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## Short communication

# $FeCl_2/DTBP$ : An efficient and highly E-selective cross - coupling of silanes with styrene and its derivatives



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## ABSTRACT

An efficient FeCl<sub>2</sub>-catalyzed cross-coupling of silanes with styrene and its derivatives using DTBP as oxidant for selective synthesis of vinylsilanes was developed. This method presented an inexpensive, non-toxic and environmentally benign catalytic system with an appropriate substrate scope. This approach is E-specific and produced important classes of vinylsilanes in good yields. Control experiments indicated that the reaction may proceed via a radical pathway.

## 1. Introduction

Organosilicon compounds play a critical role in organic synthesis as valuable synthetic intermediates [1] and have a plethora of applications in materials science [2]. Among them, vinylsilanes become important building blocks or starting materials in organic synthesis, which rely on their unique reactivity profile and low environmental impact [3]. Thus, the construction of vinylsilanes C-Si bonds has attracted great attention from the synthetic community in the past decade. Great progress has been achieved in this area [4,5], including metathesis between vinylsilanes and olefins [6], hydrosilylation of alkynes [7,8] and dehydrogenative silvlation of alkenes [9,10]. Compared to these conventional methods, synthesis of vinylsilanes through direct C-H bond functionalization is attractive from the viewpoints of atom economy, efficiency, and environmental benignity. Several concerned methods has been reported in this field using noble metals such as Ru [11], Pt [12], Ir [13], and Rh [14] as catalysts (Scheme 1, a). However, exorbitant price and high toxicity of those catalysts limit their large scale application.

Unlike other transition metals, iron is the most abundant metal in the earth's crust after aluminum [15], and therefore is much cheaper than the precious metals [16,17]. On the other hand, various iron species are incorporated in biological systems [18]. Some relatively low toxic iron species have already been extensively used in pharmaceutical industry, the food industry, and cosmetics [19]. Over the past few decades, iron catalysts have been reported in various reactions, such as oxidation, addition, substitution, and cyclization, etc. [20,21] Nevertheless, the iron-catalyzed C–Si bond-forming reactions are underdeveloped. The synthesis of vinylsilanes catalyzed by Fe (CO)<sub>5</sub> have already been reported by Nesmeyanov in 1962 (Scheme 1, b) [22], afterwards, some similar reactions catalyzed by Fe species have turned up gradually [23,24]. Plietker's group reported hydrosilylation of internal alkynes catalyzed by Fe complexes [25], and in the same year, subsequently, Thomas and co-workers discovered an iron-catalyzed hydrosilylation of alkenes and alkynes with extra ligand [26]. In addition, Marciniec's group researched the addition of HSiR<sub>3</sub> with styrene by Fe(0) catalysts [27,28]. Recently, Huang's group summarized the advances in base-metal-catalyzed alkene hydrosilylation [29]. Oestreich and co-workers proposed a Fe-catalyzed silylation of electronrich arenes by an electrophilic aromatic substitution [30]. However, disadvantages exist with the above protocols, which usually use iron complexes that are difficult to synthesis and unstable as catalysts, or need extra additives.

Recently, our group reported an efficient synthesis of vinylsilanes via combining silicon-centered radicals with styrenes which catalyzed by copper (Scheme 1, c) [31]. We consider that the single electron transfer between copper salt and oxidant could initiate a radical, which then promoted the formation of the silyl radical by a hydrogen abstraction process. In addition, those already reported transformations indicated that iron salts could also trigger radical generation with some specific oxidants, such as DTBP [32,33], DDQ [34], TBHP [35], etc. Based on those reports, we wondered whether silyl radical could be formed in the presence of iron salt and certain oxidant. Herein we present a direct FeCl<sub>2</sub>-catalyzed C—H silylation process of styrene and its derivatives (Scheme 1, d). Our protocol possesses several advantages such as low cost and low toxicity, environmental friendliness and high stereoselectivity.

