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Ligand Controlled Highly Selective Copper-Catalyzed Borylcuprations of Allenes with Bis(pinacolato)diboron

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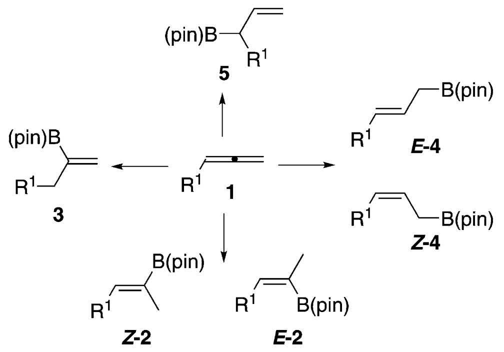
Abstract: Copper-catalyzed highly selective borylcuprations of allenes with bis(pinacolato)diboron produce two different types of alkenylboranes by applying a ligand effect. In the presence of tris(*para*-methoxyphenyl)phosphine [P(C_6H_4OMe-*p*)$_3$], the reaction of aryl-1,2-dienes affords 2-alken-2-yl boronates as the only product with exclusive *Z*-geometry; the regioselectivity is switched to afford the 1-alken-2-yl boronates as the major products when the bidentate phosphine 2,2′-bis(diphenylphosphino)biphenyl is used as the ligand.

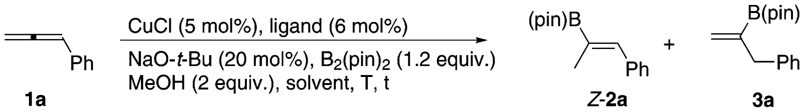
Keywords: allenes; bis(pinacolato)diboron; copper; regioselectivity; stereoselectivity



Scheme 1. Monohydroboration of allenes.

Organoboranes are important intermediates widely used in various carbon-carbon bond forming reactions,[1] such as Pd-catalyzed Suzuki cross-coupling reaction,[2] transition metal-catalyzed 1,2-addition of carbonyl compounds[3] and 1,4-addition of electron-deficient alkenes or alkynes.[4] Hydroboration of allenes may be an efficient method to afford organoboranes. However, a significant regio- and stereoselectivity issue arises: in principle, it is possible to produce six regio- and stereoisomers even if the further hydroboration reaction to the remaining C=C bond is not considered (Scheme 1). In traditional uncatalyzed hydroboration of allenes with boranes, the regio- and stereoselectivity were usually controlled by the substrates and hydroboration agents and the reaction requires high temperature with low conversions and yields:[5] hydroboration of propadiene with 4,4,6-trimethyl-1,3,2-dioxaborinane at 130 °C afforded a mixture of 2-allylborane and 2-isopropenylborane in ~86:14 regioselectivity in 25% yield, while hydroboration of propadiene with 9-BBN afforded only the dihydroboration product in 48% yield and 50% conversion; hydroboration of 3-methyl-1,2-butadiene and 2,3-pentadiene with 4,4,6-trimethyl-1,3,2-dioxaborinane afforded a mixture of **2** and **4**; using 9-BBN as hydroboration agent, the hydroboration of 3-methyl-1,2-butadiene and 2,3-pentadiene afforded **4** as the only product. Roush's group recently reported the hydroboration of allenes with 10-TMS-9-borabicyclo-[3.3.2]decane for the synthesis of γ-substituted (*Z*)-allylic boranes.[6] Miyarua and co-workers first reported the Pt(dba)$_2$-catalyzed hydroboration of terminal allenes with pinacolborane affording one of three possible monohydroboration products **2–4** (Scheme 1) by choosing an appropriate phosphine ligand:[7] for example, hydroboration of alkoxyallenes with Pt(dba)$_2$/PCy$_3$ afforded allylborane exclusively in moderate to good yields; the addition of pinacolborane with aliphatic and aromatic allenes with Pt(dba)$_2$/2P(*t*-Bu$_3$) occurred at the internal double bond to selectively provide 1-alken-2-yl boronates at 50 °C in toluene. In this report, we wish to report a highly selective copper-catalyzed hydroboration of allenes with bis(pinacolato)diboron forming 2-alken-2-yl *Z*-**2** or 1-alken-2-yl boronates **3**, respectively, by applying a ligand effect (Scheme 1).

