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Silylated Vinyloxiranes – Recent Advances and Synthetic Applications

Frédéric Marion,[a] Sandrine Calvet,[a] Jean-Charles Marié,[a] Christine Courillon,*[a] and Max Malacria*[a]

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Stereoselective preparation of α-silylated α-quaternary unsaturated aldehydes **2** from variously substituted silylated vinyloxiranes is achieved with the aid of palladium(0) catalysis under smooth experimental conditions. One example of a versatile application of this rearrangement reaction, in the case of the *tert*-butyldimethyl(3-vinyloxiran-2-yl)silane derivative **1a**, has resulted in one-pot diastereoselective syntheses of the highly functionalized polysubstituted δ-lactones **33**–**39**, the reactivity of which has been studied.

Introduction

(α,β-Epoxy-γ,δ-alkenyl)-*tert*-butyldimethylsilane derivatives **1** (Scheme 1) have been described only rarely in the literature and are presented as essentially unstable entities.[1,2] One field of research in our group involves the synthetic development of compounds **1**, which are versatile precursors for different highly functionalized skeletons; indeed, we have previously reported their palladium-catalysed rearrangement into α-silylated γ,δ-unsaturated aldehydes **2**. The unexpectedly high stabilities of these aldehydes and their ambident structures prompted us to prepare more sophisticated derivatives incorporating quaternary carbon atoms α to their aldehyde functions. These α-silylated α-substituted γ,δ-unsaturated aldehydes should be useful building blocks in further synthesis, and so we prepared the corresponding precursors – β-substituted (α,β-epoxy-γ,δ-alkenyl)-*tert*-butyldimethylsilanes – and studied their rearrangement under palladium(0) catalysis conditions.

In the first part of this paper we show the influence of the structure of the starting silylated vinyloxirane on the rate of the rearrangement. The nature of the substituent on the double bond may accelerate or decelerate the rearrangement, whilst the configuration – *cis* or *trans* – of the epoxide also has an effect on the rate and therefore in the choice of experimental conditions best used in the reaction. All these structural factors are studied and interpreted in order to provide better understanding of the mechanism of this transposition reaction.

[a] Université Pierre et Marie Curie, Laboratoire de Chimie Organique, associé au CNRS, FR 2769,
4 place jussieu, 75252 Paris cedex 05, France
Fax: +33-1-4427-7360
E-mail: christine.courillon@upmc.fr
max.malacria@upmc.fr

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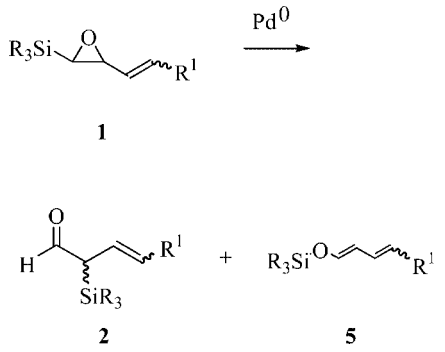
In the second part of this paper we describe an interesting synthetic application of the presented rearrangement, in a study of the one-pot stereoselective transformation of the title compounds into α,β-unsaturated γ-silylated δ-substituted lactones **3**, via the aldehydes **2** (Scheme 9). The main structural moiety in compounds **3** is a 6-substituted 5,6-dihydro-α-pyrone, widely found in natural products, as reported recently by Davies-Coleman.[3] The food industry relies a lot on δ-lactones as flavours or as preservatives in meat, dairy products or fruits,[4] whilst agrochemistry also offers some important examples of α,β-unsaturated δ-lactones as insect antifeedants[5] or phytochemical agents.[6] The pharmaceutical industry has itself developed the synthesis of a large number of α,β-unsaturated δ-lactones with different therapeutic profiles, such as antiparasitic,[7] antifungal[8] or antitumoral[9] active compounds. The numerous properties of α,β-unsaturated δ-lactones and the wide variety of molecules containing this moiety as a pharmacophore illustrate the multiple reasons for interest in their synthesis and the importance of their reactivity. δ-Alkylated γ-silylated α,β-unsaturated δ-lactones **3** display various chemical functions, such as an α,β-unsaturated ester, an allylsilane, an electron-poor carbon–carbon double bond and a carbon–silicon bond. Here we describe the preparation and some aspects of the reactivity of the α,β-unsaturated γ-silylated δ-substituted lactone **3a**.

Results and Discussion

Palladium-Catalysed Rearrangement of Silylated Vinyloxiranes

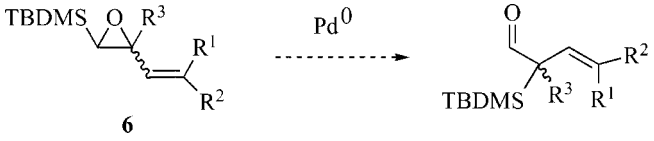
Rearrangements of vinyloxiranes[10] and of epoxysilanes[11,12] have been described in the literature as interesting synthetic pathways. Robertson reported the radical rearrangement of β-vinylepoxysilane[13] and we published the

transposition[14] of (α,β-epoxy-γ,δ-alkenyl)-*tert*-butyldimethylsilanes **1** into α-silylated γ,δ-unsaturated aldehydes **2** in the presence of catalytic amounts of palladium(0): the silicon shift occurs with total transfer of the chirality[15] and the retention of the double bond configuration.[16] We established that the presence of bulky substituents on the silicon and π-acceptor ligands for palladium were necessary to favour the preparation of the aldehyde and to avoid the formation of the unsaturated silylated enol ether **5** by a Brook rearrangement process[17] (Scheme 1).



Scheme 1.

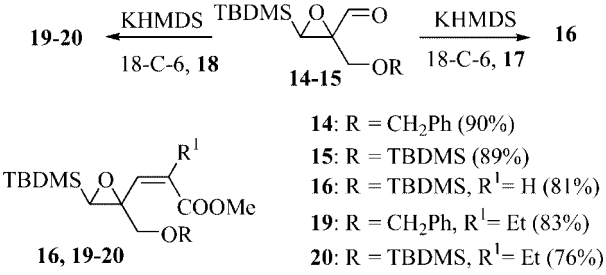
We investigated the scope of this original reaction, which occurs quickly and under smooth conditions (such as at room temperature and in a neutral medium). For further synthetic purposes, we also subjected the α,β-epoxy β-substituted γ,δ-vinylsilanes **6** to the palladium-catalysed transformation (Scheme 2).



Scheme 2.

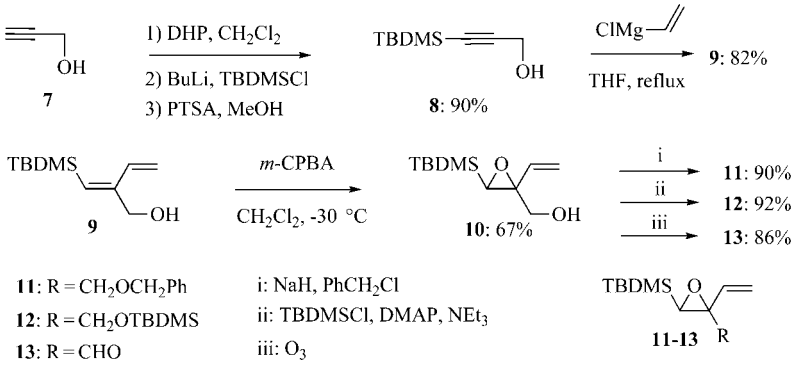
The already described six-step general procedure for the preparation of compounds **1** starts from propargylic alcohol and ends with an olefination reaction to yield the properly substituted double bond.[15] By the same procedure, we prepared the trisubstituted epoxysilanes **6** from propargylic alcohol (**7**), which was silylated in a three-step transformation to provide compound **8**. Diastereoselective addition of vinylmagnesium bromide at the triple bond by Fallis' procedure[18] afforded the butadiene derivative **9** in 82% yield, and further chemoselective oxidation with *m*-chloroperbenzoic acid gave the unsaturated epoxy alcohol **10** in 67% yield. Compound **10** serves as a common synthetic precursor to different epoxysilanes **6**. Indeed, protection of **10** as a benzyl or *tert*-butyldimethylsilyl ether or ozonolysis gave compounds **11**, **12**, and **13**, respectively, and these are interesting candidates for the rearrangement reaction (Scheme 3).

Compounds **11** and **12** were oxidized by ozonolysis to give aldehydes **14** and **15**, which were subjected to Still and Gennari olefination conditions to give the unsaturated esters **16** and **17** on treatment with the phosphonate **18** [$(CF_3CH_2O)_2POCH_2COOMe$], whereas the phosphonate **19** [$(CF_3CH_2O)_2POCHEtCOOMe$] gave the esters **20** and **21**[19] (Scheme 4).



Scheme 4.

