Stereocontrolled Formation of Vinylsilanes via Homolytic Substitution at Silicon

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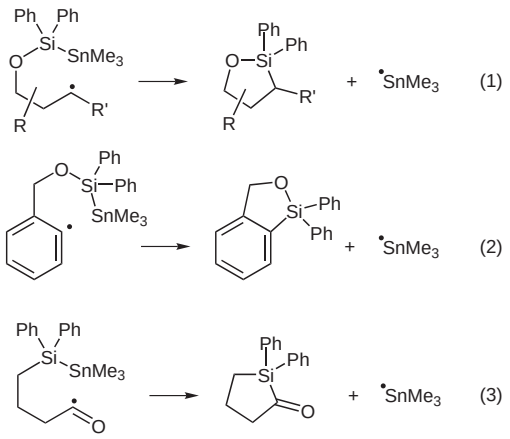
Abstract: Intramolecular homolytic substitution reactions at silicon by vinyl radicals are described. The reaction can be used for the formation of 5- and 6-membered cyclic alkoxysilanes bearing a vinyl silane functionality. These processes provide a new entry into highly substituted vinyl silanes. The reactions occur with moderate to excellent selectivities.

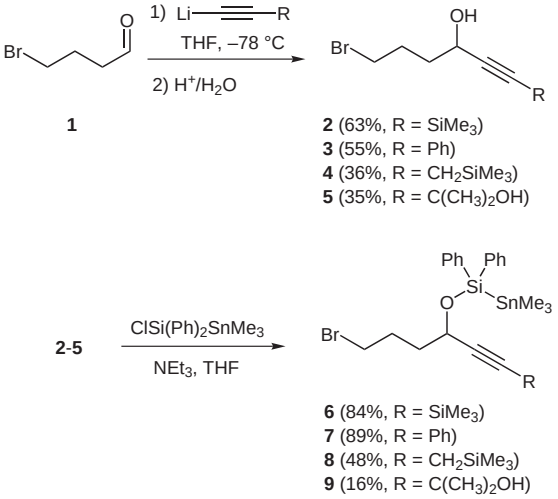
Key words: radical chemistry, silicon, stereoselective synthesis, vinyl silanes, tin

Intramolecular homolytic substitution reactions (S_Hi) at carbon using C-centered radicals are not well established.[2] However, the analogous reactions at heavier group XIV elements have been studied in more detail.[3] These processes have been successfully used for the construction of Si-,[4] Ge-[4a,c,5] and Sn-containing[4a,c,6] heterocycles. Some years ago we reported on the S_Hi reaction of alkyl and aryl radicals at silicon.[7] The trimethyltin group turned out to be a highly efficient leaving group in these homolytic substitutions (Scheme 1, equations 1 and 2).[8] More recently, we showed that acyl radicals undergo S_Hi reactions at silicon to provide cyclic acyl silanes (Scheme 1, equation 3).[9] Herein, we wish to report a new method for the stereocontrolled formation of cyclic vinyl silanes using the S_Hi reaction of vinyl radicals at silicon.



Scheme 1 S_Hi at silicon using alkyl, aryl and acyl radicals

We decided to study 5-*exo*-type cyclizations first. The requested vinyl radicals can readily be generated via intramolecular addition of carbon-centered radicals to triple bonds.[8d,10] The syntheses of the radical precursors are presented in Scheme 2. Bromoaldehyde **1** was prepared from the corresponding alcohol[11] via Swern oxidation. Li-acetylide addition at low temperature provided the secondary alcohols **2**–**5** in moderate to good yields. All compounds discussed in the present paper were prepared as racemates. However, it is important to note that acetylide additions to aldehydes can meanwhile be performed with high enantioselectivities.[12] Silylation of the alcohols using $ClSi(Ph)_2SnMe_3$[13] eventually afforded the stannylated silyl ethers **6**–**9**, ready to be used in homolytic substitution reactions.



Scheme 2 Preparation of the radical precursors

The first cyclization experiments were conducted using bromide **6**. Cylizations under typical atom transfer conditions ($Bu_3SnSnBu_3$, 0.1 equivalent, benzene, hν)[14] failed. Pleasingly, addition of Bu_3SnH (1 equivalent) and α,α′-azo-*bis*-isobutyronitrile (AIBN, 0.12 equivalent) in benzene via syringe pump to bromide **6** in benzene (0.02 M) over seven hours provided the desired cyclic vinyl silane **10** in 62% isolated yield (Scheme 3, Table 1, entry 1). The product is formed via initial 5-*exo*-*dig*-cyclization of radical **14** to generate vinyl radical **15**. S_Hi reaction at silicon eventually afforded the cyclic alkoxysilane **10** and the trimethyl tin radical. Since a chain carrying tin radical is formed during the cyclization (unimolecular chain trans-

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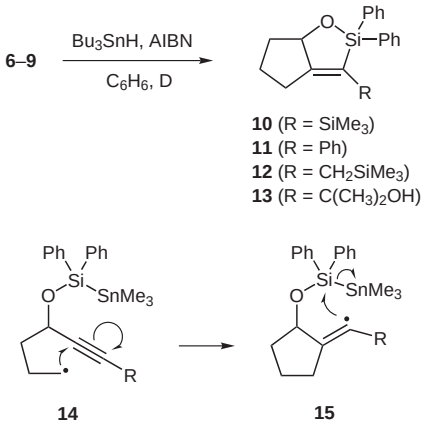
fer process),[8] the reaction should be conducted using substoichiometric amounts of tin hydride. Therefore, the reaction was repeated using 0.5 equivalent of Bu_3SnH under otherwise identical conditions. Indeed, all of the starting material was consumed and **10** was isolated in 84% yield (entry 2). With 0.4 equivalent of tin hydride a slightly lower yield was obtained (71%). In addition, 23% of unreacted starting material was identified (entry 3). The same experiment using 36% AIBN afforded a similar result (entry 4). The yield dropped to 25% if 0.2 equivalent of Bu_3SnH was used. Along with **10** the starting material was recovered in 55% yield (entry 5). The following experiments were conducted under the optimized conditions using 0.5 equivalent of tin hydride.

Transformation of the phenyl-substituted acetylene **7** provided vinyl silane **11** in 86% yield (entry 6). A lower yield was obtained for the reaction using bromide **8**. The desired silane **12** was isolated in 43% yield (entry 7). A similar yield was obtained for the reaction using **9** (→ **13**, 47%, entry 8). In the reactions with **8** and **9**, unreacted starting material was recovered in 35% and 7%, respectively.



Scheme 3 5-*exo*-*dig* Cyclization with subsequent S_Hi at Si

Table 1 S_Hi Reaction at Silicon with Vinyl Radicals

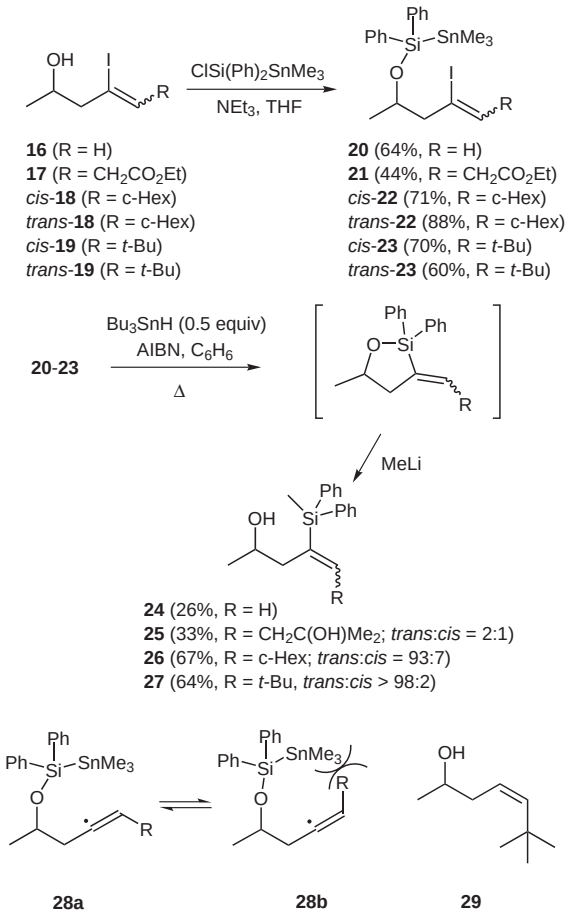
Entry	Starting material	Bu_3SnH (equiv)	Product	Yield [%]
1	**6**	1.0	**10**	62
2	**6**	0.5	**10**	84
3	**6**	0.4	**10**	71[a]
4	**6**	0.4[b]	**10**	78[a]
5	**6**	0.2	**10**	25[a]
6	**7**	0.5	**11**	86
7	**8**	0.5	**12**	43
8	**9**	0.5	**13**	47

[a] Yield determined by ^{1}H NMR spectroscopy.
[b] 36% AIBN was used.

