

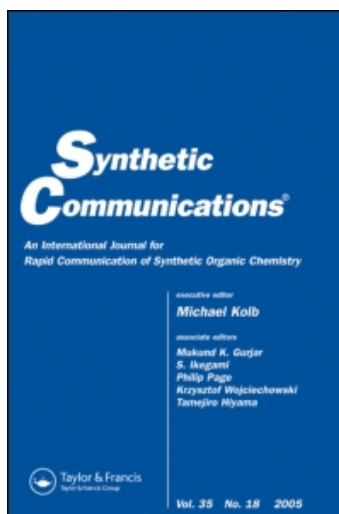
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### Efficient and Mild Iron-Catalyzed Direct Allylation of Benzyl Alcohols and Benzyl Halides with Allyltrimethylsilane

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## EFFICIENT AND MILD IRON-CATALYZED DIRECT ALLYLATION OF BENZYL ALCOHOLS AND BENZYL HALIDES WITH ALLYLTRIMETHYLSILANE

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*An efficient and mild iron-catalyzed direct allylation of benzyl alcohols and benzyl halides with allyltrimethylsilane has been developed. The present reaction would provide an excellent alternative to published methods because of its excellent yields, sustainable catalyst, and mild conditions.*

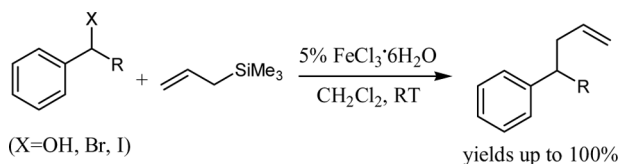
**Keywords:** Allylation; benzyl alcohols; benzyl halides; iron catalysis

The development of direct carbon–carbon (C–C) bond construction that uses low-cost, environmentally benign, and sustainable catalysts is a critical challenge for organic chemists. Recently, catalytic systems using iron as the active catalyst have received great attention, and some efficient iron-catalyzed systems have been developed for C–C couplings.<sup>[1]</sup> Herein, we report an efficient and mild iron-catalyzed direct allylation of benzyl alcohols and benzyl halides with allyltrimethylsilane.

Although few C–C bond constructions using benzyl alcohols have been achieved because of the poor leaving ability of the hydroxide group, it remains very attractive because it would be atom-efficient and environmentally benign, as water is the only by-product.<sup>[2]</sup> In past years, some efficient methods have been explored to prepare terminal olefins via direct allylation of benzyl alcohols with allyltrimethylsilane using various catalysts, such as BF<sub>3</sub>,<sup>[3]</sup> bis(fluorosulfonyl)imide,<sup>[4]</sup> B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>,<sup>[5]</sup> InCl<sub>3</sub>,<sup>[6]</sup> InBr<sub>3</sub>,<sup>[7]</sup> BiCl<sub>3</sub>,<sup>[8]</sup> ZrCl<sub>4</sub>,<sup>[9]</sup> and H-montmorillonite.<sup>[10]</sup> However, many of these systems suffer from harsh reaction conditions<sup>[3–5,10]</sup> and relatively expensive metal catalysts.<sup>[6–9]</sup> Therefore, development of more efficient and mild catalysts to promote the direct allylation of benzyl alcohols remains attractive. We successfully accomplished an efficient and mild catalytic allylation of benzyl alcohols and halides with allyltrimethylsilane by using 5 mol% of FeCl<sub>3</sub>·6H<sub>2</sub>O as the active catalyst (Scheme 1, Table 1). To the best of our knowledge, this is the first example of an iron-catalyzed allylation of benzyl alcohols and halides with allylsilane. (It puzzled us that a very low yield (5%) of the allylated product was obtained using benzhydrol

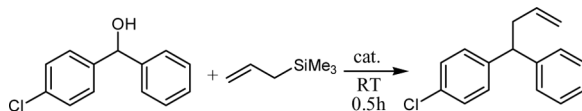
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**Scheme 1.** Iron-catalyzed allylation of benzyl alcohols and halides with allyltrimethylsilane.

**Table 1.** Optimization of the typical reaction conditions<sup>a</sup>



Entry	Catalyst (mol%)	Solvent	Isolated yield (%)
1	FeCl <sub>3</sub> (5)	CH <sub>2</sub> Cl <sub>2</sub>	100
2	FeCl <sub>3</sub> · 6H <sub>2</sub> O (5)	CH <sub>2</sub> Cl <sub>2</sub>	100 <sup>b</sup> 84 <sup>c</sup>
3	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> (5)	CH <sub>2</sub> Cl <sub>2</sub>	0
4	FeCl <sub>2</sub> (5)	CH <sub>2</sub> Cl <sub>2</sub>	0
5	CuBr <sub>2</sub> (5)	CH <sub>2</sub> Cl <sub>2</sub>	0
6	CuBr (5)	CH <sub>2</sub> Cl <sub>2</sub>	0
7	FeCl <sub>3</sub> · 6H <sub>2</sub> O (2)	CH <sub>2</sub> Cl <sub>2</sub>	94
8	FeCl <sub>3</sub> · 6H <sub>2</sub> O (1)	CH <sub>2</sub> Cl <sub>2</sub>	86
9	FeCl <sub>3</sub> · 6H <sub>2</sub> O (5)	CHCl <sub>3</sub>	0
10	FeCl <sub>3</sub> · 6H <sub>2</sub> O (5)	DCE	60
11	FeCl <sub>3</sub> · 6H <sub>2</sub> O (5)	CH <sub>3</sub> CN	0
12	FeCl <sub>3</sub> · 6H <sub>2</sub> O (5)	H <sub>2</sub> O	0
13	FeCl <sub>3</sub> · 6H <sub>2</sub> O (5)	Hexane	0
14	FeCl <sub>3</sub> · 6H <sub>2</sub> O (5)	THF	0