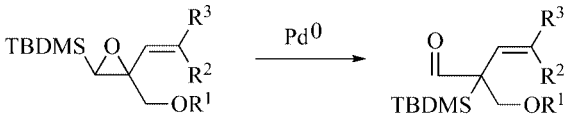
Silylated vinyloxiranes **11**–**12**, **16**, and **19**–**20** are challenging new substrates for the palladium rearrangement, each possessing a quaternary carbon atom in the position β to the silicon atom and displaying a *syn* relationship between the C–C double bond and the silyl group. Compound **12** rearranged into aldehyde **22** at room temperature in 98% yield, whereas compound **11** gave aldehyde **21** in 91% yield after 3 h at room temperature in THF. These two results involve silylated vinyloxiranes with terminal double bonds, which rearranged easily with catalytic amounts of palladium(0). They demonstrate that the rearrangement also occurs in the case of oxiranes with *cis* configurations, but with longer reaction times. When the vinyl moiety was substi-



Scheme 3.

tuted with a methyl ester function, as in compound **16**, the reaction required heating at reflux in THF, lasted longer and finally allowed the formation of aldehyde **23** in 91% yield. Vinyloxiranes containing trisubstituted olefin moieties either underwent degradation or did not react, as is reported for compounds **19** and **20**, each of which possesses an ethyl group and an ester function at the terminal carbon (Table 1). Apparently the more substituted the double bond, the more drastic the reaction conditions need to be.

Table 1. Rearrangement of β-substituted (α,β-epoxy-γ,δ-alkenyl)-*tert*-butyldimethylsilanes.



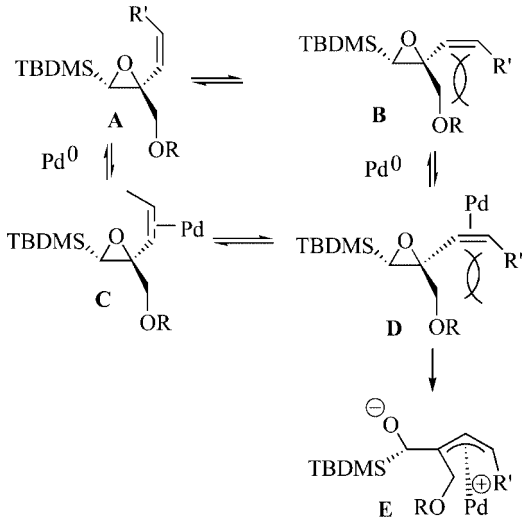
11-12 16, 19-20 **21-23**

substrate	T (°C)	t (h)	yield (%)	product
11	r.t.	1	100	**21**: $R^1 = CH_2Ph$, $R^2 = R^3 = H$
12	r.t.	3	91	**22**: R^1 = TBDMS, $R^2 = R^3 = H$
16	76	6	81	**23**: R^1 = TBDMS, R^2 = COOMe $R^3 = H$
19	76	24	-	slow degradation
20	76	24	83	**20**

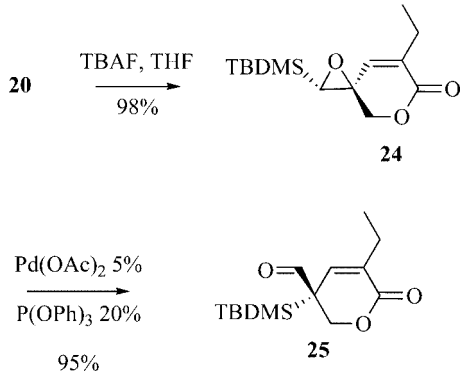
The degradation or lack of reactivity in the cases of vinylepoxysilanes **19** and **20** prompted us to study the importance of the conformation of the oxirane for the rearrangement. A limiting factor of the rearrangement reaction is probably the steric hindrance produced by the substituents on the quaternary carbon atom. In the case of the trisubstituted olefins **20** and **21**, this steric factor prevents the double bond from lining up with the epoxide: the palladium can still bind to the vinyl group but the planarity required for the formation of a π-allyl complex is lacking. This factor is not so important in the case of unsubstituted olefins. The formation of the palladium π-allyl complex **E** can only result from the palladium-associated form **D**, which can exist when the steric interactions between the double bond and the ether function are sufficiently low (Scheme 5).

We therefore decided to "freeze" the double bond in a cyclic form and so prepared the epoxylactone **24** in a yield of 98% from compound **20**. In compound **24**, the blocked conformation of the double bond should allow the easy occurrence of the rearrangement. The lactone **24** indeed reacted very easily in THF at room temperature in the presence of palladium(0) and gave the aldehyde **25** in a very good yield of 95% (Scheme 6).

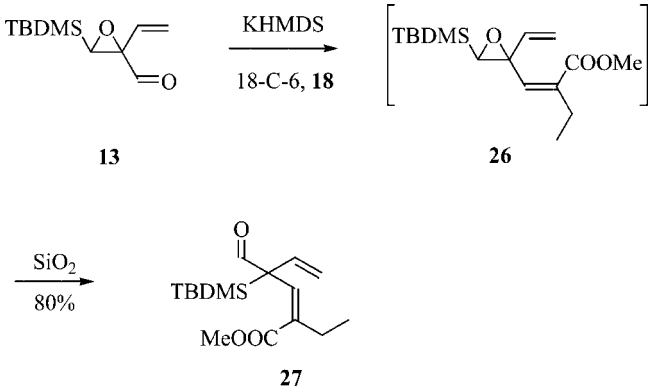
Some silylated vinyloxiranes are unstable towards the acidic[14] or metallic rearrangement conditions. The bisvinylic derivative **26** was prepared by a Still and Gennari olefination and rearranged spontaneously on silica gel to give the aldehyde **27** in a yield of 80%[19] (Scheme 7).



Scheme 5.



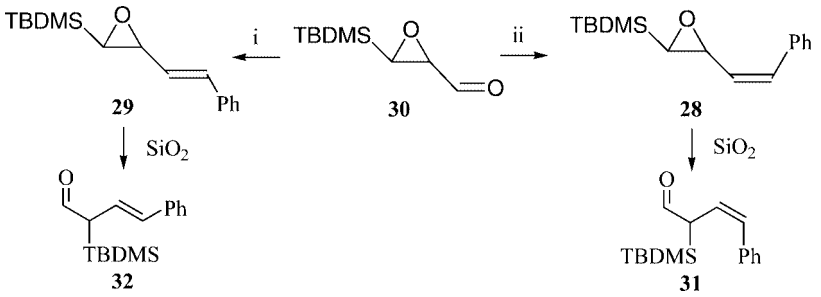
Scheme 6.



Scheme 7.

We also observed the spontaneous rearrangement of the phenyl-substituted compounds **28** and **29**, which were prepared by olefination of the epoxy aldehyde **30** and could not be isolated on silica gel since they rearrange directly into the diastereomeric aldehydes **31** and **32** (Scheme 8). However we were able to purify **28** and **29** on alumina.

The chemical behaviour of compounds **28** and **29** shows that the stability of silylated vinyloxiranes depends very strongly on the substitution on the olefinic moiety.



Scheme 8.

The results reported above demonstrate that the palladium-catalysed 1,2-silicon shift can be extended to silylated vinyloxiranes containing quaternary atoms β to their silicon atoms, yielding unsaturated aldehydes with α-quaternary silylated carbon atoms. In view of our recent work on α-alkylated (α,β-epoxy-γ,δ-alkenyl)-*tert*-butyldimethylsilanes, which rearrange into α-alkylated α,β-silylated-β,γ-unsaturated ketones,[20] this stereoselective reaction offers a wide scope and represents some interesting developments in the field of the synthesis of silylated unsaturated δ-lactones.

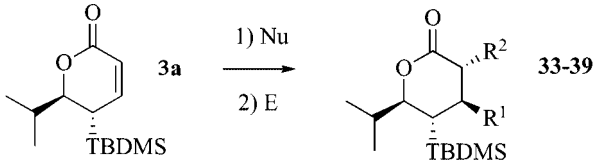
γ-Silylated δ-Substituted α,β-Unsaturated δ-Lactones

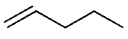
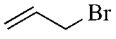
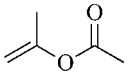
We have recently reported a short diastereoselective route to enantiomerically pure δ-alkylated γ-silylated α-pyrones **3** from the previously described silylated vinyloxirane **1a**[21] (Scheme 9).

Our interest in compounds **3** is justified by their high degree of functionalization and therefore their potential reactivity as, for instance, unsaturated esters. Conjugated addition of nucleophiles to conformationally stable α-pyrones is well documented[22–26] in the literature and the reported studies indicate an axial approach of the nucleophile, which adds *anti* to the δ-substituent.[27] This is the case when carbanions or heteroatomic nucleophiles add to δ-lactones substituted/or not at the γ-position. This stereoelectronic control may be explained in terms of the stability of the energetically favoured chair-like transition state.

In our case, the diastereoselectivity of the addition of organometallic derivatives to compound **3a** is governed by the silicon atom bound to the lactone at the γ position.[28] This reverses the stereochemical fate of this conjugated addition, which now takes place *anti* to the silyl group and therefore *syn* to the isopropyl substituent, in the equatorial position on the six-membered ring, as described in Table 2. The transition state probably has the twisted form imposed by steric hindrance from the *tert*-butyldimethylsilyl group.

