

## Reactions of alcohols and silyl ethers in the presence of an indium/silicon-based catalyst system: Deoxygenation and allyl substitution\*

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**Abstract:** An In(III)/Si catalyst system effects the direct allyl substitution of alcohols and silyl ethers under mild conditions. A deoxygenation of alcohols is also promoted by  $\text{InCl}_3$  catalyst. This method requires no pretreatment or protection of hydroxy groups or deprotection of siloxy groups. The completion of the catalytic allylation depends on the low oxophilicity and high halophilicity of In(III) halide species, and other representative Lewis acids such as  $\text{AlCl}_3$  and  $\text{BF}_3$  have no catalytic activity for the allylations. The oxophilicity and halophilicity are also demonstrated by NMR studies.

**Keywords:** indium; silicon; combined system; alcohol; silyl ether; direct substitution.

### INTRODUCTION

To complete C–C bond formation, the coupling reactions between organometallic reagents and electrophiles have been widely employed in the presence of transition-metal catalysts in which organic halide electrophiles are well utilized. In contrast, alcohols are scarcely employed as the coupling partner. Because the leaving ability of hydroxy group is very low, metallic reagents and catalysts are often decomposed by alcohols [1–7]. However, the direct use of alcohols offers the scope of an eco-friendly process since protection of the hydroxy group would thus be unnecessary. In the conventional coupling reaction, alkyl halides are the most common starting materials. However, these alkyl halides are produced from the corresponding alcohols. Moreover, silylation is often used to protect alcohols, so the direct coupling of the derived silyl ethers would be more difficult.

Although In(III) halides have attracted much attention in current organic syntheses because of their moisture tolerance and novelty, they only serve as alternatives to representative and conventional Lewis acids in many cases [8–10]. Since the acidity of In(III) halides is not so strong, the range of application is limited. We have recently reported that this range can be considerably expanded by combination with Si compounds to achieve deoxygenative functionalizations of carbonyl compounds [11–13]. Herein, we report the direct substitution of alcohols and silyl ethers in the presence of the In–Si combined catalysts, in which no pretreatment of hydroxy and siloxy group is required at all.

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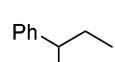
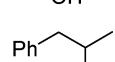
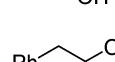
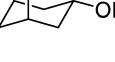
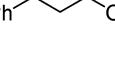
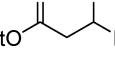
## RESULTS AND DISCUSSION

### Deoxygenation of alcohols

At first, we examined the In(III) halide-catalyzed direct reduction of alcohols to the corresponding alkanes. This deoxygenation of alcohols is a milestone of our development of direct substitution reactions of hydroxy groups, although it is not actually “direct substitution”, as discussed below [14]. The In(III) trichloride-catalyzed system resulted in the successful reduction of a wide variety of secondary or tertiary alcohols, and tolerated the presence of functional moieties such as esters and halides groups within respective alcohols.

The reaction conditions were optimized by performing the deoxygenation of decan-2-ol (entries 1–6, Table 1). The favorite reaction proceeded under the conditions using  $\text{Ph}_2\text{SiHCl}$  (2 equiv) and  $\text{InCl}_3$  (5 mol %) in refluxing 1,2-dichloroethane (DCE). Typical strong Lewis acids such as  $\text{AlCl}_3$  and  $\text{BF}_3\cdot\text{Et}_2\text{O}$  instead of  $\text{InCl}_3$  were ineffective, perhaps because these strong Lewis acids are decomposed by alcohols. The correct choice of solvent was also essential, since DCE gave a 76 % yield, whereas the

**Table 1** Deoxygenation of various alcohols.

R-OH	+	$\text{Ph}_2\text{SiHCl}$	catalyst (5 mol %) $\xrightarrow{\hspace{1cm}}$	R-H			
entry			catalyst	solvent	T (°C)	t (h)	yield (%)
1			$\text{InCl}_3$	DCE	80	4	76
2			-	DCE	80	4	5
3	$\text{CH}_3(\text{CH}_2)_7\text{CHCH}_3$		$\text{AlCl}_3$	DCE	80	4	23
4			$\text{BF}_3\cdot\text{OEt}_2$	DCE	80	4	trace
5			$\text{InCl}_3$	hexane	70	4	33
6			$\text{InCl}_3$	THF	63	4	0
7			$\text{InCl}_3$	$\text{CH}_2\text{Cl}_2$	rt	1	90
8			$\text{InCl}_3$	DCE	80	6	87
9			$\text{InCl}_3$	DCE	80	3	99
10			$\text{InCl}_3$	DCE	80	3	99
11			$\text{InCl}_3$	DCE	80	5	0
12			$\text{InCl}_3$	DCE	50	0.5	68
13			$\text{InCl}_3$	DCE	rt	3	95

