Allylic Compounds

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Synthesis of Branched Alkylboronates by Copper-Catalyzed Allylic Substitution Reactions of Allylic Chlorides with 1,1-Diborylalkanes

*Junghoon Kim, Sangwoo Park, Jinyoung Park, and Seung Hwan Cho**

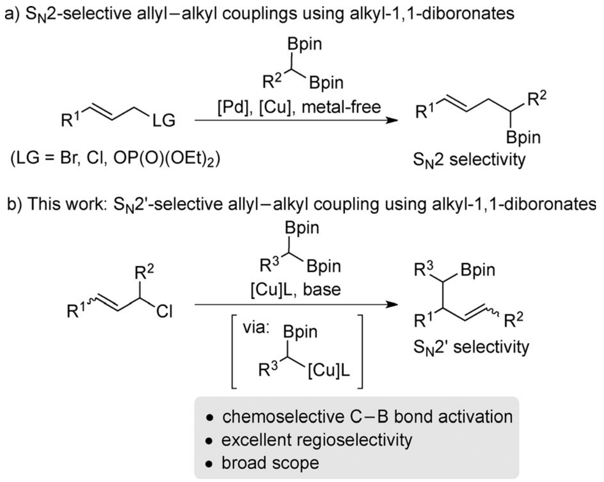
Abstract: *Reported herein is a copper-catalyzed S_N2'-selective allylic substitution reaction using readily accessible allylic chlorides and 1,1-diborylalkanes, a reaction which proceeds with chemoselective C–B bond activation of the 1,1-diborylalkanes. In the presence of a catalytic amount of [Cu(IMes)Cl] [IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazole-2-ylidene] and LiOtBu as a base, a range of primary and secondary allylic chlorides undergo the S_N2'-selective allylic substitution reaction to produce branched alkylboronates. The synthetic utilities of the obtained alkylboronates are also presented.*

Transition-metal-catalyzed allylic alkylation is one of the most powerful tools for C–C bond formation in organic synthesis.[1] Among these reactions, copper-catalyzed allylic alkylation is an efficient strategy for synthesizing branched alkyl compounds.[2,3] Although significant progress has been made in the copper-catalyzed allylic alkylations of allylic electrophiles with organometallic reagents (e.g. dialkylzinc, alkyllithium, alkylaluminum, alkylzirconium and Grignard reagent), limited functional-group compatibility and the air/moisture sensitivity of organometallic reagents often limit their synthetic applications.[4,5] Moreover, these reactions typically require cryogenic temperatures to achieve high levels of selectivity.

Organoboron compounds are versatile reagents in organic synthesis because of their wide availability and air stability.[6] Although several catalytic methods have been reported for S_N2'-selective allylic substitution using organoboron compounds,[7] most of them use aryl,[8] alkenyl,[9] allenyl,[10] propargyl,[11] and allyl boron[7,12] derivatives, while only a few examples using alkylboron reagents have been reported. Only in the last few years S_N2'-selective allylic alkylation processes have been developed. However, they are limited to alkyl-9-BBN (generated in situ from alkenes).[13] Despite these advances, because of the structural diversity, new sources of alkylboron reagents which are readily accessible, scalable, and air-stable should be discovered.

Recently, multiborylated compounds, including 1,1-diborylalkanes, have emerged as efficient substrates for synthesizing alkylboron compounds through chemoselective transformations. Since the pioneering work by Shibata and co-workers,[14] substantial progress has been made in the development of chemoselective C–C bond-forming reactions of 1,1-diborylalkanes.[15,16] However, the regioselective coupling of allylic electrophiles with 1,1-diborylalkanes has rarely been studied. In 2013, Shibata et al. reported the Suzuki–Miyaura cross-coupling of allylic bromides and diborylmethane, thus affording S_N2-selective products in the presence of a palladium catalyst.[14c] Morken and co-workers reported the alkoxide-promoted S_N2-type alkylation of allylic chlorides with alkyl-1,1-diboronates, thus providing linear alkylboronates.[16g] Fu and Xiao also reported that cinnamyl phosphate and diborylmethane participated in the copper-catalyzed allylic alkylation reaction to form linear alkylboronates (Scheme 1 a).[17] Herein, we report a Cu/(NHC)-catalyzed (NHC = N-heterocyclic carbene) S_N2'-selective allylic alkylation reaction of allylic chlorides with 1,1-diborylalkanes. This method has a wide substrate scope, is highly regioselective for the S_N2' product, and paves a path for the future development of enantioselective and diastereoselective variants (Scheme 1 b).

