Selected Paper

Rhodium-Catalyzed Acylation of Vinylsilanes with Acid Anhydrides

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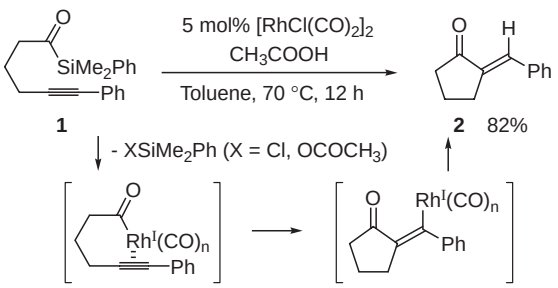
A catalytic acylation of vinylsilane with acid anhydride is accomplished by the use of $[RhCl(CO)_2]_2$, in which the transmetalation between vinylsilane and rhodium(I) carbonyl complex plays a key role. The application of this acylation reaction to (1-acyloxyvinyl)silanes provides synthetic methods for α-acyloxy enones, α-diketones, and their derivatives.

The acylation of vinylsilanes proceeds in a regioselective manner to afford α,β-unsaturated ketones and is generally performed by treatment with acid halides or acid anhydrides in the presence of Lewis acids.[1] Because more than a stoichiometric amount of strong Lewis acids such as $AlCl_3$ is indispensable in this type of acylation, the development of a catalytic process has been desired from a synthetic point of view.[2] Recently, we developed a catalytic acyclation of vinylsilanes with acid anhydrides by the use of a rhodium complex.[3] This paper gives a full account of the catalytic acylation reaction.

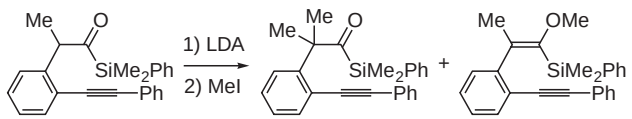
Results and Discussion

Rhodium-Catalyzed Acylation of Vinylsilanes with Acid Anhydrides. We studied the transition metal-catalyzed intramolecular acylation of acetylenic acylsilanes where the key step is the transmetalation between a rhodium(I) carbonyl complex, $[RhCl(CO)_2]_2$, and acetylenic acylsilane **1**. The reaction proceeds via generation of acylrhodium intermediates, which in turn add to the intramolecular acetylenic moiety to give alkylidenecyclopentanones **2** (Scheme 1).[4]

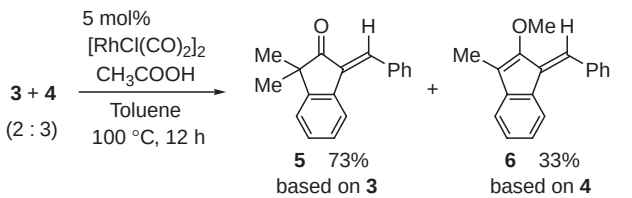
We wondered whether the transmetalation proceeds in the keto form (acylsilane) or the enol form ((1-hydroxyvinyl)-silane), because α-proton of acylsilane is acidic, as the pK_a of acetyltrimethylsilane is reported to be 16.4.[5] α,α-Dimethylacylsilane **3** and (1-methoxyvinyl)silane **4**, which correspond to the fixed keto and enol forms of acylsilane **1**, respectively, were prepared and the mixture was submitted to the intramolecular acylation reaction (Eq. 1 and 2). As both of the expected cyclization products **5** and **6** were obtained from these two substrates, the transmetalation may occur from either keto or enol form of acylsilanes.



Scheme 1. Rhodium-catalyzed acylation of alkyne with acylsilane **1**.



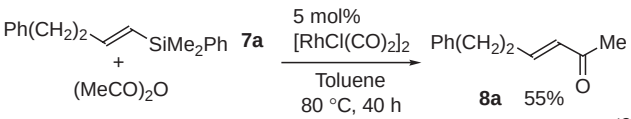
(1)



(2)

Since it was found that $[RhCl(CO)_2]_2$ had the ability to activate not only the sp^2 C–Si bond of acylsilane **3** but also that of (1-alkoxyvinyl)silane **4**, we tried to incorporate this transmetalation process to develop a catalytic acylation of vinylsilanes with acid anhydrides.

Firstly, 1-alkenylsilane **7a** was treated with 3 molar amounts of acetic anhydride and 5 mol% of $[RhCl(CO)_2]_2$ in toluene, vinylsilane **7a** was consumed gradually at 80 °C and it was found the acylation product, α,β-unsaturated ketone **8a**, was obtained in 55% yield (Eq. 3).



(3)

To obtain insight into the initial step of this catalytic acylation, vinylsilane **7a** and acetic anhydride were allowed to react independently with a stoichiometric amount of $[RhCl(CO)_2]_2$ and each of these reactions was monitored by ^1H NMR. When vinylsilane **7a** was treated with a stoichiometric amount of $[RhCl(CO)_2]_2$ in toluene at 80 °C, chloro(dimethyl)phenylsilane, dimethyl(phenyl)silanol, and 1,1,3,3-tetramethyl-1,3-diphenyldisiloxane were detected in 38%, 9%, and 33% yields, respectively (Eq. 4). To the contrary, no reaction was observed in the reaction of acetic anhydride and a stoichiometric amount of $[RhCl(CO)_2]_2$ at 80 °C for 5 h (Eq. 5).

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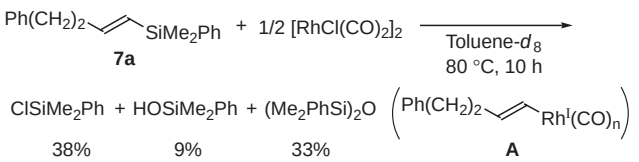
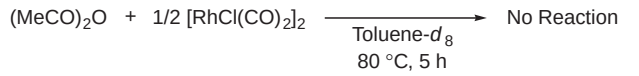


(4)



(5)

These facts indicate that vinylrhodium intermediate **A** is generated by the transmetalation between $[RhCl(CO)_2]_2$ and vinylsilane **7a** at the initial stage. As depicted in Scheme 2, the oxidative addition of acetic anhydride to the vinylrhodium **A** and the reductive elimination occur successively to give α,β-unsaturated ketone **8a**.[6]

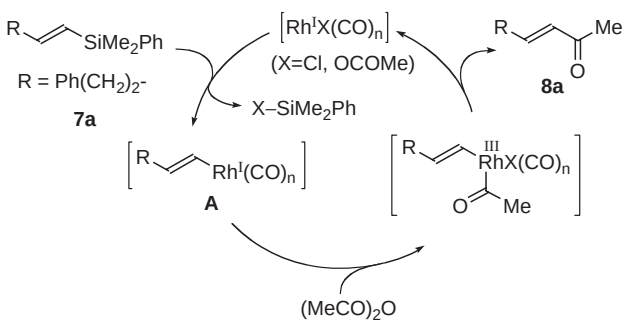
For the transmetalation between transition metal complexes and vinylsilanes, the use of fluoride ion or the introduction of alkoxy or hydroxy groups on the silyl group is essential to activate vinylsilanes, as reported in the transition metal-catalyzed arylation of vinylsilanes.[7–9] It is quite noteworthy that the present metal exchange between $[RhCl(CO)_2]_2$ and non-activated vinylsilane **7a** proceeds without any promoter, although the details of the transmetalation step are not yet clarified.

This rhodium-catalyzed acylation reaction was screened under various reaction conditions concerning solvents, temperature, and acid anhydrides (Table 1).

At a higher reaction temperature in 1,4-dioxane, the acylation proceeded faster and α,β-unsaturated ketone **8a** was obtained in 84% yield (Entries 2 and 3). Primary, secondary, and tertiary acid anhydrides could be employed for the acylation (Entries 4, 5, and 6). In the reaction with benzoic anhydride, the desired phenyl vinyl ketone **8e** was obtained in 74% yield with 5% yield of decarbonylation product **9** (Entry 7).[10]

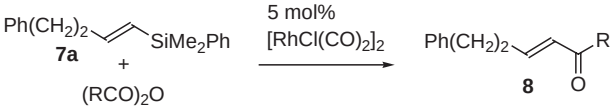
Simple vinylsilanes which have methyl- and phenyl-substituted silyl groups (Me_3Si, Me_2PhSi, $MePh_2Si$) can be employed in the rhodium-catalyzed acylation. The bulkiness of the silyl group, however, influenced the reaction rate, as shown in Table 2, and triphenyl(vinyl)silane **7d** was acylated quite slowly (Entry 4).

Acylations of several dimethyl(phenyl)vinylsilanes **7a**, **f–i** were examined, as described in Table 3. As well as (2-alkyl-



Scheme 2. Proposed mechanism of the rhodium(I)-catalyzed acylation of vinylsilane **7a**.