Table 1. Optimization of reaction conditions for copper-catalyzed regio- and stereoselective hydroboration of allenes using monodentate phosphine ligands to produce stereodefined 2-alken-2-yl boronate **Z-2a**.[a]



1a *Z*-**2a** **3a**

Entry	Ligand	Solvent	*T* [°C]/*t* [h]	*Z*-**2a**/**3a**[b]	Yield of *Z*-**2a** [%][c]
1	PPh_3	THF	40/1.2	89/11	72
2[d]	PPh_3	THF	40/9	–	5 (82)[e]
3	TFP	THF	40/5	73/27	54
4	P(*t*-Bu)$_3$	THF	40/1.3	80/20	73
5	P(*n*-Bu)$_3$	THF	40/1.3	88/12	64
6	P(*o*-tol)$_3$	THF	40/1.3	80/20	67
7	L[f]	THF	40/1	90/10	78
8	PCy_3	THF	40/1	92/8	79
9	PCy_3	THF	rt/1.3	93/7	80
10	PCy_3	THF	0/1	89/11	66
11	PCy_3	CH_3CN	r.t./1.5	85/15	34
12	PCy_3	$PhCH_3$	r.t./1	89/11	76
13	PCy_3	CH_2Cl_2	r.t./1	92/8	71
14	PCy_3	Et_2O	r.t./1	97/3	76
15	PCy_3[g]	Et_2O	r.t./1	88/12	69
16	L	Et_2O	r.t./1	100/0	72

[a] *Reaction conditions:* 0.2 mmol of allene, 0.24 mmol of bis(pinacolato)diboron, 5 mol% CuCl, 6 mol% monodentate ligand, 20 mol% NaO-*t*-Bu, and 0.4 mmol of MeOH were used.

[b] The selectivity was determined by analysis of ^{1}H NMR spectra of the crude reaction products.

[c] The yield was determined by ^{1}H NMR spectra analysis using 1,3,5-trimethylbenzene as the internal standard.

[d] NaO-*t*-Bu was not added.

[e] The number in the parenthesis is the recovery of the starting material as determined by ^{1}H NMR spectra analysis using 1,3,5-trimethylbenzene as the internal standard.

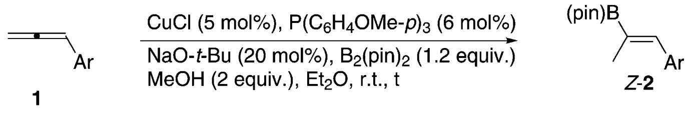
[f] L = P(C_6H_4OMe-*p*)$_3$, TFP = tri(2-furyl)phosphine, P(*o*-tol)$_3$ = tri(*o*-tolyl)phosphine.

[g] 10 mol% PCy_3 was used.

Initially, we used phenylallene **1a** as the model substrate to explore such a feasibility: When we treated **1a** with bis(pinacolato)diboron in the presence of 5 mol% Pd(PPh_3)$_4$[8–11] and 1 equiv. AcOH in THF under reflux,[12–15] disappointedly, the result was complicated. Then we used CuCl (5 mol%) combined with 6 mol% PPh_3 instead of Pd(PPh_3)$_4$ as the catalyst recently developed for hydroboration of alkynes by Yun et al.[16] In the presence of 20 mol% NaO-*t*-Bu and 2 equiv. of MeOH, as expected, the reaction in THF at 40 °C afforded a mixture of 2-alken-2-yl boronate *Z*-**2a** and 1-alken-2-yl boronate **3a** in a regioselectivity of ~8:1 with *Z*-**2a** being the major product in 72% yield (entry 1, Table 1). Although the regioselectivity is poor, it is interesting to note that in both products the boryl group is connected to the central carbon atom of allenes, indicating allyl copper compounds. Then, a series of monodentate phosphine ligands was screened to improve the regioselectivity and PCy_3 was shown to be the best (entry 8). The reaction could not proceed without NaO-*t*-Bu (entry 2). The effects of the solvents and temperature were then examined (entries 9–14). A comprehensive study on the solvent effect indicated that Et_2O is the best solvent affording *Z*-**2a** with the highest regioselectivity (entry 14). Running the reaction at 0 °C gave no better result (entry 10). When we used the P(C_6H_4OMe-*p*)$_3$ instead of PCy_3 as the ligand by considering the electron-rich nature of these two ligands, fortunately, the product *Z*-**2a** was afforded with an excellent regio- and stereoselectivity (entry 16).

