Selected Paper

Lewis Base-Catalyzed [2,3]-Wittig Rearrangement of Silyl Enolates Generated from α-Allyloxy Carbonyl Compounds

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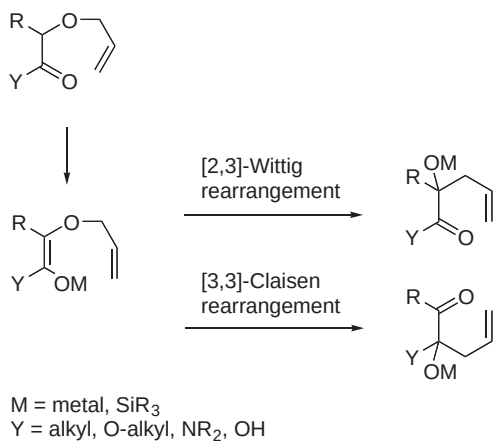
Lewis base-catalyzed [2,3]-Wittig rearrangement of silyl enolates generated from α-allyloxy carbonyl compounds is described. The [2,3]-Wittig rearrangement of silyl enolates generated from α-allyloxy ketones proceeded smoothly by using a Lewis base catalyst, such as lithio or sodio 2-pyrrolidone, in DMF at room temperature without an accompanying [3,3]-Claisen rearrangement. The nature of the catalyst determines the pathway to proceed either by [2,3]-Wittig or [3,3]-Claisen rearrangement. In addition [2,3]-Wittig rearrangement of silyl enolates generated from α-allyloxy esters was tried. It was found that ammonium carboxylates, such as 4-methoxybenzoate, effectively promoted the reaction to afford the [2,3]-Wittig rearrangement product in good yield. This is the first example of the Lewis base-catalyzed [2,3]-Wittig rearrangement of silyl enolates generated from α-allyloxy carbonyl compounds.

A sigmatropic rearrangement is one of the most useful and important tools for the formation of new carbon–carbon bonds. Metal enolates, generated from α-allyloxy carbonyl compounds, were known to give rearrangement products via two different sigmatropic pathways:[1] [2,3]-Wittig and [3,3]-Claisen rearrangements (Scheme 1). The reaction pathway is determined by the nature of the enolates, i.e. [2,3]-Wittig rearrangement occurred when the metal enolates generated from esters,[2] amides,[3] or carboxylic acids[4] were used. However, both sigmatropic rearrangements took place when the metal enolates were generated from ketones.[5] Although the rearrangement of silyl enolates generated from ketones or esters, proceeded via thermal [3,3]-Claisen rearrangement,[2a,5b,6] Nakai et al. reported that the [2,3]-Wittig rearrangement of trimethylsilyl (TMS) enolates generated from α-allyloxy esters took place in the presence of a catalytic amount of silyl triflate.[7]

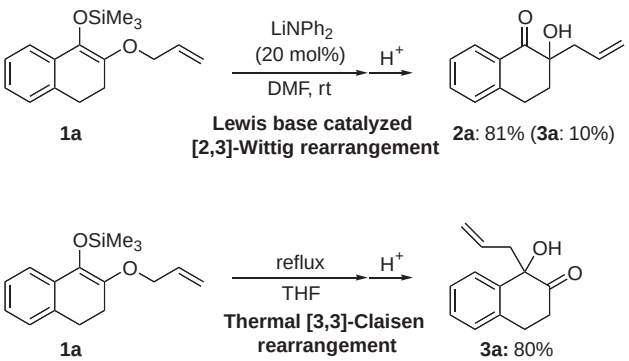
In the course of our investigations on the nucleophilic activation of TMS enolates by using a Lewis base catalyst, it was found that both the nitrogen anions generated from amides, or imides, and the oxygen anions generated from carboxylic acids, or alcohols, were efficient catalysts for promoting aldol,[8] Michael,[9] and Mannich-type[10] reactions. In order to demonstrate further the usefulness of the above mentioned catalysts, Lewis base-catalyzed intramolecular reaction of silyl enolates was then considered.[11] In this paper, we report a Lewis base-catalyzed [2,3]-Wittig rearrangement of silyl enolates which were generated from α-allyloxy carbonyl compounds.



Scheme 1.

Results and Discussion

Metal Amide-Catalyzed [2,3]-Wittig Rearrangement of Silyl Enolates, Generated from α-Allyloxy Ketones. A Lewis base-catalyzed intramolecular reaction was tried by using a TMS enolate, generated from 2-allyloxy-1-tetralone **1a**, as a model (Scheme 2). The reaction proceeded smoothly when **1a** was treated with a catalytic amount of lithium diphenylamide in DMF at room temperature and afforded the [2,3]-Wittig rearrangement product **2a** in 81% yield, as well as the [3,3]-Claisen rearrangement product **3a** in 10% yield. On the other hand, the [3,3]-Claisen rearrangement product **3a** was



Scheme 2.

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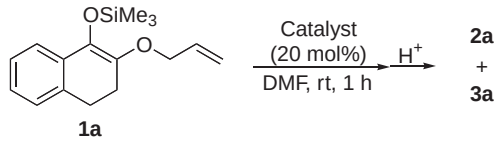
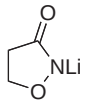
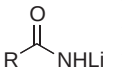
Table 1. Screening of Lewis Base Catalyst



Entry	Catalyst	Yield[a]/%	
		2a	**3a**
1[b]	none	n.d.	80
2	$LiNPh_2$	81	10
3	$LiN(SiMe_3)_2$	83	n.d.
4	LiN*i*-Pr_2	76	trace
5	 M = Li	93	n.d.
6	M = Na	92	n.d.
7	M = K	90	n.d.
8		92	n.d.
9	 R = Me	91	n.d.
10	R = Ph	81	n.d.
11	R = CF_3	36	13
12	Succinimide Li[c]	66	12
13	Phthalimide Li[d]	32	23
14	PhOLi	13	trace
15[e]	$PhONBu_4$	45	trace
16[f]	AcOLi	n.d.	n.d.
17[e]	$AcONMe_4$	n.d.	n.d.
18	4-$MeOC_6H_4CO_2NBu_4$	n.d.	n.d.

a) Isolated yield. b) Reaction was carried out in THF at 50 °C for 6.5 h and another 2 h under reflux conditions. c) Lithium salt of succinimide. d) Lithium salt of phthalimide. e) Reaction time: 0.5 h. f) Reaction time: 5 h.

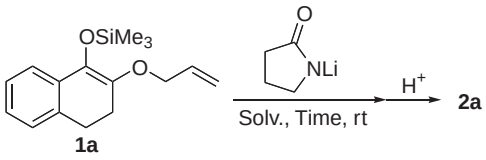
afforded selectively in high yield by the thermolysis of **1a** in THF. These results strongly suggest that the activation by Lewis base, or thermolysis, of the silyl enolate controlled the two rearrangements.

Then, the reaction conditions were optimized in order to increase the amount of **2a**, and Lewis base catalysts were screened first (Table 1). It was found that the Lewis base catalysts, such as lithium hexamethyldisilazide (LHMDS), lithio 2-pyrrolidone, and lithium acetoamide, were effective and the [2,3]-Wittig rearrangement product **2a** was afforded in good yields without the corresponding [3,3]-Claisen rearrangement product **3a** (Entries 3–10). When lithium succinimide, or lithium phthalimide, was used (Entries 12 and 13), on the other hand, the [2,3]-Wittig rearrangement product **2a** was obtained in low to moderate yields along with a small amount of **3a**.

Influence of the counter cation of the catalyst was next examined by using sodio or potassio 2-pyrrolidone. The desired product **2a** was also produced selectively in good yields (Entries 6 and 7).

Additional Lewis base catalysts, such as the corresponding phenoxide or carboxylates, were examined since they had already been shown to be effective in aldol,[8] Michael,[9] and Mannich-type[10] reactions. However, the desired rearrangement product **2a** was obtained only in low yield when lithium or tetrabutylammonium phenoxide was used, and no rearrangements took place when the carboxylates were used (Entries 14–18).

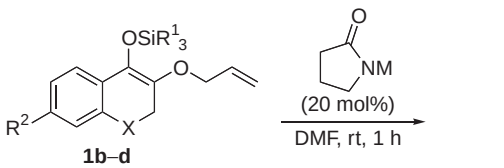
Table 2. Screening of the Solvent



Entry	Solvent	Cat./mol %	Time/h	Yield[a]/%
1	DMF	20	1	93
2	DMSO	30	1	90
3	Pyridine	20	24	37
4	THF	30	48	15
5	MeCN	30	48	15
6	CH_2Cl_2	30	48	trace

a) Isolated yield. **3a** was not detected.

Table 3. Lewis Base-Catalyzed [2,3]-Wittig Rearrangement of Silyl Enolates **1b–1d**



1b: SiR^1_3 = $SiMe_3$ R^2 = OMe X = CH_2
1c: $SiMe_3$ CN CH_2
1d: $SiEt_3$ H O

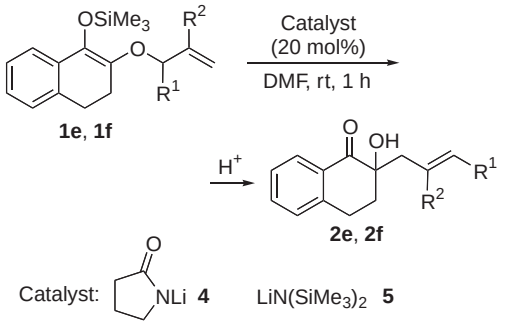
Entry	Substrate	Catalyst	Yield[a]/%	
			2b–2d	**3b–3d**
1	**1b**	none[b]	n.d.	92
2	**1b**	M = Li	71	12
3	**1b**	M = Na	98	n.d.
4	**1c**	none[b]	n.d.	73
5	**1c**	M = Li	64	16
6	**1c**	M = Na	91	n.d.
7	**1d**	none[b]	n.d.	75
8	**1d**	M = Li	78	n.d.
9	**1d**	M = Na	85	n.d.

a) Isolated yield. b) Reaction was carried out in THF under reflux conditions without catalyst.

Next, the effects of solvents were examined in the presence of lithio 2-pyrrolidone at room temperature (Table 2). It was found that when DMF and DMSO were used, the rearrangement product **2a** was produced in high yields (Entries 1 and 2) while other solvents, such as THF and MeCN, produced **2a** only in small amounts (Entries 3–6). In all cases, no [3,3]-Claisen rearrangement product **3a** was detected.

After optimizing the reaction conditions, Lewis base-catalyzed [2,3]-Wittig rearrangement was studied by using silyl enolates, prepared from 6-substituted 2-allyloxy-1-tetralones **1b** and **1c** and 3-allyloxy-4-chromanone **1d** (Table 3). Lithio 2-pyrrolidone (20 mol %), which worked effectively for the

Table 4. Effect of Allyloxy Part of Silyl Enolates



Entry		R^1	R^2	Catalyst	Yield[a]/%
1	**1e**	H	Me	**4**	50[b]
2	**1e**	H	Me	**5**	84[c]
3	**1f**	Me	H	**4**	76[c]
4	**1f**	Me	H	**5**	85[b]

a) Isolated yield. b) **3** was not detected. c) Trace amount of **3** was detected.

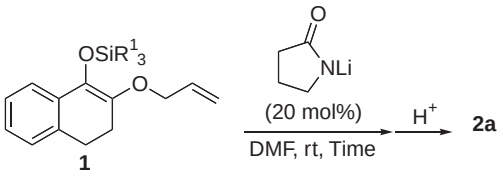
[2,3]-Wittig rearrangement of silyl enolate **1a**, was employed, and the reaction proceeded smoothly to afford the corresponding [2,3]-Wittig rearrangement products **2b**–**2d** in moderate yields along with a small amounts of the [3,3]-Claisen rearrangement products **3b** or **3c** (Entries 2, 5, and 8). In order to increase the selectivity, several other catalysts were screened. The sodium cation was found to be the most effective counter cation for 2-pyrrolidone and promoted the reaction to afford the [2,3]-Wittig rearrangement product selectively (Entries 3, 6, and 9).

On the other hand, when thermolysis of **1b**–**1d** was tried in refluxing THF, the corresponding [3,3]-Claisen rearrangement products **3b**–**3d** were afforded selectively (Entries 1, 4, and 7). These results indicate that the above two rearrangements are controlled by the reaction conditions, i.e., either Lewis base activation or thermolysis of the silyl enolate.

