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Synthesis of α-Silylmethyl-α,β-Unsaturated Imines by the Rhodium-Catalyzed Silylimination of Primary-Alkyl-Substituted Terminal Alkynes

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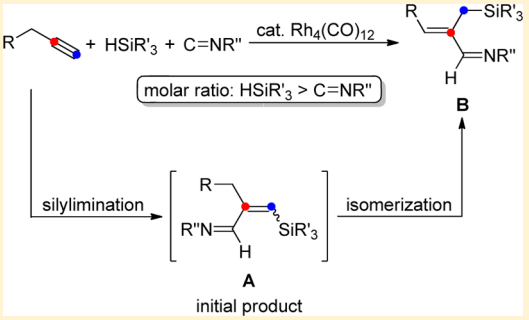
Supporting Information

ABSTRACT: In contrast to our previous report on the rhodium-catalyzed reaction of terminal alkynes with equimolar amounts of hydrosilanes and isocyanides leading to (*E*)- or (*Z*)-β-silyl-α,β-unsaturated imines **A**, the addition of an excess molar amount of hydrosilanes relative to isocyanides in the reaction of primary-alkyl-substituted terminal alkynes results in the production of α-silylmethyl-α,β-unsaturated imines **B**. Various isocyanides bearing *tert*-butyl and 1-adamantyl groups gave **B** with good product selectivity. *Z* isomers were formed stereoselectively in many cases. Regarding the mechanism for this reaction, when the hydrosilane was added to the reaction mixture in two portions, unsaturated imines **A** were initially formed, which then underwent double-bond isomerization, probably catalyzed by a Rh−H species, to give **B**.



INTRODUCTION

The catalytic addition of silyl functionalities across carbon−carbon multiple bonds has seen significant development in the past two decades, and the advances in this area have been summarized in several reviews.[1] The regio- and stereoselective addition of silicon compounds to C≡C triple bonds in the presence of Lewis acids or transition-metal complexes is an efficient strategy for preparing stereodefined vinylsilanes. We recently reported the rhodium-catalyzed addition of silyl and imino groups to alkynes via the use of a combination of hydrosilanes and isocyanides, leading to the formation of β-silyl-α,β-unsaturated imines **A** (Scheme 1).[2] The reaction, which is referred to as silylimination, allowed the stereoselective production of (*E*)- and (*Z*)-vinylsilanes from terminal alkynes, depending on the specific isocyanide employed in the reaction. This indicates that silylimination with equimolar amounts of tertiary-alkyl-substituted isocyanides, such as *tert*-butyl isocyanide and 1,1,3,3-tetramethylbutyl isocyanide (*tert*-octyl isocyanide), and hydrosilanes results in the formation of *Z* isomers, while the use of an aryl-substituted isocyanide gave *E* isomers. In the related silylformylation reaction, in which carbon monoxide is used in place of isocyanides, *Z* isomers were obtained stereoselectively.[3] During the course of our study on the *Z*-selective silylimination of primary-alkyl-substituted alkynes with *tert*-octyl isocyanide, however, we found that α-silylmethyl-α,β-unsaturated imines **B**, which contain an allylsilane, were also formed when an excess molar amount of hydrosilane relative to isocyanide was used in the reaction. Allylsilanes have been utilized extensively for regio- and stereoselective C−C bond formation with carbon electrophiles such as aldehydes and acetals in the presence of the Lewis acid, a reaction known as the Hosomi−Sakurai reaction.[4] Alper and a co-worker reported that α,β-unsaturated aldehydes corresponding to **B** were produced in the reaction of terminal alkynes with hydrosilanes under CO/H_2 pressure. However, in some cases, further hydrogenation of the C−C double bond occurred, resulting in the formation of saturated aldehydes, which depends on the nature of the substituent in the starting alkyne.[5] Propargyl alcohols and their derivatives[6] and propargylamines[7] were also converted into type **B** aldehydes, along with the elimination of R_3Si-Y (Y = OR′, NR′$_2$). Herein we report the optimization of the reaction conditions for the selective formation of **B** and the scope and limitations of the substrates. The reason for the product switch caused by the

Scheme 1. Rhodium-Catalyzed Silylimination of Terminal Alkynes Leading to β-Silyl-α,β-unsaturated Imines A or α-Silylmethyl-α,β-unsaturated Imines B

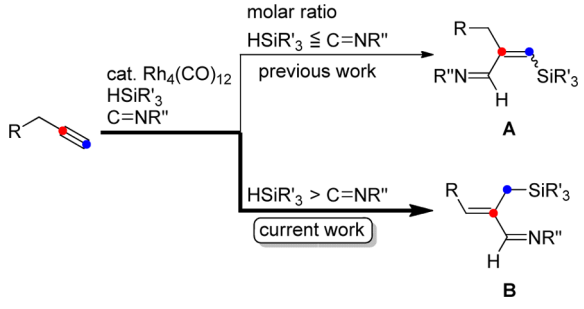


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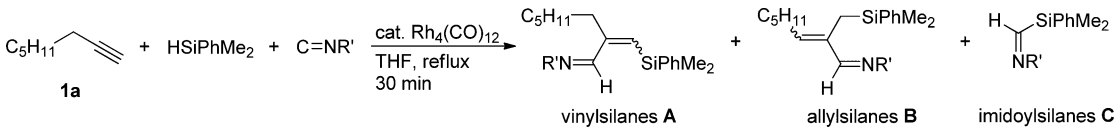
Table 1. Product Distribution of Vinylsilanes A, Allylsilanes B, and Imidoylsilanes C in the $Rh_4(CO)_{12}$-Catalyzed Reaction of 1-Octyne (1a) with Dimethylphenylsilane and Isocyanides[a]



		isocyanide		A		B		
entry	amt of $HSiPhMe_2$ (mmol)	R′	amt (mmol)	yield (%)	*E*/*Z*	yield (%)	*E*/*Z*	C yield (mmol)
1	2	^{t}Oct	2	88 (**2a**$_{Oct}$)	30/70	trace		0.87
2	2.5		2	57	45/55	32 (**3a**$_{Oct}$)	22/78	0.73
3	3		2	9	73/27	78	18/82	0.67
4	2		3	90	30/70	0		0.90
5	3		3	90	29/71	0		1.00
6	2.5	Ad	2	0		93 (**3a**$_{Ad}$)	4/96	0.70
7	2.5	^{t}Bu	2	trace		92 (**3a**$_{Bu}$)	4/96	0.42
8	2.5	Cy	2	7 (**2a**$_{Cy}$)	99/1	71 (**3a**$_{Cy}$)	18/82	0.90
9[b]	2.5	Xy	2	89 (**2a**$_{Xy}$)	86/14	0		0.14

[a]Reaction conditions: **1a** (1 mmol), $Rh_4(CO)_{12}$ (0.015 mmol), THF (8 mL) at 70 °C for 30 min. Product yields and *E*/*Z* ratios were determined by ^{1}H NMR spectroscopy. [b]The reaction was run for 4 h.

difference in the molar ratio of the hydrosilane to the isocyanide was also studied.

