Synthesis of Acylsilanes via Silastannation of Alkynes by a Palladium–Isocyanide Catalyst

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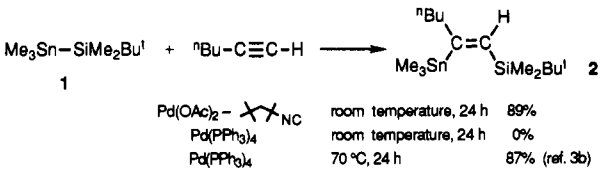
Summary: Silastannation of 1-alkoxyalkynes was carried out at room temperature by use of a palladium acetate/tert-alkyl isocyanide catalyst, to produce 1-alkoxy-1-silyl-2-stannylalkenes. Palladium-mediated coupling of the organotin moieties with organic halides followed by acid-catalyzed hydrolysis provided a variety of acylsilanes.

The usefulness of silicon- and tin-containing compounds in organic synthesis and also in material chemistry is well documented.[1] Bis(silylation) and silastannation of unsaturated organic molecules with disilanes and silylstannanes are of interest, as they provide a synthetic route to those compounds. The reactions of alkynes with organodisilanes[2] and silylstannanes[3] so far reported have mostly been achieved by the catalysis of palladium phosphine complexes.[4] Recently, we have developed a new palladium catalyst system, palladium acetate/*tert*-alkyl isocyanide, for bis(silylation) of alkynes and alkenes.[5] Herein we report a new synthetic method for acylsilanes involving silastannation of alkoxyalkynes promoted by palladium acetate/*tert*-alkyl isocyanide as a key step.

Results and Discussion

Silastannation of Alkynes Catalyzed by Palladium(II) Acetate/*tert*-Alkyl Isocyanide. A toluene solution of organosilylstannane 1, 1-hexyne (1.3 equiv), palladium(II) acetate (0.04 equiv), and 1,1,3,3-tetramethylbutyl isocyanide (0.30 equiv) was stirred at room temperature for 1 day. As is the case with $Pd(PPh_3)_4$,[3] organosilylstannane 1 underwent regioselective *syn* addition to the C–C triplet bond affording the corresponding (*Z*)-1-silyl-2-stannylalkene **2**, with a stannyl group attached to an internal carbon. The high catalytic activity of $Pd(OAc)_2$/isocyanide over $Pd(PPh_3)_4$ should be noted; *i.e.*, whereas silastannation of 1-hexyne in THF employing $Pd(PPh_3)_4$ as a catalyst requires heating at around 70 °C,[3b] $Pd(OAc)_2$/1,1,3,3-tetramethylbutyl isocyanide completed the reaction at room temperature (Scheme I). However, silastannation of alkenes or of ordinary internal alkynes failed even with the present catalyst system.

Scheme I



The new active palladium catalyst was applied to silastannation of 1-alkoxyalkynes. In the presence of $Pd(OAc)_2$/1,1,3,3-tetramethylbutyl isocyanide, 1-ethoxyalkynes **3** including a substituted **3b** successfully underwent silastannation at room temperature giving *syn* addition products **4** (Table I). The stereochemical assignment was based on a NOE experiment. The organosilyl group was regioselectively introduced on the carbon bearing ethoxy group, except for run 4, to give 1-ethoxy-1-silyl-2-stannylalkenes **4**. This regiochemistry was secured by transformation to acylsilanes described below. Notably, $^2J_{Sn-H}$ of **4a** and **4c** are 24.6 and 23.4 Hz, respectively, and are much smaller than those of ordinary vinyltin compounds (86–106 Hz).[6] In contrast, silastannation of ethoxyalkynes with $Pd(PPh_3)_4$ was unsuccessful; no reaction proceeded at room temperature, and at higher temperatures, **3a** readily underwent polymerization, affording intractable material. Although $Pd(PPh_3)_4$ promoted silastannation of a substituted ethoxyalkyne **3b** with **1** at 70 °C, a mixture of regioisomers (35:65) was produced (78%).

Cross-Coupling Reaction of 4 with Organic Halides. 1-Ethoxy-1-silyl-2-stannylalkenes **4a**, and **4b**, hardly accessible using other catalysts, are interesting synthetic blocks of potential use, and their transformations involving C–C bond formation were next examined.[7] Cross-coupling reactions of **4**, as alkenyltin compounds, with organic halides employing palladium catalysts such as $Pd(PPh_3)_4$, $PhCH_2PdCl(PPh_3)_2$, and $Pd_2(dba)_3{\cdot}CHCl_3$ were retarded, presumably due to the steric hindrance caused by the neighboring organosilyl group, producing a considerable amount of proto-destannylated compound together with the desired coupling product. However, the modified Stille reaction using CuI as a cocatalyst[8] of $PhCH_2PdCl(PPh_3)_2$ gave satisfactory results (Table II). Allyl, phenyl, benzyl,

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(2) (a) Okinoshima, H.; Yamamoto, K.; Kumada, M. *J. Organomet. Chem.* **1975,** *86,* C27. (b) Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *J. Am. Chem. Soc.* **1975,** *97,* 931. (c) Watanabe, H.; Kobayashi, M.; Higuchi, K.; Nagai, Y. *J. Organomet. Chem.* **1980,** *186,* 51. (d) Yamashita, H.; Catellani, M.; Tanaka, M. *Chem. Lett.* **1991,** 241.

