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Synthesis of Conjugated Allenes through Copper-Catalyzed γ-Selective and Stereospecific Coupling between Propargylic Phosphates and Aryl- or Alkenylboronates

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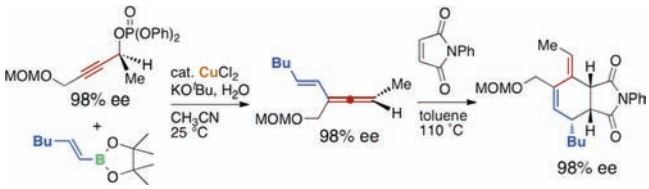
ABSTRACT



A Cu-catalyzed γ-selective coupling reaction between propargylic phosphates and aryl- or alkenylboronates afforded aryl- or alkenyl-conjugated allenes. The reaction showed excellent functional group compatibility in both the propargylic substrates and the boronates. The reaction of an enantioenriched propargylic phosphate proceeded with excellent chirality transfer with 1,3-*anti* stereochemistry to give axially chiral aryl- and alkenylallenes.

Allenes are important building blocks that have unique reactivity due to the orthogonal consecutive π-bonds.[1,2] Additionally, they are found in many natural products.[3,4] Among a number of routes to allenes, the γ-substitution (formal S_N2' displacement) of propargylic alcohol derivatives with organocuprate reagents is most straightforward.[5−8] However, the method often suffers from problems of functional group compatibility because the organocopper reagents must be prepared from highly reactive organometallic reagents such as Grignard or organolithium reagents.[4o,9] Furthermore, the use of sp^2-carbon nucleophiles, such as aryl- or alkenylmetal reagents, has not been well exploited due to the poor nucleophilicity of these reagents relative to that of the alkylcopper species.[9] Therefore, the organocopper-based method is not generally applicable for the synthesis of aryl- or alkenyl-conjugated allenes.

Previously, we found that the copper-catalyzed allyl–aryl coupling between allylic phosphates and arylboronates

(1) Reviews on allenes: (a) *Modern Allene Chemistry*; Krause, N., Hashmi, A. S. K., Eds.; Wiley-VCH: Weinheim, Germany, 2004; Vols. 1 and 2.

(2) Reviews on the synthetic applications of allenes: (a) Ma, S. *Acc. Chem. Res.* **2003**, *36*, 701–712. (b) Sydnes, L. K. *Chem. Rev.* **2003**, *103*, 1133–1150. (c) Ma, S. *Chem. Rev.* **2005**, *105*, 2829–2871. (d) Ma, S. *Acc. Chem. Res.* **2009**, *42*, 1679–1688.

(3) Reviews on allenic natural products and pharmaceuticals: Hoffmann-Röder, A.; Krause, N. *Angew. Chem., Int. Ed.* **2004**, *43*, 1196–1216.

(4) Reviews on the synthesis of allenes: (a) Krause, N.; Hoffmann-Röder, A. *Tetrahedron* **2004**, *60*, 11671–11694. (b) Brummond, K. M.; DeForrest, J. E. *Synthesis* **2007**, 795–818. (c) Yu, S.; Ma, S. *Chem. Commun.* **2011**, 5384–5418. For selected examples on the synthesis of allenes since 2007, see: (d) Deutsch, C.; Lipshutz, B. H.; Krause, N. *Angew. Chem., Int. Ed.* **2007**, *46*, 1650–1653. (e) Hayashi, S; Hirano, K.; Yorimitsu, H.; Oshima, K. *J. Am. Chem. Soc.* **2008**, *130*, 5048–5049. (f) Ready, J. M.; Pu, X. *J. Am. Chem. Soc.* **2008**, *130*, 10874–10875. (g) Kobayashi, K.; Naka, H.; Wheatley, A. E.; Kondo, Y. *Org. Lett.* **2008**, *10*, 3375–3377. (h) Tang, M.; Fan, C.-A.; Zhang, F.-M.; Tu, Y.-Q.; Zhang, W.-X.; Wang, A.-X. *Org. Lett.* **2008**, *10*, 5585–5588. (i) Zhong, C.; Sasaki, Y.; Ito, H.; Sawamura, M. *Chem. Commun.* **2009**, 5850–5852. (j) Deutsch, C.; Lipshutz, B. H.; Krause, N. *Org. Lett.* **2009**, *11*, 5010–5012. (k) Kuang, J.; Ma, S. *J. Am. Chem. Soc.* **2010**, *132*, 1786–1787. (l) Bolte, B.; Odabacian, Y.; Gagosz, F. *J. Am. Chem. Soc.* **2010**, *132*, 7294–7296. (m) Ohmiya, H.; Yang, M.; Yamauchi, Y.; Ohtsuka, Y.; Sawamura, M. *Org. Lett.* **2010**, *12*, 1796–1799. (n) Xiao, Q.; Xia, Y.; Li, H.; Zhang, Y.; Wang, J. *Angew. Chem., Int. Ed.* **2011**, *50*, 1114–1117. (o) Ohmiya, H.; Yokobori, U.; Makida, Y.; Sawamura, M. *Org. Lett.* **2011**, *13*, 6312–6315. (p) Vyas, D. J.; Hazra, C. K.; Oestreich, M. *Org. Lett.* **2011**, *13*, 4462–4465.

