Tetrahedron 65 (2009) 5541–5551

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Stereospecific α-methallylation of hydroxyaldehydes by silatropic ene cyclisation

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ARTICLE INFO

Article history:
Received 8 January 2009
Received in revised form 30 January 2009
Accepted 31 January 2009
Available online 14 April 2009

ABSTRACT

We describe the thermal rearrangement of aldehydes bearing an α-(allyl- or crotylsilyl)oxy substituent. The transformations are best described mechanistically as intramolecular silatropic ene reactions based on stereoselectivity, kinetic and computed transition state data. The overall process constitutes a stereospecific (meth)allylation of α-hydroxyaldehydes, under neutral conditions, in which the hydroxyl protecting group is also the (meth)allylating agent.

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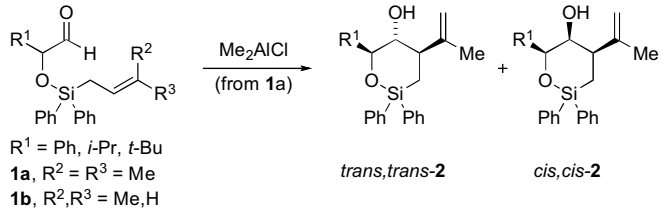
1. Introduction

Our group has been involved in a long-running investigation of alternative methodology for producing stereodefined polyols based on silicon-tethered carbonyl ene cyclisation and oxidative cleavage. As part of this study we observed that α-prenylsilyloxy aldehyde precursors (**1a**, Scheme 1) cyclised rapidly in the presence of Me_2AlCl to give 1,2-oxasilinanes (**2**) with the *trans*,*trans*-diastereomer predominating in all cases, although the dr was usually only moderate.[1] Based on the results of all-carbon substrates[2] we decided to investigate the stereospecificity of the reactions of *E*- and *Z*-α-crotylsilyloxy aldehydes (**1b**), expecting improved ratios of diastereomeric products.[3] We now describe full details[4] of the preparation and reactivity of suitable test substrates, and report further kinetic and computational studies that add to our mechanistic understanding of the observed cyclisations.



Scheme 1. 1,2-Oxasilinanes by silicon-tethered Type I ene cyclisations.

2. Synthesis of crotyl precursors

We selected substrates **6** and **10** (Scheme 2) for initial study since our previous work had shown that phenyl substituents on silicon conferred a reasonable degree of stability (in contrast to methyl) without hampering oxidative cleavage of the C–Si bond (in contrast to *tert*-butyl).[5] Piers' method[6] for hydroxyl silylation was found to be reliable, even with allylic silanes, therefore access to the *Z*-crotyl derivative **6** required the preparation of *Z*-crotyldiphenylsilane (**4**). This silane was prepared by reduction[7] of 2-butynyldiphenylsilane (**3**)[8] and, following purification by chromatography, was found to be free of the *E*-isomer as judged by examination of the 600 MHz ^{1}H NMR spectrum.[9] This reagent was then used to silylate (±)-ethyl mandelate and the resulting ester (**5**) reduced to provide the desired *Z*-crotyl precursor (**6**) in acceptable yield.

At the time of this study, existing methods[10] for the preparation of a suitable *E*-crotyl silane were either inapplicable to our specific requirements or gave poor results in our hands. However, based on Hodgson's[11] report that the double bond in 1,1-bis(trialkylsilyl)-alkenes could be migrated into the presumably more stable allylic position we expected that it would be possible to isomerise the double bond in readily-prepared 3-butenyl (i.e., homoallylic) silanes into the allylic position. Good precedent for this idea was provided by Matsuda's evaluation of a range of Ir(I) and Rh(I) complexes for their potential to isomerise several simple tetraalkylsilanes.[12] We soon established that commercially-available $[(COD)Ir(PPh_2Me)_2]^+PF_6^-$, although not identified as the optimum pre-catalyst in Matsuda's study, was an effective reagent for complete C=C isomerisation of the product (**8**) of silylation of ethyl mandelate with 3-butenyldiphenylsilane (**7**).[13] DIBAL reduction of the so-formed ester (**9**) gave aldehyde **10** to complete a practical, efficient synthesis of the *E*-crotyl precursor (Scheme 2).

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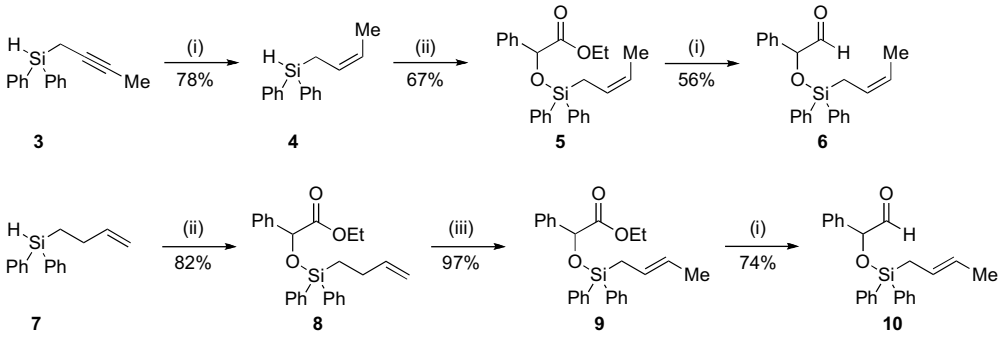
doi:10.1016/j.tet.2009.01.117

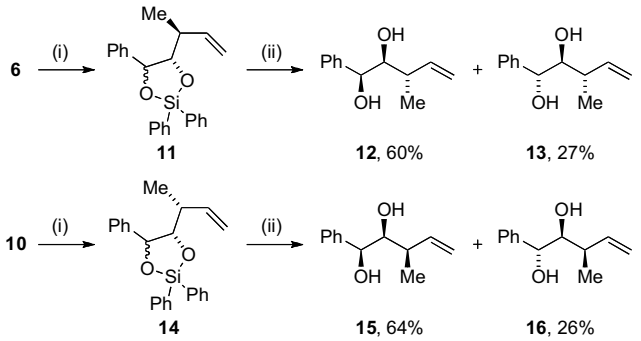


Scheme 2. Reagents: (i) DIBAL then H_3O^+; (ii) ethyl mandelate, cat. $B(C_6F_5)_3$; (iii) cat. $[(COD)Ir(PPh_2Me)_2]^+$ PF_6^-.

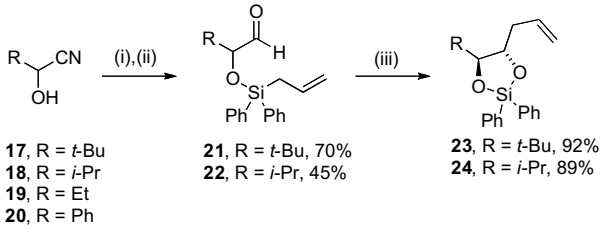
3. Ene cyclisations

With short, efficient routes to both *E*- and *Z*-crotyl precursors it was disappointing to find that these substrates decomposed or generated complex product mixtures either under the 'standard' conditions (Me_2AlCl, CH_2Cl_2, rt) or with a variety of alternative Lewis acids at various temperatures. This increased sensitivity towards Lewis acids led us to attempt ene cyclisations under neutral conditions; accordingly, aldehydes **6** and **10** were heated at 80 °C in $CDCl_3$ and the reactions monitored by ^1H NMR spectroscopy. In each case, there was a smooth progression from the α-silyloxyaldehyde to a pair of 1,3,2-dioxasilolanes (**11** or **14**, Scheme 3), which were assigned as epimers at the benzylic position. The stereochemistry at the allylic position (Me/O *anti* in **11**, *syn* in **14**) was dictated by that of the crotyl unit in the starting material. On a preparative scale these intermediates could be desilylated to give a high yield of diols **12** and **13** (from **11**) and **15** and **16** (from **14**) that could be readily separated by chromatography.

We sought to confirm the stereochemistry in these compounds by correlation with simpler analogues and, initially, simple allyl substrates were examined to establish the trend of predominant formation of 1,3,2-dioxasilolane precursors of the *syn*-diols. Preparation of test substrates was readily achieved by silylation of cyanohydrins **17**–**20**[14] (Scheme 4) with allyldiphenylchlorosilane (prepared in situ from dichlorodiphenylsilane and allylmagnesium bromide)[15] followed by DIBAL reduction. Although this sequence worked well for cyanohydrins **17** and **18**, derived, respectively, from pivalaldehyde and isobutyraldehyde, the DIBAL reductions were not productive in generating the more labile aldehydes derived from propionaldehyde- and benzaldehyde-cyanohydrin (**19** and **20**, respectively). However, substrates **21** and **22** proved sufficient for the purposes of this study and, when heated to 80 °C for 16 h, a single compound was obtained in each case (**23** and **24**, respectively), the stereochemistry being confirmed by NOE experiments as indicated in Figure 1.



Scheme 3. Thermal rearrangement of (*Z*)- and (*E*)-crotylsilyloxyaldehydes; stereospecific silatropic ene cyclisation. Reagents: (i) $CHCl_3$, 80 °C; (ii) KF, $KHCO_3$, aq MeOH.



Scheme 4. Complete stereoselectivity in the silatropic ene cyclisations of simple isopropyl and *tert*-butyl-substituted allylsilyloxy aldehydes. Reagents: (i) $Ph_2(allyl)SiCl$, imidazole; (ii) DIBAL; (iii) C_6H_6, 80 °C.

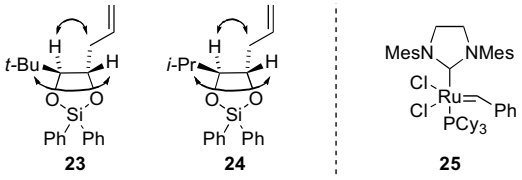


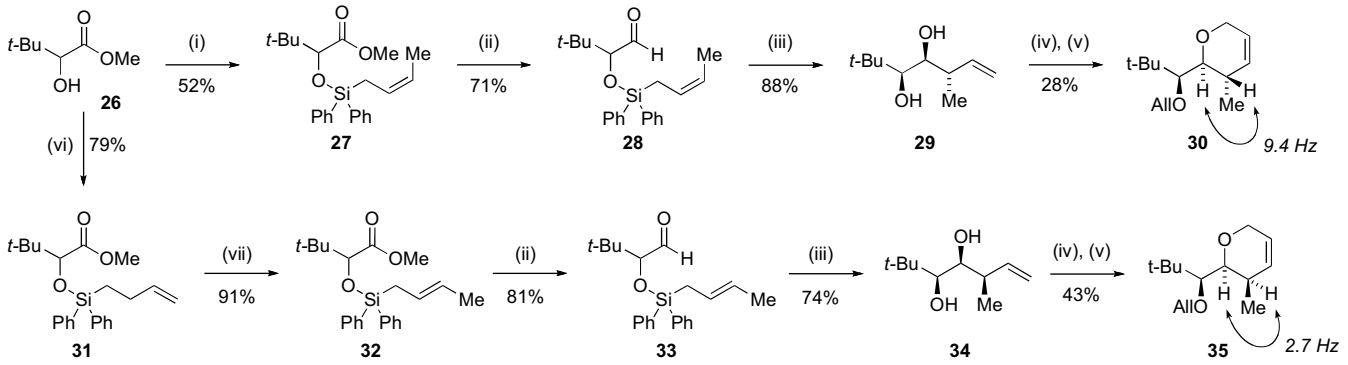
Figure 1. Diagnostic NOE enhancements supporting *trans*-stereochemistry in **23** and **24** (only small enhancements were observed between the allylic CH_2 and the *t*-Bu or *i*-Pr substituents). Grubbs II catalyst **25** for Scheme 5.

The *tert*-butyl-substituted compounds were stable, easy to handle and gave essentially perfect stereocontrol during the rearrangement step, and showed simple NMR spectra with minimal ^1H–^1H coupling to the ring protons. For these reasons, *tert*-butyl variants (**28** and **33**, Scheme 5) of the *Z*- and *E*-crotyl precursors were then prepared. Once again, cyclisation proceeded extremely cleanly to give single diastereoisomers of the 1,3,2-dioxasilolane intermediates (not shown), which were desilylated with hydrogen peroxide added to ease separation of the diols from phenylsilyl residues.

