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A Convenient Method for the Preparation of Secondary Propargylic Ethers. The Reactions of Acetals with 1-Trimethylsilyl-1-alkynes Promoted by the Combined Use of Catalytic Amounts of Tin(IV) Chloride and Zinc Chloride

Masaji Hayashi,* Atsuro Inubushi, and Teruaki Mukaiyama
Department of Applied Chemistry, Faculty of Science, Science University of Tokyo,
Kagurazaka, Shinjuku-ku, Tokyo 162
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In the coexistence of catalytic amounts of $SnCl_4$ and $ZnCl_2$, acetals undergo a coupling with 1-trimethylsilylalkynes to give secondary propargylic ethers in good yields. Similarly, propargylic ethers are directly produced from aldehydes by the treatment with alkoxytrimethylsilanes and 1-trimethylsilylalkynes under the same conditions. This catalyst system also efficiently promotes aldol reaction of silyl enol ethers with acetals or aldehydes, and the Michael reaction of silyl enol ethers with α,β-unsaturated ketones.

Over the years there have been a large body of efforts directed to the construction of carbon skeleton by employment of various kinds of silyl carbon nucleophiles, and those to develop catalysts which efficiently promote the coupling with electrophiles have been extensively studied.[1)] Recently, various carbon–carbon bond forming reactions[2)] were shown to be achieved by the use of a catalytic amount of Lewis acids such as trityl salts developed by us[2b)] for example, and it becomes apparent that a stoichiometric amount of Lewis acid, such as $TiCl_4$ or $SnCl_4$,[3)] is not necessarily required in these types of acid-promoted reactions of carbonyl compounds with silyl nucleophiles. During our continuing work on the development of efficient promotors, a convenient carbon–carbon bond forming reaction was developed by the combined use of catalytic amounts of various neutral molecules and weakly acidic Lewis acids such as TrCl–$SnCl_2$, TMSCl–$SnCl_2$.[4)] Thus divalent tin is able to accept halogen ion from the above mentioned active organic halide or silyl halide to generate cationic species (Tr^+, TMS^+-like cation etc.). In an extension of this concept, we considered that higher capability of $SnCl_2$ could accept halogen ion from the other Lewis acid such as $TiCl_4$ to generate $TiCl_3^+$–$SnCl_3^-$, or by the combination of Lewis acids such as $ZnCl_2$–$SnCl_4$ to generate $ZnCl^+$–$SnCl_5^-$, and that such species should be applicable for the activation of electrophiles, as promotors, in various reactions with moderately reactive silyl nucleophiles.

We screened further more effective combination of various Lewis acids and it was found that the combined use of $SnCl_4$ and $ZnCl_2$ is quite efficient for a coupling reaction of acetals with 1-trimethylsilyl-1-alkynes, as we have briefly reported in a preliminary communication.[5)] We now describe in full the results of our investigation on the above coupling reaction using this new catalyst system and further the application to aldol and the Michael reactions.

Results and Discussion

Ethynylation (1). The reaction of 1-trimethylsilyl-1-alkynes with acetals generally requires an equimolar amount or a large exess of Lewis acids, such as $TiCl_4$,[6)] and it was also shown that the above mentioned reaction was hardly promoted by a catalytic amount of Lewis acid. In the first place, we examined the reaction of 3-phenylpropanal dimethyl acetal (**2**) with (trimethylsilylethynyl)benzene (**1**) in the presence of 10 mol% each of two metal salts (A and B), as shown in Table 1. The reactions were carried out as follows: A suspension of 10 mol% each of catalysts A and B in CH_2Cl_2, was stirred for 30 min at room temperature. After cooling to 0 °C, **2** was added, followed by the addition of **1** at the same temperature, and the reaction mixture was stirred at 0 °C. Usual workup of the

