3) was added dropwise *t*-butyllithium (9.3 cm^3 of a 1.7 M solution in pentane, 15.8 mmol). After 20 min the previously prepared chlorosilane solution was added by cannula to the organolithium reagent at −78°C and the mixture was allowed to warm up to rt over 15 h. The reaction mixture was added to water (40 cm^3), extracted with ether (3×20 cm^3) and the combined organic portions washed successively with 0.5 M aqueous sodium thiosulfate solution (20 cm^3), brine (20 cm^3), then dried (magnesium sulfate) and concentrated in vacuo. The resulting oil was purified by chromatography (100:0→100:1 petrol/ether) to yield the *silane* **19** as a colourless oil (454 mg, 42%). R_f 0.65 (50:1 petrol/ether); Accurate mass: Found 206.1132, $C_9H_{21}ClNSi$ ($MNH_4^+-CH_4$) requires 206.11318; ν_{max}/cm^{-1} 2957s, 2932s, 2912s, 1622s, 1446s, 1371m, 1290m, 1248s, 1149m, 1040w, 958m, 862s, 837s, 816s, 773m, 733m, 697m, 653m; δ_H (500 MHz; $CDCl_3$) 0.09 (6H, s, $SiMe_2$), 0.56–0.60 (2H, m, $SiCH_2$), 1.43–1.49 (2H, m, CH_2CH_2Si), 1.77–1.83 (2H, m, CH_2CH_2Cl), 1.78 (3H, s) and 1.85 (3H, s, Me_2C=), 3.55 (2H, t, J=6.8 Hz, CH_2Cl), 5.17 (1H, s, =CHSi); δ_C (125 MHz; $CDCl_3$) −1.7, 15.8, 21.3, 23.3, 29.4, 36.2, 44.8, 122.7, 152.4; *m/z* (CI) 208 (10%), 206 (25), 189 (10), 169 (35), 168 (98), 166 (100), 167 (55), 152 (30), 150 (80), 151 (60), 149 (100), 133 (15), 131 (70), 130 (100), 113 (65), 110 (80), 91 (50), 74 (40), 59 (15).

(*E*)-1-Chloro-5,5-dimethyl-5-silaoct-6-ene (20). To a cooled (−20°C) suspension of lithium shot (35 mg, 5.0 mmol) in ether (6 cm^3) was added dropwise (*E*)-1-bromopropene (245 μL, 2.87 mmol) and the mixture was stirred until the lithium had dissolved (ca 1 h). From this point the procedure followed that used in the preparation of **19** (above); from chlorodimethyl(dimethylamino)silane (345 μL, 2.27 mmol) the *silane* **20** was obtained as a colourless oil (208 mg, 48%) after chromatography. R_f 0.62 (50:1 petrol/ether); Accurate mass: Found 192.0975, $C_8H_{19}ClNSi$ ($MNH_4^+-CH_4$) requires 192.09753; ν_{max}/cm^{-1} 2991m, 2956s, 2936s, 2913s, 2874m, 1621s, 1445m, 1290w, 1248s, 1053m, 985s, 958w, 838s, 794s, 741m, 710m, 653s; δ_H (500 MHz; $CDCl_3$) 0.04 (6H, s, $SiMe_2$), 0.53–0.56 (2H, m, $SiCH_2$), 1.42–1.48 (2H, m, CH_2CH_2Si), 1.76–1.83 (2H, m, CH_2CH_2Cl), 1.82 (3H, dd, J=6.2, 1.6 Hz, MeC=), 3.54 (2H, t, J=6.7 Hz, CH_2Cl), 5.63 (1H, dq, J=18.4, 1.6 Hz, =CHSi), 6.07 (1H, dq, J=18.4, 6.2 Hz, MeC*H*=); δ_C (125 MHz; $CDCl_3$) −3.1, 15.0, 21.2, 22.6, 36.2, 44.8, 130.0, 142.8; *m/z* (CI) 192 (5%), 175, (5), 168 (10), 166 (30), 151 (10), 149 (25), 138 (10), 136 (30), 116 (100), 99 (60), 74 (15), 59 (20).

(*Z*)-1-Chloro-5,5-dimethyl-5-silaoct-6-ene (21). To a cooled (−20°C) suspension of lithium shot (80 mg, 11.6 mmol) in ether (9 cm^3) was added dropwise (*Z*)-1-bromopropene (565 μL, 6.65 mmol) and the mixture stirred until the lithium had dissolved (ca 1 h). From this point the procedure followed that used in the preparation of **19**

(above); from chlorodimethyl(dimethylamino)silane (0.8 cm^3, 5.26 mmol) the *silane* **21** was obtained as a colourless oil (819 mg, 82%) after chromatography. R_f 0.62 (50:1 petrol/ether); Accurate mass: Found 192.0975, $C_8H_{19}ClNSi$ ($MNH_4^+-CH_4$) requires 192.09753; ν_{max}/cm^{-1} 2957s, 2935s, 1610s, 1446m, 1382w, 1290m, 1249s, 1160w, 1053m, 957m, 838s, 770s, 732m, 653s; δ_H (500 MHz; $CDCl_3$) 0.13 (6H, s, $SiMe_2$), 0.60–0.64 (2H, m, $SiCH_2$), 1.45–1.51 (2H, m, CH_2CH_2Si), 1.77–1.83 (2H, m, CH_2CH_2Cl), 1.78 (3H, dd, J=6.7, 1.5 Hz, MeC=), 3.55 (2H, t, J=6.7 Hz, CH_2Cl), 5.48 (1H, dq, J=13.9, 1.5 Hz, =CHSi), 6.44 (1H, dq, J=13.9, 6.7 Hz, MeC*H*=); δ_C (125 MHz; $CDCl_3$) −1.7, 15.7, 19.1, 21.3, 36.1, 44.7, 128.6, 143.8; *m/z* (CI) 192 (5%), 175 (5), 168(10), 166 (25), 151 (10), 149 (25), 138 (15), 136 (35), 116 (100), 110 (10), 99 (20), 74 (15), 59 (15).

