Functional Group Tolerable Synthesis of Allylsilanes through Copper-Catalyzed γ-Selective Allyl–Alkyl Coupling between Allylic Phosphates and Alkylboranes

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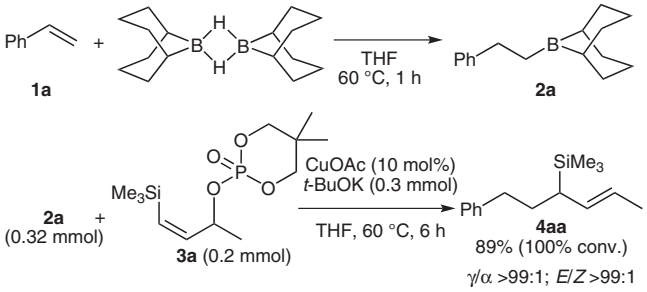
Abstract: A copper-catalyzed γ-selective allyl–alkyl coupling between γ-silylated allylic phosphates and alkylboron compounds (alkyl-9-BBN, prepared by hydroboration of alkenes with 9-BBN-H) produced allylsilanes. The reaction tolerated various functional groups in both the alkylboranes and the allylic phosphates, and afforded functionalized allylsilanes.

Key words: allylsilane, copper, allylic substitution, alkylborane, regioselectivity

Allylsilanes are versatile synthetic intermediates in organic synthesis.[1] Thus, the development of facile and efficient methods for the synthesis of allylsilanes is important. Among the available methods for preparing allylsilanes,[2–14] two types of the S_N2' displacement strategies, γ-substitutions of γ-silylated allylic alcohol derivatives with organocuprate reagents[15,16] and silylations of allylic alcohol derivatives with silylcuprate reagents,[17,18] are particularly useful because the substrates and the reagents are readily available and the reactions are highly reliable in terms of product yield and selectivity.

Previously, we developed the copper-catalyzed allyl–alkyl coupling reaction between allylic phosphates and alkylboranes (alkyl-9-BBN) that proceeds with excellent γ- and *E*-selectivities.[19a] Herein, we report that this copper-catalyzed protocol is applicable to the reaction between γ-silylated allylic phosphates and alkylboranes (alkyl-9-BBN), which appeared to be a straightforward, functional group-tolerable approach to allylsilanes.[19–22] The wide availability of alkylboranes via the established alkene hydroboration reaction is an attractive feature of this transformation.

Alkylborane **2a** (0.32 mmol), which was prepared via hydroboration of styrene (**1a**) with 9-borabicyclo[3.3.1]nonane (9-BBN-H) dimer and γ-trimethylsilyl allylic substrate **3a** (0.2 mmol) bearing a cyclic phosphate leaving group were subjected to the standard reaction conditions for the copper-catalyzed allyl–alkyl coupling [**2a**/**3a**/CuOAc/*t*-BuOK (1.6:1:0.1:1.5), THF, 60 °C] (Scheme 1).[19a] The reaction afforded allylsilane **4aa** in 89% yield (based on **3a**; 100% conversion of **3a**) with complete γ- and *E*-selectivities. The use of a diethyl phosphate as a leaving group gave a slightly decreased product yield compared to the cyclic phosphate (80% yield). The reaction of (*E*)-**3a** proceeded with significantly decreased *E*-selectivity (*E*/*Z* = 71:29) (data not shown).[23]



Scheme 1

The hydroboration-coupling one-pot protocol affords a variety of allylsilanes (Table 1). Allylic phosphates **3b**–**d** with other silyl substituents such as $PhMe_2Si$, Ph_2MeSi, and $BnMe_2Si$ instead of Me_3Si at the γ-position were also converted to the corresponding allylsilanes derivatives **4ab**, **ac**, **ad** in high yields (entries 1–3). The reaction tolerates a variety of functional groups including ester, methoxy, silyl ether, phthalimide, acetal, thiophene, bromo, and amide moieties in alkenes and allylic phosphates (entries 4–13).

The tolerance of the reaction toward steric demand in both the alkylboranes **2** and allylic phosphates **3** is also shown in Table 1. The sterically more demanding alkylborane **2b**, which was derived from the alkene **1b** bearing a tertiary alkyl substituent, served as a substrate to afford the corresponding allylsilanes **4ba** in high yield (entry 4). The reaction of the β-branched alkylborane **2i**, which was prepared from α-methylstyrene (**1i**), was also successful affording **4ia** as a 1:1 diastereomeric mixture (Table 1, entry 12). Unfortunately, however, the use of secondary alkylborane reagents prepared from internal alkenes resulted in no reaction (data not shown). The allylic phosphate **3e** with a CH_2CH_2OTIPS group instead of a Me group at the α-position also underwent the reaction (entry 13). A sterically more demanding α-substituent such as an *i*-Pr group was also tolerated (entry 14).

