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Pd-Catalyzed Coupling Reaction of Acetylenes, Iodotrimethylsilane, and Organozinc Reagents for the Stereoselective Synthesis of Vinylsilanes

Naoto Chatani, Nobuyoshi Amishiro, Takaya Morii, Toshiaki Yamashita,[†] and Shinji Murai*

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan

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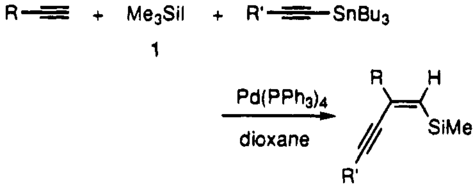
The reaction of terminal acetylenes with Me_3SiI (**1**) and organozinc reagents in the presence of $Pd(PPh_3)_4$ results in addition of the trimethylsilyl group of **1** and an alkyl group of the organozinc reagent to the acetylenes. In all cases the trimethylsilyl group adds to the terminal carbon of the acetylenes. Both aromatic and aliphatic terminal acetylenes undergo the coupling reaction with high regio- and stereoselectivities. The yield and stereoselectivity are relatively sensitive to the nature of the organozinc reagent used. The reaction of phenylacetylene (**2**) using Bu_2Zn gives the corresponding coupling product in high yield with high stereoselectivity (>98%). In contrast, the use of BuZnI results in 92% stereoselectivity. The stereoselectivity for the reaction using $(Me_3SiCH_2)_2Zn$ is lower than those for Me_2Zn, Et_2Zn, and Bu_2Zn. For organozinc reagents, alkylzinc works well while phenyl-, ethynyl-, and allylzinc do not. The reaction using Me_3SiCl, Me_3SiBr, Me_3SiSPh, $Me_3SiSePh$, and Me_3SiOTf in place of **1** does not proceed. The reaction with Me_3SiMe_2SiI and $Me_3SiMe_2SiMe_2SiI$ in place of **1** gives the corresponding vinyldisilane and -trisilane, respectively.

Introduction

The stereoselective synthesis of vinylsilanes is important because vinylsilanes have been recognized as versatile building blocks in organic synthesis.[1] A wide variety of starting materials such as ketones, vinyl halides, and olefins have been used for the preparation of vinylsilanes. Acetylenes are also a substrate of choice. One of the more straightforward routes to stereodefined vinylsilanes is transition-metal-catalyzed hydrosilylation of acetylenes, and many papers dealing with this reaction have appeared so far.[2] Hydrometalation[3] or carbometalation[4] of silylacetylenes has been extensively studied in recent years for the stereoselective preparation of vinylsilanes. Stoichiometric silylmetalation of acetylenes with Si−M (M = Li, Mg, Al, Cu, and Zn) species followed by treatment with electrophiles is also one of the attractive methods.[5] Despite the wide availability of synthetic methods of vinylsilanes as described above, there still exists a need for new selective and convenient procedures.

We have been studying the development of catalytic synthesis of vinylsilanes on the basis of new methodology, which involves silylmetalation[6] of an olefin or an acetylene with Si−M (M = transition metal) as the key catalytic species. Along this line, we have reported new synthetic methods of vinylsilanes by the Fe,[7a] Ru,[7b] Os,[7a] Co,[7c] and Rh[7d]-catalyzed dehydrogenative silylation of olefins with hydrosilanes as well as the Pd- and Ni-catalyzed addition reactions of Me_3SiCN to acetylenes.[8]



(1)

Very recently, we reported a new Pd-catalyzed coupling reaction of acetylenes with iodotrimethylsilane (Me_3SiI, **1**) and organostannanes leading to silyl-substituted conjugated enynes (eq 1).[9] This new catalytic reaction involves oxidative addition of the Si−I bond in **1** to Pd(0) leading to a silylpalladium(II) species (**I**) and silylpal-

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[†] On leave from Miyakonojo National College of Technology.

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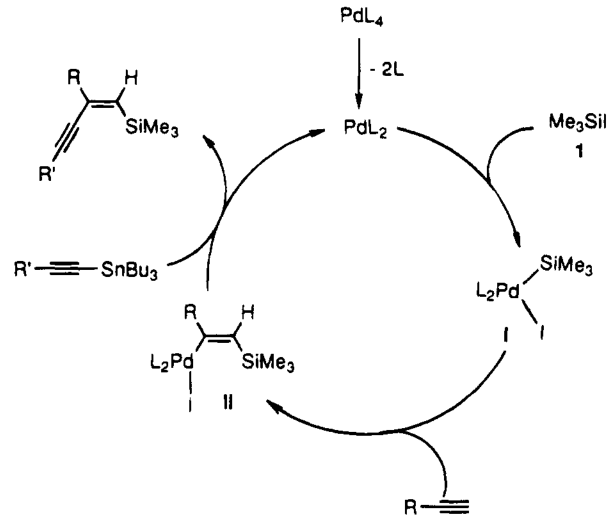
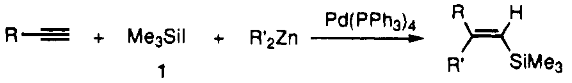
0022-3263/95/1960-1834$09.00/0

Scheme 1



ladation of an acetylene with the Si−Pd species **I** followed by coupling with organostannanes (Scheme 1). This catalytic cycle seems to be reasonable in the light of related precedents in the literature. In 1988, Tanaka reported a stoichiometric reaction of bromo- and iodotrimethylsilane with $Pt(PEt_3)_3$ leading to silylplatinum(II) complexes, $Me_3SiPtX(PEt_3)_2$ (X = Br or I) as the first example of the oxidative addition of a silicon−halogen bond to a transition metal complex.[10] Although silylpalladation has not been a well-established process for stoichiometric organometallic reactions, a number of catalytic reactions are believed to involve silylpalladation as the key steps.[6] The examples of Pd-catalyzed reactions of acetylenes are bis-silylation with disilanes (Si−Si),[11] silylstannation with silylstannanes (Si−Sn),[12] silylcyanation with a silylcyanide (Si−CN),[8] and ring opening addition of a silacyclobutane.[13] Recently, Tanaka reported an explicit example of the insertion of an acetylene into a Si−Pt bond, i.e., the reaction of an acetylene with $Me_3SiPtI(PEt_3)_2$ affording a (β-silylvinyl)platinum complex (similar to **II** in Scheme 1).[14] It was also reported that the reaction of bis(silyl)palladium complexes, $(R_3Si)_2PdL_2$, with acetylenes gave bis(silyl)ethenes as the result of silylpalladation.[15]