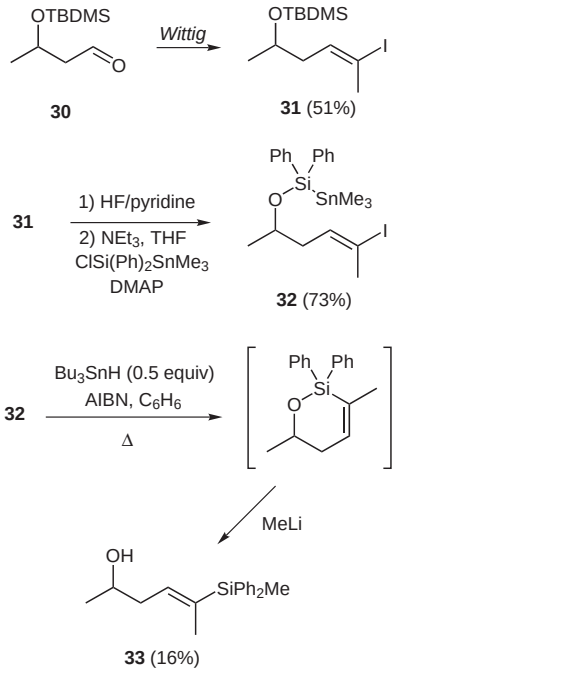
We next studied S_Hi reactions at Si leading to exocylic vinyl silanes. To this end, iodo alcohols **16**–**19** were prepared from pent-4-yn-2-ol via HI addition (→ **16**, 70%)[15] or radical I-transfer chemistry[14] using ethyl iodoacetate (→ **17**, 76%, *cis*:*trans* = 86:14), cyclohexyliodide (→ **18**, 26%, *cis*:*trans* = 84:16) or *tert*-butyliodide (→ **19**, 30%, *cis*:*trans* = 82:18). The *cis*/*trans* isomers of **18** and **19** were readily separated by chromatography. Unfortunately, the two isomers of the I-transfer product **17** could not be separated. Silylation as described above afforded the stannylated silyl ethers **20**–**23** (Scheme 4). Silyl ether **21** was used as *trans*/*cis* mixture of isomers for the subsequent S_Hi reaction, whereas for **22** and **23** each isomer was independently tested in the S_Hi reaction. Homolytic substitutions were performed under the optimized conditions. The cyclic alkoxysilanes were difficult to isolate. Therefore, the crude products were treated with an excess of MeLi to provide the corresponding ring-opened vinyl silanes **24**–**27** in moderate to good yields (Scheme 4). It is known that alkyl substituted vinyl radicals are linear.[16] Thus, for steric reasons cyclization of **28b** leading to the *cis*-double bond should be less favored as compared to the cyclization via radical **28a**. In fact, the size of the substituent R influences the stereochemical outcome to a large extent. Cyclization of **21** bearing a primary alkyl substituent cyclized with a 2:1 selectivity favoring the *trans* compound (→ **25**, 33%). A sharp increase of the selectivity was observed upon switching to a system bearing a secondary R-substituent. Thus, S_Hi reaction of the cyclohexyl derivative *cis*-**22** provided after ring-opening vinyl silane **26** in 67% yield with high selectivity (*trans*:*cis* = 93:7). An even better result was obtained for the *tert*-butyl compound *cis*-**23** where cyclization occurred with complete stereocontrol (→ **27**, 64%, only *trans*). The assignment of the relative configuration is based on the stereospecific protodesilylation of **27** using tetrabutylammoniumfluoride (TBAF) to form **29**. The *cis* double bond in **29** was unambiguously assigned using ^{1}H NMR spectroscopy. The relative configuration for the other compounds was assigned in analogy.

Based on the mechanistic scheme it is obvious that the relative configuration of the starting vinyl iodide has no influence on the selectivity. Indeed, we showed that cyclization of *trans*-**22** and *cis*-**22** occurs with the same selectivity. Furthermore, as for the corresponding *cis* derivative, S_Hi reaction of *trans*-**23** provided only *trans*-**27** in 57% yield. The *cis* isomer was not identified in the crude ^{1}H NMR spectrum.

Encouraged by the results obtained for 5-*exo*-type cyclizations we decided to study a system leading to a 6-membered cyclic alkoxysilane. The desired vinyl iodide **32** was prepared starting from aldehyde **30**[17] via Wittig reaction (→ **31**, 51%),[18] deprotection and subsequent silylation. S_Hi reaction using our standard protocol and MeLi treatment afforded homoallylic alcohol **33** albeit in low yield (16%, Scheme 5). Obviously, the S_Hi reaction is slow and the unwanted direct reduction of the reactive vi-



Scheme 4 Stereoselective S_Hi reaction at Si



Scheme 5 S_Hi reaction at Si via a 6-*exo*-type cyclization

nyl radical cannot completely be suppressed, even using low tin hydride concentrations.

In conclusion, we have shown that S_Hi reactions of vinyl radicals at silicon leading to 5-membered cyclic alkoxysilanes are efficient processes. These processes occur with high stereocontrol providing a new entry into trisubstituted olefins. The cyclic alkoxysilanes and the corresponding ring-opened vinylsilanes are useful building blocks in organic synthesis. Stereospecific protodesilylation, bromo- and iododesilylation are well established processes in organic synthesis. Moreover, cyclic alkoxysilanes have been shown by Denmark to be useful substrates for transition metal mediated C–C-bond forming reactions.[19] Studies along this line are underway.

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX-500, DRX-400, ARX-300 or ARX-200 spectrometer. IR spectra were recorded on a Bruker IFS-200 or a Nicolet Magna-IR 750 spectrophotometer. Mass spectra were recorded as EI-MS on a Varian CH7, as HRMS on a MAT 95S and as ESI-MS on a MAT TSQ 700 or a Bruker MicroTof. Elemental analyses were performed on a Heraeus CHN-Rapid analyzer. Solvents were purified by standard methods. Air and moisture sensitive compounds were handled under argon using Schlenk techniques.

Preparation of the Propargylic Alcohols 2–5 (GP 1); General Procedure

The alkyne was dissolved in THF and cooled to –78 °C (acetone/dry ice). An equimolar amount of *n*-BuLi (1.52 M in hexane) was added over 20 min. Stirring was continued for another 20 min, and a solution of 4-bromobutanal in a small amount of THF was carefully added. After stirring at –78 °C for 2 h, sat. aq NH_4Cl was added and the mixture was allowed to warm to r.t. A small amount of H_2O was added, the organic layer was separated and the aqueous layer was extracted twice with EtOAc. The organic phases were combined, washed once with sat. aq NaCl and dried ($MgSO_4$). After evaporation of the solvent, the crude product was purified by flash chromatography (FC) (SiO_2).

6-Bromo-1-(trimethylsilyl)hex-1-yn-3-ol (2)

According to GP 1 with ethynyl(trimethyl)silane (3.2 mL, 22.6 mmol), *n*-BuLi (1.52 M in hexane, 14.8 mL, 22.5 mmol) and 4-bromobutanal (3.3 g, 21.9 mmol) in THF (52 mL). FC (MTBE–pentane, 1:10) afforded **2** (3.54 g, 63%).

IR (film): 3368, 2960, 2899, 2172, 1440, 1250, 1046, 843, 760, 700, 648, 563 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 4.38 (t, *J* = 6.3 Hz, 1 H, HCO), 3.43 (t, *J* = 6.5 Hz, 2 H, CH_2Br), 2.30–1.70 (m, 5 H, CH_2CH_2, OH), 0.14 [s, 9 H, $(CH_3)_3Si$].

^{13}C NMR (50 MHz, $CDCl_3$): δ = 106.0 (C), 89.9 (C), 61.9 (CH), 35.9 (CH_2), 33.3 (CH_2), 28.3 (CH_2), –0.2 (CH_3).

Anal. Calcd for $C_9H_{17}BrOSi$ (249.22): C, 43.37; H, 6.88. Found: C, 43.01; H, 6.86.

6-Bromo-1-phenylhex-1-yn-3-ol (3)

According to GP 1 with phenylacetylene (2.8 mL, 25.5 mmol), *n*-BuLi (1.52 M in hexane, 16.7 mL, 25.5 mmol) and 4-bromobutanal (3.75 g, 24.5 mmol) in THF (56 mL). FC (MTBE–pentane, 1:5) afforded **3** (3.44 g, 55%).

IR (film): 3363, 3057, 2959, 2870, 1753, 1598, 1489, 1442, 1335, 1041, 757, 691 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.45–7.39 (m, 2 H, H_{arom}), 7.35–7.27 (m, 3 H, H_{arom}), 4.65 (t, *J* = 6.1 Hz, 1 H, CHO), 3.50 (t, *J* = 6.6 Hz, 2 H, CH_2Br), 2.17–2.07 (m, 2 H, CH_2CH_2), 1.99–1.92 (m, 2 H, CH_2CH_2).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 131.7 (CH), 128.5 (CH), 128.3 (CH), 122.3 (C), 89.4 (C), 85.3 (C), 62.1 (CH), 36.2 (CH_2), 33.3 (CH_2), 28.5 (CH_2).

MS (EI): *m*/*z* = 254/252 $[M]^+$, 173 $[M - Br]^+$, 153, 146, 131, 102, 75.

HRMS: *m*/*z* $[M]^+$ calcd for $C_{12}H_{13}BrO$, 252.0149; found, 252.0134.

7-Bromo-1-(trimethylsilyl)hept-2-yn-4-ol (4)

According to GP 1 with 1-(trimethylsilyl)-2-propyne (1.0 g, 8.9 mmol), *n*-BuLi (1.52 M in hexane, 5.6 mL, 8.9 mmol) and 4-bromobutanal (1.28 g, 8.5 mmol) in THF (28 mL). FC (MTBE–pentane, 5:1) afforded **4** (817 mg, 36%).

IR (film): 3407, 2957, 2219, 1955, 1588, 1439, 1249, 1050, 849, 761, 698, 668, 561 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.40 (td, *J* = 6.1, 2.2 Hz, 1 H, HCO), 3.45 (t, *J* = 6.6 Hz, 2 H, CH_2Br), 2.08–1.76 (m, 5 H, CH_2CH_2, OH), 1.49 (d, *J* = 2.2 Hz, 2 H, CH_2TMS), 0.10 [s, 9 H, $(CH_3)_3Si$].

^{13}C NMR (75 MHz, $CDCl_3$): δ = 84.1 (C), 79.5 (C), 62.1 (CH), 36.7 (CH_2), 33.4 (CH_2), 28.6 (CH_2), 7.0 (CH_2), -2.1 (CH_3).

HRMS: *m*/*z* $[M - H]^+$ calcd for $C_{10}H_{18}BrOSi$, 261.0310; found, 261.0306.

8-Bromo-2-methyloct-3-yne-2,5-diol (5)

According to GP 1 with 2-methyl-3-butyn-2-ol (2.45 mL, 25.0 mmol), *n*-BuLi (1.52 M in hexane, 32.0 mL, 50 mmol) and 4-bromobutanal (3.75 g, 24.8 mmol) in THF (56 mL). FC (MTBE–pentane, 1:2) afforded **5** (2.06 g, 35%).

IR(film): 3340, 2980, 2933, 2873, 1630, 1441, 1364, 1242, 1163, 1048, 951, 668, 559 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.44 (t, *J* = 6.1 Hz, 1 H, HCO), 3.46 (t, *J* = 6.8 Hz, 2 H, CH_2Br), 2.08–1.98 (m, 2 H, CH_2CH_2), 1.88–180 (m, 2 H, CH_2CH_2), 1.75 (br s, 2 H, two OH), 1.51 [s, 6 H, $C(CH_3)_2$].

