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Silylcuprates from Allene and Their Reaction with α,β-Unsaturatedd Nitriles and Imines. Synthesis of Silylated Oxo Compounds Leading to Cyclopentane and Cycloheptane Ring Formation

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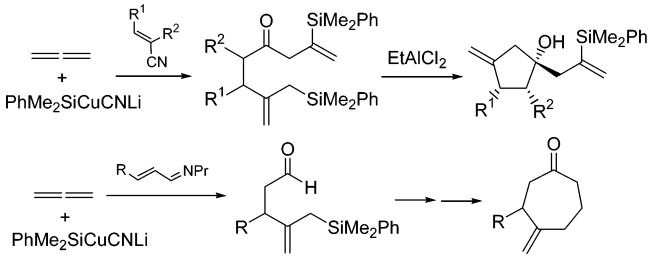

The silylcupration of allenes and the subsequent capture of the intermediate cuprate with α,β-unsaturated nitriles is reported. The influence of the substitution of the nitrile, the nature of the silylcopper species, and the temperature on the selectivity of the reaction is studied. An interesting diaddition process was observed (1,2-addition and 1,4-addition), leading to oxo compounds which simultaneously have an allylsilane and a vinylsilane group. The different reactivity of these two units has been employed in the intramolecular allylsilane-terminated cyclization of these adducts, where the vinylsilane moiety remains unchanged. To shed some light on the reaction pathway, the behavior of α,β-unsaturatedd imines was also checked and a new and convenient way for cycloheptane annulation presented. In light of the former results a feasible mechanism is proposed.

Introduction

Organosilanes are interesting building blocks in organic synthesis due to the large number of transformations that the C−Si bond can undergo.[1] Among them allyl- and vinylsilanes have gained considerable importance as usual synthetic intermediates in organic synthesis. Silylmetalation of multiple bonds is one of the most attractive strategies for the efficient synthesis of these compounds.[2] In particular the silylcupration of allenes provides an easy entry to the synthesis of allyl- and vinylsilanes,[3] since it allows the introduction of two different metals (Si and Cu) across a C−C multiple bond. It has been shown that the silylcupration of allenes occurs syn-stereospecifically,[4] giving rise to the formation of intermediate cuprates, which react with electrophiles to afford either vinyl- or allylsilanes. The regiochemistry of the addition depends on various factors such as the nature of the cuprate, the substitution of the allene, the temperature of the reaction, and the nature of the silyl group. Thus, the reaction of 1,2-propadiene with higher order silylcyanocuprates **1** containing the dimethylphenylsilyl group gives,[5,6] at any temperature between −78 and 0 °C, a vinylsilane−allylcuprate intermediate **2**, which readily reacts with a wide variety of electro-

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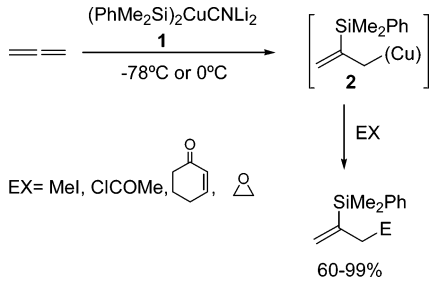
SCHEME 1



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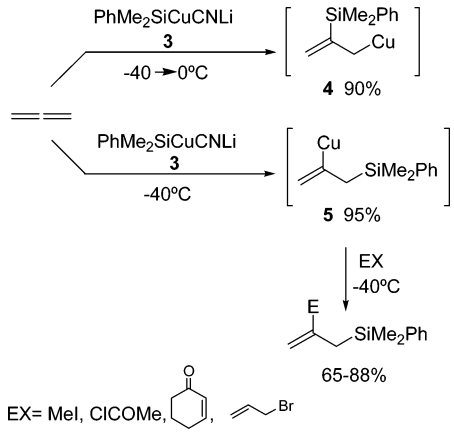


philes, leading to the corresponding vinylsilanes (Scheme 1).

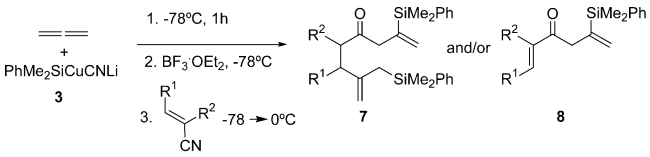
Interestingly the use of a lower order cuprate, the (dimethylphenylsilyl)cuprate reagent **3**, in an analogous addition to allene, provides a completely different regiochemistry pattern.[7] The reaction now shows temperature dependence, giving the vinylsilane−allylcopper intermediate **4**, at 0 °C, and the allylsilane−vinylcopper intermediate **5**, at −40 °C, which might account for the reversibility of the reaction. This result has great interest since it opens a route for the synthesis of functionalized allylsilanes, by reaction of **5** with electrophiles (Scheme 2).

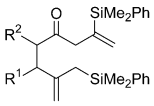
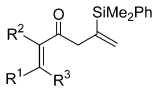
Results and Discussion

In general the reactive species at low temperature is **5**. Thus, at −40 °C, α,β-unsaturatedd oxo compounds react with **5** to give exclusively the products of Michael addition. However, at −40 °C saturated ketones are unreactive toward species **5**, but they readily react with **4** as the temperature warms to 0 °C, giving now the vinylsilane resulting from 1,2-addition. These results account for the rapid interconversion between species **4** and **5** as the temperature increases. Surprisingly, when the electrophile used is an unsaturatedd nitrile, diaddition of both species can occur.

We now report the full results[8] of an unusual tandem diaddition process of the copper species **4** and **5** to α,β-unsaturatedd nitriles to give products which have both an allylsilane group and a vinylsilane group.

TABLE 1. Silylcupration of Allenes and Reaction with Alkenenitriles Using the Lower Order Cuprate 3



Entry	Alkenenitrile[a]	Product	Yield[b]
			
1	**6a**, $R^1 = R^2 = H$	**7a**, $R^1 = R^2 = H$	87%
2	**6b**, $R^1 = H$, $R^2 = Me$	**7b**, $R^1 = H$, $R^2 = Me$	83%
3	**6c**, $R^1 = H$, $R^2 = Cl$	**7c**, $R^1 = H$, $R^2 = Cl$	78%
4	**6d**, $R^1 = Me$, $R^2 = H$	**7d**, $R^1 = Me$, $R^2 = H$	83%
			
5	**6e**, $R^1 = Me$, $R^2 = Et$, $R^3 = H$	**8e**, $R^1 = Me$, $R^2 = Et$, $R^3 = H$	60%
6	**6f**, $R^1 = R^2 = -(CH_2)_{3}-$, $R^3 = Me$	**8f**, $R^1 = R^2 = -(CH_2)_{3}-$, $R^3 = Me$	50%
7	**6g**, $R^1 = R^2 = -(CH_2)_{4}-$, $R^3 = H$	**8g**, $R^1 = R^2 = -(CH_2)_{4}-$, $R^3 = H$	55%
8	**6h**, $R^1 = R^2 = -(CH_2)_{5}-$, $R^3 = H$	**8h**, $R^1 = R^2 = -(CH_2)_{5}-$, $R^3 = H$	53%
9	**6i**, $R^1 = Et$, $R^2 = H$, $R^3 = H$	**7i** + **8i** (2:1)	81%
10	**6j**, $R^1 = R^2 = -(CH_2)_{3}-$, $R^3 = H$	**7j** + **8j** (5:1)	79%
11	**6k**, $R^1 = Ph$, $R^2 = H$, $R^3 = H$	**7k** + **8k** (5:1)	81%

[a] Ratio cuprate:nitrile = 2:1. [b] Yield of isolated product referred to nitrile.

Organocopper reagents are relatively unreactive toward alkenenitriles.[9] Particularly reactive cuprates are generally required for efficient organocopper additions to these substrates. Thus reaction of the higher order cuprate $Me_2CuLi{\cdot}LiCN$ with α,β-unsaturatedd nitriles causes 1,2-addition,[10] whereas addition of trimethylsilyl chloride ((TMS)Cl) redirects the reaction toward double 1,2- and 1,4-addition.[11] Boron-containing cuprate reagents promote conjugate additions to alkenenitriles with moderated yields.[12]

The reaction of the lower order silylcopper reagent **3**, prepared by stirring at 0 °C 1 equiv of (dimethylphenylsilyl)lithium and copper(I) cyanide in tetrahydrofuran (THF) for 30 min, with allene at −78 °C for 1 h, followed by addition of $BF_3{\cdot}OEt_2$ and subsequent slow addition of nitriles **6a**−**k** (−78 to 0 °C) affords the ketones **7a**−**k** and **8i**−**k** (Table 1). The reaction (one pot) is clean and high-yielding and seems to be produced by addition of the allylcopper species **4** to the nitrile and conjugate addition of the vinylcopper species **5** to the double bond.