RESULTS AND DISCUSSION

As reported in our previous study, when 1-octyne (1 mmol; **1a**) was reacted with dimethylphenylsilane (2 mmol) and *tert*-octyl isocyanide (2 mmol) in the presence of $Rh_4(CO)_{12}$ (0.015 mmol) in THF under reflux for 30 min, the vinylsilane **2a**$_{Oct}$ was produced in 88% yield with an *E*/*Z* ratio of 30/70. *N*-*tert*-Octylformimidoylsilane[8,9] was also produced as a byproduct (entry 1, Table 1). Whereas **2a**$_{Oct}$ was isolated by column chromatography on Al_2O_3 followed by bulb-to-bulb distillation under reduced pressure in 48% yield, the imidoylsilane disappeared during the chromatographic operation. Attempts to isolate the imidoylsilane by bulb-to-bulb distillation from the reaction mixture were also unsuccessful. The fact that moderate *Z* selectivity was observed in the reaction of primary-alkyl-substituted alkynes prompted us to reinvestigate the reaction conditions in order to improve the stereoselectivity of this reaction. To our surprise, we found that the allylsilane **3a**$_{Oct}$ was formed in 32% yield along with **2a**$_{Oct}$ in 57% yield when the amount of $HSiPhMe_2$ was increased to 2.5 mmol (entry 2). The addition of 3 mmol of $HSiPhMe_2$ resulted in a further increase in the yield of **3a**$_{Oct}$ to 78% (entry 3). On the other hand, when an excess or an equimolar amount of $HSiPhMe_2$ relative to *tert*-octyl isocyanide was added to the reaction system, **2a**$_{Oct}$ was obtained in 90% yield (entries 4 and 5, and also entry 1). A series of isocyanides (2 mmol) were next examined in the reaction of 1-octyne (1 mmol) and $HSiPhMe_2$ (2.5 mmol). Other tertiary-alkyl-substituted isocyanides such as *tert*-butyl isocyanide and 1-adamantyl isocyanide (AdN═C) reacted to give the corresponding allylsilanes **3a**$_{Ad}$ and **3a**$_{Bu}$ in 93 and 92% yields, respectively, with good *Z* selectivity (entries 6 and 7). Despite the fact that the reaction with cyclohexyl isocyanide also afforded mainly the desired **3a**$_{Cy}$ (entry 8), the use of 2,6-dimethylphenyl isocyanide (XyN═C) resulted in the production of the vinylsilane **2a**$_{xy}$ with no detectable formation of the allylsilane (entry 9). $HSiEt_2Me$ was also applicable to the reaction with AdN═C, giving the allylsilane **3a′**$_{Ad}$ in 80% yield with an 85% *Z* selectivity. Although we isolated **2a**$_{xy}$ by bulb-to-bulb distillation under reduced pressure in 62% yield, no allylsilane-type imines could be obtained in pure form. Therefore, the compounds were isolated as aldehydes after hydrolysis (see the Experimental Section).

With the optimized reaction conditions in hand, various terminal alkynes were examined in terms of producing the corresponding allylsilanes (Table 2). Functional groups such as phenyl (entry 2), ester (entry 3), cyano (entry 4), amide (entry 5), THP (entry 6), and siloxy groups (entry 7) did not interfere with the reaction. The reaction of prop-2-yn-1-ylcyclohexane (**1h**) under the standard reaction conditions afforded a mixture of **3h** in 79% yield and the byproduct vinylsilane **2h** in 5% yield. **2h** disappeared completely when the added $HSiPhMe_2$ was increased to 4 mmol, and **3h** was obtained in 83% yield with a 93% *Z* selectivity (entry 8). Similar reactivities were observed in the reaction of **1i** (entry 9). Whereas benzylacetylene (**1j**) was also transformed under the standard reaction conditions into the phenyl-substituted product **3j** (entry 10), the vinylsilanes **2k**,**l** were formed as the sole products in the reactions of adamantylmethylacetylene (**1k**, entry 11) and cyclohexylacetylene (**1l**, entry 12).

We envisioned several pathways that could explain the formation of allylsilanes, especially the origin of the alkene isomerization, as shown in Scheme 2. Alper proposed the formation of the silylallene dihydridorhodium complex **X** as a key intermediate in the aforementioned reaction of terminal alkynes with hydrosilanes under CO/H_2 pressure.[5] Considering the similarity of the products in both reactions, it appears that the catalytic reaction also involves the formation of intermediate **X**, in which a hydrogen and an imino group are added to the carbon−carbon double bond of the allene ligand (path a). In an analogous fashion, the isomerization of an alkyne to an allene **Y** and the subsequent silylimination of the carbon−carbon double bond is also a possibility (path b). However, the formation of vinylsilanes followed by the isomerization of the carbon−carbon double bond to afford allylsilanes is the most likely explanation (path c), because of the fact the product ratio of **3a**$_{Oct}$/**2a**$_{Oct}$ increased with increasing amounts of hydrosilane (entries 1−3 in Table 1).

To confirm that the present reaction proceeds via path c, an excess molar amount of hydrosilane relative to isocyanide was added to the reaction mixture in two portions (Scheme 3).

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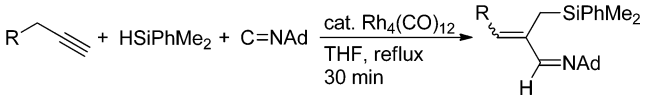
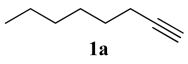
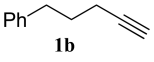
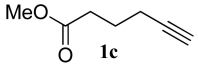
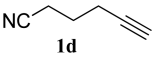
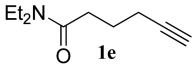
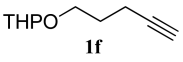
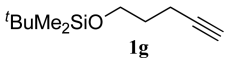
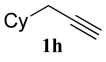
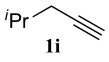
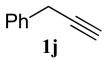
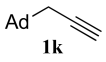
Table 2. Silylimination of Some Terminal Alkynes[a]