^{13}C NMR (75 MHz, $CDCl_3$): δ = 89.9 (C), 82.5 (C), 65.1 (C), 61.3 (CH), 36.0 (CH_2), 33.4 (CH_2), 31.3 (CH_3), 28.4 (CH_2).

MS (EI): *m*/*z* = 221/219 $[M - CH_3]^+$, 203/201, 151/149, 113, 95, 79, 67, 59, 55, 43, 41.

HRMS: *m*/*z* $[M - CH_3 - H_2]^+$ calcd for $C_8H_{10}{}^{81}BrO_2$, 218.9844; found, 218.9860.

Silylation (GP 2); General Procedure

Diphenyl(trimethylstannyl)silylchloride was dissolved under argon in THF and cooled to 0 °C. The alcohol and NEt_3 or NEt_3 and catalytic amounts of DMAP were successively added. After stirring at 0 °C for 2 h the solvent was removed by evaporation. The residue was suspended in pentane, filtered and washed several times with a mixture of pentane–MTBE (1:1). The filtrate was collected and the solvent removed by evaporation. The crude product was purified by FC.

1-(3-Bromopropyl)-3-(trimethylsilyl)-2-propynyldiphenyl(trimethylstannyl)silyl Ether (6)

According to GP 2 with diphenyl(trimethylstannyl)silylchloride (0.78 g, 2.0 mmol), **2** (0.58 g, 2.3 mmol) and NEt_3 (0.34 mL, 2.4 mmol) in THF (8 mL). FC (MTBE–pentane, 1:100) afforded **6** (999 mg, 84%).

IR (film): 3067, 3049, 2961, 2911, 2171, 1333, 1250, 1105, 1072, 844, 762, 738, 699, 518, 494 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.55 (m, 4 H, H_{arom}), 7.38 (m, 6 H, H_{arom}), 4.45 (t, *J* = 6.1 Hz, 1 H, HCO), 3.40 (t, *J* = 6.8 Hz, 2 H, $BrCH_2$), 2.02 (m, 2 H, CH_2CH_2), 1.89 (m, 2 H, CH_2CH_2), 0.22 [s, 9 H, $(CH_3)_3Sn$], 0.09 [s, 9 H, $(CH_3)_3Si$].

^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.2/137.1 (C), 134.5/134.6 (CH), 129.8/129.7 (CH), 128.0/127.9 (CH), 105.9 (C), 90.5 (C), 64.6 (CH), 36.8 (CH_2), 33.5 (CH_2), 28.5 (CH_2), –0.2 (CH_3), –10.1 (CH_3).

MS (EI): *m*/*z* = peak pattern at 579 $[M - Me]^+$, 431/429, 389/387, 363/361, 279, 261, 197, 187, 135, 73 $[TMS]^+$, 71, 59.

HRMS: *m*/*z* $[M - CH_3]^+$ calcd for $C_{23}H_{32}BrOSi_2Sn$, 579.0190; found, 579.0203.

1-(3-Bromopropyl)-3-phenyl-2-propynyldiphenyl(trimethylstannyl)silyl Ether (7)

According to GP 2 with diphenyl(trimethylstannyl)silylchloride (1.57 g, 4.2 mmol), **3** (1.14 g, 4.5 mmol) and NEt_3 (0.68 mL, 4.9 mmol) in THF (16 mL). FC (MTBE–pentane, 1:100) afforded **7** (2.22 g, 89%).

IR (film): 3066, 2963, 2912, 2224, 1956, 1489, 1442, 1428, 1336, 1105, 1069, 757, 739, 699, 520, 493 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.60–7.55 (m, 4 H, H_{arom}), 7.40–7.32 (m, 6 H, H_{arom}), 7.29–7.20 (m, 5 H, H_{arom}), 4.70 (t, *J* = 5.7 Hz, 1 H, HCO), 3.44 (t, *J* = 6.6 Hz, 2 H, CH_2Br), 2.18–1.92 (m, 4 H, CH_2CH_2), 0.19 [s, 9 H, $(CH_3)_3Sn$].

^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.3 (C), 134.5/134.4 (CH), 131.7 (CH), 129.8/129.7 (CH), 128.4 (CH), 128.1 (CH), 128.1/128.0 (CH), 122.5 (C), 89.6 (C), 86.1 (C), 64.6 (CH), 36.9 (CH_2), 33.5 (CH_2), 28.5 (CH_2), –10.1 (CH_3).

MS (EI): *m*/*z* = peak pattern at 583 $[M - Me]^+$, 435/433 $[M - SnMe_3]^+$, 393/391, 363/361, 326, 283, 199/197, 155, 131, 71.

HRMS: *m*/*z* $[M - CH_3]^+$ calcd for $C_{26}H_{28}{}^{81}BrOSiSn$, 583.0094; found, 583.0110.

1-(3-Bromopropyl)-4-(trimethylsilyl)-2-butynyldiphenyl(trimethylstannyl)silyl Ether (8)

According to GP 2 with diphenyl(trimethylstannyl)silylchloride (390 mg, 1.0 mmol), **4** (289 mg, 1.10 mmol) and NEt_3 (0.17 mL, 1.2 mmol) in THF (5 mL). FC (MTBE–pentane, 1:100) afforded **8** (301 mg, 48%).

IR (film): 2962, 2906, 1428, 1261, 1102, 799, 699, 518, 491 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.57–7.51 (m, 4 H, H_{arom}), 7.38–7.33 (m, 6 H, H_{arom}), 4.48 (t, *J* = 6.8 Hz, 1 H, HCO), 3.39 (t, *J* = 6.6 Hz, 2 H, CH_2Br), 2.08–1.98 (m, 2 H, CH_2CH_2), 1.87–180 (m, 2 H, CH_2CH_2), 1.39 (d, *J* = 2.2 Hz, 2 H, CH_2TMS), 0.19 [s, 9 H, $(CH_3)_3Sn$], 0.05 [s, 9 H, $(CH_3)_3Si$].

^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.6/137.5 (C), 134.5/134.4 (CH), 129.8/129.7 (CH), 128.0/127.9 (CH), 84.8 (C), 79.4 (C), 64.7 (CH), 37.5 (CH_2), 33.6 (CH_2), 28.6 (CH_2), 7.3 (CH_2), –2.0 (CH_3), –10.1 (CH_3).

MS (EI): *m*/*z* = peak pattern at 593 $[M - Me]^+$, 445/443 $[M - SnMe_3]^+$, 363, 293, 135, 73 $[TMS]^+$.

HRMS: *m*/*z* $[M - CH_3]^+$ calcd for $C_{23}H_{34}{}^{81}BrO^{120}SnSi_2$, 595.0355; found, 595.0349.

8-Bromo-5-{[diphenyl(trimethylstannyl)silyl]oxy}-2-methyloct-3-yn-2-ol (9)

According to GP 2 with diphenyl(trimethylstannyl)silylchloride (400 mg, 1.05 mmol), **5** (270 mg, 1.15 mmol), NEt_3 (0.17 mL,

1.2 mmol) and DMAP (19 mg, 0.15 mmol) in THF (5 mL). FC (MTBE–pentane, 1:10) afforded **9** (100 mg, 16%).

IR (film): 3397, 3048, 2959, 2919, 2866, 1893, 1646, 1428, 1357, 1340, 1154, 1119, 1102, 1053, 799, 740, 700, 568, 517, 484 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.60–7.50 (m, 4 H, H_{arom}), 7.38 (m, 6 H, H_{arom}), 4.50 (t, *J* = 6.0 Hz, 1 H, HCO), 3.42 (t, *J* = 6.6 Hz, 2 H, $BrCH_2$), 2.03 (m, 2 H, CH_2CH_2), 1.90 (m, 2 H, CH_2CH_2), 1.31 [s, 6 H, $C(CH_3)_2$], 0.21 [s, 9 H, $(CH_3)_3Sn$].

^{13}C NMR (75 MHz, $CDCl_3$): δ = 137,4 (C), 134.8/134.6 (CH), 129.9/129.8 (CH), 128.1/128,0 (CH), 90.5 (C), 82.3 (C), 64.3 (CH), 49.4 (C), 36.8, 33.4, 31.0 (CH_3), 31.0 (CH_3), 28.5, 27.0, –10.3 (CH_3).

MS (EI): *m*/*z* = 417/415 $[M – SnMe_3]^+$, 399/397, 363/361, 294, 247, 199/197, 155, 139, 93.

HRMS: *m*/*z* $[M – SnMe_3]^+$ calcd for $C_{21}H_{24}{}^{81}BrO_2Si$, 417.0708; found, 417.0692.

S_Hi Reaction (GP 3); General Procedure

The bromide was dissolved under argon in benzene and heated to reflux. A solution of Bu_3SnH and AIBN in benzene was added via syringe pump during 7 h. After completed addition stirring was continued for 15 min. The mixture was allowed to cool to r.t. After evaporation of the solvent the crude product was purified by FC.

2,2-Diphenyl-3-(trimethylsilyl)-4,5,6,6a-tetrahydro-2*H*-cyclopenta[*d*][1,2]oxasilole (10)

According to GP 3 with **6** (121 mg, 0.20 mmol) in benzene (5 mL) and a solution of Bu_3SnH (27 µL, 0,10 mmol) and AIBN (4 mg, 24 µmol) in benzene (5 mL). FC (MTBE–pentane, 1:50) afforded **10** (60 mg, 84%).

IR (KBr): 3068, 2960, 1582, 1428, 1246, 1109, 1034, 987, 916, 894, 815, 699, 512 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 7.69–7.55 (m, 4 H, H_{arom}), 7.46–7.31 (m, 6 H, H_{arom}), 4.92 (dd, *J* = 11.3, 7.0 Hz, 1 H, OCH), 2.52–1.36 (m, 6 H, $CH_2CH_2CH_2$), 0.01 [s, 9 H, $(CH_3)_3Si$].

