Synthesis and Characterization of 1,2-Disubstituted Vinylsilanes and Their Geometric Differentiation with $^3J(^{29}Si,^1H)$-Coupling Constants. Application of a Novel Heteronuclear *J*-Resolved NMR Experiment

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The $^3J(^{29}Si,^1H)$-coupling constants of a number of vinylsilanes have been accurately determined with the ACT-*J*-NMR experiment. For all investigated samples the values of the $^3J_{trans}$-coupling constants were found to be significantly larger than the corresponding values of the $^3J_{cis}$-coupling constants (8.8−20.5 Hz *versus* 3.1−11.9 Hz). Since substituent effects were characterized over a wide range, a conclusive assignment of the double-bond geometry of a particular vinylsilane by means of a single $^3J(^{29}Si,^1H)$-coupling constant is now possible even though the ranges of the $^3J_{cis}$- and the $^3J_{trans}$-values overlap.

Introduction

Vinylsilanes are important reactive intermediates used in modern organic synthesis for a variety of chemical transformations.[4−8] Among those, the electrophilic substitution of the trialkylsilyl moiety at the olefin is the most thoroughly explored and synthetically most often applied reaction. The transformation generally proceeds not only with satisfying chemical yields but also with high degrees of stereoselectivity, usually with preservation of the double-bond geometry. To take advantage of this stereochemical feature it is necessary to have stereocontrolled access to substituted vinylsilanes, and, of course, it is equally important to have a tool at hand to unequivocally distinguish between *E*/*Z* double-bond isomers. The latter is usually not a problem for 2-monosubstituted vinylsilanes, where the differentiation of the geometric isomers is possible by means of $^3J(^1H,^1H)$-coupling constants. The geometries of more highly substituted vinylsilanes, however, are not that easily assigned. Though nuclear Overhauser effects should be helpful for the determination of the spatial arrangement of NMR-active groups attached to a double bond, we have often obtained inconclusive results due to low signal intensities and vague signal interpretation in spectral regions that were obscured by several resonances. Frequently, isomeric silanes had to be converted to the corresponding alkenes by protiodesilylation, where the geometry of the respective products, and thus the structure of the parent silanes, could often be determined by spectroscopic means.[8] This is certainly a laborious and inefficient way to solve the problem and is furthermore accompanied by a substantial loss of valuable material. In a study of (1,2-dialkylvinyl)silanes, Chan et al. have reported that the geometry of such compounds can be estimated with high confidence by a combination of NMR spectroscopy (relative chemical shifts) and GLC (relative retention times).[9] However, a prerequisite for this method is the investigation of, and therefore also access to, both isomers of the respective compounds.

Two groups have used $^3J(^{29}Si,^1H)$-coupling constants to assess the double-bond geometry of 1,2-disubstituted vinylsilanes.[10,11] It was found that, as in the case of $(^1H,^1H)$ couplings, the $^3J(^{29}Si,^1H)_{trans}$ values are significantly larger than the $^3J(^{29}Si,^1H)_{cis}$ values. However, the method has been limited so far to structurally rather simple compounds. With more complex molecules, the determination of the heteronuclear *J*-coupling constants was found to be fairly difficult due to complex multiplet structures. Additionally, from our point of view, the assignment of the double-bond geometry of a particular 1,2-disubstituted vinylsilane on the basis of the value of a single heteronuclear ^3J-coupling constant, without spectroscopic data of its double-bond isomer, can be problematic since a basic set of experimental data for differently substituted vinylsilanes is missing in the literature. In this paper we present the results of a broader investigation of $^3J(^{29}Si,^1H)$-coupling constants, applying a novel and easily performed heteronuclear *J*-resolved NMR experiment (the ACT-*J*-NMR experiment[12]). The results provide a basis for the future use

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(4) Armitage, D. A. In *Comprehensive Organometallic Chemistry*; Abel, E. W., Ed.; Pergamon Press: Oxford, 1982; Vol. 2, p 1.

(5) Magnus, P. D.; Sarkar, T.; Djuric, S. In *Comprehensive Organometallic Chemistry*; Abel, E. W., Ed.; Pergamon Press: Oxford, 1982; Vol. 7, p 515.

(6) Fleming, I. In *Comprehensive Organic Chemistry*; Jones, D. N., Ed.; Pergamon Press: Oxford, 1979; Vol. 3, p 539.

(7) Colvin, E. W. *Silicon Reagents in Organic Synthesis*; Academic Press: London, 1988.

(8) Colvin, E. W. *Silicon in Organic Synthesis*; R. E. Krieger Publishing Company: Malabar, FL, 1985.

(9) Chan, T. H.; Mychajlowskij, W.; Amoroux, R. *Tetrahedron Lett.* **1977**, 1605.

(10) Behrens, U.; Wolff, C.; Hoppe, D. *Synthesis* **1991**, *47*, 644.

(11) Rossi, R.; Carpita, A.; Bellina, F.; De Santis, M. *Gazz. Chim. Ital.* **1991**, *121*, 261.

(12) Koźmiński, W.; Bienz, S.; Bratovanov, S.; Nanz, D. *J. Magn. Reson.* **1997**, *125*, 193.

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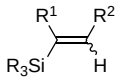
Table 1. Compilation of $^3J(^{29}Si,^1H)$-Coupling Constant Values of Substituted Vinylsilanes



samples				$^3J(^{29}Si,^1H)$-coupling constants (Hz)	
no.	R^1	R^2 [a]	R_3Si[a]	*cis*	*trans*
1a	$(i\text{-Pr})_2Al$	Ph	TBDMS	11.5, 11.9[b]	20.5[b]
2a	H	Ph	TBDMS	7.0	13.0
2b	H	Ph	A	7.0	14.0
2d	H	$HO_2CC_2H_4$	TBDMS	6.9	13.7
3a	Cl	Ph	TBDMS	4.4	8.8
4a	Br	Ph	TBDMS	4.4	9.4
5a	I	Ph	TBDMS	5.1	10.7
5b	I	Ph	A	*c*	10.6
5c	I	$THPOC_3H_6$	TBDMS	4.8	10.5
6a	PhCO	Ph	TBDMS	7.4	12.7
6b	PhCO	Ph	A	7.7	*c*
6e	PhCO	Ph	TMS	8.0[d]	15.4[d]
6f	PhCO	Bu	TMS	6.9[d]	12.8[d]
7c	Me	$THPOC_3H_6$	TBDMS	7.5	13.0
8	EtO_2C	MTH	TMS	7.6[d]	
9a	LiO	H	TBDMS	3.1[e]	12.1, 12.5[e]
9b	LiO	Ph	TBDMS	3.6	*f*
10a	TMSO	H	TBDMS	3.5	10.4
10b	TMSO	Ph	TBDMS	3.5	9.4
10c	TMSO	Me	TBDMS	3.4	9.6

[a] A = [(benzyloxy)methyl]-*tert*-butylmethylsilyl, TBDMS = *tert*-butyldimethylsilyl, TMS = trimethylsilyl, THP = tetrahydropyran-2-yl, MTH = 4-methylthiophene-2-yl. [b] Several alane species, giving a single hydrolysis product, have been detected, and the ^3J values of the major components have been determined. [c] Only one out of the two possible isomers was accessible. [d] Data from ref 11. [e] Several enolate species (probably aggregates with solvent molecules) have been detected, and the ^3J values of the major components have been determined. [f] The *Z*-configured enolate isomerized to the more stable *E* isomer.

of NMR for a simple and nondestructive geometric differentiation of vinylsilanes.

Results and Discussion

In Table 1 we summarize the values of a number of $^3J(^{29}Si,^1H)$-coupling constants of 2-mono- and 1,2-disubstituted vinylsilanes. Either the respective samples were prepared and measured by ourselves (preparation and ACT-*J*-NMR experiments, see below; ACT for active coupling-pattern tilting) or the NMR data was taken from the literature (for **6d**,**e** and **8**[11]). The substituents at C(1) were varied with care to induce and characterize effects on the $^3J(^{29}Si,^1H)$-coupling constant in as broad a range as possible.

For all compounds listed in Table 1, the $^3J(^{29}Si,^1H)_{trans}$-coupling constants are, as expected (and presupposed by others), significantly larger than the $^3J(^{29}Si,^1H)_{cis}$-coupling constants. The absolute *J* values, however, vary over a range of several hertz for the different compounds. The $^3J_{cis}$-couplings vary between 3.1 and 11.9 Hz, the $^3J_{trans}$-couplings between 8.8 and 20.5 Hz. In analogy to $(^1H,^1H)$-couplings, they roughly decrease with increasing electronegativity of the substituents at the double-bond; conjugative effects of substituents are negligible. Among the investigated samples, vinyl halides, vinyl ethers, and enolates showed the smallest coupling constants ($J_{trans} = 8.8-10.7$, $J_{cis} = 3.4-3.5$ Hz), vinylalanes the largest ($J_{trans} = 20.5$ Hz, $J_{cis} = 11.5, 11.9$ Hz). Vinylsilanes that are substituted with only carbon residues displayed $^3J(^{29}Si,^1H)$-coupling constants of 6.9−8.0 Hz (J_{cis}) and 12.7−15.2 Hz (J_{trans}).