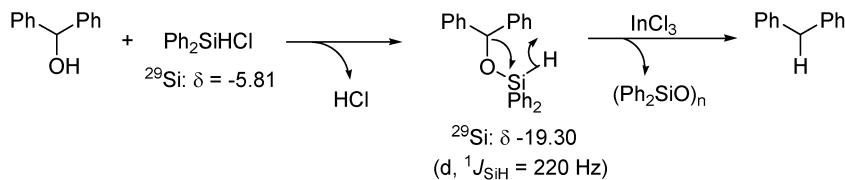
<sup>a</sup> ROH(1.0 mmol),  $\text{Ph}_2\text{SiHCl}$  (2.0 mmol),  $\text{InCl}_3$  (0.05 mmol), Solvent (1mL).

DCE:  $\text{ClCH}_2\text{CH}_2\text{Cl}$

reaction was completely depressed in the coordinative solvents such as tetrahydrofuran (THF) (entry 6). The interaction between alcohols and In(III) trichloride is perhaps interfered by the coordinative solvents. Hexane, a noncoordinative solvent, gave a moderate yield (33 %), although it was clearly less effective than DCE.

A wide range of alcohols were applicable as summarized in Table 1. Benzylic alcohol was easily reduced at room temperature to give a high yield (entry 7). Secondary and tertiary alkyl alcohols were found to be effectively reduced (entries 8–10), while the primary one gave no product (entry 11). This system is so mild that chemoselective deoxygenation of alcohols could be achieved even in the presence of feasible functionalities (entries 12 and 13). It is very noteworthy to achieve the opposite selectivity to the conventional reagents such as  $\text{LiAlH}_4$ , which reduced ester and chloro groups.

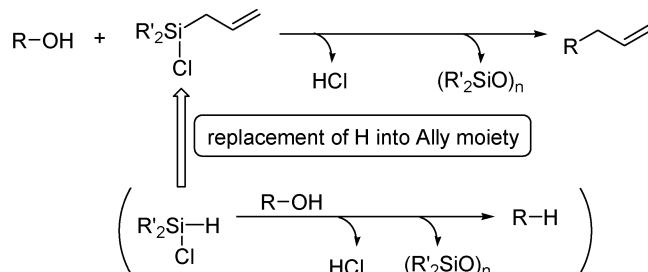
Scheme 1 illustrates a plausible reaction path which was revealed by NMR studies. The mixing of benzhydrol and  $\text{Ph}_2\text{SiHCl}$  in  $\text{CD}_2\text{Cl}_2$  at room temperature spontaneously led to the disappearance of the signals corresponding to benzhydrol in  $^1\text{H}$  and  $^{13}\text{C}$  NMR. In  $^{29}\text{Si}$  NMR, the resulting solution showed a new doublet signal due to the coupling of a Si–H bond ( $-19.30$  ppm,  $J = 220$  Hz). The fine evolution of HCl gas strongly suggests the generation of the silyl ether bearing Si–H bond. After the termination of the evolution, an addition of 5 mol % of  $\text{InCl}_3$  effected the formation of deoxygenation product, diphenylmethane. A similar evolution of HCl was observed in the reaction using 2-decanol at  $80\text{ }^\circ\text{C}$ , and the successive  $\text{InCl}_3$ -catalyzed deoxygenation was found to take place even at room temperature. The proposed reaction path is strongly suggested by these data.