The effect of the allyloxy group of the TMS enolate on this rearrangement was further examined by using **1e** and **1f** (Table 4). When the reactions were carried out in the presence of lithio 2-pyrrolidone (**4**), the corresponding [2,3]-Wittig rearrangement products **2e** and **2f** were obtained in moderate yields (Entries 1 and 3). The Lewis base catalysts were further examined in order to improve the yields, and LHMDS (**5**) was found to be the best catalyst for these enolates. The desired [2,3]-Wittig rearrangement products were afforded in better yields when LHMDS was used than when lithio 2-pyrrolidone was used (Entries 2 and 4). The rearrangement product **2f** was obtained as an *E*-isomer, which was determined based on the previously reported ^{1}H and ^{13}C NMR data.[12]

Catalytic Cycle of Lewis Base-Catalyzed [2,3]-Wittig Rearrangement. In order to understand the mechanism for this reaction, the following experiments were tried. First, the steric effect of the silyl group on this reaction was examined by using 20 mol % of lithio 2-pyrrolidone (**4**) (Table 5). The bulkiness of the silyl group of the enolate was found to strongly influence the reactivity of this rearrangement (Entries 1–4). However, in the case of dimethylphenylsilyl derivative **1j**, which has a bulky, electrophilic phenyl group, **2a** was afforded in good yield (Entry 5). This result indicated that the electrophilicity of the silyl group also influenced the reaction. Therefore, the reaction was thought to proceed via the activation of silyl enolates by coordinating the Lewis base catalyst to the silicon atom of the enolate, which is similar to other Lewis base-catalyzed reactions.[8–10]

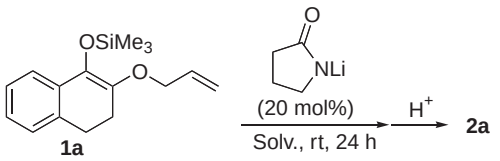
Table 5. Effect of Silyl Group

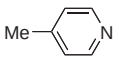
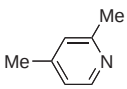
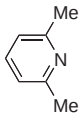


Entry		$SiR^1{}_3$	Time/h	Yield[a]/%
1	**1a**	$SiMe_3$	1	93
2	**1g**	$SiEt_3$	2	91[b]
3	**1h**	Si*i*-Pr_3	24	7
4	**1i**	$SiMe_2$*t*-Bu	24	20
5	**1j**	$SiMe_2Ph$	2	79

a) Isolated yield. b) Trace amount of **3a** was detected.

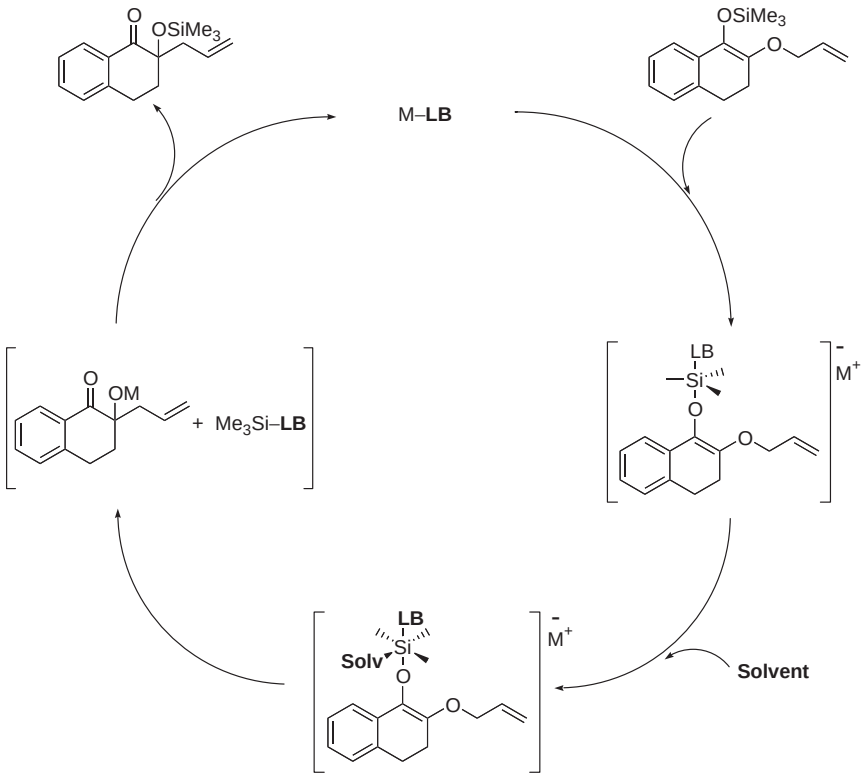
Table 6. Steric Effect of Solvent



Entry	Solvent		Yield[a]/%
1		Pyridine	37
2		4-Picoline	56
3		2-Picoline	4
4		2,4-Lutidine	9
5		2,6-Lutidine	n.d.

a) Isolated yield. **3a** was not detected.

As mentioned above, a highly nucleophilic solvent, such as DMF or DMSO, was needed in order to complete the reaction. To examine the effect of solvents, the [2,3]-Wittig rearrangement was performed in substituted pyridines by using TMS enolate **1a** in the presence of a catalytic amount of lithio 2-pyrrolidone (Table 6). The reaction proceeded smoothly in 4-picoline, and **2a** was afforded in better yield than in pyridine (Entries 1 and 2). However, only a small amount of the rearrangement product was detected when 2-substituted pyridines, such as 2-picoline, 2,4-lutidine, or 2,6-lutidine, were used (Entries 3–5). This also indicated that the reactivity would decrease remarkably if bulky substituents existed around the

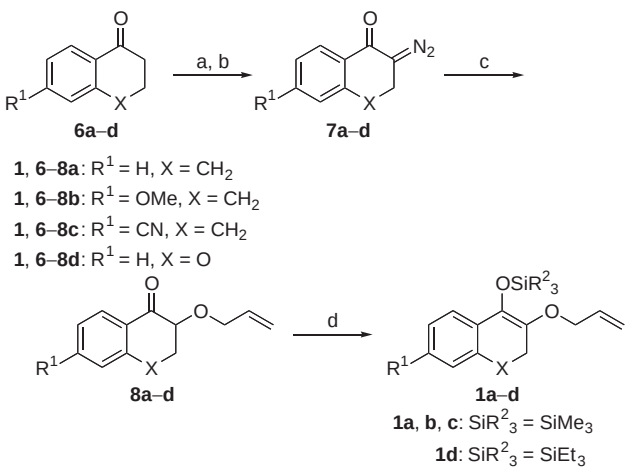


Scheme 3. Proposed catalytic cycle for Lewis base-catalyzed [2,3]-Wittig rearrangement of silyl enolates generated from α-allyloxy ketones.

nitrogen atom of the solvent. Thus, it was suggested that a solvent molecule coordinated to the silicon atom of the enolate.

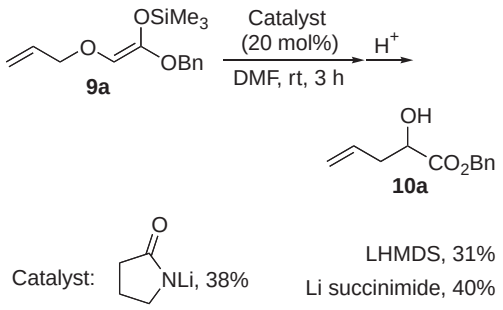
Based on these results, a catalytic cycle for this reaction was proposed (Scheme 3). Namely, the initial coordination of a Lewis base to the silicon atom of the enolate worked to form a pentacoordinated hypervalent silicate, and further coordination of the solvent to the silicate afforded a hexacoordinated hypervalent silicate. Thus, the reactivity of the enolate increased sufficiently enough to undergo [2,3]-Wittig rearrangement, even at room temperature. Subsequent silylation of alkoxide by the silylated Lewis base afforded *O*-silyl ether together with the regeneration of the Lewis base to complete the catalytic cycle.

Preparation of Silyl Enolates Generated from 2-Allyloxy-1-tetralones or 3-Allyloxy-4-chromanone. α-Allyloxy ketones **8a**–**8d** were prepared from the corresponding carbonyl compounds **6a**–**6d** via α-diazo ketones **7a**–**7d** (Scheme 4), which were prepared by the formylation[13] and deformylative diazo transfer reactions[14] of carbonyl compounds. The α-diazo ketones were then treated with allyl alcohol in the presence of a catalytic amount of diethyl ether–boron trifluoride (1/1) ($Et_2O \cdot BF_3$) to obtain the desired α-allyloxy ketones **8a**–**8d** by eliminating the diazo group.[15] Silyl enolates **1a**–**1d** were synthesized from the α-allyloxy ketones **8a**–**8d** by successive treatments with lithium diisopropylamide (LDA), or LHMDS, and with chlorotrimethylsilane (TMSCl), or chlorotriethylsilane (TESCl), in THF at −78 °C. After purification of the crude silyl enolates by column chromatography (neutral silica gel), they were used in the Lewis base-catalyzed [2,3]-Wittig rearrangement reactions. Since the thermal [3,3]-Claisen rearrangement of TNS enolate took place spontaneously at room temperature, triethylsilyl (TES) enolate **1d** was used because it can be isolated by using column chromatography at room temperature.



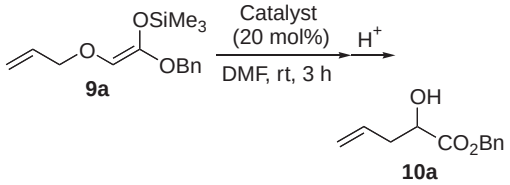
Scheme 4. Reagents and conditions: a) MeONa, HCO_2Et, Benzene, rt; b) Et_2NH, TsN_3, Et_2O, rt; c) $Et_2O \cdot BF_3$, Allyl-OH, −20 °C; d) LDA or LHMDS, TMSCl (**1d**: TESCl), THF, −78 °C.

Ammonium Carboxylate-Catalyzed [2,3]-Wittig Rearrangement of Silyl Enolates Generated from α-Allyloxy Esters. In order to increase the synthetic utility of this Lewis base-catalyzed [2,3]-Wittig rearrangement, a reaction using silyl enolates, generated from α-allyloxy esters, was tried



Scheme 5.

Table 7. Screening of Lewis Base Catalyst



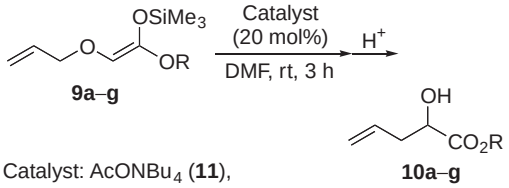
Entry	Catalyst	Yield[a]/%
1	PhOLi	32
2	$PhONBu_4$	24
3	AcOLi	34
4	AcONa	38
5	AcOK	48
6	$AcONBu_4$	70
7	t-$BuCO_2NBu_4$	71
8	$PhCO_2NBu_4$	49
9	4-$ClC_6H_4CO_2NBu_4$	30
10	4-$NO_2C_6H_4CO_2NBu_4$	trace
11	4-$MeOC_6H_4CO_2NBu_4$	83
12	2-$MeOC_6H_4CO_2NBu_4$	80
13	2,4-$(MeO)_2C_6H_3CO_2NBu_4$	71
14	3,4,5-$(MeO)_3C_6H_2CO_2NBu_4$	42
15	4-$Me_2NC_6H_4CO_2NBu_4$	66

a) Isolated yield.

because their reactivity towards the rearrangement was known to decrease compared to that of α-allyloxy ketones.[2c,6c] [2,3]-Wittig rearrangement using silyl enolate **9a** was carried out in DMF in the presence of a catalytic amount of lithium amide at room temperature (Scheme 5). The desired [2,3]-Wittig rearrangement product **10a** was obtained in low yield; however, similar reactions using silyl enolates generated from ketones was promoted effectively.

Next, reactions using a Lewis base catalyst having an oxygen anion generated from a phenol or carboxylic acid were tried (Table 7). When lithium phenoxide, or lithium acetate, was used, **10a** was obtained in low yields (Entries 1 and 3). In addition, the yield was influenced by the counter cation of the acetates (Entries 3–5), and tetrabutylammonium acetate ($AcONBu_4$) behaved as a useful catalyst to afford **10a** in 70% yield (Entry 6). Various ammonium carboxylates were then screened in order to improve the efficiency of the reaction. Tetrabutylammonium pivalate having a sterically hindered t-butyl group showed the same reactivity to $AcONBu_4$; however, the yield decreased when $PhCO_2NBu_4$ was used (Entries 7 and 8). The effect of the substituent on the phenyl group of $PhCO_2NBu_4$ was also examined, and the yields became lower when tetrabutylammonium chlorobenzoate, or nitrobenzoate, which has an electron-withdrawing group, was used. On the other hand, better yields were obtained when an electron-donating group was on the phenyl ring (Entries 9–15), and tetrabutylammonium 4-methoxybenzoate was shown to be the best catalyst for this reaction (Entry 11). It is interesting to note that the desired product **10a** was afforded in lower yield when benzoates having a stronger electron-donating group, such as dimethoxy, trimethoxy, or dimethylamino group than the methoxy group were used (Entries 12–15). Formation of [3,3]-Claisen rearrangement product was not observed in any cases.