On the basis of these results, the double-bond configurations of 1,2-disubstituted vinylsilanes can now be assigned with high confidence using single $^3J(^{29}Si,^1H)$-coupling constant values that can be obtained readily by ACT-*J*-NMR spectroscopy. The only prerequisite for the method is that the nature of the substituents attached to the double bond be known. Even though the ranges of the ^3J constants for $(^{29}Si,^1H)_{cis}$- and $(^{29}Si,^1H)_{trans}$-couplings overlap, the substituent effects are characteristic enough to avoid misinterpretation of the spectral data in most cases. With the ACT-*J*-NMR experiment and the data in Table 1, the double-bond geometries of the compounds **11a**,**b** and **12**,[13] which could not be determined before, were unambiguously assigned as *E* on the basis of the respective $^3J(^{29}Si,^1H)$ values (Figure 1).

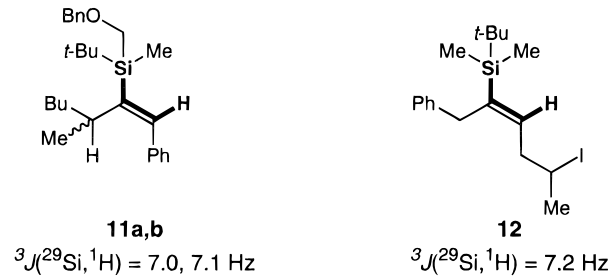


Figure 1. Samples, where the double-bond geometries were determined on the basis of the respective $^3J(^{29}Si,^1H)$-coupling constants.

NMR Experiment. The $^3J(^{29}Si,^1H)$-coupling constants were determined from heteronuclear *J* spectra with pure phase, tilted cross-peak patterns, and homonuclear *I*-spin decoupled signals in F_1, which allows the accurate determination of *I*-spin couplings, irrespective of further homonuclear couplings. The basic pulse sequence of the active coupling-pattern tilting (ACT)-*J*-NMR spectroscopy used in this study is displayed in Figure 2. It is discussed in detail elsewhere.[12] As a representative example for the result of the experiment, the spectrum of a mixture of *E*- and *Z*-configured **7c** is

(13) Bratovanov, S.; Fässler, J.; Bienz, S. Unpublished results.

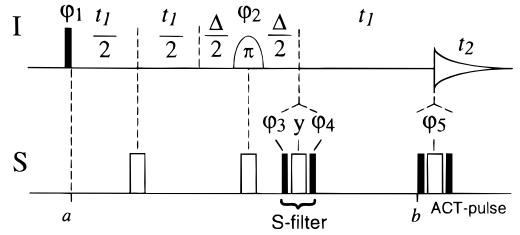


Figure 2. Pulse sequence used for the heteronuclear ACT-*J*-NMR experiments. Narrow dark and wide unfilled bars represent $\pi/2$ and π pulses, respectively. Multiplet or spectral-region selective π pulses are represented by bell-shaped patterns. $\Delta/2$ in the isotopomer-selection part of the sequence is set to $(4J_{SI})^{-1}$. Compensation is made for *I*-spin chemical-shift and homonuclear coupling evolution during all of the *S*-spin pulses by allowing short delays between the two *I*-spin pulses.

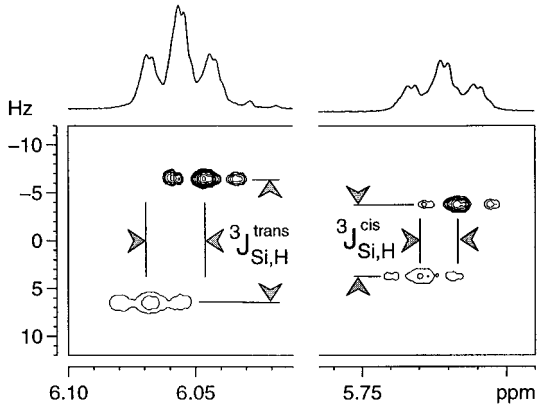


Figure 3. Representative heteronuclear (^{29}Si,^{1}H) ACT-*J*-NMR spectrum of an *E*/*Z* mixture of **7c**. Proton chemical shifts along F_2 are correlated with heteronuclear couplings along F_1. For negative peaks, only two levels are plotted. The spectrum was obtained in 1 h from an approximately 0.12 M $CDCl_3$ solution (*E* isomer, the *E*/*Z* ratio was approximately 3:2) on a Bruker AMX-600 MHz spectrometer at 300 K.

displayed in Figure 3. Although the signals of each of the two vinylic protons of (*E*)-**7c** and (*Z*)-**7c** represent at least a quartet × triplet, the only splitting observed in the F_1 dimension in the ACT-*J*-NMR spectrum is caused by the additional heteronuclear coupling of the ^{29}Si isotopomers. Since half of the cross-peak components are suppressed, accurate values for the heteronuclear coupling can be read from slices that are extracted along either the F_1 or the F_2 dimension. Hence the experiment allows the exact determination of the heteronuclear vicinal (^{29}Si,^{1}H)-coupling constant also in more complex molecules. It is more sensitive and yields more accurate *J*-constant values than silicon-detected spectra. It allows furthermore the unambiguous assignment of the *I*-spin coupling partners of a given Si nucleus. We consider the ACT-*J*-NMR experiment to be the method of choice not only for the measurement of (^{29}Si,^{1}H)-coupling constants of vinylsilanes but generally for the determination of a particular heteronuclear coupling constant as long as the assignment of the X-nucleus is unambiguous.

Preparation of the Sample Molecules. Our sample compounds were prepared according to Schemes 1 and 2. Reaction of the alkynylsilanes **13a**−**c**, obtained from *tert*-butyldimethylsilyl chloride (TBDMSCl) or [(benzyloxy)methyl](*tert*-butyl)methylsilyl chloride (ACl)[14] and the appropriate acetylides, with diisopropylaluminum hydride (DIBAH) gave rise to the alanes **1a**−**c** (Scheme 1). The double-bond geometry of these α-metalated vinylsilanes can be controlled by the proper choice of conditions in the alanation reaction:[15,16] the treatment of **13a**,**c** with DIBAH in the presence of Et_2O produced (*Z*)-**1a**,**c**; the corresponding (*E*)-**1a**,**c** arose when the alanations were performed in hexane. In the case of alane **1b**, only the (*Z*)-configured isomer could be obtained, irrespective of the reaction conditions. The (benzyloxy)methyl portion of the silicon moiety probably takes over the function of a donating additive, inhibiting the isomerization of *syn*-addition product to the (*E*)-configured α-metalated species. The alanes **1a**−**c**, when treated with an aqueous NH_4Cl solution or with I_2, gave the 2-monosubstituted vinylsilanes **2a**−**c** and the 1,2-disubstituted iodovinylsilanes **5a**−**c**, respectively, with preservation of the double-bond geometry. Compounds **2c** were converted to the derivatives **2d** by hydrolytic removal of the tetrahydropyran-2-yl (THP) protective group and oxidation of the respective alcohols to the carboxylic acids. Quenching of the stereoisomeric alanes **1a** with Br_2, *N*-bromosuccinimide, or *N*-chlorosuccinimide afforded the respective vinyl halides **3a** and **4a**. The benzoyl-substituted vinylsilanes **6a**,**b** have been prepared from the corresponding vinyl iodides **5a**,**b** by a reaction sequence consisting of metal halogen exchange with BuLi, treatment of the intermediary vinyllithium species with benzaldehyde, and oxidation of the resultant alcohols with CrO_3 or MnO_2. With this method, silane **6b** could only be obtained in the *E*-configured form: the vinyllithium intermediate deriving from vinyl iodide (*E*)-**5b** isomerized immediately under the reaction conditions. Compounds **7c** have been obtained from compounds **5c** by their reaction with Me_2Cu and MeI. In the case of (*E*)-**5c**, partial double-bond isomerization occurred during the transformation to (*Z*)-**7c**. The enolates of the type **9** and enol ethers of the type **10**, finally, were obtained from the respective acylsilanes **14a**−**c** by their sequential treatment with LDA (formation of **9a**−**c**) and TMSCl (formation of **10a**−**c**, Scheme 2).

