36. Chiral Acylsilanes in Organic Synthesis

Part 3[1])

Silicon-Directed Stereoselective Preparation and *Ireland* Ester-Enolate Rearrangement of *O*-Acyl-Substituted α-Silylated Allyl Alcohols

by **Valentin Enev**[2]), **Diana Stojanova**, and **Stefan Bienz***

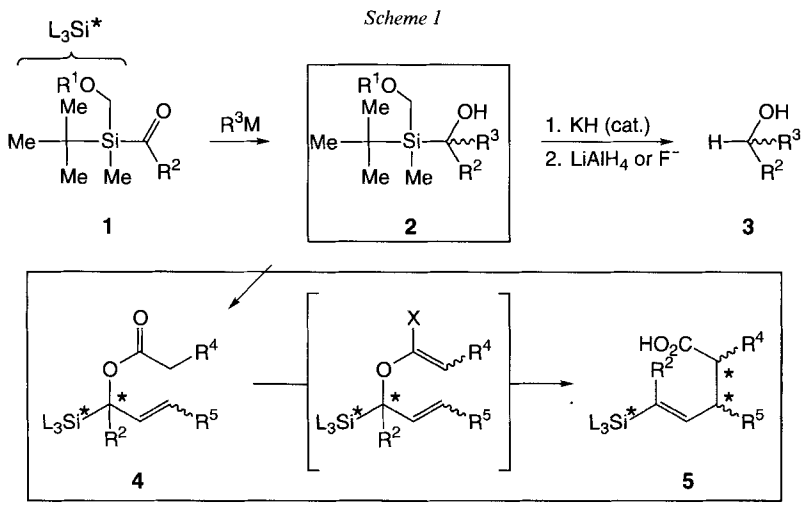
Organisch-chemisches Institut der Universität Zürich, Winterthurerstrasse 190, CH–8057 Zürich

(15.XI.95)

Stereocontrolled addition of alk-1-enylmetal reagents to the chiral (alkoxymethyl)-substituted acylsilanes (±)-**6** gave rise to α-silylated allyl alcohols, which were converted to the corresponding acetates or propionates **11**–**16** (*Scheme 2*). Deprotonation and silylation with Me_3SiCl afforded – in an *Ireland* ester-enolate-accelerated *Claisen* rearrangement – stereoselectively α,δ-silylated γ,δ-unsaturated carboxylic acids **18**–**24** (*Scheme 4*). The Me_3Si groups in α-position to the COOH group of these compounds were removed chemoselectively in presence of the chiral silyl group in δ-position by treatment with $Bu_4NF \cdot 3\ H_2O$ or $Et_3N \cdot 3$ HF (→ **27**–**32**; *Scheme 5*). The reaction sequence allows a novel stereocontrolled access to chiral C-frameworks possessing a vinylsilane moiety with its full reaction potential.

1. Introduction. – We have already demonstrated with our previous studies on chiral acylsilanes of type **1** that chiral (alkoxymethyl)-substituted silicon compounds can be efficiently used as auxiliaries for the stereoselective preparation of geminally (α) silyl-substituted alcohols of type **2** (*Scheme 1*) [1] [2]. Removal of the silyl group by *Brook*

Scheme 1



[1]) Part 2: [1].

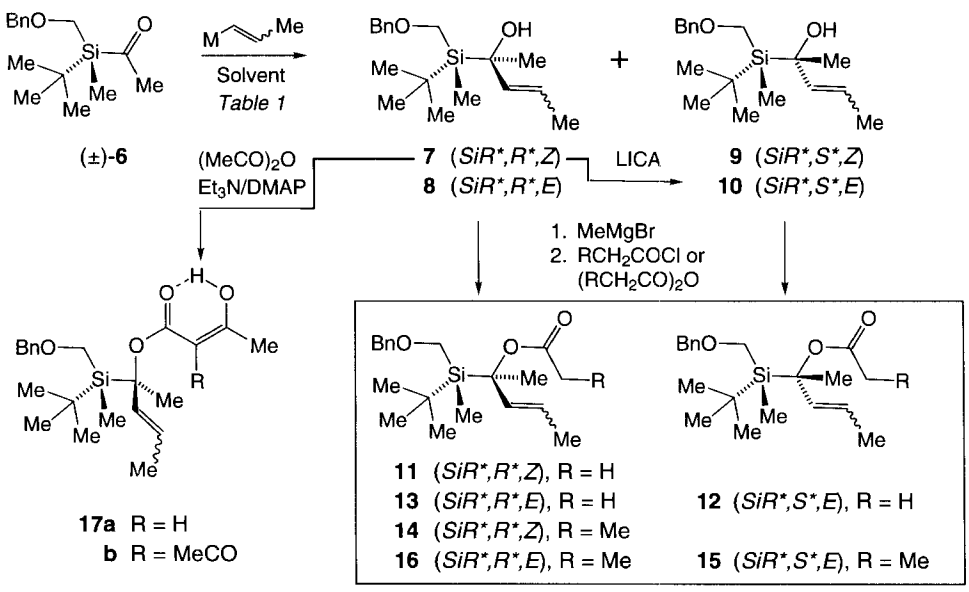
[2]) Postdoctoral fellow on leave from the Bulgarian Academy of Science, Sofia.

rearrangement followed by reduction or fluoride treatment proceeds with high stereospecificity and gives rise to Si-free secondary alcohols **3** [3] [4].

The synthetic use of chiral α-silylated alcohols, however, cannot exclusively lay in the stereospecific preparation of chiral secondary alcohols. We were rather tempted to employ compounds of type **2** as starting materials for further stereoselective transformations. Among those, the *Ireland* ester-enolate-accelerated *Claisen* rearrangement [5–8] of *O*-acyl-substituted α-silylated allyl alcohols **4** was considered to be particularly attractive. This reaction should allow a novel and stereocontrolled access to chiral γ,δ-unsaturated δ-silylated carboxylic-acid derivatives of type **5**, compounds that would not only possess an interesting chiral C-framework but would also allow to profit from the full reaction repertoire offered for vinylsilanes. They would, therefore, comprise themselves a high potential for further – eventually stereoselective – chemical transformations.

2. Results and Discussion. – 2.1. *Stereoselective Preparation of* O-*Acyl-Substituted α-Silylated Allyl Alcohols.* To study the *Ireland* ester-enolate rearrangement of *O*-acyl-substituted α-silylated allyl alcohols **4**, we first prepared some α-silylated allyl alcohol precursors with the methodology discussed earlier [1] [2]. The 'chelate-controlled' addition of several propenylmetal reagents to the racemic [(benzyloxy)methyl]-substituted acetylsilane (±)-**6**[3]) afforded preferentially the corresponding α-silylated allyl alcohols **7** and **8** in high chemical and stereochemical yields (*Scheme 2*). The stereoselectivities of

Scheme 2



DMAP = 4-(dimethylamino)pyridine, LICA = lithium cyclopropyl(isopropyl)amide

[3]) Optically active (+)- and (−)-**6** are available by bioreduction of (±)-**6** with *Trigonopsis variabilis* (DSM 70714) [3] [4] [9]. Since the stereochemistry of the investigated reactions is readily recognized by means of relative configurations, however, the more accessible racemic material is used in this study.

these reactions depend – as already experienced earlier – crucially on the reaction conditions and the nature of organometallic reagents.

Best results were obtained in Et_2O with organometallic reagents freshly prepared from prop-1-enyl bromide by sequential treatment with a *ca.* five-fold excess of elemental Li (2% Na) and ½ equiv. of $MgBr_2$. Addition of acetylsilane (±)-**6** to the organometal suspensions gave the (*SiR*,R**)-configurated[4]) products **7** and **8** in diastereoisomer ratios (d.r.) of up to 95:5 (*cf. Table 1*). The actual nature of the organometallic species involved in the transformation is not known. However, the use of a large excess of Li with 2% Na as well as of the $MgBr_2$ additive in their preparations was necessary to obtain the high stereoselectivities: the reactions with prop-1-enyl *Grignard* reagents, with prop-1-enyl lithium (without $MgBr_2$ additive), or with prop-1-enyl lithium/$MgBr_2$ (without excess of Li or with Li (0% Na)) resulted all in lower stereochemical (see *Table 1*) and, partly, lower chemical yields.

Table 1. *Metallation of* (E/Z)*-1-Bromoprop-1-ene and Subsequent Reaction with Acylsilane* (±)-**6**

Conditions				**7/9** (d.r.)	**8/10** (d.r.)
Metallation with	Additive (equiv.)	Solvent	Temp.		
Mg	–	THF	–80°	2:1	5:1
Mg	–	Et_2O	–80°	1.5:1[a])	2:1[a])
Mg	CuI (1)	Et_2O/THF 1:1	–80°	1:1	2:1
Mg	CuI (1)	Et_2O	–80°	1:1	4:1
Li (2% Na)	Li (3)	Et_2O	–80°	5:1	1:1
Li (2% Na)	$MgBr_2$ (0.5)	Et_2O	–90°	16:1	19:1
Li (2% Na)	$MgBr_2$ (0.5), Li (3)	Et_2O	–90°	24:1	> 25:1
Li (0% Na)	$MgBr_2$ (0.5), Li (3)	Et_2O	–90°	13:1	7:1

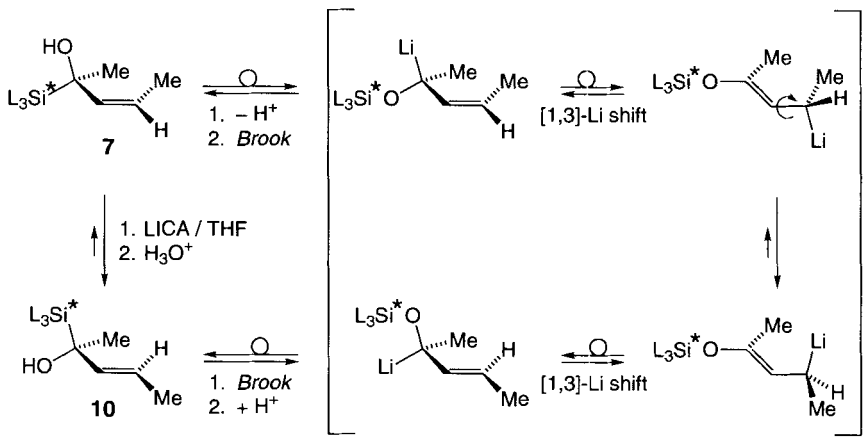
[a]) The reaction was very slow; after 2 h (standard conditions), only 10% of the products were formed. These ratios are, therefore, not reliable.

Whereas the isomers **7** and **8** were thus directly accessible in high diastereoisomer purities, the isomers **9** and **10** were, on this direct path, only obtained as minor components, together with **7** or **8**, respectively. Indirectly, highly enriched **10** was accessible from (*Z*)-isomer **7** by a base-induced rearrangement: treatment of **7** with lithium cyclopropyl(isopropyl)amide (LICA) in THF produced stereospecifically (*E*)-isomer **10** (80%), under simultaneous inversion of the C=C bond geometry and of the configuration at the OH-substituted center. A mechanism involving stereocontrolled *Brook/retro-Brook* rearrangements and [1,3]-Li shifts, as shown in *Scheme 3*, would account for the stereochemical course of the reaction.

The acylation of the α-silylated allyl alcohols **7**, **8**, and **10** to the acetates **11–13** (65–86%) and the propionates **14–16** (63–91% yields) was performed by treatment of the respective magnesium alkoxides with acid anhydrides or acyl chlorides (*Scheme 2*). The unusual conditions indicate that these transformations were not trivial. The reactions of **7**

[4]) The relative configurations are assigned on the basis of the X-ray crystal structure of **22** (for structure, see *Fig.* below) and on the assumption of similar stereochemical courses of the reactions leading from **11–16** to **18–24**. The relative configurations contradict our earlier tentative assignments based on a model of a chair-like transition state in the addition step.

