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Iridium-Catalyzed (*Z*)-Trialkylsilylation of Terminal Olefins

Biao Lu and J. R. Falck*

Departments of Biochemistry and Pharmacology, University of Texas Southwestern Medical Center, Dallas, Texas 75390

j.falck@utsouthwestern.edu

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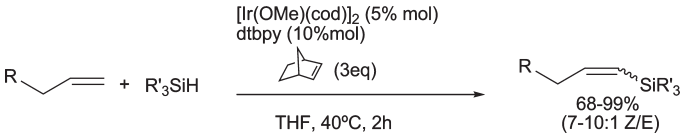

A complex of commercial $[Ir(OMe)(cod)]_2$ and 4,4-di-*tert*-butyl-2,2-bipyridine (dtbpy) catalyzes the *Z*-selective, dehydrative silylation of terminal alkenes, but not 1,2-disubstituted alkenes, with triethylsilane or benzyldimethylsilane in THF at 40 °C. Yields and *Z*-stereoselectivity were significantly improved by 2-norbornene, in contrast with other sacrificial alkenes. The reaction is compatible with many functional groups including epoxides, ketones, amides, alcohols, esters, halides, ketals, and silanes. α,*β*-Unsaturated esters were unreactive. The reaction probably proceeds through a Heck-type mechanism.

Introduction

The unique reactivity profile[1] of trialkylsilylalkenes (vinylsilanes) combined with their low environmental impact[2] and distinctive physical properties[3] has led to ever-widening roles for them as synthetic intermediates[4] and as building blocks in numerous material science/polymer applications.[5] Accordingly, a variety of procedures are extant for the preparation of vinylsilanes, *inter alia*, additions of vinyllithiums or Grignard reagents to silyl electrophiles,[6] Wittig/Peterson olefinations,[7] alkyne hydrosilyation,[8] and Suzuki cross-coupling.[9,10] In more recent years, the direct silylation of alkenes mediated by transition metal catalysts,[11] e.g., iron,[12] cobalt,[13] palladium,[14] rhodium,[15] ruthenium,[16] iridium,[17] and rhenium[18] complexes, was introduced. Additionally, Kambe et al. reported the zirconocene catalyzed silylation of alkenes using chlorosilanes,[19] while Yorimitsu and Oshima developed an elegant silylation of terminal

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(10) Other procedures: (a) Horino, Y.; Luzung, M. R.; Toste, F. D. *J. Am. Chem. Soc.* **2006**, *128*, 11364–11365. (b) Ohmiya, H.; Yorimitsu, H.; Oshima, K. *Org. Lett.* **2006**, *8*, 3093–3096. (c) Barbero, A.; Pulido, F. J. *Acc. Chem. Res.* **2004**, *37*, 817–825.

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(15) Cipot, J.; McDonald, R.; Ferguson, M. J.; Schatte, G.; Stradiotto, M. *Organometallics* **2007**, *26*, 594–608. . Notably, the iridium analogue and Et_3SiH reduce terminal olefins.

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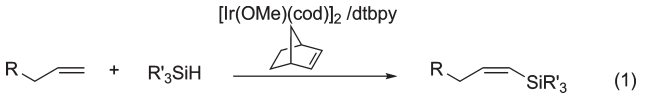
alkenes via Ni-catalyzed exchange with silacyclobutanes.[20] However, there are some important limitations associated with the stoichiometric and catalytic reactions. The former involve strongly basic or harsh reaction conditions or multistep processes and/or give modest yields; the latter require high alkene to silane ratios, conjugated or polyolefinic substrates, or noncommercial reagents, and/or are *E*-selective. Herein, we offer a high-yield *Z*-selective C−H silylation of terminal alkenes utilizing an iridium−dtbpy complex promoted by 2-norborene (eq 1) and some insights into the parameters that influence stereoselectivity.



(1)

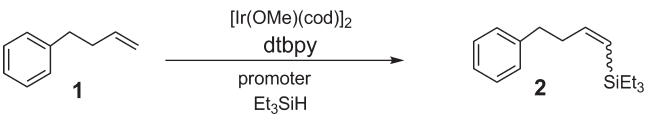
Results and Discussion

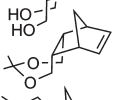
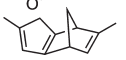
Motivated by our recent iridium-catalyzed C−H functionalization/silylation of heteroarenes and the mechanistic understanding gained therein,[21] we sought to extend this methodology to the more challenging case of isolated alkenes.[16,22] Initial attempts to silylate the model olefin 4-phenyl-1-butene **1** using $[Ir(OMe)(cod)]_2$/4,4-di-*tert*-butyl-2,2-bipyridine (dtbpy) (cod = cycloocta-1,5-diene)[23] and triethylsilane at either 80 or 40 °C in THF proved disappointing and gave rise to vinyl silane **2** in poor yield (Table 1, entries 1 and 2). The reversal of stereoselectivity toward the thermodynamically less favored *Z*-configuration at the lower temperature and the absence of aryl silylation, however, did not escape notice. Inclusion of mono- (entry 3), di- (entry 4), tri- (entry 5), and tetra-substituted (entry 6) olefins as sacrificial hydrogen repositories had little influence on the yield or stereoselectivity. In sharp contrast, 2-norbornene dramatically boosted yields (entries 7 and 8) and, in the latter case, the *Z*/*E*-ratio; at room temperature, the reaction was too sluggish to be useful (entry 9). Decreasing the amount of olefinic promoter and triethysilane resulted in a proportionate lessening of both conversion and *Z*-isomer (entry 10). Silylations also proceeded well in DME (entry 11), dioxane (entry 12), and even ether (entry13), albeit with reduced stereoselectivity; toluene and dichloromethane were unsatisfactory (< 5%). Commercial bicyclic (entries 14−16) and tricyclic (entry 17) promoters related to norbornene were less efficacious, except for a slight increase in the *Z*-selectivity in some instances. It is noteworthy that the dtbpy ligand also plays an important role by inhibiting the isomerization of olefin. Other similar ligands were not helpful (see Supporting Information).

