Rhodium-Catalyzed Hydroallylation of Activated Alkenes

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Rhodium-catalyzed hydroallylation of activated alkenes have been reported. This concept is manipulated by a one-pot operation of neutral components, an allylic carbonate, an α,β-unsaturated ketone or ester and a hydrosilane, which are activated in a specific order by [Rh(cod){$P(OPh)_3$}$_2$]OTf (**2e**, cod = 1,5-cyclooctadiene) under almost neutral conditions. In the absence of rhodium catalyst, no reaction proceeds at all. In this procedure, a variety of γ,δ-unsaturated ketones or esters are obtained in a moderate to an excellent yield. For example, slow addition of 3-methoxycarbonyloxy-1-phenyl-1-butene (**4**) in CH_2Cl_2 to a solution of methyl methacrylate (**7a**), diethylmethylsilane (**8**), and 1 mol % of **2e** in CH_2Cl_2 afforded a mixture of methyl 5-phenyl-2,2,3-trimethyl-4(*E*)-pentenoate (**9a**) and methyl 2,2-dimethyl-3-phenyl-4(*E*)-hexenoate (**10a**) in 93% yield. Although the distinction between the two allylic termini during the hydroallylation with linear carbonate is relatively difficult, introduction of a trialkylsilyl group to either of the two allylic termini is a powerful tool for regioselective allylation, which preferentially proceeds at the terminus opposite the one bearing a trialkylsilyl group.

Introduction

Carbon−carbon bond forming reactions catalyzed by rhodium complexes have recently attracted much attention.[1] In particular, rhodium-catalyzed reactions with activated alkenes were energetically investigated.[1b,c] In these reactions, the reductive aldol type coupling is one of the most powerful tools for construction of β-hydroxy carbonyl compounds.[2] This protocol is composed of three components, a carbonyl compound, an α,β-unsaturated ketone, aldehyde, or ester, and a reducing reagent supplied as a form of R_3SiH[3] or molecular hydrogen.[4] A rhodium enolate or an oxa-π-allyl rhodium complex, which is generated by the hydrometalation of H−RhL_n to an α,β-unsaturated carbonyl compound, is regarded as a key intermediate in the nucleophilic attack to an aldehyde to form a Rh−aldolate complex. It should be noted that this catalytic process avoids the operation to isolate the metal enolate and concomitant formation of a stoichiometric amount of metal waste. Both of them have been inseparable from aldol type reactions until recently. Although it is expected that rhodium enolate would have a potential nucleophilicity to a variety of electrophiles, the precedents of this type of coupling are limited to the case using carbonyl compounds as an electrophile except for our reports.[5]

On the other hand, rhodium-catalyzed allylic alkylation with carbon nucleophiles has been recognized as a powerful tool for constructing organic compounds with a ternary or quaternary carbon center with high regioselectivity.[6] The success of regiocontrol is attributed to the selective formation of a σ-allyl rhodium intermediate and the subsequent nucleophilic displacement on the allylic terminus opposite the one connecting to the Rh metal. Despite this clear demonstration, successful examples are limited to the reaction between an allylic substrate and an activated carbon nucleophile with two electron-withdrawing

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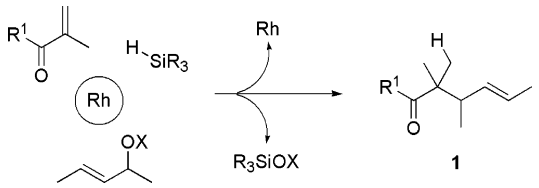
Scheme 1

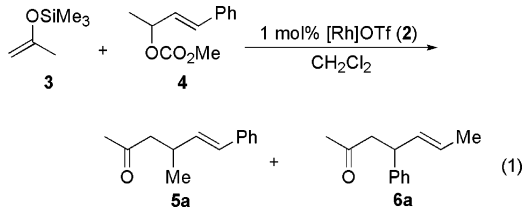


substituents such as a dialkoxycarbonyl group. Furthermore, the nucleophile used is required to be activated by a stoichiometric amount of base or by transmetalation. Thus, the reaction leaves the issue of inevitable formation of waste derived from used base or metal reagents.

We developed rhodium-catalyzed carbon−carbon bond forming reactions under neutral conditions in which hydrosilane plays an important role in the activation of a catalyst precursor. In some cases, the silyl group incorporated into the resulting products becomes an effective clue for a subsequent transformation.[7] Along this line, we focused on rhodium-catalyzed hydroallylation of α,β-unsaturated carbonyl compounds (Scheme 1), in which the intermediacy of a Rh−enolate is supposed.[5a] We report herein the full details of rhodium-catalyzed formal hydroallylation toward the α,β-unsaturated carbonyl compounds, which produces **1** in a one-pot reaction of a hydrosilane, an α,β-unsaturated carbonyl compound, and an allylic carbonate.

Results and Discussion

Reaction of 2-Trimethylsilyloxypropene (3) with 3-Methoxycarbonyloxy-1-phenyl-1-butene (4). First of all, an allylic alkylation with an enoxysilane is attempted to verify catalytic efficacy of Rh(I) complex **2** in the test reaction between 2-trimethylsilyloxypropene (**3**) and 3-methoxycarbonyloxy-1-phenyl-1-butene (**4**) under almost neutral conditions (eq 1).



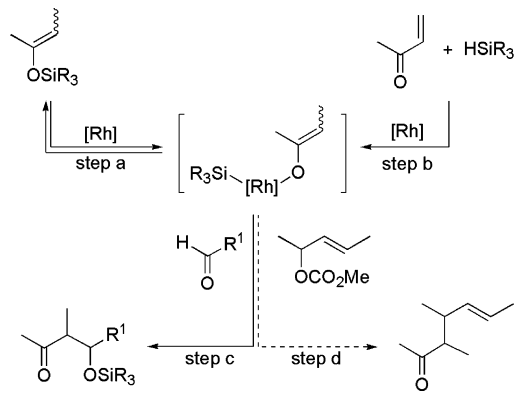
When a CH_2Cl_2 solution of **3** and **4** was heated at 80 °C for 19 h in a sealed tube containing 1 mol % of [Rh(cod)(dppb)]OTf (**2a**, cod = 1,5-cyclooctadiene, dppb = 1,4-bis(diphenylphosphino)butane), the reaction proceeded to give a mixture of 4-methyl-6-phenyl-(*E*)-5-hexen-2-one (**5a**) and 4-phenyl-(*E*)-5-hepten-2-one (**6a**) in 58% yield (**5a**:**6a** = 53:47, entry 1 in Table 1). It should be noted that congener complexes bearing PF_6^- and BF_4^- as a counteranion do not work as a catalyst in this type of test reaction. On the other hand, the yield of **5a** and **6a** was appreciably improved when $[Rh(cod)(PMe_2Ph)_2]$OTf (**2b**) was used as a catalyst instead of **2a** (76%, entry 2 in Table 1). In allylic substitutions with enoxysilanes catalyzed by Mo(II) and W(II) complexes, it is revealed that Lewis acidic character on Mo(II) and W(II) complexes accelerates the reaction rate.[8] A similar accelerating effect was also observed in our model reaction. When complex **2b** was replaced by $[Rh(cod)(PMePh_2)_2]$OTf (**2c**), the yield of **5a** and **6a** increased to 86% under similar conditions (entry 3 in Table 1). Even at

Table 1. Allylic Alkylation of 3 with 4 Catalyzed by 2[a]

			products	
entry	[Rh]OTf	time (h)	yield (%)[b]	ratio[c] (**5a**:**6a**)
1	[Rh(cod)(dppb)]OTf (**2a**)[d]	19	58[e]	53:47
2	[Rh (cod)$(PMe_2Ph)_2$]OTf (**2b**)	19	76[e]	55:45
3	[Rh (cod)$(PMePh_2)_2$]OTf (**2c**)	19	86[e]	52:48
4	[Rh (cod)$(PMePh_2)_2$]OTf (**2c**)	72	85	57:43

[a] A mixture of **3** (4 equiv) and **4** was added to a solution of **2** (1 mol % for **4**) in CH_2Cl_2 at 25 °C, and the mixture was stirred under the conditions shown. [b] Isolated yield. [c] Determined by GLC analysis. [d] dppb = 1,4-bis(diphenylphosphino)butane. [e] The reaction was performed at 80 °C in a sealed tube.

Scheme 2



25 °C, allylic carbonate **4** was completely consumed to give **5a** and **6a** in 85% yield, although prolonged reaction time was necessary for the disappearance of **4** (entry 4 in Table 1). These results seem to be consistent with Kocovsky's mechanistic consideration[8] that the central metal first interacts with an allylic component; however, intermediacy of a rhodium enolate complex is another rationale for eq 1 according to our experiments in Rh-catalyzed aldol type coupling.[3b,j,9] An identical aldol type product is formed from different reaction systems with the assistance of a rhodium complex: (i) interaction between an enoxysilane and an aldehyde and (ii) interaction among an α,β-enone, a hydrosilane, and an aldehyde. A rhodium enolate formed through step a or step b is regarded as a key intermediate to give an aldol type product in both systems as shown in Scheme 2. The fact that a mixture of **5a** and **6a** was obtained as a major product in eq 1 implies possible participation of a rhodium enolate in this transformation. If this is the case, step d in Scheme 2 becomes a plausible element as the product-determining step. As a result, a new reaction system composed of an α,β-enone, a hydrosilane, and an allylic carbonate would be disclosed as an alternative route for eq 1 (step b and step d in Scheme 2).