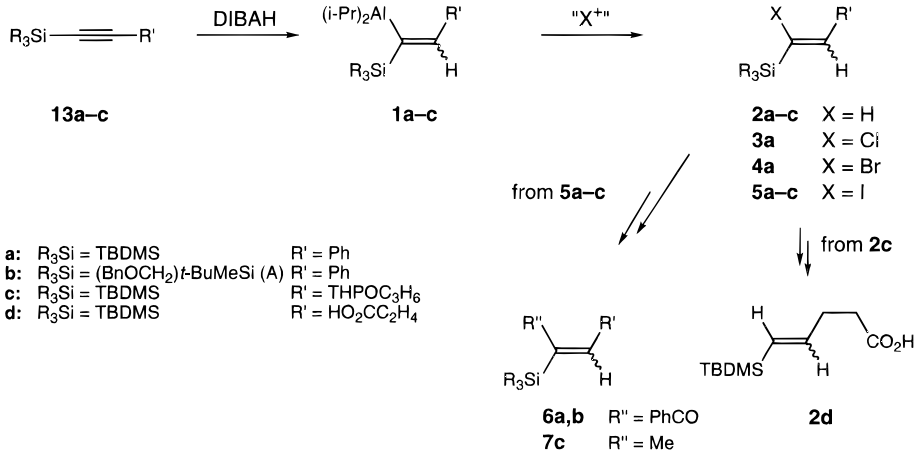
The double-bond geometries of the sample molecules of the type **1**−**7** were deduced from NMR information and chemical correlations. Since the double bond configurations of compounds **2a**−**d** are readily determined by means of $^3J(^1H,^1H)$-coupling constants, the assignments of the geometries of the precursor alanes **1a**−**c** and of the directly related derivatives of the type **3**−**7** could be based on the structures of the pertinent silanes **2a**−**c**. The double-bond geometry of (*E*)-**6b**, which is opposite to that of the precursor (*E*)-**5b** concerning the spatial arrangement of the Si and the H atoms, was determined by its correlation to (*E*)-**2b**. The latter compound was obtained by hydrolysis of the vinyllithium species that also led to (*E*)-**6b**. The double-bond geometries of the vinyl ethers and enolates followed from thermodynamic considerations and ^{1}H-increment calculations.

Experimental Section

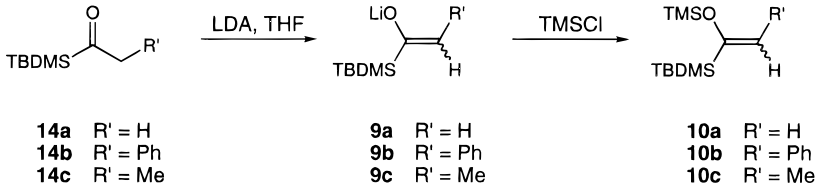
General Comments. Unless otherwise stated: all organic solvents were distilled prior to use. For the reactions, Et_2O

(14) Bienz, S.; Chapeaurouge, A. *Helv. Chim. Acta* **1991**, *74*, 1477.
(15) Wilson, S. R.; Jacob, L. A. *J. Org. Chem.* **1986**, *51*, 4833.
(16) Bratovanov, S.; Bienz, S. *Main Group Met. Chem.* **1996**, *19*, 769.

Scheme 1



Scheme 2



and THF were dried over Na in the presence of diphenylketyl; CH_2Cl_2 was dried over molecular sieves (3 Å). All reactions were carried out under an Ar atmosphere. Solutions of salts and acids for workup procedures were prepared in deionized H_2O. Extracts were dried ($MgSO_4$) and evaporated *in vacuo*. Column chromatography was performed on Merck 60 silica gel (40−63 μm). Melting points were taken on a Mettler FP-5/FP-52. ^{1}H NMR spectra were measured at 300 MHz in $CDCl_3$ on a Bruker AC-300 or a Bruker ARX-300; δ (ppm) values are relative to $CHCl_3$ (δ 7.26) with J in hertz, and multiplicities are denoted as s = singlet, d = doublet, t = triplet, and m = multiplet. ^{13}C NMR spectra were measured at 75.6 MHz in $CDCl_3$ on a Bruker ARX-300; δ (ppm) values are relative to $CDCl_3$ (δ 77.0). Multiplicities were obtained from DEPT experiments. ACT-*J*-NMR spectra were acquired according to ref 12 on a Bruker AMX-600, and J values are given in hertz. CI MS (chemical ionization mass spectrometry) was performed with NH_3 as the reactant gas on a Finnigan SSQ 700 or a Finnigan MAT 90. Only the base peak and quasi-molecular ion are given; data in *m*/*z* (relative abundance in percent, where appropriate).

1. (*E*)-1-(*tert*-Butyldimethylsilyl)-1-(diisopropylalanyl)-2-phenylethene ((*E*)-1a). To a solution of **13a** (100 mg, 0.46 mmol) in hexane (5 mL) was added diisobutylaluminum hydride (DIBAH, 0.83 mL, 1 M in CH_2Cl_2) and the mixture was refluxed for 2 h. The solution was cooled to 23 °C, and the solvent was evaporated. The NMR sample of the thus obtained (*E*)-**1a** was prepared by repeated evaporation of the solvent and redissolving of the residue in $CDCl_3$. ^{1}H NMR (several species; only the signals of the vinylic protons of the two major components are given): 8.02, 7.99 (br s, HC═). ACT-*J*-NMR: $^3J(^{29}Si,^1H)$ = 11.9 (δ ^{1}H = 8.02), 11.5 (δ ^{1}H = 7.99).

2. (*Z*)-1-(*tert*-Butyldimethylsilyl)-1-(diisopropylalanyl)-2-phenylethene ((*Z*)-1a). Analogously to the procedures described in 1, **13a** (100 mg, 0.46 mmol) was reacted in 1:1 octane/Et_2O (4 mL) with DIBAH (0.83 mL, 1 M in CH_2Cl_2) at reflux for 12 h to yield (*Z*)-**1a**. The NMR sample was prepared by evaporation of the Et_2O and mixing of 0.4 mL of the obtained solution with 0.2 mL of d_8-THF. ^{1}H NMR (several species, only the signal of the vinylic proton of the major component is given): 8.22 (br s, HC═). ACT-*J*-NMR: $^3J(^{29}Si,^1H)$ = 20.5.

3. (*E*)-1-(*tert*-Butyldimethylsilyl)-2-phenylethene ((*E*)-2a). To a solution of **13a** (60 mg, 0.28 mmol) in hexane (5 mL) was added DIBAH (0.28 mL, 1.5 M in toluene). It was refluxed for 2 h, then cooled to 23 °C, and quenched with saturated aqueous NH_4Cl solution (2 mL). Extraction with Et_2O and filtration through a plug of SiO_2 (hexane) gave (*E*)-**2a** (33 mg, 0.23 mmol, 81%) as a colorless oil. ^{1}H NMR: 7.39−7.17 (m, 5 aromatic H); 6.82 (d, J = 19.2, Ph*H*C═); 6.41 (d, J = 19.2, SiHC═); 0.85 (s, *t*-Bu); 0.05 (s, Me_2Si). ^{13}C NMR: 144.8 (d, PhH*C*═); 138.4 (s, aromatic C); 128.4 (d, 2 aromatic C); 127.8 (d, aromatic C); 126.7 (q, SiHC═); 126.2 (d, 2 aromatic C); 26.4 (q, Me_3C); 17.0 (s, Me_3C); −6.2 (s, Me_2Si). ACT-*J*-NMR: $^3J(^{29}Si,^1H)$ = 7.0. CI-MS: 147 [M + H]$^+$. Anal. Calcd for $C_{14}H_{22}Si$ (M_r = 218.417): C, 76.99; H, 10.15. Found: C, 77.12; H, 10.01.

4. (*Z*)-1-(*tert*-Butyldimethylsilyl)-2-phenylethene ((*Z*)-2a). Analogously to the procedure described in 3, **13a** (60 mg, 0.28 mmol) was reacted with DIBAH (0.28 mL, 1.5 M in toluene) in toluene/Et_2O (1:1, 4 mL) to yield (*Z*)-**2a** (30 mg, 0.21 mmol, 74%), a colorless oil. ^{1}H NMR: 7.48 (d, J = 15.4, Ph*H*C═); 7.31−7.23 (m, aromatic H); 5.89 (d, J = 15.4, SiHC═); 0.92 (s, *t*-Bu); −0.06 (s, Me_2Si). ^{13}C NMR: 147.6 (d, PhH*C*═); 141.0 (s, aromatic C); 129.8 (d, SiHC═); 128.0, 127.8 (2d, 2 × 2 aromatic C); 126.3 (d, aromatic C); 26.4 (q, Me_3C); 16.8 (s, Me_3C); −4.5 (q, Me_2Si). ACT-*J*-NMR: $^3J(^{29}Si,^1H)$ = 13.0. CI-MS: 147 [M + H]$^+$. Anal. Calcd for $C_{14}H_{22}Si$ (M_r = 218.417): C, 76.99; H, 10.15. Found: C, 77.23; H, 10.32.

