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Lewis acid-catalyzed three-component condensation reactions of aldehydes, alkoxysilanes, and allenylsilanes: synthesis of α-propargyl ethers

Lui Niimi, Shuichi Hiraoka and Tsutomu Yokozawa*

Department of Applied Chemistry, Kanagawa University, Kanagawa-ku, 3-27-1 Rokkakubashi, Yokohama 221-8686, Japan

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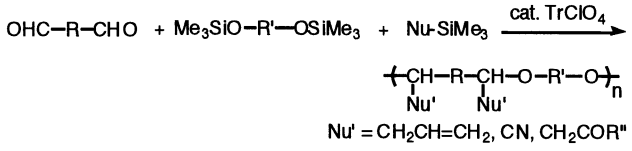
Abstract—Lewis acid-catalyzed reaction of acetals with allenylsilanes and the three-component reactions of aldehydes, alkoxysilanes, and allenylsilanes are described. Both reactions are strongly dependent on the substituent at the α-position of allenylsilanes. Allenylsilanes having bulky substituents such as the *tert*-butyl and isopropyl groups result in the corresponding α-propargyl ethers in high yields, whereas allenylsilanes having the methyl and ethyl groups afford not only the corresponding α-propargyl ethers in low yield but also cyclopropyl ketones and α,β-unsaturated ketones as by-products.

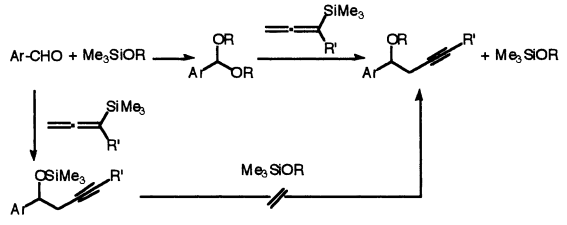
1. Introduction

Three-component condensation reactions make two bonds in one-pot and yield a broad variety of compounds by changing three kinds of reactants. These reactions are recently applied to combinatorial synthesis.[1] There are documented examples of the three-component condensation reactions of aldehydes, alkoxysilanes, and a variety of silyl nucleophiles, which yield ethers,[2] homoallyl ethers,[3] α-alkoxynitriles,[4] and β-alkoxyketones.[5] Furthermore, these reactions with amine derivatives instead of alkoxysilanes produce *N*-homoallylcarbamates,[6] pyridine and quinoline derivatives,[7] β-amino esters,[8a] β-amino ketones,[8b] and δ-lactams.[9] We have applied the three-component ether synthesis to polycondensation, in which the polyether backbone is constructed from dialdehydes and diol disilyl ethers, and functional side chains are simultaneously introduced to polyethers by silyl nucleophiles. The polyethers with the allyl,[10] cyano,[4] and keto[5a,b] side chains have been synthesized by the three-component polycondensations using allylsilane, cyanosilane, and silyl enol ethers, respectively (Scheme 1). Polyethers having the propargyl side chains would be more versatile, because the carbon–carbon triple bond is easily transformed to other functional groups[11] and cross-linking would occur by not only photochemical reaction[12] but also bidentate metals that form acetylides.[13] It has been reported that the reactions of allenylsilanes with aldehydes and acetals in the presence of $TiCl_4$ yield α-propargyl alcohols and ethers, respectively.[14] However, there is no report about the three-component condensation of aldehydes, alkoxysilanes, and allenylsilanes, which will afford the α-propargyl ethers in one-pot and can be applied to the synthesis of polyethers having the propargyl side chains.



Scheme 1.

On the basis of the reported reaction mechanism of the Lewis acid-catalyzed three-component condensations,[5a] the condensation of aldehydes, alkoxysilanes, and allenylsilanes would also take place via similar reaction mechanism (Scheme 2). Aldehyde first reacts with 1 equiv. of alkoxysilane to give acetal; 1:1 mixture of aldehyde and acetal in the initial reaction mixture. Acetal next reacts with allenylsilane to yield the desired α-propargyl ether, as well as the regeneration of 1 equiv. of alkoxysilane. If the aldehyde reacts fast with allenylsilane, the adduct obtained would not further react with alkoxysilane.



Scheme 2.

Keywords: Lewis acid-catalyst; allenylsilane; α-propargyl ether.

* Corresponding author. Tel.: +81-45-481-5661x3151; fax: +81-45-491-7915; e-mail: yokozawa@cc.kanagawa-u.ac.jp

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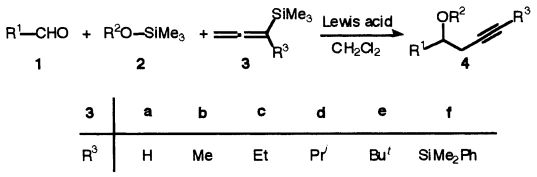


Scheme 3.