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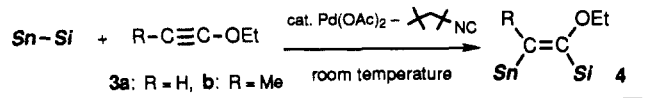
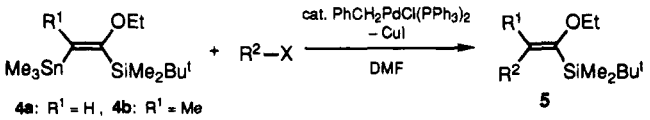
Table I. Silastannation of 1-Ethoxyalkynes

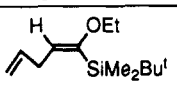
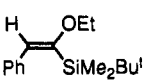
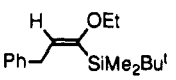
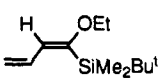
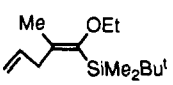
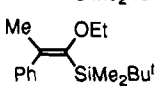
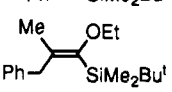


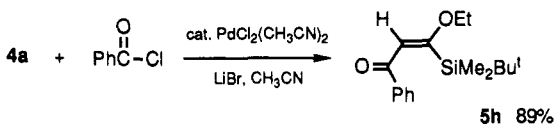
run	Sn–Si	3	4, % yield[a]
1	Me_3Sn–$SiMe_2Bu^t$	**3a**	**4a**, 92 (>95:5)
2	Me_3Sn–$SiMe_2Bu^t$	**3b**	**4b**, 99 (>95:5)
3	$^nBu_3Sn$–$SiMe_3$	**3a**	**4c**, 75 (>95:5)
4	Me_3Sn–$SiMe_3$	**3a**	**4d**, 99 (55:45)[b]

[a] The ratios in parentheses refer to the regioselectivity. [b] The regiochemical assignment is tentative.

Table II. Cross-Coupling of 4 with Organic Halides



run	4	R^2–X	product	5, % yield
1	**4a**			**5a**, 95
2	**4a**	Ph–I		**5b**, 77
3	**4a**	$PhCH_2Br$		**5c**, 88
4	**4a**			**5d**, 66
5	**4b**			**5e**, 97
6	**4b**	Ph–I		**5f**, 68
7	**4b**	$PhCH_2Br$		**5g**, 79



and vinyl groups could be introduced in the product **5** with retention of the stereochemistries. Benzoyl chloride also coupled with **4** in the presence of LiBr affording α,β-unsaturated ketone **5h**.

Iodination of **4** provided an alternative route to the cross-coupling reaction. On treatment with 1.1–1.3 equiv of iodine, the Sn–C_{sp^2} bond of **4** was oxidatively cleaved to give the corresponding alkenyl iodide **6**, the Si–C_{sp^2} bond being intact. Palladium catalyzed coupling of **6** with a terminal alkyne[9] or with an alkynylstannane[10] gave rise to enynes **7** in high yield.

Synthesis of Acylsilanes. Particularly good use of the cross-coupling products has been made for preparation of acylsilanes. 1-Ethoxy-1-silylalkenes, on treatment with aqueous acid,[11] were hydrolyzed to furnish the corresponding acylsilanes **8** in good yield. Enyne **7b** afforded β-keto acylsilane **8f** via addition of H_2O to the C–C triple

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Scheme II

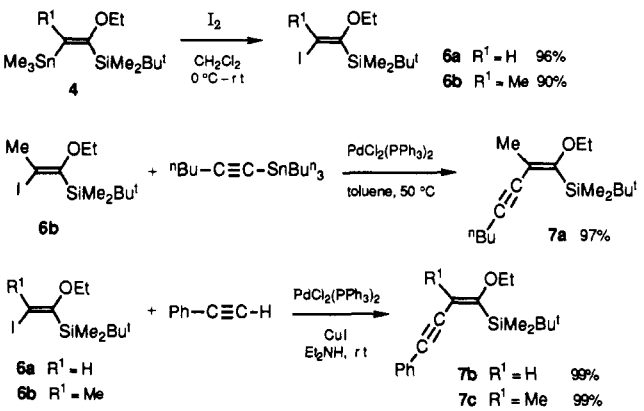
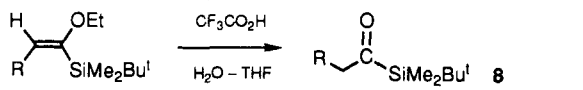
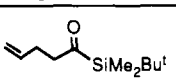
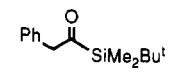
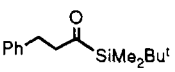
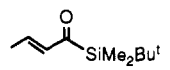
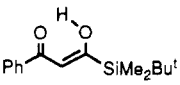
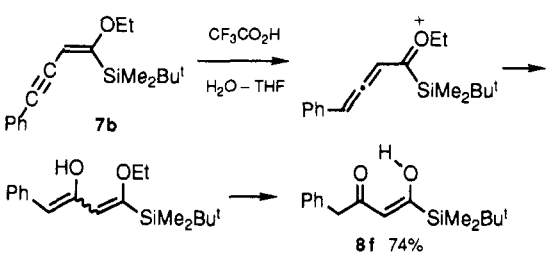


Table III. Synthesis of Acysilanes 8



run	vinyl ether	product	8, % yield
1	**5a**		**8a**, 99
2	**5b**		**8b**, 88
3	**5c**		**8c**, 78
4	**5d**		**8d**, 70
5	**5h**		**8e**, 74[a]

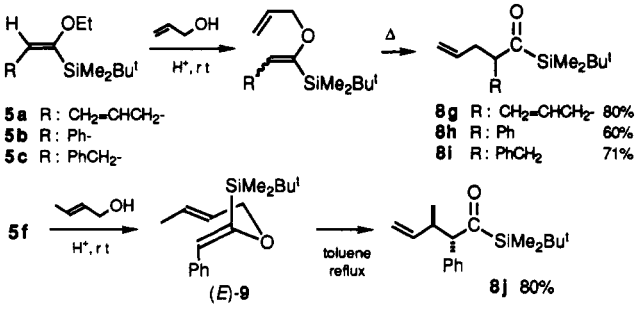
[a] HCl was used as an acid.



bond as well as hydrolysis of the vinyl ether moiety. In ^{13}C NMR spectra of acylsilanes **8a–d**, the resonances of silyl-substituted carbonyl carbons appeared in the range δ 230–245. For β-keto acylsilanes **8e,f**, silyl-substituted carbonyl resonances were not observed, suggesting the predominance of enol forms.