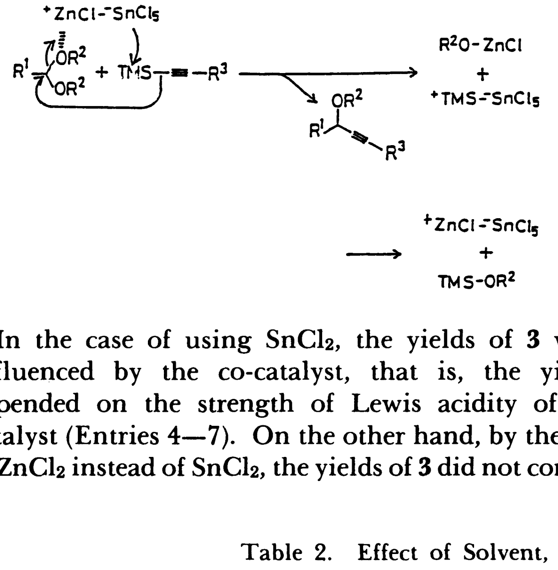
Table 1. Ethynylation of 3-Phenylpropanol Dimethyl Acetal with (Trimethylsilylethynyl)benzene in the Presence of Various Combination of Metal Salts[a)]

Entry No.	Catalyst[b)] A	Catalyst[b)] B	Time/h	Yield/%[c)]
1	TrCl	$SnCl_2$	24	Trace
2	TMSCl	$SnCl_2$	3.5	Trace
3	SnF_2	$TiCl_4$	24	6
4	$SnCl_2$	$TiCl_4$	24	47
5	$SnCl_2$	$SnCl_4$	3.5	39
6	$SnCl_2$	$TiCl_2(OTf)_2$	24	50
7	$SnCl_2$	$ZnCl_2$	2.5	0
8	$SnBr_2$	$TiCl_4$	24	33
9	$ZnCl_2$	$TiCl_4$	3.5	49
10	$ZnCl_2$	$SnCl_4$	3.5	68
11	$ZnBr_2$	$SnCl_4$	3.5	53
12	$SnCl_2$	—	3.5	0
13	$ZnCl_2$	—	3.5	0
14	$TiCl_4$	—	24	7
15	$SnCl_4$	—	3.5	30

a) Reaction were carried out in CH_2Cl_2 with 1.0 equivalent of **1**. b) 10 mol% of catalysts were used except for Entry 15. c) Isolated yield.

reaction mixture afforded 1,5-diphenyl-3-methoxy-1-pentyne (**3**).

Conventionally employed promotors, such as TrCl–$SnCl_2$ or TMSCl–$SnCl_2$[4] were not effective in the above mentioned reaction (Entries 1 and 2). The results indicate that these catalysts are insufficient to activate the acetal to produce the coupling product with **1**. Now, from the point of view that $SnCl_2$ is a potential metal salt to accept halogen ion from organic halide or silyl halide, it was assumed that more active cationic species than Tr^+–$SnCl_3^-$ or TMS^+–$SnCl_3^-$ should be generated by the combined use of strong Lewis acids ($TiCl_4$, $SnCl_4$, etc.) and weak Lewis acids ($SnCl_2$, $ZnCl_2$, etc.). As the result, in almost cases the reactions proceeded effectively to afford the desired product (**3**) in high yields (Entries 3—11). The combination of $SnCl_4$ and $ZnCl_2$ gave the best result concerning the yield of **3**. The mechanism of the reformation of $SnCl_4$–$ZnCl_2$ catalyst system could be explained as follows; In $ZnCl^+$–$SnCl_5^-$-like species initially generated,[7] $ZnCl^+$ activates oxygen atom of the acetal and at the same time $SnCl_5^-$ attacks silicon atom of the 1-trimethylsilyl-1-alkyne to activate the acetylene by way of forming TMS^+–$SnCl_5^-$-like species, which is in turn transformed into TMS–OR^2 and the original catalytic species. In the case of the combined use of $TiCl_4$ and $SnCl_2$, initially $TiCl_3^+$–$SnCl_3^-$-like species will be generated.



In the case of using $SnCl_2$, the yields of **3** were influenced by the co-catalyst, that is, the yields depended on the strength of Lewis acidity of co-catalyst (Entries 4—7). On the other hand, by the use of $ZnCl_2$ instead of $SnCl_2$, the yields of **3** did not consist with the Lewis acidity[7] of the co-catalyst (Entries 9 and 10). As shown in Entries 3,4,8 and 10,11, the substituents of tin(II) or zinc(II) salts remarkably influenced on the turn-over of the catalyst. It is assumed that Sn(II) with more electronegative atom can accept halogen ion from co-catalyst such as $TiCl_4$ to generate $TiCl_3^+$, and that Zn(II) with more electronegative atom as Cl can generate stronger cationic species as $ZnCl^+$, and consequently the oxygen atom of the acetal group would be activated more effectively. In the case of SnF_2, the yield was not so high because of its insolubility to the solvent.

