Palladium-Catalyzed Silastannation of Secondary Propargylic Alcohols and their Derivatives

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Dedicated to Prof. T. Mukaiyama on the occasion of his 77th birthday

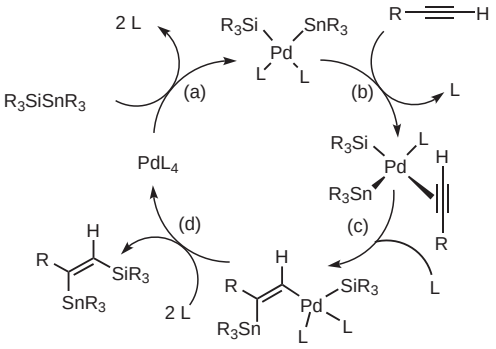
Abstract: A series of terminal propargylic alcohols and their derivatives were subjected to Pd-catalyzed silastannation. In all reactions, complete regio- and stereoselectivities were observed with the tributyltin moiety exclusively adding to the internal carbon of the triple bond in a *cis* fashion, including the first example of a diyne bis-silastannation. Silastannation reaction products could sequentially be protiodesilylated or iododestannylated, thus providing synthetic routes to 1,1-*gem*-disubstituted alkenylstannanes and iodides, respectively.

Key words: palladium, catalysis, propargylic alcohols, silastannation, iododestannylation, Stille reaction

Metal-catalyzed element–element addition to alkynes represents a unique route to bis-functionalized alkenes.[1] Several combinations of elements, such as B–B, Si–Si, Sn–Sn, Ge–Ge, B–Si, Sn–B, Ge–Sn, and Si–Sn, may be added to the triple bond via metal-catalysis, where the Group 10 metals Pd, Ni, and Pt, typically in combination with a phosphine ligand, have been primary choices of catalysts. The reaction products are valuable intermediates in the synthesis of tri- and tetrasubstituted alkenes, e.g. via subsequent metal-catalyzed cross-coupling reactions,[2] such as the Stille,[3] or Suzuki reactions.[4]

The Pd-catalyzed silastannation of alkynes was first reported by the groups of Mitchell,[5] and Chenard.[6] When performed on terminal alkynes, the reaction proceeds in a *syn*-fashion with excellent regio- and stereoselectivity, attaching the trialkyltin moiety to the internal carbon of the triple bond. For nonterminal alkynes, the picture is more complicated, as mixtures of regioisomers are generally formed.[7,8] Exceptions, however, have been observed in the case of alkoxyalkynes, where the Si moiety may add to the α-position of the alkoxy group using Ito's catalyst [$Pd(OAc)_2$/*tert*-alkyl isocyanide],[9]or to the β-position via $Pd(Ph_3P)_4$ catalysis.[10] In $Pd(Ph_3P)_4$-catalyzed silastannation of N-substituted aminoalkynes, the Si moiety adds to the α-position of the amino group with complete regioselectivity.[11]

Concerning the reaction mechanism, Ito and Nakatsuji have performed a theoretical study, including the issue of regioselectivity,[12] which gives support to the generally accepted catalytic cycle (Scheme 1). The catalytic cycle is believed to involve the following steps: (a) oxidative addition of R_3SiSnR_3 to a coordinately unsaturated Pd species; (b) coordination of the alkyne; (c) insertion of the alkyne into the Pd–Sn bond; and (d) reductive elimination to afford the silastannated product and complete the catalytic cycle.



Scheme 1 Catalytic cycle of the Pd-catalyzed silastannation of terminal alkynes.

Bearing in mind the synthetic potential of vinyl silanes,[13] and vinyl stannanes,[14] surprisingly few research groups have utilized the Pd-catalyzed silastannation for synthetic purposes. Reported applications of the reaction products comprise precursors of vinyllithium species via Li–Sn transmetalation, followed by reaction with electrophiles,[7,15] Lewis-acid mediated acylation, replacing the Si, or Sn moieties,[15] Stille reactions with benzyl, allyl, aryl, vinyl, and acyl halides,[7,9,16] halodestannylation,[7,9,15] halodealkylation at tin,[7] and formation of 1-silacyclopentadienes,[17] allenes,[7] and acyl silanes.[9] In their original reports, Chenard reported the failure of propargylic substrates in Pd-catalyzed silastannation reactions,[15] whereas Mitchell has demonstrated moderately successful silastannation of some 1-methylpropargylic alcohols.[7]

In connection with a research program dealing with the total synthesis of certain natural products, we have had occasion to reinvestigate the silastannation of propargylic alcohols, and we now wish to report the extension of the reaction scope to a broader selection of these substrates, and their derivatives, including the first bis-silastannation of a diyne. In addition, applications of the reaction products for the synthesis of 1,1-*gem*-disubstituted alkenyl-

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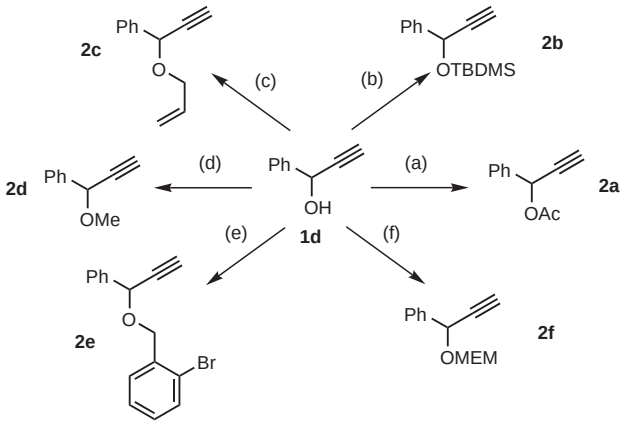
stannanes and iodides, and as coupling partners in Stille reactions, are also described.

Following a modified procedure of Midland,[18] the terminal propargylic alcohols **1d**–**i** were readily obtained by treating the parent aldehydes with lithium acetylide. Likewise, diyne **1j** was obtained by treating ethyl benzoate with a further equivalent of lithium acetylide. As illustrated for 1-phenylpropyn-1-ol (**1d**), further derivatizations were accomplished via standard protective group methods to give substrates **2a**–**f** (Scheme 2).



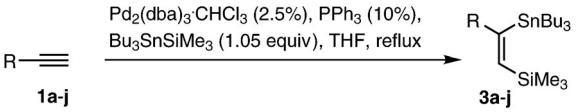
Scheme 2 *Reagents and conditions*: (a) Ac_2O, 4-DMAP, Et_3N, CH_2Cl_2, r.t., 85%; (b) TBDMSCl, imidazole, DMF, r.t., 92%; (c) NaH, CH_2=$CHCH_2Br$, KI, THF, r.t., 59%; (d) NaH, MeI, THF, r.t., 56%; (e) NaH, 2-Br-$C_6H_4CH_2Br$, TBAI, THF, r.t., 72%; (f) MEMCl, DIPEA, CH_2Cl_2, 0 °C, 80%.