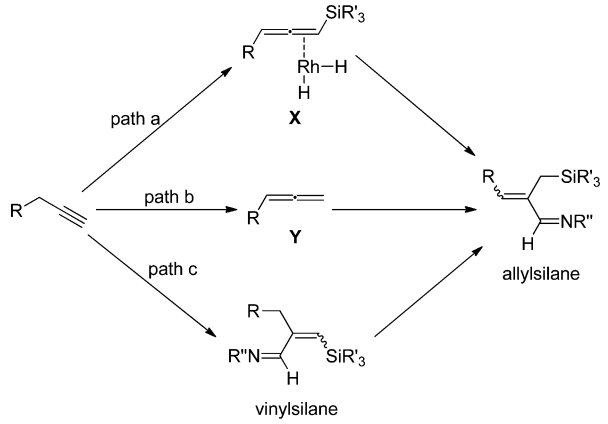


entry	alkyne	yield (%)	*E*/*Z*
1	 **1a**	93 (**3a**$_{Ad}$)	4/96
2	 **1b**	90 (**3b**)	4/96
3	 **1c**	84 (**3c**)	4/96
4	 **1d**	82 (**3d**)	3/97
5	 **1e**	92 (**3e**)	1/99
6	 **1f**	91 (**3f**)	4/96
7	 **1g**	96 (**3g**)	3/97
8[b,c]	 **1h**	83 (**3h**)	7/93
9[b,d]	 **1i**	82 (**3i**)	10/90
10	 **1j**	94 (**3j**)	21/79
11	 **1k**	93 (**2k**)	<1/>99
12	 **1l**	98 (**2l**)	11/89

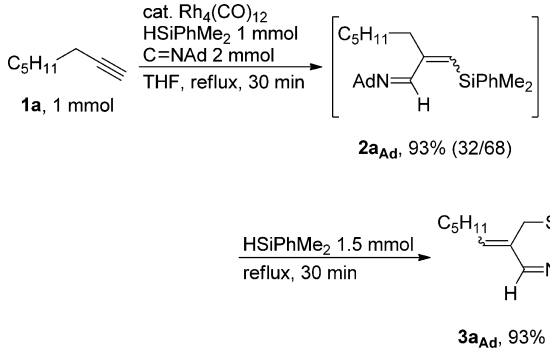
[a]Reaction conditions: alkyne (1 mmol), $HSiPhMe_2$ (2.5 mmol), 1-adamantyl isocyanide (2 mmol), in THF (8 mL), at 70 °C for 30 min. Product yields and *E*/*Z* ratios were determined by ^1H NMR spectroscopy. [b]$HSiPhMe_2$ (4 mmol) was used. [c]When the reaction was run under the standard reaction conditions, **3h** was obtained in 79% yield (*E*/*Z* = 12/88) along with the vinylsilane **2h** in 5% yield (*E*/*Z* = 29/71). [d]When the reaction was run under the standard reaction conditions, **3i** was obtained in 75% yield (*E*/*Z* = 21/79) along with the vinylsilane **2i** in 7% yield (*E*/*Z* = 22/78).

First, **1a** was treated with 1 mmol of $HSiPhMe_2$ and 2 mmol of AdN=C at 70 °C for 30 min. As expected, the vinylsilane **2a**$_{Ad}$ was formed, as confirmed by an ^1H NMR spectrum of an aliquot of the reaction mixture. At this point, an additional 1.5 mmol of $HSiPhMe_2$ was added to the reaction mixture, with the result that the total molar amount of $HSiPhMe_2$ exceeded that of AdN=C. After the resulting reaction mixture was stirred for 30 min at 70 °C, **2a**$_{Ad}$ was quantitatively transformed into **3a**$_{Ad}$. This provides evidence consistent with the silylimination of an alkyne and the subsequent isomerization of the carbon−carbon double bond of the initial product vinylsilanes. The rearrangement of vinylsilanes to allylsilanes has also been observed in some rhodium-catalyzed hydrosilylations of 1-hexyne.[10] Ohmura and Suginome reported on the migration of the double-bond of 2-borylvinylsilanes to the corresponding allylsilanes catalyzed by a palladium complex.[11]

Scheme 2. Possible Pathways for the Formation of Allylsilanes



Scheme 3. Sequential Addition of $HSiPhMe_2$ to the Reaction of 1a with C=NAd



A proposed mechanism for the catalytic reaction is presented in Scheme 4, which involves three types of catalytic cycles. Initially, $Rh_4(CO)_{12}$ reacts with a hydrosilane to generate the Rh-SiR′$_3$ species **I** and the Rh−H species **II** or a complex containing both Rh−Si and Rh−H bonds, although the details of the actual catalyst species are unclear at this time. Vinylsilanes **A** are then formed according to the catalytic cycle **i**. The addition of **I** to the alkyne C−C triple bond gives the *β*-silylvinylrhodium complex **III**. The subsequent insertion of an isocyanide into the Rh−C bond in **III** then affords the iminorhodium complex **IV**, which reacts with a hydrosilane to give **A**, with the regeneration of **I**. **I** also functions as a catalyst for the formation of imidoylsilanes **C** via the insertion of an isocyanide into the Rh−Si bond in **I** to generate **V** (cycle **ii**). In the case where the molar amount of hydrosilane in the reaction mixture is equal to or lower than that of the isocyanide, the hydrosilane would be completely consumed, with **A** and **C** being produced, and **II** would also disappear from the reaction mixture. As a consequence, **A** would remain without reacting further. On the other hand, **II** would continue to be present in the reaction mixture when an excess molar amount of hydrosilane relative to isocyanide is added. Therefore, the addition of **II** to the vinylsilane **A** would give **VI**, as depicted in cycle **iii**.[12] The Rh species is eliminated with the less sterically hindered *β*-hydrogen close to the substituent R to afford the allylsilane **B**. A *β*-hydride elimination of the 1-silylalkan-2-