Another synthetic route to acylsilanes via C–C bond formation was established by use of the Claisen rearrangement. Ether exchange of 1-ethoxy-1-silylalkenes with allyl alcohol afforded allyl vinyl ethers, which on heating underwent Claisen rearrangement to introduce an allyl unit onto the α-positions of the acylsilanes produced. The exchange reaction of **5f** with *trans*-crotyl alcohol produced (*E*)-**9** selectively (*E*:*Z* = 95:5). The Claisen rearrangement of (*E*)-**9**, isolated by column chromatography, proceeded with complete stereospecificity to give a β,γ-branched acylsilane **8j**.[12] This stereospecificity is ascribed to the accepted chairlike transition state in the rearrangement.[13]

Scheme III



In conclusion, silastannation of alkoxyalkynes catalyzed by palladium acetate/*tert*-alkyl isocyanide provides facile synthetic blocks which give a new access to a variety of acylsilanes through palladium-mediated cross-coupling reactions.

Experimental Section

General Considerations. Column chromatography was performed with silica gel (Wakogel C-200). Preparative thin-layer chromatography (TLC) was performed with silica gel 60 PF_{254} (E. Merck, Darmstadt). Reversed phase column chromatography was performed with Cosmosil 75C_{18}-OPN (nacalai, Kyoto). ^1H and ^{13}C NMR spectra (200 and 50 MHz, respectively) were acquired in chloroform-*d*, unless otherwise noted. Na_2SO_4 was used to dry an organic layer. All reactions were performed under a dry nitrogen atmosphere.

Unless otherwise noted, materials were obtained from commercial sources. THF was distilled from sodium diphenyl ketyl, toluene was distilled from $LiAlH_4$, and DMF, CH_3CN, and Et_2NH were distilled from CaH_2.

(*Z*)-1-(*tert*-Butyldimethylsilyl)-1-ethoxy-2-(trimethylstannyl)ethene (4a). To a mixture of $Pd(OAc)_2$ (135 mg, 0.60 mmol) and 1,1,3,3-tetramethylbutyl isocyanide (835 mg, 6.0 mmol) in toluene (18 mL) at room temperature was added **3a** (1.50 g, 21.4 mmol) in hexane (2.3 mL). On addition of **3a**, the dark red solution turned to yellow. (*tert*-Butyldimethylsilyl)-trimethyltin (5.30 g, 19.0 mmol) was added to the mixture, which was stirred for 10 h. The second portion of **3a** (400 mg, 5.7 mmol) in hexane (0.6 mL) was added, and the mixture was stirred for a further 8 h. Then the mixture was diluted with hexane, filtered through a short column of Florisil pretreated with Et_3N, and dried. Kugelrohr distillation afforded **4a** as a colorless oil (6.10 g, 92%): bp 83 °C (0.1 mmHg); IR (neat) 1540, 1250 cm^{-1}; ^1H NMR δ 0.11 (s, 6 H), 0.18 (s, 9 H with Sn–H coupling of 54.6 and 52.2 Hz), 0.92 (s, 9 H), 1.27 (t, J = 7.0 Hz, 3 H), 3.69 (q, J = 7.0 Hz, 2 H), 5.14 (s, 1 H with Sn–H coupling of 24.6 Hz); ^{13}C NMR (Sn–C coupling in parentheses) δ –6.2 (356.6, 340.9 Hz), –5.1, 14.6, 16.8, 27.1, 60.1, 104.3 (502.5, 480.4 Hz), 173.2. Anal. Calcd for $C_{13}H_{30}OSiSn$: C, 44.72; H, 8.66. Found: C, 44.92; H, 8.81.

(*Z*)-1-(*tert*-Butyldimethylsilyl)-1-ethoxy-2-(trimethylstannyl)-1-propene (4b). To a mixture of $Pd(OAc)_2$ (18 mg, 0.08 mmol) and 1,1,3,3-tetramethylbutyl isocyanide (67 mg, 0.48 mmol) in toluene (2 mL) was added **3b** (337 mg, 4.0 mmol) and (*tert*-butyldimethylsilyl)trimethyltin (1.12 g, 4.0 mmol). After stirring for 14 h, the mixture was diluted with hexane, filtered through a short column of Florisil pretreated with Et_3N, and dried. Kugelrohr distillation afforded **4b** as a colorless oil (1.46 g, 99%): bp 86 °C (0.1 mmHg); IR (neat) 1556, 1250 cm^{-1}; ^1H NMR δ 0.11 (s, 6 H), 0.21 (s, 9 H with Sn–H coupling of 53.4 and 51.0 Hz), 0.93 (s, 9 H), 1.25 (t, J = 7.0 Hz, 3 H), 1.94 (s, 3 H with Sn–H coupling of 50.6 and 48.5 Hz), 3.55 (q, J = 7.0 Hz, 2 H); ^{13}C NMR (Sn–C coupling in parentheses) δ –5.8 (343.0, 328.2 Hz), –3.9, 15.5, 17.2, 19.1, 27.4, 66.0, 138.7 (481.8, 460.2 Hz), 167.0. Anal. Calcd for $C_{14}H_{32}OSiSn$: C, 46.30; H, 8.88. Found: C, 46.04; H, 8.61.