5,5,7-Trimethyl-5-silaoct-6-enal (22). A mixture of chloride **19** (335 mg, 1.64 mmol), sodium hydrogen carbonate (180 mg, 2.13 mmol) and sodium iodide (0.49 g, 3.27 mmol) in DMSO (3 cm^3) was heated (115°C) for 3 h. The cooled reaction mixture was added to water (30 cm^3), extracted with ether (3×10 cm^3) and the combined organic portions washed with water (2×15 cm^3), brine (15 cm^3), dried (magnesium sulfate) and concentrated in vacuo. The resulting oil was purified by chromatography (50:1 petrol/ether) to yield the *aldehyde* **22** as a colourless oil (128 mg, 42%). R_f 0.57 (3:1 petrol/ether); Accurate mass: Found 169.1049, $C_9H_{17}OSi$ (MH^+-CH_4) requires 169.10487; ν_{max}/cm^{-1} 2954s, 2932s, 2910s, 2716m, 1728s, 1622s, 1445m, 1414m, 1371m, 1248s, 1177m, 1149m, 1058m, 1017w, 860s, 837s, 816s, 775m, 696m; δ_H (500 MHz; $CDCl_3$) 0.09 (6H, s, $SiMe_2$), 0.59–0.62 (2H, m, $SiCH_2$), 1.63–1.69 (2H, m, CH_2CH_2Si), 1.77 (3H, s) and 1.84 (3H, s, Me_2C=), 2.44 (2H, td, J=7.2, 1.9 Hz, CH_2CHO), 5.15 (1H, s, =CHSi), 9.75 (1H, t, J=1.9 Hz, CHO); δ_C (125 MHz; $CDCl_3$) −1.8, 16.4, 17.0, 23.3, 29.4, 47.4, 122.4, 152.7, 203.0; *m/z* (CI) 169 (20%), 167 (10), 141 (10), 129 (100), 113 (25), 73 (25), 59 (15).

(*E*)-5,5-Dimethyl-5-silaoct-6-enal (23). A procedure analogous to that used for the preparation of aldehyde **22** was used to prepare *aldehyde* **23** which was obtained from chloride **20** (289 mg, 1.51 mmol) as a colourless oil (70 mg, 27%; 41% based on recovered chloride **20**, 98 mg) after chromatography (45:1 petrol/ether). R_f 0.53 (3:1 petrol/ether); Accurate mass: Found 188.1471, $C_9H_{22}NOSi$ (MNH_4^+) requires 188.14707; ν_{max}/cm^{-1} 2955s, 2816m, 2716m, 1728s, 1621s, 1443m, 1414m, 1249s, 1177w, 1058m, 986m, 838s, 783s, 745m, 710m; δ_H (500 MHz; $CDCl_3$) 0.04 (6H, s, $SiMe_2$), 0.54–0.58 (2H, m, $SiCH_2$), 1.65 (2H, ca. quin., J=7.3 Hz, CH_2CH_2Si), 1.82 (3H, dd, J=6.2, 1.6 Hz, MeC=), 2.45 (2H, td, J=7.3, 1.9 Hz, CH_2CHO), 5.62 (1H, dq, J=18.4, 1.6 Hz, =CHSi), 6.06 (1H, dq, J=18.4, 6.2 Hz, MeC*H*=), 9.75 (1H, t, J= 1.9 Hz, CHO); δ_C (125 MHz; $CDCl_3$) −3.2, 15.6, 16.9, 22.6, 47.4, 129.7, 143.0, 203.1; *m/z* (CI) 188 (MNH_4^+, 35%), 155 (40), 142 (30), 129 (100), 116 (30), 99 (20), 74 (15), 59 (15).

(*Z*)-5,5-Dimethyl-5-silaoct-6-enal (24). A procedure analogous to that used for the preparation of aldehyde **22** was used to prepare *aldehyde* **24** which was obtained from chloride **21** (0.81 g, 4.25 mmol) as a colourless oil (302 mg, 42%) after chromatography (50:1 petrol/ether). R_f 0.53 (3:1 petrol/ether); Accurate mass: Found 188.1471, $C_9H_{22}NOSi$ (MNH_4^+) requires 188.14707; ν_{max}/cm^{-1} 2956s, 2715m, 1734s, 1611s, 1420m, 1357w, 1249s, 1177m, 1057m, 837s, 778s, 652s; δ_H (500 MHz; $CDCl_3$) 0.13 (6H, s, $SiMe_2$), 0.61–0.65 (2H, m, $SiCH_2$), 1.64–1.70 (2H, m, CH_2CH_2Si), 1.77 (3H, dd, J=6.8, 1.5 Hz, MeC=), 2.46 (2H, td, J=7.2, 1.9 Hz, CH_2CHO), 5.46 (1H, dq, J=13.9, 1.5 Hz, =CHSi), 6.43 (1H, dq, J=13.9, 6.8 Hz, MeC*H*=), 9.75 (1H, t, J=1.9 Hz, CHO); δ_C (125 MHz; $CDCl_3$) −1.8, 16.3, 16.9, 19.1, 47.3, 128.2, 144.0, 203.0; *m/z* (CI) 188 (MNH_4^+, 30%), 155 (30), 129 (100), 116 (25), 74 (10), 59 (10).