^{13}C NMR (50 MHz, $CDCl_3$): δ = 180.8 (C), 135.3/135.2 (CH), 139.1/130.0 (CH), 127.8/127.7 (CH), 126.5 (C), 88.5 (CH), 32.2 (CH_2), 27.0 (C), 26.6 (CH_2), 21.9 (CH_2), 0.1 (CH_3).

MS (EI): *m*/*z* = 350 $[M]^+$, 277 $[M – SiMe_3]^+$, 200, 179, 139, 99, 75, 73 $[SiMe_3]^+$.

HRMS: *m*/*z* $[M]^+$ calcd for $C_{21}H_{26}OSi_2$, 350.1522; found, 350.1536.

Anal. Calcd for $C_{21}H_{26}OSi_2$ (350.152): C, 71.94; H, 7.47. Found: C, 71.94; H, 7.58.

2,2,3-Triphenyl-4,5,6,6a-tetrahydro-2*H*-cyclopenta[*d*][1,2]oxasilole (11)

According to GP 3 with **7** (1.8 g, 3.0 mmol) in benzene (40 mL) and a solution of Bu_3SnH (0.41 mL, 1.5 mmol) and AIBN (0.06 g, 0,36 mmol) in benzene (40 mL). FC (MTBE–pentane, 1:50) afforded **11** (920 mg, 86%).

IR (KBr): 3065, 2945, 2860, 1603, 1492, 1446, 1427, 1269, 1118, 1098, 1023, 978, 825, 770, 740, 698, 563, 520, 491 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.72–7.66 (m, 4 H, H_{arom}), 7.55–7.10 (m, 11 H, H_{arom}), 5.13 (dd, *J* = 11.3, 6.7 Hz, 1 H, CHO), 2.85–2.54 (m, 2 H, CH_2–C=C), 2.39–2.27 (m, 1 H, CH_2CH_2), 2.16–2.03 (m, 2 H, CH_2CH_2), 1.68–1.46 (m, 1 H, CH_2CH_2).

^{13}C NMR (75 MHz, $CDCl_3$): 164.7 (C), 137.9 (C), 135.5 (CH), 135.3 (C), 134.8 (CH), 134.3 (C), 130.5 (CH), 130.2 (CH), 128.7 (C), 128.5 (CH), 128.4 (CH), 128.0 (CH), 128.0 (CH), 126.3 (CH), 87.0 (CH), 32.2 (CH_2), 25.4 (CH_2), 22.3 (CH_2).

MS (EI): *m*/*z* = 354 $[M]^+$, 326, 276, 249, 207, 199, 129, 104, 62, 54.

HRMS: *m*/*z* $[M]^+$ calcd for $C_{24}H_{22}OSi$: 354.1440; found, 354.1441.

2,2-Diphenyl-3-[(trimethylsilyl)methyl]-4,5,6,6a-tetrahydro-2*H*-cyclopenta[*d*][1,2]oxasilole (12)

According to GP 3 with **8** (105 mg, 172 µmol) in benzene (5 mL) and a solution of Bu_3SnH (23 µL, 86 µmol) and AIBN (3 mg, 18 µmol) in benzene (4 mL). FC (MTBE–pentane, 1:100) afforded **12** (27 mg, 43%).

IR (KBr): 3066, 2957, 2892, 1619, 1427, 1244, 1192, 1086, 859, 832, 737, 699, 577, 521, 487 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.63–7.60 (m, 4 H, H_{arom}), 7.39–7.30 (m, 6 H, H_{arom}), 5.07 (dd, *J* = 10.5, 6.8 Hz, 1 H, HCO), 2.32–2.28 (m, 1 H, CH_2C=C), 2.18–2.08 (m, 1 H, CH_2C=C), 1.94–1.68 (m, 2 H, $CH_2CH_2CH_2$), 1.66 (s, 2 H, CH_2TMS), 1.31–1.28 (m, 2 H, CH_2CHO), –0.25 [s, 9 H, $(CH_3)_3Si$].

^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.3 (C), 135.1/135.0 (CH), 134.5 (C), 130.1/131.0 (CH), 127.9/127.7 (CH), 126.6 (C), 86.5 (CH), 33.1 (CH_2), 23.1 (CH_2), 21.8 (CH_2), 19.6 (CH_2), –1.1 (CH_3).

MS (EI): *m*/*z* = 364 $[M]^+$, 349 $[M – CH_3]^+$, 336, 290, 277, 271, 199, 195, 193, 179, 135, 123.

HRMS: *m*/*z* $[M]^+$ calcd for $C_{22}H_{28}OSi_2$, 364.1679; found, 364.1685.

2-(2,2-Diphenyl-4,5,6,6a-tetrahydro-2*H*-cyclopenta[*d*][1,2]oxasilol-3-yl)propan-2-ol (13)

According to GP 3 with **9** (91 mg, 157 µmol) in benzene (5 mL) and a solution of Bu_3SnH (21 µL, 76 µmol) and AIBN (3 mg, 18 µmol) in benzene (4 mL). FC (MTBE–pentane, 1:10) afforded **13** (25 mg, 47%).

IR (KBr): 3396, 3067, 2980, 2929, 1428, 1363, 1335, 1249, 1166, 1106, 1071, 997, 956, 771, 739, 699, 519, 493 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.79–7.66 (m, 4 H, H_{arom}), 7.46–7.34 (m, 6 H, H_{arom}), 4.94 (dd, *J* = 11.2, 6.6 Hz, 1 H, HCO), 2.55–2.33 (m, 2 H, CH_2C=C), 2.26–2.18 (m, 1 H, $CH_2CH_2CH_2$), 2.07–1.81 (m, 2 H, CH_2CHO), 1.58 (br s, 1 H, OH), 1.53–1.31 (m, 1 H, $CH_2CH_2CH_2$), 1.37 (s, 3 H, CH_3), 1.27 (s, 3 H, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.1 (C), 138.9 (C), 135.9 (CH), 135.3 (C), 135.3 (C), 135.2 (CH), 130.1 (CH), 130.0 (CH), 127.9 (CH), 127.9 (CH), 86.9 (CH), 73.0 (C), 32.5 (CH_2), 31.0 (CH_3), 29.9 (CH_3), 24.7 (CH_2), 22.1 (CH_2).

MS (EI): *m*/*z* = 336 $[M]^+$, 318, 308, 290, 277, 259, 243, 199, 182, 139, 120, 104, 62.

HRMS: *m*/*z* $[M]^+$ calcd for $C_{21}H_{24}O_2Si$, 336.1545; found, 336.1539.

4-Iodopent-4-en-2-ol (16)

NaI (4.3 g, 28.6 mmol) was dissolved in MeCN (25 mL). TMS-Cl (2.76 mL, 28.6 mmol) and H_2O (0.26 mL, 14.3 mmol) were successively added and the mixture was stirred for 10 min. Pent-4-yn-2-ol (1.12 mL, 11.9 mmol) was added and the mixture stirred for 14 h at r.t. After addition of H_2O (50 mL), the resulting was mixture was extracted 3 times with Et_2O (20 mL). The combined organic phases were washed with aq K_2CO_3 (5%, 20 mL), twice with aq $Na_2S_2O_3$ (5%, 20 mL) and twice with H_2O (20 mL). The organic layer was dried with $MgSO_4$. Removal of the solvent by evaporation afforded **16** (1.78 g, 70%). The product was used without further purification.

^1H NMR (200 MHz, $CDCl_3$): δ = 6.17 (s, 1 H, H_{vinyl}), 5.85 (s, 1 H, H_{vinyl}), 4.23–3.92 (m, 1 H, CHOH), 2.76–2.25 (m, 2 H, $CHOHCH_2$), 1.58 (br s, 1 H, OH), 1.26 (d, *J* = 6.2 Hz, 3 H, CH_3).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 123.6 (CH_2), 102.6 (C), 65.8 (CH), 49.5 (CH_2), 17.2 (CH_3).

Atom Transfer Reactions (GP 4); General Procedure
Pent-4-yn-2-ol, iodoalkane and hexabutyldistannane were dissolved in benzene and irradiated for the given time in a sealed tube with a 300 W sun lamp. The reaction mixture was cooled to r.t. and the solvent was removed by evaporation. The crude product was purified by FC.

6-Hydroxy-4-iodohept-3-onic Acid Ethyl Ester (17)
According to GP 4 with pent-4-yn-2-ol (205 L, 2.5 mmol), iodoacetic acid ethyl ester (214 mg, 1.0 mmol) and $Bu_3SnSnBu_3$ (50 L, 0.1 mmol) in benzene (1.8 mL). Irradiation for 3 h and FC (pentane–MTBE, 10:1, then 3:1) afforded **17** (227 mg, 76%, *cis*/*trans* = 86:14).

IR (film): 3435, 2976, 2931, 1736, 1645, 1456, 1371, 1274, 1180, 1098, 1027, 940, 855, 792 cm^{-1}.

***cis*-17**
^1H NMR (200 MHz, $CDCl_3$): δ = 5.91 (t, *J* = 6.5 Hz, 1 H, ClCH), 4.20–3.97 (m, 1 H, C*H*OH), 4.14 (q, *J* = 7.1 Hz, 2 H, OCH_2), 3.19 (d, *J* = 6.4 Hz, 2 H, CH_2CO), 2.62 (d, *J* = 6.2 Hz, 2 H, CH_2Cl), 2.09 (d, *J* = 3.2 Hz, 1 H, OH), 1.26 (t, *J* = 7.4 Hz, 3 H, OCH_2CH_3), 1.23 (d, *J* = 6.2 Hz, 3 H, $CHOHCH_3$).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.9 (C), 130.8 (CH), 108.6 (C), 66.4 (CH), 61.6 (CH_2), 54.9 (CH_2), 42.3 (CH_2), 22.3 (CH_3), 14.6 (CH_3).

***trans*-17**
^1H NMR (200 MHz, $CDCl_3$): δ = 6.47 (t, *J* = 7.5 Hz, 1 H, ClCH), 4.20–3.97 (m, 1 H, C*H*OH), 4.13 (q, *J* = 7.1 Hz, 2 H, OCH_2), 2.62 (d, *J* = 7.9 Hz, 2 H, CH_2CO), 2.42 (dd, *J* = 14.6, 3.6 Hz, 1 H, CH_2Cl), 2.34 (dd, *J* = 13.2, 3.6 Hz, 1 H, CH_2Cl), 2.02 (s, 1 H, OH), 1.26 (t, *J* = 7.1 Hz, 3 H, OCH_2CH_3), 1.26 (d, *J* = 6.2 Hz, 3 H, $CHOHCH_3$).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.7 (C), 135.2 (CH), 102.1 (C), 66.8 (CH), 61.4 (CH_2), 48.8 (CH_2), 36.6 (CH_2), 22.7 (CH_3), 14.5 (CH_3).