(*Z*)-1-Ethoxy-2-(tributylstannyl)-1-(trimethylsilyl)ethene (4c). The title compound was prepared by a procedure similar to that used for **4a** (75%): bp 130 °C (0.1 mmHg); IR (neat) 1542, 1250 cm^{-1}; ^1H NMR δ 0.14 (s, 9 H), 0.8–1.0 (m, 15 H), 1.2–1.4 (m, 6 H), 1.26 (t, J = 6.9 Hz, 3 H), 1.4–1.6 (m, 6 H), 3.70 (q, J = 6.9 Hz, 2 H), 5.07 (s, 1 H with Sn–H coupling of 23.5 Hz); ^{13}C NMR δ –1.0, 11.6, 13.7, 14.5, 27.3, 29.1, 60.2, 101.2, 173.6. Anal. Calcd for $C_{19}H_{42}OSiSn$: C, 52.66; H, 9.77. Found: C, 52.51; H, 9.49.

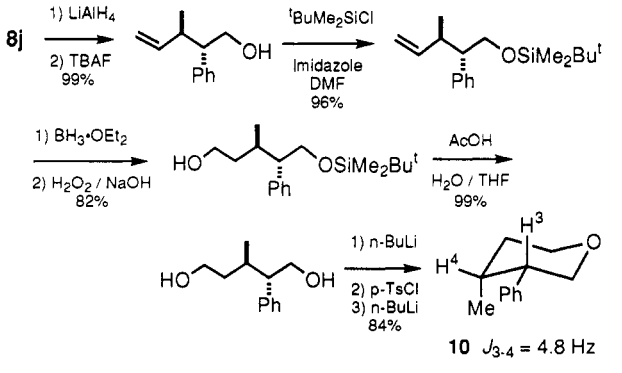
(*Z*)-1-(Trimethylsilyl)-1-ethoxy-2-(trimethylstannyl)-ethene (4d) and (*Z*)-1-(Trimethylsilyl)-2-ethoxy-2-(trimethylstannyl)ethene. The title compounds were obtained as a mixture by a procedure similar to that used for **4a** (99%): bp 65–70 °C (0.1 mmHg); IR (neat) 1546, 1250 cm^{-1}; ^1H NMR (**4d**) δ 0.09 (s, 9 H), 0.24 (s, 9 H with Sn–H coupling of 55.5 and 53.2 Hz), 1.25 (t, J = 6.9 Hz, 3 H), 3.68 (q, J = 6.9 Hz, 2 H), 5.11 (s, 1 H with Sn-H coupling of 28.2 Hz); ^1H NMR (the regioisomer) δ 0.15 (s, 9 H), 0.18 (s, 9 H with Sn–H coupling of 54.7 and 52.2 Hz), 1.25 (t, J = 6.9 Hz, 3 H), 3.68 (q, J = 6.9 Hz, 2 H), 5.01 (s, 1 H); ^{13}C NMR (a mixture of regioisomers, Sn–C coupling in parentheses) δ –7.2 (349.5, 334.5 Hz), –6.6 (355.9, 340.2), –0.9, 1.2, 14.3, 14.5, 60.3, 60.8, 102.9, 105.5, 174.1, 178.5. Anal. Calcd for $C_{10}H_{24}OSiSn$: C, 39.11; H, 7.88. Found: C, 39.09; H, 8.02.

(*Z*)-1-(*tert*-Butyldimethylsilyl)-1-ethoxy-1,4-pentadiene (5a). To a mixture of $PhCH_2PdCl(PPh_3)_2$ (43 mg, 0.060 mmol) and CuI (18 mg, 0.096 mmol) in DMF (5 mL) at room temperature were successively added allyl bromide (3.63 g, 30 mmol) and **4a** (1.92 g, 5.5 mmol). The mixture was stirred at 50 °C for 7 h and then passed through a short column of silica gel pretreated with Et_3N. Evaporation followed by Kugelrohr distillation afforded **5a** (1.19 g, 95%): IR (neat) 1644, 1608, 1252 cm^{-1}; ^1H NMR (C_6D_6) δ 0.25 (s, 6 H), 1.04 (s, 9 H), 1.09 (t, J = 7.0 Hz, 3 H), 2.81–2.92 (m, 2 H), 3.42 (q, J = 7.0 Hz, 2 H), 5.00–5.28 (m, 3 H), 5.76–6.00 (m, 1 H); ^{13}C NMR (C_6D_6) δ –5.3, 13.9, 16.6, 26.0, 31.4, 61.1, 110.4, 113.4, 137.9, 159.4. Anal. Calcd for $C_{13}H_{26}OSi$: C, 68.96; H, 11.57. Found: C, 69.09; H, 11.53.

(*Z*)-1-(*tert*-Butyldimethylsilyl)-1-ethoxy-2-phenylethene (5b). By a procedure similar to that for **5a** (60 °C, 9 h), the title compound was obtained from **4a** (1.15 g, 3.30 mmol) and phenyl iodide (690 mg, 3.30 mmol): IR (neat) 1606, 1590, 1250 cm^{-1}; ^1H NMR (C_6D_6) δ –0.03 (s, 6 H), 1.09 (s, 9 H), 1.13 (t, J = 6.9 Hz, 3 H), 3.48 (q, J = 6.9 Hz, 2 H), 6.46 (s, 1 H), 7.0–7.3 (m, 5 H); ^{13}C NMR (C_6D_6) δ –5.4, 13.7, 16.5, 26.5, 61.3, 114.7, 125.5, 127.3, 129.5, 137.2, 162.6. Anal. Calcd for $C_{16}H_{26}OSi$: C, 73.22; H, 9.98. Found: C, 73.51; H, 10.20.