To test the viability of the envisioned strategy, we identified an appropriate allylic electrophile for reacting with the diborylmethane **2a** in the presence of a catalytic amount of [Cu(IMes)Cl] [IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazole-2-ylidene] and Li*Ot*Bu as a base. Although only a negligible amount of product was formed in the presence of cinnamyl acetate (Table 1, entry 1) and *tert*-butyl cinnamyl carbamate (entry 2), the use of methyl cinnamyl carbamate afforded an almost 1:1 mixture of the S_N2' and S_N2 products **4a** and **5a**, respectively, in a low yield (entry 3). When cinnamyl ethyl phosphate was used, a 92:8 mixture of products **4a** and **5a** was obtained, with **4a** as the major isomer



Scheme 1. Chemo- and regioselective allylic alkylation of allylic electrophiles with 1,1-diborylalkanes. pin = pinacol.

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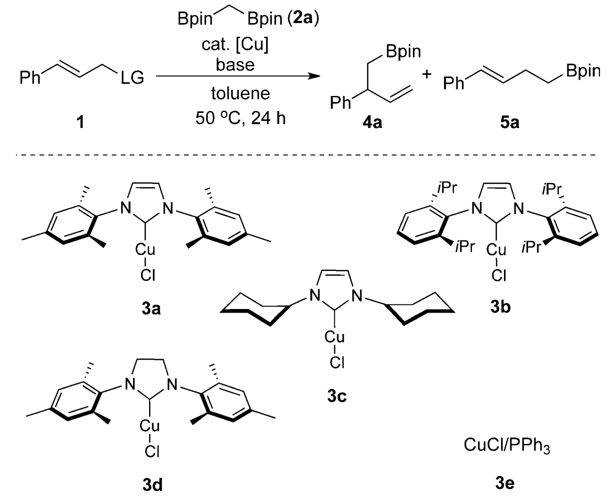
Table 1: Optimization study.[a]



Entry	cat. [Cu]	LG	**2a** (equiv)	Yield [%][b]	S_N2'/S_N2[c]
1	**3a**	OAc	1.5	trace	–
2	**3a**	OCO_2tBu	1.5	trace	–
3	**3a**	OCO_2Me	1.5	17	53:47
4	**3a**	$OP(O)(OEt)_2$	1.5	68	92:8
5	**3a**	Cl	1.5	84	92:8
6	**3a**	Br	1.5	43	74:26
7	**3a**	Cl	2.0	94 (78)[d]	93:7
8[e]	**3a**	Cl	2.0	82	84:16
9[f]	**3a**	Cl	2.0	73	51:49
10	**3b**	Cl	2.0	80	85:15
11	**3c**	Cl	2.0	99	39:61
12	**3d**	Cl	2.0	87	87:13
13	**3e**	Cl	2.0	96	58:42
14	–	Cl	2.0	<1	–

[a] Reaction conditions: **1** (0.2 mmol), **2a** (1.5–2.0 equiv), cat. [Cu] (10 mol%), LiO*t*Bu (3.0 equiv) in toluene at 50 °C for 24 h. [b] Determined by ^1H NMR analysis with anisole as the internal standard. [c] S_N2'/S_N2 selectivity was determined by ^1H NMR analysis of the crude reaction mixture. [d] Yield of isolated product is shown within parentheses. [e] NaO*t*Bu was used as the base. [f] KO*t*Bu was used as the base. LG = leaving group.