1-Chloro-5,5-dimethyl-5-silaoct-6-yne (25). To a cooled (−78°C) solution of (*Z*)-1-bromopropene (560 μL, 6.59 mmol) in THF (4 cm^3) was added dropwise *n*-butyllithium (4 cm^3 of a 2.3 M solution in hexanes, 9.2 mmol). After 2 h chlorodimethyl(dimethylamino)silane (770 μL, 5.07 mmol) was added then the rest of the procedure followed that used in the preparation of **19** (above). The *silane* **25** was obtained as a colourless oil (462 mg, 48%) after chromatography (100:0→100:1 petrol/ether). R_f 0.33 (50:1 petrol/ether); Accurate mass: Found 190.0819, $C_8H_{17}ClNSi$ ($MNH_4^+-CH_4$) requires 190.08188; ν_{max}/cm^{-1} 2958s, 2935s, 2920s, 2874m, 2183s, 1446m, 1413m, 1291m, 1250s, 1161w, 1028s, 958m, 842s, 823s, 781s, 768s, 732m, 708m, 678m, 644m; δ_H (500 MHz; $CDCl_3$) 0.13 (6H, s, $SiMe_2$), 0.58–0.61 (2H, m, $SiCH_2$), 1.49–1.55 (2H, m, CH_2CH_2Si), 1.82 (2H, ca. quin., J=6.8 Hz, CH_2CH_2Cl), 1.88 (3H, s, MeC≡), 3.55 (2H, t, J=6.8 Hz, CH_2Cl); δ_C (125 MHz; $CDCl_3$) −1.7, 4.8, 15.5, 21.1, 35.8, 44.7, 82.6, 103.6; *m/z* (CI) 206 ($M(^{35}Cl)NH_4^+$, 5%), 190 (10), 173 (10), 168 (20), 166 (50), 151 (10), 149 (20), 134 (10), 114 (100), 110 (30), 97 (70), 91 (20), 74 (30).

5,5-Dimethyl-5-silaoct-6-ynal (26). A procedure analogous to that used for the preparation of aldehyde **22** was used to prepare *aldehyde* **26** which was obtained from chloride **25** (450 mg, 2.38 mmol) as a colourless oil (188 mg, 47%) after chromatography (45:1 petrol/ether). R_f 0.43 (3:1 petrol/ether); Accurate mass: Found 186.1314, $C_9H_{20}NOSi$ (MNH_4^+) requires 186.13142; ν_{max}/cm^{-1} 2958m, 2920m, 2819w, 2718w, 2182s, 1727s, 1413w, 1251s, 1178w, 1146w, 1058m, 1028s, 842s, 819s, 779s, 696w; δ_H (500 MHz; $CDCl_3$) 0.11 (6H, s, $SiMe_2$), 0.58–0.61 (2H, m, $SiCH_2$), 1.68–1.74 (2H, m, CH_2CH_2Si), 1.85 (3H, s, MeC≡), 2.47 (2H, td, J=7.3, 1.8 Hz, CH_2CHO), 9.74 (1H, t, J=1.8 Hz, CHO); δ_C (125 MHz; $CDCl_3$) −1.8, 4.8, 16.0, 16.7, 47.0, 82.3, 103.8, 202.8; *m/z* (CI) 186 (MNH_4^+, 15%), 153 (20), 140 (100), 129 (85), 125 (20), 114 (30), 97 (35), 74 (10).

Treatment of aldehyde (22) with dimethylaluminium chloride. To a solution of aldehyde **22** (60 mg, 0.325 mmol) in DCM (16 cm^3) at rt was added dropwise dimethylaluminium chloride (490 μL of a 1.0 M solution in hexanes, 0.49 mmol). After 35 min 1 M aqueous sodium hydroxide solution (10 cm^3) was added and the mixture stirred vigorously for 45 min. Water (15 cm^3) was added to the separated aqueous layer that was then extracted with ether (2×10 cm^3) and the combined organic portions

were washed with brine (20 cm^3), dried (magnesium sulfate) and concentrated in vacuo. The resulting oil was purified by chromatography (10:1 petrol/ether) to yield a mixture of *dienes* **27** and **28** (7.7:1) as a colourless oil (17 mg, 29%). R_f 0.47 (major) and 0.59 (minor) (1:1 petrol/ether); Accurate mass: Found 185.1366, $C_{10}H_{21}OSi$ (MH^+) requires 185.13617; ν_{max}/cm^{-1} 3306br s, 3019s, 2960s, 2914s, 1661w, 1622w, 1443m, 1410m, 1378m, 1319w, 1252s, 1172m, 1039m, 987s, 958s, 856s, 778s, 702m; *m/z* (CI) 202, (MNH_4^+, 10%), 186 (10), 185 (MH^+, 65), 184 (40), 169 (10), 166 (20), 149 (20), 108 (25), 92 (40), 75 (100), 74 (70). The NMR spectra were sufficiently resolved to allow discernment of the peaks corresponding to the separate isomers. Data for *(E)-2,8-dimethyl-2-sila-5,7-nonadien-2-ol (**27**):* δ_H (500 MHz; $CDCl_3$) 0.15 (6H, s, $SiMe_2$), 0.72–0.75 (2H, m, $SiCH_2$), 1.66 (1H, br s, OH), 1.74 and 1.76 (2×3H, 2×s, Me_2C=), 2.19 (2H, ca. q, *J*=6.9 Hz, CH_2), 5.61 (1H, dt, *J*=15.0, 6.9 Hz, CH_2CH=), 5.79 (1H, d, *J*=10.8 Hz, Me_2C=C*H*), 6.24 (1H, dd, *J*=15.0, 10.8 Hz, CH_2CH=C*H*); δ_C (125 MHz; $CDCl_3$) −0.2, 17.6, 18.2, 25.9, 26.4, 124.9, 125.7, 134.0, 133.0 (minor peaks in the spectrum attributed to the minor stereoisomer were observed at: 21.1, 26.3, 120.1, 123.8, 131.8, 135.4). Data for *(Z)-2,8-dimethyl-2-sila-5,7-nonadien-2-ol (**28**):* δ_H (500 MHz; $CDCl_3$) 0.16 (6H, s, $SiMe_2$), 0.71–0.74 (2H, m, $SiCH_2$), 1.74 and 1.75 (2×3H, 2×s, Me_2C=), 1.82 (1H, br s, OH), 2.27 (2H, ca. q, *J*=7.6 Hz, CH_2), 5.36 (1H, dt, *J*=10.1, 7.6 Hz, CH_2CH=), 6.07–6.15 (2H, m, Me_2C=C*H*C*H*=).