(*Z*)-1-(*tert*-Butyldimethylsilyl)-1-ethoxy-3-phenyl-1-propene (5c). By a procedure similar to that for **5a** (70 °C, 7 h), the title compound was obtained from **4a** (524 mg, 1.50 mmol) and benzyl bromide (257 mg, 1.50 mmol): IR (neat) 1608, 1250

(12) For assignment of the stereochemistry, the acylsilane **8j** was converted to a tetrahydropyran **10** via the route shown below. The *cis* relationship of the vicinal 3- and 4-protons of **10** was elucidated on the basis of the coupling constant (J_{3-4} = 4.8 Hz) in ^1H NMR. **10**: ^1H NMR δ 0.77 (d, J = 7.2 Hz, 3 H), 1.5–1.7 (m, 2 H), 2.00–2.25 (m, 1 H), 2.84 (ddd, J = 5.3, 4.8, 3.5 Hz, 1 H), 3.55–3.70 (m, 1 H), 3.84 (dd, J = 11.4, 3.5 Hz, 1 H), 3.90–4.05 (m, 1 H), 4.11 (dd, J = 11.4, 5.3 Hz, 1 H), 7.1–7.4 (m, 5 H); ^{13}C NMR δ 17.2, 30.9, 32.6, 45.2, 66.4, 69.9, 126.1, 127.9, 129.1, 141.9; IR (neat) 1102 cm^{-1}; HRMS calcd for $C_{12}H_{16}O$ 176.1197, found 176.1206.



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cm^{-1}; ^{1}H NMR (C_6D_6) δ 0.22 (s, 6 H), 1.01 (s, 9 H), 1.03 (t, J = 6.9 Hz, 3 H), 3.33 (q, J = 6.9 Hz, 2 H), 3.42 (d, J = 7.8 Hz, 2 H), 5.26 (t, J = 7.8 Hz, 1 H), 7.1–7.3 (m, 5 H); ^{13}C NMR (C_6D_6) δ –5.1, 13.8, 16.7, 26.1, 33.2, 61.2, 112.1, 125.3, 127.3, 127.7, 141.5, 159.4. Anal. Calcd for $C_{17}H_{28}OSi$: C, 73.85; H, 10.21. Found: C, 73.87; H, 10.50.

(*Z*)-1-(*tert*-Butyldimethylsilyl)-1-ethoxy-1,2-butadiene (5d). By a procedure similar to that for **5a** (room temperature, 2 days), the title compound was obtained from **4a** (349 mg, 1.0 mmol) and vinyl bromide (1.07 g, 10.0 mmol): IR (neat) 1620, 1262 cm^{-1}; ^{1}H NMR (C_6D_6) δ 0.26 (s, 6 H), 1.02 (s, 9 H), 1.05 (t, J = 7.0 Hz, 3 H), 3.42 (q, J = 7.0 Hz, 2 H), 4.9–5.0 (m, 1 H), 5.05–5.20 (m, 1 H), 6.08 (d, J = 11.3 Hz, 1 H), 6.76 (ddd, J = 9.5, 11.3, 16.6 Hz, 1 H); ^{13}C NMR (C_6D_6) δ –5.3, 13.6, 16.7, 25.9, 61.5, 111.4, 116.3, 133.4, 164.4; HRMS calcd for $C_{12}H_{24}OSi$ 212.1597, found 212.1586.

(*Z*)-1-(*tert*-Butyldimethylsilyl)-1-ethoxy-2-methyl-1,4-pentadiene (5e). By a procedure similar to that for **5a** (50 °C, 14 h), the title compound was obtained from **4b** (91 mg, 0.25 mmol) and allyl bromide (151 mg, 1.25 mmol): ^{1}H NMR δ 0.15 (s, 6 H), 0.93 (s, 9 H), 1.24 (t, J = 7.0 Hz, 3 H), 1.70 (s, 3 H), 2.78 (dt, J = 6.4, 1.5 Hz, 2 H), 3.50 (q, J = 7.0 Hz, 2 H), 5.03 (dt J = 10.4, 1.5 Hz, 1 H), 5.05 (dt, J = 16.8, 1.5 Hz, 1 H), 5.70 (ddt, J = 16.8, 10.4, 6.4 Hz, 1 H); ^{13}C NMR δ –3.7, 15.5, 15.6, 17.7, 27.3, 38.6, 66.3, 116.1, 136.7, 138.8, 154.9; IR (neat) 1642, 1616, 1252 cm^{-1}. Anal. Calcd for $C_{14}H_{28}OSi$: C, 69.93; H, 11.74. Found: C, 69.80; H, 11.78.

(*Z*)-1-(*tert*-Butyldimethylsilyl)-1-ethoxy-2-methyl-2-phenylethene (5f). By a procedure similar to that for **5a** (50 °C, 20 h), the title compound was obtained from **4b** (91 mg, 0.25 mmol) and phenyl iodide (51 mg, 0.25 mmol): IR (neat) 1670, 1598, 1256 cm^{-1}; ^{1}H NMR δ –0.34 (s, 6 H), 0.87 (s, 9 H), 1.31 (t, J = 7.0 Hz, 3 H), 2.02 (s, 3 H), 3.68 (q, J = 7.0 Hz, 2 H), 7.1–7.3 (m, 5 H); ^{13}C NMR δ –4.2, 15.7, 17.4, 20.5, 27.4, 66.6, 126.8, 127.7, 129.2, 142.6, 142.7, 157.2; HRMS calcd for $C_{17}H_{28}OSi$ 276.1910, found 276.1930.

(*Z*)-1-(*tert*-Butyldimethylsilyl)-1-ethoxy-2-methyl-3-phenyl-1-propene (5g). By a procedure similar to that for **5a** (50 °C, 24 h), the title compound was obtained from **4b** (91 mg, 0.25 mmol) and benzyl bromide (43 mg, 0.25 mmol): IR (neat) 1694, 1604, 1258 cm^{-1}; ^{1}H NMR δ 0.19 (s, 6 H), 0.95 (s, 9 H), 1.27 (t, J = 7.0 Hz, 3 H), 1.61 (s, 3 H), 3.40 (s, 2 H), 3.56 (q, J = 7.0 Hz, 2 H), 7.1–7.3 (m, 5 H); ^{13}C NMR δ –3.6, 15.5, 15.7, 18.0, 27.3, 40.2, 66.5, 126.0, 128.3, 128.5, 139.3, 139.9, 155.8; HRMS calcd for $C_{18}H_{30}OSi$ 290.2067, found 290.2064.

