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Configuration-Dependent Ring Opening of Silyloxiranes: Synthesis of Functionalized Alkenes or Tetrahydrofurans

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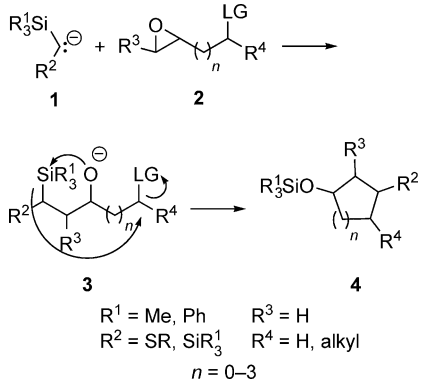
cis- and *trans*-Silyloxiranes with a potential tosylate or bromide leaving group in the β position are available by the diastereospecific reduction of the corresponding alkynes with DIBAL-H and hydrosilylation with silanes, respectively. In the reaction with the anion of a silylthioacetal, the outcome of the reaction is configuration dependent: the *cis*-oxiranes add nucleophilic methanthiolate and give a *cis*-vinyl sulfide unit in a Peterson olefination. In contrast, the *trans*-oxiranes lead to functionalized tetrahydrofurans with silyl(methylthio) substitution on the ring and in the exocyclic α position.

Introduction

The ease, reliability, and stereoselectivity of oxirane ring opening by nucleophiles is well established[1–3] and may even be considered as an example of "click chemistry".[4] The picture becomes more diverse if functionalized oxiranes of type **2** (R^3 = H) are employed and silyl-stabilized carbanions **1** are used as nucleophiles; here, cycloalkanes **4** are formed in a domino process (Scheme 1).[5–7] In addition to the use of alkyl- and aryl-substituted oxiranes, there is also a rich chemistry of silyloxiranes.[8,9] A noteworthy feature is the regioselectivity of silyloxirane ring opening, which usually occurs by nucleophilic attack on the silyl-substituted carbon atom, that is, in a contrasteric fashion.[8,9] With this background, it seemed to be of special interest to study the effect of silyl substitution in functionalized silyloxiranes **2** (R^3 = silyl). In the expected ring-opening product **3** (R^3 = silyl) there may be an interesting competition of 1,3- and 1,4-silyl migration. However, the present study shows that quite different reaction channels are available for the reaction of carbanion **1** (e.g., **23**$^-$) and silyloxiranes **2** (R^3 = silyl; e.g., **8**, **13**, **15**).

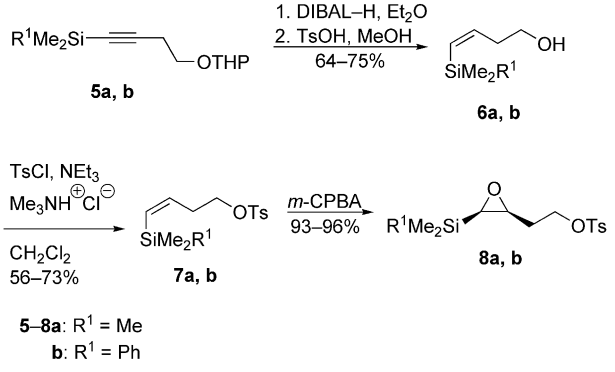


Scheme 1. Domino synthesis of cycloalkanes **4** from silyl-substituted carbanions **1** and functionalized oxiranes **2**.

Results and Discussion

Synthesis of *cis*-Silyloxiranes 8

Silyl substitution in oxiranes **2** (R^3 = silyl) creates a new stereocenter, giving rise to diastereomers. So it seemed desirable to control the relative configuration at both oxirane carbon atoms. Diastereoselective *cis*-reduction of alkynes **5a**,**b**[10] was achieved by using Negishi's method of DIBAL-H reduction.[11] The hydroxy group was liberated in the usual way by acid-catalyzed hydrolysis, and resulting enols **6a**,**b** were tosylated to **7a**,**b** in the presence of trimethylammonium chloride as catalyst;[12] we had observed earlier that this method is particularly useful for tricky tosylation



Scheme 2. Synthesis of *cis*-silyloxiranes.

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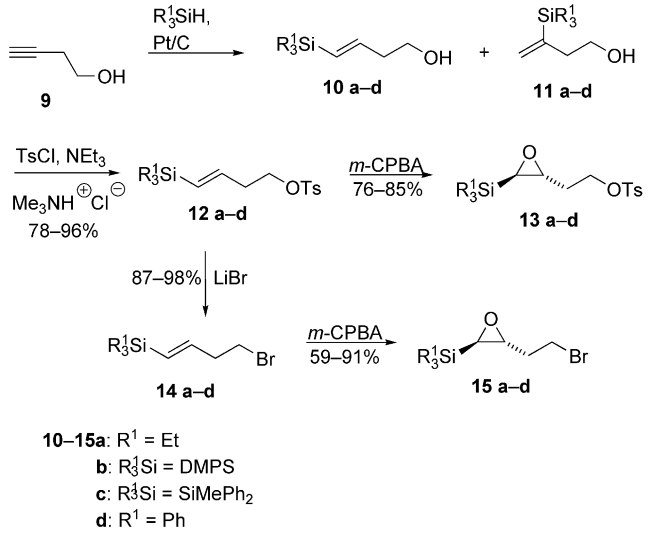
reactions.[13] Epoxidation of functionalized *cis*-vinylsilanes **7a**,**b** to silyloxiranes **8a**,**b** by *m*-CPBA was straightforward (Scheme 2).

Synthesis of *trans*-Silyloxiranes 13 and 15

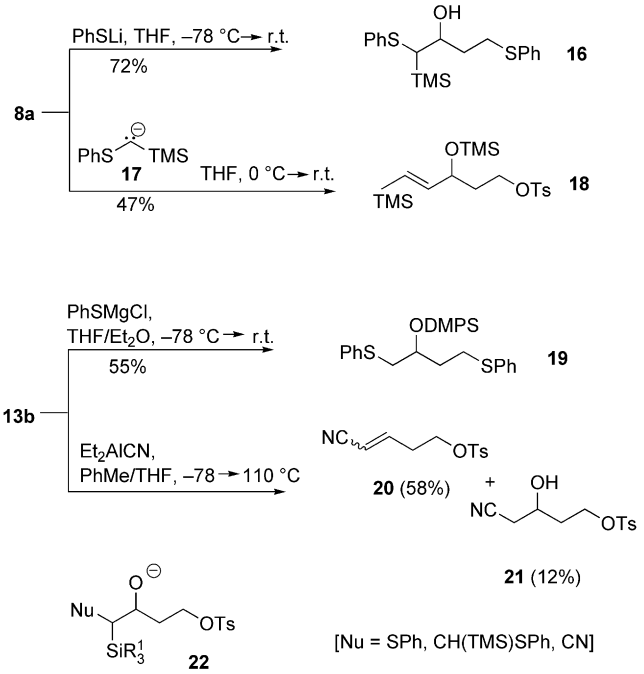
The *trans* arrangement of the substituents on oxirane targets **13** and **15** was again secured by a diastereoselective alkyne reduction, here of 3-butynol (**9**), but now by using a hydrosilylation approach with platinum on carbon as catalyst (Scheme 3).[14,15] This gave the desired *trans* selectivity, but provided a mixture of regioisomers **10/11**, which could conveniently be separated by chromatography after tosylation to give **12/13**, again by employing the Tanabe method.[12] Isolated tosylates **12** can be oxidized to give *trans*-silyloxiranes **13** or treated with lithium bromide in S_N2 chemistry to give bromides **14** and finally by epoxidation to give *trans*-silyloxiranes **15** with bromine as a potential leaving group.



Scheme 3. Synthesis of *trans*-oxiranes.

Model Ring-Opening Reactions of Oxiranes 8a and 13b

In model reactions, ring opening of *cis*-oxirane **8a** and *trans*-oxirane **13b** by thiophenoxide as an example of a strong nucleophile and by a carbanion, respectively, was tested. Diverse products **16**, **18**–**21** were isolated, but all were apparently formed via intermediate **22**, that is, by the usual contrasteric ring opening of silyloxiranes.[8,9] With thiophenoxide, both epoxide ring opening and tosylate substitution were observed to give bis(sulfide)s **16** and **19**. Silyl migration was seen for the DMPS group to give **19**, but the reaction conditions allowed silanol elimination in the Peterson olefination step to be avoided.[9,16] Starting from oxirane **8a**, the TMS group, which is known to migrate less readily than DMPS,[17] was still found on the carbon atom in product **16** (Scheme 4). Formation of **18** demonstrated a 1,3-silyl shift of the original oxirane silicon and a preference of thiophenoxide elimination for a Peterson reaction.

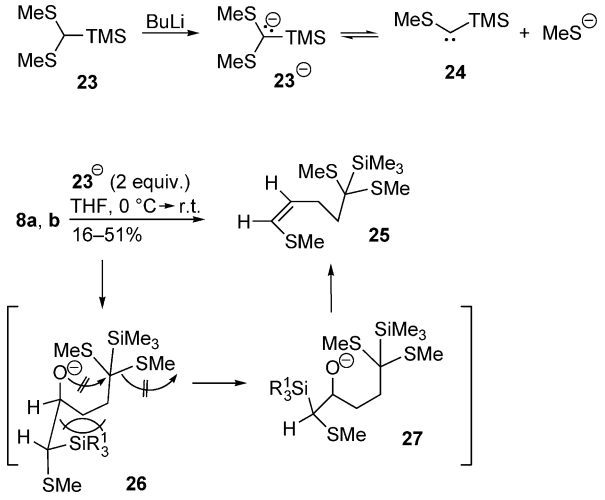


Scheme 4. Model ring-opening reactions of silyloxiranes **8a** and **13b**.

The Peterson olefination step occurred more readily if cyanide was used as nucleophile to give unsaturated nitrile **20**, however, along with desilylated ring-opening product **21**. The formation of vinylsilane **18** from oxirane **8a** and carbanion **17** shows that thiophenol was eliminated more readily from the primary ring-opening product of type **22** than silanol in a Peterson olefination. This is in line with the good leaving-group properties of thiophenol.[18]

Reactions of *cis*-Silyloxiranes 8 with Silylthioacetal 23

In the domino process starting from carbanion **1** and epoxy tosylate **2** (LG = Ts; Scheme 1), anion **23**$^-$ was found to react particularly smoothly.[5–7] So, **23**$^-$ was also employed in the reaction with silyloxiranes **8**, **13**, and **15**. Using **8a**,**b**, alkenyl sulfides **25** were isolated. So, thioacetal **23** reacted as a source of methanethiolate. The *cis* configuration of **25** is suggested by a 9.3 Hz olefinic ^3J coupling constant. Apparently, the steric screening of the oxiranes by the silyl substituent prevents attack of carbanion **23**$^-$. Instead, the reaction is probably initiated by oxirane ring opening by methanethiolate to give intermediate **26**, which suffers from a *gauche* interaction between the silyl group and the alkyl chain. So, rapid rotation to intermediate **27** with a *cis* arrangement of the silyl group and the alkoxide oxygen atom will occur; *syn* elimination of silyloxide finally gives *cis*-alkene **25**. In a parallel reaction, the tosylate group was displaced by a second equivalent of **23**$^-$ (Scheme 5).



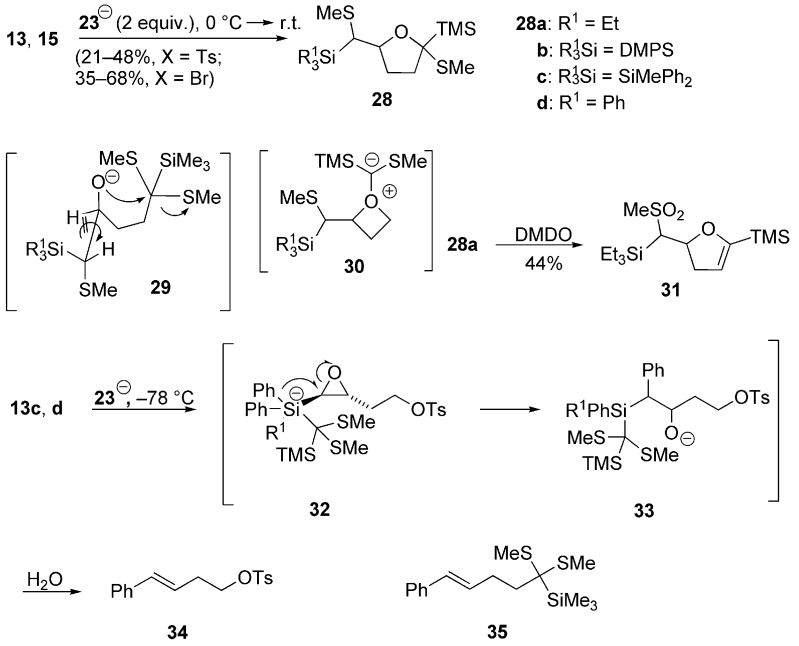
Scheme 5. Ring opening of *cis*-silyloxiranes **8** by carbanion **23**$^-$.