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Scheme 1. Strategies for transition-metal catalyzed silylation.



Fable 1		
a	C .1	

Optimization of the reaction conditions.<sup>a</sup>

+ H	H-SiEt <sub>3</sub> —	20 mol% [cat] ►	SiEt <sub>3</sub>					
		oxidant	dant L					
1a	2a	110 0, 2411	3a					
Entry		Catalyst		Oxidant	Solvent	Yield <sup>b</sup> /%		
1		FeCl <sub>2</sub>		DTBP	t-BuOH	78		
2		Fe(OAc) <sub>2</sub>		DTBP	t-BuOH	45		
3		FeCl <sub>3</sub>		DTBP	t-BuOH	-		
4		Fe(OTf) <sub>3</sub>		DTBP	t-BuOH	-		
5		Fe(acac) <sub>3</sub>		DTBP	t-BuOH	-		
6		FeCl <sub>2</sub>		TBHP	t-BuOH	11		
7		FeCl <sub>2</sub>		DCP	t-BuOH	8		
8		FeCl <sub>2</sub>		DDQ	t-BuOH	-		
9		FeCl <sub>2</sub>		DTBP	MeCN	11		
10		FeCl <sub>2</sub>		DTBP	DMSO	50		
11		FeCl <sub>2</sub>		DTBP	DMF	25		
12		FeCl <sub>2</sub>		DTBP	CH <sub>2</sub> Cl <sub>2</sub>	-		
13 <sup>c</sup>		FeCl <sub>2</sub>		DTBP	t-BuOH	80 (75) <sup>f</sup>		
14 <sup>d</sup>		FeCl <sub>2</sub>		DTBP	t-BuOH	72		
15 <sup>e</sup>		FeCl <sub>2</sub>		DTBP	t-BuOH	45		
16		-		DTBP	t-BuOH	0		
17		FeCl <sub>2</sub>		-	t-BuOH	0		

The significance of bold is the optimum conditions.

<sup>a</sup> Reaction conditions: catalyst (0.1 mmol), styrene (0.5 mmol), HSiEt<sub>3</sub> (2.5 mmol), oxidant (1.0 mmol), solvent (3 mL), at 110 °C for 24 h under Ar.

<sup>b</sup> Determined by GC.

<sup>c</sup> Temperature was 100 °C.

<sup>d</sup> Temperature was 90 °C.

e 10 mol% FeCl2 was used.

<sup>f</sup> Isolated yield.

#### 2. Results and discussion

The reaction of styrene (1a) and triethylsilane (2a) was chosen as a model reaction to optimize the reaction conditions (Table 1). With DTBP as the oxidant, triethylstyrylsilane (3a) was obtained in 78% yield, when FeCl<sub>2</sub> was used as the catalyst (Table 1, entry 1). A 45% yield of product 3a was achieved in the presence of  $Fe(OAc)_2$  (Table 1, entry 2). FeCl<sub>3</sub>, Fe(OTf)<sub>3</sub> and Fe(acac)<sub>3</sub> were not effective for the formation of 3a (Table 1, entries 3–5). Different oxidants were also screened, less product was formed when other oxidant, such as TBHP, DCP and DDQ were used instead of DTBP (Table 1, entries 6–8). Further

screening of solvents and temperatures revealed that *t*-BuOH was superior as a suitable solvent (Table 1, entries 9–12) and 100 °C was the optimum temperature (Table 1, entries 13 and 14). The amount of the catalyst was also explored, and the best yield could be obtained in the presence of a 20 mol% of catalyst (Table 1, entry 15). The conversion of the reaction in the optimum conditions is 98%. Finally, the starting materials remained unreacted when the reaction was carried out in the absence of FeCl<sub>2</sub> or DTBP (Table 1, entries 16 and 17). Moreover, the GC–MS spectrum shows there are no byproducts such as products of hydrogen addition and Z - products in the reaction mixture.