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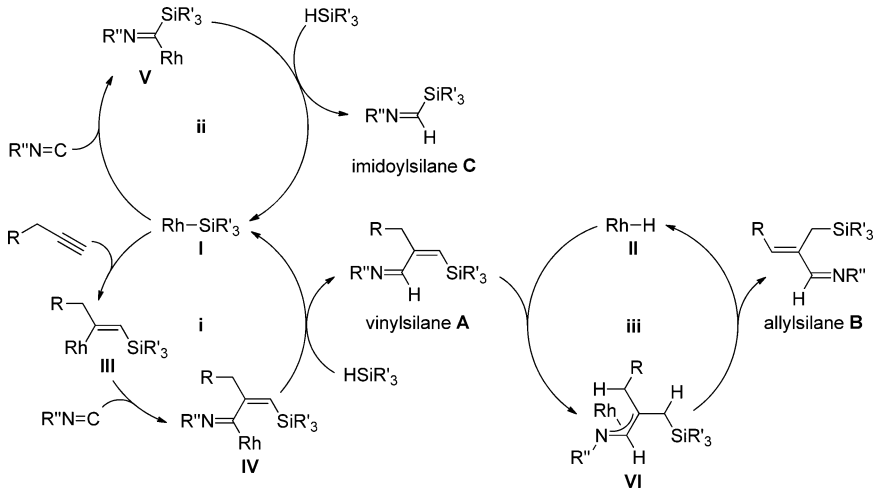
Scheme 4. Proposed Reaction Mechanism



ylmetal species leading to allylsilanes was proposed in the transition-metal-catalyzed silyl-Heck reactions of primary-alkyl-substituted alkenes.[13] The fact that the reaction of **1k** resulted in the production of not the allylsilane but, rather, the vinylsilane can be attributed to the shorter bond length of the carbon−carbon bond (ca. 154 pm) in comparison to that of the carbon−silicon bond (ca. 188 nm),[14] thereby resulting in an increase in the steric influence of the adamantyl group.

CONCLUSION

In conclusion, we report on a switch in end products, caused by the molar ratio of hydrosilanes and isocyanides in the rhodium-catalyzed reaction of primary-alkyl-substituted terminal alkynes with hydrosilanes and isocyanides. The addition of an excess molar amount of hydrosilane relative to the isocyanide in the reaction resulted in the production of α-silylmethyl-α,β-unsaturated imines. The choice of isocyanides bearing *tert*-butyl and 1-adamantyl groups gave the desired allylsilane-type compounds with good product selectivity. A variety of functional groups are tolerated in the reaction. Mechanistic studies revealed that tandem rhodium-catalyzed reactions involving silylimination, leading to the production of β-silyl-α,β-unsaturated imines and the subsequent carbon−carbon double bond isomerization, are involved in the formation of the final product.

EXPERIMENTAL SECTION

General Methods. ^{1}H NMR and ^{13}C NMR spectra were recorded on 400 and 100 MHz spectrometers (all compounds except $\mathbf{2a}_{Oct}$ and $\mathbf{2a}_{Xy}$) or 270 and 68 MHz spectrometers ($\mathbf{2a}_{Oct}$ and $\mathbf{2a}_{Xy}$) using $CDCl_3$ and C_6D_6 as solvents. Data are reported as follows: chemical shifts in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, c = complex), coupling constant (Hz), integration, and interpretation. Infrared spectra (IR) were recorded using ATR (all compounds except $\mathbf{2a}_{Oct}$ and $\mathbf{2a}_{Xy}$) or in KRS-5 cells ($\mathbf{2a}_{Oct}$ and $\mathbf{2a}_{Xy}$). Absorption data are reported in reciprocal centimeters with the following relative intensities: s (strong), m (medium), or w (weak). Mass spectra were obtained using a spectrometer with a quadrupole mass analyzer at 70 eV. High-resolution mass spectra (HRMS) were obtained using a spectrometer with a double-focusing mass analyzer. Analytical gas chromatography (GC) was carried out on a chromatograph equipped with a flame ionization detector. High-performance liquid chromatography (HPLC) was performed on a chromatograph equipped with a UV detector. THF was purified by passage through activated alumina under a positive pressure of N_2. All alkynes except **1e**,**g**,**k** were purchased. **1e**,**k** were prepared as described below. **1g** was prepared following a procedure described in the literature.[15] All alkynes were purified by distillation over CaH_2 prior to use. Among the isocyanides shown in Table 1, 1-adamantyl isocyanide[16] and 2,6-dimethylphenyl isocyanide[17] were prepared following procedures described in the literature. 1,1,3,3-Tetramethylbutyl isocyanide (*tert*-octyl isocyanide), *tert*-butyl isocyanide, and cyclohexyl isocyanide were commercially available and were used as received without any further purifications. $HSiPhMe_2$ and $HSiEt_2Me$ were purchased and were distilled over CaH_2 before use. $Rh_4(CO)_{12}$ was purchased from Strem and was used without further purification.

Preparation of *N*,*N*-Diethylhex-5-ynamide (1e).[18] The procedure reported by Merlic et al.[19] was modified by using diethylamine in place of dibutylamine to produce **1e** from hex-5-ynoic acid (2.5 mL, 22.5 mmol) in 76% yield (2.86 g) as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 1.11 (t, J = 7.1 Hz, 3H), 1.19 (t, J = 7.1 Hz, 3H), 1.88 (quint, J = 7.1 Hz, 2H), 1.98 (t, J = 2.7 Hz, 1H), 2.28 (td, J = 6.7, 2.4 Hz, 2H), 2.45 (t, J = 7.1 Hz, 2H), 3.33−3.38 (m, J = 7.2 Hz, 4H). ^{13}C NMR ($CDCl_3$): δ 13.0, 14.2, 17.8, 23.8, 31.2, 39.9, 41.7, 68.7, 83.8, 171.1. IR (ATR): 3297 w, 2972 w, 2935 w, 2874 w, 2151 w, 1632 s cm^{-1}. MS: m/z (relative intensity) 167 (5), 115 (67), 100 (34), 86 (11), 72 (40), 67 (21), 58 (100), 55 (20). HRMS: calcd for $C_{10}H_{17}NO$ (M^+): 167.1310. Found 167.1309.

Preparation of 1-(Prop-2-yn-1-yl)adamantane (1k). This compound was produced from 2-(adamantan-1-yl)acetaldehyde[20] (3.89 g, 22.0 mmol) following a method for the synthesis of 3-ethylhept-1-yne described in the patent[21] in 41% yield (1.59 g) as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 1.57 (bs, 6H), 1.62−1.70 (c, 6H), 1.94 (m, 2H), 1.98 (c, 4H). ^{13}C NMR ($CDCl_3$): δ 28.5, 32.4, 33.6, 36.8, 41.8, 70.0, 81.8. IR (ATR): 3308 w, 2899 s, 2847 m, 2116 w cm^{-1}. MS: m/z (relative intensity) 136 (11), 135 (100), 107 (15), 93 (31), 91 (12), 79 (34), 77 (12), 67 (13). Anal. Calcd for $C_{13}H_{18}$: C, 89.59; H, 10.41. Found: C, 89.30; H, 10.57.