The parallel product with the trapping of methanethiolate by **8** should be carbene **24** (Scheme 5). So far, a carbenoid reactivity of silylthioacetal anions had only been observed for the corresponding phenylthio-substituted compounds, in which thiophenoxide is a potentially better leaving group than methanethiolate in **23**$^-$.[19,20] However, carbene **24** can be generated independently from a diazo precursor.[20] In the present reaction, no product of carbene **24** could be detected. Similar to the complex reaction of carbethoxycarbene with 2-phenyloxirane,[21] carbene **24** may enter diverse reaction pathways with **8** and so escape detection.

Reactions of *trans*-Silyloxiranes 13 and 15 with Silylthioacetal 23

trans-Silyloxiranes **13** and **15** and carbanion **23**$^-$ react quite differently from the corresponding *cis* compounds **8a**,**b**. In the main reaction product, the tosylate or bromide leaving group is no longer present and one equivalent of **23**$^-$ is incorporated, though the two methylthio groups are nonequivalent in the ^{1}H NMR spectra. Moreover, prochiral methyl or methylene groups introduced by the silyl substituents in **13a**,**b** and **15a**,**b** are magnetically nonequivalent, indicating their position on an asymmetric carbon atom. In accord with the coupling pattern and ^{1}H–^{13}C correlation analysis, the structure of tetrahydrofurans **28** is suggested. These heterocycles are formed in fair yields as single diastereomers from tosylates **13**, but in better yields from bromides **15** (Scheme 6). Chemical proof of structure can be seen in the oxidation of tetrahydrofuran **28a** with dimethyldioxirane (DMDO) to dihydrofuran **31**, where one methylthio group was oxidized to a sulfone, whereas the other was eliminated probably as methanesulfinate.

To account for the formation of tetrahydrofurans **28** from silyloxiranes **13** and **15** we invoked again substitution of the leaving group by silylthioacetal unit **23**$^-$ and opening of the oxirane ring by methanethiolate to give intermediate **29**. In contrast to **26**, this compound does not suffer from *gauche* interactions and so there was no special driving force to rotate around the former oxirane C–C bond. This gives room for S_Ni attack of the alkoxide on the silylthioacetal unit to give the tetrahydrofuran ring of **28** and to regenerate methanethiolate. However, in another mechanism, methanethiolate opens the oxirane prior to the S_N2 reaction between silylthioacetal anion **23**$^-$ and the tosylate



Scheme 6. Ring opening of *trans*-silyloxiranes **13** and **15** by carbanion **23**$^-$.

or bromide leaving group. The formed alkoxide then has a chance to displace the leaving group in an S_Ni process to give an oxetane. Now, carbene **24** may add to the nucleophilic ring oxygen atom of the oxetane to give ylide **30** and from there ring enlargement to tetrahydrofuran product **28**. This has precedent in similar oxetane ring-enlargement reactions.[22,23] Both mechanisms account for product formation and the diastereoselectivity of the reaction resulting from stereospecific oxirane ring opening. However, the latter mechanism implies that *cis*-**8** and *trans*-silyloxiranes **13** and **15** react with **23**$^-$ by quite different mechanisms and so may be less probable (Scheme 6).

Phenylsilyl-substituted silyloxiranes **13c**,**d** and carbanion **23**$^-$ yield phenylalkenes **34** and **35** when the reaction is run at –78 °C or as side products in the reaction of **13d** with **23**$^-$ at 0 °C. We explain this by primary formation of hypervalent silyl species **32**, which then undergoes phenyl transfer from the silyl residue of the original silyloxirane to the neighboring oxirane carbon atom. So, alkoxide **33** is formed and allows Peterson olefination to alkene **34**. Alkene **35** seems to be a secondary product formed by tosylate displacement with anion **23**$^-$. The phenyl transfer from the silicon atom to the vicinal carbon atom has precedent in related reactions.[24]

Conclusions

The present work reveals a striking difference in the behavior of *cis*-**8** and *trans*-silyloxiranes **13** and **15** towards carbanion **23**$^-$, but in no case was a reaction observed that is comparable to that shown by alkyl-substituted oxiranes **2** (Scheme 1). The underlying principle seems to be the steric hindrance of the silyloxiranes. This apparently does not allow opening of the oxirane unit by bulky anion **23**$^-$, but rather attack of methanethiolate as formed in the equilibrium with carbene **24** (Scheme 5).

Experimental Section

General: Melting points are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded with Bruker Avance DPX 200 and Avance 400 instruments in $CDCl_3$ as solvent. TMS (δ = 0.00 ppm) or the signal of the solvent ($CDCl_3$: δ = 7.26 ppm) served as internal standard in ^{1}H NMR spectra. The solvent peak ($CDCl_3$ at δ = 77.0 ppm) was used as reference for ^{13}C spectra. For assignment of the number of substituents attached to the specified carbon atom, each carbon is described as + (primary or tertiary carbon), – (secondary carbon) or o (quaternary carbon), as determined by the DEPT-135 method. When necessary, NMR spectroscopic data were assigned by using H–H and C–H correlated spectra. MS were recorded with a Varian instrument Saturn 2100T or Hewlett–Packard 5989B; high-resolution MS (HRMS) measurements were carried out at the Institut für Organische Chemie, Leibniz Universität Hannover. LRMS (ESI) spectra were recorded with a Hewlett Packard/Agilent instrument LC-MSD Serie 1100 at a dry gas temperature of 300 °C, a capillary voltage of 3000 V and a fragmentor voltage of 0 V. Samples were dissolved in HPLC-grade methanol and sprayed directly from methanol. IR spectra were recorded with a Bruker Vektor 22 FTIR spectrometer. TLC was performed on Merck 60 F254 precoated silica plates and spots were detected by UV fluorescence quenching or by spraying with a solution of vanillin/sulfuric acid in ethanol and subsequent heating. Flash chromatography was performed with silica gel 60 (Merck, 230–400 mesh). Ethyl acetate (EA) and petroleum ether (PE) with the boiling range 60–70 °C were used in the separations. All solvents were distilled before use. All reactions involving carbanions were carried out under a nitrogen atmosphere. GC measurements were done by using Hewlett Packard instruments HP 5890 II and HP 6890 with flame ionization detector and connected with integrator HP 3396. A 30-m capillary column DB-5 of J & W Scientific was used. Nitrogen was used as the carrier gas. Initial column pressure was 1.3 bar. For GCMS coupling, helium was used as the carrier gas.

1-Trimethylsilyl-4-(2-tetrahydropyranyloxy)-1-butyne (5a) by Silylation: Following a literature method,[10] a solution of BuLi (2.45 M in hexane, 2.91 mL, 7.13 mmol) was added dropwise to 1-(2-tetrahydropyranyloxy)-3-butyne (1.000 g, 6.48 mmol)[25] in absolute THF (22 mL) at –78 °C under an atmosphere of nitrogen. After stirring for 40 min, chlorotrimethylsilane (1.22 mL, 9.72 mmol) was added dropwise at the same temperature. Stirring was continued for 1.5 h, and the mixture warmed to room temperature overnight. Ether (50 mL) and water (10 mL) were added, and after separation of the layers the aqueous layer was extracted with diethyl ether (2 × 20 mL). The combined organic phase was dried ($MgSO_4$) and the solvent was removed under vacuum. The product was used as such. Yield: 1.424 g (97%), with spectroscopic data as given in the literature.[26]

1-Dimethylphenylsilyl-4-(2-tetrahydropyranyloxy)-1-butyne (5b): Prepared analogously from the alkyne (324 mg, 2.1 mmol), though finally purified by flash chromatography (PE/EA, 5:1) to give a yellowish oil. Yield: 381 mg (63%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.36 (s, 6 H, $SiCH_3$), 1.33–2.17 (m, 6 H, pyran-CH_2), 2.50 (t, J = 7.0 Hz, 2 H, CH_2CH$_2$OTHP), 3.27–3.97 (m, 4 H, CH_2OTHP and pyran-CH_2), 4.58 (s, 1 H, pyran-CH), 7.20–7.72 (m, 5 H, Ar-H) ppm.

***cis*-4-(Trimethylsilyl)-3-buten-1-ol (6a):** Following a Negishi method,[11] a DIBAL-H solution (1 M in hexane, 6.92 mL, 6.92 mmol) was added dropwise to **5a** (1.424 g, 6.29 mmol) in absolute ether (20 mL) at 0 °C under an atmosphere of nitrogen. The reaction mixture was warmed to room temperature over 30 min and stirred for another 30 min. Then the mixture was heated at reflux for 4 h. After cooling to 0 °C, the reaction was quenched with 2 M HCl. A deposit was removed by filtration and thoroughly washed with diethyl ether. The organic phase was washed with saturated $NaHCO_3$ solution (2×), saturated NaCl solution, and dried ($MgSO_4$). The solvent was evaporated under vacuum, the residue was taken up in methanol (7 mL), and a tip of the spatula-size amount of TsOH·H_2O was added. The mixture was then stirred overnight. After addition of saturated $NaHCO_3$ solution/ether the mixture was filtered, and the residue was washed thoroughly with ether. The organic phase was washed with saturated NaCl solution (2×) and dried ($MgSO_4$), and the solvent was removed under vacuum. Yield: 680 mg (75%) with spectroscopic data as given in ref.[27]

***cis*-4-(Dimethylphenylsilyl)-3-buten-1-ol (6b):** Was prepared analogously from **5b** (380 mg, 1.32 mmol) to give 173 mg (64%) as a yellow oil with spectroscopic data as in ref.[10]

***cis*-4-(Tosyloxy)-1-(trimethylsilyl)-1-butene (7a):** Was prepared by the method of Tanabe[12] to give a colorless oil (56%) with spectroscopic data as reported before.[27]

***cis*-1-(Diphenylmethylsilyl)-4-(tosyloxy)-1-butene (7b):** Was prepared analogously to **7a** from **6b** (62 mg. 0.30 mmol) to give **7b** (81 mg, 73%) as a colorless oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.34 (s, 6 H, $SiCH_3$), 2.37 (dq, J = 6.9, 1.3 Hz, 2 H, CH_2CH_2OTs), 2.45 (s, 3 H, CH_3 of Ts), 3.93 (t, J = 6.8 Hz, 2 H, CH_2OTs), 5.80 (dt, J = 14.1, 1.3 Hz, 1 H, SiC*H*=CH), 6.26 (dt, J = 14.3, 7.1 Hz, 1 H, SiCH=C*H*), 7.28–7.37 (m, 5 H, Ar-H), 7.45–7.52 (m, 2 H, Ar-H), 7.71–7.79 (m, 2 H, Ar-H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = –1.1 (+, 2 C, $SiCH_3$), 21.6 (+, 1 C, CH_3 of Ts), 32.8 (–, 1 C, CH_2CH_2OTs), 69.3 (–, 1 C, CH_2OTs), 127.9 (+, 4 C, C-Ar), 129.0 (+, 1 C, Si*C*H=CH), 129.8 (+, 2 C, C-Ar), 131.5 (+, 1 C, C-Ar), 133.0 (q, 1 C, C-Ar), 133.6 (+, 2 C, C-Ar), 138.8 (q, 1 C, C-Ar), 143.2 (+, 1 C, SiCH=*C*H), 144.7 (q, 1 C, C-Ar) ppm. IR (NaCl): $\tilde{\nu}$ = 3068, 2957, 1600, 1495, 1428, 1362, 1307, 1250, 1176, 1112, 1097, 1072, 1041, 1020, 967, 915, 819, 780, 733, 703, 664 cm^{-1}. MS (DCP, 70 eV): *m*/*z* (%) = 345 (15) [M^+ – Me], 291 (14), 230 (10), 229 (70), 173 (20), 155 (14) [Ts], 149 (15), 145 (21), 135 (34) [$SiMe_2Ph$], 131 (15), 130 (16), 121 (10), 113 (10), 105 (16) [SiPh], 92 (10), 91 (100) [Bn], 83 (11), 75 (10) [C_2H_7OSi], 65 (37) [C_5H_5], 59 (14). HRMS (ESI): calcd. for $C_{19}H_{24}O_3SSi$ [M + Na]$^+$ 383.1113; found 383.1111.