Table 8. Tetrabutylammonium Carboxylate-Catalyzed [2,3]-Wittig Rearrangement of α-Allyloxy Ketene Silyl Acetals

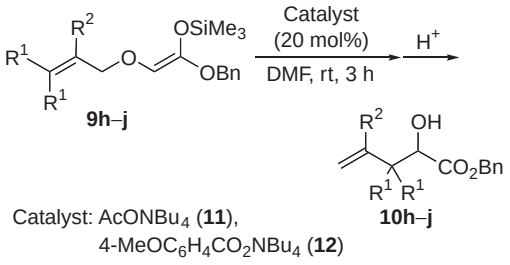


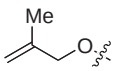
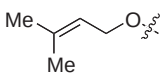
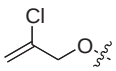
Entry	R		Cat.	Yield[a]/%
1	$PhCH_2$	**9a**	**11**	70
2	$PhCH_2$	**9a**	**12**	83
3	4-$MeOC_6H_4CH_2$	**9b**	**11**	82
4	4-$MeOC_6H_4CH_2$	**9b**	**12**	77
5	4-$ClC_6H_4CH_2$	**9c**	**11**	63
6	4-$ClC_6H_4CH_2$	**9c**	**12**	84
7	4-$CF_3C_6H_4CH_2$	**9d**	**11**	40
8	4-$CF_3C_6H_4CH_2$	**9d**	**12**	49
9	Ph	**9e**	**11**	n.d.
10	Ph	**9e**	**12**	n.d.
11	$PhCH_2CH_2$	**9f**	**11**	64
12	$PhCH_2CH_2$	**9f**	**12**	70
13	Et	**9g**	**11**	75
14	Et	**9g**	**12**	73

a) Isolated yield.

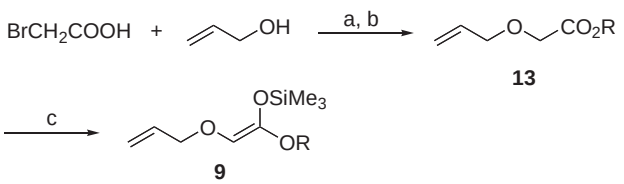
Next, the ammonium carboxylate-catalyzed [2,3]-Wittig rearrangement was tried by using various TMS enolates, **9a**–**9g**, in the presence of $AcONBu_4$ (**11**) or tetrabutylammonium 4-methoxybenzoate (**12**), in DMF at room temperature (Table 8). Both TMS enolates **9b** and **9c**, having either an electron-donating or -withdrawing substituent in a phenyl group of the ester moiety, respectively, afforded the [2,3]-Wittig rearrangement products in good yields (Entries 3–6). However, enolate **9d**, which has a strong electron-withdrawing substituent, such as trifluoromethyl group, afforded the desired product **10d** in moderate yields (Entries 7 and 8). When the TMS enolate **9f**, or **9g**, generated from alkyl ester were used, the corresponding [2,3]-Wittig rearrangement product **10f** or **10g** were also obtained in good yields (Entries 11–14). On the other

Table 9. Effect of Allyloxy Group of Silyl Enolates



Entry	Substrate	Cat.	Yield[a]/%
1	 **9h**	**11**	23
2		**12**	40
3	 **9i**	**11**	16
4		**12**	17
5	 **9j**	**11**	77
6		**12**	80

a) Isolated yield.



Scheme 6. Reagents and conditions: a) NaH, THF, reflux; b) EDC·HCl, DMAP, ROH, THF, 0 °C; c) LHMDS, TMSCl, THF, −78 °C.

hand, the [2,3]-Wittig rearrangement product was not detected when **9e** was used (Entries 9 and 10).

Further, the effect of the allyloxy part of TMS enolates was examined (Table 9). The rearrangement of the TMS enolate **9h** was tried, but the corresponding rearrangement product **10h** was obtained in low yield. The yield of the desired **10i** was also low when the TMS enolate **9i** was used. Thus, the reactivity was strongly influenced by the steric effect of the allyloxy substituent. Next, the TMS enolate **9j**, which has a chlorine atom on the allyloxy moiety was examined, and the reaction proceeded smoothly to afford the corresponding product **10j** in good yield. These results suggested a possibilities of more effective acceleration of this rearrangement involving the silyl enolates having an electron-withdrawing substituent on the allyloxy group.

Preparation of Silyl Enolates Generated from 3-Oxa-5-hexenoate Esters. α-Allyloxy esters **13** were synthesized by the esterification of carboxylic acid,[16] which was prepared from bromoacetic acid and allyl alcohol (Scheme 6).[17] The desired silyl enolates **9** were synthesized from **13** by reacting with LHMDS, followed by successive reaction with chlorotrimethylsilane (TMSCl) in THF at −78 °C.

Conclusion

The Lewis base-catalyzed [2,3]-Wittig rearrangement of silyl enolates, which were generated from α-allyloxy carbonyl compounds in DMF at room temperature was established. It was shown that the effectiveness of the catalyst on this reaction depended on the structures of silyl enolates, i.e., enolates generated from ketones were catalyzed by various metal amides while only ammonium carboxylates were the effective catalysts in the case of those generated from esters. The reaction pathway, i.e., [2,3]-Wittig or [3,3]-Claisen rearrangement, was controlled via Lewis base activation or thermolysis of silyl enolate, respectively.

Experimental

General. All melting points were determined using a Yanagimoto micro melting point apparatus (Yanaco MP-S3) and were not corrected. Infrared (IR) spectra were recorded using a Bio-Rod FTS-165 or a Horiba FT-720 FT-IR spectrometer. ^{1}H NMR spectra were recorded using a JEOL JNM-EX270L (270 MHz) spectrometer; chemical shifts (δ) are reported in parts per million relative to tetramethylsilane, except for the measurements involving silyl enolates. Chemical shifts of the silyl enolates are reported in parts per million relative to the solvent resonance as the internal standard (C_6D_6, 7.20 ppm). Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. ^{13}C NMR spectra were recorded using an EX270L (68 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in parts per million relative to tetramethylsilane, with the solvent resonance as the internal standard ($CDCl_3$, 77.0 ppm; C_6D_6, 128.0 ppm; DMSO-d_6, 39.5 ppm). High resolution mass spectra (HRMS) were recorded on a JEOL AX505WA (EI, CI) or a SX102A (EI, CI, FAB) mass spectrometer. High resolution mass spectrometry analyses and several of the IR measurements were carried out by Mitsui Chemical Analysis & Consulting Service INC. Analytical TLC was performed using Merck preparative TLC plates (silica gel 60 GF254, 0.25 mm). Column chromatography was carried out using Merck silica gel 60 (0.063–0.200 mm) unless otherwise noted. Preparative thin-layer chromatography (PTLC) was carried out using silica gel Wakogel B-5F. All reactions were carried out under an argon atmosphere in dried glassware, unless otherwise noted. Anhydrous *N*,*N*-dimethylformamide (DMF) was purchased form Kanto Chemical and dried further with calcium hydride; anhydrous tetrahydrofuran (THF) was purchased form Kanto Chemical; dichloromethane was distilled from diphosphorus pentaoxide, then from calcium hydride, and finally dried over MS 4A; benzene was distilled from diphosphorus pentaoxide and dried over MS 4A; and diethyl ether was dried over MS 4A. All reagents were purchased from Tokyo Kasei Kogyo, Kanto Chemical, Wako Pure Chemical Industries, Kokusan Chemical, or Aldrich Chemical, and were used without further purification, unless otherwise noted.

Preparation of the Lewis Bases. Lithium acetate was purchased from Wako Pure Chemical Industries. Sodium and potassium acetates were purchased from Kokusan Chemical. Tetramethylammonium acetate and potassium phthalimide were purchased from Tokyo Kasei Kogyo. Lithium phenoxide solution (1.0 M in THF) and tetrabutylammonium acetate were purchased from Aldrich Chemical. Other Lewis base catalysts were prepared by follwing the methods.

Metal Amides. Lithium amides were prepared from corresponding precursors and MeLi (1.0 M in Et_2O) in THF at 0 °C to give a 0.1 M solution of the lithium amides. Sodio and potassio 2-pyrrolidones were prepared from 2-pyrrolidone and sodium hexamethyldisilazide (1.0 M in THF) or potassium hexamethyldisilazide (0.5 M in toluene) in THF at 0 °C to give 0.1 M solution of

Lewis base. These Lewis base catalyst were used without further purification.

Tetrabutylammonium Phenoxide and Carboxylates.[18] To a MeOH solution of phenol or carboxylic acid was added tetrabutylammonium hydroxide in MeOH at room temperature. After stirring for 30 min, the solvent was removed under reduced pressure and the residue was azeotroped with toluene three times. Then, the residue was dissolved in THF, or toluene, to give 0.1 M solution of Lewis base. These Lewis base catalyst were used without further purification.

General Procedure for the Preparation of α-Diazo Ketones (7a–7d).[13,14] To a suspension of sodium methoxide (46.8 mmol) in benzene (45 mL) was added ethyl formate (46.8 mmol). The ice-cooled mixture was treated with a solution of the ketone **6**[19] (23.4 mmol) in benzene (45 mL) and the temperature was allowed to warm to room temperature. After the reaction mixture was stirred for 12 h, the reaction was quenched with ice-water and then acidified with aqueous HCl (2.0 M). The mixture was extracted with Et_2O, and the combined organic layer was washed with H_2O and brine, and dried over Na_2SO_4. After filtration and evaporation of the solvent under reduced pressure, the formed α-formyl ketone was used in the next step without further purification.

To a solution of the above α-formyl ketone and *p*-toluenesulfonyl azide[20] (25.7 mmol) in Et_2O (50 mL) at 0 °C was added diethylamine (46.8 mmol) and then temperature was allowed to rise to room temperature. The reaction mixture was stirred for 1–2 h and then H_2O was added. The mixture was extracted with Et_2O, and the combined organic layer was washed with H_2O and brine, and dried over Na_2SO_4. After filtration and evaporation of the solvent under reduced pressure, the crude α-diazo ketone **7** was purified by the method mentioned below.

2-Diazo-1-tetralone (7a):[21] The crude compound was purified by column chromatography (silica gel, 30% EtOAc–hexane) to afford **7a** (65%) as yellow solid. Mp 48–49 °C (lit.[21b] 47–49 °C); IR (KBr, cm^{-1}) 2071, 1623, 1591, 1310; ^{1}H NMR ($CDCl_3$) δ 8.01 (dd, $J = 7.6$, 1.6 Hz, 1H), 7.44 (td, $J = 7.6$, 1.6 Hz, 1H), 7.35 (t, $J = 7.6$ Hz, 1H), 7.21 (d, $J = 7.6$ Hz, 1H), 3.08–2.96 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 183.4, 139.9, 133.1, 132.3, 128.0, 126.9, 125.7, 62.7, 27.8, 20.8.

2-Diazo-6-methoxy-1-tetralone (7b):[22] The crude compound was purified by column chromatography (silica gel, 30% EtOAc–hexane) to afford diazo ketone **7b** (71%) as orange solid. Mp 68–70 °C (lit.[22] 75–76 °C); IR (KBr, cm^{-1}) 2840, 2078, 1618, 1592, 1247; ^{1}H NMR ($CDCl_3$) δ 7.95 (d, $J = 8.6$ Hz, 1H), 6.84 (dd, $J = 8.6$, 2.5 Hz, 1H), 6.67 (d, $J = 2.5$ Hz, 1H), 3.84 (s, 3H), 2.97–2.96 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 182.7, 162.7, 142.3, 128.0, 126.5, 112.9, 112.5, 61.8, 55.4, 28.2, 20.9.

6-Cyano-2-diazo-1-tetralone (7c): The crude compound was purified by recrystallization from EtOAc–hexane to afford the diazo ketone **7c** (81%) as blown solid. Mp 150–152 °C; IR (KBr, cm^{-1}) 2225, 2071, 1622, 1299; ^{1}H NMR ($CDCl_3$) δ 8.09 (d, $J = 8.0$ Hz, 1H), 7.63 (d, $J = 8.0$ Hz, 1H), 7.27 (s, 1H), 3.12–3.00 (m, 4H); ^{13}C NMR (DMSO-d_6) δ 181.3, 141.6, 135.8, 132.3, 130.4, 125.6, 118.1, 114.3, 63.9, 26.5, 19.2.

3-Diazo-4-chromanone (7d):[21a,23] The crude compound was purified by column chromatography (silica gel, 20% EtOAc–hexane) to afford the diazo ketone **7d** (70%) as yellow solid. Mp 61–64 °C (lit.[23] 52–55 °C); IR (KBr, cm^{-1}) 2113, 1627, 1604, 1333; ^{1}H NMR ($CDCl_3$) δ 7.91 (dd, $J = 7.7$, 1.6 Hz, 1H), 7.43 (td, $J = 7.7$, 1.6 Hz, 1H), 7.09 (t, $J = 7.7$ Hz, 1H), 6.96 (d, $J = 7.7$ Hz, 1H), 5.20 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 178.3, 159.1, 134.6, 126.1, 122.3, 122.2, 117.5, 62.1, 58.7.

