A Stereoselective Approach to (*Z*)-1-Silyl-2-aryl-1,3-dienes from 4-(Phenylselanyl)but-1-yne via Palladium-Catalyzed Silylstannylation and Selenoxide Elimination

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Abstract: The palladium-catalyzed silylstannylation of 4-(phenylselanyl)but-1-yne proceeded regio- and stereoselectively, followed by selenoxide elimination via oxidation to give (*Z*)-1-(trimethylsilyl)-2-(tributylstannyl)buta-1,3-diene in good yield. This conjugated diene underwent the Stille coupling reaction with various aryl iodides in the presence of $Pd(PPh_3)_4$ to afford (*Z*)-2-aryl-1-(trimethylsilyl)buta-1,3-dienes with high stereoselectivity. Reversing the order of selenoxide elimination and Stille coupling reaction in the synthetic procedure also resulted in good yields of (*Z*)-2-aryl-1-(trimethylsilyl)buta-1,3-dienes.

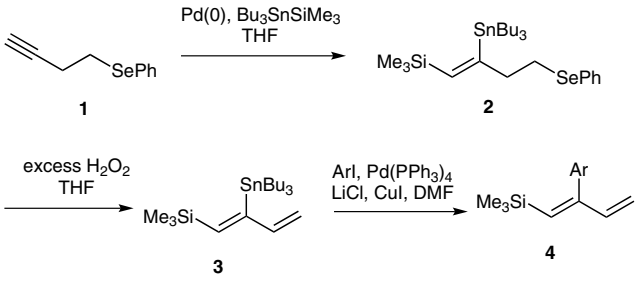
Key words: silylstannylation, selenide, Stille coupling reaction, selenoxide elimination, conjugated dienes, stereoselectivity

Conjugated dienes are useful intermediates in organic synthesis because they can be utilized in numerous transformations,[1] such as Diels–Alder reactions, and are frequently found as significant constituents in natural products and their analogues.[2] In particular, functionalized 1,3-dienes bearing metals and heteroatoms, for example Danishefsky's diene and Rawal's diene, can play an important role in cycloadditions and behave highly effective tools for the control of regio- and stereoselectivities by the presence of their functional groups.[3] The synthetic approaches to bimetal-substituted 1,3-dienes, which are substituted at the 1,2-,[4] 1,3-,[5] 2,3-,[6] and 1,4-positions,[7] containing B, Si, Ge, and Sn, are described in literature. However, useful methods for the stereoselective synthesis of silicon/tin 1,2-bimetal-substituted 1,3-dienes are limited.[8]

The palladium-catalyzed silylstannylation of terminal alkynes is very interesting and well established,[9,10] because the resulting compounds have two different metal functionalities that can be useful for further transformations, such as Stille coupling,[10g,11] iododestannylation,[8,10g,11a,12] Sn–Li exchange reactions,[9a,10b,d] and Lewis acid mediated acylation.[10d] Furthermore, the silylstannylation reaction generally proceeds with excellent regio- and stereoselectivities to give 1,2-bimetal-substituted alkenes in which the stannyl group is attached to the inner carbon.[10e]

Recently, we reported the stereoselective synthesis of monosubstituted 1,3-dienes via conjugated addition of vinylic organocuprates, generated from the transmetalation of vinylzirconates, containing a phenylselanyl group to enones, followed by selenoxide elimination via oxidation.[13]

Herein, we describe a simple and stereoselective synthesis of (*Z*)-1-silyl-2-aryl-1,3-dienes by the combination of palladium-catalyzed silylstannylation of the terminal triple bond of 4-(phenylselanyl)but-1-yne (**1**), oxidative elimination of the phenylselanyl group, and the Stille coupling reaction with various aryl iodides (Scheme 1).