Though useful and interesting, the reaction of eq 1 suffers from limitations. The most significant one is that alkylstannane reagents cannot participate in the reaction. Alkyl groups could not be incorporated into the acetylenes by this route. To make the coupling reaction more useful and general, we have examined the possibility of using other organometallic reagents (R−M; R = alkynyl, alkyl, vinyl, Ph; M = Al, B, Hg, Si, Zn, Zr) which are known to act as coupling reagents in Pd-catalyzed reactions of vinyl halides.[16] Among these examined, dialkylzinc reagents were found to participate cleanly in the coupling reaction. Described below is a new route to stereodefined vinylsilanes through the Pd-catalyzed coupling reaction of acetylenes, iodotrimethylsilane (Me_3SiI, **1**), and organozinc reagents (eq 2).



(2)

Results and Discussion

The Pd-catalyzed coupling reaction (eq 2) can be applied to a variety of acetylenes and organozinc reagents. The results are summarized in Table 1. Both aromatic and aliphatic terminal acetylenes undergo the coupling reaction. Most importantly, the coupling reaction proceeds regio- and stereoselectively. In all cases the trimethylsilyl group added to the terminal carbon of the acetylenes, and the alkyl group from dialkyl zinc reagents was introduced to the internal carbon.

When the reaction of phenylacetylene (**2**) with **1** (2 equiv) and Me_2Zn (1 equiv) in the presence of 5 mol % of $Pd(PPh_3)_4$ was run in dioxane at 25 °C for 8 h, (*E*)-2-phenyl-1-(trimethylsilyl)prop-1-ene (**3a**) was obtained

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Table 1. Pd-Catalyzed Reaction of Acetylenes with Me$_3$SiI and Organozinc Reagents[a]

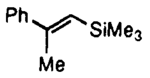
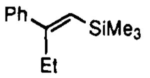
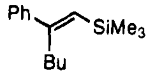
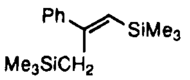
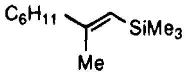
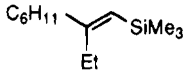
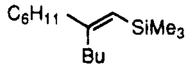
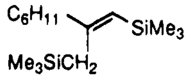
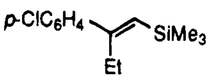
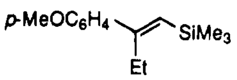
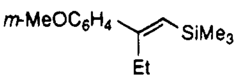
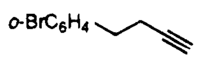
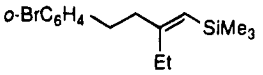
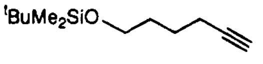
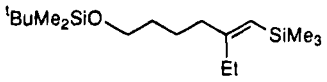
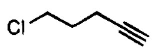
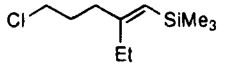
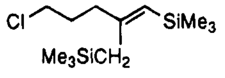
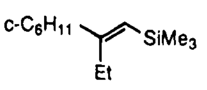
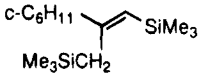
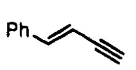
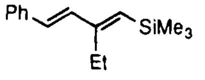
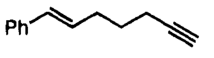
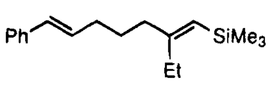
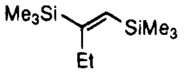
entry	acetylene	organozinc	product	time/h	yield/% [b]
1	Ph—≡ **2**	Me$_2$Zn	 **3a**	8	61 (>98)
2 [c]	**2**	Me$_2$Zn	**3a**	2	77 (>98)
3	**2**	Et$_2$Zn	 **3b**	1	90 (>98)
4	**2**	BuZnI [d]	 **3c**	1	41(92)
5	**2**	Bu$_2$Zn [e]	**3c**	1	73 (>98)
6	**2**	Bu$_3$ZnLi [f]	Ph—≡—SiMe$_3$	1	50
7	**2**	(Me$_3$SiCH$_2$)$_2$Zn [e]	 **3d**	1	66 (92)
8	C$_6$H$_{11}$—≡ **4**	Me$_2$Zn	 **5a**	11	48 (>98)
9 [c]	**4**	Me$_2$Zn	**5a**	2	57 (>98)
10	**4**	Et$_2$Zn	 **5b**	1	68 (>98)
11	**4**	Bu$_2$Zn [e]	 **5c**	1	73 (>98)
12	**4**	(Me$_3$SiCH$_2$)$_2$Zn [e]	 **5d**	1	64 (90)
13	*p*-ClC$_6$H$_4$—≡ **6**	Et$_2$Zn	 **7b**	1	89 (>98)
14	*p*-MeOC$_6$H$_4$—≡ **8**	Et$_2$Zn	 **9b**	1	71(62)
15	*m*-MeOC$_6$H$_4$—≡ **10**	Et$_2$Zn	 **11b**	1	98(93)
16	 **12**	Et$_2$Zn	 **13b**	1	80 (>98)
17	 **14**	Et$_2$Zn	 **15b**	1	60 (>98)

Table 1 (Continued)

entry	acetylene	organozinc	product	time/h	yield/%[b]
18	 **16**	Et_2Zn	 **17b**	1	76 (>98)
19	**16**	$(Me_3SiCH_2)_2Zn$[e]	 **17d**	7	66 (92)
20	c-C_6H_{11}—≡ **18**	Et_2Zn	 **19b**	1	64 (>98)
21	**18**	$(Me_3SiCH_2)_2Zn$[e]	 **19d**	1	44 (70)
22	 **20**	Et_2Zn	 **21b**	1	73 (60)
23	 **22**	Et_2Zn	 **23b**	1	79 (>98)
24	Me_3Si—≡ **24**	Et_2Zn[g]	 **25b**	1	27 (94)