The scope of this methodology was explored with a representative panel of alkenes (Table 2). Notably, only terminal alkenes proved reactive as illustrated by the nearly quantitative transformation of diene **3** to vinyl silane **4** (entry 1); all subsequent studies, therefore, were conduct with this in mind. Fortunately, the reaction conditions were compatible with a variety of functionalities including carbonate **5**, methyl ester **7**, and amide **9**, which furnished **6** (entry 2), **8** (entry 3), and **10** (entry 4), respectively, in good to excellent yields and *Z*-selectivities. Even the readily reduced epoxide **13** and methyl ketone **15** were well behaved and gave rise to the corresponding vinylsilanes **12** (entry 5) and **14** (entry 6). The smooth transformation of TBS ether **15** and acetal **17** into **16** (entry 7) and **18** (entry 8) using commercial benzyldimethylsilane, instead of triethylsilane, demonstrates that other silyl moieties are accessible including those suitable for transition-metal-catalyzed cross-coupling reactions.[24]

Aryl groups were likewise good substrates and afforded silylated benzoate **20**, benzyl ether **22**, 4-fluorophenyl **24**, and 2-bromophenyl **26** beginning from **19** (entry 9), **21** (entry 10), **23** (entry 11), and **25** (entry 12), respectively. To our delight,

TABLE 1. Influence of Promoters and Reaction Parameters on (*Z*)-Selectivity and Yield of 2[a]



entry	promoter	temp (°C)	solvent	yield (%)[b]	*Z*:*E*[c]
1	none	80	THF	<10	5:95[d]
2	none	40	THF	16	4:1
3		40	THF	< 5	nd[e]
4		40	THF	16	4:1
5		40	THF	< 5	nd[f]
6		40	THF	< 5	nd[f]
7		80	THF	91	2.5:1[f]
8		40	THF	92	9:1
9		23	THF	<5	nd[e,f]
10		40	THF	60	5:1[g]
11		40	DME	90	8:1
12		40	dioxane	88	7:1
13		40	ether	91	3:1
14		40	THF	22	9:1
15		40	THF	21	10:1
16		40	THF	71	10:1
17		40	THF	20	4:1

[a]Reaction conditions: $[Ir(OMe)(cod)]_2$ (5 mol %), dtbpy (10 mol %), promoter (3 equiv, if used), and Et_3SiH (3 equiv) in THF for 2 h. [b]Combined yield. [c]Measured by crude ^1H NMR. [d]Conducted for 15 h. [e]nd = not determined. [f]Conducted for 24 h. [g]Using 1.5 equiv each of promoter and Et_3SiH.

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TABLE 2. Trialkylsilylation of Terminal Alkenes[a]

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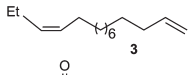
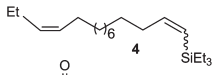
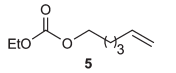
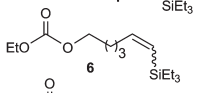
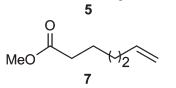
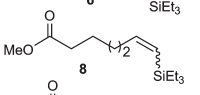
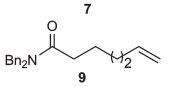
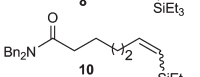
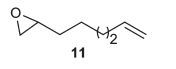
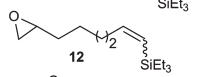
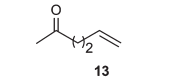
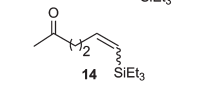
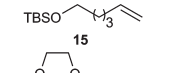
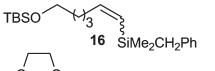
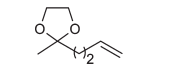
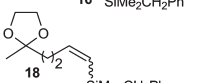
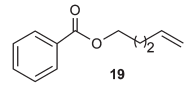
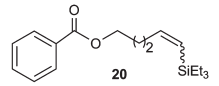
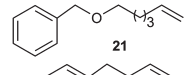
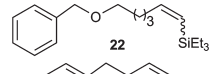
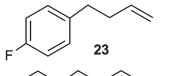
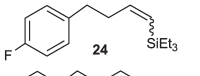
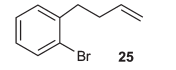
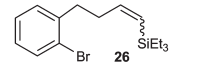
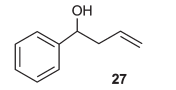
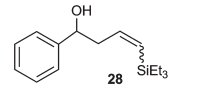
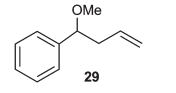
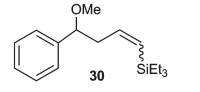
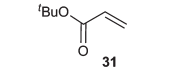
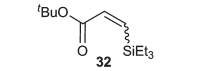
1	 3	 4	99	8:1
2	 5	 6	96	8:1
3	 7	 8	84	7:1
4	 9	 10	87	10:1
5	 11	 12	98	10:1
6	 13	 14	71	7:1
7	 15	 16	68	9:1
8	 17	 18	71	9:1
9	 19	 20	95	9:1
10	 21	 22	84	10:1
11	 23	 24	88	8:1
12	 25	 26	98	7:1
13	 27	 28	77	8:1
14	 29	 30	96	8:1
15	 31	 32	0	na[d]