Scheme 1

We initiated the investigation by optimizing the reaction conditions (Pd catalyst, concentration, and reaction time) for the palladium-catalyzed silylstannylation of **1** (Table 1). The reaction of **1** with trimethyl(tributylstannyl)silane in the presence of $Pd(PPh_3)_4$ (5 mol%) was carried out in tetrahydrofuran (1.0 M) at 60 °C for 24 hours to give (*Z*)-1-silyl-2-stannyl-substituted homoallylic selenide **2** in 34% yield with exclusive regio- and stereoselectivities (entry 1). Increasing the reaction time did not appreciably improve the yield of **2** (entries 2 and 3). When the reaction was conducted using a 2.0 M solution of **1** in tetrahydrofuran, the desired product **2** was obtained in 43% yield (entry 4). Changing the catalyst from $Pd(PPh_3)_4$ to $Pd(dba)_2$ and a phosphite or phosphine gave improved yields (entries 6 and 7), but the use of $Pd(PPh_3)_2Cl_2$ gave traces of **2** only (entry 5). The reaction under the best conditions [$Pd(dba)_2$ (2 mol%)/$P(OEt_3)$ (4 mol%), THF, 60 °C, 24 hours] afforded the silylstannylated product **2** in 65% yield (entry 6). Unfortunately, the use of the catalyst combination of $Pd_2(dba)_3{\cdot}CHCl_3$ (1 mol%) and triphenylphosphine (4 mol%), which is known to be highly effective for the silylstannylation of propargylic alcohols and their derivatives,[10g] gave an unsatisfactory result in

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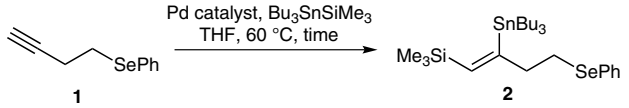
this reaction (entry 8). In all entries, the silylstannylation of **1** was incomplete and unreacted alkyne **1** was recovered. Furthermore, attempts were made to optimize the $Pd(dba)_2/P(OEt)_3$ catalytic system for this silylstannylation under various reaction conditions (solvent, reaction temperature, and concentration of catalyst) to improve the yield **2**. However, the conditions given in entry 6 still gave the best result. The efficiency of the palladium-catalyzed silylstannylation of **1** was not high, which would be due to the influence of the selenium atom in **1**. The configuration of **2** was determined to be the *trans* between tin and the vinyl proton by the NMR coupling constants [$J(^{117}Sn, H) = 168$ Hz and $J(^{119}Sn, H) = 176$ Hz]. In general, when the proton and tin are in a *trans* relationship, the coupling constants are 160–200 Hz, whereas the coupling constants in *cis* and geminal geometries are 80–100 Hz.[10d,i,14]

Table 1 Palladium-Catalyzed Silylstannylation of 4-(Phenylselanyl)but-1-yne (**1**)[a]

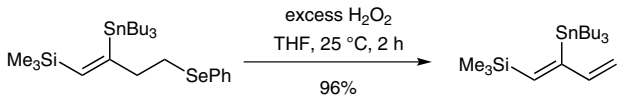


1 **2**

Entry	Pd catalyst (mol%)	Time (h)	Yield[b] (%)
1[c]	$Pd(PPh_3)_4$ (5)	24	34
2[c]	$Pd(PPh_3)_4$ (5)	48	36
3[c]	$Pd(PPh_3)_4$ (5)	96	40
4	$Pd(PPh_3)_4$ (5)	24	43
5	$Pd(PPh_3)_2Cl_2$ (5)	24	trace
6	$Pd(dba)_2$ (2)/$P(OEt)_3$ (4)	24	65
7	$Pd(dba)_2$ (2)/Bu_3P (4)	24	56
8	$Pd_2(dba)_3{\cdot}CHCl_3$ (1)/Ph_3P (4)	24	45

[a] All reactions were carried out with a 2.0 M solution of **1** in THF.
[b] Isolated yield.
[c] The reaction was carried out with 1.0 M solution of **1** in THF.

Oxidation of the adduct **2** containing a phenylselanyl group with hydrogen peroxide in tetrahydrofuran resulted in *syn* elimination of the corresponding selenoxide leading to solely the (*Z*)-isomer of 1-silyl-2-stannylbuta-1,3-diene **3** in 96% yield without isomerization of the alkene moiety (Scheme 2). The stereochemistry of **3** was also assigned by the coupling constants between tin and the vinyl proton [$J(^{117}Sn, H) = 162$ Hz and $J(^{119}Sn, H) = 167$ Hz].