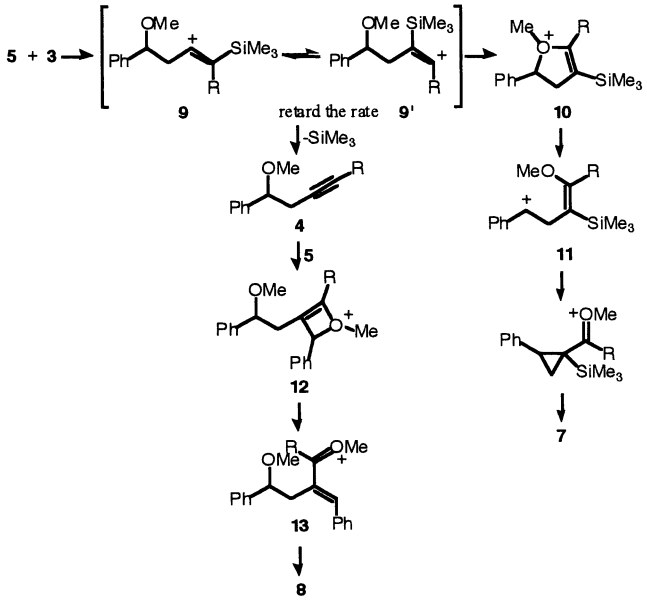
Therefore, this reaction should satisfy the following three requirements: (1) acetalization and the reaction of acetal with allenylsilane proceed by the same Lewis acid; (2) aldehyde reacts with alkoxysilane faster than with allenylsilane; (3) allenylsilane reacts with acetal faster than with aldehyde. The reported reactions of allenylsilanes by $TiCl_4$[14] would not be applied to this three-component condensation, because allenylsilane reacts both with aldehyde and acetal, and it would be difficult to form acetal by $TiCl_4$. Accordingly, another Lewis acid reaction system should be developed for the three-component condensation of aldehydes, alkoxysilanes, and allenylsilanes.

In this paper, we report the triphenylmethyl (trityl) perchlorate-catalyzed condensations of aldehydes, alkoxysilanes, and allenylsilanes, where α-propargyl ethers were obtained in one-pot in good yields when the allenylsilanes possessed the bulky alkyl groups at the α-position. First, we studied the reactions of a variety of allenylsilanes with an acetal which is an intermediate in the three-component condensation. Next, we checked whether the reaction of allenylsilanes with aldehydes proceeded under the same conditions of the reactions with acetals, and then studied the three-component condensations of aldehydes, alkoxysilanes, and allenylsilanes (Scheme 3).

2. Result and discussion

2.1. Reaction of acetal with allenylsilanes

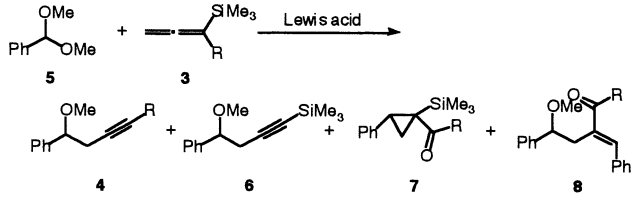
At first, the reactions of benzaldehyde dimethyl acetal **5**



Scheme 4.

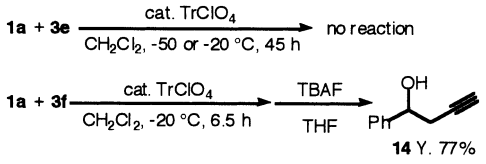
with various allenylsilanes **3a–f** were carried out in the presence of trityl perchlorate ($TrClO_4$) trimethylsilyl trifluoromethanesulfonate (triflate) (TMSOTf), tin (II) triflate ($Sn(OTf)_2$), and scandium triflate ($Sc(OTf)_3$) in CH_2Cl_2, respectively (Table 1). The yields of α-propargyl ethers **4** were strongly dependent on the substituents at the α-position of **3**. Allenylsilanes **3e** and **3f** having bulky substituents resulted in **4** in high yields with 5 mol% of $TrClO_4$; TMSOTf, $Sn(OTf)_2$, and $Sc(OTf)_3$ gave **4** in moderate yields, respectively. On the other hand, the reaction of unsubstituted **3a** with **5** hardly proceeded with 5 mol% of $TrClO_4$. Even increase in the amount of the catalyst up to 50 mol% afforded not only **4** in low yields but also trimethylsilyl-substituted α-propargyl ether **6**, which may be formed by the elimination of proton from β-silyl vinyl cationic intermediate **9** in Scheme 4. Further in this reaction, methyl triphenylmethyl ether (Tr–OMe)[15]

Table 1. Reaction of acetal **5** with allenyltrimethyl silanes **3**



R in **3**	Lewis acid (mol%)	Conditions	Yield (%)[a]			
			4	**6**	**7**	**8**
H:**3a**	$TrClO_4$ (50)	−20°C, 2 h	3	20	0	0
Me:**3b**	TMSOTf (100)	−78°C, 1.5 h	14	0	31	23
Et:**3c**	TMSOTf (100)	−78°C, 1.5 h	4	0	6	38
Bu^t:**3e**	$TrClO_4$ (5)	−50°C, 9.5 h	99	0	0	0
	TMSOTf (5)	−50°C, 8 h and −20°C, 13 h	81	0	0	0
	$Sn(OTf)_2$ (5)	−50°C, 9 h; −20°C, 13 h and 0°C, 9 h	59	0	0	0
	$Sc(OTf)_3$ (5)	−50°C, 4 h	60	0	0	0
$SiMe_2Ph$:**3f**	$TrClO_4$ (5)	−20°C, 3.5 h	85[b]	0	0	0

The reaction was carried out in CH_2Cl_2 ([**5**]0=[**3**]0=0.5 M).
[a] Isolated yield.
[b] Isolated yield after desilylation of the mixture **6** and **4f**.



Scheme 5.

was also obtained in 23% yield based on **5**, implying that $TrClO_4$ did not work well as a catalyst. Accordingly, TMSOTf was used for the reaction of **3b**, **3c** with **5**, because TMSOTf is easily regenerated after the reaction of **3** with the silyl oxonium triflate generated from **5** and TMSOTf. However, the reaction of **3b**, **3c** with **5** hardly proceeded with 5 mol% of TMSOTf. Even addition of 1 equiv. of TMSOTf resulted in the corresponding **4** in poor yield, and surprisingly cyclopropyl ketones **7**[16] and α,β-unsaturated ketones **8** were obtained as major products.

