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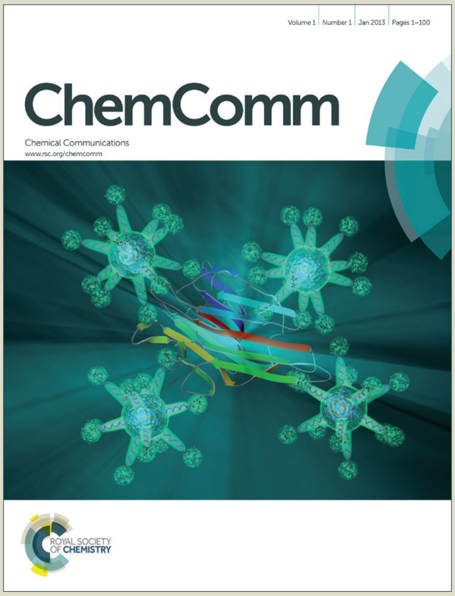

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Cite this: DOI: 10.1039/c0xx00000x

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ARTICLE TYPE

Synthesis of Multi-Substituted Vinylsilanes *via* Copper(I)-Catalyzed Hydrosilylation Reactions of Allenes and Propiolate Derivatives with Silylboronate

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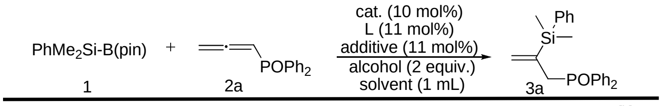
Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

An efficient and general copper(I)-catalyzed method for the synthesis of multi-substituted vinylsilanes is reported. Multi-substituted allenes with electron-withdrawing groups and propiolate derivatives reacted well with (dimethylphenylsilyl)boronic acid pinacol ester to afford silyl-substituted butenoate derivatives and *β*-silyl-substituted acrylate derivatives respectively. The corresponding products could be obtained in moderate to high yields and with good to excellent stereoselectivities.

The development of new and efficient methods for the synthesis of versatile vinylsilanes has attracted the interest of many organic chemists.[1] Accordingly, various noble transition-metal catalyzed hydrosilylation of alkynes using silanes have been reported to furnish this class of compounds in good yields.[2] Recently, silylboronate reagents developed by Suginome's group have been widely used for the silylation reactions to forge new C–Si bonds.[3] The research groups of Ito,[4] Tanaka,[5] Suginome with Ohmura,[6] Oestreich,[7] Moberg,[8] Sato,[9] Cheng,[10] Hayashi,[11] Hoveyda,[12] Riant,[13] and Sawamura[14] *et al.* have contributed greatly in this field. Among the metals, copper salts have been recognized to be good choice as catalysts because of their low cost and environmental friendly merits.[15] However, not much attention has been focused on the copper-catalyzed Si–B activation and transformations. The pioneering work of silylcupration reaction of alkynes with $Me_2PhSi–BEt_3Li$ has been reported by Oshima and co-workers.[16] In this work, for most of cases, a mixture vinylsilanes regioisomers was obtained. It was not until about 25 years later that Loh and co-workers developed a CuCl/Johnphos system catalyzed silylcupration reaction of terminal alkynes using Suginome's reagent ((dimethylphenylsilyl)boronic acid pinacol ester **1**) in the presence of MeOH to afford the corresponding branched vinylsilanes in good yields and high selectivities.[17] Subsequently Tsuji and co-workers elegantly described a Cu(I)-catalyzed silacarboxylation reaction of internal alkynes with carbon dioxide and silylborane.[18] In 2013, Hoveyda's group reported an efficient NHC-Cu-catalyzed hydrosilylation of terminal alkynes also using **1** to generate linear (*E*)-β-vinylsilanes.[19] So far, there is no report on the copper-catalyzed hydrosilylation of electron-deficient allenes or propiolate derivatives.[20] The needs to use strong base NaO^{t}Bu to initiate the copper(I) catalytic cycle in the previously reported works by using silylboronate reagent **1** limits the use of this method for base sensitive substrates.[17-19] To circumvent this issue in order to generate multi-substituted vinylsilanes, we report a copper(I)-catalyzed protosilylation reaction of allenes and propargyl ester derivatives to produce multi-substituted vinylsilanes in very high stereoselectivites under very mild reaction conditions.