[a] Reaction conditions: acetylene (2.5 mmol), Me_3SiI (5 mmol), organozinc reagent (2.5 mmol), $Pd(PPh_3)_4$ (0.05 mmol), dioxane (5 mL), at 25 °C. [b] Yields are based on acetylene used. Stereoselectivity is in parentheses. [c] At 40 °C. [d] Prepared from ZnI_2 and RLi (1 equiv). [e] Prepared from ZnI_2 and RLi (2 equiv). See text and experimental section. [f] Prepared from ZnI_2 and RLi (3 equiv). [g] Et_2Zn (1.25 mmol) was used.

stereoselectively in 61% yield after column chromatography (entry 1). A higher temperature (40 °C) shortened the reaction time and improved the yield to 77% (entry 2). In contrast, the reaction of **2** with **1** and Et_2Zn was complete within 1 h even at 25 °C, and (*E*)-2-phenyl-1-(trimethylsilyl)but-1-ene (**3b**) was obtained in 90% yield with virtually complete regio- and stereoselectivities (entry 3). The choice of solvent was crucial to the success of the reaction. Toluene, THF, and CH_2Cl_2 were ineffective, and using Et_2O as solvent gave **3b** in only 14% yield (>98% stereoselectivity). 1,4-Dioxane was the solvent of choice. The observed yields and stereoselectivities were sensitive to the nature of the zinc reagent used. The reaction with BuZnI, generated in situ by the treatment of ZnI_2 with 1 equiv of BuLi followed by filtration of LiI formed,[17] gave 2-phenyl-1-(trimethylsilyl)hex-1-ene (**3c**) in 41% yield with 92% stereoselectivity (entry 4). The use of Bu_2Zn, generated in situ from ZnI_2 and 2 equiv of BuLi followed by filtration of LiI, led to an increased yield (73%) and high stereoselectivity (>98%) (entry 5). However, the reaction of **2** with **1** and Bu_3ZnLi, obtained in situ from ZnI_2 and 3 equiv of BuLi followed by filtration of LiI, did not undergo the coupling reaction, but produced 1-(trimethylsilyl)phenylacetylene as the sole product (entry 6). The stereoselectivity in the reaction with $(Me_3SiCH_2)_2Zn$, prepared similarly from ZnI_2 and 2 equiv of Me_3SiCH_2Li, was slightly low. When the reaction of **2** with $(Me_3SiCH_2)_2Zn$ was run at 25 °C, stereoselectivity was decreased to 92% (66% yield) (entry 7). The reaction did not take place with other zinc reagents such as $(CH_2{=}CHCH_2)_2Zn$, Ph_2Zn, and $(PhC{\equiv}C)_2Zn$, nor did the reaction proceed when **1** was replaced with other silicon reagents such as Me_3SiCl, Me_3SiBr, Me_3SiSPh, $Me_3SiSePh$, Me_3SiOAc, $Me_3SiOC(O)OEt$, $Me_3SiOC(O)SPh$, and Me_3SiOTf.

The coupling reaction of 1-octyne (**4**), **1**, and organozinc reagents was also highly regio- and stereoselective (entries 8–12). Whether both of the ethyl groups or one of the ethyl groups in Et_2Zn is utilized for the coupling reaction was examined by varying the ratio of the reactants. The reaction where the ratio of **4**/**1**/Et_2Zn = 2.5 mmol/5 mmol/2.5 mmol resulted in 68% yield and >98% stereoselectivity (entry 10); **4**/**1**/Et_2Zn = 2.5/5/1.25, 84% yield and 91% selectivity; **4**/**1**/Et_2Zn = 2.5/3.5/1.25, 76% yield and 93% selectivity. These results show that both of ethyl groups in Et_2Zn are utilized in the coupling reaction. Thus, the first transfer of the ethyl group from Et_2Zn gave **5b** and EtZnI, and from the latter again the

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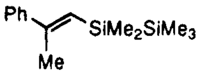
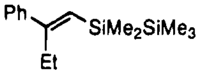
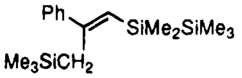
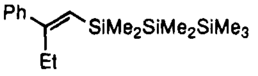
(17) For successful coupling reaction, it was necessary to separate the organozinc reagent from LiI that accompanied its formation. Without the filtration, no reaction took place. See Experimental Section.

Table 2. Pd-Catalyzed Coupling Reaction of Phenylacetylene (2) with Iodosilanes and Organozinc Reagents[a]

entry	iodosilane	organozinc	product	time/h	yield/% [b]
1	$Me_3SiSiMe_2I$	Me_2Zn	 **26a**	4	73 (>98)
2 [c]		Et_2Zn	 **26b**	2.5	64 (>98)
3		$(Me_3SiCH_2)_2Zn$ [d]	 **26d**	4	90 (82)
4	$Me_3SiSiMe_2SiMe_2I$	Et_2Zn	 **27b**	2	53 (88)

[a] Reaction conditions: phenylacetylene (2.5 mmol), iodosilane (5 mmol), organozinc reagent (2.5 mmol), $Pd(PPh_3)_4$ (0.05 mmol), dioxane (5 mL), at 40 °C. [b] Yields are based on acetylene used. Stereoselectivity is in parentheses. [c] At 25 °C. [d] Prepared from ZnI_2 and RLi (2 equiv). See experimental section. [e] Et_2Zn (1.25 mmol) was used.

ethyl group was transferred leading to **5b** and ZnI_2. The lower stereoselectivity of the second transfer than the first one was suggested by the lower selectivities of 91 and 93% for runs using a half amount (1.25 mmol) of Et_2Zn. The similar decrease in selectivity was noted in the reaction of **2** (entry 5 vs 4).