The combination of Zn(II)–Sn(IV) proved better than those of Sn(II)–Sn(IV), Zn(II)–Ti(IV), Sn(II)–Ti(IV) in the present reaction. However, these tendencies can not be explained by considering solely the Lewis acid strength of $SnCl_4$ and $TiCl_4$,[7] and it may be pointed out that the difference of the affinities of central metal as Ti, Si, and Zn toward oxygen atom reflects on the regeneration step of the catalysts. By the use of 20 mol% of $SnCl_4$ as catalyst in the absence of other co-catalyst (Entyl 15), the same reaction resulted in the formation of **3** in a moderate yield.

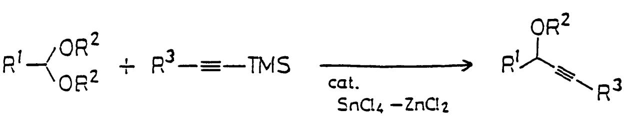
Next, we examied the optimum reaction conditions by using the above reaction as a model, and the results are summarized in Table 2. As shown in the Table, the coupling reaction proceeded effectively in CH_2Cl_2 at 0 °C in the coexistence of 10 mol% each of $SnCl_4$ and $ZnCl_2$. It should be noted that the ratio of $SnCl_4$/$ZnCl_2$ influences the yield of **3**, assuming that the unbalance of the amounts of $SnCl_4$ and $ZnCl_2$ should give rise to decrease in the population of a key species $ZnCl^+$–$SnCl_5^-$.

Then we examined the coupling reaction of various 1-trimethylsilyl-1-alkynes (**5**) with dimethyl acetals (**4**) in the presence of catalytic amounts of $SnCl_4$–$ZnCl_2$ as shown in Table 3, and the corresponding secondary propargylic ethers (**6**) were obtained in good yields. In the case of the reaction of aromatic or conjugated aldehyde dimethyl acetal (Entries 1,10,11), the side reactions forming a dipropargyl derivative (for example, **7** or **8**) took place because of the high reactivities of benzyl or allyl cations. Concerning the effect of acetals, the yield of propargylic ethers indicates a

Table 2. Effect of Solvent, Ratio of $SnCl_4$/$ZnCl_2$ and Temperature

Entry No.	1/2	Solvent	$SnCl_4$/$ZnCl_2$	Temp/°C	Time/h	Yield/%[a]
1	1/1	CH_2Cl_2	10/10	0	3.5	68
2	1/1	CH_3CN	10/10	20	24	9
3	1/1	Et_2O	10/10	20	24	0
4	1/1	Toluene	10/10	20	24	0
5	1/1.5	CH_2Cl_2	10/10	20	3.5	85
6	1/1.5	CH_2Cl_2	20/10	20	3.5	71
7	1/1.5	CH_2Cl_2	10/20	20	3.5	58
8	1/1.5	CH_2Cl_2	10/10	−20	7	74

a) Isolated yield. Yields are based on **1**.



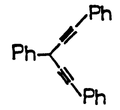
4 5 6

Table 3. Ethynylation of Acetals with 1-Trimethylsilyl-1-alkynes[a]

Entry No.	R^1	R^2	R^3	4/5	Time/h	Yield/%[b]
1	Ph	$\mathrm{CH_3}$	Ph	1/1	3.5	33
2	$\mathrm{Ph(CH_2)_2}$	$\mathrm{CH_3}$	Ph	1.5/1	3.5	85
3[c]	$\mathrm{Ph(CH_2)_2}$	$\mathrm{CH_3}$	$\mathrm{CH_3}$	2/1	3.5	82
4	$\mathrm{Ph(CH_2)_2}$	$\mathrm{CH_3}$	$\mathrm{CH_3(CH_2)_4}$	1.4/1	3.5	78
5	$\mathrm{Ph(CH_2)_2}$	$\mathrm{PhCH_2}$	Ph	1.5/1	3.5	44
6	$\mathrm{PhCH(CH_3)}$	$\mathrm{CH_3}$	Ph	1.5/1	10.5	13
7	$\mathrm{CH_3(CH_2)_7}$	$\mathrm{CH_3}$	Ph	1.5/1	3.5	79
8	$\mathrm{CH_3(CH_2)_7}$	$\mathrm{CH_3}$	$\mathrm{CH_3}$	2/1	3.5	74
9	$\mathrm{CH_3(CH_2)_7}$	$\mathrm{CH_3}$	$\mathrm{CH_3(CH_2)_4}$	1.5/1	48	71
10	$\mathrm{PhCH{=}CH}$	$\mathrm{CH_3}$	Ph	1/1	3.5	29
11	$\mathrm{CH_3CH{=}CH}$	$\mathrm{CH_3}$	Ph	1/1	3.5	15
12	$\mathrm{CH_3}$	$\mathrm{CH_3CH_2}$	Ph	1.5/1	3.5	53