5. (*E*)-1-{[(Benzyloxy)methyl]-*tert*-butylmethylsilyl}-2-phenylethene ((*E*)-2b). To a solution of (*E*)-**5b** (100 mg, 0.22 mmol) in THF (5 mL) was added BuLi (0.24 mL, 2 M in pentane) at −80 °C. The reaction mixture was stirred for 1 h at −10 °C and then quenched with H_2O (3 mL) to give, after extraction with Et_2O and filtration through SiO_2 (hexane), (*E*)-**2b** (60 mg, 0.19 mmol, 83%) as a colorless oil. ^{1}H NMR: 7.45−7.24 (m, 10 aromatic H); 6.98 (d, J = 19.3, Ph*H*C═); 6.58 (d, J = 19.3, SiHC═); 4.50 (s, PhCH_2O); 3.35 (s, SiCH_2O); 0.97 (s, *t*-Bu); 0.19 (s, MeSi). ^{13}C NMR: 146.1 (d, PhH*C*═); 139.0, 138.3 (2s, 2 aromatic C); 128.4, 128.2, 128.0, 127.5, 127.2, 126.3, 125.7 (7d, 10 aromatic C); 123.7 (d, SiHC═); 77.0 (t, PhCH_2O); 61.0 (t, SiCH_2O); 26.8 (q, Me_3C); 16.9 (s, Me_3C); −9.0 (q, MeSi). ACT-*J*-NMR: $^3J(^{29}Si,^1H)$ = 7.0. CI-MS: 342 [M + NH_4]$^+$. Anal. Calcd for $C_{21}H_{28}OSi$ (M_r = 324.543): C, 77.72; H, 8.70. Found: C, 77.51; H, 8.33.

6. (*Z*)-1-{[(Benzyloxy)methyl]-*tert*-butylmethylsilyl}-2-phenylethene ((*Z*)-2b). Analogously to the procedure described in 3, **13a** (100 mg, 0.31 mmol) was reacted with DIBAH (0.31 mL, 1.5 M in toluene) in toluene/Et_2O (1:1, 4 mL)

to yield (*Z*)-**2b** (80 mg, 0.24 mmol, 80%), a colorless oil. ^{1}H NMR: 7.54 (d, J = 15.4, Ph*H*C=); 7.32−7.22 (m, 10 aromatic H); 5.85 (d, J = 15.4, SiHC=); 4.38 (s, PhCH_2O); 3.17 (s, SiCH_2O); 0.95 (s, *t*-Bu); −0.08 (s, MeSi). ^{13}C NMR: 147.4 (d, PhH*C*=); 138.6, 137.3 (2s, 2 aromatic C); 126.6, 126.5, 126.2, 126.0, 125.7, 125.6 (6d, 10 aromatic C); 125.2 (d, SiHC=); 76.9 (t, Ph*C*H$_2$O); 61.5 (t, SiCH$_2$O); 26.9 (q, *Me*$_3$C); 15.5 (s, Me$_3$*C*); −9.0 (q, MeSi). ACT-*J*-NMR: $^3J(^{29}\mathrm{Si},^1\mathrm{H})$ = 14.0. CI-MS: 342 $[M + NH_4]^+$. Anal. Calcd for $C_{21}H_{28}OSi$ (M_r = 324.543): C, 77.72; H, 8.70. Found: C, 77.59; H, 8.62.

7. (*E*)-5-(*tert*-Butyldimethylsilyl)pent-4-enoic Acid ((*E*)-2d). Analogously to the procedure described in 3, **13c** (1.0 g, 3.6 mmol) was reacted with DIBAH (3 mL, 1.5 M in toluene) in hexane (50 mL) to yield (*E*)-**2c** (640 mg, 2.25 mmol, 64%), a colorless oil. A solution of (*E*)-**2c** (400 mg, 1.41 mmol) in AcOH/THF/H_2O (4:2:1, 20 mL) was then refluxed for 10 h, poured on aqueous $NaHCO_3$ solution, and extracted with hexane. Chromatography (hexane/EtOAc, 20:1) gave the corresponding deprotected alcohol (160 mg, 0.80 mmol, 57%) as a colorless oil. This alcohol (710 mg, 3.55 mmol) was dissolved in acetone (50 mL) and treated with Jones reagent[17] until the brown color persisted. To the mixture were added saturated aqueous $NaHCO_3$ and aqueous NaOH solutions, and the acetone was evaporated. The residue was washed with Et_2O, acidified with aqueous HCl solution (10%), and extracted with Et_2O to give (*E*)-**2d** (610 mg, 2.81 mmol, 80%) as a colorless solid material. ^{1}H NMR: 11.44 (s, CO_2H); 6.04 (dm, J = 18.6, (CH$_2$)*H*C=); 5.70 (d, J = 18.6, SiHC=); 2.50−2.42 (m, (CH$_2$)$_2$); 0.85 (s, *t*-Bu); 0.00 (s, Me$_2$Si). ^{13}C NMR: 178.4 (s, CO); 143.9 (d, (CH$_2$)H*C*=); 127.2 (d, SiHC=); 31.9 (t, HO$_2$C*C*H$_2$); 30.0 (t, (*C*H$_2$)HC=); 25.0 (q, *Me*$_3$C); 15.1 (s, Me$_3$*C*); −7.5 (q, Me$_2$Si). ACT-*J*-NMR: $^3J(^{29}\mathrm{Si},^1\mathrm{H})$ = 6.9. CI-MS: 232 $[M + NH_4]^+$. Anal. Calcd for $C_{11}H_{22}O_2Si$ (M_r = 214.383): C, 61.63; H, 10.34. Found: C, 61.31; H, 10.12.

8. (*Z*)-5-(*tert*-Butyldimethylsilyl)-pent-4-enoic Acid ((*Z*)-2d). Analogously to the procedure described in 7, **13c** (380 mg, 4.46 mmol) was reacted with DIBAH (3.6 mL, 1.5 M in toluene) in the presence of *N*-methylpyrrolidine (841 mg, 9.86 mmol) to yield (*E*)-**2c** (740 mg, 2.61 mmol, 58%), a colorless oil, which was further converted to (*Z*)-**2d** (390 mg, 1.81 mmol, 57%), a colorless oil. ^{1}H NMR: 11.10 (s, CO_2H); 6.33 (dm, J = 14.2, (CH$_2$)*H*C=); 5.57 (d, J = 14.2, SiHC=); 2.49−2.39 (m, (CH$_2$)$_2$); 0.88 (s, *t*-Bu); 0.10 (s, Me$_2$Si). ^{13}C NMR: 179.1 (s, CO); 146.6 (d, CH$_2$*C*H); 128.2 (d, SiCH); 34.0 (t, CO*C*H$_2$); 28.4, (t, CH*C*H$_2$); 26.2 (q, *Me*$_3$C); 16.7 (s, Me$_3$*C*); −4.3 (q, Me$_2$Si). ACT-*J*-NMR: $^3J(^{29}\mathrm{Si},^1\mathrm{H})$ = 13.7. CI-MS: 232 $[M + NH_4]^+$. Anal. Calcd for $C_{11}H_{22}O_2Si$ (M_r = 214.383): C, 61.63; H, 10.34. Found: C, 61.47; H, 10.31.

9. (*E*)-1-(*tert*-Butyldimethylsilyl)-1-chloro-2-phenylethene ((*E*)-3a). Analogously to the procedure described in 3, **13a** (100 mg, 0.46 mmol) was reacted with DIBAH (0.4 mL, 1.5 M in toluene) in hexane (4 mL). It was quenched with *N*-chlorosuccinimide (NCS, 104 mg, 0.78 mmol) prior to hydrolytic workup to give (*E*)-**3a** (88 mg, 0.35 mmol, 75%) as a colorless oil. ^{1}H NMR: 7.73−7.26 (m, 5 aromatic H); 6.87 (s, HC=); 1.01 (s, *t*-Bu); 0.27 (s, Me$_2$Si). ^{13}C NMR: 137.4 (d, HC=); 135.8 (s, aromatic C); 135.4 (s, SiC=); 129.4, 128.0 (2d, 2 × 2 aromatic C); 127.8 (d, aromatic C); 26.7 (q, *Me*$_3$C); 17.2 (s, Me$_3$*C*); −6.1 (s, Me$_2$Si). ACT-*J*-NMR: $^3J(^{29}\mathrm{Si},^1\mathrm{H})$ = 4.4. CI-MS: 253 $[M + H]^+$. Anal. Calcd for $C_{14}H_{21}ClSi$ (M_r = 252.862): C, 66.50; H, 8.37. Found: C, 66.19; H, 7.96.