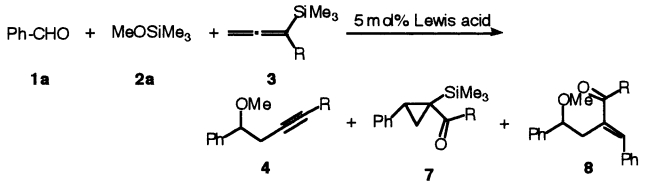
Scheme 4 accounts for the formation of **7** and **8** from the reaction of **5** and **3**. As Danheiser explained the formation of a dihydrofurane product from the reaction of an aldehyde with an allenylsilane in the presence of $TiCl_4$,[14a] dihydropyranium **10** is formed by the intramolecular cyclization of intermediate cation **9′**, which is subjected to a rapid 1,2-trimethylsilyl shift,[17,18] thus establishing an equilibrium with an isomeric vinyl cation **9**. Since **10** is an activated enol benzyl ether, **10** undergoes rearrangement via the proposed intermediate benzyl cation **11** to afford **7**, in analogy with the rearrangement of enol benzylic ethers by triisobutylaluminium.[19] Enone **8** would be formed by the tandem reaction of the desired product **4** with further 1 equiv. of **5**. Thus, **4** undergoes [2+2] cycloaddition with **5** activated by TMSOTf to give **12**,[20] followed by ring-opening isomerization and hydrolysis to give **8**.

In this case, steric hindrance by the *tert*-butyl and phenyldimethylsilyl groups from C-1 of the allenes would retard the rate of intramolecular cyclization of **9′** and undergo very rapid elimination of the trimethylsilyl group in order to relieve steric congestion to yield **4**. Furthermore, the steric hindrance would also retard the [2+2] cycloaddition of **4** with **5** leading to **8**.

2.2. Reaction of aldehyde with allenylsilanes

As mentioned in Section 1, it is necessary for the three-component condensation that allenylsilanes react with acetals faster than with aldehydes or does not react with aldehydes under the conditions where allenylsilanes react with acetals. Therefore, we tested the reaction of benzaldehyde **1a** with **3e** or **3f** which reacted with **5** to give **4** in high yields (Scheme 5). Fortunately, the reaction of **1a** with **3e** did not proceed in the presence of $TrClO_4$ at −50 and even at −20°C. On the other hand, **3f** smoothly reacted with **1a** under the same conditions to give α-propargyl alcohol **14** in 77% yield after the removal of the silyl groups by the treatment with tetrabuthylammonium fluoride (TBAF). These results show that bissilylallene **3f** possesses higher reactivity toward electrophiles than monosilylallene **3e**.

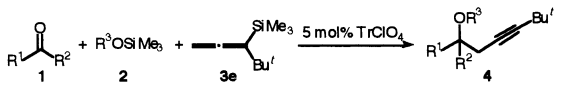
Table 2. Three-component condensation reaction of benzaldehyde **1a**, methoxytrimethylsilane **2a**, and allenyltrimethylsilane **3**

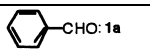
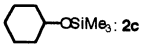
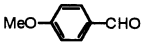
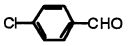
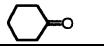


R in **3**	Lewis acid	Temperature (°C)	Time (h)	Yield (%)[a]		
				4	**7**	**8**
Me:**3b**	$TrClO_4$	−20	1.0	8[b]	0	9[b]
	TMSOTf	−20	1.0	12[b]	0	16[b]
	TMSOTt[c]	−78	1.5	17[b]	15[b]	4[b]
Et:**3c**	$TrClO_4$	−20	1.0	5[b]	0	8[b]
Pr^i:**3d**		−20	21.0	67	0	0
Bu^t:**3e**		−50	8.5	93	0	0
3e		−20	1.5	81	0	0
$SiMe_2Ph$:**3f**		−20	8.0	60[d,e] (R=$SiMe_3$/$SiMe_2Ph$=52/48)[f]	0	0
3f	TMSOTf	−20	5.0	49[d] (R=$SiMe_3$/$SiMe_2Ph$=50/50)[f]	0	0
3f	$TrClO_4$	−78	7.0	70[d] (R=$SiMe_3$/$SiMe_2Ph$=54/46)[f]	0	0
3f[g]		−78	1.0	46[d,h]	0	0

The reaction was carried out in CH_2Cl_2 ([**1a**]$_0$=[**2a**]$_0$=[**3**]$_0$=0.5 M).
[a] Isolated yield.
[b] ^1H NMR yield.
[c] 100 mol% of TMSOTf was used.
[d] Isolated yield after desilylation.
[e] Dimethylphenyl-1-propynyl silane was also obtained in 15% yield.
[f] The ratio was determined by ^1H NMR.
[g] 1.5 equiv. of **3f** was used.
[h] 1-Phenyl-3-butyn-1-ol (**14**) was also obtained in 16% yield.

Table 3. Three-component condensation reaction of carbonyl compounds **1**, alkoxytrimethylsilanes **2**, and 1-Bu^t-allenyltrimethylsilane **3e**



Entry	1	2	Conditions	Yield (%)[a]
1	 CHO: **1a**	$MeOSiMe_3$:**2a**	−50°C, 8.5 h	93
2	**1a**	 $OSiMe_3$: **2b**	−50°C, 15 h	84
3	**1a**	 $OSiMe_3$: **2c**	−20°C, 42 h	91
4	 MeO, CHO	**2a**	−50°C, 25 h and −20°C, 8.5 h	64
5	 Cl, CHO	**2a**	−50°C, 8.5 h	89
6	 CHO	**2b**	−20°C, 20 h	38
7	 O	**2a**	−20°C, 14 h; 0°C, 7 h and rt 22 h	12

The reaction was carried out with 5 mol% of $TrClO_4$ in CH_2Cl_2 ($[\mathbf{1}]_0=[\mathbf{2}]_0=[\mathbf{3e}]_0=0.5$ M).
[a] Isolated yield.