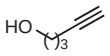
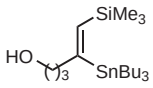
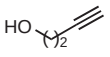
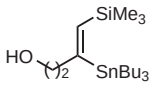
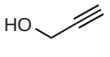
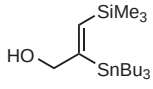
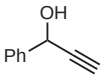
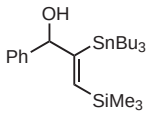
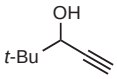
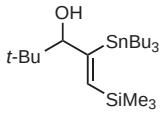
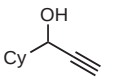
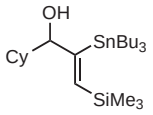
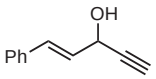
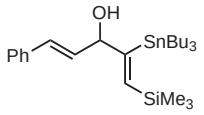
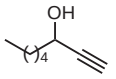
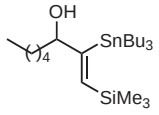
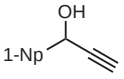
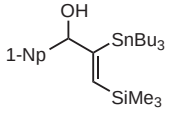
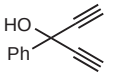
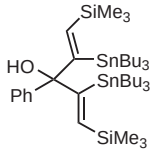
In a first round of silastannation experiments, a series of unprotected propargylic alcohols **1c**–**j**, together with terminal alkynes **1a**,**b** were tested. Initial studies on the choice of catalyst revealed that $Pd_2(dba)_3{\cdot}CHCl_3$, in combination with 1–2 equivalents of Ph_3P per Pd, generally gave the most satisfying results, when compared to $Pd(Ph_3P)_4$ and other standard catalysts. As illustrated in Table 1, good to excellent yields were obtained, with the expected regio- and stereoselectivity. All silastannations listed in Table 1 were carried out with catalyst loadings corresponding to 5% Pd.[19] Notably, the sterically congested diyne **1j** was efficiently silastannated (entry 10), thereby providing the first example of a bis-silastannation (none of the mono-silastannated product was observed).

In general, the stereochemistry of the silastannation products **3a**–**j**, **4b**–**d**, and **4f**–**h** was assigned by inspection of the coupling constants from Sn to the vinyl proton, e.g. $J(^{119}Sn,H)$ was found to be in the range of 165–182 Hz, which is strongly evident of a *trans*-relationship between Sn and the vinyl proton.

These promising results encouraged us to examine the importance of the O-protecting group. For this purpose, propargylic alcohol derivatives **2a**–**h** were subjected to the silastannation protocol (Table 2).

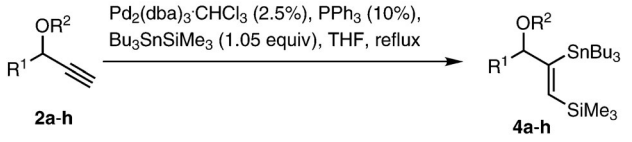
Table 1 Pd-Catalyzed Silastannation of Propargylic Alcohols



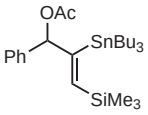
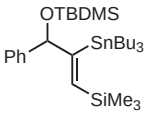
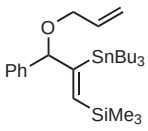
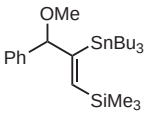
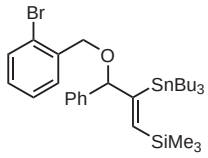
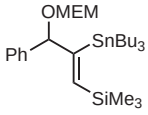
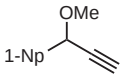
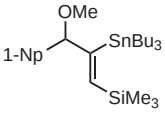
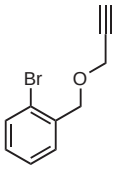
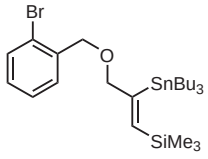
Entry	Alkyne	Product	Yield (%)[a]
1	 **1a**	 **3a**	83
2	 **1b**	 **3b**	95
3	 **1c**	 **3c**	85
4	 **1d**	 **3d**	85
5	 **1e**	 **3e**	80
6	 **1f**	 **3f**	72
7	 **1g**	 **3g**	67
8	 **1h**	 **3h**	74
9	 **1i**	 **3i**	72
10[b]	 **1j**	 **3j**	71

[a] Isolated yield after flash column chromatography.
[b] 2.10 equiv of $Bu_3SnSiMe_3$ were employed.

Table 2 Pd-Catalyzed Silastannation of *O*-Protected Propargylic Alcohols



2a-h **4a-h**

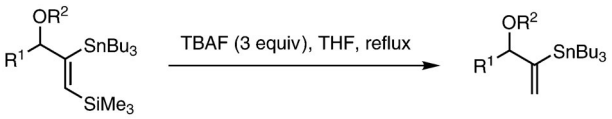
Entry	Alkyne	Product	Yield (%)[a]
1	**2a**	 **4a**	0
2	**2b**	 **4b**	85
3	**2c**	 **4c**	61
4	**2d**	 **4d**	>95
5	**2e**	 **4e**	0
6	**2f**	 **4f**	88
7[b]	 **2g**	 **4g**	>95
8[c]	 **2h**	 **4h**	78

[a] Isolated yield after flash column chromatography.
[b] Substrate **2g** was made from the corresponding alcohol **1i** via the NaH/MeI protocol (72%; see the experimental section for details).
[c] Substrate **2h** was made from the corresponding alcohol **1c** via the NaH/2-$BrC_6H_4CH_2Br$/TBAI protocol (79%; see the experimental section for details).

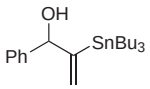
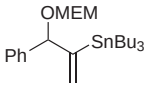
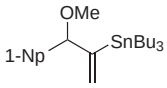
Although the propargylic acetate **2a** fails to produce any of the desired product **4a** under the reaction conditions (entry 1),[15] the silastannation products were formed in good to excellent yields when other common protecting groups, such as TBDMS, allyl, bromobenzyl, and MEM, were employed (entries 2–4, 6–8). Notably, the methyl ethers **2d** and **2g** were found to give the corresponding silastannation products **4d** and **4g** in near quantitative yields (entries 4 and 7). It is also noteworthy that, whereas the silastannation of the 1-phenyl derivative **2e** fails and results in decomposition, the silastannation of the less substituted **2h** was effected without any competing side-reactions or cross-coupling of the aryl bromide (Entry 8).

In Pd-catalyzed hydrostannation of terminal propargylic alcohol derivatives,[20] the steric bulk of the substrate and the nature of the phosphine ligand are highly important for the reaction regioselectivity, where main products normally are the *trans*-disubstituted alkenylstannanes resulting from the overall *cis*-addition of Bu_3SnH, attaching the Sn moiety with high β-selectivity to the triple bond.[21] Although some efforts have been aimed at higher α-selectivities, e.g. via Mo-catalysis,[22] the direct access to 1,1-*gem*-disubstituted alkenylstannanes from propargylic alcohol derivatives is difficult. Pleasingly, selected O-protected silastannation products **4f** and **4g** were smoothly desilylated using the conditions of Ritter,[23] to provide the 1,1-*gem*-disubstituted alkenylstannanes in high yields (Table 3). Unexpectedly, total decomposition was observed when attempts were made to desilylate the unprotected derivative **3d**.

Table 3 Desilylation of Silastannation Products



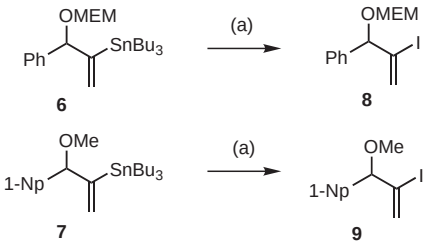
3d, **4f**, **4g** **5-7**

Entry	Substrate	Product	Yield (%)[a]
1	**3d**	 **5**	0
2	**4f**	 **6**	85
3	**4g**	 **7**	89

[a] Isolated yield after flash column chromatography.

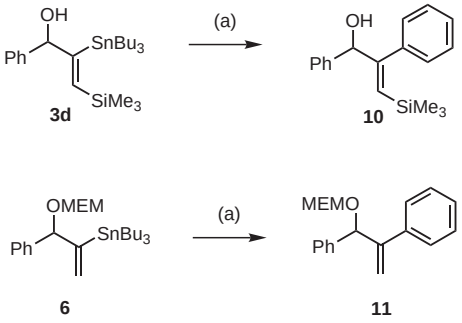
When treated with a suitable source of electrophilic halogen, vinyl stannanes may be converted to vinyl halides under mild reaction conditions. By simple treatment with iodine, the alkenylstannanes **6** and **7** were cleanly convert-

ed into the corresponding 1,1-*gem*-disubstituted alkenyl iodides, **8** and **9,** respectively, thereby establishing a convenient regio- and stereoselective overall route to this compound class from terminal alkynes (Scheme 3).