10. (*Z*)-1-(*tert*-Butyldimethylsilyl)-1-chloro-2-phenylethene ((*Z*)-3a). Analogously to the procedure described in 3, **13a** (100 mg, 0.46 mmol) was reacted with DIBAH (0.4 mL, 1.5 M in toluene) in toluene/Et_2O (1:1, 4 mL). It was quenched with NCS (104 mg, 0.78 mmol) prior to hydrolytic workup to give (*Z*)-**3a** (80 mg, 0.32 mmol, 69%) as a colorless oil. ^{1}H NMR: 7.73 (s, HC=); 7.31−7.22 (m, 5 aromatic H); 1.00 (s, *t*-Bu); 0.11 (s, Me$_2$Si). ^{13}C NMR: 144.9 (d, HC=); 138.4 (s, aromatic C); 136.8 (s, SiC=); 128.5, 127.5 (2d, 2 × 2 aromatic C); 127.1 (d, aromatic C); 27.3 (q, *Me*$_3$C); 17.5 (s, Me$_3$*C*); −4.2 (s, Me$_2$Si). ACT-*J*-NMR: $^3J(^{29}\mathrm{Si},^1\mathrm{H})$ = 8.8. CI-MS: 253 $[M + H]^+$. Anal. Calcd for $C_{14}H_{21}ClSi$ (M_r = 252.862): C, 66.50; H, 8.37. Found: C, 66.23; H, 8.11.

11. (*E*)-1-Bromo-1-(*tert*-butyldimethylsilyl)-2-phenylethene ((*E*)-4a). Analogously to the procedure described in 3, **13a** (100 mg, 0.46 mmol) was reacted with DIBAH (1 mL, 1.5 M in toluene) in toluene/Et_2O (1:1, 4 mL). It was quenched with *N*-bromosuccinimide (140 mg, 0.79 mmol) prior to hydrolytic workup to give (*E*)-**4a** (98 mg, 0.33 mmol, 71%) as a colorless oil. ^{1}H NMR: 8.07 (s, HC=); 7.31−7.17 (m, 5 aromatic H); 0.99 (s, *t*-Bu); −0.12 (s, Me$_2$Si). ^{13}C NMR: 148.8 (d, HC=); 138.1 (s, aromatic C); 130.4 (s, SiC=); 128.1, 127.7 (2d, 2 × 2 aromatic C); 127.6 (d, aromatic C); 27.5 (q, *Me*$_3$C); 17.7 (s, Me$_3$*C*); −3.3 (s, *Me*$_2$Si). ACT-*J*-NMR: $^3J(^{29}\mathrm{Si},^1\mathrm{H})$ = 9.4. Anal. Calcd for $C_{14}H_{21}BrSi$ (M_r = 297.318): C, 56.56; H, 7.12. Found: C, 56.81; H, 7.36.

12. (*Z*)-1-Bromo-1-(*tert*-butyldimethylsilyl)-2-phenylethene ((*Z*)-4a). To a solution of (*Z*)-**5a** (100 mg, 0.29 mmol) in hexane (5 mL) was added at −80 °C BuLi (2.2 mL, 2 M in pentane). It was stirred for 1 h and quenched at −80 °C with Br_2 (123 mg, 0.77 mmol, dissolved in hexane (1 mL)). After additional stirring for 15 min, a saturated aqueous NH_4Cl solution (5 mL) was added. It was extracted with Et_2O and filtered through a plug of SiO_2 (hexane) to give (*Z*)-**4a** (72 mg, 0.24 mmol, 83%) as a colorless oil. ^{1}H NMR: 7.67−7.25 (m, 5 aromatic H); 7.23 (s, HC=); 1.00 (s, *t*-Bu); 0.27 (s, Me$_2$Si). ^{13}C NMR: 140.3 (d, HC=); 136.6 (s, aromatic C); 129.1 (d, aromatic C); 129.1(s, SiC=); 128.0, 127.9 (2d, 2 × 2 aromatic C); 26.9 (q, *Me*$_3$C); 17.4 (s, Me$_3$*C*); −5.5 (s, Me$_2$Si). ACT-*J*-NMR: $^3J(^{29}\mathrm{Si},^1\mathrm{H})$ = 4.4. Anal. Calcd for $C_{14}H_{21}BrSi$ (M_r = 297.318): C, 56.56; H, 7.12. Found: C, 56.62; H, 7.48.

13. (*E*)-1-(*tert*-Butyldimethylsilyl)-1-iodo-2-phenylethene ((*E*)-5a). Analogously to the procedure described in 3, **13a** (3.0 g, 14.0 mmol) was reacted with DIBAH (14.0 mL, 1.5 M in toluene) in toluene/Et_2O (1:1, 100 mL). It was quenched with I_2 (5.29 g, 20.83 mmol) prior to hydrolytic workup to give (*E*)-**5a** (3.61 g, 10.52 mmol, 75%) as a colorless oil. ^{1}H NMR: 8.54 (s, HC=); 7.29−7.15 (m, 5 aromatic H); 1.02 (s, *t*-Bu); −0.09 (s, Me$_2$Si). ^{13}C NMR: 158.9 (d, HC=); 142.4 (s, aromatic C); 129.6 (d, 3 aromatic C); 129.5 (d, 2 aromatic C); 111.0 (s, SiC=); 29.9 (q, *Me*$_3$C); 19.9 (s, Me$_3$*C*); 0.0 (s, Me$_2$Si). ACT-*J*-NMR: $^3J(^{29}\mathrm{Si},^1\mathrm{H})$ = 10.7. CI-MS: 345 $[M + H]^+$. Anal. Calcd for $C_{14}H_{21}ISi$ (M_r = 344.313): C, 48.84; H, 6.15. Found: C, 48.62; H, 6.04.

14. (*Z*)-1-(*tert*-Butyldimethylsilyl)-1-iodo-2-phenylethene ((*Z*)-5a). Analogously to the procedure described in 3, **13a** (198 mg, 0.92 mmol) was reacted with DIBAH (0.8 mL, 1.5 M in toluene) in hexane (8 mL). It was quenched with I_2 (323 mg, 1.31 mmol) prior to hydrolytic workup to give (*Z*)-**5a** (265 mg, 0.77 mmol, 84%) as a slightly yellow oil. ^{1}H NMR: 7.59−7.19 (m, 5 aromatic H, HC=); 0.96 (s, *t*-Bu); 0.23 (s, Me$_2$Si). ^{13}C NMR: 146.8 (d, HC=); 139.6 (s, aromatic C); 128.3 (d, 3 aromatic C); 128.0 (d, 2 aromatic C); 107.3 (s, SiC=); 27.2 (q, *Me*$_3$C); 17.7 (s, Me$_3$*C*); −4.5 (s, Me$_2$Si). ACT-*J*-NMR: $^3J(^{29}\mathrm{Si},^1\mathrm{H})$ = 3.4. CI-MS: 345 $[M + H]^+$. Anal. Calcd for $C_{14}H_{21}ISi$ (M_r = 344.313): C, 48.84; H, 6.15. Found: C, 49.59; H, 6.27.

15. (*E*)-1-{[(Benzyloxy)methyl]-*tert*-butylmethylsilyl}-1-iodo-2-phenylethene ((*E*)-5b). Analogously to the procedure described in 3, **13b** (2.28 g, 7.09 mmol) was reacted with DIBAH (7.1 mL, 1.5 M in toluene) in hexane (100 mL). It was quenched with I_2 (3.24 g, 12.77 mmol) prior to hydrolytic workup to give (*E*)-**5b** (2.65 g, 5.88 mmol, 83%) as a slightly yellow oil. ^{1}H NMR: 8.56 (s, HC=); 7.35−7.17 (m, 10 aromatic H); 4.33, 4.27 (*AB*, J = 12.1, PhCH_2O); 3.14, 3.01 (*AB*, J = 13.0, SiCH$_2$O); 1.08 (s, *t*-Bu); 0.03 (s, MeSi). ^{13}C NMR: 157.8 (d, HC=); 140.5, 138.8 (2s, 2 aromatic C); 128.1 (d, 2 aromatic C); 127.8 (d, 3 aromatic C); 127.7, 127.5 (2d, 2 × 2 aromatic C); 127.2 (d, aromatic C); 105.6 (s, SiC=); 76.8 (t, Ph*C*H$_2$O); 62.2 (t, SiCH$_2$O); 28.4 (q, *Me*$_3$C); 18.2 (s, Me$_3$*C*); −4.5 (q, MeSi). ACT-*J*-NMR: $^3J(^{29}\mathrm{Si},^1\mathrm{H})$ = 10.6. CI-MS: 468 (10, $[M + NH_4]^+$); 238 (100). Anal. Calcd for $C_{21}H_{27}IOSi$ (M_r =

(17) Bowder, K.; Heilbron, J. M.; Jones, E. R. H.; Weedon, B. C. L. *J. Chem. Soc.* **1946**, 39.

450.439): C, 56.00; H, 6.04. Found: C, 55.64; H, 6.13.