With the optimized conditions in hand, we turn to explore the

## Table 2





<sup>a</sup>Reaction conditions: FeCl<sub>2</sub> (0.1 mmol), olefins (0.5 mmol), HSiEt<sub>3</sub> (2.5 mmol), DTBP (1.0 mmol), *t*-BuOH (3 mL), at 100 °C for 24 h under Ar. Isolated yields.

functional group tolerance of our protocol. A series of styrene derivatives (**1b-1j**) with triethylsilane (**2a**) were subjected to the optimized reaction conditions (20 mol% FeCl<sub>2</sub>, DTBP, *t*-BuOH, 100 °C), the corresponding vinylsilanes (Table 2, **3b-3j**) were obtained in moderate to good yields as shown in Table 2. *p*-Substituted styrene derivatives containing electron-donating groups (Table 2, **3b-3d**) worked slightly better than that containing electron-withdrawing groups (Table 2, **3e-3g**). In general, *p*-substituted styrene derivatives with electronwithdrawing or electron-donating groups reacted smoothly under the optimized conditions, producing corresponding vinylsilanes with satisfactory yields. Furthermore, *m*-substituted and *o*-substituted styrene derivatives were both compatible with this reaction (Table 2, **3h** and **3i**), and the halo-substituted vinylsilanes were conductive to further functionalization. In addition, 2, 4, 6-trimethylstyrene was also suitable for this transformation (Table 2, **3j**). Meanwhile, the protocol was effective on sterically hindered  $\alpha$ -phenylstyrene (Table 2, **3k**). Our protocol was also suitable for heteroaromatic alkenes and aliphatic olefins, affording corresponding silylation products in moderate yield (Table 2, **3l–3n**). To test some sensitive groups of styrene derivatives under such oxidative conditions, we tried 4-NH<sub>2</sub>, 4-COOCH<sub>3</sub> and 4-CN styrene, but only the ester and nitrile were suitable for this transformation (Table 2, **3o** and **3p**).

To further study the possible reaction mechanisms for the silylation, control experiments under the standard reaction conditions were carried out. The product (**3a**) was not detected in the presence of radical inhibitors, 2, 2, 6, 6- tetramethyl-1-piperidinyloxy (TEMPO) or butylated hydroxytoluene (BHT), indicating that the current reaction includes a radical process. A possible mechanism outlined in Scheme 2 was proposed for the present process. Initially, in the presence of Fe<sup>2+</sup> species, DTBP is split into Fe<sup>3+</sup> (Ot-Bu) and the *t*-BuO· radical. The reacts *t*-BuO· reacts with HSiEt<sub>3</sub> to lead to the SiEt<sub>3</sub>· radical and *t*-BuOH, and then addition across styrene affords benzylic radical **A**. Single-electron-transfer (SET) between benzylic radical and Fe<sup>3+</sup> (Ot-Bu) gives benzylic cation **B**, Fe<sup>2+</sup> species and *t*-BuO<sup>-</sup>. Finally,  $\beta$ -H elimination of benzylic cation **B** with *t*-BuO<sup>-</sup> gives desired product **3a** and *t*-BuOH. And the FeCl<sub>2</sub> was regenerated to reinitiate the reaction cycle.

#### 3. Conclusions

In conclusion, we have developed an efficient Fe-catalyzed direct C–H silylation of styrene and its derivatives using silanes with peroxides for selective synthesis of vinylsilanes. This approach is highly Eselective and produced important classes of vinylsilanes in good yields. This protocol tolerates a wide variety of functional groups, and proposes an inexpensive, non-toxic and environmentally benign character. Moreover, the preliminary mechanistic studies disclose that the reaction may proceed via a radical pathway. Further investigations and studies are being directed toward understanding the reaction mechanistic and the application to other substrates for the synthesis of natural bioactive products.



Scheme 2. Proposed reaction mechanism.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.catcom.2017.12.023.

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