Chemo- and Regioselective Intramolecular Hydrosilylative Carbocyclization of Allenynes

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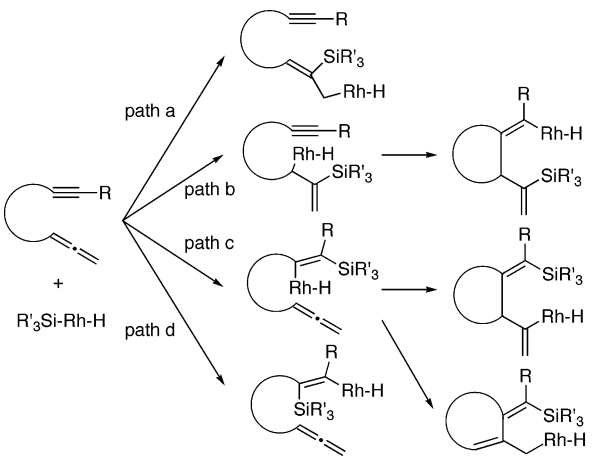
Rhodium complex catalyzed hydrosilylative carbocyclization of various allenynes and trialkoxysilanes proceeded smoothly under an atmosphere of carbon monoxide to give hydrosilylated cyclic products. The intramolecular coupling of allene and alkyne is chemo- and regioselective: silylrhodation to an internal olefinic moiety of the allene proceeded exclusively, and subsequent carbometalation to the alkyne provided cyclic 1,4-dienes. The use of alkoxysilane and the substituents on the allene terminus play pivotal roles in the selectivity.

Introduction

Transition-metal-catalyzed carbocyclization is a powerful and reliable synthetic method for the construction of various types of ring systems.[1] In particular, silylcarbocyclization, in which silicon-initiated carbometalation is a key step, is an established procedure. After Tamao and Ito reported the first example of nickel complex catalyzed silylcarbocyclization of 1,7-diynes,[2] Ojima comprehensively studied rhodium complex catalyzed silylcarbocyclization.[3] Enynes,[3a,e] diynes,[3b,4] triynes,[3c] and enediynes[3d] can all be used as substrates, and various types of functionalized cyclic systems have been obtained. Recently, cationic palladium[5] and platinum[6] complexes have been found to be efficient catalysts. However, to the best of our knowledge, the hydrosilylative carbocyclization of allenynes has not yet been reported.[7]

When an allenyne is subjected to hydrosilylation using a rhodium complex, there are several plausible pathways, depending upon the chemoselectivity between the alkyne and allene, the regioselectivity of the two olefinic moieties of the allene, and the direction of silylrhodation to an unsaturated bond. Scheme 1 shows four selected pathways, where silylation occurs at an sp carbon. On the basis of our study of transition-metal-catalyzed reactions using allenynes,[8] we considered that the regioselectivity could be controlled by the methyl substituents on the allene terminus.

Scheme 1



We report here the first example of hydrosilylative carbocyclization of allenynes catalyzed by a rhodium complex. The intramolecular coupling of allene and alkyne with various silanes was examined. A mechanistic study using a deuterated silane and the synthetic transformations of the obtained vinylsilanes are also described.

Results and Discussion

We chose allenyne **1a** as a model substrate and examined rhodium complex catalyzed silylcarbocyclization using dimethylphenylsilane under several reaction conditions (Table 1). The silylative coupling proceeded

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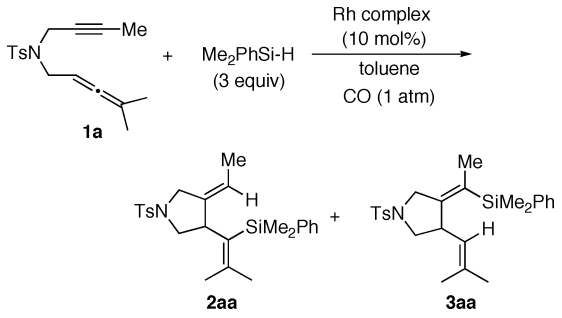
Table 1. Hydrosilylative Carbocyclization of Allenyne 1a under Various Conditions



entry	Rh complex	temp/°C	time/h	yield/%	**2aa**/**3aa**
1	$Rh(acac)(CO)_2$	120	0.5	85	2/1
2	$Rh(acac)(CO)_2$	60	0.5	90	7/1
3	$Rh(acac)(CO)_2$	room temp	1	47	9/1
4	$^1/_2[RhCl(cod)]_2$	40	1	67	12/1
5	$^1/_2[RhCl(cod)]_2 + 2PPh_3$	90	2	31	2/1
6	$^1/_2[RhCl(cod)]_2$ + DPPP[a]	90	6	64	3/1