(*Z*)-1-(*tert*-Butyldimethylsilyl)-1-ethoxy-2-benzoylethene (5h). To a mixture of $PdCl_2(CH_3CN)_2$ (19.5 mg, 0.075 mmol) and $LiBr{\cdot}H_2O$ (790 mg, 7.5 mmol) in CH_3CN (7 mL) at room temperature were successively added benzoyl chloride (211 mg, 1.50 mmol) and **4a** (524 mg, 1.50 mmol). After the mixture stirred at 70 °C for 30 min, column chromatography on silica gel pretreated with Et_3N (ether:hexane 1:10) afforded **5h** (388 mg, 89%) as a pale yellow oil: IR (neat) 1654, 1600, 1582, 1538, 1256 cm^{-1}; ^{1}H NMR (C_6D_6) δ 0.52 (s, 6 H), 1.04 (t, J = 7.0 Hz, 3 H), 1.22 (s, 9 H), 3.33 (q, J = 7.0 Hz, 2 H), 6.52 (s, 1 H), 7.1–7.2 (m, 3 H), 7.9–8.1 (m, 2 H); ^{13}C NMR (C_6D_6) δ –5.7, 13.2, 17.7, 26.9, 63.2, 109.3, 127.3, 131.0, 139.4, 183.8, 188.0. Anal. Calcd for $C_{17}H_{26}O_2Si$: C, 70.29; H, 9.02. Found: C, 70.01; H, 9.07.

(*Z*)-1-(*tert*-Butyldimethylsilyl)-1-ethoxy-2-iodoethane (6a). A mixture of **4a** (511 mg, 1.46 mmol) and I_2 (409 mg, 1.61 mmol) in CH_2Cl_2 (40 mL) was stirred at 0 °C for 2 h and at room temperature for 10 h. Then the mixture was diluted with aqueous $Na_2S_2O_3$ and extracted with CH_2Cl_2. Organic extracts were washed with H_2O, dried, and evaporated. The residue was subjected to column chromatography on silica gel pretreated with Et_3N to afford **6a** (442 mg, 96%): IR (neat) 1588, 1252 cm^{-1}; ^{1}H NMR δ 0.30 (s, 6 H), 0.96 (s, 9 H), 1.28 (t, J = 6.9 Hz, 3 H), 3.70 (q, J = 6.9 Hz, 2 H), 5.60 (s, 1 H); ^{13}C NMR (C_6D_6) δ –4.5, 13.3, 17.2, 26.2, 56.6, 61.6, 165.9. Anal. Calcd for $C_{10}H_{21}IOSi$: C, 38.46; H, 6.78; I, 40.64. Found: C, 38.67; H, 7.02; I, 40.76.

(*Z*)-1-(*tert*-Butyldimethylsilyl)-1-ethoxy-2-iodo-1-propene (6b). A mixture of **4b** (3.40 g, 9.36 mmol) and I_2 (3.09 g, 12.2 mmol) in CH_2Cl_2 (90 mL) was stirred at 0 °C for 1 h and at room temperature for 1 day. The workup procedure similar to that used for **6a** afforded **6b** (2.75 g, 90%) as a colorless oil: IR (neat) 1578, 1250 cm^{-1}; ^{1}H NMR δ 0.29 (s, 6 H), 0.99 (s, 9 H), 1.24 (t, J = 7.0 Hz, 3 H), 2.58 (s, 3 H), 3.57 (q, J = 7.0 Hz, 2 H); ^{13}C NMR δ –2.5, 15.3, 18.5, 27.7, 28.5, 66.8, 103.7, 162.7. Anal. Calcd for $C_{11}H_{23}IOSi$: C, 40.49; H, 7.10; I, 38.90. Found: C, 40.51; H, 7.33; I, 39.12.

(*Z*)-1-(*tert*-Butyldimethylsilyl)-1-ethoxy-2-methyldec-1-en-3-yne (7a). To $PdCl_2(PPh_3)_2$ (10.5 mg, 15 μmol) in toluene (4 mL) was added tributyl(hex-1-ynyl)tin (111 mg, 0.30 mmol) and **6b** (98 mg, 0.30 mmol). The mixture was stirred at 50 °C for 10 h, and then most of the toluene was removed under reduced pressure. Filtration of the residue through a pad of Florisil followed by column chromatography on silica gel afforded **7a** (82 mg, 97%) as a pale yellow oil: IR (neat) 1580, 1258 cm^{-1}; ^{1}H NMR δ 0.20 (s, 6 H), 0.80–1.00 (m, 3 H), 0.95 (s, 9 H), 1.25 (t, J = 7.0 Hz, 3 H), 1.3–1.6 (m, 4 H), 1.86 (s, 3 H), 2.30 (t, J = 7.0 Hz, 2 H), 3.54 (q, J = 7.0 Hz, 2 H); ^{13}C NMR δ –4.5, 13.6, 15.6, 18.1, 18.3, 19.4, 22.2, 27.3, 30.7, 66.7, 81.7, 94.0, 123.6, 166.1. Anal. Calcd for $C_{17}H_{32}OSi$: C, 72.79; H, 11.50. Found: C, 72.69; H, 11.77.