Table 1. Optimization of the reaction conditions[a]



entry	catalyst	ligand	additive	alcohol	solvent	T (°C)	yield (%)[b]
1	CuCl	dppe	KO^{t}Bu	MeOH	THF	30	32
2	CuCl	dppe	--	MeOH	THF	30	trace
3	CuCl	dppe	NEt_3	MeOH	THF	30	14
4	CuCl	dppe	NEt_3	MeOH	toluene	30	no reaction
5	CuCl	dppe	NEt_3	MeOH	DMSO	30	38
6	CuCl	dppe	NEt_3	--	MeOH	30	69
7	CuCl	dppe	NEt_3	--	^{t}BuOH	30	75
8	CuBr	dppe	NEt_3	--	^{t}BuOH	30	75
9	CuI	dppe	NEt_3	--	^{t}BuOH	30	74
10	CuBr	dppf	NEt_3	--	^{t}BuOH	30	70
11	CuBr	Johnphos	NEt_3	--	^{t}BuOH	30	68
12	CuBr	Xantphos	NEt_3	--	^{t}BuOH	30	67
13	CuBr	dppe	--	--	^{t}BuOH	30	no reaction
14	--	dppe	NEt_3	--	^{t}BuOH	30	no reaction
15	CuBr	--	NEt_3	--	^{t}BuOH	30	46
16	CuBr	dppe	NEt_3	--	^{t}BuOH	40	81

[a] All reactions unless otherwise stated were carried out with **2a** (0.3 mmol), 1 (0.33 mmol), 10 mol% of copper catalyst (0.03 mmol), 11 mol % ligand, 11 mol % additive and 2 equiv. alcohol in the given solvent (1.0 mL). [b] Isolated yield.

Initially, **1** and **2a** were chosen as the model substrates to optimize this reaction. In the presence of strong base KO^{t}Bu, only 32% yield of the desired product was obtained (Table 1, entry 1). To clarify what leads to the relatively low yield of the product, a few control experiments were carried out. We found that when **2a**, CuCl (10 mol %) and KO^{t}Bu (11 mol %) in THF were stirred for 24 hours in the absence of **1**, the starting material **2a** would be decomposed. Without the use of KO^{t}Bu, only trace amount of the desired product was obtained but most of **2a** could be recovered

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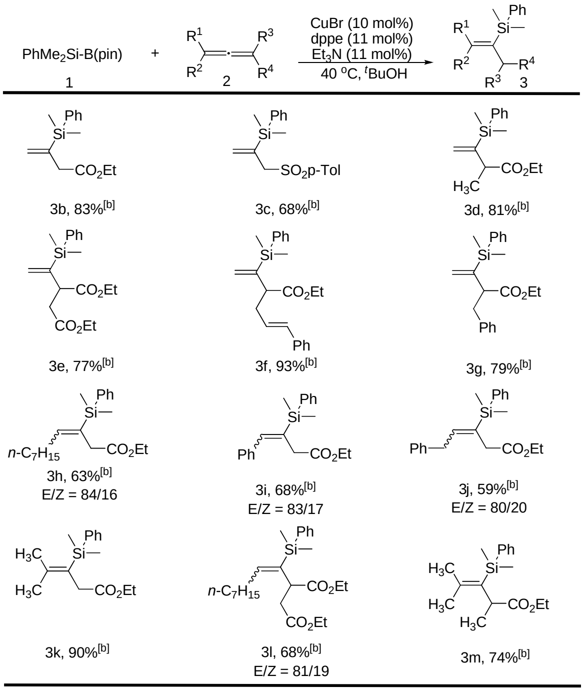
(Table 1, entry 2). On this basis, we attempted to use less basic Et$_3$N as the additive. To our delight, 14% product's yield could be obtained with the recovery of starting material **2a** (Table 1, entry 3). Diverse solvents were then screened and it was found that the yield of the desired product could be improved to 69% by using protic solvent such as methanol (Table 1, entry 6). The use of *tert*-butanol gave the best result in terms of yield (Table 1, entries 7-12 and 16). We observed that other phosphine ligands were efficient but not necessary to afford the desired product **3a** in this reaction (Table 1, entries 10-12 and 15). Further control experiments were carried out and it was shown that both the copper catalyst and Et$_3$N were crucial in this catalytic reaction (Table 1, entries 13 and 14). Ultimately, the optimized reaction conditions were established as follows: 10 mol% CuBr as catalyst and 11 mol% of dppe as ligand with 11 mol% Et$_3$N as additive in *tert*-butanol, heated at 40 °C.