Scheme 3 Reagents and conditions: (a) I_2, CH_2Cl_2, 0 °C. Yields: 88% (**8**); 95% (**9**).

Stille couplings of selected stannanes of the present study were briefly examined. When stannanes **3d** and **6** were subjected to standard coupling procedures with iodobenzene, e.g. $Pd_2(dba)_3{\cdot}CHCl_3$, in combination with a phosphine ligand (a total of 15 phosphine ligands were tested), in THF (reflux), or DMF (70 °C), with or without catalytic amounts of Cu(I) sources,[24] no general method could be established to provide the desired coupling products **10** and **11** in good yields. The literature clearly indicates that the Stille reaction of hindered stannanes with aryl halides *is* difficult,[3] often affording very low yields and mixtures of isomeric coupling products. Most likely, this limitation on the Stille reaction is associated with steric hindrance, and alternative reaction modes, such as the *cine* substitution,[25] have been reported to set in. Accordingly, our attention turned to Corey's improved procedure for Cu-mediated Stille reactions.[26] The procedure relies on the use of a large excess of CuCl (5 equiv) and LiCl (6 equiv) in DMSO, providing the coupling products in satisfying yields (Scheme 4).



Scheme 4 *Reagents and conditions*: (a) PhI, $Pd_2(dba)_3{\cdot}CHCl_3$ (0.05 equiv, PPh_3 (0.2 equiv), CuCl (5 equiv), LiCl (6 equiv), DMSO, 60 °C. Yields: 65% (**10**); 81% (**11**).

In summary, a series of terminal propargylic alcohols and their O-protected derivatives were subjected to $Pd_2(dba)_3{\cdot}CHCl_3/PPh_3$-catalyzed silastannation with $Bu_3SnSiMe_3$. A range of protecting groups for the propargylic alcohol were found to be compatible with the reaction, as illustrated by the tolerance of methyl, allyl, MEM, TBDMS, and 2-bromobenzyl ethers. The reaction conditions also apply for a diyne to give the corresponding bis-silastannated product. The reaction products are valuable precursors for 1,1-*gem*-disubstituted alkenylstannanes, and iodides, which may be obtained by sequential treatment with TBAF, and iodine. Problems with traditionally sluggish Stille reactions of sterically hindered silastannation products, and 1,1-*gem*-disubstituted alkenylstannanes in general, appear to be easily overcome using Corey's CuCl/LiCl-mediated Stille coupling protocol. Thus, the combination of regioselective silastannation with efficient cross-coupling reactions provides entry to useful building blocks for further synthetic use.

^1H (300 MHz) and ^{13}C (75 MHz) NMR spectra were recorded using $CDCl_3$ as the solvent, and signal positions (δ values) were measured relative to the signals for $CHCl_3$ (7.27) and $CDCl_3$ (77.0), respectively. Tin–hydrogen coupling constants, *J*(Sn,H), are given as the ^{117}Sn and ^{119}Sn values, or average values. IR spectra were obtained for thin films on AgCl plates, and only the strongest/structurally most important peaks are listed. Microanalyses were performed by the Microanalysis Laboratory, Department of Physical Chemistry, University of Vienna, Austria, and at the Department of Chemistry, University of Bath, England. HRMS was performed at the Department of Chemistry, University of Copenhagen, Denmark, and the Department of Chemistry, University of Bath, England. Molecular mass determinations (high-resolution mass spectrometry) for substances containing Bu_3Sn are based on ^{120}Sn and typically made on the $[M - Bu]^+$, unless otherwise stated. All compounds on which HRMS were performed exhibited clean ^1H NMR spectra and showed one spot on TLC analysis, using UV light, and a solution of 5–10% phosphomolybdic acid in ethanol for visualization.

Column chromatography was performed using Amicron Matrex silica gel (35–70 μm). All solvents were distilled prior to use. THF was distilled under nitrogen from Na-benzophenone. CH_2Cl_2 and DMF were dried over calcium hydride and distilled under nitrogen. DMSO was dried over 4Å MS, and degassed (4×) by the freeze-pump-thaw process (–78 °C, r.t., argon). CuCl was prepared according to Österlöf.[27] CuCN and LiCl were oven-dried prior to use and used without further purification. Commercially available compounds were used as received unless otherwise indicated. All reactions were carried out under dry argon using carefully flame-dried glassware. Argon gas was dried by passage through P_2O_5 and silica gel.

Terminal Propargylic Alcohols 1d–j; General Procedure

A 250 mL round-bottomed flask containing THF (100 mL) was cooled to –78 °C. A balloon filled with approximately 4 L of acetylene was attached to the system via a needle. The liquid was stirred for 1 h in which time the balloon contracted corresponding to the amount of absorbed acetylene.[28] To the resultant solution was added *n*-BuLi (1.6 M in hexanes, 37 mL 55 mmol) during 20 min via a syringe, and the solution was stirred for 10 min. To the reaction mixture was dropwise added a solution of the appropriate aldehyde (50 mmol) in THF (15 mL) at –78 °C. The mixture was stirred for 1 h at –78 °C, and then allowed to reach r.t. during which time the balloon expanded to accommodate the excess of acetylene, and subsequently quenched with H_2O (20 mL). To the mixture was added 2–3 portions of K_2CO_3 until the aqueous phase looked pasty. The THF was decanted off and the aqueous phase was extracted with Et_2O (2 × 30 mL). The combined organic phases were dried ($MgSO_4$), filtered and rotary evaporated. This gave a thick, orange oil, which was purified by flash column chromatography on silica gel (hexane–EtOAc, 4:1) to afford the propargylic alcohol.

1-Phenylprop-2-yn-1-ol (1d)[29]
Yield: 81%; thick, clear yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.55–7.25 (m, 5 H), 5.38 (d, *J* = 2 Hz, 1 H), 2.62 (d, *J* = 2 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.2, 128.7, 128.5, 126.8, 83.8, 75.0, 64.2.

4,4-Dimethylpent-1-yn-3-ol (1e)[30]
Yield: 68%, clear yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.04 (d, *J* = 2 Hz, 1 H), 2.48 (d, *J* = 2 Hz, 1 H), 1.03 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 83.6, 73.6, 70.9, 35.4, 25.0.

1-Cyclohexylprop-2-yn-1-ol (1f)[31]
Yield: 70%; clear colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.23–4.10 (m, 1 H), 2.48 (d, *J* = 2 Hz, 1 H), 1.85–0.90 (m, 11 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 83.9, 73.6, 67.0, 43.9, 28.3, 27.9, 26.4, 25.8 (two signals).

1-Phenylpent-1-en-4-yn-3-ol (1g)[32]
Yield: 81%; yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.55–7.15 (m, 5 H), 6.80 (dd, *J* = 16, 2 Hz, 1 H), 6.30 (dd, *J* = 16, 6 Hz, 1 H), 5.06 (m, 1 H), 2.63 (d, *J* = 2 Hz, 1 H), 2.02 (br s, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 135.9, 132.4, 128.7, 128.3, 127.5, 126.9, 82.8, 74.7, 62.8.

Oct-1-yn-3-ol (1h)[33]
Yield: 70%; clear yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.35–4.15 (m, 1 H), 2.33 (d, *J* = 2 Hz, 1 H), 1.85–0.75 (m, 11 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 84.6, 72.3, 61.3, 37.0, 29.9, 24.1, 22.0, 13.3.