General Procedure for the $Rh_4(CO)_{12}$-Catalyzed Reaction of 1-Octyne with $HSiPhMe_2$ and Isocyanides Leading to β-Silyl-α,β-unsaturated Imines ($\mathbf{2a}_{Oct}$ and $\mathbf{2a}_{Xy}$). A 20 mL reaction flask, equipped with a reflux condenser, was dried for 1 h in an oven at 110 °C and then purged with N_2. After the flask was cooled to room temperature, $Rh_4(CO)_{12}$ (11.2 mg, 0.015 mmol), THF (8 mL), and the isocyanide (2 mmol) were placed in the flask. The mixture was stirred at room temperature for 5 min. $HSiPhMe_2$ (0.31 mL, 2 mmol) and alkyne (1 mmol) were added to the resulting yellow solution. The reaction mixture was refluxed in an oil bath at 75 °C until the starting alkyne disappeared. After the mixture was cooled to room temperature, the volatiles were removed in vacuo. The product was isolated by bulb-to-bulb distillation under reduced pressure or by column chromatography on Al_2O_3 (0.063−0.200 mm, Activity Stage I, neutral) followed by bulb-to-bulb distillation under reduced pressure.

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*(E)- and (Z)-N-2-(Dimethylphenylsilylmethylene)oct-1-ylidene-2,4,4-trimethylpentan-2-amine (**2a**$_{Oct}$).* The compound was isolated by alumina column chromatography (1.8 cm i.d. × 8 cm height, R_f = 0.11 in hexane/EtOAc 200/1) followed by bulb-to-bulb distillation (170 °C/0.7 mmHg) in 48% yield (184 mg) as a colorless oil (*E*/*Z* = 23/77). ^{1}H NMR (C_6D_6): δ 0.43 (s, 6H), 0.46 (s, 6H), 0.89−0.94 (c, 3H), 1.00 (s, 9H), 1.05 (s, 9H), 1.07 (s, 6H), 1.22 (s, 6H), 1.28−1.50 (c, 6H), 1.58 (s, 2H), 1.63−1.73 (c, 2H), 1.65 (s, 2H), 2.65 (t, *J* = 8.1 Hz, 2H), 2.74 (t, *J* = 7.9 Hz, 2H), 6.06 (s, 1H), 6.29 (s, 1H), 7.17−7.27 (c, 3H), 7.54−7.59 (c, 2H), 7.82 (s, 1H), 8.18 (s, 1H). ^{13}C NMR (C_6D_6): δ −0.7, 0.1, 14.6, 23.2, 23.3, 29.6, 29.9, 30.07, 30.12, 30.5, 30.7, 31.7, 32.2, 32.3, 32.36, 32.38, 32.40, 34.9, 56.7, 56.8, 60.7, 61.2, 128.25, 128.33, 129.3, 129.4, 134.1, 134.2, 134.6, 136.3, 139.1, 139.9, 156.3, 158.6, 159.2, 159.4. IR (neat): 3064 w, 2960 s, 2904 m, 1630 m cm^{-1}. MS: *m*/*z* (relative intensity) 385 (4), 314 (14), 272 (23), 250 (36), 188 (21), 140 (71), 138 (24), 136 (11), 135 (55), 121 (11), 84 (10), 74 (16), 73 (11), 59 (27), 58 (33), 57 (100), 55 (16). Anal. Calcd for $C_{25}H_{43}NSi$: C, 77.85; H, 11.24; N, 3.63. Found: C, 77.88; H, 11.51; N, 3.63.

*(E)- and (Z)-N-2-(Dimethylphenylsilylmethylene)oct-1-ylidene-2,6-dimethylaniline (**2a**$_{Xy}$).* The compound was isolated by bulb-to-bulb distillation (192 °C/1 mmHg) in 62% yield (232 mg) as a pale yellow oil (*E*/*Z* = 89/11). ^{1}H NMR (C_6D_6): δ 0.27 (s, 6H), 0.42 (s, 6H), 0.85−0.95 (c, 3H), 1.26−1.51 (c, 6H), 1.60−1.71 (c, 2H), 2.03 (s, 6H), 2.11 (s, 6H), 2.74 (t, *J* = 8.1 Hz, 2H), 2.82 (t, *J* = 8.0 Hz, 2H), 6.07 (s, 1H), 6.48 (s, 1H), 6.85−7.03 (c, 3H), 7.20−7.23 (c, 3H), 7.39−7.49 (c, 2H), 7.50−7.54 (c, 2 H), 7.53 (s, 1H), 8.18 (s, 1H). ^{13}C NMR (C_6D_6): δ −0.9, 0.1, 14.6, 18.7, 18.8, 23.26, 23.31, 29.9, 30.5, 30.7, 31.5, 32.4, 35.4, 123.9, 124.0, 126.6, 126.8, 128.4, 129.5, 129.6, 134.0, 134.2, 138.6, 139.0, 139.5, 140.7, 151.8, 151.9, 157.4, 158.0, 163.0, 167.0. IR (neat): 3068 w, 3020 w, 2960 s, 2932 s, 2860 m, 1626 s, 1594 m cm^{-1}. MS: *m*/*z* (relative intensity) 377 (5), 243 (18), 242 (100), 135 (61), 132 (21), 120 (30), 105 (20), 79 (14), 77 (13), 59 (19). Anal. Calcd for $C_{25}H_{35}NSi$: C, 79.51; H, 9.34; N, 3.71. Found: C, 79.53; H, 9.59; N, 3.93.

General Procedure for the $Rh_4(CO)_{12}$-Catalyzed Reaction of Alkynes with Hydrosilanes and Isocyanides Leading to α-Silylmethyl-α,β-unsaturated Imines (3a$_{Ad}$-3j) and Subsequent Hydrolysis of the Product Imines to Aldehydes (4a−j). A 20 mL reaction flask, equipped with a reflux condenser, was dried for 1 h in an oven at 110 °C and then purged with N_2. After the flask was cooled to room temperature, $Rh_4(CO)_{12}$ (11.2 mg, 0.015 mmol), THF (8 mL), and the isocyanide (2 mmol) were placed in the flask. The mixture was stirred at room temperature for 5 min. $HSiPhMe_2$ (0.38 mL, 2.5 mmol) and alkyne (1 mmol) were added to the resulting yellow solution. The reaction mixture was refluxed in an oil bath at 75 °C for 30 min. After the mixture was cooled to room temperature, the volatiles were removed in vacuo. The yield and *E*/*Z* ratio of the resulting imine were determined by ^{1}H NMR spectroscopy with phthalan as an internal standard. The imine was hydrolyzed to give an aldehyde by passage through a silica gel column containing 10 wt % water (3.3 cm i.d. × 15 cm height, 0.075−0.150 mm) in hexane/AcOEt (20/1) as an eluent. Analytically pure *Z* isomer was obtained by column chromatography on Al_2O_3 (1.7 cm i.d. × 15 cm height, 0.063−0.200 mm, Activity Stage I, neutral; all aldehydes except **4b**,**d**,**g**−**i**), flash column Chromatography on SiO_2 (1.7 cm i.d. × 15 cm height, 0.040−0.063 mm; **4b**,**d**,**g**,**h**), or by HPLC (Nacalai COSMOSIL Cholester (2.0 cm i.d. × 15 cm height; **4i**).