Thus, conditions **A** [5 mol% CuCl, 6 mol% P(C_6H_4OMe-*p*)$_3$, 20 mol% NaO-*t*-Bu, 2 equiv. MeOH, Et_2O, and room temperature) were applied for the highly regio- and stereoselective hydroboration of aryl-1,2-allenes affording *Z*-**2**. We investigated the scope of the reaction using different aryl-substituted allenes with B_2(pin)$_2$ (Table 2): the arylallenes with electron-donating substituents at the *para* or *meta* position can afford *Z*-**2b**–*Z*-**2f** as the only isomer in good yields (entries 3–7); heteroaryl substituents, such as 2-thienyl and 3-thienyl, were also tolerated (entries 8 and 9). In addition, the reaction of **1a** proceeded smoothly to afford *Z*-**2a** on a *one-gram scale* in 69% yield (entry 2). It should be noted that the selectivity for the reaction of alkylallenes with B_2(pin)$_2$ under conditions A is poor.

Table 2. Copper-catalyzed addition of bis(pinacolato)diboron with different arylallenes under conditions **A** affording stereodefined 2-alken-2-yl boronates **Z-2**.[a]



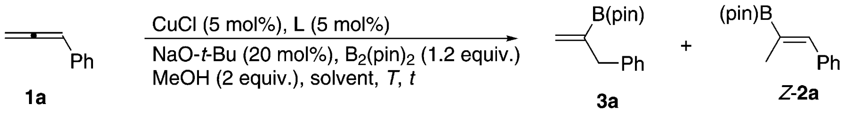
Entry	Ar	t [min]	Isolated yield of *Z*-**2** [%]
1	Ph (**1a**)	40	72 (*Z*-**2a**)
2[b]	Ph (**1a**)	20	69 (*Z*-**2a**)
3	*p*-Me-C_6H_4 (**1b**)	30	71 (*Z*-**2b**)
4	*m*-Me-C_6H_4 (**1c**)	50	70 (*Z*-**2c**)
5	*p*-MeO-C_6H_4 (**1d**)	50	66 (*Z*-**2d**)
6	*p*-Bu-C_6H_4 (**1e**)	40	73 (*Z*-**2e**)
7	*p*-*i*-Pr-C_6H_4 (**1f**)	50	63 (*Z*-**2f**)
8	*3*-thienyl (**1g**)	30	76 (*Z*-**2g**)
9	*2*-thienyl (**1h**)	40	64 (*Z*-**2h**)

[a] The reaction was carried out with allene (0.5 mmol), CuCl (5 mol%), P(C_6H_4OMe-*p*)$_3$ (6 mol%), NaO-*t*-Bu (20 mol%), B_2(pin)$_2$ (0.6 mmol), MeOH (1.0 mmol), and Et_2O (2 mL) at room temperature. The reaction was monitored by TLC on silica gel.

[b] The reaction is carried out in a one-gram scale.

Furthermore, it was observed that the regioselectivity may be switched when bidentate phosphine ligands were applied (Table 3). Firstly, the reaction with dppe afforded a mixture of 2-alken-2-yl boronate *Z*-**2a** and 1-alken-2-yl boronate **3a** in a reversed regioselectivity of ~3:7 with **3a** being the major product in 47% yield (entry 1)! Then, a series of bidentate phosphine ligands was screened and BIPHEP gave the best regioselectivity for producing **3a** (entry 6). We also investigated the effects of the solvents and temperature, no better results was observed when other solvents used (entries 9–12); running the reaction at 0 °C gave no better result (entry 8).