***cis*-4-(Tosyloxy)-1-(trimethylsilyl)-1,2-epoxybutane (8a):** A solution of *m*-CPBA (1 mmol) in CH_2Cl_2 was added to a solution of the vinylsilane (1 mmol) in CH_2Cl_2 at 0 °C. Then, the cooling bath was removed, and the mixture stirred at room temperature overnight. The resulting mixture was washed with saturated $NaHCO_3$ solution (1×) and with aqueous $Na_2S_2O_3$ solution (10%, 1×) and then finally dried ($MgSO_4$). The solvent was removed under vacuum, and the residue was purified by flash chromatography to give the silyloxiranes. Product **8a** (448 mg, 93%) was obtained from **7a** (457 mg, 1.53 mmol) as a colorless oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.09 (s, 9 H, $SiCH_3$), 1.65 (dt, J = 8.2, 6.0 Hz, 1 H, CH_2CH_2OTs), 1.72 (dt, J = 7.7, 5.7 Hz, 1 H, CH_2CH_2OTs), 2.19 (d, J = 5.1 Hz, 1 H, Me_3SiCH), 2.45 (s, 3 H, CH_3 of Ts), 3.12 (ddd, J = 7.7, 5.1, 4.3 Hz, 1 H, $Me_3SiCHCH$), 4.14–4.22 (m, 2 H, CH_2OTs), 7.35 (d, J = 8.1 Hz, 2 H, Ar-H), 7.80 (d, J = 8.1 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = –1.9 (+, 3 C, $SiCH_3$), 21.6 (+, 1 C, CH_3 of Ts), 31.3 (–, 1 C, CH_2CH_2OTs), 52.3 (+,1 C, Me_3SiCH), 53.8 (+, 1 C, $Me_3SiCHCH$), 68.0 (–, 1 C, CH_2OTs), 127.9 (+, 2 C, C-Ar), 129.9 (+, 2 C, C-Ar), 132.8 (q, 1 C, C-Ar), 144.9 (q, 1 C, C-Ar) ppm. IR (NaCl): $\tilde{\nu}$ = 2958, 2901, 1923, 1598, 1495, 1420, 1363, 1307, 1291, 1251, 1211, 1177, 1146, 1120, 1097, 1045, 1019, 978, 919, 843, 760, 692, 664 cm^{-1}. MS (DCP, 70 eV): *m*/*z* (%) = 155 (6) [Ts], 143 (11) [M^+ – OTs], 142 (20), 129 (11), 91 (48) [Bn], 75 (20) [C_2H_7OSi], 74 (12), 73 (100) [TMS], 70 (13), 65 (20) [C_5H_5], 59 (14). HRMS (ESI): calcd. for $C_{14}H_{22}O_4SSi$ [M + Na + MeCN]$^+$ 378.1171; found 378.1176.

***cis*-1-(Dimethylphenylsilyl)-4-(tosyloxy)-1,2-epoxybutane (8b):** According to the procedure given for **8a**, product **8b** (69 mg, 96%) was obtained from **7b** (69 mg, 0.19 mmol) as a yellowish oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.36 and 0.39 (each s, 3 H, $SiCH_3$), 1.49–1.66 (m, 1 H, CH_2CH_2OTs), 1.86 (ddt, J = 14.5, 7.2 Hz, 4.5 H, 1 H, CH_2CH_2OTs), 2.39 (d, J = 5.1 Hz, 1 H, $PhMe_2SiCH$), 2.45 (s, 3 H, CH_3 of Ts), 3.14 (dt, J = 7.6, 4.8 Hz, 1 H, $PhMe_2SiCHCH$), 4.06 (dd, J = 7.2, 5.6 Hz, 2 H, CH_2OTs), 7.28–7.41 (m, 5 H, Ar-H), 7.46–7.56 (m, 2 H, Ar-H), 7.72–7.81 (m, 2 H, Ar-H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = –3.4 and –3.1 (each +, 1 C, $SiCH_3$), 21.6 (+, 1 C, CH_3 of Ts), 31.0 (–, 1 C, CH_2CH_2OTs), 50.0 (+, 1 C, $PhMe_2SiCH$), 53.9 (+, 1 C, $PhMe_2SiCHCH$), 67.9 (–, 1 C, CH_2OTs), 127.9 (+, 2 C, C-Ar), 128.0 (+, 2 C, C-Ar), 129.6 (+, 1 C, C-Ar), 129.9 (+, 2 C, C-Ar), 132.8 (q, 1 C, C-Ar), 133.8 (+, 2 C, C-Ar), 136.3 (q, 1 C, C-Ar), 144.8 (q, 1 C, C-Ar) ppm. IR (NaCl): $\tilde{\nu}$ = 3069, 3049, 2958, 2925, 2182, 1921, 1770, 1727, 1598, 1495, 1428, 1361, 1307, 1291, 1252, 1212, 1177, 1115, 1097, 1019, 978, 918, 880, 816, 780, 737, 704, 664 cm^{-1}. MS (DCP, 70 eV): *m*/*z* (%) = 229 (19), 149 (16), 136 (12), 135 (100) [$SiMe_2Ph$], 130 (24), 117 (12), 113 (45), 107 (10), 105 (14) [SiPh], 91 (74) [Bn], 85 (12), 83 (15), 75 (14) [C_2H_7OSi], 70 (28), 65 (35) [C_5H_5], 57 (12), 55 (10). HRMS (ESI): calcd. for $C_{19}H_{24}O_4SSi$ [M + Na]$^+$ 399.1062; found 399.1062.

General Procedure for Hydrosilylation Using Pt/C: On the basis of a literature procedure,[14] under an atmosphere of nitrogen, alkyne **9** (1 mmol) was introduced into a Schlenk tube together with the silane (1 mmol) and a tip of a spatula-size amount of Pt/C, and the mixture warmed to 90 °C for 7 h. After cooling, the mixture was adsorbed to silica and purified by flash chromatography. The following compounds were obtained:

***trans*-1-(Triethylsilyl)-1-buten-4-ol (10a):** A 3:1 mixture (881 mg, 68%) of **10a** and 2-(triethylsilyl)-1-buten-4-ol (**11a**) was obtained as a colorless liquid from **9** (0.4 mL, 5.28 mmol) and triethylsilane after flash chromatography (PE/EA, 20:1). The spectroscopic data of **10a** were as given in ref.[28]

***trans*-1-(Dimethylphenylsilyl)-1-buten-4-ol (10b):** Product **10b** (519 mg, 48%) was obtained as a colorless liquid along with a mixture (582 mg) of **10b** and 2-(dimethylphenylsilyl)-1-buten-4-ol (**11b**) from **9** (0.4 mL, 5.28 mmol) and dimethylphenylsilane (0.82 mL, 5.28 mmol) by flash chromatography (PE/EA, 30:1; 20:1; 10:1). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.35 (s, 6 H, $SiCH_3$), 1.51 (br. s, 1 H, OH), 2.44 (ddt, J = 6.2, 0.8 Hz, 2 H, CH_2CH_2OH), 3.71 (t, J = 6.3 Hz, 2 H, CH_2OH), 5.92 (dt, J = 18.7, 0.9 Hz, 1 H, SiC*H*=CH), 6.11 (dt, J = 18.6, 6.0 Hz, 1 H, SiCH=C*H*), 7.32–7.39 (m, 3 H, Ar-H), 7.48–7.56 (m, 2 H, Ar-H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = –2.6 [+, 2 C, $Si(CH_3)_2Ph$], 40.0 (–, 1 C, CH_2CH_2OH), 61.5 (–, 1 C, CH_2OH), 127.8 (+, 2 C, C-Ar), 128.9 (+, 1 C, C-Ar), 131.6 (+, 1 C, Si*C*H=CH), 133.8 (+, 2 C, C-Ar), 138.7 (q, 1 C, C-Ar), 144.5 (+, 1 C, SiCH=*C*H) ppm. IR (NaCl): $\tilde{\nu}$ = 3346, 3068, 3050, 2955, 1953, 1881, 1817, 1618, 1427, 1335, 1248, 1189, 1158, 1114, 1047, 988, 823, 783, 758, 731, 699, 638 cm^{-1}. MS (DCP, 70 eV): *m*/*z* (%) = 191 (47) [M^+ – Me], 178 (30), 163 (73), 161 (31), 145 (39), 137 (68), 135 (88) [$SiMe_2Ph$], 130 (33), 129 (32) [M^+ – Ph], 121 (51), 105 (37) [SiPh], 91 (37) [Bn], 75 [C_2H_7OSi]. HRMS (ESI): calcd. for $C_{12}H_{18}OSi$ [M + Na]$^+$ 229.1025; found 229.1026.

***trans*-1-(Diphenylmethylsilyl)-1-buten-4-ol (10c) and 2-(Diphenylmethylsilyl)-1-buten-4-ol (11c):** Starting from **9** (0.4 mL, 5.28 mmol) and methyldiphenylsilane (1.05 mL, 5.28 mmol) and after flash chromatography (PE/EA, 15:1), **10c** (1008 mg, 71%) and **11c** (336 mg, 26%) were isolated as colorless liquids. Data for **10c**: ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.63 (s, 3 H, $SiCH_3$), 1.50 (br. s, 1 H, OH), 2.43–2.54 (m, 2 H, CH_2CH_2OH), 3.72 (t, J = 6.4 Hz, 2 H, CH_2OH), 6.11–6.16 (m, 2 H, HC=C), 7.33–7.41 (m, 6 H, Ar-H), 7.49–7.56 (m, 4 H, Ar-H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = –3.8 (+, 1 C, $SiCH_3$), 40.2 (–, 1 C, CH_2CH_2OH), 61.4 (–, 1 C, CH_2OH), 127.8 (+, 4 C, C-Ar), 129.2 (+, 2 C, C-Ar), 129.4 (+, 1 C, Si*C*H=CH), 134.8 (+, 4 C, C-Ar), 136.6 (q, 2 C, C-Ar), 146.7 (+, 1 C, $Ph_2MeSiCH$=*C*H) ppm. IR (NaCl): $\tilde{\nu}$ = 3570, 3346, 3068, 3048, 2998, 2955, 1957, 1885, 1821, 1737, 1616, 1589, 1567, 1486, 1428, 1328, 1251, 1218, 1190, 1157, 1112, 1046, 988, 853, 792, 735, 700, 663 cm^{-1}. MS (DCP, 70 eV): *m*/*z* (%) = 253 (28) [M^+ – Me], 225 (25) [M^+ – Me – C_2H_4], 223 (16) [M^+ – C_2H_5O], 207 (11), 197 (79) [$SiMePh_2$], 191 (43) [M^+ – Ph], 183 (29), 137 (100), 121 (32), 105 (46) [SiPh], 91 (25) [Bn], 77 (18) [Ph]. HRMS (ESI): calcd. for $C_{17}H_{20}OSi$ [M + Na]$^+$ 291.1181; found 291.1188. Data for **11c**: ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.68 (s, 3 H, $SiCH_3$), 1.42 (br. s, 1 H, OH), 2.48 (t, J = 6.5 Hz, 2 H, CH_2CH_2OH), 3.56 (t, J = 6.6 Hz,

1 H, CH_2OH), 5.54 (d, J = 2.7 Hz, 1 H, CH_2=C), 5.93 (dt, J = 2.8, 1.4 Hz, 1 H, CH_2=C), 7.34–7.43 (m, 6 H, Ar-H), 7.49–7.57 (m, 4 H, Ar-H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = –4.0 (+, 1 C, $SiCH_3$), 39.4 (–, 1 C, CH_2CH_2OH), 61.5 (–, 1 C, CH_2OH), 127.9 (+, 4 C, C-Ar), 129.5 (+, 2 C, C-Ar), 131.2 (–, 1 C, CH_2=C), 135.0 (+, 4 C, C-Ar), 135.5 (q, 2 C, C-Ar), 144.9 (q, 1 C, CH_2=C) ppm. IR (NaCl): $\tilde{\nu}$ = 3569, 3346, 3068, 3049, 3011, 2955, 1958, 1885, 1823, 1774, 1655, 1589, 1567, 1486, 1428, 1327, 1305, 1252, 1218, 1191, 1157, 1111, 1045, 999, 936, 886, 855, 790, 727, 699, 679 cm^{-1}. MS (DCP, 70 eV): m/z (%) = 253 (15) [M^+ – Me], 223 (3) [M^+ – C_2H_5O], 199 (56), 197 (89) [$SiMePh_2$], 191 (43) [M^+ – Ph], 137 (100), 105 (44) [SiPh], 91 (15) [Bn], 77 (26) [Ph]. HRMS (ESI): calcd. for $C_{17}H_{20}OSi$ ([M + Na]$^+$) 291.1181; found 291.1179.