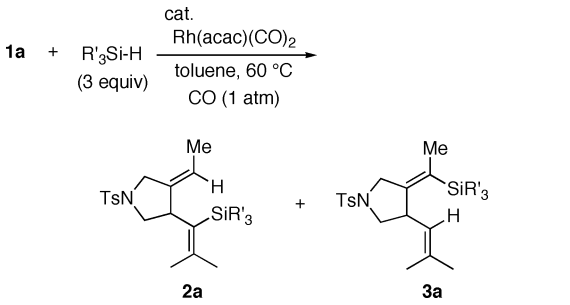
[a] DPPP = 1,3-bis(diphenylphosphino)propane.

smoothly under an atmosphere of carbon monoxide using $Rh(acac)(CO)_2$ as a catalyst in toluene. At 120 °C, allenyne **1a** was consumed within 30 min and the hydrosilylated product was obtained in high yield; however, the chemoselectivity (**2aa** via path b vs **3aa** via path c) was low (entry 1). When the reaction temperature was lowered, the selectivity was improved and the vinylsilane **2aa** was the major product (entries 2 and 3). In the silylcarbocyclization of enynes, silylrhodation to the alkyne moiety, not the alkene, proceeded exclusively, following carbometalation to the alkene moiety. Interestingly, in the reaction of the allenyne, silylrhodation to the allene moiety, not the alkyne, is predominant. When $[RhCl(cod)]_2$ was used as a catalyst, the chemoselectivity was further improved; however, the yield was lower because of the formation of several unidentified side products (entry 4). The addition of phosphine ligands diminished the catalytic activity of the rhodium complex; moreover, the chemoselectivity was not sufficient (entries 5 and 6).

Using $Rh(acac)(CO)_2$ as a catalyst, several silanes were examined for the improvement of chemoselectivity (Table 2). With a more bulky triethylsilane, the formation of **3a** was suppressed, but the yield of **2a** was low (entry 1). When alkoxysilanes were used in place of trialkylsilanes, vinylsilane **2a** was the only silylative product identified and was obtained in high yield (entries 2−4). Trimethoxy- and triethoxysilane gave satisfying results, and 2 mol % of rhodium catalyst was sufficient to give a high yield in a short reaction time (entries 5 and 6). Moreover, the catalytic reaction proceeded even with as little as 0.5 mol % catalyst (entry 7). The reaction of allenyne proceeded even at room temperature under an atmosphere of CO (entry 8).[9]

The silylcarbocyclization of various allenynes and two trialkoxysilanes was examined using 5 mol % catalyst (Table 3). In the reported rhodium complex catalyzed silylcarbocyclization of enynes and diynes, the alkyne

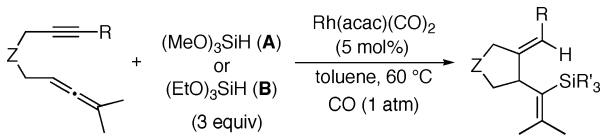
Table 2. Hydrosilylative Carbocyclization of Allenyne 1a with Various Silanes



entry	silane	cat./mol %	time/h	yield/%	**2a**/**3a**[a]
1	Et_3SiH	10	0.5	32	>20/1
2	$(MeO)_2MeSiH$	10	0.5	73	>20/1
3	$(MeO)_3SiH$	10	0.5	77	>20/1
4	$(EtO)_3SiH$	10	0.5	85	>20/1
5	$(MeO)_3SiH$	2	0.75	80	>20/1
6	$(EtO)_3SiH$	2	0.75	84	>20/1
7	$(EtO)_3SiH$	0.5	8	66	>20/1
8[b]	$(MeO)_3SiH$	10	6	53	>20/1

[a] The formation of **3a** could not detected by NMR spectra. [b] The reaction was examined at room temperature.

Table 3. Hydrosilylative Carbocyclization of Various Allenynes



entry	Z	R	allenyne	silane	time/h	yield/%
1[a]	TsN	Me	**1a**	A	0.75	80 (**2ab**)
2	TsN	Me	**1a**	B	0.5	82 (**2ac**)
3	TsN	*n*-Bu	**1b**	A	1	79 (**2bb**)
4	TsN	*n*-Bu	**1b**	B	1.5	72 (**2bc**)
5	TsN	Ph	**1c**	A	0.75	50 (**2cb**)
6	TsN	Ph	**1c**	B	1.5	52 (**2cc**)
7[a]	O	Me	**1d**	A	1	63 (**2db**)
8[a]	O	Me	**1d**	B	1	73 (**2dc**)
9	O	Ph	**1e**	A	0.75	54 (**2eb**)
10	O	Ph	**1e**	B	1	46 (**2ec**)
11	$(EtO_2C)_2C$	Ph	**1f**	A	1.5	49 (**2fb**)
12	$(EtO_2C)_2C$	Ph	**1f**	B	1.5	61 (**2fc**)