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Table 1 Synthesis of Allylsilanes[a]

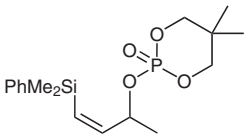
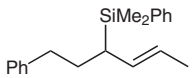
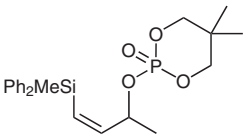
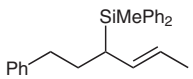
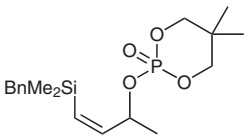
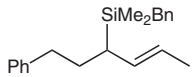
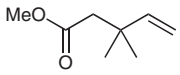
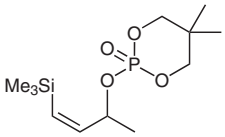
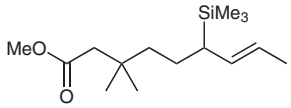
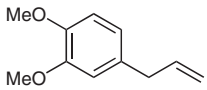
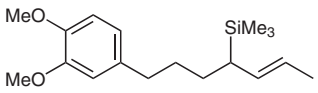
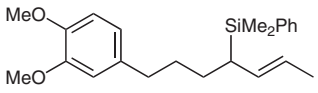
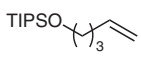
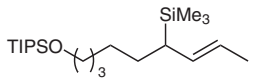
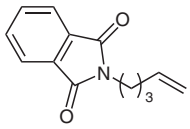
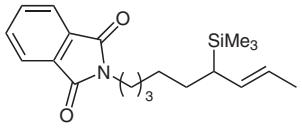
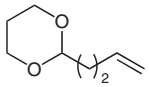
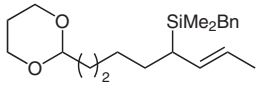
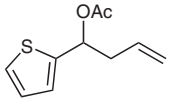
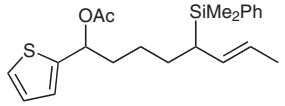
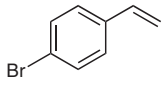
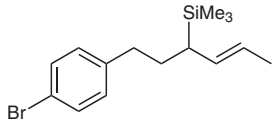
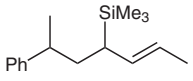
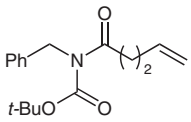
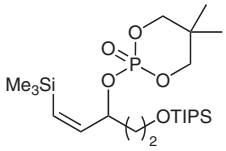
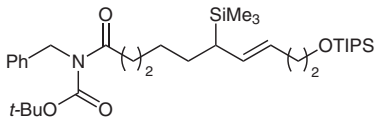
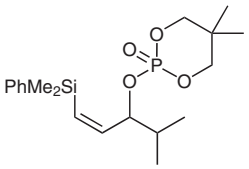
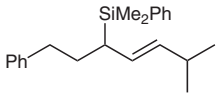
Entry	Alkene	Phosphate	Product	Yield (%)[b,c]
1	**1a**	 **3b**	 **4ab**	94
2	**1a**	 **3c**	 **4ac**	92
3	**1a**	 **3d**	 **4ad**	94
4	 **1b**	 **3a**	 **4ba**	82
5	 **1c**	**3a**	 **4ca**	81
6	**1c**	**3b**	 **4cb**	87
7	 **1d**	**3a**	 **4da**	78
8	 **1e**	**3a**	 **4ea**	72
9	 **1f**	**3d**	 **4fd**	79
10	 **1g**	**3b**	 **4gb**	73[d]

Table 1 Synthesis of Allylsilanes[a] (continued)

Entry	Alkene	Phosphate	Product	Yield (%)[b,c]
11	 **1h**	**3a**	 **4ha**	88
12	 **1i**	**3a**	 **4ia**	79[d]
13	 **1j**	 **3e**	 **4je**	76
14	**1a**	 **3f**	 **4af**	92

[a] The reaction was carried out with **3** (0.2 mmol), alkylborane **2** (0.32 mmol), CuOAc (10 mol%), and *t*-BuOK (0.3 mmol, 1 M in THF) in THF at 60 °C for 6 h. Alkylborane **2** was prepared in advance by hydroboration of **1** with 9-BBN dimer in THF at 60 °C for 1 h and used without purification.
[b] Isolated yield based on **3**.
[c] Isomeric ratios (γ/α = >99:1, *E*/*Z* = >99:1). Determined by ^{1}H NMR spectroscopy or GC analysis of the crude product.
[d] Diastereomeric ratio (1:1).

In conclusion, we have developed a versatile, functional group-tolerable approach to allylsilanes through a copper-catalyzed γ-selective cross-coupling reaction between γ-silylated allylic phosphates and alkylboranes.

All reactions were carried out under N_2 or argon atmosphere. Materials were obtained from commercial suppliers or prepared according to standard procedures, unless otherwise noted. *t*-BuOK (1.0 M THF solution) and CuOAc were purchased from Aldrich Chemical Co., stored under N_2, and used as received. THF was purchased from Kanto Chemical Co. and stored under argon. NMR spectra were recorded on a Varian Gemini 2000 spectrometer, operating at 300 MHz for ^{1}H NMR and 75.4 MHz for ^{13}C NMR. Chemical shift values for ^{1}H and ^{13}C are referenced to Me_4Si and the residual solvent resonances, respectively. Chemical shifts are reported in δ ppm. Mass spectra were obtained with Thermo Fisher Scientific Exactive, Jeol JMS-T100LP, or Jeol JMS-700TZ at the Instrumental Analysis Division, Equipment Management Center, Creative Research Institution, Hokkaido University. Elemental analysis was performed at the Instrumental Analysis Division, Equipment Management Center, Creative Research Institution, Hokkaido University. Melting point was measured on a Yanaco MP-500D apparatus. TLC analyses were performed on commercial glass plates bearing 0.25 mm layer of Merck Silica gel 60F_{254}. Silica gel (Kanto Chemical Co., Silica gel 60 N, spherical, neutral) and Al_2O_3 (Nacalai Tesuque, Alumina Activated 200) were used for column chromatography. GLC analyses were conducted on a Shimadzu GC-14B equipped with a flame ionization detector. Gel permeation chromatography (GPC) was performed by LC-908 (Japan Analytical Industry Ltd., two in-line JAIGEL-2H, $CHCl_3$, 3.5 mL/min, UV and RI detectors). Alkenes **1a–j** are literature known compounds. Allylsilane **4ab** is reported in literature.[14]

