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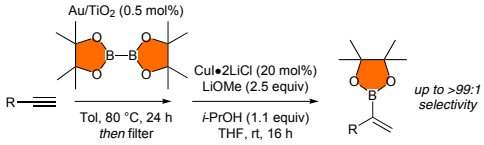
Tandem Diboration–Protoboration of Terminal Alkynes: A Practical Route to α-Substituted Alkenyl Boronates

Ziyin Kong
Jimin Park
Muchun Fei
Josephine Warfield
Dunwei Wang
James P. Morken*

Department of Chemistry, Merkert Chemistry Center, Boston College, Chestnut Hill, Massachusetts 02467, USA
morken@bc.edu



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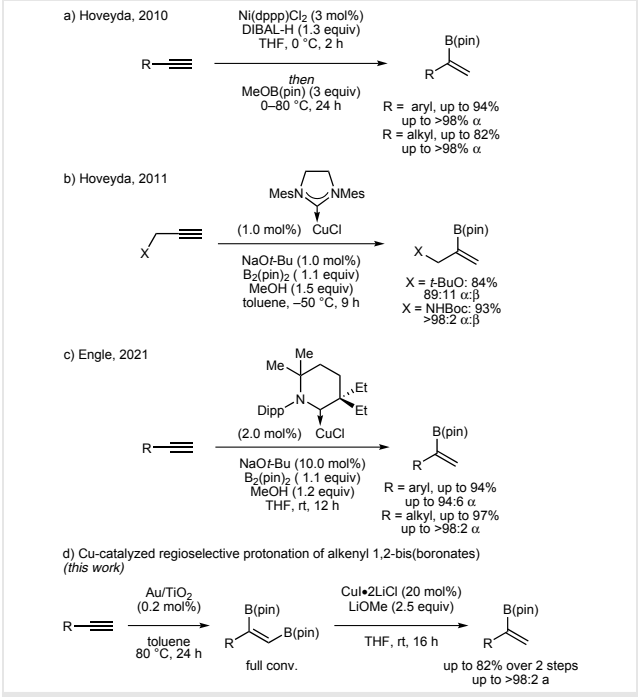
Abstract A practical method is introduced for the catalytic conversion of terminal alkynes into α-substituted vinyl boronic esters. The process employs catalytic amounts of nanoparticle-supported gold catalysts and catalytic amounts of copper to effect the overall transformation.

Key words boron, cross-coupling, AuNPs, alkynes, protonation

Alkenyl boronates have gained prominence as versatile building blocks in organic synthesis, engaging in a wide range of stereospecific transformations, particularly metal-catalyzed cross-coupling reactions.[1] These applications have made alkenylboronic esters indispensable not only for routine organic synthesis, but also for the synthesis of natural products and pharmaceutical targets. To construct alkenyl boronates, the hydroboration or protoboration of terminal alkynes emerges as one direct synthesis route.[2] In this regard, various strategies have been established to control the regioselectivity of hydroboration, resulting in products that deliver boron to either the terminal or internal carbon of the 1-alkyne. In contrast to the relatively accessible 1,2-disubstituted *E*- or *Z*-alkenyl boronate products generated by addition of boron to the terminal carbon,[3] the synthesis of α-substituted alkenyl boronates by borylation of the internal carbon poses more significant challenges due to heightened steric demands. In this report, we describe a simple protocol for the construction of 2-boryl-1-alkenes from terminal alkynes through the sequential action of a heterogeneous and a homogeneous catalyst.

Conventionally, α-substituted alkenyl boronates have been synthesized from 2-haloalkenes by lithium–halogen exchange, followed by reaction with electrophilic boronates.[4] Alternatively, Pd-catalyzed borylation of 2-haloalkenes using bis(pinacolato)diboron as described by Miyaura[5] could yield the derived boronates with controlled regioselectivity.