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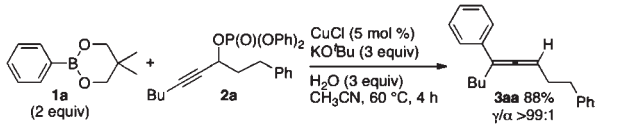
proceeded in the presence of KO^{t}Bu and water (3 equiv each) with excellent γ-selectivity and stereospecifity.[10b] On the basis of this knowledge, we envisioned that arylboron compounds could be coupled regioselectively with propargyl alcohol derivatives under copper-catalyzed conditions for constructing aryl- or alkenyl-conjugated allenes.

Here we report a copper-catalyzed γ-selective coupling between propargylic phosphates and aryl- or alkenylboronates as an approach to conjugated allenes.[10−13] The reaction is compatible with various functional groups in both propargylic phosphates and boronates, affording functionalized aryl- and alkenylallenes that are difficult to prepare by other methods. The reaction of enantioenriched propargylic phosphates took place with excellent point-to-axial chirality transfer with *anti* stereochemistry to give axially chiral conjugated allenes.

Specifically, the reaction of propargylic phosphate **2a** with 5,5-dimethyl-2-phenyl-1,3,2-dioxaborinane (**1a**) (2 equiv) in the presence of CuCl (5 mol %), KO^{t}Bu (3 equiv), and H_2O (3 equiv) in CH_3CN at 60 °C for 4 h afforded arylallene product **3aa** in 88% isolated yield. The ^{1}H NMR analysis of the crude product confirmed that no α-substitution product (alkyne) was formed (γ/α > 99:1) (Scheme 1).

The optimum reaction conditions are similar to those of the copper-catalyzed allyl−aryl coupling between allylic phosphates and arylboronates.[10b] Some noteworthy points are described below. No reaction occurred in the absence of CuCl. $CuCl_2$ was as effective as CuCl (82% yield). The use of a small amount of H_2O (3 equiv) is critical: the reaction without H_2O resulted in a complex mixture. The amount of KO^{t}Bu is also critical: reducing it from 3 to 2 equiv decreased the yield from 88 to 44% under otherwise identical conditions, and no reaction occurred in the absence of KO^{t}Bu. Reducing the amount of boronate **1a** to 1 equiv caused considerable hydrolysis of **2a**. The use of phenylboronic acid pinacol ester in place of the neopentyl glycolato **1a** decreased the yield of **3aa** (60%). Phenylboronic acid was also usable instead of **1a**, but the yield of **3aa** was further decreased to 40%. Changing the leaving group to diethyl- or diisopropyl phosphates inhibited the reaction.

Scheme 1



The reaction showed a range of substrate scope of arylboronates (**1**) and propargylic phosphates (**2**), affording a variety of allenes (Table 1). Functionalities such as MeO, CF_3, Cl, ketone, ester, and silyl ether in **1** or **2** were compatible with the Cu system (entries 2−7).