Table 1. Rhodium(I)-Catalyzed Acylation of Dimethyl(phenyl)vinylsilanes **7a**[a]



Entry	Solvent	$\frac{(RCO)_2O}{R}$	Temp/°C	Time/h	Yield/%	
1	Toluene	Me	80	40	**8a**	55
2	Toluene	Me	100	18	**8a**	87
3	1,4-Dioxane	Me	90	7	**8a**	84
4	1,4-Dioxane	Et	90	18	**8b**	67
5	1,4-Dioxane	*i*-Pr	90	18	**8c**	72
6	1,4-Dioxane	*t*-Bu	90	6	**8d**	78
7	1,4-Dioxane	Ph	90	18	**8e**	74[b]

a) Molar ratio $[RhCl(CO)_2]_2$:vinylsilane **7a**:$(RCO)_2O$ = 0.05:1:3. b) Decarbonylation product **9** was obtained in 5% yield.

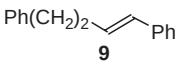
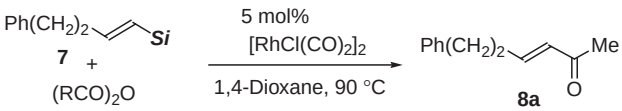


Table 2. Rhodium(I)-Catalyzed Acylation of Various Vinylsilanes **7**[a]



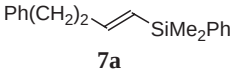
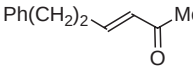
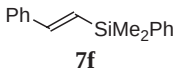
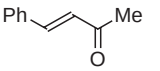
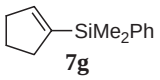
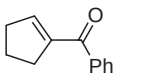
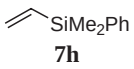
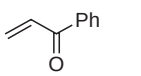
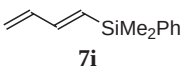
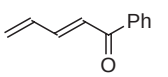
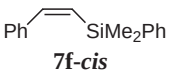
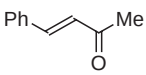
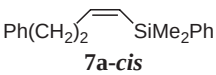
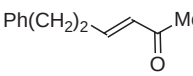
Entry	*Si*		Time/h	Yield/%	(Recovery of vinylsilane)
1	$SiMe_3$	(**7b**)	18	82	
2	$SiMe_2Ph$	(**7a**)	7	84	
3	$SiMePh_2$	(**7c**)	30	71	(8)
4	$SiPh_3$	(**7d**)	40	21	(64)

a) Molar ratio $[RhCl(CO)_2]_2$:vinylsilane **7**:$(RCO)_2O$ = 0.05:1:3.

vinyl)silane **7a**, (2-arylvinyl)silane **7f** and cyclic vinylsilane **7g** reacted smoothly to afford **8f** and **8g** (Entries 2 and 3). In the reaction of unsubstituted vinylsilane **7h** and 1,3-butadienylsilane **7i**, the yields decreased due to polymerization caused by the nucleophilic attack of vinylrhodium intermediates to the produced α,β-unsaturated ketones,[9b,c,11] as exemplified by the formation of 1-phenylpent-4-en-1-one **10** (Entries 4 and 5). The acylation of *cis*-vinylsilane proceeded slowly compared to its *trans*-isomer, shown in Entries 6 and 7. In the case of (2-arylvinyl)silane **7f-*cis***, benzylideneacetone **8f** was obtained in 53% yield, whereas the acylation of (2-alkylvinyl)-silane **7a-*cis*** afforded α,β-enone **8a** and other acylation products: **11-*trans***, **11-*cis***, and **12** in 60% total yield (Entries 6 and 7).

Synthesis of α-Diketones from (1-Acyloxyvinyl)silanes. α-Diketones are versatile synthetic intermediates, particularly in the synthesis of various heterocyclic compounds.[12] Although many methods have been developed for the synthesis of α-diketones through (i) oxidation,[13] (ii) use of masked acyl anion synthons,[14] and (iii) other approaches,[15] it is not always easy to prepare unsymmetrical α-diketones in a simple manner. We expected this rhodium-catalyzed acylation might pro-

Table 3. Synthesis of α,β-Unsaturated Ketones **8** by Rhodium(I)-Catalyzed Acylation of Vinylsilanes **7**[a)]

Entry	Vinylsilane	$(RCO)_2O$ / R	Time/h	Product (Yield/%)[b)]
1	 **7a**	Me	7	 **8a** (84)
2	 **7f**	Me	24	 **8f** (78)
3	 **7g**	Ph	24	 **8g** (68)
4	 **7h**	Ph	18	 **8h** (39)[c)]
5	 **7i**	Ph	30	 **8i** (43)
6	 **7f-*cis***	Me	24	 **8f** (53)[d)]
7	 **7a-*cis***	Me	24	 **8a** (18)[e)]

a) Molar ratio $[RhCl(CO)_2]_2$:vinylsilane **7**:$(RCO)_2O$ = 0.05:1:3. The reaction was conducted in 1,4-dioxane at 90 °C. b) Isolated yield. c) **10** was obtained in 2% yield. d) **7f-*cis*** was recovered in 15% yield. e) **11-*trans***, **11-*cis***, and **12** were obtained in 26%, 5%, and 11% yields.

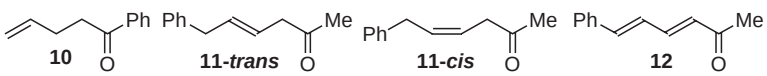
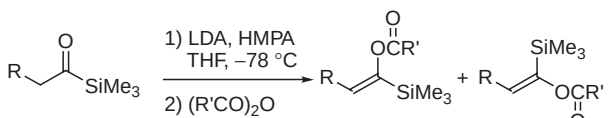


Table 4. Synthesis of (1-Acyloxyvinyl)silanes **14–16** from Acylsilane **13**



13a (R = $Ph(CH_2)_2$)
13b (R = Ph)

14, **16** **15**

Entry	R	R′	Products/%			
1[a)]	$Ph(CH_2)_2$	Me	**14a**	61	**15**	22
2	$Ph(CH_2)_2$	Me	**14a**	86		—
3	$Ph(CH_2)_2$	Ph	**14b**	86		—
4	Ph	Ph	**16**	87		—

a) The reaction was carried out without HMPA.

vide a practical synthetic method for unsymmetrical α-diketones from (1-acyloxyvinyl)silane, because obtained α-acyloxy enones could be converted to α-diketones by hydrolysis of the vinyl ester part.[16]

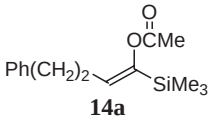
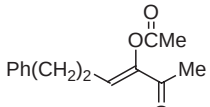
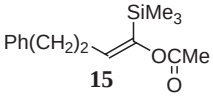
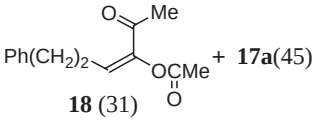
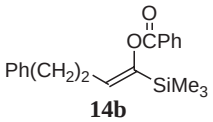
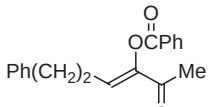
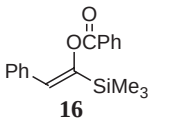
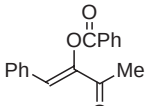
(1-Acyloxyvinyl)silanes **14–16** were prepared by *O*-acylation of lithium enolate of the corresponding acylsilanes **13** (Table 4).[17] *O*-Acetylation with acylsilane **13a** gave a mixture of stereoisomers of (1-acyloxyvinyl)silanes **14a** and **15** (Entry 1). By the addition of HMPA (Entries 2, 3, and 4), the stereoselectivity is improved to give ((*E*)-1-acyloxyvinyl)silanes **14a**, **14b**, and **16** excusively.[18]

When (1-acetoxyvinyl)silane **14a** was treated with acetic anhydride and 5 mol% of $[RhCl(CO)_2]_2$ in toluene at 80 °C, the reaction proceeded more rapidly as compared to (non-acetoxyvinyl)silane **7b**, to afford α-acetoxy enone **17a** in 94% yield (Table 5, Entry 1).[19] In the reaction of ((*Z*)-1-acetoxyvinyl)silane **15**, a mixture of α-acetoxy enones **17a** and the stereoisomer **18** was obtained in 76% total yield (Entry 2). (1-Benzoyloxyvinyl)silanes **14b** and **16** reacted smoothly as well as the α-acetoxy derivatives, giving α-benzoyloxy enones **17b** and **19** in excellent yields (Entries 3 and 4).[20]

The acylation of (1-benzoyloxyvinyl)silane **14b** with various acid anhydrides was screened as summarized in Table 6. Both primary and secondary carboxylic acid anhydrides gave acylation products **17b–d** in excellent yields (Entries 1–4), whereas the acylation with pivalic anhydride gave only 7% yield of **17e** (Entry 5). In the reaction with benzoic anhydride, benzoylation product **17f** was obtained in 66% yield with 24% yield of phenylated product **20** (Entry 6). Trifluoroacetylation also proceeded and the corresponding diketone **21** was obtained as the hydrate form in 79% yield after the purification by silica gel column chromatography (Entry 7).