On the other hand, the Hoveyda group introduced a one-pot procedure for generating 2-borylalkenes from terminal alkynes. In this work, an α-selective hydroalumination, assisted by catalytic amount of commercially available $Ni(dppp)Cl_2$, was conducted. The in situ generated alkenylaluminum species can then directly react with methoxy(pinacolato)boron to afford 2-borylalkenes in good yield and site-selectivity (Scheme 1a).[6]



Scheme 1 Overview of synthesis of α-substituted vinyl boronates

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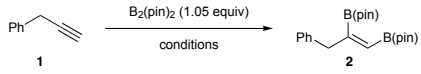
More recently, the Hoveyda group presented an alternative method involving catalytic copper-boylation/protonation using an NHC–Cu complex. With this method, propargyl alcohols, propargyl amines, and aryl acetylenes could be transformed into the corresponding α-substituted alkenyl boronates directly and in exceptional site selectivity and efficiency (up to >98:2, 95% yield, Scheme 1b).[7] The regioselectivity was attributed to electronic and steric interactions during the copper-borylation step, where the NHC(copper) complex adds distal to the electron-withdrawing propargylic heteroatom of the substrate. A reaction that applies to unactivated terminal alkyne substrates was developed by Engle, Jazzar, and Bertrand, who found that borylation of the internal carbon could be achieved when a strongly electron-donating cyclic (alkyl)(amino)carbene (CAAC) ligand is employed.[8] In this case, the use of the sterically flexible and electron-donating CAAC ligand favors the formation of 2-boryl-1-alkenes (Scheme 1c).

While hydroboration approaches to α-alkenyl boronates have been well-investigated, we considered that a scalable process that operated on a variety of different terminal alkynes, that employed readily available catalysts, and used operationally simple procedures might extend the utility of 2-borylalkenes in organic synthesis. Recently, our group and others reported stereospecific and site-selective cross-coupling of vicinal 1,2-bis(boronates).[9] In one report,[9g] a synergistic activation by an adjacent nonreacting boronate unit was found to enable rapid and site-selective transmetalation to copper. It was envisioned that extending this site-selective functionalization to alkenyl 1,2-bis(boronates) might offer an alternate avenue for the synthesis of α-substituted alkenyl boronates (Scheme 1d). However, there are multiple challenges to address in adopting this strategy. In contrast to their alkyl boronate counterparts, alkenyl boronates exhibit greater Lewis acidity, rendering them more reactive in cross-coupling reactions. While instances exist where both boronates in 1,2-diboryl alkenes can participate in Suzuki cross-coupling,[10] the regioselective monofunctionalization of alkenyl bis(boronates) remains unexplored. Additionally, although these intermediates can be generated through transition-metal- or non-transition-metal-catalyzed diboration of terminal alkynes,[11] we considered that preparative access to 1,2-diborylalkenes could be improved.

Table 1 Optimization of Catalytic Diboration of 3-Phenyl-1-propyne[a]



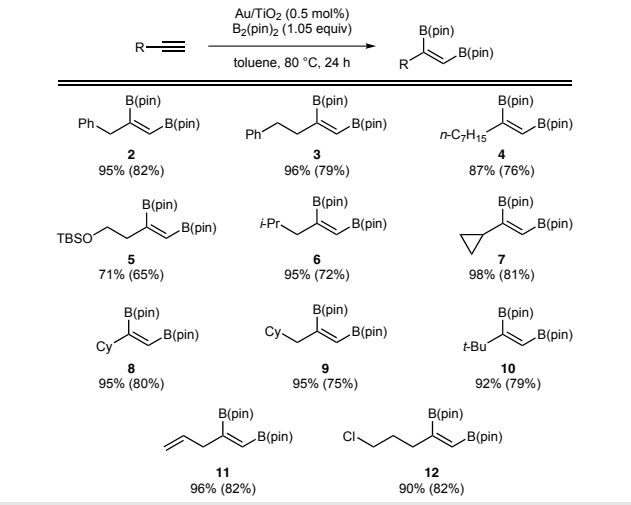
Entry	Catalyst	Loading (%)	Solvent	Temp (°C)	Yield (%)
1	$Pt(PPh_3)_4$	3	DMF	80	97
2	$Pt(PPh_3)_4$	0.5	DMF	80	48
3	$Pt(dba)_3/PPh_2(o\text{-}Tol)$	1	DMF	80	95
4	Pt/C (10%)	3	DMF	80	42
5	1% Au/TiO_2[b]	0.5	toluene	70	96
6	3% Au/TiO_2[c]	0.5	toluene	70	96
7	3% Au/TiO_2[c]	0.5	EtOAc	70	94
8	3% Au/TiO_2[c]	0.5	MeCN	70	87
9	3% Au/TiO_2[c]	0.5	MTBE	70	84
10	3% Au/TiO_2[c,d]	0.5	toluene	70	<5
11	3% Au/TiO_2[c]	0.2	toluene	70	95
12	3% Au/WO_3	0.5	toluene	70	85
13	3% Au/TiO_2[e]	0.5	toluene	70	94
14	3% Pt/TiO_2[c]	1	toluene	70	<5