16. (*E*)-5-(*tert*-Butyldimethylsilyl)-5-iodopent-4-enyl Tetrahydropyran-2-yl Ether ((*E*)-5c). Analogously to the procedure described in 3, **13c** (2.0 g, 7.1 mmol) was reacted with DIBAH (9.5 mL, 1.5 M in toluene) in hexane (100 mL) and in the presence of *N*-methylpyrrolidine (1.2 g, 14.3 mmol). It was quenched with I_2 (4.0 g, 14.3 mmol) prior to hydrolytic workup to give (*E*)-**5c** (2.65 g, 5.88 mmol, 83%) as a slightly yellow oil. ^{1}H NMR: 7.36 (t, J = 7.9, HC=); 4.56 (br t, J = 2.8, OCHO); 3.87−3.67, 3.53−3.33 (2m, 2 OCH_2); 2.35−2.06 (m, (CH_2)HC=); 1.87−1.48 (m, 4 CH_2); 0.96 (s, *t*-Bu); 0.28 (s, Me_2Si). ^{13}C NMR: 159.1 (d, HC=); 103.9 (s, SiC=); 99.8 (d, OCHO); 67.6, 63.2 (2t, 2 OCH_2); 34.1, 31.8, 30.3 (3t, 3 CH_2); 28.3 (q, Me_3C); 26.6, 20.6 (2t, 2 CH_2); 19.6 (s, Me_3C); 0.0 (q, Me_2Si). ACT-*J*-NMR: $^3J(^{29}Si,^1H) = 10.5$. CI-MS (isobutane): 411 (6, $[M + H]^+$), 85 (100). Anal. Calcd for $C_{16}H_{31}IO_2Si$ (M_r = 410.414): C, 46.83; H, 7.61. Found: C, 46.98; H, 7.88.

17. (*Z*)-5-(*tert*-Butyldimethylsilyl)-5-iodopent-4-enyl Tetrahydropyran-2-yl Ether ((*Z*)-5c). Analogously to the procedure described in 3, **13c** (3.0 g, 10.7 mmol) was reacted with DIBAH (9.0 mL, 1.5 M in toluene) in hexane (100 mL). It was quenched with I_2 (6.8 g, 26.7 mmol) prior to hydrolytic workup to give (*Z*)-5-(*tert*-butyldimethylsilyl)-5-iodopent-4-en-1-ol (2.10 g, 6.40 mmol, 60%). This alcohol (550 mg, 1.70 mmol) was dissolved in CH_2Cl_2 (10 mL) and treated with dihydropyran (710 mg, 8.44 mmol) and catalytic amounts of *p*-toluenesulfonic acid at 0 °C for 90 min. It was quenched with a saturated aqueous NH_4Cl solution, extracted with Et_2O, and chromatographed (hexane/EtOAc, 20:1) to give (*Z*)-**5c** (600 mg, 1.46 mmol, 86%) as a colorless oil. ^{1}H NMR: 6.17 (t, J = 7.9, HC=); 4.58 (t, J = 2.8, OCHO); 3.88−3.70, 3.52−3.36 (2m, 2 OCH_2); 2.37−2.16 (m, (CH_2)HC=); 1.85−1.48 (m, 4 CH_2); 0.93 (s, *t*-Bu); 0.16 (s, Me_2Si). ^{13}C NMR: 150.7 (d, HC=); 110.2 (s, SiC=); 99.7 (d, OCHO); 67.8, 63.3, (2t, 2 OCH_2); 37.4, 31.8, 29.2 (3t, 3 CH_2); 28.3 (q, Me_3C); 26.6, 20.6, (2t, 2 CH_2); 18.5 (s, Me_3C); −3.5 (q, Me_2Si). ACT-*J*-NMR: $^3J(^{29}Si,^1H) = 4.8$. CI-MS: 428 (8, $[M + NH_4]^+$), 102 (100). Anal. Calcd for $C_{16}H_{31}IO_2Si$ (M_r = 410.414): C, 46.83; H, 7.61. Found: C, 47.07; H, 7.44.

18. (*E*)-1-(*tert*-Butyldimethylsilyl)-2-phenylethenyl Phenyl Ketone ((*E*)-6a). To a solution of (*Z*)-**5a** (162 mg, 0.47 mmol) in THF (10 mL) was added BuLi (0.52 mL, 2 M in pentane) at −10 °C. After 2 h at −20 °C, PhCHO (121 mg, 1.14 mmol) was added, and it was quenched immediately with a saturated aqueous NH_4Cl solution. It was extracted with Et_2O and chromatographed (hexane/EtOAc, 25:1) to give (*E*)-2-(*tert*-butyldimethylsilyl)-1,3-diphenylprop-2-en-1-ol (113 mg, 0.35 mmol, 75%), which was oxidized with Jones reagent[17] in acetone to give (*E*)-**6a** (98 mg, 0.30 mmol, 87%), arising as a colorless oil. ^{1}H NMR: 7.81−7.04 (m, 10 aromatic H); 6.98 (s, Ph*H*C=); 0.91 (s, *t*-Bu); 0.07 (s, Me_2Si). ^{13}C NMR: 202.1 (s, C=O); 145.2 (s, aromatic C); 141.3 (d, HC=); 138.6 (s, SiC=); 136.3 (s, 2 aromatic C); 132.8 (d, aromatic C); 129.1, 128.7, 128.3, 128.2 (4d, 4 × 2 aromatic C); 128.1 (d, aromatic C); 26.7 (q, Me_3C); 18.1 (s, Me_3C); −5.7 (q, Me_2Si). ACT-*J*-NMR: $^3J(^{29}Si,^1H) = 7.4$. CI-MS: 323 $[M + H]^+$. Anal. Calcd for $C_{21}H_{26}OSi$ (M_r = 322.527): C, 78.21; H, 8.13. Found: C, 77.84; H, 8.29.

19. (*Z*)-1-(*tert*-Butyldimethylsilyl)-2-phenylethenyl Phenyl Ketone ((*Z*)-6a). Analogously to the procedure described in 18, (*E*)-**5a** (325 mg, 0.94 mmol) was reacted with BuLi (2.08 mmol, 2 M in pentane) in hexane (−80 °C, 2 h) and with PhCHO (243 mg, 2.28 mmol) to yield (*Z*)-2-(*tert*-butyldimethylsilyl)-1,3-diphenylprop-2-en-1-ol (220 mg, 0.68 mmol, 72%). This alcohol was dissolved in CH_2Cl_2 (5 mL) and treated with MnO_2 (296 mg, 3.40 mmol) at reflux for 2 h. It was filtered, the solvent evaporated, and the residue chromatographed (hexane/EtOAc, 25:1) to give (*Z*)-**6a** (187 mg, 0.58 mmol, 86%) as a colorless oil. ^{1}H NMR: 7.78−7.11 (m, 10 aromatic H); 7.33 (s, Ph*H*C=); 0.69 (s, *t*-Bu); −0.27 (s, Me_2Si). ^{13}C NMR: 201.7 (s, C=O); 149.6 (d, HC=); 145.2 (s, aromatic C); 138.1 (s, SiC=); 137.7 (s, 2 aromatic C); 132.6 (d, aromatic C); 130.1, 128.3 (2d, 2 × 2 aromatic C); 128.2 (d, aromatic C); 127.9, 127.8 (2d, 2 × 2 aromatic C); 27.6 (q, Me_3C); 18.1 (s, Me_3C); −2.8 (q, Me_2Si). ACT-*J*-NMR: $^3J(^{29}Si,^1H) = 12.7$. CI-MS: 323 $[M + H]^+$. Anal. Calcd for $C_{21}H_{26}OSi$ (M_r = 322.527): C, 78.21; H, 8.13. Found: C, 77.96; H, 8.22.

20. (*E*)-1-{[(Benzyloxy)methyl]-*tert*-butylmethylsilyl}-2-phenylethenyl Phenyl Ketone ((*E*)-6b). Analogously to the procedure described in 18, (*E*)-**5b** (523 mg, 1.16 mmol) was reacted with BuLi (2.56 mmol, 2 M in pentane) in THF (−10 °C, 1h) and with PhCHO (300 mg, 2.81 mmol) to yield (*E*)-2-{[(benzyloxy)methyl]-*tert*-butylmethylsilyl}-1,3-diphenylprop-2-en-1-ol (400 mg, 0.93 mmol, 80%), which was oxidized with Jones reagent[17] in acetone to give (*E*)-**6b** (380 mg, 0.89 mmol, 95%) as a colorless oil. ^{1}H NMR: 7.86−7.05 (m, 15 aromatic H); 7.05 (s, Ph*H*C=); 4.32 (s, PhCH_2O); 3.38, 3.33 (AB, J_{AB} = 13.1, $SiCH_2O$); 0.99 (s, *t*-Bu); 0.13 (s, MeSi). ^{13}C NMR: 201.9 (s, C=O); 142.8 (s, aromatic C); 142.4 (d, HC=); 138.6 (s, SiC=); 136.6, 136.3 (2s, 2 aromatic C); 132.7, 129.2, 128.9, 128.2, 128.1, 127.4, 127.2 (7d, 15 aromatic C); 77.1 (t, PhCH_2O); 60.4 (t, $SiCH_2O$); 27.1 (q, Me_3C); 18.2 (s, Me_3C); −8.5 (q, MeSi). ACT-*J*-NMR: $^3J(^{29}Si,^1H) = 7.7$. CI-MS: 429 $[M + H]^+$. Anal. Calcd for $C_{28}H_{32}O_2Si$ (M_r = 428.652): C, 78.46; H, 7.52. Found: C, 78.60; H, 7.79.