**Scheme 1** Reaction path of the deoxygenation of alcohol.

### Direct allyl substitution of alcohols

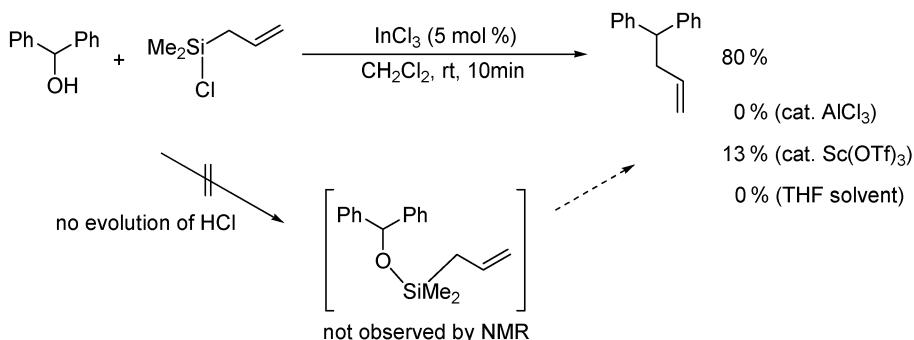
We planned the direct allyl substitution of alcohols as shown in Scheme 2, in which an intramolecular allyl substitution had been expected, followed by the evolution of hydrogen chloride [15–17].



**Scheme 2** An assumption of direct allyl substitution of alcohol.

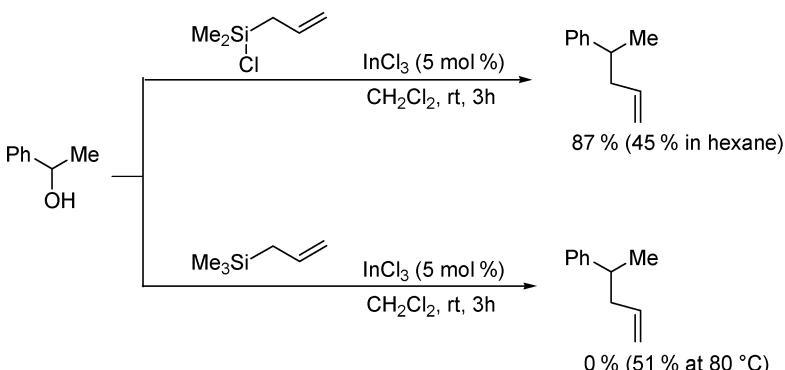
As expected, the allyl substitution using allylchlorodimethylsilane proceeded at room temperature to give the desired product in 80 % yield (Scheme 3). In this system, we observed the results similar to the deoxygenation of alcohols. Thus, representative Lewis acids such as  $\text{AlCl}_3$  and  $\text{Sc}(\text{OTf})_3$  gave only low yields, while In(III) trichloride was found to be characteristically effecting the allyl substitu-

tion. THF completely disturbed the reaction course. However, careful observation and NMR investigation gave a little surprise that the evolution of hydrogen chloride and the expected intermediate silyl ether were not observed. These results observed strongly suggest that the chloro group on silyl compounds is not required for the allyl substitution of alcohols.



**Scheme 3** Direct allylation of alcohols.

Hence, allyl substitution of 1-phenylethanol was attempted by using allyltrimethylsilane instead of allylchlorodimethylsilane (Scheme 4). However, no reaction took place at room temperature and even at 80 °C gave only 51 % yield. In contrast, using the chloroallylsilane gave 87 % yield at room temperature (45 % yield was obtained even in hexane solution). The chloro group is apparently essential for the allyl substitution, and the alternative reaction path, including no evolution of HCl, should be considered.

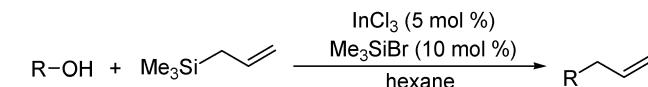


**Scheme 4** Effect of chloro atom on silicon.

On the basis of these results, the investigation focused on the effect of additives of the silicon compounds bearing a halide moiety ( $\text{Me}_3\text{SiBr}$ ). Fortunately, the addition of a catalytic amount (10 mol %) of trimethylsilyl bromide was found to promote the allyl substitution, furnishing the desired product in 77 % yield at room temperature for 2 h even in hexane solvent (entry 1, Table 2). The addition of  $\text{Me}_3\text{SiCl}$  instead of  $\text{Me}_3\text{SiBr}$  gave only 13 % yield. When no additives were employed, the allyl substitution did not take place even under hexane refluxing for 8 h. General Lewis acids such as  $\text{BF}_3 \cdot \text{OEt}_2$ ,  $\text{AlCl}_3$ , and  $\text{Yb}(\text{OTf})_3$  did not show the catalytic activity even when combined with  $\text{Me}_3\text{SiBr}$ . Of course,  $\text{Me}_3\text{SiBr}$  had no effect by itself. The allyl substitution was not promoted in THF, perhaps its coordinating ability disturbed the interaction between  $\text{InCl}_3$  and  $\text{Me}_3\text{SiBr}$ . The interaction of  $\text{InCl}_3$  and