***trans*-1-(Triphenylsilyl)-1-buten-4-ol (10d):** Product **10d** (328 mg, 47%) was obtained from **9** (0.16 mL, 2.10 mmol) and triphenylsilane (548 mg, 2.10 mmol) after flash chromatography (PE/EA, 10:1). M.p. 113 °C. The spectroscopic data agree with the data in ref.[28]

***trans*-4-(Tosyloxy)-1-(triethylsilyl)-1-butene (12a):** According to the procedure given for **7a**,**b**, product **12a** (1.073 g, 78%) was obtained from **10a** (757 mg, 4.06 mmol) after flash chromatography (PE/EA, 40:1). The spectroscopic data agree with the values in ref.[29]

***trans*-1-(Dimethylphenylsilyl)-4-(tosyloxy)-1-butene (12b):** According to the procedure given for **7a**,**b**, product **12b** (422 mg, 97%) was obtained from **10b** (249 mg, 1.21 mmol) as a colorless oil after flash chromatography (PE/EA, 25:1). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.30 (s, 6 H, $SiCH_3$), 2.44 (s, 3 H, CH_3 of Ts), 2.45–2.55 (m, 2 H, CH_2CH_2OTs), 4.10 (t, J = 6.8 Hz, 2 H, CH_2OTs), 5.81 (dt, J = 18.6, 1.3 Hz, 1 H, SiCH=CH), 5.95 (dt, J = 18.6, 5.2 Hz, 1 H, SiCH=CH), 7.28–7.51 (m, 7 H, Ar-H), 7.78 (d, J = 8.3 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = –2.7 (+, 2 C, $SiCH_3$), 21.6 (+, 1 C, CH_3 of Ts), 35.7 (–, 1 C, CH_2CH_2OTs), 69.1 (–, 1 C, CH_2OTs), 127.8 (+, 2 C, C-Ar), 127.9 (+, 2 C, C-Ar), 129.0 (+, 1 C, C-Ar), 129.8 (+, 2 C, C-Ar), 132.2 (+, 1 C, SiCH=CH), 133.1 (q, 1 C, C-Ar), 133.7 (+, 2 C, C-Ar), 138.4 (q, 1 C, C-Ar), 141.8 (+, 1 C, SiCH=CH), 144.7 (q, 1 C, C-Ar) ppm. IR (NaCl): $\tilde{\nu}$ = 3068, 2956, 2899, 1618, 1598, 1495, 1427, 1364, 1307, 1249, 1211, 1176, 1113, 1098, 1042, 1020, 974, 918, 817, 784, 733, 701, 664 cm^{-1}. MS (DCP, 70 eV): m/z (%) = 345 (8) [M^+ – Me], 317 (21) [M^+ – Me – C_2H_4], 291 (48), 229 (100), 211 (12), 205 (14) [M^+ – Ts], 173 (13), 161 (18) [$C_{10}H_{13}Si$], 149 (11) [$C_9H_{13}Si$], 145 (14), 135 (33) [$PhMe_2Si$], 131 (14), 130 (14), 91 (46) [Bn], 65 (17) [C_5H_5]. HRMS (ESI): calcd. for $C_{19}H_{24}O_3SSi$ [M + NH_4]$^+$ 378.1559; found 378.1557.

***trans*-1-(Diphenylmethylsilyl)-4-(tosyloxy)-1-butene (12c):** According to the procedure given for **7a**,**b**, product **12c** (388 mg, 82%) was obtained from **10c** (300 mg, 1.12 mmol) as a colorless oil after flash chromatography (PE/EA, 12:1). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.58 (s, 3 H, $SiCH_3$), 2.42 (s, 3 H, CH_3 of Ts), 2.54 (dt, J = 6.7, 4.6 Hz, 2 H, CH_2CH_2OTs), 4.11 (t, J = 6.7 Hz, 2 H, CH_2OTs), 5.95–6.01 (m, 2 H, SiCH=CH), 7.28–7.40 (m, 8 H, Ar-H), 7.41–7.50 (m, 4 H, Ar-H), 7.75 (d, J = 8.3 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = –3.9 (+, 1 C, $SiCH_3$), 21.6 (+, 1 C, CH_3 of Ts), 35.8 (–, 1 C, CH_2CH_2OTs), 68.9 (–, 1 C, CH_2OTs), 127.8 (+, 4 C, C-Ar), 129.3 (+, 2 C, C-Ar), 129.8 (+, 2 C, C-Ar), 130.1 (+, 1 C, C-Ar), 133.1 (q, 1 C, C-Ar), 134.8 (+, 4 C, C-Ar), 136.2 (q, 2 C, C-Ar), 144.0 (+, 1 C, C-Ar), 144.7 (q, 1 C, C-Ar) ppm. IR (NaCl): $\tilde{\nu}$ = 3068, 3048, 3022, 2958, 1959, 1822, 1726, 1618, 1598, 1488, 1428, 1362, 1307, 1292, 1253, 1217, 1176, 1112, 1042, 1020, 974, 918, 758, 701, 664 cm^{-1}. MS (DCP, 70 eV): m/z (%) = 353 (12) [M^+ – C_4H_5O], 291 (100) [M^+ – C_9H_7O], 197 (25) [$SiMe_2Ph$], 155 (11) [Ts], 91 (93) [Bn], 65 (38) [C_5H_5]. HRMS (ESI): calcd. for $C_{24}H_{26}O_3SSi$ [M + Na]$^+$ 445.1270; found 445.1270.

***trans*-4-Tosyloxy-1-(triphenylsilyl)-1-butene (12d):** According to the procedure given for **7a**,**b**, product **12d** (284 mg, 96%) was obtained from **10d** (200 mg, 0.61 mmol) after flash chromatography (PE/EA, 20:1) as a colorless solid. M.p. 95 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.40 (s, 3 H, CH_3 of Ts), 2.58 (dq, J = 6.5, 1.1 Hz, 2 H, CH_2CH_2OTs), 4.12 (t, J = 6.7 Hz, 2 H, CH_2OTs), 5.98 (dt, J = 18.5, 6.0 Hz, 1 H, Ph_3SiCH=CH), 6.23 (dt, J = 18.5, 1.2 Hz, 1 H, Ph_3SiCH=CH), 8.31–7.50 (m, 17 H, Ar-H), 7.73 (d, J = 8.3 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.6 (+, 1 C, CH_3 of Ts), 35.9 (–, 1 C, CH_2CH_2OTs), 68.7 (–, 1 C, CH_2OTs), 127.9 (+, C-Ar), 128.3 (+, 1 C, Ph_3SiCH=CH), 129.6 (+, C-Ar), 129.8 (+, C-Ar), 145.9 (+, 1 C, Ph_3SiCH=CH) ppm. IR (KBr): $\tilde{\nu}$ = 3064, 1617, 1596, 1484, 1427, 1359, 1189, 1178, 1157, 1112, 987, 927, 860, 819, 786, 744, 727, 705, 661 cm^{-1}. HRMS (ESI): calcd. for $C_{29}H_{28}O_3SSi$ [M + Na]$^+$ 507.1426; found 507.1413.

***trans*-4-(Tosyloxy)-1-(triethylsilyl)-1,2-epoxybutane (13a):** According to the procedure given for **8a**,**b**, product **13a** (178 mg, 81%) was obtained from **12a** (211 mg, 0.62 mmol) as a colorless liquid after flash chromatography (PE/EA, 30:1). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.47–0.61 (m, 6 H, SiCH_2CH$_3$), 0.94 (t, J = 7.9 Hz, 9 H, $SiCH_2CH_3$), 1.78–2.03 (m, 2 H, CH_2CH_2OTs), 2.00 (d, J = 3.6 Hz, 1 H, Et_3SiCH), 2.44 (s, 3 H, CH_3 of Ts), 2.83 (ddd, J = 6.4, 4.5, 3.6 Hz, 1 H, Et_3SiCHCH), 4.12–4.20 (m, 2 H, CH_2OTs), 7.34 (d, J = 7.9 Hz, 2 H, Ar-H), 7.79 (d, J = 8.3 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 1.7 (–, 3 C, SiCH$_2$CH$_3$), 7.2 (+, 3 C, $SiCH_2CH_3$), 21.6 (+, 1 C, CH_3 of Ts), 33.8 (–, 1 C, CH_2CH_2OTs), 48.4 (+, 1 C, Et_3SiCH), 52.0 (+, 1 C, Et_3SiCHCH), 67.6 (–, 1 C, CH_2OTs), 127.9 (+, 2 C, C-Ar), 129.9 (+, 2 C, C-Ar), 132.9 (q, 1 C, C-Ar), 144.9 (q, 1 C, C-Ar) ppm. IR (NaCl): $\tilde{\nu}$ = 2955, 2876, 1598, 1495, 1460, 1417, 1363, 1293, 1239, 1178, 1097, 1018, 977, 916, 872, 816, 738, 664 cm^{-1}. MS (DCP, 70 eV): m/z (%) = 327 (35) [M^+ – Et], 257 (100), 185 (33) [M^+ – OTs], 155 (16) [Ts], 149 (15), 115 (62) [$SiEt_3$], 91 (54) [Bn], 87 (25), 65 (21) [C_5H_5], 59 (22). HRMS (ESI): calcd. for $C_{17}H_{28}O_4SSi$ [M + Na]$^+$ 379.1375; found 379.1376.

***trans*-1-(Dimethylphenylsilyl)-4-(tosyloxy)-1,2-epoxybutane (13b):** According to the procedure given for **8a**,**b**, product **13b** (186 mg, 91%) was obtained from **12b** (196 mg, 0.54 mmol) as a colorless oil after flash chromatography (PE/EA, 10:1). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.29 and 0.32 (each s, 3 H, $SiCH_3$), 1.76–1.91 (m, 1 H, CH_2CH_2OTs), 1.93–2.08 (m, 1 H, CH_2CH_2OTs), 2.15 (d, J = 3.5 Hz, 1 H, $PhMe_2$SiCH), 2.44 (s, 3 H, CH_3 of Ts), 2.81 (ddd, J = 6.4, 4.5, 3.4 Hz, 1 H, SiCHCH), 4.15 (dd, J = 6.9, 5.6 Hz, 2 H, CH_2OTs), 7.29–7.43 (m, 5 H, Ar-H), 7.48–7.56 (m, 2 H, Ar-H), 7.77 (d, J = 8.3 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = –5.3 and –5.2 (each +, 1 C, $SiCH_3$), 21.6 (+, 1 C, CH_3 of Ts), 33.5 (–, 1 C, CH_2CH_2OTs), 51.1 (+, 1 C, $PhMe_2$SiCH), 52.6 (+, 1 C, SiCHCH), 67.5 (–, 1 C, CH_2OTs), 127.9 (+, 2 C, C-Ar), 128.0 (+, 2 C, C-Ar), 129.6 (+, 1 C, C-Ar), 129.9 (+, 2 C, C-Ar), 132.8 (q, 1 C, C-Ar), 133.9 (+, 2 C, C-Ar), 135.7 (q, 1 C, C-Ar), 144.9 (q, 1 C, C-Ar) ppm. IR (NaCl): $\tilde{\nu}$ = 2960, 1598, 1428, 1361, 1293, 1250, 1189, 1177, 1116, 1097, 1037, 976, 917, 872, 817, 789, 736, 704, 664 cm^{-1}. HRMS (ESI): calcd. for $C_{19}H_{24}O_4SSi$ [M + Na]$^+$ 399.1062; found 399.1060.

***trans*-1-(Diphenylmethylsilyl)-4-(tosyloxy)-1,2-epoxybutane (13c):** According to the procedure given for **8a**,**b**, product **13c** (114 mg, 76%) was obtained from **12c** (144 mg, 0.34 mmol) as a slightly yellow oil after flash chromatography (PE/EA, 10:1). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.55 (s, 3 H, $SiCH_3$), 1.78–2.13 (m, 2 H, CH_2CH_2OTs), 2.41 (d, J = 3.6 Hz, 1 H, Ph_2MeSiCH), 2.43 (s, 3 H,

CH_3 of Ts), 2.79 (ddd, J = 6.2, 4.6, 3.4 Hz, 1 H, SiCHC*H*), 4.10–4.18 (m, 2 H, CH_2OTs), 7.26–7.45 (m, 8 H, Ar-H), 7.49–7.59 (m, 4 H, Ar-H), 7.73 (d, J = 8.3 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = –6.4 (+, 1 C, $SiCH_3$), 21.6 (+, 1 C, CH_3 of Ts), 33.3 (–, 1 C, *C*H_2CH_2OTs), 50.3 (+, 1 C, $Ph_2MeSiCH$), 52.6 (+, 1 C, SiCH*C*H), 67.4 (–, 1 C, *C*H_2OTs), 127.9 (+, 2 C, C-Ar), 128.0 (+, 4 C, C-Ar), 129.9 (+, 4 C, C-Ar), 132.8 (q, 1 C, C-Ar), 133.6 (q, 1 C, C-Ar), 133.8 (q, 1 C, C-Ar), 134.8 (+, 4 C, C-Ar), 144.8 (q, 1 C, C-Ar) ppm. IR (NaCl): $\tilde{\nu}$ = 3069, 2962, 1893, 1735, 1598, 1489, 1428, 1361, 1293, 1253, 1177, 1115, 1037, 975, 917, 871, 790, 731, 701, 664 cm^{-1}. MS (DCP, 70 eV): *m*/*z* (%) = 361 (11) [M^+ – Ph], 291 (24), 267 (4) [M^+ – OTs], 197 (100) [$SiMePh_2$], 175 (42), 155 (8) [Ts], 130 (23), 105 (13) [SiPh], 91 (41) [Bn], 65 (16) [C_5H_5]. HRMS (ESI): calcd. for $C_{24}H_{26}O_4SSi$ [M + Na]$^+$ 461.1219; found 461.1218.