21. (*E*/*Z*)-5-(*tert*-Butyldimethylsilyl)-5-methylpent-4-enyl Tetrahydropyran-2-yl Ether ((*E*/*Z*)-7c). To a solution of Me_2CuLi (1.40 mmol) in Et_2O (5 mL) was added (*E*)-**5c** (115 mg, 0.28 mmol) dissolved in Et_2O (1 mL) at −30 °C. It was stirred for 1 h, MeI (800 mg, 5.60 mmol) was added, and the mixture was allowed to warm to 0 °C. After 12 h, it was quenched with saturated aqueous NH_4Cl solution, extracted with Et_2O, and chromatographed (hexane/EtOAc, 40:1) to give an inseparable mixture of (*E*/*Z*)-**7c** (64 mg, 0.21 mmol, 76%) as a slightly yellow oil. Spectral data from the mixture (approximately 1:1) are as follows. ^{1}H NMR: 6.05, 5.72 (2tq, J = 7.5, 1.4, J = 6.8, 1.7, HC=); 4.58−4.56 (m, OCHO); 3.89−3.68, 3.52−3.34 (2m, 2 OCH_2); 2.26−2.13 (m, (CH_2)HC=); 1.89−1.52 (m, therein 1.77, 1.68 (2d, J = 1.4, J = 1.7, MeC=) and 4 CH_2); 0.88, 0.84 (2s, *t*-Bu); 0.11, 0.01 (2s, Me_2Si). ^{13}C NMR: 143.5, 141.0 (2d, HC=); 134.2, 132.6 (2s, Me*C*=); 98.8, 98.6 (2d, OCHO); 67.1 (t, OCH_2); 62.2, 62.1 (2t, OCH_2); 30.7, 30.3, 29.5, 29.4 (4t, 2 CH_2); 27.0, 26.9 (2q, Me_3C); 26.4 (q, $^1/_2$ *Me*C=); 25.5, 25.0, 19.6, 19.5, (4t, 3 CH_2); 19.4, 18.1 (2s, Me_3C); 16.0 (q, $^1/_2$ *Me*C=); −3.8, −6.3 (2q, Me_2Si). ACT-*J*-NMR: $^3J(^{29}Si,^1H)_{cis} = 7.5$ (δ ^{1}H: 5.72); $^3J(^{29}Si,^1H)_{trans} = 13.0$ (δ ^{1}H: 6.05). CI-MS: 316 (7, $[M + NH_4]^+$), 215 (100). Anal. Calcd for $C_{17}H_{34}O_2Si$ (M_r = 298.545): C, 68.39; H, 11.48. Found: C, 68.15; H, 11.53.

22. (*E*)-5-(*tert*-Butyldimethylsilyl)-4-methylpent-4-enyl Tetrahydropyran-2-yl Ether ((*E*)-7c). Analogously to the procedure described in 21, (*Z*)-**5c** (150 mg, 0.37 mmol) was reacted with Me_2CuLi (1.83 mmol) and MeI (1.05 g, 7.32 mmol) to yield (*E*)-**7c** (64 mg, 0.21 mmol, 76%), a slightly yellow oil. ^{1}H NMR: 5.72 (t, J = 6.8, HC=); 4.58−4.56 (m, OCHO); 3.89−3.68, 3.52−3.34 (2m, 2 OCH_2); 2.26−2.13 (m, (CH_2)HC=); 1.89−1.52 (m, therein 1.68 (d, J = 1.7, MeC=) and 4 CH_2); 0.84 (2s, *t*-Bu); 0.01 (2s, Me_2Si). ^{13}C NMR: 141.0 (d, HC=); 134.2 (s, Me*C*=); 98.8 (d, OCHO); 67.1, 62.2 (2t, 2 OCH_2); 30.7, 29.4 (2t, 2 CH_2); 27.0, 26.9 (2q, Me_3C); 25.5, 25.0, 19.6 (3t, 3 CH_2); 18.1 (s, Me_3C); 16.0 (q, *Me*C=); −6.3 (2q, Me_2Si). ACT-*J*-NMR: $^3J(^{29}Si,^1H) = 7.5$. CI-MS: 316 (7, $[M + NH_4]^+$), 215 (100). Anal. Calcd for $C_{17}H_{34}O_2Si$ (M_r = 298.545): C, 68.39; H, 11.48. Found: C, 68.42; H, 11.54.

23. Lithium 1-(*tert*-Butyldimethylsilyl)ethenolate (9a). Prepared directly in the NMR tube: To the solution of *tert*-butyldimethylsilyl methyl ketone[18] (30 mg, 0.19 mmol) in d_8-THF (0.2 mL) was added LDA (0.29 mmol, 0.78 M in d_8-THF) at −80 °C. The NMR experiments were performed at −30 °C. ^{1}H NMR data are as follows (several species; only the signals of the vinylic protons of the two major components (ratio 1:2) are given). Isomer A: 4.19 (d, J = 1.7, H_{trans}C=); 3.74 (d, J = 1.7, H_{cis}C=). Isomer B: 4.15 (d, J = 2.0, H_{trans}C=); 3.62 (d, J = 1.7, H_{cis}C=). ACT-*J*-NMR: $^3J(^{29}Si,^1H)_{cis} = 3.1$, $^3J(^{29}Si,^1H)_{trans}$ = 12.1 (δ ^{1}H = 4.19), 12.5 (δ ^{1}H = 4.15).

(18) Fässler, J., Ph.D. Thesis, University of Zurich, in preparation.

24. Lithium (*E*)-1-(*tert*-Butyldimethylsilyl)-2-phenylethenolate ((*E*)-9b). Prepared directly in the NMR tube: To the solution of benzyl *tert*-butyldimethylsilyl ketone[18] (29 mg, 0.12 mmol) in d_8-THF (0.35 mL) was added LDA (0.19 mmol, 0.71 M in d_8-THF) at −80 °C. The NMR experiments were performed after 1 h at −60 °C. ^{1}H NMR: 7.60 (br t, J = 7.2, aromatic H); 7.10 (br d, J = 7.6, 2 aromatic H); 6.80 (br t, J = 7.3, 2 aromatic H); 5.26 (s, HC=); 1.10 (s, *t*-Bu); 0.17 (s, Me_2Si). ACT-*J*-NMR: $^3J(^{29}Si,^1H)$ = 3.6.

25. 1-(*tert*-Butyldimethylsilyl)-1-(trimethylsiloxy)ethene (10a). To a solution of LDA (0.8 mmol, 0.8 M in THF) was added at −80 °C *tert*-butyldimethylsilyl methyl ketone[18] (98 mg, 0.62 mmol) dissolved in THF (1 mL). After 1 h, TMSCl (103 mg, 0.95 mmol) was added at −80 °C and the temperature was raised to 0 °C over a period of 2 h. The mixture was poured on a column of basic Al_2O_3, and **10a** (137.7 mg, 0.59 mmol, 97%), arising as a slightly yellow oil, was eluted with Et_2O. ^{1}H NMR (C_6D_6): 4.95 (d, J = 1.2, $H_{trans}C$=); 4.59 (d, J = 1.2, $H_{cis}C$=); 1.04 (s, *t*-Bu); 0.19 (s, Me_3Si); 0.11 (s, Me_2Si). ^{13}C NMR (C_6D_6): 166.2 (s, OC=); 105.6 (t, H_2C=); 27.3 (q, Me_3C); 17.0 (s, Me_3C); 1.0 (q, Me_3Si); −6.0 (q, Me_2Si). ACT-*J*-NMR: $^3J(^{29}Si,^1H)_{cis}$ = 3.5; $^3J(^{29}Si,^1H)_{trans}$ = 10.4. CI-MS: 231 $[M + H]^+$. Anal. Calcd for $C_{11}H_{26}OSi_2$ (M_r = 230.501): C, 57.32; H, 11.37. Found: C, 55.84; H, 10.65 (volatile).