Functional groups such as siloxy, chloro, bromo, and even methoxy group that are known to react with **1**[18] remained intact under the reaction conditions (entries 13–19). A decrease in stereoselectivity was observed in the case of (*p*-methoxyphenyl)acetylene (**8**) but not in the case for (*m*-methoxyphenyl)acetylene (**10**) (entries 14 and 15), suggesting *Z*/*E* isomerization in a vinylpalladium intermediate.[19] The reaction of 4-(2-bromophenyl)butyne (**12**) afforded the corresponding product **13b** without cleavage of an aromatic–bromine bond, although Pd-catalyzed coupling of halobenzenes with organozinc reagents are known (entry 16).[20] The reaction of (4-acetyl- and (4-cyanophenyl)acetylene gave a complex mixture along with the expected product. The reaction of a conjugated enyne **20** with **1** and Et_2Zn gave **21b** in a moderate yield and with low stereoselectivity (entry 22). The reaction of (trimethylsilyl)acetylene (**24**) with Et_2Zn under the standard conditions gave the coupling product **25b** only in 4% yield. The yield was improved to some extent (27%) when the mount of Et_2Zn used was out in half (entry 24).[21] Coupling reaction of internal acetylenes such as diphenylacetylene and 1-phenylpropyne did not take place.

We thought it would be interesting to examine whether a Si–I bond or a Si–Si bond is cleaved in the reaction using iododisilane ($Me_3SiSiMe_2I$) in place of **1**, because Pd-catalyzed bis-silylation of acetylenes with halodisilanes to give bis(silyl)ethenes is well known.[11] The results are summarized in Table 2. The reaction of **2** with $Me_3SiSiMe_2I$ and Me_2Zn in the presence of $Pd(PPh_3)_4$ in dioxane at 40 °C gave (*E*)-1-[dimethyl(trimethylsilyl)silyl]-2-phenylprop-1-ene (**26a**) without the cleavage of the Si–Si bond (entry 1). The result is in accordance with the observation that $Me_3SiSiMe_2I$ undergoes oxidative addition to $Pt(PEt_3)_3$ selectively at the Si–I bond.[22] Reaction in the presence of Et_2Zn and $(Me_3SiCH_2)_2Zn$ gave the corresponding vinyldisilanes (entries 2 and 3) as well. The present reaction was also extended to the coupling reaction with iodotrisilane ($Me_3SiMe_2SiMe_2SiI$) to give the corresponding vinyltrisilane **27b** (entry 4). The data illustrated in Table 2 indicate that the method described herein has considerable promise as a synthetic tool for new silicon-containing materials, since the resulting reaction products contain Si–Si bonds.[11j,k]

Concluding Remarks

We have studied the Pd-catalyzed coupling reaction of acetylenes, Me_3SiI, and organozinc reagents on the basis of the working hypothesis that the reaction proceeds via a mechanism closely related to that shown in Scheme 1. However, the mechanism of the present reaction is not fully understood. One can consider an alternative that the reaction procceds via carbozincation[23] of acetylenes with R_2Zn followed by quenching with Me_3SiI. This possibility can be excluded for the following reasons. If the reaction involves carbozincation, Me_3SiCl, Me_3SiBr,

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(18) For reviews on Me_3SiI, see: Schmidt, V. A. H. *Chem. Zeit.* **1980**, *104*, 253. Olah, G. A.; Narang, S. C. *Tetrahedron* **1982**, *38*, 2225. Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer-Verlag: Berlin, 1983; pp 21–39. Olah, G. A.; Prakash, G. K. S. In *Advances in Silicon Chemistry*; Larson, G. L., Ed.; JAI Press Inc.: Greenwich, 1991; Vol 1, pp 2–64.

(19) A similar decrease in stereoselectivity was encountered in the Pd-catalyzed reaction of (*o*- and (*p*-methoxyphenyl)acetylenes with Me_3SiCN or Me_3GeCN. This would be due to the isomerization of vinylpalladium complex (similar to **II** in Scheme 1) via a zwitterionic carbene complex. The electron-donating methoxy group stabilizes the zwitterion by the mesomeric effect. For a discussion on the isomerization, see: Chatani, N.; Morimoto, T.; Muto, T.; Murai, S. *J. Organomet. Chem.* **1994**, *473*, 335.

(20) Isobutyl, isobutenyl, benzyl, phenyl, and phenylethynyl substituents can be introduced into an aromatic ring by Pd-catalyzed halobenzenes with organozinc reagents. Hamon, D. P. G.; Massy-Westropp, R. A.; Newton, J. L. *Tetrahedron Lett.* **1993**, *34*, 5333.

(21) Et_2Zn may react with **1** to some extent.

(22) Yamashita, H.; Kobayashi, T.; Hayashi, T.; Tanaka, M. *Chem. Lett.* **1990**, 1447.

(23) For a paper on Cp_2ZrI_2-promoted ethylzincation of acetylenes, see: Negishi, E.; Van Horn, D. E.; Yoshida, T.; Rand, C. L. *Organometallics* **1983**, *2*, 563.

or Me_3SiOTf should be usable in place of **1** in the present reaction. This is not the case. In addition, treatment of **2** with Et_2Zn (2 equiv) in the presence of $Pd(PPh_3)_4$ in dioxane at 25 °C for 1 h did not give, after hydrolysis, 2-phenyl-1-butene. Whatever the mechanistic details, this new catalytic process provides a new synthetic method of vinylsilanes from an acetylene, Me_3SiI, and an organozinc reagent. The Pd-catalyzed coupling reaction is applicable to both aromatic and aliphatic acetylenes. Regioselectivity is complete; a silyl group adds to the terminal carbon of an acetylene. Stereoselectivity is high; a silyl group and an alkyl group add to an acetylene in the syn manner. The alkylative coupling with R_2Zn[24] may serve as the complimentary method for ethynylative coupling where $RC{\equiv}CSnR'_3$ is involved.[9] The observed wide functional group compatibility enhances the utility of the present reaction.