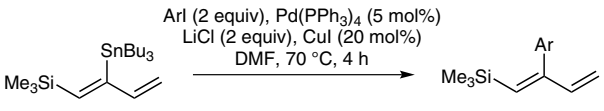
2 **3**

Scheme 2

From the viewpoint of synthetic efficiency, one-pot synthetic procedures are very useful. A one-pot procedure for the palladium-catalyzed silylstannylation of **1** followed by the oxidation with hydrogen peroxide was carried out. However, a vigorously exothermic reaction between the catalyst [$Pd(dba)_2/P(OEt)_3$] and hydrogen peroxide occurred, and the desired product was not obtained.

For further transformations, the Stille coupling reaction at the vinyltin group of the conjugated diene **3** was examined. The cross-coupling of **3** with a variety of aryl iodides (2 equiv) using $Pd(PPh_3)_4$ (5 mol%) in the presence of copper(I) iodide (20 mol%) and lithium chloride (2 equiv) as additives in *N*,*N*-dimethylformamide at 70 °C gave (*Z*)-2-aryl-1-(trimethylsilyl)buta-1,3-dienes **4a**–**f** in moderate to good yields (Table 2). Stille coupling of **3** with iodobenzene, 1-iodonaphthalene, or aryl iodides with an electron-deficient substituent in the *para* position provided the conjugated dienes **4a**,**b**,**e**,**f** in 70–84% yields (entries 1, 2, 5, and 6). In the case of 4-methyl- and 4-methoxyphenyl coupling partners, the corresponding products **4c** and **4d** were obtained, but the yields decreased to 52% and 54%, respectively (entries 3 and 4).

Table 2 Stille Coupling Reaction of (*Z*)-1-Silyl-2-stannylbuta-1,3-diene **3** with Aryl Iodides



3 **4**

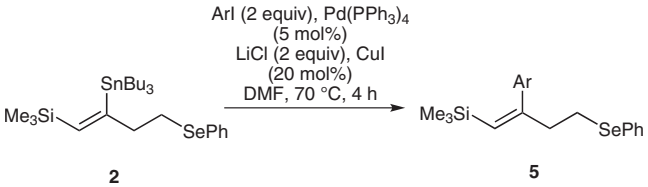
Entry	ArI	Product	Yield[a] (%)
1	Ph	**4a**	70
2	1-naphthyl	**4b**	82
3	$4\text{-}MeC_6H_4$	**4c**	52
4	$4\text{-}MeOC_6H_4$	**4d**	54
5	$4\text{-}O_2NC_6H_4$	**4e**	84
6	$4\text{-}ClC_6H_4$	**4f**	77

[a] Isolated yield.

On the other hand, reversing the order of the selenoxide elimination and the Stille coupling reaction in the synthetic sequence also afforded conjugated dienes **4**. The cross-coupling reaction of the silylstannylated product **2** with various aryl iodides under the same conditions as described above gave (*Z*)-2-aryl-1-(trimethylsilyl)-substituted homoallylic selenides **5a**–**f** stereoselectively (Table 3). The Stille coupling reaction with iodobenzene, 1-iodonaphthalene, and electron-rich aryl iodides resulted the desired products **5a**–**d** in 63–65% yields (entries 1–4). In this reaction, the use of electron-deficient aryl iodides was highly effective (91% and 71% yields, entries 5 and 6, respectively). Next, oxidation of the cross-coupling products **5a**–**f** with hydrogen peroxide afforded efficiently (*Z*)-2-aryl-1-(trimethylsilyl)-substituted conjugated dienes

4a–f in high yields (78–87%) via *syn* elimination of the corresponding selenoxides, regardless of the substituent on the aromatic ring (Table 4).

Table 3 Stille Coupling Reaction of the Silylstannylated Compound **2** with Aryl Iodides

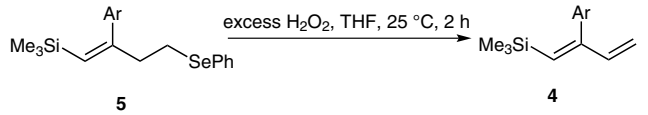


2 **5**

Entry	ArI	Product	Yield[a] (%)
1	Ph	**5a**	63
2	1-naphthyl	**5b**	64
3	4-MeC_6H_4	**5c**	65
4	4-$MeOC_6H_4$	**5d**	65
5	4-$O_2NC_6H_4$	**5e**	91
6	4-ClC_6H_4	**5f**	71

[a] Isolated yield.

