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

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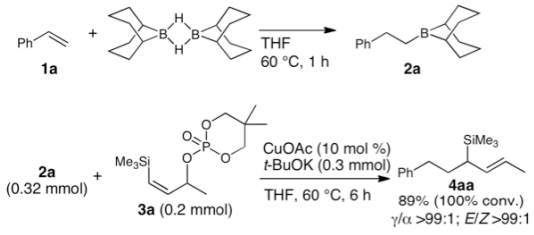
Abstract: A copper-catalyzed γ-selective allyl–alkyl coupling between γ -silylated allylic phosphates and alkylboron compounds (alkyl-9-BBN, prepared by hydroboration of alkenes with 9-BBN-H) produced allylsilanes. The reaction tolerated various functional groups in both the alkylboranes and the allylic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

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

Allylsilanes are versatile synthetic intermediates in organic synthesis.[1] The development of facile and efficient methods for the sythesis of allylsilanes is important. Among the available methods for accessing to 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.

Previouly 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.



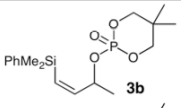
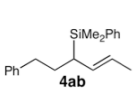
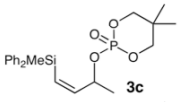
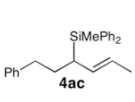
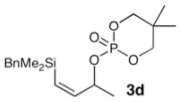
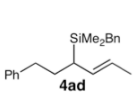
Scheme 1.

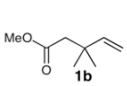
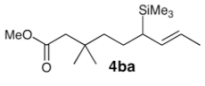
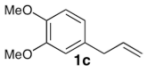
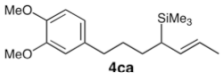
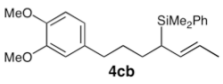
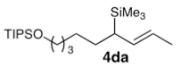
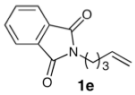
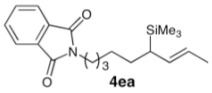
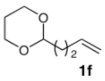
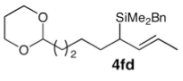
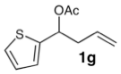
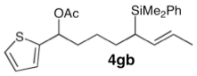
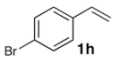
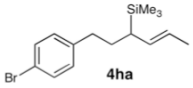
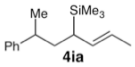
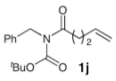
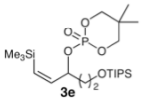
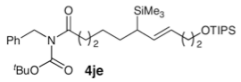
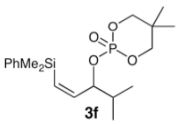
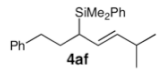
Alkylborane **2a** (0.32 mmol), which was prepared via hydroboration of styrene (**1a**) with 9-borabicyclo[3.3.1]nonane (9-BBN-H) dimer, and γ-trimethylsilyl allylic substrates **3a** (0.2 mmol) bearing a cyclic phosphate leaving group were subjected to the standard reaction conditions for the copper-catalyzed 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% convn 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]

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 a 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 to give **4ia** as a 1:1 diastereomeric mixture (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 undewent the reaction (entry 13). A sterically more demanding α-substituent such as an ^{i}Pr group was also tolerated (entry 14).

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		**3a**		82
5		**3a**		81
6	**1c**	**3b**		87
7		**3a**		78
8		**3a**		72
9		**3d**		79
10		**3b**		73[d]
11		**3a**		88
12		**3a**		79[d]
13				76
14	**1a**			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 or GC of the crude product. [d] Diasteremeric 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 nitrogen 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 nitrogen, and used as it is. Tetrahydrofuran (THF) was purchased from Kanto Chemical Co., 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 aluminum oxide (Nacalai Tesuque, Alumina Activated 200) were used for column chromatography. Gas chromatographic (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** were well known compounds. Allylsilane **4ab** was found in literature.[14]