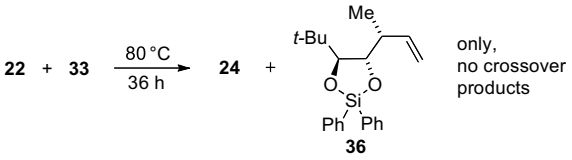
The relative stereochemistry at the two hydroxylated positions was clear by ^1H NMR analysis of the intermediate 1,3,2-dioxasilolanes but, to secure the stereochemistry at the allylic position, the diallyl ethers of diols **29** and **34** were subjected to ring closing metathesis with the second generation Grubbs catalyst (**25**, Fig. 1) to give samples of the dihydropyrans **30** and **35**. Seven-membered ring products (not shown) formed the majority of the mass balance in these metatheses.[16] The coupling constant between the allylic and ring-oxygen methine protons was large (*J* 9.4 Hz) in the case of **30** and small (*J* 2.7 Hz) in the case of **35** in support of *anti* and *syn* assignments, respectively, of the precursor diols **29** and **34**.

4. Kinetics and mechanism

An intramolecular rearrangement involving Si–O bond formation in concert with allylation can be drawn (Fig. 5) that accounts for the connectivity and stereochemistry in the product. However,



Scheme 5. Stereospecific alkenyl diol synthesis in *tert*-butyl substrates and confirmation of OH/Me relative stereochemistry. Reagents: (i) **4**, cat. $B(C_6F_5)_3$, (ii) DIBAL then Swern oxidation; (iii) C_6H_6, 80 °C then KF, H_2O_2, aq MeOH; (iv) NaH, excess allyl bromide (All-Br); (v) cat. **25**; (vi) **7**, cat. $B(C_6F_5)_3$; (vii) cat. $[(COD)Ir(PPh_2Me)_2]^+PF_6^-$.



Scheme 6. Crossover experiment to confirm the intramolecular nature of the observed rearrangements.

to confirm that intermolecular processes were not operating a mixture of isopropyl/allyl substrate **22** and *tert*-butyl/*E*-crotyl substrate **33** was heated for 36 h at 80 °C. Analysis of the reaction mixture both by high field ^{1}H NMR spectroscopy and high resolution GC mass spectrometry revealed the production of only two siladioxolanes (**24** and **36**, Scheme 6) in support of a purely intramolecular reaction.

To gain further insight into this rearrangement, a series of NMR experiments were performed in which an 84±8 mM solution (20±2 mg in 700 μL of toluene-d_8) of substrate **21** was heated within the NMR probe whilst the reaction was followed by ^{1}H NMR spectroscopy. Experiments were performed at 5 °C intervals from 60 to 80 °C whilst the ratios of aldehyde/1,3,2-dioxasilolane (**21**/**23**) were established at 10–30 min intervals by integration[17] of the well-separated C*H*=CH_2 methine resonances in each component (Fig. 2).

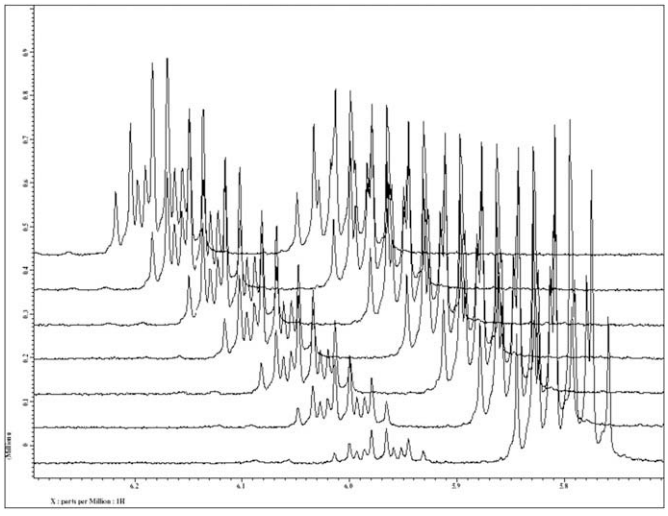


Figure 2. Stack plot of typical 500 MHz ^{1}H NMR experiment (**21**→**23** at 70 °C; plots shown at 30 min intervals).

The resulting data gave a good straight-line fit in a plot of ln(relative concentration **21**) versus time for each temperature run, indicating first order kinetics with respect to the substrate. This was confirmed by additional experiments performed at 70 °C, with 10±2, 20±2 and 30±2 mg of aldehyde **21** in 700 μL of toluene-d_8, which showed the rate constant for the rearrangement to have a negligible dependence on concentration. From these experiments, the Arrhenius activation energy (E_a) was calculated (Fig. 3) to be 70.0 kJ mol^{-1}.[18]

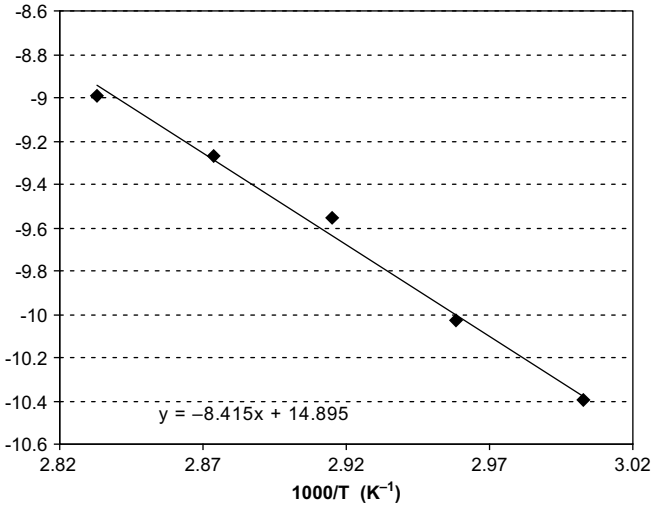


Figure 3. Plot of ln(rate constant) versus reciprocal temperature for the activation energy calculation.

By way of comparison, a conformer distribution for aldehyde **21** was obtained[19] (AM1) and key members of the 99 lowest energy conformers were selected for higher-level geometry optimisations (B3LYP/6-31G*). At this level of theory the first conformer (in the original list) to approximate a five-membered Si–O–C–C=O cyclic arrangement was 4.3 kJ mol^{-1} higher in energy than the first conformer to contain a *cisoid* O–C–C=O arrangement. A transition state was calculated using this conformation as a starting point that showed a similar degree of C–C and O–Si bond formation, with the forming and breaking C–C bonds being of roughly equal length (Fig. 4). This transition state was calculated to be 84 kJ mol^{-1} higher than the low energy *cisoid* aldehyde (**21**) conformer.

In our original working model for these reactions we envisaged a cooperative[20] pre-activation of both the aldehyde and silicon atom by their mutual coordination, and subsequent allylic transfer through a chair-like assembly from the face opposite the alkyl substituent (path ***a***, Fig. 5). This arrangement results in anti-Felkin–Anh

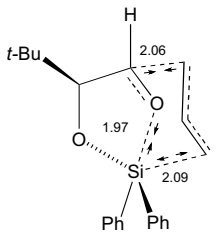


Figure 4. Calculated transition state for the cyclisation of **21**→**23** showing partial-bond lengths and vibrations.

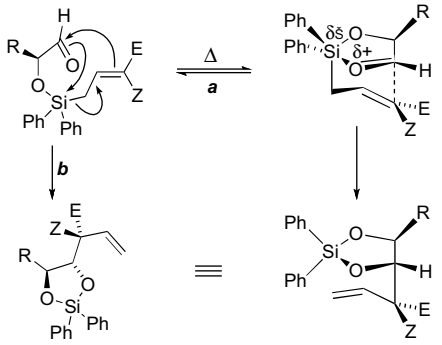


Figure 5. Silatropic ene cyclisation by pre-association of the carbonyl oxygen and silicon atoms (path ***a***) or by concerted Si–O and C–C bond formation (path ***b***).

selectivity and, because the CHR group is forced into a pseudoaxial position, the usual sense of stereoselectivity between the allylic and newly-formed hydroxylated positions (*E*→*anti*, *Z*→*syn*) is reversed.[21] This model predicts that the level of facial selectivity should be determined by the effective size of the alkyl group and, indeed, the *t*-Bu and *i*-Pr cases proceeded with excellent stereoselectivity in contrast to the Ph cases. Subsequent experiments[22] showed that di(isopropyl)-substituted silyl precursors cyclise at a comparable rate to the diphenyl analogues discussed above, suggesting that pre-coordination may not be important and that the reaction follows a concerted pathway (path ***b***, Fig. 5).[23]

5. Summary

This process represents an addition to the known allylations that proceed in the absence of added catalysts. In other systems, the silicon atom may be rendered Lewis acidic, either by virtue of attached electronegative substituents[24] or constraint within a four-membered ring;[20,25] in these cases, complexation to an aldehyde precedes allyl delivery and an ordered intramolecular reaction follows with consequently high stereocontrol. Leighton has been very active in this general field and has reported, inter alia, a variety of elegant systems for intramolecular carbonyl allylation from silicon intermediates.[26] Nevertheless, our examples appear to be the first in which a simple diarylsilyloxy substituent activates the proximal carbonyl group in this way.

6. Experimental

6.1. (But-2-ynyl)diphenylsilane (3)

tert-Butyllithium (13.2 mL, 1.7 M in hexanes, 22 mmol) was added dropwise to a solution of 2-butyne (1.56 mL, 20 mmol) and TMEDA (3.01 mL, 20 mmol) in THF (20 mL) at −78 °C and the mixture was stirred for 30 min. The reaction mixture was allowed to warm to rt over 30 min, re-cooled to −78 °C and chlorodiphenylsilane (3.9 mL, 20 mmol) was added. The resulting solution was stirred for 30 min at −78 °C, rt for 30 min and then partitioned between water (20 mL) and ether (40 mL). The aqueous layer was extracted with ether (40 mL) and the combined organic extracts were washed with brine (20 mL) then dried over $MgSO_4$. The solvent was removed under reduced pressure and the resulting oil was purified by flash column chromatography on silica gel (petrol) to give the product (**3**) as a colourless oil (2.92 g, 62%). R_f 0.13 (petrol); Found C 81.35, H 6.99, $C_{16}H_{16}Si$ requires C 81.30, H 6.82%; ν_{max}/cm^{-1} (thin film) 3069m, 3049m, 2916m, 2135s (SiH), 1428s, 1179m, 1117s, 818br s, 734s, 698s, 675s; δ_H (200 MHz, $CDCl_3$) 1.77 (3H, t, *J* 2.7, CH_3), 2.08 (2H, dq, *J* 3.3, 2.7, $SiCH_2$), 5.00 (1H, t, *J* 3.3, SiH), 7.36–7.47 (6H, m) and 7.64–7.69 (4H, m, 2×Ph); δ_C (50 MHz, $CDCl_3$) 0.0, 0.6, 71.9, 72.7, 124.9, 126.9, 130.0, 132.4; *m*/*z* (EI^+) 236 (M^+, 18%), 183 (100), 105 (52); HRMS (EI^+) found 236.1022, $C_{16}H_{16}Si$ [M^+] requires 236.1016.

6.2. (*Z*-But-2-enyl)diphenylsilane (4)

Silane **3** (1.22 g, 5.18 mmol) was dissolved in a solution of DIBAL (10.4 mL, 1 M in hexanes, 10.4 mmol) and the mixture was heated to reflux for 4 h. The reaction mixture was then poured into a mixture of ice (50 mL), 1 M hydrochloric acid (25 mL) and ether (50 mL) and stirred for 15 min. The aqueous layer was extracted with ether (50 mL) and the combined organic extracts were washed with 1 M hydrochloric acid (25 mL), brine (50 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure and the resulting oil was purified by flash column chromatography on silica gel (petrol) to give the product (**4**) as a colourless oil (965 mg, 78%). R_f 0.25 (petrol); ν_{max}/cm^{-1} (thin film) 3069m, 3017m, 2125s (SiH), 1429s, 1151m, 1118s, 990m, 846s, 808s, 731m, 711s, 698s, 647m; δ_H (200 MHz, $CDCl_3$) 1.54 (3H, d, *J* 5.6, $CHCH_3$), 2.15 (2H, dd, *J* 6.7, 3.6, $SiCH_2$), 4.90 (1H, t, *J* 3.6, SiH), 5.40–5.48 (1H, m) and 5.51–5.58 (1H, m, CH=CH), 7.37–7.46 (6H, m) and 7.47–7.65 (4H, m, 2×Ph); δ_C (100 MHz, $CDCl_3$) 12.6, 13.5, 123.3, 124.7, 128.0, 129.7, 134.1, 135.2; *m*/*z* (CI^+) 256 (MNH_4^+, 42%), 239 (MH^+, 16), 183 (100); HRMS (CI^+) found 256.1520, $C_{16}H_{22}NSi$ [MNH_4^+] requires 256.1516.