26. (*E*/*Z*)-1-(*tert*-Butyldimethylsilyl)-1-(trimethylsiloxy)-2-phenylethene ((*E*/*Z*)-10b). Analogously to the procedure described in 25, benzyl *tert*-butyldimethylsilyl ketone[18] (60 mg, 0.26 mmol) was reacted with LDA (0.4 mmol) and TMSCl (55 mg, 0.51 mmol) to yield (*E*/*Z*)-**10b** (63 mg, 0.20 mmol, 80%, ratio *ca*. 2:1), a colorless oil. ^{1}H NMR (C_6D_6): 7.55−6.93 (m, 5 aromatic H); 6.90 (s, $PhH_{trans}C$=); 6.13 (s, $PhH_{cis}C$=); 1.12, 1.11 (2s, *t*-Bu); 0.28, 0.18, 0.16, 0.08 (4s, Me_2Si and Me_3Si). ^{13}C NMR (C_6D_6): 159.0, 157.3 (2s, SiC=); 136.0, 135.6 (2s, 2 aromatic C); 129.0, 128.5 (2d, PhC=); 125.6, 125.5, 124.4, 123.9 (4d, 5 aromatic C); 26.3, 25.9 (2q, Me_3C); 16.2, 16.1 (2s, Me_3C); 0.0, −0.4 (2q, Me_3Si); −5.7, −6.9 (2q, Me_2Si). ACT-*J*-NMR: $^3J(^{29}Si,^1H)_{cis}$ = 3.5; $^3J(^{29}Si,^1H)_{trans}$ = 9.4. CI-MS: 307 $[M + H]^+$. Anal. Calcd for $C_{17}H_{30}OSi_2$ (M_r = 306.600): C, 66.60; H, 9.86. Found: C, 66.21; H, 10.16.

27. (*E*/*Z*)-1-(*tert*-Butyldimethylsilyl)-1-(trimethylsiloxy)prop-1-ene ((*E*/*Z*)-10c). To a solution of LDA (0.8 mmol, 0.8 M in THF) was added at −80 °C *tert*-butyldimethylsilyl methyl ketone (81 mg, 0.51 mmol) dissolved in THF (1 mL). After 30 min, *N*,*N*′-dimethyl-*N*,*N*′-propenylurea (65 mg 0.50 mmol) was added, and after 1 h, MeI (217 mg, 1.53 mmol) was added. The mixture was warmed to 0 °C, and stirring was continued for 1 h (formation of *tert*-butyldimethylsilyl ethyl ketone). The solution was cooled to −80 °C, treated with LDA (0.55 mmol, 0.4 M in THF), stirred for an additional 1 h, and treated with TMSCl (60 mg, 0.55 mmol). The temperature was slowly raised to 0 °C, the mixture poured on a column of basic Al_2O_3, and (*E*/*Z*)-**10c** (93 mg, 0.38 mmol, 75%, ratio *ca*. 6:1), arising as a slightly yellow oil, eluted with Et_2O. ^{1}H NMR (C_6D_6): 5.63 (q, J = 7.3, $H_{trans}C$=); 5.14 (q, J = 6.7, $H_{cis}C$=); 1.62, 1.63 (2d, J = 7.3, 6.7, MeC=); 1.07, 1.08 (2s, *t*-Bu); 0.26, 0.24 (2s, Me_3SiO); 0.14, 0.13 (2s, Me_2Si). ^{13}C NMR (C_6D_6, major isomer only): 156.8 (s, SiC=); 119.7 (d, MeCH); 26.9 (q, Me_3C); 16.8 (s, Me_3C); 11.6 (q, MeCH); 1.0 (q, Me_3SiO); −6.7 (q, Me_2Si). ACT-*J*-NMR: $^3J(^{29}Si,^1H)_{cis}$ = 3.4; $^3J(^{29}Si,^1H)_{trans}$ = 9.6. CI-MS: 245 $[M + H]^+$. Anal. Calcd for $C_{12}H_{28}OSi_2$ (M_r = 244.528): C, 58.94; H, 11.54. Found: C, 59.29; H, 11.43.

28. 1-(*tert*-Butyldimethylsilyl)-2-phenylethyne (13a). To a solution of phenylacetylene (5.8 mL, 50 mmol) in THF (30 mL) was added at −80 °C BuLi (60 mmol, 2 M in pentane). After 1 h, *tert*-butyldimethylsilyl chloride (TBDMSCl, 5.0 g, 40.9 mmol) was added, the temperature was slowly raised to 23 °C (2 h), and the solution was stirred for an additional 16 h. It was recooled to −50 °C, quenched with aqueous HCl solution (10%), extracted with Et_2O, and distilled (bulb-to-bulb, *ca*. 100 °C/10^{-4} Torr) to give **13a** (5.9 g, 27.5 mmol, 82%) as a colorless oil. ^{1}H NMR: 7.49−7.29 (m, 5 aromatic H); 1.01 (s, *t*-Bu); 0.19 (s, Me_2Si). ^{13}C NMR: 132.0 (d, 2 aromatic C); 128.3 (d, aromatic C); 128.2 (d, 2 aromatic C); 123.2 (s, aromatic C); 105.7 (s, PhC≡); 92.4 (s, SiC≡); 26.1 (q, Me_3C); 16.6 (s, Me_3C); −4.7 (q, Me_2Si). CI-MS: 217 $[M + H]^+$. Anal. Calcd for $C_{14}H_{20}Si$ (M_r = 216.402): C, 77.71; H, 9.32. Found: C, 76.98; H, 8.56 (volatile).

29. 1-{[(Benzyloxy)methyl]-*tert*-butylmethylsilyl}-2-phenylethyne (13b). Analogously to the procedure described in 28, phenylacetylene (1.54 mL, 14.1 mmol) was reacted with BuLi (14.8 mmol) and [(benzyloxy)methyl]-*tert*-butylmethylsilyl chloride[14] (1.95 g, 7.60 mmol) to yield **13b** (2.42 g, 7.52 mmol, 98%), arising as a colorless oil after chromatography (hexane/CH_2Cl_2, 1:1). ^{1}H NMR: 7.53−7.21 (m, 10 aromatic H); 4.51(s, $PhCH_2O$); 3.37, 3.31 (AB, J = 13.0, $SiCH_2O$); 1.02 (s, *t*-Bu); 0.24 (s, MeSi). ^{13}C NMR: 138.8 (s, aromatic C); 132.0, 128.5 (2d, 2 × 2 aromatic C); 128.2 (d, aromatic C); 128.1 (d, 2 aromatic C); 127.5 (d, 3 aromatic C); 123.0 (s, aromatic C); 106.8 (s, PhC≡); 90.1 (s, SiC≡); 76.8 (t, $PhCH_2O$); 60.9 (t, $SiCH_2O$); 26.5 (q, Me_3C); 19.9 (s, Me_3C); −7.5 (q, MeSi). CI-MS: 323 $[M + H]^+$. Anal. Calcd for $C_{21}H_{26}OSi$ (M_r = 322.527): C, 78.21; H, 8.13. Found: C, 78.33; H, 8.14.

30. 5-(*tert*-Butyldimethylsilyl)pent-4-ynyl Tetrahydropyran-2-yl Ether (13c). To a solution of pent-4-yn-1-ol (440 mg, 5.22 mmol) in THF (7.5 mL) was added dropwise at 0 °C MeMgBr (13.5 mmol, 3 M in Et_2O). The mixture was refluxed for 1 h, cooled to −50 °C, and treated with TBDMSCl (903 mg, 6.01 mmol) dissolved in THF (5 mL). After 12 h, a saturated aqueous NH_4Cl solution was added, the mixture was extracted with Et_2O, the solvent was evaporated, and the residue was chromatographed (hexane/EtOAc, 12:1) to give 5-(*tert*-butyldimethylsilyl)pent-4-yn-1-ol (950 mg, 4.80 mmol, 91%). This alcohol (250 mg, 1.26 mmol) was dissolved in CH_2Cl_2 (5 mL) and the mixture treated with dihydropyran (530 mg, 6.32 mmol) and catalytic amounts of *p*-toluenesulfonic acid at 0 °C. After 90 min, it was quenched with saturated aqueous NH_4Cl solution, the mixture was extracted with Et_2O, the solvent was evaporated, and the residue was chromatographed (hexane/EtOAc, 20:1) to give **13c** (284 mg, 1.01 mmol, 80%) as a colorless oil. ^{1}H NMR: 4.58 (br t, J = 4.1, OCHO); 3.88−3.78, 3.51−3.42 (2m, 2 OCH_2); 2.33 (t, J = 7.0, CH_2C≡); 1.83−1.47 (m, 4 CH_2); 0.91 (s, *t*-Bu); 0.06 (s, Me_2Si). ^{13}C NMR: 106.4 (s, CH_2C≡); 97.9 (d, OCHO); 81.9 (s, SiC≡); 64.9, 61.2, (2t, 2 OCH_2); 29.8, 28.1 (2t, 2 CH_2); 25.2 (q, Me_3C); 24.6, 18.6, 15.8, (3t, 3 CH_2); 15.6 (s, Me_3C); −5.0 (q, Me_2Si). CI-MS (isobutane): 283 (46, $[M + H]^+$), 151 (100). Anal. Calcd for $C_{16}H_{30}O_2Si$ (M_r = 282.502): C, 68.03; H, 10.70. Found: C, 67.85; H, 10.44.

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Supporting Information Available: IR spectral data for (*E*)- and (*Z*)-**2a**,**b**,**d**, **-3a**, **-4a**, **-5a**,**c**, and **-6a**, (*E*)-**5b**, **-6b**, and **-7c**, (*E*/*Z*)-**7c** and **-10b**,**c**, **10a**, and **13a**−**c** (6 pages). Ordering information is given on any current masthead page.

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