1-Naphthylprop-2-yn-1-ol (1i)[34]
Yield: 70%; fluffy, white solid; mp 61–62 °C (Lit.[35] mp 61–63 °C).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.29 (m, *J* = 8 Hz, 1 H), 7.92–7.83 (m, 3 H), 7.62–7.45 (m, 3 H), 6.14 (s, 1 H), 2.35 (br s, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 135.0, 133.9, 130.3, 129.3, 128.6, 126.4, 125.8, 125.1, 124.5, 123.7, 83.2, 75.4, 62.5.

3-Phenylpenta-1,4-diyn-3-ol (1j)[36]
Yield: 74%; thick, clear yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.78–7.63 (m, 2 H), 7.37–7.10 (m, 3 H), 2.88 (br s, 1 H), 2.69 (s, 2 H)

^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.7, 128.9, 128.4, 125.7, 83.3, 73.7, 64.6.

Acetic Acid 1-Phenylprop-2-ynyl Ester (2a)[37]
The alcohol **1d** (524 mg, 4.0 mmol) was dissolved in CH_2Cl_2 (7 mL). To the mixture was added 4-dimethylaminopyridine (244 mg, 2.0 mmol) in one portion, followed by Et_3N (567 mg, 5.6 mmol), and Ac_2O (490 mg, 4.8 mmol). After stirring for 2 h at r.t., TLC indicated the complete conversion of the substrate. The reaction mixture was poured into a separating funnel containing H_2O (15 mL) and CH_2Cl_2 (8 mL). The organic phase was isolated, and the aqueous phase was extracted with CH_2Cl_2 (2 × 8 mL). The combined organic layers were washed with brine (3 × 5 mL), dried ($MgSO_4$), filtered and rotary evaporated. The residue was purified by flash column chromatography on silica gel (hexane–EtOAc, 10:1) to give the crude title compound **2a** (590 mg, 85%) as a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.58–7.49 (m, 2 H), 7.42–7.30 (m, 3 H), 6.45 (d, *J* = 2 Hz, 1 H), 2.64 (d, *J* = 2 Hz, 1 H), 2.12 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.6, 136.5, 129.0, 128.7, 127.6, 75.3, 65.3, 21.0.

(1-*tert*-Butyldimethylsilyloxyprop-2-ynyl)benzene (2b)[38]
The alcohol **1d** (1.06 g, 8.0 mmol), *tert*-butyldimethylsilyl chloride (1.45 g, 9.6 mmol), and imidazole (2.45 g, 36.0 mmol) was dissolved in DMF (10 mL) and stirred overnight. H_2O (10 mL) and pentane (50 mL) were added, and the organic phase was separated. The aqueous phase was extracted with portions of pentane (2 × 25 mL). The combined organics were washed with H_2O (5 × 10 mL), and brine (5 mL), dried ($MgSO_4$), filtered and rotary evaporated. The residue was purified by flash column chromatography on silica gel (hexane–EtOAc, 20:1) to give the crude title compound **2b** (1.81 g, 92%) as a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.46–7.39 (m, 2 H), 7.32–7.17 (m, 3 H), 5.41 (d, *J* = 2 Hz, 1 H), 2.48 (d, *J* = 2 Hz, 1 H), 0.87 (s, 9 H), 0.11 (s, 3 H), 0.07 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.1, 128.1, 127.6, 125.8, 84.6, 73.4, 64.4, 25.6, 18.1, –4.7, –5.1.

(1-Allyloxyprop-2-ynyl)benzene (2c)
A solution of the alcohol **1d** (132 mg, 1.0 mmol) in THF (2 mL) was added dropwise to a suspension of NaH (24 mg, 1.0 mmol) in THF (2 mL). A crystal of KI was added, before the dropwise addition of allyl bromide (182 mg, 1.5 mmol). The mixture was stirred until TLC indicated a complete conversion, and H_2O (2 mL) and Et_2O (30 mL) were added to the reaction mixture. The organic phase was isolated, and the aqueous phase was extracted with Et_2O (2 × 20 mL). The combined organic phases were washed with brine (2 × 5 mL), dried ($MgSO_4$), filtered and rotary evaporated. The residue was purified by flash column chromatography on silica gel (hexane–EtOAc, 20:1) to give the title compound **2c** (102 mg, 59%) as a colorless oil.

IR (neat): 3032, 2860, 1647, 1452, 1060, 1009, 926, 759, 742, 699 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.56–7.49 (m, 2 H), 7.43–7.31 (m, 3 H), 6.04–5.90 (m, 1 H), 5.35 (ddd, *J* = 17, 3, 2 Hz, 1 H), 5.24 (ddd, *J* = 10, 3, 2 Hz, 1 H), 5.22 (d, *J* = 2 Hz, 1 H), 4.22 (dddd, *J* = 12, 5, 2, 1 Hz, 1 H), 4.13 (dddd, *J* = 13, 6, 2, 1 Hz, 1 H), 2.65 (d, *J* = 2 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.1, 134.1, 128.5, 128.4, 127.3, 117.7, 81.6, 75.5, 70.3, 69.1.

Anal. Calcd for $C_{12}H_{12}O$: C, 83.67; H, 7.04. Found: C, 83.39; H, 6.83.

(1-Methoxyprop-2-ynyl)benzene (2d)[39]
To a suspension of NaH (182 mg, 7.6 mmol) in THF (5 mL) at r.t. was added dropwise a solution of propargyl alcohol **1d** (1.00 g, 7.6 mmol) in THF (5 mL). The reaction mixture was stirred for 10 min, before the dropwise addition of MeI (1.61 g, 11.4 mmol) dissolved in THF (5 mL). The mixture was left stirring overnight, then diluted with H_2O (5 mL), and extracted with portions of CH_2Cl_2 (4 × 50 mL). The combined organic extracts were washed with brine (2 × 5 mL), then dried, filtered and concentrated by rotary evaporation. The residue was purified by flash column chromatography on silica gel (hexane–EtOAc, 5:1) to give the title compound **2d** (624 mg, 56%) as a colorless oil (turning brown, if not stored in the dark).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.62–7.29 (m, 5 H), 5.10 (d, *J* = 2 Hz, 1 H), 3.46 (3 H, s), 2.66 (d, *J* = 2 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.0, 128.5, 128.3, 127.3, 81.3, 75.7, 72.8, 55.9.

1-Bromo-2-(1-phenylprop-2-ynyloxymethyl)benzene (2e)
To a suspension of NaH (120 mg, 5 mmol) in THF (5 mL) at r.t. was added dropwise a solution of propargyl alcohol **1d** (280 mg, 5 mmol) in THF (5 mL). The reaction mixture was stirred for 10 min, before the addition of a crystal of Bu_4NI, followed by dropwise addition of 2-bromobenzyl bromide (1.00 g, 4 mmol) dissolved in THF (5 mL). The mixture was left stirring overnight, then diluted with H_2O (5 mL), and extracted with portions of CH_2Cl_2 (4 × 50 mL). The combined organic extracts were washed with brine (10 mL), then dried, filtered and concentrated by rotary evaporation. The residue was purified by flash column chromatography on silica gel (hexane–EtOAc, 30:1) to give the title compound **2e** (867 mg, 72%) as a colorless oil.

IR (neat): 1717, 1599, 1495, 1240, 1095, 754, 692 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.62–7.24 (m, 8 H), 7.19–7.11 (m, 1 H), 5.31 (d, *J* = 2 Hz, 1 H), 4.82 (d, *J* = 13 Hz, 1 H), 4.72 (d, *J* = 13 Hz, 1 H), 2.71 (d, *J* = 2 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.7, 136.9, 132.4, 129.6, 129.0, 128.5, 128.4, 127.3 (two peaks), 122.9, 81.1, 76.2, 71.0, 69.6.