[a] These entries were examined using 2 mol % catalyst.

terminus is usually limited to hydrogen or alkyl groups. In the case of allene−alkyne coupling, both alkyls (entries 1−4) and an aryl group can be tolerated (entries 5 and 6). Oxygen-bridge allenynes **1d**,**e** are also good substrates, and the corresponding cyclic vinylsilanes **2db**,**dc** and **2eb**,**ec** were obtained in acceptable yields (entries 7−10). Allenylpropargylmalonate **1f** could also be transformed into the silylative product **2fb**,**fc** (entries 11 and 12). In each case, vinylsilanes **2a**−**f** were the only fully characterized products and the other silylative coupling products, including **3**, could not be isolated. Moreover, neither a cross-conjugated triene by an ene-type reaction[8a,10] nor bicyclic enones by a Pauson−Khand-type reaction[8b,11] could be detected.

(9) Under an atmosphere of argon or a high pressure of carbon monoxide (5 atm), silylcarbocyclization proceeded, yet in lower yield (48 and 55%, respectively), along with the formation of many unidentified products.

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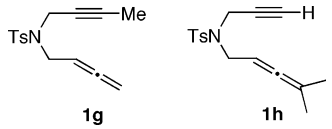
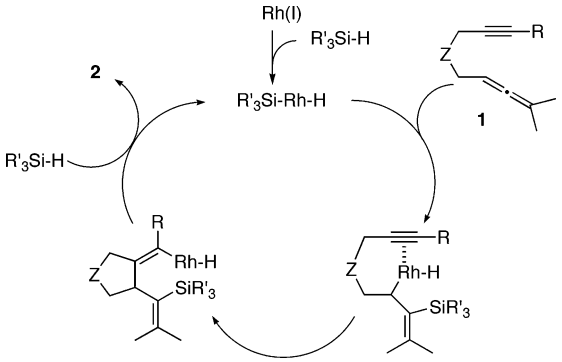
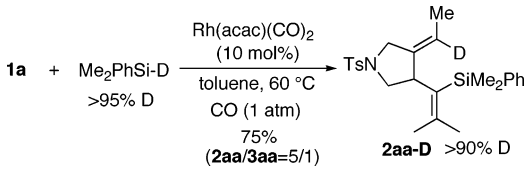


Figure 1. Other allenynes possessing no substituent on allene or alkyne terminus.

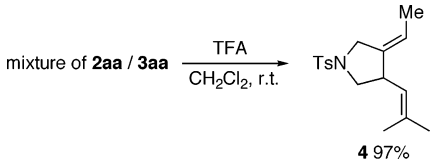
Scheme 2



Scheme 3



Scheme 4



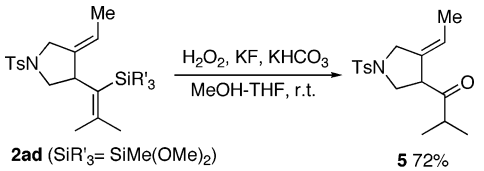
When allenynes **1g**,**h** (Figure 1) were examined under the same reaction conditions, respectively, many silylated products were obtained, although none of them could be isolated or fully characterized. These results imply that the substituents on both the allene and alkyne termini play pivotal roles in the highly chemo- and regioselective silylcarbocyclization of allenynes.

The proposed mechanism is depicted in Scheme 2. Regioselective silylmetalation to the allene moiety could be achieved by the methyl groups on the allene terminus. Subsequent carbometalation gives the cyclic vinyl rhodium complex and reductive elimination provides the product **2** and regenerates the catalyst. The *Z* form of the obtained vinylsilane **2ab** was ascertained by NOE spectra. The results of a labeling experiment also support the above mechanism: when silylcarbocyclization was examined using the deuterated silane (>95% D),[12] the vinylic position derived from the alkyne moiety was labeled by deuterium at over 90% (Scheme 3).

The mixture of vinylsilanes **2aa**/**3aa** was desilylated by trifluoroacetic acid, and the cyclic 1,4-diene **4** was obtained as the sole product (Scheme 4). Alkoxyvinylsilane **2ad** (entry 2 in Table 1) was readily transformed into the isopropyl ketone **5** by Tamao oxidation (Scheme 5).[13]

(12) Zheng, G. Z.; Chan, T. H. *Organometallics* **1995**, *14*, 70.
(13) Tamao, K.; Maeda, K. *Tetrahedron Lett.* **1986**, *27*, 65.