γ-Silylated Allylic Phosphates 3a–d; (*Z*)-2-{[4-(Dimethylphenylsilyl)but-3-en-2-yl]oxy}-5,5-dimethyl -1,3,2-dioxaphosphinane 2-Oxide (3b); Typical Procedure

THP-protection of commercially available but-3-yn-2-ol followed by silylations gave γ-silylated propargylic alcohol derivatives. Next, DIBAL-H reduction followed by deprotection afforded γ-silylated allylic alcohols. Finally, allylic phosphates **3a–d** were prepared by the phosphorylation of the γ-silylated allylic alcohols (*vide infra* for the product yield of the phosphorylation). The phosphorylation of (*Z*)-4-(dimethylphenylsilyl)but-3-en-2-ol to **3b** is representative.

To a solution of (*Z*)-4-(dimethylphenylsilyl)but-3-en-2-ol (413 mg, 2.0 mmol) in THF (16.0 mL) and TMEDA (4.0 mL) was added *n*-BuLi (1.3 mL, 1.63 M, 2.1 mmol) at –78 °C. After stirring at –78 °C for 45 min, 2-chloro-5,5-dimethyl-1,3,2-dioxaphosphinane 2-oxide (Aldrich Chemical Co., 480 mg, 2.6 mmol) was added to the reaction mixture. The mixture was stirred for an additional 5 min at –78 °C, then warmed to r.t., and stirred for 3 h. The resulting solution was quenched with sat. aq NH_4Cl (15 mL). The aqueous layer was extracted with EtOAc (3 × 20 mL). The organic layers were combined and washed with brine (20 mL), dried ($MgSO_4$), filtered, and concentrated under vacuum to leave an oil. After passing through a short plug of Al_2O_3 with Et_2O (40 mL), the solvent was evaporated, and the residue was purified with GPC to provide **3b** (517 mg, 1.46 mmol, 73%) as a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.44 (s, 3 H), 0.48 (s, 3 H), 0.84 (s, 3 H), 1.23 (s, 3 H), 1.28 (d, *J* = 6.3 Hz, 3 H), 3.69–4.04 (m, 4 H), 5.04 (dq, *J* = 9.0, 6.3 Hz, 1 H), 5.86 (d, *J* = 14.2 Hz, 1 H), 6.38 (dd, *J* = 14.2, 9.0 Hz, 1 H), 7.26–7.37 (m, 3 H), 7.54–7.56 (m, 2 H).

^{13}C NMR (75.4 MHz, $CDCl_3$): δ = –1.54, –1.27, 20.26 (d, *J* = 4.0 Hz), 21.58, 22.19 (d, *J* = 4.0 Hz), 31.92 (d, *J* = 5.7 Hz), 75.18 (d, *J* = 5.1 Hz), 77.35 (d, *J* = 6.8 Hz), 77.73 (d, *J* = 6.8 Hz), 128.00, 129.24, 130.37, 133.75, 138.54, 147.67 (d, *J* = 5.7 Hz).

HRMS-ESI: *m/z* $[M + Na]^+$ calcd for $C_{17}H_{27}O_4PSi$ + Na: 377.44290; found: 377.13084.

(*Z*)-5,5-Dimethyl-2-{[4-(trimethylsilyl)but-3-en-2-yl]oxy}-1,3,2-dioxaphosphinane 2-Oxide (3a)
Yield: 345 mg (59%); white solid; mp 45.6–45.8 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.17 (s, 9 H), 0.87 (s, 3 H), 1.25 (s, 3 H), 1.44 (d, *J* = 5.1 Hz, 3 H), 3.78–4.11 (m, 4 H), 5.13 (dq, *J* = 9.0, 5.1 Hz, 1 H), 5.71 (d, *J* = 14.1 Hz, 1 H), 6.29 (dd, *J* = 14.1, 9.0 Hz, 1 H).

^{13}C NMR (75.4 MHz, $CDCl_3$): δ = –0.20, 20.21 (d, *J* = 1.1 Hz), 21.55, 22.59 (d, *J* = 4.6 Hz), 31.91 (d, *J* = 5.7 Hz), 75.14 (d, *J* = 5.1 Hz), 77.36 (d, *J* = 6.8 Hz), 77.75 (d, *J* = 6.8 Hz), 132.39, 146.26 (d, *J* = 5.7 Hz).

HRMS-ESI: *m/z* $[M + Na]^+$ calcd for $C_{12}H_{25}O_4PSi$ + Na: 315.11574; found: 315.11519.