[a] Unless otherwise indicated, reaction was conducted at 1 mmol scale in the indicated solvent (1 mL) for 24 h. Percentage yields of products determined by ^1H NMR spectroscopy.
[b] Commercially available through Strem catalog, catalog number 79-0165.
[c] Prepared in-house.
[d] Catalyst calcinated at 400 °C for 5 h before use.
[e] Gold loaded on P25 TiO_2 instead of anatase TiO_2.

We began our exploration of catalytic diboration of 4-phenyl-1-butyne using commercially available Pt complexes. Following the seminal work of Miyaura and Suzuki on the *cis*-selective alkyne diboration,[12a] as well as the work of a number of others,[12] we began by employing $Pt(PPh_3)_4$ as the catalyst. This approach resulted in a high-yielding diboration reaction with a catalyst loading of 3 mol% (Table 1, entry 1). However, the yield was diminished when the catalyst loading was reduced to 0.5 mol% (Table 1, entry 2). When a platinum complex ($Pt(dba)_3$) modified by the addition of a monophosphine was examined, improved efficiency was observed (Table 1, entry 3).[13] In an effort to establish a practical method that required minimal workup and purification procedures, investigation of heterogeneous catalysts was initiated. Metal complexes supported on nanoparticle supports are an emerging class of catalysts that offer both cost-effectiveness and the potential for catalyst recycling, thereby minimizing waste generation.[14] These solid-supported catalysts, free from ligands, facilitate surface-based reactions, averting the risk of catalyst decomposition by metal aggregation – an issue highlighted in earlier work by Miyaura and colleagues involving 'ligandless' platinum.[15] Drawing inspiration from Grirrane, commercially available 10% Pt/C was examined and found to deliver the desired product with a 42% yield (Table 1, entry 4).[16] Notably, the heterogeneous metal could be conveniently removed by simple filtration through Celite. Following Stratakis' conditions, the desired diboration reaction could also be achieved using commercially available Au/TiO_2 with catalyst loading as low as 0.5 mol% (Table 1, entry 5). Preparation of related complexes was investigated, and it was found that a straightforward procedure involving doping $HAuCl_4$ onto anatase TiO_2, followed by reduction with $NaBH_4$, yielded an Au/TiO_2 heterogeneous catalyst showing comparable reactivity to the commercial material. While the use of tol-

uene as a solvent resulted in the highest reaction yields (Table 1, entry 6), more environmentally friendly solvents such as ethyl acetate, acetonitrile, and MTBE provided only slightly diminished reaction efficiency (Table 1, entries 7–9). Of note, the preparation of Au/TiO_2 was straightforward and did not require high-temperature calcination for effective catalysis. Intriguingly, the calcinated catalyst was largely ineffective for diboration and did not provide detectable amounts of product (Table 1, entry 10). Furthermore, the as-synthesized Au/TiO_2 nanoparticles exhibited good efficiency, even at a loading as low as 0.2 mol% (Table 1, entry 11). Gold nanoparticles loaded onto alternative supporting materials such as P25 TiO_2 and WO_3 exhibited similar reactivity (Table 1, entries 12, 13). In contrast, Pt nanoparticles, synthesized using a similar approach, did not exhibit catalytic competency under the same conditions (Table 1, entry 14).