Anal. Calcd for $C_{16}H_{13}BrO$: C, 63.81; H, 4.35. Found: C, 63.60; H, 4.22.

[1-(2-Methoxyethoxymethoxy)prop-2-ynyl]benzene (2f)
The propargyl alcohol **1d** (1.32 g, 10.0 mmol) was dissolved in CH_2Cl_2 (20 mL). The solution was cooled to 0 °C, before the addition of methoxyethoxymethyl chloride (1.87 g, 15 mmol), followed by dropwise addition of *i*-Pr_2EtN (1.94 g, 15 mmol). The reaction mixture was stirred overnight at r.t., and then poured into a separating funnel containing H_2O (5 mL). The organic phase was separated, and the aqueous phase was extracted with CH_2Cl_2 (2 × 10 mL). The combined organic phases were washed with brine (5 mL), dried ($MgSO_4$), filtered, and rotary evaporated. The residue was purified by flash column chromatography on silica gel (hexane–EtOAc, 5:1) to give the title compound **2f** (1.76 g, 80%) as a colorless oil.

IR (neat): 3290, 1654, 1456, 1108, 1034, 908, 850, 750, 700 cm^{-1}.

^1H NMR ($CDCl_3$, 300 MHz): δ = 7.55–7.50 (m, 2 H), 7.42–7.30 (m, 3 H), 5.46 (d, *J* = 2 Hz, 1 H), 5.09 (d, *J* = 7 Hz, 1 H), 4.77 (d, *J* = 7 Hz, 1 H), 3.84–3.68 (m, 2 H), 3.60–3.54 (m, 2 H), 3.40 (s, 3 H), 2.60 (d, *J* = 2 Hz, 1 H).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 138.3, 128.6, 127.5, 92.9, 81.5, 75.3, 71.7, 67.4, 67.2, 59.0.

Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 70.88; H, 7.20.

1-(1-Methoxyprop-2-ynyl)naphthalene (2g)
Following the procedure for the synthesis of **2d**, the reaction of NaH (182 mg, 7.6 mmol), propargyl alcohol **1i** (1.39 g, 7.6 mmol), and MeI (1.61 g, 11.4 mmol) gave, after flash column chromatography on silica gel (hexane–EtOAc, 10:1), the title compound **2g** (1.08 g, 72%) as a yellow oil (turning gradually darker).

IR (neat): 3050, 2935, 1598, 1510, 1462, 1300, 1188, 1165, 1071, 974, 802, 781, 650 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.28–8.20 (m, 1 H), 7.92–7.78 (m, 3 H), 7.62–7.40 (m, 3 H), 5.72 (d, *J* = 2 Hz, 1 H), 3.43 (s, 3 H), 2.71 (d, *J* = 2 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 134.0, 133.1, 130.8, 129.5, 128.6, 126.3, 125.8, 125.0, 124.0, 81.1, 76.4, 71.3, 55.8.

No satisfactory elemental analysis could be obtained.

1-Bromo-2-prop-2-ynyloxymethylbenzene (2h)[40]
Following the procedure for the synthesis of **2e**, the reaction of propargyl alcohol **1c** (840 mg, 15 mmol), NaH (360 mg, 15), 2-bromobenzyl bromide (2.68 g, 11.2 mmol), and a crystal of Bu_4NI gave after flash column chromatography on silica gel (hexane–EtOAc, 30:1) the title compound **2h** (1.99 g, 79%) as a colorless oil.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.52–7.32 (m, 2 H), 7.32–6.99 (m, 2 H), 4.61 (s, 2 H), 4.11 (d, *J* = 2 Hz, 1 H), 2.42 (d, *J* = 2 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 136.7, 132.4, 129.2, 129.0, 127.2, 122.8, 79.4, 74.8, 70.9, 57.7.

Silastannation of Terminal Propargylic Alcohols and their Derivatives; General Procedure
A solution of Ph_3P (48 mg, 0.18 mmol), tris(dibenzylideneacetone)dipalladium(0)-$CHCl_3$ complex (45 mg, 0.043 mmol) was stirred for 10 min in THF (10 mL). To the mixture was added trimethyl(tributylstannyl)silane (3.81 g, 10.5 mmol) and the propargylic alcohol (10 mmol) in THF (5 mL). The resulting solution was refluxed overnight. The dark brown reaction mixture was cooled to r.t. and diluted with Et_2O (100 mL), filtered through a pad of Celite, and concentrated by rotary evaporation. The residue was purified by flash column chromatography on silica gel (hexane–EtOAc, 1:0–10:1) to afford the silastannane.

(*Z*)-4-Tributylstannyl-5-trimethylsilylpent-4-en-1-ol (3a)
Yield: 83%; colorless oil.

IR (neat): 3318, 2956, 1458, 1376, 1247, 1071, 837, 688 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 6.40 [t, *J* = 2 Hz, *J*(^{119}Sn,H) = 179 Hz, *J*(^{117}Sn,H) = 172 Hz, 1 H], 3.64 (t, *J* = 7 Hz, 2 H), 2.36 [dt, *J* = 2, 8 Hz, *J*(Sn,H) = 43 Hz, 2 H], 1.68–1.24 (m, 14 H), 1.01–0.83 (m, 15 H), 0.11 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.9, 144.1, 62.5, 43.6, 32.8, 29.4, 27.5, 13.6, 11.3, 0.2.

Anal. Calcd for $C_{20}H_{44}OSiSn$: C, 53.70; H, 9.91. Found: C, 53.84; H, 10.20.

(*Z*)-3-Tributylstannyl-4-trimethylsilylbut-3-en-1-ol (3b)
Yield: 95%; colorless oil.

IR (neat): 3348, 2956, 1461, 1247, 1044, 843 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 6.47 [s, *J*(^{119}Sn,H) = 173 Hz, *J*(^{117}Sn,H) = 166 Hz, 1 H], 3.57 (q, *J* = 6 Hz, 2 H), 2.56 [t, *J* = 6 Hz, *J*(Sn,H) = 44 Hz, 2 H], 1.58–1.21 (m, 13 H), 1.06–0.80 (m, 15 H), 0.11 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 161.3, 148.4, 60.8, 50.0, 29.1, 27.4, 13.4, 11.2, 0.1.

HRMS (FAB): *m*/*z* calcd for $C_{15}H_{33}OSiSn$ [M – C_4H_9]$^+$: 377.1323; found: 377.1335.

Anal. Calcd for $C_{19}H_{42}OSiSn$: C, 52.66; H, 9.77. Found: C, 52.93; H, 9.88.

(*Z*)-2-Tributylstannyl-3-trimethylsilylprop-2-en-1-ol (3c)[7]
Yield: 85%; colorless oil.

IR (neat): 3319, 2956, 1458, 1376, 1247, 1062, 1021, 839, 690 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 6.63 [t, *J* = 2 Hz, *J*(^{119}Sn,H) = 169 Hz, *J*(^{117}Sn,H) = 162 Hz, 1 H], 4.25 [dd, *J* = 2, 6 Hz, *J*(Sn,H) = 26 Hz, 2 H], 1.65–1.25 (m, 12 H), 1.12–0.87 (m, 15 H), 0.14 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.6, 140.5, 128.3, 73.6, 29.2, 27.4, 13.7, 11.0, 0.11.

Anal. Calcd for $C_{18}H_{40}OSiSn$: C, 51.56; H, 9.62. Found: C, 51.44; H, 9.66.

(*Z*)-1-Phenyl-2-tributylstannyl-3-trimethylsilylprop-2-en-1-ol (3d)
Yield: 85%; thick, slightly yellow oil.