(*Z*)-5,5-Dimethyl-2-{[4-(methyldiphenylsilyl)but-3-en-2-yl]oxy}-1,3,2-dioxaphosphinane 2-Oxide (3c)
Yield: 687 mg (83%); colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.78 (s, 3 H), 0.81 (s, 3 H), 1.19 (d, *J* = 6.3 Hz, 3 H), 1.21 (s, 3 H), 3.66–3.98 (m, 4 H), 4.93 (dq, *J* = 9.0, 6.3 Hz, 1 H), 6.08 (d, *J* = 14.4 Hz, 1 H), 6.53 (dd, *J* = 14.4, 9.0 Hz, 1 H), 7.33–7.39 (m, 6 H), 7.53–7.58 (m, 4 H).

^{13}C NMR (75.4 MHz, $CDCl_3$): δ = –2.57, 20.26 (d, *J* = 1.1 Hz), 21.53, 21.88 (d, *J* = 4.0 Hz), 31.88 (d, *J* = 5.7 Hz), 75.20 (d, *J* = 5.1 Hz), 77.34 (d, *J* = 6.8 Hz), 77.64 (d, *J* = 6.8 Hz), 128.04, 128.10, 128.14, 129.49, 129.60, 134.61, 134.75, 136.30, 136.68, 149.30 (d, *J* = 6.3 Hz).

HRMS-ESI: *m/z* $[M + Na]^+$ calcd for $C_{22}H_{29}O_4PSi$ + Na: 439.14704; found: 439.14649.

(*Z*)-2-{[4-(Benzyldimethylsilyl)but-3-en-2-yl]oxy}-5,5-dimethyl-1,3,2-dioxaphosphinane 2-Oxide (3d)
Yield: 667 mg (91%); colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.16 (s, 3 H), 0.17 (s, 3 H), 0.87 (s, 3 H), 1.24 (s, 3 H), 1.37 (d, *J* = 6.3 Hz, 3 H), 2.19 (s, 2 H), 3.76–4.09 (m, 4 H), 5.08 (dq, *J* = 9.0, 6.3 Hz, 1 H), 5.68 (d, *J* = 14.4 Hz, 1 H), 6.32 (dd, *J* = 14.4, 9.0 Hz, 1 H), 7.00–7.10 (m, 3 H), 7.19–7.24 (m, 2 H).

^{13}C NMR (75.4 MHz, $CDCl_3$): δ = –2.05, –2.00, 20.25, 21.55, 22.51 (d, *J* = 4.6 Hz), 26.17, 31.94 (d, *J* = 5.7 Hz), 75.20 (d, *J* = 5.1 Hz), 77.38 (d, *J* = 6.8 Hz), 77.75 (d, *J* = 6.8 Hz), 124.19, 128.22, 128.28, 130.46, 139.51, 147.16 (d, *J* = 5.7 Hz).

HRMS-ESI: *m/z* $[M + Na]^+$ calcd for $C_{18}H_{29}O_4PSi$ + Na: 391.14704; found: 391.14649.

(*Z*)-5,5-Dimethyl-2-{[5-(triisopropylsilyloxy)-1-(trimethylsilyl)pent-1-en-3-yl]oxy}-1,3,2-dioxaphosphinane 2-Oxide (3e)
THP-protection of 5-[(triisopropylsilyl)oxy]pent-1-yn-3-ol followed by silylation gave the γ-silylated propargylic alcohol derivative. Next, DIBAL-H reduction followed by deprotection afforded the γ-silylated allylic alcohol. Finally, the phosphorylation of the γ-silylated allylic alcohol (661 mg, 2.0 mmol) provided the allylic phosphate **3e** (171 mg, 1.0 mmol, 50%) as a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.18 (s, 9 H), 0.88 (s, 3 H), 1.06–1.14 (m, 21 H), 1.23 (s, 3 H), 1.81–1.91 (m, 1 H), 1.96–2.07 (m, 1 H), 3.82–3.94 (m, 4 H), 4.01–4.10 (m, 2 H), 5.13 (m, 1 H), 5.76 (d, *J* = 14.4 Hz, 1 H), 6.34 (dd, *J* = 14.4, 9.3 Hz, 1 H).

^{13}C NMR (75.4 MHz, $CDCl_3$): δ = –0.15, 11.77, 17.88, 20.35, 21.57, 31.95 (d, *J* = 5.7 Hz), 39.71 (d, *J* = 6.3 Hz), 59.03, 76.04 (d, *J* = 5.7 Hz), 77.39 (d, *J* = 5.1 Hz), 77.58 (d, *J* = 6.9 Hz), 133.44, 145.14 (d, *J* = 2.7 Hz).

HRMS-ESI: *m/z* $[M + Na]^+$ calcd for $C_{22}H_{47}O_5PSi_2$ + Na: 501.25973; found: 501.25919.