Experimental Section

General Comments. ^1H NMR and ^{13}C NMR were recorded in $CDCl_3$ with tetramethylsilane as an internal standard. Elemental analyses were performed by Elemental Analyses Section of Osaka University. Me_3SiI (**1**) was purchased from Aldrich Chemical Co. and used without further purification. Dioxane was distilled from CaH_2. Et_2Zn was commercially available as 25 w/v % solution in hexane from Wako Chemical Co. or 1.0 M solution in hexane from Aldrich Chemical Co. Me_2Zn was supplied as 2.0 M solution in hexane from Nippon Alkyl Aluminum Co. Acetylenes **6**, **8**, **10**, and **18** were prepared according to the method of Corey.[25] 4-(1-Bromophenyl)butyne (**12**) was prepared by the reaction of 1-bromobenzyl bromide with propargyl magnesium bromide.[26] A conjugated enyne **20** was prepared according to the known method.[27] Me_3SiMe_2SiI[28] and $Me_3SiMe_2SiMe_2SiI$[29] were prepared by reported methods. Vinylsilanes **3a–c** are known compounds and have already been fully characterized.[30]

General Procedure for the Coupling Reaction with Me_2Zn and Et_2Zn. In a 10-mL reaction flask were placed $Pd(PPh_3)_4$ (0.05 mmol, 58 mg), dioxane (5 mL), phenylacetylene (**2**) (2.5 mmol, 255 mg), and Et_2Zn (25 w/v % in hexane, 2.5 mmol, 1.2 mL). On addition of iodotrimethylsilane (Me_3SiI, **1**) (5 mmol, 0.71 mL) to the solution, a slightly exothermic reaction was observed. The mixture was allowed to react at 25 °C with stirring for 1 h under N_2. The reaction mixture was diluted with moist hexane (50 mL) to decompose excess Et_2Zn. Evaporation of the solvent in vacuo gave a brown oil, which was purified by column chromatography (silica gel, hexane) to give (*E*)-2-phenyl-1-(trimethylsilyl)but-1-ene (**3b**) (460 mg, 90%) as a colorless oil. An analytical sample was obtained by bulb-to-bulb distillation.

General Procedure for the Coupling Reaction Using Bu_2Zn. A 100-mL three-necked round bottomed flask equipped with a dropping funnel was flame-dried in a stream of N_2. In the flask was placed ZnI_2 (15 mmol, 4.78 g), which was dried over P_2O_5, and the flask was again flame-dried. Dioxane (10 mL) was added to the flask in one portion. After cooling to 0 °C with an ice bath, 1.6 M BuLi in hexane (30 mmol, 19 mL) was added dropwise over 30 min. A white precipitate was immediately formed. After stirring at 0 °C for 1 h, the mixture was warmed to 25 °C where it was kept for 2 h. The precipitates were filtered through a filter funnel with a glass frit and washed with 5 mL of dioxane twice. The solution was diluted with dioxane to make the solution about 0.6 M in dioxane (a total volume of 25 mL). The solution was used for the coupling reaction without titration.

In a 10-mL reaction flask were placed $Pd(PPh_3)_4$ (0.05 mmol, 58 mg), dioxane (1 mL), phenylacetylene (**2**) (2.5 mmol, 255 mg), Bu_2Zn in dioxane (5 mL), and iodotrimethylsilane (Me_3SiI, **1**) (5 mmol, 0.71 mL) in this order. The mixture was allowed to stir at 25 °C for 1 h under N_2. The reaction mixture was diluted with moist hexane (50 mL) to decompose unreacted organozinc compound. Evaporation of the volatiles in vacuo gave a brown oil, which was purified by column chromatography (silica gel, hexane) to give (*E*)-2-phenyl-1-(trimethylsilyl)hex-1-ene (**3c**) (423 mg, 73%) as a colorless oil. An analytical sample was obtained by bulb-to-bulb distillation.

The reaction using $(Me_3SiCH_2)_2Zn$ was carried out in a similar way.

(*E*)-2-Phenyl-1,3-bis(trimethylsilyl)-2-phenylprop-1-ene (3d): bp 74–80 °C (10 Torr); ^1H NMR ($CDCl_3$) δ −0.19 (s, 9 H), 0.16 (s, 9 H), 2.18 (s, 2 H), 5.46 (s, 1 H), 7.19–7.35 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ −1.00, 0.40, 26.32, 124.78, 126.45, 127.10, 127.93, 146.16, 156.20; IR (neat) 2964, 2904, 1592, 1572, 1248, 848; MS, *m/z* (rel intensity) 262 (M^+, 7), 174 (18), 159 (21), 73 (100). Anal. Calcd for $C_{15}H_{26}Si_2$: C, 68.62; H, 9.98. Found: C, 68.56; H, 10.13.

(*E*)-2-Methyl-1-(trimethylsilyl)oct-1-ene (5a): bp 101–103 °C (10 Torr); ^1H NMR ($CDCl_3$) δ 0.09 (s, 9 H), 0.89 (t, J = 6.6 Hz, 3 H), 1.23–1.46 (m, 8 H), 1.76 (d, J = 0.7 Hz, 3 H), 2.05 (td, J = 7.8, 1.5 Hz, 2 H), 5.18 (brs, 1 H); ^{13}C NMR ($CDCl_3$) δ 0.11, 14.09, 21.55, 22.63, 27.85, 28.99, 31.79, 42.68, 122.61, 155.71; IR (neat) 2936, 2864, 1622, 1248, 838; MS, *m/z* (rel intensity) 198 (M^+, 1), 128 (20), 73 (100). Anal. Calcd for $C_{12}H_{26}Si$: C, 72.64; H, 13.21. Found: C, 72.64; H, 13.39.

(*E*)-2-Ethyl-1-(trimethylsilyl)oct-1-ene (5b): bp 114–116 °C (7 Torr); ^1H NMR ($CDCl_3$) δ 0.09 (s, 9 H), 0.89 (t, J = 6.6 Hz, 3 H), 1.01 (t, J = 7.6 Hz, 3 H), 1.23–1.48 (m, 8 H), 2.07 (t, J = 7.8 Hz, 2 H), 2.13(q, J = 7.6 Hz, 2 H), 5.15 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 0.37, 13.79, 14.08, 22.65, 28.12, 28.93, 29.16, 31.82, 38.34, 122.00, 161.74; IR (neat) 2968, 2864, 1616, 1468, 1248, 842; MS, *m/z* (rel intensity) 212 (M^+, 0), 142 (15), 73 (100). Anal. Calcd for $C_{13}H_{28}Si$: C, 73.50; H, 13.28. Found: C, 73.51; H, 13.50.