(*Z*)-1-(*tert*-Butyldimethylsilyl)-1-ethoxybut-1-en-3-yne (7b). To a mixture of $PdCl_2(PPh_3)_2$ (8.8 mg, 13 μmol) and CuI (9.5 mg, 50 μmol) in Et_2NH (2.5 mL) were added **6a** (144 mg, 0.46 mmol) and phenylethyne (51 mg, 0.50 mmol). The mixture was stirred at room temperature for 12 h, and then most of the Et_2NH was removed under reduced pressure. Filtration of the residue through a pad of Florisil pretreated with Et_3N followed by column chromatography on silica gel pretreated with Et_3N afforded **9a** (131 mg, 99%) as a pale yellow oil: IR (neat) 2200, 1560, 1252 cm^{-1}; ^{1}H NMR δ 0.31 (s, 6 H), 0.98 (s, 9 H), 1.31 (t, J = 6.9 Hz, 3 H), 3.75 (q, J = 6.9 Hz, 2 H), 5.56 (s, 1 H), 7.2–7.4 (m, 5 H); ^{13}C NMR (C_6D_6) δ –6.1, 13.3, 17.0, 26.0, 62.0, 88.1, 91.0, 93.7, 124.3, 127.3, 127.7, 130.1, 173.6; HRMS calcd for $C_{18}H_{26}OSi$ 286.1746, found 286.1750.

(*Z*)-1-(*tert*-Butyldimethylsilyl)-1-ethoxy-2-methylbut-1-en-3-yne (7c). By a procedure similar to that for **7b**, the title compound was prepared from **6b** (99%): IR (neat) 2208, 1600, 1250 cm^{-1}; ^{1}H NMR δ 0.28 (s, 6 H), 0.99 (s, 9 H), 1.30 (t, J = 7.0 Hz, 3 H), 1.99 (s, 3 H), 3.63 (q, J = 7.0 Hz, 2 H), 7.2–7.5 (m, 5 H); ^{13}C NMR δ –4.3, 15.7, 18.0, 18.4, 27.3, 67.0, 91.3, 93.0, 122.9, 123.9, 127.8, 128.3, 131.0, 168.4; HRMS calcd for $C_{19}H_{28}OSi$ 300.1902, found 300.1928.

1-(*tert*-Butyldimethylsilyl)-4-penten-1-one (8a). A mixture of **5a** (30 mg, 0.13 mmol), H_2O (15 mg, 0.83 mmol), and CF_3CO_2H (75 mg, 0.66 mmol) in THF (0.3 mL) was stirred at room temperature for 11 h with minimum exposure to light. The mixture was diluted with saturated aqueous Na_2CO_3, extracted with ether, dried over $MgSO_4$, and evaporated. Column chromatography of silica gel (hexane:AcOEt 20:1) afforded **8a** (26 mg, 99%): ^{1}H NMR δ 0.19 (s, 6 H), 0.93 (s, 9 H), 2.19–2.34 (m, 2 H), 2.69 (t, J = 7.2 Hz, 2 H), 4.91–4.99 (m, 1 H), 5.00 (dq, J = 17.1, 1.7 Hz, 1 H), 5.80 (ddt, J = 17.1, 10.2, 6.6 Hz, 1 H); ^{13}C NMR δ –7.0, 16.5, 26.0, 26.4, 49.3, 114.8, 137.7, 246.3; IR (neat) 1680, 1640 cm^{-1}. Anal. Calcd for $C_{11}H_{22}OSi$: C, 66.60; H, 11.18. Found: C, 66.59; H, 11.19.

The syntheses of **8b–d**[14–16] and **8f** were carried out according to the preceding procedure for **8a**.

1-(*tert*-Butyldimethylsilyl)-4-phenyl-1,3-butanedione (8f): ^{1}H NMR δ 0.11 (s, 6 H), 0.92 (s, 9 H), 3.66 (s, 2 H), 5.70 (s, 1 H), 7.2–7.4 (m, 5 H), 14.4 (br s, 1 H); ^{13}C NMR δ –7.5, 16.4, 26.3, 48.4, 109.8, 126.9, 128.6, 129.4, 134.8, 191.8, 201.0; IR (neat) 1580 cm^{-1}. Anal. Calcd for $C_{16}H_{24}O_2Si$: C, 69.52; H, 8.75. Found: C, 69.30; H, 8.61.

1-(*tert*-Butyldimethylsilyl)-3-phenyl-1,3-propanedione (8e). A solution of **5h** (40 mg, 0.15 mmol) in aqueous HCl (1 N, 1.7 mL)–THF (5 mL) was stirred at 70 °C for 5 h with minimum

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exposure to light. The mixture was diluted with saturated aqueous Na_2CO_3, extracted with ether, dried, and evaporated. Reversed phase column chromatography (CH_3CN) afforded **8e** (27 mg, 74%): ^1H NMR (C_6D_6) δ 0.07 (s, 6 H), 0.92 (s, 9 H), 6.40 (s, 1 H), 6.9–7.1 (m, 3 H), 7.8–7.9 (m, 2 H), 16.1 (br s, 1 H); ^{13}C NMR (C_6D_6) δ –8.2, 15.7, 25.6, 105.5, 127.3, 127.7, 131.6, 136.7, 191.7, 193.5; IR (neat) 1602, 1574 cm^{-1}. Anal. Calcd for $C_{15}H_{22}O_2Si$: C, 68.65; H, 8.45. Found: C, 68.72; H, 8.31.