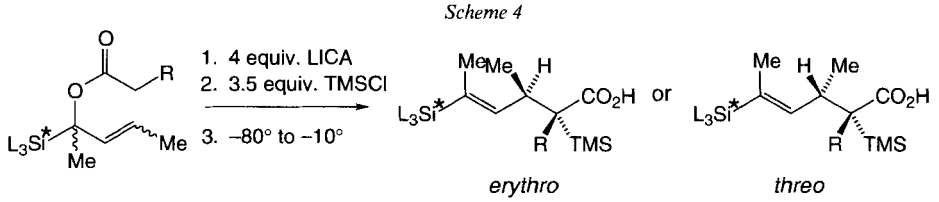
Scheme 3



with acyl chlorides or anhydrides in presence of amine bases were sluggish, probably due to steric hindrance at the chiral C-center. Activation of the acyl component by catalytic amounts of 4-(dimethylamino)pyridine (DMAP) and prolonged reaction times afforded mainly bis- and tris-acylated products of type **17**, and because of the facile *Brook*-rearrangement already mentioned above, acylation of **7**, **8**, and **10** could not be performed *via* the alkali alkoxides.

2.2. Claisen-*Type Rearrangements*. In analogy to the traditional protocol, our acetates **11**–**13** and propionates **14**–**16** were deprotonated at –80° with an excess of LICA. The enolates were silylated at this temperature by addition of trimethylchlorosilane (Me_3SiCl), and the resulting mixtures were subsequently allowed to reach –30 to 0° for the thermal rearrangements. To our surprise, not the simple rearrangement products, but the silylated derivatives **18**–**24** were obtained by this procedure (*Scheme 4*). The rear-

Scheme 4



11 (*SiR*,R*,Z*), R = H
12 (*SiR*,S*,E*), R = H
13 (*SiR*,R*,E*), R = H
14 (*SiR*,R*,Z*), R = Me
15 (*SiR*,S*,E*), R = Me
16 (*SiR*,R*,E*), R = Me

18 (*SiS*,2R*,3R**), R = H
18 (*SiS*,2R*,3R**), R = H $\xleftarrow{\Delta t}$ **19** (*SiS*,2S*,3R**), R = H
21 (*SiS*,2S*,3S**), R = H ← **20** (*SiS*,2R*,3S**), R = H
22 (*SiS*,2R*,3R**), R = Me
23 (*SiS*,2S*,3R**), R = Me
24 (*SiS*,2R*,3S**), R = Me

25 (*SiR*,R*,Z*), R = Me_3Si
26 (*SiR*,R*,Z*), R = (*t*-Bu)Me_2Si

TMS = Me_3Si

rangements proceeded highly stereospecifically. Each starting material[5]) gave initially rise to a single product only: the compounds **11** and **14**, possessing (*Z*)-configurated C=C bonds, produced the (*E*)-*erythro*(*SiS**,*R**) on the C-skeleton)-configurated carboxylic acids **18** and **22**, whereas **12**, **13**, **15**, and **16** with the (*E*)-C=C bond delivered the (*E*)-*threo*(*SiS**,*S** on the C-skeleton)-configurated products **19**, **20**, **23**, and **24**, respectively. In the case of the (*E*)-configurated acetates **12** and **13**, the epimerization products **18** and **21** were found together with the primary rearrangement products **19** and **20**, respectively, after a prolonged reaction time. Evidently, partial deprotonation of the α-monosubstituted carboxy compounds (in the reaction mixture in form of the Me_3Si esters) takes place under the basic conditions, and reprotonation leads to the epimerization products. Since the Me_3Si group is removed in a later step, the observed isomerization is not relevant.

The C=C bond geometries of the starting materials **11–16** and the rearrangement products **18–24** were secured by NMR experiments. The coupling constants of the olefinic protons for the starting esters **11–16** (and the corresponding alcohol precursors **7**, **8**, and **10**) are characteristic for the C=C bond geometry ($^3J_{cis}$ = 12.1–12.3 Hz, $^3J_{trans}$ = 15.4–15.7 Hz). For the rearrangement products, irradiations at the absorption frequencies of the olefinic protons or olefinic methyl protons led to nuclear *Overhauser* effects (NOE) of the signals deriving from the *cis*-arranged groups (see *Exper. Part*). The assignment of the *erythro*- or *threo*-configurations of the products followed from the single-crystal X-ray analysis of **22** (*Fig.*) and from the assumption of similar stereochemical reaction courses for all enolizations/rearrangements.

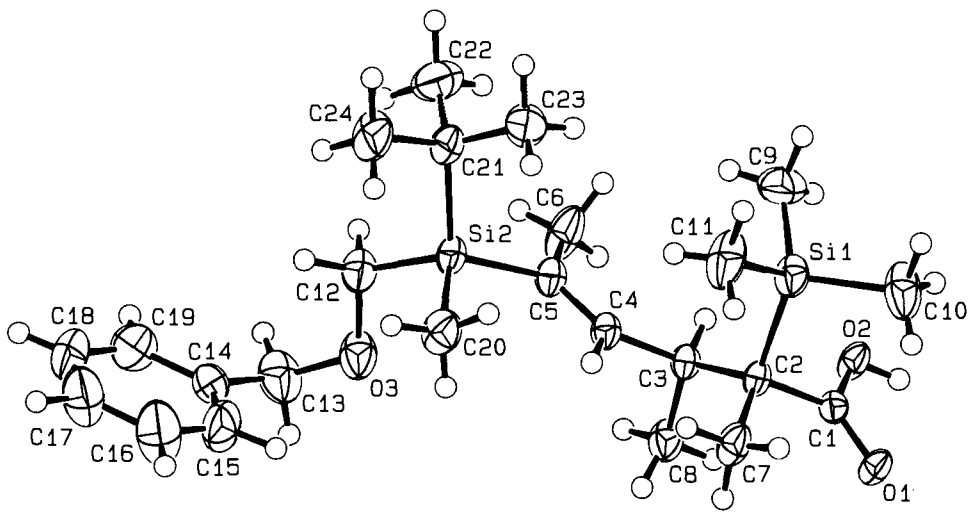


Figure. *View* (ORTEP [10]) *of the molecular structure of* **22**

It is, to the best of our knowledge, the first time that exlusively C-silylated products were obtained by the *Ireland* ester-enolate rearrangement. C-Silylated products have been previously obtained, too, but to a much lesser extent [5] [6]. They were tentatively explained in terms of a silylation reaction occurring after the enolate rearrangement. Our results, however, demonstrate clearly that the silylation had taken place before the

[5]) The starting esters were used as mixtures of diastereoisomers in different ratios, and the product mixtures reflected, within the limits of error, in all cases the original ratio of the starting materials.

rearrangement happened: otherwise, the reactions of **11** and **12** – possessing opposite C=C bond geometries as well as relative configurations at the Si- and C-atom – should have led to the same product(s). Since it is well known that alkonates of sterically hindered alcohols favor α-silylation upon treatment with strong bases and Me_3SiCl [11], our result is not too astonishing. Accordingly, the ester enolates of **11**–**16** were initially α-silylated, subsequently stereoselectively re-enolized and *O*-silylated using a second equivalent of base and Me_3SiCl, and then, upon warming up, the α-silylated ketene acetals rearranged. The use of a large excess of base is in fact necessary for the high-yielding rearrangement reactions. The treatment of **11**, *e.g.*, with 1 equiv. of LICA only, followed by the addition of 2 equiv. of Me_3SiCl delivered 36% of the corresponding α-silylated starting material **25** as the product; no rearrangement was observed at all under these conditions. The use of (*tert*-butyl)chlorodimethylsilane ((*t*-Bu)Me_2SiCl) instead of Me_3SiCl for the reaction, which should lead to the preferred *O*-silylation of ester enolates [11] and, hence, diminish the formation of α-silylated rearrangement products [6], gave still rise to only α-silylated starting material (see **26**) besides deacylated and isomerized product **10**.

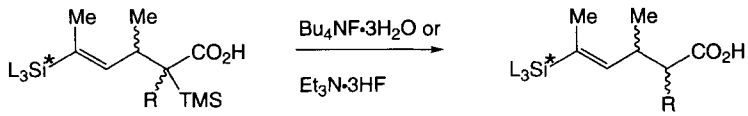
The stereochemistry of the transformations **11**–**16** to **18**–**24** contradicts our expectation of a reaction proceeding *via* (*E*)-configurated ketene-acetal intermediates, which should preferentially be formed by kinetic deprotonation and silylation of carboxylic esters with LICA in THF [6] [12], and cyclic chair-like transition states. The observed stereochemical outcome can be explained by two reaction paths: either by a reaction course proceeding *via* a chair-like transition state where the bulky silyl group is placed in pseudoequatorial position and the (trimethylsilyl)ketene acetal is (*Z*)-configurated, or by a transformation advancing *via* a boat-like transition state, where the silyl group is again placed in pseudoequatorial position, but the (trimethylsilyl)ketene acetal is (*E*)-configurated. From model studies, we assumed that the first reaction course has to be preferred: due to two bulky groups that are attached to the O-atoms and to the C(α)'s of the ester moieties, the $A_{1,3}$-strain should destabilize a 'closed' chair-like transition state, which was postulated by *Ireland* and coworkers [6] [12] to be responsible for the formation of the (*E*)-configurated enolate[6]). As a consequence, the 'acyclic' stereocontrol of enolization should be operative, as it is described for ester deprotonations in the presence of donating cosolvents. The result would be the preferred formation of (*Z*)-enolates. In fact, the stereochemical outcome of the *Ireland* rearrangement is the same whether the deprotonations are done in 45% DMPU/THF or THF alone (DMPU = 3,4,5,6-tetrahydro-1,3-dimethylpyrimidin-2(1*H*)-one), supporting our assumption.

2.3. *Removal of the Trimethylsilyl Group.* The Me_3Si groups of **18**–**24** were removed selectively in presence of the olefinic silyl groups (*Scheme 5*). Treatment of the compounds with Bu_4NF or $Et_3N \cdot 3$ HF gave rise to the Me_3Si-free products **27**–**32** in good yields. The starting acids **18** and **19** produced the same product **27**, proving that they share in fact the relative configuration at the Si and C(3) centers. Likewise, **20** and **22**/**23** afforded the product **28** or the mixture of products **29**/**30** (*ca.* 2:3). The acid **24** gave rise to the mixture of **31**/**32** (*ca.* 2:3). The formation of mixtures of products from single precursors (**29**/**30** from **22** or **23**, and **31**/**32** from **24**, resp.) shows that the removal of the

---

[6]) The stereochemical notion is used, in which the enolate O-atom is assigned priority over the alkoxy group, regardless of the nature of the associated cation, as suggested by *Evans* [13].

Scheme 5



18/19 (*SiS*,2R*/S*,3R**), R = H
20 (*SiS*,2R*/S*,3S**), R = H

22/23 (*SiS*,2R*/S*,3R**), R = Me
24 (*SiS*,2R*,3S**), R = Me

27 (*SiS*,3R**), R = H
28 (*SiS*,3S**), R = H

29/30 (*SiS*,2R*/S*,3R**), R = Me
31/32 (*SiS*,2R*/S*,3S**), R = Me

TMS = Me_3Si

Me_3Si group proceeds with low stereoselectivity. Evidently, the reaction passes through a carbanionic intermediate that does, unfortunately, not retain the stereochemical information of the precursor. Since the Me group is located in α-position to a carboxy group, however, it might be possible to epimerize the respective chiral center in a later stage of a synthesis.

We thank the members of our analytical laboratories for their excellent services, particularly Dr. *A. Linden* for the X-ray analysis, and the *Swiss National Science Foundation* for their generous financial support. We are especially grateful to Prof. Dr. *M. Hesse* who provided us with laboratory space, equipment, and regular occasions for scientific discussions. We like to express our thanks to Dipl.-chem. *J. Fässler*, too, who independently reproduced some of the presented experiments.

Experimental Part

General. Unless otherwise stated: all org. solvents were distilled prior to use. For the reactions, THF and Et_2O were dried over Na-ketyl. All reactions were carried out under Ar. Soln. of salts and acids for workup procedures were prepared in deionized H_2O. Extracts were dried (Na_2SO_4) and evaporated *in vacuo*. Chromatography: silica gel *Merck 60* (40–63 μm). M.p.: *Mettler FP-5/FP-52*. IR Spectra (neat): *Perkin-Elmer 781*; data in cm^{-1}. ^{1}H-NMR: at 300 MHz in $CDCl_3$; *Bruker AC-300*; in δ in ppm rel. to $CHCl_3$ (= 7.26 ppm), *J* in Hz. ^{13}C-NMR: at 75.6 MHz in $CDCl_3$; *Bruker ARX-300*; δ in ppm rel. to $CDCl_3$ (= 77.0 ppm); multiplicities from DEPT experiments. CI-MS (chemical-ionization mass spectrometry): with NH_3 as the reactant gas; *Finnigan MAT 90* or *Varian MAT 711*; data in *m/z*.