(*E*)-2-Butyl-1-(trimethylsilyl)oct-1-ene (5c): bp 115–116 °C (7 Torr); ^1H NMR ($CDCl_3$) δ 0.09 (s, 9 H), 0.89 (t, J = 6.8 Hz, 3 H), 0.92 (t, J = 7.1 Hz, 3 H), 1.22–1.44 (m, 12 H), 2.02–2.14 (m, 4 H), 5.15 (t, J = 1.4 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 0.46, 14.11, 22.65, 23.08, 28.15, 29.14, 31.48 31.82, 35.94, 38.94, 122.46, 160.44; IR (neat) 2960, 2864, 1616, 1246, 842; MS, *m/z* (rel intensity) 240 (M^+, 5), 128 (31), 73 (100); HRMS calcd for $C_{15}H_{32}Si$ 240.2273, found 240.2289.

(*E*)-1-(Trimethylsilyl)-2-[(trimethylsilyl)methyl)]oct-1-ene (5d): bp 108–114 °C (9 Torr); ^1H NMR ($CDCl_3$) δ 0.05 (s, 9 H), 0.08 (s, 9 H), 0.89 (t, J = 6.6 Hz, 3 H), 1.27–1.44 (m, 8 H), 1.73 (s, 2 H), 1.99 (dt, J = 0.8, 7.8 Hz, 2 H), 4.99 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ −0.59, 0.56, 14.09, 22.65, 27.16, 28.09, 29.05, 31.80, 41.75, 119.05, 157.89; IR (neat) 2964, 2864, 1604, 1248, 1152, 846; MS, *m/z* (rel intensity) 270 (M^+, 3), 125 (13), 112 (11), 73 (100). Anal. Calcd for $C_{15}H_{34}Si_2$: C, 66.58; H, 12.66. Found: C, 66.40; H, 12.82.

(*E*)-2-(4-Chlorophenyl)-1-(trimethylsilyl)but-1-ene (7b): bp 125–128 °C (5 Torr); ^1H NMR ($CDCl_3$) δ 0.20 (s, 9 H), 0.97 (t, J = 7.6 Hz, 3 H), 2.61 (q, J = 7.6 Hz, 2 H), 5.73 (s, 1 H), 7.29–7.35 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 0.16, 13.97, 27.78, 127.56, 127.99, 128.23, 132.91, 141.74, 157.72; IR (neat) 2968, 1598, 1564, 1494, 1248, 1096, 1012, 924, 862, 838; MS, *m/z* (rel intensity) 240 (M^+ for ^{37}Cl, 3), 225 (18), 223 (49), 171 (36), 170 (14), 169 (100), 73 (34). Anal. Calcd for $C_{13}H_{19}ClSi$: C, 65.38; H, 8.02; Cl, 14.84. Found: C, 65.57; H, 8.14; Cl, 14.75.

(*E*)-2-(4-Methoxyphenyl)-1-(trimethylsilyl)but-1-ene (9b-*E*): bp 121–125 °C (3 Torr); ^1H NMR ($CDCl_3$) δ 0.18 (s, 9 H), 0.99 (t, J = 7.6 Hz, 3 H), 2.61 (q, J = 7.6 Hz, 2 H), 3.81 (s, 3 H), 5.68 (s, 1 H), 6.83–6.86, 7.23–7.37 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 0.27, 14.18, 27.80, 55.23, 113.46, 125.25, 127.29, 135.58, 158.26, 158.95; IR (neat) 2964, 1612, 1576, 1286, 1246, 1178, 1038, 862, 836; MS, *m/z* (rel intensity) 235 (M^+, 3), 234 (15), 219 (27), 166 (14), 165 (100), 73 (30). Anal. Calcd for $C_{14}H_{22}OSi$: C, 71.73; H, 9.46. Found: C, 71.63; H, 9.53.

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(*Z*)-2-(4-Methoxyphenyl)-1-(trimethylsilyl)but-1-ene (9b-*Z*): ^{1}H NMR ($CDCl_3$) δ −0.17 (s, 9 H), 1.00 (t, J = 7.6 Hz, 3 H), 2.39 (qd, J = 7.6, 1.3 Hz, 2 H), 3.81 (s, 3 H), 5.51 (s, 1 H), 6.82−6.85 (m, 2 H), 7.05−7.08 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 0.17, 12.69, 35.30, 55.20, 113.05, 124.98, 128.98, 136.81, 158.58, 160.89; MS, *m/z* (rel intensity) 235 (M^+, 3), 234 (17), 219 (30), 166 (15), 165 (100), 73 (34).

(*E*)-2-(3-Methoxyphenyl)-1-(trimethylsilyl)but-1-ene (11b): bp 130−135 °C (3 Torr); ^{1}H NMR ($CDCl_3$) δ 0.19 (s, 9 H), 0.98 (t, J = 7.6 Hz, 3 H), 2.61 (q, J = 7.6 Hz, 2 H), 3.83 (s, 3 H), 5.73 (s, 1 H), 6.78−6.82 (m, 1 H), 6.93−7.04 (m, 2 H), 7.19−7.26 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 0.20, 14.09, 27.95, 55.23, 112.19, 112.39, 118.79, 127.03, 129.03, 145.00, 158.89, 159.48; IR (neat) 2964, 1602, 1578, 1490, 1286, 1248, 848; MS, *m/z* (rel intensity) 235 (M^+, 3), 234 (15), 220 (19), 219 (27), 203 (17), 166 (13), 165 (93), 135 (12), 102 (12), 73 (34). Anal. Calcd for $C_{14}H_{22}OSi$: C, 71.73; H, 9.46. Found: C, 71.71; H, 9.49.

(*E*)-4-(2-Bromophenyl)-2-ethyl-1-(trimethylsilyl)but-1-ene (13b): bp 140−143 °C (2 Torr); ^{1}H NMR ($CDCl_3$) δ 0.11 (s, 9 H), 1.06 (t, J = 7.6 Hz, 3 H), 2.20 (q, J = 7.6 Hz, 2 H), 2.33−2.39 (m, 2 H), 2.82−2.88 (m, 2 H), 5.22 (brs, 1 H), 7.02−7.08 (m, 1 H), 7.21−7.23 (m, 2 H), 7.51−7.54 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 0.34, 13.82, 29.11, 35.38, 38.33, 123.22, 124.38, 127.32, 127.47, 130.45, 132.73, 141.59, 160.14; IR (neat) 3068, 2964, 1616, 1572, 1472, 1444, 1246, 1046, 838; MS, *m/z* (rel intensity) 312 (M^+ for ^{81}Br, 0), 298 (4), 297 (18), 295 (18), 190 (10), 157 (36), 139 (36), 137 (35), 129 (41), 73 (100). Anal. Calcd for $C_{15}H_{23}BrSi$: C, 57.87; H, 7.45; Br, 25.66. Found: C, 57.87; H, 7.60; Br, 25.61.