(*S*)-(*Z*)-2-{[1-(Dimethylphenylsilyl)-4-methylpent-1-en-3-yl]oxy}-5,5-dimethyl-1,3,2-dioxaphosphinane 2-Oxide (3f)
THP-protection of 4-methylpent-1-yn-3-ol followed by silylation gave the γ-silylated propargylic alcohol derivative. Next, DIBAL-H reduction followed by deprotection afforded the γ-silylated allylic alcohol. Finally, the phosphorylation of the γ-silylated allylic alcohol (468 mg, 2.0 mmol) provided the allylic phosphate **3f** (451 mg, 1.18 mmol, 59%); white solid; mp 91.5–91.7 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.46 (s, 3 H), 0.50 (s, 3 H), 0.81 (d, *J* = 6.6 Hz, 3 H), 0.85 (s, 3 H), 0.89 (d, *J* = 6.6 Hz, 3 H), 1.24 (s, 3 H), 1.77 (sext, *J* = 6.6 Hz, 1 H), 3.71–4.06 (m, 4 H), 4.68–4.76 (m, 1 H), 5.95 (d, *J* = 14.4 Hz, 1 H), 6.37 (dd, *J* = 14.4, 9.6 Hz, 1 H), 7.34–7.37 (m, 3 H), 7.57–7.58 (m, 2 H).

^{13}C NMR (75.4 MHz, $CDCl_3$): δ = –1.43, –1.31, 17.15, 17.99, 20.34 (d, *J* = 1.1 Hz), 21.63, 31.92 (d, *J* = 5.7 Hz), 33.47 (d, *J* = 5.7 Hz), 77.27 (d, *J* = 6.3 Hz), 77.68 (d, *J* = 6.8 Hz), 82.59 (d, *J* = 6.3 Hz), 127.95, 129.18, 132.94, 133.90, 138.69, 144.54 (d, *J* = 2.9 Hz).

HRMS-ESI: *m/z* $[M + Na]^+$ calcd for $C_{19}H_{31}O_4PSi$ + Na: 405.16269; found: 405.16241.

Allylsilanes; (*E*)-Trimethyl(1-phenylhex-4-en-3-yl)silane (4aa); Typical Procedure
In a glove box, (9-BBN-H)$_2$ (40.3 mg, 0.165 mmol), THF (0.06 mL), and styrene (**1a**; 0.041 mL, 0.36 mmol) were sequentially placed in a screw-top test tube containing a magnetic stirring bar. Also in the glove box, CuOAc (2.5 mg, 0.02 mmol) was placed in another vial containing a magnetic stirring bar. Both the two vials were then sealed with a cap equipped with a Teflon-coated silicon rubber septum, and were removed from the glove box. After stirring the THF solution at 60 °C for 1 h to prepare the alkylborane **2a**, *t*-BuOK (1 M in THF, 0.3 mL, 0.3 mmol) prepared in advance at 25 °C was added. Next, this mixture was transferred to the vial containing the Cu salt. Finally, allylic phosphate **3a** (56.1 mg, 0.2 mmol) was added. After stirring for 6 h at 60 °C, CH_2Cl_2 (0.3 mL) was added to the mixture. Then, the mixture was filtered through a short plug of silica gel, which was washed with Et_2O (8 mL). After removal of the solvent under reduced pressure, flash chromatography on silica gel (hexane) provided **4aa** (41.5 mg, 0.178 mmol, 89%) as a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = –0.05 (s, 9 H), 1.40–1.46 (m, 1 H), 1.52–1.78 (m, 2 H), 1.71 (d, *J* = 4.8 Hz, 3 H), 2.43 (ddd, *J* = 13.5, 9.6, 6.9 Hz, 1 H), 2.77 (ddd, *J* = 13.5, 9.3, 4.5 Hz, 1 H), 5.23 (dd, *J* = 15.0, 7.8 Hz, 1 H), 5.30 (dq, *J* = 15.0, 4.8 Hz, 1 H), 7.15–7.19 (m, 3 H), 7.25–7.30 (m, 2 H).

^{13}C NMR (75.4 MHz, $CDCl_3$): δ = –3.37, 18.11, 31.08, 32.71, 35.59, 123.16, 125.60, 128.29, 128.59, 132.17, 143.18.

Anal. Calcd for $C_{15}H_{24}Si$: C, 77.51; H, 10.41. Found: C, 77.70; H, 10.76.

(*E*)-Dimethylphenyl(1-phenylhex-4-en-3-yl)silane (4ab)
Yield: 55.4 mg (94%); colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.21 (s, 3 H), 0.24 (s, 3 H), 1.53–1.76 (m, 3 H), 1.69 (d, *J* = 4.8 Hz, 3 H), 2.39 (ddd, *J* = 13.5, 9.0, 7.2 Hz, 1 H), 2.72 (ddd, *J* = 13.5, 9.6, 4.2 Hz, 1 H), 5.22 (dd, *J* = 15.0, 7.5 Hz, 1 H), 5.29 (dq, *J* = 15.0, 4.8 Hz, 1 H), 7.07–7.10 (m, 2 H), 7.13–7.18 (m, 1 H), 7.22–7.26 (m, 2 H), 7.29–7.34 (m, 3 H), 7.37–7.45 (m, 2 H).

^{13}C NMR (75.4 MHz, $CDCl_3$): δ = –5.37, –4.39, 18.09, 30.91, 32.07, 35.34, 123.90, 125.58, 127.63, 128.25, 128.60, 128.89, 131.61, 134.15, 138.13, 142.90.

Anal. Calcd for $C_{20}H_{26}Si$: C, 81.57; H, 8.96. Found: C, 81.45; H, 9.04.