Table 3. Optimization of reaction conditions for copper-catalyzed regio- and stereoselective hydroboration of allenes using bidentate phosphine ligands yielding 1-alken-2-yl boronate **3a**.[a]



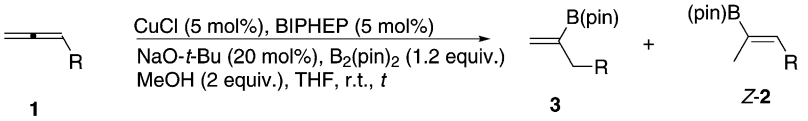
Entry	Ligand	Solvent	T [°C]/t [h]	**3a**/*Z*-**2a**[b]	Yield of **3a** [%][c]
1	dppe	THF	40/1.1	71/29	47
2	Xantphos	THF	40/1	74/26	23
3	DPEphos	THF	40/1.2	84/16	70
4	dppf	THF	40/1.1	93/7	56
5	BINAP	THF	40/1.1	93/7	57
6	BIPHEP	THF	40/1	95/5	62
7	BIPHEP	THF	r.t./1	95/5	63
8	BIPHEP	THF	0/1	95/5	57
9	BIPHEP	CH_3CN	r.t./1	–	NR
10	BIPHEP	Et_2O	r.t./1	89/11	57
11	BIPHEP	$PhCH_3$	r.t./1	93/7	67
12	BIPHEP	CH_2Cl_2	r.t./1	93/7	69

[a] *Reaction conditions:* 0.2 mmol of allene, 0.24 mmol of bis(pinacolato)diboron, 5 mol% CuCl, 5 mol% bidentate ligand, 20 mol% NaO-*t*-Bu, and 0.4 mmol of MeOH were used.

[b] The selectivity was determined by ^{1}H NMR spectra analysis of the crude reaction products prior to purification.

[c] The yield was determined by ^{1}H NMR spectra analysis using 1,3,5-trimethylbenzene as the internal standard. dppe = 1,2-bis(diphenylphosphino)ethane, Xantphos = 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene, DPEphos = (oxydi-2,1-phenylene)bis(diphenylphosphine), dppf = 1,1′-bis(diphenylphosphino)ferrocene, BINAP = (±)-2,2′-bis(diphenylphosphino)-1,1′-binaphthalene, BIPHEP = 2,2′-bis(diphenylphosphino)biphenyl.

Table 4. Copper-catalyzed addition of bis(pinacolato)diboron with different allenes under conditions **B** to afford 1-alken-2-yl boronates **3**.[a]



Entry	R	t [min]	Isolated yield of ($\mathbf{3}+Z$-$\mathbf{2}$) [%]	Ratio ($\mathbf{3}/Z$-$\mathbf{2}$)[b]
1	Ph (**1a**)	40	67 (**3a**)	≥95/5
2[c]	Ph (**1a**)	20	70 (**3a**)	≥95/5
3	*p*-Me-C_6H_4 (**1b**)	40	70 (**3b**)	≥94/6
4	*m*-Me-C_6H_4 (**1c**)	50	64 (**3c**)	≥95/5
5	*p*-Bu-C_6H_4 (**1e**)	40	70 (**3d**)	≥94/6
6	*p*-Cl-C_6H_4 (**1i**)	45	73 (**3e**)	≥96/4[d]
7	*m*-Cl-C_6H_4 (**1j**)	60	60 (**3f**)	≥96/4
8	*o*-Cl-C_6H_4 (**1k**)	45	62 (**3g**)	>99/1
9	*p*-Br-C_6H_4 (**1l**)	45	73 (**3h**)	≥96/4[d]
10	*o*-Br-C_6H_4 (**1m**)	90	54 (**3i**)	>99/1
11	*p*-EtO_2C-C_6H_4 (**1n**)	70	76 (**3j**)	≥96/4[d]
12[e]	Bn (**1o**)	50	64 (**3k**)	99/1
13[e]	C_8H_{17} (**1p**)	50	71 (**3l**)	≥96/4
14[e]	C_6H_{13} (**1q**)	60	63 (**3m**)	≥97/3[f]

[a] The reaction was carried out with allene (0.5 mmol), CuCl (5 mol%), BIPHEP (5 mol%), NaO-*t*-Bu (20 mol%), $B_2(pin)_2$ (0.6 mmol), MeOH (1.0 mmol), and THF (2 mL) at room temperature.

[b] The selectivity was determined by ^{1}H NMR spectra analysis of the products obtained before and after separation.

[c] The reaction is carried out on a one-gram scale.

[d] The selectivity before separation is 97/3.

[e] The ligand is dppf.

[f] The selectivity before separation is 98/2.