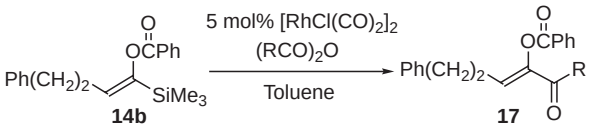
Thus obtained α-benzoyloxy ketones were supposed to be hydrolyzed under acidic conditions to give α-diketones, whereas no reaction occurred when α-benzoyloxy ketone **17b** was refluxed for 30 min in 3 M HCl (1 M = 1 mol dm^{-3}) according to the reported procedure for the conversion of enol esters to ketones.[16] It was found that α-benzoyloxy ketones **17b** and **19** could be converted in good yield to α,α-dialkoxy ketones **22a**, **b** and **23** by treatment with K_2CO_3 in methanol

Table 5. Rhodium(I)-Catalyzed Acetylation of (1-Acyloxyvinyl)silanes **14–16** with Acetic Anhydride[a)]

Entry	Vinylsilane	Time/h	Product (Yield/%)[b)]
1	 **14a**	1.5	 **17a** (94)
2[c)]	 **15**	5	 **18** (31) + **17a**(45)
3	 **14b**	3	 **17b** (99)
4	 **16**	6	 **19** (93)

a) Molar ratio $[RhCl(CO)_2]_2$:vinylsilane:$(MeCO)_2O$ = 0.05:1:3. The reaction was conducted in toluene at 80 °C. b) Isolated yield. c) The reaction was conducted at 100 °C.

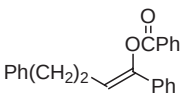
Table 6. Rh(I)-Catalyzed Acylation of (1-Benzoyloxyvinyl)silane **14b** with Acid Anhydrides[a)]

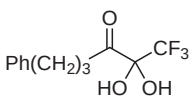


14b **17**

Entry	R	Temp/°C	Time/h	Yield/%	
1	Me	80	3	**17b**	99
2	Me	80	12	**17b**	87[b)]
3	Et	80	2	**17c**	99
4	*i*-Pr	80	3	**17d**	97
5	*t*-Bu	80	24	**17e**	7[c)]
6	Ph	80	5	**17f**	66[d)]
7	CF_3	50	4	**17g**	(79)[e)]

a) Molar ratio $[RhCl(CO)_2]_2$:vinylsilane **14b**:$(RCO)_2O$ = 0.05:1:3. b) 1.2 molar amounts of $(MeCO)_2O$ was used. c) **14b** was recovered in 8% yield. d) Decarbonylation product **20** was obtained in 24% yield. e) Hydrate **21** was obtained in 79% yield.

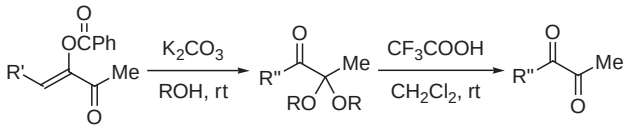

20

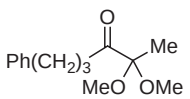
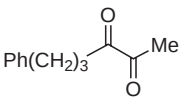
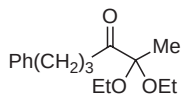
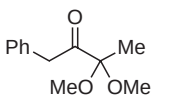
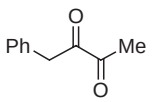

21

(Table 7, Entries 1 and 3) or ethanol (Entry 2).[21,22] These α,α-dialkoxy were readily transformed to α-diketones **24** and **25** by dissolving in a 1:10 mixture of trifluoroacetic acid–dichloromethane (Table 7).[22]

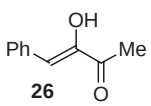
Thus, the present rhodium-catalyzed acylation of (1-acyloxyvinyl)silanes provided a preparative method of unsymmetrical α-diketones and also of α-acyloxy enones and α,α-dialkoxy ketones, which are regarded as regioselectively-masked α-diketones at each of the carbonyl groups.

Table 7. Conversion of α-Benzoyloxy Enones to α,α-Dialkoxy Ketones and α-Diketones.



Entry	Enone	ROH (Time)	α,α-Dialkoxy ketone	α-Diketone
1	**17b**	MeOH (5 min)	 **22a** 92%	 **24** quant
2	**17b**	EtOH (30 min)	 **22b** 95%	**24** 80%
3	**19**	MeOH (5 min)	 **23** 99%	 **25** 95%[a)]

a) After Florisil® column chromatography, the mixture of **25** and **26** were obtained in 1:1 ratio.


26

Experimental

General. ^1H NMR spectra were recorded with a Bruker Avance 500 (500 MHz) and a Bruker DRX 500 (500 MHz) spectrometer in $CDCl_3$ [using $CHCl_3$ (for ^1H, $\delta = 7.24$) as internal

standard] or toluene-d_8 [using $C_6D_5CHD_2$ (for ^1H, $\delta = 2.09$) as internal standard]. ^{13}C NMR spectra were recorded with a Bruker Avance 500 (125 MHz) and a Bruker DRX 500 (125 MHz) spectrometer in $CDCl_3$ [using $CDCl_3$ (for ^{13}C, $\delta = 77.0$) as internal standard]. IR spectra were recorded on a Horiba FT 300-S by ATR method. High resolution mass spectra were taken with a JEOL MS-700M mass spectrometer. Melting points (mp) were uncorrected. Elemental analyses were carried out at The Elemental Analysis Laboratory, Department of Chemistry, Faculty of Science, The University of Tokyo. Silica Gel 60 (spherical) (Kanto Chemical) was used for column chromatography, and Wakogel® B-5F (Wako Pure Chemical Industries) was used for preparative thin-layer chromatography. Toluene and 1,4-dioxane were freshly distilled from lithium aluminium hydride before use. Tetrahydrofuran (THF) was purchased in anhydrous form from Kanto Chemical Co., Inc. Dichloromethane was distilled from phosphorus pentoxide and calcium hydride, successively, and dried over MS 4A. Toluene-d_8 (ACROS) and chloroform-*d* (Nippon Sanso) were used as received. Acetic anhydride, propionic anhydride, and trifluoroacetic anhydride were distilled from phosphorus pentoxide before use. Benzoic anhydride was recrystallized from diethyl ether. Acetic acid was distilled from $KMnO_4$, and stored under argon. Hexamethylphosphoric triamide was distilled from calcium hydride, dried over MS 4A, and stored under argon. Tetracarbonyldichlorodirhodium ($[RhCl(CO)_2]_2$) was prepared according to the literature procedure.[23]

Preparation of Acylsilane 3 and (1-Methoxyvinyl)silane 4. To a solution of LDA (0.339 mmol) in THF (2 mL) was added 1-dimethyl(phenyl)silyl-2-(2-phenylethynylphenyl)propan-1-one (104 mg, 0.282 mmol) in THF (1 mL) at −78 °C, and the solution was stirred for 30 min at this temperature and at 0 °C for an additional 1 h. After addition of MeI (200 mg, 1.41 mmol), the solution was stirred at room temperature. Then the solution was quenched with saturated NH_4Cl solution and the organic layer was extracted with ethyl acetate. The combined organic extracts were washed with water and dried over magnesium sulfate. After evaporation of the solvent, the crude products were purified by thin-layer chromatography (silica gel, hexane:diethyl ether = 15:1) to afford a 2:3 mixture of 1-dimethyl(phenyl)silyl-2-methyl-2-(2-phenylethynylphenyl)propan-1-one (**3**) and (*Z*)-1-dimethyl(phenyl)silyl-1-methoxy-2-(2-phenylethynylphenyl)prop-1-ene (**4**) (88.4 mg, 0.231 mmol), in 82% total yield.

1-Dimethyl(phenyl)silyl-2-(2-phenylethynylphenyl)propan-1-one: Colorless oil; IR (ZnSe) 1637, 1493, 1248, 1111, 816, 756, 690 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.24 (3H, s), 0.33 (3H, s), 1.24 (3H, d, $J = 6.8$ Hz), 4.56 (1H, q, $J = 6.8$ Hz), 6.81–6.82 (1H, m), 7.13–7.22 (4H, m), 7.27–7.30 (1H, m), 7.32–7.36 (5H, m), 7.45–7.48 (2H, m), 7.49–7.51 (1H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ −4.3, −4.1, 15.9, 55.7, 87.7, 93.5, 123.1, 123.7, 126.9, 127.8, 128.4, 128.4, 128.4, 128.6, 129.5, 131.5, 132.7, 133.9, 134.7, 141.0, 243.2; Anal. Found: C, 81.33; H, 6.70%. Calcd for $C_{25}H_{24}OSi$: C, 81.47; H, 6.56%.

1-Dimethyl(phenyl)silyl-2-methyl-2-(2-phenylethynylphenyl)propan-1-one (3) and (*Z*)-1-Dimethyl(phenyl)silyl-1-methoxy-2-(2-phenylethynylphenyl)prop-1-ene (4): These compounds were obtained as a mixture (**3**:**4** = 2:3). The stereo configuration of the alkene part of **4** is not determined. Colorless oil; IR (ZnSe) 1635, 1493, 1246, 1111, 818, 754, 688 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) **3** δ 0.13 (6H, s), 1.37 (6H, s), 7.13–7.51 (14H, m); **4** δ 0.05 (6H, brs), 2.09 (3H, s), 3.46 (3H, s), 7.01–7.03 (1H, m), 7.13–7.51 (13H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ −3.1, −2.3, −1.9, 18.4, 23.5, 57.3, 59.4, 88.5, 89.0, 92.4, 94.4, 122.9, 123.0, 123.4, 126.4, 127.0, 127.1, 127.4, 127.5, 127.8, 128.1, 128.2, 128.3, 128.3, 128.6, 128.7, 129.0, 129.7, 130.9, 131.4, 131.4, 131.9, 133.7, 133.8, 133.8, 136.0, 138.6, 141.1, 144.0, 145.2, 158.0, 242.7; HRMS (FAB^+) Found: m/z 383.1808. Calcd for $C_{26}H_{27}OSi$: $(M + H)^+$, 383.1831.