Consequently, **3e** (R=Bu^t) was suited for the three-component reaction because **3e** reacted only with acetal even in the presence of aldehyde.

2.3. Reaction of aldehyde, alkoxysilane, and allenylsilanes

To establish the optimal condition for the three-component condensation of **1**, **2**, and **3**, the reactions of benzaldehyde **1a**, methoxytrimethylsilane **2a**, and a variety of **3** were carried out (Table 2). In analogy with the reaction of acetal **5** with a variety of **3**, allenylsilanes **3b**, **3c** (R=Me, Et) resulted in **4** and **8** in low yields, as well as polymeric compounds, whereas **3d**, **3e**, and **3f** (R=Pr^i, Bu^t, $PhMe_2Si$) having bulky substituents did **4** in good yields, respectively. In the reactions of **1a**, **2a** and **3f** at −20°C, the yield of **4** was moderate irrespective of the catalysts $TrClO_4$ or TMSOTf, and dimethylphenyl-1-propynylsilane was obtained as a by-product.[15a] The reaction at −78°C depressed this side reaction to increase the yield of **4**. There was no selectivity of the silyl groups which were eliminated during reaction; this might be because there was no π-face selectivity at the γ-carbon of **3f**, if **3f** undergoes anti S'_E reaction like allylsilanes.[21] Me_3Si-substituted-**4** and $PhMe_2Si$-substituted-**4** were obtained in the ratio about 1:1. It should be noted that **3f**, which can react not only with acetal but also with the aldehyde, gave the three-component condensed product **4** without the formation of the adduct **14** of **3f** and aldehyde **1a**. This implies that the reaction of **3f** with acetal is faster than that with aldehyde. In the reaction using 1.5 equiv. of **3f**, however, **14** was obtained in 16% yield to decrease the yield of **4**.

With the optimized conditions in hand, we next carried out the reaction of a variety of **1**, **2**, and **3e**. The results are summarized in Table 3. In the reaction of **1a**, **2**, and **3e**, silyl ethers **2a**, **2b** of primary alcohols resulted in the corresponding **4** in good yields at −50°C, but the reaction of secondary **2c** required raising reaction temperature for obtaining **4** in high yield (entries 1–3). Regarding the substituent effects of aromatic aldehydes, the electron-withdrawing group was more effective for obtaining **4** than the electron-donating group (entry 4 vs. 5). The reaction of aliphatic aldehyde or ketone proceeded slowly, and the corresponding **4** was obtained in low yields even at higher temperature and longer time (entries 6, 7).

3. Conclusions

Three-component reaction of aldehydes **1**, alkoxysilanes **2**, and allenylsilanes **3** was studied. The substituents at the α-position of **3** were found to affect the reaction strongly; bulky substituents such as the *tert*-butyl and isopropyl groups made the three-component reaction proceed smoothly to give α-propargyl ethers **4** in good yields, whereas the methyl- and ethyl-substituted **3** gave cyclopropyl ketones and α,β-unsaturated ketones as by-products. The reaction developed here would apply to the three-component polycondensation of dialdehydes, diol disilyl ethers, and **3** having bulky substituents, which would yield functional polyethers having the propargyl side chains in one-pot. The study along this line is in progress.

4. Experimental

4.1. General

All reactions were carried out under argon atmosphere. Column chromatography was carried out on Merck silica gel 60 using hexane and a hexane/diethyl ether gradient as eluent. The purity of new compounds was confirmed by elemental analysis. ^{1}H NMR spectra were obtained on a JEOL A-500 and FX-200 operating in the pulsed Fourier transform (FT) modes with tetramethylsilane (TMS) as an internal standard. ^{13}C NMR spectra were also obtained on a JEOL A-500 and FX-200 operating in the FT modes with TMS as an internal standard. IR spectra were recorded on a Hitachi 270-30 and JASCO FT/IR-410. Isolation of some products was carried out with a recycling preparative high-performance liquid chromatography (HPLC) Japan Analytical Industry LC-908 (eluent, chloroform) using two Tosoh TSK gel G2000H columns. Elemental analyses were performed by Perkin-Elmer 2400 II CHN. Commercially available dry dichloromethane and tetrahydrofuran were used as received. Benzaldehyde **1a**, *p*-anisaldehyde,

4-chlorobenzaldehyde, propionaldehyde, isobutyraldehyde, cyclohexanone, methoxytrimethylsilane **2a**, benzaldehyde dimetyl acetal **5**, and TMSOTf were used as received. $TrClO_4$ was prepared from triphenylmethanol and 70% perchloric acid according to the reported procedure.[22] Octyloxytrimethylsilane **2b** was prepared from octanol, 1,1,1,3,3,3-hexamethyldisilazane (HMDS), and a catalytic amount of chlorotrimethylsilane. Cyclohexyloxytrimethylsilane was prepared from cyclohexanol, HMDS, and a catalytic amount of saccharin.[23] Trimethylsilylallene **3a** was prepared from 3-trimethylsilyl-2-propyn-1-ol and *o*-nitrobenzenesulfonylhydrazide in the presence of triphenylphosphine and diethylazodicarboxylate in CH_2Cl_2.[24] α-Substituted trimethylsilylallene **3b**–**3e** were prepared from the corresponding organoheterocuprates and 3-trimethylsilyl-2-propyn-1-mesylates.[25]