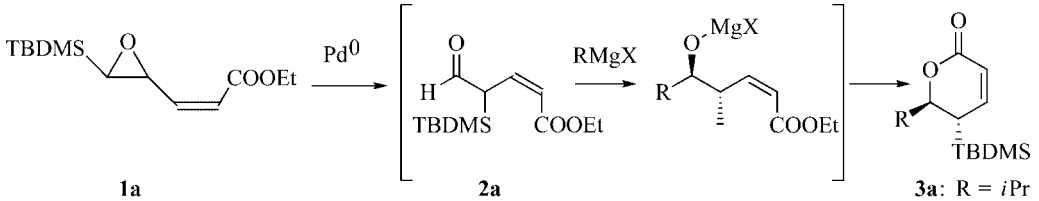
Table 2. Reactivity of δ-alkylated γ-silylated α-pyrones.



entry	Nu	E	**product** : R^1 , R^2	*d.e.* (%)	yield (%)
1	a	H_2O	**33**: *n*Bu, H	> 98	93
2	b	"	**33**: *n*Bu, H	> 98	86
3	c	"	**34**: CH_2-Ph, H	> 98	75
4	d	"	**35**:  , H	> 98	72
5	b		**36**: *n*Bu, 	>98	77
6	b		**37**: *n*Bu, 	>98	66
7	b	PhCHO	**38**: *n*Bu, PhCHOH	>98	79
8	b	CH_3I	**39**: *n*Bu, CH_3	70	89

[a] nBu_2CuLi, $BF_3{\cdot}Et_2O$. [b] *n*BuLi, $ZnCl_2$ in a 3:1 ratio. [c] $PhCH_2Li$, $ZnCl_2$. [d] Cp_2ZrHCl, hexyne, CuCN, MeLi, $BF_3{\cdot}Et_2O$.

Copper derivatives have been reported[29] as versatile reagents for conjugated additions onto enoate-type acceptors. In view of Yamamoto's work,[30] we investigated cuprous derivatives, cuprates and cyanocuprates[31] with the δ-lactone **3a**. No reaction occurred unless the ester moiety was



Scheme 9.

activated with ether/boron trifluoride complex. Treatment with the three described reagents gave 10 to 30% yields of the 1,4 adduct in the cases of cuprous derivatives and cyanocuprates, whilst dialkylcuprates gave the best results, with a 93% yield of the adduct **33** (Entry 1). Conjugate addition of vinylcuprates, prepared from the tributylvinyltin derivatives, with or without boron trifluoride, failed with δ-lactone **3a**. Finally, compound **3a** reacted under Lipshutz's conditions[32] and the hexenyl adduct **35** was isolated in 72% yield and in high diastereomeric purity (Entry 4). We found that preparation of alkynyl adducts could not be achieved under Nilsson's conditions,[33] and nor could a phenyl Grignard reagent add to the unsaturated lactone in the presence of cuprous iodide.

We were able to cause and successfully control the formation of a new C–C bond in the position next to the carbon bearing the silicon atom. Since we are able to effect desilylation of these lactonic substrates, we have demonstrated the potential to apply our results to the synthesis of natural and/or biologically interesting compounds.[21,34] The newly formed stereogenic centre in the position β to the lactone may be alkylic, vinylic or homobenzylic, which opens a wide range of further synthetic developments.[28]

We thus pursued our task by creating a second stereogenic centre in the α-position on the lactone ring. This could be done in a one-pot transformation involving conjugate addition followed by trapping of the intermediary enolate by an electrophile.

With compound **3a**, tributylzincate (Entry 2) adds in 86% yield and with the same high diastereoselectivity as dibutylcuprate (Entry 1). Treatment with allyl bromide (Entry 5) gave a 77% yield of the tetrasubstituted lactone **36**, in which the α-carbon has the relative *anti* configuration to the β-carbon. Trapping with acetyl chloride afforded a 66% yield of the ylidene derivative **37**, probably obtained by reaction of the intermediary ketyl derivative with an excess of acetyl chloride (Entry 6). We were also able to control an extracyclic carbon centre in the addition of benzaldehyde to the zinc enolate. Compound **38** was therefore isolated in only one diastereomeric form and in 79% yield.

Conclusion

In conclusion we stress that the rearrangements of silylated vinyloxiranes take place here as the first of four steps, all successively accomplished in a one-pot diastereoselective procedure. This work allows the creation of four contiguous stereogenic centres and therefore brings a highly versatile tool to asymmetric synthesis. This offers a novel and interesting route to diastereomerically pure δ-lactones, compared to the existing methods, which give the δ- and β-substituents *anti* to each other.

Experimental Section

^{1}H NMR and ^{13}C NMR spectra were recorded at room temperature at 400 MHz and 200 MHz, respectively, on an ARX 400 Bruker spectrometer. Chemical shifts are reported in ppm referenced to the residual proton resonances of the solvents. Coupling constants are expressed in Hertz. We use (I), (II), (III) and (IV) to characterize primary, secondary, tertiary and quaternary carbons. Infrared (IR) spectra were recorded with a Bruker tensor 27 (ATR diamond) spectrometer. Thin-layer chromatography (TLC) was performed on Merck silica gel (60 F 254). Silica gel (Merck Geduran SI, 40–63 mm) was also used for column chromatography.

All melting points are uncorrected. THF and Et_2O were distilled from sodium benzophenone ketyl, CH_2Cl_2, pentane and toluene were distilled from CaH_2, and amines from KOH.

(*E*)-2-[(*tert*-Butyldimethylsilyl)methylene]but-3-en-1-ol (9): Vinylmagnesium chloride (15 wt.-% in THF, 160 mmol) was added dropwise at 0 °C to a solution of propargylic alcohol (50 mmol) in THF (50 mL). When the addition was complete, the reaction mixture was heated at reflux for 16 h. After cooling to ambient temperature, the crude mixture was poured into iced NH_4Cl aqueous solution. Extraction with Et_2O, drying over $MgSO_4$ and concentration under reduced pressure gave the crude product, which was purified on silica gel with petroleum ether/ethyl acetate as the eluent (8:2). (yield 85%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 6.60 (dd, J = 18.2, 11.3 Hz, 1 H, H–C=CH_2), 5.87 (s, 1 H, H–C=C), 5,25 (d, J = 18.2 Hz, 1 H, H–CH=CH), 5.15 (d, J = 11.3 Hz, 1 H, H–CH=CH), 4.35 (s, 2 H, CH_2OH), 0.89 [s, 9 H, $SiC(CH_3)_3$], 0.13 [s, 6 H, $Si(CH_3)_2$] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.9 (IV), 136.1 (III), 127.6 (III), 115.1 (II), 65.0 (II), 26.4 (3 C, I), 17.5 (IV), –3.5 (2 C, I) ppm. IR (ATR): $\tilde{\nu}$ = 3300, 2930, 2910, 2860, 2840, 1610, 1560, 1460, 1450, 1240, 830 cm^{-1}. HRMS calcd. for $C_{11}H_{22}OSi$ 198.144; found m/z 199.152 [M + H]$^+$.

(*trans*-3-Benzyloxymethyl-3-vinyloxiran-2-yl)-*tert*-butyldimethylsilane (11): A solution of alcohol (10 mmol) in THF (25 mL) was added at 0 °C to NaH (11 mmol) in THF (25 mL). After gas evolution has ceased, benzyl bromide (11 mmol) and Bu_4NI (1 mmol) were successively added at ambient temperature and the reaction mixture was stirred for 1 h. NH_4Cl was then added, and extraction with Et_2O was followed by drying with $MgSO_4$ and concentration under reduced pressure to give the crude product, which was purified on silica gel with E.P./Et_2O (9:1) (yield 90%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.31 (m, 5 H, HAr), 5.89 (dd, J = 17.2, 10.8 Hz, 1 H, H–C=CH_2), 5.45 (dd, J = 17.2, 1.5 Hz, 1 H, H–CH=CH), 5.30 (dd, J = 10.8, 1.5 Hz, 1 H, H–CH=CH), 4.63 (d, J = 11.8 Hz,1 H, OCH_2Ar), 4.52 (d, J = 11.8 Hz, 1 H, OCH_2Ar), 3.80 (d, J = 11.3 Hz, 1 H, OCH_2–C), 3.50 (d, J = 11.3 Hz, 1 H, OCH_2–C), 2.41 (s, 1 H, H–CSiO), 0.94 [s, 9 H, $SiC(CH_3)_3$], 0.04 (s, 3 H, $SiCH_3$), –0.01 (s, 3 H, $SiCH_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.2 (IV), 135.2 (III), 128.4 (2 C, III), 127.7 (2 C, III), 127.6 (III), 118.1 (II), 74.2 (II), 73.0 (II), 62.0 (IV), 54.0 (III), 26.6 (3 C, I), 16.9 (IV), –5.8 (I), –6.1 (I) ppm. IR (ATR): $\tilde{\nu}$ = 3089, 3064, 3030, 2927, 2855, 1463, 1362, 1248, 1100, 990, 927, 834 cm^{-1}. HRMS calcd. for $C_{18}H_{28}O_2Si$ 304.186; found m/z 305.193 [M + H]$^+$.