***trans*-4-(Tosyloxy)-1-(triphenylsilyl)-1,2-epoxybutane (13d):** According to the procedure given for **8a**,**b**, product **13d** (226 mg, 85%) was obtained from **12d** (257 mg, 0.53 mmol) as a colorless solid after flash chromatography (PE/EA, 10:1). M.p. 118 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.87–2.08 (m, 2 H, CH_2CH_2OTs), 2.42 (s, 3 H, CH_3 of Ts), 2.69 (d, J = 3.3 Hz, 1 H Ph_3SiCH), 2.79 (ddd, J = 6.0, 4.7, 3.4 Hz, 1 H, $Ph_3SiCHCH$), 4.07–4.21 (m, 2 H, CH_2OTs), 7.20–8.13 (m, 19 H, Ar-H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.6 (+, 1 C, CH_3 of Ts), 33.2 (–, 1 C, *C*H_2CH_2OTs), 49.6 (+, 1 C, Ph_3SiCH), 52.9 (+, 1 C, Si*C*HCH), 67.3 (–, 1 C, *C*H_2OTs), 127.8 (+, 2 C, C-Ar), 128.1 (+, 6 C, C-Ar), 129.9 (+, 2 C, C-Ar), 130.1 (+, 3 C, C-Ar), 132.7 (q, 1 C, C-Ar), 133.8 (+, 1 C, C-Ar), 134.7 (q, 1 C, C-Ar), 135.9 (+, 6 C, C-Ar), 144.8 (q, 2 C, C-Ar) ppm. IR (KBr): $\tilde{\nu}$ = 3067, 1700, 1596, 1574, 1485, 1428, 1359, 1304, 1263, 1178, 1114, 987, 920, 901, 877, 819, 780, 748, 700, 659 cm^{-1}. HRMS (ESI): calcd. for $C_{29}H_{28}O_4SSi$ [M + Na]$^+$ 523.1375; found 523.1375.

***trans*-4-Bromo-1-(triethylsilyl)-1-butene (14a):** Following a procedure by Negishi,[11] LiBr (155 mg, 1.79 mmol) was added to **12a** (304 mg, 0.89 mmol) in absolute acetone (20 mL) under an atmosphere of nitrogen, and the mixture was heated at reflux for 10 h. Then, the mixture was poured into water and extracted with petroleum ether (4×). The combined organic phase was dried ($MgSO_4$), and the solvents were removed under vacuum. Product **14a** (194 mg, 87%) was obtained as a colorless liquid. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.48–0.68 (m, 6 H, $SiCH_2$), 0.88–0.98 [m, 9 H, $Si(CH_2CH_3)_3$], 2.62–2.74 (m, 2 H, CH_2CH_2Br), 3.42 (t, J = 7.1 Hz, 2 H, CH_2CH_2Br), 5.68 (dt, J = 18.7, 1.2 Hz, 1 H, SiC*H*=CH), 5.98 (dt, J = 18.7, 6.0 Hz, 1 H, SiCH=C*H*) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 3.4 [-, 3 C, $Si(CH_2CH_3)_3$], 7.3 [+, 3 C, $Si(CH_2CH_3)_3$], 31.9 (–, 1 C, CH_2Br), 39.9 (–, 1 C, *C*H_2CH_2Br), 129.9 (+, 1 C, Et_3SiCH=CH), 143.9 (+, 1 C, Et_3SiCH=*C*H) ppm. IR (NaCl): $\tilde{\nu}$ = 2954, 2875, 2733, 1615, 1459, 1417, 1378, 1329, 1303, 1273, 1238, 1205, 1126, 1015, 932, 784, 720, 636 cm^{-1}. GC–MS (70eV): *m*/*z* (%) = 221 (71), 219 (68) [M^+ – Et], 193 (22), 191 (24), 167 (28), 165 (39), 163 (21), 151 (12), 141 (37) [M^+ – C_2H_4 – Br], 139 (34), 137 (32), 127 (22), 116 (18), 115 (100) [$SiEt_3$], 113 (21), 111 (36), 109 (14), 101 (27), 87 (15), 83 (34), 81 (16), 55 (23). HRMS (EI): calcd. for $C_8H_{16}BrSi$ [M – Et]$^+$ 219.0205; found 219.0206.

***trans*-4-Bromo-1-(dimethylphenylsilyl)-1-butene (14b):** According to the procedure given for **14a**, product **14b** (127 mg, 86%) was obtained from **12b** (198 mg, 0.55 mmol) and LiBr (95 mg, 1.10 mmol) as a colorless liquid. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.35 (s, 6 H, $SiCH_3$), 2.66–2.78 (m, 2 H, CH_2CH_2Br), 3.44 (t, J = 7.2 Hz, 2 H, CH_2Br), 5.83–5.97 (m, 1 H, SiC*H*=CH), 6.08 (dt, J = 18.6, 5.6 Hz, 1 H, SiCH=C*H*), 7.34–7.40 (m, 3 H, Ar-H), 7.49–7.56 (m, 2 H, Ar-H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = –2.6 (+, 2 C, $SiCH_3$), 31.5 (–, 1 C, CH_2Br), 39.7 (–, 1 C, *C*H_2CH_2Br), 127.8 (+, 2 C, C-Ar), 129.0 (+, 1 C, C-Ar), 131.4 (+, 1 C, Si*C*H=CH), 133.8 (+, 2 C, C-Ar), 138.6 (q, 1 C, C-Ar), 144.5 (+, 1 C, SiCH=*C*H) ppm. IR (NaCl): $\tilde{\nu}$ = 3068, 3049, 2957, 1615, 1487, 1427, 1330, 1273, 1248, 1205, 1113, 991, 911, 841, 785, 731, 699, 637 cm^{-1}. GC–MS (70eV): *m*/*z* (%) = 253 (9) [M^+ – Me], 240 (14) [M^+ – 2Me], 190 (19), 189 (100) [M^+ – Br], 161 (15) [M^+ – Br – C_2H_4], 135 (12) [$SiMe_2Ph$]. HRMS (EI): calcd. for $C_{11}H_{14}BrSi$ [M – Me]$^+$ 253.0048; found 253.0046.

***trans*-4-Bromo-1-(methyldiphenylsilyl)-1-butene (14c):** According to the procedure given for **14a**, product **14c** (277 mg, 92%) was obtained as a slightly yellowish oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.64 (s, 3 H, $SiCH_3$), 2.71–2.82 (m, 2 H, CH_2CH_2Br), 3.45 (t, J = 7.0 Hz, 2 H, CH_2Br), 6.07–6.12 (m, 2 H, SiC*H*=C*H*), 7.33–7.42 (m, 6 H, Ar-H), 7.50–7.58 (m, 4 H, Ar-H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = –3.8 (+, 1 C, $SiCH_3$), 31.4 (–, 1 C, CH_2Br), 39.7 (–, 1 C, *C*H_2CH_2Br), 127.8 (+, 4 C, C-Ar), 129.3 (+, 2 C, C-Ar), 129.3 (+, 1 C, Si*C*H=CH), 134.8 (+, 4 C, C-Ar), 136.4 (q, 2 C, C-Ar), 146.7 (+, 1 C, SiCH=*C*H) ppm. IR (NaCl): $\tilde{\nu}$ = 3068, 3048, 2998, 2958, 2924, 2852, 1957, 1885, 1821, 1615, 1589, 1487, 1428, 1330, 1303, 1272, 1251, 1206, 1111, 1067, 1029, 994, 911, 794, 734, 699, 659, 636 cm^{-1}. MS (DCP, 70 eV): *m*/*z* (%) = 315 (12) [M^+ – Me], 302 (14) [M^+ – C_2H_4], 287 (6) [M^+ – Me – C_2H_4], 224 (20), 197 (24) [$SiMePh_2$], 180 (50), 130 (30), 105 (74) [SiPh], 104 (100), 91 (36), 77 (20) [Ph]. HRMS (EI): calcd. for $C_{16}H_{16}BrSi$ [M – Me]$^+$ 315.0205; found 315.0206.

***trans*-4-Bromo-1-(triphenylsilyl)-1-butene (14d):** According to the procedure given for **14a**, product **14d** (288 mg, 98%) was obtained from **12d** (365 mg, 0.75 mmol) and LiBr (131 mg, 1.51 mmol) The product was not further purified, but oxidized to **15d**. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.75–2.87 (m, 2 H, CH_2CH_2Br), 3.47 (t, J = 7.0 Hz, 2 H, CH_2Br), 6.10 (dt, J = 18.4, 6.0 Hz, 1 H, Ph_3SiCH=C*H*), 6.34 (dt, J = 18.6, 1.1 Hz, 1 H, Ph_3SiCH=CH), 7.31–7.69 (m, 15 H, Ar-H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 31.3 (–, 1 C, CH_2Br), 39.7 (–, 1 C, *C*H_2CH_2Br), 127.5 (+,1 C, Ph_3SiCH=CH), 127.9 (+, 6 C, C-Ar), 129.6 (+, 3 C, C-Ar), 134.4 (q, 3 C, C-Ar), 135.9 (+, 6 C, C-Ar), 148.6 (+,1 C, Ph_3SiCH=*C*H) ppm.

***trans*-4-Bromo-1-(triethylsilyl)-1,2-epoxybutane (15a):** According to the procedure given for **8**, product **15a** (105 mg, 66%) was obtained from **14a** (153 mg, 0.61 mmol) as a colorless oil after flash chromatography (PE/EA, 400:1). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.52–0.66 (m, 6 H, $SiCH_2CH_3$), 0.98 (t, J = 7.7 Hz, 9 H, $SiCH_2CH_3$), 2.07–2.19 (m, 2 H, CH_2CH_2Br), 2.12 (d, J = 3.3 Hz, 1 H, $Et_3SiCHCH$), 2.96 (ddd, J = 5.3, 5.3, 3.5 Hz, 1 H, $Et_3SiCHCH$), 3.51 (t, J = 6.7 Hz, 2 H, CH_2Br) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = –1.8 (–, 3 C, $SiCH_2CH_3$), 7.2 (+, 3 C, $SiCH_2CH_3$), 29.4 (–, 1 C, CH_2Br), 37.4 (–, 1 C, *C*H_2CH_2Br), 50.2 (+, 1 C, $Et_3SiCHCH$), 54.1 (+, 1 C, $Et_3SiCHCH$) ppm. IR (NaCl): $\tilde{\nu}$ = 2955, 2912, 2876, 1459, 1416, 1293, 1264, 1236, 1209, 1016, 974, 920, 869, 721 cm^{-1}. MS (DCP, 70 eV): *m*/*z* (%) = 209 (40), 207 (34), 167 (65), 165 (71), 155 (14), 139 (100), 138 (10), 137 (88), 127 (21), 115 (79) [$SiEt_3$], 111 (11), 109 (15), 103 (12), 99 (15), 87 (100) [$C_4H_{11}Si$], 85 (16), 75 (34), 71 (24), 69 (24), 67 (12), 59 (86), 58 (21), 57 (31), 55 (31), 53 (19). HRMS (ESI): calcd. for $C_{10}H_{21}BrOSi$ [M + Na]$^+$ 287.0443; found 287.0445.