Scheme 5



Conclusions

In conclusion, this is the first report of the cyclization/hydrosilylation of allenynes. Rhodium complex catalyzed chemo- and regioselective reactions could be realized by using alkoxysilane and the methyl substituents on the allene terminus. The present coupling proceeds under an atmosphere of carbon monoxide, and nitrogen-, oxygen-, and carbon-bridged allenynes can be transformed into the cyclic vinylsilanes.

Experimental Section

General Considerations. IR spectra were recorded with a JASCO FT/IR-5000 spectrometer. NMR spectra were measured with a Varian VXR-300 spectrometer using tetramethylsilane as an internal standard, and $CDCl_3$ was used as solvent. High-resolution mass spectra were measured with a JEOL JMS-SX102A instrument. Elemental analyses were measured with Perkin-Elmer PE2400. Toluene was distilled from calcium hydride and dried over molecular sieves 4A (MS 4A). All reactions were examined using a CO balloon.

Typical Procedure for Hydrosilylative Carbocyclization of Allenynes (Table 2, Entry 6). (Acetylacetonato)dicarbonylrhodium(I) (2.2 mg, 8.46×10^{-3} mmol, 2 mol %) and triethoxysilane (209 mg, 1.27 mmol) in dry toluene (3.6 mL) were stirred under an atmosphere of carbon monoxide at room temperature. After the mixture was changed to a homogeneous solution, a solution of *N*-(but-2-ynyl)-*N*-(4-methylpenta-2,3-dienyl)tosylamine (**1a**; 128 mg, 0.423 mmol) in dry toluene (5.1 mL) was added to the mixture and stirred for 30 min at 60 °C. The solvent was removed under reduced pressure to give the crude product, which was further purified by thin-layer chromatography to give the pure product **2ac** (166.0 mg, 84%).

***(Z)*-4-(1-(Dimethylphenylsilyl)-3-ethylidene-2-methylprop-1-enyl)-1-tosylpyrrolidine (2aa).** Yellow oil. IR (neat): 1601, 1350, 1164, 832, 816 cm^{-1}. ^1H NMR: δ −0.08 (s, 3H), 0.15 (s, 3H), 1.51−1.54 (m, 3H), 1.65 (s, 3H), 1.69 (s, 3H), 2.39 (s, 3H), 2.90 (dd, J = 9.6, 9.6 Hz, 1H), 3.51 (d, J = 14.4 Hz, 1H), 3.63 (dd, J = 9.6, 9.6 Hz, 1H), 3.85−3.88 (m, 1H), 4.06 (d, J = 14.4 Hz, 1H), 5.08−5.16 (m, 1H), 7.23−7.36 (m, 7H), 7.68 (d, J = 8.4 Hz, 2H). ^{13}C NMR: δ 0.8, 1.3, 14.6, 21.6, 26.8, 46.2, 50.4, 52.6, 116.3, 127.5, 127.6, 128.0, 128.3, 129.5, 132.5, 133.4, 139.7, 140.6, 143.4, 149.1. HRMS (FAB): found, 440.2065; calcd for $C_{25}H_{34}NO_2SSi$ (MH^+), 440.2080.

***(Z)*-3-Ethylidene-4-(2-methyl-1-(trimethoxysilyl)prop-1-enyl)-1-tosylpyrrolidine (2ab).** Colorless solid (hexane). Mp: 93−94 °C. IR (neat): 1601, 1346, 1164, 1089, 814 cm^{-1}. ^1H NMR: δ 1.50−1.55 (m, 3H), 1.75 (s, 3H), 1.92 (s, 3H), 2.42 (s, 3H), 2.96 (dd, J = 8.7, 10.4 Hz, 1H), 3.22 (s, 9H), 3.45−3.49 (m, 1H), 3.55 (dd, J = 8.7, 8.7 Hz, 1H), 3.74−3.80 (m, 1H), 4.10 (d, J = 14.1 Hz, 1H), 4.93−5.02 (m, 1H), 7.34 (d, J = 8.1 Hz, 2H), 7.74 (d, J = 8.1 Hz, 2H). ^{13}C NMR: δ 14.6, 21.5, 25.5, 44.9, 49.7, 50.4, 52.6, 115.3, 124.5, 128.0, 129.6, 132.3, 140.4, 143.2, 151.9; Anal. Calcd for $C_{20}H_{31}NO_5SSi$: C, 56.44; H, 7.34; N, 3.29. Found: C, 56.42; H, 7.47; N, 3.18.