in 68% yield (entry 4). Comparable selectivity ($S_N2'/S_N2 = 92:8$) was obtained when cinnamyl chloride (entry 5) was used as the allylic electrophile, but with an improved yield (84%). However, when cinnamyl bromide was used, a poor yield was obtained (entry 6). To our delight, using 2 equivalents of **2a** with cinnamyl chloride provided the best yield (94%) and highest S_N2' selectivity (entry 7). The use of other alkoxide bases (entries 8 and 9) and solvents resulted in lower yields and reduced S_N2' selectivity.[18] Moreover, the replacement of IMes with other NHC ligands such as IPr, ICy, and SIMes (entries 10–12) resulted in lower S_N2'/S_N2 ratios. When the NHC was replaced with a phosphine ligand, poor regioselectivity was obtained (entry 13). This result indicated that S_N2' selectivity is highly favored by the presence of a NHC ligand. No reaction occurred when the copper catalyst was absent (entry 14).

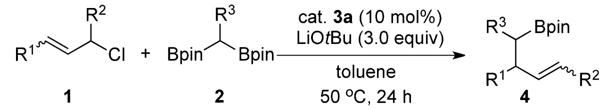
With optimized reaction conditions in hand, the substrate scope with respect to the allylic chlorides **1** and 1,1-diborylalkanes **2** was investigated (Table 2). To our delight, both aromatic and aliphatic allylic chlorides successfully afforded the corresponding alkylboronates in good yields and with good to excellent S_N2' selectivity. The reactions with cinnamyl chlorides bearing methyl (entry 2) and chloro (entry 3) substituents in the *para*-position of the arene ring afforded the products **4b** (68%) and **4c** (86%) in good selectivities of 95:5 and 96:4 S_N2'/S_N2, respectively.

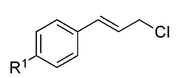
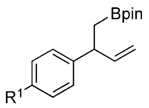
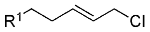
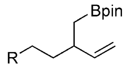
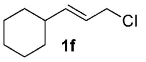
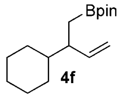
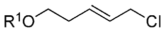
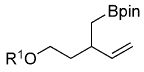
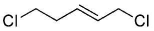
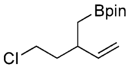
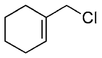
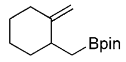
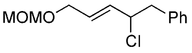
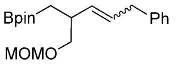
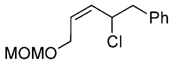
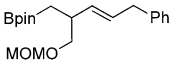
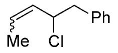
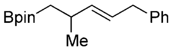
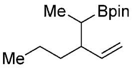
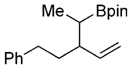
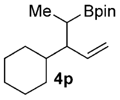
Notably, aliphatic allylic chlorides underwent allylic alkylation with a high yields and greater than 99:1 S_N2'/S_N2 selectivity. The reactions of acyclic and cyclic allylic chlorides (**1d–f**) afforded the products **4d–f** with a high level of S_N2' selectivity ($S_N2'/S_N2 > 99:1$). Various functional groups, including silyl ether (**4g**), pivalate (**4h**), and chloride (**4i**), were well tolerated, thus affording the corresponding branched alkylboronates in moderate to good yields (76–82%) and with excellent selectivities ($S_N2'/S_N2 > 99:1$). A boronate bearing an exocyclic methylene, **4j**, was synthesized in 78% yield with complete S_N2' selectivity by the reaction of the cyclohexenyl derivative **1j** with **2a** under copper catalysis. That the developed catalytic conditions are applicable to secondary allylic chlorides is of particular note. The reaction of the allylic chloride (*E*)-**1k** with **2a** in the presence of 20 mol% copper catalyst afforded **4k** in 62% yield with complete S_N2' selectivity and moderate stereoselectivity (*E*/*Z* 86:14). In contrast, when the *Z*-allylic chloride **1l** was used, (*E*)-**4l** was obtained exclusively. Importantly, the reaction with an isomeric mixture of a secondary allylic chloride **1m** (*E*/*Z* 1:2.6) afforded the corresponding alkylboronate **4m** in 80% yield and with excellent regio- ($S_N2'/S_N2 > 99:1$) and stereoselectivity ($E/Z > 99:1$).

