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Rhodium-Catalyzed Silylative Cyclization of 1,6-Heptadiyne Derivatives: A Versatile Route for the Synthesis of a 1,2-Dialkylidenecyclopentane Skeleton

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The reaction of 1,6-heptadiyne derivatives with a hydrosilane in the presence of a catalytic amount of $RhCl(PPh_3)_3$ (**3a**) affords 1,2-dialkylidenecyclopentane derivatives (**4**) in moderate yields. This skeleton is constructed by the insertion of two alkyne moieties involved in the same molecule into the Rh−Si bond and the Rh−vinyl bond, consecutively. The key intermediate in this process is $Rh(H)(SiR_3)(Cl)(PPh_3)_2$ (**8**), the formation of which is observed in a solution of $CDCl_3$ by ^1H NMR analysis. 1,6-Heptadiynes react smoothly with hydrosilanes to give **4** at room temperature in the presence of an equimolar amount of **8**. The quantity of **8** can be reduced to 3 mol % of the starting diynes to complete the identical reaction at 80 °C. $Rh_4(CO)_{12}$ (**3b**) or a cationic rhodium complex $[Rh(cod)(dppb)]PF_6$ (**3c**) is also effective as a catalyst precursor for the present transformation, although the selectivity of **4** is rather low. The stereochemistry of the silylvinylidene moiety of **4** has the *E*-configuration in the reaction catalyzed by **3a** or **8**, while **4** with the *Z*-configuration is obtained from the reaction catalyzed by **3b**. Two exo-methylene groups on the contiguous carbons of the products **4** behave as a diene unit for the Diels−Alder reaction with some dienophiles. Hydrogenation of **4** proceeds smoothly in the 1,4-addition mode to give the allylsilane **25** in high yield under 1 atm of H_2.

Introduction

Transition-metal-catalyzed carbocyclization of alkenes and alkynes is one of the most effective procedures for construction of a variety of carbocyclic and heterocyclic compounds.[1] In particular, the cyclization of diynes[2] and enynes[3,4] is one of the most popular methods for the formation of 1,2-dialkylidenecycloalkane skeletons, which are widely used as building blocks for the synthesis of complex molecules.[1,2c,4] In these reactions, the cyclization of diynes with reagents having H−X or X−X′ bonds[5,6] (X, X′ = metals or heteroatoms) have additional effectiveness, because the resultant cyclic compounds involving metals or heteroatoms allow numerous synthetic transformations. Although this type of cyclization has been extensively studied for other starting substrates such as eneynes,[6d,e,i,7] dienes,[8] alleneynes,[9] bis(dienes),[10] or other unsaturated substrates,[8j,11] these substrates do not form cyclic structures including alkylidene groups on the contiguous positions.

The current method for the synthesis of 1,2-dialkylidenecycloalkanes from a diyne or an enyne requires stoichiometric amounts of low-valent titanium and/or zirconium fragments. This is the most serious problem from the viewpoint of metal economy and green chemistry. Palladium[2−4,6] and nickel[3,6] catalysts have been successfully applied to this type of transformation in

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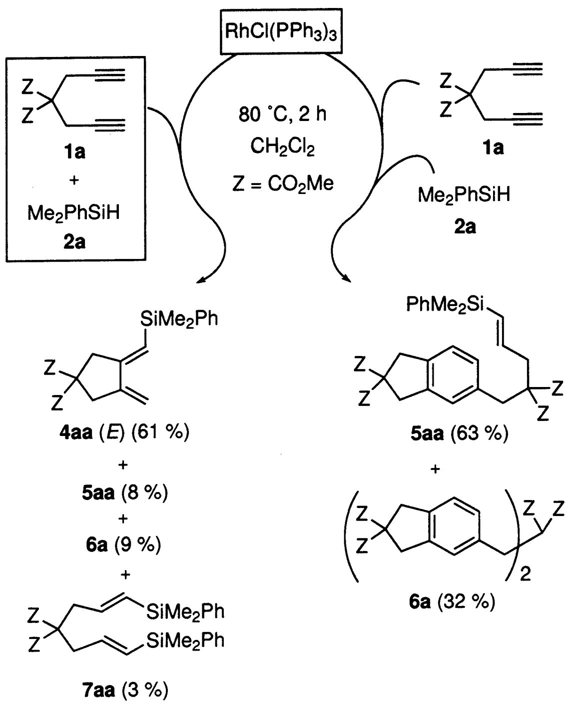
which a relatively high concentration of catalyst (5−10 mol %) was necessary. Therefore, exploitation of a highly active catalyst is desired from the point of synthetic organic chemistry.

On the other hand, we have developed the rhodium-catalyzed silylformylation of alkynes[12] and some related transformations of diynes,[13] enynes,[14] propargylic alcohols,[15] and propargylic amines.[16] Oxidative addition of a hydrosilane toward a low-valent rhodium species is regarded as the first step in the catalytic cycle of these reactions. The final products can be formed as a result of the subsequent steps, insertion of unsaturated bonds into a Rh−Si bond and insertion of CO into the resultant Rh−C bond. The results of 1,6-diynes and 1,6-enynes suggest that the C≡C bond or the C=C bond located in the specific position of the same molecule inserts into the Rh−C bond prior to CO. According to this insight, the Rh-catalyzed reaction of a 1,6-diyne with a hydrosilane would form 1,2-dialkylidenecyclopentane frameworks in the absence of CO. Thus, we designed these reactions and found that either a 1,2-dialkylidenecyclopentane or an indane derivative is obtained as a major product from the identical starting substrates depending on reaction conditions as shown in Scheme 1.[17] We describe here the details of these catalytic reactions and some characteristic reactions of **4aa** to demonstrate a part of the versatile availability of this compound.

Results and Discussion

Oxidative Addition of a Hydrosilane to Wilkinson's Complex and Silylative Cyclization of 1,6-Diynes. We initially designed the silylative cyclization

Scheme 1. Outline for Silylative Cyclization of 1a with 2a



of 4,4-dimethoxycarbonyl-1,6-heptadiyne (**1a**) with Me$_2$PhSiH (**2a**) using RhCl(PPh$_3$)$_3$ (**3a**) as a catalyst precursor (3 mol % for **1a**) because this complex is known as a good mediator for cyclization of 1,6-diyne derivatives.[18] However, the expected 1,2-dialkylidenecyclopentane **4aa** was not obtained at all. Instead of **4aa**, indane derivative **5aa** was isolated in 63% yield with the concomitant formation of a trimer of **1a** (**6a**, 32%) (right side of Scheme 1). Dominant formation of **5** suggests that a 1,6-diyne interacts with the rhodium of **3a** prior to the hydrosilane. If the hydrosilane interacts with the rhodium prior to a 1,6-diyne, 1,2-dialkylidenecyclopentane **4** should become the major product. Thus, a CH$_2$Cl$_2$ solution of an equivalent mole each of **1a** and **2a** was added into a solution of **3a**. In sharp contrast to the above result, **4aa** was obtained as a major product (61% yield) with the concomitant formation of **5aa**, **6a**, and **7aa** (left side of Scheme 1). Although **4aa** was obtained as a major product, it is desired to find a more efficient catalyst applicable to a wider type of 1,6-diynes. Thus, we focused our attention on the oxidative addition of a hydrosilane to **3a**. Although some complexes have been isolated and the structure of those were unambiguously determined by X-ray analysis,[19] we designed the reaction of hydrosilane **2** with **3a** and observed its ^{1}H NMR behavior in relation to the catalytic reactions described above.

As a representative example, 0.04 mmol of **2a** was added to a solution of **3a** (0.04 mmol) in CDCl$_3$ (0.6 mL) at −78 °C, and then the resultant solution was gradually warmed to room temperature. The sample was promptly monitored by ^{1}H NMR spectroscopy. A characteristic peak was observed at δ −15.27, which is

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Scheme 2. Oxidative Addition of Hydrosilane 2 to $RhCl(PPh_3)_3$ (3a)

$$\underset{\mathbf{3a}}{RhCl(PPh_3)_3} + \underset{\mathbf{2}}{R_3SiH} \underset{CDCl_3}{\overset{r.\,t.}{\rightleftharpoons}} \underset{\mathbf{8}}{Rh(H)(SiR_3)(Cl)(PPh_3)_2}$$

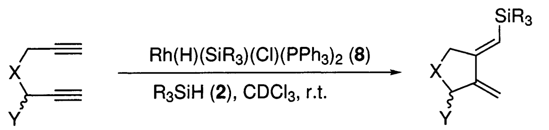
entry	R_3SiH	product	^1H NMR (δ) Rh-H(dt, Hz)	Rh-SiMe(s)
1	Me_2PhSiH (**2a**)	**8a**	-15.27 (J = 22.8 and 15.5)	0.09
2	Et_2MeSiH (**2b**)	**8b**	-15.34 (J = 23.4 and 14.7)	-0.21
3	$MePh_2SiH$ (**2c**)	**8c**	-15.07 (J = 22.2 and 16.0)	0.29
4	$EtMe_2SiH$ (**2d**)	**8d**	-15.36 (J = 23.7 and 14.9)	-0.15

assigned to the hydride signal of $Rh(H)(SiMe_2Ph)(Cl)(PPh_3)_3$, **8a**. This signal showed the coupling pattern of the doublet of a triplet (J = 22.8 and 15.5 Hz, in Scheme 2), which is similar to the one reported previously.[19,20] Because **8a** was not very stable and its decomposition was observed in the NMR sample tube within 30 min, our attempts to isolate **8a** were unsuccessful.

Other hydrosilanes also reacted with **3a** to give **8** which show the corresponding Rh−H signal in the ^1H NMR spectrum as shown in Scheme 2. Because these rhodium(III) complexes are suitable as a model for an intermediate in the silylative cyclization of 1,6-heptadiynes, the behavior of **8** was monitored in a mixture containing an equivalent mole each of **1** and **2**.

A $CDCl_3$ solution of 0.04 mmol each of **1a** and **2a** was added to a $CDCl_3$ solution of $Rh(H)(SiMe_2Ph)(Cl)(PPh_3)_2$, **8a**, prepared in advance by mixing 0.04 mmol of **3a** and 0.04 mmol of **2a** in an NMR sample tube at −78 °C. The mixture was kept for 10 min at ambient temperature until the temperature of the contents was raised to 25 °C. A few minutes later, the ^1H NMR spectrum of the mixture showed unambiguously the presence of *E*-**4aa**, the formation of which was confirmed by the appearance of three peaks, δ 4.99, 5.46, and 6.15, assigned to the vinylic protons of **4aa**. As summarized in Table 1, **8** derived from some other hydrosilanes mediated a similar silylative cyclization of **1a** with the corresponding hydrosilane (entries 2−4 in Table 1). Other diynes, **1b**−**f**, reacted with **2a** in the presence of a stoichiometric amount of **8a** at 25 °C. All of these diynes formed **4** with acceptable selectivity in the reaction time for 30−90 min (entries 5−9 in Table 1). These results suggest that a low-valent rhodium species should interact with a hydrosilane prior to the interaction with a 1,6-diyne for the selective synthesis of **4** in a catalytic reaction of **1** with **2**.

Table 1. Silylative Cyclization of 1 with 2 Mediated by a Stoichiometric Amount of $Rh(H)(SiR_3)(Cl)(PPh_3)_2$ Species[a]



1 **4**

entry	diyne **1**	X	Y	R_3SiH (**2**)	time (min)	product (%)[b]
1	**1a**	$(MeO_2C)_2C$	H	**2a**	5	**4aa** (94)
2	**1a**	$(MeO_2C)_2C$	H	**2b**	10	**4ab** (77)
3	**1a**	$(MeO_2C)_2C$	H	**2c**	10	**4ac** (80)
4	**1a**	$(MeO_2C)_2C$	H	**2d**	5	**4ad** (83)
5	**1b**	H_2C	H	**2a**	30	**4ba** (78)
6	**1c**	BnN	H	**2a**	90	**4ca** (90)
7	**1d**	$CH_2{=}CHCH_2N$	H	**2a**	30	**4da** (84)
8	**1e**	O	H	**2a**	90	**4ea** (89)
9	**1f**	$(H_3C)_2C$	OSi^tBuMe_2	**2a**	30	**4fa** (94)

[a] A $CDCl_3$ solution containing 0.04 mmol each of **1** and **2** was added to a clear solution of **8** prepared by stirring a mixture of 0.04 mmol each of **2** and **3a** for 30 min at −78 °C in $CDCl_3$. The resulting mixture was additionally stirred for a period shown at 25 °C. [b] Yield was determined by ^1H NMR analysis.

Table 2. Silylative Cyclization of 1 with 2 Catalyzed by Rhodium Complex[a]

entry	diyne **1**	R_3SiH **2**	[Rh]	products (yield %)[b] **4**[c]	**5**	**6**	**7**
1	**1a**	**2a**	**8a**	**4aa** (61)	**5aa** (10)	**6a** (5)	**7aa** (7)
2[d]	**1a**	**2a**	**3b**	**4aa** (29)	**5aa** (17)	**6a** (20)	
3[e]	**1a**	**2a**	**3c**	**4aa** (35)	**5aa** (42)	**6a** (21)	
4	**1a**	**2b**	**8b**	**4ab** (50)	**5ab** (19)	**6a** (26)	
5[f]	**1a**	**2c**	**8c**	**4ac** (25)	**5ac** (27)	**6a** (23)	
6[f]	**1a**	**2d**	**8d**	**4ad** (62)	**5ad** (10)	**6a** (5)	
7[f,g]	**1a**	**2e**	**3c**			**6a** (37)	
8	**1b**	**2a**	**8a**	**4ba** (53)		**6b** (7)	**7ba** (12)
9	**1b**	**2b**	**8b**	**4bb** (39)	**5bb** (33)	**6b** (14)	**7bb** (7)
10	**1b**	**2d**	**8d**	**4bd** (44)	**5bd** (21)	**6b** (29)	
11	**1c**	**2a**	**8a**	**4ca** (53)	**5ca** (9)		
12	**1d**	**2a**	**8a**	**4da** (52)	**5da** (10)		**7da** (6)
13	**1e**	**2a**	**8a**		**5ea** (28)		**7ea** (9)

[a] To a solution of **3** or previously produced **8** (3 mol % for **1**) in CH_2Cl_2 at 25 °C was added a solution of **1** and **2**. The resulting mixture was then heated for 2 h at 80 °C (bath temp). All the reaction was performed except for some runs. [b] Isolated yield. [c] The stereochemistry of the silylmethylene moiety was *E*-configured except for entry 2 (only *Z*-**4aa** was obtained). [d] 80 °C for 6 h. [e] 45 °C for 24 h. [f] Dimer of **1a** (**9a**) was also obtained in 12% (entry 5), 9% (entry 6), and 54% yield, respectively, with products shown in each entry. [g] 80 °C for 15 h.