Preparation of γ-Silylated Allylic Phosphates 3a–d

THP-protection of commercially available 3-butyn-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)-3-buten-2-ol to **3b** is representative. To a solution of (*Z*)-4-(dimethylphenylsilyl)-3-buten-2-ol (413 mg, 2.0 mmol) in THF (16.0 mL) and TMEDA (4.0 mL), ^{n}BuLi (1.3 mL, 1.63 M, 2.1 mmol) was added at –78 ˚C. After being stirred 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 reaction mixture was stirred for an additional 5 minutes at –78 °C, then warmed to room temperature, and stirred for 3 hours. The resulting solution was quenched with saturated NH_4Cl aq. Aqueous layer was extracted with ethyl acetate. The organic layers were combined and washed with brine, dried over $MgSO_4$, filtered, and concentrated under vacuum to leave an oil. After passing through a short plug of aluminum oxide with diethyl ether, an eluent was concentrated, and the residue was purified with GPC to provide **3b** in 73% yield (517 mg, 1.46 mmol).

(*Z*)-5,5-Dimethyl-2-{[4-(trimethylsilyl)-3-buten-2-yl]oxy}-1,3,2-dioxaphosphinane 2-Oxide (3a)

White solid; yield: 345 mg (59%); mp 45.6–45.8 ˚C.

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

^{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 $C_{12}H_{25}O_4PSiNa$, 315.11574; found, 315.11519.

(*Z*)-2-{[4-(Dimethylphenylsilyl)-3-buten-2-yl]oxy}-5,5-dimethyl-1,3,2-dioxaphosphinane 2-Oxide (3b)

Colorless oil; yield: 517 mg (73%).

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

^{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 $C_{17}H_{27}O_4PSiNa$, 377.44290; found, 377.13084.

(Z)-5,5-Dimethyl-2-{[4-(methyldiphenylsilyl)-3-buten-2-yl]oxy}-1,3,2-dioxaphosphinane 2-Oxide (3c)

Colorless oil; yield: 687 mg (83%).

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

^{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 $C_{22}H_{29}O_4PSiNa$, 439.14704; found, 439.14649.

(*Z*)-2-{[4-(Benzyldimethylsilyl)-3-buten-2-yl]oxy}-5,5-dimethyl-1,3,2-dioxaphosphinane 2-Oxide (3d)

Colorless oil; yield: 667 mg (91%).

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

^{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 $C_{18}H_{29}O_4PSiNa$, 391.14704; found, 391.14649.

(Z)-5,5-Dimethyl-2-{[5-(triisopropylsilyloxy)-1-(trimethylsilyl)-1-penten-3-yl]oxy}-1,3,2-dioxaphosphinane 2-Oxide (3e)

THP-protection of 5-[(triisopropylsilyl)oxy]-1-pentyn-3-ol followed by silylation gave γ-silylated propargylic alcohol derivative. Next, DIBAL-H reduction followed by deprotection afforded γ-silylated allylic alcohol. Finally, the phosphorylation of the γ-silylated allylic alcohol (2.0 mmol) provided allylic phosphate **3e** in 50% (171 mg, 1.0 mmol).

Colorless oil.

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

^{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 $C_{22}H_{47}O_5PSi_2Na$, 501.25973; found, 501.25919.

(*S*)-(*Z*)-2-{[1-(Dimethylphenylsilyl)-4-methyl-1-penten-3-yl]oxy}-5,5-dimethyl-1,3,2-dioxaphosphinane 2-Oxide (3f)

THP-protection of 4-methyl-1-pentyn-3-ol followed by silylation gave γ-silylated propargylic alcohol derivative. Next, DIBAL-H reduction followed by deprotection afforded γ-silylated allylic alcohol. Finally, the phosphorylation of the γ-silylated allylic alcohol (2.0 mmol) provided allylic phosphate **3f** in 59% (451 mg, 1.18 mmol).

White solid; mp 91.5–91.7 ˚C.