a) Reaction was carried out in CH_2Cl_2 at room temperature in the coexistence of 10 mol% each of $SnCl_4$ and $ZnCl_2$. b) Isolated yield. c) 20 mol% each of $SnCl_4$ and $ZnCl_2$ was used.

tendency to decrease as R^2 substituent becomes more bulky (Entry 12), and cyclic acetals such as 1,3-dioxolane did not react with 1-trimethylsilyl-1-alkynes under the above condition. When benzyl acetal was used as a substrate, unknown side reactions accompanied. The reaction of α-substituted aldehyde dimethyl acetal with **5** was very slow to afford **6** in poor yield (Entry 6). In addition, under the above conditions, silylalkynes having bulky substituents on the silicon atom, such as (triphenylsilylethynyl)benzene, did not react with acetals.



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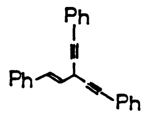

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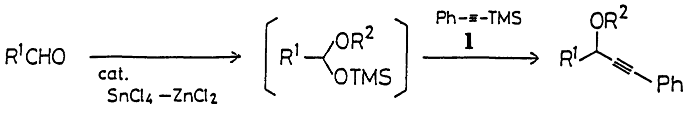
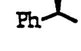
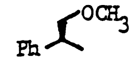
Ethynylation (2). From the synthetic point of view, it is more desirable to prepare the above-mentioned propargylic ethers directly from the corresponding aldehydes. On the basis of such consideration, the reaction of in situ formed hemiacetal-type compounds (**9**) with **5** was examined. As shown in Table 4, in the coexistence of 20 mol% each of $SnCl_4$ and $ZnCl_2$, adducts **9** were initially formed from alkoxytrimethylsilanes and aldehydes, and **9** in turn reacted with **5** to form the desired secondary propargylic ethers **6**. In the case of benzyloxytrimethylsilane, the yield was not so high (Entry 1) and unknown side reactions accompanied as same as the above mentioned reaction.



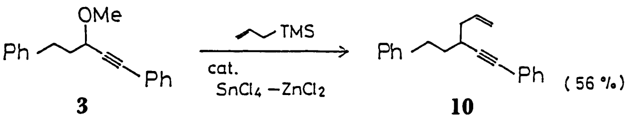
9 6

Table 4. Synthesis of Secondary Propargylic from Aldehydes[a]

Entry No.	R^1	R^2	Time/h	Yield/%[b]
1	$\mathrm{Ph(CH_2)_2}$	$\mathrm{PhCH_2}$	6	67
2	$\mathrm{Ph(CH_2)_2}$	$\mathrm{CH_3}$	6	78
3	$\mathrm{Ph(CH_2)_2}$	$\mathrm{CH_2CH_2}$	6	77
4	$\mathrm{CH_3(CH_2)_5}$	$\mathrm{CH_3}$	6	73
5	$\mathrm{Ph(CH_2)_2}$	 c)	21	37(20%d.e.)
6	$\mathrm{Ph(CH_2)_2}$		22	0

a) Reaction was carried out in CH_2Cl_2 at −78 °C for 4 h, then at room temperature for 6 h in the coexistence of 20 mol% each of $SnCl_4$ and $ZnCl_2$. b) Isolated yield. Yields are based on aldehydes. c) *S*-configuration.

Allylation of Propargylic Ethers. It was reported that allyl ethers reacts with silyl nucleophiles, such as allylsilane[8] or silyl enol ethers,[9] in the presence of a catalytic amount of $TrClO_4$ to result in the formation of a new carbon skeleton having tertiary carbon. These facts and the above-mentioned side reaction to form bis propargyl compounds **7** or **8** suggested us to develop a convenient method for the two carbon–carbon bond formations by one-pot procedure, that is, the secondary propargylic ethers thus obtained had a potentiality to couple with the second nucleophile such as allylsilane. Expectedly, **3** smoothly reacted with allyltrimethylsilane at 0 °C in the coexistance of 20 mol% each of $SnCl_4$ and $ZnCl_2$ to afford the 1,5-enyne compound (**10**) in 56% yield. And **10** was also obtained according to the above-mentioned methods from acetal (**1**) (in 29% yield), from 3-phenylpropanal (in 60% yield) by one-pot procedure.