1. *Addition Reaction of the Acylsilane.* 1.1. *(*R*,R*,Z*)- and (*R*,R*,E*)-2-{[(Benzyloxy)methyl](*tert*-butyl)methylsilyl}pent-3-en-2-ol* (**7** and **8**, resp.). To a suspension of 300 mg (*ca.* 43 mmol) of Li (2% Na, 15% suspension in hexane), activated with *ca.* 10 mg of 1,2-dibromoethane, in 5 ml of dry Et_2O were added 1.0 ml (11.6 mmol) of neat 1-bromoprop-1-ene ((*E*/*Z*)-mixture) at −10°. After 1 h, 5.0 ml of 1M $MgBr_2$ in benzene/Et_2O 1:1 (5.0 mmol) were added dropwise at −90°, and, after another 30 min, a soln. of 900 mg (3.41 mmol) of (±)-**6** in 1 ml of dry Et_2O followed. The mixture was kept at −90 to −85° for 40 min, then quenched with sat. NH_4Cl soln., and acidified with dil. HCl soln. Extraction with Et_2O and chromatography (hexane/Et_2O 96:4) gave 500 mg (48%) of **7** and 220 mg (21%) of **8** as colorless oils. The yields and the stereoselectivities varied depending on the reaction conditions (see *Table 1*).

Data of **7**: IR: 3480*s* (br.), 3090*w*, 3060*w*, 3025*m*, 3000*m*, 2955*s*, 2930*s*, 2855*s*, 2815*m*, 1495*w*, 1465*m*, 1455*m*, 1405*w*, 1380*s*, 1365*s*, 1280*w*, 1250*s*, 1210*m*, 1150*m*, 1095*s*, 1070*s*, 1030*m*, 975*w*, 955*w*, 935*w*, 900*m*, 825*s*, 805*m*, 785*m*, 765*m*, 735*s*, 700*s*. ^{1}H-NMR: 7.38–7.27 (*m*, 5 arom. H); 5.35, 5.25 (*AB* of *ABX*$_3$, J_{AB} = 12.1, J_{AX} = 6.8, J_{BX} = 1.3, MeC*H*=C*H*); 4.54, 4.47 (*AB*, *J* = 11.8, PhCH_2O); 3.50, 3.38 (*AB*, *J* = 12.5, SiCH_2O); 3.36 (*s*, OH); 1.89 (*dd*, *J* = 6.8, 1.3, *Me*CH=CH); 1.47 (*s*, C(OH)*Me*); 0.97 (*s*, *t*-Bu); 0.12 (*s*, MeSi). ^{13}C-NMR: 137.8 (*s*, arom. C); 134.8 (*d*, CH=); 128.3, 127.7 (2*d*, each 2 arom. C); 127.6 (*d*, arom. C); 122.3 (*d*, CH=); 77.6 (*t*, PhCH_2O); 72.0 (*s*,

C(OH)Me); 61.3 (*t*, $SiCH_2O$); 27.9 (*q*, Me_3C); 27.7 (*q*, *Me*C=); 17.7 (*s*, Me_3C); 14.2 (*q*, C(OH)*Me*); −9.8 (*s*, MeSi). CI-MS (isobutane): 307 ($[M + H]^+$), 289 ($[M + H - H_2O]^+$).

Data of **8**: IR: 3480*s* (br.), 3090*w*, 2060*w*, 3025*m*, 2960*s*, 2930*s*, 2860*s*, 2820*m*, 1495*w*, 1465*m*, 1455*m*, 1380*s*, 1365*s*, 1250*s*, 1210*w*, 1160*w*, 1090*s*, 1070*s*, 1030*m*, 1010*w*, 975*s*, 935*w*, 900*m*, 855*m*, 825*s*, 805*m*, 785*m*, 765*m*, 735*s*, 700*s*. ^{1}H-NMR: 7.39–7.28 (*m*, 5 arom. H); 5.58, 5.46 (*AB* of *ABX*$_3$, J_{AB} = 15.4, J_{AX} = 1.1, J_{BX} = 6.1, MeC*H*=C*H*); 4.50 (*s*, $PhCH_2O$); 3.46, 3.34 (*AB*, *J* = 12.5, $SiCH_2O$); 3.27 (*s*, OH); 1.70 (*dd*, *J* = 6.1, 1.1, *Me*CH=CH); 1.40 (*s*, C(OH)*Me*); 0.96 (*s*, *t*-Bu); 0.03 (*s*, MeSi). ^{13}C-NMR: 137.9 (*s*, arom. C); 137.1 (*d*, CH=); 128.3, 127.7 (2*d*, each 2 arom. C); 127.6 (*d*, arom. C); 120.5 (*d*, CH=); 77.6 (*t*, $PhCH_2O$); 69.2 (*s*, *C*(OH)Me); 60.9 (*t*, $SiCH_2O$); 27.9 (*q*, Me_3C); 26.1 (*q*, *Me*C=); 17.8 (*q*, C(OH)*Me*); 17.7 (*s*, Me_3C); −10.3 (*q*, MeSi). CI-MS (isobutane): 307 ($[M + H]^+$), 289 ($[M + H - H_2O]^+$).

1.2. *(*R*,S*,E*)-2-{[(Benzyloxy)methyl](*tert*-butyl)methylsilyl}pent-3-en-2-ol* (**10**). To a soln. of 0.35 ml (2.8 mmol) of cyclohexyl(isopropyl)amine in 1.5 ml of THF, 1.3 ml (2.6 mmol) of 2M BuLi in pentane were added at 0° (→2.6 mmol of LICA). After 5 min, the mixture was cooled to −10°, and 153 mg (0.50 mmol) of **7** in 0.5 ml of THF were added. The mixture was stirred for 2.5 h, quenched with sat. NH_4Cl soln., acidified with dil. HCl soln., extracted, and chromatographed (hexane/Et_2O 96:4): 123 mg (80%) of **10**. Colorless oil. IR: 3470*s* (br.), 3090*w*, 3060*w*, 3030*m*, 2960*s*, 2930*s*, 2860*s*, 2820*m*, 1495*w*, 1465*m*, 1455*m*, 1380*s*, 1365*s*, 1250*s*, 1205*w*, 1160*w*, 1090*s*, 1070*s*, 1030*m*, 1010*w*, 970*s*, 935*w*, 905*m*, 860*m*, 825*s*, 800*m*, 785*m*, 765*m*, 735*s*, 700*s*. ^{1}H-NMR: 7.39–7.28 (*m*, 5 arom. H); 5.65, 5.44 (*AB* of *ABX*$_3$, J_{AB} = 15.4, J_{AX} = 1.4, J_{BX} = 6.3, MeC*H*=C*H*); 4.49 (*s*, $PhCH_2O$); 3.51 (*s*, OH); 3.49, 3.33 (*AB*, *J* = 12.6, $SiCH_2O$); 1.70 (*dd*, *J* = 6.3, 1.4, *Me*CH=CH); 1.32 (*s*, C(OH)*Me*); 0.96 (*s*, *t*-Bu); 0.07 (*s*, MeSi). ^{13}C-NMR: 137.9 (*s*, arom. C); 137.7 (*d*, CH=); 128.3, 127.8 (2*d*, each 2 arom. C); 127.7 (*d*, arom. C); 120.0 (*d*, CH=); 77.6 (*t*, $PhCH_2O$); 69.3 (*s*, *C*(OH)Me); 60.9 (*t*, $SiCH_2O$); 27.8 (*q*, Me_3C); 26.0 (*q*, *Me*C=); 17.8 (*q*, C(OH)*Me*); 17.7 (*s*, Me_3C); −10.0 (*q*, MeSi). CI-MS (isobutane): 307 ($[M + H]^+$), 289 ($[M + H - H_2O]^+$).

2. *Acylation of the α-Silylated Allyl Alcohols.* 2.1. *(*R*,R*,Z*)-1-{[(Benzyloxy)methyl](*tert*-butyl)methylsilyl}-1-methylbut-2-enyl Acetate* (**11**). To a soln. of 80 mg (0.26 mmol) of **7** in 2 ml of Et_2O, 0.12 ml (0.36 mmol) of 3M MeMgBr in Et_2O were added at −80°. After 10 min, 0.09 ml (0.15 mmol) of AcCl were added, and the previously formed precipitate dissolved almost completely. The mixture was slowly allowed to warm to 23° (*ca.* 2 h), and stirring was continued for another 30 min. Quenching with sat. $NaHCO_3$ soln., extraction with Et_2O, and chromatography (hexane/Et_2O 96:4) gave 77 mg (85%) of **11**. Colorless oil. IR: 3090*w*, 3060*w*, 3025*m*, 2960*s*, 2930*s*, 2855*s*, 2815*m*, 1740*s*, 1500*w*, 1465*m*, 1455*m*, 1405*w*, 1370*s*, 1250*s*, 1230*s*, 1150*w*, 1095*s*, 1070*s*, 1030*m*, 1010*m*, 975*w*, 935*m*, 905*w*, 830*s*, 785*m*, 770*m*, 735*s*, 700*s*. ^{1}H-NMR: 7.36–7.15 (*m*, 5 arom. H); 5.48 (*dq*, *J* = 12.3, 1.5, MeCH=C*H*); 5.34 (*dq*, *J* = 12.3, 7.2, MeC*H*=CH); 4.47 (*s*, $PhCH_2O$); 3.40, 3.34 (*AB*, *J* = 12.9, $SiCH_2O$); 1.99 (*s*, MeCOO); 1.83 (*s*, C(OR)Me); 1.66 (*dd*, *J* = 7.2, 1.5, *Me*CH=CH); 1.05 (*s*, *t*-Bu); 0.15 (*s*, MeSi). ^{13}C-NMR: 170.0 (*s*, CO); 138.8 (*s*, arom. C); 133.7 (*d*, CH=); 128.1, 127.3 (2*d*, each 2 arom. C); 127.2 (*d*, arom. C); 120.7 (*d*, CH=); 80.4 (*s*, *C*(OR)Me); 77.2 (*t*, $PhCH_2O$); 60.0 (*t*, $SiCH_2O$); 28.2 (*q*, Me_3C); 23.3 (*q*, *Me*C=); 21.9 (*q*, *Me*CO); 18.7 (*s*, Me_3C); 14.0 (*q*, C(OR)*Me*); −9.6 (*q*, MeSi). CI-MS: 366 ($[M + NH_4]^+$).

2.2. *(*R*,S*,E*)-1-{[(Benzyloxy)methyl](*tert*-butyl)methylsilyl}-1-methylbut-2-enyl Acetate* (**12**). Analogously to **11**, 131 mg (0.43 mmol) of **10** gave, after deprotonation (at −70°) with 1.29 mmol of MeMgBr and reaction with 1.72 mmol of Ac_2O (slowly warmed up to 0° and immediately quenched), 115 mg (77%) of **12** as a colorless oil and 12 mg (9%) of recovered **10**. IR: 3090*w*, 3060*w*, 3030*m*, 2960*s*, 2935*s*, 2860*s*, 2815*m*, 1740*s*, 1500*w*, 1465*m*, 1455*m*, 1370*s*, 1230*s*, 1160*w*, 1095*s*, 1070*s*, 1030*s*, 1010*m*, 970*m*, 935*m*, 900*w*, 830*s*, 805*m*, 780*m*, 735*m*, 700*s*. ^{1}H-NMR: 7.33–7.20 (*m*, 5 arom. H); 5.69 (*dq*, *J* = 15.7, 1.5, MeCH=C*H*); 5.21 (*dq*, *J* = 15.7, 6.6, MeC*H*=CH); 4.42 (*s*, $PhCH_2O$); 3.29 (*s*, $SiCH_2O$); 1.92 (*s*, MeCOO); 1.68 (*s*, C(OR)Me); 1.66 (*dd*, *J* = 6.6, 1.5, *Me*CH=CH); 0.98 (*s*, *t*-Bu); 0.00 (*s*, MeSi). ^{13}C-NMR: 170.4 (*s*, CO); 138.8 (*s*, arom. C); 134.6 (*d*, CH=); 128.1, 127.3 (2*d*, each 2 arom. C); 127.2 (*d*, arom. C); 120.7 (*d*, CH=); 79.9 (*s*, *C*(OR)Me); 77.1 (*t*, $PhCH_2O$); 59.8 (*t*, $SiCH_2O$); 28.1 (*q*, Me_3C); 22.1 (*q*, *Me*C=); 21.1 (*q*, *Me*CO); 18.4 (*s*, Me_3C); 17.9 (*q*, C(OR)*Me*); −9.9 (*q*, MeSi). CI-MS: 366 ($[M + NH_4]^+$).