The tolerance of the reaction toward steric demand in both arylboronates (**1**) and propargylic phosphates (**2**) is shown in Table 1, entries 1 and 8−11. *o*-Tolylboronate (**1b**) was coupled with **2a** in a reasonable yield (entry 1). The propargylic phosphates **2c**, **2d**, and **2e** with Me, $MeOCH_2$, and bulkier *i*-Bu groups, respectively, instead of the Bu group at the γ-position in **2** were phenylated effectively to afford the corresponding allenes **3ac**, **3ad**, and **3ae** (entries 8−10). A sterically more demanding α-substituent such as an *i*-Pr group was also tolerated (entry 11).

The Cu catalyst system was also applicable to the synthesis of conjugated alkenylallenes (Scheme 2 and Table 2). Specifically, the treatment of *trans*-1-hexen-1-ylboronic acid pinacol ester (**1h**) (3 equiv) with **2a** in the

(5) Pioneering works on γ-substitution of propargylic alcohol derivatives with organocuprate reagents by Crabee and co-workers: (a) Rona, P.; Crabbe, P. *J. Am. Chem. Soc.* **1968**, *90*, 4733–4744. (b) Rona, P.; Crabbe, P. *J. Am. Chem. Soc.* **1969**, *91*, 3289–3292.

(6) Reviews on γ-substitution of propargylic alcohol derivatives with organocuprate reagents: (a) Krause, N.; Hoffmann-Röder, A. In *Modern Organocopper Chemistry*; Krause, N., Ed.; Wiley-VCH: Weinheim, Germany, 2002; pp 145−163. (b) Hoffmann-Röder, A.; Krause, N. In *Modern Allene Chemistry*; Krause, N., Hashmi, A. S. K., Eds.; Wiley-VCH: Weinheim, Germany, 2004; pp 51−92. (c) Ogasawara, M.; Hayashi, T. In *Modern Allene Chemistry*; Krause, N., Hashmi, A. S. K., Eds.; Wiley-VCH: Weinheim, Germany, 2004; pp 93−140. (d) Ohno, H.; Nagaoka, Y.; Tomioka, K. In *Modern Allene Chemistry*; Krause, N., Hashmi, A. S. K., Eds.; Wiley-VCH: Weinheim, Germany, 2004; pp 141−181.

(7) The synthesis of optically active allenes by the S_N2' ring opening reaction of alkynyl-substituted β-lactones:Wan, Z.; Nelson, S. G. *J. Am. Chem. Soc.* **2000**, *122*, 10470–10471.

(8) The synthesis of optically active vinylallenes by 1,5-substitution of enyne acetates:Krause, N.; Purpura, M. *Angew. Chem., Int. Ed.* **2000**, *39*, 4355–4356.

(9) The transition-metal (Pd, Rh)-catalyzed substitutions of propargylic derivatives with aryl- or alkenylboron compounds: (a) Moriya, T.; Miyaura, N.; Suzuki, A. *Synlett* **1994**, 149–152. (b) Yoshida, M.; Gotou, T.; Ihara, M. *Tetrahedron Lett.* **2004**, *45*, 5573–5575. (c) Yoshida, M.; Ueda, H.; Ihara, M. *Tetrahedron Lett.* **2005**, *46*, 6705–6708. (d) Yoshida, M.; Okada, T.; Ihara, M. *Tetrahedron* **2007**, *63*, 6996–7002. (e) Molander, G. A.; Sommers, E. M.; Baker, S. R. *J. Org. Chem.* **2006**, *71*, 1563–1568. (f) Murakami, M.; Igawa, H. *Helv. Chim. Acta* **2002**, *85*, 4182–4188. (g) Miura, T.; Shimada, M.; Ku, S.-Y.; Tamai, T.; Murakami, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 7101–7103.