<sup>a</sup>Reaction conditions: 1-phenyl-1-*p*-chlorophenyl methanol (0.5 mmol), allyltrimethylsilane (1.0 mmol), rt, 0.5 h.

<sup>b</sup>Alcohol/allylsilane = 1:3.

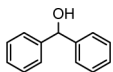
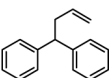
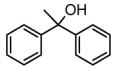
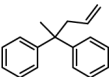
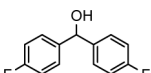
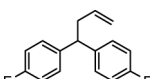
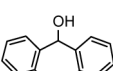
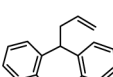
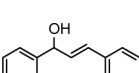
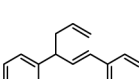



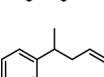
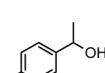
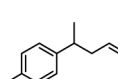
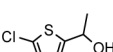
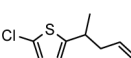
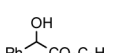



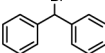
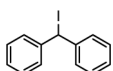
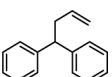
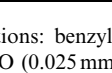
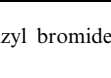
<sup>c</sup>Alcohol/allylsilane = 1:1.

and allyltrimethylsilane catalyzed by 5% FeCl<sub>3</sub>, according to Ref. 8. However, we obtained nearly quantitative yield of the desired product by using 5% FeCl<sub>3</sub> under a similar condition.)

## EXPERIMENTAL

For the initial research, we select 1-phenyl-1-*p*-chlorophenyl methanol and allyltrimethylsilane as standard substrates to optimize suitable conditions for this substitution reaction (Table 1). The desired allylation product was obtained in quantitative yield using 5 mol% of anhydrous FeCl<sub>3</sub> at room temperature in CH<sub>2</sub>Cl<sub>2</sub> (entry 1). It is interesting that 100% isolated yield of the product was also obtained by using 5 mol% of FeCl<sub>3</sub> · 6H<sub>2</sub>O as catalyst (entry 2). The yield of product decreased

**Table 2.** Allylation of benzyl alcohols and halides with allyltrimethylsilane<sup>a</sup>

Entry	Benzyl alcohols or halides	Products	Time (min)	Isolated yield (%)
1			30	98
2			30	80
3			30	94
4			30	100
5			30	71
6			60	88
7			60	25
8			40	84
9			30	95
10		—	180	0
11		—	180	0
12		—	180	0
13		—	180	0
14		—	50	Mixture
15			30	93
16			30	91

<sup>a</sup>Reaction conditions: benzyl alcohol or benzyl bromide (0.5 mmol), allyltrimethylsilane (1.0 mmol), 5 mol%  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (0.025 mmol),  $\text{CH}_2\text{Cl}_2$ , rt.

to 84% while the reaction was carried out with equal amount of alcohol and silane. However, other iron salts and copper salts were inactive to this reaction (entries 3–6). Decrease or increase of the catalyst dosage was less efficient than 5 mol% (entries 7 and 8). Further investigation of solvent effect showed that  $\text{CH}_2\text{Cl}_2$  is a more effective solvent (entries 9–14).

Various alcohols have been tested as substrates for the allylation reaction (Table 2). It is seen from Table 2 that diaryl methanols gave good to excellent, even quantitative, yields of the products (entries 1–4). 1,3-Diphenyl-allyl alcohol also gave a good yield of the corresponding allylation product (entry 5). An excellent yield was obtained by using 1,2,3,4-tetrahydro naphthalen-1-ol as the substrate (entry 6). 1-Phenyl ethanol gave a very poor yield of the product (entry 7), whereas 1-*p*-methyl-phenyl ethanol gave 84% isolated yield (entry 8). 1-(5-Chloro-thiophen-2-yl)-ethanol also gave excellent yield of the desired product (entry 9). However, hydroxy-phenyl-acetic acid ethyl ester (entry 10), 1-phenyl-ethane-1,2-diol (entry 11), 2-phenyl-ethanol (entry 12), and phenylmethanol (entry 13) were inactive in this system. 3-Phenyl-prop-2-en-1-ol gave a mixture under the condition in entry 14. It is noteworthy that benzyl halides such as bromo-diphenyl-methane and iodo-diphenyl-methane also gave excellent yields of the allylation products (entries 15 and 16).

In conclusion, this work demonstrates an efficient and mild iron-catalyzed allylation of benzyl alcohols and halides with allyltrimethylsilane. Compared with the systems reported before, the present method provides a better alternative because of its sustainable catalyst and mild conditions. Extension of this system to other substrates is under way in our laboratory.

## ACKNOWLEDGMENT

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