4.1.1. Preparation of 3f. THF (33 mL) was added to the flask which was charged with lithium (0.84 g, 121.6 mmol), followed by cooling the solution to 0°C.[26] Dimethylphenylsilyl chloride (9.3 mL, 55.4 mmol) was added to the flask at 0°C. The resulting red solution was transferred by cannula into a slurry of CuCN (4.95 g, 55.2 mmol) in THF (10 mL) at −78°C. The reaction mixture was stirred for 10 min and warmed up to −20°C over 30 min, and then cooled again to −78°C. BF_3–OEt_2[27,28] (7.0 mL, 55.2 mmol) was added and stirred for 10 min at −78°C, and a solution of 3-trimethylsilyl-2-propyn-1-mesylate (10.36 g, 50.2 mmol) in THF (50 mL) was added. After stirring for 3 h at −78°C, the reaction mixture was poured into a saturated NH_4Cl solution, and diluted with hexane. The black emulsion was filtered through Celite. The organic layer was washed with saturated NH_4Cl solution, and the aqueous layer was extracted with hexane. The organic layer was combined and dried over $MgSO_4$. The solution was filtered and concentrated in vacuo. The residue was purified by column chromatography on silica gel, followed by HPLC to afford **3f** (1.70 g, 14%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55–7.49 (m, 2H), 7.36–7.30 (m, 3H), 3.94 (s, 2H), 0.41 (s, 6H), 0.00 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.6, 139.0, 134.0, 129.1, 127.7, 59.4, 46.3, −0.1, −1.5; IR (neat) 3069, 2958, 2898, 1912, 1543, 1249, 776, 699 cm^{-1}. Anal. Calcd for $C_{14}H_{22}Si_2$: C, 68.22; H, 9.00. Found: C, 68.01; H, 8.70.

4.1.2. Reaction of 5 with 3a. A round-bottomed flask, equipped with a three-way stopcock, was charged with $TrClO_4$ (0.017 g, 0.05 mmol) and purged with argon. CH_2Cl_2 (1.0 mL) was added to the flask, followed by cooling the solution to −20°C. A solution of **5** (0.152 g, 1.0 mmol) in CH_2Cl_2 (0.5 mL) was added at −20°C. After 5 min, a solution of **3a** (0.112 g, 1.0 mmol) in CH_2Cl_2 (0.4 mL) was added. After 3 h, a solution of $TrClO_4$ (0.153 g, 0.45 mmol) in CH_2Cl_2 (1.5 mL) was added at −20°C. The solution was stirred at −20°C for 2 h. The reaction mixture was quenched with a few drops of ammoniacal methanol. The reaction mixture was diluted with diethyl ether and washed with water. The organic layer was dried over $MgSO_4$. The solution was filtered and concentrated in vacuo. The residue was purified by column chromatography on silica gel, followed by HPLC to afford methyl triphenylmethyl ether[15] (0.062 g, 23%), 4-methoxy-4-phenyl-1-butyne **4a** (0.005 g, 3%), and 4-methoxy-4-phenyl-1-trimethylsilyl-1-butyne **6** (0.047 g, 20%). **4a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38–7.31 (br s, 5H), 4.31 (dd, *J*=6.3, 6.8 Hz, 1H), 3.28 (s, 3H), 2.68 (ddd, *J*=2.8, 6.8, 16.8 Hz, 1H), 2.56 (ddd, *J*=2.8, 6.3, 16.8 Hz, 1H), 1.98 (t, *J*=2.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.5, 128.4, 128.1, 126.7, 82.0, 80.9, 69.9, 57.0, 28.0; IR (neat) 3293, 2935, 2824, 2121, 1602, 1103, 756, 701 cm^{-1}. Anal. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.86; H, 7.50. **6**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36–7.24 (m, 5H), 4.29 (dd, *J*=6.3, 6.8 Hz, 1H), 3.28 (s, 3H), 2.72 (dd, *J*=6.3, 16.6 Hz, 1H), 2.55 (dd, *J*=6.8, 16.6 Hz, 1H), 0.11 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.7, 128.3, 128.0, 126.8, 103.5, 86.7, 82.3, 57.1, 29.5, 0.04; IR (neat) 2959, 2179, 1249, 1104, 758, 700 cm^{-1}. Anal. Calcd for $C_{14}H_{20}OSi$: C, 72.36; H, 8.67. Found: C, 72.29; H, 8.86.