(*E*)-Methyldiphenyl(1-phenylhex-4-en-3-yl)silane (4ac)
Yield: 65.6 mg (92%); colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.48 (s, 3 H), 1.59–1.71 (m, 1 H), 1.66 (d, *J* = 4.2 Hz, 3 H), 1.78–1.86 (m, 1 H), 2.05–2.10 (m, 1 H), 2.45 (dt, *J* = 13.8, 8.4 Hz, 1 H), 2.76 (ddd, *J* = 13.8, 9.0, 4.8 Hz, 1 H), 5.27–5.29 (m, 2 H), 7.07–7.49 (m, 15 H).

^{13}C NMR (75.4 MHz, $CDCl_3$): δ = –5.82, 18.09, 30.21, 30.96, 35.04, 124.89, 125.65, 127.63, 127.76, 128.25, 128.73, 129.08, 129.20, 130.97, 135.07, 135.10, 135.84, 136.40, 142.62.

Anal. Calcd for $C_{25}H_{28}Si$: C, 84.21; H, 7.91. Found: C, 83.88; H, 7.95.

(*E*)-Benzyldimethyl(1-phenylhex-4-en-3-yl)silane (4ad)
Yield: 58.0 mg (94%); colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = –0.12 (s, 3 H), –0.10 (s, 3 H), 1.48–1.80 (m, 3 H), 1.72 (d, *J* = 5.1 Hz, 3 H), 2.06 (s, 2 H), 2.42 (ddd, *J* = 13.5, 9.0, 7.2 Hz, 1 H), 2.77 (ddd, *J* = 13.5, 9.6, 4.2 Hz, 1 H), 5.25 (dd, *J* = 16.2, 8.4 Hz, 1 H), 5.31 (dq, *J* = 16.2, 5.1 Hz, 1 H), 6.93–6.95 (m, 2 H), 7.03–7.08 (m, 1 H), 7.15–7.21 (m, 5 H), 7.26–7.31 (m, 2 H).

^{13}C NMR (75.4 MHz, $CDCl_3$): δ = –5.40, –5.29, 18.12, 23.69, 31.14, 31.31, 35.41, 123.91, 123.93, 125.67, 128.20, 128.27, 128.33, 128.62, 131.69, 140.37, 142.96.

Anal. Calcd for $C_{21}H_{28}Si$: C, 81.75; H, 9.15. Found: C, 81.53; H, 9.40.

(*E*)-Methyl 3,3-Dimethyl-6-(trimethylsilyl)non-7-enoate (4ba)
Yield: 44.3 mg (82%); colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = –0.05 (s, 9 H), 0.98 (s, 6 H), 1.04–1.26 (m, 3 H), 1.42–1.47 (m, 2 H), 1.66 (d, *J* = 4.8 Hz, 3 H), 2.19 (s, 2 H), 3.65 (s, 3 H), 5.15 (dd, *J* = 15.3, 7.8 Hz, 1 H), 5.21 (dq, *J* = 15.3, 4.8 Hz, 1 H).

^{13}C NMR (75.4 MHz, $CDCl_3$): δ = –3.26, 18.02, 23.04, 27.12, 27.22, 33.24, 33.47, 42.34, 45.77, 51.01, 122.49, 132.51, 173.09.

Anal. Calcd for $C_{15}H_{30}O_2Si$: C, 66.61; H, 11.18. Found: C, 66.59; H, 11.20.

(*E*)-[7-(3,4-Dimethoxyphenyl)hept-2-en-4-yl]trimethylsilane (4ca)

Yield: 49.7 mg (81%); colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = –0.06 (s, 9 H), 1.26–1.54 (m, 4 H), 1.65 (d, *J* = 4.8 Hz, 3 H), 1.71–1.78 (m, 1 H), 2.46 (ddd, *J* = 15.0, 8.1, 6.6 Hz, 1 H), 2.58 (ddd, *J* = 15.0, 9.6, 5.1 Hz, 1 H), 3.86 (s, 3 H), 3.87 (s, 3 H), 5.17 (dd, *J* = 15.3, 7.2 Hz, 1 H), 5.24 (dq, *J* = 15.3, 4.8 Hz, 1 H), 6.70–6.72 (m, 2 H), 6.77–6.80 (m, 1 H).

^{13}C NMR (75.4 MHz, $CDCl_3$): δ = –3.34, 18.01, 28.42, 31.34, 32.75, 35.23, 55.68, 55.82, 111.08, 111.69, 120.14, 122.59, 132.34, 135.69, 146.99, 148.75.

Anal. Calcd for $C_{18}H_{30}O_2Si$: C, 70.53; H, 9.87. Found: C, 70.52; H, 10.02.

(*E*)-[7-(3,4-Dimethoxyphenyl)hept-2-en-4-yl]dimethyl(phenyl)silane (4cb)
Yield: 64.1 mg (87%); colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.22 (s, 3 H), 0.24 (s, 3 H), 1.28–1.70 (m, 5 H), 1.64 (d, *J* = 4.8 Hz, 3 H), 2.38 (ddd, *J* = 14.4, 8.4, 6.0 Hz, 1 H), 2.51 (ddd, *J* = 14.4, 9.3, 4.5 Hz, 1 H), 3.84 (s, 3 H), 3.85 (s, 3 H), 5.18 (dd, *J* = 15.3, 7.5 Hz, 1 H), 5.22 (dq, *J* = 15.3, 4.8 Hz, 1 H), 6.63–6.66 (m, 2 H), 6.74–6.77 (m, 1 H), 7.30–7.38 (m, 3 H), 7.38–7.49 (m, 2 H).