Next, the reactions of substituted 1,1-diboronates were investigated. However, when the allylic chloride **1d** and ethyl-1,1-diboronate **2b** ($R^3 = Me$) were subjected to the optimized reaction conditions, only a trace amount of the desired product was formed. Therefore, we immediately reinvestigated the reaction parameters using **1d** and **2b** as model substrates. After extensive re-optimization,[18] we were pleased to find that the reaction required a higher catalyst loading (20 mol%) and a 5:1 mixture of 1,4-dioxane and toluene as the solvent to afford the corresponding product **4n** in 80% yield and with 96:4 S_N2'/S_N2 selectivity. It should be emphasized that this avenue opens up new possibilities for the development of a copper-catalyzed diastereoselective allylic substitution reaction. By using these modified reaction conditions, the reactions of aliphatic allylic chlorides **1e** and **1f** with **2b** afforded the products **4o** and **4p**, respectively, in satisfactory yields (55–71%) and good S_N2' selectivity (S_N2'/S_N2 95:5).

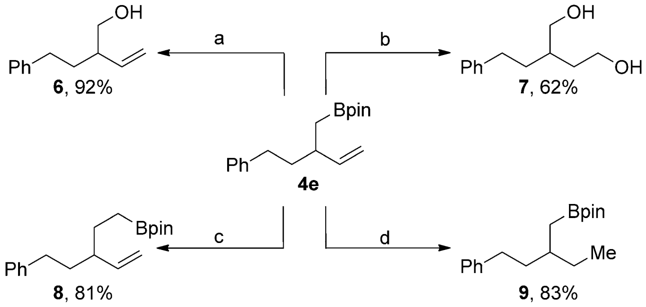
To demonstrate the versatility of the products obtained in this study, further transformations of **4e** were investigated (Scheme 2). The oxidation of **4e** in the presence of sodium perborate in a mixture of THF/H_2O at room temperature afforded the corresponding alcohol **6** in 92% yield. Product **4e** was transformed into the 1,4-diol **7** by a sequence of hydroboration and oxidation reactions (62% yield over two steps). Moreover, treatment with iodochloromethane and *n*BuLi afforded the one-carbon homologated product **8** in 81% yield. The product **4e** was hydrogenated with $TsNHNH_2$ and NaOAc, thus affording the aliphatic alkylboronate **9** in 83% yield, in which the Bpin unit remained intact.

Table 2: Substrate scope.[a]

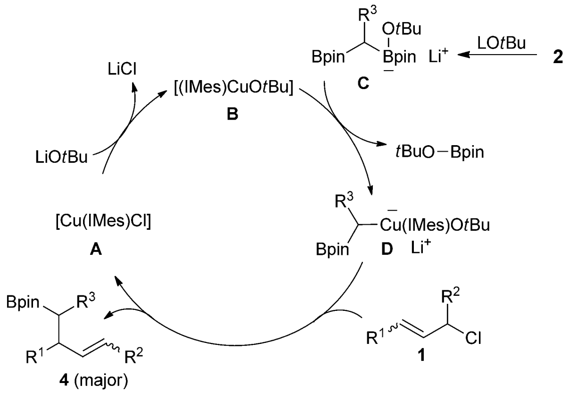


Entry	Allylic chloride	R³	Product	S_N2'/S_N2[b]	Yield [%][c]
					
1	**1a** (R^1 = H)	**2a** (R^3 = H)	**4a**	93:7	78
2	**1b** (R^1 = Me)	**2a**	**4b**	95:5	68
3	**1c** (R^1 = Cl)	**2a**	**4c**	96:4	86
					
4	**1d** (R^1 = Me)	**2a**	**4d**	>99:1	82
5	**1e** (R^1 = Ph)	**2a**	**4e**	>99:1	76
6	 **1f**	**2a**	 **4f**	>99:1	60
					