The most obvious explanation for these results is a reversible reaction, with the vinylcopper species **5** being

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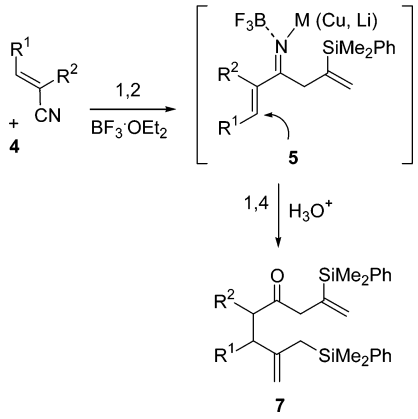
(11) Alexakis, A.; Berlan, J.; Besace, Y. *Tetrahedron Lett*. **1986**, *27*, 1047−1050.
(12) Yamamoto, Y.; Yamamoto, S.; Yatagai, H.; Ishihara, Y.; Maruyama, K. *J. Org. Chem*. **1982**, *47*, 119−126.

SCHEME 3



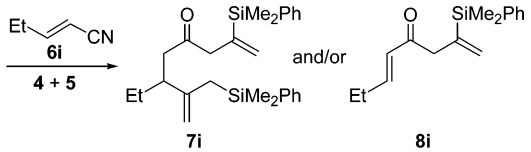
the kinetic intermediate (−78 to −40 °C), and the allylcopper species **4** being the thermodynamic intermediate (−40 to 0 °C). The preference of species **5** for Michael addition and of species **4** for 1,2 addition must be related to the higher hardness of cuprate **4** toward **5**.

As can be observed in Table 1, alkenenitriles fall into three groups: alkenenitriles **6a**−**d**, which are good Michael acceptors, give regioselectively the products of double 1,2- and 1,4-addition **7a**−**d** (entries 1−4). However less reactive alkenenitriles **6e**−**h** give regioselectively the products of 1,2-monoaddition **8e**−**h** (entries 5−8) probably due to alkyl substitution, which simultaneously leads to electronic and steric deactivation toward conjugate addition. Finally, nitriles **6i**−**k**, having an intermediate electronic character, give mixtures of the product of double and monoaddition, being the major one, in every case, the product of diaddition (entries 9−11).

Regarding the diaddition products, the order in which the two steps of addition (1,2 and 1,4) take place is not totally certain. It seems feasible, in view of the absence of 1,4-monoaddition products, that the reaction proceeds by initial addition of species **4** to the nitrile, followed by conjugate addition of species **5** to the intermediate α,β-unsaturatedd ketimine (Scheme 3). Further support for this mechanistic pathway is the easy reaction of α,β-unsaturatedd imines with **5** (see below, Table 5) and the fact that the intermediate of the silylcupration of allene, using the lower order cuprate **3**, is unreactive toward the pentanenitrile enolate (prepared by reaction of pentanenitrile with lithium diisoprpylamide (LDA), at −78 °C, 30 min). The latter result seems to discard the opposite order of addition (first $A_{1,4}$ and second $A_{1,2}$). Effectively, the second step of this sequence (1,2-addition of **4** to the resulting intermediate, formally a nitrile enolate) does not seem very probable in view of the unsuccessful result obtained with pentanenitrile. (Scheme 3).

Moreover, the selectivity of the reaction (double addition versus 1,2-addition) depends also upon the temperature of the process (Table 2). Thus the reaction of nitrile **6i** with the intermediate of the silylcupration of allene (**4** and/or **5**) gives a 2:1 mixture of **7i** and **8i** when the reaction is carried out at −78 °C, warming up from −78 to 0 °C (entry 1). However when the reaction was repeated from −78 to −50 °C, quenching the intermediate at −50 °C, the diaddition product **7i** was obtained exclusively (entry 3). And when the reaction was done

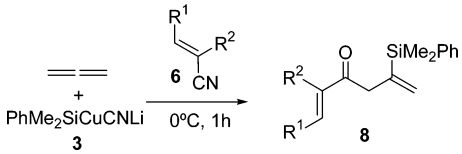
TABLE 2. Dependence of the Reaction with Temperature



entry[a]	temp (°C)	product (ratio)	yield[b] (%)
1	−78 → 0	**7i** + **8i** (2:1)	81
2	−50 → 0	**7i** + **8i** (1:1)	73
3	−78 → −50	7i	78
4	0	8i	61

[a] Ratio cuprate:nitrile = 2:1. [b] Referred to converted nitrile.

TABLE 3. Reaction with Alkenenitriles at 0 °C



entry[a]	alkenenitrile	product	yield[b] (%)
1	**6d**	**8d**	58
2	**6i**	**8i**	61
3	**6j**	**8j**	59
4	**6k**	**8k**	64

[a] Ratio nitrile:cuprate = 1:1. [b] Isolated product.

at 0 °C (for 1 h, quenching at that temperature) only the 1,2-addition product **8i** was obtained (entry 4).

These results reinforce the mechanistic proposal since they show that, under thermodynamic conditions, cuprate **4** is the only species present, being the monoaddition 1,2 product obtained. However under kinetic conditions, even though cuprate **5** is the major one in the equilibrium, the product of double addition is obtained through an initial and rapid 1,2-addition of the minor cuprate **4** and subsequent addition of **5**.

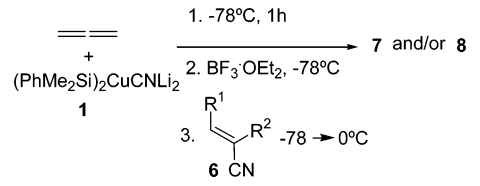
The selective generation of the product of 1,2-monoaddition at 0 °C was shown to be general for other nitriles, as seen in Table 3. This selectivity is also found when the ratio of nitrile to cuprate is 2:1.

The influence of the nature of the silylcuprate in the selectivity of the reaction was also examined. Thus reaction of the higher order silylcopper reagent **1** with allene at −78 °C for 1 h, followed by addition of BF_3·OEt_2 and subsequent slow addition of nitriles **6b**−**d**,**i**,**k** (−78 to 0 °C) affords the ketones **7c**,**d**,**i**,**k** and **8b**−**d**,**i**,**k** (Table 4).

Now the product of 1,2-addition is the only or a major isomer, which is consistent with the allylcopper intermediate **2** being the major species in the equilibrium (Scheme 1).

To corroborate the mechanistic proposal and the existence of an intermediate imine (Scheme 3), we studied the silylcupration of allene with the lower order cuprate **3** and the reaction of the intermediate cuprate with α,β-unsaturatedd imines **9a**−**d**. The reaction leads with high yields to the corresponding oxoallylsilanes **10a**−**d** (Table 5). Moreover this methodology constitutes an alternative to the synthesis of these interesting aldehydes, which are not readily available by silylcupration of allene and

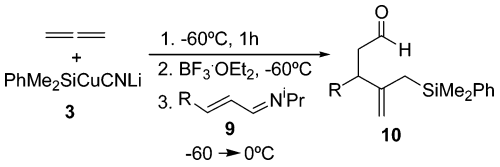
TABLE 4. Silylcupration of Allenes and Reaction with Alkenenitriles Using the Higher Order Cuprate 1



entry[a]	alkenenitrile	product	yield[b] (%)
1	**6b**, R^1 = H, R^2 = Me	8b	75
2	**6c**, R^1 = H, R^2 = Cl	**7c** + **8c** (1:4)	72
3	**6d**, R^1 = Me, R^2 = H	**7d** + **8d** (1:2)	65
4	**6i**, R^1 = Et, R^2 = H	**7i** + **8i** (1:2)	68
5	**6k**, R^1 = Ph, R^2 = H	**7k** + **8k** (1:2)	60

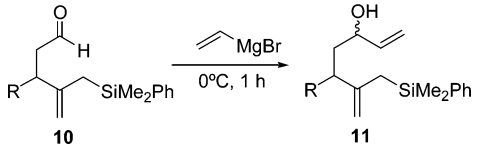
[a] Ratio nitrile:cuprate = 1:2. [b] Isolated product.