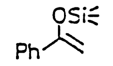
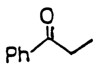
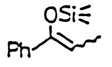
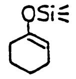
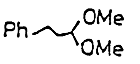


Aldol Reaction. This new catalyst system ($SnCl_4$–$ZnCl_2$) also promoted the aldol reaction of silyl enol ethers and aldehydes or acetals smoothly and some experimental results are shown in Table 5. The ratios of anti/syn (threo/erythro) adducts are slightly different from those in the cases of using other promotors, such as $TrClO_4$,[1] TrCl–$SnCl_2$, or TMSCl–$SnCl_2$.[4]

The Michael Reaction. Tin(IV) chloride and zinc chloride catalyst system also promoted the Michael reaction of silyl enol ethers with α,β-unsaturated ketones as shown in Table 6. The uk (anti) adducts[4] were obtained preferentially similar to the reactions using other promotors (Tr^+ or TMS^+-like cation). These diastereoselectivities are almost the same as consistent with those of Tr^+ or TMS^+-like cation-promoted Michael reactions.

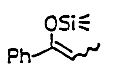
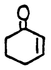
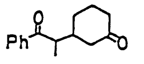
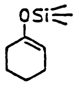
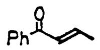
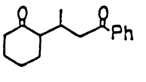
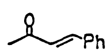
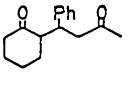
Allylation of Aldehydes. Under the acidic condition, allyltrimethylsilane generally reacts with aldehyde to give a complicated product mixture by the occurrence of further reactions, which contains the reaction of hemiacetal (**11**) formed by the addition of initially formed silyl alkoxide to the starting aldehyde followed by the addition of the allyltrimethylsilane. In contrast, by using the present catalyst system, the desired homoallyl alcohols were obtained in good yields as shown below.

Table 5. Aldol Reaction of Aldehydes or Dimethyl Acetals with Trimethylsilyl Enol Ethers

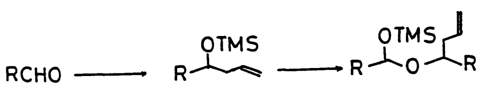
Entry No.	Nucleophiles	Electrophiles	Time/h	Yield/%	Ratio of anti/syn[b]
1			2	65	—
2		PhCHO	2	99	58:42
3		PhCH(OMe)$_2$	4	99	73:27
4		PhCHO	4	83	32:69
5		PhCH(OMe)$_2$	2	87	36:64
6			2	58	89:11
7			2	80	87:13

a) All products gave satisfactory NMR and IR spectra.[3] b) Determined by ^{1}H NMR.[4]

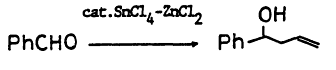
Table 6. Michael Reaction of α,β-Unsaturated Ketones with Trimethylsilyl Enol Ethers

Entry No.	Nuleophile	Electrophile	Products[a]	Time/h	Yielde/%	Ratio of anti/syn[b]
1				4	87	87:23
2				2	84	65:35
3				3	100	55:45

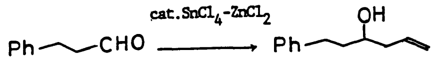
a) All products gave satisfactory NMR and IR spectra. b) Determined by ^{1}H NMR.



11 16



61%



74%

It is concluded that the catalytic use of equimolar amounts of $SnCl_4$ and $ZnCl_2$ effectively promotes the reaction of 1-trimethylsilyl-1-alkynes with acetals, and also secondary propargylic ethers thus obtained are converted into 1,5-enyne compounds by the further reaction with allyltrimethylsilane in the same flask. The present cationic promotors based on the combination of two metal salts will open many synthetic and theoritical possibilities in carbon–carbon bond forming reactions.