With the optimized conditions in hand, we applied conditions **B** (5 mol% CuCl, 5 mol% BIPHEP, 20 mol% NaO-*t*-Bu, 2 equiv, MeOH, THF, and room temperature) to investigate the scope of the hydroboration of allenes to afford **3** (Table 4). The substituent on the aryl group shows very limited effect on the yields: arylallenes with either an electron-withdrawing or electron-donating substituent at the *ortho*, *meta*, or *para* position of the aryl group all reacted smoothly to afford **3b**–**3j** in good yields and excellent regioselectivity (entries 3–11); alkyl- or benzyl-substituted allenes also afford the corresponding 1-alken-2-yl boronates in good yields and excellent regioselectivitity (entries 12–14). In addition, the reaction of **1a** proceeded smoothly to afford **3a** on a *one-gram scale* in 70% overall yield with the same regioselectivity (entry 2). The structure of compound **3h** was confirmed by an X-ray single crystal diffraction study (Figure 1).[17] It should be pointed out that the recently developed hydroboration of alkyl- or benzyl-substituted terminal alkynes by Hoveyda et al. provides a mixture of two regioisomers with the traditional hydroboration products being the major[16c] and, thus, failed to provide such products **3** from the corresponding alkynes highly selectively.[18]

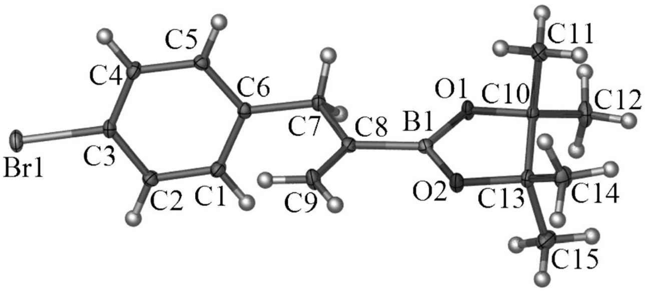
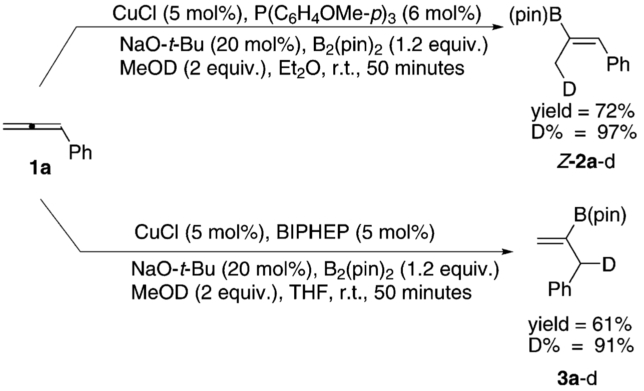


Figure 1. ORTEP representation of **3h**.

To explore the mechanism, a deuterium-labeling experiment was tried: it is interesting to observe that the reaction can afford 72% of *Z*-**2a**-d with 97% D incorporation and 61% of **3a**-d in ≥94:6 regioselectivity with 91% D incorporation at the allylic position (Scheme 2).

Based on these observations, a rationale for the observed regioselectivity was proposed (Scheme 3).[19] Firstly, the copper-boryl complex LCu-B(pin) adds to the terminal or internal double bond of allene with boron always connected to the middle carbon atom: For $P(C_6H_4OMe$-$p)_3$, the reaction proceeds with the more-substituted C=C bond forming **Int 1** while for sterically bulky BIPHEP the terminal C=C was reacted producing **Int 2**. Then γ-protonolysis of the allylic C−Cu bond in **Int 1** and **Int 2** by MeOH produces the



Scheme 2. Deuterium labeling experiments.

Z-**2** and **3**, respectively. Obviously, the steric hindrance of the ligand determines the regioselectivity. This also nicely explains the stabilization effect of the aryl group for selectivity shown in Table 2. Of course, an α-protonation mechanism may not be completely excluded.

In summary, we have developed an efficient non-classic hydroboration of allenes with bis(pinacolato)diboron based on copper catalysis, which affords two different types of vinylboronates with high regio- and stereoselectivity by using different ligands. These borylated products are not readily available from the classic hydroboration of alkynes or the recently developed reaction of alkynes with bis(pinacolato)diboron and obviously will be very useful intermediates for subsequent elaboration to more complex structures although the effect of ligands on the regio- and stereoselectivity requires further attention. Studies including synthetic applications and the factors controlling the regio- and stereoselectivity are under way in this laboratory.