$\text{Me}_3\text{SiBr}$  does not seem to be so strong, but apparently it is essential for the effective allyl substitution under appropriate conditions. Table 2 shows that a variety of alcohols could be transformed into the corresponding allylation products. Benzylic and tertiary alkyl alcohols gave high yields. In addition, tertiary cyclohexenyl alcohol gave the product, having allylated at the less hindered site via the formation of allyl cation intermediate (entry 4). These results strongly suggested that the participation of a cation generated from the removal of the hydroxy group was promoted by the combination catalyst of In and Si.

**Table 2** Direct allyl substitution of alcohol with allyltrimethylsilane.



entry	R-OH	T (°C)	t (h)	yield (%)
1 <sup>a</sup>		rt	2	77 (13 <sup>b</sup> )
2		50	0.5	75
3		70	4	68
4		0	3	98
5		70	2	85

<sup>a</sup> Ineffective catalysts;  $\text{BF}_3 \cdot \text{Et}_2\text{O}$ ,  $\text{AlCl}_3$ ,  $\text{Yb}(\text{OTf})_3$ ,  $\text{Sc}(\text{OTf})_3$ ,  $\text{BiCl}_3$ ,  $\text{B}(\text{C}_6\text{F}_5)_3$ , <sup>b</sup>  $\text{Me}_3\text{SiCl}$  was used instead of  $\text{Me}_3\text{SiBr}$ .

We monitored the activation of the hydroxy group by the catalysts with NMR studies, in which a low reactive primary alcohol was employed because only the interaction between Lewis acids and 1-octanol was expected, and the results are noted in Table 3. The values of the  $\Delta\delta(^{13}\text{C})$  indicate the degree of the interaction between Lewis acid and hydroxy group. Two types of interactions, I and II, can be proposed. If the former is plausible, the value should be smaller than the sum of  $\text{Me}_3\text{SiX}$  and  $\text{InX}_3$ , for example,  $\text{Me}_3\text{SiCl}$  (+0.156),  $\text{InCl}_3$  (+2.559), and the sum (+2.715). However, the value obtained

**Table 3** Effect of Lewis acids on  $\delta(^{13}\text{C})$  chemical shift of  $\alpha$ -carbon in 1-octanol.

Lewis acid	$\delta(^{13}\text{C})/\text{ppm}$	$\Delta(^{13}\text{C})/\text{ppm}$	Lewis acid	$\delta(^{13}\text{C})/\text{ppm}$	$\Delta(^{13}\text{C})/\text{ppm}$
none	62.681	0			
$\text{Me}_3\text{SiCl}$	62.837	+0.156	$\text{InCl}_3 + \text{Me}_3\text{SiCl}$	65.997	+3.316
$\text{Me}_3\text{SiBr}$	63.964	+1.283	$\text{InCl}_3 + \text{Me}_3\text{SiBr}$	66.294	+3.613
$\text{InCl}_3$	65.240	+2.559	$\text{InBr}_3 + \text{Me}_3\text{SiCl}$	67.372	+4.691
$\text{InBr}_3$	65.199	+2.518	$\text{InBr}_3 + \text{Me}_3\text{SiBr}$	70.203	+7.522



(+3.316) is larger than the sum, and so the type II interaction is plausible in which the combined catalyst ( $\text{Me}_3\text{SiX}\cdots\text{InX}_3$ ) interacted with the hydroxy group.

The interaction leading to the combination was demonstrated by  $^{29}\text{Si}$  NMR (Fig. 1). Upon mixing equal amounts of  $\text{Me}_3\text{SiBr}$  and  $\text{InCl}_3$ , facile halogen exchange gave a broadened signal of  $\text{Me}_3\text{SiCl}$  at 33.0 ppm. In the combination of  $\text{Me}_3\text{SiCl}$  and  $\text{InBr}_3$ , only the broadening of  $\text{Me}_3\text{SiCl}$  was observed. This broadening plausibly indicates the range of interaction between  $\text{Me}_3\text{SiCl}$  and In(III) halide. The combination of  $\text{Me}_3\text{SiBr}$  and  $\text{InBr}_3$  caused the largest broadening, which was conformable to the largest down field shift noted in Table 3. In the case of  $\text{AlCl}_3$  and  $\text{BF}_3\cdot\text{OEt}_2$ , immediate halogen exchange with  $\text{Me}_3\text{SiBr}$  also took place at room temperature to generate  $\text{Me}_3\text{SiCl}$  and  $\text{Me}_3\text{SiF}$ , respectively, but no broadening was observed perhaps because of the weak interaction. Only In halides could form a combined catalyst with silyl halides.