Since oxidative addition of an enoxysilane to a low-valent rhodium complex requires relatively high temperature, it is difficult to enhance drastically the rate and the product yield in eq 1 by conventional modification of a catalyst precursor. Therefore, we focused on three-component coupling composed of methyl vinyl ketone (**7e**), diethylmethylsilane (**8**), and allylic carbonate (**4**) with the assistance of rhodium complex **2c**. Contrary to aldol type couplings, a complex mixture was obtained in the first trial of this reaction system. This result

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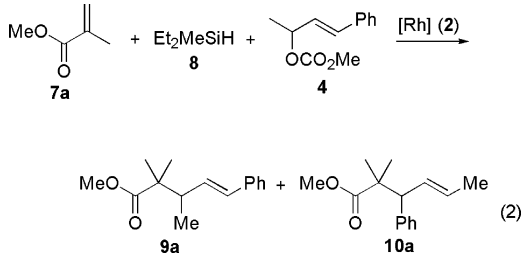
Table 2. Hydroallylation of 7b with 4 and 8 Catalyzed by 2[a]

entry	[Rh]OTf	time (h)	products: yield (%)[b]	products: ratio[c] (**9a**:**10a**)
1	[Rh(cod)(dppb)]OTf (**2a**)[d]	19	55[e]	41:59
2	[Rh(cod)($PMePh_2$)$_2$]OTf (**2c**)	42	90	38:62
3	[Rh(cod)(PPh_3)$_2$]OTf (**2d**)	4	76	34:66
4	[Rh (cod){$P(OPh)_3$}$_2$]OTf (**2e**)	1	38[f]	35:65

[a] A mixture of **7a** (2 equiv), **8** (2 equiv), and **4** was added to a solution of **2** (1 mol % for **4**) in CH_2Cl_2 at 25 °C, and the mixture was stirred under the conditions shown. [b]Isolated yield. [c]Determined by GLC analysis. [d]dppb = 1,4-bis(diphenylphosphino)butane. [e]The reaction was performed at 80 °C in a sealed tube. [f]In addition to **9a** and **10a**, 1-phenyl-1-butene (**11**) was isolated in 61% yield.

suggests that a rhodium enolate derived from **7e** and **8** does not possess sufficient nucleophilicity toward **4** under the conditions, although this three-component coupling is realized to give corresponding products in high yield under modified reaction conditions (vide infra). Thus, our focus is shifted to the rhodium enolate derived from methyl methacrylate (**7a**).

Reaction of Methyl Methacrylate (7a) with 3-Methoxycarbonyloxy-1-phenyl-1-butene (4). A formal hydroallylation toward an activated alkene was accomplished by the catalysis of a Rh(I) complex, **2**. Methyl methacrylate (**7a**) interacted with diethylmethylsilane (**8**) and 3-methoxycarbonyloxy-1-phenyl-1-butene (**4**) to form a mixture of **9a** and **10a** in a CH_2Cl_2 solution containing 1 mol % of the cationic rhodium(I) complex **2** (eq 2). It should be noted that these substrates do not interact



with each other in the absence of **2**. The product yield was extremely affected by the catalyst precursor. Since the rhodium complex possessing a bidentate phosphine ligand (**2a**) exhibited less catalytic activity for this transformation at 25 °C (entry 1 in Table 2), some trials were conducted in the presence of [Rh(cod)(PR_3)$_2$]OTf (**2c**−**e**) as a catalyst precursor. As a result, **2c** gave an acceptable yield of products, although a long reaction time was necessary for complete consumption of **4** (entry 2 in Table 2). Although the rate of consumption of **4** was accelerated by the catalysis **2d** or **2e**, the yields of **9a** and **10a** did not increase much (entries 3 and 4 in Table 2). 1-Phenyl-1-butene (**11**) became a major product (61% based on **4**) when **2e** was employed as a catalyst precursor (entry 4 in Table 2). It should be noted that the corresponding complexes bearing BF_4^- or PF_6^- as an anionic part did not give any product under similar conditions.

The formation of **11** can be rationalized by the prior interaction of **4** with **8** since either **7a** or **4** is potentially susceptible to **8** in the presence of **2**. It is anticipated that the yields of **9a** and **10a** are improved if the reaction between **4** and **8** can be suppressed to a minimum during the hydroallylation. As expected, the yield of this hydroallylation increased outstandingly as a result of tuning conditions: the use of **2e** as a catalyst precursor and the *slow addition* of **4** into the reaction system (Scheme 3). The yields of **9a** and **10a** increased to 93% (entry 1 in Table 3) when a solution of **4** in CH_2Cl_2 (4 mL) was slowly added to a CH_2Cl_2 solution of **7a**, **8**, and **2e** (1 mol % for **4**) at the rate taking 1 h for completion, and then the resulting mixture was stirred for 1 h. In this operation, **11** was not detected at all. Interestingly, this procedure made it possible to acquire the products **9a** and **10a** within 2 h (compare entry 2 in Table 2 with entry 1 in Table 3). The identical products **9a** and **10a** were also selectively obtained in the reactions using Me_2PhSiH (83%, entry 2 in Table 3) or $EtMe_2SiH$ (83%, entry 3 in Table 3) instead of Et_2MeSiH (**8**) under similar conditions. This protocol for the hydroallylation of **7a** is generally applicable

Scheme 3

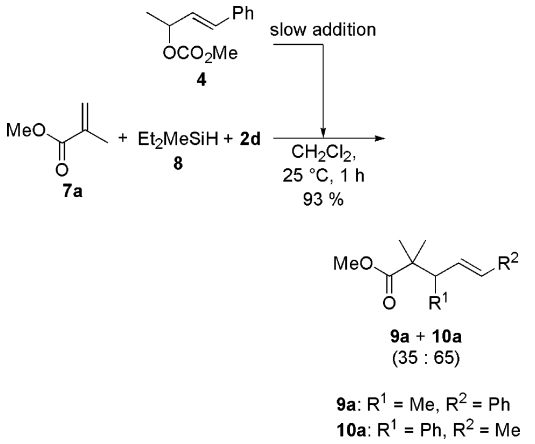


Table 3. Hydroallylation of 7 with 4 and 8 Catalyzed by 2e[a]

entry	substrate	yield (%)[c]	products[b]	ratio (**9**:**10**)[d]
1	**7a**	93	**9a** + **10a**	35:65
2		83[e]		32:68
3		83[f]		35:65
4	**7b**	99	**9b** + **10b**	33:67
5	**7c**	96	**9c** + **10c**	51:49
6	**7d**	64[g]	**9d** + **10d**	52:48
7	**7e**	96[h]	**9e** + **10e**	48:52
8	**7f**	99	**9f** + **10f**	48:52
9	**7g**	90[i]	**9g** + **10g**	46:54

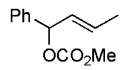
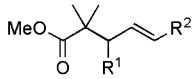
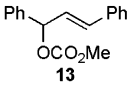
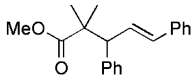
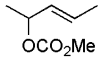
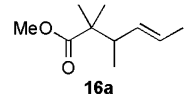
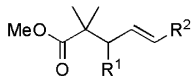
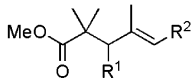
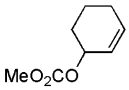
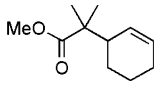
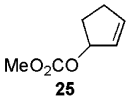
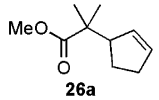
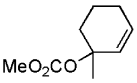
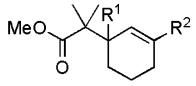
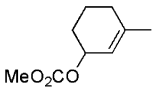
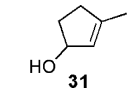
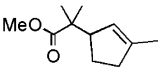
[a] Unless otherwise noted, a solution of **4** was added at the rate taking about 1 h to a mixture of **7** (2 equiv), **8** (2 equiv), and **2e** (1 mol %) in CH_2Cl_2 at 25 °C, and the resulting mixture was stirred for 1 h. [b]**9**; R^1 = Me, R^2 = Ph, **10**; R^1 = Ph, R^2 = Me. [c] Isolated yield. [d]Determined by GLC analysis. [e]Me_2PhSiH was used instead of **8**. [f]$EtMe_2SiH$ was used instead of **8**. [g]The time for stirring was 2 h. [h]A mixture of **7e** and **8** was added to a solution of **4** and **2e** in CH_2Cl_2. [i]The time for stirring was 12 h.

to other types of α,β-unsaturated esters and ketones. These results are summarized in Table 3. Acyclic α,β-unsaturated esters were efficiently converted to the corresponding γ,δ-unsaturated esters in high yields (entries 1−5 in Table 3). α-Methylene-γ-butyrolactone (**7d**) resulted in moderate yields of **9d** and **10d** (entry 6 in Table 3), whereas **7f** and **7g** gave the corresponding products in an excellent yield (entries 8 and 9 in Table 3). In sharp contrast to the results of **7f** and **7g**, the modified protocol did not improve yields of **9e** and **10e** in the reaction of **7e**. Thus, a second modification was adopted in the mixing of **7e**, **4**, and **8**. A mixture of **7e** and **8** in CH_2Cl_2 was slowly added to a CH_2Cl_2 solution of **4** and **2d** to afford the corresponding products in 96% yield (entry 7 in Table 3). These clear-cut results imply that an intermediate composed of **7e**, **8**, and **2e** (**34**, vide infra) would not be tolerant of the presence of **4** in far lower concentration than that of **7e**.

Reaction of 7a with a Variety of Allylic Carbonates. Many types of allylic carbonates behaved as an allylating reagent as well as **4**, although yields of the coupling products significantly fluctuate according to the structure of the allyic carbonates used. These results are summarized in Table 4. Allylic carbonates **13** and **15** were suitable for the present transformation in the presence of **2e** with high efficiency. Their reaction time shown in Table 4 means a period from the start of mixing each substrate to the start of the evaporation of volatiles. Therefore, it would not reflect the precise time required for complete consumption of **13** and **15**. Disappearance of these starting substrates was not detected in the TLC analyses because R_f values of the starting substrates unfortunately coincided with those of the corresponding products. Carbonates derived from primary alcohols (**17** and **20**) required forcing conditions to form substituted products **18a** + **19a** and **21a** + **22a** in acceptable yields (entries 4 and 5 in Table 4). In contrast to these results, alicyclic carbonates showed high reactivity comparable to **4** (entries 6−9 in Table 4). In the reaction of **25**, less active **2d** was more suitable than **2e** as a catalyst for the formation of **26a**. When **2e** was used as a catalyst, coupling of **7a** with **25** became a minor path despite the fast consumption of **25** (entry 7 in Table 4). It is worth noting that a certain type of allylic alcohol is applicable to this three-component coupling without converting the hydroxy group to an ester group. For example, 3-methyl-2-cyclopentene-1-ol (**31**) reacted with **7a** and **8** to give **32a** in 57% yield as the sole product (entry 10 in Table 4).