IR (neat): 3423, 2920, 1460, 1247, 1053, 960, 862, 836, 742, 699 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.31–7.17 (m, 5 H), 6.66 [d, *J* = 2 Hz, *J*(^{119}Sn,H) = 167 Hz, *J*(^{117}Sn,H) = 159 Hz, 1 H], 5.20 [dd, *J* = 2, 4 Hz, *J*(Sn,H) = 37 Hz, 1 H], 1.91 (d, *J* = 4 Hz, 1 H), 1.37–1.04 (m, 12 H), 0.85–0.66 (m, 15 H), 0.13 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.4, 142.2, 141.9, 128.2, 127.4, 127.1, 83.8, 29.0, 27.4, 13.6, 11.6, 0.3.

Anal. Calcd for $C_{24}H_{44}OSiSn$: C, 58.19; H, 8.95. Found: C, 58.38; H, 8.73.

(*Z*)-4,4-Dimethyl-2-tributylstannyl-1-trimethylsilylpent-1-en-3-ol (3e)
Yield: 80%; colorless oil.

IR (neat): 3482, 2954, 1464, 1376, 1361, 1248, 1070, 1003, 860, 758, 690 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 6.55 [d, *J* = 1 Hz, *J*(^{119}Sn,H) = 180 Hz, *J*(^{117}Sn,H) = 173 Hz, 1 H], 3.91 [dd, *J* = 1, 2 Hz, *J*(Sn,H) = 42 Hz), 1 H], 1.61–1.25 (m, 12 H), 1.03–0.86 (m, 15 H), 0.89 (s, 9 H), 0.15 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.0, 144.6, 128.3, 88.3, 35.9, 29.3, 27.6, 26.5, 13.7, 12.8, 0.4.

Anal. Calcd for $C_{22}H_{48}OSiSn$: C, 55.58; H, 10.18. Found: C, 55.90; H, 10.15.

(*Z*)-1-Cyclohexyl-2-tributylstannyl-3-trimethylsilylprop-2-en-1-ol (3f)
Yield: 72%; colorless oil.

IR (neat): 2955, 2924, 1451, 1247, 1072, 1012, 862, 836 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 6.40 [d, *J* = 1 Hz, *J*(^{119}Sn,H) = 176 Hz, *J*(^{117}Sn,H) = 168 Hz, 1 H], 3.76 [d, *J* = 7 Hz, *J*(Sn,H) = 47 Hz), 1 H], 1.90–0.78 (m, 38 H), 0.12 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.7, 142.0, 88.0, 42.0, 30.5, 29.3, 27.5, 27.4, 26.5, 26.4, 26.2, 13.7, 11.9, 0.3.

Anal. Calcd for $C_{24}H_{50}OSiSn$: C, 57.48; H, 10.05. Found: C, 58.17; H, 10.11.

(*Z*)-5-Phenyl-2-tributylstannyl-1-trimethylsilylpenta-1,4-dien-3-ol (3g)
Yield: 67%; colorless oil.

IR (neat): 3427, 2954, 1603, 1460, 1376, 1247, 967, 859, 750, 692 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.42–7.19 (m, 5 H), 6.65 [d, *J* = 1 Hz, *J*(^{119}Sn,H) = 168 Hz, *J*(^{117}Sn,H) = 161 Hz, 1 H], 6.53 (d, *J* = 18 Hz, 1 H), 6.17 (d, *J* = 6 Hz, 1 H), 6.12 (d, *J* = 6 Hz, 1 H), 4.84–4.78 [m, *J*(Sn,H) = 40 Hz, 1 H], 1.78 (d, *J* = 4 Hz, 1 H), 1.59–1.21 (m, 12 H), 1.02–0.81 (m, 15 H), 0.15 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.4, 142.4, 136.8, 131.2, 130.8, 128.5, 127.6, 126.5, 83.1, 29.2, 27.5, 13.6, 11.9, 0.3.

Anal. Calcd for $C_{26}H_{46}OSiSn$: C, 59.89; H, 8.89. Found: C, 60.01; H, 9.14.

(*Z*)-2-Tributylstannyl-1-trimethylsilyloct-1-en-3-ol (3h)
Yield: 74%; colorless oil.

IR (neat): 3452, 2956, 2928, 1464, 1247, 1026, 860, 736 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 6.51 [d, *J* = 1 Hz, *J*(^{119}Sn,H) = 174 Hz, *J*(^{117}Sn,H) = 166 Hz, 1 H], 4.06 (m, 1 H), 1.58–1.25 (m, 20 H), 1.03–0.82 (m, 18 H), 0.13 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.8, 140.4, 83.0, 37.0, 31.8, 29.3, 27.5, 25.6, 22.6, 14.0, 13.7, 11.8, 0.3.

Anal. Calcd for $C_{23}H_{50}OSiSn$: C, 56.55; H, 10.13. Found: C, 56.85; H, 9.87.

HRMS (FAB): *m/z* calcd for $C_{19}H_{39}SiSn$ [M – C_4H_9 – H_2O]$^+$: 415.1851; found: 415.1851.

(*Z*)-1-(1-Naphthyl)-2-tributylstannyl-3-trimethylsilylprop-2-en-1-ol (3i)
Yield: 72%; colorless oil.

IR (neat): 3364, 2955, 1458, 1246, 1048, 864, 780 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.25–8.19 (m, 1 H), 7.89–7.76 (m, 3 H), 7.57–7.39 (m, 3 H), 6.85 [d, *J* = 2 Hz, *J*(^{119}Sn,H) = 171 Hz, *J*(^{117}Sn,H) = 163 Hz, 1 H], 6.07 [dd, *J* = 2, 6 Hz, *J*(Sn,H) = 23 Hz, 1 H], 1.97 (d, *J* = 6 Hz, 1 H), 1.41–1.08 (m, 12 H), 0.96–0.68 (m, 15 H), 0.18 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.3, 140.7, 137.9, 134.1, 131.8, 128.7, 128.6, 126.1, 125.6, 125.6, 125.0, 124.2, 77.8, 29.1, 27.4, 13.6, 11.6, 0.3.

Anal. Calcd for $C_{28}H_{46}OSiSn$: C, 61.65; H, 8.50. Found: C, 61.57; H, 8.83.

(*Z*,*Z*)-3-Phenyl-2,4-bis(tributylstannyl)-1,5-bis(trimethylsilyl)penta-1,4-dien-3-ol (3j)
Yield: 71%; colorless oil.

IR (neat): 2954, 1464, 1376, 1247, 1072, 1004, 860, 701 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.32–7.12 (m, 5 H), 5.95 [s, *J*(^{119}Sn,H) = 182 Hz, *J*(^{117}Sn,H) = 174 Hz, 2 H], 2.46 (s, 1 H), 1.55–1.23 (m, 12 H), 0.98–0.72 (m, 15 H), 0.11 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 173.2, 144.8, 143.9, 127.7, 127.6, 126.7, 92.6, 29.3, 27.6, 13.7, 13.3, 0.5.

Anal. Calcd for $C_{41}H_{80}OSi_2Sn_2$: C, 55.79; H, 9.14. Found: C, 56.01; H, 9.25.

(*Z*)-[1-(*tert*-Butyldimethylsilyloxy)-2-tributylstannyl-3-trimethylsilylallyl]benzene (4b)
Yield: 85%; colorless oil.