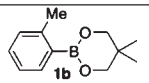
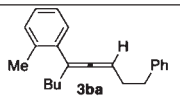
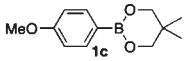
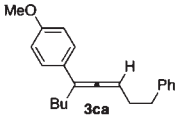
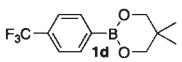
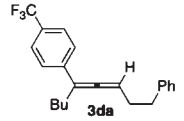
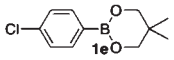
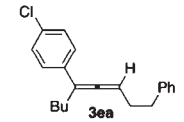
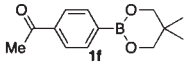
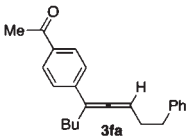
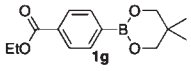
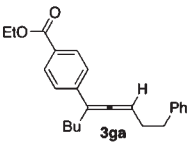
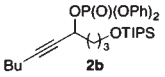
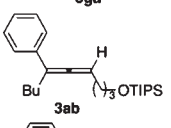
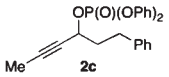
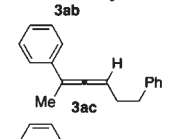
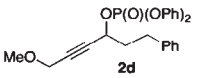
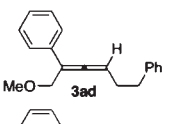
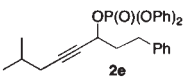
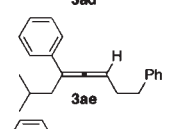
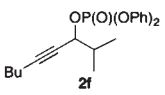
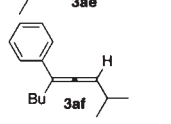
(10) Cu-catalyzed γ-selective and stereospecific allyl−aryl and allyl−alkyl couplings with organoboron compounds: (a) Ohmiya, H.; Yokobori, U.; Makida, Y.; Sawamura, M. *J. Am. Chem. Soc.* **2010**, *132*, 2895–2897. (b) Ohmiya, H.; Yokokawa, N.; Sawamura, M. *Org. Lett.* **2010**, *12*, 2438–2440. (c) Whittaker, A. M.; Rucker, R. P.; Lalic, G. *Org. Lett.* **2010**, *12*, 3216–3218. For related studies with palladium catalysts, see also: (d) Ohmiya, H.; Makida, Y.; Tanaka, T.; Sawamura, M. *J. Am. Chem. Soc.* **2008**, *130*, 17276–17277. (e) Ohmiya, H.; Makida, Y.; Li, D.; Tanabe, M.; Sawamura, M. *J. Am. Chem. Soc.* **2010**, *132*, 879–889. (f) Li, D.; Tanaka, T.; Ohmiya, H.; Sawamura, M. *Org. Lett.* **2010**, *12*, 3344–3347. (g) Makida, Y.; Ohmiya, H.; Sawamura, M. *Chem. Asian J.* **2011**, *6*, 410–414.

(11) Our studies on regioselective transformations of propargylic alcohol derivatives: (a) Ito, H.; Sasaki, Y.; Sawamura, M. *J. Am. Chem. Soc.* **2008**, *130*, 15774–15775. (b) Ohmiya, H.; Ito, H.; Sawamura, M. *Org. Lett.* **2009**, *11*, 5618–5620. See also refs 4i, 4m, and 4o.

(12) Cu-catalyzed conjugate additions with alkylboron compounds (alkyl-9-BBN): (a) Ohmiya, H.; Yoshida, M.; Sawamura, M. *Org. Lett.* **2011**, *13*, 482–485. (b) Ohmiya, H.; Shido, Y.; Yoshida, M.; Sawamura, M. *Chem. Lett.* **2011**, *40*, 928–930. Cu-catalyzed carboxylations with alkylboron compounds (alkyl-9-BBN) to carbon dioxide: (c) Ohmiya, H.; Tanabe, M.; Sawamura, M. *Org. Lett.* **2011**, *13*, 1086–1088.

(13) Cu-catalyzed C−C bond formations with aryl- and alkenylboron reagents: (a) Takaya, J.; Tadami, S.; Ukai, K.; Iwasawa, N. *Org. Lett.* **2008**, *10*, 2697–2700. (b) Ohishi, T.; Nishiura, M.; Hou, Z. *Angew. Chem., Int. Ed.* **2008**, *47*, 5792–5795. (c) Yamamoto, Y.; Kirai, N.; Harada, Y. *Chem. Commun.* **2008**, 2010–2012. (d) Tomita, D.; Kanai, M.; Shibasaki, M. *Chem. Asian J.* **2006**, *1*, 161–166. (e) Tomita, D.; Yamatsugu, K.; Kanai, M.; Shibasaki, M. *J. Am. Chem. Soc.* **2009**, *131*, 6946–6948. (f) Takatsu, K.; Shintani, R.; Hayashi, T. *Chem. Commun.* **2010**, 6822–6824. (g) Takatsu, K.; Shintani, R.; Hayashi, T. *Angew. Chem., Int. Ed.* **2011**, *50*, 5548–5552. (h) Yang, C.-T.; Zhang, Z.-Q.; Liu, T.-C.; Liu, L. *Angew. Chem., Int. Ed.* **2011**, *50*, 3904–3907. (i) Shintani, R.; Takatsu, K.; Takeda, M.; Hayashi, T. *Angew. Chem., Int. Ed.* **2011**, *50*, 8656–8659. See also refs 10b and 10c.