6.3. (±)-Ethyl [(*Z*-but-2-enyl)diphenylsilanyloxy]-phenylacetate (5)

Silane **4** (456 mg, 1.93 mmol) and ethyl mandelate (347 mg, 1.93 mmol) were dissolved in dichloromethane (8 mL). Tris(pentafluorophenyl)borane (49 mg, 0.097 mmol) was added and the resulting solution was heated at reflux for 1 h, then allowed to cool to rt and poured into a mixture of water (10 mL) and ether (10 mL). The aqueous layer was extracted with ether (2×10 mL) and the combined organic extracts were washed with brine (10 mL) and then dried over $MgSO_4$. The solvent was removed under reduced pressure and the resulting oil was purified by flash column chromatography on silica gel (petrol/ether, 25:1) to give the product (**5**) as a colourless oil (532 mg, 67%). R_f 0.44 (petrol/ether, 5:1); ν_{max}/cm^{-1} (thin film) 3069m, 3049m, 3016m, 2980m, 2915m, 1753s, 1429s, 1369m, 1263m, 1177s, 1118s, 1072m, 1029m, 880m, 838m, 738s, 699s, 650m; δ_H (300 MHz, $CDCl_3$) 1.12 (3H, t, *J* 7.1, CH_2CH_3), 1.41 (3H, d, *J* 6.6, $CHCH_3$), 2.18 (2H, d, *J* 8.1, $SiCH_2$), 4.02–4.10 (2H, m, CH_2O), 5.27 (1H, s, CHO), 5.33–5.53 (2H, m, CH=CH), 7.31–7.49 (11H, m) and 7.59–7.66 (4H, m, 3×Ph); δ_C (50 MHz, $CDCl_3$) 12.6, 14.0, 15.7, 61.1, 74.8, 123.6, 123.9, 126.7, 127.8, 128.4, 130.1, 133.9, 135.0, 138.7, 138.8, 171.7; *m*/*z* (ES^+) 855 (M_2Na^+, 8%), 439 (MNa^+, 73), 361 (100); HRMS (ESI^+) found 439.1733, $C_{26}H_{28}NaO_3Si$ [MNa^+] requires 439.1700.

6.4. (±)-[(*Z*-But-2-enyl)diphenylsilanyloxy]-phenylacetaldehyde (6)

Ester **5** (522 mg, 1.25 mmol) was dissolved in a mixture of dichloromethane (2.5 mL) and heptane (3.75 mL) and cooled to

−78 °C. DIBAL (1.88 mL, 1 M in hexanes, 1.88 mmol) was added dropwise and the resulting solution was stirred for 1 h. Methanol (5 mL) and aqueous pH 7.4 buffer solution (5 mL) were added, then the reaction mixture was warmed to rt and added to 60% aqueous tartaric acid solution (10 mL) and ether (10 mL). The aqueous layer was extracted with ether (3×20 mL) and the combined organic extracts were washed with brine (20 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure and the resulting oil was purified by flash column chromatography on silica gel (petrol/ether, 15:1) to give the product (**6**) as a colourless oil (260 mg, 56%), which solidified to give a waxy solid on standing. R_f 0.30 [petrol/ether, 5:1 (streaks)]; mp 69–76 °C; ν_{max}/cm^{-1} (thin film) 3070m, 3050m, 3017m, 2917m, 2858m, 2806m, 1737s, 1590m, 1490m, 1453m, 1429s, 1192m, 1118s, 1074s, 1049m, 1028m, 966m, 923m, 857m, 763m, 740s, 699s; δ_H (200 MHz, $CDCl_3$) 1.39 (3H, d, *J* 5.1, $CHCH_3$), 2.16 (2H, dd, *J* 6.8, 0.9, $SiCH_2$), 5.10 (1H, d, *J* 1.7, CHO), 5.33–5.43 (2H, m, CH=CH), 7.31–7.49 (11H, m) and 7.54–7.65 (4H, m, 3×Ph), 9.55 (1H, d, *J* 1.7, CH=O); δ_C (75 MHz, $CDCl_3$) 12.9, 15.9, 80.8, 123.6, 124.4, 127.0, 128.2, 129.0, 130.5, 133.9, 135.1, 136.3, 138.2, 199.0; *m*/*z* (CI^+) 390 (MNH_4^+, 50%), 373 (MH^+, 81), 355 (30), 317 [$M-(C_4H_7)^+$, 100]; HRMS (CI^+) found 373.1631, $C_{24}H_{25}O_2Si$ [MH^+] requires 373.1618.

6.5. (But-3-enyl)diphenylsilane (7)

Magnesium powder (243 mg, 10 mmol), a few crystals of iodine and ether (5 mL) were heated together at reflux for 15 min. A few drops of neat 1-bromobut-3-ene were added to initiate the reaction and then a solution of the remaining 1-bromobut-3-ene (1.02 mL, 10 mmol in total) in ether (5 mL) was added dropwise over 5 min. The mixture was heated at reflux for a further 90 min then chlorodiphenylsilane (1.76 mL, 9.0 mmol) was added dropwise. The mixture was heated at reflux for a further 15 min then cooled to rt, filtered through a plug of silica gel, washing through with ether (2×50 mL). The combined organic portions were washed successively with water (50 mL) and brine (50 mL) then dried over $MgSO_4$. The solvent was removed under reduced pressure and the resulting oil was purified by flash column chromatography on silica gel (petrol/ether, 20:1) to give the product (**7**) as a colourless oil (1.68 g, 78%). R_f 0.30 (petrol); Found C 80.36, H 7.72, $C_{16}H_{18}Si$ requires C 80.61, H 7.61%; ν_{max}/cm^{-1} (thin film) 3069s, 3001m, 2914m, 2120s (SiH), 1639m, 1428s, 1117s, 996m, 904s, 807s, 732s, 699s; δ_H (200 MHz, $CDCl_3$) 1.33 (2H, td, *J* 8.2, 3.6, $SiCH_2$), 2.28 (2H, td, *J* 8.2, 6.2, CH_2CH_2CH), 4.97 (1H, t, *J* 3.6, SiH), 4.96–5.05 (1H, m) and 5.03–5.14 (1H, m, $=CH_2$), 5.98 (1H, ddt, *J* 16.8, 10.3, 6.2, $CH=CH_2$), 7.39–7.53 (6H, m) and 7.60–7.68 (4H, m, 2×Ph); δ_C (50 MHz, $CDCl_3$) 11.4, 28.5, 113.5, 128.0, 129.7, 134.3, 135.3, 140.7; *m*/*z* (EI^+) 238 (M^+, 9%), 210 (23), 183 (100), 160 (25), 132 (17), 105 (78), 78 (97); HRMS (EI^+) found 238.1171, $C_{16}H_{18}Si$ [M^+] requires 238.1172.

6.6. (±)-Ethyl [(but-3-enyl)diphenylsilanyloxy]-phenylacetate (8)

Silane (**7**) (1.51 g, 6.34 mmol) and ethyl mandelate (1.14 g, 6.34 mmol) were dissolved in dichloromethane (10 mL). Tris-(pentafluorophenyl)borane (162 mg, 0.317 mmol) was added and the resulting solution was heated at reflux for 2 h. The mixture was allowed to cool to rt and then partitioned between water (10 mL) and ether (10 mL). The aqueous layer was extracted with ether (2×10 mL) and the combined organic extracts were washed with brine (10 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure and the resulting oil was purified by flash column chromatography on silica gel (petrol/ether, 25:1) to give the product (**8**) as a colourless oil (2.15 g, 82%). R_f 0.32 (petrol/ether, 10:1); Found C 74.93, H 6.74, $C_{26}H_{28}O_3Si$ requires C 74.96, H 6.77%; ν_{max}/cm^{-1} (thin film) 3070m, 2979m, 2910m, 1753s, 1639m, 1454m, 1429s, 1370m, 1264s, 1178br s, 1117br s, 1028s, 894s, 836s, 699s; δ_H (200 MHz, $CDCl_3$) 1.12 (3H, t, *J* 7.2, CH_2CH_3), 1.21–1.34 (2H, m, $SiCH_2$), 2.09–2.23 (2H, m, CH_2CH_2CH), 3.94–4.11 (2H, m, CH_2O), 4.89 (1H, dd, *J* 10.1, 3.5) and 4.96 (1H, dd, *J* 17.0, 3.5, $=CH_2$), 5.23 (1H, s, CHO), 5.87 (1H, ddt, *J* 17.0, 10.1, 6.2, $CH=CH_2$), 7.30–7.67 (15H, m, 3×Ph); δ_C (50 MHz, $CDCl_3$) 13.2, 14.0, 26.9, 61.1, 74.7, 113.0, 126.7, 127.9, 128.4, 128.9, 130.1, 134.1, 134.9, 138.8, 141.0, 171.7; *m*/*z* (CI^+) 434 (MNH_4^+, 40%), 361 (30), 339 (100), 196 (33), 182 (31); HRMS (CI^+) found 434.2142, $C_{26}H_{32}NO_3Si$ [MNH_4^+] requires 434.2146.

6.7. (±)-Ethyl [(*E*-but-2-enyl)diphenylsilanyloxy]-phenylacetate (9)

(1,5-Cyclooctadiene)-bis(methyldiphenylphosphine) iridium(I) hexafluorophosphate (14 mg, 0.016 mmol) was dissolved in degassed dichloromethane (1 mL) and the solution cooled to −78 °C. The catalyst was activated under an atmosphere of hydrogen (balloon) until a colour change from clear blood-red to colourless or clear yellow was observed. The remaining hydrogen was removed and the solution placed under an atmosphere of argon and warmed to 0 °C. A solution of ester **8** (664 mg, 1.60 mmol) in degassed dichloromethane (7 mL) was added by cannula and the resulting solution was stirred for a further 45 min at 0 °C, monitoring by ^1H NMR. Upon completion, the solvent was removed under reduced pressure, the resulting material was triturated with ether (20 mL) and the extract filtered though a silica pad. The solvent was removed under reduced pressure and the resulting oil was purified by flash column chromatography on silica gel (petrol/ether, 20:1→15:1) to give the product (**9**) as a colourless oil (647 mg, 97%). R_f 0.40 (petrol/ether, 10:1); Found C 74.81, H 6.90, $C_{26}H_{28}O_3Si$ requires C 74.96, H 6.77%; ν_{max}/cm^{-1} (thin film) 3070m, 3015m, 2934m, 2916m, 1753s, 1454m, 1429s, 1394m, 1370m, 1264s, 1177br s, 1118br s, 1072s, 1029s, 965m, 838s, 763s, 727s, 699s; δ_H (200 MHz, $CDCl_3$) 1.14 (3H, t, *J* 7.2, CH_2CH_3), 1.57 (3H, d, *J* 5.7, $CHCH_3$), 2.15 (2H, d, *J* 6.8, $SiCH_2$), 3.97–4.13 (2H, m, CH_2O), 5.32 (1H, s, CHO), 5.25–5.47 (2H, m, CH=CH), 7.33–7.51 (11H, m) and 7.58–7.68 (4H, m, 3×Ph); δ_C (50 MHz, $CDCl_3$) 14.0, 18.1, 20.1, 61.1, 74.8, 124.3, 126.0, 126.7, 127.8, 128.4, 128.5, 130.1, 134.1, 135.0, 138.8, 171.7; *m*/*z* (CI^+) 434 (MNH_4^+, 35%), 361 (100), 341 (27), 196 (31), 182 (43), 165 (15), 105 (21); HRMS (CI^+) found 434.2137, $C_{26}H_{32}NO_3Si$ [MNH_4^+] requires 434.2146.

6.8. (±)-[(*E*-But-2-enyl)diphenylsilanyloxy]-phenylacetaldehyde (10)

Ester **9** (758 mg, 1.82 mmol) was dissolved in a mixture of dichloromethane (4 mL) and heptane (6 mL) and cooled to −78 °C. DIBAL (2.73 mL, 1 M in hexanes, 2.73 mmol) was added dropwise and the resulting solution was stirred at −78 °C for 1 h. Methanol (5 mL) and aqueous pH 7.4 buffer solution (5 mL) were added, the mixture warmed to rt and then added to a mixture of 60% aqueous tartaric acid solution (10 mL) and ether (10 mL). The aqueous layer was extracted with ether (3×20 mL) and the combined organic extracts were washed with brine (20 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure and the resulting oil was purified by flash column chromatography on silica gel (petrol/ether, 15:1) to give the product (**10**) as a colourless oil (499 mg, 74%). R_f 0.31 [petrol/ether, 15:1 (streaks)]; ν_{max}/cm^{-1} (thin film) 3070m, 3016m, 2933m, 2856m, 2806m, 1737s, 1453s, 1429m, 1118s, 957s, 923s, 857s, 740m, 699s; δ_H (200 MHz, $CDCl_3$) 1.55 (3H, d, *J* 5.9, $CHCH_3$), 2.13 (2H, d, *J* 5.2, $SiCH_2$), 5.12 (1H, d, *J* 1.7, CHO), 5.19–5.46 (2H, m, CH=CH), 7.31–7.50 (11H, m) and 7.55–7.64 (4H, m, 3×Ph), 9.58 (1H, d, *J* 1.7, CH=O); δ_C (50 MHz, $CDCl_3$) 18.1, 20.1, 80.4, 124.0, 126.4, 126.8, 128.0, 128.5, 128.8, 130.3, 133.8, 134.8, 136.2, 199.0; *m*/*z* (CI^+) 390 (MNH_4^+, 50%), 373 (73), 355 (33), 317

(100), 299 (10); HRMS (CI^+) found 373.1624, $C_{24}H_{25}O_2Si$ [MH^+] requires 373.1618.