MS (EI): *m*/*z* = 298 $[M]^+$, 254 $[M - OEt]^+$, 225, 181, 127 $[I]^+$, 99, 45.

HRMS: *m*/*z* $[M]^+$ calcd for $C_9H_{15}IO_3$, 298.0066; found, 298.0060.

5-Cyclohexyl-4-iodopent-4-en-2-ol (18)
According to GP 4 with pent-4-yn-2-ol (1.05 mL, 12.5 mmol), cyclohexyliodide (2.625 g, 12.5 mmol) and $Bu_3SnSnBu_3$ (250 L, 0.5 mmol) in benzene (9 mL). Irradiation for 62 h and FC (pentane–MTBE, 5:1) afforded *cis*-**18** (659 mg, 22%) and *trans*-**18** (290 mg, 4%), (*cis*/*trans* = 84:16).

***cis*-18**
IR (film) : 3365, 2925, 2850, 1625, 1448, 1083, 937, 896, 638 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 6.21 (d, *J* = 9.6 Hz, 1 H, ClCH), 4.18–3.97 (m, 1 H, C*H*OH), 2.63 (ddd, *J* = 13.8, 8.2, 0.4 Hz, 1 H, CH_2Cl), 2.40 (ddd, *J* = 14.0, 4.1, 0.7 Hz, 1 H, $ClCH_2$), 2.29 (qt, *J* = 10.4, 3.5 Hz, 1 H, ICCHC*H*), 1.76–0.76 (m, 11 H, H_{CyHex}, OH), 1.25 (d, *J* = 6.3 Hz, 3 H, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 150.4 (CH), 97.0 (C), 66.8 (CH), 48.1 (CH_2), 40.8 (CH), 33.0, 32.9, 26.0, 25.9, 16.7, 22.2 (CH_3).

MS (ESI): *m*/*z* = 317 $[M + Na]^+$.

HRMS: *m*/*z* $[M]^+$ calcd for $C_{11}H_{19}INaO$, 317.0373; found, 317.0385.

***trans*-18**
IR (film): 3350, 2925, 2850, 1638, 1448, 1120, 1086, 965, 938, 893, 815, 620, 506 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 5.44 (d, *J* = 8.3 Hz, 1 H, ClCH), 4.18–3.97 (m, 1 H, C*H*OH), 2.56 (ddd, *J* = 13.8, 4.5, 1.0 Hz, 1 H, CH_2Cl), 2.51 (ddd, *J* = 13.8, 8.2, 0.4 Hz, 1 H, $ClCH_2$), 2.38–2.10 (m, 1 H, ICCHC*H*), 1.82–0.95 (m, 11 H, H_{CyHex}, OH), 1.21 (d, *J* = 6.3 Hz, 3 H, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.8 (CH), 101.6 (C), 65.6 (CH), 54.6 (CH_2), 45.7 (CH), 31.8, 28.3, 26.2, 25.9, 22.0 (CH_3).

MS (ESI): *m*/*z* = 317 $[M + Na]^+$.

HRMS: *m*/*z* $[M]^+$ calcd for $C_{11}H_{19}InaO$, 317.0373; found, 317.0381.

4-Iodo-6,6-dimethylhept-4-en-2-ol (19)
According to GP 4 with pent-4-yn-2-ol (210 mg, 2.5 mmol), *t*-butyliodide (455 mg, 2.5 mmol) and $Bu_3SnSnBu_3$ (250 L, 0.5 mmol) in benzene (4.5 mL). Irradiation for 24 h and FC (pentane–MTBE, 5:1) afforded *cis*-**19** (151 mg, 25%) and *trans*-**19** (50 mg, 5%), (*cis*/*trans* = 82:18).

***cis*-19**
IR (film): 3375, 2961, 1616, 1461, 1364, 1255, 1119, 1085, 941, 656 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 6.38 (s, 1 H, H_{vinyl}), 4.20–4.05 (m, 1 H, C*H*OH), 2.69 (dd, *J* = 14.6, 8.3 Hz, 1 H, CH_2), 2.39 (dd, *J* = 14.4, 4.1 Hz, 1 H, CH_2), 1.76 (br s, 1 H, OH), 1.20 (d, *J* = 6.3 Hz, 3 H, $CHOHCH_3$), 1.09 [s, 9 H, $C(CH_3)_3$].

^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.6 (CH), 100.6 (C), 67.9 (CH), 48.8 (CH_2), 37.5 (C), 31.3 (CH_3), 22.2 (CH_3).

MS (ESI): *m*/*z* = 291 $[M + Na]^+$.

***trans*-19**
IR (film): 3437, 2963, 1458, 1413, 1363, 1261, 1094, 1021, 865, 802 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 5.98 (s, 1 H, H_{vinyl}), 4.20–4.00 (m, 1 H, C*H*OH), 2.57 (dd, *J* = 4.6, 3.6 Hz, 2 H, CH_2), 1.55 (br s, 1 H, OH), 1.15 (d, *J* = 6.3 Hz, 3 H, $CHOHCH_3$), 1.13 [s, 9 H, $C(CH_3)_3$].

^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.3 (CH), 97.0 (C), 66.0 (CH), 57.6 (CH_2), 33.7 (C), 29.9 (CH_3), 21.8 (CH_3).

MS (ESI): *m*/*z* = 291 $[M + Na]^+$.

4-Iodo-2-(diphenyltrimethylstannylsilanoxy)-pent-4-ene (20)
According to GP 2 with diphenyl(trimethylstannyl)silyl-chloride (1.00 g, 2.62 mmol), **16** (667 mg, 3.15 mmol) and Et_3N (265 mg, 3.15 mmol) in THF (20 mL). FC (MTBE–pentane, 25:1) afforded **20** (773 mg, 61%).

IR (film): 3086, 2972, 1428, 1125, 1087, 997, 739, 717, 700, 520, 493 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 7.60–7.48 (m, 4 H, H_{arom}), 7.45–7.31 (m, 6 H, H_{arom}), 6.08 (d, *J* = 1.0 Hz, 1 H, H_{vinyl}), 5.71 (d, *J* = 1.2 Hz, 1 H, H_{vinyl}), 4.26–4.13 (m, 1 H, C*H*OH), 2.69 (dd, *J* = 16.5, 4.9 Hz, 1 H, $CHOSiCH_2$), 2.45 (ddd, *J* = 14.2, 6.2, 1.1 Hz, 1 H, $CHOSiCH_2$), 1.19 (d, *J* = 6.2 Hz, 3 H, $CHOHCH_3$), 0.23 [s, 9 H, $Sn(CH_3)_3$].

^{13}C NMR (50 MHz, $CDCl_3$): δ = 137.9 (C), 134.6 (CH), 130.4 (CH), 129.8 (CH_2), 128.1 (CH), 107.4 (C), 70.4 (CH), 54.7 (CH_2), 22.9 (CH_3), –10.0 (CH_3).

MS (EI): *m*/*z* = 393 $[M - SnMe_3]^+$, 309 $[ISiPh_2SnMe_3]^+$, 199, 197 $[SiPh_2Me]^+$, 195 $[M - OSiPh_2SnMe_3]^+$, 181, 105, 77 $[Ph]^+$, 41, 39.

HRMS: *m*/*z* $[M - SnMe_3]^+$ calcd for $C_{17}H_{18}IOSi$, 393.0172; found, 393.0188.

Ethyl 6-{[Diphenyl(trimethylstannyl)silyl]oxy}-4-iodohept-3-enoate (21)

According to GP 2 with diphenyl(trimethylstannyl)silyl-chloride (718 mg, 1.88 mmol), **17** (618 mg, 2.07 mmol) and Et_3N (210 mg, 2.08 mmol) in THF (20 mL). FC (MTBE–pentane, 5:1) afforded **21** (532 mg, 44%, *cis*/*trans*: 80:20).

IR (film): 3451, 2975, 2927, 1736, 1427, 1371, 1274, 1178, 1127, 1102, 1050, 997, 771, 741, 718, 700, 524, 493 cm^{-1}.

***cis*-21**

^1H NMR (200 MHz, $CDCl_3$): δ = 7.81–7.27 (m, 10 H, H_{arom}), 5.90 (t, *J* = 6.3 Hz, 1 H, CICH), 4.35–4.15 (m, 1 H, CHOSi), 4.15 (q, *J* = 7.2 Hz, 2 H, OCH_2), 3.07 (d, *J* = 6.8 Hz, 2 H, CH_2CO), 2.82 (ddd, *J* = 14.0, 6.7, 0.9 Hz, 1 H, CH_2CI), 2.61 (ddd, *J* = 14.0, 6.1, 0.9 Hz, 1 H, CH_2CI), 1.26 (t, *J* = 7.1 Hz, 3 H, OCH_2CH_3), 1.19 (d, *J* = 6.0 Hz, 3 H, $CHOHCH_3$), 0.23 [s, 9 H, $Sn(CH_3)_3$].

^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.0 (C), 138.2 (C), 134.9 (CH), 130.3 (CH), 130.0, (CH), 128.4 (CH), 108.0 (C), 71.0 (CH), 61.3 (CH_2), 54.9 (CH_2), 42.3 (CH_2), 22.1 (CH_3), 14.6 (CH_3), –9.8 ($SnCH_3$).

***trans*-21**

^1H NMR (200 MHz, $CDCl_3$): δ = 7.81–7.27 (m, 10 H, H_{arom}), 6.39 (t, *J* = 7.4 Hz, 1 H, CICH), 4.35–4.15 (m, 1 H, CHOSi), 4.11 (q, *J* = 7.1 Hz, 2 H, OCH_2), 2.62 (d, *J* = 7.9 Hz, 2 H, CH_2CO), 2.74 (dd, *J* = 14.5, 7.3 Hz, 1 H, CH_2CI), 2.48 (dd, *J* = 14.2, 5.6 Hz, 1 H, CH_2CI), 1.26 (t, *J* = 7.1 Hz, 3 H, OCH_2CH_3), 1.19 (d, *J* = 6.3 Hz, 3 H, $CHOHCH_3$), 0.24 [s, 9 H, $Sn(CH_3)_3$].