Table 4 Selenoxide Elimination via Oxidation of the Coupling Products **5**



5 **4**

Entry	Substrate	Ar	Product	Yield[a] (%)
1	**5a**	Ph	**4a**	83
2	**5b**	1-naphthyl	**4b**	78
3	**5c**	4-MeC_6H_4	**4c**	84
4	**5d**	4-$MeOC_6H_4$	**4d**	85
5	**5e**	4-$O_2NC_6H_4$	**4e**	86
6	**5f**	4-ClC_6H_4	**4f**	87

[a] Isolated yield.

In conclusion, we have developed a simple and useful method for the stereoselective synthesis of (*Z*)-1-silyl-2-aryl-1,3-dienes by the combination of palladium-catalyzed silylstannylation, oxidative deselenation, and the Stille coupling reaction.

^1H, ^{13}C, and ^{77}Se NMR spectra were recorded on a Jeol JNM-LA-400 (^1H; 399.7 MHz, ^{13}C; 100.4 MHz, and ^{77}Se; 76.2 MHz, respectively) spectrometer relative to TMS or the residual solvent signals [$CDCl_3$: δ = 7.26 (^1H) and 77.0 (^{13}C)] as internal standard, or $(PhSe)_2$ as external standard [$CDCl_3$: δ = 464.1 (^{77}Se)]. IR spectra were obtained on a Shimadzu FTIR-8300 spectrophotometer. Mass spectra (EI) were recorded on a Jeol JMS-700 or JMS-SX 102A mass spectrometer. Melting points were measured on a Gallenkamp MFB-595 apparatus and are uncorrected. Column chromatography used Kanto Chemical silica gel 60 N (40–50 μm). THF was distilled from Na benzophenone ketyl under N_2. DMF was dried over CaH_2 and distilled under reduced pressure. Other reagents were commercially available and used without further purification. All reactions were performed under an argon atmosphere with flame-dried glassware using a vacuum pump unless otherwise described. 4-(Phenylselanyl)but-1-yne (**1**)[13] and trimethyl(tributylstannyl)silane[15] were synthesized according to published procedures.

(*Z*)-Trimethyl[4-(phenylselanyl)-2-(tributylstannyl)but-1-enyl]silane (2)

A THF (5 mL) soln of $Pd(dba)_2$ (0.116 g, 0.202 mmol) and $P(OEt)_3$ (0.069 g, 0.415 mmol) was stirred at r.t. for 5 min. To the mixture was added trimethyl(tributylstannyl)silane (6.30 g, 17.4 mmol) and 4-(phenylselanyl)but-1-yne (**1**, 2.19 g, 10.5 mmol). After heating at 60 °C for 24 h, the mixture was cooled to r.t., diluted with Et_2O (20 mL), and concentrated. The residue was purified by column chromatography (silica gel, hexane) to afford **2** (3.93 g, 65%) as a colorless oil.

IR (neat): 3059, 2853, 1598, 1556, 1477, 1464, 1246, 837, 733, 691 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.09 (s, 9 H), 0.86–0.92 (m, 15 H), 1.25–1.47 (m, 12 H), 2.62 (t, *J* = 8.2 Hz, 2 H), 2.86 (t, *J* = 8.2 Hz, 2 H), 6.41 (s, $J(^{117}Sn,H)$ = 168 Hz, $J(^{119}Sn,H)$ = 176 Hz, 1 H), 7.23–7.27 (m, 3 H), 7.50–7.52 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.1, 11.2, 13.7, 27.4, 27.5, 29.2, 47.2, 126.8, 129.0, 130.4, 133.0, 145.4, 163.5.

^{77}Se NMR (76 MHz, $CDCl_3$): δ = 302.5.