Silylative Cyclization of 1,6-Heptadiynes Catalyzed by $Rh(H)(SiR_3)(Cl)(PPh_3)_2$. As described above, the selective synthesis of 1,2-dialkylidenecyclopentanes (**4**) was achieved using a stoichiometric amount of $Rh(H)(SiR_3)(Cl)(PPh_3)_2$ species (**8**). From the viewpoint of organic synthesis, however, it is strongly desired to diminish the quantity of **8** for accomplishing this transformation. Thus, a mixture of **1a** and 1.2 equiv of **2a** was added to a CH_2Cl_2 solution containing **8a** (3 mol % for **1a**) prepared from 0.02 mmol of **2a** and **3a** in situ. After refluxing the resultant mixture for 2 h, the desired **4aa** was isolated in 61% yield with the concomitant formation of **5aa** (10%), **6a** (5%), and **7aa** (7%) (entry 1 in Table 2). Although selectivity in forming **4aa** was not enhanced so much by this procedure (compare Scheme 1 with entry 1 in Table 2), **8a** is far superior to $Rh_4(CO)_{12}$ (**3b**) and a cationic rhodium complex $[Rh(cod)(dppb)]PF_6$ (**3c**, cod = 1,5-cyclooctadiene, dppb = 1,4-bis(diphenylphosphino)butane) as a catalyst precursor under similar conditions (entries 2 and 3 in Table 2). It should be emphasized that **4ab** or **4ad** become a major product with the catalysis of **8b** or **8d** in the reactions of **1a** with Et_2MeSiH (**2b**) and $EtMe_2SiH$ (**2d**), respectively (entries 4 and 6 in Table 2). In marked contrast to these results, the formation of **4ac** competed with the formation of **5ac** when $MePh_2SiH$ (**2c**) was used in the

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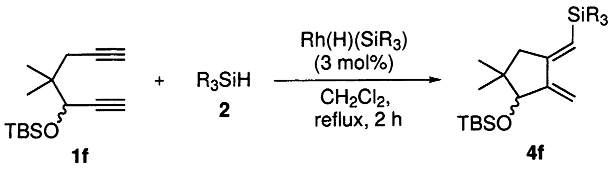
Scheme 3. Selective Synthesis of 4f



Rh(H)(SiR$_3$)
= Rh(H)(SiR$_3$)(Cl)(PPh$_3$)$_2$ (**8**)
TBSO = ^{t}BuMe$_2$SiO

4fa; R$_3$Si = Me$_2$PhSi 67 %
4fb; R$_3$Si = Et$_2$MeSi 73 %
4fd; R$_3$Si = EtMe$_2$Si 63 %

reaction with **1a** (entry 5 in Table 2). These results suggest that bulky substituents on a hydrosilane suppress the pathway to form **4**. In fact, a bulkier ^{t}BuMe$_2$SiH (**2e**) gave no silylative product (**4ae** and/or **5ae**) with the catalysis of **3c** in a reaction with **1a**, but **6a** and the dimer of **1a** (**9a**, Scheme 5) were obtained in 37 and 57% yield, respectively (entry 7 in Table 2). This result seems to reflect the lower reactivity of **2e** in the oxidative addition of **3c**.

Some other 1,6-diynes gave **4** as a major product despite the moderate selectivity (entries 8–13 in Table 2). It is notable that the *N*-allyl moiety remains intact in the product after the reaction of *N*-allyl-*N*,*N*-dipropargylamine **1d** with **2a**, in which **4da** was a major product under similar conditions (entry 12 in Table 2). This result allows deducing that two acetylenic bonds of **1d** participate in the silylative cyclization in preference to the olefinic part included in the identical molecule. Unexpectedly, **4ea** was not obtained in the reaction of dipropargyl ether **1e** with **2a** under similar conditions, but **5ea** (28%) and **7ea** (9%) were isolated (entry 13 in Table 2). The failure of this improved procedure in the reaction of **1e** is surprising, though **1e** reacted with **2a** to give **4ea** with the assist of a stoichiometric amount of **8a** in a yield comparable to other diynes (entry 8 in Table 1). This result may reflect that the reversible way to form **3a** from **8a** is prior to the consecutive insertion of the second acetylenic moiety.

In sharp contrast to the results described above, **4fa** was isolated as the sole product despite the moderate yield (67%) in the reaction of **1f** with **2a** catalyzed by **8a** (Scheme 3). This fact shows that the less hindered acetylenic part inserts into the Rh–Si bond prior to the hindered one and that the bulky ^{t}BuMe$_2$SiO group plays a sufficient role in differentiating the two acetylenic bonds in **1f**. Similar results were observed in the reaction of **1f** with other hydrosilanes, **2b** and **2d**, to give **4fb** and **4fd** in 73 and 63% yield, respectively.

Although any information on the intermediate has not been obtained at present, the catalytic cycle shown in Scheme 4 can be accepted as one of the plausible pathways to form **4** and **5**. In cycle 1, a hydride–rhodium(III)–silyl species, H-[Rh]-SiR$_3$, **10**, is formed by oxidative addition of a hydrosilane[21] to a low-valent rhodium(I) in the first step. One acetylenic moiety of **1** inserts into the Rh–Si bond of **10** to give a β-silylvinyl-[Rh] species, **11**, which is converted to **12** by the subsequent intramolecular insertion of the remaining acetylenic moiety into the Rh–C bond. Reductive elimination of **4** from **12** regenerates the low-valent rhodium species and restarts the catalytic cycle.

In cycle 2, a low-valent rhodium species interacts with **1** to give rhodacyclopentadiene **13** at the first stage. This type of oxidative coupling is well-documented in the reaction of a rhodium complex with 1,6-diyne derivatives.[18] The resulting **13** reacts with the second molecule of **1** to give the rhodacycloheptatriene derivatives **14**, from which **15** is derived by reductive elimination of the aromatic ring. The final product **5** is formed by the subsequent hydrosilylation of the remaining acetylenic bond of **15**, in which the rhodium metal is coordinated by an acetylenic bond and the resulting aromatic ring of the indane derivative. The latter type of intramolecular interaction around the rhodium seems to be a principal factor in forming **16** selectively, which is a precursor for the hydrosilylation of the remaining acetylenic bond in **15**. In this context, the regioselective formation of **5** is in sharp contrast to the controlled hydrosilylation of free **9a** with Me$_2$PhSiH by the catalytic use of **3c**. In the latter controlled experiment, a mixture of two regioisomers, **5aa** and **17**, was obtained (Scheme 5).

In addition, it is notable that the stereochemistry of the silylvinylidene moiety in **4** is regulated to the *E*-configuration in the reactions using **3a**, **3c**, and **8** as a catalyst precursor (Table 1, Table 2, and Scheme 3), whereas the *Z*-configuration is observed in the reaction catalyzed by **3b** (entry 2 in Table 2). This discrepancy of the stereochemistry can be explained by assuming the intervention of a zwitterionic structure, **18**, as shown in Scheme 6.[22] Insertion of the alkyne bond into the Rh–SiR$_3$ bond occurs in *syn* fashion to give *Z*-**11**. Electron-withdrawing ligands such as CO favor intramolecular coordination of the second alkyne bond toward the metal center. Subsequently, the spontaneous insertion of the coordinated acetylene into the Rh–C bond does not give time for the rotation around the C=C bond, which brings about the isomerization from *Z*-**11** to *E*-**11**. On the other hand, electron-donating ligands such as PPh$_3$ retard the rate of insertion at the second stage. As a result, **11**, containing electron-donating ligands, has sufficient time for the conversion from the *Z*-form to the *E*-form via **18**. The resulting *E*-**11** cyclizes to give *E*-**12**, which is the immediate precursor of *E*-**4**. Isomerization of the formed *Z*-**4** to *E*-**4** under the reaction conditions is another explanation for the formation of *E*-**4**. However, this process can be excluded on the basis of the fact that the isolated *Z*-**4aa** remained intact after refluxing a CH$_2$Cl$_2$ solution containing *Z*-**4aa**, **2a**, and **3a** or **8a** for 2 h.

In contrast to 1,6-heptadiyne derivatives, 1,7-octadiyne **19** was not suitable for the present type of silylative cyclization. Either of the two acetylenic bonds in **19** was hydrosilylated independently to give **21** (*E*:*Z* = 75:25) as a major product in the rhodium-catalyzed reaction of **19** with 1 equiv of **2a** (entry 1 in Table 3).

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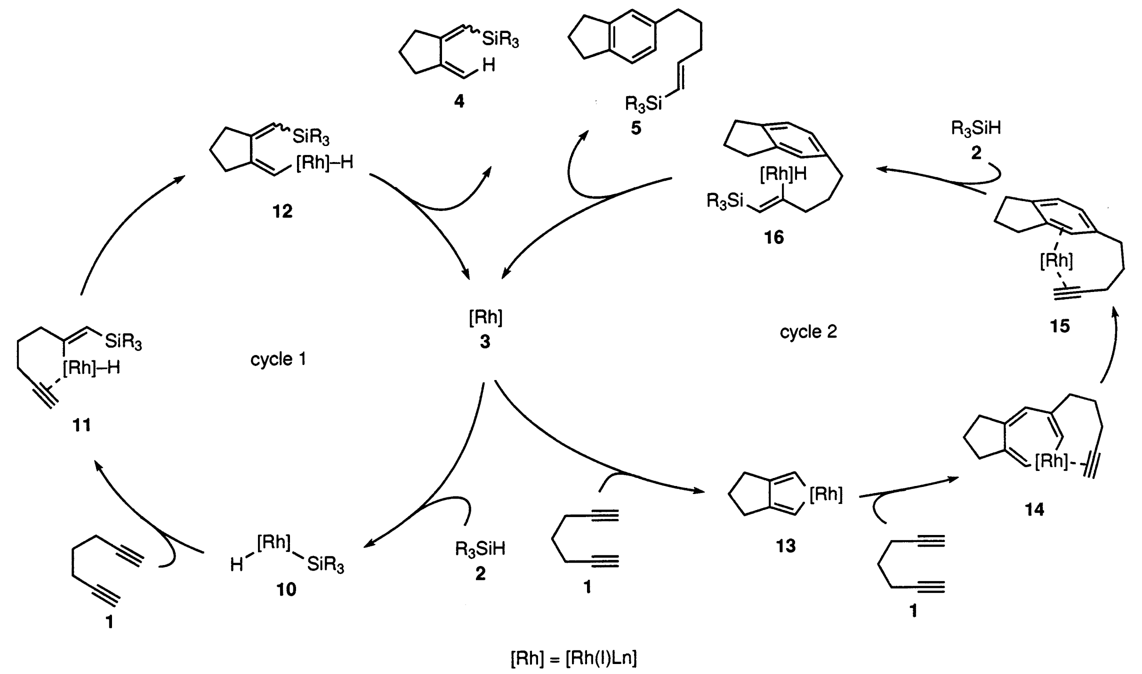
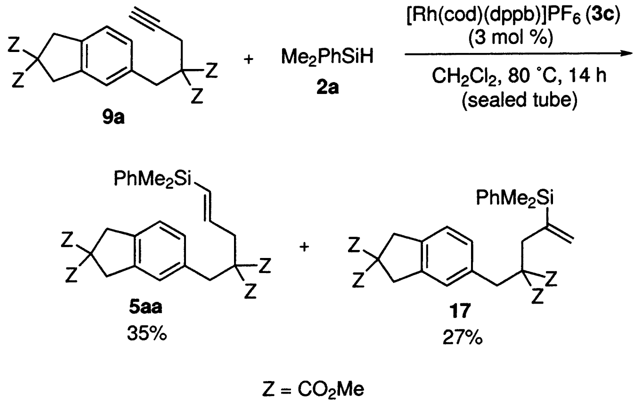
(21) (a) Ojima, I.; Li, Z.; Zhu, J. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; John Wiley & Sons: New York, 1998; Vol. 2, p 1687, and references therein. (b) Hiyama, T.; Kusumoto, T. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, U.K., 1991; Vol. 8, p 763. (c) Ojima, I. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: Chichester, U.K., 1989; p 1479.

(22) (a) Tanke, R. S.; Crabtree, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 7984. See also: (b) Ojima, I.; Clos, N.; Donovan, R. J.; Ingallina, P. *Organometallics* **1990**, *9*, 3127.

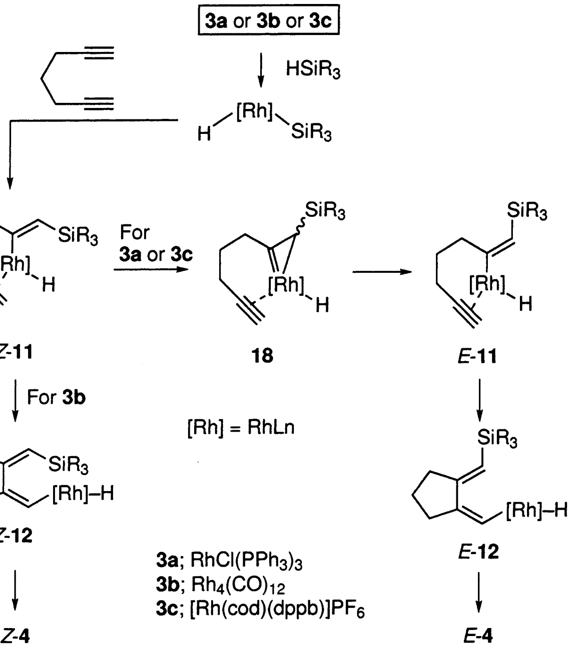
Scheme 4. Plausible Pathway for the Formation of 4 or 5



Scheme 5. Controlled Hydrosilylation of Isolated 9a with 2a Catalyzed by 3c



Scheme 6. Proposed Mechanism for the Formation of *E*-4 or *Z*-4



Cyclized product **20** was given only as a minor component. This trend was not improved by the use of **3b** instead of **8a** (entry 2 in Table 3). These results contrast with the nickel-catalyzed reaction in which 1,7-diynes react with a hydrosilane to give selectively 1,2-dialkylidenecyclohexanes, and 1,6-diynes do not afford any cyclic product.[6g]

Subsequent Modification of 1,2-Dialkylidenecyclopentane Derivatives. 1,2-Dialkylidenecyclopentanes **4** formed by rhodium-catalyzed silylative cyclization of 1,6-heptadiynes **1** possess two exo-methylene groups on the contiguous carbons. This type of compounds would behave as a diene unit in Diels–Alder reactions.[23] In fact, the reaction of **4aa** with some dienophiles proceeded readily to form [4+2] adducts. The results are summarized in Table 4. Dimethyl acetylenedicarboxylate (**23a**) reacted with **4aa** to give **24a** in 55% yield (entry 1 in Table 4). Tricyclic compounds were readily constructed by the reactions of **4aa** with cyclic dienophiles, **23b** and **23c**, respectively (entries 2 and 3 in Table 4). Because the resultant product **24** contains the partial structure regarded as a substituted allylsilane, application of a well-documented method[24] makes it possible to introduce some electrophiles at the angular position of **24**.

On the other hand, another type of allylsilane **25aa** was selectively formed in 88% yield by the hydrogenation of **4** on Pd (10% Pd–C, 1 atm of H_2, EtOH, entry 1 in Table 5). As a result, our two-step operation toward

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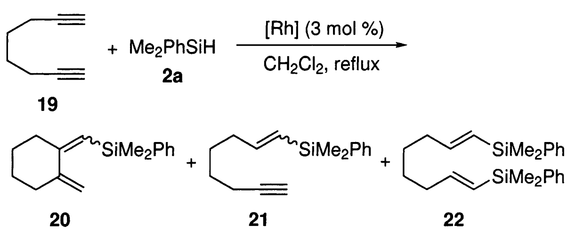
(23) Oppolzer, W. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon: Oxford, 1991; Vol. 5, p 315.

(24) (a) Luh, T.-Y.; Liu, S.-T. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; John Wiley & Sons: New York, 1998; Vol. 2, p 1793, and references therein. (b) Fleming, I.; Barbero, A.; Walter, D. *Chem. Rev.* **1997**, *97*, 2063. (c) Colvin, E. W. *Silicon in Organic Synthesis*; Butterworth: London, 1981; pp 97–124.