[a]Reaction conditions: $[Ir(OMe)(cod)]_2$ (5 mol %), dtbpy (10 mol %), 2-norbornene (3 equiv), and R_3SiH (3 equiv) in THF for 2 h at 40 °C. [b]Combined isolated yield. [c]Measured by ^1H NMR. [d]na = not applicable.

even the free alcohol **27** generated silylated **28** (entry 13) in useful yield, as did the related methyl ether **29** (entry 14). The corresponding allylic alcohol and methyl ether, on the other hand, produced complex product mixtures. NMR analysis of the crude mixtures suggested migration of the olefin might be a contributing factor. Also, conjugated alkenes, e.g., *tert*-butyl acrylate **31** (entry 15), produced numerous unidentified products and little of the desired *Z*-vinylsilane.

The details of the reaction mechanism are uncertain at the present time, but a tentative sequence similar to earlier proposals[25] is likely (Figure 1). Initial oxidative insertion of the iridium into the silane followed by addition to the more reactive 2-norbornyl olefin generates intermediate ***i***. Heck-type addition[25] to the terminal alkene forms intermediate ***ii***.

(25) Iridium-catalyzed Heck reaction: Koike, T.; Du., X.; Sanada, T.; Danda, Y.; Mori, A. *Angew. Chem., Int. Ed.* **2003**, *42*, 89–92.

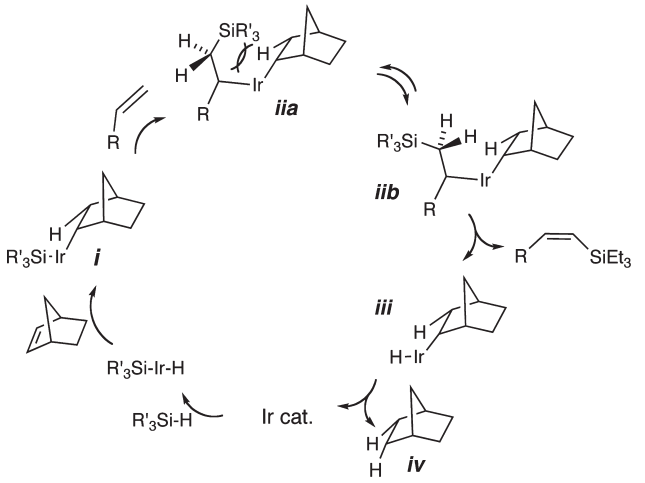


FIGURE 1. Proposed mechanism of Ir-catalyzed trialkylsilylation showing influence of ligand.

As a result of the unfavorable steric interactions present in ***iia***, intermediate ***iib*** is likely the predominate conformation. *syn*-β-Hydride elimination from ***iib*** would lead to *Z*-vinylsilane and iridium-hydride complex ***iii***. Reductive elimination of norbornane ***iv*** regenerates the catalyst and completes the catalytic cycle. Furthermore, this proposal highlights an underappreciated role for some so-called "sacrificial olefins" such as 2-norbornene, i.e., they can also influence the stereoselectivity of the reaction and thus should be taken into consideration when selecting reagent combinations.

Conclusion

In summary, we describe a mild, *Z*-stereoselective dehydrogenative trialkylsilylation of terminal alkenes utilizing a commercial iridium catalyst. Additionally, we demonstrate that 2-norbornene strongly promotes the reaction and also influences its stereoselectivity. Extensions of these concepts will follow in due course.

Experimental Section

General Information. All reactions were carried out under an argon atmosphere. Anhydrous solvents were freshly distilled from sodium benzophenone ketyl, except for CH_2Cl_2, which was distilled from CaH_2. Extracts were dried over anhydrous Na_2SO_4 and then filtered prior to removal of all volatiles under reduced pressure. Unless otherwise noted, commercially available materials were used without further purification. $[Ir(OMe)(COD)]_2$ was purchased from Strem or Aldrich Chemical Co. Flash chromatography (FC) was performed using silica gel 60 (240−400 mesh). Thin layer chromatography was performed using purchased precoated plates (silica gel 60 PF254, 0.25 mm).

^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ unless stated otherwise. Chemical shifts (δ) are given in ppm relative to residual solvent (usually chloroform δ 7.26 for ^1H NMR or δ 77.23 for proton decoupled ^{13}C NMR), and coupling constants (*J*) are in Hz. Multiplicity is tabulated as s for singlet, d for doublet, t for triplet, q for quadruplet, and m for multiplet. The prefix app is applied in cases where the true multiplicity is unresolved and br when the signal in question is broadened.

General Procedure for Iridium-Catalyzed (*Z*)-Trialkylsilylation. A flame-dried Schlenk tube was charged with terminal alkene (0.2 mmol), $[Ir(OMe)(cod)]_2$ (6.6 mg, 0.01 mmol), and

dtbpy (5.4 mg, 0.02 mmol), then evacuated and flushed with argon three times. Under a positive flow of argon, 2-norbornene (56 mg, 0.6 mmol) and dry THF (1 mL) were added. After stirring for 5 min, trialkylsilane (0.6 mmol) was added dropwise, and the reaction mixture was stirred at 40 °C for 2 h. The solvent was concentrated under reduced pressure, and the residue was purified by flash chromatography using silica gel to give the vinylsilane generally as a *Z*/*E*-mixture. More extensive purification via PTLC was required to obtain the individual *Z*- and *E*-isomers.