*(E)- and (Z)-2-Dimethylphenylsilylmethyloct-2-enal (**4a**).* This compound was isolated in 91% yield (250 mg) as a pale yellow oil (R_f = 0.14 in hexane/EtOAc 20/1) with an *E*/*Z* ratio of 3/97. *Z*-**4a** was obtained by column chromatography on Al_2O_3 (R_f = 0.24 in hexane/EtOAc 20/1). The stereochemistry of the compound was determined by an NOE experiment. ^{1}H NMR ($CDCl_3$): δ 0.27 (s, 6H), 0.88 (t, *J* = 7.1 Hz, 3H), 1.22−1.32 (c, 6H), 1.95 (s, 2H), 2.01 (q, *J* = 7.1 Hz, 2H), 6.28 (t, *J* = 7.1 Hz, 1H), 7.34−7.36 (c, 3H), 7.51 (m, 2H), 9.32 (s, 1H). ^{13}C NMR ($CDCl_3$): δ −2.8, 13.9, 14.3, 22.4, 28.1, 29.2, 31.5, 127.7, 129.0, 133.5, 138.4, 141.0, 152.6, 194.9. IR (ATR): 3069 w, 3049 w, 2956 w, 2927 w, 2858 w, 2708 w, 1683 s cm^{-1}. MS: *m*/*z* (relative intensity) 274 (8), 137 (14), 136 (13), 135 (100), 127 (11), 107 (12), 75 (21). Anal. Calcd for $C_{17}H_{26}OSi$: C, 74.39; H, 9.55. Found: C, 74.25; H, 9.62.

*(E)- and (Z)-2-Diethylmethylsilylmethyloct-2-enal (**4a**′).* This compound was isolated in 75% yield (178 mg) as a pale yellow oil (R_f = 0.10 in hexane/EtOAc 20/1) with an *E*/*Z* ratio of 3/97. *Z*-**4a**′ was obtained by column chromatography on Al_2O_3 (R_f = 0.23 in hexane/EtOAc 20/1). ^{1}H NMR ($CDCl_3$): δ −0.12 (s, 3H), 0.41−0.52 (c, 4H), 0.88−0.92 (c, 9H), 1.30−1.36 (c, 4H), 1.46−1.50 (m, 2H), 1.69 (s, 2H), 2.26 (q, *J* = 7.3 Hz, 2H), 6.27 (t, *J* = 7.3 Hz, 1H), 9.30 (s, 1H). ^{13}C NMR ($CDCl_3$): δ −5.7, 5.4, 7.2, 11.4, 14.0, 22.5, 28.3, 29.3, 31.6, 141.9, 151.7, 195.1. IR (ATR): 2954 m, 2930 w, 2874 w, 2813 w, 2707 w, 1685 s cm^{-1}. MS: *m*/*z* (relative intensity) 225 (6), 211 (42), 141 (43), 113 (22), 101 (64), 89 (67), 75 (10), 73 (100), 61 (33). HRMS: calcd for $C_{14}H_{28}OSi$ (M^+) 240.1909, found 240.1910.

*(E)- and (Z)-2-Dimethylphenylsilylmethyl-5-phenylpent-2-enal (**4b**).* This compound was isolated in 83% yield (257 mg) as a colorless oil (R_f = 0.14 in hexane/EtOAc 20/1) with an *E*/*Z* ratio of 3/97. *Z*-**4b** was obtained by flash column chromatography on SiO_2. ^{1}H NMR ($CDCl_3$): δ 0.28 (s, 6H), 1.94 (s, 2H), 2.34 (q, *J* = 7.5 Hz, 2H), 2.63 (t, *J* = 7.5 Hz, 2H), 6.30 (t, *J* = 7.2 Hz, 1H), 7.09 (d, *J* = 6.8 Hz, 2H), 7.20−7.40 (c, 6H), 7.52 (m, 2H), 9.32 (s, 1H). ^{13}C NMR ($CDCl_3$): δ −2.7, 14.5, 30.8, 34.4, 126.2, 127.8, 128.2, 128.4, 129.2, 133.6, 138.3, 140.7, 141.6, 150.8, 194.8. IR (ATR): 3066 w, 3026 w, 2955 w, 2898 w, 2863 w, 2719 w, 1681 s cm^{-1}. MS: *m*/*z* (relative intensity) 293 (6), 136 (13), 135 (100), 107 (10), 91 (32), 75 (19). Anal. Calcd for $C_{20}H_{24}OSi$: C, 77.87; H, 7.84. Found: C, 77.62; H, 8.11.

*(E)- and (Z)-Methyl 6-Dimethylphenylsilyl-5-formylhex-4-enoate (**4c**).* This compound was isolated in 80% yield (230 mg) as a colorless oil (R_f = 0.26 in hexane/EtOAc 5/1) with an *E*/*Z* ratio of 3/97. *Z*-**4c** was obtained by column chromatography on Al_2O_3 (R_f = 0.19 in hexane/EtOAc 10/1). ^{1}H NMR ($CDCl_3$): δ 0.28 (s, 6H), 1.97 (s, 1H), 2.24−2.30 (c, 4H), 3.67 (s, 3H), 6.21 (t, *J* = 6.6 Hz, 1H), 7.31−7.35 (c, 3H), 7.50 (m, 2H), 9.32 (s, 1H). ^{13}C NMR ($CDCl_3$): δ −2.8, 14.5, 24.4, 32.4, 51.7, 127.7, 129.1, 133.5, 138.1, 142.0, 149.0, 172.6, 194.6. IR (ATR): 3070 w, 3048 w, 3000 w, 2954 w, 2901 w, 2822 w, 2712 w, 1738 m, 1681 s cm^{-1}. MS: *m*/*z* (relative intensity) 290 (1), 151 (11), 136 (13), 135 (100), 107 (13), 105 (11), 89 (11), 75 (14). HRMS: calcd for $C_{16}H_{22}O_3Si$ (M^+) 290.1338, found 290.1337.