Treatment of aldehyde (23) with dimethylaluminium chloride. To a solution of aldehyde **23** (70 mg, 0.41 mmol) in DCM (21 cm^3) at rt was added dropwise dimethylaluminium chloride (620 μL of a 1.0 M solution in hexanes, 0.62 mmol). After 1 h water (30 cm^3) was added and the mixture stirred vigorously for 10 min. Water (40 cm^3) was added to the separated aqueous layer that was then extracted with ether (2×15 cm^3) and the combined organic portions were washed with water (25 cm^3), brine (25 cm^3), dried (magnesium sulfate) and concentrated in vacuo. The resulting oil was purified by chromatography (15:1→10:1 petrol/ether) to yield a mixture of the inseparable *dienes* **29** and **30** (1.8:1) as a colourless oil (33 mg, 48%). R_f 0.50 (1:1 petrol/ether); Accurate mass: Found 171.1201, $C_9H_{19}OSi$ (MH^+) requires 171.12052; ν_{max}/cm^{-1} 3306br m, 3018m, 2959s, 2915m, 1441w, 1252s, 1057w, 986s, 947m, 907m, 858s, 783s, 699w. The NMR spectra were sufficiently resolved to allow discernment of the peaks corresponding to the separate isomers. Data for *(5E,7E)-2-methyl-2-sila-5,7-nonadien-2-ol (**29**):* δ_H (500 MHz; $CDCl_3$) 0.18 (6H, s, $SiMe_2$), 0.74–0.78 (2H, m, $SiCH_2$), 1.77 (3H, d, *J*=6.4 Hz, MeC=), 2.04 (1H, br s, OH), 2.19 (2H, ca. q, *J*=6.9 Hz, CH_2), 5.59–5.69 and 6.02–6.09 (2×2H, 2×m, 4×CH=); δ_C (125 MHz; $CDCl_3$) −0.2, 17.3, 18.0, 26.1, 126.9, 129.2, 131.5, 134.1; *m/z* (CI) 188 (MNH_4^+, 25%), 171 (MH^+, 45), 170 (30), 166 (10), 152 (10), 149 (10), 94 (30), 92 (80), 91 (45), 75 (100), 74 (80). Data for *(5Z,7E)-2-methyl-2-sila-5,7-nonadien-2-ol (**30**):* δ_H (500 MHz; $CDCl_3$) 0.20 (6H, s, $SiMe_2$), 0.74–0.78 (2H, m, $SiCH_2$), 1.82 (3H, d, *J*=6.8 Hz, MeC=), 2.04 (1H, br s, OH), 2.30 (2H, ca. q, *J*=7.5 Hz, CH_2), 5.36 (1H, dt, *J*=10.5, 7.5 Hz, CH_2CH=), 5.72 (1H, dq, *J*=14.8, 6.8 Hz, MeC*H*=), 5.95 (1H, t, *J*=10.9 Hz, CH_2CH=C*H*), 6.38 (1H, dd, *J*=14.8, 11.2 Hz, MeCH=C*H*); δ_C (125 MHz; $CDCl_3$) −0.2, 18.0, 18.3, 21.2, 126.7, 127.5, 129.3, 132.0; *m/z* (CI) 188 (MNH_4^+, 20%), 171 (MH^+, 45), 170 (25), 152 (10), 94 (30), 92 (70), 91 (45), 75 (100), 74 (85).

Treatment of aldehyde (24) with dimethylaluminium chloride. To a solution of aldehyde **24** (101 mg, 0.592 mmol) in DCM (30 cm^3) at rt was added dropwise dimethylaluminium chloride (890 μL of a 1.0 M solution in hexanes, 0.89 mmol). After 35 min 1 M aqueous sodium hydroxide solution (15 cm^3) was added and the mixture stirred vigorously for 2 h. Water (15 cm^3) was added to the separated aqueous layer that was then extracted with ether (2×15 cm^3) and the combined organic portions were washed with brine (25 cm^3), dried (magnesium sulfate) and concentrated in vacuo. The resulting oil was purified by chromatography (10:1 petrol/ether) to yield a mixture of all four stereoisomers (**29**–**31**) of *2-methyl-2-sila-5,7-nonadien-2-ol* as a colourless oil (62 mg, 62%). R_f 0.50 (1:1 petrol/ether); Accurate mass: Found 171.1202, $C_9H_{19}OSi$ (MH^+) requires 171.12052; ν_{max}/cm^{-1} 3306br s, 3019m, 2958s, 2915s, 1252s, 1179w, 986s, 946m, 907s, 857s, 782s, 694m; δ_H (500 MHz; $CDCl_3$) in addition to the NMR data reported above for **29** and **30** further peaks corresponding to the other diastereomers were discernible (highly complex spectrum); δ_C (125 MHz; $CDCl_3$) −0.2, 13.1, 13.2, 17.3, 17.8, 18.0, 18.2, 21.1, 21.2, 26.0, 26.4, 122.3, 124.0, 124.2, 126.2, 126.7, 126.9, 127.5, 129.17, 129.24, 129.3, 131.5, 132.0, 134.1, 136.5; *m/z* (CI) 188 (MNH_4^+, 30%), 171 (MH^+, 35), 170 (30), 166 (20), 152 (10), 149 (25), 94 (35), 92 (80), 91 (40), 75 (100), 74 (70).