The product was determined to be a *Z* isomer on the basis of the observation of NOEs in Figure 2.

***(Z)*-3-Ethylidene-4-(2-methyl-1-(triethoxysilyl)prop-1-enyl)-1-tosylpyrrolidine (2ac).** White solid (hexane). Mp: 50−51 °C. IR (neat): 1601, 1348, 1164, 1079, 832, 814 cm^{-1}. ^1H NMR: δ 1.00 (t, J = 7.1 Hz, 9H), 1.48−1.52 (m, 3H), 1.74

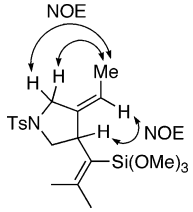


Figure 2. Determination of stereochemistry of **2ab** by NOEs.

(s, 3H), 1.94 (s, 3H), 2.42 (s, 3H), 3.04 (dd, J = 8.4, 10.5 Hz, 1H), 3.42−3.60 (m, 7H), 3.74 (d, J = 13.5 Hz, 1H), 3.72−3.77 (m, 1H), 4.10 (d, J = 13.5 Hz, 1H), 4.91−4.99 (m, 1H), 7.32 (d, J = 8.1 Hz, 2H), 7.73 (d, J = 8.1 Hz, 2H). ^{13}C NMR: δ 14.5, 18.0, 21.5, 21.6, 25.7, 45.3, 50.4, 52.6, 57.7, 114.8, 124.9, 127.9, 129.3, 132.7, 140.4, 143.2, 151.7. HRMS (FAB): found, 468.2276; calcd for $C_{23}H_{38}NO_5SSi$ (MH^+), 468.2240.

(*Z*)- 4-(2-Methyl-1-(trimethoxysilyl)prop-1-enyl)-3-pentylidene-1-tosylpyrrolidine (2bb). White solid. Mp: 89−91 °C (hexane). IR (neat): 1601, 1348, 1164, 1087, 812 cm^{-1}. ^{1}H NMR: δ 0.84−0.88 (m, 3H), 1.23−1.28 (m, 4H), 1.75 (s, 3H), 1.82−1.92 (m, 2H), 1.93 (s, 3H), 2.42 (s, 3H), 2.94 (dd, J = 8.7, 10.2 Hz, 1H), 3.22 (s, 9H), 3.47 (d, J = 14.1 Hz, 1H), 3.57 (dd, J = 8.7, 8.7 Hz, 1H), 3.63−3.74 (m, 1H), 4.10 (d, J = 14.1 Hz, 1H), 4.88−4.94 (m, 1H), 7.33 (d, J = 8.0 Hz, 2H), 7.73 (d, J = 8.0 Hz, 2H). ^{13}C NMR: δ 14.0, 21.5, 22.3, 25.5, 29.3, 31.5, 44.9, 49.7, 50.4, 52.5, 121.2, 124.3, 127.9, 129.2, 132.3, 139.3, 143.1, 151.9. HRMS (FAB): found 468.2231; calcd for $C_{23}H_{38}NO_5SSi$ (MH^+), 468.2240.

(*Z*)-4-(2-Methyl-1-(triethoxysilyl)prop-1-enyl)-3-pentylidene-1-tosylpyrrolidine (2bc). Colorless oil. IR (neat): 1601, 1344, 1162, 1077, 955, 756 cm^{-1}. ^{1}H NMR: δ 0.84−0.89 (m, 3H), 1.00 (t, J = 7.1 Hz, 9H), 1.23−1.30 (m, 4H), 1.74 (s, 3H), 1.84−1.89 (m, 2H), 1.95 (s, 3H), 2.42 (s, 3H), 3.04 (dd, J = 8.6, 10.7 Hz, 1H), 3.43−3.59 (m, 7H), 3.68−3.82 (m, 2H), 4.11 (dd, J = 0.9, 13.2 Hz, 1H), 4.87−4.93 (m, 1H), 7.31 (d, J = 8.1 Hz, 2H), 7.42 (d, J = 8.1 Hz, 2H). ^{13}C NMR: δ 14.0, 18.0, 21.5, 21.6, 22.4, 25.7, 29.3, 31.5, 45.3, 50.4, 52.5, 57.7, 120.7, 124.8, 127.8, 129.3, 132.7, 139.2, 143.2, 151.8. HRMS (FAB): found, 510.2714; calcd for $C_{26}H_{44}NO_5SSi$ (MH^+), 510.2709.