***trans*-3-(*tert*-Butyldimethylsilyl)-2-(*tert*-butyldimethylsilyloxymethyl)-2-vinyloxirane (12):** TBDMSCl (11 mmol), Et_3N (11 mmol) and DMAP (0.5 mmol) were successively added to a solution of alcohol (10 mmol) in CH_2Cl_2 (50 mL). The medium was stirred for 1 h and extracted with water and CH_2Cl_2. Drying with $MgSO_4$ and concentration under reduced pressure gave the crude product, which was purified on silica gel with E.P./Et_2O (9:1) (yield 93%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 5.86 (dd, J = 17.7, 10.8 Hz, 1 H, H–C=CH_2), 5.40 (dd, J = 17.7, 2.0 Hz, 1 H, H–CH=CH), 5.23 (dd, J = 10.8, 2.0 Hz, 1 H, H–CH=CH), 3.83 (d, J = 11.3 Hz 1 H, OCH_2–C), 3.65 (d, J = 11.3 Hz, 1 H, OCH_2–C), 2.50 (s, 1 H, H–CSiO),

0.93 [s, 9 H, $SiC(CH_3)_3$], 0.87 [s, 9 H, $SiC(CH_3)_3$], 0.04 (s, 3 H, $SiCH_3$), 0.03 (s, 3 H, $SiCH_3$), 0.02 (s, 3 H, $SiCH_3$), –0.03 (s, 3 H, $SiCH_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.6 (III), 117.8 (II), 67.1 (II), 63.0 (IV), 54.11 (III), 26.6 (3 C, I), 25.9 (3C.I), 18.4 (IV), 16.92 (IV), –5.2 (I), –5.9 (I), –6.2 (I) ppm. IR (ATR): $\tilde{\nu}$ = 2928, 2857, 2360, 1471, 1362, 1250, 1101, 1006, 834 cm^{-1}. Elemental analysis (%) calcd for $C_{17}H_{36}O_2Si_2$ (328.23): C 62.13, H 11,04; found C 61.92, H 11.23.

***trans*-3-(*tert*-Butyldimethylsilyl)-2-vinyloxirane-2-carbaldehyde (13):** DMSO (100 mmol), Et_3N (50 mmol) and SO_3–pyridine (30 mmol) were successively added at 0 °C to a solution of **9** (10 mmol) in CH_2Cl_2 (100 mL). After 1 h at room temperature, the reaction mixture was quenched with NH_4Cl and extracted with CH_2Cl_2. After drying with $MgSO_4$ and concentration under reduced pressure, purification on silica gel with E.P./Et_2O (9:1) gave compound **13** in a yield of 95%. ^1H NMR (200 MHz, $CDCl_3$): δ = 8.75 (s, 1 H, CHO), 6.10 (dd, J = 17.7, 10.8 Hz, 1 H, H–C=CH_2), 5.55 (dd, J = 17.7, 1.5 Hz, 1 H, H–CH=CH), 5.43 (dd, J = 10.8, 1.5 Hz, 1 H, H–CH=CH), 2.64 (s, 1 H, H–CSiO), 0.96 [s, 9 H, $SiC(CH_3)_3$], 0.06 (s, 3 H, $SiCH_3$), 0.00 (s, 3 H, $SiCH_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.9 (III), 128.3 (III), 120.2 (II), 94.6 (IV), 53.3 (III), 26.3 (3 C, I), 16.9 (IV), –5.9 (I), –6.4 (I) ppm. IR (ATR): $\tilde{\nu}$ = 1715 cm^{-1}.

General Procedure for Ozonolysis: Ozone was bubbled at –78 °C into a solution of starting compounds **11** or **12** (100 mmol) in CH_2Cl_2 (300 mL) and MeOH (200 mL) until a blue coloration appeared. Excess ozone was then removed by bubbling of N_2 until the coloration disappeared. Me_2S (200 mmol) was then added at –78 °C and the mixture was allowed to warm slowly to room temperature. Concentration under reduced pressure gave the crude products **14** or **15**, which were purified on silica gel with petroleum ether/ethyl acetate as the eluent (9:1).

***cis*-2-Benzyloxymethyl-3-(*tert*-butyldimethylsilyl)oxirane-2-carbaldehyde (14):** Yield 90%. ^1H NMR (200 MHz, $CDCl_3$): δ = 9.27 (s, 1 H, CHO), 7.31 (m, 5 H, HAr), 4.57 (s, 2 H, OCH_2Ar), 4.10 (d, J = 11.3 Hz, 1 H, OCH_2–C), 3.60 (d, J = 11.3 Hz, 1 H, OCH_2–C), 2.68 (s, 1 H, H–CSiO), 0.95 [s, 9 H, $SiC(CH_3)_3$], 0.12 (s, 3 H, $SiCH_3$), 0.01 (s, 3 H, $SiCH_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.9 (III), 137.7 (IV),128.4 (2 C, III), 127.8 (2 C, III), 127.7 (III), 73.6 (II), 69.0 (II), 65.8 (IV), 52.8 (III), 26.4 (3 C, I), 16.8 (IV), –5, 7 (I), –5.9 (I) ppm. IR (ATR): $\tilde{\nu}$ = 2950, 2927, 2856, 1726, 1464, 1250, 1077 cm^{-1}.

***cis*-3-(*tert*-Butyldimethylsilyl)-2-(*tert*-butyldimethylsilyloxymethyl)-oxirane-2-carbaldehyde (15):** Yield 87%. ^1H NMR (200 MHz, $CDCl_3$): δ = 9.27 (s, 1 H, CHO), 4.12 (d, J = 11.8 Hz, 1 H, Si-OCH_2–C), 3.87 (d, J = 11.8 Hz, 1 H, $SiOCH_2$–C), 2.74 (s, 1 H, H–CSiO), 0.95 [s, 9 H, $SiC(CH_3)_3$], 0.85 [s, 9 H, $SiC(CH_3)_3$], 0.12 (s, 3 H, $SiCH_3$), 0.05 (s, 3 H, $SiCH_3$), 0.04 (s, 3 H, $SiCH_3$), 0.00 (s, 3 H, $SiCH_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.5 (III), 66.8 (IV), 61.6 (II), 52.3 (III), 26.3 (3 C, I), 25.8 (3 C, I), 18.3 (IV), 16.8 (IV), –5.5 (2 C, I), –6.1 (I) ppm. IR (ATR): $\tilde{\nu}$ = 2940, 2920, 1740, 1460, 1250, 1100, 830 cm^{-1}. $C_{16}H_{34}O_3Si_2$ (330.20): C 56.91, H 10.19; found C 56.95, H 10.38.

General Procedure for Olefination: KHMDS (72 mmol) and a solution of aldehyde (60 mmol) in THF (50 mL) were added at –78 °C to a solution of 18-C-6 (120 mmol) and phosphonate **17** or **18** (66 mmol) in THF (550 mL). The reaction mixture was allowed to warm slowly to room temperature and quenched with NH_4Cl. Extraction with Et_2O followed by drying over $MgSO_4$ and concentration under reduced pressure gave the crude product, which was purified on silica gel with E.P./Et_2O (9:1).

Methyl (*Z*)-3-[(*trans*)-3-(*tert*-Butyldimethylsilyl)-2-(*tert*-butyldimethylsilyloxymethyl)oxiran-2-yl]-2-propenoate (16): Yield 81%. ^1H NMR (200 MHz, $CDCl_3$): δ = 6.34 (d, J = 12.0 Hz, 1 H, CH=), 5.93 (d, J = 12.0 Hz, 1 H, CH=), 4.24 (d, J = 11.3 Hz 1 H, OCH_2), 3.72 (s, 3 H, CH_3), 3.61 (d, J = 11.3 Hz, 1 H, OCH_2), 2.62 (s, 1 H, HCSiO), 0.93 [s, 9 H, $SiC(CH_3)_3$], 0.85 [s, 9 H, $Si(CH_3)_3$], 0.021 (s, 3 H, $SiCH_3$), 0.004 (s, 3 H, $SiCH_3$), –0.096 (s, 3 H, $SiCH_3$), –0,128 (s, 3 H, $SiCH_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.0 (IV), 146.4 (III),122.7 (III), 67.7 (III), 63.5 (IV), 54.2 (I), 51.7 (III), 26.8 (3 C, I), 18.7 (IV), 4.9 (I), –5.0 (I), –6.5 (I), –6.7 (I) ppm. IR (ATR): $\tilde{\nu}$ = 2980, 2840, 1720, 1630, 1470, 1250 cm^{-1}.

Methyl 2-[(*Z*)-(*trans*)-2-Benzyloxymethyl-3-(*tert*-butyldimethylsilyl)-oxiran-2-ylmethylene]butyrate (19): Yield 83%. ^1H NMR (200 MHz, $CDCl_3$): δ = 7.26 (m, 5 H, HAr), 6.00 (t, J = 1.5 Hz, 1 H, H–C=), 4.61 (d, J = 11.8 Hz, 1 H, OCH_2Ar), 4.51 (d, J = 11.8 Hz, 1 H, OCH_2Ar), 3.99 (d, J = 10.8 Hz, 1 H, OCH_2–C), 3.69 (s, 3 H, OCH_3), 3.48 (d, J = 10.8 Hz, 1 H, OCH_2–C), 2.54 (s, 1 H, H–CSiO), 2.31 (qd, J = 7.4, 1.5 Hz, 2 H, CH_3–CH_2–C=CH), 1.03 (t, J = 7.4 Hz, 3 H, CH_3–CH_2–C=CH), 0.94 [s, 9 H, $SiC(CH_3)_3$], –0.08 (s, 3 H, $SiCH_3$), –0.10 (s, 3 H, $SiCH_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.8 (IV), 138.3 (IV), 136.8 (IV), 134.9 (III), 128.3 (2 C, III), 127.6 (2 C, III), 127.5 (III), 74.5 (II), 73.2 (II), 62.0 (IV), 53.9 (I), 51.5 (III), 26.9 (II), 26.5 (3 C, I), 16.9 (IV), 12.5 (I), –6.7 (I), –6.8 (I) ppm. HRMS calcd. for $C_{22}H_{34}O_4Si$ 390.223; found m/z 391.230 $[M + H]^+$.