LRMS (EI): *m*/*z* (%) = 155 (80), 178 (91), 283 (85), 558 (100), 573 (12) $[M - 1]^+$.

HRMS (EI): *m*/*z* $[M - 3\ H]^+$ calcd for $C_{25}H_{43}SiSeSn$: 571.1321; found: 571.1319.

(*Z*)-Trimethyl[2-(tributylstannyl)buta-1,3-dienyl]silane (3)

To a soln of **2** (0.500 g, 0.874 mmol) in THF (5 mL) was added 30% aq H_2O_2 (1.0 mL) at 0 °C. After stirring for 2 h at r.t., the reaction was quenched with sat. $NaHCO_3$ and extracted with Et_2O (2 × 20 mL). The combined organic layers were washed with brine (2 × 20 mL), dried ($MgSO_4$), concentrated, and purified by column chromatography (silica gel, hexane) to afford **3** (0.350 g, 96%) as a colorless oil.

IR (neat): 3082, 2855, 1607, 1464, 1248, 984, 899, 837 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = –0.14 (s, 9 H), 0.87–1.01 (m, 15 H), 1.28–1.53 (m, 12 H), 4.93 (dd, *J* = 1.2, 10.5 Hz, 1 H), 5.04 (dd, *J* = 1.2, 17.2 Hz, 1 H), 6.51 (ddd, *J* = 1.2, 10.5, 17.2 Hz, 1 H), 6.62 (s, $J(^{117}Sn,H)$ = 162 Hz, $J(^{119}Sn,H)$ = 167 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.30, 11.7, 13.6, 27.4, 29.1, 113.5, 147.8, 148.8, 162.3.

LRMS (EI): *m*/*z* (%) = 73 (67), 177 (79), 235 (85), 291 (100), 359 (47), 416 (21) $[M]^+$.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{19}H_{40}SiSn$: 416.1921; found: 416.1919.

Stille Coupling Reaction; General Procedure

A 3-necked flask was charged with LiCl (0.024 g, 0.566 mmol) and flame-dried under vacuum. After cooling, $Pd(PPh_3)_4$ (0.015 g, 0.013 mmol) and CuI (0.011 g, 0.578 mmol) were added, then the mixture was degassed with an argon purge. A soln of an aryl iodide (0.5 mmol) and the alkenylstannnane **3** or **2** (0.25 mmol) in DMF (5mL) was introduced, and the mixture was heated at 70 °C for 4 h. After cooling to r.t., the mixture was diluted with E_2O (30 mL) and washed with H_2O (20 mL). The aqueous layer was further extracted with Et_2O (2 × 20 mL). The combined organic layers were washed with H_2O (2 × 20 mL) and brine (2 × 20 mL), dried ($MgSO_4$), and concentrated. The residue was purified by column chromatography

(silica gel, hexane–EtOAc, 1:0–20:1) to afford the cross-coupling product.

(*Z*)-Trimethyl(2-phenylbuta-1,3-dienyl)silane (4a)
Colorless oil; yield: 35 mg (70%).

IR (neat): 3089, 2955, 2897, 1562, 1493, 1246, 860, 837 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = –0.19 (s, 9 H), 4.74 (d, *J* = 17.3 Hz, 1 H), 5.11 (d, *J* = 10.5 Hz, 1 H), 5.85 (s, 1 H), 6.61 (dd, *J* = 10.5, 17.3 Hz, 1 H), 7.12–7.14 (m, 2 H), 7.29–7.33 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = –0.29, 117.0, 127.1, 127.7, 129.4, 134.2, 140.1, 143.0, 156.3.

LRMS (EI): *m*/*z* (%) = 43 (94), 118 (84), 135 (91), 187 (100), 202 (95) $[M]^+$.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{13}H_{18}Si$: 202.1178; found: 202.1180.

(*Z*)-Trimethyl[2-(1-naphthyl)buta-1,3-dienyl]silane (4b)
Colorless oil; yield: 52 mg (82%).