Compound 2: combined yield 92%, *Z*/*E* = 9:1.

(*Z*)-Triethyl(4-phenylbut-1-enyl)silane. ^{1}H NMR (300 MHz) δ 7.32−7.18 (m, 5H), 6.42 (dt, *J* = 14.1, 6.6 Hz, 1H), 5.44 (d, *J* = 14.1 Hz, 1H), 2.69 (t, *J* = 7.2 Hz, 2H), 2.46−2.38 (m, 2H), 0.93 (t, *J* = 7.5 Hz, 9H), 0.59 (q, *J* = 7.5 Hz, 6H); ^{13}C NMR (75 MHz) δ 149.1, 142.1, 128.6, 128.6, 126.2, 126.1, 36.4, 36.3, 7.7, 4.9. HRMS (EI) calcd for $C_{16}H_{26}Si$ $[M]^+$ *m*/*z* 246.1804, found 246.1805.

(*E*)-Triethyl(4-phenylbut-1-enyl)silane. ^{1}H NMR (300 MHz) δ 7.30−7.17 (m, 5H), 6.07 (dt, *J* = 18.9 Hz, 6.3 Hz, 1H), 5.57 (d, *J* = 18.9 Hz, 1H), 2.72 (t, *J* = 7.5 Hz, 2H), 2.47−2.40 (m, 2H), 0.91 (t, *J* = 7.5 Hz, 9H), 0.53 (q, *J* = 7.5 Hz, 6H); ^{13}C NMR (75 MHz) δ 147.7, 142.1, 128.7, 128.4, 126.7, 125.9, 39.0, 35.6, 7.6, 3.7.

Compound 4: combined yield 99%, *Z*/*E* = 8:1.

1-Triethylsilyl-pentadeca-1(*Z*),12(*Z*)-diene. ^{1}H NMR (300 MHz) δ 6.37 (dt, *J* = 13.8, 7.5 Hz, 1H), 5.39 (d, *J* = 13.8 Hz, 1H), 5.36−5.31 (m, 2H), 2.10−1.99 (m, 6H), 1.36−1.28 (m, 14H), 0.98−0.92 (m, 12H), 0.64−0.56 (m, 6H); ^{13}C NMR (75 MHz) δ 150.6, 131.7, 129.6, 125.1, 34.3, 30.0 (2 × C), 29.78 (2 × C), 29.75, 29.6, 29.5, 27.3, 20.7, 14.6, 7.8, 4.9. HRMS (EI) calcd for $C_{21}H_{42}Si$ $[M]^+$ *m*/*z* 322.3056, found 322.3063.

1-Triethylsilyl-pentadeca-1(*E*),12(*Z*)-diene. ^{1}H NMR (300 MHz) δ 6.02 (dt, *J* = 18.6 Hz, 6.3 Hz, 1H), 5.52 (d, *J* = 18.6 Hz, 1H), 5.44−5.38 (m, 2H), 2.12−1.93 (m, 6H), 1.40−1.26 (m, 14H), 0.96−0.0.88 (m, 12H), 0.58−0.50 (m, 6H); ^{13}C NMR (75 MHz) δ 149.1, 132.1, 129.6, 125.7, 37.3, 32.8, 29.9, 29.8, 29.7, 29.4, 29.3, 29.0, 25.8, 14.2, 7.6, 3.7.

Compound 6: combined yield 96%, *Z*/*E* = 8:1.

Ethyl 6-(Triethylsilyl)hex-5(*Z*)-enyl Carbonate. ^{1}H NMR (300 MHz) δ 6.35 (dt, *J* = 14.4, 7.2 Hz, 1H), 5.42 (d, *J* = 14.4 Hz, 1H), 4.19 (q, *J* = 6.9 Hz, 2H), 4.14 (t, *J* = 6.6 Hz, 2H), 2.17−2.09 (m, 2H), 1.72−1.66 (m, 2H), 1.52−1.44 (m, 2H), 1.31 (t, *J* = 6.6 Hz, 3H), 0.96−0.91 (m, 9H), 0.64−0.56 (m, 6H); ^{13}C NMR (75 MHz) δ 155.5, 149.5, 126.1, 68.0, 64.1, 33.7, 28.5, 26.1, 14.5, 7.7, 4.9. HRMS (EI) calcd for $C_{15}H_{31}O_3Si$ $[M + H]^+$ *m*/*z* 287.2042, found 287.2039.

(*E*)-Ethyl 6-(Triethylsilyl)hex-5-enyl Carbonate. ^{1}H NMR (300 MHz) δ 6.00 (dt, *J* = 18.6, 6.3 Hz, 1H), 5.42 (d, *J* = 18.6 Hz, 1H), 4.19 (q, *J* = 7.2 Hz, 2H), 4.13 (t, *J* = 6.6 Hz, 2H), 2.18−2.12 (m, 2H), 1.71−1.62 (m, 2H), 1.52−1.46 (m, 2H), 1.31 (t, *J* = 7.2 Hz, 3H), 0.96−0.89 (m, 9H), 0.58−0.49 (m, 6H); ^{13}C NMR (75 MHz) δ 155.5, 147.9, 126.7, 68.0, 64.1, 36.6, 28.3, 25.1, 14.5, 7.6, 3.7.