2.3. *(*R*,R*,E*)-1-{[(Benzyloxy)methyl](*tert*-butyl)methylsilyl}-1-methylbut-2-enyl Acetate* (**13**). Analogously to **11**, 70 mg (0.23 mmol) of **8** gave, after deprotonation with 0.33 mmol of MeMgBr and reaction with 0.70 mmol of Ac_2O (slowly warmed up to 0° and immediately quenched), 57 mg (71%) of **13**. Colorless oil. IR: 3095*w*, 3060*w*, 3030*m*, 2960*s*, 2935*s*, 2860*s*, 2815*m*, 1740*s*, 1500*w*, 1465*m*, 1455*m*, 1370*s*, 1250*s*, 1230*s*, 1165*w*, 1095*s*, 1070*s*, 1030*s*, 1010*m*, 970*s*, 935*m*, 905*w*, 830*w*, 805*m*, 785*m*, 770*m*, 735*m*, 700*s*. ^{1}H-NMR: 7.36–7.25 (*m*, 5 arom. H); 5.67 (*dq*, *J* = 15.6, 1.4, MeCH=C*H*); 5.29 (*dq*, *J* = 15.6, 6.5, MeC*H*=CH); 4.52, 4.47 (*AB*, *J* = 12.0, $PhCH_2O$); 3.33 (*s*, $SiCH_2O$); 2.01 (*s*, MeCOO); 1.74 (*s*, C(OR)Me); 1.72 (*dd*, *J* = 6.5, 1.4, *Me*CH=CH); 1.04 (*s*, *t*-Bu); 0.15 (*s*, MeSi). ^{13}C-NMR: 170.4 (*s*, CO); 138.8 (*s*, arom. C); 134.5 (*d*, CH=); 128.1, 127.4 (2*d*, each 2 arom. C); 127.2 (*d*, arom. C); 120.6 (*d*, CH=); 79.8 (*s*, *C*(OR)Me); 77.1 (*t*, $PhCH_2O$); 59.8 (*t*, $SiCH_2O$); 28.1

(*q*, Me_3C); 22.1 (*q*, *Me*C=); 21.2 (*q*, *Me*CO); 18.4 (*s*, Me_3C); 17.9 (*q*, C(OR)*Me*); −9.9 (*q*, MeSi). CI-MS: 366 ($[M + NH_4]^+$).

2.4. *(*R**,R*,Z)-1-{[(Benzyloxy)methyl](*tert*-butyl)methylsilyl}-1-methylbut-2-enyl Propanoate* (**14**). Analogously to **11**, 79 mg (0.26 mmol) of **7** gave, after deprotonation with 0.36 mmol of MeMgBr and reaction with 0.97 mmol of propanoyl chloride, 86 mg (91%) of **14**. Colorless oil. IR: 3095*w*, 3060*w*, 3030*m*, 2965*s*, 2930*s*, 2860*s*, 2815*m*, 1740*s*, 1500*w*, 1465*m*, 1405*w*, 1380*m*, 1365*s*, 1250*s*, 1205*s*, 1175*s*, 1150*m*, 1095*s*, 1075*s*, 1030*m*, 1010*w*, 990*w*, 935*w*, 905*m*, 825*s*, 805*m*, 785*m*, 770*m*, 735*s*, 695*s*. ^{1}H-NMR: 7.34–7.21 (*m*, 5 arom. H); 5.46 (*dq*, *J* = 12.3, 1.5, MeCH=C*H*); 5.34 (*dq*, *J* = 12.3, 7.1, MeC*H*=CH); 4.44 (*s*, PhCH_2O); 3.38, 3.31 (*AB*, *J* = 12.9, SiCH_2O); 2.24 (*q*, *J* = 7.6, MeCH_2); 1.80 (*s*, C(OR)Me); 1.66 (*dd*, *J* = 7.2, 1.5, *Me*CH=CH); 1.07 (*t*, *J* = 7.6, *Me*CH_2); 1.02 (*s*, *t*-Bu); 0.08 (*s*, MeSi). ^{13}C-NMR: 173.4 (*s*, CO); 138.8 (*s*, arom. C); 132.9 (*d*, CH=); 128.1, 127.4 (2*d*, each 2 arom. C); 127.2 (*d*, arom. C); 120.6 (*d*, CH=); 80.2 (*s*, *C*(OR)Me); 77.2 (*t*, PhCH_2O); 60.0 (*t*, SiCH_2O); 28.4 (*t*, MeCH_2); 28.2 (*q*, Me_3C); 23.4 (*q*, *Me*C=); 18.5 (*s*, Me_3C); 14.0 (*q*, C(OR)*Me*); 9.1 (*q*, *Me*CH_2); −9.7 (*q*, MeSi). CI-MS: 380 ($[M + NH_4]^+$).

2.5. *(*R**,S*,E)-1-{[(Benzyloxy)methyl](*tert*-butyl)methylsilyl}-1-methylbut-2-enyl Propanoate* (**15**). Analogously to **11**, 100 mg (0.33 mmol) of **10** gave, after deprotonation (at −70°) with 0.90 mmol of MeMgBr and reaction with 1.15 mmol of propano anhydride (slowly warmed up to +5° and immediately quenched), 89 mg (75%) of **15**. Colorless oil. IR: 3095*w*, 3060*w*, 3030*m*, 2965*s*, 2935*s*, 2860*s*, 2815*m*, 1740*s*, 1500*w*, 1465*s*, 1455*s*, 1380*s*, 1365*s*, 1270*m*, 1250*s*, 1210*s*, 1175*s*, 1110*m*, 1095*s*, 1075*s*, 1030*m*, 1010*w*, 990*w*, 970*m*, 935*w*, 905*m*, 830*s*, 805*s*, 785*s*, 770*m*, 735*s*, 700*s*. ^{1}H-NMR: 7.36–7.24 (*m*, 5 arom. H); 5.71 (*dq*, *J* = 15.7, 1.5, MeCH=C*H*); 5.24 (*dq*, *J* = 15.7, 6.5, MeC*H*=CH); 4.46 (*s*, PhCH_2O); 3.30 (*s*, SiCH_2O); 2.23 (*q*, *J* = 7.5, MeCH_2); 1.71 (*s*, C(OR)Me); 1.70 (*dd*, *J* = 6.5, 1.5, *Me*CH=CH); 1.08 (*t*, *J* = 7.5, *Me*CH_2); 1.02 (*s*, *t*-Bu); 0.04 (*s*, MeSi). ^{13}C-NMR: 173.7 (*s*, CO); 138.8 (*s*, arom. C); 134.7 (*d*, CH=); 128.1, 127.3 (2*d*, each 2 arom. C); 127.2 (*d*, arom. C); 120.6 (*d*, CH=); 79.6 (*s*, *C*(OR)Me); 77.1 (*t*, PhCH_2O); 59.8 (*t*, SiCH_2O); 28.6 (*t*, MeCH_2); 28.1 (*q*, Me_3C); 21.1 (*q*, *Me*C=); 18.4 (*s*, Me_3C); 18.0 (*q*, C(OR)*Me*); 9.1 (*q*, *Me*CH_2); −9.9 (*q*, MeSi). CI-MS: 380 ($[M + NH_4]^+$).

2.6. *(*R**,R*,E)-1-{[(Benzyloxy)methyl](*tert*-butyl)methylsilyl}-1-methylbut-2-enyl Propanoate* (**16**). Analogously to **11**, 65 mg (0.21 mmol) of **8** gave, after deprotonation with 0.30 mmol of MeMgBr and reaction with 0.61 mmol of propanoic anhydride (slowly warmed up to −5° and immediately quenched), 48 mg (63%) of **16** as a colorless oil and 19 mg (29%) of recovered **8**. IR: 3095*w*, 3060*w*, 3030*m*, 2965*s*, 2935*s*, 2860*s*, 2815*m*, 1740*s*, 1500*w*, 1465*s*, 1455*s*, 1380*s*, 1365*s*, 1270*m*, 1250*s*, 1210*s*, 1175*s*, 1105*m*, 1095*s*, 1075*s*, 1030*m*, 1010*w*, 990*w*, 970*w*, 935*w*, 905*m*, 830*s*, 805*s*, 785*s*, 770*m*, 735*s*, 700*s*. ^{1}H-NMR: 7.34–7.21 (*m*, 5 arom. H); 5.73 (*dq*, *J* = 15.6, 1.4, MeCH=C*H*); 5.25 (*dq*, *J* = 15.6, 6.4, MeC*H*=CH); 4.47, 4.44 (*AB*, *J* = 12.0, PhCH_2O); 3.30 (*s*, SiCH_2O); 2.25 (*q*, *J* = 7.5, MeCH_2); 1.70 (*s*, C(OR)Me); 1.69 (*dd*, *J* = 6.4, 1.4, *Me*CH=CH); 1.09 (*t*, *J* = 7.5, *Me*CH_2); 1.00 (*s*, *t*-Bu); 0.12 (*s*, MeSi). ^{13}C-NMR: 173.7 (*s*, CO); 138.8 (*s*, arom. C); 134.7 (*d*, CH=); 128.1, 127.4 (2*d*, each 2 arom. C); 127.2 (*d*, arom. C); 120.5 (*d*, CH=); 79.5 (*s*, *C*(OR)Me); 77.1 (*t*, PhCH_2O); 59.8 (*t*, SiCH_2O); 28.6 (*t*, MeCH_2); 28.1 (*q*, Me_3C); 21.3 (*q*, *Me*C=); 18.4 (*s*, Me_3C); 18.0 (*q*, C(OR)*Me*); 9.1 (*q*, *Me*CH_2); −9.9 (*q*, MeSi). CI-MS: 380 ($[M + NH_4]^+$).

2.7. *(*R**,R*,Z)-1-{[(Benzyloxy)methyl](*tert*-butyl)methylsilyl}-1-methylbut-2-enyl 3-Oxobutanoate* (**17a**) *and (*R**,R*,Z)-1-{[(Benzyloxy)methyl](*tert*-butyl)methylsilyl}-1-methylbut-2-enyl 2-Acetyl-3-oxobutanoate* (**17b**). To a soln. of 110 mg (0.36 mmol) of **7** and 5 mg (0.04 mmol) of 4-(dimethylamino)pyridine in 0.3 ml of Et_3N, 120 mg (1.2 mmol) of Ac_2O were added at 0°. The mixture was warmed to 23°, stirred for 5 h, quenched with sat. $NaHCO_3$ soln., and acidified with dil. HCl soln. Extraction with Et_2O and chromatography (hexane/AcOEt 90:10) gave 56 mg (36%) of **17a** and 25 mg (18%) of **17b** as colorless oils.

Data of **17a**: IR: 3095*w*, 3060*w*, 3030*m*, 2965*s*, 2930*s*, 2860*s*, 2815*m*, 1740*s*, 1720*s*, 1500*w*, 1465*m*, 1405*w*, 1380*m*, 1365*s*, 1250*s*, 1205*s*, 1175*s*, 1150*m*, 1095*s*, 1075*s*, 1030*m*, 1010*w*, 990*w*, 935*w*, 905*m*, 825*s*, 805*m*, 785*m*, 770*m*, 735*s*, 695*s*. ^{1}H-NMR (enol form): 14.12 (*s*, OH); 7.36–7.15 (*m*, 5 arom. H); 5.46 (*dq*, *J* = 12.3, 1.5, MeCH=C*H*); 5.33 (*dq*, *J* = 12.3, 7.2, MeC*H*=CH); 5.12 (*s*, COCH=); 4.45 (*s*, PhCH_2O); 3.40, 3.34 (*AB*, *J* = 12.9, SiCH_2O); 2.17 (*s*, *Me*C(OH)=); 1.80 (*s*, C(OR)Me); 1.68 (*dd*, *J* = 7.2, 1.5, *Me*CH=CH); 1.01 (*s*, *t*-Bu); 0.05 (*s*, MeSi). ^{13}C-NMR: 187.3 (*s*, Me*C*(OH)=); 168.4 (COO); 138.8 (*s*, arom. C); 133.7 (*d*, CH=); 128.1, 127.3 (2*d*, each 2 arom. C); 127.2 (*d*, arom. C); 120.7 (*d*, CH=); 102.3 (*d*, CO*C*H=); 80.4 (*s*, *C*(OR)Me); 77.2 (*t*, PhCH_2O); 60.0 (*t*, SiCH_2O); 28.2 (*q*, Me_3C); 24.9 (*q*, *Me*C(OH)=); 23.3 (*q*, *Me*C=); 18.7 (*s*, Me_3C); 14.0 (*q*, C(OR)*Me*); −9.6 (*q*, MeSi). CI-MS: 408 ($[M + NH_4]^+$).