IR (neat): 3044, 2955, 2897, 1562, 1246, 864, 837, 779 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = –0.37 (s, 9 H), 4.54 (d, *J* = 17.4 Hz, 1 H), 5.06 (d, *J* = 10.4 Hz, 1 H), 6.14 (s, 1 H), 6.74 (dd, *J* = 10.4, 17.4 Hz, 1 H), 7.23 (d, *J* = 6.0 Hz, 1 H), 7.41–7.48 (m, 3 H), 7.78–7.84 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = –0.75, 117.1, 125.1, 125.6, 125.6, 126.5, 127.0, 127.5, 128.0, 135.9, 142.9.

LRMS (EI): *m*/*z* (%) = 73 (91), 152 (40), 165 (65), 178 (99), 185 (67), 209 (26), 221 (45), 237 (55), 252 (100) $[M]^+$.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{17}H_{20}Si$: 252.1334; found: 252.1336.

(*Z*)-Trimethyl[2-(*p*-tolyl)buta-1,3-dienyl]silane (4c)
Colorless oil; yield: 28 mg (52%).

IR (neat): 3028, 2955, 2924, 1608, 1246, 864, 841 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = –0.18 (s, 9 H), 2.37 (s, 3 H), 4.76 (d, *J* = 17.6 Hz, 1 H), 5.10 (d, *J* = 10.4 Hz, 1 H), 5.82 (s, 1 H), 6.60 (dd, *J* = 10.4, 17.6 Hz, 1 H), 7.01 (d, *J* = 8.0 Hz, 2 H), 7.13 (d, *J* = 8.0 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = –0.20, 21.2, 116.8, 128.4, 129.3, 134.1, 136.6, 137.1, 143.1, 156.4.

LRMS (EI): *m*/*z* (%) = 73 (63), 91 (66), 119 (100), 149 (80), 201 (71), 216 (70) $[M]^+$.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{14}H_{20}Si$: 216.1334; found: 216.1336.

(*Z*)-[2-(4-Methoxyphenyl)buta-1,3-dienyl]trimethylsilane (4d)
Colorless oil; yield: 31 mg (54%).

IR (neat): 3090, 2955, 2897, 1612, 1508, 1288, 1246, 1173, 1038, 864, 837 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = –0.17 (s, 9 H), 3.83 (s, 3 H), 4.77 (d, *J* = 17.3 Hz, 1 H), 5.10 (d, *J* = 10.7 Hz, 1 H), 5.82 (s, 1 H), 6.60 (dd, *J* = 10.7, 17.3 Hz, 1 H), 6.87 (d, *J* = 8.8 Hz, 2 H), 7.05 (d, *J* = 8.8 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = –0.18, 55.2, 113.1, 116.7, 130.5, 132.5, 134.2, 143.2, 156.0, 158.7.

LRMS (EI): *m*/*z* (%) = 43 (72), 118 (76), 165 (99), 217 (96), 232 (100) $[M]^+$.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{14}H_{20}OSi$: 232.1284; found: 232.1278.

(*Z*)-Trimethyl[2-(4-nitrophenyl)buta-1,3-dienyl]silane (4e)
Pale yellow solid; yield: 52 mg (84%); mp 69–70 °C.

IR (KBr): 3078, 2955, 1597, 1570, 1512, 1342, 1246, 868, 833 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = –0.18 (s, 9 H), 4.61 (d, *J* = 17.4 Hz, 1 H), 5.15 (d, *J* = 10.5 Hz, 1 H), 5.95 (s, 1 H), 6.60 (dd, *J* = 10.5, 17.4 Hz, 1 H), 7.32 (d, *J* = 8.1 Hz, 2 H), 8.22 (d, *J* = 8.1 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = –0.28, 117.4, 123.1, 130.4, 135.9, 142.2, 147.1, 147.5, 153.8.

LRMS (EI): *m*/*z* (%) = 43 (82), 118 (73), 180 (70), 232 (100), 247 (90) $[M]^+$.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{13}H_{17}O_2NSi$: 247.1029; found: 247.1031.

(*Z*)-[2-(4-Chlorophenyl)buta-1,3-dienyl]trimethylsilane (4f)
Pale yellow oil; yield: 45 mg (77%).