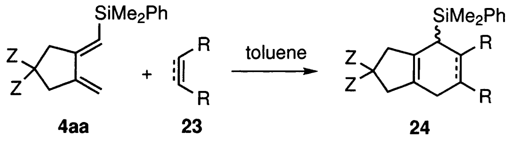
Table 3. Silylative Cyclization of 19 with 2a Catalyzed by 3[a]

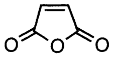
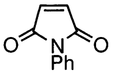


entry	[Rh]	time (h)	yield (%)[b]		
			20 (*E*:*Z*)	**21** (*E*:*Z*)	**22**
1	**8a**	3	9 (77:23)	51 (75:25)	
2	**3b**	14	16 (16:84)	29 (56:44)	trace
3	**3c**	14		40 (100:0)	14

[a] To a solution of rhodium complex (3 mol % for **19**) in CH_2Cl_2 was added a solution of **19** and **2a** at 25 °C. The resulting mixture was then refluxed for a period shown. [b] Isolated yield. The ratio of stereoisomers was determined by ^{1}H NMR analysis.

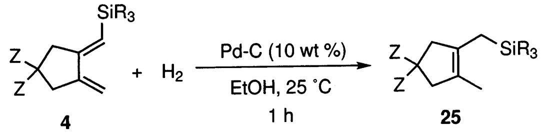
Table 4. Diels–Alder Reactions between 4a and Some Dienophiles[a]



entry	dienophile		conditions (°C / h)	yield of **24** (%)[b]
1	$MeO_2C{-}{\equiv}{-}CO_2Me$	**23a**	120 / 4	**24a** (55)
2[c]		**23b**	110 / 2	**24b** (66)[d]
3		**23c**	110 / 6	**24c** (82)[d]

[a] A toluene (1 mL) solution of the isolated **4aa** (0.25–0.3 mmol) and a dienophile (1 equiv for **4aa**) was heated under the conditions shown. [b] Isolated yield. [c] 1.2 mol equiv of dienophile was used. [d] The ratio of two diastereomers was almost 1:1.

Table 5. Hydrogenation of 4 Catalyzed by Pd–C[a]

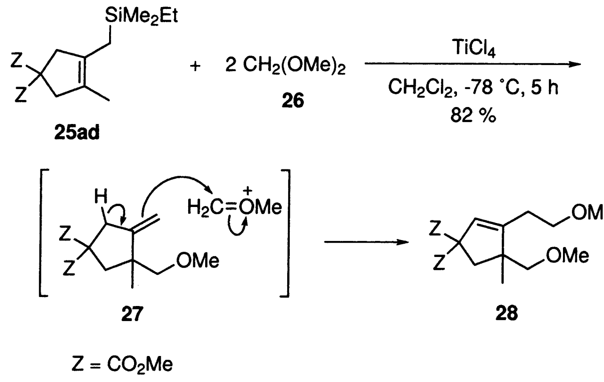


entry	**4** (R_3Si)	product (yield %)[b]
1	**4aa** (Me_2PhSi)	**25aa** (88)
2	**4ab** (Et_2MeSi)	**25ab** (83)
3	**4ad** ($EtMe_2Si$)	**25ad** (94)

[a] An EtOH (5 mL) solution of **4** (0.25–0.3 mmol) was degassed under reduced pressure and charged with H_2 at 25 °C. The resulting mixture prepared by repeating this operation three times was stirred for 1 h at 25 °C. [b] Isolated yield.

1,6-diynes, silylative cyclization and the subsequent hydrogenation of **4**, provides a new route to construct frameworks containing an allylsilyl part. Similar partial hydrogenation of the 1,3-diene part of **4** proceeded uniformly regardless of the substituents in the R_3Si group under 1 atm of hydrogen (entries 2 and 3 in Table 5).

Scheme 7. TiCl₄-Mediated Homologation of 25ad with 26



Allylsilane **25ad** reacted with dimethoxymethane **26** to give **28** (82%) in the presence of 3 equiv of $TiCl_4$ in CH_2Cl_2 at −78 °C, as shown in Scheme 7, although it did not react at all with benzaldehyde and 3-phenylpropanal in the presence of $TiCl_4$ or TBAF. The result demonstrates that allylsilane **25** is available for a two-stage carbon–carbon bond formation.

Conclusions

Selective formation of 1,2-dialkylidenecyclopentanes has been accomplished in the reactions of 1,6-heptadiyne with a hydrosilane by the catalysis of $Rh(H)(SiR_3)(Cl)(PPh_3)_2$. When a 1,6-diyne and a hydrosilane were added successively into a solution containing $RhCl(PPh_3)_3$, an indane framework was obtained as a major product. On the other hand, 1,2-dialkylidenecyclopentane was mainly produced by adding a mixture of a 1,6-diyne and a hydrosilane into the catalyst solution. The resultant 1,2-dialkylidenecyclopentane behaved as a molecule susceptible to Diels–Alder reactions and to the partial hydrogenation of the 1,3-diene unit giving allylsilanes. Thus, the present silylative cyclization provides a new route for the construction of allylsilanes the olefinic bond of which is the moiety of a cyclopentene ring.

Experimental Section

General Procedures. All silylative cyclizations were carried out in a 20 mL round-bottomed flask under N_2 or Ar atmosphere unless otherwise indicated. Anhydrous solvents were transferred via an oven-dried syringe. The following solvents and reagents were distilled prior to use: CH_2Cl_2 and toluene from CaH_2; EtOH from magnesium metal. $CDCl_3$ and all other solvents were utilized at their commercial level of purity. The following preparations were based on standard literature procedures: $Rh_4(CO)_{12}$,[25] $RhCl(PPh_3)_3$,[26] $[Rh(cod)(dppb)]PF_6$,[27] **1a**,[28] **1c**,[29] **1d**,[30] and **1e**.[31] Diyne **1f**[32a] was prepared from 2,2-dimethyl-4-propyn-1-al.[32b] Nucleophilic attack for this aldehyde with ethynylmagnesium bromide[32c] gave a secondary alcohol which was protected with ^{t}BuMe$_2$SiOTf in the presence of Et_3N. Diyne **1b**, silanes, and other reagents were obtained from Aldrich, Lancaster, Tokyo Kasei, Shin-Etsu Chemicals, or Wako Chemicals. Those were used as received.

All reactions were monitored by thin-layer chromatography carried out on 0.25 mm E. Merck silica gel plates (60 F-254) using UV light as visualizing agent and 7% ethanolic phosphomolybdic acid and heat as developing agent. E. Merck silica gel (60, particle size 0.063–0.200 mm) was used for column chromatography. Proton nuclear magnetic resonance (^{1}H NMR) data were obtained at 200 MHz on Varian GEM-200, 300 MHz on a Varian Mercury 300 spectrometer, or 500 MHz on a Varian INOVA-500 spectrometer. Chemical shifts are reported in delta (δ) units, in parts per million (ppm) relative to the singlet at 7.26 ppm for chloroform-*d*. Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; m, multiplet; and b, broad. Coupling constants are reported in hertz (Hz). Carbon-13 nuclear magnetic resonance (^{13}C NMR) data were obtained at 50 MHz on a Varian GEM-200, at 75 MHz on a Varian Mercury 300 spectrometer, or at 125.7 MHz on a Varian INOVA-500 spectrometer and are reported in ppm with the center line of a triplet at 77.00 ppm for chloroform-*d*. Routine ^{13}C spectra were fully decoupled by broad-band decoupling. Infrared data were recorded in 0.2 mm path length sodium chloride cavity cells on a JASCO IR-810 spectrometer. Absorbance frequencies are reported in reciprocal centimeters (cm^{-1}). Melting points were obtained on a Büchi 510-K apparatus in sealed capillary tubes and are uncorrected. Boiling points are also uncorrected. Kügelrohr distillation was performed in a SIBATA GTO-350RS oven. Elemental analyses were performed by the Microanalytical Center of Kyoto University.

Typical Procedure for Silylative Cyclization of 1,6-Diynes Catalyzed by Rhodium Complex (cycle 2 in Scheme 5). To a solution of RhCl(PPh$_3$)$_3$ (**3a**, 13.5 mg, 0.014 mmol) in 2 mL of CH_2Cl_2 were added a CH_2Cl_2 solution (2 mL) of 4,4-bis(carbomethoxy)-1,6-heptadiyne (**1a**, 100 mg, 0.48 mmol) and a solution of Me$_2$PhSiH (**2a**, 65.5 mg, 0.48 mmol) in CH_2Cl_2 (1 mL) in this fashion. The resulting mixture was refluxed for 2 h. The solvent was evaporated and the residue was purified by flash column chromatography (eluent hexane/ethyl acetate = 50:1−5:1). As a result, **5aa** (83.3 mg, 0.15 mmol) was obtained in 63% yield as colorless liquid with a concomitant formation of **6a** (a colorless solid, 51.5 mg, 0.082 mmol, 32% yield), which was recrystallized from a mixed solvent of hexane and ethyl acetate to give colorless needles.

Property of 5aa: colorless liquid, bp 320 °C/4 Torr, eluent hexane/ethyl acetate = 10:1. IR (neat): 1736 (C=O), 1252 (Si−CH$_3$) cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$): δ 0.33 (s, 6H, SiCH_3), 2.62 (d, J = 6.8 Hz, 2H, =CCH_2), 3.18 (s, 2H, CH_2), 3.53−3.54 (m, 4H, CH_2, cyclic), 3.65 (s, 6H, OCH_3), 3.74 (s, 6H, OCH_3), 5.88 (d, J = 18.4 Hz, 1H, =CHSi), 6.00 (dt, J = 18.4, and 6.8 Hz, 1H, CH=CSi), 6.85 (d, J = 7.8 Hz, 1H, Ar), 6.87 (s, 1H, Ar), 7.06 (d, J = 7.8 Hz, 1H, Ar), 7.35−7.37 (m, 3H, SiC$_6H_5$), 7.50−7.52 (m, 2H, SiC$_6H_5$). ^{13}C NMR (125 MHz, CDCl$_3$): δ −2.69 (SiCH$_3$), 38.45 (=CCH$_2$), 39.73 (CH$_2$), 40.28 (CH$_2$, cyclic), 40.47 (CH$_2$, cyclic), 52.24 (OCH$_3$), 52.95 (OCH$_3$), 59.20 (C(CO$_2$Me)$_2$), 60.34 (C(CO$_2$Me)$_2$), 124.02 (Ar), 125.71 (Ar), 127.76 (SiC_6H$_5$ and Ar), 128.67 (=CHSi or SiC_6H$_5$), 128.99 (=CHSi or SiC_6H$_5$), 133.78 (SiC_6H$_5$), 134.66 (Ar), 138.45 (SiC_6H$_5$), 138.62 (Ar), 140.02 (Ar), 142.22 (C=CSi), 171.15 (C=O), 172.03 (C=O). Anal. Calcd for $C_{30}H_{36}O_8Si$: C, 65.19; H, 6.57. Found: C, 64.90; H, 6.40.

Property of 6a: colorless needles from ethyl acetate and hexane, mp 123.0−125.0 °C, eluent hexane/ethyl acetate = 5:1. IR (KBr): 1738 (C=O) cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ 3.15 (s, 4H, CH_2), 3.55 (s, 8 H, CH_2, cyclic), 3.61 (s, 6H, OCH_3), 3.74 (s, 12H, OCH_3), 6.92−7.11 (m, 6H, Ar). ^{13}C NMR (50 MHz, CDCl$_3$): δ 39.07 (CH$_2$), 40.13 (CH$_2$, cyclic), 40.33 (CH$_2$, cyclic), 52.03 (OCH$_3$), 52.85 (OCH$_3$), 60.28 (C(CO$_2$Me)$_2$), 60.45 (C(CO$_2$Me)$_2$), 124.07 (Ar), 125.94 (Ar), 128.91 (Ar), 135.07 (Ar), 138.72 (Ar), 140.12 (Ar), 171.55 (C=O), 172.28 (C=O). Anal. Calcd for $C_{33}H_{36}O_{12}$: C, 63.45; H, 5.81. Found: C, 63.31; H, 5.84.

Typical Procedure for Silylative Cyclization of 1,6-Diynes Catalyzed by Rhodium Complex (cycle 1 in Scheme 5). To a solution of 40.8 mg (0.044 mmol) of RhCl(PPh$_3$)$_3$ (**3a**) in 2 mL of CH_2Cl_2 was added a mixture of 300.5 mg (1.44 mmol) of **1a** and 197.3 mg (1.45 mmol) of **2a** in CH_2Cl_2 (2 mL), and the resulting mixture was refluxed for 2 h at 80 °C (bath temp). Volatile components were evaporated, and the residue was purified by flash column chromatography (eluent hexane/ethyl acetate = 50:1−5:1). As a result, **4aa** (304.3 mg, 0.88 mmol) was obtained in 61% yield as a colorless liquid with a concomitant formation of **5aa** (colorless liquid, 33.3 mg, 0.060 mmol, 8% yield), **6a** (colorless solid, 28.1 mg, 0.045 mmol, 9% yield), and **7aa** (colorless liquid, 20.2 mg, 0.042 mmol, 3% yield). Pure **6a** was obtained as colorless needles by recrystallization from hexane and ethyl acetate.

Property of 4aa (*E*): colorless liquid, eluent hexane/ethyl acetate = 50:1. IR (neat): 1739 (C=O), 1249 (Si−CH$_3$) cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$): δ 0.42 (s, 6H, SiCH_3), 2.96 (d, J = 2.3 Hz, 2H, CH_2), 3.03 (dd, J = 2.2 and 2.1 Hz, 2H, CH_2), 3.68 (s, 6H, OCH_3), 4.99 (t, J = 2.1 Hz, 1H, =CH_2), 5.46 (t, J = 2.2 Hz, 1H, =CH_2), 6.15 (t, J = 2.3 Hz, 1H, =CHSi), 7.35−7.37 (m, 3H, SiC$_6H_5$), 7.53−7.56 (m, 2H, SiC$_6H_5$). ^{13}C NMR (125 MHz, CDCl$_3$): δ −1.64 (SiCH$_3$), 40.38 (CH$_2$), 40.99 (CH$_2$), 52.78 (OCH$_3$), 57.55 (C(CO$_2$Me)$_2$), 106.10 (=CH$_2$), 117.23 (=CHSi), 127.78 (SiC_6H$_5$), 128.93 (SiC_6H$_5$), 133.73 (SiC_6H$_5$), 138.66 (SiC_6H$_5$), 145.59 (C=CH$_2$), 153.30 (C=CHSi), 171.53 (C=O). Anal. Calcd for $C_{19}H_{24}O_4Si$: C, 66.25; H, 7.02. Found: C, 66.01; H, 7.08.

Property of 7aa: colorless liquid, bp 230 °C/4 Torr, eluent hexane/ethyl acetate = 50:1. IR (neat): 1736 (C=O), 1247 (Si−CH$_3$) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ 0.30 (s, 12H, SiCH_3), 2.71 (d, J = 5.9 Hz, 4H, CH_2), 3.63 (s, 6H, OCH_3), 5.82 (d, J = 18.3 Hz, 2H, =CHSi), 5.92 (dt, J = 18.3 and 5.9 Hz, 2H, CH=CSi), 7.32−7.35 (m, 6H, SiC$_6H_5$), 7.46−7.49 (m, 4H, SiC$_6H_5$). ^{13}C NMR (75 MHz, CDCl$_3$): δ −2.59 (SiCH$_3$), 40.29 (CH$_2$), 52.24 (OCH$_3$), 57.75 (C(CO$_2$Me)$_2$), 127.59 (SiC_6H$_5$), 128.81 (SiC_6H$_5$), 133.61 (SiC_6H$_5$), 133.64 (C=CSi), 138.26 (SiC_6H$_5$), 141.68 (C=CSi), 170.83 (C=O). Anal. Calcd for $C_{27}H_{36}O_4Si_2$: C, 67.46; H, 7.55. Found: C, 67.22; H, 7.81.