Rhodium-Catalyzed Reaction with Acylsilane 3 and (1-Methoxyvinyl)silane 4. To a toluene solution (2.3 mL) of a 2:3 mixture of 1-dimethyl(phenyl)silyl-2-methyl-2-(2-phenylethynylphenyl)propan-1-one (**3**) and (*Z*)-1-dimethyl(phenyl)silyl-1-methoxy-2-(2-phenylethynylphenyl)prop-1-ene (**4**) (88.4 mg, 0.231 mmol) was added $[RhCl(CO)_2]_2$ (4.8 mg, 0.012 mmol) and acetic acid (139 mg, 2.31 mmol) and the mixture was heated at 100 °C (the oil bath temperature) for 12 h. After evaporation of the solvent, the crude products were purified by thin-layer chromatography (silica gel, hexane:diethyl ether = 8:1) to afford (*E*)-3-benzylidene-1,1-dimethylindan-2-one (**5**) (15.4 mg, 0.062 mmol) in 73% yield based on **3** and (*E*)-1-benzylidene-2-methoxy-3-methyl-1*H*-indene (**6**) (12.0 mg, 0.048 mmol) in 33% yield based on **4**.

(*E*)-3-Benzylidene-1,1-dimethylindan-2-one (5): Yellow oil; IR (ZnSe) 1726, 1622, 1092, 760, 696 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.38 (6H, s), 7.09–7.45 (6H, m), 7.55 (1H, s), 7.59–7.61 (2H, m), 7.69 (1 H, d, $J = 7.9$ Hz); HRMS (FAB^+) Found: m/z 249.1299. Calcd for $C_{18}H_{17}O$: $(M + H)^+$, 249.1279.

(*E*)-1-Benzylidene-2-methoxy-3-methyl-1*H*-indene (6): Yellow oil; IR (ZnSe) 1622, 1456, 1325, 1086, 754, 698 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.14 (3H, s), 3.95 (3H, s), 6.90 (1H, dd, $J = 7.3$, 7.3 Hz), 7.08 (1H, d, $J = 7.3$ Hz), 7.18 (1H, dd, $J = 7.3$, 7.3 Hz), 7.23 (1H, s), 7.36 (1H, d, $J = 7.3$ Hz), 7.40–7.43 (3H, m), 7.55–7.56 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 9.1, 61.6, 117.7, 119.5, 122.3, 124.1, 128.0, 128.0, 128.1, 128.3, 129.4, 130.0, 134.6, 136.5, 143.7, 155.1; HRMS (FAB^+) Found: m/z 249.1277. Calcd for $C_{18}H_{17}O$: $(M + H)^+$, 249.1279.

NMR Experiment in the Reaction of Vinylsilane 7a and $[RhCl(CO)_2]_2$. Toluene-d_8 solution (0.7 mL) of $[RhCl(CO)_2]_2$ (10.0 mg, 0.026 mmol), (*E*)-1-dimethyl(phenyl)silyl-4-phenylbut-1-ene (**7a**) (13.6 mg, 0.051 mmol), and mesitylene (5.3 mg, 0.044 mmol) in an NMR tube was heated at 80 °C. The reaction was followed by taking ^1H NMR measurements every one hour. After 10 h, the formation of chlorodimethyl(phenyl)silane ($\delta = 0.43$), dimethyl(phenyl)silanol ($\delta = 0.23$), and 1,1,3,3-tetramethyl-1,3-diphenyldisiloxane ($\delta = 0.31$) was detected in 38%, 9%, and 33% yields, respectively. Chemical shift values of products were in good agreement with those of authentic samples,[24] and their yields were estimated based on mesitylene as internal standard.

Typical Procedure for Preparation of Vinylsilane 7.[25] To a stirred solution of (*E*)-1-iodo-4-phenylbut-1-ene (1.53 g, 5.93 mmol) in THF/Et_2O/pentane (14.4 mL, 4:1:1), cooled to −100 °C, was added *t*-butyllithium (1.5 M in pentane, 8.0 mL, 11.9 mmol) over 10 min. The solution was stirred for 2 h at −100 °C, and then allowed to warm to −78 °C. Chlorodimethyl(phenyl)silane (1.22 g, 7.12 mmol) was added, and stirring was continued for 5 min at −78 °C, and then for 45 min at room temperature. The reaction mixture was poured on to diethyl ether and brine, and the aqueous layer was extracted with diethyl ether. The combined organic extracts were washed with brine and dried over magnesium sulfate. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (hexane) to afford (*E*)-1-dimethyl(phenyl)silyl-4-phenylbut-1-ene (**7a**) (1.35 g, 5.05 mmol) in 85% yield.

(*E*)-1-Dimethyl(phenyl)silyl-4-phenylbut-1-ene (7a): Color-

less oil; IR (ZnSe) 1616, 1427, 1248, 1113, 841, 822, 698 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.29 (6H, s), 2.42–2.47 (2H, m), 2.70–2.73 (2H, m), 5.76 (1H, dt, $J = 18.5$, 1.5 Hz), 6.14 (1H, dt, $J = 18.5$, 6.2 Hz), 7.15–7.18 (3H, m), 7.24–7.27 (2H, m), 7.31–7.35 (3H, m), 7.44–7.48 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ −2.5, 35.1, 38.5, 125.8, 127.7, 128.2, 128.3, 128.5, 128.8, 133.8, 139.1, 141.8, 148.1; HRMS (FAB^+) Found: m/z 267.1589. Calcd for $C_{18}H_{23}Si$: $(M + H)^+$, 267.1569.

(*E*)-4-Phenyl-1-trimethylsilylbut-1-ene (7b):[26] Colorless oil; IR (ZnSe) 2954, 1616, 1246, 864, 833, 696 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.02 (9H, s), 2.37–2.42 (2H, m), 2.68–2.71 (2H, m), 5.65 (1H, dt, $J = 18.6$, 1.4 Hz), 6.06 (1H, dt, $J = 18.6$, 6.1 Hz), 7.15–7.18 (3H, m), 7.23–7.27 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ −1.2, 35.2, 38.5, 125.7, 128.2, 128.4, 130.4, 142.0, 146.1.

(*E*)-1-Methyldiphenylsilyl-4-phenylbut-1-ene (7c):[27] Colorless oil; IR (ZnSe) 1614, 1427, 1250, 1111, 791, 733, 696 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.57 (3H, s), 2.50 (2H, ddt, $J = 1.4$, 6.2, 7.4 Hz), 2.74 (2H, t, $J = 7.4$ Hz), 5.94 (1H, dt, $J = 18.5$, 1.4 Hz), 6.16 (1H, dt, $J = 18.5$, 6.2 Hz), 7.15–7.20 (3H, m), 7.24–7.28 (2H, m), 7.31–7.38 (6H, m), 7.45–7.47 (4H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ −3.7, 34.9, 38.5, 125.8, 126.2, 127.7, 128.3, 128.5, 129.1, 134.8, 136.8, 141.6, 150.2; HRMS (EI^+) Found: m/z 328.1621. Calcd for $C_{23}H_{24}Si$: M^+, 328.1647.

(*E*)-4-Phenyl-1-triphenylsilylbut-1-ene (7d): Colorless oil; IR (ZnSe) 1616, 1427, 1109, 997, 737, 698 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.53–2.57 (2H, m), 2.73–2.77 (2H, m), 6.13–6.22 (2H, m), 7.14–7.20 (3H, m), 7.22–7.29 (3H, m), 7.31–7.35 (6H, m), 7.37–7.41 (3H, m), 7.45–7.47 (5H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 34.9, 38.6, 124.4, 125.8, 127.8, 128.3, 128.5, 129.4, 134.8, 135.9, 141.6, 152.2; Anal. Found: C, 85.97; H, 6.83%. Calcd for $C_{28}H_{26}Si$: C, 86.10; H, 6.71%.

(*E*)-1-Dimethyl(phenyl)silyl-2-phenylethylene (7f):[28] Colorless oil; IR (ZnSe) 1604, 1574, 1495, 1427, 1248, 1113, 989, 829, 698 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.42 (6H, s), 6.58 (1H, d, $J = 19.1$ Hz), 6.93 (1H, d, $J = 19.1$ Hz), 7.23–7.37 (6H, m), 7.43–7.44 (2H, m), 7.55–7.57 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ −2.5, 126.5, 127.0, 127.8, 128.1, 128.5, 129.0, 133.9, 138.1, 138.5, 145.3.

1-Dimethyl(phenyl)silylcyclopentene (7g):[29] Colorless oil; IR (ZnSe) 2954, 1250, 1111, 1057, 827, 795, 771, 698 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.34 (6H, s), 1.81 (2H, quint, $J =$ 7.5 Hz), 2.34–2.40 (4H, m), 6.04–6.06 (1H, m), 7.32–7.35 (3H, m), 7.48–7.51 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ −3.0, 24.1, 35.0, 36.0, 127.7, 128.8, 133.8, 138.8, 142.4, 142.6.