Mechanistic Consideration of Rhodium-Catalyzed Hydroallylation. The results hitherto described suggest clearly that the interaction between **7** and **8** on the rhodium metal must have priority over the one between **4** and **8** for accomplishing the selective coupling of these three substrates. It is well-established that the oxidative addition of hydrosilanes to transition metals is an important step in the hydrosilylation of unsaturated bonds.[10,11] Thus, Scheme 4 can be proposed as a possible rationale for the present coupling in which **7a** and **4** are presented as a typical example. H−[Rh]−SiR_3 species **33** is formed by the oxidative addition of hydrosilane to the cationic rhodium complex **2** during the first stage. Insertion of an α,β-unsaturated ester **7a** into the hydride−rhodium bond of **33** gives the rhodium enolate species **34a**.[9d,12−14] Sigma-bond methathesis

Table 4. Hydroallylation of 7a with 8 and Allylic Carbonates Catalyzed by 2e[a]

entry	allylic carbonate	time (h)[d]	yield (%)[b]	products
1	 **12**	1	89	 **9a** R^1 = Me R^2 = Ph **10a** R^1 = Ph R^2 = Me **9a**:**10a** = 35:65[c]
2	 **13**	45	78	 **14a**
3	 **15**	6	76	 **16a**
4	 **17**	24	51[e]	 **18a** R^1 = H R^2 = Ph **19a** R^1 = Ph R^2 = H **18a**:**19a** = 58:42[c]
5	 **20**	31	76[e]	 **21a** R^1 = H R^2 = Ph **22a** R^1 = Ph R^2 = H **21a**:**22a** = 56:44[c]
6	 **23**	13	83	 **24a**
7	 **25**	1	62[f]	 **26a**
8	 **27**	1	71	 **28a** R^1 = Me R^2 = H **29a** R^1 = H R^2 = Me **28a**:**29a** = 5:95[c]
9	 **30**	2	77	**28a** + **29a** **28a**:**29a** = 93:7[c]
10	 **31**	5	57	 **32a**

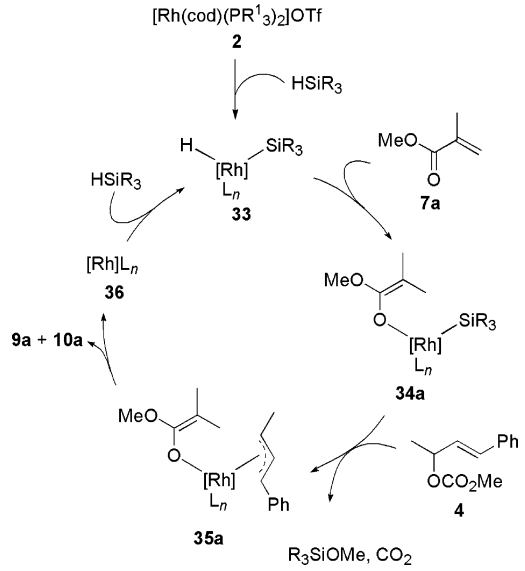
[a] Unless otherwise noted, a solution of allylic carbonate was added at the rate taking about 1 h to a mixture of **7a** (2 equiv), **8** (2 equiv), and **2e** (1 mol %) in CH_2Cl_2 at 25 °C. [b] Isolated yield. [c]Determined by GLC analysis. [d]Time for stirring. [e]A mixture of **7a**, **8**, and **17** or **20** in CH_2Cl_2 was refluxed for given reaction time in the presence of **2e** (1 mol %). [f]**2d** was used in place of **2e** as a catalyst.

(10) (a) Chalk, A. J.; Hallod, J. F. *J. Am. Chem. Soc.* **1965**, *87*, 16. (b) Muir, K. W.; Ibers, J. A. *Inorg. Chem.* **1970**, *9*, 440. (c) Aiszenberg, M.; Milstein, D. *J. Am. Chem. Soc.* **1995**, *117*, 6456. (d) Osakada, K.; Koizumi, T.; Yamamoto, T. *Organometallics* **1997**, *16*, 2063.

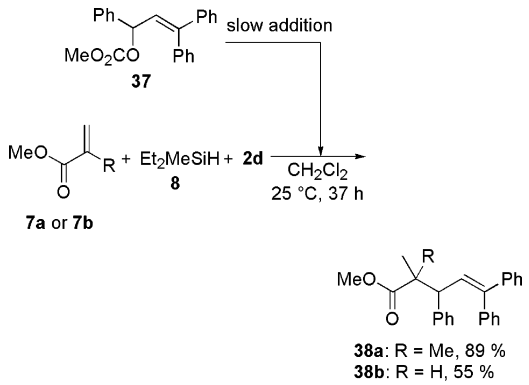
(11) For review see: (a) Speier, J. L. *Adv. Organomet. Chem.* **1979**, *17*, 407. (b) Ojima, I. In *The Chemistry of Organic Silicon Compounds*, Part 2; Patai, S., Rappoport, Z., Eds.; John Wiley and Sons: Chichester, U.K., 1989; p 1479. (c) Hiyama, T.; Kusumoto, T. In *Comprehensive Organic Synthesis;* Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 8, p 763. (d) Marciniec, B. *Comprehensive Handbook on Hydrosilylation*; Pergamon Press: Oxford, 1992. (e) Ojima, I.; Li, Z.; Zhu, J. In *The Chemistry of Organic Silicon Compounds*, Vol. 2; Rappoport, Z., Apeloig, Y., Eds.; John Wiley: New York, 1998; Chapter 29, p 1687. See also: (f) Maruyama, Y.; Yamamura, K.; Sagawa, T.; Katayama, H.; Ozawa, F. *Organometallics* **2000**, *19*, 1308.

(12) (a) Slough, G. A.; Hayashi, R.; Ashbaugh, J. R.; Shamblin, S. L.; Aukamp, A. M. *Organometallics* **1994**, *13*, 890. (b) Slough, G. A.; Ashbaugh, J. R.; Zannoni, L. A. *Organometallics* **1994**, *13*, 3587. (c) For an example of an η^1 oxygen-bound rhodium enolate, see: Slough, G. A.; Bergman, R. G.; Heathcock, C. H. *J. Am. Chem. Soc.* **1989**, *111*, 938.

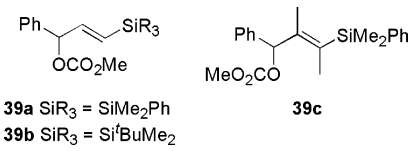
Scheme 4



Scheme 5



Scheme 6



of allylic carbonate **4** with the Rh−SiR_3 bond in **34a** generates the η^3-allyl rhodium enolate **35a**, methoxytrialkylsilane, and carbon dioxide. Reductive elimination from **35a** gives a mixture of products **9a** and **10a** and a low-valent rhodium species, **36**, which interacts with hydrosilane to regenerate **33**. Participation of η^3-allyl complex **35** in Scheme 4 is consistent with the fact that a similar result was obtained from the reaction of a regioisomer of **4**, 1-methoxycarbonyloxy-1-phenyl-2-butene, **12** (entry 1 in Table 4).

Regiocontrol with the Assistance of the R_3Si Group in the Allylic Moiety. In all examples presented here, the α-carbon of **7** is exclusively allylated, whereas the discrimination between the two allylic termini is relatively difficult during the reaction of linear carbonates (Table 3 and entries 1, 4, and 5 in Table 4). In contrast, the regiochemistry of the alicyclic ones seems to be remarkably affected by the steric factor. The methoxycarbonyloxy group of **27** and **30** was replaced to form a C−C bond at the less substituted terminus of the corresponding allylic group with a high selectivity of 95% and 93%, respectively (entries 8 and 9 in Table 4). An extreme effect of the additional methyl group on the regiochemistry is exemplified in the reaction of 3-methyl-2-cyclopenten-1-ol (**31**) to give **32a** as the sole product under similar conditions (entry 10 in Table 4). These results imply that obvious differentiation in the steric environment between the two allylic termini of the starting allylic moiety brings about higher order of the regiocontrol in acyclic allylic carbonates. In fact, hydroallylation of **7a** or **7b** with carbonate **37** in the presence of **8** and **2e** proceeded with high selectivity to give γ,δ-unsaturated ester **38a** or **38b** as the sole product in 89% and 55% yield, respectively (Scheme 5).

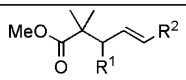
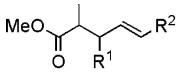
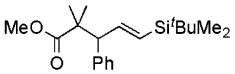
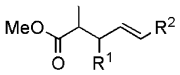
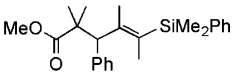
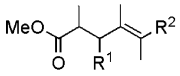
Thus, we planned introducing a triorganosilyl group into either site of the allylic termini of allylic carbonates as a directing auxiliary[15] because of its favorable characteristics: sufficient bulkiness affecting the selection of the reaction site and ready replaceablity to a proton after the reaction. To demonstrate this strategy, three types of silyl-modified allylic carbonates, **39a**, **39b**, and **39c**, were employed as allylating reagents (Scheme 6 and Table 5). These allylic carbonates showed sufficient reactivity as an allylating reagent in the present three-component coupling. For example, the reaction of **39a** with **7b** and **8** in the presence of **2e** (1 mol % for **39a**) proceeded at 25 °C to form γ-trialkylsilyl-γ,δ-unsaturated ester (**40ba**) in an excellent yield with a selectivity of 86% (entry 2 in Table 5). The selectivity for **40ba** was much higher than the one in the reactions of **4** and **12**. More appreciable improvement in the selectivity for **40** was realized by increasing the steric bulkiness at the nucleophilic site in addition to the introduction of a silyl group. Methyl methacrylate **7a** was converted to **40aa** with a selectivity of 95% in the reaction with **39a** (entry 1 in Table 5, cf. entry 1 in Table 4). Such appreciable improvement in the regioselectivity as shown in these results implies that the steric bulkiness of the Me_2PhSi group in **39a** plays an important role in the selection between two allylic termini of **39a**. If this is the case, increasing the steric bulkiness of the R_3Si group located in **39** might improve the selectivity to form **40** in this three-component coupling. To corroborate this primitive hypothesis, a *tert*-butyldimethylsilyl (^{t}BuMe_2Si) group was employed in place of the Me_2PhSi group. In fact, the reaction of 1-*tert*-butyldimethylsilyl-3-methoxycarbonyloxy-3-phenyl-1(*E*)-propene (**39b**) with **7b** and **8** proceeded smoothly to afford **40bb** with a selectivity of more than 95% (entry 4 in Table 5). Especially, it should be stressed that methyl 5-*tert*-butyldimethylsilyl-2,2-dimethyl-3-phenyl-4(*E*)-pentenoate (**40ab**) was obtained as the sole product in the reaction of **39b** with **7a** and

(13) A similar sequence is postulated in the reactions constructing aldol type products from an α,β-enone, a hydrosilane, and an aldehyde. See ref 3. Rhodium enolate complexes are formed by the interaction of a chlororhodium species with an enolate anion.