IR (neat): 3090, 2955, 2897, 1597, 1489, 1246, 860, 833 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = –0.18 (s, 9 H), 4.69 (d, *J* = 17.2 Hz, 1 H), 5.11 (d, *J* = 10.4 Hz, 1 H), 5.86 (s, 1 H), 6.58 (dd, *J* = 10.4, 17.2 Hz, 1 H), 7.07 (dd, *J* = 2.0, 6.3 Hz, 2 H), 7.32 (dd, *J* = 2.0, 6.3 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = –0.21, 117.0, 128.0, 130.8, 133.0, 135.0, 138.6, 142.8, 155.0.

LRMS (EI): *m*/*z* (%) = 59 (65), 73 (45), 169 (99), 221 (100), 236 (95) $[M]^+$.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{13}H_{17}SiCl$: 236.0788; found: 236.0792.

(*Z*)-Trimethyl[2-phenyl-4-(phenylselanyl)but-1-enyl]silane (5a)
Colorless oil; yield: 57 mg (63%).

IR (neat): 3055, 2951, 2897, 1593, 1477, 1439, 1246, 841, 737, 702 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = –0.20 (s, 9 H), 2.78 (t, *J* = 8.0 Hz, 2 H), 2.89 (t, *J* = 8.0 Hz, 2 H), 5.59 (s, 1 H), 7.10–7.13 (m, 2 H), 7.20–7.28 (m, 6 H), 7.40–7.42 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = –0.04, 25.6, 43.1, 126.7, 127.2, 127.9, 128.1, 128.8, 129.0, 130.3, 132.5, 142.9, 157.5.

^{77}Se NMR (76 MHz, $CDCl_3$): δ = 298.0.

LRMS (EI): *m*/*z* (%) = 73 (100), 105 (8), 135 (13), 187 (12), 215 (5), 287 (26), 360 (19) $[M]^+$.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{19}H_{24}SiSe$: 360.0812; found: 360.0817.

(*Z*)-Trimethyl[2-(1-naphthyl)-4-(phenylselanyl)but-1-enyl]silane (5b)
Pale yellow oil; yield: 66 mg (64%).

IR (neat): 3055, 2951, 1609, 1578, 1477, 1246, 837, 779, 733, 691 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = –0.37 (s, 9 H), 2.87–2.91 (m, 2 H), 2.95–2.99 (m, 2 H), 5.92 (s, 1 H), 7.19–7.22 (m, 4 H), 7.39–7.47 (m, 5 H), 7.78 (d, *J* = 8.3 Hz, 1 H), 7.83–7.86 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = –0.57, 25.7, 43.1, 125.0, 125.7, 125.8, 125.9, 126.6, 127.4, 128.2, 129.0, 130.4, 130.7, 131.5, 132.3, 133.5, 140.4, 155.7.

^{77}Se NMR (76 MHz, $CDCl_3$): δ = 298.0.

LRMS (EI): *m*/*z* (%) = 73 (100), 180 (57), 252 (9), 337 (2), 410 (7) $[M]^+$.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{23}H_{26}SiSe$: 410.0969; found: 410.0968.

(*Z*)-Trimethyl[4-(phenylselanyl)-2-(*p*-tolyl)but-1-enyl]silane (5c)
Colorless oil; yield: 61 mg (65%).

IR (neat): 3055, 2951, 2897, 1597, 1578, 1477, 1246, 841, 733, 691 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = –0.17 (s, 9 H), 2.35 (s, 3 H), 2.78 (t, *J* = 8.0 Hz, 2 H), 2.90 (t, *J* = 8.0 Hz, 2 H), 5.57 (s, 1 H), 7.02 (d, *J* = 8.1 Hz, 2 H), 7.10 (d, *J* = 8.1 Hz, 2 H), 7.22–7.26 (m, 3 H), 7.42–7.44 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.04, 21.2, 25.7, 43.1, 126.6, 128.0, 128.4, 128.5, 128.9, 130.4, 132.4, 136.8, 139.9, 157.6.

^{77}Se NMR (76 MHz, $CDCl_3$): δ = 298.1.

LRMS (EI): *m*/*z* (%) = 73 (100), 115 (11), 149 (12), 301 (22), 374 (19) $[M]^+$.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{20}H_{26}SiSe$: 374.0969; found: 374.0965.