Compound 8: combined yield 84%, *Z*/*E* = 7:1.

Methyl 7-(Triethylsilyl)hept-6(*Z*)-enoate. ^{1}H NMR (300 MHz) δ 6.35 (dt, *J* = 14.4, 7.2 Hz, 1H), 5.41 (d, *J* = 14.1 Hz, 1H), 3.67 (s, 3H), 2.32 (t, *J* = 7.5 Hz, 1H), 2.15−2.07 (m, 2H), 1.70−1.60 (m, 2H), 1.45−1.38 (m, 2H), 0.96−0.90 (m, 9H), 0.64−0.55 (m, 6H); ^{13}CNMR (75 MHz, $CDCl_3$) δ 174.4, 149.7, 125.9, 51.7, 34.2, 33.9, 29.5, 24.9, 7.8, 4.9. HRMS (EI) calcd for $C_{14}H_{28}O_2Si$ $[M]^+$ *m*/*z* 256.1859, found 256.1855.

Methyl 7-(Triethylsilyl)hept-6(*E*)-enoate. ^{1}H NMR (300 MHz) δ 6.00 (dt, *J* = 18.6, 6.0 Hz, 1H), 5.55 (d, *J* = 18.6 Hz, 1H), 3.67 (s, 3H), 2.32 (t, *J* = 7.5 Hz, 1H), 2.17−2.10 (m, 2H), 1.69−1.58 (m, 2H), 1.48−1.40 (m, 2H), 0.96−0.89 (m, 9H), 0.57−0.47 (m, 6H); ^{13}C NMR (75 MHz) δ 174.4, 148.1, 126.4, 51.7, 36.8, 34.2, 28.4, 24.6, 7.6, 3.7.

Compound 10:, combined yield 87%, *Z*/*E* = 10:1.

***N*,*N*-Dibenzyl-7-(triethylsilyl)hept-6(*Z*)-enamide.** ^{1}H NMR (300 MHz) δ 7.39−7.14 (m, 10H), 6.35 (dt, *J* = 14.1, 7.2 Hz, 1H), 5.39 (d, *J* = 14.1 Hz, 1H), 4.61 (s, 2H), 4.44 (s, 2H), 2.43 (t, *J* = 7.2 Hz, 2H), 2.15−2.07 (m, 2H), 1.78−1.70 (m, 2H), 1.45−1.38 (m, 2H), 0.95−0.89 (m, 9H), 0.62−0.54 (m, 6H); ^{13}C NMR (75 MHz) δ 173.7, 149.8, 137.7, 136.8, 129.2, 128.8, 128.5, 127.8, 127.6, 126.5, 125.7, 50.1, 48.3, 34.0, 33.4, 29.8, 25.4, 7.8, 4.9. HRMS (EI) calcd for $C_{27}H_{40}NOSi$ $[M + H]^+$ *m*/*z* 422.2879, found 422.2877.

***N*,*N*-Dibenzyl-7-(triethylsilyl)hept-6(*E*)-enamide.** ^{1}H NMR (300 MHz) δ 7.39−7.14 (m, 10H), 6.00 (dt, *J* = 18.6, 6.0 Hz, 1H), 5.52 (d, *J* = 18.6 Hz, 1H), 4.60 (s, 2H), 4.44 (s, 2H), 2.43 (t, *J* = 7.2 Hz, 2H), 2.16−2.09 (m, 2H), 1.78−1.70 (m, 2H), 1.49−1.39 (m, 2H), 0.93−0.88 (m, 9H), 0.56−0.46 (m, 6H); ^{13}C NMR (75 MHz) δ 173.8, 148.3, 137.7, 136.8, 129.2, 128.8, 128.5, 127.8, 127.6, 126.5, 126.2, 50.1, 48.2, 37.0, 33.3, 28.8, 25.2, 7.6, 3.7.

Compound 12: combined yield 98%, *Z*/*E* = 10:1.

(*Z*)-Triethyl(8-(oxiran-2-yl)oct-1-enyl)silane. ^{1}H NMR (300 MHz) δ 6.37 (dt, *J* = 14.1, 7.2 Hz, 1H), 5.39 (d, *J* = 14.1 Hz, 1H), 2.92−2.89 (m, 1H), 2.75 (dd, *J* = 3.9, 4.8 Hz, 1H), 2.47 (dd, *J* = 2.7, 4.8 Hz, 1H), 2.13−2.06 (m, 2H), 1.54−1.34 (m, 10H), 0.96−0.90 (m, 9H), 0.64−0.55 (m, 6H); ^{13}C NMR (75 MHz) δ 150.4, 125.3, 52.6, 47.4, 34.2, 32.7, 29.9, 29.6, 29.5, 26.1, 7.8, 4.9. HRMS (EI) calcd for $C_{16}H_{32}OSi$ $[M]^+$ *m*/*z* 268.2222, found 268.2222.

(*E*)-Triethyl(8-(oxiran-2-yl)oct-1-enyl)silane. ^{1}H NMR (300 MHz) δ 6.02 (dt, *J* = 18.9 Hz, 6.3 Hz, 1H), 5.53 (d, *J* = 18.9 Hz, 1H), 2.92−2.88 (m, 1H), 2.75 (dd, *J* = 3.9, 4.8 Hz, 1H), 2.47 (dd, *J* = 2.7, 4.8 Hz, 1H), 2.15−2.08 (m, 2H), 1.54−1.34 (m, 10H), 0.95−0.89 (m, 9H), 0.58−0.50 (m, 6H); ^{13}C NMR (75 MHz) δ 148.8, 125.8, 52.6, 47.4, 37.2, 32.7, 29.5, 29.2, 28.9, 26.1, 7.6, 3.7.