Oxidative Addition of 2 to 3a in an NMR Tube (Scheme 2). The reaction was performed in an NMR tube. To a solution of RhCl(PPh$_3$)$_3$ (36.2 mg, 0.04 mmol) in CDCl$_3$ (0.3 mL) was added a solution of **2a** (5.2 mg, 0.04 mmol) in CDCl$_3$ (0.3 mL) at −78 °C under an argon atmosphere. The tube was degassed and backfilled with argon twice and sealed. The content was gradually warmed to ambient temperature and measured in the ^{1}H NMR spectrum. Selected spectral data in ^{1}H NMR were cited in Scheme 2.

Silylative Cyclization of 1 with 2 Mediated by Rh(H)(SiR$_3$)(Cl)(PPh$_3$)$_2$ in an NMR Tube. Typical Procedure in Table 1. The reaction was performed in an NMR tube. To a solution of RhCl(PPh$_3$)$_3$ (36.2 mg, 0.04 mmol) in CDCl$_3$ (0.3 mL) was added a solution of **2a** (5.2 mg, 0.04 mmol) in CDCl$_3$ (0.3 mL) at −78 °C under argon atmosphere. The mixture was degassed and backfilled with argon twice, and then the tube was sealed. The content was gradually raised to ambient temperature and measured in the ^{1}H NMR spectrum. After 120 min, the sealed tube was opened and a mixture of **1a** (8.0 mg, 0.04 mmol) and **2a** (6.2 mg, 0.05 mmol) in CDCl$_3$ (0.2 mL) was added at −78 °C. The tube was degassed and backfilled with argon twice and resealed. The content was gradually raised to ambient temperature and analyzed in the ^{1}H NMR spectrum. The reaction was complete after 30 min.

Property of 4ab: colorless liquid, eluent hexane/ethyl acetate = 50:1. IR (neat): 1738 (C=O), 1250 (Si−CH$_3$) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ 0.08 (s, 3H, SiCH_3), 0.60 (q, J = 8.0 Hz, 4H, SiCH_2CH$_3$), 0.92 (t, J = 8.0 Hz, 6H, SiCH$_2$CH_3),

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3.00−3.02 (m, 4H, CH_2), 3.70 (s, 6H, OCH_3), 4.91 (bs, 1H, =CH_2), 5.37 (t, J = 2.1 Hz, 1H, =CH_2), 5.95 (t, J = 2.1 Hz, 1H, =C*H*Si). ^{13}C NMR (75 MHz, CDCl$_3$): δ −5.04 (Si*C*H$_3$), 5.92 (Si*C*H$_2$CH$_3$), 7.47 (SiCH$_2$*C*H$_3$), 40.44 (*C*H$_2$), 41.18 (*C*H$_2$), 52.74 (O*C*H$_3$), 57.63 (*C*(CO$_2$Me)$_2$), 105.36 (=*C*H$_2$), 117.26 (=*C*HSi), 145.45 (*C*=CH$_2$), 152.12 (*C*=CHSi), 171.37 (*C*=O). Anal. Calcd for $\mathrm{C_{16}H_{26}O_4Si}$: C, 61.90; H, 8.44. Found: C, 61.64; H, 8.66.

Property of 4ac: colorless liquid, eluent hexane/ethyl acetate = 50:1. IR (neat): 1736 (C=O), 1251 (Si−CH$_3$) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ 0.71 (s, 3H, SiCH_3), 2.86 (d, J = 2.4 Hz, 2H, CH_2), 3.03 (dd, J = 2.4 and 1.9 Hz, 2H, CH_2), 3.66 (s, 6H, OCH_3), 5.03 (t, J = 1.9 Hz, 1H, =CH_2), 5.53 (t, J = 2.4 Hz, 1H, =CH_2), 6.32 (t, J = 2.4 Hz, 1H, =C*H*Si), 7.33−7.40 (m, 6H, SiC$_6H_5$), 7.46−7.58 (m, 4H, SiC$_6H_5$). ^{13}C NMR (75 MHz, CDCl$_3$): δ −2.61 (Si*C*H$_3$), 40.50 (*C*H$_2$), 41.27 (*C*H$_2$), 52.77 (O*C*H$_3$), 57.60 (*C*(CO$_2$Me)$_2$), 106.50 (=*C*H$_2$), 115.20 (=*C*HSi), 127.80 (Si*C*$_6$H$_5$), 129.16 (Si*C*$_6$H$_5$), 134.58 (Si*C*$_6$H$_5$), 136.56 (Si*C*$_6$H$_5$), 145.62 (*C*=CH$_2$), 154.81 (*C*=CHSi), 171.32 (*C*=O). Anal. Calcd for $\mathrm{C_{24}H_{26}O_4Si}$: C, 70.90; H, 6.45. Found: C, 70.61; H, 6.68.

Property of 4ad: colorless liquid, eluent hexane/ethyl acetate = 40:1. IR (neat): 1738 (C=O), 1248 (Si−CH$_3$) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ 0.12 (s, 6H, SiCH_3), 0.61 (q, J = 7.8 Hz, 2H, SiCH_2CH$_3$), 0.94 (t, J = 7.8 Hz, 3H, SiCH$_2$CH_3), 3.02−3.04 (m, 4H, CH_2), 3.73 (s, 6H, CO$_2$CH_3), 4.93 (m, 1H, =CH_2), 5.39 (t, J = 2.4 Hz, 1H, =CH_2), 5.99 (t, J = 2.2 Hz, 1H, =C*H*Si). ^{13}C NMR (75 MHz, CDCl$_3$): δ −2.70 (Si*C*H$_3$), 7.51 (Si*C*H$_2$CH$_3$), 7.82 (SiCH$_2$*C*H$_3$), 40.50 (*C*H$_2$), 41.11 (*C*H$_2$), 52.86 (O*C*H$_3$), 57.71 (*C*(CO$_2$Me)$_2$), 105.49 (=*C*H$_2$), 118.46 (=*C*HSi), 145.52 (*C*=CH$_2$), 151.87 (*C*=CHSi), 171.47 (*C*=O). Anal. Calcd for $\mathrm{C_{15}H_{24}O_4Si}$: C, 60.78; H, 8.16. Found: C, 60.56; H, 8.10.

Property of 4ba: colorless liquid, eluent hexane. IR (neat): 2955 (C−H), 1247 (Si−CH$_3$) cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$): δ 0.39 (s, 6H, SiCH_3), 1.63 (tt, J = 7.5 and 7.2 Hz, 2H, CH_2), 2.33 (dt, J = 7.2 and 2.2 Hz, 2H, CSi=CCH_2), 2.41 (ddt, J = 7.5, 2.3 and 2.2 Hz, 2H, C=CCH_2), 4.91 (t, J = 2.2 Hz, 1H, =CH_2), 5.40 (t, J = 2.2 Hz, 1H, =CH_2), 6.08 (t, J = 2.3 Hz, 1H, =C*H*Si), 7.34−7.36 (m, 3H, SiC$_6H_5$), 7.54−7.56 (m, 2H, SiC$_6H_5$). ^{13}C NMR (125 MHz, CDCl$_3$): δ −1.46 (Si*C*H$_3$), 23.98 (*C*H$_2$), 33.42 (*C*H$_2$), 33.90 (*C*H$_2$), 104.11 (=*C*H$_2$), 114.51 (=*C*HSi), 127.74 (Si*C*$_6$H$_5$), 128.79 (Si*C*$_6$H$_5$), 133.77 (Si*C*$_6$H$_5$), 139.42 (Si*C*$_6$H$_5$), 150.21(*C*=CH$_2$), 158.24 (*C*=CHSi). Anal. Calcd for $\mathrm{C_{15}H_{20}Si}$: C, 78.88; H, 8.83. Found: C, 78.63; H, 8.76.

Property of 4ca: pale yellow liquid, eluent hexane/ethyl acetate = 40:1. IR (neat): 2954 (C−H), 1247 (Si−CH$_3$) cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$): δ 0.37 (s, 6H, SiCH_3), 3.21 (d, J = 2.1 Hz, 2H, CH_2), 3.25 (dd, J = 2.1 and 2.0 Hz, 2H, CH_2), 3.59 (s, 2H, CH_2), 4.90 (m, 1H, =CH_2), 5.42 (t, J = 2.1 Hz, 1H, =CH_2), 6.09 (t, J = 2.1 Hz, 1H, =C*H*Si), 7.24−7.30 (m, 5H, C$_6H_5$), 7.33−7.35 (m, 3H, SiC$_6H_5$), 7.50−7.52 (m, 2H, SiC$_6H_5$). ^{13}C NMR (75 MHz, CDCl$_3$): δ −1.53 (Si*C*H$_3$), 58.89 (*C*H$_2$), 59.66 (*C*H$_2$), 60.53 (*C*H$_2$), 103.71 (=*C*H$_2$), 114.71 (=*C*HSi), 126.94 (Ar), 127.72 (Si*C*$_6$H$_5$), 128.14 (Ar), 128.71 (Ar), 128.90 (Si*C*$_6$H$_5$), 133.65 (Si*C*$_6$H$_5$), 138.15 (Ar or Si*C*$_6$H$_5$), 138.48 (Ar or Si*C*$_6$H$_5$), 145.74 (*C*=CH$_2$), 153.24 (*C*=CHSi). Anal. Calcd for $\mathrm{C_{21}H_{25}NSi}$: C, 78.94; H, 7.89; N, 4.38. Found: C, 78.73; H, 7.84; N, 4.39.

Property of 4da: pale yellow liquid, eluent hexane/ethyl acetate = 30:1. IR (neat): 1248 (Si−CH$_3$) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ 0.39 (s, 6H, SiCH_3), 3.07 (ddd, J = 6.5, 1.5, and 1.1 Hz, 2H, NCH_2), 3.20 (d, J = 2.0 Hz, 2H, CH_2), 3.28 (dd, J = 2.2 and 2.2 Hz, 2H, CH_2), 4.94 (t, J = 2.0 Hz, 1H, C=CH_2), 5.09 (ddt, J = 10.2, 1.5, and 1.1 Hz, 1H, CH=CH_2), 5.16 (ddt, J = 15.9, 1.5, and 1.5 Hz, 1H, CH=CH_2), 5.43 (t, J = 2.2 Hz, 1H, =CH_2), 5.85 (ddt, J = 15.9, 10.2, and 6.5 Hz, 1H, C*H*=CH$_2$), 6.10 (t, J = 2.2 Hz, 1H, =C*H*Si), 7.33−7.37 (m, 3H, SiC$_6H_5$), 7.52−7.55 (m, 2H, SiC$_6H_5$). ^{13}C NMR (75 MHz, CDCl$_3$): δ −1.49 (Si*C*H$_3$), 58.93 (*C*H$_2$), 59.15 (*C*H$_2$), 59.44 (*C*H$_2$), 103.69 (C=*C*H$_2$), 114.70 (=*C*Si), 117.23 (CH=*C*H$_2$), 127.74 (Si*C*$_6$H$_5$), 128.91 (Si*C*$_6$H$_5$), 133.66 (Si*C*$_6$H$_5$), 135.14 (*C*H=CH$_2$), 138.52 (Si*C*$_6$H$_5$), 145.68 (*C*=CH$_2$), 153.19 (*C*=CHSi). Anal. Calcd for $\mathrm{C_{17}H_{23}NSi}$: C, 75.78; H, 8.60; N, 5.20. Found: C, 75.57; H, 8.70; N, 4.94.

Spectral data for 4ea: (This compound was not isolated. Characteristic signals corresponding to **4ea** were detected in a mixture of stoichiometric amount of **1e**, **2a**, and **17a**. Therefore, signals around the aryl region could not be assigned precisely.) ^{1}H NMR (300 MHz, CDCl$_3$): δ 0.34 (s, 6H, SiCH_3), 4.29 (d, J = 2.1 Hz, 2H, CH_2), 4.42 (dd, J = 2.7 and 1.5 Hz, 2H, CH_2), 4.96 (m, 1H, =CH_2), 5.46 (t, J = 2.7 Hz, 1H, =CH_2), 6.14 (t, J = 2.1 Hz, 1H, =C*H*Si).

Property of 4fa: colorless liquid, eluent hexane. IR (neat): 2956 (C−H), 1249 (Si−CH$_3$) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ 0.09 (s, 3H, SiCH_3), 0.10 (s, 3H, SiCH_3), 0.380 (s, 3H, SiCH_3), 0.384 (s, 3H, SiCH_3), 0.74 (s, 3H, CH_3), 0.95 (s, 9H, SiC(CH_3)$_3$), 0.98 (s, 3H, CH_3), 2.03 (dd, J = 16.2 and 2.9 Hz, 1H, CH_2), 2.20 (dd, J = 16.2 and 2.0 Hz, 1H, CH_2), 4.05 (dd, J = 2.4 and 2.1 Hz, 1H, OC*H*), 4.99 (d, J = 2.1 Hz, 1H, =CH_2), 5.48 (d, J = 2.4 Hz, =CH_2), 6.13 (dd, J = 2.9 and 2.0 Hz, 1H, =C*H*Si), 7.34−7.36 (m, 3H, SiC$_6H_5$), 7.53−7.56 (m, 2H, SiC$_6H_5$). ^{13}C NMR (75 MHz, CDCl$_3$): δ −4.28 (Si*C*H$_3$), −4.06 (Si*C*H$_3$), −1.22 (Si*C*H$_3$), −1.13 (Si*C*H$_3$), 18.30 (Si*C*Me$_3$), 20.25 (*C*H$_3$), 26.03 (SiC(*C*H$_3$)$_3$), 26.20 (*C*H$_3$), 40.16 (*C*Me$_2$), 44.71 (*C*H$_2$), 82.11 (O*C*H), 105.61 (=*C*H$_2$), 116.30 (=*C*HSi), 127.65 (Si*C*$_6$H$_5$), 128.72 (Si*C*$_6$H$_5$), 133.68 (Si*C*$_6$H$_5$), 139.24 (Si*C*$_6$H$_5$), 152.31 (*C*=CH$_2$), 154.08 (*C*=CHSi). Anal. Calcd for $\mathrm{C_{23}H_{38}OSi_2}$: C, 71.43; H, 9.90. Found: C, 71.39; H, 10.00.

Typical Procedure for Silylative Cyclization of 1,6-Diynes Catalyzed by Rh(H)(SiR$_3$)(Cl)(PPh$_3$)$_2$ Cited in Table 2. To a solution of **3a** (20.3 mg, 0.022 mmol) in 2 mL of CH$_2$Cl$_2$ was added a CH$_2$Cl$_2$ solution (0.1 mL) of **2a** (2.9 mg, 0.021 mmol), and the resulting mixture was stirred for 10 min. To this solution a mixture of **1a** (152.2 mg, 0.73 mmol) and **2a** (101.9 mg, 0.75 mmol) in CH$_2$Cl$_2$ (2 mL) was added, and then the mixture was refluxed for 2 h at 80 °C (bath temp). Volatile components were evaporated, and the residue was purified by flash column chromatography (eluent hexane/ethyl acetate = 50:1−5:1). As a result, **4aa** (154.1 mg, 0.45 mmol) was obtained in 61% yield as a colorless liquid with a concomitant formation of **5aa** (colorless liquid, 19.8 mg, 0.036 mmol, 10% yield), **6a** (colorless solid, 8.1 mg, 0.013 mmol, 5% yield), and **7aa** (colorless liquid, 25.0 mg, 0.052 mmol, 7% yield).