Methyl 2-[(*Z*)-(*trans*)-3-(*tert*-Butyldimethylsilanyl)-2-(*tert*-butyldimethylsilyloxymethyl)oxiran-2-ylmethylene]butyrate (20): Yield 83%. ^1H NMR (200 MHz, $CDCl_3$): δ = 5.97 (t, J = 1.5 Hz, 1 H, H–C=C), 3.95 (d, J = 11.3 Hz, 1 H, OCH_2), 3.74 (s, 3 H, OCH_3), 3.60 (d, J = 11.3 Hz, 1 H, OCH_2–C), 2.55 (s, 1 H, H–CSiO), 2.28 (qd, J = 7.4, 1.5 Hz, 2 H, CH_3–CH_2–C=CH), 1.03 (t, J = 7.4 Hz, 3 H, CH_3–CH_2–C=CH), 0.92 [s, 9 H, $SiC(CH_3)_3$], 0.85 [s, 9 H, $SiC(CH_3)_3$], 0.02 (s, 3 H, $SiCH_3$), 0.00 (s, 3 H, $SiCH_3$), –0.10 (s, 3 H, $SiCH_3$), –0.12 (s, 3 H, $SiCH_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.1 (IV), 136.7 (IV), 134.6 (III), 67.2 (II), 62.9 (IV), 53.5 (I), 51.6 (III), 26.9 (II), 26.5 (3 C,I), 25.8 (3 C,I), 18.3 (IV), 17.0 (IV), 12.5 (I), –5.3 (2C,I), –6.7 (2C,I) ppm.

Palladium-Catalysed Rearrangement of Vinyl Epoxy Silanes: Triphenyl phosphite (0.2 equiv., 0.4 mmol) was added by syringe to a stirred solution of palladium diacetate (0.05 equiv., 0.1 mmol) in freshly distilled THF (3 mL). A solution of the vinyl epoxy silane (1 equiv., 2 mmol) in THF (10 mL) was cannulated into the pale yellow reaction mixture. After completion of the rearrangement (checked by TLC), solvent was removed and the residue was purified by chromatography on silica gel with petroleum ether/ethyl acetate as the eluent.

Acid-Catalysed Rearrangement of Vinyl Epoxy Silanes: APTS (0.5 mmol) was added at ambient temperature to a solution of starting material (10 mmol) in CH_2Cl_2 (50 mL). After completion of the rearrangement (checked by TLC), $NaHCO_3$ was added and the resulting organic phase was dried with $MgSO_4$ and concentrated under reduced pressure. The residue was purified by chromatography on silica gel with petroleum ether/ethyl acetate as the eluent.

2-Benzyloxymethyl-2-(*tert*-butyldimethylsilyl)but-3-enal (21): Yield 100%. ^1H NMR (200 MHz, $CDCl_3$): δ = 9.73 (s, 1 H, CHO), 7.29 (m, 5 H, HAr), 6.26 (dd, J = 18.2, 11.3 Hz, 1 H, H–C=CH_2), 5.17 (dd, J = 11.3, 1.0 Hz, 1 H, H–CH=CH), 5.10 (dd, J = 18.2, 1.0 Hz, 1 H, H–CH=CH), 4.49 (s, 2 H, OCH_2Ar), 4.08 (d, J = 9.8 Hz, 1 H, OCH_2–C), 3.90 (d, J = 9.8 Hz, 1 H, OCH_2–C), 0.88 [s, 9 H, $SiC(CH_3)_3$], 0.05 (s, 3 H, $SiCH_3$), 0.04 (s, 3 H, $SiCH_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.4 (III), 138.1 (IV), 133.8 (III),

128.6 (2 C, III), 127.9 (3 C, III), 113.6 (II), 73.6 (II), 69.1 (II), 60.3 (IV), 28.1 (3 C, I), 19.57 (IV), –6.5 (I), –6.7 (I) ppm. IR (ATR): $\tilde{\nu}$ = 2980, 2960, 2910, 2880, 2740, 1720, 1480, 1270, 1100, 850 cm^{-1}.

2-(*tert*-Butyldimethylsilanyl)-2-(*tert*-butyldimethylsilyloxymethyl)-but-3-enal (22): Yield 91%. ^1H NMR (200 MHz, $CDCl_3$): δ = 9.74 (s, 1 H, CHO), 6.19 (dd, J = 18.2, 11.3 Hz, 1 H, H–C=CH_2), 5.15 (dd, J = 11.3, 1.0 Hz, 1 H, H–CH=CH), 5.08 (dd, J = 18.2, 1.0 Hz, 1 H, H–CH=CH), 4.26 (d, J = 9.8 Hz, 1 H, OCH_2–C), 4.08 (d, J = 9.8 Hz, 1 H, OCH_2–C), 0.90 [s, 9 H, $SiC(CH_3)_3$], 0.84 [s, 9 H, $SiC(CH_3)_3$], –0.07 (s, 3 H, $SiCH_3$), –0.06 (s, 3 H, $SiCH_3$), –0.04 (s, 3 H, $SiCH_3$), –0.03 (s, 3 H, $SiCH_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.7 (III), 135.0 (III), 114.4 (II), 63.5 (II), 61.5 (IV), 28.8 (3 C, I), 26.7 (3 C, I), 20.2 (IV), 19.2 (IV), –4.6 (2 C, I), –5.6 (I), –5.8 (I) ppm. IR (ATR): $\tilde{\nu}$ = 2980, 2960, 2880, 2740, 1720, 1640, 1480, 1400, 1370, 1200, 1090, 1020, 850 cm^{-1}. HRMS calcd. for $C_{17}H_{36}O_2Si_2$ 328.225; found m/z 329.233 $[M + H]^+$.

Methyl (*Z*)-4-(*tert*-Butyldimethylsilyl)-2-ethyl-4-formylhexa-2,5-dienoate (23): Yield 87%. ^1H NMR (200 MHz, $CDCl_3$): δ = 9.64 (s, 1 H, CHO), 6.53 (d, J = 12.7 Hz, 1 H, *H*C=CHCOOMe), 5.94 (d, J = 12.7 Hz, 1 H, =C*H*COOMe), 4.66 (d, J = 10.3 Hz, 1 H, C*H*HOSi), 4.23 (d, J = 9.8 Hz, 1 H, CH*H*OSi), 3.65 (d, J = 9.8 Hz, 1 H, $COOCH_3$), 0.89 (s, 9 H, *t*Bu), 0.79 (s, 9 H, *t*Bu), 0.17 (s, 3 H, $OSiCH_3$), 0.15 (s, 3 H, $OSiCH_3$), –0.015 (s, 3 H, $CSiCH_3$), –0.022 (s, 3 H, $CSiCH_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.2 (III), 166.2 (IV), 143.8 (III), 119.5 (III), 63.3 (II), 61.4 (IV), 51.3 (I), 29.7 (IV), 27.7 (I), 25.8 (I), 19.35 (IV), –5.5 (I), –5.6 (I), –5.7 (I), –6.5 (I) ppm. IR (ATR): $\tilde{\nu}$ = 2980, 2960, 2880, 1730, 1710, 1640, 1480, 1450, 1270, 1190, 1020, 850 cm^{-1}.

(*Z*)-(*trans*)-2-(*tert*-Butyldimethylsilanyl)-7-ethyl-1,5-dioxaspiro[2.5]-oct-7-en-6-one (24): TBAF (10 mmol) was added at room temperature to a solution of epoxide (10 mmol) in THF (100 mL). After 30 min, the reaction was quenched with NH_4Cl. Extraction with Et_2O followed by drying over $MgSO_4$ and concentration under reduced pressure gave the crude product mixed with the silanol, which was distilled off under vacuum. The residue was purified by chromatography on silica gel with petroleum ether/ethyl acetate as the eluent (8:2). Yield 70%. ^1H NMR (200 MHz, $CDCl_3$): δ = 6.23 (s, 1 H, H–C=C), 4.63 (d, J = 12.3 Hz, 1 H, OCH_2–C), 4.30 (d, J = 12.3 Hz, 1 H, OCH_2–C), 2.53 (s, 1 H, H–CSiO), 2.35 (q, J = 7.4 Hz, 2 H, CH_3–CH_2–C=CH), 1.08 (t, J = 7.4 Hz, 3 H, CH_3–CH_2–C=CH), 0.94 [s, 9 H, $SiC(CH_3)_3$], 0.12 (s, 3 H, $SiCH_3$), 0.05 (s, 3 H, $SiCH_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.7 (IV), 139.0 (IV), 137.3 (III), 72.6 (II), 57.1 (III), 55.5 (IV), 26.4 (3 C,I), 24.2 (II), 16.7 (IV), 11.9 (I), –6.2 (I), –6.4 (I) ppm. HRMS calcd. for $C_{14}H_{24}O_3Si$ 268.149; found m/z 269.156 $[M + H]^+$.