TABLE 5. Reaction with α,β -Unsaturatedd Imines



entry	imine	product	yield (%)
1	**9a**, R = H	**10a**, R = H	84
2	**9b**, R = Me	**10b**, R = Me	65
3	**9c**, R = ^{n}Pr	**10c**, R = ^{n}Pr	77
4	**9d**, R = Ph	**10d**, R = Ph	79

TABLE 6. Synthesis of Allylic Alcohols



entry	aldehyde	product	yield (%)
1	**10a**, R = H	**11a**, R = H	95
2	**10b**, R = Me	**11b**, R = Me	89
3	**10c**, R = ^{n}Pr	**11c**, R = ^{n}Pr	90
4	**10d**, R = Ph	**11d**, R = Ph	87

reaction with α,β -unsaturatedd aldehydes due to isomerization processes.[13]

Oxoallylsilanes **10** can be seen as precursors of seven-membered rings, which are useful units since they constitute the structure core of a large number of biologically important natural products,[14] such as karahanaenone or perforenone. Their synthesis is accomplished in three steps from **10**. Thus, reaction of aldehydes **10** with vinylmagnesium bromide affords in excellent yield allylic alcohols **11**, as a mixture of two diastereoisomers (Table 6).

In the case of alcohols **11d** both isomers can be separated by chromatography, one of them being a solid, the X-ray image of which is showed in Figure 1.

(13) (a) Barbero, A.; García, C.; Pulido, F. J. *Tetrahedron Lett.* **1999**, *40*, 6649−6652. (b) Barbero, A.; García, C.; Pulido, F. J. *Tetrahedron* **2000**, *56*, 2739−2751.

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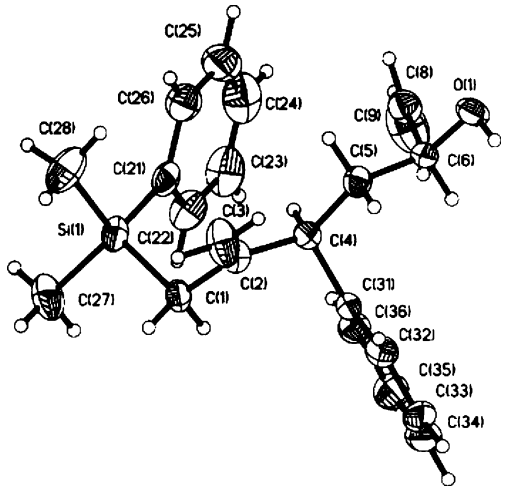
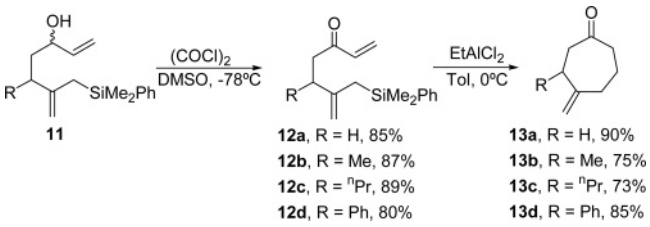


FIGURE 1. X-ray crystal structure of [3*S**,5*S**]-6-[(dimethylphenylsilyl)methyl]-5-phenyl-1,6-heptadien-3-ol.

SCHEME 4



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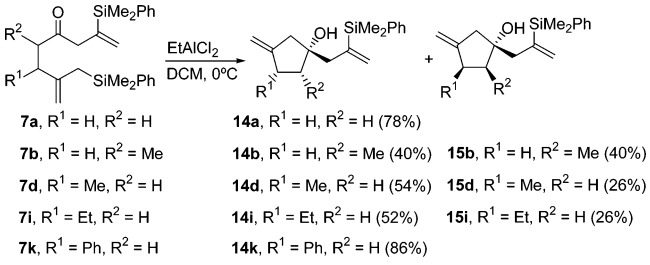


Oxidation of **11** gave the corresponding enones **12**, which were subjected to Lewis acid-catalyzed cyclization, leading in good yield to methylenecycloheptanones **13** (Scheme 4).

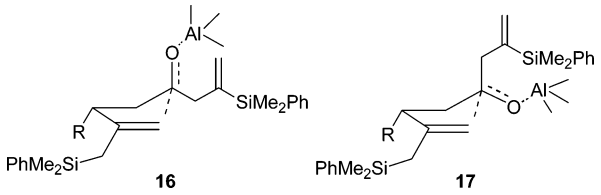
Moreover, diadducts **7** containing a nucleophilic allylsilane unit and an electrophilic carbonyl moiety undergo intramolecular allylsilane-terminated cyclization when treated with a Lewis acid, while the vinylsilane unit remains unchanged. The reaction leads with high yields to methylenecyclopentanols **14** and **15** (Scheme 5).

The stereoselectivity of the reaction is not high unless a phenyl group is present in the molecule, which might indicate the competitiveness between two relatively bulky groups (vinylsilane moiety and carbonyl complexed with the Lewis acid) for the equatorial position in the transition states **16** or **17** where the R group attains an equatorial conformation[13b] (Chart 1).

Conclusions

In summary, silylcupration of allenes and reaction with α,β -unsaturated nitriles leads to the products of 1,2-addition or to the diaddition adducts, depending on the

CHART 1



substituents of the nitrile, the temperature, and the nature of the silylcuprate. The products of double addition resulting from consecutive 1,2- and 1,4-addition show two silyl moieties (an allylsilane group and a vinylsilane group) with a very different reactivity pattern. Thus, these compounds undergo intramolecular cyclization processes in the presence of a Lewis acid, where the vinylsilane moiety remains unchanged. α,β -Unsaturated imines, in the same conditions, give oxoallylsilanes which can be easily converted to methylenecycloheptanones in high yields.

Experimental Section

Silylcupration of Allene. (a) Preparation of Intermediates 4 + 5. A solution of (dimethylphenylsilyl)lithium (6 mmol) in THF was added by syringe to a stirred suspension of copper(I) cyanide (6 mmol) in THF at 0 °C. After 30 min at this temperature the solution of (dimethylphenylsilyl)copper **3** (6 mmol) was cooled at −78 °C and a slight excess of allene was added from a balloon. The mixture was stirred for 1 h and then used immediately.

(b) Reaction of Intermediates 4 + 5 with α,β-Unsaturated Nitriles. (1) Procedure A. $BF_3.Et_2O$ (6 mmol) was added at −78 °C to the solution previously prepared and the mixture stirred for an additional period of 10 min. The nitrile (3 mmol) in THF was slowly dropped in at −78 °C and stirred at this temperature for 1 h. The reaction mixture was left to warm to 0 °C, quenched with basic saturated ammonium chloride solution, and extracted with ether. The organic layer was dried ($MgSO_4$), evaporated, and chromatographed to give the corresponding products (Table 1).

(2) Procedure B. The nitrile (3 mmol) in THF was slowly dropped in at 0 °C to the solution previously prepared and the mixture stirred for an additional period of 1 h. The reaction mixture was quenched with basic saturated ammonium chloride solution and extracted with ether. The organic layer was dried ($MgSO_4$), evaporated, and chromatographed to give the corresponding products (Table 3).

(c) 2-(Dimethylphenylsilyl)-7-[(dimethylphenylsilyl)-methyl]octa-1,7-dien-4-one (7a). Colorless oil. IR (neat, cm^{-1}): 1705, 1630, 1240, 1110. ^1H NMR ($CDCl_3$): δ 7.55−7.35 (10H, m), 5.75 (1H, d, J = 2.2 Hz), 5.64 (1H, d, J = 2.2 Hz), 4.52 (2H, s), 3.14 (2H, s), 2.34 (2H, t, J = 7.7 Hz), 2.02 (2H, t, J = 7.7 Hz), 1.74 (2H, s), 0.41 (6H, s), 0.33 (6H, s). ^{13}C NMR ($CDCl_3$): δ 208.4 (C), 145.6 (C), 143.6 (C), 138.8 (C), 137.3 (C), 134.0 (CH), 133.5 (CH), 130.5 (CH_2), 129.2 (CH), 129.0 (CH), 127.8 (CH), 127.7 (CH), 107.8 (CH_2), 50.1 (CH_2), 40.4 (CH_2), 31.8 (CH_2), 26.2 (CH_2), −3.0 (CH_3), −3.1 (CH_3). MS: *m/z* 406 (M^+, 5), 329 (M^+ − Ph, 10), 271 (M^+ − $SiMe_2Ph$, 13), 135 ($SiMe_2Ph$, 100). Anal. Calcd for $C_{25}H_{34}OSi_2$: C, 73.83; H, 8.43. Found: C, 74.18; H, 8.71.