Property of 4aa (*Z*): colorless liquid, eluent hexane/ethyl acetate = 50:1. IR (neat): 1736 (C=O), 1252 (Si−CH$_3$) cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$): δ 0.37 (s, 6H, SiCH_3), 3.02 (dd, J = 2.3 and 2.0 Hz, 2H, CH_2), 3.15 (d, J = 1.8 Hz, 2H, CH_2), 3.74 (s, 6H, OCH_3), 4.92 (t, J = 2.0 Hz, 1H, =CH_2), 5.10 (t, J = 2.3 Hz, 1H, =CH_2), 5.69 (t, J = 1.8 Hz, 1H, =C*H*Si), 7.31−7.36 (m, 3H, SiC$_6H_5$), 7.48−7.52 (m, 2H, SiC$_6H_5$). ^{13}C NMR (125 MHz, CDCl$_3$): δ −1.51 (Si*C*H$_3$), 41.99 (*C*H$_2$), 45.45 (*C*H$_2$), 52.81 (O*C*H$_3$), 56.98 (*C*(CO$_2$Me)$_2$), 112.05 (=*C*H$_2$), 121.38 (=*C*HSi), 127.76 (Si*C*$_6$H$_5$), 127.81 (Si*C*$_6$H$_5$), 133.68 (Si*C*$_6$H$_5$), 139.01 (Si*C*$_6$H$_5$), 144.39 (*C*=CH$_2$), 154.78 (*C*=CHSi), 171.73 (*C*=O). Anal. Calcd for $\mathrm{C_{19}H_{24}O_4Si}$: C, 66.25; H, 7.02. Found: C, 66.01; H, 7.08.

Property of 5ab: colorless liquid, bp 320 °C/6 Torr, eluent hexane/ethyl acetate = 10:1. IR (neat): 1737 (C=O), 1252 (Si−CH$_3$) cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$): δ 0.00 (s, 3H, SiCH_3), 0.54 (q, J = 7.9 Hz, 4H, SiCH_2CH$_3$), 0.92 (t, J = 7.9 Hz, 6H, SiCH$_2$CH_3), 2.60 (d, J = 6.7 Hz, 2H, =CCH_2), 3.18 (s, 2H, CH_2), 3.54 (s, 4H, CH_2, cyclic), 3.68 (s, 6H, OCH_3), 3.74 (s, 6H, OCH_3), 5.73 (d, J = 18.5 Hz, 1H, =C*H*Si), 5.91 (dt, J = 18.5 and 6.7 Hz, 1H, C*H*=CSi), 6.87 (d, J = 8.0 Hz, 1H, Ar), 6.90 (s, 1H, Ar), 7.07 (d, J = 8.0 Hz, 1H, Ar). ^{13}C NMR (125 MHz, CDCl$_3$): δ −6.04 (Si*C*H$_3$), 5.32 (Si*C*H$_2$CH$_3$), 7.28 (SiCH$_2$*C*H$_3$), 38.56 (=C*C*H$_2$), 39.82 (*C*H$_2$), 40.28 (*C*H$_2$, cyclic), 40.46 (*C*H$_2$, cyclic), 52.20 (O*C*H$_3$), 52.92 (O*C*H$_3$), 59.19 (*C*(CO$_2$Me)$_2$), 60.35 (*C*(CO$_2$Me)$_2$), 123.98 (Ar), 125.71 (Ar), 128.67 (Ar), 133.46 (=*C*Si), 134.75 (Ar), 138.58 (Ar), 139.98 (Ar), 141.18 (*C*=CSi), 171.18 (*C*=O), 172.01 (*C*=O). Anal. Calcd for $\mathrm{C_{27}H_{38}O_8Si}$: C, 62.52; H, 7.38. Found: C, 62.40; H, 7.22.

Property of 5ac: colorless liquid, bp 320 °C/0.3 Torr, eluent hexane/ethyl acetate = 10:1. IR (neat): 1735 (C═O), 1251 (Si−CH$_3$) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ 0.63 (s, 3 H, SiCH_3), 2.67 (d, J = 5.4 Hz, 2H, ═CCH_2), 3.19 (s, 2H, CH_2), 3.52 (s, 2H, CH_2), 3.55 (s, 2H, CH_2), 3.64 (s, 6H, CO$_2$CH_3), 3.74 (s, 6H, CO$_2$CH_3), 5.99−6.13 (m, 2H, HC═CHSi), 6.80 (d, J = 8.0 Hz, 1H, Ar), 6.85 (s, 1H, Ar), 7.05 (d, J = 8.0 Hz, 1H, Ar), 7.35−7.41 (m, 6H, SiC$_6H_5$), 7.51−7.55 (m, 4H, SiC$_6H_5$). ^{13}C NMR (75 MHz, CDCl$_3$): δ −3.78 (SiCH$_3$), 38.50 (CH$_2$), 39.78 (CH$_2$), 40.33 (CH$_2$), 40.51 (CH$_2$), 52.27 (CO$_2$$CH_3$), 52.96 (CO$_2$$CH_3$), 59.20 ($C$(CO$_2$Me)$_2$), 60.35 ($C$(CO$_2$Me)$_2$), 123.92 (Ar), 125.58 (Ar), 127.71 (SiC_6H$_5$), 128.54 (═CSi), 129.19 (SiC_6H$_5$), 134.50 (Ar), 134.66 (SiC_6H$_5$), 134.94 (Ar), 136.17 (Ar), 138.50 (Ar), 139.91 (SiC_6H$_5$), 144.35 (C═CSi), 170.92 (C═O), 171.82 (C═O). Anal. Calcd for $C_{35}H_{38}O_8Si$: C, 68.38; H, 6.23. Found: C, 68.09; H, 6.30.

Property of 9a: colorless needles from ethyl acetate and hexane, mp 112.0−114.0 °C, eluent hexane/ethyl acetate = 5:1. IR (KBr): 1732 (C═O) cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ 2.14 (t, J = 2.7 Hz, 1H, C≡CH), 2.68 (d, J = 2.7 Hz, 2H, ≡CCH_2), 3.35 (s, 2H, CH_2), 3.55 (s, 4H, CH_2, cyclic), 3.74 (s, 12H, OCH_3), 6.93 (d, J = 7.8 Hz, 1H, Ar), 6.97 (s, 1H, Ar), 7.09 (d, J = 7.8 Hz, 1H, Ar). ^{13}C NMR (50 MHz, CDCl$_3$): δ 21.98 (≡CCH$_2$), 37.11 (CH$_2$), 40.15 (CH$_2$, cyclic), 40.35 (CH$_2$, cyclic), 52.65 (OCH$_3$), 52.88 (OCH$_3$), 58.19 (C(CO$_2$Me)$_2$), 60.24 (C(CO$_2$Me)$_2$), 72.17 (HC≡C), 79.20 (HC≡C), 124.31 (Ar), 125.65 (Ar), 128.66 (Ar), 134.36 (Ar), 139.03 (Ar), 140.38 (Ar), 170.31 (C═O), 172.29 (C═O). Anal. Calcd for $C_{22}H_{24}O_8$: C, 63.45; H, 5.81. Found: C, 63.17; H, 5.83.

Property of 5ad: colorless liquid, bp 260 °C/0.08 Torr, eluent hexane/ethyl acetate = 8:1. IR (neat): 1737 (C═O), 1250 (Si−CH$_3$) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ 0.03 (s, 6H, SiCH_3), 0.52 (q, J = 7.8 Hz, 2H, SiCH_2CH$_3$), 0.93 (t, J = 7.8 Hz, 3H, SiCH$_2$CH_3), 2.59 (d, J = 6.7 Hz, 2H, ═CCH_2), 3.18 (s, 2H, CH_2), 3.54 (s, 4H, CH_2C(CO$_2$Me)$_2$CH_2), 3.68 (s, 6H, CO$_2$CH_3), 3.74 (s, 6H, CO$_2$CH_3), 5.74 (d, J = 18.8 Hz, 1H, ═CHSi), 5.91 (dt, J = 18.8 and 6.7 Hz, 1H, CH═CSi), 6.87 (d, J = 7.7 Hz, 1H, Ar), 6.90 (s, 1H, Ar), 7.07 (d, J = 7.7 Hz, 1H, Ar). ^{13}C NMR (75 MHz, CDCl$_3$): δ −3.49 (SiCH$_3$), 7.35 (SiCH$_2$CH$_3$), 7.41 (SiCH$_2$$CH_3$), 38.45 ($CH_2$), 39.82 ($CH_2$), 40.34 ($CH_2$), 40.54 ($CH_2$), 52.23 (CO$_2$$CH_3$), 52.97 (CO$_2$$CH_3$), 59.23 ($C$(CO$_2$Me)$_2$), 60.38 ($C$(CO$_2$Me)$_2$), 123.89 (Ar), 125.63 (Ar), 128.57 (═CSi), 134.63 (Ar, 2C), 138.46 (Ar), 139.86 (Ar), 140.60 (C═CSi), 171.00 (C═O), 171.83 (C═O). Anal. Calcd for $C_{26}H_{36}O_8Si$: C, 61.88; H, 7.19. Found: C, 61.63; H, 7.12.

Property of 6b: colorless liquid, eluent hexane. IR (neat): 2935 (C−H) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.93 (quint., J = 7.8 Hz, 2H, CH_2), 2.06 (quint., J = 7.4 Hz, 4H, CH_2, cyclic), 2.63 (t, J = 7.8 Hz, 4H, CH_2), 2.88 (t, J = 7.4 Hz, 8H, CH_2, cyclic), 6.96 (d, J = 7.5 Hz, 2H, Ar), 7.07 (s, 2H, Ar), 7.14 (d, J = 7.5 Hz, 2H, Ar). ^{13}C NMR (50 MHz, CDCl$_3$): δ 25.35 (CH$_2$$CCH_2$, cyclic), 32.31 ($CH_2$, cyclic), 32.65 ($CH_2$, cyclic), 33.43 (CH$_2$$C$C H$_2$), 35.23 ($CH_2$), 124.20 (Ar), 124.56 (Ar), 126.35 (Ar), 140.44 (Ar), 141.65 (Ar), 144.50. Anal. Calcd for $C_{21}H_{24}$: C, 91.25; H, 8.75. Found: C, 91.09; H, 8.83.

Property of 7ba: colorless liquid, bp 170 °C/0.1 Torr, eluent hexane. IR (neat): 2954 (C−H), 1247 (Si−CH$_3$) cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$): δ 0.32 (s, 12H, SiCH_3), 1.54 (quint., J = 7.5 Hz, 2H, CH_2), 2.14−2.18 (m, 4H, CH_2), 5.76 (dt, J = 18.5 and 1.5 Hz, 2H, ═CHSi), 6.11 (dt, J = 18.5 and 6.8 Hz, 2H, CH═CSi), 7.34−7.37 (m, 3H, SiC$_6H_5$), 7.51−7.53 (m, 2H, SiC$_6H_5$). ^{13}C NMR (75 MHz, CDCl$_3$): δ −2.46 (SiCH$_3$), 27.52 (CH$_2$), 36.22 (CH$_2$), 127.69 (SiC_6H$_5$), 127.72 (═CSi), 128.79 (SiC_6H$_5$), 133.80 (SiC_6H$_5$), 139.27 (SiC_6H$_5$), 148.84 (C═CSi). Anal. Calcd for $C_{23}H_{32}Si_2$: C, 75.75; H, 8.84. Found: C, 75.91; H, 8.90.

Property of 4bb: colorless liquid, eluent hexane. IR (neat): 2953 (C−H), 1249 (Si−CH$_3$) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ 0.08 (s, 3H, SiCH_3), 0.61 (q, J = 7.8 Hz, 4H, SiCH_2CH$_3$), 0.95 (t, J = 7.8 Hz, 6H, SiCH$_2$CH_3), 1.68 (tt, J = 7.3 and 7.2 Hz, 2H, CH_2), 2.41 (ddt, J = 7.3, 2.3 and 2.1 Hz, 2H, CH$_2$═CCH_2), 2.44 (dt, J = 7.2 and 2.3 Hz, 2H, SiC═CCH_2), 4.87 (m, 1H, ═CH_2), 5.35 (t, J = 2.3 Hz, 1H, ═CH_2), 5.93 (t, J = 2.3 Hz, 1H, ═CHSi). ^{13}C NMR (75 MHz, CDCl$_3$): δ −4.81 (SiCH$_3$), 6.18 (SiCH$_2$CH$_3$), 7.65 (SiCH$_2$$CH_3$), 24.17 ($CH_2$), 33.56 ($CH_2$), 34.02 ($CH_2$), 103.44 (═$CH_2$), 114.68 (═$C$Si), 150.11 ($C$═CH$_2$), 157.00 ($C$═CSi). Anal. Calcd for $C_{12}H_{22}Si$: C, 74.14; H, 11.41. Found: C, 73.84; H, 11.71.

Property of 5bb: colorless liquid, bp 200 °C/6 Torr, eluent hexane. IR (neat): 2951 (C−H), 1259 (Si−CH$_3$) cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ 0.02 (s, 3H, SiCH_3), 0.52 (q, J = 7.8 Hz, 4H, SiCH_2CH$_3$), 0.91 (t, J = 7.8 Hz, 6H, SiCH$_2$CH_3), 1.71 (tt, J = 7.7 and 7.3 Hz, 2H, CH$_2$CH_2CH$_2$), 2.05 (quint., J = 7.4 Hz, 2H, CH$_2$CH_2CH$_2$, cyclic), 2.16 (dt, J = 7.3 and 6.6 Hz, 2H, ═CCH_2), 2.57 (t, J = 7.7 Hz, 2H, ArCH_2), 2.87 (t, J = 7.4 Hz, 4H, CH_2, cyclic), 5.59 (dt, J = 18.7 and 1.5 Hz, 1H, ═CHSi), 6.05 (dt, J = 18.7 and 6.6 Hz, 1H, CH═CSi), 6.95 (d, J = 7.6 Hz, 1H, Ar), 7.05 (s, 1H, Ar), 7.13 (d, J = 7.6 Hz, 1H, Ar). ^{13}C NMR (50 MHz, CDCl$_3$): δ −6.17 (SiCH$_3$), 5.29 (SiCH$_2$CH$_3$), 7.18 (SiCH$_2$$CH_3$), 25.38 (CH$_2$$CH_2CH_2$, cyclic), 30.79 (═C$CH_2$), 32.34 ($CH_2$, cyclic), 32.68 ($CH_2$, cyclic), 35.12 ($CH_2$), 36.33 (Ar$CH_2$), 124.22 (Ar), 124.61 (Ar), 126.39 (Ar), 127.54 (═CHSi), 140.62 (Ar), 141.68 (Ar), 144.53 (Ar), 148.08 (C═CHSi). Anal. Calcd for $C_{19}H_{30}Si$: C, 79.64; H, 10.55. Found: C, 79.67; H, 10.71.