Compound 14: combined yield 71%, *Z*/*E* = 7:1.

6-(Triethylsilyl)hex-5(*Z*)-en-2-one. Yield 62% following PTLC separation. ^{1}H NMR (300 MHz) δ 6.31 (dt, *J* = 14.1, 7.2 Hz, 1H), 5.45 (d, *J* = 14.1 Hz, 1H), 2.53−2.48 (m, 2H), 2.40−2.34 (m, 2H), 2.15 (s, 3H), 1.49−1.42 (m, 2H), 0.96−0.90 (m, 9H), 0.65−0.57 (m, 6H); ^{13}C NMR (75 MHz) δ 208.3, 147.9, 127.0, 43.8, 30.2, 28.3, 7.7, 4.8. HRMS (EI) calcd for $C_{12}H_{24}OSi$ $[M]^+$ *m*/*z* 212.1596, found 212.1599.

6-(Triethylsilyl)hex-5(*E*)-en-2-one. Yield 9% following PTLC separation. ^{1}H NMR (300 MHz) δ 6.01 (dt, *J* = 18.6, 6.3 Hz, 1H), 5.57 (d, *J* = 18.6 Hz, 1H), 2.56−2.52 (m, 2H), 2.43−2.36 (m, 2H), 2.15 (s, 3H), 1.49−1.42 (m, 2H), 0.93−0.88 (m, 9H), 0.57−0.49 (m, 6H); ^{13}C NMR (75 MHz) δ 208.6, 146.3, 127.1, 42.9, 31.1, 30.2, 7.6, 3.6.

Compound 16: combined yield 71%, *Z*/*E* = 7:1.

(*Z*)-Benzyl(6-(*tert*-butyldimethylsilyloxy)hex-1-enyl)dimethylsilane. ^{1}H NMR (300 MHz) δ 7.25−7.18 (m, 2H), 7.09−7.00 (m, 3H), 6.33 (dt, *J* = 14.1, 7.5 Hz, 1H), 5.44 (d, *J* = 14.1 Hz, 1H), 3.59 (t, *J* = 6.3 Hz, 1H), 2.15 (s, 2H), 2.09−2.02 (m, 2H), 1.53−1.46 (m, 2H), 1.41−1.35 (m, 2H), 0.90 (s, 9H), 0.09 (s, 6H), 0.04 (s, 6H); ^{13}C NMR (75 MHz) δ 150.4, 140.4, 128.4, 128.3, 127.0, 124.1, 63.3, 33.7, 32.7, 26.9, 26.2, 26.1, 18.6, −1.4, −5.1. HRMS (EI) calcd for $C_{21}H_{39}Si_2$ $[M + H]^+$ *m*/*z* 363.2539, found 363.2541.

(*E*)-Benzyl(6-(*tert*-butyldimethylsilyloxy)hex-1-enyl)dimethylsilane. ^{1}H NMR (300 MHz) δ 7.25−7.18 (m, 2H), 7.09−7.00 (m, 3H), 5.99 (dt, *J* = 18.9, 7.5 Hz, 1H), 5.58 (d, *J* = 18.9 Hz, 1H), 3.60 (t, *J* = 6.3 Hz, 1H), 2.10 (s, 2H), 2.12−2.08 (m, 2H), 1.53−1.47 (m, 2H), 1.45−1.40 (m, 2H), 0.05 (s, 9H), 0.01 (s, 6H), 0.04 (s, 6H); ^{13}C NMR (75 MHz) δ 148.6, 140.4, 128.4, 128.2, 127.9, 124.0, 63.3, 36.7, 32.5, 26.4, 26.2, 18.6, −3.1, −5.0.

Compound 18: combined yield 71%, *Z*/*E* = 7:1.

(*Z*)-Benzyldimethyl(4-(2-methyl-1,3-dioxolan-2-yl)but-1-enyl)silane. ^{1}H NMR (300 MHz) δ 7.23−7.18 (m, 2H), 7.09−7.00 (m, 3H), 6.33 (dt, *J* = 14.1, 7.2 Hz, 1H), 5.45 (d, *J* = 14.1 Hz, 1H), 3.98−3.86 (m, 4H), 2.17 (s, 2H), 2.17−2.10 (m, 2H), 1.68−1.63

(m, 2H), 1.30 (s, 3H), 0.11 (s, 6H); ^{13}C NMR (75 MHz) δ 149.6, 140.3, 128.4, 128.3, 127.2, 124.1, 109.9, 64.9, 39.1, 28.7, 26.9, 24.1, −1.5. HRMS (EI) calcd for $C_{17}H_{26}O_2Si$ $[M]^+$ m/z 290.1702, found 290.1704.