^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.0 (C), 138.2 (C), 135.0 (CH), 134.7 (CH), 130.0, (CH), 128.4 (CH), 101.1 (C), 70.8 (CH), 61.3 (CH_2), 48.9 (CH_2), 36.6 (CH_2), 23.3 (CH_3), 14.5 (CH_3), –9.8 (CH_3).

MS (EI): *m*/*z* = peak pattern at 627 $[M – Me]^+$, 593, 517, 439, 337, 227, 105, 78.

HRMS: *m*/*z* $[M – Me]^+$ calcd for $C_{23}H_{30}IO_3SiSn$, 626.9896; found, 626.9885.

***cis*-5-Cyclohexyl-4-iodo-2-{[diphenyl(trimethylstannyl)silyl]oxy}-pent-4-ene (*cis*-22)**

According to GP 2 with diphenyl(trimethylstannyl)silyl–chloride (454 mg, 1.19 mmol), *cis*-**18** (368 mg, 1.25 mmol) and Et_3N (127 mg, 1.25 mmol) in THF (15 mL). FC (MTBE–pentane–Et_3N, 10:1:0.04) afforded *cis*-**22** (673 mg, 88%).

IR (film): 3469, 3067, 2969, 2924, 2850, 2359, 1428, 1126, 1103, 1070, 698, 518, 491 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.58–7.47 (m, 4 H, H_{arom}), 7.41–7.30 (m, 6 H, H_{arom}), 5.39 (d, *J* = 8.3 Hz, 1 H, CICH), 4.31–3.19 (m, 1 H, C*H*OH), 2.78 (ddd, *J* = 13.7, 6.1, 0.8 Hz, 1 H, CH_2CI), 2.52 (ddd, *J* = 14.4, 7.1, 0.5 Hz, 1 H, $CICH_2$), 2.25–2.09 (m, 1 H, ICCHC*H*), 1.77–0.97 (m, 11 H, H_{CyHex}), 1.15 (d, *J* = 6.0 Hz, 3 H, $CHOHCH_3$), 0.23 [s, 9 H, $Sn(CH_3)_3$].

^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.5 (CH), 136.4 (C), 133.3 (CH), 128.6 (CH), 125.9 (CH), 100.8 (C), 68.6 (CH), 54.7 (CH_2), 44.5 (CH), 31.9, 25.2, 24.9, 21.9 (CH_3), –9.7 (CH_3).

MS (EI): *m*/*z* = 475 $[M – SnMe_3]^+$, 309 $[ISiPh_2]^+$, 249, 199, 197 $[SiMePh_2]^+$, 81, 55, 41.

***trans*-5-Cyclohexyl-4-iodo-2-{[diphenyl(trimethylstannyl)silyl]oxy}-pent-4-ene (*trans*-22)**

According to GP 2 with diphenyl(trimethylstannyl)silyl-chloride (128 mg, 0.34 mmol), *trans*-**18** (100 mg, 0.34 mmol) and Et_3N (41 mg, 0.40 mmol) in THF (10 mL). FC (MTBE–pentane–Et_3N, 10:1:0.04) afforded *trans*-**22** (154 mg, 71%).

IR (film): 3440, 3069, 3049, 2967, 2926, 2851, 1626, 1448, 1428, 1126, 1102, 1078, 699, 520, 494 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.60–7.47 (m, 4 H, H_{arom}), 7.44–7.30 (m, 6 H, H_{arom}), 6.07 (d, *J* = 9.6 Hz, 1 H, CICH), 4.31–4.16 (m, 1 H, C*H*OH), 2.66 (ddd, *J* = 14.7, 6.1, 0.4 Hz, 1 H, CH_2CI), 2.55 (dd, *J* = 14.1, 7.1 Hz, 1 H, $CICH_2$), 2.29 (qt, *J* = 10.5, 3.5 Hz, 1 H, ICCHC*H*), 1.75–0.73 (m, 11 H, H_{CyHex}), 1.17 (d, *J* = 6.0 Hz, 3 H, $CHOHCH_3$), 0.24 [s, 9 H, $Sn(CH_3)_3$].

^{13}C NMR (75 MHz, $CDCl_3$): δ = 150.5 (CH), 139.0, 138.7 (C), 135.5, 135.4 (CH), 130.6, (CH), 128.9 (CH), 97.3 (C), 70.9 (CH), 47.6 (CH_2), 40.1 (CH), 32.0, 25.1, 25.0, 25.9, 21.9 (CH_3), –11.3 (CH_3).

MS (EI): *m*/*z* = 475 $[M – SnMe_3^+]$, 309 $[ISiPh_2]^+$, 249, 199, 197 $[SiMePh_2]^+$, 81, 55, 41.

***cis*-4-Iod-6,6-dimethyl-2-{[diphenyl(trimethylstannyl)silyl]oxy}-hept-4-ene (*cis*-23)**

According to GP 2 with diphenyl(trimethylstannyl)silyl-chloride (742 mg, 2.14 mmol), *cis*-**19** (521 mg, 1.95 mmol) and Et_3N (217 mg, 2.14 mmol) in THF (20 mL). FC (MTBE–pentane–Et_3N, 10:1:0.04) afforded *cis*-**23** (838 mg, 70%).

Mp 40 °C.

IR (KBr): 3474, 3068, 3049, 2961, 2907, 2870, 2358, 1428, 1131, 1103, 1079, 987, 699, 519, 493 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.69–7.54 (m, 4 H, H_{arom}), 7.46–7.31 (m, 6 H, H_{arom}), 6.35 (s, 1 H, CICH), 4.40–4.27 (m, 1 H, C*H*OH), 2.61 (dd, *J* = 14.3, 6.6 Hz, 1 H, CH_2), 2.41 (dd, *J* = 14.3, 6.3 Hz, 1 H, CH_2), 1.04 (d, *J* = 5.0 Hz, 3 H, $CHOHCH_3$), 0.94 [s, 9 H, $C(CH_3)_3$], 0.27 [s, 9 H, $Sn(CH_3)_3$].

^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.3 (CH), 138.0, 137.9 (C), 134.6 (CH), 129.8 (CH), 128.1, 128.0 (CH), 100.2 (C), 72.3 (CH), 48.6 (CH_2), 37.3 (C), 31.3 (CH_3), 22.9 (CH_3), –10.0 (CH_3).

MS (EI): *m*/*z* 449 $[M – SnMe_3]^+$, 353, 309 $[ISiPh_2]^+$, 249, 199, 197 $[SiMePh_2]^+$, 123, 57 $[^tBu]^+$.

HRMS: *m*/*z* $[M – SnMe_3]^+$ calcd for $C_{21}H_{26}IOSi$, 449.0798; found, 449.0795.

***trans*-4-Iodo-6,6-dimethyl-2-{[diphenyl(trimethylstannyl)silyl]oxy}-hept-4-ene (*trans*-23)**

According to GP 2 with diphenyl(trimethylstannyl)silyl-chloride (251 mg, 0.66 mmol), *trans*-**19** (176 mg, 0.66 mmol) and Et_3N (73 mg, 0.72 mmol) in THF (10 mL). FC (MTBE–pentane–Et_3N, 10:1:0.04) afforded *trans*-**23** (242 mg, 60%).

IR (film): 3067, 2963, 2906, 1428, 1376, 1362, 1198, 1103, 1078, 770, 737, 699, 519, 493 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 7.61–7.48 (m, 4 H, H_{arom}), 7.46–7.30 (m, 6 H, H_{arom}), 6.02 (s, 1 H, CH), 4.39–4.19 (m, 1 H, C*H*OH), 2.80 (dd, *J* = 13.9, 6.4 Hz, 1 H, CH_2), 2.55 (dd, *J* = 13.8, 6.3 Hz, 1 H, CH_2), 1.17 [s, 9 H, $C(CH_3)_3$)], 1.16 (d, *J* = 6.0 Hz, 3 H, $CHOHCH_3$), 0.24 [s, 9 H, $Sn(CH_3)_3$].

^{13}C NMR (50 MHz, $CDCl_3$): δ = 146.1 (CH), 138.2, 137.9 (C), 134.6, 134.5 (CH), 129.8 (CH), 128.1 (CH), 97.3 (C), 70.5 (CH), 57.7 (CH_2), 33.5 (C), 29.9 (CH_3), 22.7 (CH_3), –10.0 (CH_3).

MS (EI): *m*/*z* = peak pattern at 599 $[M – CH_3]^+$, 449, 353, 309 $[ISiPh_2]^+$, 249 $[M – OSiPh_2SnMe_3]^+$, 199, 197 $[SiMePh_2]^+$, 123, 57 $[^tBu]^+$.

HRMS(EI): *m*/*z* $[M – Me]^+$ calcd for $C_{23}H_{32}IOSiSn$, 599.0289; found, 599.0299.

4-[Methyl(diphenyl)silyl]pent-4-en-2-ol (24)

According to GP 3 with **20** (210 mg, 377 mol) in benzene (18 mL) and a solution of Bu_3SnH (55 mg, 186 μmol) and AIBN (15 mg,

75 μmol) in benzene (1 mL). Treatment at 0 °C with MeLi (1.67 M in Et_2O, 2.36 mL), stirring overnight at r.t., aqueous workup and FC (MTBE–pentane, 5:1) afforded **24** (28 mg, 26%).