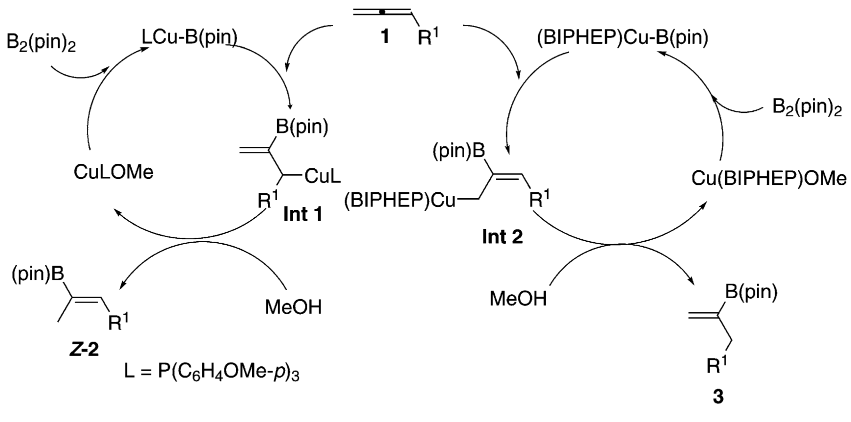
Experimental Section

Typical Procedure for the Preparation of *Z*-2

To an oven-dried Schlenk tube equipped with a magnetic stirring bar were added sequentially bis(pinacolato)diboron (2.6200 g, 10.33 mmol), $P(C_6H_4OMe\text{-}p)_3$ (182.0 mg, 0.52 mmol), CuCl (42.6 mg, 0.43 mmol), NaO-*t*-Bu (165.4 mg, 1.72 mmol), **1a** (1.0102 g, 8.61 mmol), MeOH (0.7 mL, $d = 0.7915\ \text{g cm}^{-3}$, 551.7 mg, 17.22 mmol), and Et_2O (20 mL) under argon. The mixture was stirred at room temperature for 20 min as monitored by TLC. Upon completion, the resulting mixture was filtered through a short column of silica gel eluting with Et_2O and concentrated. The residue was purified by chromatography on silica gel (eluent: petroleum ether/ethyl ether = 50/1) to afford *Z*-**2a** as a liquid; yield: 1.4544 g (69%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.41$–7.30 (m, 4H), 7.28–7.20 (m, 2H), 1.99 (s, 3H, CH_3), 1.32 [s, 12H, B(pin)]; ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 142.3$, 137.8, 129.3, 127.9, 127.0, 83.3, 24.7, 15.8; IR (neat): $\nu = 2978$, 1618, 1491, 1448, 1405, 1367, 1346, 1311, 1272, 1209, 1145, 1104 cm^{-1}; MS (70 eV, EI): *m*/*z* (%) = 244 (M^+, 71.67), 43 (100).

Typical Procedure for the Preparation of 3

To an oven-dried Schlenk tube equipped with a magnetic stirring bar were added sequentially bis(pinacolato)diboron (2.6200 g, 10.33 mmol), BIPHEP (224.7 mg, 0.43 mmol), CuCl (42.6 mg, 0.43 mmol), NaO-*t*-Bu (165.4 mg, 1.72 mmol), **1a** (1.0010 g, 8.61 mmol), MeOH (0.7 mL, $d = 0.7915\ \text{g cm}^{-3}$, 551.7 mg, 17.22 mmol), and THF (20 mL) under argon. The mixture was stirred at room temperature for 20 min as monitored by TLC. Upon completion, the resulting mixture was filtered through a short column of silica gel eluting with Et_2O and concentrated. The residue was purified by chromatography on silica gel (eluent: petroleum ether/ethyl ether = 50/1) to afford a mixture of **3a** and *Z*-**2a**, molar ratio by NMR: $\geq 95:5$) as a liquid; yield: 1.4630 g (70%). **3a**: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.28$–7.08 (m, 5H, Ar-H), 5.83 (s, 1H, one proton of $=CH_2$), 5.58–5.48 (br s, 1H, one proton of $=CH_2$), 3.47 (s, 2H, CH_2), 1.19 [s, 12H, B(pin)]; ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 140.6$, 129.7, 129.0, 128.0, 125.6, 83.4, 41.3, 24.8, 24.6; IR (neat): $\nu = 2979$, 1618, 1494, 1429, 1364, 1310, 1272, 1210, 1136, 1111, 1073,



Scheme 3. Ligand-controlled borylcuprations followed by γ-protonolysis.