4,4,7-Trimethyl-4-silaoct-6-enal (33). To a cooled (−78°C) solution of tributylprenylstannane[26] (2.26 cm^3, 6.63 mmol) in THF (11 cm^3) was added dropwise *n*-butyllithium (4.2 cm^3 of a 1.6 M solution in hexanes, 6.72 mmol). After 30 min chlorodimethyl(dimethylamino)-silane (775 μL, 5.10 mmol) was added and the mixture stirred at rt for 1 h and at 40°C for 2 h. To the cooled (0°C) silane mixture was added dropwise acetyl chloride (360 μL, 5.10 mmol) and the mixture was allowed to warm up to rt over 15 min then stirred at rt for 1 h. To a cooled (−78°C) solution of *N*-allylpyrrolidine[10] (1 cm^3, 7.65 mmol) in THF (20 cm^3) was added dropwise *s*-butyllithium (12.7 cm^3 of a 1.2 M solution in cyclohexane, 15.2 mmol) and the solution was allowed to warm up to −10°C over 2 h then stirred at −10°C for 3.5 h. To the cooled (−78°C) allyllithium solution was added by cannula the previously prepared chlorosilane solution and the mixture allowed to warm up to rt over 19 h. The reaction mixture was added to a mixture of water (30 cm^3) and 1 M hydrochloric acid (8 cm^3), extracted with ether (3×20 cm^3) and the combined organic portions were washed successively with water (2×30 cm^3), brine (30 cm^3), then dried (magnesium sulfate) and concentrated in vacuo. The resulting oil was purified by chromatography (100:0→70:1 petrol/ether) to yield the *aldehyde* **33** as a colourless oil (480 mg, 51%). R_f 0.52 (3:1 petrol/ether); Accurate mass: Found 115.0579, $C_5H_{11}OSi$ ($MH^+-C_5H_{10}$) requires 115.05792; ν_{max}/cm^{-1} 2959s, 2918m, 2809w, 2715w, 1728s, 1410m, 1377w, 1249s, 1180m, 1158m, 1096w, 1035w, 994w, 837s, 692w; δ_H (500 MHz; $CDCl_3$) −0.01 (6H, s, $SiMe_2$),

0.74–0.77 (2H, m, $SiCH_2$), 1.40 (2H, d, J=8.4 Hz, CH_2CHC=), 1.54 and 1.68 (2×3H, 2×s, Me_2C=), 2.35–2.39 (2H, m, CH_2CHO), 5.10 (1H, t, J=8.4 Hz, C*H*=), 9.73 (1H, t, J=1.8 Hz, CHO); δ_C (125 MHz; $CDCl_3$) −3.7, 6.6, 16.8, 17.5, 25.7, 38.3, 119.1, 129.3, 203.0; *m/z* (CI) 127 (15%), 116 (40), 115 (100), 102 (10), 99 (15), 91 (10), 85 (20), 76 (20), 74 (25), 59 (30).

Treatment of aldehyde (33) with dimethylaluminium chloride. To a solution of aldehyde **33** (99 mg, 0.54 mmol) in DCM (27 cm^3) at rt was added dropwise dimethylaluminium chloride (810 μL of a 1.0 M solution in hexanes, 0.81 mmol). After 35 min 1 M aqueous sodium hydroxide solution (15 cm^3) was added and the mixture stirred vigorously for 10 min. Water (10 cm^3) was added to the separated aqueous layer that was then extracted with ether (2×15 cm^3) and the combined organic portions were washed with brine (20 cm^3), dried (magnesium sulfate) and concentrated in vacuo. The resulting oil was purified by chromatography (30:1→15:1 petrol/ether) to yield *silacycles* **34** (51 mg, 52%) and **35** (9 mg, 9%), and a fraction containing a mixture of the two (1 mg, 1%) as colourless oils. Data for *trans-4,4-dimethyl-2-(propen-2-yl)-4-silacyclohexanol (**34**):* R_f 0.47 (1:1 petrol/ether); Accurate mass: Found 202.1627, $C_{10}H_{24}NOSi$ (MNH_4^+) requires 202.16272; ν_{max}/cm^{-1} 3436br m, 2954s, 2917s, 2884s, 1645m, 1456m, 1412m, 1373m, 1250s, 1166m, 1056m, 1036m, 1010s, 965m, 886m, 842s, 792s, 736s, 704m; δ_H (500 MHz; $CDCl_3$) 0.06 and 0.13 (2×3H, 2×s, $SiMe_2$), 0.61 (1H, td, J=14.1, 5.0 Hz) and 0.81 (1H, dddd, J=14.1, 5, 2.9, 2 Hz, $SiCH_2$), 0.71 (1H, d, J=12.6 Hz) and 0.72–0.76 (1H, m, CH_2CHC=), 1.53 (1H, tdd, J=14.1, 10.8, 3.3 Hz) and 2.22–2.30 (2H, m, CH_2CHOH and CHC=) 1.76 (3H, s, MeC=), 2.00 (1H, br s, OH), 3.32 (1H, td, J=10.8, 3.4 Hz, C*H*OH), 4.88 and 4.90 (2×1H, 2×s, $=CH_2$); δ_C (125 MHz; $CDCl_3$) −4.4, −2.3, 11.4, 17.4, 17.8, 31.4, 51.7, 72.5, 112.5, 149.0; *m/z* (CI) 202 (MNH_4^+, 10%), 185 (MH^+, 10), 169 (5), 168 (5), 167 (30), 139 (15), 115 (100), 109 (10), 92 (25), 74 (35). Data for *cis-4,4-dimethyl-2-(propen-2-yl)-4-silacyclohexanol (**35**):* R_f 0.60 (1:1 petrol/ether); Accurate mass: Found 202.1627, $C_{10}H_{20}NOSi$ (MNH_4^+) requires 202.16272; ν_{max}/cm^{-1} 3470br w, 2960s, 2923s, 1641w, 1455w, 1445w, 1406w, 1371w, 1248s, 1180m, 1061m, 863s, 842s; δ_H (500 MHz; $CDCl_3$) 0.46 and 0.49 (2×3H, 2×s, $SiMe_2$), 0.47 (1H, d, J=14.0 Hz) and 1.02 (1H, t, J=14.0 Hz, CH_2CHC=), 0.53 (1H, dtd, J=14.5, 3.8, 1.9 Hz) and 0.86 (1H, td, J=14.5, 5.3 Hz, $SiCH_2$), 1.47 (1H, br s, OH), 1.69 (1H, tdd, J=14.5, 3.4, 1.9 Hz) and 2.34 (1H, dq, J=14.5, 4.4 Hz, CH_2CHOH), 1.86 (3H, s, MeC=), 2.26 (1H, d, J=14.0 Hz, CHC=), 3.98 (1H, br s, C*H*OH), 4.96 and 4.99 (2×1H, 2×s, $=CH_2$); δ_C (125 MHz; $CDCl_3$) −4.7, −1.9, 6.3, 11.8, 22.7, 29.4, 46.7, 68.2, 110.7, 150.2; *m/z* (CI) 202 (MNH_4^+, 10%), 185 (MH^+, 5), 169 (5), 167 (15), 115 (100), 109 (10), 92 (10), 74 (35), 59 (10).