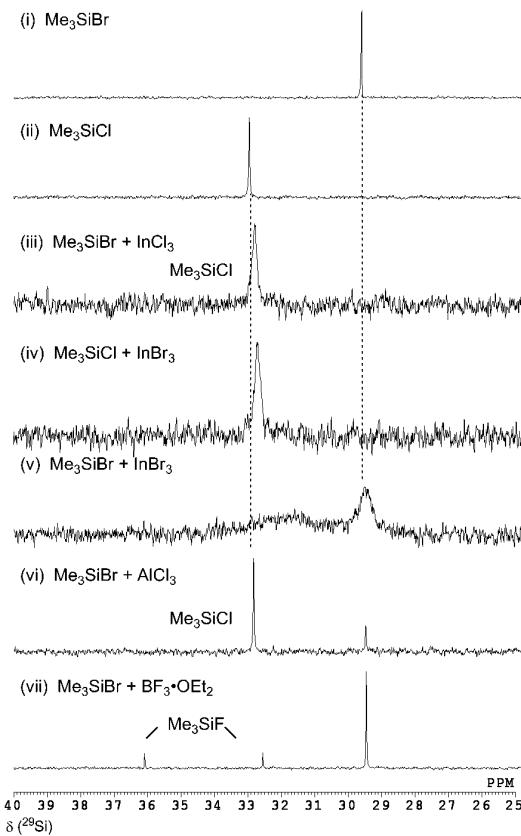


Fig. 1  $^{29}\text{Si}$  NMR of the mixture  $\text{Me}_3\text{SiX}$  and Lewis acid in  $\text{MeCN}$  at rt.

The oxophilicity of In(III) halides was compared with that of  $\text{AlCl}_3$  and  $\text{BF}_3\cdot\text{OEt}_2$  by monitoring the  $^{29}\text{Si}$  NMR of the interactive reaction of these Lewis acids with  $\text{Me}_3\text{SiOMe}$  as shown in Fig. 2. No change of  $\text{Me}_3\text{SiOMe}$  was observed in the case of In(III) halides, while immediate transmetallation between  $\text{AlCl}_3$  (or  $\text{BF}_3\cdot\text{OEt}_2$ ) and  $\text{Me}_3\text{SiOMe}$  took place.

These results (Figs. 1 and 2) reveal the strong halophilicity of In halides and are capable enough to form the combined Lewis acid even in the presence of an oxygen atom, in which the Si center has a cationic character. And on the basis of these investigations, a plausible mechanism is proposed

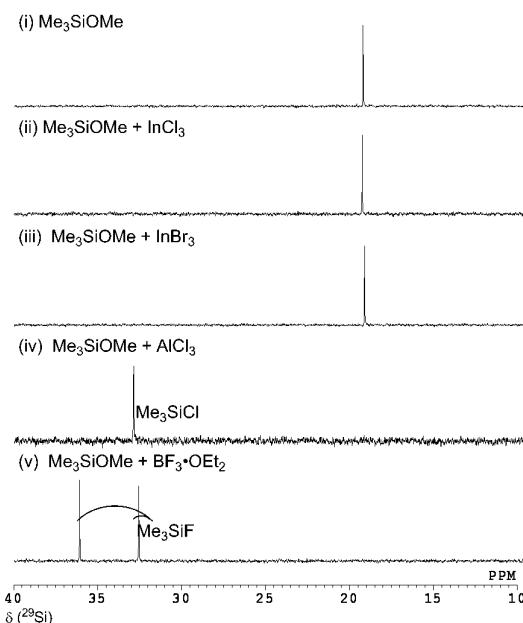
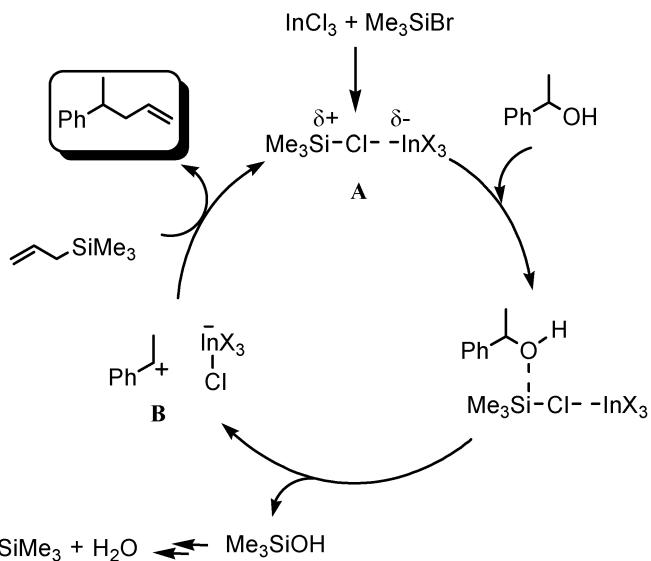