(*E*)-Benzyldimethyl(4-(2-methyl-1,3-dioxolan-2-yl)but-1-enyl)-silane. ^{1}H NMR (300 MHz) δ 7.22−7.17 (m, 2H), 7.08−6.97 (m, 3H), 6.02 (dt, J = 18.6, 6.3 Hz, 1H), 5.61 (d, J = 18.6 Hz, 1H), 3.97−3.88 (m, 4H), 2.25−2.17 (m, 2H), 2.10 (s, 2H), 1.75−1.70 (m, 2H), 1.32 (s, 3H), 0.01 (s, 6H); ^{13}C NMR (75 MHz) δ 148.1, 140.4, 128.5, 128.2, 127.7, 124.1, 110.0, 64.9, 38.2, 31.4, 26.4, 24.2, −3.1.

Compound 20: combined yield 95%, Z/E = 9:1.

(*Z*)-5-(Triethylsilyl)pent-4-enyl Benzoate. ^{1}H NMR (300 MHz) δ 8.07−8.04 (m, 2H), 7.56−7.53 (m, 1H), 7.47−7.41 (m, 2H), 6.41(dt, J = 14.1, 7.2 Hz, 1H), 5.48 (d, J = 14.1 Hz, 1H), 4.34 (t, J = 6.3 Hz, 2H), 2.32−2.25 (m, 2H), 1.91−1.82 (m, 2H), 0.95−0.90 (m, 9H), 0.65−0.57 (m, 6H); ^{13}C NMR (75 MHz) δ 166.9, 148.6, 133.1, 130.6, 129.8, 128.5, 126.8, 64.8, 30.8, 29.1, 7.7, 4.9. HRMS (EI) calcd for $C_{18}H_{28}O_2Si$ $[M]^+$ m/z 304.1859, found 304.1874.

(*E*)-(6-(Benzyloxy)hex-1-enyl)triethylsilane. ^{1}H NMR (300 MHz) δ 8.07−8.04 (m, 2H), 7.58−7.53 (m, 1H), 7.47−7.42 (m, 2H), 6.41(dt, J = 18.6, 6.3 Hz, 1H), 5.62 (d, J = 18.6 Hz, 1H), 4.33 (t, J = 6.6 Hz, 2H), 2.33−2.26 (m, 2H), 1.94−1.84 (m, 2H), 0.97−0.90 (m, 9H), 0.58−0.50 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.9, 147.0, 133.1, 130.6, 129.8, 128.5, 127.3, 64.7, 33.5, 28.0, 7.6, 3.7.

Compound 22: combined yield 84%, Z/E = 10:1.

(*Z*)-(6-(Benzyloxy)hex-1-enyl)triethylsilane. ^{1}H NMR (300 MHz) δ 7.35−7.26 (m, 5H), 6.36 (dt, J = 14.1, 7.5 Hz, 1H), 5.40 (d, J = 14.1 Hz, 1H), 4.51 (s, 2H), 3.48 (t, J = 6.6 Hz, 2H), 2.16−2.09 (m, 2H), 1.67−1.60 (m, 2H), 1.49−1.44 (m, 2H), 0.96−0.90 (m, 9H), 0.64−0.55 (m, 6H); ^{13}C NMR (75 MHz) δ 150.1, 138.8, 128.6, 127.8, 127.7, 125.6, 73.1, 70.5, 34.0, 29.7, 26.6, 7.8, 4.9. HRMS (EI) calcd for $C_{19}H_{31}OSi$ $[M + H]^+$ m/z 303.2144, found 303.2160.

(*E*)-(6-(Benzyloxy)hex-1-enyl)triethylsilane. ^{1}H NMR (300 MHz) δ 7.35−7.26 (m, 5H), 6.02 (dt, J = 18.6 Hz, 6.3 Hz, 1H), 5.40 (d, J = 18.6 Hz, 1H), 4.51 (s, 2H), 3.48 (t, J = 6.6 Hz, 2H), 2.17−2.11 (m, 2H), 1.66−1.58 (m, 2H), 1.51−1.45 (m, 2H), 0.95−0.90 (m, 9H), 0.59−0.50 (m, 6H); ^{13}C NMR (75 MHz) δ 148.5, 138.9, 128.6, 127.8, 127.7, 126.2, 73.0, 70.5, 37.0, 29.4, 25.6, 7.6, 3.7.

Compound 24: combined yield 88%, Z/E = 8:1.

(*Z*)-Triethyl(4-(4-fluorophenyl)but-1-enyl)silane. ^{1}H NMR (300 MHz) δ 7.15−7.10 (m, 2H), 6.99−6.94 (m, 2H), 6.39 (dt, J = 14.1, 7.2 Hz, 1H), 5.45 (d, J = 14.1 Hz, 1H), 2.66 (t, J = 7.5 Hz, 2H), 2.42−2.35 (m, 2H), 0.95−0.88 (m, 9H), 0.62−0.54 (m, 6H); ^{13}C NMR (75 MHz) δ 163.1, 159.9, 148.8, 137.65, 137.6, 130.0, 129.9, 126.5, 115.4, 115.1, 36.3, 35.5, 7.7, 4.9. HRMS (EI) calcd for $C_{16}H_{25}FSi$ $[M]^+$ m/z 246.1710, found 264.1715.

(*E*)-Triethyl(4-(4-fluorophenyl)but-1-enyl)silane. ^{1}H NMR (300 MHz) δ 7.14−7.09 (m, 2H), 6.98−6.92 (m, 1H), 6.01 (dt, J = 18.9 Hz, 6.0 Hz, 1H), 5.56 (d, J = 18.9 Hz, 1H), 2.69 (t, J = 7.2 Hz, 2H), 2.44−2.37 (m, 2H), 0.93−0.88 (m, 9H), 0.57−0.49 (m, 6H); ^{13}C NMR (75 MHz) δ 163.0, 159.8, 147.3, 137.75, 137.71, 130.0, 129.9, 127.1, 115.3, 115.0, 39.0, 34.7, 7.6, 3.7.