(14) In relation to this, it is proposed that the preferential insertion is of a carbonyl group of an enone into a R_3Si−Rh bond in the explanation of hydrosilylation of an α,β-enone. (a) Ojima, I.; Kogure, T.; Nagai, Y. *Tetrahedron Lett.* **1972**, 5035. (b) Yoshii, E.; Kobayashi, Y.; Koizumi, T.; Oribe, T. *Chem. Pharm. Bull.* **1974**, *22*, 2767. (c) Ojima, I.; Kumagai, M.; Nagai, Y. *J. Organomet. Chem.* **1976**, *111*, 43. (d) Ojima, I.; Kogure, T. *Organometallics* **1982**, *1*, 1390. (e) Chan, T. H.; Zheng, G. Z. *Tetrahedron Lett.* **1993**, *34*, 3095. (f) Zheng, G. Z.; Chan, T. H. *Organometallics* **1995**, *14*, 70.

(15) Several studies on palladium-catalyzed allylation of nucleophiles with allylic esters having a trialkylsilyl group have been reported. (a) Hirao, T.; Enda, J.: Ohshiro, Y.; Agawa, T. *Tetrahedron Lett.* **1981**, *22*, 3079. (b) Trost, B. M.; Self, C. R. *J. Am. Chem. Soc.* **1983**, *105*, 5942. (c) Ohta, T.; Hosokawa, T.; Murahashi, S.-I.; Miki, K.; Kasai, N. *Organometallics* **1985**, *4*, 2080. (d) Tsuji, J.; Yuhara, M.; Minato, M.; Yamada, H. *Tetrahedron Lett.* **1988**, *29*, 343. (e) Inami, H.; Ito, T.; Urabe, H.; Sato, F. *Tetrahedron Lett.* **1993**, *34*, 5919. (f) Trost, B. M.; Ariza, X. *J. Am. Chem. Soc.* **1999**, *121*, 10727. (g) Commandeur, C.; Thorimbert, S.; Malacria, M. *J. Org. Chem.* **2003**, *68*, 5588. (h) Sakaguchi, K.; Yamada, T.; Ohfune, Y. *Tetrahedron Lett.* **2005**, *46*, 5009. See also: (i) Kang, J.; Cho, W.; Lee, W. K. *J. Org. Chem.* **1984**, *49*, 1840.

Table 5. Hydroallylation of 7a with 8 and 39 Catalyzed by 2e[a]

entry	7	39	time (h)[d]	yield (%)[b]	products
1	**7a**	**39a**	23	80	 **40aa** R^1 = Ph R^2 = $SiMe_2Ph$ **41aa** R^1 = $SiMe_2Ph$ R^2 = Ph **40aa**:**41aa** = 95:5[c]
2	**7b**	**39a**	19	96	 **40ba** R^1 = Ph R^2 = $SiMe_2Ph$ **41ba** R^1 = $SiMe_2Ph$ R^2 = Ph **40ba**:**41ba** = 86:14[c]
3	**7a**	**39b**	7	88	 **40ab**:**41ab** = 100:0[c]
4	**7b**	**39b**	34	83	 **40bb** R^1 = Ph R^2 = Si^tBuMe_2 **41bb** R^1 = Si^tBuMe_2 R^2 = Ph **40bb**:**41bb** = >95:<5[c]
5	**7a**	**39c**	4	89	 **40ac**:**41ac** = 100:0[c]
6	**7b**	**39c**	24	80	 **40bc** R^1 = Ph R^2 = $SiMe_2Ph$ **41bc** R^1 = $SiMe_2Ph$ R^2 = Ph **40bc**:**41bc** = 97:3[c]

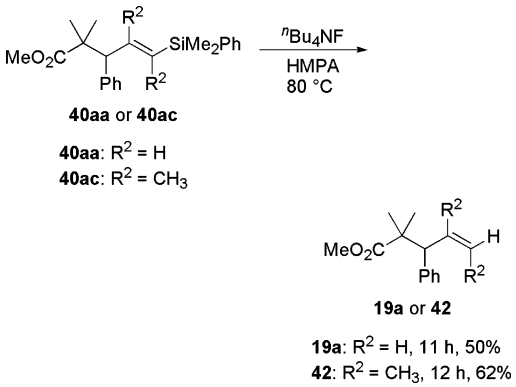
[a] Unless otherwise noted, a solution of **39** was added at the rate taking about 1 h to a mixture of **7** (2 equiv), **8** (2 equiv), and **2e** (1 mol %) in CH_2Cl_2 at 25 °C. [b]Isolated yield. [c]Determined by ^1H NMR analysis. [d]Time for stirring.

8 by the catalysis of **2e** (entry 3 in Table 5). When two allylic termini of **39** have a different number of substituents except for the leaving group, the presence of a dimethylphenylsilyl group contributes to realize more clear-cut discrimination of the reaction site. In the reaction of **39c** with **7b** and **8**, **40bc** was isolated in 80% yield with a high level of regioselectivity (97%, entry 6 in Table 5). It should be noted that **40ac** was obtained in 89% yield as the sole product in the reaction of **39c** with **7a** and **8** (entry 5 in Table 5). These results demonstrate that introduction of a bulkier triorganosilyl group into allylic carbonates promises high regioselectivity in the present type of coupling reactions.

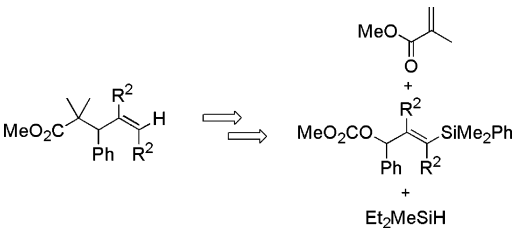
In general, a triorganosilyl group can be regarded as equivalent to a proton, because the corresponding silyl group is readily replaced by H under mild conditions. Therefore, if the silyl group involved in **40** could be replaced by H, this silyl-modified hydroallylation provides a practical route for precise regiocontrol of the two unsymmetrically substituted allylic termini. In fact, the Me_2PhSi group of **40aa** and **40ac** was replaced by H to give **19a** and **42** in 50% and 62% yield, respectively, after treatment with $^nBu_4NF$ (1 M solution in THF) in HMPA for 11 or 12 h at 80 °C (Scheme 7).[16] This successful protodesilylation of **40aa** and **40ac** clearly demonstrates that the retro-synthesis as shown in Scheme 8 is appreciable as a

(16) Oda, H.; Sato, M.; Morizawa, Y.; Oshima, K.; Nozaki, H. *Tetrahedron Lett.* **1983**, *24*, 2877.

Scheme 7



Scheme 8



feasible route for the regioselective allylic substitutions.[17] In addition to the regiocontrol in hydroallylation, it is also important to control the stereochemistry of the reaction path. In contrast to successful regiocontrol, diastereochemical control to form products is insufficient at this stage (entries 4−9 in Table 3, Scheme 5, and entries 2, 4, and 6 in Table 5). Although access to similar frameworks is possible through classical methods such as allylation of enolate anions[6h,18] and allylation of enoxysilanes,[8,19] there is no general and facile methodology to control the stereochemistry in the substitution at the allylic termini. Therefore, the present three-component coupling retains a sufficient usefulness not only in the novelty of the reaction but also in synthetic organic chemistry despite this defect. This protocol makes it possible to design diverse types of homoallylic carbonyl compounds under almost neutral conditions. This

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method provides a powerful tool for a large-scale synthesis of designed building blocks, since it is operated as a catalytic process.

Conclusions

A one-pot method for the synthesis of γ,δ-unsaturated carbonyl compounds has been developed. This methodology provides a convenient route for the formal hydroallylation of α,β-unsaturated carbonyl compounds by the catalysis of a cationic rhodium(I) complex. A trialkylsilyl group on either carbon of two allylic termini plays an important role in enhancing the regioselectivity of the allylic substitution because of its remarkable bulkiness. Removal of the trialkylsilyl group by protodesilylation is another advantage. These results provide a reliable protocol for regiocontrolled allylic alkylation in which the choice of catalyst is also critical.

Experimental Section

General Considerations. All hydroallylations 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 $Mg(OEt)_2$. $CDCl_3$ and all other solvents were utilized at their commercial level of purity. α,β-Unsaturated compounds **7a**, **7b**, **7c**, **7d**, **7e**, **7f**, and **7g** and hydrosilanes **8**, Me_2PhSiH, and $EtMe_2SiH$ were purchased from Tokyo Kasei, Aldrich, or Shin-Etsu Chemicals. They were used as received. Allylic carbonates were derived from the corresponding alcohols by the standard procedures.[20] Cationic rhodium(I) complexes **2a**−**e** were prepared by a similar procedure reported for $[Rh(cod)(PPh_3)_2]BF_4$.[21]

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. Medium-pressure preparative liquid chromatography was performed on a YFLC-600 system equipped with a silica gel (particle size 0.040−0.063 mm) column.

Proton nuclear magnetic resonance (^{1}H NMR) data were obtained at 300 MHz on a Varian Mercury 300 spectrometer or at 500 MHz on a Varian VXR-500 spectrometer. Chemical shifts are reported in delta (δ) units, in parts per million (ppm) relative to the singlet at 7.26 ppm for $CHCl_3$ in 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 75 MHz on a Varian Mercury 300 spectrometer or at 125.7 MHz on a Varian VXR-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 broadband 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.

Preparation of (*E*)-1-(Dimethylphenylsilyl)-3-(methoxycarbonyloxy)-3-phenylpropene, 39a. In a 20 mL round-bottomed flask, to a solution of (*Z*)-3-(dimethylphenylsilyl)-2-(trimethylsilyl)-propenal[22] (1.47 g, 5.6 mmol) in C_6H_6 (10 mL) was added an aqueous solution of HI (50%, 0.1 mL). The resultant mixture was stirred for 15 h at 25 °C, and to this mixture was added a saturated aqueous solution of sodium thiosulfate (10 mL). The resulting mixture was stirred for 10 min at 25 °C. Phases were separated and the aqueous layer was extracted with ethyl acetate (10 mL × 3). The organic layer and ethyl acetate extracts were combined, washed once with brine, and then dried over magnesium sulfate. The solvent was evaporated to give (*E*)-3-(dimethylphenylsilyl)-2-(trimethylsilyl)propenal in 93% yield (1.37 g, 5.2 mmol) as dark red liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.17 (s, 9H, $Si(CH_3)_3$), 0.52 (s, 6H, $Si(CH_3)_2$), 7.36−7.40 (m, 3H, Ph), 7.51−7.53 (m, 2H, Ph), 10.00 (s, 1H, C*H*O).