Table 2. Synthesis of multi-substituted vinylsilanes using various allenes[a]

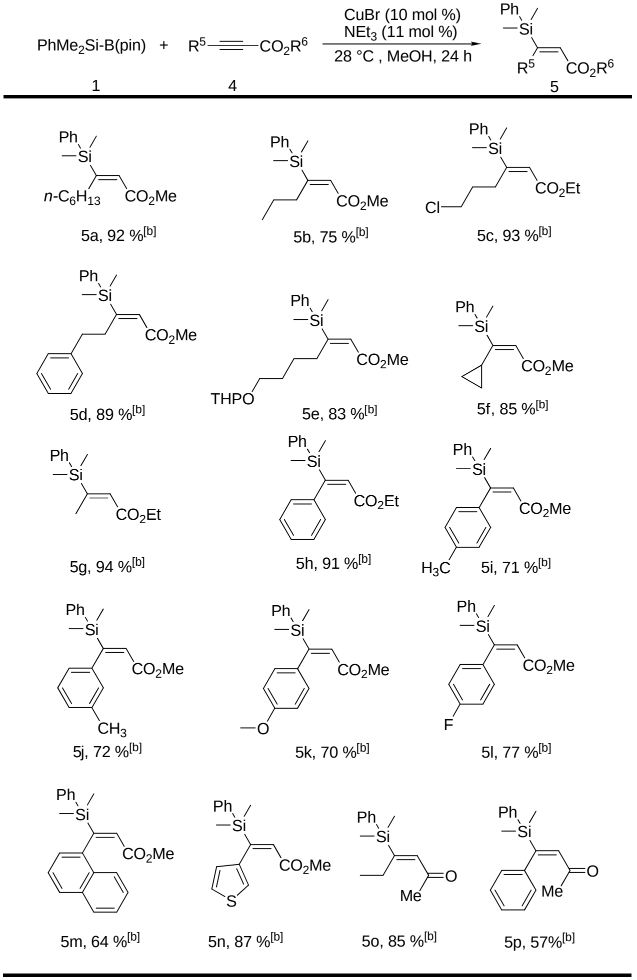


3b, 83%[b]
3c, 68%[b]
3d, 81%[b]
3e, 77%[b]
3f, 93%[b]
3g, 79%[b]
3h, 63%[b] E/Z = 84/16
3i, 68%[b] E/Z = 83/17
3j, 59%[b] E/Z = 80/20
3k, 90%[b]
3l, 68%[b] E/Z = 81/19
3m, 74%[b]

[a] Unless noted otherwise, the reaction conditions are as follows: allene (0.3 mmol), **1** (0.33 mmol), CuBr (10 mol%), dppe (11 mol%) and Et$_3$N (11 mol %) in ^{t}BuOH (1.0 mL) were heated at 40 °C for 24 h. [b] Isolated yields.

With the optimizated conditions in hand, we next tested the scope of allenes for this Cu(I)-catalyzed hydrosilylation reaction using (dimethylphenylsilyl)boronic acid pinacol ester **1**. The results are shown in Table 2. Firstly, we extended this reaction to the monosubstituted allenic ester and sulfone. The desired products were obtained in good yields respectively (Table 2, entries **3b** and **3c**). In all the cases using 1,1-disubstituted allenes, very high yields of the β-silylation products were also obtained (Table 2, entries **3d**-**3g**). 1,3-Disubstituted allenes were also treated as substrates in our reaction and the corresponding trisubstituted vinylsilanes also could be generated in reasonable yields (Table 2, entries **3h**, **3i** and **3j**). Furthermore, we noticed that the multi-substituted allenes (Table 2, entries **3k**, **3l** and **3m**) are good substrates for this reaction. In all cases, only the β-substituted products were obtained in high yields.

Table 3. Synthesis of multi-substituted vinylsilanes using internal alkynes[a]



5a, 92 %[b]
5b, 75 %[b]
5c, 93 %[b]
5d, 89 %[b]
5e, 83 %[b]
5f, 85 %[b]
5g, 94 %[b]
5h, 91 %[b]
5i, 71 %[b]
5j, 72 %[b]
5k, 70 %[b]
5l, 77 %[b]
5m, 64 %[b]
5n, 87 %[b]
5o, 85 %[b]
5p, 57%[b]

[a] Unless noted otherwise, the reaction conditions are as follows: alkyne (0.3 mmol), **1** (0.6 mmol), CuBr (10 mol%) and Et$_3$N (11 mol%) in MeOH (1.0 mL) were stirred at 28 °C for 24 h. [b] Isolated yields.