*(E)- and (Z)-5-Cyano-2-dimethylphenylsilylmethylpent-2-enal (**4d**).* This compound was isolated in 80% yield (203 mg) as a colorless oil (R_f = 0.11 in hexane/EtOAc 5/1) with an *E*/*Z* ratio of 3/97. *Z*-**4d** was obtained by flash column chromatography on SiO_2. ^{1}H NMR ($CDCl_3$): δ 0.30 (s, 6H), 1.95 (s, 2H), 2.06 (t, *J* = 7.2 Hz, 2H), 2.17 (q, *J* = 7.2 Hz, 2H), 6.16 (t, *J* = 7.2 Hz, 1H), 7.35−7.38 (c, 3H), 7.47 (m, 2H), 9.36 (s, 1H). ^{13}C NMR ($CDCl_3$): δ −3.0, 15.1, 16.0, 24.7, 118.5, 127.9, 129.4, 133.6, 137.7, 143.2, 144.9, 194.1. IR (ATR): 3069 w, 3048 w, 2957 w, 2900 w, 2827 w, 2713, 2247 w, 1682 s cm^{-1}. MS: *m*/*z* (relative intensity) 243 (1), 136 (14), 135 (100), 105 (11). Anal. Calcd for $C_{15}H_{19}NOSi$: C, 69.99; H, 7.44; N, 5.44. Found: C, 69.85; H, 7.55; N, 5.44.

*(E)- and (Z)-6-Dimethylphenylsilyl-5-formyl-N,N-diethylhex-4-enamide (**4e**).* This compound was isolated in 89% yield (292 mg) as a colorless oil (R_f = 0.40 in EtOAc) with an *E*/*Z* ratio of 1/99. *Z*-**4e** was obtained by column chromatography on Al_2O_3 (R_f = 0.38 in EtOAc). ^{1}H NMR ($CDCl_3$): δ 0.28 (s, 6H), 1.11 (t, *J* = 7.3 Hz, 3H), 1.13 (t, *J* = 7.3 Hz, 3H), 1.99 (s, 2H), 2.17 (t, *J* = 7.3 Hz, 2H), 2.37 (q, *J* = 7.3 Hz, 2H), 3.21 (q, *J* = 7.3 Hz, 2H), 3.36 (q, *J* = 7.3 Hz, 2H), 6.30 (t, *J* = 7.3 Hz, 1H), 7.33−7.34 (c, 3H), 7.50 (m, 2H), 9.32 (s, 1H). ^{13}C NMR ($CDCl_3$): δ −2.9, 12.9, 14.0, 14.2, 24.7, 31.0, 39.9, 41.5, 127.5, 128.8, 133.4, 138.0, 141.2, 150.8, 170.0. 195.7. IR (ATR): 3068 w, 3048 w, 2971 w, 2933 w, 2902 w, 2818 w, 2710, 1680 m cm^{-1}. MS: *m*/*z* (relative intensity) 316 (4), 231 (18), 196 (19), 137 (12), 136 (14), 135 (100), 115 (19), 107 (14), 105 (14), 100 (69), 75 (40), 74 (17), 72 (51), 58 (12). Anal. Calcd for $C_{19}H_{29}NO_2Si$: C, 68.83; H, 8.82; N, 4.22. Found: C, 68.49; H, 8.98; N, 4.23.

*(E)- and (Z)-2-Dimethylphenylsilylmethyl-5-(tetrahydro-2H-pyranyl)oxypent-2-enal (**4f**).* This compound was isolated in 90% yield (300 mg) as a colorless oil (R_f = 0.06 in hexane/EtOAc 20/1) with an *E*/*Z* ratio of 3/97. *Z*-**4f** was obtained by column

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chromatography on Al_2O_3 (R_f = 0.13 in hexane/EtOAc 10/1). ^{1}H NMR ($CDCl_3$): δ 0.27 (s, 6H), 1.50−1.79 (c, 6H), 1.97 (s, 2H), 2.32 (q, J = 6.7 Hz, 2H), 3.34 (dt, J = 9.6, 6.7 Hz, 1H), 3.49 (m, 1H), 3.71 (dt, J = 9.6, 6.7 Hz, 1H), 3.81 (m, 1H), 4.53 (m, 1H), 6.37 (t, J = 6.7 Hz, 1H), 7.33−7.36 (c, 3H), 7.50 (m, 2H), 9.35 (s, 1H). ^{13}C NMR ($CDCl_3$): δ −2.8, −2.7, 14.4, 19.4, 25.3, 29.8, 30.5, 62.3, 65.5, 98.8, 127.7, 129.1, 133.5, 138.3, 142.3, 148.3, 194.7. IR (ATR): 3068 w, 3049 w, 2971 w, 2947 m, 2902 w, 2870 w, 2709 w, 1680 s cm^{-1}. MS: m/z (relative intensity) 247 (1), 135 (48), 95 (100), 75 (13), 67 (17), 57 (14). HRMS: calcd for $C_{19}H_{28}O_3Si$ (M^+ + H) 333.1886, found 333.1881.

*(E)- and (Z)-5-tert-Butyldimethylsiloxy-2-dimethylphenylsilylmethyloct-2-enal (**4g**).* This compound was isolated in 93% yield (338 mg) as a colorless oil (R_f = 0.08 in hexane/EtOAc 20/1) with an E/Z ratio of 3/97. Z-**4g** was obtained by flash column chromatography on SiO_2. ^{1}H NMR ($CDCl_3$): δ 0.03 (s, 6H), 0.27 (s, 6H), 0.88 (s, 9H), 1.96 (s, 2H), 2.22 (q, J = 7.0 Hz, 2H), 3.56 (t, J = 7.0 Hz, 2H), 6.37 (t, J = 7.0 Hz, 1H), 7.34−7.36 (c, 3H), 7.50 (m, 2H), 9.34 (s, 1H). ^{13}C NMR ($CDCl_3$): δ −5.3, −2.7, 14.5, 18.3, 25.9, 32.8, 61.4, 127.7, 129.1, 133.6, 138.4, 142.2, 148.8, 194.9. IR (ATR): 3069 w, 3049 w, 2954 w, 2929 w, 2897 w, 2816 w, 2710 w, 1685 m cm^{-1}. MS: m/z (relative intensity) 347 (1), 210 (12), 209 (18), 136 (13), 135 (100), 129 (19), 91 (11), 89 (27), 75 (41), 73 (54). Anal. Calcd for $C_{20}H_{34}O_2Si_2$: C, 66.24; H, 9.45. Found: C, 66.03; H, 9.45.