(d) 2-(Dimethylphenylsilyl)-7-[(dimethylphenylsilyl)-methyl]-5-methylocta-1,7-dien-4-one (7b). Colorless oil. IR (neat, cm^{-1}): 1695, 1640, 1240, 1110. ^1H NMR ($CDCl_3$): δ 7.56−7.27 (10H, m), 5.70 (1H, d, J = 2.6 Hz), 5.63 (1H, d, J = 2.6 Hz), 4.58 (2H, s), 3.17 (1H, d, J = 16.4 Hz), 3.10 (1H, d, J = 16.4 Hz), 2.61−2.53 (1H, m), 2.12 (1H, dd, J = 14.3 and 6.3 Hz), 1.72 (1H, d, J = 13 Hz), 1.70 (1H, dd, J = 14.3 and 4.4 Hz), 1.65 (1H, d, J = 13 Hz), 0.88 (3H, d, J = 6.7 Hz), 0.40 (6H, s), 0.34 (6H, s). ^{13}C NMR ($CDCl_3$): δ 212.1 (C), 143.8 (C), 143.5 (C), 138.5 (C), 137.5 (C), 134.0 (CH), 133.6 (CH), 130.5 (CH_2), 129.1 (CH), 129.0 (CH), 127.8 (CH), 110.3 (CH_2), 48.6 (CH_2), 43.6 (CH), 41.3 (CH_2), 25.5 (CH_2), 16.0 (CH_3), −2.9 (CH_3), −3.0 (CH_3). MS: *m/z* 420 (M^+, 3), 405 (M^+ − CH_3, 7), 343 (M^+ − Ph, 10), 285 (M^+ − $SiMe_2Ph$, 20), 135 ($SiMe_2Ph$, 100). Anal. Calcd for $C_{26}H_{36}OSi_2$: C, 74.22; H, 8.62. Found: C, 74.53; H, 8.89.

(e) 5-Chloro-2-(dimethylphenylsilyl)-7-[(dimethylphenylsilyl)methyl]-octa-1,7-dien-4-one (7c). Colorless oil. IR (neat, cm^{-1}): 1707, 1630, 1240, 1110. ^1H NMR ($CDCl_3$): δ 7.51−7.20 (10H, m), 5.71 (1H, d, J = 2.2 Hz), 5.63 (1H, d, J = 2.2 Hz), 4.64 (1H, s), 4.62 (1H, s), 4.15 (1H, dd, J = 8.8 and 5.7 Hz), 3.36 (1H, d, J = 16.8 Hz), 3.28 (1H, d, J = 16.8 Hz), 2.35 (1H, dd, J = 15.1 and 5.7 Hz), 2.17 (1H, dd, J = 15.1 and 8.8 Hz), 1.75 (1H, d, J = 13.6 Hz), 1.66 (1H, d, J = 13.6 Hz), 0.38 (6H, s), 0.31 (6H, s). ^{13}C NMR ($CDCl_3$): δ 202.3 (C), 142.6 (C), 141.2.5 (C), 138.3 (C), 137.1 (C), 134.0 (CH), 133.5 (CH), 131.3 (CH_2), 129.2 (CH), 127.8 (CH), 111.9 (CH_2), 60.0 (CH), 46.0 (CH_2), 41.4 (CH_2), 25.7 (CH_2), −3.0 (CH_3−Si). MS: *m/z* 440 (M^+, 5), 286 (M^+ − 2×Ph, 12), 271 (M^+ − 2×Ph-CH_3, 100). Anal. Calcd for $C_{25}H_{33}ClOSi_2$: C, 68.06; H, 7.54. Found: C, 68.38; H, 7.81.

(f) 2-(Dimethylphenylsilyl)-7-[(dimethylphenylsilyl)-methyl]-6-methylocta-1,7-dien-4-one (7d). Colorless oil. IR (neat, cm^{-1}): 1680, 1580, 1240, 1110. ^1H NMR ($CDCl_3$): δ 7.53−7.27 (10H, m), 5.73 (1H, d, J = 2.4 Hz), 5.62 (1H, d, J = 2.4 Hz), 4.55 (1H, s), 4.51 (1H, s), 3.09 (2H, s), 2.40−2.29 (2H, m), 2.18−2.08 (1H, dd, J = 15.2 and 7.8 Hz), 1.74 (1H, d, J = 13.9 Hz), 1.67 (1H, d, J = 13.9 Hz), 0.87 (3H, d, J = 6.7 Hz), 0.39 (6H, s), 0.32 (6H, s). ^{13}C NMR ($CDCl_3$): δ 208.1 (C), 151.0 (C), 143.6 (C), 139.0 (C), 137.4 (C), 134.0 (CH), 133.6 (CH), 130.6 (CH_2), 129.2 (CH), 129.0 (CH), 127.8 (CH), 127.7 (CH), 106.6 (CH_2), 50.5 (CH_2), 48.4 (CH_2), 36.1 (CH), 25.1 (CH_2), 19.4 (CH_3), −2.8 (CH_3), −2.9 (CH_3). MS: *m/z* 420 (M^+, 5), 405 (M^+ − CH_3, 7), 343 (M^+ − Ph, 10), 135 ($SiMe_2Ph$, 100). Anal. Calcd for $C_{26}H_{36}OSi_2$: C, 74.22; H, 8.62. Found: C, 74.66; H, 8.95.

(g) 6-Ethyl-2-(dimethylphenylsilyl)-7-[(dimethylphenylsilyl)methyl]-octa-1,7-dien-4-one (7i). Colorless oil. IR (neat, cm^{-1}): 1695, 1630, 1240, 1110. ^1H NMR ($CDCl_3$): δ 7.55−7.23 (10H, m), 5.73 (1H, d, J = 2.5 Hz), 5.6 (1H, d, J = 2.5 Hz), 4.59 (1H, s), 4.55 (1H, s), 3.10 (2H, s), 2.26−2.11 (3H, m), 1.68 (2H, s), 1.29−1.22 (2H, m), 0.72 (3H, t, J = 7.3 Hz), 0.40 (6H, s), 0.33 (6H, s). ^{13}C NMR ($CDCl_3$): δ 208.2 (C), 148.6 (C), 143.6 (C), 139.1 (C), 137.4 (C), 134.0 (CH), 133.6 (CH), 130.6 (CH_2), 129.2 (CH), 129.0 (CH), 127.8 (CH), 127.7 (CH), 108.4 (CH_2), 50.5 (CH_2), 46.4 (CH_2), 43.0 (CH), 25.8 (CH_2), 24.6 (CH_2), 11.3 (CH_3), −2.6 (CH_3), −2.7 (CH_3). MS: *m/z* 357 (M^+ − Ph, 5), 299 (M^+ − $SiMe_2Ph$, 12), 135 ($SiMe_2Ph$, 100). Anal. Calcd for $C_{27}H_{38}OSi_2$: C, 74.59; H, 8.81. Found: C, 74.98; H, 9.11.

(h) *cis*-2-[1-(Dimethylphenylsilyl)methyl]ethenylcyclopentyl 2-(Dimethylphenylsilyl)-2-propenyl Ketone (7j). Colorless oil. IR (neat, cm^{-1}): 1695, 1620, 1240, 1100. ^1H NMR ($CDCl_3$): δ 7.54−7.27 (10H, m), 5.70 (1H, d, J = 2.3 Hz), 5.61 (1H, d, J = 2.3 Hz), 4.59 (1H, s), 4.51 (1H, s) 3.17 (2H, s), 2.77 (1H, m), 2.57 (1H, q, J = 8.3 Hz), 1.80−1.35 (6H, m), 1.70 (2H, s), 0.39 (6H, s), 0.33 (6H, s). ^{13}C NMR ($CDCl_3$): δ 210.9 (C), 148.7 (C), 143.7 (C), 139.0 (C), 137.5 (C), 134.0 (CH), 133.9 (CH), 133.6 (CH), 130.5 (CH_2), 129.1 (CH), 129.0 (CH), 127.7 (CH), 107.2 (CH_2), 55.3 (CH), 50.2 (CH), 49.7 (CH_2), 32.4 (CH_2), 30.0 (CH_2), 24.8 (CH_2), 24.7 (CH_2), −2.7 (CH_3), −3.0 (CH_3). MS: *m/z* 446 (M^+, 5), 431 (M^+ − CH_3, 7), 369 (M^+ − Ph, 10), 311 (M^+ − $SiMe_2Ph$, 15), 135 ($SiMe_2Ph$, 100). Anal. Calcd for $C_{28}H_{38}OSi_2$: C, 75.27; H, 8.57. Found: C, 75.58; H, 8.84.