Data of **17b**: IR: 3095*w*, 3060*w*, 3030*m*, 2965*s*, 2930*s*, 2860*s*, 2815*m*, 1740*s*, 1720*s*, 1500*w*, 1465*m*, 1405*w*, 1380*m*, 1365*s*, 1250*s*, 1205*s*, 1175*s*, 1150*m*, 1095*s*, 1075*s*, 1030*m*, 1010*w*, 990*w*, 935*w*, 905*m*, 825*s*, 805*m*, 785*m*, 770*m*, 735*s*, 695*s*. ^{1}H-NMR (enol form): 14.23 (*s*, OH); 7.36–7.15 (*m*, 5 arom. H); 5.44 (*dq*, *J* = 12.3, 1.5, MeCH=C*H*); 5.33 (*dq*, *J* = 12.3, 7.2, MeC*H*=CH); 4.45 (*s*, PhCH_2O); 3.42, 3.36 (*AB*, *J* = 12.9, SiCH_2O); 2.19 (*s*, *Me*C(OH)=, MeCO); 1.81 (*s*, C(OR)Me); 1.70 (*dd*, *J* = 7.2, 1.5, *Me*CH=CH); 0.98 (*s*, *t*-Bu); 0.07 (*s*, MeSi).

^{13}C-NMR: 194.2 (*s*, Me*C*(OH)=, Me*C*O); 166.9 (*s*, COO); 138.7 (*s*, arom. C); 132.7 (*d*, CH=); 128.4, 127.4 (2*d*, each 2 arom. C); 127.2 (*d*, arom. C); 120.6 (*d*, CH=); 109.6 (*s*, *C*OC=); 81.8 (*s*, *C*(OR)Me); 77.1 (*t*, PhCH_2O); 60.2 (*t*, SiCH_2O); 28.7 (*q*, *Me*$_3$C); 25.1 (*q*, *Me*C(OH)=, *Me*CO); 23.2 (*q*, *Me*C=); 21.6 (*q*, *Me*CO); 19.0 (*s*, Me$_3$*C*); −9.5 (*q*, MeSi). CI-MS: 450 ([*M* + NH_4]$^+$).

3. Ireland *Ester-Enolate Rearrangement*. 3.1. *(*SiS*,2R*,3R,E*)-5-{[(Benzyloxy)methyl](*tert*-butyl)methylsilyl}-3-methyl-2-(trimethylsilyl)hex-4-enoic Acid* (**18**). To a soln. of 0.19 ml (1.5 mmol) of cyclohexyl(isopropyl)amine in 2 ml of THF, 0.6 ml (1.2 mmol) of 2M BuLi in pentane were added at 0° (→1.2 mmol of LICA). After 5 min, it was cooled to −80°, 101 mg (0.29 mmol) of **11** were added, and after 15 min, 0.13 ml (1.0 mmol) of Me_3SiCl followed. The mixture was warmed to −10°, quenched with sat. NH_4Cl soln., and acidified with dil. HCl soln. Extraction with Et_2O and chromatography (CH_2Cl_2/MeOH 150:1) gave 91 mg (75%) of **18** as a colorless oil. The same product was obtained in 61% yield when the reaction was performed in 45% DMPU/THF. IR ($CHCl_3$): 3600–2400*s* (br.), 3095*w*, 3060*w*, 3030*w*, 3000*m*, 2960*s*, 2930*s*, 2900*s*, 2860*s*, 2815*m*, 1680*s*, 1610*w*, 1500*w*, 1470*m*, 1465*m*, 1455*m*, 1410*m*, 1390*m*, 1380*m*, 1365*m*, 1335*w*, 1280*s*, 1250*s*, 1195*m*, 1150*m*, 1100*s*, 1070*s*, 1030*w*, 1010*w*, 980*m*, 960*m*, 935*m*, 905*m*, 885*m*, 845*s*, 825*s*, 700*s*. ^{1}H-NMR: 7.38–7.25 (*m*, 5 arom. H); 5.67 (*dq*, *J* = 9.4, 1.7, CH=); 4.47 (*s*, PhCH_2O); 3.35, 3.29 (*AB*, *J* = 12.8, SiCH_2O); 3.19–3.07 (*m*, MeC*H*); 1.99 (*d*, *J* = 10.6, Me_3SiC*H*); 1.78 (*d*, *J* = 1.6, *Me*C=); 1.06 (*d*, *J* = 6.5, *Me*CH); 0.94 (*s*, *t*-Bu); 0.10 (*s*, MeSi); 0.09 (*s*, Me_3Si). ^{1}H-NOE: irrad. at 5.67→NOE at 3.35, 3.29 (2.3%), 3.19–3.07 (0.8%), 1.99 (4.2%), 1.06 (2.1%), 0.94 (1.6%), and 0.10/0.09 (4.5%), irrad. at 1.78→NOE at 3.35, 3.29 (0.9%), 3.19–3.07 (3.0%), 1.06 (0.9%), 0.94 (1.8%), and 0.10/0.09 (1.8%). ^{13}C-NMR: 181.8 (*s*, COOH); 146.5 (*d*, CH=); 138.9 (*s*, arom. C); 130.9 (*s*, Me*C*=); 128.1, 127.5 (2*d*, each 2 arom. C); 127.4 (*d*, arom. C); 77.0 (*t*, PhCH_2O); 60.9 (*t*, SiCH_2O); 44.7 (*d*, Me_3SiCH); 32.3 (*d*, MeCH); 27.4 (*Me*$_3$C); 21.5 (*q*, *Me*C=); 17.5 (*s*, Me$_3$*C*); 16.1 (*q*, *Me*CH); −1.8 (*q*, Me_3Si); −9.1 (*q*, MeSi). CI-MS: 438 ([*M* + NH_4]$^+$), 421 ([*M* + H]$^+$), 420 ([*M* + NH_4 − H_2O]$^+$), 403 ([*M* + H − H_2O]$^+$).

3.2. *(*SiS*,2S*,3R*,E*)-5-{[(Benzyloxy)methyl](*tert*-butyl)methylsilyl}-3-methyl-2-(trimethylsilyl)hex-4-enoic Acid* (**19**). Analogously to **18**, 84 mg (0.14 mmol) of **12**, reacted with 1.08 mmol of LICA and 0.87 mmol of Me_3SiCl and warmed to 10°, gave, after chromtography (hexane/Et_2O 80:20), 30 mg (30%) of **19** and 37 mg (37%) of **18** (for data of **18**, see *3.1*). **19**: M.p. 46.5–49.0° (from oil). IR ($CHCl_3$): 3600–2400*s* (br.), 3095*w*, 3060*w*, 3030*w*, 3005*m*, 2960*s*, 2930*s*, 2895*s*, 2855*s*, 2810*m*, 1685*s*, 1615*w*, 1495*w*, 1470*m*, 1455*m*, 1430*m*, 1410*m*, 1390*w*, 1375*m*, 1365*m*, 1330*w*, 1280*s*, 1250*s*, 1195*w*, 1160*w*, 1100*s*, 1070*s*, 1030*w*, 1010*w*, 980*m*, 950*w*, 935*m*, 905*m*, 845*s*, 825*s*, 700*s*. ^{1}H-NMR: 7.37–7.24 (*m*, 5 arom. H); 5.76 (*dq*, *J* = 9.3, 1.6, CH=); 4.48 (*s*, PhCH_2O); 3.36, 3.30 (*AB*, *J* = 12.0, SiCH_2O); 3.20–3.07 (*m*, MeC*H*); 1.97 (*d*, *J* = 9.1, Me_3SiC*H*); 1.75 (*d*, *J* = 1.6, *Me*C); 1.05 (*d*, *J* = 6.8, *Me*CH); 0.91 (*s*, *t*-Bu); 0.16 (*s*, Me_3Si); 0.14 (*s*, MeSi). ^{1}H-NOE: irrad. at 5.76→NOE at 3.36, 3.30 (2.2%), 3.20–3.07 (1.1%), 1.97 (3.4%), 1.05 (2.1%), 0.97 (1.8%), and 0.16/0.14 (4.7%); irrad. at 1.75→NOE at 3.36, 3.30 (1.4%), 3.20–3.07 (3.2%), 1.05 (0.7%), 0.91 (1.6%), and 0.14/0.12 (1.8%). ^{13}C-NMR: 180.9 (*s*, COOH); 147.1 (*d*, CH=); 139.1 (*s*, arom. C); 130.2 (*s*, Me*C*=); 128.1, 127.4 (2*s*, each 2 arom. C), 127.1 (*d*, arom. C); 77.0 (*t*, PhCH_2O); 61.0 (*t*, SiCH_2O); 44.4 (*d*, Me_3SiCH); 32.9 (*d*, MeCH); 27.3 (*Me*$_3$C); 20.3 (*q*, *Me*C=); 17.3 (*s*, Me$_3$*C*); 15.9 (*q*, *Me*CH); −1.4 (*q*, Me_3Si); −8.9 (*q*, MeSi). CI-MS: 438 ([*M* + NH_4]$^+$), 421 ([*M* + H]$^+$), 420 ([*M* + NH_4 − H_2O]$^+$), 403 ([*M* + H − H_2O]$^+$).

3.3. *(*SiS*,2S*,3S*,E*)-5-{[(Benzyloxy)methyl](*tert*-butyl)methylsilyl}-3-methyl-2-(trimethylsilyl)hex-4-enoic Acid* (**20**) *and (*SiS*,2S*,3S*,E*)-5-{[(Benzyloxy)methyl](*tert*-butyl)methylsilyl}-3-methyl-2-(trimethylsilyl)hex-4-enoic Acid* (**21**). Analogously to **18**, 49 mg (0.14 mmol) of **13**, reacted with 0.56 mmol of LICA and 0.47 mmol of Me_3SiCl and warmed to 0°, gave, after chromatography (CH_2Cl_2/MeOH 150:1), 32 mg (55%) of **20** and 4 mg (7%) of **21**.

Data of **20**: M.p 111.0–113.0° (hexane). IR ($CHCl_3$): 3600–2400*s* (br.), 3095*w*, 3060*w*, 3030*w*, 3000*m*, 2960*s*, 2930*s*, 2900*s*, 2855*s*, 2810*m*, 1685*s*, 1615*w*, 1495*w*, 1470*m*, 1460*m*, 1455*m*, 1410*m*, 1390*w*, 1375*m*, 1365*m*, 1330*w*, 1280*s*, 1250*s*, 1195*w*, 1160*w*, 1100*s*, 1070*s*, 1030*w*, 1010*w*, 980*m*, 955*w*, 935*m*, 905*m*, 845*s*, 825*s*, 700*s*. ^{1}H-NMR: 7.35–7.25 (*m*, 5 arom. H); 5.83 (*dq*, *J* = 9.3, 1.6, CH=); 4.48, 4.46 (*AB*, *J* = 12.5, PhCH_2O); 3.34, 3.31 (*AB*, *J* = 13.0, SiCH_2O); 3.18–3.05 (*m*, MeC*H*); 1.98 (*d*, *J* = 8.6, Me_3SiC*H*); 1.74 (*d*, *J* = 1.6, *Me*C=); 1.05 (*d*, *J* = 6.8, *Me*CH); 0.90 (*s*, *t*-Bu); 0.15 (*s*, Me_3Si); 0.10 (*s*, MeSi). ^{1}H-NOE: irrad. at 5.83→NOE at 3.34, 3.31 (2.5%), 3.18–3.05 (0.9%), 1.98 (3.1%), 1.05 (2.2%), 0.90 (1.6%), and 0.10 (2.1%); irrad. at 1.74→NOE at 3.34, 3.31 (0.9%), 3.18–3.05 (30%), 1.05 (0.5%), 0.90 (1.6%), 0.15 (0.7%), and 0.10 (0.8%). ^{13}C-NMR: 180.9 (*s*, COOH); 148.0 (*d*, CH=); 139.1 (*s*, arom. C); 130.0 (*s*, Me*C*=); 128.1, 127.4 (2*d*, each 2 arom. C); 127.2 (*d*, arom. C); 77.1 (*t*, PhCH_2O); 60.9 (*t*, SiCH_2O); 44.3 (*d*, Me_3SiCH); 32.9 (*d*, MeCH); 27.2 (*q*, *Me*$_3$C); 20.4 (*q*, *Me*C=); 17.3 (*s*, Me$_3$*C*); 16.9 (*q*, *Me*CH); −1.4 (*q*, Me_3Si); −8.9 (*q*, MeSi). CI-MS: 438 ([*M* + NH_4]$^+$), 421 ([*M* + H]$^+$), 420 ([*M* + NH_4 − H_2O]$^+$), 403 ([*M* + H − H_2O]$^+$).