Property of 7bb: colorless liquid, bp 170 °C/5 Torr, eluent hexane. IR (neat): 2953 (C−H), 1250 (Si−CH$_3$) cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$): δ 0.01 (s, 6H, SiCH_3), 0.52 (q, J = 8.0 Hz, 8H, SiCH_2CH$_3$), 0.92 (t, J = 8.0 Hz, 12H, SiCH$_2$CH_3), 1.50 (quint., J = 7.3 Hz, 2H, CH_2), 2.12 (ddt, J = 7.3, 6.7 and 1.5 Hz, 4H, ═CCH_2), 5.57 (dt, J = 18.8 and 1.5 Hz, 2H, ═CHSi), 6.02 (dt, J = 18.8 and 6.7 Hz, 2H, CH═CSi). ^{13}C NMR (75 MHz, CDCl$_3$): δ −5.78 (SiCH$_3$), 5.64 (SiCH$_2$CH$_3$), 7.50 (SiCH$_2$$CH_3$), 27.94 ($CH_2$), 36.41 ($CH_2$), 127.21 (═$C$Si), 147.78 ($C$═CSi). Anal. Calcd for $C_{17}H_{36}Si_2$: C, 68.83; H, 12.23. Found: C, 68.61; H, 12.25.

Property of 4bd: colorless liquid, eluent hexane. IR (neat): 2953 (C−H), 1247 (Si−CH$_3$) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ 0.10 (s, 6H, SiCH_3), 0.60 (q, J = 8.0 Hz, 2H, SiCH_2CH$_3$), 0.95 (t, J = 8.0 Hz, 3H, SiCH$_2$CH_3), 1.68 (tt, J = 7.3 and 7.2 Hz, 2H, CH_2), 2.41 (ddt, J = 7.3, 2.4 and 2.1 Hz, 2H, C═CCH_2), 2.45 (dt, J = 7.2 and 2.4 Hz, 2H, SiC═CCH_2), 4.87 (m, 1H, ═CH_2), 5.35 (t, J = 2.4 Hz, 1H, ═CH_2), 5.94 (t, J = 2.4 Hz, 1H, ═CHSi). ^{13}C NMR (75 MHz, CDCl$_3$): δ −2.54 (SiCH$_3$), 7.60 (SiCH$_2$CH$_3$), 8.05 (SiCH$_2$$CH_3$), 24.17 ($CH_2$), 33.57 (═C$CH_2$), 33.87 (═C$CH_2$), 103.48 (═$CH_2$), 115.76 (═$C$HSi), 150.11 ($C$═CH$_2$), 156.71 ($C$═CHSi). Anal. Calcd for $C_{11}H_{20}Si$: C, 73.25; H, 11.18. Found: C, 72.98; H, 11.62.

Property of 5bd: colorless liquid, eluent hexane. IR (neat): 2952 (C−H), 1246 (Si−CH$_3$) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ 0.03 (s, 6H, SiCH_3), 0.53 (q, J = 7.9 Hz, 2H, SiCH_2CH$_3$), 0.94 (t, J = 7.9 Hz, 3H, SiCH$_2$CH_3), 1.75 (quint., J = 7.2 Hz, 2H, CH_2), 2.07 (tt, J = 7.6 and 7.4 Hz, 2H, CH_2), 2.18 (dt, J = 7.4 and 6.1 Hz, 2H, ═CCH_2), 2.60 (t, J = 7.6 Hz, 2H, CH_2), 2.89 (t, J = 7.2 Hz, 4H, CH_2), 5.64 (dt, J = 18.8 and 1.5 Hz, 1H, ═CHSi), 6.06 (dt, J = 18.8 and 6.1 Hz, 1H, CH═CSi), 6.96 (d, J = 7.5 Hz, 1H, Ar), 7.07 (s, 1H, Ar), 7.15 (d, J = 7.5 Hz, 1H, Ar). ^{13}C NMR (75 MHz, CDCl$_3$): δ −3.34 (SiCH$_3$), 7.49 (SiCH$_2$CH$_3$), 7.59 (SiCH$_2$$CH_3$), 25.62 ($CH_2$), 30.92 ($CH_2$), 32.55 ($CH_2$), 32.89 ($CH_2$), 35.33 ($CH_2$), 36.41 ($CH_2$), 123.98 (Ar), 124.35 (Ar), 126.14 (Ar), 128.62 (═CSi), 140.28 (Ar), 141.34 (Ar), 144.17 (Ar), 147.24 (C═CSi). Anal. Calcd for $C_{18}H_{28}Si$: C, 79.34; H, 10.36. Found: C, 79.08; H, 10.38.

Property of 5ca: pale yellow liquid, bp 310 °C/0.1 Torr, eluent hexane/ethyl acetate = 2:1. IR (neat): 1248 (Si−CH$_3$) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ 0.33 (s, 6H, SiCH_3), 3.12 (d, J = 5.8 Hz, 2H, ═CCH_2), 3.55−3.57 (m, 4H, PhCH_2), 3.93 (s, 6H, CH_2), 5.99 (d, J = 18.8 Hz, 1H, ═CHSi), 6.18 (dt, J = 18.8 and 5.8 Hz, 1H, CH═CSi), 7.10−7.61 (m, 18H, Ar). ^{13}C NMR (75 MHz, CDCl$_3$): δ −2.38 (SiCH$_3$), 58.01 (CH$_2$), 58.73 (CH$_2$), 58.90 (CH$_2$), 59.07 (CH$_2$), 60.33 (CH$_2$), 121.90 (Ar), 122.76 (Ar), 126.70 (Ar), 127.08 (Ar), 127.44 (Ar), 127.63

(Si*C*$_6$H$_5$), 128.05 (Ar), 128.30 (Ar), 128.73 (Ar or Si*C*$_6$H$_5$), 128.76 (Ar or Si*C*$_6$H$_5$), 130.52 (=*C*Si), 133.67 (Si*C*$_6$H$_5$), 138.11 (Ar), 138.53 (Ar), 138.75 (Ar), 139.40 (Ar), 139.94 (Si*C*$_6$H$_5$), 146.05 (*C*=CSi). Anal. Calcd for $C_{35}H_{38}N_2Si$: C, 81.22; H, 7.62; N, 5.57. Found: C, 81.32; H, 7.73; N, 5.46.

Property of 5da: pale yellow liquid, eluent hexane/ethyl acetate = 2:1. IR (neat): 1248 (Si−CH$_3$) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): *δ* 0.33 (s, 6H, SiC*H*$_3$), 3.07 (d, *J* = 6.6 Hz, 2H, NC*H*$_2$), 3.14 (dd, *J* = 5.8 and 1.2 Hz, 2H, NC*H*$_2$), 3.40 (ddd, *J* = 6.6, 1.3, and 1.3 Hz, 2H, NC*H*$_2$), 3.55 (s, 2H, NC*H*$_2$), 3.92 (s, 4H, NC*H*$_2$), 5.12−5.20 (m, 3H, =C*H*$_2$), 5.29 (ddt, *J* = 17.1, 2.0, and 1.4 Hz, 1H, =C*H*$_2$), 5.88 (ddt, *J* = 17.1, 10.2, and 6.5 Hz, 1H, =C*H*CH$_2$), 5.96 (dt, *J* = 18.6 and 1.2 Hz, =C*H*Si), 5.99 (ddt, *J* = 17.1, 10.2, and 6.6 Hz, 1H, =C*H*CH$_2$), 6.16 (dt, *J* = 18.8 and 5.8 Hz, 1H, C*H*=CSi), 7.12−7.17 (m, 3H, Ar), 7.32−7.37 (m, 3H, SiC$_6$*H*$_5$), 7.48−7.54 (m, 2H, SiC$_6$*H*$_5$). ^{13}C NMR (75 MHz, CDCl$_3$): *δ* −2.40 (SiCH$_3$), 56.67 (N*C*H$_2$), 57.77 (N*C*H$_2$), 58.57 (N*C*H$_2$), 58.72 (N*C*H$_2$), 58.92 (N*C*H$_2$), 59.10 (N*C*H$_2$), 117.16 (=*C*H$_2$), 117.51 (=*C*H$_2$), 121.85 (Ar), 122.89 (Ar), 127.63 (Si*C*$_6$H$_5$), 128.79 (Si*C*$_6$H$_5$), 130.74 (=*C*Si), 133.66 (Si*C*$_6$H$_5$), 135.58 (=*C*H), 137.74 (Ar), 138.56 (Ar), 138.74 (Ar), 139.96 (Si*C*$_6$H$_5$), 145.79 (*C*=CSi). Anal. Calcd for $C_{26}H_{34}N_2Si$: C, 77.56; H, 8.51; N, 6.96. Found: C, 77.33; H, 8.50; N, 6.71.

Property of 7da: pale yellow liquid, eluent hexane/ethyl acetate = 50:1. IR (neat): 1247 (Si−CH$_3$) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): *δ* 0.34 (s, 12H, SiC*H*$_3$), 3.09 (d, *J* = 6.6 Hz, 2H, C*H*$_2$), 3.16 (dd, *J* = 6.0 and 1.2 Hz, 4H, C*H*$_2$), 5.14 (d, *J* = 10.7 Hz, 1H, =C*H*$_2$), 5.15 (d, *J* = 16.7 Hz, 1H, =C*H*$_2$), 5.86 (ddt, *J* = 16.7, 10.7, and 6.6 Hz, 1H, =C*H*), 5.95 (d, *J* = 18.5 Hz, =C*H*Si), 6.16 (dt, *J* = 18.5 and 6.0 Hz, 2H, =C*H*), 7.34−7.36 (m, 3H, SiC$_6$*H*$_5$), 7.50−7.53 (m, 2H, SiC$_6$*H*$_5$). ^{13}C NMR (75 MHz, CDCl$_3$): *δ* −2.43 (SiCH$_3$), 56.86 (N*C*H$_2$), 59.36 (N*C*H$_2$, 2C), 117.78 (=*C*H$_2$), 127.65 (Si*C*$_6$H$_5$), 128.82 (Si*C*$_6$H$_5$), 131.18 (=*C*Si), 133.66 (Si*C*$_6$H$_5$), 135.26 (=*C*H), 138.67 (=*C*H), 145.30 (*C*=CSi). Anal. Calcd for $C_{25}H_{35}NSi_2$: C, 74.01; H, 8.70; N, 3.45. Found: C, 73.74; H, 9.00; N, 3.46.

Property of 5ea: colorless liquid, eluent hexane/ethyl acetate = 30:1. IR (neat): 2848 (C−H), 1247 (Si−CH$_3$) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): *δ* 0.36 (s, 6H, SiC*H*$_3$), 4.10 (dd, *J* = 4.5 and 1.3 Hz, 2H, =CC*H*$_2$), 4.54 (s, 2H, OC*H*$_2$), 5.11 (s, 4H, OC*H*$_2$), 6.09 (dt, *J* = 18.9 and 1.3 Hz, 1H, =C*H*Si), 6.21 (dt, *J* = 18.9 and 4.5 Hz, 1H, =C*H*), 7.23 (d, *J* = 6.0 Hz, 1H, Ar), 7.24 (s, 1H, Ar), 7.25 (d, *J* = 6.0 Hz, 1H, Ar), 7.34−7.37 (m, 3H, SiC$_6$*H*$_5$), 7.51−7.55 (m, 2H, SiC$_6$*H*$_5$). ^{13}C NMR (75 MHz, CDCl$_3$): *δ* −2.55 (SiCH$_3$), 72.27 (O*C*H$_2$), 73.01 (O*C*H$_2$), 73.39 (O*C*H$_2$), 73.43 (O*C*H$_2$), 120.33 (Ar), 120.74 (Ar), 126.93 (Ar), 127.66 (Si*C*$_6$H$_5$), 128.89 (Si*C*$_6$H$_5$), 129.73 (=*C*Si), 133.69 (Si*C*$_6$H$_5$), 137.45 (Ar), 138.29 (Si*C*$_6$H$_5$), 138.48 (Ar), 139.35 (Ar), 143.87 (=*C*). Anal. Calcd for $C_{20}H_{24}O_2Si$: C, 74.03; H, 7.45. Found: C, 73.85; H, 7.44.

Property of 7ea: colorless liquid, eluent hexane/ethyl acetate = 50:1. IR (neat): 2954 (C−H), 1247 (Si−CH$_3$) cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$): *δ* 0.35 (s, 12H, SiC*H*$_3$), 4.05 (dd, *J* = 4.5 and 1.2 Hz, 4H, OC*H*$_2$), 6.06 (d, *J* = 18.8 Hz, 2H, SiC*H*=), 6.18 (dt, *J* = 18.8 and 4.5 Hz, 2H, SiC=C*H*), 7.33−7.36 (m, 6H, SiC$_6$*H*$_5$), 7.51−7.54 (m, 4H, SiC$_6$*H*$_5$). ^{13}C NMR (75 MHz, CDCl$_3$): *δ* −2.53 (SiCH$_3$), 73.18 (O*C*H$_2$), 127.66 (Si*C*$_6$H$_5$), 128.88 (Si*C*$_6$H$_5$), 129.61 (=*C*Si), 133.71 (Si*C*$_6$H$_5$), 138.33 (Si*C*$_6$H$_5$), 143.91 (=*C*). Anal. Calcd for $C_{22}H_{30}OSi_2$: C, 72.07; H, 8.25. Found: C, 71.85; H, 8.46.

Property of 4fb: colorless liquid, eluent hexane. IR (neat): 2954 (C−H), 1251 (Si−CH$_3$) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): *δ* 0.07 (s, 3H, SiC*H*$_3$), 0.09 (s, 6H, OSiC*H*$_3$), 0.59 (q, *J* = 7.7 Hz, 4H, SiC*H*$_2$CH$_3$), 0.77 (s, 3H, C*H*$_3$), 0.936 (t, 6H, *J* = 7.7 Hz, SiCH$_2$C*H*$_3$), 0.939 (s, 9H, OSiC(C*H*$_3$)$_3$), 2.11 (dd, *J* = 16.3 and 2.8 Hz, 1H, C*H*$_2$), 2.27 (dd, *J* = 16.3 and 1.8 Hz, 1H, C*H*$_2$), 4.05 (dd, *J* = 2.4 and 2.1 Hz, 1H, OC*H*), 4.94 (d, *J* = 2.1 Hz, 1H, =C*H*$_2$), 5.42 (d, *J* = 2.4 Hz, 1H, =C*H*$_2$), 5.96 (dd, *J* = 2.8 and 1.8 Hz, 1H, =C*H*). ^{13}C NMR (75 MHz, CDCl$_3$): *δ* −4.72 (SiCH$_3$), −4.28 (SiCH$_3$), −4.06 (SiCH$_3$), 6.24 (Si*C*H$_2$CH$_3$), 7.61 (SiCH$_2$*C*H$_3$), 18.30 (Si*C*(CH$_3$)$_3$), 20.29 (*C*H$_3$), 26.03 (SiC(*C*H$_3$)$_3$), 26.29 (*C*H$_3$), 40.08 (*C*(CH$_3$)$_2$), 44.85 (*C*H$_2$), 82.14 (O*C*H$_2$), 104.98 (=*C*H$_2$), 116.57 (=*C*Si), 152.35 (=*C*), 152.81 (=*C*). Anal. Calcd for $C_{19}H_{40}OSi_2$: C, 68.11; H, 11.43. Found: C, 67.87; H, 11.56.