(*Z*)-[2-(4-Methoxyphenyl)-4-(phenylselanyl)but-1-enyl]trimethylsilane (5d)
Pale yellow oil; yield: 63 mg (65%).

IR (neat): 3055, 2951, 2835, 1609, 1508, 1246, 1173, 837, 737, 691 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = –0.17 (s, 9 H), 2.77 (t, *J* = 8.0 Hz, 2 H), 2.89 (t, *J* = 8.0 Hz, 2 H), 3.81 (s, 3 H), 5.56 (s, 1 H), 6.82 (d, *J* = 8.4 Hz, 2 H), 7.05 (d, *J* = 8.4 Hz, 2 H), 7.22–7.25 (m, 3 H), 7.41–7.44 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.07, 25.8, 43.1, 55.2, 113.2, 126.6, 128.5, 129.0, 129.2, 130.4, 132.5, 135.2, 157.2, 158.8.

^{77}Se NMR (76 MHz, $CDCl_3$): δ = 297.8.

LRMS (EI): *m*/*z* (%) = 73 (100), 115 (9), 165 (11), 217 (16), 317 (18), 390 (19) $[M]^+$.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{20}H_{26}OSiSe$: 390.0918; found: 390.0919.

(*Z*)-Trimethyl[2-(4-nitrophenyl)-4-(phenylselanyl)but-1-enyl]silane (5e)
Yellow oil; yield: 92 mg (91%).

IR (neat): 3091, 2954, 1595, 1516, 1310, 1010, 853, 837, 735 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = –0.17 (s, 9 H), 2.80–2.82 (m, 2 H), 2.85–2.88 (m, 2 H), 5.74 (s, 1 H), 7.24–7.26 (m, 3 H), 7.31 (d, *J* = 8.5 Hz, 2 H), 7.43–7.46 (m, 2 H), 8.18 (d, *J* = 8.5 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = –0.05, 25.3, 42.6, 123.3, 124.8, 127.0, 129.0, 129.1, 131.5, 132.8, 138.7, 150.0, 154.9.

^{77}Se NMR (76 MHz, $CDCl_3$): δ = 299.4.

LRMS (EI): *m*/*z* (%) = 73 (66), 171 (40), 332 (97), 390 (56), 405 (100) $[M]^+$.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{19}H_{23}O_2NSiSe$: 405.0663; found: 405.0661.

(*Z*)-[2-(4-Chlorophenyl)-4-(phenylselanyl)but-1-enyl]trimethylsilane (5f)
Pale yellow oil; yield: 70 mg (71%).

IR (neat): 3059, 2953, 1609, 1580, 1477, 1248, 1090, 839, 735, 691 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = –0.17 (s, 9 H), 2.75–2.78 (m, 2 H), 2.86–2.89 (m, 2 H), 5.63 (s, 1 H), 7.06 (d, *J* = 8.3 Hz, 2 H), 7.23–7.28 (m, 5 H), 7.41–7.43 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.01, 25.5, 42.9, 126.8, 128.1, 129.0, 129.4, 129.8, 130.1, 132.6, 133.0, 141.3, 156.1.

^{77}Se NMR (76 MHz, $CDCl_3$): δ = 298.1.

MS (EI): *m*/*z* (%) = 73 (100), 129 (7), 169 (14), 221 (9), 321 (29), 394 (19) $[M]^+$.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{19}H_{23}SiSeCl$: 394.0423; found: 394.0422.

Selenoxide Elimination (4 from 5); General Procedure

To a soln of **5** (0.15 mmol) in THF (5 mL) was added 30% aq H_2O_2 (0.3 mL) at 0 °C. After stirring for 2 h at r.t., the reaction was quenched with sat. $NaHCO_3$ and extracted with Et_2O (2 × 20 mL). The combined organic layers were washed with brine (2 × 20 mL), dried ($MgSO_4$), concentrated, and purified by column chromatography (silica gel, hexane) to afford **4**. Yields: **4a**: 25 mg (83%); **4b**: 30 mg (78%); **4c**: 27 mg (84%); **4d**: 30 mg (85%); **4e**: 32 mg (86%); **4f**: 31 mg (87%).

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