(*Z*)-3-Benzylidene-4-(2-methyl-1-(trimethoxysilyl)prop-1-enyl)-1-tosylpyrrolidine (2cb). Pale yellow solid. Mp: 113−114 °C. IR (neat): 1601, 1348, 1168, 1091, 814 cm^{-1}. ^{1}H NMR: δ 1.82 (s, 3H), 1.98 (s, 3H), 2.42 (s, 3H), 2.99 (dd, J = 9.2, 10.4 Hz, 1H), 3.22 (s, 9H), 3.65 (dd, J = 9.2, 9.2 Hz, 1H), 3.84 (dt, J_d = 14.3, J_t = 2.4 Hz, 1H), 3.93−4.00 (m, 1H), 4.44 (dt, J_d = 14.3, J_t = 2.4 Hz, 1H), 5.82 (q, J = 2.5 Hz, 1H), 7.16−7.35 (m, 7H), 7.76 (d, J = 8.4 Hz, 2H). ^{13}C NMR: δ 21.6, 21.7, 25.6, 46.7, 49.9, 51.7, 51.8, 121.4, 124.5, 126.4, 127.6, 128.0, 128.4, 129.4, 132.4, 137.1, 142.5, 143.4, 152.7. HRMS (FAB): found, 488.1920; calcd for $C_{25}H_{34}NO_5SSi$ (MH^+), 488.1972.

(*Z*)-3-Benzylidene-4-(2-methyl-1-(triethoxysilyl)prop-1-enyl)-1-tosylpyrrolidine (2cc). White solid. Mp: 82−84 °C (hexane). IR (neat): 1601, 1346, 1166, 1077, 957, 756 cm^{-1}. ^{1}H NMR: δ 0.97 (t, J = 6.9 Hz, 9H), 1.81 (s, 3H), 2.00 (s, 3H), 2.41 (s, 3H), 3.09 (dd, J = 8.4, 10.2 Hz, 1H), 3.43−3.58 (m, 6H), 3.63 (dd, J = 8.4, 8.4 Hz, 1H), 3.88 (dt, J_d = 14.4, J_t = 2.7 Hz, 1H), 3.93−3.99 (m, 1H), 4.44 (d, J = 14.4 Hz, 1H), 5.95 (d, J = 2.7 Hz, 1H), 7.07−7.34 (m, 7H), 7.75 (d, J = 8.1 Hz, 2H). ^{13}C NMR: δ 18.0, 21.5, 21.7, 25.8, 47.0, 51.7, 51.8, 57.8, 121.1, 125.0, 126.3, 127.5, 127.9, 128.3, 129.4, 132.7, 137.2, 142.5, 143.4, 152.5. HRMS (FAB): found, 530.2368; calcd for $C_{28}H_{40}NO_5SSi$ (MH^+), 530.2396.

(*Z*)-3-Ethylidene-4-(2-methyl-1-(trimethoxysilyl)prop-1-enyl)-2,3,4,5-tetrahydrofuran (2db). Colorless oil. IR (neat) 1607, 1191, 1087, 801 cm^{-1}. ^{1}H NMR: δ 1.55−1.58 (m, 3H), 1.83 (s, 3H), 1.99 (s, 3H), 3.50 (s, 9H), 3.72 (dd, J = 6.8, 10.1 Hz, 1H), 3.76−3.85 (m, 1H), 4.00 (dd, J = 6.8, 6.8 Hz, 1H), 4.29 (dd, J = 1.8, 12.9 Hz, 1H), 4.48 (d, J = 12.9 Hz, 1H), 4.99−5.09 (m, 1H). ^{13}C NMR: δ 14.7, 21.7, 25.7, 46.6, 50.0, 67.0, 72.6, 112.4, 124.3, 144.1, 151.4. HRMS (FAB): found, 273.1543; calcd for $C_{13}H_{25}O_4Si$ (MH^+), 273.1522.

(*Z*)-3-Ethylidene-4-(2-methyl-1-(triethoxysilyl)prop-1-enyl)-2,3,4,5-tetrahydrofuran (2dc). Colorless oil. IR (neat): 1605, 1296, 1079 cm^{-1}. ^{1}H NMR: δ 1.20 (t, J = 7.0 Hz, 9H), 1.53−1.56 (m, 3H), 1.82 (s, 3H), 2.00 (s, 3H), 3.67−3.87 (m, 8H), 3.98 (dd, J = 3.8, 4.7 Hz, 1H), 4.40 (dd, J = 1.2, 12.9 Hz, 1H), 4.47 (d, J = 12.9 Hz, 1H), 4.96−5.05 (m, 1H). ^{13}C NMR: δ 14.7, 18.2, 21.8, 25.8, 46.7, 57.9, 70.1, 72.8, 112.0, 124.9, 144.2, 151.0. HRMS (FAB): found, 315.1986; calcd for $C_{16}H_{31}O_4Si$ (MH^+), 315.1992.