(*E*)-1-Dimethyl(phenyl)silylbuta-1,3-diene (7i):[30] Colorless oil; IR (ZnSe) 1572, 1427, 1248, 1113, 1011, 833, 812, 729, 698 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.36 (6H, s), 5.14 (1H, dd, $J = 1.6$, 10.0 Hz), 5.24 (1H, dd, $J = 1.6$, 17.0 Hz), 5.99 (1H, dd, $J = 0.6$, 18.3 Hz), 6.38 (1H, ddt, $J = 0.6$, 17.0, 10.0 Hz), 6.58 (1H, dd, $J = 10.0$, 18.3 Hz), 7.33–7.37 (3H, m), 7.50–7.54 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ −2.6, 118.2, 127.8, 129.0, 132.3, 133.8, 138.5, 139.7, 146.2.

(*Z*)-1-Dimethyl(phenyl)silyl-4-phenylbut-1-ene (7a-*cis*) was prepared according to the literature procedure;[31] Colorless oil; IR (ZnSe) 2956, 1604, 1248, 1111, 818, 698 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.33 (6H, s), 2.30–2.35 (2H, m), 2.54–2.57 (2H, m), 5.66 (1H, dt, $J = 14.0$, 1.2 Hz), 6.45 (1H, dt, $J = 14.0$, 7.4 Hz), 7.00–7.02 (2H, m), 7.13–7.16 (1H, m), 7.20–7.23 (2H, m), 7.31–7.34 (3H, m), 7.50–7.53 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ −0.9, 35.7, 35.7, 125.8, 127.5, 127.8, 128.2, 128.4, 128.8, 133.7, 139.6, 141.6, 149.6; HRMS (FAB^+) Found: m/z 267.1586. Calcd for $C_{18}H_{23}Si$: $(M + H)^+$, 267.1569.

(*Z*)-1-Dimethyl(phenyl)silyl-2-phenylethene (7f-*cis*)[28] was prepared according to the literature procedure;[31] Colorless oil; IR (ZnSe) 1248, 1111, 810, 777, 696 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.25 (6H, s), 5.99 (1H, d, $J = 15.1$ Hz), 7.17–7.21 (5H, m), 7.31–7.35 (3H, m), 7.48 (1H, d, $J = 15.1$ Hz), 7.52–7.55 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ −1.1, 127.5, 127.8, 127.8, 128.2, 128.8, 130.1, 133.7, 139.6, 139.6, 148.1.

Typical Procedure for Rhodium-Catalyzed Acylation of Vinylsilane 7. To a 1,4-dioxane solution (9.3 mL) of (*E*)-1-dimethyl(phenyl)silyl-4-phenylbut-1-ene (**7a**) (248 mg, 0.930 mmol) was added $[RhCl(CO)_2]_2$ (18.1 mg, 0.047 mmol) and acetic anhydride (284 mg, 2.79 mmol) and the mixture was heated at 90 °C (the oil bath temperature) for 7 h. After evaporation of the solvent, the crude products were purified by thin-layer chromatography (silica gel, hexane:ethyl acetate = 9:1) to afford (*E*)-6-phenylhex-3-en-2-one (**8a**) (136 mg, 0.781 mmol) in 84% yield.

(*E*)-6-Phenylhex-3-en-2-one (8a):[32] Colorless oil; IR (ZnSe) 1672, 1626, 1360, 1254, 976, 700 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.21 (3H, s), 2.53 (2H, ddt, $J = 1.5$, 6.8, 7.4 Hz), 2.77 (2H, t, $J = 7.4$ Hz), 6.47 (1H, dt, $J = 16.0$, 1.5 Hz), 6.80 (1H, dt, $J = 16.0$, 6.8 Hz), 7.16–7.21 (3H, m), 7.27–7.30 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 26.8, 34.1, 34.3, 126.2, 128.3, 128.5, 131.6, 140.6, 147.1, 198.6.

(*E*)-7-Phenylhept-4-en-3-one (8b): Colorless oil; IR (ZnSe) 1697, 1672, 1630, 1496, 1454, 1358, 1201, 976, 700 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.07 (3H, t, $J = 7.3$ Hz), 2.49–2.54 (4H, m), 2.77 (2H, t, $J = 7.4$ Hz), 6.10 (1H, dt, $J = 15.9$, 1.5 Hz), 6.83 (1H, dt, $J = 15.9$, 6.8 Hz), 7.15–7.20 (3H, m), 7.26–7.29 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 8.1, 33.2, 34.1, 34.4, 126.2, 128.3, 128.5, 130.5, 140.7, 145.6, 201.0; HRMS (FAB^+) Found: m/z 189.1282. Calcd for $C_{13}H_{17}O$: $(M + H)^+$, 189.1279.

(*E*)-2-Methyl-7-phenylhept-4-en-3-one (8c): Colorless oil; IR (ZnSe) 1695, 1670, 1626, 1456, 1383, 1207, 980, 698 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.07 (6H, d, $J = 6.9$ Hz), 2.50–2.54 (2H, m), 2.75–2.79 (2H, m), 2.77 (1H, sep, $J = 6.9$ Hz), 6.15 (1H, dt, $J = 15.7$, 1.5 Hz), 6.88 (1H, dt, $J = 15.7$, 6.9 Hz), 7.15–7.20 (3H, m), 7.25–7.29 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 18.4, 34.1, 34.5, 38.5, 126.1, 128.3, 128.4, 128.8, 140.8, 145.7, 203.9; HRMS (FAB^+) Found: m/z 203.1437. Calcd for $C_{14}H_{19}O$: $(M + H)^+$, 203.1436.

(*E*)-2,2-Dimethyl-7-phenylhept-4-en-3-one (8d): Colorless oil; IR (ZnSe) 1689, 1624, 1477, 1456, 1078, 698 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.10 (9H, s), 2.48–2.53 (2H, m), 2.74–2.77 (2H, m), 6.44 (1H, dt, $J = 15.3$, 7.0 Hz), 6.94 (1H, dt, $J = 15.3$, 1.5 Hz), 7.15–7.19 (3H, m), 7.25–7.28 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 26.1, 34.2, 34.5, 42.8, 124.8, 126.0, 128.3, 128.4, 140.9, 146.0, 204.2; HRMS (FAB^+) Found: m/z 217.1584. Calcd for $C_{15}H_{21}O$: $(M + H)^+$, 217.1592.

(*E*)-1,5-Diphenylpent-2-en-1-one (8e):[32] Colorless oil; IR (ZnSe) 1668, 1618, 1446, 1282, 980, 694 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.64 (2H, ddt, $J = 1.4$, 6.9, 7.4 Hz), 2.84 (2H, t, $J = 7.4$ Hz), 6.85 (1H, dt, $J = 15.4$, 1.4 Hz), 7.07 (1H, dt, $J = 15.4$, 6.9 Hz), 7.19–7.22 (3H, m), 7.27–7.31 (2H, m), 7.43–7.46 (2H, m), 7.52–7.56 (1H, m), 7.86–7.88 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 34.5, 34.5, 126.2, 126.5, 128.4, 128.4, 128.5, 128.5, 132.6, 137.8, 140.8, 148.4, 190.8.

(*E*)-1,4-Diphenylbut-1-ene (9):[32] Colorless oil; IR (ZnSe) 1496, 1456, 1448, 1030, 962, 739, 696 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.49–2.54 (2H, m), 2.76–2.79 (2H, m), 6.24

(1H, dt, $J = 15.8$, 6.8 Hz), 6.40 (1H, dt, $J = 15.8$, 1.3 Hz), 7.16–7.21 (4H, m), 7.25–7.32 (6H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 34.9, 35.9, 125.9, 126.0, 126.9, 128.3, 128.5, 128.5, 130.0, 130.4, 137.7, 141.8.

(*E*)-4-Phenylbut-3-en-2-one (Benzylideneacetone) (8f):[33] White crystals; mp 59–60 °C; IR (ZnSe) 1666, 1608, 1358, 1255, 974, 748, 690 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.37 (3H, s), 6.70 (1H, d, $J = 16.3$ Hz), 7.37–7.40 (3H, m), 7.50 (1H, d, $J = 16.3$ Hz), 7.52–7.55 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 27.3, 126.9, 128.1, 128.8, 130.3, 134.2, 143.2, 198.1.

Cyclopent-1-en-1-yl Phenyl Ketone (8g):[34] Colorless oil; IR (ZnSe) 1637, 1608, 1446, 1354, 1296, 1273, 708 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.96–2.02 (2H, m), 2.58–2.62 (2H, m), 2.70–2.75 (2H, m), 6.51–6.53 (1H, m), 7.39–7.42 (2H, m), 7.48–7.51 (1H, m), 7.70–7.72 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.8, 31.8, 34.3, 128.1, 128.8, 131.7, 139.0, 144.5, 146.9, 194.2.