General Procedure for the Preparation of α-Allyloxy Ketones (8a–8f).[15] To a solution of α-diazo ketone **7** (18.59 mmol) in allyl alcohol (40 mL) at −20 °C (0 °C in the case of **7c**) was added a solution of $Et_2O \cdot BF_3$ (0.930 mmol) in allyl alcohol (20 mL). After the reaction mixture was stirred for 3–5 h at −20 °C (room temperature in the case of **7c**), the reaction was quenched with saturated aqueous $NaHCO_3$. The mixture was extracted with Et_2O, and the combined organic layer was washed with H_2O and brine, then dried over $MgSO_4$, and filtered. The filtrate was concentrated under reduced pressure, and the crude product was purified by column chromatography (silica gel, 20% EtOAc–hexane) to afford the allyloxy ketone **8**.

2-Allyloxy-1-tetralone (8a):[12] Yield: 72%; Pale yellow oil; IR (neat, cm^{-1}) 3071, 1692, 1647, 1601, 1101, 924; ^{1}H NMR ($CDCl_3$) δ 8.02 (dd, $J = 7.6$, 1.4 Hz, 1H), 7.48 (td, $J = 7.6$, 1.4 Hz, 1H), 7.31 (t, $J = 7.6$ Hz, 1H), 7.24 (d, $J = 7.6$ Hz, 1H), 5.96 (ddt, $J = 17.3$, 10.3, 5.2 Hz, 1H), 5.33 (d, $J = 17.3$ Hz, 1H), 5.21 (d, $J = 10.3$ Hz, 1H), 4.43–4.36 (m, 1H), 4.21–4.08 (m, 2H), 3.20–2.99 (m, 2H), 2.41–2.18 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 196.6, 143.3, 134.4, 133.4, 131.7, 128.4, 127.4, 126.5, 117.3, 79.1, 71.3, 30.0, 27.4.

2-Allyloxy-6-methoxy-1-tetralone (8b): The crude product was purified by column chromatography (silica gel, EtOAc: hexane:CH_3Cl = 1:4:4). Yield: 72%; Blown oil; IR (neat, cm^{-1}) 3080, 2841, 1686, 1601, 1252, 1098, 929; ^{1}H NMR ($CDCl_3$) δ 7.99 (d, $J = 8.7$ Hz, 1H), 6.82 (dd, $J = 8.7$, 2.6 Hz, 1H), 6.67 (d, $J = 2.6$ Hz, 1H), 5.96 (ddt, $J = 17.3$, 10.4, 5.6 Hz, 1H), 5.31 (d, $J = 17.3$ Hz, 1H), 5.19 (d, $J = 10.4$ Hz, 1H), 4.42–4.34 (m, 1H), 4.22–4.13 (m, 1H), 4.04 (dd, $J = 10.2$, 4.5 Hz, 1H), 3.83 (s, 3H), 3.15–2.90 (m, 2H), 2.38–2.13 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 195.2, 163.5, 145.8, 134.5, 129.8, 125.2, 117.1, 113.2, 112.2, 78.8, 71.2, 55.4, 30.0, 27.6; HRMS (CI) Found: m/z 233.1176, Calcd for $C_{14}H_{17}O_3$ $(M + H)^+$: 233.1178.

2-Allyloxy-6-cyano-1-tetralone (8c): Yield: 61%; Pale yellow solid. Mp 55–59 °C; IR (KBr, cm^{-1}) 3064, 2231, 1702, 1648, 1607, 1110, 930; ^{1}H NMR ($CDCl_3$) δ 8.10 (d, $J = 7.6$ Hz, 1H), 7.61–7.58 (m, 2H), 5.95 (ddt, $J = 17.3$, 10.4, 5.4 Hz, 1H), 5.32 (d, $J = 17.3$ Hz, 1H), 5.22 (d, $J = 10.4$ Hz, 1H), 4.38–4.30 (m, 1H), 4.20–4.10 (m, 2H), 3.25–2.98 (m, 2H), 2.44–2.21 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 195.1, 143.8, 134.5, 133.9, 132.4, 129.8, 128.2, 117.8, 117.6, 116.5, 78.5, 71.3, 29.4, 26.7; HRMS (CI) Found: m/z 228.1024, Calcd for $C_{14}H_{14}NO_2$ $(M + H)^+$: 228.1025.

3-Allyloxy-4-chromanone (8d):[23] Yield: 61%; Pale yellow oil; IR (neat, cm^{-1}) 3080, 1703, 1646, 1607, 1478, 1104, 1053, 934; ^{1}H NMR ($CDCl_3$) δ 7.89 (dd, $J = 7.6$, 1.6 Hz, 1H), 7.47 (td, $J = 7.6$, 1.6 Hz, 1H), 7.03 (t, $J = 7.6$ Hz, 1H), 6.96 (d, $J = 7.6$ Hz, 1H), 5.93 (ddt, $J = 17.3$, 10.3, 5.4 Hz, 1H), 5.32 (d, $J = 17.3$ Hz, 1H), 5.23 (d, $J = 10.3$ Hz, 1H), 4.53–4.34 (m, 3H), 4.23–4.11 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 190.7, 160.9, 135.9, 133.6, 127.3, 121.5, 119.7, 118.2, 117.6, 74.5, 71.9, 69.7.

2-(2-Methylallyloxy)-1-tetralone (8e): Yield: 51%; Yellow oil; IR (neat, cm^{-1}) 3074, 2937, 1698, 1658, 1602, 1104, 901; ^{1}H NMR ($CDCl_3$) δ 8.02 (dd, $J = 7.6$, 1.4 Hz, 1H), 7.47 (td, $J = 7.6$, 1.4 Hz, 1H), 7.30 (t, $J = 7.6$ Hz, 1H), 7.23 (d, $J = 7.6$ Hz, 1H), 5.02–5.01 (m, 1H), 4.92–4.91 (m, 1H), 4.28 (d, $J = 12.7$ Hz, 1H), 4.09 (d, $J = 12.7$ Hz, 1H), 4.07 (dd, $J = 10.4$, 4.7 Hz, 1H), 3.20–2.95 (m, 2H), 2.41–2.17 (m, 2H), 1.77 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 196.6, 143.3, 141.9, 133.3, 131.8, 128.4, 127.4, 126.5, 112.3, 78.9, 74.1, 30.0, 27.3, 19.6; HRMS (CI) Found m/z: 217.1225, Calcd for $C_{14}H_{17}O_2$ $(M + H)^+$: 217.1229,

2-(1-Methylallyloxy)-1-tetralone (8f): The crude product

was obtained as diastereomeric mixture, and they were separated by column chromatography (silica gel, 10% EtOAc–hexane). Less-polar isomer: Yield: 19%; Yellow oil; IR (neat, cm^{-1}) 3074, 2979, 2931, 1698, 1641, 1602, 1101, 940; ^1H NMR ($CDCl_3$) δ 8.01 (dd, $J = 7.6$, 1.4 Hz, 1H), 7.46 (td, $J = 7.6$, 1.4 Hz, 1H), 7.30 (t, $J = 7.6$ Hz, 1H), 7.22 (d, $J = 7.6$ Hz, 1H), 5.75 (ddd, $J = 17.3$, 10.3, 7.4 Hz, 1H), 5.24–5.13 (m, 2H), 4.38–4.28 (m, 1H), 4.12 (dd, $J = 10.9$, 4.9 Hz, 1H), 3.16–2.96 (m, 2H), 2.30–2.16 (m, 2H), 1.35 (d, $J = 6.4$ Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 197.6, 143.3, 139.7, 133.2, 131.9, 128.4, 127.3, 126.5, 116.4, 77.1, 76.9, 30.8, 27.7, 21.6; HRMS (CI) Found m/z: 217.1227, Calcd for $C_{14}H_{17}O_2$ $(M + H)^+$: 217.1229. More-polar isomer: Yield: 35%; Yellow oil; IR (neat, cm^{-1}) 3074, 2977, 2931, 1699, 1643, 1603, 1101, 927; ^1H NMR ($CDCl_3$) δ 8.03 (dd, $J = 7.6$, 1.4 Hz, 1H), 7.47 (td, $J = 7.6$, 1.4 Hz, 1H), 7.30 (t, $J = 7.6$ Hz, 1H), 7.23 (d, $J = 7.6$ Hz, 1H), 5.89 (ddd, $J = 17.3$, 10.5, 7.0 Hz, 1H), 5.23 (d, $J = 17.3$ Hz, 1H), 5.12 (d, $J = 10.5$ Hz, 1H), 4.25–4.15 (m, 2H), 3.18–2.90 (m, 2H), 2.42–2.11 (m, 2H), 1.34 (d, $J = 6.2$ Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 196.2, 143.1, 139.9, 133.2, 131.9, 128.3, 127.5, 126.5, 115.7, 77.5, 75.6, 29.7, 27.5, 21.0; HRMS (CI) Found m/z: 217.1233, Calcd for $C_{14}H_{17}O_2$ $(M + H)^+$: 217.1229.

General Procedure for the Preparation of the Silyl Enolates Generated from α-Allyloxy Ketones (1a–1j). To a solution of diisopropylamine (1.30 mmol) in THF (1.5 mL) was added butyllithium (1.6 M in hexane, 1.20 mmol) at 0 °C, and then the mixture was cooled to −78 °C. The reaction mixture was successively added a solution of allyloxy ketone **8** (1.00 mmol) in THF (1.5 mL) and chlorotrimethylsilane (1.30 mmol) in THF (1.5 mL), and then, the temperature was allowed to rise to room temperature. After evaporation of the solvent, the residue was diluted with petroleum ether and filtered through a short pad of celite. The filtrate was concentrated under reduced pressure, and the crude product was purified by column chromatography (silica gel; spherical and neutral, 5% EtOAc–hexane) to afford the silyl enolate **1** as pale yellow oil.

2-Allyloxy-1-trimethylsilyloxy-3,4-dihydronaphthalene (1a): Yield: 76%; Pale yellow oil; IR (neat, cm^{-1}) 3068, 2954, 1655, 1250, 1092, 930, 845; ^1H NMR (C_6D_6) δ 7.69 (d, $J = 7.6$ Hz, 1H), 7.24–7.20 (m, 1H), 7.05 (t, $J = 7.6$ Hz, 1H), 6.98 (d, $J = 7.6$ Hz, 1H), 5.87 (ddt, $J = 17.3$, 10.5, 5.3 Hz, 1H), 5.25 (d, $J = 17.3$ Hz, 1H), 5.05 (d, $J = 10.5$ Hz, 1H), 4.15 (d, $J = 5.4$ Hz, 2H), 2.64 (t, $J = 8.1$ Hz, 2H), 2.22 (t, $J = 8.1$ Hz, 2H), 0.37 (s, 9H); ^{13}C NMR (C_6D_6) δ 139.4, 135.4, 135.0, 133.6, 133.2, 126.8, 126.8, 126.0, 121.6, 116.7, 69.4, 29.0, 25.0, 1.0; HRMS (CI) Found m/z: 235.1454, Calcd for $C_{16}H_{23}O_2Si$ $(M + H)^+$: 275.1467.

2-Allyloxy-6-methoxy-1-trimethylsilyloxy-3,4-dihydronaphthalene (1b): Hexamethyldisilazane was used instead of the diisopropylamine in the general procedure. Yield: 55%; Colorless oil; IR (neat, cm^{-1}) 3080, 2954, 2833, 1658, 1250, 1105, 924, 845; ^1H NMR (C_6D_6) δ 7.61 (d, $J = 8.9$ Hz, 1H), 6.77–6.73 (m, 2H), 5.92 (ddt, $J = 17.3$, 10.4, 5.4 Hz, 1H), 5.28 (d, $J = 17.3$ Hz, 1H), 5.06 (d, $J = 10.4$ Hz, 1H), 4.18 (d, $J = 5.4$ Hz, 2H), 3.41 (s, 3H), 2.63 (t, $J = 8.0$ Hz, 2H), 2.26 (t, $J = 8.0$ Hz, 2H), 0.40 (s, 9H); ^{13}C NMR (C_6D_6) δ 158.7, 137.3, 135.5, 135.2, 133.5, 128.2, 122.8, 116.6, 113.9, 111.1, 69.7, 54.9, 29.4, 25.2, 1.0; HRMS (CI) Found m/z: 305.1564, Calcd for $C_{17}H_{25}O_3Si$ $(M + H)^+$: 305.1573.