4.1.3. Reaction of 5 with 3b. A solution of TMSOTf (1.8 mL, 10.0 mmol) in CH_2Cl_2 (5.0 mL) was added to a flask, followed by cooling to −78°C. A solution of **5** (1.52 g, 10.0 mmol) and **3b** (1.26 g, 10.0 mmol) in CH_2Cl_2 (5.0 mL) was added at −78°C. The solution was stirred at −78°C for 1.5 h. The reaction mixture was quenched with saturated $NaHCO_3$ solution, followed by dilution with diethyl ether. The organic layer was washed with water and dried over $MgSO_4$. The solution was filtered and concentrated in vacuo. The residue was purified by column chromatography on silica gel, followed by HPLC to afford 5-methoxy-5-phenyl-2-pentyne **4b** (0.240 g, 14%), methyl 2-phenyl-1-trimethylsilylcyclopropyl ketone **7b** (0.711 g, 31%), and 3-(2-methoxy-2-phenylethyl)-4-phenyl-3-buten-2-one **8b** (0.324 g, 23%). **4b**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.32 (br s, 5H), 4.25 (dd, *J*=6.1, 6.8 Hz, 1H), 3.25 (s, 3H), 2.69–2.41 (m, 2H), 1.74 (t, *J*=2.6 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 141.0, 128.3, 127.8, 126.7, 82.5, 77.3, 75.5, 56.9, 28.3, 3.5; IR (neat) 3022, 2974, 2914, 1599, 1095, 696 cm^{-1}. Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.43; H, 8.26. **7b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28–7.19 (m, 5H), 2.58 (dd, *J*=6.4, 8.8 Hz, 1H), 2.16 (s, 3H), 1.71 (dd, *J*=4.7, 8.8 Hz, 1H), 1.42 (dd, *J*=4.7, 6.4 Hz, 1H), −0.19 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.3, 137.9, 129.8, 128.1, 127.0, 31.6, 30.9, 27.5, 14.8, −0.8; IR (neat) 2954, 2898, 1672, 1603, 1252, 771, 700 cm^{-1}. Anal. Calcd for $C_{14}H_{20}OSi$: C, 72.36; H, 8.67. Found: C, 72.05; H, 8.74. **8b**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.55 (s, 1H), 7.48–7.22 (m, 10H), 4.42 (dd, *J*=5.4, 8.6 Hz, 1H), 3.16 (s, 3H), 3.00 (dd, *J*=8.6, 13.6 Hz, 1H), 2.82 (dd, *J*=5.4, 13.6 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.5, 142.0, 141.6, 139.3, 135.5, 129.3, 128.5, 128.4, 128.3, 127.5, 126.6, 82.3, 56.9, 35.5, 26.3; IR (neat) 3022, 2974, 2920, 1659, 1101, 732, 690 cm^{-1}. Anal. Calcd for $C_{19}H_{20}O_2$: C, 81.40; H, 7.19. Found: C, 81.26; H, 7.28.

4.1.4. Reaction of 5 with 3c. In the presence of TMSOTf (1.62 mL, 9.0 mmol), the reaction of **5** (1.37 g, 9.0 mmol) with **3c** (1.26 g, 9.0 mmol) was performed in a similar manner as above to yield 1-methoxy-1-phenyl-3-hexyne **4c** (0.058 g, 4%), ethyl 2-phenyl-1-trimethylsilylcyclopropyl ketone **7c** (0.117 g, 6%), 2-(2-methoxy-2-phenylethyl)-1-phenyl-1-pentene-3-one **8c** (0.471 g, 38%). **4c**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38–7.23 (m, 5H), 4.26 (dd, *J*=6.0, 6.3 Hz, 1H), 3.27 (s, 3H), 2.64 (dd, *J*=6.0, 16.5 Hz, 1H), 2.50 (dd, *J*=6.3, 16.5 Hz, 1H), 2.13 (q, *J*=7.5 Hz, 2H), 1.07 (t, *J*=7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.1, 128.3, 127.9, 126.8, 83.6, 82.7, 75.8, 57.1, 28.4, 14.2, 12.5;

IR (neat) 2975, 2932, 1600, 1102, 757, 700 cm^{-1}. Anal. Calcd for $C_{13}H_{16}O$: C, 82.94; H, 8.57. Found: C, 82.53; H, 8.75. **7c**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.28–7.20 (m, 5H), 2.51 (q, J=7.4 Hz, 2H), 2.49 (dd, J=5.8, 10.6 Hz, 1H), 1.73 (dd, J=4.6, 10.6 Hz, 1H), 1.39 (dd, J=4.6, 5.8 Hz, 1H), 1.10 (t, J=7.4 Hz, 3H), −0.19 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 211.9, 138.1, 129.8, 128.1, 127.0, 33.2, 31.0, 30.7, 14.2, 8.5, −0.7; IR (neat) 3061, 3028, 2974, 2899, 1673, 1603, 1249, 765, 700 cm^{-1}. Anal. Calcd for $C_{15}H_{22}OSi$: C, 73.11; H, 9.00. Found: C, 73.14; H, 9.00. **8c**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.52 (s, 1H), 7.44 (d, J=7.5 Hz, 2H), 7.38–7.22 (m, 8H), 4.40 (dd, J=5.6, 8.6 Hz, 1H), 3.16 (s, 3H), 3.01 (dd, J=8.6, 13.3 Hz, 1H), 2.84 (dd, J=5.6, 13.3 Hz, 1H), 2.80 (q, J=7.3 Hz, 2H), 1.15 (t, J=7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.4, 142.1, 140.1, 139.1, 135.7, 129.3, 128.40, 128.36, 127.6, 126.7, 82.4, 57.0, 35.8, 31.2, 8.8; IR (neat) 3028, 2977, 2936, 1667, 1625, 1102, 754, 700 cm^{-1}. Anal. Calcd for $C_{20}H_{22}O_2$: C, 81.60; H, 7.53. Found: C, 81.24; H, 7.42.

4.1.5. Reaction of 5 with 3e. In the presence of $TrClO_4$ (0.051 g, 0.15 mmol), the reaction of **5** (0.459 g, 3.0 mmol) with **3e** (0.505 g, 3.0 mmol) was performed in a similar manner to the reaction of **5** with **3a**. The solution was stirred at −50°C for 9.5 h. The reaction mixture was quenched with a few drops of ammoniacal methanol. The solvent was evaporated and the residue was purified by column chromatography on silica gel to afford 1-methoxy-5,5-dimethyl-1-phenyl-3-hexyne **4e** (0.630 g, 99%): ^1H NMR (200 MHz, $CDCl_3$) δ 7.32 (br s, 5H), 4.23 (dd, J=6.3, 7.2 Hz, 1H), 3.27 (s, 3H), 2.66 (dd, J=6.3, 16.3 Hz, 1H), 2.46 (dd, J=7.2, 16.3 Hz, 1H), 1.13 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 141.1, 128.1, 127.8, 126.9, 90.9, 82.8, 74.8, 57.0, 31.2, 28.2, 27.3; IR (neat) 2966, 2931, 2866, 1601, 1104, 753, 697 cm^{-1}. Anal. Calcd for $C_{15}H_{20}O$: C, 83.29; H, 9.32. Found: C, 83.06; H, 9.48.