1030 cm^{-1}; MS (70 eV, EI): m/z (%) = 244 (M^+, 1.80), 41 (100); HR-MS: m/z = 244.1637, calcd. for $C_{15}H_{21}BO_2$ (M^+): 244.1635.

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References

[1] a) J. Tsuji, *Palladium Reagents and Catalysts*, John Wiley & Sons, Chichester, England, **2004**, pp 289–310; b) D. S. Matteson, *Chem. Rev.* **1989**, *89*, 1535; c) D. S. Matteson, *Acc. Chem. Res.* **1988**, *21*, 294. For applications of vinylboronates in C–C bond formation, see: d) M. Tobisu, N. Chatani, *Angew. Chem.* **2009**, *121*, 3617; *Angew. Chem. Int. Ed.* **2009**, *48*, 3565; e) S. Kotha, K. Lahiri, D. Kashinath, *Tetrahedron* **2002**, *58*, 9633.

[2] For reviews, see: a) N. Miyaura, A. Suzuki, *Chem. Rev.* **1995**, *95*, 2457; b) A. Suzuki, *J. Organomet. Chem.* **1999**, *576*, 147.

[3] a) T. Ohishi, M. Nishiura, Z. Hou, *Angew. Chem.* **2008**, *120*, 5876; *Angew. Chem. Int. Ed.* **2008**, *47*, 5792; b) R. Shintani, M. Takeda, Y. T. Soh, T. Ito, T. Hayashi, *Org. Lett.* **2011**, *13*, 2977; c) J. Takaya, S. Tadami, K. Ukai, N. Iwasawa, *Org. Lett.* **2008**, *10*, 2697.

[4] a) M. Sakai, H. Hayashi, N. Miyaura, *Organometallics* **1997**, *16*, 4229; b) S. Sakuma, M. Sakai, R. Itooka, N. Miyaura, *J. Org. Chem.* **2000**, *65*, 5951.

[5] a) R. H. Fish, *J. Am. Chem. Soc.* **1968**, *90*, 4435; b) D. S. Sethi, G. C. Joshi, D. Devaprabhakara, *Can. J. Chem.* **1969**, *47*, 1083; c) H. C. Brown, R. Liotta, G. W. Kramer, *J. Am. Chem. Soc.* **1979**, *101*, 2966.

[6] a) J. Kister, A. C. DeBaillie, R. Lira, W. R. Roush, *J. Am. Chem. Soc.* **2009**, *131*, 14174; b) D. H. Ess, J. Kister, M. Chen, W. R. Roush, *Org. Lett.* **2009**, *11*, 5538.

[7] Y. Yamamoto, R. Fujikawa, A. Yamada, N. Miyaura, *Chem. Lett.* **1999**, *28*, 1069.

[8] For Pt-catalyzed diboration of allenes, see: a) T. Ishiyama, T. Kitano, N. Miyaura, *Tetrahedron Lett.* **1998**, *39*, 2357; b) M. Wang, L. Cheng, Z. Wu, *Organometallics* **2008**, *27*, 6464.

[9] For Pd-catalyzed diboration occurring to the terminal C=C bond in mono-substituted allenes, see: F.-Y. Yang, C.-H. Cheng, *J. Am. Chem. Soc.* **2001**, *123*, 761.

[10] For Pd-catalyzed enatioselective diboration occurring to the more-substituted C=C bond in allenes, see: a) N. F. Pelz, A. R. Woodward, H. E. Burks, J. D. Sieber, J. P. Morken, *J. Am. Chem. Soc.* **2004**, *126*, 16328; b) A. R. Woodward, H. E. Burks, L. M. Chan, and J. P. Morken, *Org. Lett.* **2005**, *7*, 5505; c) N. F. Pelz, J. P. Morken, *Org. Lett.* **2006**, *8*, 4557; d) H. E. Burks, S. Liu, J. P. Morken, *J. Am. Chem. Soc.* **2007**, *129*, 8766.