(*E*)-6-(*tert*-Butyldimethylsiloxy)-2-ethyl-1-(trimethylsilyl)hex-1-ene (15b): bp 132−134 °C (3 Torr); ^{1}H NMR ($CDCl_3$) δ 0.05 (s, 6 H), 0.09 (s, 9 H), 0.89 (s, 9 H), 1.00 (t, J = 7.6 Hz, 3 H), 1.43−1.57 (m, 4 H), 2.11 (t, J = 7.6Hz, 2 H), 2.14 (t, J = 7.6 Hz, 2 H), 3.62 (t, J = 6.4 Hz, 2 H), 5.15 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ −5.25, 0.36, 13.76, 18.37, 24.21, 25.98, 28.84, 32.58, 37.93, 63.20 122.32, 161.30; IR (neat) 2960, 2864, 1616, 1248, 840; MS, *m/z* (rel intensity) 314 (M^+, 0), 148 (16), 147 (100), 133 (19), 75 (13), 73 (45). Anal. Calcd for $C_{17}H_{38}OSi_2$: C, 64.89; H, 12.17. Found: C, 64.79; H, 12.39.

(*E*)-6-Chloro-2-ethyl-1-(trimethylsilyl)pent-1-ene (17b): bp 96−97 °C (7 Torr); ^{1}H NMR ($CDCl_3$) δ 0.10 (s, 9 H), 1.02 (t, J = 7.6 Hz, 3 H), 1.85−1.96 (m, 2 H), 2.10−2.24 (m, 4 H), 3.58 (t, J = 6.6 Hz, 2 H), 5.18 (t, J = 1.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 0.28, 13.70, 28.93, 31.04, 35.16, 44.71, 123.51, 159.30; IR (neat) 2964, 1616, 1248, 842; MS, *m/z* (rel intensity) 204 (M^+ for ^{35}Cl, 1), 95 (47), 93 (100), 73 (38). Anal. Calcd for $C_{10}H_{21}ClSi$: C, 58.64; H, 10.33; Cl, 17.31. Found: C, 58.67; H, 10.51; Cl, 17.33.

(*E*)-6-Chloro-1-(trimethylsilyl)-2-[(trimethylsilyl)methyl]hex-1-ene (17d): bp 108−117 °C (10 Torr); ^{1}H NMR ($CDCl_3$) δ 0.06 (s, 9 H), 0.08 (s, 9 H), 1.73 (s, 2 H), 1.86−1.96 (m, 2 H), 2.12−2.18 (m, 2 H), 3.52 (t, J = 6.8 Hz, 2 H), 5.01 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ −0.62, 0.46, 27.22, 30.99, 38.50, 44.70, 120.40, 155.54; IR (neat) 2960, 2904, 1606, 1248, 1156, 860, 766; MS, *m/z* (rel intensity) 262 (M^+ for ^{35}Cl, 2), 93 (15), 73 (100). Anal. Calcd for $C_{12}H_{27}ClSi_2$: C, 54.81; H, 10.35; Cl, 13.48. Found: C, 54.71; H, 10.58; Cl, 13.44.

(*E*)-2-Cyclohexyl-1-(trimethylsilyl)but-1-ene (19b): bp 128−132 °C (10 Torr); ^{1}H NMR ($CDCl_3$) δ 0.09 (s, 9 H), 1.00 (t, J = 7.6 Hz, 3 H), 1.11−1.30 (m, 5 H), 1.70−1.88 (m, 6 H), 2.15 (q, J = 7.6 Hz, 2 H), 5.14 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 0.48, 14.44, 26.45, 26.99, 28.78, 33.22, 45.33, 119.20, 167.03; IR (neat) 2936, 2860, 1614, 1454, 1248, 898, 844; MS, *m/z* (rel intensity) 210 (M^+, 5), 195 (11), 139 (13), 136 (21), 73 (100). Anal. Calcd for $C_{13}H_{26}Si$: C, 74.20; H, 12.45. Found: C, 74.17; H, 12.57.

2-Cyclohexyl-1,3-bis(trimethylsilyl)prop-1-ene (19d): bp 105−116 °C (10 Torr); ^{1}H NMR ($CDCl_3$) δ [0.01 (*Z*), 0.04 (*E*), s, 9 H, $SiCH_3$], [0.066 (*E*), 0.07 (*Z*), s, 9 H], 1.07−1.74 (m, 11 H), [1.54 (*Z*), 1.77 (*E*), s, 2 H], [4.92 (*Z*), 4.96 (*E*), s, 1 H]; ^{13}C NMR ($CDCl_3$) δ [-0.49 (*E*), −0.42 (*Z*)], [0.60 (*Z*), 0.65 (*E*)], 23.75, 26.06, 26.33, 26.44, 27.05, 27.68, 32.96, 47.45, [115.52 (*E*), 120.99 (*Z*)], 163.16; IR (neat) 2936, 2860, 1602, 1246, 848; MS, *m/z* (rel intensity) 269 (M^+, 3), 165 (17), 73 (100). Anal. Calcd for $C_{15}H_{32}Si_2$: C, 67.08; H, 12.01. Found: C, 67.04; H, 12.27.