Experimental

The IR spectra were determined on Hitachi Model 260-30 spectrometer. The ^1H NMR spectra were recorded with a Hitachi R-24B, a Varian EM-390, and a JEOL GX-400 spectrometers in $CDCl_3$ with trimethylsilane as an internal standard. The mass spectra were taken on a JEOL JMS-D300. Diethyl ether was freshly distilled from sodium benzophenone ketyl. Dichloromethane was distilled from CaH_2 and stored over Molecular Sieve. Purification of products was performed by column chromatography on silica gel (Wakogel C-200, C-300 or Merck, Art. 9385 Kieselgel 60, 230—400 mesh), preparative TLC on silica gel (Wakogel B-5F).

1-Trimethylsilyl-1-alkynes **1a—g** were prepared by trimethylsilylation of the corresponding lithium acetylide (butyllithium and alkynes), and purified by distillation or column chromatography on silica gel. Dimethyl acetals **2a—h** were prepared by transacetalization of the corresponding aldehydes with trimethyl orthoformate in the presence of *p*-TsOH·H_2O.

Preparation of Propargylic Ethers (6). (Table 3) A typical reaction procedure is described for 3-phenylpropanal dimethyl acetal with (trimethylsilylethynyl)benzene (Entry 2): a CH_2Cl_2 (4 ml) suspension of $SnCl_4$ (0.11 mmol) and $ZnCl_2$ (0.11 mmol) was stirred for 30 min at room temperature, to which were added succeccively (trimethylsilylethynyl)benzene (1.0 mmol) in CH_2Cl_2 (3 ml) and 3-phenylpropanal dimethyl acetal (1.5 mmol) in CH_2Cl_2. The reaction mixture was stirred for 3.5 h at the same temperature, then quenched with aqueous solution of sodium hydrogencarbonate. The organic materials were extracted with CH_2Cl_2, and the combined extracts were dried over $MgSO_4$. After evaporation of the solvent, the residue was purified by preparative TLC (silica gel) to afford 1,5-diphenyl-3-methoxy-1-pentyne (**1a**) (0.85 mmol, 85%). IR (neat) 2835, 2240, 1610, 1500 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.87—2.30 (m, 2H), 2.72—2.97 (m, 2H), 3.45 (s, 3H), 4.11 (t, J=6 Hz, 1H), 6.95—7.60 (m, 10H); MS *m/z* 250 (M$^+$). Found: C, 86.29; H, 7.26%. Calcd for $C_{18}H_{18}O$: C, 86.36; H, 7.25%.

Other analysis data are presented: 1,3-Diphenyl-3-methoxy-1-propyne (Entry 1). IR (neat) 2815, 2215, 1600, 1490 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.47 (s, 3H), 5.27 (s, 1H), 7.2—7.6 (9m, 10H); MS, *m/z* 222 (M$^+$).

6-Phenyl-4-methoxy-1-hexyne (Entry 3). IR (neat) 2825, 2235, 1610, 1500; ^1H NMR ($CDCl_3$) δ=1.84 (d, 3H, J=1.8 Hz), 1.75—2.20 (m, 2H), 2.53—2.97 (m, 2H), 3.53 (s, 3H), 3.63—4.08 (m, 1H), 7.17 (s, 5H); MS, *m/z* 188 (M$^+$).

3-Methoxy-1-phenyl-1-decyne (Entry 4). IR (neat) 2815, 2220, 1600, 1495 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.63—1.73 (m, 11H), 1.73—2.46 (m, 4H), 3.38 (s, 3H), 3.55—4.16 (m, 1H), 7.18 (s, 5H); MS, *m/z* 244 (M$^+$). Found: C, 83.61; H, 9.95%. Calcd for $C_{17}H_{24}O$: C, 83.55; H, 9.90%.

1,5-Diphenyl-3-benzyloxy-1-pentyne (Entry 5). IR (neat) 2225, 1610, 1495, 1270, 1040 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.93—2.40 (m, 2H), 2.58—3.06 (m, 2H), 4.28 (dd, 1H, J=6.5, 6.5 Hz), 4.28 (d, 2H, J=11 Hz), 6.85—7.27 (m, 15H); MS, *m/z* 326 (M$^+$). Found: C, 88.45; H, 6.78%. Calcd for $C_{24}H_{22}O$: C, 88.31; H, 6.79%.