6.9. (±)-(3*SR*,4*SR*,5*SR*)-3-Methyl-5-phenylpent-1-en-4,5-diol (12) and (±)-(3*SR*,4*SR*,5*RS*)-3-methyl-5-phenylpent-1-en-4,5-diol (13)

Aldehyde **6** (171 mg, 0.46 mmol) was dissolved in chloroform (10 mL) and the solution was heated at 80 °C for 36 h in a sealed tube. The solvent was removed under reduced pressure and the resulting oil was dissolved in a mixture of methanol (3 mL), ether (3 mL) and water (3 mL). KF (145 mg, 2.5 mmol) and $KHCO_3$ (100 mg, 1.0 mmol) were added and the resulting mixture was stirred at rt for a further 16 h. Water was added (10 mL) and the reaction mixture was extracted with ether (3×20 mL). The combined organic extracts were washed with brine (20 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure and the resulting oil was purified by flash column chromatography on silica gel (petrol/ether, 3:2) to give the major product (**12**) as a white crystalline solid (59 mg, 67%) and the minor product (**13**) as a white crystalline solid (26 mg, 29%). Data for **12**: R_f 0.22 (petrol/ether, 1:1); mp 72–76 °C; ν_{max}/cm^{-1} (KBr) 3371br s, 2970m, 2965s, 2962m, 1450m, 1430m, 1199m, 1122s, 1078m, 1008s, 915m, 912m, 845m, 769m, 699m, 521m; δ_H (200 MHz, $CDCl_3$) 1.08 (3H, d, *J* 6.9, CH_3), 2.16–2.26 (1H, m, C*H*CH_3), 2.46 (1H, d, *J* 3.6, PhCH(O*H*)), 2.83 (1H, d, *J* 4.0, $CH(CH_3)$CH(O*H*)), 3.54–3.61 (1H, m, $CH(CH_3)$C*H*(OH)), 4.59 (1H, dd, *J* 6.5, 3.6, PhC*H*), 5.11 (1H, dd, *J* 17.2, 1.8) and 5.16 (1H, dd, *J* 10.4, 1.8, $=CH_2$), 5.91 (1H, ddd, *J* 17.2, 10.4, 8.4, C*H*$=CH_2$), 7.30–7.41 (5H, m, Ph); δ_C (100 MHz, $CDCl_3$) 17.7, 39.6, 75.2, 78.9, 116.6, 126.8, 128.0, 128.5, 139.1, 141.2; *m*/*z* (CI^+) 210 (MNH_4^+, 8%), 193 (MH^+, 100), 175 (39), 157 (30), 120 (32), 91 (16); HRMS (CI^+) found 210.1494, $C_{12}H_{20}NO_2$ [MNH_4^+] requires 210.1489. Data for **13**: R_f 0.30 (petrol/ether, 1:1); δ_H (200 MHz, $CDCl_3$) 1.10 (3H, d, *J* 6.9, C*H*$_3$), 2.40–2.50 (1H, m, C*H*CH_3), 3.67 (1H, dd, *J* 6.3, 5.0, $CH(CH_3)$C*H*(OH)), 4.65 (1H, d, *J* 6.3, PhC*H*), 5.07–5.19 (2H, m, $=CH_2$), 5.93 (1H, ddd, *J* 17.0, 10.7, 8.4, C*H*$=CH_2$), 7.28–7.51 (5H, m, Ph).

6.10. (±)-(3*RS*,4*SR*,5*SR*)-3-Methyl-5-phenylpent-1-en-4,5-diol (15) and (±)-(3*RS*,4*SR*,5*RS*)-3-methyl-5-phenylpent-1-en-4,5-diol (16)

Aldehyde **10** (95 mg, 0.26 mmol) was dissolved in chloroform (10 mL) and the solution heated at 80 °C for 36 h in a sealed tube. The solvent was removed under reduced pressure and the resulting oil was dissolved in a mixture of methanol (3 mL), ether (3 mL) and water (3 mL). KF (44 mg, 0.8 mmol) was added and the resulting mixture was stirred at rt for a further 16 h. Water was added (10 mL) and the reaction mixture was extracted with ether (3×20 mL). The combined organic extracts were washed with brine (20 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure and the resulting oil was purified by flash column chromatography on silica gel (petrol/ether, 3:2) to give a major product (**15**) as a white crystalline solid (35 mg, 71%) and a minor product (**16**) as a white crystalline solid (14 mg, 28%). Data for **15**: R_f 0.24 (petrol/ether, 1:1); mp 67–68 °C; ν_{max}/cm^{-1} (KBr) 3368br s, 2972m, 1453m, 1430m, 1199m, 1126s, 1073m, 1008s, 911m, 760m, 718m, 699s, 520m; δ_H (400 MHz, $CDCl_3$) 1.07 (3H, d, *J* 6.8, CH_3), 2.26 (1H, dqd, *J* 7.4, 6.8, 5.2, C*H*CH_3), 2.42 (1H, d, *J* 4.4, $CH(CH_3)$CH(O*H*)), 2.89 (1H, d, *J* 4.2, PhCH(O*H*)), 3.59 (1H, ddd, *J* 5.2, 4.6, 4.4, $CH(CH_3)$C*H*(OH)), 4.67 (1H, dd, *J* 4.6, 4.2, PhC*H*), 5.02–5.06 (1H, m) and 5.09–5.13 (1H, m, $=CH_2$), 5.82 (1H, ddd, *J* 17.5, 10.1, 7.4, C*H*$=CH_2$), 7.29–7.41 (5H, m, Ph); δ_C (50 MHz, $CDCl_3$) 14.0, 39.5, 74.5, 78.6, 115.2, 126.6, 127.9, 128.6, 141.2, 141.5; *m*/*z* (CI^+) 210 (MNH_4^+, 7%), 193 (MH^+, 20), 192 (M^+, 100), 175 (37), 157 (33), 143 (15), 120 (35), 105 (16), 91 (28); HRMS (CI^+) found 210.1496, $C_{12}H_{20}NO_2$ [MNH_4^+] requires 210.1489. Data for **16**: R_f 0.24 (petrol/ether, 1:1); δ_H (400 MHz, $CDCl_3$) 1.09 (3H, d, *J* 7.0, CH_3), 2.40–2.49 (1H, m, C*H*CH_3), 3.64–3.67 (1H, m, $CH(CH_3)$C*H*(OH)), 4.66 (1H, d, *J* 6.1, PhC*H*), 5.09–5.16 (2H, m, $=CH_2$), 5.92 (1H, ddd, *J* 17.3, 10.4, 8.4, C*H*$=CH_2$), 7.31–7.43 (5H, m, Ph).

6.11. General procedure for cyanohydrin synthesis[14]

To a solution of $NaHSO_3$ (7.6 g, 73.1 mmol) in water (20 mL) at 0 °C was added the requisite aldehyde (20 mmol) and the mixture was stirred for 30 min. A solution of KCN (5.2 g, 80.0 mmol) in water (100 mL) was added dropwise over 10 min and the resulting solution was stirred at rt for 2 h. The reaction mixture was extracted with ether (3×50 mL) and the combined organic extracts were washed successively with 5 M hydrochloric acid (50 mL), brine (50 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure and the product was used without further purification.

6.12. (±)-2-Hydroxy-3,3-dimethylbutyronitrile (17)

Clear waxy solid (1.96 g, 87%); mp 43–45 °C (lit.[27] 42.5–44 °C); ν_{max}/cm^{-1} (thin film) 3445br s, 2967s, 2912m, 2876m, 2247w, 1479m, 1467m, 1398m, 1370s, 1243m, 1076s, 1023s, 949m, 934m; δ_H (200 MHz, $CDCl_3$) 1.07 (9H, s, $C(CH_3)_3$), 2.96 (1H, br s, OH), 4.13 (1H, s, C*H*(OH)); δ_C (50 MHz, $CDCl_3$) 24.9, 35.4, 70.6, 119.2.

6.13. (±)-2-Hydroxy-3-methylbutyronitrile (18)

Yellow oil (1.88 g, 95%); ν_{max}/cm^{-1} (thin film) 3436br s, 2970s, 2937s, 2879s, 2248w, 1639m, 1470s, 1391m, 1373m, 1064s, 1017m, 973m, 954m; δ_H (200 MHz, $CDCl_3$) 1.06 (3H, d, *J* 5.7) and 1.10 (3H, d, *J* 5.7, $CH(CH_3)_2$), 2.03 (1H, dhept, *J* 5.9, 5.7, C*H*$(CH_3)_2$), 3.21 (1H, br s, OH), 4.27 (1H, d, *J* 5.9, C*H*(OH)); δ_C (50 MHz, $CDCl_3$) 17.2, 17.7, 33.1, 67.0, 119.2.

6.14. General procedure for cyanohydrin silylation

To a solution of dichlorodiphenylsilane (2.03 g, 8.0 mmol) in ether (20 mL) at 0 °C was added allylmagnesium bromide (8.0 mL, 1 M in ether, 8.0 mmol) and the resulting solution was stirred at rt for 1 h. The solvent was removed under reduced pressure and the resulting oil was dissolved in DMF (10 mL). This solution was then added via cannula to a solution of imidazole (545 mg, 8.0 mmol) and the requisite cyanohydrin (**17** or **18**, 4.0 mmol) in DMF (10 mL) and the mixture stirred for 16 h at rt. The reaction was quenched with water (30 mL) and the mixture extracted with ether (3×30 mL). The combined organic extracts were washed with brine (20 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure and the resulting oil was purified by flash column chromatography on silica gel (petrol/ether, 25:1).

6.15. (±)-2-(Allyldiphenylsilanyloxy)-3,3-dimethylbutyronitrile

Colourless oil (963 mg, 72%); R_f 0.57 (petrol/ether, 10:1); Found C 75.14, H 7.58, $C_{21}H_{25}NOSi$ requires C 75.18, H 7.51%; ν_{max}/cm^{-1} (thin film) 3072m, 2966m, 1631m, 1478m, 1429s, 1368m, 1161m, 1111s, 1035m, 902m, 831s, 775m, 738s, 699s; δ_H (400 MHz, $CDCl_3$) 1.03 (9H, s, $Si(CH_3)_3$), 2.29 (1H, ddt, *J* 14.3, 7.8, 1.2) and 2.35 (1H, ddt, *J* 14.3, 7.8, 1.2, $SiCH_2$), 4.01 (1H, s, CHO), 4.95 (1H, ddt, *J* 10.1, 1.8, 1.2) and 5.00 (1H, ddt, *J* 17.0, 1.8, 1.2, $=CH_2$), 5.83 (1H, ddt, *J* 17.0, 10.1, 7.8, C*H*$=CH_2$), 7.40–7.51 (6H, m) and 7.62–7.64 (4H, m, 2×Ph); δ_C (100 MHz, $CDCl_3$) 21.4, 25.1, 36.3, 71.5, 116.1, 118.8, 128.0, 128.1, 130.6, 131.9, 132.4, 132.5, 134.4, 134.8, 135.1; *m*/*z* (CI^+) 353 (MNH_4^+, 100%), 311 (34), 294 (23), 267 (14), 225 (5), 215 (10), 198 (11); HRMS (CI^+) found 353.2053, $C_{21}H_{29}N_2OSi$ [MNH_4^+] requires 353.2044.