1-Phenylprop-2-en-1-one (8h):[35] Colorless oil; IR (ZnSe) 1672, 1608, 1448, 1404, 1232, 993, 727 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.92 (1H, dd, $J = 1.6$, 10.6 Hz), 6.42 (1H, dd, $J = 1.6$, 17.1 Hz), 7.14 (1H, dd, $J = 10.6$, 17.1 Hz), 7.45–7.48 (2H, m), 7.54–7.58 (1H, m), 7.92–7.94 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 128.6, 128.7, 130.2, 132.4, 133.0, 137.3, 191.1.

1-Phenylpent-4-en-1-one (10):[36] Colorless oil; IR (ZnSe) 1730, 1685, 1448, 1325, 1273, 1128 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.46–2.51 (2H, m), 3.06 (2H, t, $J = 7.4$ Hz), 5.00 (1H, dd, $J = 1.5$, 10.3 Hz), 5.07 (1H, dd, $J = 1.5$, 17.1 Hz), 5.89 (1H, ddt, $J = 10.3$, 17.1, 6.5 Hz), 7.43–7.46 (2H, m), 7.53–7.58 (1H, m), 7.94–7.96 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.1, 37.7, 115.3, 128.0, 128.6, 133.0, 136.9, 137.3, 199.4.

(*E*)-1-Phenylpenta-2,4-dien-1-one (8i):[37] Yellow oil; IR (ZnSe) 1662, 1587, 1448, 1273, 1219, 1016, 688 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.57 (1H, dd, $J = 0.6$, 10.2 Hz), 5.70 (1H, dd, $J = 0.6$, 16.9 Hz), 6.58 (1H, ddt, $J = 0.5$, 16.9, 10.2 Hz), 6.98 (1H, dd, $J = 0.5$, 15.1 Hz), 7.38 (1H, dd, $J = 10.2$, 15.1 Hz), 7.44–7.47 (2H, m), 7.53–7.56 (1H, m), 7.92–7.94 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 126.2, 126.8, 128.4, 128.6, 132.7, 135.4, 137.9, 144.7, 190.7.

6-Phenylhex-4-en-2-one (11-*trans* and 11-*cis*):[38] **11-*trans***, **11-*cis***, and **8a** were obtained as a mixture (**11-*trans***:**11-*cis***:**8a** = 53:10:37). Their yields were estimated by allylic proton ratios of ^{1}H NMR. Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) **11-*trans*** δ 2.14 (3H, s), 3.14 (2H, d, $J = 6.7$ Hz), 3.38 (2H, d, $J = 6.5$ Hz), 5.59–5.73 (2H, m), 7.16–7.30 (5H, m); **11-*cis*** δ 2.17 (3H, s), 3.28 (2H, d, $J = 7.3$ Hz), 3.37–3.40 (2H, m), 5.77–5.83 (2H, m), 7.16–7.30 (5H, m).

(*E*,*E*)-6-Phenylhexa-3,5-dien-2-one (12):[39] Colorless oil; IR (ZnSe) 1653, 1614, 1587, 997, 881, 827, 690 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.30 (3H, s), 6.24 (1H, d, $J = 15.5$ Hz), 6.87 (1H, dd, $J = 10.4$, 15.6 Hz), 6.94 (1H, d, $J = 15.6$ Hz), 7.28 (1H, dd, $J = 10.4$, 15.5 Hz), 7.29–7.37 (3H, m), 7.45–7.47 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 27.4, 126.2, 127.2, 128.8, 129.2, 130.5, 135.9, 141.3, 143.5, 198.5.

Typical Procedure for Preparation of Acylsilane 13. The preparation in the literature was slightly modified.[40] To a solution of 1-(phenoxymethyl)benzotriazole (1.20 g, 5.34 mmol) in THF (75 mL) at −78 °C was added butyllithium (1.57 M in hexane, 3.4 mL, 5.34 mmol) and the solution was stirred for 5 min at this temperature. Chlorotrimethylsilane (580 mg, 5.34 mmol) was added, and the mixture was stirred at this temperature for 15 min, adding a second portion of butyllithium (1.57 M in hexane, 3.4 mL, 5.34 mmol). After addition of 3-phenylpropyl bromide (957 mg, 4.81 mmol), the solution was kept at −78 °C for 5 min and then at room temperature for an additional 1 h. Then the solution was quenched with saturated NH_4Cl solution and the organic layer was extracted with ethyl acetate. The combined organic extracts were washed with water and dried over magnesium sulfate. The solvent was removed under reduced pressure, and the obtained residue was dissolved in 20 mL of 80% acetic acid and the solution was heated at 80 °C for 30 min. After cooling, the solution was extracted with diethyl ether, and the combined extracts were washed with brine and dried over magnesium sulfate. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (hexane–ethyl acetate 50:1) to afford 4-phenyl-1-trimethylsilylbutan-1-one (**13a**) in 55% yield (2 steps).

4-Phenyl-1-trimethylsilylbutan-1-one (13a): Colorless oil; IR (ZnSe) 1641, 1496, 1454, 1248, 839, 739, 698 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.16 (9H, s), 1.83 (2H, tt, $J = 7.2$, 7.4 Hz), 2.57 (2H, t, $J = 7.4$ Hz), 2.60 (2H, t, $J = 7.2$ Hz), 7.13–7.18 (3H, m), 7.24–7.27 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ −3.3, 23.6, 35.1, 47.5, 125.8, 128.2, 128.4, 141.8, 248.0; Anal. Found: C, 70.78; H, 9.12%. Calcd for $C_{13}H_{20}OSi$: C, 70.85; H, 9.15%.

2-Phenyl-1-trimethylsilylethanone (13b): Colorless oil; IR (ZnSe) 1651, 1635, 1250, 845, 748, 702 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.09 (9H, s), 3.83 (2H, s), 7.10–7.12 (2H, m), 7.21–7.24 (1H, m), 7.28–7.31 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ −2.8, 55.5, 126.8, 128.6, 129.9, 133.1, 244.2; Anal. Found: C, 68.49; H, 8.31%. Calcd for $C_{11}H_{16}OSi$: C, 68.69; H, 8.39%.

Typical Procedure for Preparation of (1-Acyloxyvinyl)-silane 14–16. To a solution of LDA (5.51 mmol) in THF 20 mL was added hexamethylphosphoric triamide (8.98 g, 50.1 mmol) at −78 °C, and the solution was stirred for 5 min at this temperature. THF (5 mL) solution of 4-phenyl-1-trimethylsilylbutan-1-one (**13a**) (1.10 g, 5.01 mmol) was added, and the mixture was stirred at this temperature for 2 h. After addition of benzoic anhydride (1.70 g, 7.51 mmol), the solution was kept at −78 °C for 5 min and then at room temperature for an additional 1 h. Then the solution was quenched with saturated NH_4Cl solution and the organic layer was extracted with ethyl acetate. The combined organic extracts were washed with water and dried over magnesium sulfate. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (hexane:ethyl acetate = 50:1) to afford (*E*)-4-phenyl-1-trimethylsilylbut-1-en-1-yl benzoate (**14b**) in 86% yield.

(*E*)-4-Phenyl-1-trimethylsilylbut-1-en-1-yl Acetate (14a): Colorless oil; IR (ZnSe) 1743, 1369, 1219, 839, 771, 698 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.10 (9H, s), 2.11 (3H, s), 2.30–2.34 (2H, m), 2.63–2.67 (2H, m), 5.49 (1H, t, $J = 7.0$ Hz), 7.15–7.19 (3H, m), 7.25–7.28 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ −1.5, 20.6, 27.6, 35.0, 125.9, 128.3, 128.4, 130.5, 141.6, 155.3, 169.2; Anal. Found: C, 68.46; H, 8.42%. Calcd for $C_{15}H_{22}O_2Si$: C, 68.65; H, 8.45%.

(*Z*)-4-Phenyl-1-trimethylsilylbut-1-en-1-yl Acetate (15): Colorless oil; IR (ZnSe) 1738, 1367, 1232, 1047, 839, 698 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.16 (9H, s), 2.09 (3H, s), 2.39–2.44 (2H, m), 2.67–2.70 (2H, m), 5.85 (1H, t, $J = 8.2$ Hz), 7.17–7.21 (3H, m), 7.27–7.30 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ −1.0, 20.8, 29.6, 36.1, 126.0, 128.4, 128.4, 133.3, 141.1, 154.9, 170.6.

(*E*)-4-Phenyl-1-trimethylsilylbut-1-en-1-yl Benzoate (14b): Colorless oil; IR (ZnSe) 1720, 1452, 1263, 1246, 1095, 839, 706 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.17 (9H, s), 2.42 (2H, dt, $J = 7.1$, 7.5 Hz), 2.71 (2H, t, $J = 7.5$ Hz), 5.61 (1H, t,

$J = 7.1$ Hz), 7.15–7.18 (3H, m), 7.24–7.27 (2H, m), 7.44–7.47 (2H, m), 7.56–7.59 (1H, m), 8.05–8.07 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ −1.3, 27.7, 35.1, 125.9, 128.3, 128.4, 128.4, 129.8, 130.0, 130.7, 133.0, 141.6, 155.6, 164.8; Anal. Found: C, 74.05; H, 7.49%. Calcd for $C_{20}H_{24}O_2Si$: C, 74.03; H, 7.45%.