Having established a route for the scalable synthesis of 1,2-diborylalkenes, the conditions were applied to a representative subset of alkyne substrates (Scheme 2).[17] Aryl- and alkyl-substituted alkynes both underwent efficient diboration. Furthermore, with alkynes bearing sterically demanding substituents (isopropyl, cyclohexyl, cyclopropyl, and cyclohexylmethyl) proved compatible with the process, yielding the desired product in nearly quantitative yield. More sterically demanding *tert*-butylacetylene yielded the desired diboryl product as well. Additionally, alkene groups and halogens did not interfere with the reaction in any detectable way. However, chelating functional groups such as alcohols, phenyl or benzyl-protected alcohols, or nitrogen-containing heterocycles are currently not tolerated (see the Supporting Information for this data).

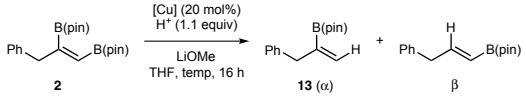


Scheme 2 Scope of Au/TiO2 catalyzed diboration of terminal alkyne. *Reagents and conditions*: terminal alkyne (1.05 mmol), 3% Au/TiO_2 (5 µmol), $B_2(pin)_2$(1.00 mmol), toluene (1 mL), 80 °C, 24 h. Percentage yields of products determined by ^1H NMR spectroscopy. Percentage yield in parentheses represents the isolated yield.

It is important to note that the chromatographic purification of 1,2-diborylalkenes is not straightforward. The use of an extended silica gel column can lead to a reduction in product recovery, as the comparison between isolated purified yields and those versus an internal standard indicates. This observation might be attributed to the undesirable over-absorption of these compounds on the silica gel as previously noted by Isobe[18] and others,[19] suggesting that short silica gel columns should be employed to mitigate this issue.

With an effective scalable diboration in hand, the site-selective protodeboration was examined. Conditions from a previous study[9g] employing Cu catalysis and LiOMe as the activator were examined first. When employing MeOH as the proton source and heating the reaction to 60 °C, the product arising from protodeboration of both boronates was observed, and only 15% of the desired product was generated (Table 2, entry 1). However, by conducting the reaction at room temperature, selective protonation at the less hindered alkenyl boronate was the predominant product, with protonation of the internal boronate as the minor product (Table 2, entry 2). To enhance the regioselectivity of the protonation, various proton sources with higher pK_a

Table 2 Optimization of Cu-Catalyzed Selective Protonation of 1,2-Alkenyl Bis(boronates)



Entry	Temp (°C)	Cu source	H^+	Yield (%)[a]	α:β
1	60	CuCN	MeOH	15	N/A
2	rt	CuCN	MeOH	60	90:10
3	rt	CuCN	acetone	65	95:5
4[b]	rt	CuCN	acetone	53	96:4
5	rt	CuCN	acetone	47	96:4
6	rt	CuCN	DMA	63	94:6
7	rt	CuCN	MeCN	36	90:10
8	rt	CuCN	EtOAc	34	91:9
9	rt	CuCN·2LiCl	acetone	92	96:4
10	rt	CuCN·2LiCl	DMA	93	94:6
11	rt	CuCN·2LiCl	*i*-PrOH	94	98:2
12	rt	CuCN·2LiCl	*t*-BuOH	90	97:3
13	rt	CuCN·2LiCl	TFIP	81	97:3
14	rt	CuCl·2LiCl	*i*-PrOH	72	99:1
15	rt	CuBr·2LiCl	*i*-PrOH	77	99:1
16	rt	CuI·2LiCl	*i*-PrOH	88	97:3

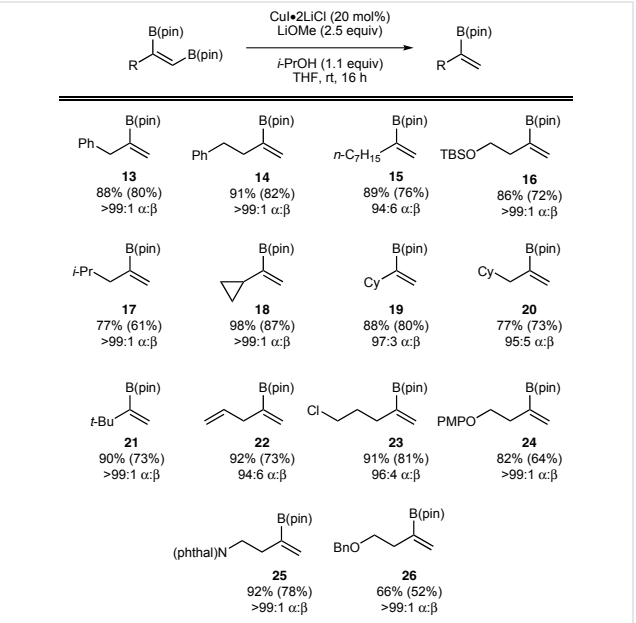
[a] Unless otherwise indicated, reaction was conducted at 0.2 mmol scale in THF (1 mL) for 24 h. Yields and regioselectivity are determined by ^1H NMR spectroscopy with the unpurified material.
[b] Reaction employed 50 mol% CuCN.