Compound 26: combined yield 88%, Z/E = 7:1.

(*Z*)-(4-(2-Bromophenyl)but-1-enyl)triethylsilane. ^{1}H NMR (300 MHz) δ 7.55−7.52 (m, 1H), 7.24−7.21 (m, 2H), 7.09−7.03 (m, 1H), 6.43 (dt, J = 14.1, 7.2 Hz, 1H), 5.46 (d, J = 14.1 Hz, 1H), 2.81 (t, J = 7.5 Hz, 2H), 2.46−2.38 (m, 2H), 0.96−0.89 (m, 9H), 0.63−0.55 (m, 6H); ^{13}C NMR (75 MHz) δ 148.6, 141.3, 133.0, 130.7, 127.8, 127.6, 126.6, 124.6, 36.5, 34.4, 7.7, 4.8. HRMS (EI) calcd for $C_{16}H_{25}BrSi$ $[M]^+$ m/z 324.0909, found 324.0906.

(*E*)-(4-(2-Bromophenyl)but-1-enyl)triethylsilane. ^{1}H NMR (300 MHz) δ 7.52 (d, J = 7.8 Hz, 1H), 7.24−7.20 (m, 2H), 7.07−7.02 (m, 1H), 6.07 (dt, J = 18.6 Hz, 6.3 Hz, 1H), 5.57 (d, J = 18.6 Hz, 1H), 2.84 (t, J = 7.5 Hz, 2H), 2.46−2.40 (m, 2H), 0.93−0.88 (m, 9H), 0.57−0.50 (m, 6H); ^{13}C NMR (75 MHz) δ 147.0, 141.3, 132.9, 130.7, 127.7, 127.5, 127.2, 124.6, 37.2, 35.8, 7.6, 3.7.

Compound 28: combined yield 77%, Z/E = 8:1.

(*Z*)-Triethyl(4-hydroxyl-4-phenylbut-1-enyl)silane. Yield 68% following PTLC separation. ^{1}H NMR (300 MHz) δ 7.38−7.26 (m, 5H), 6.41 (dt, J = 14.1, 7.2 Hz, 1H), 5.64 (d, J = 14.1 Hz, 1H), 4.77−4.73 (m, 1H), 2.61−2.55 (m, 2H), 2.03−2.00 (m, 1H), 0.96−0.91 (m, 9H), 0.66−0.58 (m, 6H); ^{13}C NMR (75 MHz) δ 145.1, 144.2, 129.9, 128.7, 127.8, 126.0, 74.1, 43.9, 7.7, 4.8. HRMS (EI) calcd for $C_{16}H_{26}OSi$ $[M]^+$ m/z 262.1753, found 262.1751.

(*E*)-Triethyl(4-hydroxyl-4-phenylbut-1-enyl)silane. Yield 8% following PTLC separation. ^{1}H NMR (300 MHz) δ 7.36−7.24 (m, 5H), 6.01 (dt, J = 18.6 Hz, 6.3 Hz, 1H), 5.71 (d, J = 18.6 Hz, 1H), 4.78−4.73 (m, 1H), 2.62−2.55 (m, 2H), 2.03−2.02 (m, 1H), 0.93−0.88 (m, 9H), 0.58−0.50 (m, 6H); ^{13}C NMR (75 MHz) δ 144.1, 143.7, 131.6, 128.6, 127.7, 126.0, 73.4, 47.4, 7.6, 3.6.

Compound 30: combined yield 96%, Z/E = 8:1.

(*Z*)-Triethyl(4-methoxy-4-phenylbut-1-enyl)silane. Yield 85% following PTLC separation. ^{1}H NMR (300 MHz) δ 7.39−7.26 (m, 5H), 6.36 (dt, J = 14.4 Hz, 7.2 Hz, 1H), 5.50 (d, J = 14.4 Hz, 1H), 4.14 (t, J = 6.6 Hz, 1H), 3.22 (s, 3H), 2.67−2.59 (m, 2H), 2.49−2.40 (m, 2H), 0.93−0.88 (m, 9H), 0.61−0.53 (m, 6H); ^{13}C NMR (75 MHz) δ 145.6, 141.9, 128.6, 127.9, 127.8, 126.9, 84.2, 56.9, 42.5, 7.7, 4.8. HRMS (EI) calcd for $C_{17}H_{28}OSi$ $[M]^+$ m/z 276.1909, found 276.1907.

(*E*)-Triethyl(4-methoxy-4-phenylbut-1-enyl)silane. Yield 10% following PTLC separation. ^{1}H NMR (300 MHz) δ 7.36−7.24 (m, 5H), 5.95 (dt, J = 18.6 Hz, 6.3 Hz, 1H), 5.55 (d, J = 18.6 Hz, 1H), 4.14 (t, J = 6.6 Hz, 1H), 3.22 (s, 3H), 2.67−2.59 (m, 2H), 2.49−2.40 (m, 2H), 0.90−0.85 (m, 9H), 0.54−0.46 (m, 6H); ^{13}C NMR (75 MHz) δ 144.1, 141.9, 129.3, 128.5, 127.7, 127.0, 84.0, 56.9, 45.9, 7.5, 3.6.

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Supporting Information Available: Analytical data, and ^{1}H and ^{13}C NMR spectra for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.