(*E*)-2-Phenyl-1-trimethylsilylvinyl Benzoate (16): Colorless oil; IR (ZnSe) 1720, 1282, 1243, 1105, 1093, 1068, 841, 708, 692 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.26 (9H, s), 6.36 (1H, s), 7.17–7.20 (1H, m), 7.24–7.27 (2H, m), 7.47–7.50 (4H, m), 7.59–7.62 (1H, m), 8.11–8.13 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ −0.9, 127.6, 128.3, 128.4, 128.6, 129.1, 129.7, 130.0, 133.2, 134.3, 156.6, 164.9; Anal. Found: C, 72.92; H, 6.90%. Calcd for $C_{18}H_{20}O_2Si$: C, 72.93; H, 6.80%.

Typical Procedure for Rhodium-Catalyzed Acylation of (1-Acyloxyvinyl)silane 14–16. To a toluene solution (6.8 mL) of (*E*)-4-phenyl-1-trimethylsilylbut-1-en-1-yl benzoate (**14b**) (222 mg, 0.684 mmol) was added $[RhCl(CO)_2]_2$ (13.8 mg, 0.035 mmol) and acetic anhydride (209 mg, 2.05 mmol) and the mixture was heated at 80 °C (the oil bath temperature) for 3 h. After evaporation of the solvent, the crude products were purified by thin-layer chromatography (silica gel, hexane:ethyl acetate = 5:1) to afford (*Z*)-2-oxo-6-phenylhex-3-en-3-yl benzoate (**17b**) (199 mg, 0.675 mmol) in 99% yield.

(*Z*)-2-Oxo-6-phenylhex-3-en-3-yl Acetate (17a): Colorless oil; IR (ZnSe) 1761, 1685, 1371, 1205, 1099, 771, 700 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.23 (3H, s), 2.26 (3H, s), 2.49 (2H, dt, $J = 7.4$, 7.5 Hz), 2.76 (2H, t, $J = 7.5$ Hz), 6.43 (1H, t, $J = 7.4$ Hz), 7.16–7.22 (3H, m), 7.27–7.31 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.2, 25.1, 27.8, 34.2, 126.3, 128.2, 128.5, 131.5, 140.4, 146.4, 168.5, 191.2; Anal. Found: C, 72.23; H, 7.11%. Calcd for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94%.

(*E*)-2-Oxo-6-phenylhex-3-en-3-yl Acetate (18): Colorless oil; IR (ZnSe) 1755, 1699, 1365, 1209, 1095, 700 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.12 (3H, s), 2.19 (3H, s), 2.75 (2H, t, $J = 7.5$ Hz), 2.84–2.89 (2H, m), 5.75 (1H, t, $J = 7.8$ Hz), 7.17–7.19 (3H, m), 7.26–7.29 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.7, 27.7, 28.5, 35.1, 126.1, 128.4, 128.5, 131.8, 140.7, 144.2, 170.0, 194.5.

(*Z*)-2-Oxo-6-phenylhex-3-en-3-yl Benzoate (17b): Colorless oil; IR (ZnSe) 1734, 1685, 1452, 1246, 1088, 1068, 1024, 771, 704 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.32 (3H, s), 2.56 (2H, dt, $J = 7.5$, 7.5 Hz), 2.80 (2H, t, $J = 7.5$ Hz), 6.57 (1H, t, $J = 7.5$ Hz), 7.16–7.22 (3H, m), 7.26–7.29 (2H, m), 7.46–7.49 (2H, m), 7.60–7.63 (1H, m), 8.10–8.12 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 25.3, 27.9, 34.2, 126.3, 128.3, 128.5, 128.5, 128.6, 130.2, 131.5, 133.7, 140.4, 146.5, 164.2, 191.3; Anal. Found: C, 77.45; H, 6.22%. Calcd for $C_{19}H_{18}O_3$: C, 77.53; H, 6.16%.

(*Z*)-3-Oxo-1-phenylbut-1-en-2-yl Benzoate (19): White crystal; mp 81–82 °C; IR (ZnSe) 1734, 1682, 1244, 1088, 708, 690 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.47 (3H, s), 7.28 (1H, s), 7.32–7.34 (3H, m), 7.50–7.53 (2H, m), 7.58–7.67 (3H, m), 8.18–8.20 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 25.4, 128.0, 128.6, 128.7, 128.8, 130.1, 130.3, 130.3, 131.9, 133.9, 144.7, 164.2, 192.1; Anal. Found: C, 76.76; H, 5.44%. Calcd for $C_{17}H_{14}O_3$: C, 76.68; H, 5.30%.

(*Z*)-3-Oxo-7-phenylhept-4-en-4-yl Benzoate (17c): Colorless oil; IR (ZnSe) 1734, 1687, 1452, 1244, 1219, 1090, 771, 708 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.11 (3H, t, $J = 7.3$ Hz), 2.55 (2H, dt, $J = 7.5$, 7.5 Hz), 2.66 (2H, q, $J = 7.3$ Hz), 2.80 (2H, t, $J = 7.5$ Hz), 6.57 (1H, t, $J = 7.5$ Hz), 7.16–7.21 (3H, m), 7.26–7.29 (2H, m), 7.46–7.49 (2H, m), 7.60–7.63 (1H, m), 8.11–8.13 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 7.9, 27.8, 30.6, 34.2, 126.2, 128.3, 128.5, 128.5, 128.7, 130.2, 130.3, 133.7, 140.5, 146.1, 164.3, 194.4; Anal. Found: C, 77.90; H, 6.74%. Calcd for $C_{20}H_{20}O_3$: C, 77.90; H, 6.54%.

(*Z*)-2-Methyl-3-oxo-7-phenylhept-4-en-4-yl Benzoate (17d): Colorless oil; IR (ZnSe) 1734, 1684, 1452, 1240, 1084, 1063, 1024, 700 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.14 (6H, d, $J = 6.8$ Hz), 2.58 (2H, dt, $J = 7.5$, 7.5 Hz), 2.81 (2H, t, $J = 7.5$ Hz), 3.09 (1H, sep, $J = 6.8$ Hz), 6.57 (1H, t, $J = 7.5$ Hz), 7.17–7.22 (3H, m), 7.26–7.29 (2H, m), 7.46–7.49 (2H, m), 7.59–7.63 (1H, m), 8.10–8.12 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 18.9, 27.9, 34.3, 34.8, 126.3, 128.3, 128.5, 128.5, 128.7, 130.2, 130.4, 133.6, 140.5, 145.5, 164.3, 197.9; Anal. Found: C, 78.22; H, 7.04%. Calcd for $C_{21}H_{22}O_3$: C, 78.23; H, 6.88%.

(*Z*)-2,2-Dimethyl-3-oxo-7-phenylhept-4-en-4-yl Benzoate (17e): Colorless oil; IR (ZnSe) 1734, 1684, 1456, 1259, 1082, 1066, 706 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.22 (9H, s), 2.49 (2H, dt, $J = 7.5$, 7.5 Hz), 2.77 (2H, t, $J = 7.5$ Hz), 6.43 (1H, t, $J = 7.5$ Hz), 7.14–7.17 (3H, m), 7.24–7.27 (2H, m), 7.46–7.49 (2H, m), 7.59–7.62 (1H, m), 8.07–8.09 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 27.6, 28.0, 34.3, 43.0, 126.2, 128.4, 128.5, 128.6, 128.8, 129.8, 130.2, 133.7, 140.6, 144.7, 164.2, 200.0; HRMS (FAB$^+$) Found: m/z 337.1831. Calcd for $C_{22}H_{25}O_3$: $(M + H)^+$, 337.1804.

(*Z*)-1-Oxo-1,5-diphenylpent-2-en-2-yl Benzoate (17f): Colorless oil; IR (ZnSe) 1732, 1662, 1599, 1452, 1259, 1128, 1063, 706 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.68 (2H, dt, $J = 7.4$, 7.4 Hz), 2.82 (2H, t, $J = 7.4$ Hz), 6.22 (1H, t, $J = 7.4$ Hz), 7.17–7.22 (3H, m), 7.27–7.30 (2H, m), 7.39–7.42 (2H, m), 7.46–7.54 (3H, m), 7.57–7.63 (1H, m), 7.75–7.77 (2H, m), 8.11–8.12 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.0, 34.4, 126.3, 128.2, 128.4, 128.5, 128.5, 128.6, 129.4, 130.2, 132.4, 133.1, 133.7, 136.8, 140.5, 146.1, 164.3, 189.7; Anal. Found: C, 80.78; H, 5.78%. Calcd for $C_{24}H_{20}O_3$: C, 80.88; H, 5.66%.

(*Z*)-1,4-Diphenylbut-1-en-1-yl Benzoate (20): Colorless oil; IR (ZnSe) 1732, 1495, 1450, 1240, 1088, 1066, 1026, 708 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.52 (2H, dt, $J = 7.3$, 7.5 Hz), 2.82 (2H, t, $J = 7.5$ Hz), 5.98 (1H, t, $J = 7.3$ Hz), 7.19–7.22 (3H, m), 7.27–7.33 (5H, m), 7.44–7.48 (2H, m), 7.51–7.54 (2H, m), 7.63–7.66 (1H, m), 8.19–8.21 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.0, 35.1, 117.2, 124.4, 125.9, 128.2, 128.3, 128.4, 128.5, 128.6, 129.2, 130.1, 133.6, 134.9, 141.4, 146.6, 164.3; HRMS (FAB$^+$) Found: m/z 329.1555. Calcd for $C_{23}H_{21}O_2$: $(M + H)^+$, 329.1542.