6.16. (±)-2-(Allyldiphenylsilanyloxy)-3-methylbutyronitrile

Colourless oil (925 mg, 72%); R_f 0.51 (petrol/ether, 10:1); ν_{max}/cm^{-1} (thin film) 3072m, 3052m, 2967s, 2932m, 2876m, 2240w, 1631s, 1590m, 1468m, 1429s, 1390m, 1371m, 1354m, 1186m, 1161s, 1118s, 1063s, 1028m, 998m, 902m, 834m, 809m, 769m, 738s, 699s; δ_H (400 MHz, $CDCl_3$) 0.99 (3H, d, *J* 7.0) and 1.09 (3H, d, *J* 6.7, CH(C*H*$_3$)$_2$), 2.03 (1H, app. heptd, *J* 7.0, 5.3, C*H*(CH$_3$)$_2$), 2.30 (1H, ddt, *J* 15.6, 7.7, 1.2) and 2.35 (1H, ddt, *J* 15.6, 7.7, 1.2, SiC*H*$_2$), 4.27 (1H, d, *J* 5.3, CHO), 4.98 (1H, ddt, *J* 10.1, 1.7, 1.2) and 5.05 (1H, ddt, *J* 17.0, 1.7, 1.2, =CH$_2$), 5.87 (1H, ddt, *J* 17.0, 10.1, 7.7, C*H*=CH$_2$), 7.41–7.51 (6H, m) and 7.62–7.65 (4H, m, 2×Ph); δ_C (100 MHz, $CDCl_3$) 17.1, 17.6, 21.5, 33.9, 68.0, 116.0, 118.6, 127.9, 128.0, 130.6, 131.9, 132.4, 132.5, 134.4, 134.8, 134.9; *m*/*z* (CI$^+$) 339 (MNH_4^+, 100%), 297 (43), 270 (18), 253 (14), 198 (13); HRMS (CI$^+$) found 339.1893, $C_{20}H_{27}N_2OSi$ [MNH_4^+] requires 339.1887.

6.17. General procedure for silylcyanohydrin reduction

To a solution of the requisite silylcyanohydrin (1.0 mmol) in dichloromethane (10 mL) at −78 °C was added DIBAL (1.5 mL, 1 M in pentane, 1.5 mmol) and the mixture was stirred for 1 h. A saturated solution of tartaric acid in methanol (5 mL) was added and the reaction mixture partitioned between water (20 mL) and ether (40 mL). The aqueous layer was extracted with ether (40 mL) and the combined organic extracts were washed with saturated aqueous tartaric acid (30 mL) and brine (20 mL) then dried over $MgSO_4$. The solvent was removed under reduced pressure and the resulting oil was purified by flash column chromatography on silica gel (petrol/ether, 25:1).

6.18. (±)-2-(Allyldiphenylsilanyloxy)-3,3-dimethylbutyraldehyde (21)

Colourless oil (328 mg, 97%); R_f 0.52 (petrol/ether, 10:1); ν_{max}/cm^{-1} (thin film) 3071s, 3001m, 2962s, 2871s, 1733s, 1631m, 1590m, 1478m, 1421s, 1396m, 1366s, 1158s, 1118s, 1307s, 998m, 900s, 847s, 770s, 737s, 598s; δ_H (400 MHz, $CDCl_3$) 0.99 (9H, s, C(CH$_3$)$_3$), 2.22 (1H, ddt, *J* 14.4, 7.6, 1.4) and 2.27 (1H, ddt, *J* 14.4, 7.6, 1.4, SiCH$_2$), 3.69 (1H, d, *J* 2.8, CHO), 4.90–4.98 (2H, m, =CH$_2$), 5.81 (1H, ddt, *J* 17.0, 10.1, 7.6, C*H*=CH$_2$), 7.38–7.48 (6H, m) and 7.61–7.66 (4H, m, 2×Ph), 9.60 (1H, d, *J* 2.8, CH=O); δ_C (100 MHz, $CDCl_3$) 21.9, 25.8, 36.1, 84.9, 115.6, 127.8, 128.0, 130.2, 130.2, 132.5, 133.7, 134.8, 134.8, 134.9, 203.6; δ_{Si} (99 MHz, toluene-d_8) −6.35; *m*/*z* (CI$^+$) 356 (MNH_4^+, 100%), 339 (MH^+, 63), 297 (96), 281 (38), 216 (29); HRMS (CI$^+$) found 339.1781, $C_{21}H_{27}O_2Si$ [MH^+] requires 339.1775.

6.19. (±)-2-(Allyldiphenylsilanyloxy)-3-methylbutyraldehyde (22)

Colourless oil (206 mg, 64%); R_f 0.45 (petrol/ether, 10:1); ν_{max}/cm^{-1} (thin film) 3071m, 3001m, 2965s, 2875m, 1736s, 1630m, 1467m, 1428s, 1388m, 1368m, 1188m, 1161s, 1118s, 1069s, 1028m, 998m, 928m, 901s, 846m, 770m, 737s, 699s; δ_H (400 MHz, $CDCl_3$) 0.96 (3H, d, *J* 6.8) and 0.97 (3H, d, *J* 6.8, CH(C*H*$_3$)$_2$), 2.05–2.12 (1H, m, C*H*(CH$_3$)$_2$), 2.23 (1H, ddt, *J* 14.0, 7.9, 1.2) and 2.28 (1H, ddt, *J* 14.0, 7.9, 1.2, SiCH$_2$), 3.93 (1H, dd, *J* 4.4, 1.6, CHO), 4.90–4.94 (1H, m) and 4.93–4.99 (1H, m, =CH$_2$), 5.83 (1H, ddt, *J* 17.2, 10.1, 7.9, C*H*=CH$_2$), 7.38–7.48 (6H, m) and 7.61–7.64 (4H, m, 2×Ph), 9.58 (1H, d, *J* 1.6, CH=O); δ_C (100 MHz, $CDCl_3$) 16.9, 18.6, 22.0, 31.7, 82.4, 115.6, 127.8, 127.9, 130.2, 130.2, 132.6, 133.8, 133.9, 134.8, 134.9, 203.9; *m*/*z* (CI$^+$) 342 (MNH_4^+, 91%), 325 (MH^+, 70), 283 (100); HRMS (CI$^+$) found 325.1626, $C_{20}H_{25}O_2Si$ [MH^+] requires 325.1618.

6.20. General procedure for silatropic ene reaction

A solution of aldehyde **21** or **22** (0.48–0.83 mmol) in either benzene (10 mL) or toluene (10 mL) was heated for 18 h at 80 °C in a base-washed sealed tube. The solvent was removed under reduced pressure to give the product, which was used without further purification.

6.21. (±)-4,5-*trans*-4-Allyl-5-*tert*-butyl-2,2-diphenyl-[1,3,2]-dioxasilolane (23)

On a 0.83 mmol scale the reaction gave **23** as a colourless oil (258 mg, 92%); ν_{max}/cm^{-1} (thin film) 3072m, 2958s, 2908m, 2870m, 1479m, 1430s, 1365m, 1126s, 1117s, 1053s, 1018s, 997m, 908m, 862m, 806m, 794s, 719s, 699s; δ_H (400 MHz, $CDCl_3$) 0.97 (9H, s, C(CH$_3$)$_3$), 2.33–2.48 (2H, m, CH$_2$), 3.74 (1H, d, *J* 5.9, *t*-BuC*H*O), 4.28 (1H, ddd, *J* 7.6, 5.9, 4.4, CH$_2$C*H*O), 5.10–5.15 (2H, m, =CH$_2$), 5.92–6.02 (1H, m, C*H*=CH$_2$), 7.39–7.52 (6H, m) and 7.69–7.73 (4H, m, 2×Ph); δ_C (100 MHz, $CDCl_3$) 25.8, 37.7, 42.7, 76.1, 87.6, 117.4, 127.8, 128.0, 130.8, 130.9, 131.9, 133.2, 134.5, 135.0, 135.1; δ_{Si} (99 MHz, toluene-d_8) −5.02; *m*/*z* (CI$^+$) 356 (MNH_4^+, 66%), 339 (MH^+, 61), 297 (100), 281 (43), 216 (34); HRMS (CI$^+$) found 339.1792, $C_{21}H_{27}SiO_2$ [MH^+] requires 339.1775.

6.22. (±)-4,5-*trans*-4-Allyl-5-isopropyl-2,2-diphenyl-[1,3,2]-dioxasilolane (24)

On a 0.48 mmol scale the reaction gave **24** as a colourless oil (137 mg, 89%); ν_{max}/cm^{-1} (thin film) 3072m, 2962s, 2874m, 1469m, 1430s, 1388m, 1125s, 1059s, 1027s, 917m, 741m, 718s, 700s; δ_H (400 MHz, $CDCl_3$) 1.06 (3H, d, *J* 6.8) and 1.07 (3H, d, *J* 6.5, CH(C*H*$_3$)$_2$), 1.82–1.90 (1H, m, C*H*(CH$_3$)$_2$), 2.47 (2H, app. dd, *J* 7.2, 6.4, CH$_2$), 3.82 (1H, dd, *J* 5.8, 5.8, *i*-PrC*H*O), 4.21 (1H, td, *J* 6.4, 5.8, CH$_2$C*H*O), 5.15–5.22 (2H, m, =C*H*$_2$), 6.00 (1H, ddt, *J* 17.7, 10.4, 7.2, C*H*=CH$_2$), 7.42–7.52 (6H, m) and 7.73–7.76 (4H, m, 2×Ph); δ_C (100 MHz, $CDCl_3$) 17.5, 19.5, 32.2, 40.9, 77.7, 84.8, 117.6, 127.8, 127.9, 130.4, 130.9, 132.4, 132.7, 134.5, 135.0, 135.3; *m*/*z* (CI$^+$) 342 (MNH_4^+, 21%) 325 (MH^+, 54), 283 (100), 216 (45), 199 (16), 183 (15), 109 (13); HRMS (CI$^+$) found 325.1625, $C_{20}H_{25}O_2Si$ [MH^+] requires 325.1618.

6.23. (±)-2-Hydroxy-3,3-dimethylbutyric acid[28]

A solution of cyanohydrin **17** (2.26 g, 20 mmol) in 35% hydrochloric acid (20 mL) was stirred for 16 h at rt and then heated at reflux for 4 h. The solution was allowed to cool to rt, then NaCl (1.0 g) was added and the reaction mixture extracted with ether (3×20 mL). The combined organic extracts were dried over $MgSO_4$ and the solvent was removed under reduced pressure to give the acid as a white crystalline solid (2.56 g, 97%). ν_{max}/cm^{-1} (KBr) 3426br s, 2965br s, 1714s, 1481s, 1371s, 1283m, 1225s, 1184m, 1085s, 1025m; δ_H (200 MHz, $CDCl_3$) 1.00 (9H, s, C(CH$_3$)$_3$), 3.87 (1H, s, C*H*(OH)); δ_C (50 MHz, $CDCl_3$) 26.2, 35.7, 78.7, 178.7.

6.24. (±)-Methyl (2-hydroxy-3,3-dimethyl)butyrate (26)

To a solution of 2-hydroxy-3,3-dimethylbutyric acid (2.30 g, 17.0 mmol) in methanol (20 mL) was added acetyl chloride (120 μL, 1.7 mmol) and the reaction mixture was heated at reflux for 16 h. The solvent was removed under reduced pressure and the resulting oil was dissolved in ethyl acetate (40 mL). The solution was washed with saturated aqueous $NaHCO_3$ solution (3×40 mL) and brine (40 mL) then dried over $MgSO_4$. The solvent was removed under reduced pressure to give the product (**26**) as a colourless oil (1.66 g, 66%). R_f 0.13 (petrol/ether, 10:1); ν_{max}/cm^{-1} (thin film) 3504br s, 2959s, 2909s, 2873s, 1736s, 1480s, 1439s, 1397m, 1368s, 1275s, 1222s, 1173s, 1089s, 1024s, 987m, 802m, 749m; δ_H (200 MHz,

$CDCl_3$) 0.91 (9H, s, $C(CH_3)_3$), 2.83 (1H, br s, OH), 3.73 (3H, s, OCH_3), 3.77 (1H, s, C*H*(OH)); δ_C (50 MHz, $CDCl_3$) 26.1, 35.6, 52.4, 78.9, 175.2; *m*/*z* (CI^+) 164 (MNH_4^+, 100%), 147 (MH^+, 62), 99 (11); HRMS (CI^+) found 147.1019, $C_7H_{15}O_3$ [MH^+] requires 147.1016.