***trans*-4-Bromo-1-(dimethylphenylsilyl)-1,2-epoxybutane (15b):** According to the procedure given for **8**, product **15b** (120 mg, 91%) was obtained from **14b** (123 mg, 0.46 mmol) as a colorless oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.34 and 0.36 (each s, 3 H, CH_3), 2.09–2.19 (m, 2 H, CH_2CH_2Br), 2.26 (d, J = 3.5 Hz, 1 H, $PhMe_2S$-

iC*H*), 2.93 (dt, *J* = 5.4, 3.4 Hz, 1 H, SiCHC*H*), 3.49 (t, *J* = 6.7 Hz, 2 H, CH_2Br), 7.32–7.43 (m, 3 H, Ar-H), 7.50–7.61 (m, 2 H, Ar-H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = –5.2 and –5.1 (each +, 1 C, $SiCH_3$), 29.3 (–, 1 C, CH_2Br), 37.0 (–, 1 C, *C*H_2CH_2Br), 51.2 (+, 1 C, $PhMe_2SiCH$), 54.6 (+, 1 C, SiCH*C*H), 128.0 (+, 2 C, C-Ar), 129.6 (+, 1 C, C-Ar), 133.9 (+, 2 C, C-Ar), 135.8 (q, 1 C, C-Ar) ppm. IR (NaCl): ṽ = 3070, 3049, 2961, 1728, 1589, 1488, 1428, 1291, 1250, 1209, 1116, 999, 923, 834, 787, 735, 701, 635 cm^{-1}. GC–MS (70eV): *m*/*z* (%) = 256 (8) [$M^+ - C_2H_4$], 209 (23), 191 (35), 177 (14), 135 (100) [$SiMe_2Ph$], 131 (43), 117 (19), 105 (18), 91 (16), 75 (27) [C_2H_7OSi]. HRMS (ESI): calcd. for $C_{12}H_{17}BrOSi$ [M + Na]$^+$ 307.0130; found 307.0136.

***trans*-4-Bromo-1-(methyldiphenylsilyl)-1,2-epoxybutane (15c):** According to the procedure given for **8**, product **15c** (211 mg, 84%) was obtained from **14c** (239 mg, 0.72 mmol) as a colorless oil after flash chromatography (PE/EA, 30:1). ^1H NMR (200 MHz, $CDCl_3$): δ = 0.61 (s, 3 H, CH_3), 2.19 (dt, *J* = 6.6, 5.6 Hz, 2 H, C*H*$_2$CH$_2$Br), 2.54 (d, *J* = 3.5 Hz, 1 H, $Ph_2MeSiCH$), 2.94 (dt, *J* = 5.4, 3.4 Hz, 1 H, SiCHC*H*), 3.49 (t, *J* = 6.7 Hz, CH_2Br), 7.33–7.45 (m, 6 H, Ar-H), 7.56–7.64 (m, 4 H, Ar-H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = –6.4 (+, 1 C, CH_3), 29.1 (–, 1 C, CH_2Br), 36.9 (–,1 C, *C*H_2CH_2Br), 50.3 (+, 1 C, $Ph_2MeSiCH$), 54.7 (+, 1 C, SiCH*C*H), 128.0 (+, 4 C, C-Ar), 129.9 (+, 2 C, C-Ar), 133.7 (q, 1 C, C-Ar), 134.0 (q, 1 C, C-Ar), 134.8 (+, 2 C, C-Ar), 134.9 (+, 2 C, C-Ar) ppm. IR (NaCl): ṽ = 3069, 3048, 2999, 2965, 1589, 1487, 1428, 1290, 1253, 1209, 1115, 998, 922, 869, 791, 730, 700, 656 cm^{-1}. GC–MS (70eV): *m*/*z* (%) = 318 (16) [$M^+ - C_2H_4$], 253 (32), 197 (44) [$SiMePh_2$], 181 (66), 175 (33), 165 (32), 131 (100). HRMS (ESI): calcd. for $C_{17}H_{19}BrOSi$ [M + NH_4]$^+$ 364.0732; found 364.0730.

***trans*-4-Bromo-1-(triphenylsilyl)-1,2-epoxybutane (15d):** According to the procedure given for **8**, product **15d** (120 mg, 59%) was obtained from **14d** (200 mg,0.50 mmol) as a colorless solid after flash chromatography (PE/EA, 60:1). M.p. 93 °C. ^1H NMR (200 MHz, $CDCl_3$): δ = 2.23 (dt, *J* = 6.8, 5.4 Hz, 2 H, C*H*$_2$CH$_2$Br), 2.80 (d, *J* = 3.3 Hz, 1 H, C*H*$SiPh_3$), 2.93 (dt, *J* = 5.4, 3.3 Hz, 1 H, SiCHC*H*), 3.47 (t, *J* = 6.8 Hz, 2 H, CH_2Br), 7.34–7.62 (m, 15 H, Ar-H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 28.9 (–, 1 C, CH_2Br), 37.0 (–, 1 C, *C*H_2CH_2Br), 49.5 (+, *C*$HSiPh_3$), 54.9 (+, 1 C, SiCH*C*H), 128.1 (+, 2 C, C-Ar), 130.1 (+, 1 C, C-Ar), 131.9 (q, 1 C, C-Ar), 135.9 (+, 2 C, C-Ar) ppm. IR (KBr): ṽ = 3066, 2919, 1587, 1484, 1427, 1211, 1185, 1113, 997, 870, 811, 789, 741, 699 cm^{-1}. HRMS (ESI): calcd. for $C_{22}H_{21}BrOSi$ [M + Na]$^+$ 431.0443; found 431.0444.

Synthesis of 1,4-Bis(phenylthio)-1-(trimethylsilyl)butan-2-ol (16) by Reaction of *cis*-Silylepoxide 8a with Lithium Thiophenoxide: On the basis of a literature procedure,[30] BuLi (2.45 M in hexane, 0.26 mL, 0.33 mmol) was added dropwise to thiophenol (0.06 mL, 0.6 mmol) in absolute THF (1 mL) at –78 °C under an atmosphere of nitrogen. After 10 min at –78 °C, **8a** (78 mg, 0.25 mmol) in absolute THF (1 mL) was added dropwise. The reaction mixture was allowed to reach room temperature within 2 h. Then, saturated aqueous NH_4Cl (3 mL) and water (4 mL) were added, the phases were separated, and the aqueous phase was extracted with diethyl ether (2×). The combined organic phase was washed with NaOH (5%, 10 mL), dried ($MgSO_4$), and the solvents removed in vacuo. After flash chromatography (PE/EA, 10:1), a colorless oil was isolated. Yield: 65 mg (72%). ^1H NMR (200 MHz, $CDCl_3$): δ = 0.18 (s, 9 H, $SiCH_3$), 1.57–1.92 (m, 2 H, C*H*$_2$CH$_2$SPh), 2.11 (br. s, 1 H, OH), 2.57 (d, *J* = 3.5 Hz, 1 H, PhSC*H*TMS), 2.75–3.04 (m, 2 H, C*H*$_2$SPh), 4.03 (dt, *J* = 9.0, 3.7 Hz, 1 H, C*H*OH), 7.12–7.41 (m, 10 H, Ar-H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = –1.7 (+, 3 C, $SiCH_3$), 30.7 (–, 1 C, *C*H_2CH_2SPh), 36.4 (–, 1 C, *C*H_2SPh), 43.6 (+, 1 C, PhS*C*HTMS), 71.1 (+, 1 C, CHOH), 126.0 (+, 1 C, C-Ar), 126.5 (+, 1 C, C-Ar), 128.8 (+, 2 C, C-Ar), 129.0 (+, 2 C, C-Ar), 130.1 (+, 2 C, C-Ar), 136.2 (q, 1 C, C-Ar), 138.1 (q, 1 C, C-Ar) ppm. IR (NaCl): ṽ = 3473, 3058, 3018, 2954, 2899, 1943, 1583, 1479, 1439, 1378, 1249, 1216, 1091, 1067, 1043, 1025, 1000, 841, 740, 691, 665, 618 cm^{-1}. MS (DCP) (70 eV) *m*/*z* (%) = 362 (1) [M^+], 253 [M^+ – SPh], 163 (100) [M^+ – SPh – TMSOH], 149 (14), 123 (23), 109 (10) [SPh], 73 (50) [TMS]. HRMS (ESI): calcd. for $C_{19}H_{26}OS_2Si$ [M + Na]$^+$ 385.1092; found 385.1093.

Synthesis of *trans*-5-(Tosyloxy)-1-(trimethylsilyl)-3-(trimethylsilyloxy)-1-pentene (18) by Reaction of *cis*-Epoxysilane 8a with Lithiated Phenylthio(trimethylsilyl)methane (17): BuLi (2.45 M in hexane, 0.90 mL, 2.2 mmol) was added dropwise to protonated **17** (137 mg, 0.7 mmol) in absolute THF (4 mL) at 0 °C under an atmosphere of nitrogen. Stirring was continued for 20 min. Then, the yellow solution of **17** was added dropwise to **8a** (111 mg, 0.35 mmol) in absolute THF (4 mL) at 0 °C. After 15 min at 0 °C the reaction mixture was stirred at room temperature overnight. Water was added, the phases separated, and the aqueous phase was extracted with diethyl ether (3×). The combined organic phase was dried ($MgSO_4$) and the solvents were evaporated under vacuum. The product was isolated by flash chromatography as a colorless oil. Yield: 66 mg (47%). ^1H NMR (200 MHz, $CDCl_3$): δ = 0.03, 0.04 (each s, 9 H, $SiCH_3$), 1.66–1.84 (m, 2 H, C*H*$_2$CH$_2$OTs), 2.44 (s, 3 H, CH_3 of Ts), 3.99–4.21 (m, 3 H, C*H*OTMS, C*H*$_2$OTs), 5.72 (d, *J* = 18.7 Hz, 1 H, SiC*H*=CH), 5.87 (dd, *J* = 18.7, 5.0 Hz, 1 H, SiCH=C*H*), 7.34 (d, *J* = 7.9 Hz, 2 H, Ar-H), 7.79 (d, *J* = 8.3 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = –1.5, 0.1 (each +, 3 C, $SiCH_3$), 21.6 (+, 1 C, *C*H$_3$of Ts), 36.6 (–, 1 C, *C*H_2CH_2OTs), 67.2 (–, 1 C, *C*H_2OTs), 71.4 (+, 1 C, *C*HOTMS), 127.9 (+, 2 C, C-Ar), 129.8 (+, 2 C, C-Ar), 130.1 (+, 1 C, Si*C*H=CH), 133.2 (q, 1 C, C-Ar), 144.7 (q, 1 C, C-Ar), 147.4 (+, 1 C, SiCH=*C*H) ppm. IR (NaCl): ṽ = 3032, 2956, 2899, 1922, 1621, 1599, 1496, 1366, 1307, 1250, 1189, 1177, 1097, 1021, 994, 922, 839, 760, 690, 664, 637, 609 cm^{-1}. GC–MS (70 eV): *m*/*z* (%) = 385 (6) [M^+ – Me], 317 (100), 303 (10), 155 (11), 141 (16), 127 (13), 103 (24), 91 (8), 73 (20), 67 (27). HRMS (ESI): calcd. for $C_{15}H_{24}O_4SSi$ [M + Na – TMS]$^+$ 351.1062; found 351.1068.

Synthesis of 1,4-Bis(phenylthio)-2-(dimethylphenylsilyloxy)butane (19) by Reaction of *trans*-Silylepoxide 13b with Magnesium Chloride Thiophenoxide: Methylmagnesium chloride (1 M in ether, 0.06 mL, 0.17 mmol) was added dropwise to thiophenol (0.02 mL, 0.17 mmol) in absolute THF (0.3 mL) at –78 °C under an atmosphere of nitrogen. After 10 min, **13b** (65 mg, 0.17 mmol) in absolute THF (1 mL) was added dropwise to this solution. The mixture was warmed to room temperature and saturated aqueous NH_4Cl (2 mL) was added. The phases were separated, and the aqueous phase was extracted with diethyl ether (2×). The combined organic phase was washed with NaOH (5%) and dried ($MgSO_4$). The product was purified by flash chromatography (PE/EA, 10:1) to give a colorless oil. Yield: 40 mg (55%). ^1H NMR (200 MHz, $CDCl_3$): δ = 0.43 (s, 6 H, $SiCH_3$), 1.53–1.67, 1.72–1.89 (each m, 1 H, C*H*$_2$CH$_2$SPh), 2.71–3.10 (m, 4 H, C*H*$_2$SPh), 3.94–4.07 (m, 1 H, CHOSi), 7.12–7.64 (m, 15 H, Ar-H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = –3.0, –2.6 (each +, 1 C, $SiCH_3$), 30.5 (–, 1 C, *C*H_2CH_2SPh), 35.1 (–, 1 C, *C*H_2SPh), 44.3 (–, 1 C, PhS*C*H_2CHOSi), 72.3 (+, 1 C, CHOSi), 125.9 (+, 1 C, C-Ar), 126.4 (+, 1 C, C-Ar), 127.9 (+, 2 C, C-Ar), 128.9 (+, 2 C, C-Ar), 129.0 (+, 2 C, C-Ar), 129.2 (+, 2 C, C-Ar), 129.5 (+, 1 C, C-Ar), 129.9 (+, 2 C, C-Ar), 134.1 (+, 2 C, C-Ar), 136.2 (q, 1 C, C-Ar), 136.8 (q, 1 C, C-Ar), 137.5 (q, 1 C, C-Ar) ppm. IR (NaCl): ṽ = 3069, 2956, 1583, 1480, 1438, 1427, 1251, 1113, 1026, 823, 788, 738, 692 cm^{-1}. MS (DCP, 70 eV): *m*/*z* (%) = 281 (33), 229 (68), 218 (47),

180 (39), 163 (95), 155 (21), 149 (75), 137 (91), 135 (100) [$SiMe_2Ph$], 124 (64), 123 (98) [CH_2SPh], 110 (69), 109 (84) [SPh], 91 (74), 77 (39) [Ph], 65 (50). LRMS (ESI): calcd. for $C_{24}H_{28}OS_2Si$ [M + Na]$^+$ 447.1; found 447.1.