In a 50 mL round-bottomed flask, to a solution of (*E*)-3-(dimethylphenylsilyl)-2-(trimethylsilyl)propenal (1.37 g, 5.2 mmol) in MeOH (30 mL) was added an aqueous solution (1 mL) of KOH (0.13 g, 2.3 mmol). The resultant mixture was stirred for 3 h at 25 °C and the solvent was evaporated. The residue was poured into a mixture of water (10 mL) and ethyl acetate (10 mL). Phases were separated and the aqueous layer was extracted with ethyl acetate (10 mL × 3). The organic layer and ethyl acetate extracts were combined, washed once with brine, and then dried over magnesium sulfate. The solvent was evaporated to give (*E*)-3-(dimethylphenylsilyl)propenal in 94% yield (0.93 g, 4.9 mmol) as a colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.47 (s, 6H, $Si(CH_3)_2$), 6.54 (dd, J = 19.0 and 7.5 Hz, 1H, C*H*CHO), 7.28 (d, J = 19.0 Hz, 1H, SiC*H*), 7.36−7.40 (m, 3H, Ph), 7.51−7.53 (m, 2H, Ph), 9.53 (d, J = 7.5 Hz, 1H, C*H*O).

In a 50 mL two-necked flask equipped with a dropping funnel and reflux condenser were placed magnesium turnings (0.071 g, 2.9 mmol), a small piece of I_2, and THF (1 mL). To this suspension was added a solution of bromobenzene (0.38 g, 2.4 mmol) in THF (5 mL) at 25 °C. This mixture was diluted with THF (5 mL) and stirred for 1 h at 25 °C. To the flask containing PhMgBr was added (*E*)-3-(dimethylphenylsilyl)propenal (0.39 g, 2.0 mmol) in THF (5 mL) at 0 °C. After stirring for 24 h at 25 °C, to this mixture cooled to 0 °C was added an aqueous saturated solution of NH_4Cl (20 mL). Phases were separated and the aqueous layer was extracted with ethyl acetate (20 mL × 3). The organic layer and ethyl acetate extracts were combined, washed once with brine, and then dried over magnesium sulfate. The solvent was evaporated and the residue was purified by flash column chromatography (eluent; hexane:ethyl acetate = 10:1) to give (*E*)-3-(dimethylphenylsilyl)-1-phenyl-2-propen-1-ol in 49% yield (0.27 g, 1.0 mmol) as a colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.35 (s, 3H, Si−CH_3), 0.36 (s, 3H, Si−CH_3), 1.98 (d, J = 4.0 Hz, 1H, O*H*), 5.23 (m, 1H, PhC*H*), 6.15 (dd, J = 19.0 and 1.5 Hz, 1H, C=C*H*), 6.30 (dd, J = 19.0 and 5.0 Hz, 1H, SiC*H*=C), 7.35−7.38 (m, 8H, Ph), 7.50−7.52 (m, 2H, Ph).

To a 20 mL round-bottomed flask containing a solution of (*E*)-3-(dimethylphenylsilyl)-1-phenyl-2-propen-1-ol (0.27 g, 1.0 mmol) in THF (5 mL) was added ^{n}BuLi (1.56 M in hexane, 0.76 mL, 1.2 mmol) at −78 °C, and the mixture was stirred for 30 min. To this mixture was added methyl chloroformate (0.1 mL, 1.3 mmol), and resultant mixture was warmed to 25 °C. After stirring for 17 h at 25 °C, the solvent was evaporated and the residue was purified by flash column chromatography (eluent; hexane:ethyl acetate = 20:1) to give **36a** in 71% yield (0.23 g, 0.70 mmol) as a colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.336 (s, 3H, Si−CH_3), 0.342 (s, 3H, Si−CH_3), 3.77 (s, 3H, OCH_3), 6.103 (dd, J = 5.0 and 1.5 Hz, 1H, PhC*H*), 6.105 (dd, J = 19.3 and 1.5 Hz, 1H, C=C*H*), 6.23 (dd, J = 19.0 and 5.0 Hz, 1H, SiC*H*=C), 7.32−7.37 (m, 8H, Ph), 7.47−7.49 (m, 2H, Ph).

Preparation of (*E*)-1-(*tert*-Butyldimethylsilyl)-3-(methoxycarbonyloxy)-3-phenylpropene, 39b, and (*E*)-2-(Dimethylphenyl-

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silyl)-4-(methoxycarbonyloxy)-3-methyl-4-phenyl-2-butene, **39c.** Allylic carbonates (*E*)-1-(*tert*-butyldimethylsilyl)-3-(methoxycarbonyloxy)-3-phenylpropene (**39b**) and (*E*)-2-(dimethylphenylsilyl)-4-(methoxycarbonyloxy)-3-methyl-4-phenyl-2-butene (**39c**) were prepared from (*Z*)-3-(*tert*-butyldimethylsilyl)-2-(trimethylsilyl)propenal[22] and (*Z*)-3-(dimethylphenylsilyl)-2,3-dimethylpropenal,[22] respectively, according to a procedure similar to the synthesis of **39a**.

39b: colorless liquid, eluent; hexane:ethyl acetate = 30:1. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.02 (s, 3H, Si−CH_3), 0.03 (s, 3H, Si−CH_3), 3.78 (s, 3H, OCH_3), 5.97 (dd, J = 18.6 and 1.2 Hz, 1H, SiCH═C), 6.08 (dd, J = 4.8 and 1.2 Hz, 1H, PhCH), 6.17 (dd, J = 18.6 and 4.8 Hz, 1H, C═CH), 7.32−7.37 (m, 5H, Ph).

39c: colorless liquid, eluent; hexane:ethyl acetate = 49:1. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.53 (s, 3H, Si−CH_3), 0.54 (s, 3H, Si−CH_3), 1.60 (s, 3H, CH_3), 1.77 (s, 3H, CH_3), 3.75 (s, 3H, OCH_3), 6.50 (S, 1H, PhCH), 7.05−7.09 (m, 2H, Ph), 7.21−7.29 (m, 3H, Ph), 7.32−7.36 (m, 3H, Ph), 7.54−7.60 (m, 2H, Ph).

Typical Procedure for Rh-Catalyzed Allylic Alkylation of 4 with 3. In a test tube, to a solution of [Rh(cod)(PMePh$_2$)$_2$]OTf (**2c**) (6.0 mg, 0.0079 mmol) in CH_2Cl_2 (2 mL) was added a mixture of 2-trimethylsilyloxypropene (**3**) (380.3 mg, 2.9 mmol) and 3-methoxycarbonyloxy-1-phenyl-1-butene (**4**) (151.8 mg, 0.74 mmol) in CH_2Cl_2 (2 mL). This test tube was sealed and then stirred at 80 °C for 19 h. The resulting mixture was cooled to ambient temperature followed by opening a sealed tube. The solvent was removed under reduced pressure and the residue was purified by silica gel flash column chromatography (hexane:ethyl acetate = 10:1 as an eluent) to afford a mixture of 4-methyl-6-phenyl-(*E*)-5-hexen-2-one (**5a**) and 4-phenyl-(*E*)-5-hepten-2-one (**6a**) (120 mg, 0.64 mmol) as colorless liquid (86%).

The products **5a**[8] and **6a**[8] were characterized by comparing their spectral data to those reported in the literature.

Typical Procedure for Rh-Catalyzed Hydroallylation of an α,β-Unsaturated Carbonyl Compound with Hydrosilane and Allylic Carbonate. To a solution of [Rh(cod){P(OPh)$_3$}$_2$]OTf (**2e**) (8.2 mg, 0.084 mmol) in CH_2Cl_2 (4 mL) was added a mixture of methyl methacrylate (**7a**) (162 mg, 1.6 mmol) and diethylmethylsilane (**8**) (150 mg, 1.5 mmol). To the homogeneous solution resulting from stirring for 3 min was added a solution of 3-methoxycarbonyloxy-1-phenyl-1-butene (**4**) (151 mg, 0.73 mmol) in CH_2Cl_2 (4 mL) at the rate taking about 1 h under a N_2 atmosphere. The resulting mixture was then stirred for 1 h under a N_2 atmosphere. The solvent was removed under reduced pressure and the residue was purified by silica gel flash column chromatography (hexane:ethyl acetate = 120:1 as an eluent) to afford a mixture of methyl 2,2,3-trimethyl-5-phenyl-4-pentenoate (**9a**) and methyl 2,2-dimethyl-3-phenyl-4-hexenoate (**10a**) (158 mg, 0.68 mmol) as a colorless liquid (93%). The reactions of allylic carbonates and α,β-unsaturated carbonyl compounds **7a**−**g** were carried out in a similar manner. Conditions and yields are summarized in Tables 3, 4, and 5, respectively.

The products **9a**,[8] **10a**,[8,23] **18a**,[24] **24a**,[8,25a] **26a**,[8,25b,c] **28a**,[8] **29a**,[8,25a,d] and 3**2a**[8,25c−f] were characterized by comparing their spectral data to those reported in the literature.

The mixtures of **9b** and **10b**, **9c** and **10c**, **6f** and **10f**, **9g** and **10g**, **18a** and **19a**, and **21a** and **22a** could not be separated by flash column chromatography.

Properties of 3-methyl-3-(1-methyl-3-phenyl-2(*E*)-propenyl)-dihydro-2-furanone, 9d (as a 1:1 mixture of diastereoisomers): colorless liquid, eluent; hexane:ethyl acetate = 15:1. IR (neat): 1765 (C═O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.14 (d, 3H, J = 6.9 Hz), 1.19 (d, 3H, J = 6.9 Hz), 1.29 (s, 3H), 1.30 (s, 3H), 1.85−1.95 (m, 2H), 2.34 (ddd, 1H, J = 13.2, 7.6, and 7.6 Hz), 2.41 (ddd, 1H, J = 13.2, 8.7 and 8.4 Hz), 2.66 (dq, 1H, J = 9.0 and 6.9 Hz), 2.66 (dq, 1H, J = 7.8 and 6.9 Hz), 4.17−4.29 (m, 4H), 6.03 (dd, 1H, J = 15.6 and 9.0 Hz), 6.17 (dd, 1H, J = 16.1 and 7.8 Hz), 6.46 (d, 1H, J = 16.1 Hz), 6.49 (d, 1H, J = 15.6 Hz), 7.19−7.39 (m, 10 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.16, 14.40, 16.24, 21.55, 22.68, 23.17, 30.82, 30.92, 31.60, 31.70, 41.86, 43.44, 45.84, 46.14, 65.06, 65.15, 119.94, 120.01, 125.46, 126.05, 126.11, 127.28, 127.32, 128.26, 128.38, 128.43, 129.70, 130.01, 130.32, 131.51, 131.92, 136.86, 136.89, 181.05, 181.14. Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 78.30; H, 7.98.