4.1.6. Reaction of 5 with 3f. In the presence of $TrClO_4$ (0.008 g, 0.025 mmol), the reaction of **5** (0.076 g, 0.5 mmol) with **3f** (0.123 g, 0.5 mmol) was performed in a similar manner to the reaction of **5** with **3a**. The solution was stirred at −20°C for 3.5 h. The reaction mixture was quenched with a few drops of ammoniacal methanol. The solvent was evaporated and the residue was purified by column chromatography on silica gel, followed by HPLC to afford a mixture of **6** and 1-(dimethylphenylsilyl)-4-methoxy-4-phenyl-1-butyne **4f**. **4f**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.55–7.52 (m, 2H), 7.36–7.30 (m, 8H), 4.32 (dd, J=6.3, 7.2 Hz, 1H), 3.28 (s, 3H), 2.79 (dd, J=6.3, 16.8 Hz, 1H), 2.62 (dd, J=7.2, 16.8 Hz, 1H), 0.34 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.3, 138.2, 134.5, 130.0, 129.1, 128.7, 128.6, 127.6, 106.1, 85.4, 83.0, 57.8, 30.2, 0.00; IR (neat) 3067, 2959, 2932, 2906, 2179, 1589, 1249, 1104, 754, 700 cm^{-1}. Anal. Calcd for $C_{19}H_{22}OSi$: C, 77.50; H, 7.53. Found: C, 77.54; H, 7.61. The mixture was dissolved in THF (2.0 mL), and 1.0 M TBAF in THF (0.5 mL, 0.5 mmol) was added. After 1 min, the solution was filtered through silica gel. The solvent was evaporated and the residue was purified by column chromatography on silica gel to afford **4a** (0.068 g, 85%).

4.1.7. Reaction of 1a with 3f. In the presence of $TrClO_4$ (0.017 g, 0.05 mmol), the reaction of **1a** (0.106 g, 1.0 mmol) with **3f** (0.247 g, 1.0 mmol) was performed in a similar manner to the reaction of **5** with **3a**. The solution was stirred at −20°C for 6.5 h. The reaction mixture was quenched with a few drops of ammoniacal methanol. After purification by column chromatography, the residue was treated with 1.0 M TBAF in THF (1.5 mL, 1.5 mmol) to afford 1-phenyl-3-butyn-1-ol **14** (0.112 g, 77%): ^1H NMR (500 MHz, $CDCl_3$) δ 7.43–7.27 (m, 5H), 4.88 (t, J=6.3 Hz, 1H), 2.65 (dd, J=2.3, 6.3 Hz, 2H), 2.49–2.28 (br, 1H), 2.07 (t, J=2.3 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.4, 128.5, 128.0, 125.7, 80.7, 72.3, 71.0, 29.5; IR (neat) 3385, 3294, 3031, 2911, 2121, 1600, 1051, 755, 701 cm^{-1}. Anal. Calcd for $C_{10}H_{10}O$: C, 82.16; H, 6.90. Found: C, 82.18; H, 7.00.

4.2. General procedure for the reaction of 1, 2, and 3

A round-bottomed flask, equipped with a three-way stopcock, was charged with $TrClO_4$ (0.017 g, 0.05 mmol) and purged with argon. CH_2Cl_2 (1.0 mL) was added to the flask, followed by cooling the solution to −20 or −50°C. A solution of **1** (1.0 mmol) and **2** (1.0 mmol) in CH_2Cl_2 (0.5 mL) was added at −20 or −50°C. After 5 min, a solution of **3** (1.0 mmol) in CH_2Cl_2 (0.5 mL) was added. The solution was stirred at −20 or −50°C. The reaction mixture was quenched with a few drops of ammoniacal methanol. The solvent was evaporated and the residue was purified by column chromatography on silica gel to afford **4**.

4.2.1. 1-Methoxy-5-methyl-1-phenyl-3-hexyne 4d. 0.113 g, 67%. ^1H NMR (200 MHz, $CDCl_3$) δ 7.33 (br s, 5H), 4.25 (dd, J=6.3, 6.6 Hz, 1H), 3.27 (s, 3H), 2.75–2.39 (m, 3H), 1.09 (d, J=6.6 Hz, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 141.0, 128.2, 127.8, 126.8, 88.0, 82.7, 75.6, 57.0, 28.3, 23.2, 20.5; IR (neat) 3032, 2968, 2931, 1601, 1103, 756, 700 cm^{-1}. Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 82.74; H, 9.04.

4.2.2. Dimethylphenyl-1-propynylsilane. 0.013 g, 15%. ^1H NMR (500 MHz, $CDCl_3$) δ 7.64–7.62 (m, 2H), 7.37–7.36 (m, 3H), 1.93 (s, 3H), 0.39 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.7, 133.8, 129.4, 128.0, 105.0, 82.0, 5.1, −0.6; IR (neat) 3069, 2960, 2917, 2183, 1250, 730, 700 cm^{-1}. Anal. Calcd for $C_{11}H_{14}Si$: C, 75.79; H, 8.10. Found: C, 75.96; H, 7.80.