(*Z*)-3-(*tert*-Butyldimethylsilanyl)-5-ethyl-6-oxo-3,6-dihydro-2*H*-pyran-3-carbaldehyde (25): Yield 90%. ^1H NMR (200 MHz, $CDCl_3$): δ = 9.70 (s, 1 H, CHO), 6.89 (s, 1 H, H–C=C), 4.68 (dd, J = 11.8, 1.5 Hz, 1 H, OCH_2–C), 4.60 (d, J = 11.8, 1 H, OCH_2–C), 2.37 (qdd, J = 7.4, 3.5, 1.5 Hz, 2 H, CH_3–CH_2–C=CH), 1.10 (t, J = 7.4 Hz, 3 H, CH_3–CH_2–C=CH), 0.96 [s, 9 H, $SiC(CH_3)_3$], 0.16 (s, 3 H, $SiCH_3$), 0.15 (s, 3 H, $SiCH_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.9 (III), 164.2 (IV), 150.5 (IV), 137.6 (III), 68.0 (II), 54.7 (IV), 27.4 (3 C,I), 24.2 (II), 19.0 (IV), 12.8 (I), –6.5 (I), –6.8 (I) ppm. HRMS calcd. for $C_{14}H_{24}O_3Si$ 268.149; found m/z 269.156 $[M + H]^+$.

Methyl (*Z*)-4-(*tert*-Butyldimethylsilyl)-2-ethyl-4-formylhexa-2,5-dienoate (27): Yield 80%. ^1H NMR (200 MHz, $CDCl_3$): δ = 9.41 (s, 1 H, CHO), 6.40 (dd, J = 17.7, 10.8 Hz, 1 H, H–C=CH_2), 6.15 (t, J = 1.5 Hz, 1 H, H–C=C–CH_2), 4.93 (dd, J = 10.8, 1.5 Hz, 1 H, H–CH=CH) 4.70 (dd, J = 17.7, 1.5 Hz, 1 H, H–CH=CH), 3.56 (s, 3 H, OCH_3), 2.40 (qd, J = 7.4, 1.5 Hz, 2 H, CH_3–CH_2–C=CH), 1.08 (t, J = 7.4 Hz, 3 H, CH_3–CH_2–C=CH), 0.91 [s, 9 H, $SiC(CH_3)_3$], 0.11 (s, 3 H, $SiCH_3$), 0.07 (s, 3 H, $SiCH_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.0 (III), 167.5 (IV), 138.6 (IV), 135.9 (III), 133.8 (III), 112.1 (II), 60.8 (IV), 51.2 (I), 28.2 (II), 28.0 (3 C,I), 19.3 (IV), 13.5 (I), –7.4 (I), –7.6 (I) ppm. IR (neat): $\tilde{\nu}$ = 1649 cm^{-1}.

(*Z*)-(*trans*)-1-*tert*-Butyldimethylsilyl-1.2-epoxy-4-phenylbut-3-ene (28): Sodium *tert*-pentoxide (716 mg, 6.5 mmol, 1.3 equiv.) was added at room temperature, in four portions, to a suspension of benzyltriphenylphosphonium chloride (2.33 g, 6.0 mmol, 1.2 equiv.) in dry toluene (40 mL). The mixture was stirred for 10 min at room temperature and was then warmed to 55 °C for 1 h. The temperature was lowered to –60 °C and a solution of *trans* epoxy aldehyde[35] (932 mg, 5.0 mmol, 1.0 equiv.) in dry toluene (10 mL) was added dropwise by cannula. After 30 min at –60 °C, saturated aqueous NH_4Cl solution (30 mL) was added and the temperature was increased to room temperature. The aqueous layer was extracted with AcOEt, the combined organic phases were washed with brine and dried with Na_2SO_4, and the solvents were removed in vacuo. After purification of the crude product by flash chromatography on neutral deactivated alumina gel (petroleum/ethyl acetate, 98:2), the phenyl-substituted olefin was isolated as a colourless, oily mixture of the two diastereomers (Z/E = 54:1) in 80% yield (1.04 g, 4.0 mmol). In this mixture, the major product **28** can be described as follows. ^1H NMR (400 MHz, C_6D_6): δ = 7.39–7.11 (m, 5 H, Ph), 6.66 (d, J = 11.7 Hz, 1 H, =CHPh), 5.55 (dd, J = 11.7, 7.8 Hz, 1 H, C*H*=CHPh), 3.83 (br dd, J = 7.8, 2.8 Hz, 1 H, O–C*H*–CH=CHPh), 2.38 (d, J = 2.8 Hz, 1 H, SiCH–O), 1.03 (s, 9 H, *t*Bu), 0.04 (s, 3 H, CH_3Si), 0.00 (s, 3 H, CH_3Si) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 136.9 (IV), 133.5 (III), 132.5 (III), 128.9 (III), 128.4 (III), 127.5 (III), 52.0 (III), 50.5 (III), 26.5 (I), 16.7 (IV), –8.0 (I), –8.5 (I) ppm. IR (neat): $\tilde{\nu}$ = 3040, 2960, 1630, 1260, 850 cm^{-1}.

(*E*)-(*trans*)-1-*tert*-Butyldimethylsilyl-1.2-epoxy-4-phenylbut-3-ene (29): LDA solution in THF (5.90 mL of 1.0 M, 5.90 mmol, 1.1 equiv.) was added to a cooled (–78 °C) solution of diethyl benzylphosphonate (1.23 mL, 5.90 mmol, 1.1 equiv.) and dry LiCl (125 mg, 2.95 mmol, 0.5 equiv.) in THF (45 mL). The medium was allowed to warm to room temperature over 1 h and was then cooled to 0 °C. A solution of the *trans* epoxyaldehyde[18] (1.0 g, 5.37 mmol, 1.0 equiv.) in THF (5 mL) was added dropwise to the reaction mixture. The solution was stirred for 10 h at room temperature and was then hydrolysed with saturated aqueous NH_4Cl solution (30 mL). The aqueous layer was extracted with AcOEt and the combined organic phases were washed with brine and dried with Na_2SO_4, and the solvents were removed in vacuo. After purification of the crude product by flash chromatography on neutral deactivated alumina gel (petroleum/ethyl acetate, 98:2), the phenyl-substituted olefin **16** was isolated as a mixture of the two diastereomers (E/Z = 10:1). The isomer **29** could be separated by recrystallization from methanol, affording a white powder (1.26 g, 4.83 mmol) in 90% yield. m.p. 131 °C. ^1H NMR (400 MHz, C_6D_6): δ = 7.24–7.18 (m, 5 H, Ph), 6.69 (d, J = 15.8 Hz, 1 H, =CHPh), 5.98 (dd, J = 15.8, 7.6 Hz, 1 H, C*H*=CHPh), 3.36 (dd, J = 7.6, 3.1 Hz, 1 H, O–C*H*–CH=CHPh), 2.33 (d, J = 3.1 Hz, 1 H, SiCHO), 1.02 (s, 9 H, *t*Bu), 0.10 (s, 3 H, CH_3Si), 0.00 (s, 3 H, CH_3Si) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 135.5 (IV), 132.0 (III), 128.6 (III), 127.5 (III), 126.9 (III), 125.3 (III), 54.4 (III), 50.1 (III), 25.3 (I), 15.5 (IV), –9.5 (I), –9.7 (I) ppm. $C_{16}H_{24}OSi$ (260.16): C 73.79, H 9.29; found C 73.68, H 9.41.

(*Z*)-(*trans*)-2-*tert*-Butyldimethylsilyl-4-phenylbut-3-enal (31): When the silylated vinyloxirane **28** (260 mg, 1.00 mmol) was purified on silica gel instead of the previously mentioned alumina gel, the dia-

stereomer **31** could be isolated in 98% yield as a colourless oil (255 mg, 0.98 mmol). Compound **31** could also be obtained from **28** (260 mg, 1.00 mmol, 1.0 equiv.) in the presence of Lewis acids (0.10 mmol, 0.1 equiv.). With use of $BF_3{\cdot}Et_2O$ (13 mL) in Et_2O (5 mL) at –78 °C, the aldehyde **31** was obtained in 98% yield (255 mg, 0.98 mmol), whilst when the reaction was performed at 0 °C, the yield was 45% (117 mg, 0.45 mmol). With use of Ti(O*i*Pr)$_4$ (30 mL) in CH_2Cl_2 (5 mL) at –78 °C, compound **31** was obtained with 95% yield (247 mg, 0.95 mmol), when the Lewis acid used was $AlCl_3$ (13 mg) the aldehyde **31** was isolated in 51% yield (133 mg, 0.51 mmol), whilst in the presence of $MgBr_2$ (18 mg) or $ZnBr_2$ (22 mg) compound **31** was obtained in 98% yield (255 mg, 0.98 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.67 (d, J = 3.2 Hz, 1 H, CHO), 7.27 (m, 4 H, Ph: *o*, *m*), 7.17 (t, J = 4.0 Hz, 1 H, Ph: *p*), 6.45 (d, J = 12.1 Hz, 1 H, =CHPh), 6.02 (t, J = 11.7 Hz, 1 H, C*H*=CHPh), 4.15 (dd, J = 11.7, 3.2 Hz, 1 H, CHSi), 0.80 (s, 9 H, *t*Bu), 0,00 (s, 6 H, CH_3Si) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.7 (III), 136.7 (IV), 128.7 (III), 128.3 (III), 126.8 (III), 124.4 (III), 50.0 (III), 26.6 (I), 17.9 (IV), –6.3 (I), –6.6 (I) ppm. IR (neat): $\tilde{\nu}$ = 3010, 2950, 1700, 1630, 1250, 830 cm^{-1}. $C_{16}H_{24}OSi$: C, 73.79, H 9.29; found C 73.82, H 9.35.