IR (film): 3404, 3068, 2963, 2924, 1486, 1428, 1373, 1253, 1111, 935, 791, 728, 700, 536, 486 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 7.59–7.47 (m, 4 H, H_{arom}), 7.45–7.29 (m, 6 H, H_{arom}), 5.97 (dt, *J* = 2.8, 1.4 Hz, 1 H, H_{vinyl}), 5.58 (dt, *J* = 2.7, 0.6 Hz, 1 H, H_{vinyl}), 3.77–3.56 (m, 1 H, C*H*OH), 2.43 (ddd, *J* = 13.9, 1.4, 0.6 Hz, 1 H, CHOHCH_2), 2.28 (dddd, *J* = 14.6, 9.4, 1.2, 0.7 Hz, 1 H, CHOHCH_2), 1.09 (d, *J* = 6.2 Hz, 3 H, CHOHCH_3), 0.69 (s, 3 H, $SiCH_3$).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.9 (C), 135.7 (C), 135.1 (CH), 132.1 (CH_2), 129.7, 129.6 (CH), 128.1 (CH), 66.1 (C), 46.8 (CH_2), 23.0 (CH_3), –3.7 (CH_3).

MS (ESI): *m*/*z* = 305 $[M + Na]^+$.

2-Methyl-5-[methyl(diphenyl)silyl]oct-4-ene-2,7-diol (25)
According to GP 3 with **21** (177 mg, 280 mol) in benzene (10 mL) and a solution of Bu_3SnH (40 mg, 140 μmol) and AIBN (11 mg, 50 μmol) in benzene (1 mL). Treatment at 0 °C with MeLi (1.67 M in Et_2O, 1.75 mL), stirring overnight at r.t., aqueous workup and FC (pentane–EtOAc, 2:1) afforded *trans*-**25** (19 mg, 20%) and *cis*-**25** (12 mg, 13%), (*trans*/*cis* = 2:1).

***trans*-25**
IR (film): 3384, 3068, 2964, 2926, 1609, 1456, 1428, 1379, 1260, 1109, 935, 793, 737, 721, 700, 515, 478 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.58–7.46 (m, 4 H, H_{arom}), 7.43–7.31 (m, 6 H, H_{arom}), 6.15 (dd, *J* = 9.0, 6.3 Hz, 1 H, CSiCH), 3.65–3.50 (m, 1 H, C*H*OH), 2.59 (ddd, *J* = 15.0, 14.7, 8.9 Hz, 2 H, CH_2CSi), 2.19 (dd, *J* = 9.0, 6.3 Hz, 2 H, CH_2COH), 1.24 (s, 3 H, HOCCH_3), 1.21 (s, 3 H, OCCH_3), 1.06 (d, *J* = 6.3 Hz, 3 H, CHOHCH_3), 0.67 (s, 3 H, $SiCH_3$).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.2 (CH), 137.6 (C), 136.6 (C), 135.2 (CH), 129.5 (CH), 128.0 (CH), 71.1 (C), 67.2 (CH), 42.6 (CH_2), 39.8 (CH_2), 30.7, 30.0 (CH_3), 23.6 (CH_3), –3.2 (CH_3).

MS (ESI): *m*/*z* = 377 $[M + Na]^+$.

***cis*-25**
IR (film): 3339, 3068, 2967, 2927, 1612, 1456, 1428, 1376, 1260, 1110, 939, 907, 792, 726, 701, 482 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.58–7.50 (m, 4 H, H_{arom}), 7.41–7.32 (m, 6 H, H_{arom}), 6.43 (t, *J* = 7.6 Hz, 1 H, CSiCH), 3.68–3.53 (m, 1 H, C*H*OH), 2.49 (dd, *J* = 13.1, 3.1 Hz, 1 H, CHOHCH_2), 2.17–2.00 (m, 3 H), 1.09 (d, *J* = 6.1 Hz, 3 H, CHOHCH_3), 1.00 (s, 3 H, HOCCH_3), 0.95 (s, 3 H, OCCH_3), 0.69 (s, 3 H, $SiCH_3$).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.0 (CH), 137.1, 136.0 (two C), 135.1 (CH), 129.5 (CH), 128.2 (CH), 70.7 (C), 66.7 (CH), 49.1 (CH), 45.9 (CH_2), 29.7, 29.0 (CH_3), 22.8 (CH_3), –1.6 (CH_3).

MS (ESI): *m*/*z* = 377 $[M + Na]^+$.

5-Cyclohexyl-4-[methyl(diphenyl)silyl]pent-4-en-2-ol (26)
According to GP 3 with *cis*-**22** (479 mg, 750 mol) in benzene (10 mL) and a solution of Bu_3SnH (109 mg, 370 μmol) and AIBN (29 mg, 150 μmol) in benzene (1 mL). Treatment at 0 °C with MeLi (1.67 M in Et_2O, 4.4 mL), stirring overnight at r.t., aqueous workup and FC (pentane–MTBE, 5:1) afforded *trans*-**26** (143 mg, 53%) and a *cis*/*trans* mixture (39 mg, 14%, 56:44), (*trans*/*cis* = 93:7).

According to GP 3 with *trans*-**22** (11 mg, 18 mol) in benzene (1 mL) and a solution of Bu_3SnH (3 mg, 10 μmol) and AIBN (1 mg, 5 μmol) in benzene (1 mL). Treatment at 0 °C with MeLi (1.67 M in Et_2O, 0.12 mL), stirring overnight at r.t. and aqueous workup afforded the crude product mixture of **26** (*cis*/*trans* = 93:7).

IR (film): 3432, 3068, 2926, 2850, 1607, 1448, 1428, 1371, 1261, 1110, 789, 730, 700, 491, 433 cm^{-1}.

***trans*-26**
^1H NMR (300 MHz, $CDCl_3$): δ = 7.58–7.45 (m, 4 H, H_{arom}), 7.43–7.30 (m, 6 H, H_{arom}), 5.87 (d, *J* = 9.3 Hz, 1 H, SiCC*H*CH), 3.60–3.46 (m, 1 H, C*H*OH), 2.61–2.46 (m, 1 H, SiCCHC*H*), 2.42 (ddd, *J* = 13.6, 9.0, 0.2 Hz, 1 H, CH_2CSi), 2.32 (ddd, *J* = 13.7, 4.3, 0.3 Hz, 1 H, $SiCCH_2$), 1.77–0.96 (m, 11 H, H_{CyHex}, OH), 1.06 (d, *J* = 6.0 Hz, 3 H, CHOHCH_3), 0.65 (s, 3 H, $SiCH_3$).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.8 (CH), 136.7 (C), 135.2 (CH), 130.9 (C), 129.4, (CH), 128.0 (CH), 67.2 (CH), 40.2 (CH_2), 38.1 (CH), 32.9, 27.1, 25.8, 22.9 (CH_3), –3.1 (CH_3).

MS (ESI): *m*/*z* = 387 $[M + Na]^+$.

***cis*-26**
^1H NMR (300 MHz, $CDCl_3$): δ = 7.58–7.45 (m, 4 H, H_{arom}), 7.43–7.30 (m, 6 H, H_{arom}), 6.08 (d, *J* = 10.6 Hz, 1 H, SiCC*H*CH), 3.60–3.46 (m, 1 H, C*H*OH), 2.30 (td, *J* = 4.6, 3.7 Hz, 1 H, CH_2CSi), 2.08 (ddd, *J* = 13.1, 8.5, 0.2 Hz, 1 H, $SiCCH_2$), 1.97 (qt, *J* = 10.9, 3.5 Hz, 1 H, SiCCHC*H*), 1.77–0.96 (m, 11 H, H_{CyHex}, OH), 1.03 (d, *J* = 6.0 Hz, 3 H, CHOHCH_3), 0.69 (s, 3 H, $SiCH_3$).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.6 (CH), 137.2, 137.1 (C), 135.0, 134.9 (CH), 130.6 (C), 129.4, 129.3, (CH), 128.0, 127.9 (CH), 66.5 (CH), 41.6 (CH_2), 38.1 (CH), 33.0, 32.5, 25.5, 22.5 (CH_3), –3.1 (CH_3).

***trans*-6,6-Dimethyl-4-[methyl(diphenyl)silyl]hept-4-en-2-ol (27)**
According to GP 3 with *cis*-**23** (548 mg, 890 mol) in benzene (30 mL) and a solution of Bu_3SnH (130 mg, 480 μmol) and AIBN (34 mg, 180 μmol) in benzene (1 mL). Treatment at 0 °C with MeLi (1.67 M in Et_2O, 5.3 mL), stirring overnight at r.t., aqueous workup and FC (pentane–MTBE, 5:1) afforded **27** (192 mg, 64% *trans* only).

According to GP 3 with *trans*-**23** (102 mg, 166 mol) in benzene (8 mL) and a solution of Bu_3SnH (24 mg, 82 μmol) and AIBN (6 mg, 40 μmol) in benzene (1 mL). Treatment at 0 °C with MeLi (1.67 M in Et_2O, 1.0 mL), stirring overnight at r.t., aqueous workup and FC (pentane–MTBE, 5:1) afforded **27** (32 mg, 57% *trans* only).

IR (film): 3580, 3445, 3067, 2958, 2904, 1595, 1463, 1428, 1363, 1252, 1109, 1072, 1036, 939, 791, 730, 701, 516, 482 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 7.60–7.46 (m, 4 H, H_{arom}), 7.44–7.28 (m, 6 H, H_{arom}), 6.02 (s, 1 H, CSiCH), 3.75–3.51 (m, 1 H, C*H*OH), 2.63 (ddd, *J* = 13.6, 9.1, 0.8 Hz, 1 H, CH_2), 2.35 (ddd, *J* = 13.8, 4.0, 1.3 Hz, 1 H, CH_2), 1.37 (br s, 1 H, OH), 1.17 [s, 9 H, $C(CH_3)_3$], 1.08 (d, *J* = 6.0 Hz, 3 H, CHOHCH_3), 0.67 (s, 3 H, $SiCH_3$).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 158.1 (CH), 137.2, 137.1 (C), 135.2, 135.0 (CH), 132.2 (C), 129.4, 129.3 (CH), 128.0, 127.9 (CH), 67.2 (CH), 39.7 (CH_2), 35.9 (C), 31.6 (CH_3), 23.1 (CH_3), –2.8 (CH_3).

MS (ESI): *m*/*z* = 361 $[M + Na]^+$.

HRMS: *m*/*z* $[M + Na]^+$ calcd for $C_{22}H_{30}NaOSi$, 361.1964; found, 361.1967.