Table 1. Synthesis of Arylallenes[a]

entry	boronate	phosphate	product	yield (%)[b,c]
1		**2a**		69
2		**2a**		62
3		**2a**		78
4		**2a**		78
5[d]		**2a**		57
6[d]		**2a**		63
7	**1a**			74
8	**1a**			74
9	**1a**			70
10	**1a**			84
11	**1a**			75

[a] Conditions: **1** (0.6 mmol), **2** (0.3 mmol), CuCl (5 mol %), H_2O (0.9 mmol), KO^{t}Bu (0.9 mmol), CH_3CN (1 mL), 60 °C, 4 h. [b] Isolated yield. [c] Isomeric ratio (γ/α >99:1). Determined by ^{1}H NMR or GC analysis. [d] The reaction was carried out for 12 h.

presence of $CuCl_2$ (10 mol %), KO^{t}Bu (3 equiv), and H_2O (3 equiv) in CH_3CN at 30 °C for 12 h afforded alkenylallene product **3ha** in 71% isolated yield. No α-substitution product (alkyne) was observed (Scheme 2). Increasing the amounts of both boronate **1h** and KO^{t}Bu/H_2O to 3 and 4 equiv, respectively, resulted in a slight increase in the yield (77%). In contrast to the reaction of the arylboronates, the use of CuCl resulted in lower reaction efficiency (61%).

Scheme 2

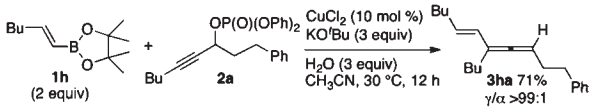
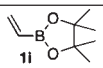
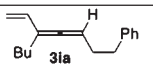
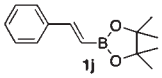
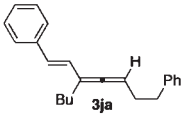
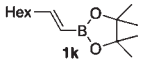
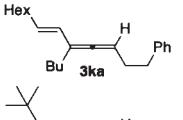
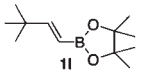
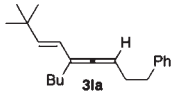
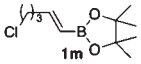
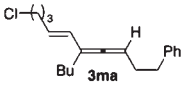
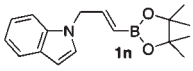
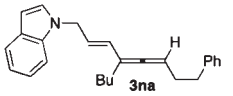
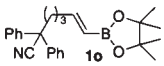
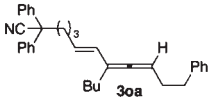
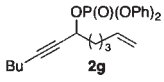
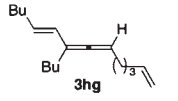


Table 2. Synthesis of Alkenylallenes[a]

entry	boronate	phosphate	product	yield (%)[c,d]
1[b]		**2a**		54
2[b]		**2a**		56
3		**2a**		72
4		**2a**		50
5		**2a**		76
6		**2a**		68
7		**2a**		55
8	**1h**			68