Properties of 3-methyl-3-(1-phenyl-2(*E*)-butenyl)dihydro-2-furanone, 10d (as a 1:1 mixture of diastereoisomers): colorless liquid, eluent hexane:ethyl acetate = 15:1. IR (neat): 1763 (C═O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ one isomer: 1.11 (s, 3H), 1.65 (dd, 3H, J = 6.4 and 1.5 Hz), 1.91 (ddd, 1H, J = 13.1, 8.1, and 7.1 Hz), 2.44 (ddd, 1H, J = 13.1, 8.5, and 5.2 Hz), 3.45 (ddd, 1H, J = 8.9, 8.5, and 7.1 Hz), 3.58 (d, 1H, J = 9.7 Hz), 4.02 (ddd, 1H, J = 8.9, 8.1, and 5.2 Hz), 5.52 (dq, 1H, J = 14.9 and 6.4 Hz), 5.77 (ddq, 1H, J = 14.9, 9.7, and 1.5 Hz), 7.18−7.33 (m, 5 H). the other isomer: 1.26 (s, 3H), 1.73 (dd, 3H, J = 6.2 and 1.5 Hz), 1.91 (ddd, 1H, J = 12.6, 7.8, and 4.8 Hz), 2.58 (ddd, 1H, J = 12.6, 8.6, and 7.9 Hz), 3.52 (d, 1H, J = 8.6 Hz), 3.91 (ddd, 1H, J = 9.0, 8.6, and 4.8 Hz), 4.11 (ddd, 1H, J = 9.0, 7.9, and 7.8 Hz), 5.64 (dq, 1H, J = 15.1 and 6.2 Hz), 5.82 (ddq, 1H, J = 15.1, 8.6, and 1.5 Hz), 7.18−7.33 (m, 5 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.17, 18.15, 18.17, 22.69, 23.44, 24.22, 31.29, 31.61, 32.06, 47.04, 47.20, 53.92, 55.09, 64.99, 65.04, 126.87, 126.89, 127.78, 128.15, 128.24, 128.43, 128.55, 128.61, 129.13, 129.19, 129.32, 129.66, 140.29, 140.44, 180.97, 181.26. Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 78.35; H, 8.01.

Properties of 3,4-Dimethyl-6-phenyl-(*E*)-5-hexen-2-one, 9e (as a 1:1 mixture of diastereoisomers): colorless liquid, eluent hexane:ethyl acetate = 120:1. IR (neat): 1715 (C═O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ one isomer: 1.08 (d, 3H, J = 6.6 Hz), 1.09 (d, 3H, J = 6.6 Hz), 2.14 (s, 3H), 2.50 (ddq, 1H, J = 7.8, 6.9, and 6.6 Hz), 2.66 (dq, 1H, J = 6.9 and 6.6 Hz), 6.13 (dd, 1H, J = 15.9 and 7.8 Hz), 6.38 (d, 1H, J = 15.9 Hz), 7.17−7.37 (m, 5 H). the other isomer: 1.08 (d, 3H, J = 6.6 Hz), 1.10 (d, 3H, J = 6.6 Hz), 2.18 (s, 3H), 2.59 (ddq, 1H, J = 8.7, 6.6, and 6.6 Hz), 2.66 (dq, 1H, J = 6.6 and 6.6 Hz), 6.01 (dd, 1H, J = 15.8 and 8.7 Hz), 6.41 (d, 1H, J = 15.8 Hz), 7.17−7.37 (m, 5 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.00, 14.59, 16.61, 19.15, 29.12, 29.22, 39.20, 39.88, 52.46, 52.79, 126.00, 127.07, 127.45, 127.83, 128.40, 129.47, 130.23, 132.60, 133.53, 137.21, 211.65, 211.98. Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 82.98; H, 9.05.

Properties of 3-methyl-4-phenyl-(*E*)-5-hepten-2-one, 10e (as a 1:1 mixture of diastereoisomers): colorless liquid, eluent; hexane:ethyl acetate = 120:1. IR (neat): 1716 (C═O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ one isomer: 0.86 (d, 3H, J = 7.0 Hz), 1.61 (d, 3H, J = 6.3 Hz), 1.86 (s, 3H), 2.90 (dq, 1H, J = 7.1 and 7.0 Hz), 3.37 (dd, 1H, J = 8.4 and 7.1 Hz), 5.44 (dq, 2H, J = 15.0 and 6.3 Hz), 5.59 (dd, 2H, J = 15.0 and 8.4 Hz), 7.14−7.41 (m, 5 H), the other isomer: 1.11 (d, 3H, J = 6.9 Hz), 1.67 (d, 3H, J = 5.7 Hz), 2.15 (s, 3H), 2.93 (dq, 1H, J = 6.9 and 6.8 Hz), 3.40 (dd, 1H, J = 8.4 and 6.8 Hz), 5.44 (dq, 2H, J = 15.0 and 5.7 Hz), 5.59 (dd, 2H, J = 15.0 and 8.4 Hz), 7.14−7.41 (m, 5 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 6.75, 6.87, 15.32, 15.61, 15.91, 18.01, 29.48, 29.62, 52.13, 52.35, 52.47, 126.28, 126.36, 126.39, 127.15, 127.44, 127.82, 128.47, 128.50, 131.45, 132.00, 132.33, 142.18, 143.15, 211.93, 212.09. Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 83.02; H, 9.05.

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Properties of methyl 2,2-dimethyl-3,5-diphenyl-4(*E*)-pentenoate, 14a: colorless liquid, eluent; hexane:ethyl acetate = 120:1. IR (neat): 1731 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.18 (s, 3H), 1.23 (s, 3H), 3.60 (s, 3H), 3.76 (d, 1H, J = 9.4 Hz), 6.46 (d, 1H, J = 15.7 Hz), 6.61 (dd, 1H, J = 15.7 and 9.4 Hz), 7.20−7.37 (m, 10 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.66, 23.34, 47.30, 51.57, 56.99, 126.15, 126.61, 127.15, 127.91, 128.31, 128.55, 128.98, 132.40, 137.20, 140.31, 177.02. Anal. Calcd for $C_{20}H_{22}O_2$: C, 81.61; H, 7.53. Found: C, 81.80; H, 7.61.

Properties of methyl 2,2,3-trimethyl-4(*E*)-hexenoate, 16a: colorless liquid, eluent; hexane:ethyl acetate = 120:1. IR (neat): 1736 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 0.90 (d, 3H, J = 6.9 Hz), 1.08 (s, 3H), 1.09 (s, 3H), 1.65 (dd, 3H, J = 6.1 and 1.4 Hz), 2.41 (dq, 1H, J = 8.3 and 6.9 Hz), 3.65 (s, 3H), 5.28 (ddq, 1H, J = 15.3, 8.3, and 1.4 Hz), 5.44 (dq, 1H, J = 15.3 and 6.1 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 15.92, 18.11, 21.07, 23.07, 44.24, 45.82, 51.52, 126.09, 132.24, 178.22. Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 70.37; H, 10.60.

Properties of methyl 2,2-dimethyl-5-phenyl-5(*E*)-pentenoate, 18a (as a mixture of regioisomers): colorless liquid, bp 140 °C/0.1 Torr. IR ($CHCl_3$): 1727 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.23 (s, 6H, CH_3), 2.44 (d, J = 7.6 Hz, 2H, CH_2), 3.68 (s, 3H, OCH_3), 6.14 (dt, J = 15.9 and 7.6 Hz, 1H, PhC=CH), 6.41 (d, J = 15.9 Hz, 1H, PhCH=C), 7.16−7.36 (m, 5H, Ph). Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 76.80; H, 8.47.

Properties of methyl 2,2-dimethyl-3-phenyl-4(*E*)-pentenoate, 19a: colorless liquid, bp 140 °C/0.1 Torr. IR (neat): 1738 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.12 (s, 3H, CH_3), 1.18 (s, 3H, CH_3), 3.60 (d, J = 9.7 Hz, 1H, PhCH), 3.61 (s, 3H, OCH_3), 5.10 (dd, J = 16.7 and 1.9 Hz, 1H, CHC=CH), 5.13 (dd, J = 10.4 and 1.9 Hz, 1H, CH_2C=CH), 6.23 (ddd, J = 16.7, 10.4, and 9.7 Hz, 1H, CHCH=C), 7.15−7.31 (m, 5H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.36 (*C*H_3), 23.29 (*C*H_3), 46.95 (CO*C*), 51.62 (O*C*H_3), 57.78 (PhC), 117.38 (C=C), 126.61 (Ph), 127.91 (Ph), 129.04 (Ph), 136.85 (Ph or C=C), 140.23 (Ph or C=C), 177.22 (*C*=O). Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 76.96; H, 8.45.

Properties of methyl 2,2,4-trimethyl-5-phenyl-4(*E*)-pentenoate, 21a, and methyl 2,2,4-trimethyl-3-phenyl-4-pentenoate, 22a (as a mixture of regioisomers): colorless liquid, bp 140 °C/0.2 Torr. IR (neat): 1731 (C=O) cm^{-1}. For **21a** ^1H NMR (300 MHz, $CDCl_3$): δ 1.25 (s, 6H, CH_3), 1.79 (s, 3H, CH_3), 2.46 (s, 2H, CH_2), 3.68 (s, 3H, OCH_3), 6.25 (s, 1H, PhCH=C), 7.17−7.34 (m, 5H, Ph). For **22a** ^1H NMR (300 MHz, $CDCl_3$): δ 1.15 (s, 3H, CH_3), 1.20 (s, 3H, CH_3), 1.58 (s, 3H, CH_3), 3.66 (s, 3H, OCH_3), 3.68 (s, 1H, PhCH), 4.95 (s, 1H, C=CH), 4.99 (s, 1H, C=CH), 7.17−7.34 (m, 5H, Ph). Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.35; H, 8.90.