Fig. 2  $^{29}\text{Si}$  NMR of the mixture of  $\text{Me}_3\text{SiOMe}$  and Lewis acid (MeCN, rt).

(Scheme 5). At first, the combined Lewis acid **A** is generated due to the strong halophilicity of  $\text{InCl}_3$ . Then the hydroxy group is activated by the Si center to promote the formation of carbocation **B**. The addition of allylsilane to **B** gives the allylated product with regeneration of the combined catalyst **A** and completes the catalytic cycle of the direct allyl substitution of alcohols. An important factor for completion of the catalytic cycle is the low oxophilicity and high halophilicity of In halides, because high oxophilicity disturbs the regeneration of the combined catalyst. An oxophilic Lewis acid like  $\text{AlCl}_3$  has no catalytic ability.



Scheme 5 Catalytic cycle of direct allylation of alcohol.

### Direct allyl substitution of silyl ethers

Recently, Gevorgyan et al. [18,19] demonstrated that the strong Lewis acid like  $B(C_6F_5)_3$  promoted the allyl substitution of the acetoxy group with allylsilane, while the direct substitution of alcohol gave a low yield, and no reaction took place in the case of trimethylsilyl ether. Furthermore, Cho et al. [20] reported that  $InBr_3$  itself also promoted the substitution of the acetoxy group, but not hydroxyl group. A Lewis acid-catalyzed leaving ability of OH, OAc, and  $OSiMe_3$  is generally arranged in the order; OAc > OH >>  $OSiMe_3$  as noted in Scheme 6. Although a few direct couplings between silyl ethers and allylic silanes, which have been catalyzed by Lewis acids such as  $Ph_3CCl/NaTFPB$  [21], Ti-fluoride complex [22], and  $ZnCl_2$  [23] have been reported, these methods are limited to the coupling reactions involving benzylic or allylic silyl ethers.

catalyst	OR		
	$OSiMe_3$	OH	OAc
$B(C_6F_5)_3$ (ref. 18, 19)	0 %	15-20 %	96 %
$InBr_3$ (ref. 20)	-	0 %	38 % (95 % at 40 °C)
In/Si combined <i>This work</i>	77 %	trace	

**Scheme 6** Leaving ability of OAc, OH, and  $OSiMe_3$  groups.

In the view of this situation, we focused on the direct substitution of siloxy group. The coupling reaction was found to be effected by the combination catalyst of  $InCl_3$  and  $Me_3SiI$ , moreover, in which the reactivity order of acetoxy and hydroxy groups could be reversed [24].