(*E*)-(*trans*)-2-(*tert*-Butyldimethylsilyl)-4-phenylbut-3-enal (32): The isomer **32**, a white solid, was isolated in 51–100% yields from **29** (260 mg, 1.0 mmol) by use of the same procedures as described for the preparation of **31**. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.81 (d, J = 3.0 Hz, 1 H, CHO), 7.35 (m, 4 H, Ph: *o*, *m*), 7.24 (t, J = 4.0 Hz, 1 H, Ph: *p*), 6.59 (d, J = 16.1 Hz, 1 H, =CHPh), 6.35 (dd, J = 15.8, 10.2 Hz, 1 H, C*H*=CHPh), 3.53 (dd, J = 9.8, 2.9 Hz, 1 H, CHSi), 0.93 (s, 9 H, *t*Bu), 0.09 (s, 3 H, CH_3Si), 0.09 (s, 3 H, CH_3Si) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.5 (III), 137.8 (IV), 129.8 (III), 128.7 (III), 127.2 (III), 126.1 (III), 123.3 (III), 54.7 (IV), 26.9 (I), 18.5 (IV), –5.9 (I), –6.3 (I) ppm. IR (neat): $\tilde{\nu}$ = 3010, 2950, 1690, 1250, 830 cm^{-1}. $C_{16}H_{24}OSi$ (260.16): C 73.79, H 9.29; found C 73.44, H 9.40.

4-Butyl-5-(*tert*-butyldimethylsilyl)-6-isopropyltetrahydropyran-2-one (33): *n*BuLi (6.16 mmol, 9.9 equiv.) and BF_3/Et_2O were added to a solution of CuI (593 mg) in THF (6 mL) and the mixture was stirred at –60 °C. Compound **3a** (158 mg, 0.62 mmol, 1 equiv.) was stirred in and the mixture was maintained at –60 °C for 3 h. Quenching with a saturated solution of ammonium chloride was followed by extraction and flash chromatography with light petroleum/ethyl acetate, 9:1, which yielded the adduct. Yield 93%. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 4.19 [dd, J = 2.2, 10.0 Hz, 1 H, H–C(OC=O)(CHSi)(CH)], 2.44 (d, J = 4.5 Hz, 2 H, CH_2–C=O), 2.14 [m, 1 H, H–C(CH_2C=O)(CHSi)(CH_2)], 1.79 [hd, J = 2.2, 3.7 Hz, 1 H, H–C(CH_3)$_2$(CH)], 1.26–1.43 [m, 6 H, $(CH_2)_4$], 1.07 (d, J = 3.7 Hz, 3 H, *CH*$_3$–CH–CH_3), 1.04 (m, 1 H, H–CSi), 0.96 (d, J = 3.7 Hz, 3 H, *CH*$_3$–CH–CH_3), 0.91 (s, 9 H, *t*BuSi), 0.89 [t, J = 7.2 Hz, 3 H, CH_3-$(CH_2)_4$], 0.11 (s, 3 H, $SiCH_3$), 0.05 (s, 3 H, $SiCH_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.0 (IV), 84.1 (III), 38.9 (II), 33.4 (III), 32.8 (II), 31.5 (II), 29.3 (II), 29.0 (II), 27.4 (3 C, I), 22.6 (I), 20.7 (IV), 14.6 (I), 14.1 (I), –5.3 (I), –5.5 (I) ppm. IR (neat): $\tilde{\nu}$ = 2850–2980, 2250, 1740, 1470, 1250 cm^{-1}. HRMS calcd. for $C_{18}H_{36}O_2Si$ 313.2563; found *m*/*z* 313.2562.

4-Benzyl-5-*tert*-butyldimethylsilyl-6-isopropyl-3,4,5,6-tetrahydropyran-2-one (34): TMEDA (3.6 mmol, 9 equiv.) and *n*BuLi (2.15 M, 1.67 mL, 3.6 mmol, 9 equiv.) were added at 0 °C to toluene (5 mL); the reaction mixture was stirred for two hours at room temperature until a red colour was observed. This mixture (9 equiv.) was added at 0 °C to a saturated solution of zinc chloride in THF (1.23 mmol, 1.6 M, 3 equiv.). The reaction medium was stirred at 0 °C for one hour and cooled to –78 °C, after which a solution of **4a** (100 mg, 0.41 mmol, 1 equiv. in 5 mL of THF) was added. The mixture was maintained at –78 °C for half an hour and then kept at 0 °C for one hour. Hydrolysis with ammonium chloride, extraction and separation by flash chromatography (petroleum ether/ethyl acetate, 95:5) afforded a pale yellow oil in a yield of 75%. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.15–7.26 (m, 5 H, Ph), 4.22 (dd, J = 11.32, 1.97 Hz, 1 H, *H*–C-O–C=O), 2,72 (m, 1 H, C*H*CH_2Ph), 2.28 to 2.42 (m, 4 H, CH_2C=O and CH_2Ph), 1.86 [hd, J = 6.89, 1.97 Hz, 1 H, $(CH_3)_2$C*H*], 1.22 (d, J = 11.32 Hz, 1 H, C*H*Si), 1.17 (d, J = 6.89 Hz, 3 H, CH_3CHCH_3), 1.01 (d, J = 6.89 Hz, 3 H, CH_3CHCH_3), 0.93 (s, 9 H, *t*Bu), 0.09 [s, 6 H, $(CH_3)_2$Si] ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 173.8, 139.0–126.6 (4 C), 83.9, 45.0, 35.6–14.4 (7 C), –5.1, –5.4 ppm. IR: $\tilde{\nu}$ = 2860–2980, 1740, 1480, 1250, 850, 710 cm^{-1}. HRMS calcd. for $C_{21}H_{34}O_2Si$ 347.2406; found *m*/*z* (%) 347.2403 [M + H]$^+$ (100), 289 (9), 215 (19).

5-(*tert*-Butyldimethylsilyl)-4-hex-1-enyl-6-isopropyltetrahydropyran-2-one (35): In a pre-cooled round-bottomed flask (–78 °C), Cp_2ZrHCl (1.29 g, 5 equiv.) in THF (20 mL) was mixed with hexyne (410 mg, 5 equiv.) and the solution was cannulated under argon into a second flask containing CuCN (447.8 mg, 5 equiv.), MeLi (6.25 mL, 1.6 M, 10 equiv.) and THF (20 mL). Addition of BF_3/Et_2O (1.3 mL, 5 equiv.) was followed by introduction lactone (254 mg) in THF (1 mL). Quenching with ammonium chloride and extraction with ether provided crude material, which was purified by flash chromatography (light petroleum/ethyl acetate, 9:1). The final product was obtained in a yield of 72%. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 5.42 [dt, J = 15.1, 6.6 Hz, 1 H, H-(CH_2)C=CH], 5.29 [dd, J = 15.1, 8.2 Hz, 1 H, H-(CH)C=CH], 4.17 [dd, J = 2.3, 10.6 Hz, 1 H, H–C(OC=O)(CHSi)(CH)], 2.84 [m, 1 H, H–C(CH_2)(CH=CH)(CHSi)], 2.55 (dd, J = 9.9, 14.0 Hz, 1 H, O=C–CH_2–CH), 2.34 (dd, J = 2.8, 14.0 Hz, 1 H, O=C–CH_2–CH), 1.97 [m, 2 H, CH_2-(CH=CH)$(CH_2)_3$], 1.83 [hd, J = 6.8, 2.4 Hz, 1 H, H–C$(CH_3)_2$(CH)], 1.28 [m, 6 H, $(CH_2)_3$], 1.08 (d, J = 6.7 Hz, 3 H, CH_3–CH–*CH*$_3$), 0.98 (d, J = 6.7 Hz, 3 H, *CH*$_3$–CH–CH_3), 0.94 (s, 9 H, *t*BuSi), 0.89 [t, J = 14.1 Hz, 3 H, *CH*$_3$-$(CH_2)_4$], 0.11 (s, 3 H, $SiCH_3$), 0.05 (s, 3 H, $SiCH_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.4 (IV), 134.2 (II), 130.9 (II), 84.1 (III), 52.7, 36.1, 35.9, 32.0, 31.6, 31.5, 27.7, 27.2, 22.2, 20.6, 17.8, 14.7, 19.9, –5.1, –5.5 ppm. IR (neat): $\tilde{\nu}$ = 2930, 2900, 2820, 1730, 1450, 1240, 820 cm^{-1}. HRMS calcd. for $C_{20}H_{38}O_2Si$ 339.271; found *m*/*z* 339.271.

General One-Pot Procedure for 1,4-Addition/Enolate Trapping: *n*-BuLi (3.6 mmol, 9 equiv.) was added to a cooled (0 °C) saturated solution of zinc chloride in THF (1.6 M, 1.2 mmol, 3 equiv.) and the resulting heterogeneous mixture was stirred at 0 °C for one hour. After the temperature had been lowered to –78 °C, a solution of **3a** (100 mg, 0.41 mmol, 1 equiv.) in THF (5 mL) was added. The reaction medium was kept for 30 min at –78 °C and warmed to 0 °C for one hour. Before addition of an excess of the electrophile (5 equiv.), the temperature was lowered to –78 °C, and the reaction mixture was then kept at 0 °C for one hour. Hydrolysis with a saturated aqueous solution of ammonium chloride was followed by extractions and flash chromatography with petroleum ether/ethyl acetate, 95:5.