1,4-Diphenyl-3-methoxy-1-pentyne (Entry 6). ^1H NMR ($CDCl_3$) δ=1.43 (d, 2H, J=7 Hz), 2.83—3.35 (m, 1H), 3.42 (s, 1H), 4.22 (dd, 1H, J=7 Hz, 6.7 Hz), 7.26 (s, 5H); MS, *m/z* 250 (M$^+$).

1-Phenyl-3-methoxy-1-undecyne (Entry 7). IR (neat) 1600, 1490 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.67—2.07 (m, 17H), 4.50 (s, 3), 4.15 (t, 1H), 7.1—7.6 (m, 5H); MS, *m/z* 258 (M$^+$).

4-Methoxy-1-hexadecyne (Entry 8). IR (neat) 2235 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.67—1.99 (m, 17H), 3.36 (s, 3H), 3.72—4.05 (m, 1H) MS, *m/z* 196 (M$^+$).

8-Methoxy-1-hexadecyne (Entry 9). ^1H NMR ($CDCl_3$) δ=1.56—1.93 (m, 26H), 1.97—2.38 (m, 2H), 3.35 (s, 3H), 3.68—4.03 (m, 1H); MS, *m/z* 252 (M$^+$).

1,5-Diphenyl-3-methoxy-1-penten-4-yne (Entry 10). IR (neat) 2815, 1675 (m), 1595, 1490, 960 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.32, 3.43 (s, 3H), 4.74 (d, 1.5H, J=5.5 Hz), 5.25 (d, 1.5 H, J=9.5 Hz), 5.72—6.27 (m, 2H), 7.1—7.25 (m, 10) (cis, trans mixture).

3-Methoxy-1-phenyl-4-hexen-1-yne (Entry 11). IR (neat) 2815, 2195, 1590, 1490, 960 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.26 (d, 3H, J=6.5 Hz), 3.28 (s, 3H), 4.78 (t, 1H, J=6.5 Hz), 5.65—6.32 (m, 2H), 7.17—7.56 (m, 5H); MS, *m/z* 186 (M$^+$).

3-Ethoxy-1-phenyl-1-butyne (Entry 12). IR (neat) 2210, 1600, 1490 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.15 (t, 3H, J=6.6 Hz), 1.35 (d, 3H, J=7.5 Hz), 3.23—4.10 (m, 2H), 4.34 (q, 1H, J=6.6 Hz), 7.09—7.58 (m, 5H); MS, *m/z* 174 (M$^+$). Found: C, 82.58; H, 8.08%. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10%.

Preparation of Propargylic Ether (6). (Table 4). A typical reaction procedure is described for 3-phenylpropanal with methoxytrimethylsilane and (trimethylsilylethynyl)-benzene (Entry 2): a CH_2Cl_2 (4 ml) suspension of $SnCl_4$ (0.2 mmol) and $ZnCl_2$ (0.2 mmol) was stirred for 30 min at room temperature, to which were added successively methoxytrimethylsilane (1.6 mmol) in CH_2Cl_2 (2 ml) and

3-phenylpropanal (1.0 mmol) in CH_2Cl_2 (2 ml) at −78 °C and stirred for 4 h, then warmed to room temperature, a solution of (trimethylsilylethynyl)benzene (1.5 mmol) in CH_2Cl_2 (2 ml) was added to the reaction mixture and stirred for 6 h at the same temperature. After quenching with aqueous solution of sodium hydrogencarbonate, the solution was extracted with CH_2Cl_2. The extracts were dried over $MgSO_4$ and condensed in vacuo. Purification by preparative TLC on silica gel (hexane:ether 1:1, v/v) afforded 1,5-diphenyl-3-methoxy-1-pentyne (0.78 mmol, 78%).

Other spectral data presented: 1,5-Diphenyl-3-ethoxy-1-pentyne (Entry 3), IR (neat) 2200, 1600, 1490 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.22 (t, 3H, J=7.5 Hz), 1.91—2.32 (m, 2H), 2.70—3.03 (m, 2H), 3.27—4.03 (m, 1H), 4.17 (q, 2H, J=7.5 Hz), 7.0—7.5 (m, 10H); MS, m/z 246 (M^+). Found: C, 86.50; H, 7.71%. Calcd for $C_{19}H_{20}O$: C, 86.32; H, 7.63%.

4-Methoxy-2-decyne (Entry 4). IR (neat) 2830, 2210, 1605, 1495 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.73—2.35 (m, 13H), 3.42 (s, 3H), 3.92—4.21 (m, 1H), 7.07—7.53 (m, 5H); MS, m/z 230 (M^+).