2-Allyloxy-6-cyano-1-trimethylsilyloxy-3,4-dihydronaphthalene (1c): Hexamethyldisilazane was used instead of the diisopropylamine in the general procedure. Yield: 89%; Pale yellow oil; IR (neat, cm^{-1}) 3082, 2956, 2222, 1645, 1252, 1107, 926, 845; ^1H NMR (C_6D_6) δ 7.33 (d, $J = 7.9$ Hz, 1H), 7.09 (d, $J = 7.9$ Hz, 1H), 6.80 (s, 1H), 5.76 (ddt, $J = 17.0$, 10.3, 5.1 Hz, 1H), 5.18 (d, $J = 17.0$ Hz, 1H), 5.02 (d, $J = 10.3$ Hz, 1H), 4.02 (d, $J = 5.1$ Hz, 2H), 2.24 (t, $J = 7.9$ Hz, 2H), 1.97 (t, $J = 7.9$ Hz, 2H), 0.28 (s, 9H); ^{13}C NMR (C_6D_6) δ 142.6, 139.5, 134.3, 133.7, 131.5, 130.7, 129.7, 121.2, 119.6, 117.2, 109.0, 69.0, 28.0, 23.9, 0.8; HRMS (CI) Found m/z: 300.1412, Calcd for $C_{17}H_{22}NO_2Si$ $(M + H)^+$: 300.1420.

3-Allyloxy-4-triethylsilyloxy-2*H*-chromene (1d): Chlorotriethylsilane was used instead of the chlorotrimethylsilane in the general procedure. Yield: 43%; Pale yellow oil; IR (neat, cm^{-1}) 3078, 2954, 2875, 1676, 1479, 1240, 1099, 1043, 920; ^1H NMR (C_6D_6) δ 7.66 (d, $J = 7.2$ Hz, 1H), 7.04 (t, $J = 7.2$ Hz, 1H), 7.01 (t, $J = 7.2$ Hz, 1H), 6.97 (d, $J = 7.2$ Hz, 1H), 5.82 (ddt, $J = 17.2$, 10.4, 5.6 Hz, 1H), 5.21 (d, $J = 17.2$ Hz, 1H), 5.04 (d, $J = 10.4$ Hz, 1H), 4.71 (s, 2H), 4.09 (d, $J = 5.6$ Hz, 2H), 1.13 (t, $J = 8.0$ Hz, 9H), 0.89 (q, $J = 8.0$ Hz, 6H); ^{13}C NMR (C_6D_6) δ 153.7, 134.3, 132.0, 131.1, 124.0, 122.1, 121.7, 119.4, 117.4, 115.6, 70.7, 66.2, 7.3, 6.9; HRMS (CI) Found m/z: 319.1724, Calcd for $C_{18}H_{27}O_3Si$ $(M + H)^+$: 319.1729.

2-(2-Methylallyloxy)-1-trimethylsilyloxy-3,4-dihydronaphthalene (1e): Yield: 60%; Pale yellow oil; IR (neat, cm^{-1}) 3070, 2954, 1655, 1250, 1092, 901, 845; ^1H NMR (C_6D_6) δ 7.66 (d, $J = 7.6$ Hz, 1H), 7.20 (t, $J = 7.6$ Hz, 1H), 7.04 (t, $J = 7.6$ Hz, 1H), 6.97 (d, $J = 7.6$ Hz, 1H), 5.10–5.09 (m, 1H), 4.88–4.87 (m, 1H), 4.10 (s, 2H), 2.66 (t, $J = 8.0$ Hz, 2H), 2.25 (t, $J = 8.0$ Hz, 2H), 1.69 (s, 3H), 0.36 (s, 9H); ^{13}C NMR (C_6D_6) δ 142.4, 139.8, 135.4, 133.6, 133.0, 126.8, 126.7, 125.9, 121.6, 112.4, 72.3, 29.1, 24.9, 19.6, 0.9; HRMS (CI) Found m/z: 289.1624, Calcd for $C_{17}H_{25}O_2Si$ $(M + H)^+$: 289.1624.

2-(1-Methylallyloxy)-1-trimethylsilyloxy-3,4-dihydronaphthalene (1f): Major diastereomer of **8f** was used for starting material. Hexamethyldisilazane was used instead of the diisopropylamine in the general procedure. Yield: 41%; Colorless oil; IR (neat, cm^{-1}) 3068, 2954, 1653, 1248, 1090, 914, 845; ^1H NMR (C_6D_6) δ 7.62 (d, $J = 7.6$ Hz, 1H), 7.20–6.98 (m, 3H), 5.84 (ddd, $J = 17.0$, 10.4, 6.4 Hz, 1H), 5.14 (d, $J = 17.0$ Hz, 1H), 4.96 (d, $J = 10.4$ Hz, 1H), 4.50–4.45 (m, 1H), 2.68 (t, $J = 8.0$ Hz, 2H), 2.25 (t, $J = 8.0$ Hz, 2H), 1.28 (d, $J = 6.4$ Hz, 3H), 0.35 (s, 9H): ^{13}C NMR (C_6D_6) δ 140.4, 138.7, 135.5, 133.8, 133.7, 126.8, 126.7, 125.9, 125.5, 121.6, 74.7, 29.2, 25.9, 21.5, 1.1; HRMS (CI) Found m/z: 289.1617, Calcd for $C_{17}H_{25}O_2Si$ $(M + H)^+$: 289.1624.

2-Allyloxy-1-triethylsilyloxy-3,4-dihydronaphthalene (1g): Chlorotriethylsilane was used instead of the chlorotrimethylsilane in the general procedure. Yield: 63%; Pale yellow oil; IR (neat, cm^{-1}) 3070, 2954, 2875, 1655, 1238, 1091, 928; ^1H NMR (C_6D_6) δ 7.76 (d, $J = 7.3$ Hz, 1H), 7.23 (t, $J = 7.3$ Hz, 1H), 7.06 (t, $J = 7.3$ Hz, 1H), 7.00 (d, $J = 7.3$ Hz, 1H), 5.88 (ddt, $J = 17.3$, 10.5, 5.4 Hz, 1H), 5.24 (d, $J = 17.3$ Hz, 1H), 5.04 (d, $J = 10.5$ Hz, 1H), 4.13 (d, $J = 5.4$ Hz, 2H), 2.65 (t, $J = 8.0$ Hz, 2H), 2.20 (t, $J = 8.0$ Hz, 2H), 1.13 (t, $J = 7.9$ Hz, 9H), 0.87 (q, $J = 7.9$ Hz, 6H); ^{13}C NMR (C_6D_6) δ 139.1, 135.4, 135.0, 133.6, 133.3, 126.8, 126.7, 126.0, 121.6, 116.7, 69.3, 29.1, 24.9, 7.4, 6.0; HRMS (CI) Found m/z: 317.1927, Calcd for $C_{19}H_{29}O_2Si$ $(M + H)^+$: 317.1937.

2-Allyloxy-1-triisopropylsilyloxy-3,4-dihydronaphthalene (1h): Triisopropylsilyl trifluoromethanesulfonate was used instead of the chlorotrimethylsilane in the general procedure. Yield: 59%; Pale yellow oil; IR (neat, cm^{-1}) 3070, 2943, 2891, 1655, 1250, 1093, 920; ^1H NMR (C_6D_6) δ 7.78 (d, $J = 7.4$ Hz, 1H), 7.20 (t, $J = 7.4$ Hz, 1H), 7.00 (t, $J = 7.4$ Hz, 1H), 6.94 (d, $J = 7.4$ Hz,

1H), 5.81 (ddt, $J = 17.0$, 10.4, 5.1 Hz, 1H), 5.14 (d, $J = 17.0$ Hz, 1H), 4.97 (d, $J = 10.4$ Hz, 1H), 4.00 (d, $J = 5.1$ Hz, 2H), 2.59 (t, $J = 8.0$ Hz, 2H), 2.11 (t, $J = 8.0$ Hz, 2H), 1.46–1.33 (m, 3H), 1.24 (d, $J = 7.0$ Hz, 18H); ^{13}C NMR (C_6D_6) δ 138.5, 135.6, 135.0, 133.4, 133.2, 126.7, 126.7, 125.8, 121.7, 116.7, 68.8, 29.1, 24.4, 18.7, 14.3; HRMS (CI) Found m/z: 359.2405, Calcd for $C_{22}H_{35}O_2Si$ $(M + H)^+$: 359.2406.

2-Allyloxy-1-*t*-butyldimethylsilyloxy-3,4-dihydronaphthalene (1i): *t*-Butyldimethylsilyl trifluoromethanesulfonate was used instead of the chlorotrimethylsilane. Yield: 40%; Pale yellow oil; IR (neat, cm^{-1}) 3070, 2954, 2931, 1655, 1250, 1090, 914, 841; ^{1}H NMR (C_6D_6) δ 7.78 (d, $J = 7.6$ Hz, 1H), 7.24–7.20 (m, 1H), 7.04 (t, $J = 7.6$ Hz, 1H), 6.98 (d, $J = 7.6$ Hz, 1H), 5.86 (ddt, $J =$ 17.0, 10.5, 5.4 Hz, 1H), 5.23 (d, $J = 17.0$ Hz, 1H), 5.09 (d, $J =$ 10.5 Hz, 1H), 4.11 (d, $J = 5.4$ Hz, 2H), 2.63 (t, $J = 8.0$ Hz, 2H), 2.19 (t, $J = 8.0$ Hz, 2H), 1.17 (s, 9H), 0.34 (s, 6H); ^{13}C NMR (C_6D_6) δ 139.4, 135.4, 135.0, 133.6, 132.9, 126.8, 126.6, 125.9, 121.8, 116.7, 69.2, 29.1, 26.5, 25.1, −3.7; HRMS (CI) Found m/z 319.1938, Calcd for $C_{19}H_{29}O_2Si$ $(M + H)^+$: 317.1937.

2-Allyloxy-1-dimethylphenylsilyloxy-3,4-dihydronaphthalene (1j): Chlorodimethylphenylsilane was used instead of the chlorotrimethylsilane in the general procedure. Yield: 50%; Pale yellow oil; IR (neat, cm^{-1}) 3070, 2956, 1657, 1427, 1252, 1090, 918, 831; ^{1}H NMR (C_6D_6) δ 7.80–7.74 (m, 3H), 7.28–7.14 (m, 4H), 7.03 (td, $J = 7.3$, 1.5 Hz, 1H), 6.96 (d, $J = 7.3$ Hz, 1H), 5.72 (ddt, $J = 17.0$, 10.5, 5.4 Hz, 1H), 5.13 (d, $J = 17.0$ Hz, 1H), 4.98 (d, $J = 10.5$ Hz, 1H), 3.98 (d, $J = 5.4$ Hz, 2H), 2.61 (t, $J = 8.0$ Hz, 2H), 2.17 (t, $J = 8.0$ Hz, 2H), 0.62 (s, 6H); ^{13}C NMR (C_6D_6) δ 139.2, 138.8, 135.1, 134.9, 133.8, 133.5, 133.3, 129.7, 128.0, 126.8, 126.8, 126.0, 121.8, 116.7, 69.3, 29.0, 24.6, −0.2; HRMS (CI) Found m/z: 337.1628, Calcd for $C_{21}H_{25}O_2Si$ $(M + H)^+$: 337.1624.

General Procedure for the Preparation of the Alkyl 3-Oxa-5-hexenoates 13a–13f and 13h–13j).[16,17] To a suspension of NaH (60% dispersion, 95.0 mmol) in THF (25 mL) at 0 °C was added a solution of allyl alcohol (40.0 mmol) in THF (15 mL), and then the temperature was allowed to rise to room temperature. After stirred for 30 min at room temperature, the reaction mixture was cooled to 0 °C and added a solution of bromoacetic acid (36.0 mmol) in THF (25 mL). The mixture was stirred for 30 min at room temperature and refluxed for 1 h, and then, the reaction was quenched with aqueous NaOH (1.0 M). The mixture was washed with AcOEt. After the aqueous layer was acidified with aqueous HCl (2.0 M), the reaction mixture was extracted with CH_2Cl_2. The combined organic layer was washed with H_2O and brine, then dried over $MgSO_4$, and filtered. The filtrate was concentrated under reduced pressure to afford 3-oxa-5-hexenoic acid as a yellow oil, which was used directly in the next step without further purification.

To a solution of above 3-oxa-5-hexenoic acid (10.3 mmol) in CH_2Cl_2 (30 mL) were successively added 4-dimethylaminopyridine (1.03 mmol), EDC [1-(3-dimethylaminopropyl)-3-ethylcarbodiimide] (11.4 mmol), and a solution of the corresponding alcohol (10.3 mmol) in CH_2Cl_2 (10 mL) at 0 °C then the temperature was allowed to rise to room temperature. After the reaction mixture was stirred overnight, H_2O was added. The mixture was extracted with CH_2Cl_2, and the combined organic layer was washed with H_2O and brine, then dried over Na_2SO_4, and filtered. The filtrate was concentrated under reduced pressure, and the crude product was purified by column chromatography (silica gel, 10% EtOAc–hexane) to afford the alkyl 3-oxa-5-hexenoate **13** as colorless oil.

Benzyl 3-Oxa-5-hexenoate (13a): Yield: 98%; IR (neat, cm^{-1}) 3068, 1757, 1648, 1195, 1133; ^{1}H NMR ($CDCl_3$) δ 7.36 (s, 5H), 5.91 (ddt, $J = 16.8$, 10.8, 5.8 Hz, 1H), 5.33–5.20 (m, 4H), 4.13–4.09 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 170.0, 135.2, 133.5, 128.4, 128.3, 128.3, 118.2, 72.4, 67.1, 66.5; HRMS (CI) Found m/z: 207.1016, Calcd for $C_{12}H_{15}O_3$ $(M + H)^+$: 207.1021.