*(E)- and (Z)-3-Cyclohexyl-2-dimethylphenylsilylmethylpropenal (**4h**).* This compound was isolated in 80% yield (230 mg) as a colorless oil (R_f = 0.24 in hexane/EtOAc 20/1) with an E/Z ratio of 1/99. Z-**4h** was obtained by flash column chromatography on SiO_2. ^{1}H NMR ($CDCl_3$): δ 0.28 (s, 6H), 1.02−1.12 (c, 5H), 1.35−1.38 (c, 2H), 1.60−1.66 (c, 3H), 1.95 (s, 2H), 2.10 (m, 1H), 6.07 (d, J = 10.1 Hz, 1H), 7.34−7.36 (c, 3H), 7.51 (m, 2H), 9.29 (s, 1H). ^{13}C NMR ($CDCl_3$): δ −2.8, 14.1, 25.1, 25.7, 31.6, 38.2, 127.7, 129.0, 133.6, 138.5, 139.0, 157.3, 195.5. IR (ATR): 3068 w, 3046 w, 2925 w, 2850 w, 2706 w, 1682 s cm^{-1}. MS: m/z (relative intensity) 286 (3), 137 (21), 136 (13), 135 (100), 119 (24), 107 (17), 106 (12), 105 (20), 92 (11), 91 (18), 75 (32). Anal. Calcd for $C_{18}H_{26}OSi$: C, 75.46; H, 9.15. Found: C, 75.46; H, 9.23.

*(E)- and (Z)-4-Methyl-2-dimethylphenylsilylmethylpropenal (**4i**).* This compound was isolated in 79% yield (196 mg) as a colorless oil (R_f = 0.25 in hexane/EtOAc 20/1) with an E/Z ratio of 10/90. Z-**4i** was obtained by HPLC (Nacalai COSMOSIL Cholester column) with ^{i}PrOH as an eluent. ^{1}H NMR ($CDCl_3$): δ 0.28 (s, 6H), 0.89 (d, J = 6.8 Hz, 6H), 1.95 (s, 2H), 2.51 (d of sext, J = 6.8 10.1 Hz, 1H), 6.06 (d, J = 10.1 Hz, 1H), 7.34−7.36 (c, 3H), 7.51 (m, 2H), 9.30 (s, 1H). ^{13}C NMR ($CDCl_3$): δ −2.7, 14.1, 21.7, 28.4, 127.7, 129.1, 133.6, 138.5, 138.8, 158.7, 195.4. IR (ATR): 3069 w, 3053 w, 2960 w, 2871 w, 1684 s cm^{-1}. MS: m/z (relative intensity) 231 (3), 137 (13), 135 (100), 75 (25). Anal. Calcd for $C_{15}H_{22}OSi$: C, 73.11; H, 9.00. Found: C, 72.72; H, 8.87.

*(E)- and (Z)-2-Dimethylphenylsilylmethyl-3-phenylpropenal (**4j**).* This compound was isolated in 92% yield (256 mg) as a colorless oil (R_f = 0.14 in hexane/EtOAc 20/1) with an E/Z ratio of 21/79. Z-**4j** was obtained by column chromatography on Al_2O_3 (R_f = 0.13 in hexane/EtOAc 20/1). ^{1}H NMR ($CDCl_3$): δ 0.24 (s, 6H), 2.40 (s, 2H), 7.10 (s, 1H), 7.29−7.40 (c, 8H), 7.49 (m, 2H), 9.50 (s, 1H). ^{13}C NMR ($CDCl_3$): δ −2.4, 15.0, 127.7, 128.5, 129.0, 129.1, 129.4, 133.7, 135.4, 138.3, 141.4, 146.9, 195.5. IR (ATR): 3068 w, 3048 w, 3023 w, 2957 w, 2898 w, 2717 w, 2708 w, 1679 s cm^{-1}. MS: m/z (relative intensity) 280 (4), 202 (15), 135 (100), 129 (11), 128 (31), 107 (16), 105 (12), 91 (10), 75 (11). HRMS: calcd for $C_{18}H_{20}OSi$ (M^+) 280.1283, found 280.1282.

*(E)- and (Z)-2-(1-Adamantylmethyl)-3-dimethylphenylsilylpropenal (**5k**).* This compound was isolated in 82% yield (278 mg) after hydrolysis of **2k** as a colorless oil (R_f = 0.20 in hexane/EtOAc 20/1) with an E/Z ratio of 1/99. Z-**5k** was obtained by flash column chromatography on SiO_2. ^{1}H NMR ($CDCl_3$): δ 0.53 (s, 6H), 1.42 (s, 6H), 1.57−1.70 (c, 6H), 1.94 (m, 3H), 2.15 (s, 2H), 6.83 (s, 1H), 7.37−7.38 (c, 3H), 7.55 (m, 2H), 9.75 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 0.0, 28.6, 33.3, 36.9, 42.4, 45.4, 128.1, 129.4, 133.5, 138.1, 152.5, 153.3, 193.3. IR (ATR): 3068 w, 3049 w, 2900 m, 2845 m, 2741 w, 2715 w, 1684 m cm^{-1}. MS: m/z (relative intensity) 325 (1), 323 (25), 261 (10), 232 (15), 137 (26), 136 (12), 135 (100), 107 (19), 93 (29), 91 (14), 79 (31), 75 (15), 67 (14). HRMS: calcd for $C_{22}H_{30}OSi$ (M^+) 338.2066, found 338.2067.

*(E)- and (Z)-2-Cyclohexyl-3-dimethylphenylsilylpropenal (**5l**).*[2] This compound was isolated in 92% yield (250 mg) after hydrolysis of **2l** as a colorless oil (R_f = 0.28 in hexane/EtOAc 20/1) with an E/Z ratio of 11/89. ^{1}H NMR ($CDCl_3$): δ 0.50 (s, 6H), 0.51 (s, 6H), 0.97 (m, 2H), 1.10−1.24 (c, 3H), 1.32−1.43 (c, 2H), 1.65−1.85 (c, 5H), 2.30 (m, 1H), 2.61 (m, 1H), 6.70 (s, 1H), 6.89 (s, 1H), 7.34−7.40 (c, 3H), 7.50−7.57 (c, 2H), 9.44 (s, 1H), 9.78 (s, 1H). ^{13}C NMR ($CDCl_3$): δ −1.7, 0.1, 25.6, 26.2, 26.5, 29.6, 32.5, 38.1, 43.0, 128.0, 128.1, 129.36, 129.41, 133.5, 133.6, 137.4, 138.1, 146.4, 151.7, 161.9, 162.3, 193.2, 196.1.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Copies of ^{1}NMR and ^{13}C spectra of compounds **1e**, **1k**, **2a**$_{Oct}$, **2a**$_{Xy}$, Z-**4a**-Z-**4j**, Z-**5k**, and **5l**, and ^{1}H−^{1}H COSY, HMBC, DEPT 135, and NOE spectra of Z-**4a**. This material is available free of charge via the Internet at http://pubs.acs.org/.

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Notes

The authors declare no competing financial interest.

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