4,4-Diisopropyl-7-methyl-3-phenyl-4-silaoct-6-en-1-ol (37). A solution of tributylprenylstannane[26] (331 mg, 0.92 mmol) in THF (2 cm^3) was cooled to −78°C and methyllithium (0.8 cm^3 of a 1.3 M solution in ether, 1.04 mmol) was added dropwise. The mixture was allowed to warm to 0°C and, after 1 h, re-cooled to −78°C. A solution of crude oxasilacyclopentane **36**[1c] (200 mg, 0.81 mmol) in THF (1 cm^3) was added dropwise then the mixture was allowed to warm to rt and stirred for 20 h. Water (20 cm^3) was added and the mixture was extracted with ether (3×10 cm^3). The organic portions were combined, washed with brine (12 cm^3), dried (magnesium sulfate) and the solvent removed in vacuo. Purification by chromatography (5:1 petrol/ether) afforded the *alcohol* (**37**) as a colourless oil (150 mg, 59%). R_f 0.42 (1:1 petrol/ether); Accurate mass: Found 336.2723, $C_{20}H_{38}NOSi$ (MNH_4^+) requires 336.27225; ν_{max}/cm^{-1} 3324s, 3023m, 2923s, 2866s, 1599m, 1492s, 1464s, 1376s, 1250m, 1157s, 1099s, 1032s, 882s, 701s; δ_H (400 MHz, $CDCl_3$) 0.88–1.11 (14H, m, 2×*i*-Pr), 1.53 (2H, app. d, J=8.1 Hz, CH_2Si), 1.64 (3H, s, CH_3C=), 1.70 (3H, s, CH_3C=), 1.86 (1H, br s, OH), 2.00–2.15 (2H, m, CH_2CH_2OH), 2.44 (1H, dd, J=12.5, 2.9 Hz, C*H*Ph), 3.38 (1H, ddd, J=10.4, 7.6, 7.3 Hz, C*H*HOH), 3.51 (1H, ddd, J=10.4, 7.6, 4.3 Hz, CH*H*OH), 5.18 (1H, br t, J=8.1 Hz, CH=), 7.10 (1H, ca. tt, J=7.2, 1.2 Hz), 7.15 (2H, ca. dt, J=7.2, 1.2 Hz) and 7.24 (2H, t, J=7.2 Hz, Ph); δ_C (100.6 MHz, $CDCl_3$) 10.9, 11.1, 11.3, 17.6, 18.3 (two peaks), 18.4, 18.5, 25.8, 29.2, 33.4, 62.0, 120.1, 124.6, 128.2, 128.3, 128.9, 143.1; *m/z* (CI) 336 (MNH_4^+, 22%), 282 (37), 249 (100), 148 (25), 118 (43).

4,4-Diisopropyl-7-methyl-3-phenyl-4-silaoct-6-enal (38). To a cooled (0°C) mixture of alcohol **37** (0.5 g, 1.57 mmol) and MS4 Å (1.6 g) in DCM (9.3 cm^3) was added PDC (0.9 g, 2.39 mmol). The reaction mixture was allowed to warm to rt and stirred for 4 h. The solution was diluted with ether (45 cm^3) and filtered through Celite®, which was thoroughly washed through with more ether. The filtrates were combined and concentrated in vacuo to give a dark yellow oil that was purified by chromatography (10:1 petrol/ether) to give *aldehyde* (**38**) as a colourless oil (0.32 g, 64%). R_f 0.63 (1:1 petrol/ether); Accurate mass: Found 334.2566, $C_{20}H_{36}NOSi$ (MNH_4^+) requires 334.25660; ν_{max}/cm^{-1} 3428w, 3024m, 2944s, 2866s, 2715m, 1724s, 1600s, 1495s, 1451s, 1384s, 1158s, 999s, 882s, 702s; δ_H (500 MHz, $CDCl_3$) 0.85–1.10 (14H, m, 2×*i*-Pr), 1.52 (2H, app. d, J=8.3 Hz, CH_2Si), 1.63 (3H, s, CH_3C=), 1.69 (3H, d, J=1 Hz, CH_3C=), 2.70 (1H, ddd, J=16, 1.8, 1.6 Hz, C*H*HCHO), 2.95–3.03 (2H, m, CH*H*CHO and PhC*H*), 5.16 (1H, br t, J=8.3 Hz, CH=), 7.09–7.26 (5H, m, Ph), 9.57 (1H, dd, J=3.2, 1.6 Hz, CHO); δ_C (125 MHz, $CDCl_3$) 10.9, 11.2, 11.3, 17.7, 18.2, 18.3 (two peaks), 18.4, 25.9, 26.8, 44.7, 119.6, 125.2, 128.3, 128.5, 129.8, 142.1, 202.7; *m/z* (CI) 334 (MNH_4^+, 42%), 247 (100), 117 (45).

Treatment of aldehyde (38) with dimethylaluminium chloride. To a stirred solution of aldehyde **38** (67 mg, 0.22 mmol) in DCM (10 cm^3) at rt was added dropwise dimethylaluminium chloride (319 μl of a 1 M solution in hexanes, 0.32 mmol) dropwise. After 35 min 1 M aqueous sodium hydroxide solution (5 cm^3) was added and the mixture stirred vigorously for 10 min. Water (8 cm^3) was added to the separated aqueous layer, which was then extracted with ether (2×3 cm^3). The combined organic portions were washed with brine (7 cm^3), dried (magnesium sulfate) and concentrated in vacuo. Purification by chromatography (10:1 petrol/ether) gave *cis, trans-4,4-diisopropyl-3-phenyl-6-(propen-2-yl)-4-silacyclohexanol (**39**)* (41 mg, 61%) and *trans, cis-4,4-diisopropyl-3-phenyl-6-(propen-2-*