(i) 2-(Dimethylphenylsilyl)hepta-1,5-dien-4-one (8d). Colorless oil. IR (neat, cm^{-1}): 1650, 1600, 1240, 1110. ^1H NMR ($CDCl_3$): δ 7.54−7.27 (5H, m), 6.70 (1H, dq, J = 15.6 and 6.9 Hz), 6.03 (1H, d, J = 15.6 Hz), 5.74 (1H, d, J = 1.2 Hz), 5.61 (1H, d, J = 1.2 Hz), 3.28 (2H, s), 1.81 (3H, d, J = 6.9 Hz), 0.43 (3H, s), 0.39 (3H, s). ^{13}C NMR ($CDCl_3$): δ 191.4 (C), 156.5 (C), 143.2 (CH), 136.4 (C), 134.6 (CH), 134.0 (CH), 131.2 (CH_2),

129.4 (CH), 127.9 (CH), 65.5 (CH_2), 18.3 (CH_3), −3.2 (CH_3), −3.8 (CH_3). MS: *m/z* 229 ($M^+ - CH_3$, 100), 135 ($SiMe_2Ph$, 32). Anal. Calcd for $C_{15}H_{20}OSi$: C, 73.71; H, 8.25. Found: C, 73.98; H, 8.51.

(j) 2-(Dimethylphenylsilyl)-5-ethylhepta-1,5-dien-4-one (8e). Colorless oil. IR (neat, cm^{-1}): 1675, 1640, 1250, 1095, 909. ^1H NMR ($CDCl_3$): δ 7.55−7.27 (5H, m), 6.45 (1H, q, *J* = 7.0 Hz), 5.66 (1H, d, *J* = 2.1 Hz), 5.56 (1H, d, *J* = 2.1 Hz), 3.39 (2H, s), 2.24 (2H, q, *J* = 7.6 Hz), 1.77 (3H, d, *J* = 7.0 Hz), 0.88 (3H, t, *J* = 7.6 Hz), 0.39 (6H, s). ^{13}C NMR ($CDCl_3$): δ 199.8 (C), 144.9 (C), 143.9 (C), 137.8 (CH), 134.0 (CH), 129.0 (CH), 129.1 (CH_2), 127.7 (CH), 44.1 (CH_2), 18.4 (CH_2), 14.3 (CH_3), 13.2 (CH_3), −3.1 (CH_3). M. S. *m/z* 272 (M^+, 5), 257 ($M^+ - CH_3$, 100), 195 (M^+ − Ph, 67), 135 ($SiMe_2Ph$, 37). Anal. Calcd for $C_{17}H_{24}OSi$: C, 74.94; H, 8.88. Found: C, 75.28; H, 9.17.

(k) 2-Methyl-1-cyclopentenyl 2-(Dimethylphenylsilyl)-2-methyl-2-propenyl Ketone (8f). Colorless oil. IR (neat; *ν*, cm^{-1}): 1655, 1600, 1240, 1090. ^1H NMR ($CDCl_3$): δ 7.54−7.27 (5H, m), 5.67 (1H, d, *J* = 2.4 Hz), 5.58 (1H, d, *J* = 2.4 Hz), 3.27 (2H, s), 2.55−2.50 (2H, m), 2.48−2.39 (2H, m), 2.00 (3H, s), 1.76 (2H, quint, *J* = 7.5 Hz), 0.39 (6H, s). ^{13}C NMR ($CDCl_3$): δ 199.1 (C), 154.6 (C), 144.1 (C), 137.6 (C), 135.1 (C), 134.0 (CH), 129.4 (CH_2), 129.0 (CH), 127.7 (CH), 49.0 (CH_2), 40.7 (CH_2), 33.9 (CH_2), 21.5 (CH_2), 16.7 (CH_3), −3.1 (CH_3). MS: *m/z* 269 ($M^+ - CH_3$, 23), 207 (M^+ − Ph, 19), 135 ($SiMe_2Ph$, 22). EI HRMS. Calcd for $C_{18}H_{24}OSi$ (M^+): 284.1596. Found: 284.1605.

(l) 1-Cyclohexenyl 2-(Dimethylphenylsilyl)-2-propenyl Ketone (8 g). Colorless oil. IR (neat, cm^{-1}): 1695, 1630, 1240, 1090. ^1H NMR ($CDCl_3$): δ 7.54−7.27 (5H, m), 6.66 (1H, s), 5.68 (1H, d, *J* = 2.2 Hz), 5.57 (1H, d, *J* = 2.2 Hz), 3.40 (2H, s), 2.14−2.10 (2H, m), 2.14−2.10 (2H, m), 1.57−1.55 (4H, m), 0.39 (6H, s). ^{13}C NMR ($CDCl_3$): δ 199.9 (C), 144.9 (C), 140.6 (CH), 138.8 (C), 137.6 (C), 134.0 (CH), 129.3 (CH_2), 129.0 (CH), 127.7 (CH), 44.1 (CH_2), 26.0 (CH_2), 23.0 (CH_2), 21.8 (CH_2), 21.4 (CH_2), −3.1 (CH_3). MS: *m/z* 284 (M^+, 5), 269 ($M^+ - CH_3$, 15), 207 (M^+ − Ph, 18), 135 ($SiMe_2Ph$, 45). Anal. Calcd for $C_{18}H_{24}OSi$: C, 76.00; H, 8.50. Found: C, 76.38; H, 8.79.

(m) 1-Cycloheptenyl 2-(Dimethylphenylsilyl)-2-propenyl Ketone (8h). Colorless oil. IR (neat, cm^{-1}): 1650, 1240, 1090. ^1H NMR ($CDCl_3$): δ 7.55−7.27 (5H, m), 6.83 (1H, t, *J* = 6.7 Hz), 5.68 (1H, d, *J* = 2.2 Hz), 5.57 (1H, d, *J* = 2.2 Hz), 3.42 (2H, s), 2.44−2.40 (2H, m), 2.27−2.21 (2H, m), 1.78−1.72 (2H, m), 1.56−1.47 (2H, m), 1.46−1.37 (2H, m), 0.40 (6H, s). ^{13}C NMR ($CDCl_3$): δ 199.9 (C), 145.7 (C), 145.2 (CH), 145.1 (C), 137.6 (C), 134.0 (CH), 129.1 (CH_2), 129.0 (CH), 127.7 (CH), 44.1 (CH_2), 32.2 (CH_2), 29.0 (CH_2), 26.0 (CH_2), 25.7 (CH_2), 25.5 (CH_2), −3.1 (CH_3). MS: *m/z* 299 (M^+ + **1**, 5), 283 ($M^+ - CH_3$, 39), 221 (M^+ − Ph, 30), 135 ($SiMe_2Ph$, 28). Anal. Calcd for $C_{19}H_{26}OSi$: C, 76.45; H, 8.78. Found: C, 76.78; H, 9.07.

(n) 2-(Dimethylphenylsilyl)octa-1,5-dien-4-one (8i). Colorless oil. IR (neat, cm^{-1}): 1660, 1620, 1240, 1110. ^1H NMR ($CDCl_3$: δ 7.55−7.27 (5H, m), 6.78−6.68 (1H, dt, *J* = 15.8 and 6.3 Hz), 6.01 (1H, dt, *J* = 15.8 and 1.6 Hz), 5.75 (1H, d, *J* = 2.2 Hz), 5.62 (1H, d, *J* = 2.2 Hz), 3.30 (2H, s), 2.19−2.14 (2H, m), 1.03 (3H, t, *J* = 7.5 Hz), 0.40 (6H, s). ^{13}C NMR ($CDCl_3$): δ 198.8 (C), 149.1 (CH), 143.9 (C), 137.4 (C), 134.0 (CH), 130.1 (CH_2), 129.1 (CH), 128.6 (CH), 127.7 (CH), 47.3 (CH_2), 25.4 (CH_2), 12.1 (CH_3), −3.2 (2×CH_3). MS: *m/z* 243 ($M^+ - CH_3$, 30), 181 (M^+ − Ph, 35), 135 ($SiMe_2Ph$, 70). Anal. Calcd for $C_{16}H_{22}OSi$: C, 74.36; H, 8.58. Found: C, 74.68; H, 8.86.