1-(*tert*-Butyldimethylsilyl)-2-(2-propenyl)-4-penten-1-one (8g). A mixture of **5a** (46 mg, 0.21 mmol), allyl alcohol (1.18 g, 20 mmol), trimethyl orthoformate (43 mg, 0.41 mmol), acetyl chloride (1.6 mg, 0.02 mmol), and molecular sieves (3 Å, 40 mg) in THF (3 mL) was stirred at room temperature for 9 h. Then, triethylamine (10 μL, 0.07 mmol) was added and the mixture was evaporated, diluted with hexane, filtered, and evaporated. The residue was dissolved in toluene, which was heated at reflux for 36 h. After evaporation, the mixture was subjected to column chromatography (hexane:AcOEt 10:1) to afford **8g** (38 mg, 80%): ^1H NMR δ 0.20 (s, 6 H), 0.93 (s, 9 H), 1.9–2.1 (m, 2 H), 2.2–2.4 (m, 2 H), 3.10 (quintet, J = 6.5 Hz, 1 H), 4.9–5.1 (m, 4 H), 5.5–5.8 (m, 2 H); ^{13}C NMR δ –6.6, 17.0, 26.5, 33.1, 55.3, 116.8, 135.9, 250.0; IR (neat) 1644 cm^{-1}; HRMS calcd for $C_{14}H_{26}OSi$ 238.1746, found 238.1748.

1-(*tert*-Butyldimethylsilyl)-2-phenyl-4-penten-1-one (8h). A mixture of **5f** (45.5 mg, 0.17 mmol), allyl alcohol (1.01 g, 17 mmol), acetyl chloride (1.4 mg, 0.02 mmol), and molecular sieves (3 Å, 30 mg) in THF (2.5 mL) was stirred at room temperature for 10 h. Then, triethylamine (10 μL, 0.07 mmol) was added and the mixture was diluted with ether, filtered, and evaporated. The residue was dissolved in toluene (2 mL), which was heated at 100 °C for 1 day. After evaporation, the mixture was subjected to column chromatography (hexane:AcOEt 10:1) to afford **8h** (29 mg, 60%): ^1H NMR δ –0.03 (s, 3 H), –0.01 (s, 3 H), 0.83 (s, 9 H), 2.30 (dt, J = 14.0, 7.0 Hz, 1 H), 2.71 (dt, J = 14.0, 7.0 Hz, 1 H), 4.09 (t, J = 7.0 Hz, 1 H), 4.88–5.00 (m, 2 H), 5.64 (ddt, J = 17.1, 10.1, 7.0 Hz, 1 H), 7.08–7.37 (m, 5 H); ^{13}C NMR δ –6.4, –6.3, 16.9, 26.4, 36.0, 64.0, 116.2, 127.1, 128.7, 129.5, 136.4, 136.5, 244.2; IR (neat) 1642 cm^{-1}. Anal. Calcd for $C_{17}H_{26}OSi$: C, 74.39; H, 9.54. Found: C, 74.19; H, 9.65.

2-Benzyl-1-(*tert*-butyldimethylsilyl)-4-penten-1-one (8i). A mixture of **5g** (35 mg, 0.13 mmol), allyl alcohol (743 mg, 12.8 mmol), trimethyl orthoformate (27 mg, 0.26 mmol), acetyl chloride (1.0 mg, 0.01 mmol), and molecular sieves (3 Å, 10 mg) in THF (2 mL) was stirred at room temperature for 10 h. Then, triethylamine (10 μL, 0.07 mmol) was added and the mixture was diluted with ether, filtered, and evaporated. The residue was dissolved in xylene (2 mL), which was heated at reflux for 6 h. After evaporation, the mixture was subjected to preparative TLC (hexane:AcOEt 10:1) to afford **8i** (26 mg, 71%): ^1H NMR δ 0.05 (s, 3 H), 0.07 (s, 3 H), 0.82 (s, 9 H), 1.90–2.04 (m, 1 H), 2.24–2.37 (m, 1 H), 2.47 (dd, J = 6.5, 13.5 Hz, 1 H), 2.94 (dd, J = 7.7, 13.5 Hz, 1 H), 3.31–3.45 (m, 1 H), 4.97–5.06 (m, 2 H), 5.71 (ddt, J = 17.5, 9.5, 7.1 Hz, 1 H), 7.10–7.30 (m, 5 H); ^{13}C NMR δ –6.9, 16.9, 26.4, 33.8, 35.3, 57.4, 117.1, 126.1, 128.4, 129.3, 135.8, 140.1, 250.7; IR (neat) 1642 cm^{-1}. Anal. Calcd for $C_{18}H_{28}OSi$: C, 74.94; H, 9.78. Found: C, 75.00; H, 9.68.

(2*R,3*S**)-1-(*tert*-Butyldimethylsilyl)-3-methyl-2-phenyl-4-penten-1-one (8j).** A mixture of **5f** (251 mg, 0.96 mmol), *trans*-crotyl alcohol (6.2 g, 86 mmol), acetyl chloride (8 mg, 0.1 mmol), and molecular sieves (3 Å, 300 mg) in THF (7.7 mL) was stirred at room temperature for 10 h. Then, triethylamine (50 μL, 0.36 mmol) was added and the mixture was subjected to column chromatography on silica gel deactivated with water. The vinyl ether (*E*)-**9** thus isolated was next dissolved in toluene (5 mL), which was heated at reflux for 5 h. After evaporation, the mixture was subjected to preparative TLC (hexane:AcOEt 10:1) to afford **8j** (222 mg, 80%): ^1H NMR δ –0.03 (s, 3 H), 0.00 (s, 3 H), 0.81 (s, 9 H), 1.01 (d, J = 6.5 Hz, 3 H), 2.85–3.10 (m, 1 H), 3.95 (d, J = 10.2 Hz, 1 H), 4.68–4.82 (m, 2 H), 5.44 (ddd, J = 17.2, 10.4, 7.3 Hz, 1 H), 7.00–7.35 (m, 5 H); ^{13}C NMR δ –6.4, –6.3, 16.9, 18.9, 26.4, 39.1, 70.0, 113.7, 127.0, 128.5, 130.3, 135.2, 141.7, 245.4; IR (neat) 1640 cm^{-1}. Anal. Calcd for $C_{18}H_{28}OSi$: C, 74.94; H, 9.78. Found: C, 74.85; H, 9.76.

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