*yl)-4-silacyclohexanol (**40**)* (9 mg, 13%) as colourless oils. Data for **39**: R_f 0.51 (1:1 petrol/ether); Accurate mass: Found 334.2566, $C_{20}H_{36}NOSi$ (MNH_4^+) requires 334.25660; ν_{max}/cm^{-1} 3384m, 3058m, 3022m, 2931s, 2865s, 1599s, 1494s, 1383s, 1112s, 880s, 774s, 698s, 668s; δ_H (500 MHz, $CDCl_3$) 0.56 (3H, d, J=7.4 Hz, Si(CH-Me*Me*)), 0.73 (1H, app. t, J=13.9 Hz, $SiCH_{eq}H_{ax}$), 0.85–0.95 (9H, m, $SiCH_{eq}H_{ax}$, Si*i*-Pr and $Si(CHMe_2)$), 0.96 (3H, d, J=7.4 Hz, Si(CH*Me*Me), 1.79 (3H, s, CH_3C=), 2.03 (1H, br s, OH), 2.15 (1H, ddd, J=13.7, 13.1, 11.4 Hz, $CH_{eq}H_{ax}CHOH$), 2.27 (1H, ddd, J=13.9, 9.2, 3.3 Hz, CHC=), 2.38 (1H, app. dt, J=13.1, 2.8 Hz, $CH_{eq}H_{ax}CHOH$), 2.51 (1H, dd, J=13.7, 2.8 Hz, C*H*Ph), 3.49 (1H, ddd, J=11.4, 9.2, 2.8 Hz, C*H*OH), 4.92 (1H, app. s, =C*H*H), 4.92 (1H, d, J=1.7 Hz, =CH*H*), 7.11–7.25 (5H, m, Ph); δ_C (125 MHz, $CDCl_3$) 9.1, 9.2, 9.9, 17.9, 18.0 (two peaks), 18.3, 18.8, 29.3, 37.9, 51.7, 72.4, 112.5, 124.4, 126.4, 128.3, 144.0, 149.0; *m/z* (CI) 334 (MNH_4^+, 9%), 317 (MH^+, 3), 299 (37), 273 (16), 148 (100). Data for **40**: R_f 0.63 (1:1 petrol/ether); Accurate mass: Found 334.2566, $C_{20}H_{36}NSiO$ (MNH_4^+) requires 334.25660; ν_{max}/cm^{-1} 3466m, 3076m, 3013m, 2940s, 2865 s, 1600s, 1495s, 1463s, 1260s, 1084s, 1017s, 798s, 699s, 666s; δ_H (500 MHz, $CDCl_3$) 0.58–1.2 (16H, m, $SiCH_2$ and 2×*i*-Pr), 1.87 (3H, s, CH_3C=), 2.24 (1H, ddd, J=14.1, 13.9, 1.6 Hz, $CH_{eq}H_{ax}CHOH$), 2.32 (1H, d, J=13.6 Hz, CHC=), 2.42 (1H, dd, J=13.9, 4.2 Hz, $CH_{eq}H_{ax}CHOH$), 2.86 (1H, dd, J=14.1, 4.2 Hz, C*H*Ph), 4.17 (1H, app. d, J=4.1 Hz, C*H*OH), 5.00 (2H, s, $=CH_2$), 7.12–7.24 (5H, m, Ph); δ_C (125 MHz, $CDCl_3$) 9.1, 9.5, 14.1, 17.9, 18.0, 18.3, 18.6, 19.2, 26.8, 36.0, 46.6, 68.3, 110.9, 124.2, 126.8, 128.1, 144.7, 149.9; *m/z* (CI) 334 (MNH_4^+, 53%), 317 (MH^+, 3), 299 (17), 273 (39), 148 (100), 131 (27), 117 (19).

4,4-Diisopropyl-7-methyl-2-phenyl-4-silaoct-6-en-1-ol (42). A solution of tributylprenylstannane[26] (470 mg, 1.31 mmol) in THF (3 cm^3) was cooled to −78°C then methyllithium (1.87 cm^3 of a 0.77 M solution in ether, 1.44 mmol) was added dropwise and the mixture was stirred at −78°C for 1 h. A solution of crude oxasilacyclopentane **41** (650 mg, 2.62 mmol) in THF (3 cm^3) was added dropwise, the reaction mixture was allowed to warm up to rt and then stirred for 19 h. Water (2 cm^3) was added and the organic product was extracted with ether (3×2 cm^3). The organic portions were combined, washed with brine (2.5 cm^3), dried (magnesium sulfate) and the solvent removed in vacuo. Purification by chromatography (5:1 petrol/ether) afforded the *alcohol* **42** as a colourless oil (107 mg, 26% from tributylprenylstannane). R_f 0.37 (1:1 petrol/ether); Accurate mass: Found 336.2723, $C_{20}H_{38}NSiO$ (MNH_4^+) requires 336.27225; ν_{max}/cm^{-1} 3364m, 3028m, 2941s, 2865s, 1602m, 1494s, 1463s, 1383s, 1098s, 1053s, 1015s, 883s, 762s; δ_H (400 MHz, $CDCl_3$) 0.80–1.12 (15H, m, C*H*HSi(*i*-Pr)$_2$), 1.22–1.38 (3H, m, CH*H*SiCH_2), 1.54 (3H, s, CH_3C=), 1.64 (3H, d, J=0.7 Hz, CH_3C=), 2.94 (1H, app. tt, J=8.5, 5.7 Hz, C*H*Ph), 3.63 (1H, dd, J=10.6, 8.5 Hz, C*H*HOH), 3.70 (1H, dd, J=10.6, 5.7 Hz, CH*H*OH), 5.02 (1H, br t, J=8.3 Hz, CH=), 7.22–7.35 (5H, m, Ph); δ_C (100.6 MHz, $CDCl_3$) 11.6, 11.8, 12.1, 13.1, 17.6, 18.1, 18.2, 18.3, 25.8, 44.2, 70.3, 120.3, 126.9, 128.1, 128.6, 144.0; *m/z* (CI) 336 (MNH_4^+, 11%), 202 (59), 148 (100), 58 (15).