4.2.3. 5,5-Dimethyl-1-octyloxy-1-phenyl-3-hexyne. 0.265 g, 84%. ^1H NMR (500 MHz, $CDCl_3$) δ 7.35–7.21 (m, 5H), 4.32 (t, J=6.8 Hz, 1H), 3.40–3.29 (m, 2H), 2.63 (dd, J=6.8, 16.3 Hz, 1H), 2.44 (dd, J=6.8, 16.3 Hz, 1H), 1.59–1.54 (m, 2H), 1.38–1.21 (m, 10H), 1.14 (s, 9H), 0.87 (t, J=7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.9, 128.0, 127.7, 126.7, 90.6, 81.1, 75.1, 69.4, 31.8, 31.2, 29.9, 29.4, 29.3, 28.5, 27.3, 26.2, 22.6, 14.1; IR (neat) 2928, 2857, 1602, 1102, 755, 700 cm^{-1}. Anal. Calcd for $C_{22}H_{34}O$: C, 84.02; H, 10.90. Found: C, 83.78; H, 11.17.

4.2.4. 1-Cyclohexyloxy-5,5-dimethyl-1-phenyl-3-hexyne. 0.258 g, 91%. ^1H NMR (500 MHz, $CDCl_3$) δ 7.38–7.22 (m, 5H), 4.51 (dd, J=6.3, 7.3 Hz, 1H), 3.27–3.21 (m, 1H), 2.57 (dd, J=7.3, 16.5 Hz, 1H), 2.40 (dd, J=6.3, 16.5 Hz, 1H), 2.00–1.92 (m, 1H), 1.81–1.63 (m, 3H), 1.52–1.27 (m, 3H), 1.23–1.11 (m, 12H); ^{13}C NMR (125 MHz,

$CDCl_3$) δ 142.8, 128.0, 127.4, 126.6, 90.3, 78.0, 75.59, 75.55, 33.3, 31.6, 31.2, 29.1, 27.3, 25.8, 24.2, 24.0; IR (neat) 2931, 2857, 1601, 1452, 1089, 755, 700 cm^{-1}. Anal. Calcd for $C_{20}H_{28}O$: C, 84.45; H, 9.92. Found: C, 84.81; H, 10.13.

4.2.5. 1-Methoxy-1-(4-methoxyphenyl)-5,5-dimethyl-3-hexyne. 0.156 g, 64%. ^1H NMR (500 MHz, $CDCl_3$) δ 7.25 (d, J=8.8 Hz, 2H), 6.88 (d, J=8.8 Hz, 2H), 4.19 (dd, J=5.8, 7.2 Hz, 1H), 3.81 (s, 3H), 3.25 (s, 3H), 2.64 (dd, J=5.8, 16.1 Hz, 1H), 2.44 (dd, J=7.2, 16.1 Hz, 1H), 1.13 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.2, 133.1, 128.0, 113.5, 90.8, 82.3, 74.9, 56.8, 55.3, 31.2, 28.2, 27.3; IR (neat) 2967, 2857, 1601, 1452, 1089, 755, 700 cm^{-1}. Anal. Calcd for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 78.12; H, 8.96.

4.2.6. 1-(4-Chlorophenyl)-1-methoxy-5,5-dimethyl-3-hexyne. 0.224 g, 89%. ^1H NMR (500 MHz, $CDCl_3$) δ 7.32 (d, J=8.5 Hz, 2H), 7.27 (d, J=8.5 Hz, 2H), 4.21 (dd, J=5.6, 7.6 Hz, 1H), 3.26 (s, 3H), 2.64 (dd, J=5.6, 16.5 Hz, 1H), 2.44 (dd, J=7.6, 16.5 Hz, 1H), 1.13 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.5, 133.4, 128.7, 128.3, 91.3, 82.0, 74.2, 57.0, 31.1, 28.0, 27.3; IR (neat) 2967, 2929, 1598, 1107, 825 cm^{-1}. Anal. Calcd for $C_{15}H_{19}ClO$: C, 71.84; H, 7.64. Found: C, 72.14; H, 7.94.

4.2.7. 2,2-Dimethyl-6-octyloxy-3-octyne. 0.015 g, 38%. ^1H NMR (500 MHz, $CDCl_3$) δ 3.55 (dt, J=6.5, 9.3 Hz, 1H), 3.40 (dt, J=6.7, 9.3 Hz, 1H), 3.28–3.23 (m, 1H), 2.38 (dd, J=5.5, 16.5 Hz, 1H), 2.22 (dd, J=6.8, 16.5 Hz, 1H), 1.22–1.71 (m, 14H), 1.19 (s, 9H), 0.93 (t, J=7.3 Hz, 3H), 0.88 (t, J=7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 90.1, 79.8, 75.6, 70.0, 31.8, 31.3, 30.2, 29.9, 29.5, 29.3, 26.9, 26.2, 23.9, 22.6, 14.1, 9.6; IR (neat) 2927, 2857, 1111 cm^{-1}. Anal. Calcd for $C_{19}H_{34}O$: C, 81.13; H, 12.86. Found: C, 81.06; H, 13.14.

4.2.8. 1-(4,4-Dimethyl-2-pentynyl)-1-methoxycyclohexane. 0.025 g, 12%. ^1H NMR (500 MHz, $CDCl_3$) δ 3.21 (s, 3H), 1.87 (s, 2H), 1.75–1.69 (m, 2H), 1.61–1.42 (m, 8H), 1.20 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 91.1, 74.9, 74.8, 48.6, 33.2, 31.2, 27.9, 27.4, 25.7, 21.8; IR (neat) 2967, 2932, 2861, 1455, 1081 cm^{-1}. Anal. Calcd for $C_{14}H_{24}O$: C, 80.71; H, 11.61. Found: C, 80.52; H, 11.37.

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