4-Methoxybenzyl 3-Oxa-5-hexenoate (13b): Yield: 86%; IR (neat, cm^{-1}) 3080, 2839, 1753, 1647, 1614, 1516, 1250, 1195, 1131; ^{1}H NMR ($CDCl_3$) δ 7.31 (d, $J = 6.8$ Hz, 2H), 6.88 (d, $J = 6.8$ Hz, 2H), 5.90 (ddt, $J = 17.2$, 10.3, 5.8 Hz, 1H), 5.29 (d, $J = 17.2$ Hz, 1H), 5.22 (d, $J = 10.3$ Hz, 1H), 5.13 (s, 2H), 4.10–4.07 (m, 4H), 3.81 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 170.1, 159.5, 133.5, 130.2, 127.3, 118.1, 113.8, 72.3, 67.1, 66.3, 55.2; HRMS (EI) Found m/z: 236.1045, Calcd for $C_{13}H_{16}O_4$ $(M)^+$: 236.1049.

4-Chlorobenzyl 3-Oxa-5-hexenoate (13c): Yield: 90%; IR (neat, cm^{-1}) 3082, 1758, 1647, 1600, 1494, 1193, 1133, 1095; ^{1}H NMR ($CDCl_3$) δ 7.36–7.28 (m, 4H), 5.91 (ddt, $J = 17.8$, 11.0, 5.8 Hz, 1H), 5.34–5.21 (m, 2H), 5.16 (s, 2H), 4.13–4.08 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 169.9, 134.2, 133.7, 133.4, 129.7, 128.6, 118.2, 72.4, 67.0, 65.6; HRMS (CI) Found m/z: 241.0633, Calcd for $C_{12}H_{14}ClO_3$ $(M + H)^+$: 241.0631.

4-Trifluoromethylbenzyl 3-Oxa-5-hexenoate (13d): Yield: 83%; IR (neat, cm^{-1}) 3084, 1761, 1648, 1623, 1327, 1191, 1128; ^{1}H NMR ($CDCl_3$) δ 7.63 (d, $J = 8.1$ Hz, 2H), 7.48 (d, $J = 8.1$ Hz, 2H), 5.92 (ddt, $J = 17.3$, 10.3, 5.8 Hz, 1H), 5.35–5.21 (m, 4H), 4.16–4.10 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 169.8, 139.2, 133.4, 130.2 (q, $J_{CCF} = 32.3$ Hz), 128.1, 125.3 (q, $J_{CCCF} = 3.9$ Hz), 123.8 (q, $J_{CF} = 271.1$ Hz), 118.1, 72.3, 66.9, 65.4; HRMS (CI) Found m/z: 275.0895, Calcd for $C_{13}H_{14}F_3O_3$ $(M + H)^+$: 275.0895.

Phenyl 3-Oxa-5-hexenoate (13e): Yield: 55%; IR (neat, cm^{-1}) 3078, 1774, 1647, 1593, 1493, 1195, 1123; ^{1}H NMR ($CDCl_3$) δ 7.39 (t, $J = 7.6$ Hz, 2H), 7.24 (t, $J = 7.6$ Hz, 1H), 7.11 (d, $J = 7.6$ Hz, 2H), 5.97 (ddt, $J = 17.3$, 10.3, 5.9 Hz, 1H), 5.36 (d, $J = 17.3$ Hz, 1H), 5.28 (d, $J = 10.3$ Hz, 1H), 4.35 (s, 2H), 4.19 (d, $J = 5.9$ Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 168.8, 150.0, 133.5, 129.4, 126.0, 121.2, 118.5, 72.6, 67.1; HRMS (CI) Found m/z: 193.0866, Calcd for $C_{11}H_{13}O_3$ $(M + H)^+$: 193.0867.

Phenylethyl 3-Oxa-5-hexenoate (13f): Yield: 81%; IR (neat, cm^{-1}) 3086, 3030, 1755, 1648, 1604, 1195, 1134; ^{1}H NMR ($CDCl_3$) δ 7.34–7.20 (m, 5H), 5.90 (ddt, $J = 17.5$, 10.4, 5.7 Hz, 1H), 5.28 (d, $J = 17.5$ Hz, 1H), 4.72 (d, $J = 10.4$ Hz, 1H), 4.38 (t, $J = 7.0$ Hz, 2H), 4.07–4.04 (m, 4H), 2.97 (t, $J = 7.0$ Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 170.1, 137.2, 133.5, 128.7, 128.3, 126.5, 118.0, 72.2, 67.0, 65.1, 35.0; HRMS (CI) Found m/z: 221.1177, Calcd for $C_{13}H_{17}O_3$ $(M + H)^+$: 221.1178.

Benzyl 5-Methyl-3-oxa-5-hexenoate (13h): Yield: 58%; IR (neat, cm^{-1}) 3069, 2945, 2914, 1758, 1657, 1193, 1133; ^{1}H NMR ($CDCl_3$) δ 7.37–7.34 (m, 5H), 5.19 (s, 2H), 4.97 (s, 1H), 4.93 (s, 1H), 4.09 (s, 2H), 4.00 (s, 2H), 1.74 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 170.0, 140.9, 135.2, 128.4, 128.2, 128.2, 113.2, 75.2, 66.8, 66.4, 19.4; HRMS (CI) Found m/z: 221.1178, Calcd for $C_{13}H_{17}O_3$ $(M + H)^+$: 221.1178.

Benzyl 6-Methyl-3-oxa-5-heptenoate (13i): Yield: 75%; IR (neat, cm^{-1}) 3066, 2973, 2915, 1756, 1674, 1191, 1134; ^{1}H NMR ($CDCl_3$) δ 7.37–7.34 (m, 5H), 5.35 (t, $J = 7.2$ Hz, 1H), 5.19 (s, 2H), 4.09–4.05 (m, 4H), 1.74 (s, 3H), 1.65 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 170.2, 138.4, 135.2, 128.3, 128.2, 128.2, 119.8, 67.4, 66.7, 66.3, 25.8, 17.9; HRMS (FAB) Found m/z: 233.1183, Calcd for $C_{14}H_{17}O_3$ $(M - H)^+$: 233.1177.

Benzyl 5-Chloro-3-oxa-5-hexenoate (13j): Yield: 26%; IR (neat, cm^{-1}) 3035, 1751, 1638, 1193, 1113, 898; ^{1}H NMR ($CDCl_3$) δ 7.36 (s, 5H), 5.48 (s, 1H), 5.40 (s, 1H), 5.20 (s, 2H), 4.18 (s, 4H); ^{13}C NMR ($CDCl_3$) δ 169.5, 137.0, 135.1, 128.5,

128.4, 128.3, 114.3, 73.5, 67.1, 66.7; HRMS (CI) Found m/z: 241.0629, Calcd for $C_{12}H_{14}ClO_3$ $(M+H)^+$: 241.0631.

Preparation of Ethyl 3-Oxa-5-hexenoate (13g).[24] To a suspension of NaH (60% dispersion, 105.6 mmol) in DMF (70 mL) at 0 °C was added ethyl glycolate (10.00 g, 96.1 mmol), and then the temperature was allowed to rise to room temperature. After stirring for 2 h at room temperature, the reaction mixture was cooled to 0 °C and allyl bromide (13.04 g, 107.8 mmol) was added. The mixture was stirred for 2 h at room temperature and quenched with saturated aqueous NH_4Cl (1.0 M). The mixture was extracted with Et_2O, and the combined organic layer was washed with H_2O and brine, then dried over Na_2SO_4, and filtered. The filtrate was concentrated under reduced pressure, and the crude product was distilled to afford the ethyl 3-oxa-5-hexenoate (**13g**) (8.31 g, 60%) as colorless oil. Bp 72–74 °C (lit.[24] 70–74 °C); IR (neat, cm^{-1}) 3084, 2985, 1756, 1648, 1205, 1136; ^1H NMR ($CDCl_3$) δ 5.92 (ddt, J = 17.3, 10.3, 5.7 Hz, 1H), 5.31 (d, J = 17.3 Hz, 1H), 5.24 (d, J = 10.3 Hz, 1H), 4.23 (q, J = 7.1 Hz, 2H), 4.12–4.08 (m, 4H), 1.29 (t, J = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 170.1, 133.5, 118.0, 72.2, 67.0, 60.8, 14.2; HRMS (CI) Found m/z: 145.0860, Calcd for $C_7H_{13}O_3$ $(M+H)^+$: 145.0865.

General Procedure for the Preparation of the Silyl Enolates Generated from α-Allyloxy Esters (9a–9j). To a solution of hexamethyldisilazane (2.46 mmol) in THF (1.5 mL) at 0 °C was added butyllithium (1.6 M in hexane, 2.27 mmol), and then mixture was cooled to −78 °C. The reaction mixture was successively added a solution of allyloxy ester **13** (1.89 mmol) in THF (1.5 mL) and chlorotrimethylsilane (2.46 mmol) in THF (1.5 mL), and then, the temperature was allowed to rise to room temperature. After evaporation of the solvent, the residue was diluted with petroleum ether and filtered through a short pad of celite. The filtrate was concentrated under reduced pressure to afford the silyl enolate **9** as pale yellow or colorless oil. The yield was determined by ^1H NMR analysis using 1,3,5-trimethylbenzene as an internal standard, and the purity of the enolate was calculated. The crude silyl enolates were used without further purification.

1-Benzyloxy-1-trimethylsilyloxy-3-oxa-1,5-hexadiene (9a): Yield: 85%; IR (neat, cm^{-1}) 3066, 2958, 1747, 1709, 1647, 1252, 849; ^1H NMR (C_6D_6) δ 7.30–7.11 (m, 5H), 5.82 (ddt, J = 17.3, 10.4, 5.4 Hz, 1H), 5.51 (s, 1H), 5.21 (d, J = 17.3 Hz, 1H), 5.04 (d, J = 10.4 Hz, 1H), 4.65 (s, 2H), 3.92 (td, J = 5.4, 1.5 Hz, 2H), 0.32 (s, 9H); ^{13}C NMR (C_6D_6) δ 148.4, 137.5, 134.8, 128.5, 128.0, 127.9, 116.7, 113.8, 73.3, 70.6, 0.7.

1-(4-Methoxybenzyloxy)-1-trimethylsilyloxy-3-oxa-1,5-hexadiene (9b): Yield: 76%; IR (neat, cm^{-1}) 3078, 2956, 2837, 1749, 1707, 1614, 1516, 1252, 849; ^1H NMR (C_6D_6) δ 7.22 (d, J = 8.6 Hz, 2H), 6.78 (d, J = 8.6 Hz, 2H), 5.82 (ddt, J = 17.0, 10.5, 5.4 Hz, 1H), 5.51 (s, 1H), 5.21 (d, J = 17.0 Hz, 1H), 5.04 (d, J = 10.5 Hz, 1H), 4.63 (s, 2H), 3.93 (d, J = 5.4 Hz, 2H), 3.31 (s, 3H), 0.33 (s, 9H); ^{13}C NMR (C_6D_6) δ 159.8, 148.3, 134.9, 129.9, 129.4, 116.6, 114.0, 113.8, 73.3, 70.4, 54.8, 0.8.

1-(4-Chlorobenzyloxy)-1-trimethylsilyloxy-3-oxa-1,5-hexadiene (9c): Yield: 54%; IR (neat, cm^{-1}) 3082, 2958, 1751, 1709, 1645, 1601, 1493, 1252, 849; ^1H NMR (C_6D_6) δ 7.11 (d, J = 8.5 Hz, 2H), 6.97 (d, J = 8.5 Hz, 2H), 5.80 (ddt, J = 17.3, 10.3, 5.7 Hz, 1H), 5.46 (s, 1H), 5.20 (d, J = 17.3 Hz, 1H), 5.04 (d, J = 10.3 Hz, 1H), 4.48 (s, 2H), 3.91 (d, J = 5.7 Hz, 2H), 0.31 (s, 9H); ^{13}C NMR (C_6D_6) δ 147.9, 135.9, 134.7, 133.8, 129.4, 128.7, 116.8, 114.0, 73.3, 69.7, 0.7.

1-(4-Trifluoromethylbenzyloxy)-1-trimethylsilyloxy-3-oxa-1,5-hexadiene (9d): Yield: 70%; IR (neat, cm^{-1}) 3081, 2960, 1751, 1709, 1647, 1622, 1327, 1254, 849; ^1H NMR (C_6D_6) δ 7.35 (d, J = 8.1 Hz, 2H), 7.08 (d, J = 8.1 Hz, 2H), 5.79 (ddt, J = 17.3, 10.3, 5.4 Hz, 1H), 5.48 (s, 1H), 5.19 (d, J = 17.3 Hz, 1H), 5.04 (d, J = 10.3 Hz, 1H), 4.51 (s, 2H), 3.91 (dt, J = 5.4, 1.5 Hz, 2H), 0.31 (s, 9H); ^{13}C NMR (C_6D_6) δ 147.9, 141.5, 134.6, 129.7 (q, J_{CCF} = 32.3 Hz), 127.9, 125.4 (q, J_{CCCF} = 3.9 Hz), 124.7 (q, J_{CF} = 247.4 Hz), 116.9, 114.1, 73.3, 69.6, 0.7.