1,5-Diphenyl-3-(1-phenylethoxy)-1-pentyne (Entry 5). ^1H NMR ($CDCl_3$) δ=1.27, 1.43 (d, 3H, J=6.5 Hz), 1.80—2.28 (m, 2H), 2.57—3.03 (m, 2H), 4.03 (q, 1H, J=6.5 Hz), 4.1—5.0 (m, 1H), 6.90—7.47 (m, 10H); MS, m/z 340 (M^+).

Preparation of 1,5-Diphenyl-3-methoxy-1-pentene (Cis-Isomer): 1,5-Diphenyl-3-methoxy-1-pentyne (1 mmol) was dissolved in AcOEt (5 ml) and hydrogenated with Lindler catalyst (50 mg) and quinoline (30 mg) at 1 atm. The catalyst was removed by filtration and the solvent was condensed in vacuo. Then the residue was purified by preparative TLC on silica gel to afford 1,5-diphenyl-3-methoxy-1-pentene (0.89 mmol, 89%). IR (neat) 2810, 1600, 1490, 1405 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.63—2.07 (m, 2H), 2.55—2.90 (m, 2H), 3.11 (s, 3H), 3.82—4.27 (m, 1H), 5.50 (dd, 1H, J=12 Hz, 8.5 Hz), 6.52 (d, 1H, J=12 Hz), 6.77—7.40 (m, 10H); MS, m/z 252 (M^+). Found: C, 85.90; H, 7.97%. Calcd for $C_{18}H_{20}O$: C, 85.67; H, 7.99%.

Allylation of Propargylic Ethers: A CH_2Cl_2 suspension of $SnCl_4$ (0.4 mmol) and $ZnCl_2$ (0.4 mmol) was stirred for 30 min at room temperature, to which were added successively methoxytrimethylsilane (1.5 mmol) in CH_2Cl_2 (2 ml) and 3-phenylpropanal (1.0 mmol) in CH_2Cl_2 (2 ml) at 0 °C, and stirred for 4 h. Then to the reaction mixture was added (trimethylsilylethynyl)benzene (1.5 mmol) in CH_2Cl_2 (2 ml) at the same temperature and stirred for 6 h. After warming to room temperature allyltrimethylsilane (5 mmol) in CH_2Cl_2 (3 ml) was added and stirred for 15 h at the same temperature. Usual workup and purification by preparative TLC on silica gel afforded 1-phenyl-3-(2-phenylethyl)-5-hexen-1-yne (0.6 mmol, 60%). IR (neat) 1640, 1595, 1485, 910 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.58—3.03 (m, 3H), 4.90—5.29 (m, 2H), 5.57—6.34 (m, 1H), 7.05—7.66 (m, 10H); MS, m/z 260 (M^+).

Aldol Reaction and the Michael Reaction: Representative procedure is described for the reaction of silyl enol ether of propiophenone and benzaldehyde; a CH_2Cl_2 (4 ml) suspension of $SnCl_4$ (0.1 mmol) and $ZnCl_2$ (0.1 mmol) was stirred for 30 min at room temperature, to which was added a CH_2Cl_2 solution (2 ml) of silyl enol ether of propiophenone (1.1 mmol) and a CH_2Cl_2 (2 ml) solution of benzaldehyde (1.0 mmol) successively at −78 °C. The reaction mixture was further stirred for 2 h at this temperature, and the reaction quenched with satd. $NaHCO_3$ solution. The organic materials were extracted with CH_2Cl_2 twice, and the combined extracts were washed with brine and dried over Na_2SO_4. After evaporation of the solvent, the crude product was purified by silica gel thin layer chromatography to give the product in 99% yield.

Allylation of Aldehydes: A typical procedure is described for the reaction of 3-phenylpropnal with allyltrimethylsilane; a CH_2Cl_2 (4 ml) suspension of $SnCl_4$ (0.1 mmol) and $ZnCl_2$ (0.1 mmol) was stirred for 30 min at room temperature, to which was added allyltrimethylsilane (1.2 mmol) in CH_2Cl_2 (2 ml) and benzaldehyde (1.0 mmol) in CH_2Cl_2 (2 ml) successively at 0 °C. The reaction mixture was further stirred for 2 h at this temperature. Usual workup and purification by preparative TLC on silica gel afforded the product in 74% yield.

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