^{13}C NMR (75.4 MHz, $CDCl_3$): δ = –5.37, –4.39, 18.01, 28.47, 31.22, 32.28, 35.10, 55.68, 55.83, 111.09, 111.68, 120.12, 123.37, 127.60, 128.86, 131.77, 134.12, 135.63, 138.33, 146.99, 148.75.

Anal. Calcd for $C_{23}H_{32}O_2Si$: C, 74.95; H, 8.75. Found: C, 75.11; H, 8.77.

(*E*)-Triisopropyl[(6-(trimethylsilyl)non-7-en-1-yl)oxy]silane (4da)
Yield: 67.5 mg (78%); colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = –0.06 (s, 9 H), 1.05–1.07 (m, 21 H), 1.15–1.57 (m, 9 H), 1.65 (d, *J* = 4.8 Hz, 3 H), 3.66 (t, *J* = 13.2 Hz, 2 H), 5.16 (dd, *J* = 14.7, 6.9 Hz, 1 H), 5.23 (dq, *J* = 14.7, 4.8 Hz, 1 H).

^{13}C NMR (75.4 MHz, $CDCl_3$): δ = –3.32, 11.90, 17.92, 18.02, 25.56, 28.81, 29.08, 32.88, 32.89, 63.50, 122.35, 132.63.

HRMS-APCI: *m*/*z* $[M]^+$ calcd for $C_{21}H_{46}OSi_2$: 370.3087; found: 370.3083.

(*E*)-2-[6-(Trimethylsilyl)non-7-en-1-yl]isoindoline-1,3-dione (4ea)
Yield: 49.5 mg (72%); white solid; mp 54.2–54.4 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = –0.08 (s, 9 H), 1.14–1.49 (m, 9 H), 1.63 (d, *J* = 5.1 Hz, 3 H), 3.67 (t, *J* = 7.2 Hz, 2 H), 5.13 (dd, *J* = 15.0, 6.9 Hz, 1 H), 5.20 (dq, *J* = 15.0, 5.1 Hz, 1 H), 7.71 (m, 2 H), 7.85 (m, 2H).

^{13}C NMR (75.4 MHz, $CDCl_3$): δ = –3.35, 17.80, 26.70, 28.48, 28.65, 28.90, 32.85, 38.06, 122.47, 123.20, 132.26, 132.42, 133.90, 168.63.

Anal. Calcd for $C_{20}H_{29}NO_2Si$: C, 69.92; H, 8.51; N, 4.08. Found: C, 70.14; H, 8.68; N, 3.99.

(*E*)-[9-(1,3-Dioxan-2-yl)non-2-en-4-yl](benzyl)dimethylsilane (4fd)
Yield: 57.0 mg (79%); colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = –0.11 (s, 3 H), –0.10 (s, 3 H), 1.16–1.63 (m, 12 H), 1.66 (d, *J* = 4.8 Hz, 3 H), 2.02–2.16 (m, 1 H), 2.06 (s, 2 H), 3.76 (td, *J* = 12.3, 2.1 Hz, 2 H), 4.10 (dd, *J* = 10.8, 5.1 Hz, 2 H), 4.50 (t, *J* = 5.1 Hz, 1 H), 5.16 (dd, *J* = 15.3, 7.8 Hz, 1 H), 5.21 (dq, *J* = 15.3, 4.8 Hz, 1 H), 6.97–7.00 (m, 2 H), 7.03–7.08 (m, 1 H), 7.18–7.23 (m, 2 H).

^{13}C NMR (75.4 MHz, $CDCl_3$): δ = –5.32, –5.28, 18.02, 23.75, 23.82, 25.74, 28.77, 29.08, 29.24, 31.70, 35.17, 66.86, 102.47, 123.09, 123.86, 128.14, 128.29, 132.08, 140.49.

Anal. Calcd for $C_{22}H_{36}O_2Si$: C, 73.28; H, 10.06. Found: C, 73.21; H, 10.33.

(*E*)-5-(Dimethylphenylsilyl)-1-(thiophen-2-yl)oct-6-en-1-yl Acetate (4gb)
Yield: 56.4 mg (73%); colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.22 (s, 3 H), 0.23 (s, 3 H), 1.07–1.50 (m, 5 H), 1.62 (d, *J* = 4.8 Hz, 1.5 H), 1.63 (d, *J* = 4.8 Hz, 1.5 H), 1.79–1.93 (m, 2 H), 2.02 (s, 3 H), 5.07–5.24 (m, 2 H), 5.94 (t, *J* = 7.2 Hz, 0.5 H), 5.95 (t, *J* = 7.2 Hz, 0.5 H), 6.92–6.98 (m, 2 H), 7.23–7.26 (m, 1 H), 7.34–7.35 (m, 3 H), 7.44–7.48 (m, 2 H).

^{13}C NMR (75.4 MHz, $CDCl_3$): δ = –5.46, –5.41, –4.46, –4.42, 17.97 (2 C), 21.09 (2 C), 24.87, 25.00, 28.29, 28.31, 32.02, 32.24, 35.68, 35.90, 71.09, 71.30, 123.56, 123.62, 125.11, 125.20, 125.77, 125.91, 126.50, 126.52, 127.63, 127.65, 128.91, 131.43, 131.49, 134.09, 134.11, 138.15, 138.19, 143.64, 143.84, 170.41, 170.44.