6.25. (±)-Methyl 2-[(*Z*-but-2-enyl)diphenylsilanyloxy]-3,3-dimethylbutyrate (27)

Silane **4** (827 mg, 3.47 mmol) and hydroxyester **26** (507 mg, 3.47 mmol) were dissolved in dichloromethane (10 mL). Tris-(pentafluorophenyl)borane (89 mg, 0.17 mmol) was added and the reaction mixture was heated at reflux for 3 h. The reaction mixture was allowed to cool to rt and then poured into water (10 mL) and ether (20 mL). The aqueous layer was extracted with ether (2×30 mL) and the combined organic extracts were washed with brine (20 mL) and then dried over $MgSO_4$. The solvent was removed under reduced pressure and the resulting oil was purified by flash column chromatography on silica gel (petrol/ether, 25:1) to give the product (**27**) as a colourless oil (695 mg, 52%). R_f 0.44 (petrol/ether, 10:1); Found C 72.22, H 7.99, $C_{23}H_{30}O_3Si$ requires C 72.21, H 7.90%; ν_{max}/cm^{-1} (thin film) 2957m, 1752s, 1429m, 1364m, 1272m, 1218m, 1162m, 1118s, 1037m, 993m, 846m, 780m, 739m, 700s, 647m; δ_H (400 MHz, $CDCl_3$) 0.96 (9H, s, $C(CH_3)_3$), 1.40 (3H, dd, *J* 6.8, 1.2, =CHC*H*$_3$), 2.14 (2H, app. dd, *J* 8.1, 1.4, $SiCH_2$), 3.41 (3H, s, OCH_3), 3.93 (1H, s, CHO), 5.33–5.41 (1H, m, =C*H*CH_3), 5.45–5.52 (1H, m, CH_2C*H*=), 7.34–7.46 (6H, m) and 7.59–7.64 (4H, m, 2×Ph); δ_C (100 MHz, $CDCl_3$) 12.6, 15.1, 25.9, 35.4, 50.9, 80.4, 123.7, 125.6, 127.6, 127.6, 129.9, 132.0, 134.0, 134.1, 135.1, 135.1, 172.4; *m*/*z* (CI^+) 400 (MNH_4^+, 59%), 327 (100), 305 (42), 299 (30), 213 (33); HRMS (CI^+) found 400.2306, $C_{23}H_{34}NO_3Si$ [MNH_4^+] requires 400.2302.

6.26. (±)-2-[(*Z*-But-2-enyl)diphenylsilanyloxy]-3,3-dimethylbutanol

To a stirred solution of ester **27** (666 mg, 1.74 mmol) in dichloromethane (10 mL) at −78 °C was added DIBAL (3.66 mL, 1 M in dichloromethane, 3.66 mmol). The resulting solution was stirred for 1 h then a saturated solution of tartaric acid in methanol (5 mL) was added. The reaction mixture was allowed to warm to rt and then partitioned between ether (30 mL) and 1 M hydrochloric acid (20 mL). The aqueous layer was extracted with ether (20 mL) and the combined organic portions were washed with 1 M hydrochloric acid (20 mL) and brine (20 mL) then dried over $MgSO_4$. The solvent was removed under reduced pressure and the resulting oil was purified by flash column chromatography on silica gel (petrol/ether, 10:1) to give the product as a colourless oil (509 mg, 83%). R_f 0.24 (petrol/ether, 10:1); ν_{max}/cm^{-1} (thin film) 3582br s, 3015m, 2958m, 2870m, 1428m, 1395m, 1362m, 1111s, 1032m, 996m, 951m, 782m, 738m, 700s, 646m; δ_H (400 MHz, $CDCl_3$) 0.90 (9H, s, $C(CH_3)_3$), 1.41 (3H, dd, *J* 6.4, 1.7, =CHC*H*$_3$), 2.15–2.25 (2H, m, $SiCH_2$), 3.48 (1H, dd, *J* 7.2, 2.5, CHO), 3.57 (1H, dd, *J* 11.6, 7.2) and 3.64 (1H, dd, *J* 11.6, 2.5, C*H*$_2$OH), 5.38 (1H, dqt, *J* 11.6, 6.4, 1.6, =C*H*CH_3), 5.50 (1H, dtq, *J* 11.6, 8.4, 1.7, CH_2C*H*=), 7.36–7.47 (6H, m) and 7.61–7.69 (4H, m, 2×Ph); δ_C (100 MHz, $CDCl_3$) 12.8, 15.8, 26.5, 34.6, 64.1, 82.5, 123.8, 124.1, 127.8, 127.9, 129.8, 132.0, 134.9, 134.9, 135.0, 135.1; *m*/*z* (ESI−) 353 ($M-H^+$, 100%), 311 (20); HRMS (ESI−) found 353.1935, $C_{22}H_{29}O_2Si$ ($M-H^+$) requires 353.1942.

6.27. (±)-2-[(*Z*-But-2-enyl)diphenylsilanyloxy]-3,3-dimethylbutyraldehyde (28)

To a stirred solution of oxalyl chloride (170 μL, 1.94 mmol) in dichloromethane (5 mL) at −78 °C was added DMSO (220 μL, 3.1 mmol). After 10 min a cooled solution of (±)-2-[(*Z*-but-2-enyl)-diphenylsilanyloxy]-3,3-dimethylbutanol (550 mg, 1.55 mmol) in dichloromethane (5 mL) was added via cannula. After a further 10 min triethylamine (860 μL, 6.2 mmol) was added and the resulting cloudy solution was stirred for 15 min at −78 °C and then allowed to warm to rt over 1 h. The reaction mixture was partitioned between water (20 mL) and ether (40 mL) and the aqueous layer was extracted with ether (40 mL). The combined organic extracts were washed with brine (20 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure and the resulting oil was purified by flash column chromatography on silica gel (petrol/ether, 25:1) to give the product (**28**) as a colourless oil (469 mg, 86%). R_f 0.58 (petrol/ether, 10:1); ν_{max}/cm^{-1} (thin film) 3071m, 3017m, 2961s, 2871m, 1732s, 1590m, 1478m, 1429s, 1396m, 1365m, 1154s, 1118s, 1037m, 991m, 899m, 847m, 779s, 738s, 699s, 648s; δ_H (400 MHz, $CDCl_3$) 0.98 (9H, s, $C(CH_3)_3$), 1.41 (3H, dd, *J* 6.5, 1.2, =CHC*H*$_3$), 2.11–2.21 (2H, m, $SiCH_2$), 3.65 (1H, d, *J* 2.8, CHO), 5.35–5.51 (2H, m, CH=CH), 7.37–7.47 (6H, m) and 7.60–7.64 (4H, m, 2×Ph), 9.58 (1H, d, *J* 2.8, CH=O); δ_C (100 MHz, $CDCl_3$) 12.6, 15.4, 25.9, 36.0, 84.8, 123.4, 124.0, 126.9, 127.8, 130.1, 130.2, 133.9, 134.1, 134.9, 135.0, 203.8; *m*/*z* (CI^+) 370 (MNH_4^+, 8%), 353 (MH^+, 19), 297 (100), 216 (36), 155 (11), 137 (17), 78 (16); HRMS (CI^+) found 353.1941, $C_{22}H_{29}O_2Si$ [MH^+] requires 353.1931.

6.28. (±)-(4*SR*,5*SR*,3′*SR*)-5-*tert*-Butyl-4-(but-1′-en-3′-yl)-2,2-diphenyl-[1,3,2]-dioxasilolane

A solution of aldehyde **28** (466 mg, 1.3 mmol) in benzene (10 mL) was heated for 36 h at 80 °C in a base-washed sealed tube. After cooling, the solvent was removed under reduced pressure to give the product, which was used without further purification, as a colourless oil (459 mg, 99%). ν_{max}/cm^{-1} (thin film) 3071m, 2960s, 2907m, 2870m, 1479m, 1430s, 1365m, 1117s, 1061s, 1012s, 996s, 970m, 932m, 916m, 854s, 812m, 740s, 699s; δ_H (400 MHz, $CDCl_3$) 0.93 (9H, s, $C(CH_3)_3$), 1.17 (3H, d, *J* 6.9, CHC*H*$_3$), 2.21–2.29 (1H, m, C*H*CH_3), 3.88 (1H, d, *J* 5.6, *t*-BuC*H*O), 4.12 (1H, dd, *J* 5.6, 4.0, CHC*H*O), 4.93 (1H, ddd, *J* 17.2, 2.0, 0.8) and 4.98 (1H, dd, *J* 10.0, 2.0, =CH_2), 5.71 (1H, ddd, *J* 17.2, 10.0, 8.6, C*H*=CH_2), 7.37–7.50 (6H, m) and 7.65–7.70 (4H, m, 2×Ph); δ_C (100 MHz, $CDCl_3$) 18.3, 25.9, 34.8, 44.2, 80.1, 85.8, 116.0, 127.7, 127.7, 130.0, 130.7, 132.4, 132.9, 135.2, 135.3, 139.6; *m*/*z* (CI^+) 370 (MNH_4^+, 4%), 353 (MH^+, 14), 297 (100), 216 (46), 137 (17), 94 (12), 78 (13); HRMS (CI^+) found 370.2208, $C_{22}H_{32}NO_2Si$ [MNH_4^+] requires 370.2197.

6.29. (±)-(3*SR*,4*SR*,5*SR*)-3,6,6-Trimethylhept-1-en-4,5-diol (29)

To a stirred solution of (±)-(4*SR*,5*SR*,3′*SR*)-5-*tert*-butyl-4-(but-1′-en-3′-yl)-2,2-diphenyl-[1,3,2]-dioxasilolane (423 mg, 1.2 mmol) in a mixture of ether (5 mL), water (5 mL) and methanol (5 mL) were added KF (313 mg, 5.4 mmol) and hydrogen peroxide (2 mL, 30% aq). The resulting solution was stirred at rt for 16 h. The solvent was removed under reduced pressure and the resulting material triturated with ether (40 mL) and the extract washed with water (20 mL). The aqueous layer was extracted with ether (40 mL) and the combined organic extracts were washed with brine (20 mL) and then dried over $MgSO_4$. The solvent was removed under reduced pressure and the resulting oil was purified by flash column chromatography on silica gel (petrol/ether, 5:1→1:1) to give the product (**29**) as a white solid (181 mg, 88%). R_f 0.15 (petrol/ether, 5:1); ν_{max}/cm^{-1} (KBr) 3434br s, 3292br s, 3082m, 2963s, 1478m, 1429m, 1127s, 1085s, 1056s, 1013m, 997m, 955m, 909s, 720s, 699s; δ_H (400 MHz, $CDCl_3$) 0.93 (9H, s, $C(CH_3)_3$), 1.04 (3H, d, *J* 6.8, CHC*H*$_3$), 2.26–2.35 (1H, m, C*H*CH_3), 2.47–2.37 (1H, br s, O*H*), 2.65 (1H, br s, O*H*), 3.20 (1H, br d, *J* 2.4, *t*-BuC*H*(OH)), 3.49 (1H, app. br d, *J* 7.2, CHC*H*(OH)), 5.12–5.17 (2H, m, =CH_2), 5.76 (1H, ddd, *J* 18.0, 9.6, 8.7, C*H*=CH_2); δ_C (100 MHz, $CDCl_3$) 16.5, 26.1, 35.0, 43.8, 71.4, 77.4, 116.9, 140.6; *m*/*z* (CI^+) 190 (MNH_4^+, 23%), 173 (MH^+, 81), 155 (66), 137 (100), 121 (22), 99 (17), 92 (24); HRMS (CI^+) found 190.1812, $C_{10}H_{24}NO_2$ [MNH_4^+] requires 190.1807.

6.30. (±)-(3*SR*,4*SR*,5*SR*)-4,5-Di(allyloxy)-3,6,6-trimethylhept-1-ene

A mixture of diol **29** (48 mg, 0.3 mmol) and NaH (70 mg, 60% in mineral oil, 1.8 mmol) was stirred for 15 min in THF (2 mL) and DMF (2 mL). The solution was cooled to 0 °C and allyl bromide (150 μL, 1.8 mmol) was added dropwise. The reaction mixture was allowed to warm to rt and then stirred for 16 h. The resulting solution was partitioned between water (30 mL) and ether (30 mL), the aqueous layer was extracted with ether (30 mL) and the combined organic extracts were washed with brine (20 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure and the resulting oil was purified by flash column chromatography on silica gel (petrol/ether, 25:1) to give the title compound as a colourless oil (54 mg, 72%). R_f 0.68 (petrol/ether, 10:1); ν_{max}/cm^{-1} (thin film) 2956s, 2926s, 2870s, 2853s, 1480m, 1459m, 1422m, 1362m, 1145m, 1086s, 1002m, 914s; δ_H (400 MHz, $CDCl_3$) 0.93 (9H, s, $C(CH_3)_3$), 1.12 (3H, d, *J* 6.8, $CHCH_3$), 2.11–2.19 (1H, m, $CHCH_3$), 2.95 (1H, d, *J* 6.8, *t*-BuC*H*O), 3.26 (1H, dd, *J* 6.8, 2.7, CHC*H*O), 3.85 (1H, ddt, *J* 12.7, 6.1, 1.4), 3.91 (1H, ddt, *J* 12.7, 6.1, 1.4), 4.28 (1H, ddt, *J* 9.2, 5.6, 1.8) and 4.31 (1H, ddt, *J* 9.2, 5.6, 1.8, 2×OCH_2), 5.01–5.14 (4H, m), 5.23 (1H, ddt, *J* 17.6, 5.6, 1.8) and 5.25 (1H, ddt, *J* 17.6, 5.6, 1.8, 3×=CH_2), 5.89–5.98 (3H, m, 3×C*H*=CH_2); δ_C (100 MHz, $CDCl_3$) 18.8, 26.5, 34.9, 43.7, 72.9, 73.4, 81.1, 86.1, 115.3, 115.5, 115.7, 135.9, 136.0, 140.2; *m*/*z* (CI^+) 253 (MH^+, 100%), 127 (66); HRMS (CI^+) found 253.2177, $C_{16}H_{29}O_2$ [MH^+] requires 253.2162.