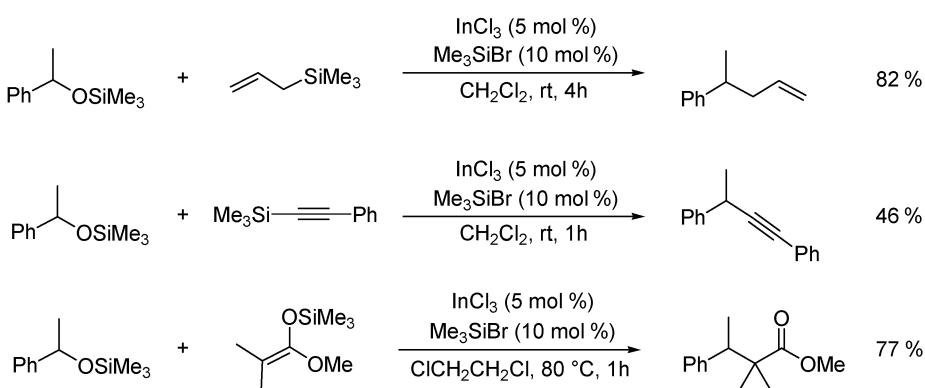
The combination catalyst  $InCl_3/Me_3SiBr$ , which has high activity for the direct allyl substitution of alcohols, gave only 34 % yield. Fortunately, the combination of  $InCl_3/Me_3SiI$ , which represents higher catalytic activity, increased the yield up to 61 % at room temperature in dichloromethane (entry 1, Table 4). The highest yield (76 %) was obtained by using  $I_2$  instead of an unstable  $Me_3SiI$ , where  $Me_3SiI$  is presumably generated in situ from  $I_2$  and allylsilane [25]. Representative Lewis acids such as  $AlCl_3$  and  $B(C_6F_5)_3$  were ineffective even in the presence of  $I_2$ . Interestingly, the mild acids,  $ZnCl_2$  and  $Yb(OTf)_3$ , gave the desired product in 27 and 26 % yields, respectively. Direct coupling of a variety of silyl ethers with allylsilanes was investigated under the optimized conditions noted in Table 4. Benzyl ether was allylated in good yield at room temperature (entry 2). It is noteworthy that the reaction temperature was lower than that of the allylation of alcohols. In the case of secondary ethers such as benzylic and norbornyl, siloxy groups were easily substituted (entries 3 and 4), and the latter (entry 4) gave a single isomer product. The reaction conditions are compatible with phthalimide moiety to give the prenylated products in moderate yield (entry 5). Entry 5 is the case for the formation of carbon skeletons connecting two quaternary carbons. Our system also tolerates the phenolic hydroxy group to give the desired product in 83 % yield (entry 6). A primary alkyl ether was inactive, and this is the limitation in this stage. The reaction mechanism is similar to that of the reaction with alcohol noted in Scheme 5, in which at first,  $I_2$  reacts with allylsilane to give  $Me_3SiI$ , which generates the combined Lewis acid. The C–O bond of silyl ether is activated by the coordination from the oxygen of siloxy group to the silicon center of the combined catalyst to form a carbocation and hexamethyldisiloxane. The coupling product was obtained with a regeneration of the combined catalyst ( $InCl_3/Me_3SiI$ ). An advantage of this system is non-protic conditions which can avoid the protonolysis of substrates.

Moreover, the coupling reactions with an alkynylsilane and a silyl ketene acetal have been also achieved by the combination catalyst of  $\text{InCl}_3$  and  $\text{Me}_3\text{SiBr}$  (Scheme 7).

**Table 4** Direct allyl substitution of silyl ethers.

		$\text{R'-OSiMe}_3$ + $\text{Me}_3\text{Si}-\text{CH}_2-\text{CH}(\text{R'})-\text{CH}_2-\text{R}'$	$\xrightarrow[\text{CH}_2\text{Cl}_2, \text{rt, 3h}]{\text{InCl}_3 (5 \text{ mol \%}), \text{I}_2 (20 \text{ mol \%})}$	
entry	silyl ether	allysilane	yield (%)	
1 <sup>a</sup>			76 (34) <sup>b</sup> (61) <sup>c</sup>	
2			70	
3			88	
4			90	
5			41	
6			83	
7			0	

<sup>a</sup> Other catalysts; AlCl<sub>3</sub> (0%), B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (0%), ZnCl<sub>2</sub> (27%), Yb(OTf)<sub>3</sub> (26%). <sup>b</sup> Me<sub>3</sub>SiBr was used instead of I<sub>2</sub>. <sup>c</sup> Me<sub>2</sub>SiL was used instead of I<sub>2</sub>.



**Scheme 7** Direct coupling by  $\text{InCl}_3/\text{Me}_3\text{SiBr}$ .

## CONCLUSION

Our recent work on the development of direct allyl substitution of hydroxy group with In(III) halide/silyl halide combined catalyst system led to the deoxygenative reduction and allyl substitution of hydroxy groups, furthermore, the allyl substitution of silyl ethers under mild conditions has been achieved. The combined system has not only the strong Lewis acidity, but also the opposite chemoselectivity compared to the conventional Lewis acids or In(III) halide itself.

## ACKNOWLEDGMENTS

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