Data of **21**: M.p. 61.5–63.8° (oil). IR ($CHCl_3$): 3600–2400*s* (br.), 3095*w*, 3060*w*, 3030*w*, 3000*m*, 2960*s*, 2930*s*, 2900*s*, 2855*s*, 2810*m*, 1685*s*, 1615*w*, 1495*w*, 1470*m*, 1460*m*, 1455*m*, 1410*m*, 1390*w*, 1375*m*, 1365*m*, 1330*w*, 1280*s*, 1250*s*, 1195*w*, 1160*w*, 1100*s*, 1070*s*, 1030*w*, 1010*w*, 980*m*, 955*w*, 935*m*, 905*m*, 845*s*, 825*s*, 700*s*. ^{1}H-NMR: 7.35–7.24 (*m*, 5 arom. H); 5.58 (*dq*, J = 9.5, 1.7, CH=); 4.49, 4.44 (*AB*, J = 12.0, PhCH_2O); 3.36, 3.31 (*AB*, J = 12.8, SiCH_2O); 3.18–3.09 (*m*, MeCH); 1.99 (*d*, J = 10.8, Me_3SiCH); 1.78 (*d*, J = 1.6, *Me*C=); 1.03 (*d*, J = 6.5, *Me*CH); 0.89 (*s*, *t*-Bu); 0.09 (*s*, Me_3Si); 0.07 (*s*, MeSi). ^{1}H-NOE: irrad. at 5.58 → NOE at 3.36, 3.31 (1.7%), 1.99 (4.8%), 1.03 (3.8%), 0.89 (3.3%), and 0.09/0.07 (15.4%); irrad. at 1.78 → NOE at 3.36, 3.31 (0.9%), 3.18–3.09 (2.8%), 1.03 (0.8%), 0.89 (1.9%), and 0.09/0.07 (3.7%). ^{13}C-NMR: 181.0 (*s*, COOH); 146.7 (*d*, CH=); 139.0 (*s*, arom. C); 131.0 (*s*, MeC=); 128.1, 127.5 (2*d*, each 2 arom. C); 127.2 (*d*, arom. C); 77.2 (*t*, PhCH_2O); 60.5 (*t*, SiCH_2O); 44.9 (*d*, Me_3SiCH); 32.4 (*d*, MeCH); 27.4 (*q*, *Me*$_3$C); 21.7 (*q*, *Me*C=); 17.5 (*s*, Me_3C); 16.1 (*q*, *Me*CH); −1.7 (*q*, Me_3Si); −8.8 (*q*, MeSi). CI-MS (isobutane): 421 ([M + H]$^+$), 403 ([M + H − H_2O]$^+$).

3.4. *(*SiS*,2R*,3R*,E)-5-{[(Benzyloxy)methyl](*tert*-butyl)methylsilyl}-2,3-dimethyl-2-(trimethylsilyl)hex-4-enoic Acid* (**22**). Analogously to **18**, 86 mg (0.27 mmol) of **14**, reacted with 0.96 mmol of LICA and 0.79 mmol of Me_3SiCl and warmed to −30°, gave, after chromatography (hexane/Et_2O 80:20), 83 mg (80%) of **22** as colorless crystals. The same product was obtained in 52% yield when the reaction was performed in 45% DMPU/THF. M.p. 66.2–68.3° (MeCN). IR ($CHCl_3$): 3600–2200*s* (br.), 3095*w*, 3060*w*, 3030*w*, 3010*m*, 2960*s*, 2930*s*, 2895*s*, 2855*s*, 2810*m*, 1675*s*, 1610*w*, 1500*w*, 1470*m*, 1465*m*, 1455*m*, 1430*w*, 1410*w*, 1385*m*, 1365*m*, 1320*w*, 1290 (sh), 1265*s*, 1250*s*, 1195*w*, 1150*w*, 1115*m*, 1090*s*, 1075*s*, 1040*w*, 1030*w*, 1010*m*, 965*m*, 935*m*, 920*m*, 840*s*, 825*s*, 700*s*. ^{1}H-NMR: 7.37–7.24 (*m*, 5 arom. H); 5.92 (*dq*, J = 9.6, 1.5, CH=); 4.47 (*s*, PhCH_2O); 3.49–3.40 (*m*, MeCH); 3.34, 3.31 (*AB*, J = 12.8, SiCH_2O); 1.79 (*d*, J = 1.5, *Me*C=); 1.16 (*s*, Me_3SiC*Me*); 0.94 (*s*, *t*-Bu); 0.94 (*d*, J = 6.5, *Me*CH); 0.10 (*s*, MeSi); 0.05 (*s*, Me_3Si). ^{1}H-NOE: irrad. at 5.92 → NOE at 3.49–3.40 (2.0%), 3.34, 3.31 (2.9%), 1.16 (3.5%), 0.95 (4.0%), and 0.10/0.05 (8.5%); irrad. at 1.79 → NOE at 3.49–3.40 (2.8%), 3.34, 3.31 (1.2%), 0.94 (3.3%), and 0.10/0.05 (3.6%). ^{13}C-NMR: 184.2 (*s*, COOH); 143.9 (*d*, CH=); 139.0 (*s*, arom. C); 131.6 (*s*, MeC=); 128.2, 127.4 (2*d*, each 2 arom. C); 127.3 (*d*, arom. C); 77.1 (*t*, PhCH_2O); 61.2 (*t*, SiCH_2O); 41.2 (*s*, Me_3SiC); 35.6 (*d*, MeCH); 27.6 (*q*, *Me*$_3$C); 17.6 (*s*, Me_3C); 17.0 (*q*, *Me*C=); 16.2 (*q*, Me_3SiC*Me*); 11.4 (*q*, *Me*CH); −3.2 (*q*, Me_3Si); −9.0 (*q*, MeSi). CI-MS (isobutane): 425 ([M + H]$^+$), 417 ([M + H − H_2O]$^+$).

For the single-crystal X-ray analysis of **22**, see below.

3.5. *(*SiS*,2S*,3R*,E)-5-{[(Benzyloxy)methyl](*tert*-butyl)methylsilyl}-2,3-dimethyl-2-(trimethylsilyl)hex-4-enoic Acid* (**23**). Analogously to **18**, 89 mg (0.25 mmol) of **15**, reacted with 1.0 mmol of LICA and 0.80 mmol of Me_3SiCl and warmed to −40°, gave, after chromatography (hexane/Et_2O 80:20), 88 mg (81%) of **23**. M.p. 68.4–71.0° (from oil). IR ($CHCl_3$): 3600–2200*s* (br.), 3095*w*, 3060*w*, 3030*w*, 3010*m*, 2960*s*, 2930*s*, 2895*s*, 2855*s*, 2810*m*, 1675*s*, 1610*w*, 1495*w*, 1470*m*, 1465*m*, 1455*m*, 1430*w*, 1410*w*, 1385*m*, 1365*m*, 1310*w*, 1255*s*, 1115*w*, 1095*s*, 1070*s*, 1050*w*, 1030*w*, 1010*m*, 1000*w*, 970*m*, 945*m*, 905*m*, 845*s*, 825*s*, 700*s*. ^{1}H-NMR: 7.37–7.23 (*m*, 5 arom. H); 5.87 (*dq*, J = 9.8, 1.7, CH=); 4.48 (*s*, PhCH_2O); 3.44–3.34 (*m*, MeCH); 3.34, 3.29 (*AB*, J = 12.9, SiCH_2O); 1.75 (*d*, J = 1.7, *Me*C=); 1.15 (*s*, Me_3SiC*Me*); 1.00 (*d*, J = 7.0, *Me*CH); 0.90 (*s*, *t*-Bu); 0.12 (*s*, Me_3Si); 0.07 (*s*, MeSi). ^{1}H-NOE: irrad. at 5.87 → NOE at 3.44–3.34/3.34, 3.29 (3.2%), 1.15 (3.9%), 1.00 (2.1%), 0.90 (2.5%), and 0.12/0.07 (4.5%); irrad. at 1.75 → NOE at 3.44–3.34/3.34, 3.29 (3.9%), 1.15 (0.5%), 0.90 (1.5%), and 0.12/0.07 (1.6%). ^{13}C-NMR: 183.7 (*s*, COOH); 143.7 (*d*, CH=); 139.2 (*s*, arom. C); 131.0 (*s*, MeC=); 128.2, 127.4 (2*d*, each 2 arom. C); 127.2 (*d*, arom. C); 77.1 (*t*, PhCH_2O); 61.3 (*t*, SiCH_2O); 41.3 (*s*, Me_3SiC); 35.3 (*d*, MeCH); 27.3 (*q*, *Me*$_3$C); 17.3 (*s*, Me_3C); 17.1 (*q*, *Me*C=); 16.1 (*q*, Me_3SiC*Me*); 12.0 (*q*, *Me*CH); −2.4 (*q*, Me_3Si); −8.8 (*q*, MeSi). CI-MS (isobutane): 435 ([M + H]$^+$), 417 ([M + H − H_2O]$^+$).

3.6. *(*SiS*,2R*,3S*,E)-5-{[(Benzyloxy)methyl](*tert*-butyl)methylsilyl}-2,3-dimethyl-2-(trimethylsilyl)hex-4-enoic Acid* (**24**). Analogously to **18**, 72 mg (0.20 mmol) of **16**, reacted with 0.80 mmol of LICA and 0.63 mmol of Me_3SiCl and warmed to −10°, gave, after chromatography (CH_2Cl_2/MeOH 150:1), 67 mg (77%) of **24**. Colorless crystals. M.p. 53.2–55.0° (oil). IR ($CHCl_3$): 3600–2200*s* (br.), 3095*w*, 3060*w*, 3030*w*, 3010*m*, 2960*s*, 2930*s*, 2895*s*, 2855*s*, 2810*m*, 1675*s*, 1610*w*, 1495*w*, 1470*m*, 1465*m*, 1455*m*, 1430*w*, 1410*w*, 1385*m*, 1365*m*, 1320*w*, 1255*s*, 1115*w*, 1095*s*, 1070*s*, 1050*w*, 1030*w*, 1010*m*, 1000*w*, 970*m*, 930*m*, 905*m*, 845*s*, 825*s*, 700*s*. ^{1}H-NMR: 7.37–7.24 (*m*, 5 arom. H); 5.90 (*dq*, J = 9.7, 1.5, CH=); 4.50, 4.45 (*AB*, J = 12.0, PhCH_2O); 3.42–3.31 (*m*, MeCH); 3.35, 3.29 (*AB*, J = 12.8, SiCH_2O); 1.74 (*d*, J = 1.5, *Me*C=); 1.16 (*s*, Me_3SiC*Me*); 1.00 (*d*, J = 7.0, *Me*CH); 0.91 (*s*, *t*-Bu); 0.12 (*s*, Me_3Si); 0.10 (*s*, MeSi). ^{1}H-NOE: irrad. at 5.90 → NOE at 3.42–3.31/3.35, 2.29 (3.6%), 1.16 (4.0%), 1.00 (2.3%), 0.91 (1.7%), and 0.12/0.10 (3.7%); irrad. at 1.74 → NOE at 3.42–3.31/3.35, 3.29 (3.8%), 1.00 (0.5%), 0.91 (2.4%), and 0.12/0.10 (1.9%). ^{13}C-NMR: 183.6 (*s*, COOH); 143.9 (*d*, CH=); 139.2 (*s*, arom. C); 130.7 (*s*, MeC=); 128.2, 127.5 (2*d*, each 2 arom. C); 127.2 (*d*, arom. C); 77.1 (*t*, PhCH_2O); 61.2 (*t*, SiCH_2O); 41.3 (*s*, Me_3SiC); 35.5 (*d*, MeCH); 27.3 (*q*, *Me*$_3$C); 17.3 (*s*, Me_3C); 17.1 (*q*, *Me*C=); 16.1 (*q*, Me_3SiC*Me*); 12.5 (*q*, *Me*CH); −2.0 (*q*, Me_3Si); −8.8 (*q*, MeSi). CI-MS (isobutane): 435 ([M + H]$^+$), 417 ([M + H − H_2O]$^+$).