After the successful synthesis of dimethylphenylsilyl-substituted butenoate derivatives, next we turn our attention to study the hydrosilylation of propiolate derivatives which would provide very useful Si-substituted acrylate derivatives.[21] We chose methyl non-2-ynoate and (dimethylphenylsilyl)boronic acid pinacol ester **1** to optimize the reaction conditions (see the details in supplementary materials). To our surprise, we found that in the absence of any phosphine ligand, the exclusive (E)-isomer **5a** could be generated in a very high yield (92%) when the reaction was carried out using 10 mol% amount of CuBr as catalyst combined with 11 mol% Et$_3$N in MeOH.[22]

Next, we examined the scope of the reaction using various propiolate derivatives. It was found that the substrates possessing aliphatic side-chains all could provide the desired products in very high yields (Table 3, entries **5a**-**5g**). Functional group including chloride (Table 3, entry **5c**), protected hydroxy (Table 3, **5e**) and bulky cyclopropane groups (Table 3, entry **5f**) are well tolerated in this reaction. β-Aromatic ring substituted propiolates also worked well in this reaction (Table 3, entries **5h**-**5m**). The electronic properties of the substitutents on the aromatic ring have no apparent effect on the products' yields. Heterocycles such as thiophene group containing substrate also furnished the

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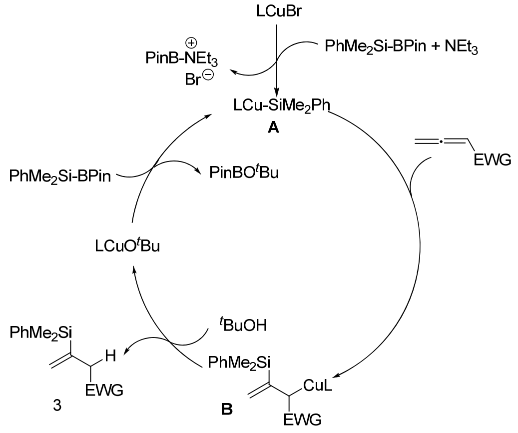
product **5p** in 87% yield (Table 3, entry **5n**). When the substrates were changed into butynone derivatives, the desired products could also be obtained in moderate to good yields (Table 3, entries **5o** and **5p**).

With the observed results, a possible mechanism was proposed as shown in Scheme 1. Firstly, the Et$_3$N could help to activate the B–Si bond *via* possible coordination between nitrogen and boron atom.[23] In the presence of copper catalyst, species **A** could be generated. Due to the electron density bias of allene with an electron-withdrawing group, an addition of Si-Cu into double bond will afford an allylic copper species **B** which could then undergo protonolysis in the presence of ^{t}BuOH to give the desired product **3**.[24] The reactive L-Cu-O^{t}Bu complex is then regenerated and will be involved in the next catalytic cycle. As for the hydrosilylation of propiolate derivatives, a similar mechanism as depicted in Scheme **1** could also be proposed. The higher reactivity of propiolate derivatives permits an easy transformation of the silyl group with the triple bond.

Scheme 1. Proposed Mechanism for the synthesis of vinylsilane from allene



Conclusions

In conclusion, we have found that copper salt can catalyze the silylation reactions of allenes and propiolate derivatives with silylboronate under mild reaction conditions. These methods provide facile access to versatile silyl-substituted homoallylic esters and β-silyl-substituted acrylates in moderate to excellent *E*/*Z* selectivities. This study also reveals that weak bases such as triethylamine could activate the Si–B bond to initiate the catalytic cycle for the transformation of silyl group into unsaturated bonds. The use of this strategy to carry out other organic transformations is in progress.

Acknowledgement

We thank Prof. S. Ma of SIOC for his generous gift of chiral allene compound for the mechanism study. We are grateful for financial support by the National Science Foundation for Young Scientists of China (No. 21202156), the Natural Science Foundation of Anhui Province (No. 1308085QB37). We also thank the Singapore Ministry of Education Academic Research Fund (MOE2011-T2-1-013, NEA1002111) for the funding of this research.

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[24] Please see a brief proof for the proposed mechanism in the SI section by using a chiral allene **2n** to generate a racemic product **3n**.

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