Property of 4fd: colorless liquid, eluent hexane. IR (neat): 2955 (C−H), 1252 (Si−CH$_3$) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): *δ* 0.09 (s, 12H, SiC*H*$_3$), 0.59 (q, *J* = 7.8 Hz, 2H, SiC*H*$_2$CH$_3$), 0.78 (s, 3H, C*H*$_3$), 0.94 (t, *J* = 7.8 Hz, 3H, SiCH$_2$C*H*$_3$), 0.95 (s, 9H, OSiC(C*H*$_3$)$_3$) 1.03 (s, 3H, C*H*$_3$), 2.12 (dd, *J* = 16.1 and 3.0 Hz, 1H, C*H*$_2$), 2.28 (dd, *J* = 16.1 and 1.9 Hz, 1H, C*H*$_2$), 4.05 (dd, *J* = 2.6 and 2.1 Hz, 1H, C*H*), 4.94 (d, *J* = 2.1 Hz, 1H, =C*H*$_2$), 5.42 (d, *J* = 2.6 Hz, 1H, =C*H*$_2$), 5.98 (dd, *J* = 3.0 and 1.9 Hz, 1H, =C*H*). ^{13}C NMR (75 MHz, CDCl$_3$): *δ* −4.28 (SiCH$_3$), −4.06 (SiCH$_3$), −2.47 (SiCH$_3$), −2.45 (SiCH$_3$), 7.57 (Si*C*H$_2$CH$_3$), 8.09 (SiCH$_2$*C*H$_3$), 18.31 (Si*C*(CH$_3$)$_3$), 20.32 (*C*H$_3$), 26.04 (SiC(*C*H$_3$)$_3$), 26.32 (*C*H$_3$), 40.08 (*C*(CH$_3$)$_2$), 44.73 (*C*H$_2$), 82.14 (O*C*H$_2$), 105.01 (=*C*H$_2$), 117.66 (=*C*Si), 152.34 (=*C*), 152.52 (=*C*). Anal. Calcd for $C_{19}H_{38}OSi_2$: C, 67.38; H, 11.31. Found: C, 67.30; H, 11.56.

Hydrosilylation of 9a with 2a Catalyzed by 3c (Scheme 6). A mixture of **9a** (112.9 mg, 0.27 mmol), **2a** (36.9 mg, 0.27 mmol), and **3c** (6.4 mg, 0.0081 mmol) in CH$_2$Cl$_2$ (2 mL) was heated at 80 °C for 14 h in a sealed tube. The solvent was evaporated, and the residue was purified by flash column chromatography (eluent hexane/ethyl acetate = 9:1) to give a mixture of **5aa** and **17** (92.7 mg, 0.17 mmol, 62%) as a colorless liquid. The ratio of **5aa** and **17** was determined by ^{1}H NMR spectra and could not be separated from each other.

Property of 20 (*E*): colorless liquid, bp 150 °C/6 Torr, eluent hexane. IR (neat): 2931 (C−H), 1247 (Si−CH$_3$) cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$): *δ* 0.36 (s, 6H, SiC*H*$_3$), 1.52−1.56 (m, 2H, C*H*$_2$), 1.59−1.64 (m, 2H, C*H*$_2$), 2.24 (t, *J* = 5.8 Hz, 2H, C*H*$_2$), 2.29 (t, *J* = 6.2 Hz, 2H, C*H*$_2$), 4.64 (dt, *J* = 2.5 and 1.3 Hz, 1H, =C*H*$_2$), 4.97 (d, *J* = 2.5 Hz, 1H, =C*H*$_2$), 5.62 (s, 1H, =C*H*), 7.34−7.35 (m, 3H, SiC$_6$*H*$_5$), 7.55−7.57 (m, 2H, SiC$_6$*H*$_5$). ^{13}C NMR (50 MHz, CDCl$_3$): *δ* −1.02 (SiCH$_3$), 26.38 (*C*H$_2$), 26.47 (*C*H$_2$), 34.66 (*C*H$_2$), 35.43 (*C*H$_2$), 108.36 (=*C*H$_2$), 119.80 (=*C*Si), 127.85 (Si*C*$_6$H$_5$), 128.84 (Si*C*$_6$H$_5$), 133.89 (Si*C*$_6$H$_5$), 140.15 (Si*C*$_6$H$_5$), 153.07 (CH$_2$=*C*), 160.41 (SiC=*C*). Anal. Calcd for $C_{14}H_{22}Si$: C, 79.27; H, 9.15. Found: C, 79.27; H, 9.24.

Property of 20 (*Z*): colorless liquid, bp 150 °C/6 Torr, eluent hexane. IR (neat): 2932 (C−H), 1250 (Si−CH$_3$) cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$): *δ* 0.33 (s, 6H, SiC*H*$_3$), 1.62−1.71 (m, 4H, C*H*$_2$), 2.14 (t, *J* = 6.0 Hz, 2H, C*H*$_2$), 2.33 (t, *J* = 5.5 Hz, 2H, C*H*$_2$), 4.62 (dt, *J* = 2.5 and 1.4 Hz, 1H, C=C*H*$_2$), 4.69 (d, *J* = 2.5 Hz, 1H, C=C*H*$_2$), 5.33 (m, 1H, C=C*H*), 7.32−7.33 (m, 3H, SiC$_6$*H*$_5$), 7.52−7.54 (m, 2H, SiC$_6$*H*$_5$). ^{13}C NMR (50 MHz, CDCl$_3$): *δ* −0.98 (SiCH$_3$), 27.64 (=C*C*H$_2$), 28.02 (=C*C*H$_2$), 36.59 (*C*H$_2$), 41.70 (*C*H$_2$), 110.01 (=*C*H$_2$), 120.21 (=*C*Si), 127.70 (Si*C*$_6$H$_5$), 128.57 (Si*C*$_6$H$_5$), 133.85 (Si*C*$_6$H$_5$), 141.24 (Si*C*$_6$H$_5$), 150.91 (CH$_2$=*C*), 161.94 (SiC=*C*). Anal. Calcd for $C_{14}H_{22}Si$: C, 79.27; H, 9.15. Found: C, 79.27; H, 9.24.

Property of 21 (*E*): colorless liquid, bp 250 °C/6 Torr, eluent hexane. IR (neat): 3306 (C≡C), 2935 (C−H), 1247 (Si−CH$_3$) cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): *δ* 0.32 (s, 6H, SiC*H*$_3$), 1.52−1.56 (m, 4H, C*H*$_2$), 1.95 (t, *J* = 2.7 Hz, 1H, C≡C*H*), 2.16−2.21 (m, 4H, C*H*$_2$), 5.77 (dt, *J* = 18.6 and 1.4 Hz, 1H, SiC*H*=C) 6.11 (dt, *J* = 18.6 and 6.0 Hz, 1H, SiC=C*H*), 7.33−7.34 (m, 3H, SiC$_6$*H*$_5$), 7.50−7.55 (m, 2H, SiC$_6$*H*$_5$). ^{13}C NMR (50 MHz, CDCl$_3$): *δ* −2.71 (SiCH$_3$), 18.10 (C≡C*C*H$_2$), 27.48 (*C*H$_2$), 27.84 (*C*H$_2$), 36.05 (C=C*C*H$_2$), 68.19 (C≡*C*H), 76.84 (*C*≡CH), 127.85 (Si*C*$_6$H$_5$), 127.93 (Si*C*=C), 128.97 (Si*C*$_6$H$_5$), 133.97 (Si*C*$_6$H$_5$), 139.45 (Si*C*$_6$H$_5$), 148.87 (SiC=*C*). Anal. Calcd for $C_{14}H_{22}Si$: C, 79.27; H, 9.15. Found: C, 79.22; H, 9.36.

Property of 21 (*Z*): colorless liquid, eluent hexane. IR (neat): 3308 (C≡C), 2939 (C−H), 1248 (Si−CH$_3$) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): *δ* 0.37 (s, 6H, SiC*H*$_3$), 1.38−1.45 (m, 4H, C*H*$_2$), 1.92 (t, *J* = 2.7 Hz, 1H, C≡C*H*), 2.02−2.12 (m, 4H, C*H*$_2$), 5.65 (dt, *J* = 14.0 and 1.2 Hz, 1H, SiC*H*=C) 6.41 (dt, *J* = 14.0 and 7.2 Hz, 1H, SiC=C*H*), 7.34−7.36 (m, 3H, SiC$_6$*H*$_5$), 7.50−7.56 (m, 2H, SiC$_6$*H*$_5$). ^{13}C NMR (75 MHz, CDCl$_3$): *δ* −0.70 (SiCH$_3$), 18.34 (C≡C*C*H$_2$), 28.09 (*C*H$_2$), 28.60 (*C*H$_2$), 33.19 ($\mathrm{C{=}C}C\mathrm{H_2}$), 68.22 ($\mathrm{C{\equiv}}C\mathrm{H}$), 77.21 ($C\mathrm{{\equiv}CH}$), 126.98 ($\mathrm{Si}C\mathrm{{=}C}$), 127.66 ($\mathrm{Si}C_6\mathrm{H_5}$), 128.70 ($\mathrm{Si}C_6\mathrm{H_5}$), 133.58 ($\mathrm{Si}C_6\mathrm{H_5}$), 140.61 ($\mathrm{Si}C_6\mathrm{H_5}$), 150.14 ($\mathrm{SiC{=}}C$). Anal. Calcd for $\mathrm{C_{14}H_{22}Si}$: C, 79.27; H, 9.15. Found: C, 79.22; H, 9.36.

Property of 22: colorless liquid, eluent hexane. IR (neat): 2954 (C−H), 1247 ($\mathrm{Si{-}CH_3}$) $\mathrm{cm^{-1}}$. ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): δ 0.35 (s, 12H, $\mathrm{SiC}H_3$), 1.43−1.46 (m, 4H, $\mathrm{C{=}CC}H_2$), 2.17−2.19 (m, 4H, $\mathrm{C}H_2$), 5.79 (d, J = 18.2 Hz, 2H, $\mathrm{SiC}H\mathrm{{=}C}$), 6.14 (dt, J = 18.2 and 6.1 Hz, 2H, $\mathrm{SiC{=}C}H$), 7.34−7.38 (m, 6H, $\mathrm{SiC_6}H_5$), 7.53−7.56 (m, 4H, $\mathrm{SiC_6}H_5$). ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$): δ −2.29 ($\mathrm{Si}C\mathrm{H_3}$), 28.24 ($\mathrm{{=}C}C\mathrm{H_2}$), 36.69 ($C\mathrm{H_2}$), 127.30 ($\mathrm{Si}C\mathrm{{=}C}$), 127.59 ($\mathrm{Si}C_6\mathrm{H_5}$), 128.70 ($\mathrm{Si}C_6\mathrm{H_5}$), 133.70 ($\mathrm{Si}C_6\mathrm{H_5}$), 139.20 ($\mathrm{Si}C_6\mathrm{H_5}$), 149.02 ($\mathrm{SiC{=}}C$). Anal. Calcd for $\mathrm{C_{24}H_{34}Si_2}$: C, 76.12; H, 9.05. Found: C, 76.32; H, 9.10.

Property of 24a: colorless liquid, eluent hexane/ethyl acetate = 10:1. IR (neat): 1736 (C=O), 1255 ($\mathrm{Si{-}CH_3}$) $\mathrm{cm^{-1}}$. ^{1}H NMR (500 MHz, $\mathrm{CDCl_3}$): δ 0.34 (s, 6H, $\mathrm{SiC}H_3$), 2.53 (m, 1H $\mathrm{Si{-}C}H$), 2.71 (m, 1H, $\mathrm{C}H_2$), 2.79 (d, J = 14.2 Hz, 1H, $\mathrm{C}H_2$), 2.82 (d, J = 14.2 Hz, 1H, $\mathrm{C}H_2$), 2.85 (d, J = 15.6 Hz, 1H, $\mathrm{C}H_2$), 2.95 (d, J = 15.6 Hz, 1H, $\mathrm{C}H_2$), 3.09 (m, 1H, $\mathrm{C}H_2$), 3.51 (s, 3H, $\mathrm{CO_2C}H_3$), 3.70 (s, 3H, $\mathrm{CO_2C}H_3$), 3.73 (s, 6H, $\mathrm{CO_2C}H_3$), 7.31−7.36 (m, 3H, $\mathrm{Si{-}C_6}H_5$), 7.45−7.46 (m, 2H, $\mathrm{Si{-}C_6}H_5$). ^{13}C NMR (125 MHz, $\mathrm{CDCl_3}$): δ −3.68 ($\mathrm{Si}C\mathrm{H_3}$), −3.63 ($\mathrm{Si}C\mathrm{H_3}$), 29.16 ($\mathrm{Si}C\mathrm{H}$), 34.19 ($C\mathrm{H_2}$), 42.79 ($C\mathrm{H_2}$), 43.21 ($C\mathrm{H_2}$), 51.89 ($\mathrm{CO_2}C\mathrm{H_3}$), 52.08 ($\mathrm{CO_2}C\mathrm{H_3}$), 52.78 ($\mathrm{CO_2}C\mathrm{H_3}$), 52.85 ($\mathrm{CO_2}C\mathrm{H_3}$), 58.56 ($C\mathrm{(CO_2Me)_2}$), 126.35 ($C\mathrm{{=}C}$), 127.64 ($\mathrm{Si}C_6\mathrm{H_5}$), 129.44 ($\mathrm{Si}C_6\mathrm{H_5}$), 131.46 ($C\mathrm{{=}C}$), 131.79 ($C\mathrm{{=}C}$), 134.02 ($\mathrm{Si}C_6\mathrm{H_5}$), 136.14 ($\mathrm{Si}C_6\mathrm{H_5}$ or $C\mathrm{{=}C}$), 136.30 ($\mathrm{Si}C_6\mathrm{H_5}$ or $C\mathrm{{=}C}$), 168.00 ($C\mathrm{{=}O}$), 168.91 ($C\mathrm{{=}O}$), 172.18 ($C\mathrm{{=}O}$), 172.48 ($C\mathrm{{=}O}$). Anal. Calcd for $\mathrm{C_{25}H_{30}O_8Si}$: C, 61.71; H, 6.21. Found: C, 61.62; H, 6.18.