General One-Pot Procedure for Vinyl Epoxy Silane Transformations: A solution of palladium acetate (0.05 mmol) and triphenyl phosphite (0.2 mmol) in THF (1 mL) was added at room temperature to a neat sample of the vinyl epoxide (1 mmol, 1 equiv.). After completion of the reaction had been checked by TLC, the temperature was lowered to –78 °C and the Grignard reagent (1.1 mmol, 1.3 M in THF) was added dropwise. After stirring for 30 min, the solution was allowed to warm to room temperature. The resulting mixture was then added at –78 °C to a white slurry of zinc chloride

(3.0 mmol, 1.6 M in THF) and lithium reagent (*n*BuLi, 8.9 mmol, 2.3 M in hexane) and stirred at this temperature until TLC indicated completion of the reaction. Hexamethyl phosphoramide (3 mL) was then added at –78 °C, followed by the electrophile (5.0 mmol of CH_3I or CH_2CHCH_2Br). The mixture was then allowed to warm slowly to 0 °C. The reaction was quenched with a saturated aqueous solution of ammonium chloride and extracted with diethyl ether. The organic layer was dried with sodium sulfate and concentrated under reduced pressure. Flash chromatography petroleum ether/diethyl ether (95:5) afforded compounds **36** and **39** in the yields of 62 and 75%, respectively.

3-Allyl-4-butyl-5-(*tert*-butyldimethylsilyl)-6-isopropyl-3,4,5,6-tetrahydropyran-2-one (36): Yield 77%. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 5.94 [m, 1 H, H-(CH_2)C=CH_2], 5.08 (dd, J = 15.7, 1.5 Hz, 1 H, H–CH=CH), 5.05 (s, 1 H, H–CH=CH_2), 4.12 [dd, J = 9.1, 3.5 Hz, 1 H, H–C(OC=O)(CHSi)(CH)], 2.42 [m, 1 H, CH_2-(CH=CH)(CH)], 2.37 [m, 1 H, CH_2-(CH=CH)(CH)], 2.05 [hd, J = 2.0 Hz, 1 H, H–C(CH_3)$_2$], 1.85 [m, 1 H, H–C(CHC=O)(CHSi)(CH_2)], 1.57–1.20 [m, 7 H, (CH_2)$_3$ + H–CSi], 0.99 (d, J = 3.0 Hz, 3 H, CH_3–CH–CH_3), 0.98 (d, J = 3.0 Hz, 3 H, CH_3–CH–CH_3), 0.091 [m, 12 H, CH_3(CH_2)$_3$ + *t*BuSi], 0.06 (s, 3 H, $SiCH_3$), 0.03 (s, 3 H, $SiCH_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.2, 136.1, 117.2, 85.7, 44.2, 38.0–14.1 (14C), –5.1, –6.1 ppm. IR (neat): $\tilde{\nu}$ = 2930, 2900, 2820, 1750, 1720, 1620, 1450, 1240, 820 cm^{-1}. HRMS calcd. for $C_{21}H_{40}O_2Si$ 353.2876; found *m*/*z* 353.2878.

Ethyl 1-[4-Butyl-5-(*tert*-butyldimethylsilyl)-6-isopropyl-2-oxodihydropyran-3-ylidene]acetate (37): Yield 66%. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 4.17 [dd, J = 12.0, 1.1 Hz, 1 H, H–C(OC=O)(CHSi)-(CH)], 2.83 [dt, J = 11.2, 3.5 Hz, 1 H, H–C(CHSi)(CH_2)(C=C)], 2.19 (s, 3 H, CH_3–C=C), 1.98 (s, 3 H, CH_3–C=O), 1.84 [h, 1 H, C*H*–(CH_3)$_2$], 1.50–1.19 [m, 7 H, (CH_2)$_3$ + HCSi], 1.08 (d, J = 7.1 Hz, 3 H, CH_3–CH–CH_3), 0.95 (m, 12 H, CH_3–CH–CH_3 + *t*BuSi), 0.88 [t, J = 7,1 Hz, 3 H, CH_3–(CH_2)$_3$], 0.13 (s, 3 H, $SiCH_3$), 0.10 (s, 3 H, $SiCH_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.1, 168.0, 150.32, 121.0, 83.2, 52.7, 40.1 –14.1 (14C), –4.4, –5.0 ppm. IR (neat): $\tilde{\nu}$ = 2940, 2920, 2850, 1760, 1720, 1660, 1460, 1370, 1260, 1240, 1170, 1010, 830 cm^{-1}. HRMS calcd. for $C_{22}H_{40}O_4Si$ 397.2774; found *m*/*z* 397.2779.

4-Butyl-5-(*tert*-butyldimethylsilyl)-3-(hydroxyphenylmethyl)-6-isopropyl-3,4,5,6-tetrahydropyran-2-one (38): Compound **38** was obtained as a diastereomerically pure pale yellow oil in a yield of 79%. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.34 (m, 5 H, Ph), 5.41 (dd, J = 3.94, 3.44 Hz, 1 H, C*H*OHPh), 4.11 (dd, J = 9.35, 2.46 Hz, 1 H, C*H*O–C=O), 3.44 (d, J = 4.92 Hz, 1 H, OH), 2.65 (dd, J = 7.39, 3.44 Hz, 1 H, C*H*C=O), 2.07 (m, 1 H, CH_3C*H*CH_3), 1.40 (dd, J = 2.46, 1.97 Hz, 1 H, C*H*Si), 1.24 [m, 7 H, CH(CH_2)$_3$], 1.10 (d, J = 6.4 Hz, 3 H, CH_3CHCH_3), 0.89 (d + s, 12 H, CH_3CHCH_3 + *t*BuSi), 0.06 [s, 6 H, (CH_3)$_2$Si] ppm. ^{13}C NMR (200 MHz, $CDCl_3$): δ = 174.6, 128.4–126.4 (4 C), 87.1, 77.1, 51.7, 38.6, 32.4–13.9 (10 C), –5.3, –6.2 ppm. IR: $\tilde{\nu}$ = 3500, 2900–3000, 1730, 1480, 1400, 1270, 850, 720 cm^{-1}. HRMS calcd. for $C_{25}H_{42}O_3Si$ 441.2801 [*M* + Na], found *m*/*z* (%) 441.2803 [*M* + Na], 341 (13), 313 (100), 297 (16), 255 (16), 107 (74).

4-Butyl-5-(*tert*-butyldimethylsilyl)-6-isopropyl-3-methyltetrahydropyran-2-one (39): Yield 75%. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 4.10 [dd, J = 9.3, 1.9 Hz, 1 H, H–C(OC=O)(CHSi)(CH)], 2.30 [m, 1 H, H–C(C=O)(CH_3)(CH)], 2.10 [m, 1 H, H–C(CHSi)(CH_2)$_3$(CH)], 1.7–1.3 [m, 8 H, (CH_2)$_3$ + HCSi + H-(CH_3)$_2$], 1.24 (d, 3 H, J = 6.8 Hz, CH_3–CH–CH_3), 1.02 (d, J = 6.1 Hz, 3 H, CH_3–CH), 1.00 (d, J = 6.8 Hz, 3 H, CH_3–CH–CH_3), 0.96 [m, 12 H, CH_3-(CH_2)$_3$ + *t*BuSi], 0.03 (s, 3 H, $SiCH_3$), 0.00 (s, 3 H, $SiCH_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 175.8, 86.1, 39.9, 39.0, 38.1, 32.7, 31.5, 29.2, 27.4, 24.0, 23.0, 20.3, 19.1, 15.8, 14.0, –5.5, –6.4 ppm. IR (neat): $\tilde{\nu}$ = 2940, 2920, 2840, 1735, 1460, 840 cm^{-1}. HRMS calcd. for $C_{19}H_{38}O_2Si$ 327.2719; found *m*/*z* 327.2724.

Supporting Information (for details see footnote on the first page of this article): ^{1}H NMR spectra of compounds **13**, **14**, **16**, **19**, **20**, **23**, **24**, and **25**.

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[34] A typical desilylation procedure was to dilute the γ-silylated δ-substituted α,β-unsaturated δ-lactone (1.9 mmol) in DMSO (8 mL) at room temperature and to add potassium fluoride (7 equiv., 13.3 mmol) and water (14 equiv., 26.6 mmol, 0.48 mL). After stirring for two days, the mixture was washed first with a saturated aqueous solution of ammonium chloride and then one of sodium chloride. The organic phases were dried with sodium sulfate and filtered, and the solvents were evaporated. After purification by flash chromatography on silica gel (petroleum ether/ethyl acetate, 85:15), the desilylated compound was obtained in a yield ranging from 54 to 76%). For instance the (–)-6-pentyl-5,6-dihydro-α-pyrone (massoilactone) was obtained in 76% yield. α_D^{20} –28.7 (*c* = 1.02, $CHCl_3$).[36] ^1H NMR (200 MHz, $CDCl_3$): δ = 6.83 (ddt, 1 H), 5.92 (dt, 1 H), 4.34 (m, 1 H), 2.23 (m, 2 H), 1.1–1.8 (m, 8 H), 0.81 (t, 1 H) ppm. ^{13}C NMR (200 MHz, $CDCl_3$): δ = 164.7, 145.4, 121.2, 77.1, 34.8, 31.5, 29.4, 22.5, 13.6 ppm. IR [cm^{-1}]: $\tilde{\nu}$ = 2900–3000, 1730, 1630, 810 cm^{-1}.
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