3.7. *(*R**,R*,Z)-1-{[(Benzyloxy)methyl](*tert*-butyl)methylsilyl}-1-methylbut-2-enyl 2-(Trimethylsilyl)acetate* (**25**). To a soln. of 0.07 ml (0.56 mmol) of cyclohexyl(isopropyl)amine in 2 ml of THF, 0.11 ml (0.22 mmol) of 2M BuLi in pentane were added at 0° (→ 0.22 mmol of LICA). After 5 min, the mixture was cooled to −80°, 70 mg (0.22 mmol) of **11** were added, and after 15 min, 0.05 ml (0.40 mmol) of Me_3SiCl followed. The mixture was warmed to 0° and quenched with sat. NH_4Cl soln. Extraction with Et_2O and chromatography (hexane/Et_2O 98:2) gave 30 mg (36%) of **25** and 33 mg (47%) of recovered **11**. IR: 3090*w*, 3060*w*, 3025*m*, 2960*s*, 2935*s*, 2890*s*, 2855*s*, 2815*m*, 1720*s*, 1500*w*, 1465*m*, 1455*m*, 1405*w*, 1375*m*, 1360*m*, 1250*s*, 1230*s*, 1140*w*, 1095*m*, 1075*s*, 1030*m*, 1010*m*, 980*w*, 940*m*, 905*w*, 855*s*, 825*m*, 780*m*, 765*m*, 735*s*, 700*s*. ^{1}H-NMR: 7.36–7.25 (*m*, 5 arom. H); 5.52 (*dq*, J = 12.4, 1.6, MeCH=C*H*); 5.31 (*dq*, J = 12.4, 7.3, MeC*H*=CH); 4.46 (*s*, PhCH_2O); 3.37, 3.33 (*AB*, J = 12.9, SiCH_2O); 1.87, 1.81 (*AB*, J = 11.7, SiCH_2COO); 1.84 (*s*, C(OR)Me); 1.70 (*dd*, J = 7.3, 1.6, *Me*CH=CH); 1.04 (*s*, *t*-Bu); 0.18 (*s*, MeSi); 0.13 (*s*, Me_3Si). ^{13}C-NMR: 172.0 (*s*, CO); 138.8 (*s*, arom. C); 133.6 (*d*, CH=); 128.1, 127.4 (2*d*, each 2 arom. C); 127.2 (*d*, arom. C); 120.0 (*d*, CH=); 80.1 (*s*, C(OR)Me); 77.2 (*t*, PhCH_2O); 60.0 (*t*, SiCH_2O); 28.4 (*q*, Me_3C); 28.6 (*t*, SiCH_2COO); 23.5 (*q*, *Me*C=); 18.5 (*s*, Me_3C); 14.2 (*q*, C(OR)*Me*); −1.2 (*q*, Me_3Si); −9.6 (*q*, MeSi). CI-MS: 438 ($[M + NH_4]^+$).

3.8. *(*R**,R*,Z)-1-{[(Benzyloxy)methyl](*tert*-butyl)methylsilyl}-1-methylbut-2-enyl α-[(*tert*-Butyl)dimethylsilyl]acetate* (**26**). To a soln. of 0.10 ml (0.8 mmol) of cyclohexyl(isopropyl)amine in 2 ml of THF, 0.35 ml (0.7 mmol) of 2M BuLi in pentane were added at 0° (→ 0.7 mmol of LICA). After 5 min, the mixture was cooled to −80°, 100 mg (0.29 mmol) of **11** were added, and after 15 min, 100 mg (0.66 mmol) of (*t*-Bu)Me_2SiCl followed. The mixture was kept at −80°, and the formation of **26** was detected by TLC. On warming to −60°, the slow formation of **10** was evidenced by TLC; no rearrangement product was detected. Before **26** decomposed completely to **10**, the mixture was quenched with sat. NH_4Cl soln. Extraction with Et_2O and chromatography (hexane/AcOEt 90:10) gave 54 mg (40%) of **26** and 40 mg (45%) of **10**. **26**: ^{1}H-NMR: 7.37–7.23 (*m*, 5 arom. H); 5.53 (*dq*, J = 11.5, 1.6, MeCH=C*H*); 5.31 (*dq*, J = 11.5, 7.0, MeC*H*=CH); 4.47 (*s*, PhCH_2O); 3.38, 3.32 (*AB*, J = 13.0, SiCH_2O); 1.85 (*d*, J = 12.0, 1 H, SiCH_2COO); 1.83 (*s*, C(OR)Me); 1.69 (*dd*, J = 7.0, 1.6, *Me*CH=CH); 1.59 (*d*, J = 12.0, 1 H, SiCH_2COO); 1.03, 0.90 (2*s*, 2 *t*-Bu); 0.16 (*s*, MeSi); 0.12 (*s*, Me_2Si).

4. *Removal of the Trimethylsilyl Group.* 4.1. *(SiS*,3R*,E)-5-{[(Benzyloxy)methyl](*tert*-butyl)methylsilyl}-3-methylhex-4-enoic Acid* (**27**). A soln. of 38 mg (0.09 mmol) of **18** and 70 mg (0.22 mmol) of $Bu_4NF \cdot 3\ H_2O$ in 1 ml of MeCN was stirred for 3 h at 23°. The mixture was acidified with dil. HCl soln., extracted with Et_2O, and chromatographed (hexane/Et_2O 60:40): 29 mg (93%) of **27** as a colorless oil. The same product was obtained in 90% yield by similar treatment of **19**. IR ($CHCl_3$): 3600–2200*s* (br.), 3095*w*, 3060*w*, 3030*w*, 3005*m*, 2960*s*, 2930*s*, 2895*s*, 2855*s*, 2810*m*, 1710*s*, 1615*w*, 1495*w*, 1470*m*, 1465*m*, 1455*m*, 1430*w*, 1410*w*, 1380*m*, 1365*m*, 1310*w*, 1290*m*, 1250*s*, 1200*m*, 1110*w*, 1090*m*, 1070*s*, 1025*w*, 1010*m*, 980*m*, 930*m*, 905*m*, 820*s*, 700*s*. ^{1}H-NMR: 7.38–7.25 (*m*, 5 arom. H); 5.56 (*dq*, J = 9.1, 1.7, CH=); 4.51, 4.46 (*AB*, J = 12.4, PhCH_2O); 3.33 (*s*, SiCH_2O); 3.21–3.06 (*m*, MeC*H*); 2.30 (*d*, J = 7.2, CH_2COOH); 1.76 (*d*, J = 1.7, *Me*C=); 1.03 (*d*, J = 6.7, *Me*CH); 0.89 (*s*, *t*-Bu); 0.10 (*s*, MeSi). ^{13}C-NMR: 178.3 (*s*, COOH); 145.9 (*d*, CH=); 139.0 (*s*, arom. C); 131.9 (*s*, MeC=); 128.2, 127.5 (2*d*, each 2 arom. C); 127.3 (*d*, arom. C); 77.1 (*t*, PhCH_2O); 60.7 (*t*, SiCH_2O); 41.4 (*t*, CH_2COOH); 29.6 (*d*, MeCH); 27.2 (*q*, Me_3C); 20.2 (*q*, *Me*C=); 17.3 (*s*, Me_3C); 16.1 (*q*, *Me*CH); −8.9 (*q*, MeSi). CI-MS: 366 ($[M + NH_4]^+$), 349 ($[M + H]^+$).

4.2. *(SiS*,3S*,E)-5-{[(Benzyloxy)methyl](*tert*-butyl)methylsilyl}-3-methylhex-4-enoic Acid* (**28**). Analogously to **27**, 26 mg (0.06 mmol) of **20**, reacted with 0.16 mmol of $Bu_4NF \cdot 3\ H_2O$, gave, after chromatography (hexane/Et_2O 60:40), 19 mg (91%) of **28**. Colorless oil. IR ($CHCl_3$): 3600–2200*s* (br.), 3095*w*, 3060*w*, 3030*w*, 3005*m*, 2960*s*, 2930*s*, 2895*s*, 2855*s*, 2810*m*, 1710*s*, 1615*w*, 1495*w*, 1470*m*, 1465*m*, 1455*m*, 1435*m*, 1410*m*, 1380*m*, 1365*m*, 1310*w*, 1290*m*, 1250*m*, 1200*m*, 1155*w*, 1110*m*, 1090*m*, 1070*s*, 1030*w*, 1010*w*, 980*m*, 935*m*, 905*m*, 820*s*, 700*s*. ^{1}H-NMR: 7.37–7.25 (*m*, 5 arom. H); 5.57 (*dq*, J = 9.1, 1.6, CH=); 4.51, 4.46 (*AB*, J = 12.3, PhCH_2O); 3.32 (*s*, SiCH_2O); 3.21–3.06 (*m*, MeC*H*); 2.31 (*d*, J = 7.2, CH_2COOH); 1.76 (*d*, J = 1.7, *Me*C=); 1.04 (*d*, J = 6.7, *Me*CH); 0.90 (*s*, *t*-Bu); 0.11 (*s*, MeSi). ^{13}C-NMR: 178.4 (*s*, COOH); 145.8 (*d*, CH=); 139.0 (*s*, arom. C); 131.7 (*s*, MeC=); 128.2, 127.5 (2*d*, each 2 arom. C); 127.3 (*d*, arom. C); 77.1 (*t*, PhCH_2O); 60.6 (*t*, SiCH_2O); 41.3 (*t*, CH_2COOH); 29.6 (*d*, MeCH); 27.2 (*q*, Me_3C); 20.2 (*q*, *Me*C=); 17.3 (*s*, Me_3C); 16.1 (*q*, *Me*CH); −9.0 (*q*, MeSi). CI-MS: 366 ($[M + NH_4]^+$), 349 ($[M + H]^+$).

4.3. *(SiS*,2R*/S*,3R*,E)-5-{[(Benzyloxy)methyl](*tert*-butyl)methylsilyl}-2,3-dimethylhex-4-enoic Acid* (**29**/**30**). Analogously to **27**, 50 mg (0.11 mmol) of **22**, reacted with 1.5 ml $Et_3N \cdot 3$ HF for 3 d, gave, after chromatography (hexane/Et_2O 60:40), 9 mg (23%) of **29** (first eluting) and 22 mg (55%) of **30** as colorless oils. The same products were obtained from **23** by similar treatment. The assignment of the relative configurations was not possible.

Data of **29**: IR ($CHCl_3$): 3600–2200*s* (br.), 3095*w*, 3060*w*, 3030*w*, 3005*m*, 2960*s*, 2930*s*, 2855*s*, 2810*m*, 1705*s*, 1610*w*, 1495*w*, 1470*m*, 1465*m*, 1455*m*, 1430*m*, 1415*m*, 1380*m*, 1365*m*, 1310*w*, 1285*m*, 1250*m*, 1215*m*, 1160*w*, 1110*m*, 1090*m*, 1070*s*, 1030*w*, 1010*w*, 980*m*, 960*w*, 930*m*, 910*m*, 825*s*, 700*s*. ^{1}H-NMR: 7.37–7.24 (*m*, 5 arom. H); 5.64 (*dq*, J = 9.4, 1.7, CH=); 4.48 (*s*, PhCH_2O); 3.32 (*s*, SiCH_2O); 3.00–2.89 (*m*, CH=MeC*H*); 2.37 (*quint.*, J = 7.0, MeC*H*COOH); 1.74 (*d*, J = 1.7, *Me*C=); 1.13 (*d*, J = 7.0, CH=*Me*CH); 0.98 (*d*, J = 6.8, *Me*CHCOOH); 0.89 (*s*, *t*-Bu); 0.09 (*s*, MeSi). ^{13}C-NMR: 181.2 (*s*, COOH); 145.1 (*d*, CH=); 139.0 (*s*, arom. C); 132.4 (*s*, MeC=); 128.2, 127.5 (2*d*, each 2 arom C); 127.2 (*d*, arom. C); 77.1 (*t*, PhCH_2O); 60.8 (*t*, SiCH_2O); 44.7 (*t*, *C*HCOOH); 35.0 (*d*, CH=MeCH); 27.2 (*q*, Me_3C); 17.3 (*s*, Me_3C); 17.0 (*q*, *Me*C=); 16.2 (*q*, *Me*CH); 13.7 (*q*, *Me*CH); –8.9 (*q*, MeSi). CI-MS (isobutane): 363 ($[M + H]^+$).