7	**1g** (R^1 = TBS)	**2a**	**4g**	>99:1	76
8	**1h** (R^1 = C(O)*t*Bu)	**2a**	**4h**	>99:1	82
9	 **1i**	**2a**	 **4i**	>99:1	82
10	 **1j**	**2a**	 **4j**	>99:1	78
11[d]	 **1k** (*E/Z* >99:1)	**2a**	 **4k** (*E/Z* 86:14)	>99:1	62
12[d]	 **1l** (*E/Z* <1:99)	**2a**	 **4l** (*E/Z* >99:1)	>99:1	77
13[d]	 **1m** (*E/Z* 1:2.6)	**2a**	 **4m** (*E/Z* >99:1)	>99:1	80
14[d,e,f]	**1d**	**2b** (R^3 = Me)	 **4n**	96:4	80
15[d,e,f]	**1e**	**2b**	 **4o**	95:5	55
16[d,e,f]	**1f**	**2b**	 **4p**	95:5	71

[a] Reaction conditions: **1** (0.2 mmol), **2a** (2.0 equiv), Cu(IMes)Cl (10 mol%), and LiO*t*Bu (3.0 equiv) in toluene at 50 °C for 24 h. [b] S_N2'/S_N2 selectivity was determined by ^{1}H NMR analysis of the crude reaction mixture. [c] Yield of isolated product. [d] [Cu(IMes)Cl] (20 mol%) was used. [e] A mixture of 1,4-dioxane/toluene (5:1 v/v) was used as the solvent instead of toluene. [f] Mixtures of diastereomers were obtained (1:1–1:1.5). MOM = methoxy methyl ether.



Scheme 2. Transformations of the allylic substitution product: a) $NaBO_3\cdot4H_2O$, THF/H_2O (1:1 v/v), RT, 5 h. b) (9-BBN)$_2$, toluene, 120 °C, 12 h, then NaOH/H_2O_2, EtOH, RT, 5 h. c) ICH_2Cl, *n*BuLi, THF, −78 °C to RT, 3 h. d) $TsNHNH_2$, NaOAc, THF/H_2O (1:1 v/v), reflux, 24 h. THF = tetrahydrofuran, Ts = 4-toluenesulfonyl.



Scheme 3. Proposed reaction mechanism.

Although more comprehensive studies are still required to elucidate the mechanistic details, a plausible mechanism is shown in Scheme 3. On the basis of the incomplete S_N2' selectivity and literature precedent,[4l,19] we assume that a monoalkylalkoxycuprate (**D**) is involved as an active species for the transformation. First, the copper alkoxide complex **B** is generated from [Cu(IMes)Cl] in the presence of LiO*t*Bu. The copper complex **B** then undergoes transmetalation with the monoborate **C**[20] to afford the heterocuprate **D**. Subseqeunt S_N2' substitution of **1** with the copper species **D** via a allylcopper(III) complex[19] affords the S_N2' product **4** and the copper(I) complex **A**. Finally, **B** is regenerated by the reaction of **A** with LiO*t*Bu.

In summary, we have developed the first copper-catalyzed S_N2'-selective allylic substitution reaction which utilizes readily accessible 1,1-diborylalkanes as the coupling partners. This new protocol provides an efficient strategy to synthesize branched alkylboronates in good yields and with a high functional-group compatibility. Further studies to develop an enantio- and diastereoselective version of this transformation are underway.

Acknowledgments

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Keywords: allylic compounds · boron · copper · N-heterocyclic carbenes · regioselectivity

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[1] For reviews on transition metal-catalyzed allylic substitution, see: a) B. M. Trost, M. L. Crawley, *Chem. Rev.* **2003**, *103*, 2921; b) Z. Lu, S. Ma, *Angew. Chem. Int. Ed.* **2008**, *47*, 258; *Angew. Chem.* **2008**, *120*, 264; c) J. F. Teichert, B. L. Feringa, *Angew. Chem. Int. Ed.* **2010**, *49*, 2486; *Angew. Chem.* **2010**, *122*, 2538; d) J. D. Weaver, A. Recio, A. J. Grenning, J. A. Tunge, *Chem. Rev.* **2011**, *111*, 1846.

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