Properties of methyl 2,2-dimethyl-3,5,5-triphenyl-4-pentenoate, 38a: colorless plates from ethyl acetate and hexane, mp 207−208 °C. IR (CCl_4): 1731 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.13 (s, 3H, CH_3), 1.17 (s, 3H, CH_3), 3.53 (s, 3H, OCH_3), 3.71 (d, J = 11.0 Hz, 1H, CH), 6.58 (d, J = 11.0 Hz, 1H, C=CH), 6.96−7.33 (m, 15H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.10 (*C*H_3), 23.73 (*C*H_3), 41.18 (CO*C*), 51.65 (*C*H or O*C*H_3), 52.54 (O*C*H_3 or *C*H), 126.48, 127.08, 127.15, 127.55 (2C), 127.85, 127.93, 128.01, 129.25, 129.72, 139.58, 141.05, 142.80, 143.25, 177.02 (*C*=O). Anal. Calcd for $C_{26}H_{26}O_2$: C, 84.29; H, 7.07. Found: C, 84.40; H, 7.25.

Properties of methyl 2-methyl-3,5,5-triphenyl-4-pentenoate, 38b (as a 1:1 mixture of diastereoisomers): colorless liquid, bp 190 °C/0.2 Torr. IR (neat): 1735 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): one isomer: δ 0.90 (d, J = 7.1 Hz, 3H, CH_3), 2.85 (dq, J = 9.3 and 7.1 Hz, 1H, CH_3CH), 3.52 (dd, J = 10.5 and 9.3 Hz, 1H, PhCH), 3.63 (s, 3H, OCH_3), 6.36 (d, J = 10.5 Hz, 1H, C=CH), 7.06−7.41 (m, 15H, Ph); the other isomer: δ 1.21 (d, J = 6.9 Hz, 3H, CH_3), 2.89 (dq, J = 8.7 and 6.9 Hz, 1H, CH_3CH), 3.36 (s, 3H, OCH_3), 3.69 (dd, J = 10.8 and 8.7 Hz, 1H, PhCH), 6.25 (d, J = 10.8 Hz, 1H, C=CH), 7.06−7.41 (m, 15H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$): δ 15.33 (CH_3), 15.58 (CH_3), 46.43 (COC), 46.84 (COC), 48.47 (CH or OCH_3), 49.24 (CH or OCH_3), 51.32 (OCH_3 or CH), 51.60 (OCH_3 or CH), 126.37, 126.48, 127.11, 127.12, 127.16, 127.19, 127.23, 127.34, 127.60, 127.78, 127.94, 127.97, 128.02, 128.13, 128.38, 128.60, 128.88, 129.66, 129.74, 129.77, 139.48, 139.52, 142.13, 142.19, 142.33, 142.36, 142.66, 143.26, 175.18 (C=O), 175.50 (C=O). Anal. Calcd for $C_{25}H_{24}O_2$: C, 84.24; H, 6.79. Found: C, 84.13; H, 6.92.

Properties of methyl 2,2-dimethyl-5-(dimethylphenylsilyl)-3-phenyl-4(*E*)-pentenoate, 40aa, and methyl 2,2-dimethyl-3-(dimethylphenylsilyl)-5-phenyl-4(*E*)-pentenoate, 41aa (as a mixture of regioisomers (95:5)): colorless liquid, bp 185−190 °C/0.4 Torr. IR (neat): 1731 (C=O), 1246 (Si-CH_3) cm^{-1}. For **40aa** ^1H NMR (300 MHz, $CDCl_3$): δ 0.32 (s, 3H, Si−CH_3), 0.33 (s, 3H, Si−CH_3), 1.10 (s, 3H, CH_3), 1.17 (s, 3H, CH_3), 3.55 (s, 3H, OCH_3), 3.67 (d, J = 9.0 Hz, 1H, CH), 5.87 (d, J = 18.3 Hz, 1H, SiCH=C), 6.47 (dd, J = 18.3 and 9.0 Hz, 1H, SiC=CH), 7.15−7.51 (m, 10H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$): δ −2.41 (Si*C*H_3), −2.38 (Si*C*H_3), 22.16(*C*H_3), 23.55 (*C*H_3), 47.12 (CO*C*), 51.56 (O*C*H_3), 60.38 (*C*H), 126.57, 127.60, 127.88, 128.81, 129.17, 131.27, 133.71, 138.52, 139.93, 146.22, 177.12 (*C*=O). For **41aa** ^1H NMR (300 MHz, $CDCl_3$): δ 0.34 (s, 3H, Si−CH_3), 0.35 (s, 3H, Si−CH_3), 1.17 (s, 3H, CH_3), 1.22 (s, 3H, CH_3), 2.44 (d, J = 10.7 Hz, 1H, CH), 3.50 (s, 3H, OCH_3), 6.08 (dd, J = 15.6 and 10.7 Hz, 1H, SiCCH), 6.19 (d, J = 15.6 Hz, 1H, PhCH=C), 7.15−7.51 (m, 10H, Ph). Anal. Calcd for $C_{22}H_{28}O_2Si$: C, 74.95; H, 8.01. Found: C, 75.10; H, 7.97.

Properties of methyl 5-(dimethylphenylsilyl)-2-methyl-3-phenyl-4(*E*)-pentenoate, 40ba, and methyl 3-(dimethylphenylsilyl)-2-methyl-5-phenyl-4(*E*)-pentenoate, 41ba (as a mixture of regioisomers (86:14), and each isomer consisted of two diastereoisomers): colorless liquid, bp 150 °C/0.5 Torr. IR (neat): 1737 (C=O), 1247 (Si−CH_3) cm^{-1}. For **40ba** ^1H NMR (500 MHz, $CDCl_3$): one isomer: δ 0.31 (s, 3H, Si−CH_3), 0.32 (s, 3H, Si−CH_3), 1.21 (d, J = 7.0 Hz, 3H, CH_3), 2.85 (dq, J = 9.3 and 7.0 Hz, 1H, CH_3CH), 3.56 (dd, J = 9.3 and 8.8 Hz, 1H, PhCH), 3.57 (s, 3H, OCH_3), 5.90 (d, J = 18.6 Hz, 1H, SiCH=), 6.17 (dd, J = 18.6 and 8.8 Hz, 1H, SiC=CH), 7.16−7.52 (m, 10H, Ph), the other isomer: δ 0.28 (s, 3H, Si−CH_3), 0.29 (s, 3H, Si−CH_3), 0.95 (d, J = 7.0 Hz, 3H, CH_3), 2.84 (dq, J = 10.3 and 7.0 Hz, 1H, CH_3CH), 3.41 (s, 3H, OCH_3), 3.50 (dd, J = 10.3 and 8.0 Hz, 1H, PhCH), 5.82 (d, J = 18.5 Hz, 1H, SiCH=), 6.24 (dd, J = 18.5 and 8.0 Hz, 1H, SiC=CH), 7.16−7.52 (m, 10H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$): δ −2.52 (Si*C*H_3), −2.48 (Si*C*H_3), −2.41 (Si*C*H_3), −2.36 (Si*C*H_3), 15.81 (*C*H_3), 15.91 (*C*H_3), 44.97 (CO*C*), 45.23 (CO*C*), 51.36 (O*C*H_3), 51.40 (O*C*H_3), 56.46 (Ph*C*), 56.56 (Ph*C*), 126.43, 126.59, 127.57, 127.63 (2C), 128.07, 128.29, 128.53, 128.61, 128.76, 128.82, 130.43, 133.66 (2C), 138.51, 138.54, 140.82, 141.82, 147.58, 148.66, 175.47 (*C*=O), 175.88 (*C*=O). For **41ba** ^1H NMR (500 MHz, $CDCl_3$): one isomer: δ 0.358 (s, 3H, Si−CH_3), 0.364 (s, 3H, Si−CH_3), 1.12 (d, J = 7.0 Hz, 3H, CH_3), 2.14 (dd, J = 8.9 and 7.2 Hz, 1H, SiCH), 2.72 (dq, J = 7.2 and 7.0 Hz, 1H, CH_3CH), 3.53 (s, 3H, OCH_3), 5.99 (d, J = 16.4 Hz, 1H, PhCH=), 6.21 (dd, J = 16.4 and 8.9 Hz, 1H, SiCCH=), 7.16−7.52 (m, 10H, Ph); the other isomer: δ 0.35 (s, 3H, Si−CH_3), 0.36 (s, 3H, Si−CH_3), 1.14 (d, J = 6.8 Hz, 3H, CH_3), 2.38 (dd, J = 10.4 and 7.4 Hz, 1H, SiCH), 2.67 (dq, J = 7.4 and 6.8 Hz, 1H, CH_3CH), 3.47 (s, 3H, OCH_3), 6.00 (d, J = 15.8 Hz, 1H, PhCH=), 6.16 (dd, J = 15.8 and 10.4 Hz, 1H, SiCCH=), 7.16−7.52 (m, 10H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$): δ −4.04 (Si*C*H_3), −3.69 (Si*C*H_3), −3.33 (Si*C*H_3), −2.84 (Si*C*H_3), 16.65 (*C*H_3), 18.03 (*C*H_3), 29.77 (2C, Si*C*), 37.18 (CO*C*), 38.66 (CO*C*), 39.89 (O*C*H_3), 40.40 (O*C*H_3), 125.72, 125.75, 126.53, 126.59, 127.91, 127.97, 128.35 (2C), 128.45, 128.70, 129.00, 129.06, 129.73, 130.11, 133.90, 134.07, 136.82, 137.48, 137.75, 137.81, 176.06 (*C*=O), 176.32 (*C*=

O). Anal. Calcd for $C_{21}H_{26}O_2Si$: C, 74.51; H, 7.74. Found: C, 74.75; H, 7.68.

Properties of methyl 5-(*tert*-buthyldimethylsilyl)-2,2-dimethyl-3-phenyl-4(*E*)-pentenoate 40ab: colorless liquid, bp 150 °C/0.1 Torr. IR (neat): 1734 (C═O), 1246 (Si−CH_3) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ −0.01 (s, 3H, Si−CH_3), 0.02 (s, 3H, Si−CH_3), 0.85 (s, 9H, SiC(CH_3)$_3$), 1.11 (s, 3H, CH_3), 1.17 (s, 3H, CH_3), 3.59 (s, 3H, OCH_3), 3.64 (d, J = 9.0 Hz, 1H, PhC*H*), 5.68 (d, J = 18.4 Hz, 1H, SiC*H*═), 6.38 (dd, J = 18.4 and 9.0 Hz, 1H, SiC═C*H*), 7.16−7.31 (m, 5H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$): δ −6.04 (Si*C*H_3), −5.84 (Si*C*H_3), 16.63 (*C*Me$_3$), 22.45 (*C*H_3), 23.40 (*C*H_3), 26.48 (C(*C*H_3)$_3$), 47.04 (CO*C*), 51.59 (O*C*H_3), 60.41 (Ph*C*), 126.49, 127.85, 129.12, 130.79, 140.31, 145.61, 177.17 (*C*═O). Anal. Calcd for $C_{20}H_{32}O_2Si$: C, 72.23; H, 9.70. Found: C, 71.93; H, 9.85.