(*E*)-2-Ethyl-4-phenyl-1-(trimethylsilyl)but-1,3-diene (21b): bp 132−139 °C (6.5 Torr); ^{1}H NMR ($CDCl_3$) δ 0.17 (s, 9 H), 1.15 (t, J = 7.6 Hz, 3 H), 2.46 (q, J = 7.6 Hz, 2 H), 5.65 (s, 1H), 6.57 (d, J = 16.4 Hz, 1 H), 6.72 (d, J = 16.5 Hz, 1 H), 7.19−7.44 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 0.17, 14.87, 25.14, 126.48, 127.36, 127.78, 128.59, 132.25, 133.55, 137.52, 177.82; IR (neat) 2964, 1602, 1580, 1248, 962, 868; MS, *m/z* (rel intensity) 230 (M^+, 11), 156 (10), 143 (11), 129 (10), 73 (100). Anal. Calcd for $C_{15}H_{22}Si$: C, 78.20; H, 9.62. Found: C, 78.06; H, 9.73.

(1*E*,6*E*)-2-Ethyl-7-phenyl-1-(trimethylsilyl)hepta-1,6-diene (23b): ^{1}H NMR ($CDCl_3$) δ 0.10 (s, 9 H), 1.01 (t, J = 7.6 Hz, 3 H), 1.60 (quint, J = 7.8 Hz, 2 H), 2.15 (q, J = 7.6 Hz, 2 H), 2.10−2.25 (m, 4 H), 5.18 (s, 1 H), 6.23 (dt, J = 15.9, 6.8 Hz, 1 H), 6.39 (d, J = 15.9 Hz, 1 H), 7.16−7.36 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 0.37, 13.80, 27.74, 28.91, 32.75, 37.72, 122.55, 125.90, 126.78, 128.46, 129.98, 130.86, 137.86, 161.06; IR (neat) 2964, 1616, 1248, 964, 842; MS, *m/z* (rel intensity) 272 (M^+, 0), 130 (59), 129 (11), 109 (33), 91 (13), 73 (26). Anal. Calcd for $C_{18}H_{28}Si$: C, 79.34; H, 10.36. Found: C, 79.08; H, 10.55.

(*E*)-1,2-Bis(trimethylsilyl)but-1-ene (25b): bp 108−112 °C; ^{1}H NMR ($CDCl_3$) δ 0.09 (s, 9 H), 0.13 (s, 9 H), 0.99 (t, J = 7.6 Hz, 3 H), 2.30 (q, J = 7.6 Hz, 2 H), 5.97 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ −0.81, 0.54, 15.61, 29.36, 140.72, 167.12; IR (neat) 2964, 1566, 1248, 928, 846; MS, *m/z* (rel intensity) 200 (M^+, 6), 185 (11), 112 (21), 111 (37), 97 (12), 73 (100). HRMS calcd for $C_{10}H_{24}Si_2$ 200.1417, found 200.1420.

(*E*)-2-Phenyl-1-[(trimethylsilyl)dimethylsilyl]prop-1-ene (26a): bp 136−139 °C (3.5 Torr); ^{1}H NMR ($CDCl_3$) δ 0.14 (s, 9 H), 0.28 (s, 6 H), 2.22 (s, 3 H), 5.98 (s, 1 H), 7.24−7.40 (m, 3 H), 7.47−7.51 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ −2.64, −1.78, 21.61, 125.41, 126.46, 127.19, 128.10, 144.17 151.31; IR (neat) 2960, 1600, 1576, 1446, 1246, 836, 802, 768; MS, *m/z* (rel intensity) 248 (M^+, 10), 175 (51), 159 (38), 135 (100), 73 (53). Anal. Calcd for $C_{14}H_{24}Si_2$: C, 67.66; H, 9.73. Found: C, 67.56; H, 9.82.

(*E*)-2-Phenyl-1-[(trimethylsilyl)dimethylsilyl]but-1-ene (26b): bp 153−155 °C (14 Torr); ^{1}H NMR ($CDCl_3$) δ 0.11 (s, 9 H), 0.24 (s, 6 H), 0.98 (t, J = 7.5 Hz, 3 H), 2.60 (q, J = 7.4 Hz, 2 H), 5.74 (s, 1 H), 7.21−7.41 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ −2.47, −1.88, 14.17, 28.50, 126.20, 126.35, 127.06, 128.13, 143.36, 158.73; IR (neat) 2960, 1598, 1574, 1246, 838, 800; MS, *m/z* (rel intensity) 262 (M^+, 12), 189 (89), 173 (43), 145 (21), 135 (100), 73 (87). Anal. Calcd for $C_{15}H_{26}Si_2$: C, 68.62; H, 9.98. Found: C, 68.48; H, 10.03.

(*E*)-2-Phenyl-1,3-bis[(trimethylsilyl)dimethylsilyl]prop-1-ene (26d): bp 147−153 °C (0.5 Torr); ^{1}H NMR ($CDCl_3$) δ −0.17 (s, 9 H), 0.11 (s, 9 H), 0.23 (s, 6 H), 2.16 (s, 2 H), 5.48 (s, 1 H), 7.22−7.35 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ −2.15, −1.72, −0.99, 27.05, 123.60, 126.42, 127.00, 127.90, 146.13, 156.13; IR (neat) 2960, 1590, 1246, 836, 804, 764; MS, *m/z* (rel intensity) 320 (M^+, 7), 247 (23), 159 (26), 135 (24), 131 (13), 73 (100). Anal. Calcd for $C_{17}H_{32}Si_3$: C, 63.67; H, 10.06. Found: C, 63.61; H, 9.88.

(*E*)-2-Phenyl-1-[[(trimethylsilyl)dimethylsilyl]dimethylsilyl]but-1-ene (27b): bp 166−167 °C (3 Torr); ^{1}H NMR ($CDCl_3$) δ 0.10 (s, 9 H), 0.14 (s, 6 H), 0.28 (s, 6 H), 0.98 (t, J = 7.6 Hz, 3 H), 2.61 (q, J = 7.6 Hz, 2 H), 5.75 (s, 1 H), 7.24−7.40 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ −6.38, −1.47, −1.39, 14.2, 28.5, 126.2, 126.8, 127.0, 128.1, 143.4, 158.6; IR (neat) 2956, 1598, 1574, 1246, 836; MS, *m/z* (rel intensity) 320 (M^+, 6), 231 (11), 189 (40), 173 (74), 145 (19), 135 (55), 116 (17), 73 (100); HRMS calcd for $C_{17}H_{32}Si_3$ 320.1813, found 320.1811.

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