Synthesis of 5-(Tosyloxy)-2-pentenenitrile (20) and 3-Hydroxy-5-(tosyloxy)pentanenitrile (21) by Reaction of *trans*-Silylepoxide 13b with Diethylaluminium Cyanide: Adopting a literature procedure,[31] diethylaluminium cyanide (1 M in toluene, 0.31 mL, 0.31 mmol) was added dropwise to **13b** (116 mg, 0.31 mmol) in toluene (3 mL) at –78 °C under an atmosphere of nitrogen. Stirring was continued for 3 h, the mixture was then warmed to room temperature and heated at reflux for 6 h. More diethylaluminium cyanide in THF (0.62 mL, 0.62 mmol) was added and the stirring continued at room temperature for 2 d. A mixture of saturated aqueous sodium potassium tartrate and EA (1:1, 4 mL) was added, and the phases were separated. The aqueous phase was extracted with EA and the combined organic phase was dried (Na_2SO_4). Flash chromatography gave products **20** and **21**. Data for **20** (*E*:*Z*, 4.5:1): Yellowish oil. Yield: 45 mg (58%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.45 (s, 3 H, CH_3 of Ts), 2.50–2.61 (m, 2 H, *E*-CH_2CH$_2$OTs), 2.68–2.79 (m, 2 H, *Z*-CH_2CH$_2$OTs), 4.11 (t, J = 6.0 Hz, 2 H, CH_2OTs), 5.36 (dt, J = 16.4, 1.7 Hz, 1 H, *E*-NC-C*H*=CH), 6.45 (dt, J = 11.1, 7.3 Hz, 1 H, *Z*-NC-CH=C*H*), 6.49 (dt, J = 16.4, 6.9 Hz, 1 H, *E*-NC-CH=C*H*), 7.32–7.40 (m, 2 H, Ar-H), 7.73–7.80 (m, 2 H, Ar-H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.6 (+, 1 C, CH_3 of Ts), 31.1 (–, 1 C, *Z*-CH_2CH$_2$OTs), 32.4 (–, 1 C, *E*-CH_2CH$_2$OTs), 67.0 (–, 1 C, *E*-CH_2OTs), 67.5 (–, 1 C, *Z*-CH_2OTs), 102.7 (+, 1 C, *Z*-NC-*C*H=CH), 103.0 (+, 1 C, *E*-NC-*C*H=CH), 116.6 (q, 1 C, CN), 127.8 (+, 2 C, C-Ar), 129.9 (+, 2 C, C-Ar), 132.4 (q, 1 C, C-Ar), 145.3 (q, 1 C, C-Ar), 148.6 (+, 1 C, *Z*-NC-CH=*C*H), 149.3 (+, 1 C, *E*-NC-CH=*C*H) ppm. IR (NaCl): $\tilde{\nu}$ = 2225, 1598, 1360, 1177, 1097, 957, 817, 757, 665 cm^{-1}. MS (DCP, 70 eV): *m*/*z* (%) = 251 (17) [M$^+$], 187 (18) [M$^+$ – SO_2], 172 (16) [M$^+$ – SO_2Me], 156 (15) [M$^+$ – $MeOSO_2$], 155 (97) [Ts], 137 (43), 91 (100) [Bn], 65 (45) [C_5H_5]. HRMS (EI): calcd. for $C_{12}H_{13}NO_3S$ [M]$^+$ 251.0616; found 251.0617. HRMS (ESI): calcd. for $C_{12}H_{14}NO_3S$ [M + H]$^+$ 252.0694; found 252.0698. Data for **21**: Yellow oil. Yield: 10 mg (12%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.74–2.07 (m, 2 H, CH_2CH$_2$OTs), 2.46 (s, 3 H, CH_3 of Ts), 2.53 (d, J = 3.7 Hz, 1 H, NC-CH_2), 2.56 (d, J = 2.8 Hz, 1 H, NC-CH_2), 2.65 (br. s, 1 H, OH), 4.01–4.20 (m, 2 H, CH_2OTs), 4.23–7.37 (m, 1 H, C*H*OH), 7.37 (d, J = 7.9 Hz, 2 H, Ar-H), 7.79 (d, J = 8.3 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.7 (+, 1 C, CH_3 of Ts), 26.2 (–, 1 C, NC-*C*H$_2$), 35.3 (–, 1 C, *C*H$_2$CH$_2$OTs), 63.8 (+, 1 C, CHOH), 66.5 (–, 1 C, *C*H$_2$OTs), 117.1 (q, 1 C, CN), 127.9 (+, 2 C, C-Ar), 130.0 (+, 2 C, C-Ar), 132.5 (q, 1 C, C-Ar), 145.3 (q, 1 C, C-Ar) ppm. IR (NaCl): $\tilde{\nu}$ = 3483, 2927, 2252, 1598, 1355, 1174, 1097, 1019, 933, 817, 768, 665 cm^{-1}. MS (DCP, 70 eV): *m*/*z* (%) = 269 (33) [M$^+$], 205 (72) [M$^+$ – SO_2], 173 (82), 172 (82), 155 (84) [Ts], 98 (40) [M$^+$ – OTs], 91 (100) [Bn], 65 (84) [C_5H_5]. HRMS (ESI): calcd. for $C_{12}H_{15}NO_4S$ [M + Na + MeCN]$^+$ 333.0885; found 333.0887.

General Procedure for the Reaction of Epoxysilanes 8, 13, and 15 with Lithiated Bis(methylthio)trimethylsilylmethane (23): BuLi (2.45 M in hexane, 1.9 mL, 2.2 mmol) was added dropwise to **23** (360 mg, 2 mmol) in absolute THF (2 mL) at – 78 °C under an atmosphere of nitrogen. Stirring was continued for 1 h at –78 °C, then at 0 °C for 30 min and finally at room temperature for 15 min. Then, the solution of the epoxide (1 mmol) in absolute THF (3 mL) was added slowly at 0 °C. The reaction mixture was stirred at room temperature overnight. The resulting mixture was poured into a mixture of saturated aqueous NH_4Cl/water/diethyl ether (1:1:1), the phases separated, and the aqueous phase extracted with diethyl ether (1×). The combined organic phase was dried ($MgSO_4$), and the solvents were evaporated under vacuum. The product was isolated by flash chromatography (PE; PE/EA, 400:1; 200:1; 100:1). The following products were obtained:

***cis*-1,5,5-Tris(thiomethyl)-5-trimethylsilyl-1-pentene (25):** From **8a** (96 mg, 0.31 mmol) or **8b** (61 mg, 0.16 mmol). Yellow oil. Yield: 14 mg (16%) from **8a**, 23 mg (51%) from **8b**. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.22 (s, 9 H, $SiCH_3$), 1.77–1.88 (m, 2 H, =CHCH_2CH_2), 2.05 (s, 6 H, SCH_3), 2.27 (s, 3 H, SCH_3), 2.29–2.40 (m, 2 H, =CHCH_2), 5.49 (dt, J = 9.3, 7.2 Hz, 1 H, =C*H*CH$_2$), 5.90 (dt, J = 9.3, 1.2 Hz, 1 H, MeSC*H*=CH) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = –1.0 (+, 3 C, $SiCH_3$), 11.2, 7.0 (each +, 1 C, SCH_3), 26.7 (–, 1 C, C=CH*C*H$_2$), 36.6 (–, 1 C, =CHCH$_2$*C*H$_2$), 47.1 [q, 1 C, *C*(SMe)TMS], 127.6 (+, 1 C, MeSCH=*C*H), 127.6 (+, 1 C, MeS*C*H=CH) ppm. IR (NaCl): $\tilde{\nu}$ = 2955, 2918, 1734, 1608, 1435, 1314, 1248, 1077, 962, 840, 757, 692, 625 cm^{-1}. GC–MS (70 eV): *m*/*z* (%) = 265 (18) [M$^+$], 233 (100) [M$^+$ – SMe], 217 (23), 193 (18) [$CH_2C(SMe)_2TMS$], 185 (18), 159 (27), 145 (56), 113 (21), 87 (60) [C_4H_7S], 73 (30) [TMS], 45 (33) [CHS]. HRMS (EI): calcd. for $C_{10}H_{21}S_2Si$ [M – SMe]$^+$ 233.0854; found 233.0852.

2-(Methylthio)-2-(trimethylsilyl)-5-(1-methylthio-1-triethylsilyl)-methyl-tetrahydrofuran (28a): From **13a** (220 mg, 0.62 mmol) or **15a** (97 mg, 0.37 mmol). Colorless oil. Yield: 108 mg (48%) from **13a**, 81 mg (60%) from **15a**. ^{1}H NMR (400 MHz): δ = 0.14 (s, 9 H, $SiCH_3$), 0.61–0.70 (m, 6 H, SiCH_2CH$_3$), 0.98 (t, J = 7.9 Hz, 9 H, SiCH$_2$CH_3), 1.74–1.92 (m, 2 H, CH_2), 2.04 (s, 3 H, SCH_3), 2.20–2.25 (m, 2 H, CH_2), 2.22 (s, 3 H, CHSCH_3), 2.31 [d, J = 4.5 Hz, 1 H, C*H*(SMe)], 4.47 (ddd, J = 8.9, 6.3, 4.5 Hz, 1 H, C*H*-THF ring) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = –2.6 (+, 3 C, $SiCH_3$), 3.3 (–, 3 C, Si*C*H$_2$CH$_3$), 7.7 (+, 3 C, SiCH$_2$*C*H$_3$), 12.8 (+, 1 C, SCH_3), 20.8 (+, 1 C, CHS*C*H$_3$), 29.4 (–, 1 C, CH_2), 36.2 (+, 1 C, *C*HSCH$_3$), 36.4 (–, 1 C, *C*H$_2$), 81.2 (+, 1 C, *C*H-THF ring), 85.3 (q, 1 C) ppm. IR (NaCl): $\tilde{\nu}$ = 2954, 2917, 2875, 1458, 1416, 1378, 1311, 1247, 1089, 1019, 953, 839, 732, 624 cm^{-1}. GC–MS (70eV): *m*/*z* (%) = 301 (60) [M$^+$ – MeSO], 287 (29) [M$^+$ – Me_2S – Me], 273 (32) [M$^+$ – Me_2S – Et], 269 (26), 243 (20), 215 (18), 185 (29), 176 (42) [$C_8H_{20}SSi$], 153 (44), 147 (64), 141 (80), 133 (30), 119 (34), 115 (100) [$SiEt_3$], 105 (27), 87 (90), 73 (87) [TMS], 59 (60). HRMS (ESI): calcd. for $C_{16}H_{36}OS_2Si_2$ [M + Na]$^+$ 387.1644; found 387.1640.