6.31. (±)-(2*SR*,3*SR*,1′*SR*)-2-(1′-Allyloxy-2′,2′-dimethylpropyl)-3-methyl-3,6-dihydro-2*H*-pyran (30)

To a stirred solution of (±)-(3*SR*,4*SR*,5*SR*)-4,5-di(allyloxy)-3,6,6-trimethylhept-1-ene (50 mg, 0.2 mmol) in degassed dichloromethane (5 mL) was added Grubbs II catalyst (**25**, 3 mg, 0.004 mmol). The resulting brown solution was stirred at rt for 4 h. The solvent was removed under reduced pressure and the resulting oil was purified by flash column chromatography on silica gel (petrol/ether, 20:1) to give the product (**30**) as a colourless oil (16 mg 35%). R_f 0.32 (petrol/ether, 10:1); ν_{max}/cm^{-1} (thin film) 3028m, 2958s, 2874s, 2811m, 1481m, 1459m, 1392m, 1360m, 1338m, 1261m, 1182m, 1135s, 1113s, 1080s, 1034m, 1013m, 920m; δ_H (400 MHz, $CDCl_3$) 0.95 (3H, d, *J* 7.0, $CHCH_3$), 1.01 (9H, s, $C(CH_3)_3$), 2.54–2.64 (1H, m, $CHCH_3$), 3.08 (1H, d, *J* 0.6, *t*-BuC*H*O), 3.22 (1H, dd, *J* 9.4, 0.6, CHC*H*O), 4.01–4.03 (1H, m), 4.05–4.07 (1H, m) and 4.12–4.24 (2H, m, 2×OCH_2), 5.13 (1H, ddt, *J* 10.0, 1.6, 1.0) and 5.25 (1H, ddt, *J* 17.2, 1.6, 1.6, =C*H*$_2$), 5.59–5.63 (1H, m) and 5.67–5.71 (1H, m, CH=CH), 5.99 (1H, ddt, *J* 17.2, 10.0, 6.0, C*H*=CH_2); δ_C (100 MHz, $CDCl_3$) 17.6, 27.6, 34.1, 36.0, 65.6, 76.1, 79.9, 85.4, 116.4, 125.1, 131.5, 135.5; *m*/*z* (CI^+) 242 (MNH_4^+, 11%), 225 (MH^+, 100), 167 (27), 127 (44), 97 (17); HRMS (CI^+) found 225.1858, $C_{14}H_{25}O_2$ [MH^+] requires 225.1849.

6.32. (±)-Methyl 2-[(but-3-enyl)diphenylsilanyloxy]-3,3-dimethylbutyrate (31)

To a solution of hydroxyester **26** (584 mg, 4.0 mmol) and silane **7** (952 mg, 4.0 mmol) in dichloromethane (10 mL) was added tris(pentafluorophenyl)borane (102 mg, 0.2 mmol) and the reaction mixture was heated at reflux for 3 h. The mixture was allowed to cool to rt and then poured into water (20 mL) and extracted with ether (3×30 mL). The combined organic extracts were washed with brine (20 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure and the resulting oil was purified by flash column chromatography on silica gel (petrol/ether, 50:1) to give the product (**31**) as a colourless oil (1.20 g, 78%). R_f 0.41 (petrol/ether, 10:1); Found C 72.32, H 8.00, $C_{23}H_{30}O_3Si$ requires C 72.21, H 7.90%; ν_{max}/cm^{-1} (thin film) 3071m, 3000m, 2976s, 2957s, 2909m, 1752s, 1639m, 1479m, 1429s, 1368m, 1271m, 1218s, 1163s, 1117s, 1037m, 996m, 909m, 890m, 844m, 740s, 700s; δ_H (400 MHz, $CDCl_3$) 0.96 (9H, s, $C(CH_3)_3$), 1.21–1.30 (2H, m, $SiCH_2$), 2.11–2.19 (2H, m, CH_2CH=), 3.41 (3H, s, OCH_3), 3.90 (1H, s, CHO), 4.90 (1H, dtd, *J* 10.2, 1.7, 1.0) and 5.00 (1H, dtd, *J* 17.1, 1.7, 1.0, =CH_2), 5.90 (1H, ddt, *J* 17.1, 10.2, 6.2, C*H*=CH_2), 7.36–7.46 (6H, m) and 7.58–7.63 (4H, m, 2×Ph); δ_C (100 MHz, $CDCl_3$) 12.7, 25.9, 26.9, 35.4, 50.9, 80.3, 112.9, 127.7, 127.7, 129.9, 130.0, 134.0, 134.2, 134.9, 135.0, 141.1, 172.4; *m*/*z* (CI^+) 400 (MNH_4^+, 49%), 327 (41), 305 (100), 230 (14), 213 (13), 183 (13); HRMS (CI^+) found 400.2297, $C_{23}H_{34}NO_3Si$ [MNH_4^+] requires 400.2302.

6.33. (±)-Methyl 2-[(*E*-but-2-enyl)diphenylsilanyloxy]-3,3-dimethylbutyrate (32)

(1,5-Cyclooctadiene) bis(methyldiphenylphosphine) iridium(I) hexafluorophosphate (24 mg, 0.028 mmol) was dissolved in degassed dichloromethane (5 mL) and the solution cooled to −78 °C. The catalyst was activated under an atmosphere of hydrogen (balloon) until a colour change from clear blood-red to colourless or clear yellow was observed. The remaining hydrogen was removed and the reaction placed under an atmosphere of argon and warmed to 0 °C. A solution of silyloxyester **31** (1.06 g, 2.78 mmol) in degassed dichloromethane (5 mL) was added via cannula and the reaction mixture was stirred at 0 °C for 30 min, with monitoring by ^1H NMR. The solvent was removed under reduced pressure, the product triturated with ether (30 mL) and the extract filtered though a silica pad. The solvent was removed under reduced pressure and the resulting oil was purified by flash column chromatography on silica gel (petrol/ether, 15:1) to give the product (**32**) as a colourless oil (960 mg, 91%). R_f 0.33 (petrol/ether, 10:1); Found C 72.29, H 8.01, $C_{23}H_{30}O_3Si$ requires C 72.21, H 7.90%; ν_{max}/cm^{-1} (thin film) 3070m, 3015m, 2957s, 2884m, 1751s, 1479m, 1429s, 1396m, 1368m, 1271m, 1218s, 1163s, 1118s, 1037s, 965m, 871m, 846m, 763m, 739s, 700s; δ_H (400 MHz, $CDCl_3$) 0.96 (9H, s, $C(CH_3)_3$), 1.59 (3H, d, *J* 6.8, $CHCH_3$), 2.13 (2H, app. d, *J* 7.2, $SiCH_2$), 3.41 (3H, s, OCH_3), 3.96 (1H, s, CHO), 5.30–5.47 (2H, m, CH=CH), 7.35–7.46 (6H, m) and 7.58–7.65 (4H, m, 2×Ph); δ_C (100 MHz, $CDCl_3$) 18.1, 19.6, 25.9, 35.4, 50.9, 80.3, 124.5, 125.9, 127.6, 127.7, 129.9, 129.9, 134.1, 134.2, 135.1, 135.5, 172.4; *m*/*z* (CI^+) 400 (MNH_4^+, 63%), 327 (100), 305 (56), 299 (31), 230 (33), 213 (25), 183 (11); HRMS (CI^+) found 400.2302, $C_{23}H_{34}NO_3Si$ [MNH_4^+] requires 400.2302.

6.34. (±)-2-[(*E*-But-2-enyl)diphenylsilanyloxy]-3,3-dimethylbutanol

To a stirred solution of ester **32** (929 mg, 2.43 mmol) in dichloromethane (10 mL) at −78 °C was added DIBAL (5.35 mL, 1 M in dichloromethane, 5.35 mmol). The resulting solution was stirred for 1 h then a saturated solution of tartaric acid in methanol (5 mL) was added. The reaction mixture was allowed to warm to rt and then partitioned between ether (30 mL) and 1 M hydrochloric acid (20 mL). The organic layer was washed with 1 M hydrochloric acid (20 mL) and the aqueous layer was extracted with ether (20 mL). The organic extracts were combined and the solvent was removed under reduced pressure. The resulting oil was purified by flash column chromatography on silica gel (petrol/ether, 10:1) to give the title compound as a colourless oil (773 mg, 90%). R_f 0.11 (petrol/ether, 10:1); ν_{max}/cm^{-1} (thin film) 3580br m, 3070m, 3014m, 2958s, 2871m, 1480m, 1436m, 1428s, 1395m, 1362m, 1159m, 1111s, 1067m, 1032s, 998m, 963m, 934m, 799m, 763m, 738s, 701s; δ_H (400 MHz, $CDCl_3$) 0.90 (9H, s, $C(CH_3)_3$), 1.60 (3H, dd, *J* 5.9, 0.7, =$CHCH_3$), 2.11–2.24 (2H, m, $SiCH_2$), 3.51 (1H, dd, *J* 7.3, 2.5, CHO), 3.54–3.66 (2H, m, CH_2OH), 5.33–5.48 (2H, m, CH=CH), 7.36–7.47 (6H, m) and 7.60–7.68 (4H, m, 2×Ph); δ_C (100 MHz, $CDCl_3$) 18.1, 20.4, 26.4, 34.6, 64.0,

82.4, 125.0, 125.9, 127.8, 127.9, 129.8, 130.0, 135.0, 135.2, 135.2, 135.8; *m*/*z* (ESI−) 353 (M−H$^+$, 100%), 253 (13); HRMS (ESI−) found 353.1947, $C_{22}H_{29}O_2Si$ [M−H$^+$] requires 353.1942.

6.35. (±)-2-[(*E*-But-2-enyl)diphenylsilanyloxy]-3,3-dimethylbutyraldehyde (33)

To a stirred solution of oxalyl chloride (220 μL, 2.5 mmol) in dichloromethane (5 mL) at −78 °C was added DMSO (280 μL, 4.0 mmol). After 10 min a cooled solution of (±)-2-[(*E*-but-2-enyl)diphenylsilanyloxy]-3,3-dimethylbutanol (714 mg, 2.0 mmol) in dichloromethane (5 mL) was added via cannula. After a further 10 min triethylamine (1.11 mL, 8.0 mmol) was added, the resulting cloudy mixture was stirred for 15 min at −78 °C and then allowed to warm to rt over 1 h. The reaction mixture was partitioned between water (20 mL) and ether (40 mL). The aqueous layer was extracted with ether (40 mL) and the combined organic extracts were washed with brine (20 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure and the resulting oil was purified by flash column chromatography on silica gel (petrol/ether, 25:1) to give the product (**33**) as a colourless oil (646 mg, 91%). R_f 0.51 (petrol/ether, 10:1); Found C 74.62, H 8.09, $C_{22}H_{28}O_2Si$ requires C 74.95, H 8.01%; ν_{max}/cm^{-1} (thin film) 3070m, 3015m, 2961s, 2935m, 2872m, 1733s, 1478m, 1429s, 1396m, 1366m, 1158m, 1117s, 1077m, 1037m, 966m, 846m, 797m, 764m, 737s, 700s; δ_H (400 MHz, $CDCl_3$) 1.00 (9H, s, $C(CH_3)_3$), 1.61 (3H, dd, *J* 5.6, 0.6, =CHC*H*$_3$), 2.15–2.17 (2H, m, $SiCH_2$), 3.69 (1H, d, *J* 2.9, CHO), 5.32–5.47 (2H, m, CH=CH), 7.39–7.49 (6H, m) and 7.62–7.66 (4H, m, 2×Ph), 9.59 (1H, d, *J* 2.9, CH=O); δ_C (100 MHz, $CDCl_3$) 10.1, 19.9, 25.9, 36.1, 84.7, 124.0, 125.3, 128.0, 128.2, 130.1, 130.1, 134.1, 134.2, 134.9, 135.1, 203.9; *m*/*z* (CI$^+$) 370 (MNH_4^+, 38%), 353 (MH$^+$, 58), 297 (98), 285 (19), 216 (100), 157 (22), 137 (43), 94 (23), 78 (61); HRMS (CI$^+$) found 353.1934, $C_{22}H_{29}O_2Si$ (MH$^+$) requires 353.1931.