(o) 1-Cyclopentenyl 2-(Dimethylphenylsilyl)-2-propenyl Ketone (8j). Colorless oil. IR (neat, cm^{-1}): 1700, 1645, 1240, 1090. ^1H NMR ($CDCl_3$): δ 7.53−7.26 (5H, m), 6.49 (1H, s), 5.71 (1H, d, *J* = 2.4 Hz), 5.57 (1H, d, *J* = 2.4 Hz), 3.42 (2H, s), 2.49−2.40 (4H, m), 1.85 (2H, quint, *J* = 7.6 Hz), 0.38 (6H, s). ^{13}C NMR ($CDCl_3$): δ 197.3 (C), 145.3 (C), 144.4 (C), 144.0 (CH), 137.4 (C), 134.0 (CH), 129.6 (CH_2), 129.0 (CH), 127.7 (CH), 46.1 (CH_2), 33.9 (CH_2), 30.5 (CH_2), 22.7 (CH_2), −3.1 (CH_3). MS: *m/z* 255 ($M^+ - CH_3$, 44), 193 (M^+ − Ph, 41), 135 ($SiMe_2Ph$, 100). Anal. Calcd for $C_{17}H_{22}OSi$: C, 75.50; H, 8.20. Found: C, 75.93; H, 8.51.

(p) 2-(Dimethylphenylsilyl)-6-phenylhexa-1,5-dien-4-one (8k). Colorless oil. IR (neat, cm^{-1}): 1650, 1600, 1240, 1110. ^1H NMR ($CDCl_3$): δ 7.59−7.37 (11H, m), 6.64 (1H, d, *J* = 16.1 Hz), 5.82 (1H, d, *J* = 2.2 Hz), 5.68 (1H, d, *J* = 2.2 Hz), 3.42 (2H, s) 0.40 (6H, s). ^{13}C NMR ($CDCl_3$): δ 198.5 (C), 143.9 (C), 142.7 (CH), 137.3 (C), 134.4 (C), 134.0 (CH), 130.4 (CH), 130.3 (CH_2), 129.2 (CH), 128.8 (CH), 128.3 (CH), 127.9 (CH), 125.4 (CH), 48.2 (CH_2), −3.2 (CH_3). MS: *m/z* 291 ($M^+ - CH_3$, 17), 229 (M^+ − Ph, 19), 135 ($SiMe_2Ph$, 100). Anal. Calcd for $C_{20}H_{22}OSi$: C, 78.38; H, 7.24. Found: C, 78.69; H, 7.51.

Silylcupration of Allene and Reaction with α,β-Unsaturated Nitriles Using Cuprate 1. A solution of (dimethylphenylsilyl)lithium (12 mmol) in THF was added by syringe to a stirred suspension of copper(I) cyanide (6 mmol) in THF at 0 °C. After 30 min at this temperature, the solution of bis(dimethylphenylsilyl)cuprate **1** (6 mmol) was cooled at −78 °C and a slight excess of allene was added from a ballon. The mixture was stirred for 1 h and then used immediately. $BF_3{\cdot}Et_2O$ (6 mmol) was added at −78 °C to the solution previously prepared and the mixture stirred for an additional period of 10 min. The nitrile (3 mmol) in THF was slowly dropped in at −78 °C and stirred at this temperature for 1 h. The reaction mixture was left to warm to 0 °C, quenched with basic saturated ammonium chloride solution, and extracted with ether. The organic layer was dried ($MgSO_4$), evaporated, and chromatographed to give the corresponding products (Table 4).

(a) 2-(Dimethylphenylsilyl)-5-methylhexa-1,5-dien-4-one (8b). Colorless oil. IR (neat, cm^{-1}): 1687, 1635, 1105. ^1H NMR ($CDCl_3$): δ 7.67−7.38 (5H, m), 5.85 (1H, s), 5.78 (1H, s), 5.74 (1H, d, *J* = 2.0 Hz), 5.68 (1H, d, *J* = 2.0 Hz), 3.55 (2H, s), 1.89 (3H, s), 0.47, 0.46 (3H, s). ^{13}C NMR ($CDCl_3$): δ 200.6 (C), 144.7 (C), 144.2 (C), 137.5 (C=), 134.1 (CH), 129.7 (CH), 129.2 (CH_2), 127.8 (CH), 125.2 (CH_2), 44.7 (CH_2), 17.7 (CH_3), −2.9 (CH_3). MS: *m/z* 229 ($M^+ - CH_3$, 100), 135 ($SiMe_2Ph$, 28). Anal. Calcd for $C_{15}H_{20}OSi$: C, 73.71; H, 8.25. Found: C, 73.98; H, 8.59.

(b) 5-Chloro-2-(dimethylphenylsilyl)hexa-1,5-dien-4-one (8c). Colorless oil. IR (neat, cm^{-1}): 1692, 1633, 1105. ^1H NMR ($CDCl_3$): δ 7.64−7.27 (5H, m), 6.17 (1H, d, *J* = 2 Hz), 5.96 (1H, d, *J* = 2 Hz), 5.72 (1H, s), 5.65 (1H, s), 3.53 (2H, s), 0.47 (6H, s). ^{13}C NMR ($CDCl_3$): δ 192.9 (C), 143.3 (C), 138.9 (C), 138.0 (C), 134.1 (CH), 130.2 (CH_2), 129.2 (CH), 127.8 (CH), 124.2 (CH_2), 44.9 (CH_2), −2.4 (CH_3), −3.2 (CH_3). MS: *m/z* 264 (M^+, 9), 229 (M^+ − Cl, 20), 135 ($SiMe_2Ph$, 35). Anal. Calcd for $C_{14}H_{17}ClOSi$: C, 63.50; H, 6.47. Found: C, 63.88; H, 8.72.

Silylcupration of Allene with α,β-Unsaturated Imines. $BF_3{\cdot}Et_2O$ (6 mmol) was added at −60 °C to the solution previously prepared, and the mixture stirred for an additional period of 10 min. The imine (6 mmol) in THF was slowly dropped in at −60 °C and stirred at this temperature for 1 h. The reaction mixture was left to warm to 0 °C, quenched with basic saturated ammonium chloride solution, and extracted with ether. The organic layer was dried ($MgSO_4$), evaporated, and chromatographed to give the products **10a**−**d**.

(a) 4-[(Dimethylphenylsilyl)methyl]pent-4-enal (10a). Colorless oil. IR (neat, cm^{-1}): 1725, 1635, 1249, 1113. ^1H NMR ($CDCl_3$): δ 9.66 (1H, t, *J* = 1.8 Hz), 7.56−7.38 (5H, m), 4.62 (2H, s), 2.50 (2H, td, *J* = 7.3 and 1.8 Hz), 2.19 (2H, t, *J* = 7.3 Hz), 1.81 (2H, s), 0.37 (3H, s), 0.36 (3H, s). ^{13}C NMR ($CDCl_3$): δ 202.1 (C), 145.0 (C), 138.6 (C), 133.6 (C), 129.1 (C), 127.8 (C), 108.3 (CH_2), 41.7 (CH_2), 30.2 (CH_2), 26.3 (CH_2), −3.0 (CH_3). MS: *m/z* 203 (M^+ − CHO, 10), 135 ($SiMe_2Ph$, 100). Anal. Calcd for $C_{14}H_{20}OSi$: C, 72.36; H, 8.67. Found: C, 72.68; H, 8.91.

(b) 4-[(Dimethylphenylsilyl)methyl]-3-methylpent-4-enal (10b). Colorless oil. IR (neat, cm^{-1}): 1725, 1633, 1249, 1113. ^1H NMR ($CDCl_3$): δ 9.54 (1H, t, *J* = 2.3 Hz), 7.56−7.37 (5H, m), 4.68 (1H, s), 4.65 (1H, s), 2.48 (1H, dd, *J* = 15.3 and 5.2 Hz), 2.45−2.34 (1H, m), 2.27 (1H, ddd, *J* = 15.3, 7.4 and 2.3 Hz), 1.82 (2H, s), 1.05 (3H, d, *J* = 6.6 Hz), 0.38 (6H, s). ^{13}C NMR ($CDCl_3$): δ 202.3 (C), 150.1 (C), 138.6 (C), 133.6 (CH), 129.1 (CH), 127.8 (CH), 107.3 (CH_2), 49.3 (CH_2), 35.2 (CH),

25.0 (CH_2), 19.7 (CH_3), −3.0 (CH_3). MS: *m/z* 231 ($M^+ - CH_3$, 5), 217 (M^+ − COH, 10), 135 ($SiMe_2Ph$, 100). Anal. Calcd for $C_{15}H_{22}OSi$: C, 73.11; H, 9.00. Found: C, 73.41; H, 9.31.