IR (neat): 2955, 2928, 1464, 1248, 1089, 1064, 884, 836, 777 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.35–7.25 (m, 5 H), 6.64 [d, *J* = 1 Hz, *J*(^{119}Sn,H) = 165 Hz, *J*(^{117}Sn,H) = 158 Hz, 1 H], 5.16 [s, *J*(Sn,H) = 55 Hz, 1 H], 1.38–1.10 (m, 12 H), 1.05–0.68 (m, 15 H), 0.96 (s, 9 H), 0.19 (s, 9 H), 0.09 (s, 3 H), 0.08 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.4, 143.2, 143.0, 127.8, 126.6, 126.5, 87.5, 29.1, 27.5, 26.2, 18.6, 13.6, 11.9, 0.2, –3.9, –4.7.

Anal. Calcd for $C_{30}H_{58}OSiSn$: C, 59.10; H, 9.59. Found: C, 59.35; H, 9.41.

(*Z*)-(3-Allyloxy-3-phenyl-2-tributylstannylpropenyl)trimethylsilane (4c)
Yield: 61%; colorless oil.

IR (neat): 2955, 1448, 1247, 1069, 861, 837, 744, 698 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.35–7.19 (m, 5 H), 6.56 [d, *J* = 1 Hz, *J*(^{119}Sn,H) = 168 Hz, *J*(^{117}Sn,H) = 161 Hz, 1 H], 6.04–5.90 (m, 1 H), 5.30 (ddt [app. ddd], *J* = 17, 4, 2 Hz, 1 H), 5.17 (ddt, *J* = 11, 4, 2 Hz, 1 H), 4.81 [d, *J* = 2 Hz, *J*(Sn,H) = 46 Hz, 1 H], 4.07 (dddd, *J* = 13, 5, 2, 2 Hz, 1 H), 3.92 (dddd, *J* = 13, 6, 2, 2 Hz, 1 H), 1.43–1.15 (m, 12 H), 0.94–0.70 (m, 15 H), 0.18 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.8, 145.3, 141.0, 135.1, 127.9, 127.2, 127.1, 116.2, 92.0, 69.5, 29.1, 27.5, 13.7, 11.8, 0.4.

Anal. Calcd for $C_{27}H_{48}OSiSn$: C, 60.55; H, 9.05. Found: C, 60.61; H, 8.76.

(*Z*)-(3-Methoxy-3-phenyl-2-tributylstannylpropenyl)trimethylsilane (4d)
Yield: >95%; colorless oil.

IR (neat): 2955, 1464, 1376, 1248, 1092, 839, 743, 699 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.35–7.20 (m, 5 H), 6.53 [d, *J* = 2 Hz, *J*(^{119}Sn,H) = 170 Hz, *J*(^{117}Sn,H) = 162 Hz], 4.64 [s, *J*(Sn,H) = 42 Hz, 1 H], 1.45–1.17 (m, 12 H), 1.00–0.68 (m, 15 H), 0.17 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.0, 144.7, 140.8, 127.9, 127.3, 127.1, 94.0, 56.5, 29.0, 27.5, 13.7, 11.8, 0.4.

Anal. Calcd for $C_{25}H_{46}OSiSn$: C, 58.94; H, 9.10; Found: C, 58.99; H, 9.12.

(*Z*)-[3-(2-Methoxyethoxymethoxy)-3-phenyl-2-tributylstannylpropenyl]trimethylsilane (4f)
Yield: 88%; colorless oil.

IR (neat): 2956, 1456, 1376, 1248, 1110, 1026, 839, 744, 700 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.37–7.20 (m, 5 H), 6.74 [d, *J* = 1 Hz, *J*(^{119}Sn,H) = 167 Hz, *J*(^{117}Sn,H) = 160 Hz, 1 H], 5.19 [s, *J*(Sn,H) = 41 Hz, 1 H], 4.86 (d, *J* = 7 Hz, 1 H), 4.76 (d, *J* = 7 Hz, 1 H), 3.87–3.79 (m, 1 H), 3.73–3.64 (m, 1 H), 3.55 (t, *J* = 5 Hz, 2 H), 3.39 (s, 3 H), 1.38–1.15 (m, 12 H), 0.96–0.70 (m, 15 H), 0.19 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.9, 145.9, 140.7, 128.0, 127.1 (two signals), 92.7, 88.1, 71.8, 67.1, 59.0, 53.4, 28.9, 27.4, 13.6, 11.7, 0.3.

Anal. Calcd for $C_{28}H_{52}O_3SiSn$: C, 57.63; H, 8.98. Found: C, 57.78; H, 8.74.

(*Z*)-[3-Methoxy-3-(naphth-1-yl)-2-tributylstannylpropenyl]trimethylsilane (4g)
Yield: >95%; colorless oil.

IR (neat): 2955, 2921, 1464, 1247, 1089, 862, 776, 674 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.09–8.01 (m, 1 H), 7.89–7.74 (m, 2 H), 7.53–7.38 (m, 4 H), 6.37 [d, *J* = 2 Hz, *J*(^{119}Sn,H) = 176 Hz, *J*(^{117}Sn,H) = 168 Hz, 1 H], 5.38 [d, *J* = 2 Hz, *J*(Sn,H) = 19 Hz, 1 H], 3.33 (s, 3 H), 1.53–1.16 (m, 12 H), 1.05–0.75 (m, 15 H), 0.18 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.6, 143.4, 136.1, 134.1, 131.8, 131.8, 128.5, 128.5, 126.8, 125.5, 125.3, 125.1, 124.9, 89.7, 57.0, 29.2, 27.5, 13.7, 11.7, 0.2.

Anal. Calcd for $C_{29}H_{48}OSiSn$: C, 62.26; H, 8.65. Found: C, 62.69; H, 8.43.

(*Z*)-[3-(2-Bromobenzyloxy)-2-tributylstannylpropenyl]trimethylsilane (4h)
Yield: 78%; colorless oil.

IR (neat): 2955, 1464, 1376, 1339, 1097, 1028, 847, 748, 691, 670 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.55–7.50 (m, 2 H), 7.34–7.28 (m, 1 H), 7.17–7.10 (m, 1 H), 6.69 [t, *J* = 1 Hz, *J*(^{119}Sn,H) = 169 Hz, *J*(^{117}Sn,H) = 161 Hz, 1 H], 4.54 (s, 2 H), 4.21 [d, *J* = 1 Hz, *J*(Sn,H) = 32 Hz, 2 H], 1.55–1.24 (m, 12 H), 1.10–0.84 (15 H, m), 0.15 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 161.2, 144.6, 138.0, 132.2, 128.8, 128.5, 127.2, 122.2, 82.8, 71.0, 29.2, 27.5, 13.7, 11.2, 0.1.

Anal. Calcd for $C_{25}H_{45}BrOSiSn$: C, 51.04; H, 7.71. Found: C, 51.30; H, 7.80.

TBAF-Mediated Desilylation of Silastannation Products; General Procedure
To a solution of the silastannane **4f**,**g** (1.09 mmol) in THF (1 mL) was added Bu_4NF (1.0 M in THF, 3.3 mL, 3.3 mmol). The reaction mixture was refluxed overnight, and partitioned between H_2O (20 mL) and Et_2O (20 mL). The organic phase was separated, and the aqueous phase was extracted with Et_2O (2 × 20 mL). The combined organic phases were dried ($MgSO_4$), filtered, and rotary evaporated. The residue was purified by flash column chromatography on silica gel (hexane–EtOAc–Et_3N, 50:1:1–50:2:1) to give the desilylated product.

Tributyl-{1-[(2-methoxyethoxymethoxy)phenylmethyl]vinyl}stannane (6)
Yield: 85%; colorless oil.