Property of 24b: colorless liquid composed of two diastereomers, bp 320 °C/0.3 Torr. IR (neat): 1778 (C=O), 1733 (C=O), 1261 ($\mathrm{Si{-}CH_3}$) $\mathrm{cm^{-1}}$. One isomer, ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): δ 0.40 (s, 3H, $\mathrm{SiC}H_3$), 0.43 (s, 3H, $\mathrm{SiC}H_3$), 1.59 (m, 1H, $\mathrm{SiC}H$), 2.17−2.22 (m, 2H, $\mathrm{C}H_2$), 2.92−3.35 (m, 6H, $\mathrm{C}H_2\mathrm{C(CO_2Me)_2C}H_2$, $\mathrm{C}H$, $\mathrm{C}H$), 3.70 (s, 3H, $\mathrm{CO_2C}H_3$), 3.74 (s, 3H, $\mathrm{CO_2C}H_3$), 7.33−7.42 (m, 3H, $\mathrm{SiC_6}H_5$), 7.45−7.51 (m, 2H, $\mathrm{SiC_6}H_5$). ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$): δ −3.70 ($\mathrm{Si}C\mathrm{H_3}$), −3.57 ($\mathrm{Si}C\mathrm{H_3}$), 24.09 ($\mathrm{Si}C\mathrm{H}$), 27.71 ($C\mathrm{H_2}$), 39.46 ($C\mathrm{H}$), 41.18 ($C\mathrm{H}$), 43.51 ($C\mathrm{H_2}$), 44.37 ($C\mathrm{H_2}$), 52.87 ($\mathrm{CO_2}C\mathrm{H_3}$), 57.49 ($C\mathrm{(CO_2Me)_2}$), 127.84 ($\mathrm{Si}C_6\mathrm{H_5}$), 128.12 ($\mathrm{Si}C_6\mathrm{H_5}$), 129.42 ($\mathrm{{=}}C$), 132.71 ($\mathrm{{=}}C$), 133.61 ($\mathrm{Si}C_6\mathrm{H_5}$), 135.51 ($\mathrm{Si}C_6\mathrm{H_5}$), 171.55 ($C\mathrm{{=}O}$), 172.27 ($C\mathrm{{=}O}$), 173.93 ($C\mathrm{O_2Me}$), 174.63 ($C\mathrm{O_2Me}$). Another isomer, ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): δ 0.46 (s, 3H, $\mathrm{SiC}H_3$), 0.48 (s, 3H, $\mathrm{SiC}H_3$), 1.59 (m, 1H, $\mathrm{SiC}H$), 2.29−2.38 (m, 2H, $\mathrm{C}H_2$), 2.92−3.35 (m, 6H, $\mathrm{C}H_2\mathrm{C(CO_2Me)_2C}H_2$, $\mathrm{C}H$, $\mathrm{C}H$), 3.68 (s, 3H, $\mathrm{CO_2C}H_3$), 3.71 (s, 3H, $\mathrm{CO_2C}H_3$), 7.33−7.42 (m, 3H, $\mathrm{SiC_6}H_5$), 7.45−7.51 (m, 2H, $\mathrm{SiC_6}H_5$). ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$): δ −1.92 ($\mathrm{Si}C\mathrm{H_3}$), −1.78 ($\mathrm{Si}C\mathrm{H_3}$), 23.65 ($\mathrm{Si}C\mathrm{H}$), 26.59 ($C\mathrm{H_2}$), 40.43 ($C\mathrm{H}$), 42.99 ($C\mathrm{H}$), 43.20 ($C\mathrm{H_2}$), 43.81 ($C\mathrm{H_2}$), 52.87 ($\mathrm{CO_2}C\mathrm{H_3}$), 57.93 ($C\mathrm{(CO_2Me)_2}$), 127.78 ($\mathrm{Si}C_6\mathrm{H_5}$), 129.93 ($\mathrm{Si}C_6\mathrm{H_5}$), 130.95 ($\mathrm{{=}}C$), 133.34 ($\mathrm{{=}}C$), 133.81 ($\mathrm{Si}C_6\mathrm{H_5}$), 136.75 ($\mathrm{Si}C_6\mathrm{H_5}$), 171.80 ($C\mathrm{{=}O}$), 171.97 ($C\mathrm{{=}O}$), 172.33 ($C\mathrm{O_2Me}$), 173.28 ($C\mathrm{O_2Me}$). Anal. Calcd for $\mathrm{C_{23}H_{26}O_7Si}$: C, 62.42; H, 5.92. Found: C, 62.05; H, 5.90.

Property of 24c: colorless needles containing two diastereoisomers which are recrystallized from ethyl acetate and hexane, mp 79.0−83.0 °C. All of the specific signals for these isomers were accidentally identical in IR, ^{1}H NMR, and ^{13}C NMR spectra. IR (KBr): 1734 (C=O), 1712 (C=O), 1263 ($\mathrm{Si{-}CH_3}$) $\mathrm{cm^{-1}}$. ^{1}H NMR (500 MHz, $\mathrm{CDCl_3}$): δ 0.48 (s, 3H, $\mathrm{SiC}H_3$), 0.53 (s, 3H, $\mathrm{SiC}H_3$), 2.18 (m, 1H, $\mathrm{SiC}H$), 2.35 (m, 1H, $\mathrm{C}H_2$), 2.51 (m, 1H, $\mathrm{C}H_2$), 2.87−2.99 (m, 4H, $\mathrm{C}H_2\mathrm{C(CO_2Me)_2C}H_2$), 3.21 (overlapping ddd, 1H, $\mathrm{NCOC}H$), 3.28 (dd, J = 8.5 and 6.0 Hz, 1H, $\mathrm{SiCC}H$), 3.66 (s, 3H, $\mathrm{CO_2C}H_3$), 3.69 (s, 3H, $\mathrm{CO_2C}H_3$), 7.22−7.25 (m, 2H, $\mathrm{NC_6}H_5$), 7.34−7.40 (m, 1H, $\mathrm{NC_6}H_5$ and m, 3H, $\mathrm{SiC_6}H_5$), 7.43−7.48 (m, 2H, $\mathrm{NC_6}H_5$), 7.55−7.58 (m, 2H, $\mathrm{SiC_6}H_5$). ^{13}C NMR (125 MHz, $\mathrm{CDCl_3}$): δ −1.62 ($\mathrm{Si}C\mathrm{H_3}$), −1.21 ($\mathrm{Si}C\mathrm{H_3}$), 24.73 ($C\mathrm{H_2}$), 26.74 ($\mathrm{Si}C\mathrm{H}$), 40.90 ($C\mathrm{H}$), 42.81 ($\mathrm{SiC}C\mathrm{H}$), 43.19 ($C\mathrm{H_2}$), 43.63 ($C\mathrm{H_2}$), 52.82 ($\mathrm{CO_2}C\mathrm{H_3}$), 52.85 ($\mathrm{CO_2}C\mathrm{H_3}$), 58.26 ($C\mathrm{(CO_2Me)_2}$), 126.40 ($\mathrm{N}C_6\mathrm{H_5}$), 127.87 ($\mathrm{Si}C_6\mathrm{H_5}$), 128.50 ($\mathrm{Si}C_6\mathrm{H_5}$), 129.09 ($\mathrm{N}C_6\mathrm{H_5}$), 129.18 ($\mathrm{N}C_6\mathrm{H_5}$), 131.92 ($\mathrm{N}C_6\mathrm{H_5}$), 133.10 ($\mathrm{{=}}C$), 133.98 ($\mathrm{Si}C_6\mathrm{H_5}$), 134.50 ($\mathrm{{=}}C$), 138.25 ($\mathrm{Si}C_6\mathrm{H_5}$), 172.14 ($\mathrm{PhN}C\mathrm{{=}O}$), 172.34 ($\mathrm{PhN}C\mathrm{{=}O}$), 177.82 ($C\mathrm{O_2Me}$), 178.83 ($C\mathrm{O_2Me}$). Anal. Calcd for $\mathrm{C_{29}H_{31}NO_6Si}$: C, 61.71; H, 6.21. Found: C, 61.62; H, 6.18.

Property of 25aa: colorless liquid, bp 195 °C/5 Torr, eluent hexane/ethyl acetate = 30:1). IR (neat): 1736 (C=O), 1252 ($\mathrm{Si{-}CH_3}$) $\mathrm{cm^{-1}}$. ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): δ 0.29 (s, 6H, $\mathrm{SiC}H_3$), 1.43 (s, 3H, $\mathrm{C}H_3$), 1.68 (s, 2H, $\mathrm{C}H_2$), 2.83 (s, 2H, $\mathrm{C}H_2$), 2.91 (s, 2H, $\mathrm{C}H_2$), 3.70 (s, 6H, $\mathrm{CO_2C}H_3$), 7.33−7.36 (m, 3H, $\mathrm{SiC_6}H_5$), 7.47−7.51 (m, 2H, $\mathrm{SiC_6}H_5$). ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$): δ −2.48 ($\mathrm{Si}C\mathrm{H_3}$), 13.74 ($\mathrm{Si}C\mathrm{H_2}$), 18.18 ($C\mathrm{H_3}$), 45.69 ($C\mathrm{H_2}$), 45.94 ($C\mathrm{H_2}$), 52.67 ($\mathrm{CO_2}C\mathrm{H_3}$), 57.20 ($C\mathrm{(CO_2Me)_2}$), 125.70 ($\mathrm{{=}}C$), 127.61 ($\mathrm{Si}C_6\mathrm{H_5}$), 128.85 ($\mathrm{Si}C_6\mathrm{H_5}$), 129.04 ($\mathrm{{=}}C$), 133.35 ($\mathrm{Si}C_6\mathrm{H_5}$), 139.01 ($\mathrm{Si}C_6\mathrm{H_5}$), 172.73 ($C\mathrm{{=}O}$). Anal. Calcd for $\mathrm{C_{19}H_{26}O_4Si}$: C, 65.86; H, 7.56. Found: C, 65.58; H, 7.79.

Property of 25ab: colorless liquid, bp 200 °C/5 Torr, eluent hexane/ethyl acetate = 30:1. IR (neat): 1737 (C=O), 1253 ($\mathrm{Si{-}CH_3}$) $\mathrm{cm^{-1}}$. ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): δ −0.07 (s, 3H, $\mathrm{SiC}H_3$), 0.49 (q, J = 7.8 Hz, 4H, $\mathrm{SiC}H_2\mathrm{CH_3}$), 0.91 (t, J = 7.8 Hz, 6H, $\mathrm{SiCH_2C}H_3$), 1.44 (s, 2H, $\mathrm{C}H_2$), 1.54 (s, 3H, $\mathrm{C}H_3$), 2.91 (s, 4H, $\mathrm{C}H_2$), 3.71 (s, 6H, $\mathrm{CO_2C}H_3$). ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$): δ −5.39 ($\mathrm{Si}C\mathrm{H_3}$), 5.63 ($\mathrm{Si}C\mathrm{H_2CH_3}$), 7.41 ($\mathrm{SiCH_2}C\mathrm{H_3}$), 13.83 ($\mathrm{Si}C\mathrm{H_2}$), 15.20 ($C\mathrm{H_3}$), 45.66 ($C\mathrm{H_2}$), 46.06 ($C\mathrm{H_2}$), 52.70 ($\mathrm{CO_2}C\mathrm{H_3}$), 57.33 ($C\mathrm{(CO_2Me)_2}$), 124.82 ($\mathrm{{=}}C$), 129.81 ($\mathrm{{=}}C$), 172.80 ($C\mathrm{{=}O}$). Anal. Calcd for $\mathrm{C_{16}H_{28}O_4Si}$: C, 61.50; H, 9.03. Found: C, 61.53; H, 9.32.

Property of 25ad: colorless liquid, bp 150 °C/0.1 Torr, eluent hexane/ethyl acetate = 30:1. IR (neat): 1736 (C=O), 1251 ($\mathrm{Si{-}CH_3}$) $\mathrm{cm^{-1}}$. ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): δ −0.04 (s, 6H, $\mathrm{SiC}H_3$), 0.48 (q, J = 7.9 Hz, 2H, $\mathrm{SiC}H_2\mathrm{CH_3}$), 0.92 (t, J = 7.9 Hz, 3H, $\mathrm{SiCH_2C}H_3$), 1.44 (s, 2H, $\mathrm{C}H_2$), 1.54 (s, 3H, $\mathrm{C}H_3$), 2.92 (s, 4H, $\mathrm{C}H_2$), 3.72 (s, 6H, $\mathrm{CO_2C}H_3$). ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$): δ −3.12 ($\mathrm{Si}C\mathrm{H_3}$), 7.40 ($\mathrm{Si}C\mathrm{H_2CH_3}$), 7.52 ($\mathrm{SiCH_2}C\mathrm{H_3}$), 13.84 ($\mathrm{Si}C\mathrm{H_2}$), 16.99 ($C\mathrm{H_3}$), 45.66 ($C\mathrm{H_2}$), 46.06 ($C\mathrm{H_2}$), 52.71 ($\mathrm{CO_2}C\mathrm{H_3}$), 57.35 ($C\mathrm{(CO_2Me)_2}$), 124.84 ($\mathrm{{=}}C$), 129.81 ($\mathrm{{=}}C$), 172.81 ($C\mathrm{{=}O}$). Anal. Calcd for $\mathrm{C_{15}H_{26}O_4Si}$: C, 60.37; H, 8.78. Found: C, 60.08; H, 8.61.

Property of 27: colorless liquid, eluent hexane/ethyl acetate = 10:1. IR (neat): 2954 (C−H), 1735 (C=O) $\mathrm{cm^{-1}}$. ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): δ 1.10 (s, 3H, $\mathrm{C}H_3$), 2.24 (d, J = 14.1 Hz, 1H, $\mathrm{CC}H_2$), 2.54 (d, J = 14.1 Hz, 1H, $\mathrm{CC}H_2$), 3.02 (m, 1H, $\mathrm{C{=}CC}H_2$), 3.05 (dd, J = 2.4 and 2.1 Hz, 1H, $\mathrm{C{=}CC}H_2$), 3.12 (s, 2H, $\mathrm{MeOC}H_2$), 3.31 (s, 3H, $\mathrm{OC}H_3$), 3.715 (s, 3H, $\mathrm{CO_2C}H_3$), 3.718 (s, 3H, $\mathrm{CO_2C}H_3$), 4.81 (dd, 1H, J = 2.1 and 2.1 Hz, $\mathrm{C{=}C}H_2$), 4.97 (dd, 1H, J = 2.1 and 1.8 Hz, $\mathrm{C{=}C}H_2$). ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$): δ 24.88 ($C\mathrm{H_3}$), 41.83 ($C\mathrm{H_2}$), 43.86 ($C\mathrm{H_2}$), 45.95 ($C\mathrm{CH_3}$), 52.74 ($\mathrm{CO_2}C\mathrm{H_3}$), 52.77 ($\mathrm{CO_2}C\mathrm{H_3}$), 57.94 ($C\mathrm{(CO_2Me)_2}$), 59.31 ($C\mathrm{H_3O}$), 80.91 ($C\mathrm{H_2O}$), 106.41 ($C\mathrm{H_2{=}C}$), 154.48 ($\mathrm{CH_2{=}}C$), 172.15 ($C\mathrm{{=}O}$). Anal. Calcd for $\mathrm{C_{13}H_{20}O_5}$: C, 60.92; H, 7.87. Found: C, 60.81; H, 8.14.

Property of 28: colorless liquid, eluent hexane/ethyl acetate = 5:1. IR (neat): 2953 (C−H), 1736 (C=O) $\mathrm{cm^{-1}}$. ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): δ 1.05 (s, 3H, $\mathrm{C}H_3$), 2.24 (d, J = 13.7 Hz, 1H, $\mathrm{CC}H_2$), 2.25 (dt, J = 7.4 and 1.7 Hz, 2H, $\mathrm{C{=}CC}H_2$), 2.56 (d, J = 13.7 Hz, 1H, $\mathrm{CC}H_2$), 3.12 (d, J = 9.0 Hz, 1H, $\mathrm{MeOC}H_2$), 3.19 (d, J = 9.0 Hz, 1H, $\mathrm{MeOC}H_2$), 3.27 (s, 3H, $\mathrm{OC}H_3$), 3.34 (s, 3H, $\mathrm{OC}H_3$), 3.55 (t, J = 7.4 Hz, 2H, $\mathrm{MeOC}H_2$), 3.70 (s, 6H, $\mathrm{CO_2C}H_3$), 5.45 (t, J = 1.7 Hz, 1H, $\mathrm{C{=}C}H$). ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$): δ 22.70 ($C\mathrm{H_3}$), 27.10 (CH_2), 42.08 ($C\mathrm{H_2}$), 51.27 ($C\mathrm{CH_3}$), 52.60 ($\mathrm{CO_2}C\mathrm{H_3}$), 52.71 ($\mathrm{CO_2}C\mathrm{H_3}$), 58.57 ($\mathrm{O}C\mathrm{H_3}$), 59.17 ($\mathrm{O}C\mathrm{H_3}$), 64.26 ($\mathrm{(MeO_2C)_2}C$), 71.01 ($\mathrm{MeO}C\mathrm{H_2}$), 78.75 ($\mathrm{MeO}C\mathrm{H_2}$), 122.07 ($C\mathrm{H{=}C}$), 150.26 ($\mathrm{CH{=}}C$), 171.72 ($C\mathrm{{=}O}$), 171.93 ($C\mathrm{{=}O}$). Anal. Calcd for $\mathrm{C_{15}H_{24}O_6}$: C, 59.98; H, 8.05. Found: C, 60.13; H, 8.27.

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