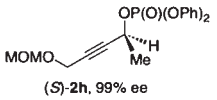
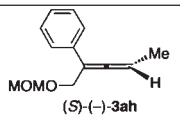
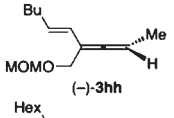
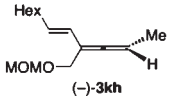
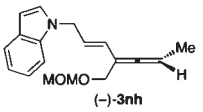
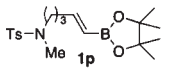
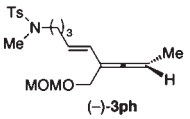
[a] Conditions: **1** (0.6 mmol), **2** (0.3 mmol), $CuCl_2$ (10 mol %), H_2O (0.9 mmol), KO^{t}Bu (0.9 mmol), CH_3CN (3 mL), 30 °C, 12 h. [b] Conditions: **1** (0.6 mmol), **2** (0.3 mmol), CuCl (5 mol %), H_2O (0.9 mmol), KO^{t}Bu (0.9 mmol), CH_3CN (3 mL), entry 1; 40 °C, entry 2; 30 °C, 12 h. [c] Isolated yield. [d] Isomeric ratio (γ/α >99:1). Determined by ^{1}H NMR or GC analysis.

The use of the neopentylglycol ester derivative as an alkenylboronate was not effective.[14]

A scope for the synthesis of alkenyl-conjugated allenes is summarized in Table 2. The protocol was applicable to the vinylboronate **1i**, affording the corresponding vinylallene **3ia** (entry 1). Both alkyl and aryl substituents were tolerated at the β-position in the alkenylboronates (entries 2−7). The styrylboronate **1j** and 1-octenylboronate **1k** underwent the reaction with **2a** in reasonable yields (entries 2 and 3). A sterically more demanding *t*-Bu substituent was tolerated at the β-position of alkenylboronate (**1l**) (entry 4).

(14) The use of the corresponding neopentylglycol ester derivative instead of **1k** decreased the yield from 72 to 26% (cf. Table 2, entry 3).

Table 3. Synthesis of Chiral Allenes

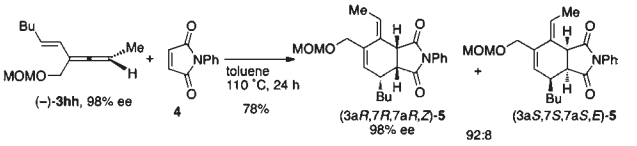
entry	boronate	phosphate	product	yield (%)[c]	ee (%)
1[a]	**1a**	 (*S*)-**2h**, 99% ee	 (*S*)-(−)-**3ah**	70[d]	99
2[b]	**1h**	(*S*)-**2h** 99% ee	 (−)-**3hh**	83[d]	98
3[b]	**1k**	(*S*)-**2h** 99% ee	 (−)-**3kh**	80[d]	99
4[b]	**1n**	(*S*)-**2h** 99% ee	 (−)-**3nh**	79[e]	99
5[b]	 **1p**	(*S*)-**2h** 99% ee	 (−)-**3ph**	83[e]	99

[a] Conditions: **1a** (0.6 mmol), **2h** (0.3 mmol), CuCl (5 mol %), H_2O (0.9 mmol), KO^{t}Bu (0.9 mmol), CH_3CN (1 mL), 25 °C, 12 h. [b] Conditions: **1** (0.6 mmol), **2h** (0.3 mmol), $CuCl_2$ (10 mol %), H_2O (0.9 mmol), KO^{t}Bu (0.9 mmol), CH_3CN (3 mL), 25 °C, 12 h. [c] Isomeric ratio (γ/α >99:1). Determined by ^{1}H NMR or GC analysis. [d] Isolated yield. [e] NMR yield. The purified material was contaminated with alkenylboronate (**1**).

However, the reaction was inhibited by the α-substitution or α,β-disubstitution in the alkenylboronates (data not shown). Various functional groups were tolerated in the alkenylboronates, and thus alkenylallenes (**3ma**, **na**, **oa**) containing Cl, indole, or CN were synthesized in moderate yields (entries 5−7). The allylic phosphate (**2g**) having an isolated terminal alkene was suitable for this protocol (entry 8).

Excellent α-to-γ chirality transfer with 1,3-*anti* stereochemistry was observed in the reaction between the phenylboronate **1a** and the enantioenriched propargylic phosphate (*S*)-**2h** (99% ee), which has α-Me and γ-MOMOCH$_2$ substituents: the reaction afforded phenylallene (*S*)-(−)-**3ah** (99% ee) without any loss of enantiomeric purity (Table 3, entry 1).[15−18] The reactions between the alkenylboronates **1h** or **1k** and (*S*)-**2h** (99% ee) also occurred with excellent chirality transfer to give the corresponding chiral alkenylallenes (−)-**3hh** (98% ee) and (−)-**3kh** (99% ee), respectively (entries 2 and 3). Functional groups such as indole and tosylamide were tolerated in the alkenylboronate (**1**), giving the corresponding allenes (−)-(*E*)-**3nh** and (−)-(*E*)-**3ph** with the high chirality transfer efficiency unchanged (entries 4 and 5).