(*Z*)-3-Benzylidene-4-(2-methyl-1-(trimethoxysilyl)prop-1-enyl)-2,3,4,5-tetrahydrofuran (2eb). Pale yellow oil. IR (neat): 1605, 1191, 1083, 801 cm^{-1}. ^{1}H NMR: δ 1.91 (s, 3H), 2.05 (s, 3H), 3.47 (s, 9H), 3.77 (dd, J = 12.2, 14.7 Hz, 1H), 4.00−4.09 (m, 2H), 4.64 (dt, J_d = 13.7, J_t = 2.2 Hz, 1H), 4.76 (dt, J_d = 13.7, J_t = 2.2 Hz, 1H), 6.05 (q, J = 2.2 Hz, 1H), 7.10−7.19 (m, 3H), 7.28−7.33 (m, 2H). ^{13}C NMR: δ 21.9, 25.7, 48.4, 50.2, 71.0, 71.8, 119.1, 124.2, 126.0, 127.5, 128.3, 137.9, 147.1, 152.3. HRMS (FAB): found, 335.1677; calcd for $C_{18}H_{27}O_4Si$ (MH^+), 335.1679.

(*Z*)-3-Benzylidene-4-(2-methyl-1-(triethoxysilyl)prop-1-enyl)-2,3,4,5-tetrahydrofuran (2ec). Yellow oil. IR (neat): 1603, 1218, 1079, 957, 756 cm^{-1}. ^{1}H NMR: δ 1.16 (t, J = 6.9 Hz, 9H), 1.90 (s, 3H), 2.06 (s, 3H), 3.64−3.80 (m, 6H), 3.87 (dd, J = 11.0, 14.0 Hz, 1H), 4.01−4.07 (m, 2H), 4.69 (dt, J_d = 13.5, J_t = 2.0 Hz, 1H), 4.75 (dt, J_d = 13.5, J_t = 2.0 Hz, 1H), 6.03 (q, J = 2.0 Hz, 1H), 7.08−7.33 (m, 5H). ^{13}C NMR: δ 18.2, 22.0, 25.9, 48.6, 58.0, 71.2, 71.9, 118.8, 124.9, 125.8, 127.4, 128.3, 138.0, 147.2, 152.0. HRMS (FAB): found, 375.2017; calcd for $C_{21}H_{31}O_4Si$ (M − 1), 375.1991.

Diethyl (*E*)-3-Benzylidene-4-(2-methyl-1-(trimethoxysilyl)prop-1-enyl)cyclopentane-1,1-dicarboxlate (2fb). Pale yellow oil. IR (neat): 1719, 1083, 756 cm^{-1}. ^{1}H NMR: δ 1.22 (t, J = 7.3 Hz, 3H), 1.26 (t, J = 7.3 Hz, 3H), 1.88 (s, 3H), 2.02 (s, 3H), 2.25 (dd, J = 12.1, 12.1, 1H), 2.49 (dd, J = 7.7, 12.1 Hz, 1H), 3.32−3.35 (m, 1H), 3.47 (s, 9H), 3.91−3.97 (m, 1H), 4.05−4.27 (m, 4H), 6.01 (d, J = 2.4 Hz, 1H), 7.12−7.17 (m, 1H), 7.32−7.52 (m, 4H). ^{13}C NMR: δ 14.1, 14.1, 21.6, 25.6, 38.8, 39.5, 47.4, 50.2, 59.9, 61.4, 61.4, 121.5, 125.6, 127.9, 128.1, 138.4, 147.0, 171.4, 171.7. HRMS (FAB): found, 476.2263; calcd for $C_{25}H_{36}O_7Si$, 476.2230.

Diethyl (*E*)-3-Benzylidene-4-(2-methyl-1-(triethoxysilyl)prop-1-enyl)cyclopentane-1,1-dicarboxylate (2fc). Yellow oil. IR (neat): 1731, 1077, 756 cm^{-1}. ^{1}H NMR: δ 1.13−1.29 (m, 15H), 1.87 (s, 3H), 2.03 (s, 3H), 2.38−2.45 (m, 2H), 3.29 (d, J = 16.8, 1H), 3.40 (dt, J_d = 16.8, J_t = 2.7, 1H), 3.66−3.79 (m, 6H), 3.90−3.98 (m, 1H), 4.07−4.25 (m, 4H), 5.98 (d, J = 2.1 Hz, 1H), 7.11−7.32 (m, 5H). ^{13}C NMR: δ 14.1, 14.1, 18.2, 21.7, 25.8, 38.8, 39.6, 47.5, 57.9, 60.0, 61.3, 61.4, 121.2, 125.5, 127.8, 128.9, 138.5, 147.0, 150.0, 171.4, 171.8. HRMS (FAB): found, 518.2704; calcd for $C_{28}H_{42}O_7Si$, 518.2700.