IR (neat): 2955, 2926, 1457, 1110, 1038, 929, 699 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.35–7.19 (m, 5 H), 5.94 [dd, *J* = 2, 2 Hz, *J*(Sn,H) = 126 Hz, 1 H], 5.38 [dd, *J* = 2, 1 Hz, *J*(Sn,H) = 60 Hz, 1 H], 5.25 [br s, *J*(Sn,H) = 21 Hz, 1 H], 4.81 (d, *J* = 7 Hz, 1 H), 4.72 (d, *J* = 7 Hz, 1 H), 3.72–3.66 (m, 2 H), 3.53–3.46 (m, 2 H), 3.36 (s, 3 H), 1.45–1.15 (m, 12 H), 0.90–067 (m, 15 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.7, 141.4, 128.1, 127.1, 126.9, 126.0, 92.7, 83.7, 71.7, 67.0, 58.9, 28.9, 27.3, 13.6, 9.9.

Anal. Calcd for $C_{25}H_{44}O_3Sn$: C, 58.72; H, 8.67. Found: C, 58.89; H, 8.58.

Tributyl[1-(methoxynaphth-1-ylmethyl)vinyl]stannane (7)
Yield: 89%; colorless oil.

IR (neat): 2954, 2925, 1464, 1376, 1101, 1094, 927, 801, 779, 699 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.18–8.10 (m, 1 H), 7.89–7.77 (m, 2 H), 7.53–7.40 (m, 4 H), 5.58 [dd (app. t), *J* = 2, 3 Hz, *J*(Sn,H) = 134 Hz, 1 H], 5.32 [m, *J*(Sn,H) = 64 Hz, *J*(Sn,H) = 26 Hz, 2 H], 3.31 (s, 3 H), 3.55–1.20 (m, 12 H), 0.95–0.67 (m, 15 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.4, 136.9, 134.1, 131.2, 128.5, 128.2, 125.8, 125.4, 125.2 (two signals), 125.1, 88.2, 56.4, 29.1, 27.0, 13.7, 10.1.

Anal. Calcd for $C_{26}H_{40}OSn$: C, 64.08; H, 8.27. Found: C, 64.08; H, 8.32.

Iododestannylation of Alkenylstannanes; General Procedure
A solution of the alkenylstannane **6**, **7** (0.50 mmol) in CH_2Cl_2 (40 mL) was cooled to 0 °C, and a solution of I_2 (ca. 130 mg, 0.5 mmol) in CH_2Cl_2 (15 mL) was added dropwise until a permanent red coloration was observed. The reaction mixture was stirred for a further 30 min, before pouring the mixture into aq sat. $Na_2S_2O_3$ (15 mL). The red/pink organic phase became immediately colorless when shaken with aq sat. $Na_2S_2O_3$ in a separating funnel. The organic phase was washed with further amounts of aq sat. $Na_2S_2O_3$ (2 × 10 mL) and brine (5 mL), then separated, dried ($MgSO_4$), and rotary evaporated. The residue was purified by flash column chromatography on silica gel (hexane–EtOAc, 30:1) to give the alkenyl iodide.

[2-Iodo-1-(2-methoxyethoxymethoxy)allyl]benzene (8)
Yield: 88%; colorless oil.

IR (neat): 2886, 1611, 1494, 1452, 1274, 1112, 1024, 912, 852, 760, 700 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.43–7.28 (m, 5 H), 6.54 (dd, *J* = 1, 2 Hz, 1 H), 6.04 (dd, *J* = 1, 2 Hz, 1 H), 5.03 (s, 1 H), 4.86 (d, *J* = 7 Hz, 1 H), 4.78 (d, *J* = 7 Hz, 1 H), 3.82–3.68 (m, 2 H), 3.60–3.46 (m, 2 H), 3.36 (s, 3 H).

^{13}C NMR (75 MHz, $CHCl_3$): δ = 138.5, 128.2, 128.0, 127.6, 127.1, 113.4, 92.9, 82.1, 71.6, 67.4, 58.9.

Anal. Calcd for $C_{13}H_{17}IO_3$: C, 44.84; H, 4.92. Found: C, 44.91; H, 4.87.

1-(2-Iodo-1-methoxyallyl)naphthalene (9)
Yield: 95%; colorless oil.

IR (neat): 2925, 1606, 1511, 1460, 1396, 1190, 1095, 910, 802, 785, 733 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.08–8.00 (m, 1 H), 7.93–7.82 (m, 2 H), 7.73–7.66 (m, 1 H), 7.57–7.45 (m, 3 H), 6.46 (dd, *J* = 2, 2 Hz, 1 H), 6.09 (dd, *J* = 1, 2 Hz, 1 H), 5.25 (s, 1 H), 3.49 (s, 3 H).

^{13}C NMR (75 MHz, $CHCl_3$): δ = 134.1, 133.9, 131.2, 129.3, 129.2, 128.3, 126.4, 126.2, 125.8, 125.5, 123.7, 112.5, 86.6, 57.8.

Anal. Calcd for $C_{14}H_{13}IO$: C, 51.87; H, 4.04. Found: C, 51.62; H, 4.31.

Stille Reactions of Alkenylstannanes; General Procedure
A Schlenk tube was charged with LiCl (127 mg, 3.0 mmol) and flame-dried under high vacuum. Upon cooling, Ph_3P (52 mg, 0.20 mmol), tris(dibenzylideneacetone)dipalladium(0)-$CHCl_3$ complex (52 mg, 0.05 mmol), and CuCl (245 mg, 2.5 mmol) were added, and the mixture was degassed (4 ×) under high vacuum with an argon purge. A solution of iodobenzene (100 mg, 0.5 mmol), and the alkenylstannane **3d**, **6** (0.6 mmol) in DMSO (5 mL) was introduced with concomitant stirring. The reaction mixture was vigorously degassed (4 ×) by the freeze-pump-thaw process (–78 °C to r.t., argon). The mixture was stirred at r..t for 1 h, and then heated to 60 °C overnight. Upon cooling, the mixture was diluted with Et_2O (60 mL), and washed with a mixture of brine (80 mL) and 5% aq ammonia (15 mL). The aqueous layer was further extracted with Et_2O (2 × 50 mL), and the combined organic layers were washed with H_2O (2 × 50 mL, brine (2 × 50 mL), then dried ($MgSO_4$), filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography on silica gel (hexane–EtOAc, 20:1) to give the cross-coupling product.

(*E*)-1,2-Diphenyl-3-trimethylsilylprop-2-en-1-ol (10)
Yield: 67%; colorless oil.

IR (neat): 3375, 2954, 1595, 1490, 1246, 1061, 877, 838, 764, 700 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.68–7.50 (8 H, m), 7.30–7.21 (2 H, m), 6.47 (1 H, d, *J* = 2 Hz), 5.74 (1 H, dd, *J* = 4, 2 Hz), 2.47 (1 H, d, *J* = 4 Hz), 0.19 (9 H, s).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.3, 141.5, 140.5, 129.1, 128.2, 127.6 (two peaks), 127.2, 126.9, 126.4, 79.7, –0.1.

Anal. Calcd for $C_{18}H_{22}OSi$: C, 76.54; H, 7.85. Found: C, 76.88; H, 7.99.

{1-[Phenyl(2-methoxyethoxymethoxy)methyl]vinyl}benzene (11)[41]
Yield: 81%; yellow oil.

IR (neat): 2925, 1457, 1377, 1260, 1172, 1106, 1040, 909, 734, 698 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.48–7.10 (m, 10 H), 5.67 (br s, 1 H), 5.52 (d, *J* = 1 Hz, 1 H), 5.46 [dd (app. t), *J* = 1, 1 Hz, 1 H], 4.87 (d, *J* = 7 Hz, 1 H), 4.77 (d, *J* = 7 Hz, 1 H), 3.72–3.65 (m, 2 H), 3.55–3.47 (m, 2 H), 3.39 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.1, 143.2, 128.2 (several signals), 127.4, 127.1, 115.3, 93.1, 79.0, 71.7, 67.2, 58.9.

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