1-Phenoxy-1-trimethylsilyloxy-3-oxa-1,5-hexadiene (9e): Yield: 73%; IR (neat, cm^{-1}) 3079, 2960, 1716, 1646, 1254, 850; ^1H NMR (C_6D_6) δ 7.24–7.10 (m, 4H), 6.88 (t, J = 7.3 Hz, 1H), 5.85–5.71 (m, 1H), 5.77 (s, 1H), 5.21 (dd, J = 15.4, 3.7 Hz, 1H), 5.04 (dd, J = 10.4, 3.2 Hz, 1H), 3.89 (dt, J = 5.1, 1.5 Hz, 2H), 0.25 (s, 9H); ^{13}C NMR (C_6D_6) δ 157.6, 143.2, 134.4, 129.7, 122.6, 119.8, 117.1, 116.6, 73.1, 0.5.

1-(2-Phenylethoxy)-1-trimethylsilyloxy-3-oxa-1,5-hexadiene (9f): Yield: 80%; IR (neat, cm^{-1}) 3086, 3028, 2956, 1755, 1709, 1643, 1604, 1252, 849; ^1H NMR (C_6D_6) δ 7.31–7.17 (m, 5H), 5.95 (ddt, J = 17.5, 10.3, 5.4 Hz, 1H), 5.57 (s, 1H), 5.35 (d, J = 17.5 Hz, 1H), 5.16 (d, J = 10.3 Hz, 1H), 4.07 (d, J = 5.4 Hz, 2H), 3.89 (t, J = 7.0 Hz, 2H), 2.90 (t, J = 7.0 Hz, 2H), 0.41 (s, 9H); ^{13}C NMR (C_6D_6) δ 148.8, 138.6, 134.9, 129.2, 128.6, 126.6, 116.6, 112.9, 73.4, 69.3, 36.1, 0.7.

1-Ethoxy-1-trimethylsilyloxy-3-oxa-1,5-hexadiene (9g): Yield: 72%; IR (neat, cm^{-1}) 3082, 2979, 1749, 1705, 1647, 1252, 849; ^1H NMR (C_6D_6) δ 5.86 (ddt, J = 17.3, 10.3, 5.4 Hz, 1H), 5.48 (s, 1H), 5.26 (d, J = 17.3 Hz, 1H), 5.06 (d, J = 10.3 Hz, 1H), 3.98 (td, J = 5.4, 1.5 Hz, 2H), 3.56 (q, J = 7.0 Hz, 2H), 1.08 (t, J = 7.0 Hz, 3H), 0.34 (s, 9H); ^{13}C NMR (C_6D_6) δ 148.8, 135.0, 116.6, 112.7, 73.4, 64.0, 14.9, 0.7.

1-Benzyloxy-5-methyl-1-trimethylsilyloxy-3-oxa-1,5-hexadiene (9h): Yield: 76%; IR (neat, cm^{-1}) 3068, 2958, 1745, 1709, 1658, 1252, 849; ^1H NMR (C_6D_6) δ 7.29 (d, J = 7.0 Hz, 2H), 7.20–7.11 (m, 3H), 5.53 (s, 1H), 5.04 (s, 1H), 4.87 (s, 1H), 4.66 (s, 2H), 3.88 (s, 2H), 1.66 (s, 3H), 0.33 (s, 9H); ^{13}C NMR (C_6D_6) δ 148.2, 142.1, 137.5, 128.5, 128.1, 127.9, 113.8, 112.5, 76.3, 70.7, 19.6, 0.7.

1-Benzyloxy-6-methyl-1-trimethylsilyloxy-3-oxa-1,5-heptadiene (9i): Yield: 88%; IR (neat, cm^{-1}) 3089, 2960, 1745, 1709, 1678, 1252, 850; ^1H NMR (C_6D_6) δ 7.30 (d, J = 6.8 Hz, 2H), 7.20–7.08 (m, 3H), 5.60 (s, 1H), 5.50–5.45 (m, 1H), 4.69 (s, 2H), 4.08 (d, J = 6.8 Hz, 2H), 1.59 (s, 3H), 1.46 (s, 3H), 0.27 (s, 9H); ^{13}C NMR (C_6D_6) δ 148.2, 137.7, 136.2, 128.5, 128.0, 127.9, 121.7, 113.9, 70.7, 69.1, 25.8, 18.1, 0.8.

1-Benzyloxy-5-chloro-1-trimethylsilyloxy-3-oxa-1,5-hexadiene (9j): Yield: 65%; IR (neat, cm^{-1}) 3066, 2956, 1751, 1637, 1252, 874, 845; ^1H NMR (C_6D_6) δ 7.27–7.02 (m, 5H), 5.41 (s, 1H), 5.34 (dd, J = 2.9, 1.4 Hz, 1H), 5.20 (dd, J = 2.2, 1.1 Hz, 1H), 4.56 (s, 2H), 3.94 (dd, J = 1.4, 1.1 Hz, 2H), 0.29 (s, 9H); ^{13}C NMR (C_6D_6) δ 149.3, 138.1, 137.2, 128.5, 128.1, 127.8, 113.3, 113.2, 74.6, 70.5, 0.6.

General Procedure of the Lewis Base-Catalyzed [2,3]-Wittig Rearrangement. The solution of the Lewis base (0.1 M in THF, 0.36 mL, 0.036 mmol) was evaporated under reduced pressure and dissolved in DMF (0.5 mL). To the DMF solution of Lewis base was added a solution of silyl enolate (0.18 mmol) in DMF (1.5 mL) at room temperature. The reaction mixture was stirred for an appropriate time at room temperature and quenched with aqueous HCl (1.0 M). After stirring further for 30 min, the mixture was extracted with Et_2O, and the combined organic layer was washed with H_2O and brine, then dried over $MgSO_4$, and filtered. The filtrate was concentrated under reduced pressure, and the crude product was purified by preparative TLC to give the corresponding [2,3]-Wittig rearrangement product.

2-Allyl-2-hydroxy-1-tetralone (2a):[12] Colorless oil; IR (neat, cm^{-1}) 3488, 3075, 2933, 1685, 1640, 1604, 1092, 918; ^1H NMR ($CDCl_3$) δ 8.02 (dd, $J = 7.6$, 1.4 Hz, 1H), 7.53 (td, $J = 7.6$, 1.4 Hz, 1H), 7.35 (t, $J = 7.6$ Hz, 1H), 7.27 (d, $J = 7.6$ Hz, 1H), 5.88 (ddt, $J = 17.0$, 10.3, 6.2 Hz, 1H), 5.17 (d, $J = 10.3$ Hz, 1H), 5.09 (d, $J = 17.0$ Hz, 1H), 3.82 (s, 1H), 3.18–2.94 (m, 2H), 2.49–2.32 (m, 3H), 2.23–2.11 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 201.0, 143.4, 134.1, 132.1, 130.1, 129.0, 128.0, 126.9, 119.1, 75.4, 40.3, 33.5, 26.1; HRMS (CI) Found m/z: 203.1072, Calcd for $C_{13}H_{15}O_2$ $(M + H)^+$: 203.1072.

2-Allyl-2-hydroxy-6-methoxy-1-tetralone (2b): Colorless oil; IR (neat, cm^{-1}) 3482, 3075, 2941, 2842, 1674, 1639, 1600, 1247, 1095, 918; ^1H NMR ($CDCl_3$) δ 7.98 (d, $J = 8.6$ Hz, 1H), 6.86 (d, $J = 8.6$ Hz, 1H), 6.70 (s, 1H), 5.89 (ddt, $J = 18.1$, 10.3, 8.1 Hz, 1H), 5.16 (d, $J = 10.3$ Hz, 1H), 5.08 (d, $J = 18.1$ Hz, 1H), 3.87 (s, 3H), 3.85 (s, 1H), 3.13–2.88 (m, 2H), 2.47–2.29 (m, 3H), 2.19–2.07 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 199.3, 164.0, 145.9, 132.2, 130.3, 123.4, 118.8, 113.7, 112.6, 75.0, 55.5, 40.6, 33.5, 26.6; HRMS (CI) Found m/z: 233.1175, Calcd for $C_{14}H_{17}O_3$ $(M + H)^+$: 233.1178.

2-Allyl-6-cyano-2-hydroxy-1-tetralone (2c): Colorless oil; IR (neat, cm^{-1}) 3497, 3080, 2937, 2234, 1685, 1643, 1608, 923; ^1H NMR ($CDCl_3$) δ 8.11 (d, $J = 7.8$ Hz, 1H), 7.64–7.61 (m, 2H), 5.85 (ddt, $J = 17.3$, 10.3, 7.6 Hz, 1H), 5.20 (d, $J = 10.3$ Hz, 1H), 5.10 (d, $J = 17.3$ Hz, 1H), 3.67 (s, 1H), 3.20–3.00 (m, 2H), 2.48–2.32 (m, 3H), 2.25–2.14 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 199.5, 143.8, 133.0, 132.9, 131.2, 130.1, 128.5, 119.7, 117.7, 117.1, 75.4, 40.1, 33.0, 25.9; HRMS (CI) Found m/z: 228.1023, Calcd for $C_{14}H_{14}NO_2$ $(M + H)^+$: 228.1025.

3-Allyl-3-hydroxy-4-chromanone (2d): Colorless oil; IR (neat, cm^{-1}) 3473, 3078, 2929, 1695, 1639, 1608, 1477, 1035, 924; ^1H NMR ($CDCl_3$) δ 7.87 (dd, $J = 7.8$, 1.6 Hz, 1H), 7.54 (td, $J = 7.8$, 1.6 Hz, 1H), 7.07 (t, $J = 7.8$ Hz, 1H), 7.00 (d, $J = 7.8$ Hz, 1H), 5.89–5.74 (m, 1H), 5.20 (d, $J = 10.3$ Hz, 1H), 5.13 (d, $J = 17.0$ Hz, 1H), 4.42 (d, $J = 11.2$ Hz, 1H), 4.17 (d, $J = 11.2$ Hz, 1H), 3.62 (s, 1H), 2.50 (d, $J = 7.3$ Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 195.7, 161.2, 136.6, 130.7, 127.5, 121.8, 120.1, 118.2, 117.9, 72.6, 72.5, 39.2; HRMS (CI) Found m/z: 205.0862, Calcd for $C_{12}H_{13}O_3$ $(M + H)^+$: 205.0865.

2-Hydroxy-2-(2-methylallyl)-1-tetralone (2e): Colorless oil; IR (neat, cm^{-1}) 3491, 3073, 2935, 1686, 1643, 1604, 1091, 895; ^1H NMR ($CDCl_3$) δ 8.00 (dd, $J = 7.6$, 1.4 Hz, 1H), 7.53 (td, $J = 7.6$, 1.4 Hz, 1H), 7.35 (t, $J = 7.6$ Hz, 1H), 7.26 (d, $J = 7.6$ Hz, 1H), 4.93–4.92 (m, 1H), 4.70 (brm, 1H), 3.88 (s, 1H), 3.23–2.95 (m, 2H), 2.42–2.31 (m, 3H), 2.24–2.12 (m, 1H), 1.80 (brm, 3H); ^{13}C NMR ($CDCl_3$) δ 201.1, 143.1, 140.8, 133.8, 130.2, 128.8, 127.8, 126.8, 115.3, 75.7, 43.6, 33.9, 26.5, 24.3; HRMS (CI) Found m/z: 217.1225, Calcd for $C_{14}H_{17}O_2$ $(M + H)^+$: 217.1229.

2-(2-Butenyl)-2-hydroxy-1-tetralone (2f):[12] Colorless oil; IR (neat, cm^{-1}) 3491, 3066, 2935, 1687, 1604, 1093, 970; ^1H NMR ($CDCl_3$) δ 8.00 (dd, $J = 7.6$, 1.3 Hz, 1H), 7.51 (td, $J = 7.6$, 1.3 Hz, 1H), 7.33 (t, $J = 7.6$ Hz, 1H), 7.25 (d, $J = 7.6$ Hz, 1H), 5.58–5.41 (m, 2H), 3.76 (s, 1H), 3.16–2.91 (m, 2H), 2.41–2.25 (m, 3H), 2.20–2.09 (m, 1H), 1.68 (d, $J = 3.8$ Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 201.0, 143.3, 133.8, 130.1, 129.8, 128.9, 127.8, 126.7, 124.1, 75.5, 39.1, 33.5, 26.2, 18.1.