Data of **30**: IR ($CHCl_3$): 3600–2200*s* (br.), 3095*w*, 3060*w*, 3030*w*, 3005*m*, 2960*s*, 2930*s*, 2855*s*, 2810*m*, 1705*s*, 1615*w*, 1495*w*, 1470*m*, 1465*m*, 1455*m*, 1430*m*, 1415*m*, 1380*m*, 1365*m*, 1290*m*, 1250*m*, 1210*m*, 1155*w*, 1110*m*, 1090*m*, 1070*s*, 1030*w*, 1010*w*, 985*m*, 955*w*, 935*m*, 905*m*, 820*s*, 700*s*. ^{1}H-NMR: 7.37–7.24 (*m*, 5 arom. H); 5.52 (*dq*, J = 9.6, 1.6, CH=); 4.49 (*s*, PhCH_2O); 3.34 (*s*, SiCH_2O); 2.96–2.83 (*m*, CH=MeC*H*); 2.31–2.25 (*m*, MeC*H*COOH); 1.75 (*d*, J = 1.6, *Me*C=); 1.11 (*d*, J = 6.9, CH=*Me*CH); 1.01 (*d*, J = 6.6, *Me*CHCOOH); 0.92 (*s*, *t*-Bu); 0.11 (*s*, MeSi). ^{13}C-NMR: 182.4 (*s*, COOH); 144.6 (*d*, CH=); 139.0 (*s*, arom. C); 132.8 (*s*, MeC=); 128.2, 127.5 (2*d*, each 2 arom. C); 127.3 (*d*, arom. C); 77.1 (*t*, PhCH_2O); 60.8 (*t*, SiCH_2O); 45.5 (*t*, *C*HCOOH); 35.5 (*d*, CH=MeCH); 27.2 (*q*, Me_3C); 18.8 (*s*, Me_3C); 17.4 (*q*, *Me*C=); 16.4 (*q*, *Me*CH); 15.2 (*q*, *Me*CH); –8.9 (*q*, MeSi). CI-MS (isobutane): 363 ($[M + H]^+$).

4.4. *(*SiS*,2*R*/S*,3*S*,E)-5-{[(Benzyloxy)methyl](*tert*-butyl)methylsilyl}-2,3-dimethylhex-4-enoic Acid* (**31**/**32**). Analogously to **27**, 38 mg (0.09 mmol) of **24**, reacted with 1.5 ml $Et_3N \cdot 3$ HF for 3 d, gave, after chromatography (hexane/Et_2O 60:40), 13 mg (41%) of **31** (first eluting) and 17 mg (53%) of **32** as colorless oils. The assignment of the relative configurations was not possible.

Data of **31**: IR ($CHCl_3$): 3600–2200*s* (br.), 3095*w*, 3060*w*, 3030*w*, 3005*m*, 2960*s*, 2930*s*, 2855*s*, 2810*m*, 1705*s*, 1610*w*, 1495*w*, 1470*m*, 1465*m*, 1455*m*, 1430*m*, 1415*m*, 1380*m*, 1365*m*, 1310*w*, 1285*m*, 1250*m*, 1215*m*, 1160*w*, 1110*m*, 1090*m*, 1070*s*, 1030*w*, 1010*w*, 980*m*, 960*w*, 930*m*, 910*m*, 825*s*, 700*s*. ^{1}H-NMR: 7.36–7.24 (*m*, 5 arom. H); 5.65 (*dq*, J = 9.3, 1.6, CH=); 4.50, 4.45 (*AB*, J = 12.2, PhCH_2O); 3.32 (*s*, SiCH_2O); 3.00–2.88 (*m*, CH=MeC*H*); 2.38 (*quint.*, J = 7.0, MeC*H*COOH); 1.73 (*d*, J = 1.6, *Me*C=); 1.14 (*d*, J = 7.0, CH=*Me*CH); 0.98 (*d*, J = 6.8, *Me*CHCOOH); 0.89 (*s*, *t*-Bu); 0.10 (*s*, MeSi). ^{13}C-NMR: 181.3 (*s*, COOH); 145.0 (*d*, CH=); 139.0 (*s*, arom. C); 132.1 (*s*, MeC=); 128.2, 127.5 (2*d*, each 2 arom. C); 127.2 (*d*, arom. C); 77.1 (*t*, PhCH_2O); 60.8 (*t*, SiCH_2O); 44.7 (*t*, *C*HCOOH); 35.0 (*d*, CH=MeCH); 27.2 (*q*, Me_3C); 17.3 (*s*, Me_3C); 16.9 (*q*, *Me*C=); 16.1 (*q*, *Me*CH); 13.5 (*q*, *Me*CH); –8.9 (*q*, MeSi). CI-MS (isobutane): 363 ($[M + H]^+$).

Data of **32**: IR ($CHCl_3$): 3600–2200*s* (br.), 3095*w*, 3060*w*, 3030*w*, 3005*m*, 2960*s*, 2930*s*, 2855*s*, 2810*m*, 1705*s*, 1615*w*, 1495*w*, 1470*m*, 1465*m*, 1455*m*, 1430*m*, 1415*m*, 1380*m*, 1365*m*, 1290*m*, 1250*m*, 1210*m*, 1155*w*, 1110*m*, 1090*m*, 1070*s*, 1030*w*, 1010*w*, 985*m*, 955*w*, 935*m*, 905*m*, 820*s*, 700*s*. ^{1}H-NMR: 7.37–7.24 (*m*, 5 arom. H); 5.52 (*dq*, J = 9.6, 1.7, CH=); 4.51, 4.46 (*AB*, J = 12.3, PhCH_2O); 3.33 (*s*, SiCH_2O); 2.95–2.82 (*m*, CH=MeC*H*); 2.33–2.23 (*m*, MeC*H*COOH); 1.75 (*d*, J = 1.6, *Me*C=); 1.12 (*d*, J = 7.0, CH=*Me*CH); 1.00 (*d*, J = 6.6, *Me*CHCOOH); 0.92 (*s*, *t*-Bu); 0.11 (*s*, MeSi). ^{13}C-NMR: 182.2 (*s*, COOH); 144.7 (*d*, CH=); 139.0 (*s*, arom. C); 132.7 (*s*, MeC=); 128.2, 127.5 (2*d*, each 2 arom. C); 127.3 (*d*, arom. C); 77.1 (*t*, PhCH_2O); 60.7 (*t*, SiCH_2O); 45.5 (*t*, *C*HCOOH); 35.5 (*d*, CH=MeCH); 27.2 (*q*, Me_3C); 18.8 (*s*, Me_3C); 17.4 (*q*, *Me*C=); 16.4 (*q*, *Me*CH); 15.3 (*q*, *Me*CH); –8.9 (*q*, MeSi). CI-MS (isobutane): 363 ($[M + H]^+$).

5. *Crystal-Structure Determination of* **22**[7]). All measurements were conducted at low-temperature on a *Rigaku-AFC5R* diffractometer using graphite-monochromated MoK_α radiation (λ = 0.71069 Å) and a 12 kW rotating anode generator. The intensities were collected using $\omega/2\theta$ scans. Three standard reflections measured every 150 reflections showed negligible variation in intensity. The intensities were corrected for *Lorentz* and polarization effects, but not for absorption. The structure was solved by direct methods using SHELXS86 [14] which revealed the positions of all non-H-atoms. The non-H-atoms were refined anisotropically. The H-atoms were located in a difference electron density map, and their positions were refined together with isotropic thermal parameters. All refinements were carried out on F using full-matrix least-squares procedures which minimized the function $\Sigma w(|F_o| - |F_c|)^2$. The data collection and refinement parameters are listed in *Table 2*. Neutral-atom scattering factors for non-H-atoms were taken from [15] and the scattering factors for H-atoms from [16]. Anomalous dispersion effects were included in F_{calc} [17]; the values for $\Delta f'$ and $\Delta f''$ were taken from [18]. All calculations were performed using the TEXSAN [19] crystallographic software package.

---

[7]) The atomic coordinates and bond lengths and angles were deposited with the *Cambridge Crystallographic Data Centre*, 12 Union Road, Cambridge CB2 1EZ, England.

Table 2. *Crystallographic Data for Compound* **22**

Crystallized from	acetonitrile	Z	2
Empirical formula	$C_{24}H_{42}O_3Si_2$	D_x [g cm^{-3}]	1.060
Formula weight	434.76	$\mu(MoK_\alpha)$ [mm^{-1}]	0.150
Crystal color, habit	colorless, prism	$2\theta_{(max)}$ [°]	55
Crystal dimensions [mm]	0.15 × 0.32 × 0.48	Total reflections	
Temperature [K]	173 (1)	measured	6526
Crystal system	triclinic	Symmetry-independent	
Space group	$P\bar{1}$	reflections	6252
Unit cell parameters		Reflections used [$I > 2\sigma(I)$]	3994
Number of centred		Parameters refined	430
reflections	25	R	0.0516
2θ range [°]	30–36	wR	0.0417
a [Å]	13.183 (3)	Weights	$[\sigma^2(F_o) + (0.005F_o)^2]^{-1}$
b [Å]	14.259 (3)	Goodness of fit	1.826
c [Å]	7.814 (3)	Final Δ_{max}/σ	0.004
α [°]	103.92 (2)	$\Delta\rho$ (max; min) [e Å^{-3}]	0.58; −0.37
β [°]	90.26 (3)		
γ [°]	73.27 (1)		
V [Å^3]	1362.0 (7)		

REFERENCES

[1] A. Chapeaurouge, S. Bienz, *Helv. Chim. Acta* **1993,** *76,* 1876.
[2] S. Bienz, A. Chapeaurouge, *Helv. Chim. Acta* **1991,** *74,* 1477.
[3] S. Bienz, S. Bratovanov, A. Chapeaurouge, P. Huber, M. Pietzsch, C. Syldatk, Proceedings of the 3rd Symposium on Biochemical Engineering, Stuttgart, 1995, in press.
[4] P. Huber, S. Bratovanov, S. Bienz, M. Pietzsch, C. Syldatk, *Tetrahedron: Assym.*, in press.
[5] R. E. Ireland, R. H. Mueller, *J. Am. Chem. Soc.* **1972,** *94,* 5897.
[6] R. E. Ireland, R. H. Mueller, A. K. Willard, *J. Am. Chem. Soc.* **1976,** *98,* 2868.
[7] S. Pereira, M. Srebnik, *Aldrichim. Acta* **1993,** *26,* 17.
[8] P. Wipf, in 'Comprehensive Organic Synthesis', Ed. B. M. Trost, Pergamon Press, Oxford, 1991, Vol. 5, p. 827.
[9] S. Bratovanov, A. Linden, S. Bienz, *Acta Crystallogr., Sect. C,* in press.
[10] C. K. Johnson,'ORTEPII. Report ORNL-5138', Oak Ridge National Laboratory, Oak Ridge, Tenn., 1976.
[11] M. W. Rathke, D. F. Sullivan, *Synth. Commun.* **1973,** *3,* 67.
[12] R. E. Ireland, P. Wipf, J. D. Armstrong, *J. Org. Chem.* **1991,** *56,* 650.
[13] D. A. Evans, in 'Asymmetric Synthesis', Ed. J. E. Morrison, Academic Press, Orlando, FL, 1984, Vol. 3, p. 9.
[14] G. M. Sheldrick, 'SHELXS86', *Acta Crystallogr., Sect. A* **1990,** *46,* 467.
[15] E. N. Maslen, A. G. Fox, M. A. O'Keefe, in 'International Tables for Crystallography', Ed. A. J. C. Wilson, Kluwer Academic Publishers, Dordrecht, 1992, Vol. C, Table 6.1.1.1, p. 477.
[16] R. F. Stewart, E. R. Davidson, W. T. Simpson, *J. Chem. Phys.* **1965,** *42,* 3175.
[17] J. A. Ibers, W. C. Hamilton, *Acta Crystallogr.* **1964,** *17,* 781.
[18] D. C. Creagh, W. J. McAuley, in 'International Tables for Crystallography', Ed. A. J. C. Wilson, Kluwer Academic Publishers, Dordrecht, 1992, Vol. C, Table 4.2.6.8, p. 219.
[19] 'Texsan, Single Crystal Structure Analysis Software, Version 5.0', Molecular Structure Corporation, The Woodlands, Texas, 1989.