Scheme 3



The utility of the enantioenriched alkenyl-conjugated allenes was demonstrated in the intermolecular Diels−Alder reaction between (−)-**3hh** (98% ee) and electron-deficient alkenes under the Reich's conditions, as shown in Scheme 3.[19] The reaction employing *N*-phenylmaleimide (**4**) as a dienophile proceeded with a reasonably high diastereoface selectivity (92:8) and complete *endo*/*exo* selectivity to install three stereogenic centers and a geometrically controlled exocyclic alkene in the 6,5-fused bicyclic framework of **5**.

In conclusion, we have developed the Cu-catalyzed coupling reaction between propargylic phosphates and aryl- or alkenylboronates as a versatile route to aryl- and alkenyl-conjugated allenes. The excellent point-to-axial chirality transfer from enantioenriched propargylic phosphates with *anti*-stereochemistry allows efficient preparation of axially chiral conjugated allenes. The wide availability and easy-to-handle nature of aryl- and alkenylboronates, the simplicity and inexpensiveness of the Cu catalyst system, and the high regio- and stereoselectivities are attractive features of this protocol.[20]

Acknowledgment. This work was supported by Grants-in-Aid for Scientific Research (B) (No. 21350020) and for Young Scientists (B) (No. 21750086), JSPS. M.Y. thanks the China Scholarship Council for a fellowship.

Supporting Information Available. Experimental details and characterization data for new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

(15) The stereoselectivity in the synthesis of axially chiral allenes from enantioenriched propargylic substrates with organocuprate reagents is not always reliable. Racemization of chiral allenes occurs under the reaction conditions. See: (a) Claesson, A.; Olsson, L.-I. *J. Chem. Soc., Chem. Commun.* **1979**, 524–525. (b) Elsevier, C. J.; Vermeer, P. *J. Org. Chem.* **1989**, *54*, 3726–3730.

(16) Alexakis and co-workers descibed stereochemical and mechanistic aspects on the formation of axially chiral allenes through the reaction between enantioenriched propargylic alcohol derivatives and organocopper reagents. Ligands for copper such as P(OMe)$_3$ or PBu$_3$ were used to improve the point-to-axial chirality transfer. Additionally, copper salts, halogens of the Grignard reagents, or leaving groups have a significant effect on the stereoselectivity. Even with these attempts, however, the chirality transfer was insufficient or incomplete in many cases. See: (a) Alexakis, A.; Marek, I.; Mangeney, P.; Normant, J. F. *J. Am. Chem. Soc.* **1990**, *112*, 8042–8047. (b) Alexakis, A.; Marek, I.; Mangeney, P.; Normant, J. F. *Tetrahedron* **1991**, *47*, 1677–1696. (c) Alexakis, A. *Pure Appl. Chem.* **1992**, *64*, 387–392.

(17) A review on enantioselective routes to chiral allenes that do not utilize propargylic compounds: Ogasawara, M. *Tetrahedron: Asymmetry* **2009**, *20*, 259–271.

(18) The absolute configuration of (*S*)-(−)-**3ah** was determined by transforming it to a known compound. See Supporting Information for details.

(19) [4 + 2]-Cycloaddition of vinylallenes: (a) Reich, H. J.; Eisenhart, E. K.; Whipple, W. L.; Kelly, M. J. *J. Am. Chem. Soc.* **1988**, *110*, 6432–6433. (b) Spino, C.; Thibault, C.; Gingras, S. *J. Org. Chem.* **1998**, *63*, 5283–5287.

(20) After submission of our manuscript, Lalic and co-workers reported the copper-catalyzed arylation of propargylic phosphates with arylboronates:Uehling, M. R.; Marionni, S. T.; Lalic, G. *Org. Lett.* **2012**, *14*, 362–365.