(c) 4-[(Dimethylphenylsilyl)methyl]-3-propylpent-4-enal (10c). Colorless oil. IR (neat, cm^{-1}): 1715, 1630, 1245, 1110. ^1H NMR ($CDCl_3$): δ 9.48 (1H, t, J = 2.1 Hz), 7.58−7.27 (5H, m), 4.70 (1H, s), 4.66 (1H, s), 2.43−2.27 (3H, m), 1.77 (2H, s), 1.57−1.13 (4H, m), 0.86 (3H, t, J = 7.1 Hz), 0.37 (3H, s), 0.36 (3H, s). ^{13}C NMR ($CDCl_3$): δ 202.7 (C), 148.2 (C), 138.7 (C), 133.7 (CH), 129.1 (CH), 127.8 (CH), 109.0 (CH_2), 47.3 (CH_2), 40.8 (CH), 35.9 (CH_2), 24.4 (CH_2), 20.2 (CH_2), 14.1 (CH_3), −2.6 (CH_3), −2.8 (CH_3). MS: *m/z* 274 (M^+, 3), 259 ($M^+ - CH_3$, 5), 245 (M^+ − CHO, 7), 139 ($M^+ - SiMe_2Ph$, 10), 135 ($SiMe_2Ph$, 100). Anal. Calcd for $C_{17}H_{26}OSi$: C, 74.39; H, 9.55. Found: C, 74.68; H, 9.86.

Síntesis of Methylenecycloheptanones. To a stirred solution of enones **12a**−**d** (3 mmol) in dry toluene (15 mL) is added $EtAlCl_2$ (1.8 M, 3 mmol) at 0 °C under nitrogen. The mixture is stirred at this temperature for 1 h, and then saturated solution of $NaHCO_3$ (2 mL) is added. Extraction (Et_2O), drying ($MgSO_4$), and chromatography gave the following compounds.

(a) 4-Methylenecycloheptanone (13a). Colorless oil. IR (neat, cm^{-1}): 1730, 1630. ^1H NMR ($CDCl_3$): δ 4.82 (1H, s), 4.78 (1H, s), 2.58 (2H, t, J = 6.2 Hz), 2.52 (2H, t, J = 6.5 Hz), 2.33−2.45 (4H, m), 1.83−1.73 (2H, m). ^{13}C NMR ($CDCl_3$): δ 215.1 (C=O), 139.5 (C), 112.6 (CH_2), 43.3 (CH_2), 43.1 (CH_2), 38.2 (CH_2), 31.8 (CH_2), 24.2 (CH_2). MS: *m/z* 124 (M^+, 19). Anal. Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74. Found: C, 77.72; H, 9.99.

(b) 3-Methyl-4-methylenecycloheptanone (13b). Colorless oil. IR (neat, cm^{-1}): 1735, 1650. ^1H NMR ($CDCl_3$): δ 4.81 (1H, s), 4.78 (1H, s), 2.49−2.21 (5H, m), 2.01−1.80 (4H, m), 1.30 (3H, d, J = 7.4 Hz). ^{13}C NMR ($CDCl_3$): δ 212.7 (C=O), 145.0 (C), 111.1 (CH_2), 49.8 (CH), 43.8 (CH_2), 41.2 (CH_2), 39.8 (CH_2), 26.4 (CH_2), 20.8 (CH_3). MS: *m/z* 138 (M^+, 12), 123 ($M^+ - CH_3$, 10). Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.59; H, 10.48.

(c) 4-Methylene-3-propylcycloheptanone (13c). Colorless oil. IR (neat, cm^{-1}): 1728, 1632. ^1H NMR ($CDCl_3$): δ 4.83 (1H, s), 4.77 (1H, s), 2.55−2.20 (5H, m), 1.70−1.50 (4H, m), 1.39−1.21 (4H, m), 0.90 (3H, t, J = 7.0 Hz). ^{13}C NMR ($CDCl_3$): δ 213.9 (C=O), 139.1 (C), 111.9 (CH_2), 51.9 (CH_2), 48.9 (CH_2), 43.3 (CH), 35.8 (CH_2), 35.4 (CH_2), 24.9 (CH_2), 20.4 (CH_2), 13.4 (CH_3). MS: *m/z* 166 (M^+, 20). Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.81; H, 11.21.

(d) 4-Methylene-3-phenylcycloheptanone (13d). Colorless oil. IR (neat, cm^{-1}): 1730, 1630. ^1H NMR ($CDCl_3$): δ 7.53−7.27 (5H, m), 4.88 (1H, s), 4.85 (1H, s), 3.83 (1H, dd, J = 7.9 and 7.7 Hz), 2.98 (1H, dd, J = 16.2 and 7.9 Hz), 2. 83 (1H, dd, J = 16.2 and 7.7 Hz), 2.66−2.48 (4H, m), 1.71−1.56 (2H, m). ^{13}C NMR ($CDCl_3$): δ 208.0 (C=O), 147.1 (C), 142.2 (C), 129.0 (CH), 127.6 (CH), 126.1 (CH), 110.2 (CH_2), 49.7 (CH_2), 47.5 (CH), 43.1 (CH_2), 29.6 (CH_2), 21.9 (CH_2). MS: *m/z* 200 (M^+, 20), 77 (Ph, 14). Anal. Calcd for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 84.29; H, 8.38.

Allylsilane-Terminated Cyclizations. $EtAlCl_2$ (2 mmol, 1.8 M) was added slowly to a solution of **7** (2 mmol) in DCM (8 mL), under nitrogen. After stirring at 0 °C for 0.5 h, brine was added (5 mL) and the mixture extracted with ether, dried, and evaporated. Purification by flash chromatography gave the products **14** and **15**.

(a) 1-[2-(Dimethylphenylsilyl)-2-propenyl]-3-methylenecyclopentan-1-ol (14a). Colorless oil. IR (neat, cm^{-1}): 3585, 1665, 1550, 1240, 1090. ^1H NMR ($CDCl_3$): δ 7.57−7.27 (5H, m), 5.91 (1H, d, J = 2.2 Hz), 5.70 (1H, d, J = 2.2 Hz), 4.89−4.80 (2H, m), 2.51−2.39 (1H, m), 2.46 (2H, s), 2.36−2.22 (1H, m), 2.29 (1H, d, J = 16.6 Hz), 2.15 (1H, d, J = 16.6 Hz), 1.65−1.57 (2H, m), 1.22 (1H, s), 0.43 (6H, s). ^{13}C NMR ($CDCl_3$): δ 150.4 (C), 147.1 (C), 138.2 (C), 133.9 (CH), 131.4 (CH_2), 129.0 (CH), 127.7 (CH), 106.8 (CH_2), 80.9 (C), 47.0 (CH_2), 46.4 (CH_2), 39.3 (CH_2), 30.2 (CH_2), −2.4 (CH_3). MS: *m/z* 257 ($M^+ - CH_3$, 7), 195 (M^+ − Ph, 30), 137 ($M^+ - SiMe_2Ph$, 68), 135 ($SiMe_2Ph$, 100). Anal. Calcd for $C_{17}H_{24}OSi$: C, 74.94; H, 8.88. Found: C, 75.28; H, 9.21.

(b) [*1R*,2R]-2-Methyl-4-methylene-1-[2-(dimethylphenylsilyl)-2-propenyl]cyclopentan-1-ol (14b).** Colorless oil. IR (neat, cm^{-1}): 3400, 1650, 1240, 1090. ^1H NMR ($CDCl_3$): δ 7.59−7.37 (5H, m), 5.92 (1H, d, J = 2.9 Hz), 5.71 (1H, d, J = 2.9 Hz), 4.84−4.82 (2H, m), 2.74−2.67 (1H, m), 2.43 (1H, d, J = 14.1 Hz), 2.43 (1H, d, J = 14.1 Hz), 2.30 (1H, d, J = 14.1 Hz), 2.07−1.89 (3H, m), 1.33−1.29 (1H, s, OH), 0.87 (3H, d, J = 7.0 Hz), 0.45 (3H, s), 0.43 (3H, s). ^{13}C NMR ($CDCl_3$): δ 148.6 (C), 147.1 (C), 138.3 (C), 133.9 (CH), 131.3 (CH_2), 129.1 (CH), 127.9 (CH), 107.2 (CH_2), 82.0 (C), 44.3 (CH_2), 44.2 (CH), 41.2 (CH_2), 38.7 (CH_2), 15.8 (CH_3), −2.2 (CH_3), −2.5 (CH_3). MS: *m/z* 271 ($M^+ - CH_3$, 7), 151 ($M^+ - SiMe_2Ph$, 12), 135 ($SiMe_2Ph$, 100). Anal. Calcd for $C_{18}H_{26}OSi$: C, 75.46; H, 9.15. Found: C, 75.78; H, 9.36.