6.36. (±)-(4*SR*,5*SR*,3′*RS*)-5-*tert*-Butyl-4-(but-1′-en-3′-yl)-2,2-diphenyl-[1,3,2]-dioxasilolane

A solution of aldehyde **33** (625 mg, 1.78 mmol) in benzene (10 mL) was heated for 36 h at 80 °C in a base-washed sealed tube. The solvent was removed under reduced pressure to give the product as a colourless oil (602 mg, 96%), which was used without further purification. ν_{max}/cm^{-1} (thin film) 3070m, 2958s, 2870m, 1478m, 1429m, 1364m, 1124s, 1117s, 1056s, 1014s, 985m, 917m, 845s, 740m, 717s, 699s, 678m; δ_H (400 MHz, $CDCl_3$) 0.90 (9H, s, $C(CH_3)_3$), 1.02 (3H, d, *J* 6.4, CHC*H*$_3$), 2.20–2.29 (1H, m, C*H*CH$_3$), 3.91 (1H, d, *J* 4.4, *t*-BuC*H*O), 4.12 (1H, dd, *J* 5.8, 4.4, CHC*H*O), 5.04 (1H, ddd, *J* 10.4, 2.0, 0.8) and 5.08 (1H, ddd, *J* 17.2, 2.0, 0.8, =CH$_2$), 5.79 (1H, ddd, *J* 17.2, 10.4, 8.4, C*H*=CH$_2$), 7.36–7.49 (6H, m) and 7.65–7.69 (4H, m, 2×Ph); δ_C (100 MHz, $CDCl_3$) 14.9, 25.9, 34.9, 44.5, 79.5, 85.8, 114.9, 127.7, 127.8, 130.6, 130.7, 132.4, 133.3, 135.0, 135.1, 141.6; *m*/*z* (CI$^+$) 370 (MNH_4^+, 11%), 353 (MH$^+$, 29), 297 (100), 285 (16), 216 (51), 199 (12); HRMS (CI$^+$) found 353.1924, $C_{22}H_{29}O_2Si$ [MH$^+$] requires 353.1931.

6.37. (±)-(3*RS*,4*SR*,5*SR*)-3,6,6-Trimethylhept-1-en-4,5-diol (34)

To a solution of (±)-(4*SR*,5*SR*,3′*RS*)-5-*tert*-butyl-4-(but-1′-en-3′-yl)-2,2-diphenyl-[1,3,2]-dioxasilolane (636 mg, 1.8 mmol) in a mixture of ether (5 mL), water (5 mL) and methanol (5 mL) were added KF (313 mg, 5.4 mmol) and hydrogen peroxide (2 mL, 30% aq) and the reaction mixture was stirred at rt for 16 h. The solvent was removed under reduced pressure and the resulting material triturated with ether (40 mL) and the extract washed with water (20 mL). The aqueous layer was re-extracted with ether (40 mL) and the combined organic extracts were washed with brine (20 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure and the resulting oil was purified by flash column chromatography on silica gel (petrol/ether, 5:1→1:1) to give the product (**34**) as a white solid (228 mg, 74%). R_f 0.50 (petrol/ether, 1:1); ν_{max}/cm^{-1} (KBr) 3472br m, 3337br m, 2959s, 2908m, 2570m, 2476m, 1429m, 1128s, 1103s, 1054s, 1014m, 996m, 908m, 740m, 718m, 698s, 523m, 490m; δ_H (400 MHz, $CDCl_3$) 0.92 (9H, s, $C(CH_3)$), 1.07 (3H, d, *J* 6.7, CHC*H*$_3$), 2.36–2.29 (1H, m, C*H*CH$_3$), 3.26 (1H, s, *t*-BuC*H*(OH)), 3.45 (1H, d, *J* 8.3, CHC*H*(OH)), 5.02 (1H, ddd, *J* 10.3, 2.0, 0.4) and 5.08 (1H, ddd, *J* 17.2, 2.0, 0.9, =CH$_2$), 5.69 (1H, ddd, *J* 17.2, 10.3, 8.7, C*H*=CH$_2$); δ_C (100 MHz, $CDCl_3$) 16.1, 25.7, 34.8, 44.0, 72.1, 76.4, 114.5, 142.0; *m*/*z* (CI$^+$) 190 (MNH_4^+, 18%), 173 (MH$^+$, 100), 171 (39), 161 (15), 137 (12); HRMS (CI$^+$) found 190.1815, $C_{10}H_{24}NO_2$ [MNH_4^+] requires 190.1802.

6.38. (±)-(3*RS*,4*SR*,5*SR*)-4,5-Di(allyloxy)-3,6,6-trimethylhept-1-ene

A mixture of diol **34** (351 mg, 2.04 mmol) and NaH (492 mg, 60% in mineral oil, 12.3 mmol) in THF (10 mL) and DMF (10 mL) was stirred for 15 min at rt. The solution was cooled to 0 °C, allyl bromide (1.06 mL, 12.3 mmol) was added dropwise and the reaction mixture was stirred for 16 h at rt. The resulting mixture was partitioned between water (30 mL) and ether (30 mL). The aqueous layer was extracted with ether (30 mL) and the combined organic extracts were washed with brine (20 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure and the resulting oil was purified by flash column chromatography on silica gel (petrol/ether, 25:1) to give the product as a colourless oil (437 mg, 85%). R_f 0.74 (petrol/ether, 10:1); ν_{max}/cm^{-1} (thin film) 2958s, 2871s, 1646m, 1481m, 1424m, 1394m, 1362m, 1106s, 998s, 914s; δ_H (400 MHz, $CDCl_3$) 0.95 (9H, s, $C(CH_3)_3$), 1.09 (3H, d, *J* 6.8, CHC*H*$_3$), 2.33–2.51 (1H, m, C*H*CH$_3$), 2.94 (1H, d, *J* 5.5, *t*-BuC*H*O), 3.35 (1H, dd, *J* 5.5, 4.1, CHC*H*O), 3.91–3.99 (2H, m), 4.23 (1H, ddt, *J* 12.6, 5.2, 1.6) and 4.33 (1H, ddt, *J* 12.6, 5.0, 1.6, 2×OCH$_2$), 4.98 (1H, ddd, *J* 10.3, 1.7, 0.8, CHCH=C*H*$_2$), 5.02 (1H, ddd, *J* 17.2, 1.8, 1.4), 5.08–5.13 (2H, m), 5.25 (1H, ddt, *J* 17.2, 1.9, 1.8) and 5.26 (1H, ddt, *J* 17.2, 1.9, 1.8, 3×=CH$_2$), 5.84–5.97 (3H, m, 3×C*H*=CH$_2$); δ_C (100 MHz, $CDCl_3$) 14.2, 26.7, 35.3, 41.9, 72.2, 73.9, 80.9, 86.2, 113.5, 115.4, 115.7, 135.8, 135.9, 142.8; *m*/*z* (CI$^+$) 270 (MNH_4^+, 3%), 253 (MH$^+$, 100), 127 (64); HRMS (CI$^+$) found 253.2173, $C_{16}H_{29}O_2$ [MH$^+$] requires 253.2162.

6.39. (±)-(2*SR*,3*RS*,1′*SR*,)-2-(1′-Allyloxy-2′,2′-dimethylpropyl)-3-methyl-3,6-dihydro-2*H*-pyran (35) and (±)-2,3-*cis*-3,4-*trans*-3-allyloxy-2-*tert*-butyl-4-methyl-2,3,4,7-tetrahydrooxepin

To a solution of (±)-(3*RS*,4*SR*,5*SR*)-4,5-di(allyloxy)-3,6,6-trimethylhept-1-ene (252 mg, 1.0 mmol) in degassed dichloromethane (10 mL) was added Grubbs II catalyst (**25**, 17 mg, 0.05 mmol) and the resulting brown reaction mixture was stirred at rt for 4 h. The solvent was removed under reduced pressure and the resulting oil was purified by flash column chromatography on silica gel (petrol/ether, 20:1) to give the major product (**35**) as a colourless oil (111 mg, 49%) and the minor seven-membered ring product as a colourless oil (66 mg, 29%). Data for **35**: R_f 0.44 (petrol/ether, 10:1); ν_{max}/cm^{-1} (thin film) 3030m, 2958s, 2880s, 2816m, 1482m, 1459m, 1394m, 1372m, 1362m, 1181s, 1143s, 1095s, 1074s, 1019m, 915m, 863m, 841m, 707m; δ_H (400 MHz, $CDCl_3$) 0.96 (9H, s, $C(CH_3)_3$), 1.10 (3H, d, *J* 6.4, CHC*H*$_3$), 2.01–2.08 (1H, m, C*H*CH$_3$), 2.98 (1H, d, *J* 5.7, *t*-BuC*H*O), 3.64 (1H, dd, *J* 5.7, 2.7, CHC*H*O), 4.00 (1H, ddt, *J* 12.3, 6.0, 1.4, C*H*H′CH=CH$_2$), 4.16–4.27 (2H, m, C*H*$_2$CH=CH), 4.31 (1H, ddt, *J* 12.3, 5.6, 1.4, CH*H*′CH=CH$_2$), 5.11 (1H, ddt, *J* 10.4, 1.9, 1.4) and 5.24 (1H, ddt, *J* 17.2, 1.9, 1.4, =C*H*$_2$), 5.64 (1H, dddd, *J* 10.0, 3.0, 1.8, 0.8) and 5.82 (1H, ddt, *J* 10.0, 5.7, 2.1, CH=CH), 5.97 (1H, dddd, *J* 17.2, 10.4, 6.0, 5.6, C*H*=CH$_2$); δ_C (100 MHz, $CDCl_3$) 14.6, 26.8, 33.5, 35.9, 67.1, 74.8, 76.4, 86.0, 116.0, 125.3, 131.6, 135.8; *m*/*z* (CI$^+$) 242 (MNH_4^+, 3%), 225 (MH$^+$, 100), 167 (16), 127 (40), 97 (11); HRMS (CI$^+$) found 225.1848, $C_{14}H_{25}O_2$ [MH$^+$] requires 225.1849. Data for minor

component: R_f 0.31 (petrol/ether, 10:1); ν_{max}/cm^{-1} (thin film) 3014s, 2956s, 2872s, 1647m, 1480m, 1459s, 1425m, 1408m, 1393m, 1360s, 1236m, 1221m, 1194m, 1170s, 1123s, 1098s, 1075s, 1018s, 997s, 922s, 690m; δ_H (400 MHz, $CDCl_3$) 0.98 (9H, s, $C(CH_3)_3$), 1.00 (3H, d, *J* 7.4, $CHCH_3$), 2.80–2.87 (1H, m, $CHCH_3$), 3.09 (1H, d, *J* 0.4, *t*-Bu*CH*O), 3.66 (1H, dd, *J* 3.7, 0.4, CHC*H*O), 3.98 (1H, ddt, *J* 12.8, 6.0, 1.4, OC*H*H′CH=CH_2), 3.98–4.01 (1H, m, OC*H*H′CH=CH), 4.14 (1H, ddt, *J* 12.8, 6.0, 1.4, OCH*H*′CH=CH_2), 4.41–4.46 (1H, m, OCH*H*′CH=CH), 5.12 (1H, ddt, *J* 10.3, 1.6, 1.4) and 5.23 (1H, ddt, *J* 17.2, 1.6, 1.4, =CH_2), 5.49–5.57 (2H, m, C*H*=C*H*), 5.97 (1H, ddt, *J* 17.2, 10.3, 6.0, C*H*=CH_2); δ_C (100 MHz, $CDCl_3$) 18.9, 27.6, 35.2, 35.9, 70.5, 70.9, 81.3, 85.3, 116.8, 127.9, 132.0, 135.7; *m*/*z* (CI^+) 242 (MNH_4^+, 11%), 225 (MH^+, 100), 167 (49); HRMS (CI^+) found 225.1849, $C_{14}H_{25}O_2$ [MH^+] requires 225.1849.

Acknowledgements

The authors would like to thank Pfizer Ltd, Oxford University and Newcastle University for funding, Professor William McFarlane (Newcastle University) for assistance with ^1H NMR kinetic studies and ^{29}Si INEPT experiments, and Professor Richard Henderson (Newcastle University) for helpful discussions.

Supplementary data

Structural information from DFT calculations. ^1H NMR kinetics data [plots of relative conc versus time, ln(relative conc) versus time, calculations of reaction rates and activation parameters]. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2009.01.117.

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