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

^{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 $C_{19}H_{31}O_4NaPSi$, 405.16269; found, 405.16241.

Typical Procedure for Synthesis of Allylsilanes

The preparation of **4aa** is representative (Scheme 1). In a grove box, $(9\text{-BBN-H})_2$ (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. The two vials were then each sealed with a cap equipped with a Teflon-coated silicon rubber septum, and were removed from the glove box. After the mixture in THF was stirred at 60 °C for 1 h to prepare alkylborane **2a**, *t*-BuOK (1 M in THF, 0.3 mL, 0.3 mmol) was added to **2a** prepared in advance at 25 °C. Next, the mixture was transferred to the vial containing the Cu salt. Finally, allylic phosphate **3a** (56.1 mg, 0.2 mmol) was added. After 6 h stirring at 60 ˚C, CH_2Cl_2 was added to the mixture. Then, the mixture was filtered through a short plug of silica gel, which was washed with diethyl ether. After the solvent was removed under reduced pressure, flash chromatography on silica gel (hexane) provided **4aa** (41.5 mg, 0.178 mmol) in 89% yield.

(*E*)-Trimethyl(1-phenyl-4-hexen-3-yl)silane (4aa)

Colorless oil; yield: 41.5 mg (89%).

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

^{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*)-Methyldiphenyl(1-phenyl-4-hexen-3-yl)silane (4ac)

Colorless oil; yield: 65.6 mg (92%).

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

^{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-phenyl-4-hexen-3-yl)silane (4ad)

Colorless oil; yield: 58.0 mg (94%).

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

^{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)-7-nonenoate (4ba)

Colorless oil; yield: 44.3 mg (82%).

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

^{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)-2-hepten-4-yl]trimethylsilane (4ca)

Colorless oil; yield: 49.7 mg (81%).

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

^{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)-2-hepten-4-yl]dimethyl(phenyl) silane (4cb)

Colorless oil; yield: 64.1 mg (87%).

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

^{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)-7-nonen-1-yl)oxy]silane (4da)

Colorless oil; yield: 67.5 mg (78%).

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

^{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)-7-nonen-1-yl]isoindoline-1,3-dione (4ea)

White solid; yield: 49.5 mg (72%); mp 54.2–54.4 ˚C.

^{1}H NMR (300 MHz, $CDCl_3$) δ –0.08 (s, 9H), 1.14–1.49 (m, 9H), 1.63 (d, *J* = 5.1 Hz, 3H), 3.67 (t, *J* = 7.2 Hz, 2H), 5.13 (dd, *J* = 15.0, 6.9 Hz, 1H), 5.20 (dq, *J* = 15.0, 5.1 Hz, 1H), 7.71 (m, 2H), 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)-2-nonen-4-yl](benzyl)dimethylsilane (4fd)

Colorless oil; yield: 57.0 mg (79%).

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

^{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)-6-octen-1-yl Acetate (4gb)

Colorless oil; yield: 56.4 mg (73%).

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

^{13}C NMR (75.4 MHz, $CDCl_3$) δ –5.46, –5.41, –4.46, –4.42, 17.97 (×2C), 21.09 (×2C), 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 $C_{22}H_{30}O_2SSiNa$, 409.16335; found, 409.16280.

(*E*)-[1-(4-Bromophenyl)-4-hexen-3-yl]trimethylsilane (4ha)

Colorless oil; yield: 54.8 mg (88%).

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

^{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-phenyl-2-hepten-4-yl)silane (4ia)

Colorless oil; yield: 38.9 mg (79%).

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

^{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)-7-decenoyl}carbamate (4je)

Colorless oil; yield: 91.7 mg (76%).

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

^{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 $C_{34}H_{61}NO_4Si_2Na$, 626.40368; found, 626.40313.

(*E*)-Dimethyl(6-methyl-1-phenyl-4-hepten-3-yl)(phenyl)silane (4af)

Colorless oil; yield: 59.4 mg (92%).

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

^{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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