Properties of methyl 5-(*tert*-buthyldimethylsilyl)-2-methyl-3-phenyl-4(*E*)-pentenoate, 40bb, and methyl 3-(*tert*-buthyldimethylsilyl)-2-methyl-5-phenyl-4(*E*)-pentenoate, 41bb (as a mixture of regioisomers (>95:<5), and each isomer consisted of two diastereoisomers): colorless liquid, bp 140 °C/0.1 Torr. IR (neat): 1740 (C═O), 1254 (Si−CH_3) cm^{-1}. For **40bb** ^1H NMR (300 MHz, $CDCl_3$): one isomer: δ −0.02 (s, 3H, Si−CH_3), 0.01 (s, 3H, Si−CH_3), 0.83 (s, 9H, SiC(CH_3)$_3$), 1.21 (d, J = 7.1 Hz, 3H, CH_3), 2.84 (dq, J = 9.6 and 7.1 Hz, 1H, CH_3C*H*), 3.52 (dd, J = 9.6 and 8.7 Hz, 1H, PhC*H*), 3.65 (s, 3H, OCH_3), 5.76 (d, J = 18.4 Hz, 1H, SiC*H*═), 6.08 (dd, J = 18.4 and 8.7 Hz, 1H, SiC═C*H*), 7.15−7.34 (m, 5H, Ph); the other isomer: δ −0.04 (s, 3H, Si−CH_3), −0.03 (s, 3H, Si−CH_3), 0.85 (s, 9H, SiC(CH_3)$_3$), 0.95 (d, J = 6.9 Hz, 3H, CH_3), 2.85 (dq, J = 10.7 and 6.9 Hz, 1H, CH_3C*H*), 3.42 (s, 3H, OCH_3), 3.49 (dd, J = 10.7 and 7.9 Hz, 1H, PhC*H*), 5.70 (d, J = 18.6 Hz, 1H, SiC*H*═), 6.16 (dd, J = 18.6 and 7.9 Hz, 1H, SiC═C*H*), 7.15−7.34 (m, 5H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$): δ −6.16 (Si*C*H_3), −6.05 (Si*C*H_3, 2C), −5.89 (Si*C*H_3), 15.80 (*C*H_3), 16.07 (*C*H_3), 16.57 (*C*Me$_3$, 2C), 26.43 (C(*C*H_3)$_3$), 26.48 (C(*C*H_3)$_3$), 44.96 (CO*C*), 45.10 (CO*C*), 51.39 (O*C*H_3), 51.54 (O*C*H_3), 56.38 (Ph*C*), 56.62 (Ph*C*), 126.34, 126.49, 127.56, 128.05, 128.26, 128.48, 129.87 (2C), 141.26, 142.10, 146.92, 148.15, 175.59 (*C*═O), 175.94 (*C*═O). Anal. Calcd for $C_{19}H_{30}O_2Si$: C, 71.64; H, 9.49. Found: C, 71.38; H, 9.71. The isomer **41bb** was characterized on the basis of some assigned signals in ^1H NMR spectrum. For **41bb** ^1H NMR (300 MHz, $CDCl_3$): δ 0.03 (s, 3H, Si−CH_3), 0.04 (s, 3H, Si−CH_3), 0.05 (s, 3H, SiCH_3), 0.06 (s, 3H, SiCH_3), 0.91 (s, 9H, SiC(CH_3)$_3$), 0.92 (s, 9H, SiC(CH_3)$_3$), 0.93 (d, J = 7.2 Hz, 3H, CH_3), 1.23 (d, J = 6.9 Hz, 3H, CH_3), 3.63 (s, 3H, OCH_3), 3.64 (s, 3H, OCH_3), 7.15−7.34 (m, 10H, Ph).

Properties of methyl 5-(dimethylphenylsilyl)-2,2,4-trimethyl-3-phenyl-4(*E*)-hexenoate, 40ac: colorless liquid, bp 190−195 °C/0.1 Torr. IR (neat): 1728 (C═O), 1249 (Si−CH_3) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 0.46 (s, 3H, Si−CH_3), 0.51 (s, 3H, Si−CH_3), 1.19 (s, 3H, CH_3), 1.31 (s, 3H, CH_3), 1.70 (s, 3H, CH_3), 1.79 (s, 3H, CH_3), 3.57 (s, 3H, OCH_3), 4.42 (s, 1H, PhC*H*), 7.10−7.34 (m, 8H, Ph), 7.47−7.51 (m, 2H, Ph). ^{13}C NMR (125 MHz, $CDCl_3$): δ −0.58 (SiCH_3), 0.42 (SiCH_3), 19.32 (*C*H_3, 2C), 23.11 (*C*H_3), 26.99 (*C*H_3), 45.80 (CO*C*), 51.77 (O*C*H_3), 57.72 (Ph*C*), 125.76, 127.61, 127.81, 128.57, 128.59, 133.00, 133.92, 139.91, 141.37, 147.25, 178.80 (*C*═O). Anal. Calcd for $C_{24}H_{32}O_2Si$: C, 75.68; H, 8.47. Found: C, 75.68; H, 8.39.

Properties of methyl 5-(dimethylphenylsilyl)-2,4-dimethyl-3-phenyl-4(*E*)-hexenoate, 40bc, and methyl 3-(dimethylphenylsilyl)-2,4-dimethyl-5-phenyl-4(*E*)-hexenoate, 41bc (as a mixture of regioisomers (97:3) each of which consists of two diastereoisomers): colorless liquid, bp 175−180 °C/0.4 Torr. For **40bc** one isomer: IR (neat): 1736 (C═O), 1252 (Si-CH_3) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 0.56 (s, 3H, Si−CH_3), 0.62 (s, 3H, Si−CH_3), 1.15 (d, J = 7.1 Hz, 3H, CH_3), 1.50 (s, 3H, CH_3), 1.65 (s, 3H, CH_3), 3.15 (dq, J = 11.0 and 7.1 Hz, 1H, CH_3C*H*), 3.50 (s, 3H, OCH_3), 4.29 (d, J = 11.0 Hz, 1H, PhC*H*), 7.12−7.23 (m, 5H, Ph), 7.34−7.36 (m, 3H, Ph), 7.54−7.59 (m, 2H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$): δ 0.58 (Si*C*H_3), 0.91 (Si*C*H_3), 14.71 (*C*H_3), 17.03 (*C*H_3), 18.98 (*C*H_3), 40.83 (CO*C*), 51.59 (O*C*H_3), 53.10 (Ph*C*), 125.98, 127.49, 127.69, 127.93, 128.61, 130.12, 133.90, 139.78, 141.64, 147.05, 176.38 (*C*═O). The other isomer: IR (neat): 1737 (C═O), 1247 (Si−CH_3) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 0.55 (s, 3H, Si−CH_3), 0.65 (s, 3H, Si−CH_3), 1.07 (d, J = 6.6 Hz, 3H, CH_3), 1.53 (s, 3H, CH_3), 1.62 (s, 3H, CH_3), 3.28 (dq, J = 11.3 and 6.6 Hz, 1H, CH_3C*H*), 3.64 (s, 3H, OCH_3), 4.14 (d, J = 11.3 Hz, 1H, PhC*H*), 7.18−7.37 (m, 8H, Ph), 7.55−7.62 (m, 2H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$): δ −0.38 (Si*C*H_3), 1.32 (Si*C*H_3), 15.08 (*C*H_3), 15.80 (*C*H_3), 18.87 (*C*H_3), 41.46 (CO*C*), 51.37 (O*C*H_3), 55.07 (Ph*C*), 126.13, 127.57, 128.13, 128.16, 128.54, 134.08, 134.69, 139.99, 140.51, 148.31, 175.96 (*C*═O). Anal. Calcd for $C_{23}H_{30}O_2Si$: C, 75.36; H, 8.25. Found: C, 75.15; H, 8.36. The isomer **41bc** was characterized on the basis of some assigned signals in ^1H NMR spectrum. For **41bc** ^1H NMR (300 MHz, $CDCl_3$): δ 0.32 (s, 3H, Si−CH_3), 0.35 (s, 3H, Si−CH_3), 0.58 (s, 3H, SiCH_3), 0.64 (s, 3H, SiCH_3), 1.13 (d, J = 6.9 Hz, 3H, CH_3), 1.16 (d, J = 6.6 Hz, 3H, CH_3), 1.51 (s, 3H, CH_3), 1.57 (s, 3H, CH_3), 1.67 (s, 3H, CH_3), 1.98 (s, 3H, CH_3), 3.50 (s, 3H, OCH_3), 3.67 (s, 3H, OCH_3), 7.15−7.34 (m, 10H, Ph).

Properties of methyl 2,2,4-trimethyl-3-phenyl-4(*Z*)-hexanoate, 42: colorless liquid. IR (neat): 1731 (C═O) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 1.16 (s, 3H, CH_3), 1.19 (s, 3H, CH_3), 1.46 (s, 3H, CH_3), 1.61 (d, J = 6.5 Hz, 3H, CH_3), 3.62 (s, 3H, OCH_3), 3.65 (s, 1H, PhC*H*), 5.52 (q, J = 6.5 Hz, 1H, C*H*═C), 7.21−7.28 (m, 5H, Ph). ^{13}C NMR (125 MHz, $CDCl_3$): δ 13.68 (*C*H_3), 17.29 (*C*H_3), 22.21 (*C*H_3), 27.26 (*C*H_3), 45.59 (CO*C*), 51.71 (O*C*H_3), 60.78 (Ph*C*), 120.24 (C═C), 126.41 (Ph), 127.65 (Ph), 130.33 (Ph), 135.99 (Ph or C═C), 139.98 (C═C or Ph), 178.69 (*C*═O). Anal. Calcd for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 77.97; H, 9.06.

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