(*Z*)-4-(1-(Dimethoxymethylsilyl)-2-methylprop-1-enyl)-3-ethylidene-1-tosylpyrrolidine (2ad). Colorless solid (hexane). Mp: 119−120 °C. IR (neat): 1601, 1348, 1164, 1087, 832 cm^{-1}. ^{1}H NMR: δ 0.03 (s, 3H), 1.50−1.53 (m, 3H), 1.73 (s, 3H), 1.90 (s, 3H), 2.42 (s, 3H), 2.94 (s, 3H), 3.03 (dd, J = 8.7, 10.4 Hz, 1H), 3.17 (s, 3H), 3.47 (d, J = 13.5 Hz, 1H), 3.57 (dd, J = 8.7, 8.7 Hz, 1H), 3.76−3.82 (m, 1H), 4.09 (d, J = 13.5 Hz, 1H), 4.89−4.96 (m, 1H), 7.33 (d, J = 8.1 Hz, 2H), 7.73 (d, J = 8.1 Hz, 2H). ^{13}C NMR: δ −2.3, 14.5, 21.6, 24.9, 45.2, 49.0, 49.2, 50.5, 52.6, 114.9, 127.7, 128.0, 129.2,132.4, 140.7, 143.2, 149.6. Anal. Calcd for $C_{20}H_{32}NO_4SSi$; C, 58.64; H, 7.63; N, 3.42. Found: C, 58.77; H, 7.70; N, 3.35.

(*Z*)-3-Ethylidene-4-(2-methylprop-1-enyl)-1-tosylpyrrolidine (4). Yellow oil. IR (neat): 1618, 1350, 1166, 1093, 812 cm^{-1}. ^{1}H NMR: δ 1.50−1.54 (m, 3H), 1.60 (d, J = 1.2 Hz, 3H), 1.69 (d, J = 1.2 Hz, 3H), 2.44 (s, 3H), 2.56 (dd, J = 9.3, 9.3 Hz, 1H), 3.39−3.42 (m, 1H), 3.59−3.64 (m, 2H), 4.00 (dt, J_d = 14.4, J_t = 1.4 Hz, 1H), 4.74−4.76 (dt, J_d = 14.4, J_t = 1.4 Hz,

1H), 5.09−5.12 (m, 1H), 7.32 (d, J = 8.7 Hz, 2H), 7.74 (d, J = 8.4 Hz, 2H). ^{13}C NMR: δ 14.5, 18.2, 21.6, 25.8, 42.3, 49.6, 53.6, 117.2, 122.3, 127.7, 129.5, 132.7, 135.4, 138.6, 143.4. HRMS (FAB): found, 306.1520; calcd for $C_{17}H_{24}NO_2S$ (MH^+), 306.1528.

(*Z*)-3-Ethylidene-4-(2-methyl-1-oxopropyl)-1-tosylpyrrolidine (5). Yellow oil. IR (neat): 1618, 1350, 1166, 1093, 812 cm^{-1}. ^{1}H NMR: δ 1.50−1.54 (m, 3H), 1.60 (d, J = 1.2 Hz, 3H), 1.69 (d, J = 1.2 Hz, 3H), 2.44 (s, 3H), 2.56 (dd, J = 9.3, 9.3 Hz, 1H), 3.39−3.42 (m, 1H), 3.59−3.64 (m, 2H), 4.00 (dt, J_d = 14.4, J_t = 1.4 Hz, 1H), 4.74−4.76 (dt, J_d = 14.4, J_t = 1.4 Hz, 1H), 5.09−5.12 (m, 1H), 7.32 (d, J = 8.7 Hz, 2H), 7.74 (d, J = 8.4 Hz, 2H). ^{13}C NMR: δ 14.5, 18.2, 21.6, 25.8, 42.3, 49.6, 53.6, 117.2, 122.3, 127.7, 129.5, 132.7, 135.4, 138.6, 143.4. HRMS (FAB): found, 306.1520; calcd for $C_{17}H_{24}NO_2S$ (MH^+), 306.1528.

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Supporting Information Available: Listings of spectral data for allenyne **1a**−**f**, ^{1}H NMR charts of **2aa** and **2aa-D**, and copies of ^{1}H and ^{13}C NMR spectra for allenynes and products lacking analyses. This material is available free of charge via the Internet at http://pubs.acs.org.

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