[11] For Pd-catalyzed silaboration of allenes, see: a) M. Suginome, Y. Ohmori, Y. Ito, *Synlett* **1999**, 1567; b) M. Suginome, Y. Ohmori, Y. Ito, *J. Organomet. Chem.* **2000**, *611*, 403; c) S. Onozawa, Y. Hatanaka, M. Tanaka, *Chem. Commun.* **1999**, 1863; d) M. Suginome, T. Ohmura, Y. Miyake, S. Mitani, Y. Ito, M. Murakami, *J. Am. Chem. Soc.* **2003**, *125*, 11174; e) T. Ohmura, H. Taniguchi, M. Suginome, *J. Am. Chem. Soc.* **2006**, *128*, 13682.

[12] a) S. Ma, N. Jiao, L. Ye, *Chem. Eur. J.* **2003**, *9*, 6049; b) S. Ma, H. Guo, F. Yu, *J. Org. Chem.* **2006**, *71*, 6634; c) H. Guo, S. Ma, *Synthesis* **2007**, 2731.

[13] C. H. Oh, T. W. Ahn, R. V. Reddy, *Chem. Commun.* **2003**, 2622.

[14] For a mechanistic study, see: R. Qian, H. Guo, Y. Liao, Y. Guo, S. Ma, *Angew. Chem.* **2005**, *117*, 4849; *Angew. Chem. Int. Ed.* **2005**, *44*, 4771.

[15] a) M. Yoshida, Y. Shoji, K. Shishido, *Org. Lett.* **2009**, *11*, 1441; b) M. Yoshida, Y. Shoji, K. Shishido, *Tetrahedron* **2010**, *66*, 5053; c) M. Osaka, M. Kanematsu, M. Yoshida, K. Shishido, *Heterocycles* **2010**, *80*, 1003.

[16] For Cu-catalyzed hydroboration of alkynes, see: a) H. R. Kim, I. G. Jung, K. Yoo, K. Jang, E. S. Lee, J. Yun, S. U. Son, *Chem. Commun.* **2010**, *46*, 758; b) H. R. Kim, J. Yun, *Chem. Commun.* **2011**, *47*, 2943; c) H. Jang, A. R. Zhugralin, Y. Lee, A. H. Hoveyda, *J. Am. Chem. Soc.* **2011**, *133*, 7859. For stoichiometric amounts of a Cu complex promoted hydroboration of alkynes, see: K. Takahashi, T. Ishiyama, N. Miyaura, *J. Organomet. Chem.* **2001**, *625*, 47.

[17] Crystal data for compound **3h**: $C_{15}H_{20}BBrO_2$; MW = 323.03, triclinic space group P-1, final R indices [I > 2σ(I)], $R1 = 0.0276$, $wR2 = 0.0751$, R indices (all data) $R1 = 0.0353$, $wR2 = 0.0815$, $a = 19.691(3)$ Å, $b = 6.1598(10)$ Å, $c = 24.966(4)$ Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$, $V = 3028.2(9)$ Å^3, $T = 173(2)$ K, $Z = 8$, reflections collected/unique 31004/2674 ($R_{int} = 0.0451$), number of observations [> 2σ(I)] 2286, parameters: 180. CCDC 845986 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

[18] For the synthesis of α-vinyl boronates *via* hydroalumination/borodealumination sequence from terminal alkynes, see: F. Gao, A. H. Hoveyda, *J. Am. Chem. Soc.* **2010**, *132*, 10961.

[19] For the mechanistic studies of Cu-catalyzed hydroboration of unsaturated bonds, see: a) D. S. Laitar, E. Y. Tsui, J. P. Sadighi, *Organometallics* **2006**, *25*, 2405; b) L. Dang, Z. Y. Lin, T. B. Marder, *Organometallics* **2008**, *27*, 4443; c) Y. Sasaki, C. M. Zhong, M. Sawamura, H. Ito, *J. Am. Chem. Soc.* **2010**, *132*, 1226; d) Y. Sasaki, Y. Horita, C. M. Zhong, M. Sawamura, H. Ito, *Angew. Chem.* **2011**, *123*, 2830; *Angew. Chem. Int. Ed.* **2011**, *50*, 2778; e) K. Takahashi, T. Ishiyama, N. Miyaura, *Chem. Lett.* **2000**, *29*, 982; f) H. Ito, H. Yamanaka, J-I. Tateiwa, A. Hosomi, *Tetrahedron Lett.* **2000**, *41*, 6821.

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