Benzyl 2-Hydroxy-4-pentenoate (10a): Colorless oil; IR (neat, cm^{-1}) 3476, 3078, 1738, 1642, 1214; ^1H NMR ($CDCl_3$) δ 7.38–7.35 (m, 5H), 5.85–5.69 (m, 1H), 5.22–5.07 (m, 4H), 4.32 (td, $J = 6.3$, 4.6 Hz, 1H), 2.77 (d, $J = 6.2$ Hz, 1H), 2.65–2.54 (m, 1H), 2.50–2.39 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 174.2, 135.0, 132.3, 128.6, 128.5, 128.4, 118.8, 69.9, 67.3, 38.6; HRMS (CI) Found m/z: 207.1020, Calcd for $C_{12}H_{15}O_3$ $(M + H)^+$: 207.1021.

4-Methoxybenzyl 2-Hydroxy-4-pentenoate (10b): Colorless oil; IR (neat, cm^{-1}) 3483, 3078, 2839, 1735, 1642, 1614, 1516, 1250, 1215; ^1H NMR ($CDCl_3$) δ 7.30 (d, $J = 6.5$ Hz, 2H), 6.89 (d, $J = 6.5$ Hz, 2H), 5.83–5.68 (m, 1H), 5.14–5.06 (m, 4H), 4.33–4.21 (m, 1H), 3.81 (s, 3H), 2.89 (d, $J = 5.9$ Hz, 1H), 2.61–2.51 (m, 1H), 2.47–2.37 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 174.1, 159.6, 132.2, 130.2, 127.0, 118.7, 113.8, 69.9, 67.2, 55.3, 38.6; HRMS (EI) Found m/z: 236.1045, Calcd for $C_{13}H_{16}O_4$ $(M)^+$: 236.1049.

4-Chlorobenzyl 2-Hydroxy-4-pentenoate (10c): Colorless oil; IR (neat, cm^{-1}) 3474, 3080, 1739, 1642, 1600, 1494, 1212, 1198, 1092; ^1H NMR ($CDCl_3$) δ 7.37–7.24 (m, 4H), 5.84–5.68 (m, 1H), 5.22–5.06 (m, 4H), 4.33 (dt, $J = 5.9$, 4.9 Hz, 1H), 2.78 (d, $J = 5.9$ Hz, 1H), 2.63–2.53 (m, 1H), 2.49–2.39 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 174.0, 134.4, 133.4, 132.0, 129.8, 128.7, 118.9, 69.9, 66.5, 38.7; HRMS (CI) Found m/z: 241.0631, Calcd for $C_{12}H_{14}ClO_3$ $(M + H)^+$: 241.0631.

4-Trifluoromethylbenzyl 2-Hydroxy-4-pentenoate (10d): Colorless oil; IR (neat, cm^{-1}) 3474, 3082, 1743, 1643, 1623, 1328, 1193, 1129; ^1H NMR ($CDCl_3$) δ 7.64 (d, $J = 8.4$ Hz, 2H), 7.48 (d, $J = 8.4$ Hz, 2H), 5.85–5.70 (m, 1H), 5.27 (d, $J = 13.0$ Hz, 1H), 5.25 (d, $J = 13.0$ Hz, 1H), 5.15–5.08 (m, 2H), 4.35 (dt, $J = 5.9$, 4.9 Hz, 1H), 2.78 (d, $J = 5.9$ Hz, 1H), 2.66–2.56 (m, 1H), 2.52–2.41 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 173.9, 138.9, 132.0, 130.6 (q, $J_{CCF} = 32.4$ Hz), 128.3, 125.5 (q, $J_{CCCF} = 3.9$ Hz), 123.8 (q, $J_{CF} = 127.1$ Hz), 119.0, 70.0, 66.3, 38.7; HRMS (CI) Found m/z: 275.0895, Calcd for $C_{13}H_{14}F_3O_3$ $(M + H)^+$: 275.0895.

Phenylethyl 2-Hydroxy-4-pentenoate (10f): Colorless oil; IR (neat, cm^{-1}) 3475, 3080, 3030, 1737, 1642, 1605, 1213, 1197, 1136; ^1H NMR ($CDCl_3$) δ 7.35–7.20 (m, 5H), 5.80–5.64 (m, 1H), 5.10–5.02 (m, 2H), 4.44–4.35 (m, 2H), 4.24 (dt, $J = 5.9$, 4.9 Hz, 1H), 2.97 (t, $J = 6.9$ Hz, 2H), 2.80 (d, $J = 5.9$ Hz, 1H), 2.57–2.47 (m, 1H), 2.42–2.32 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 174.1, 137.1, 132.2, 128.7, 128.4, 126.6, 118.6, 69.9, 66.0, 38.6, 35.0; HRMS (CI) Found m/z: 221.1177, Calcd for $C_{13}H_{17}O_3$ $(M + H)^+$: 221.1178.

Ethyl 2-Hydroxy-4-pentenoate (10g):[25] Colorless oil; IR (neat, cm^{-1}) 3467, 3080, 2983, 1730, 1642, 1267, 1203; ^1H NMR ($CDCl_3$) δ 5.91–5.73 (m, 1H), 5.20–5.12 (m, 2H), 4.31–4.19 (m, 3H), 2.89 (d, $J = 5.9$ Hz, 1H), 2.63–2.53 (m, 1H), 2.49–2.39 (m, 1H), 1.30 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 174.2, 132.3, 118.6, 69.9, 61.7, 38.7, 14.3; HRMS (CI) Found m/z: 145.0863, Calcd for $C_7H_{13}O_3$ $(M + H)^+$: 145.0865.

Benzyl 2-Hydroxy-4-methyl-4-pentenoate (10h): Colorless oil; IR (neat, cm^{-1}) 3484, 3072, 2920, 1739, 1650, 1264, 1195; ^1H NMR ($CDCl_3$) δ 7.37 (s, 5H), 5.21 (s, 2H), 4.87 (brm, 1H), 4.79 (brm, 1H), 4.38 (ddd, $J = 8.1$, 5.9, 4.1 Hz, 1H), 2.72 (d, $J = 5.9$ Hz, 1H), 2.55 (dd, $J = 14.0$, 4.1 Hz, 1H), 2.37 (dd, $J = 14.0$, 8.1 Hz, 1H), 1.76 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 174.4, 140.6, 134.9, 128.5, 128.5, 128.3, 114.1, 69.1, 67.3, 42.6, 22.5; HRMS (CI) Found m/z: 221.1176, Calcd for $C_{13}H_{17}O_3$ $(M + H)^+$: 221.1178.

Benzyl 2-Hydroxy-3,3-dimethyl-4-pentenoate (10i): Colorless oil; IR (neat, cm^{-1}) 3515, 2967, 1727, 1640, 1213, 1179; ^1H NMR ($CDCl_3$) δ 7.36 (s, 5H), 5.82 (dd, $J = 17.3$, 10.8 Hz, 1H), 5.23–4.97 (m, 4H), 3.92 (d, $J = 8.0$ Hz, 1H), 2.76 (d, $J = 8.0$ Hz, 1H), 1.07 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 173.4, 142.9, 134.9, 128.5, 128.5, 128.4, 113.5, 77.5, 67.2, 41.5, 23.6, 22.8; HRMS (CI) Found m/z: 235.1335, Calcd for $C_{14}H_{19}O_3$ $(M + H)^+$: 235.1334.

Benzyl 4-Chloro-2-hydroxy-4-pentenoate (10j): Colorless

oil; IR (neat, cm^{-1}) 3466, 3035, 1735, 1637, 1268, 1198, 889; ^1H NMR ($CDCl_3$) δ 7.37 (s, 5H), 5.30–5.23 (m, 4H), 4.52–4.49 (m, 1H), 2.91 (d, $J = 5.1$ Hz, 1H), 2.85 (dd, $J = 14.8$, 4.2 Hz, 1H), 2.68 (dd, $J = 14.8$, 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 173.6, 136.9, 134.7, 128.6, 128.6, 128.4, 116.0, 68.0, 67.8, 43.9; HRMS (CI) Found m/z: 241.0626, Calcd for $C_{12}H_{14}ClO_3$ $(M + H)^+$: 241.0631.

General Procedure for the Thermal [3,3]-Claisen Rearrangement of the Silyl Enolates. The solution of silyl enolate (0.179 mmol) in THF (3 mL) was refluxed for an appropriate time and then aqueous HCl (1.0 M) was added. After stirring for another 30 min at room temperature, the mixture was extracted with Et_2O, and the combined organic layer was washed with H_2O and brine, then dried over $MgSO_4$, and filtered. The filtrate was concentrated under reduced pressure, and the crude product was purified by preparative TLC to give the corresponding [3,3]-Claisen rearrangement product. Products and yields are as reported in the text.

1-Allyl-1-hydroxy-2-tetralone (3a):[12] Pale yellow oil; IR (neat, cm^{-1}) 3477, 3074, 2916, 1716, 1639, 1604, 920; ^1H NMR ($CDCl_3$) δ 7.61 (d, $J = 7.6$ Hz, 1H), 7.34–7.23 (m, 2H), 7.17 (d, $J = 7.6$ Hz, 1H), 5.80–5.68 (m, 1H), 5.12–5.03 (m, 2H), 4.03 (brs, 1H), 3.42–3.30 (m, 1H), 3.08 (ddd, $J = 16.5$, 7.7, 4.1 Hz, 1H), 2.88 (ddd, $J = 18.1$, 7.8, 4.1 Hz, 1H), 2.73–2.57 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 211.4, 139.5, 133.6, 131.7, 127.6, 127.6, 127.2, 125.8, 119.1, 78.8, 44.4, 33.6, 27.8.

1-Allyl-1-hydroxy-6-methoxy-2-tetralone (3b): Pale yellow oil; IR (neat, cm^{-1}) 3477, 3076, 2943, 2837, 1716, 1639, 1610, 1250, 915; ^1H NMR ($CDCl_3$) δ 7.51 (d, $J = 8.6$ Hz, 1H), 6.85 (dd, $J = 8.6$, 2.4 Hz, 1H), 6.69 (d, $J = 2.4$ Hz, 1H), 5.70 (ddt, $J = 17.4$, 10.0, 6.8 Hz, 1H), 5.11–5.01 (m, 2H), 3.97 (s, 1H), 3.80 (s, 3H), 3.37–3.25 (m, 1H), 3.02 (ddd, $J = 16.5$, 7.6, 4.6 Hz, 1H), 2.86 (ddd, $J = 17.8$, 7.8, 4.6 Hz, 1H), 2.71–2.54 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 211.3, 159.0, 135.0, 131.8, 131.7, 127.2, 118.9, 112.8, 112.8, 78.4, 55.3, 44.8, 33.8, 28.1; HRMS (CI) Found m/z: 233.1179, Calcd for $C_{14}H_{17}O_3$ $(M + H)^+$: 233.1178.

1-Allyl-6-cyano-1-hydroxy-2-tetralone (3c): Pale yellow oil; IR (neat, cm^{-1}) 3474, 3080, 2916, 2230, 1720, 1640, 1608, 924; ^1H NMR ($CDCl_3$) δ 7.73 (d, $J = 8.1$ Hz, 1H), 7.60 (d, $J = 8.1$ Hz, 1H), 7.49 (s, 1H), 5.68 (ddt, $J = 17.0$, 11.3, 7.0 Hz, 1H), 5.12 (d, $J = 11.3$ Hz, 1H), 5.06 (d, $J = 17.0$ Hz, 1H), 4.08 (brs, 1H), 3.46–3.33 (m, 1H), 3.13 (ddd, $J = 16.7$, 7.8, 3.2 Hz, 1H), 2.92 (ddd, $J = 18.6$, 7.7, 3.2 Hz, 1H), 2.74–2.54 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 209.7, 144.5, 134.9, 131.2, 130.8, 130.7, 126.9, 119.8, 118.5, 111.5, 78.8, 43.7, 32.8, 27.1; HRMS (CI) Found m/z: 228.1023, Calcd for $C_{14}H_{14}NO_2$ $(M + H)^+$: 228.1025.

4-Allyl-4-hydroxy-3-chromanone (3d): Pale yellow oil; IR (neat, cm^{-1}) 3502, 3078, 2916, 1736, 1639, 1608, 1483, 1051, 924; ^1H NMR ($CDCl_3$) δ 7.53 (dd, $J = 7.6$, 1.6 Hz, 1H), 7.29 (td, $J = 7.6$, 1.6 Hz, 1H), 7.14 (t, $J = 7.6$ Hz, 1H), 7.02 (d, $J = 7.6$ Hz, 1H), 5.77–5.67 (m, 1H), 5.15–5.07 (m, 2H), 4.78 (d, $J = 18.6$ Hz, 1H), 4.48 (d, $J = 18.6$ Hz, 1H), 3.64 (s, 1H), 2.69–2.59 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 209.2, 152.9, 131.0, 129.4, 128.2, 126.0, 123.7, 119.9, 117.6, 77.3, 71.0, 43.5; HRMS (CI) Found m/z: 205.0860, Calcd for $C_{12}H_{13}O_3$ $(M + H)^+$: 205.0865.

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