(c) [*1R*,2S]-2-Methyl-4-methylene-1-[2-(dimethylphenylsilyl)-2-propenyl]cyclopentan-1-ol (15b).** Colorless oil. IR (neat, cm^{-1}): 3400, 1650, 1240, 1090. ^1H NMR ($CDCl_3$): δ 7.59−7.37 (5H, m), 5.92 (1H, d, J = 2.9 Hz), 5.68 (1H, d, J = 2.9 Hz), 4.85 (1H, s with fine couplings), 4.81 (1H, s with fine couplings), 2.61 (1H, d, J = 13.7 Hz), 2.45 (1H, dd, J = 16.4 and 8.1 Hz), 2.25 (1H, ddd, J = 16.4, 4, 9 and 2.3 Hz), 2.15 (1H, d, J = 13.7 Hz), 2.14−2.10 (2H, m), 1.90−1.80 (1H, m), 1.06 (1H, s, OH), 0.90 (3H, d, J = 6.7 Hz), 0.43 (6H, s). ^{13}C NMR ($CDCl_3$): δ 148.9 (C), 147.4 (C), 138.4 (C), 134.0 (CH), 131.0 (CH_2), 129.1 (CH), 127.9 (CH), 106.6 (CH_2), 81.0 (C), 46.7 (CH_2), 44.8 (CH_2), 43.0 (CH), 38.7 (CH_2), 12.4 (CH_3), −2.2 (CH_3), −2.3 (CH_3). MS: *m/z* 271 ($M^+ - CH_3$, 7), 151 ($M^+ - SiMe_2Ph$, 12), 135 ($SiMe_2Ph$, 100).

(d) [*1R*,4S]-4-Methyl-3-methylene-1-[2-(dimethylphenylsilyl)-2-propenyl]cyclopentan-1-ol (14d) and [*1R*,4R**] (15d).** Colorless oils. Chromatography gave the alcohols as a mixture. (**14d**) IR (neat, cm^{-1}): 3560, 1650, 1240, 1090. ^1H NMR ($CDCl_3$): δ 7.56−7.27 (5H, m), 5.92−5.89 (1H, m), 5.71−5.69 (1H, m), 4.85−4.78 (2H, m), 2.72−2.67 (1H, m), 2.45 (1H, d, J = 10.6 Hz), 2.49−2.19 (3H, m), 1.77 (1H, ddd, J = 12.9, 7.4 and 2.4 Hz), 1.33−1.15 (2H, m), 1.04 (3H, d, J = 6.7 Hz), 0.43 (6H, s). ^{13}C NMR ($CDCl_3$): δ 155.5 (C), 147.2 (C), 138.2 (C), 133.9 (CH), 131.3 (CH_2), 129.1 (CH), 127.9 (CH), 105.4 (CH_2), 79.3 (C), 47.6 (CH_2), 47.2 (CH_2), 46.6 (CH_2), 36.3 (CH), 20.2 (CH_3), −2.3 (CH_3), −2.4 (CH_3). MS: *m/z* 286 (M^+, 16), 271 ($M^+ - CH_3$, 97), 194 ($M^+ - Ph - CH_3$, 19), 135 ($SiMe_2Ph$, 29). (**15d**) ^1H NMR ($CDCl_3$): δ 7.56−7.27 (5H, m), 5.92−5.89 (1H, m), 5.71−5.69 (1H, m), 4.85−4.78 (2H, m), 2.45 (2H, d, J = 10.6 Hz), 2.49−2.19 (4H, m), 1.98 (1H, dd, J = 13.0 and 8.9 Hz), 1.33−1.15 (2H, m), 1.09 (3H, d, J = 6.8 Hz), 0.43 (6H, s). ^{13}C NMR ($CDCl_3$): δ 155.5 (C), 147.1 (C), 138.2 (C), 133.9 (CH), 131.5 (CH_2), 129.1 (CH), 127.9 (CH), 105.4 (CH_2), 79.2 (C), 48.7 (CH_2), 47.5 (CH_2), 47.1 (CH_2), 36.3 (CH), 18.6 (CH_3), −2.5 (CH_3).

(e) [*1R*,4S]-4-Ethyl-3-methylene-1-[2-(dimethylphenylsilyl)-2-propenyl]cyclopentan-1-ol (14i) and [*1R*,4R**] (15i).** Colorless oils. Chromatography gave the alcohols as a mixture. (**14i**) IR (neat, cm^{-1}): 3560, 1650, 1240, 1090. ^1H NMR ($CDCl_3$): δ 7.59−7.27 (5H, m), 5.91−5.88 (1H, m), 5.72−5.67 (1H, m), 4.85 (1H, s with fine couplings), 4.80 (1H, s with fine couplings), 2.49−2.15 (3H, m), 2.41 (2H, s), 1.92 (1H, ddd, J = 13.2, 8.8 and 1.2 Hz), 1.71−1.55 (2H, m), 1.33−1.15 (2H, m), 0.86 (3H, t, J = 7.4 Hz), 0.43 (3H, s), 0.42 (3H, s). ^{13}C NMR ($CDCl_3$): δ 154.0 (C), 147.0 (C), 138.2 (C), 133.9 (CH), 131.6 (CH_2), 129.1 (CH), 127.9 (CH), 106.1 (CH_2), 78.9 (C), 47.7 (CH_2), 46.5 (CH_2), 44.4 (CH_2), 43.4 (CH), 28.1 (CH_2), 12.1 (CH_3), −2.4 (CH_3), −2.5 (CH_3). M. S. *m/z* 285 (M^+-CH_3, 5), 165 (M^+-$SiMe_2Ph$, 7), 135 ($SiMe_2Ph$, 100). (**15i**): ^1H NMR ($CDCl_3$): δ 7.59−7.27 (5H, m), 5.91−5.88 (1H, m), 5.72−5.67 (1H, m), 4.85 (1H, s with fine couplings), 4.80 (1H, s with fine couplings), 2.49−2.15 (3H, m), 2.41 (2H, s), 1.79 (1H, ddd, J = 13.0, 7.7 and 2.6 Hz), 1.71−1.55 (2H, m), 1.33−1.15 (2H, m), 0.85 (3H, t, J = 7.3 Hz), 0.43 (3H, s), 0.42 (3H, s). ^{13}C NMR ($CDCl_3$): δ 154.3 (C), 147.2 (C), 138.2 (C), 133.9 (CH), 131.3 (CH_2), 129.1 (CH), 127.7 (CH), 106.0 (CH_2), 79.3 (C), 47.4 (CH_2),

46.9 (CH_2), 45.8 (CH_2), 43.1 (CH), 27.2 (CH_2), 11.8 (CH_3), −2.4 (CH_3), −2.5 (CH_3).

(f) [*1R*,4S]-1-[2-(Dimethylphenylsilyl)-2-propenyl]-3-methylene-4-phenylcyclopentan-1-ol (14k).** Colorless oil. IR (neat, cm^{-1}) 3540, 1650, 1240, 1090. ^1H NMR ($CDCl_3$) δ 7.57−7.14 (10H, m), 5.94 (1H, d, J = 2.9 Hz), 5.73 (1H, d, J = 2.9 Hz), 4.93 (1H, d, J = 2.1 Hz), 4.49 (1H, d, J = 2.1 Hz), 3.59 (1H, dd, J = 9.4 and 8.7 Hz), 2.54 (1H, d, J = 15.4 Hz), 2.52 (2H, s), 2.40 (1H, d, J = 15.4 Hz), 2.26 (1H, dd, J = 13.3 and 9.4 Hz), 1.81 (1H, dd, J = 13.3 and 8.7 Hz), 1.45 (1H, s, OH), 0.45 (3H, s), 0.43 (3H, s). ^{13}C NMR ($CDCl_3$) δ 153.9 (C), 144.5 (C), 138.1 (C), 134.0 (CH), 131.7 (CH_2), 129.3 (CH), 129.1 (CH), 128.2 (CH), 128.0 (CH), 127.7 (CH), 126.0 (CH), 109.1 (CH), 106.0 (CH_2), 78.9 (C), 48.6 (CH), 48.2 (CH_2), 46.5 (CH_2), 29.6 (CH_2), −2.4 (CH_3), −2.5 (CH_3). MS: *m/z* 271 (M^+ − Ph, 5), 135 ($SiMe_2Ph$, 100). Anal. Calcd for $C_{23}H_{28}OSi$: C, 79.26; H, 8.10. Found: C, 79.58; H, 8.44.

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Supporting Information Available: General experimental methods, details of synthesis as well as spectra of compounds **11a**−**d** and **12a**−**d**, and crystallographic data collection parameters for compound **11d**. This material is available free of charge via the Internet at http://pubs.acs.org.

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