1,1,1-Trifluoro-2,2-dihydroxy-6-phenylhexan-3-one (21): White crystals; mp 69–72 °C; IR (ZnSe) 1732, 1496, 1456, 1165, 1103, 1066, 746, 700 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.99 (2H, tt, $J = 7.1$, 7.4 Hz), 2.64 (2H, t, $J = 7.4$ Hz), 2.84 (2H, t, $J = 7.1$ Hz), 4.46 (2H, s), 7.12–7.21 (3H, m), 7.27–7.30 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 24.6, 34.7, 35.4 (q, $J_{CF} = 2$ Hz), 92.1 (q, $J_{CF} = 34$ Hz), 121.4 (q, $J_{CF} = 287$ Hz), 126.2, 128.4, 128.5, 141.0, 202.5; HRMS (FAB$^+$) Found: m/z 263.0914. Calcd for $C_{12}H_{14}O_3F_3$: $(M + H)^+$, 263.0895.

Typical Procedure for Preparation of α,α-Dialkoxy Ketone (22, 23). To a methanol solution (3 mL) of potassium carbonate (494 mg, 3.57 mmol) was added (*Z*)-2-oxo-6-phenylhex-3-en-3-yl benzoate (**17b**) (105 mg, 0.357 mmol) in methanol (1 mL) at room temperature and the solution was stirred at this temperature for 5 min. Then the solution was quenched with water and the organic layer was extracted three times with diethyl ether. The combined organic extracts were dried over magnesium sulfate. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on Florisil® (hexane:ethyl acetate =

5:1) to afford 2,2-dimethoxy-6-phenylhexan-3-one (**22a**) (77.5 mg, 0.328 mmol) in 92% yield.

2,2-Dimethoxy-6-phenylhexan-3-one (22a): Colorless oil; IR (ZnSe) 2941, 1726, 1496, 1454, 1367, 1149, 1045 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.32 (3H, s), 1.90 (2H, tt, $J = 7.4$, 7.4 Hz), 2.59 (2H, t, $J = 7.4$ Hz), 2.61 (2H, t, $J = 7.4$ Hz), 3.19 (6H, s), 7.14–7.19 (3H, m), 7.23–7.28 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.8, 24.8, 35.1, 37.2, 49.7, 102.6, 125.9, 128.3, 128.4, 141.7, 209.0; HRMS (FAB^+) Found: m/z 237.1495. Calcd for $C_{14}H_{21}O_3$: $(M + H)^+$, 237.1491.

2,2-Diethoxy-6-phenylhexan-3-one (22b): Colorless oil; IR (ZnSe) 1728, 1454, 1173, 1144, 1097, 958, 700 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.18 (6H, t, $J = 7.1$ Hz), 1.34 (3H, s), 1.89 (2H, tt, $J = 7.2$, 7.2 Hz), 2.61 (2H, t, $J = 7.2$ Hz), 2.62 (2H, t, $J = 7.2$ Hz), 3.39 (2H, dq, $J = 9.2$, 7.1 Hz), 3.48 (2H, dq, $J = 9.2$, 7.1 Hz), 7.15–7.18 (3H, m), 7.24–7.28 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.3, 20.8, 24.9, 35.1, 37.1, 57.5, 102.2, 125.8, 128.3, 128.4, 141.7, 209.5; HRMS (FAB^+) Found: m/z 265.1833. Calcd for $C_{16}H_{25}O_3$: $(M + H)^+$, 265.1804.

3,3-Dimethoxy-1-phenylbutan-2-one (23): Colorless oil; IR (ZnSe) 1732, 1454, 1192, 1142, 1041, 889, 725, 696 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.34 (3H, s), 3.23 (6H, s), 3.89 (2H, s), 7.18–7.20 (2H, m), 7.21–7.25 (1H, m), 7.28–7.31 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.9, 44.5, 49.6, 102.7, 126.7, 128.3, 129.6, 133.8, 206.3; HRMS (FAB^+) Found: m/z 209.1205. Calcd for $C_{12}H_{17}O_3$: $(M + H)^+$, 209.1178.

Typical Procedure for Preparation of α-Diketone (24, 25). To a dichloromethane–trifluoroacetic acid 10:1 solution (3 mL) was added 2,2-dimethoxy-6-phenylhexan-3-one (**22a**) (77.5 mg, 0.328 mmol) at room temperature and the solution was stirred at this temperature for 1.5 h. Then the solution was quenched with saturated $NaHCO_3$ solution and the organic layer was extracted three times with dichloromethane. The combined organic extracts were dried over magnesium sulfate. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on Florisil® (hexane–ethyl acetate 5:1) to afford 6-phenylhexane-2,3-dione (**24**) (62.4 mg, 0.328 mmol) quantitatively. In the case of hydrolysis of **23**, only **25** was formed as a crude material. **25** and **26** were obtained as a mixture (1:1) after Florisil® column chromatography.

6-Phenylhexane-2,3-dione (24):[41] Yellow oil; IR (ZnSe) 1776, 1712, 1496, 1454, 1354, 700 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.92 (2H, tt, $J = 7.3$, 7.4 Hz), 2.28 (3H, s), 2.63 (2H, t, $J = 7.4$ Hz), 2.74 (2H, t, $J = 7.3$ Hz), 7.14–7.19 (3H, m), 7.24–7.28 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 23.7, 24.6, 35.0, 35.0, 126.1, 128.4, 128.5, 141.2, 197.4, 199.1.

1-Phenylbutane-2,3-dione (25): Yellow oil; IR (ZnSe) 1712, 1259, 1082, 1047, 800, 727, 694 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.30 (3H, s), 4.03 (2H, s), 7.18–7.20 (2H, m), 7.23–7.27 (1H, m), 7.29–7.33 (1H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 24.0, 42.3, 127.2, 128.7, 129.7, 132.3, 195.8, 197.3.

3-Hydroxy-4-phenylbut-3-en-2-one (26): Yellow oil; IR (mixture of **25** and **26**) (ZnSe) 3371, 1712, 1664, 1637, 1394, 1352, 1244, 692 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.49 (3H, s), 6.44 (1H, d, $J = 1.1$ Hz), 7.28–7.33 (2H, m), 7.37–7.40 (2H, m), 7.81–7.83 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 23.0, 113.8, 128.5, 128.6, 130.1, 134.0, 146.9, 195.2; HRMS (mixture of **25** and **26**) (FAB^+) Found: m/z 163.0756. Calcd for $C_{10}H_{11}O_2$: $(M + H)^+$, 163.0759.

$AlCl_3$-Mediated Acylation of (1-Benzoyloxyvinyl)silane 14b.[20] To a dichloromethane solution (2 mL) of (*E*)-4-phenyl-1-trimethylsilylbut-1-en-1-yl benzoate (**14b**) (64.4 mg, 0.20 mmol) was added acetyl chloride (31.2 mg, 0.40 mmol) and aluminium chloride (52.9 mg, 0.40 mmol), successively, and the solution was stirred at room temperature for 24 h. Then the solution was quenched with saturated $NaHCO_3$ solution and the organic layer was extracted twice with dichloromethane. The combined organic extracts were washed with brine and dried over magnesium sulfate. The solvent was removed under reduced pressure and the crude products were purified by thin-layer chromatography (silica gel, hexane:ethyl acetate = 4:1) to afford (*E*)-4-(4-acetylphenyl)-1-trimethylsilylbut-1-en-1-yl benzoate (**27**) (54.1 mg, 0.15 mmol) in 74% yield.

(*E*)-4-(4-Acetylphenyl)-1-trimethylsilylbut-1-en-1-yl Benzoate (27): Colorless oil; IR (ZnSe) 1718, 1682, 1604, 1263, 1246, 1095, 837, 706 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.14 (9H, s), 2.42 (2H, dt, $J = 7.1$, 7.4 Hz), 2.55 (3H, s), 2.75 (2H, t, $J = 7.4$ Hz), 5.57 (1H, t, $J = 7.1$ Hz), 7.22 (2H, d, $J = 8.3$ Hz), 7.43–7.46 (2H, m), 7.55–7.59 (1H, m), 7.83 (2H, d, $J = 8.3$ Hz), 8.00–8.03 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ −1.4, 26.5, 27.3, 35.0, 128.4, 128.4, 128.6, 129.8, 129.8, 129.9, 133.1, 135.1, 147.3, 156.0, 164.7, 197.8; Anal. Found: C, 72.02; H, 7.25%. Calcd for $C_{22}H_{26}O_3Si$: C, 72.09; H, 7.15%.

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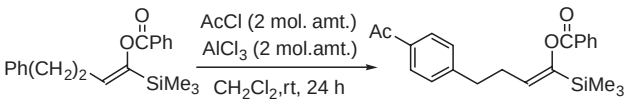

14b **27** 74%

(6)

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