HRMS-ESI: *m*/*z* $[M + Na]^+$ calcd for $C_{22}H_{30}O_2SSi + Na$: 409.16335; found: 409.16280.

(*E*)-[1-(4-Bromophenyl)hex-4-en-3-yl]trimethylsilane (4ha)
Yield: 54.8 mg (88%); colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = –0.07 (s, 9 H), 1.35–1.42 (m, 1 H), 1.49–1.73 (m, 2 H), 1.70 (d, *J* = 5.1 Hz, 3 H), 2.40 (ddd, *J* = 13.5 9.0, 7.2 Hz, 1 H), 2.71 (ddd, *J* = 13.5, 9.3, 4.5 Hz, 1 H), 5.20 (dd, *J* = 15.6, 8.1 Hz, 1 H), 5.26 (dq, *J* = 15.6, 5.1 Hz, 1 H), 7.02–7.05 (m, 2 H), 7.36–7.40 (m, 2 H).

^{13}C NMR (75.4 MHz, $CDCl_3$): δ = –3.40, 18.09, 30.83, 32.47, 34.84, 119.27, 123.39, 130.40, 131.32, 131.95, 142.02.

HRMS-EI: *m/z* $[M]^+$ calcd for $C_{15}H_{23}BrSi$: 310.0752; found: 310.0752.

(*E*)-Trimethyl(6-phenylhept-2-en-4-yl)silane (4ia)
Yield: 38.9 mg (79%); colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = –0.13 (s, 4.5 H), –0.06 (s, 4.5 H), 1.09–1.27 (m, 1 H), 1.15 (d, *J* = 6.9 Hz, 1.5 H), 1.21 (d, *J* = 6.9 Hz, 1.5 H), 1.44–1.64 (m, 2 H), 1.68 (d, *J* = 5.1 Hz, 1.5 H), 1.69 (d, *J* = 5.1 Hz, 1.5 H), 2.71–2.87 (m, 1 H), 5.03–5.34 (m, 2 H), 7.11–7.15 (m, 1 H), 7.17–7.21 (m, 2 H), 7.26–7.32 (m, 2 H).

^{13}C NMR (75.4 MHz, $CDCl_3$): δ = –3.53, –3.40, 18.08, 19.12, 23.60, 30.52, 30.66, 37.27, 37.46, 38.03, 38.40, 122.96, 123.03, 125.73, 125.76, 126.97, 127.48, 128.24, 128.35, 131.85, 132.23, 147.11, 149.29.

Anal. Calcd for $C_{16}H_{26}Si$: C, 77.97; H, 10.63. Found: C, 78.09; H, 10.89.

(*E*)-*tert*-Butyl Benzyl{10-[(triisopropylsilyl)oxy]-6-(trimethylsilyl)dec-7-enoyl}carbamate (4je)
Yield: 91.7 mg (76%); colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = –0.06 (s, 9 H), 1.06 (s, 21 H), 1.12–1.70 (m, 7 H), 1.41 (s, 9 H), 2.25 (d, *J* = 6.9 Hz, 2 H), 2.88 (td, *J* = 7.8, 2.1 Hz, 2 H), 3.65 (t, *J* = 6.9 Hz, 2 H), 4.88 (s, 2 H), 5.21–5.24 (m, 2 H), 7.23–7.32 (m, 5 H).

^{13}C NMR (75.4 MHz, $CDCl_3$): δ = –3.37, 11.86, 17.91, 24.98, 27.78, 28.58, 28.85, 32.92, 36.80, 38.21, 47.21, 64.03, 82.99, 124.36, 127.10, 127.60, 128.33, 133.52, 138.53, 153.25, 176.45.

HRMS-ESI: *m/z* $[M + Na]^+$ calcd for $C_{34}H_{61}NO_4Si_2$ + Na: 626.40368; found: 626.40313.

(*E*)-Dimethyl(6-methyl-1-phenylhept-4-en-3-yl)(phenyl)silane (4af)
Yield: 59.4 mg (92%); colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.22 (s, 3 H), 0.24 (s, 3 H), 0.96 (d, *J* = 6.6 Hz, 3 H), 0.98 (d, *J* = 6.6 Hz, 3 H), 1.50–1.78 (d, *J* = 6.6 Hz, 3 H), 2.22–2.34 (m, 1 H), 2.36–2.44 (m, 1 H), 2.67–2.76 (m, 1 H), 5.15 (dd, *J* = 15.3, 7.8 Hz, 1 H), 5.22 (dd, *J* = 15.3, 6.0 Hz, 1 H), 7.08–7.10 (m, 2 H), 7.13–7.18 (m, 1 H), 7.22–7.27 (m, 2 H), 7.30–7.34 (m, 3 H), 7.42–7.45 (m, 2 H).

^{13}C NMR (75.4 MHz, $CDCl_3$): δ = –5.34, –4.53, 22.87, 23.03, 30.81, 31.41, 31.70, 35.18, 125.58, 127.29, 127.60, 128.25, 128.63, 128.89, 134.18, 137.17, 138.07, 142.89.

HRMS-EI: *m/z* $[M]^+$ calcd for $C_{22}H_{30}Si$: 322.21168; found: 322.2115.

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