2-(Methylthio)-2-(trimethylsilyl)-5-(1-methylthio-1-dimethylphenylsilyl)methyl-tetrahydrofuran (28b): From **13b** (141 mg, 0.37 mmol) or **15b** (113 mg, 0.40 mmol). Colorless oil. Yield: 58 mg (41%) from **13b**, 105 mg (68%) from **15b**. ^{1}H NMR (400 MHz): δ = 0.12 (s, 9 H, $SiCH_3$), 0.40 and 0.42 [each s, 3 H, Si(CH_3)$_2$Ph], 1.64–1.74 (m, 1 H, CHCH_2CH$_2$), 1.83 (ddd, J = 13.0, 8.9, 6.0 Hz, 1 H, CHCH$_2$CH_2), 1.96 (s, 3 H, SCH_3), 1.97–2.02 (m, 1 H, CHCH_2CH$_2$), 2.16–2.19 (m, 1 H, CHCH$_2$CH_2), 2.34 (d, J = 4.7 Hz, 1 H, C*H*SMe), 4.40 (ddd, J = 8.5, 6.7, 4.8 Hz, 1 H, C*H*-THF ring), 7.33–7.38 (m, 3 H, Ar-H), 7.56–7.61 (m, 2 H, Ar-H) ppm. ^{13}C NMR (100 MHz): δ = –3.4 and –3.2 [each +, 1 C, Si(*C*H$_3$)$_2$Ph], –2.6 (+, 3 C, $SiCH_3$), 12.7 (+, 1 C, SCH_3), 20.2 [+, 1 C, CH(S*C*H$_3$)], 29.2 (–, 1 C, CH*C*H$_2$CH$_2$), 36.2 (–, 1 C, CHCH$_2$*C*H$_2$), 38.8 [+, 1 C, *C*H(SCH$_3$)], 81.1 (+, 1 C, *C*H-THF ring), 85.5 (q, 1 C, C-THF ring), 127.7 (+, 2 C, C-Ar), 129.2 (+, 1 C, C-Ar), 134.0 (+, 2 C, C-Ar), 137.2 (q, 1 C, C-Ar) ppm. IR (NaCl): $\tilde{\nu}$ = 3069, 3049, 2957, 2920, 1600, 1487, 1427, 1362, 1312, 1248, 1186, 1115, 1024, 956, 838, 736, 701, 648, 623 cm^{-1}. GC–MS (70eV): *m*/*z* (%) = 321 (15) [M$^+$ – MeSO], 293 (13), 209 (16), 196 (14) [$C_{10}H_{16}SSi$], 153 (20), 147 (35), 141 (49), 135 (100) [$SiMe_2Ph$], 105 (25) [SiPh], 87 (24), 73 (85) [TMS]. HRMS (ESI): calcd. for $C_{18}H_{32}OS_2Si_2$ [M + Na]$^+$ 407.1331; found 407.1338.

2-(Methylthio)-2-(trimethylsilyl)-5-(1-methylthio-1-diphenylmethylsilyl)methyl-tetrahydrofuran (28c): From **13c** (91 mg, 0.21 mmol) or from **15c** (200 mg, 0.58 mmol). Yield: 37 mg (40%) from **13c**, 120 mg (46%) from **15c**. Slightly yellowish oil. ^{1}H NMR (400 MHz): δ = 0.11 (s, 9 H, $SiCH_3$), 0.68 (s, 3 H, $SiCH_3Ph_2$), 1.66–1.74 (m, 1 H, $CHCH_2CH_2$), 1.81 (ddd, J = 12.7, 8.8, 5.8 Hz, 1 H, $CHCH_2CH_2$), 1.90 (s, 3 H, SCH_3), 1.90–1.96 (m, 1 H, $CHCH_2CH_2$), 2.18 [s, 3 H, $CH(SCH_3)$], 2.21–2.25 (m, 1 H, HCH_2CH_2), 2.80 [d, J = 4.5 Hz, 1 H, CH(SMe)], 4.48 (ddd, J = 8.5, 6.6, 4.4 Hz, 1 H, CH-THF ring), 7.34–7.69 (m, 10 H, Ar-H) ppm. ^{13}C NMR (100 MHz): δ = –4.4 (+, 1 C, $SiCH_3Ph_2$), –2.7 [+, 3 C, $Si(CH_3)_3$], 12.6 (+, 1 C, SCH_3), 20.5 [+, 1 C, $CH(SCH_3)$], 29.1 (–, 1 C, $CHCH_2CH_2$), 36.2 (–, 1 C, $CHCH_2CH_2$), 37.3 [+, 1 C, $CH(SCH_3)$], 80.9 (+, 1 C, CH-THF ring), 85.4 (q, 1 C, C-THF ring), 127.7 (+, 2 C, C-Ar), 127.8 (+, 2 C, C-Ar), 129.5 (+, 2 C, C-Ar), 134.6 (+, 2 C, C-Ar), 135.0 (+, 2 C, C-Ar), 135.1 (q, 1 C, C-Ar), 135.6 (q, 1 C, C-Ar) ppm. IR (NaCl): $\tilde{\nu}$ = 3069, 3049, 2958, 2920, 1955, 1599, 1488, 1428, 1352, 1313, 1249, 1194, 1112, 1028, 956, 890, 840, 724, 698, 628 cm^{-1}. GC–MS (70eV): m/z (%) = 383 (79) [M$^+$ – MeSO], 355 (42), 321 (28), 305 (25), 273 (34), 271 (45), 258 (80), 257 (57) [$C_{15}H_{17}SSi$], 241 (26), 221 (27), 209 (58), 197 (38) [$SiMePh_2$], 185 (100), 179 (60), 167 (26), 153 (39), 141 (81), 105 (34) [SiPh], 87 (93), 73 (89) [TMS]. HRMS (ESI): calcd. for $C_{23}H_{34}OS_2Si_2$ [M + Na]$^+$ 469.1487; found 469.1491.

2-(Methylthio)-2-(trimethylsilyl)-5-(1-methylthio-1-triphenylsilyl)-methyl-tetrahydrofura (28d): From **13d** (213 mg, 0.43 mmol) or from **15d** (95 mg, 0.23 mmol). Yield: 47 mg (21%) from **13d**, 41 mg (35%) from **15d**. Colorless oil. ^{1}H NMR (400 MHz): δ = 0.12 (s, 9 H, $SiCH_3$), 1.76–1.80 (m, 2 H, CH_2), 1.87 (s, 3 H, SCH_3), 2.09 (dd, J = 14.5, 7.4 Hz, 2 H, CH_2), 2.26 [s, 3 H, $CH(SCH_3)$], 3.19 [d, J = 3.5 Hz, 1 H, CH(SMe)], 4.71 (ddd, J = 7.3, 7.3, 3.5 Hz, 1 H, CH-THF ring), 7.33–7.48 (m, 15 H, Ar-H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = –2.6 (+, 3 C, $SiCH_3$), 12.4 (+, 1 C, SCH_3), 21.2 [+, 1 C, $CH(SCH_3)$], 28.9 (–, 1 C, CH_2), 36.3 (–, 1 C, CH_2), 36.8 [+, 1 C, $CH(SCH_3)$], 80.7 (+, 1 C, CH-THF ring), 85.3 (q, 1 C, C-THF ring), 127.8 (+, 6 C, C-Ar), 129.7 (+, 3 C, C-Ar), 133.5 (q, 3 C, C-Ar), 136.0 (+, 6 C, C-Ar) ppm. IR (NaCl): $\tilde{\nu}$ = 3069, 3049, 2998, 2956, 2919, 1960, 1893, 1824, 1679, 1589, 1567, 1485, 1428, 1311, 1248, 1218, 1190, 1158, 1110, 1027, 956, 840, 755, 700, 625 cm^{-1}. GC–MS (70eV): m/z (%) = 445 (5) [M$^+$ – MeSO], 320 (10) [$C_{20}H_{20}SSi$], 271 (7), 259 (100) [$SiPh_3$], 181 (9), 141 (11), 87 (8), 73 (29) [TMS], 45 (11). HRMS (ESI): calcd. for $C_{28}H_{36}OS_2Si_2$ [M + Na]$^+$ 531.1644; found 531.1652.

***trans*-5,5-Bis(methylthio)-5-(trimethylsilyl)-1-(phenyl)-1-pentene (35):** Was isolated along with **28d**. Yield: 32 mg (24%) from **13d**, 21 mg (29%) from **15d**. Yellow oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.23 (s, 9 H, $SiCH_3$), 1.88–1.99 [m, 2 H, $CH_2C(SMe)_2$], 2.07 (s, 6 H, SCH_3), 2.35–2.49 (m, 2 H, $PhCH{=}CHCH_2$), 6.19 (dt, J = 15.8, 6.6 Hz, 1 H, $PhCH{=}CHCH_2$), 6.42 (dt, J = 15.8, 1.2 Hz, 1 H, $PhCH{=}CH$), 7.17–7.38 (m, 5 H, Ar-H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = –0.9 (+, 3 C, $SiCH_3$), 11.3 (+, 2 C, SCH_3), 30.3 (–, 1 C, $PhCH{=}CHCH_2$), 37.5 [-, 1 C, $CH_2C(SMe)_2$], 47.1 [q, 1 C, $C(SMe)_2$], 125.9 (+, 2 C, C-Ar), 127.0 (+, 1 C, C-Ar), 128.5 (+, 2 C, C-Ar), 129.9 (+, 1 C, C-olefin), 130.2 (+, 1 C, C-olefin), 137.5 (q, 1 C, C-Ar) ppm. IR (NaCl): $\tilde{\nu}$ = 2918, 1249, 963, 840, 693. GC–MS (70eV): m/z (%) = 295 (68) [M$^+$ – Me], 263 (5) [M$^+$ – SMe], 247 (19), 193 (13) [$CH_2C(SMe)_2TMS$], 175 (17), 117 (100) [C_9H_9], 73 (42) [TMS]. HRMS (EI): calcd. for $C_{15}H_{23}S_2Si$ [M – Me]$^+$ 295.1010; found 295.1010.

***trans*-1-Phenyl-4-(tosyloxy)-1-butene (34):** BuLi (2.45 M in hexane, 1.02 mL, 2.5 mmol) was added dropwise to **23** (396 mg, 2.2 mmol) in absolute THF (5 mL) at –78 °C under an atmosphere of nitrogen. Stirring was continued for 1 h at –78 °C, then at 0 °C for 30 min, and finally at room temperature for 15 min. Then, a solution of **13c or 13d** (1 mmol) in absolute THF (5 mL) was added slowly at –78 °C. The reaction mixture was warmed to –20 °C for 1.5 h and stirred at room temperature overnight. Workup was carried out as given above for the synthesis of **26**. Yield: 35 mg (64%) from **13d** (89 mg, 0.18 mmol), 276 mg (57%) from **13c** (707 mg, 1.61 mmol). Colorless oil. The spectra agree with the data in ref.[32]

2-(Trimethylsilyl)-5-(1-methylsulfonyl-1-triethylsilyl)methyl-4,5-dihydrofuran (31): The oxidation procedure was based on a literature method.[33] Compound **28a** (169 mg, 0.46 mmol) in CH_2Cl_2 (10 mL) was diluted with acetone (2 mL) and saturated aqueous $NaHCO_3$ (35 mL). At 0 °C, Oxone (5.697 g, 9.27 mmol) in water (20 mL) was carefully added to the two-phase mixture. After another 30 min at 0 °C the mixture was stirred overnight at room temperature The phases were separated, and the aqueous phase was extracted with CH_2Cl_2 (2×). The combined organic phase was dried (Na_2SO_4), and the solvents were removed in vacuo. The product was purified by flash chromatography (PE/EA, 5:1). Yield: 66 mg (41%). Colorless solid. M.p. 44–45 °C. ^{1}H NMR (400 MHz): δ = 0.12 (s, 9 H, $SiCH_3$), 0.74–0.97 (m, 6 H, $SiCH_2CH_3$), 1.02 (t, J = 7.7 Hz, 9 H, $SiCH_2CH_3$), 2.58 (ddd, J = 15.7, 11.1, 2.8 Hz, 1 H, $CH_2CH{=}C$), 2.95 (s, 3 H, SO_2CH_3), 3.21 (ddd, J = 15.7, 12.0, 2.2 Hz, 1 H, $CH_2CH{=}C$), 3.41 (d, J = 3.3 Hz, 1 H, Et_3SiCH), 4.81 (dt, J = 11.5, 3.3 Hz, 1 H, $Et_3SiCHCH$), 5.25 (t, J = 2.4 Hz, 1 H, $CH{=}C$) ppm. ^{13}C NMR (100 MHz): δ = –2.3 (+, 3 C, $SiCH_3$), 3.8 (–, 3 C, $SiCH_2CH_3$), 7.4 (+, 3 C, $SiCH_2CH_3$), 33.3 (–, 1 C, $CH_2CH{=}C$), 45.8 (+, 1 C, SO_2CH_3), 56.6 (+, 1 C, Et_3SiCH), 80.0 (+, 1 C, $Et_3SiCHCH$), 113.2 (+, 1 C, $CH{=}C$), 161.5 (q, 1 C, $CH{=}C$) ppm. IR (NaCl): $\tilde{\nu}$ = 3045, 2954, 2885, 1733, 1597, 1463, 1416, 1364, 1316, 1292, 1245, 1204, 1127, 1076, 1025, 1005, 972, 948, 884, 838, 803, 750, 734, 720, 706, 632, 601. MS (DCP, 70 eV): m/z (%) = 348 (3) [M$^+$], 319 (27) [M$^+$ – Et], 267 (19), 165 (13), 147 (33), 119 (23), 115 (22) [$SiEt_3$], 97 (15), 87 (36), 85 (11), 83 (18), 75 (31) [C_2H_7OSi], 73 (100) [TMS], 59 (36), 58 (11), 57 (10), 55 (10). HRMS (ESI): calcd. for $C_{15}H_{32}O_3SSi_2$ [M + H]$^+$ 349.1689; found 349.1686.

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