4,4-Diisopropyl-7-methyl-2-phenyl-4-silaoct-6-enal (43). To a cooled (0°C) mixture of alcohol **42** (46 mg, 0.15 mmol) and MS4 Å (150 mg) in DCM (0.85 cm^3) was added PDC (83 mg, 0.22 mmol). The reaction mixture was allowed to warm to rt then stirred for 6 h. The mixture was diluted with ether (5 cm^3) and filtered through Celite®, the Celite® being washed thoroughly with ether and the combined filtrates concentrated in vacuo to give a pale pink oil. Purification by chromatography (10:1 petrol/ether) gave the *aldehyde* **43** as a colourless oil (24 mg, 53%). R_f 0.65 (1:1 petrol/ether); Accurate mass: Found 334.2566, $C_{20}H_{36}NOSi$ (MNH_4^+) requires 334.25660; ν_{max}/cm^{-1} 3428w, 3062m, 3028m, 2941s, 2888s, 2885s, 2714m, 1727s, 1664s, 1600m, 1581m, 1492m, 1453s, 882s, 819s, 736s, 700s; δ_H (400 MHz, $CDCl_3$) 0.82–1.06 (14H, m, 2×?*i*-Pr), 1.06–1.12 (1H, m, SiC*H*HCHPh), 1.34 (1H, app. dd, J=8.2, 3.4 Hz, SiC*H*HCH=), 1.46 (1H, dd, J=15.1, 6 Hz, SiCH*H*CHPh), 1.51–1.54 (1H, m, SiCH*H*CH=), 1.55 (3H, s, CH_3C=), 1.65 (3H, d, J=1 Hz, CH_3C=), 3.63 (1H, ca. td, J=6, 2.6 Hz, PhC*H*), 5.05 (1H, br t J=8.2 Hz, CH=), 7.22–7.93 (5H, m, Ph), 9.59 (1H, d, J=2.6 Hz, CHO); δ_C (100.6 MHz, $CDCl_3$) 10.2, 11.6, 11.8, 11.9, 17.6, 17.9, 18.1, 18.2, 25.8, 30.9, 54.8, 119.9, 127.6, 128.8, 129.0, 138.2, 142.5, 200.4; *m/z* (CI) 334 (MNH_4^+, 15%), 317 (MH^+, 7), 247 (100), 148 (75), 117 (21).

Treatment of aldehyde (43) with dimethylaluminium chloride. To a solution of aldehyde **43** (24 mg, 0.076 mmol) in DCM (5 cm^3) at rt was added dropwise dimethylaluminium chloride (114 μl of a 1 M solution in hexanes, 0.114 mmol). After 30 min 1 M aqueous sodium hydroxide solution (3 cm^3) was added and the mixture stirred vigorously for 10 min. Water (5 cm^3) was added to the separated aqueous layer, which was then extracted with ether (2×3 cm^3). The combined organic portions were washed with brine (5 cm^3), then dried (magnesium sulfate) and concentrated in vacuo. Purification by chromatography (10:1 petrol/ether) gave *trans, trans-4,4-diisopropyl-2-phenyl-6-(propen-2-yl)-4-silacyclohexanol (**44**)* (12 mg, 50%) and *cis, cis-diisopropyl-2-phenyl-6-(propen-2-yl)-4-silacyclohexanol (**45**)* (2 mg, 8.5%) as colourless oils. Data for **44**: R_f 0.65 (1:1 petrol/ether); Accurate mass: Found 334.2566, $C_{20}H_{32}SiNO$ (MNH_4^+) requires 334.25660; ν_{max} /cm^{-1} 3500m, 2939s, 2863s, 1343s, 1124s, 1013s, 882s, 780s, 698s; δ_H (400 MHz, $CDCl_3$) 0.86–1.01 (4H, m, 2×$SiCH_2$), 1.03–1.10 and 1.24–1.38 (14H, m, 2×*i*-Pr), 1.83 (3H, s, CH_3C=), 2.53 (1H, dd, J=13.7, 9.9 Hz, CH(C=)), 2.85 (1H, ddd, J=13.4, 9.9, 3.5 Hz, C*H*Ph), 3.54 (1H, br t, J=9.9 Hz, C*H*OH), 4.87 (1H, s, =C*H*H), 4.90 (1H, s, =CH*H*), 7.27–7.40 (5H, m, Ph); δ_C (100.6 MHz, $CDCl_3$) 10.5, 11.0, 12.4, 16.3, 17.7, 18.3, 18.4, 49.3, 51.5, 75.4, 111.7, 126.4, 127.2, 128.6, 147.0, 149.8; *m/z* (CI) 334 (MNH_4^+, 30%), 317 (MH^+, 8) 247 (43), 148 (100), 131 (21), 117 (18). Data for **45**: R_f 0.67 (1:1 petrol: ether); Accurate mass: Found 334.2566, $C_{20}H_{32}SiNO$ (MNH_4^+) requires 334.25660; ν_{max}/cm^{-1} 3500w, 2924s, 2865s, 1458s, 886s, 792s, 750s, 698s; δ_H (400 MHz, $CDCl_3$) 0.90–0.99 and 1.29–1.38 (14H, m, 2×*i*-Pr), 1.04–1.16 (4H, m, 2×$SiCH_2$), 1.85 (3H, s, $=CCH_3$), 2.53 (1H, dd, J=11.5, 4 Hz, C*H*(C=)), 2.80 (1H, ddd, J=11.8, 6.8, 2 Hz, C*H*Ph), 3.91 (1H, ca. dd, J=6.8, 4 Hz, C*H*OH), 5.10 (1H, s, =C*H*H), 5.11 (1H, s,

=CH*H*), 7.37–7.38 (5H, m, Ph); δ_C (125 MHz, $CDCl_3$) 10.1, 11.4, 11.7, 11.8, 18.1, 18.3, 18.4, 18.5, 22.6, 46.3, 53.4, 74.4, 112.9, 126.2, 127.2, 128.4, 148.3, 148.4; *m/z* (CI) 334 (MNH_4^+, 45%), 317 (MH^+, 5), 247 (26), 220 (28), 205 (20), 169 (28), 148 (100), 121 (40), 103 (29).

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