6,6-Dimethylhept-4-en-2-ol (29)
A solution of **27** (59 mg, 170 mol) in THF (1 mL) was treated with TBAF (1 M in THF, 0.87 mL). After stirring for 14 h at r.t. no reaction could be observed via TLC. The mixture was heated in a sealed tube and stirred for 8 h at 70 °C. After cooling to r.t., H_2O (2 mL) was added and the aqueous layer was extracted 3 times with Et_2O. The combined organic phases were dried with $MgSO_4$ and the solvent was removed by evaporation. Purification of the crude product by FC (pentane–MTBE, 5:1) afforded **29** (11 mg, 45%).

IR (film): 3445, 2957, 2924, 2854, 1739, 1462, 1377, 1261, 1112, 802, 700, 617, 522 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 5.53 [dt, *J* = 9.1, 0.8 Hz, 1 H, C*H*C$(CH_3)_3$], 5.19 (ddd, *J* = 12.1, 8.0, 7.0 Hz, 1 H, CH_2C*H*CH), 3.92–3.73 (m, 1 H, C*H*OH), 2.63 (ddd, *J* = 14.5 7.8, 1.5 Hz, 1 H, CH_2), 2.35 (ddd, *J* = 12.3, 5.3, 1.7 Hz, 1 H, CH_2), 1.58 (br s, 1 H, OH), 1.22 (d, *J* = 6.2 Hz, 3 H, CHOHCH_3), 1.11 [s, 9 H, C$(CH_3)_3$].

^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.8 (CH), 123.9 (CH), 68.3 (CH), 38.3 (CH_2), 35.6 (C), 31.5 (CH_3), 23.2 (CH_3).

3-{[*tert*-Butyl(dimethyl)silyl]oxy}butyraldehyde (30)

3-{[*tert*-Butyl(dimethyl)silyl]oxy}butyric acid ethyl ester (1.0 g, 4.03 mmol) was dissolved in toluene (14 mL) and cooled to –78 °C. DIBALH (1 M in THF, 4.07 mL, 4.07 mmol) was added. After stirring at –78 °C for 10 min sat. NH_4Cl solution (1.4 mL) was added. The mixture was allowed to warm to r.t. and stirred for 1 h. Et_2O (30 mL) was added, and after stirring for 1 h the solution was dried with $MgSO_4$. Removal of the solvent by evaporation afforded **30** (803 mg, 98%). The product was used without further purification.

^1H NMR (200 MHz, $CDCl_3$): δ = 9.74 (t, *J* = 2.5 Hz, 1 H, CHO), 4.29 (m, *J* = 5.9 Hz, 1 H, CHOSi), 2.46 (dd, *J* = 7.0, 2.8 Hz, 1 H, CH_2), 2.43 (dd, *J* = 5.4, 1.9 Hz, 1 H, CH_2), 1.18 (d, *J* = 6.0 Hz, 3 H, CHCH_3), 0.81 [s, 9 H, C$(CH_3)_3$], 0.03 (s, 3 H, SiCH_3), 0.02 (s, 3 H, SiCH_3).

***tert*-Butyl-[(4-iodo-1-methylpent-3-en-1-yl)oxy]dimethylsilane (31)**

Ethylphosphoniumbromide (2 g, 5.39 mmol) was suspended in THF (50 mL) and treated with *n*-BuLi (1.5 M, in hexane, 3.6 mL, 5.39 mmol). The ylid was transferred by cannula to a cold (–78 °C) solution of I_2 (1.367 g, 5.39 mmol) in THF (100 mL). The suspension was stirred for 10 min and warmed to –20 °C. NaHMDS (1 M in THF, 4.8 mL) was added and the mixture was stirred for another 10 min at –20 °C. The solution was cooled to –78 °C and aldehyde **30** (544 mg, 2.69 mmol) in THF (20 mL) was added. After stirring for 10 min at –78 °C the mixture was allowed to warm to r.t. and stirred for 62 h. The solvent was removed by evaporation. The residue was suspended in a mixture of pentane–MTBE (10:1) and filtered through a plug of silica. The filtrate was collected and the solvent removed by evaporation. Purification of the crude product by FC (pentane–MTBE, 10:1) afforded **31** (466 mg, 51%).

IR (film): 2956, 2929, 2856, 1652, 1472, 1427, 1376, 1255, 1132, 1094, 1061, 1002, 836, 775 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 5.47 (td, *J* = 5.2, 1.6 Hz, 1 H, CICH), 3.90–3.72 (m, 1 H, CHOSi), 2.48 (t, *J* = 1.2 Hz, 3 H, $CICH_3$), 2.19 (t, *J* = 6.8 Hz, 2 H, CH_2), 1.11 (d, *J* = 6.2 Hz, 3 H, H_3CCHOSi), 0.83 [s, 9 H, C$(CH_3)_3$], 0.00 (s, 6 H, SiCH_3).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 131.7 (CH), 101.7 (C), 68.1 (CH), 47.3 (CH_2), 34.9 (CH_3), 27.2 (CH_3), 25.0 (CH_3), 20.1 (C), –2.4 (CH_3), –2.6 (CH_3).

MS (EI): *m*/*z* = 283 $[M - {}^tBu]^+$, 185 $[ISiMe_2]^+$, 159, 155, 81, 73, 32.

HRMS: *m*/*z* $[M - {}^tBu]^+$ calcd $C_8H_{16}IOSi$, 283.0015; found, 283.0031.

5-Iodo-2-{[diphenyl(trimethylstannyl)silyl]oxy}hex-4-ene (32)

A solution of silyl ether **31** (298 mg, 0.87 mmol) in CH_2Cl_2 (20 mL) was cooled to 0 °C. HF·pyridine (0.31 mL, 12.1 mmol) was added and the solution was allowed to warm to r.t. After stirring for 14 h sat. aq Na_2CO_3 (20 mL) was added. The aqueous phase was separated and extracted 5 times with Et_2O (5 mL) the organic phases were combined and dried with $MgSO_4$. The solvent was removed by evaporation. Purification of the crude product by FC (pentane–MTBE, 5:1) afforded 5-iodohex-4-en-2-ol (121 mg, 62%).

IR (film): 3346, 2966, 2912, 1651, 1425, 1374, 1127, 1110, 1044, 938, 849, 580 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 5.47 (td, *J* = 6.8, 1.5 Hz, 1 H, CH), 4.01–3.76 (m, 1 H, C*H*OH), 2.47 (q, *J* = 1.3 Hz, 3 H, $CICH_3$), 2.21 (tq, *J* = 6.4, 1.1 Hz, 2 H, CH_2), 1.16 (d, *J* = 6.0 Hz, 3 H, H_3CCHO).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 131.7 (CH), 103.5 (C), 67.2 (CH), 46.1 (CH_2), 33.9 (CH_3), 23.2 (CH_3).

MS (ESI): *m*/*z* = 249 $[M + Na]^+$.

According to GP 2 with diphenyl(trimethylstannyl)silyl-chloride (251 mg, 660 μmol), 5-iodohex-4-ene-2-ol (150 mg, 666 μmol) and Et_3N (101 mg, 1.0 mmol) in THF (15 mL). FC (MTBE–pentane–Et_3N, 10:1:0.04) afforded **32** (278 mg, 73%).

IR (film): 3444, 3067, 2965, 2910, 2358, 1650, 1427, 1105, 1051, 1004, 793, 699, 518, 492 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.58–7.49 (m, 4 H, H_{arom}), 7.44–7.32 (m, 6 H, H_{arom}), 5.45 (tq, *J* = 6.6, 1.2 Hz, 1 H, CICH), 4.10–3.98 (m, 1 H, C*H*OH), 2.45 (d, *J* = 1.3 Hz, 3 H, $CICH_3$), 2.42–2.12 (m, 2 H, CH_2), 1.22 (d, *J* = 6.0 Hz, 3 H, H_3CCHOH), 0.30 [s, 9 H, Sn$(CH_3)_3$].

^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.0 (C), 134.6, 134.5 (CH), 132.2, 129.8 (two CH), 128.2 (CH), 102.9 (C), 70.7 (CH), 46.4 (CH_2), 33.9 (CH_3), 23.5 (CH_3), –10.2 (CH_3).

MS (EI): *m*/*z* = 407 $[M - SnMe_3]^+$, 309 $[ISiPh_2]^+$, 235, 197 $[SiPh_2Me]^+$, 105, 81.

HRMS: *m*/*z* $[M - SnMe_3]^+$ calcd $C_{18}H_{20}IOSi$, 407.0328; found, 407.0317.

5-[Methyl(diphenyl)silyl]hex-4-en-2-ol (33)

According to GP 3 with **32** (172 mg, 300 μmol) in benzene (15 mL) and a solution of Bu_3SnH (43 mg, 150 μmol) and AIBN (11 mg, 60 μmol) in benzene (1 mL). Treatment at 0 °C with MeLi (1.67 M in Et_2O, 1.8 mL), stirring overnight at r.t., aqueous workup and FC (MTBE–pentane, 5:1) afforded **33** (14 mg, 16%).

IR (film): 3364, 3068, 2966, 2927, 1617, 1428, 1373, 1253, 1111, 1080, 1046, 939, 791, 722, 700, 528, 494 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.57–7.47 (m, 4 H, H_{arom}), 7.41–7.31 (m, 6 H, H_{arom}), 6.31 (tq, *J* = 7.5, 1.6 Hz, 1 H, CSiCH), 3.63–3.48 (m, 1 H, C*H*OH), 2.04 (dq, *J* = 6.3, 1.3 Hz, 1 H, CH_2), 2.00 (dq, *J* = 6.3, 1.3 Hz, 1 H, CH_2), 1.85 (q, *J* = 1.4 Hz, 3 H, SiCCH_3), 0.94 (d, *J* = 6.3 Hz, 3 H, H_3CCHOH), 0.63 (s, 3 H, SiCH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.5 (CH), 137.0 (C), 135.0 (CH), 134.4 (C), 129.4 (CH), 128.1 (CH), 68.1 (CH), 42.0 (CH_2), 26.1 (CH_3), 22.9 (CH_3), –2.0 (CH_3).

MS (ESI): *m*/*z* = 319 $[M + Na]^+$.

HRMS: *m*/*z* $[M + Na]^+$ Calcd for $C_{19}H_{24}NaOSi$: 319.1489. Found: 319.1486.

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