values were explored. With acetone employed as the proton source, the reaction yielded the desired product with a slight improvement in regioselectivity to a ratio of 95:5 (Table 2, entry 3). Comparable outcomes were observed in solvents such as DMA, acetonitrile, and ethyl acetate (Table 2, entry 6–8). Increasing the loading of copper catalyst (Table 2, entry 4) or changing the copper salt didn't lead to improved reaction yield. Conversion of 1,2-diborylalkene to the desired 2-boryl-1-alkene could be further improved by use of freshly prepared homogenous CuCN•2LiCl in THF as copper source (Table 2, entry 9).[9e] With this modification, more hindered proton sources were examined. Finally, isopropanol (Table 2, entry 11) was identified as the most effective proton source, with 94% yield of the desired product and 98:2 selectivity being observed.

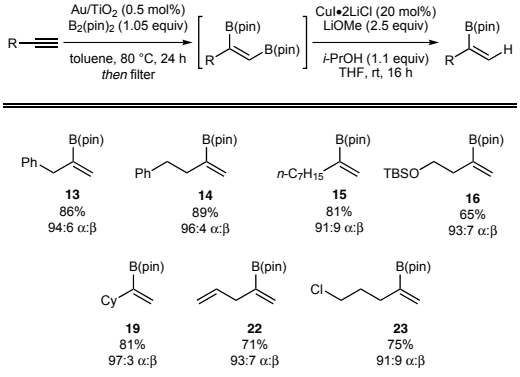
Considering aspects pertaining to practicality and scalability, other copper halides were surveyed (Table 2, entries 14–16) and it was found that CuI·2LiCl offered comparable reactivity and selectivity compared to the more toxic CuCN·2LiCl. Therefore, examination of various substrates in the reaction was conducted using CuI·2LiCl. As depicted in Scheme 3, various 1,2-alkenyl bis(boronates) underwent conversion into the corresponding 2-boryl-1-alkenes in good yield and selectivity.[20] Modifying the substituents on the diborylalkene substrate had minimal effects on the overall selectivity. For substrates with aryl groups 2–3 carbons removed from the reacting alkene, α-selectivity exceeding 99:1 was consistently observed after purification. Linear alkyl substrates reacted with slightly diminished selectivity (94:6). Substrates with other substituents, such as a silyl-protected alcohol and isobutyl group provided >99:1 selectivity with good yield. Alkynes with bulky substituents such as cyclopropyl, cyclohexyl, methyl cyclohexyl, and *tert*-butyl reacted with selectivity of >95:5 for the desired α-substituted vinyl boronates with satisfactory yields. In addition, alkene and halogen substituents were well-tolerated under these reaction conditions. Different derivatives of alcohols, such as *para*-methoxyphenyl-protected alcohol, benzyl-protected alcohol, and a phthalimide, all displayed compatibility with the reaction conditions, delivering the desired α-substituted vinyl boronates.

Lastly, a tandem diboration–protonation was investigated as a method to provide direct access to 2-boryl-1-alkenes without isolation and purification of the 1,2-diborylalkene intermediate (Scheme 4). In the sequence, the reaction mixture from the Au-catalyzed diboration was filtered through a short pad of Celite to remove the catalyst, concentrated, and the crude mixture directly subjected to Cu-catalyzed protonation. The desired α-substituted vinyl boronates could be obtained in moderate to good yield and with uncompromised regioselectivity.

In summary, a synthetic method to access 2-boryl-1-alkenes from terminal alkynes via a selective diboration–protonation sequence was demonstrated. The desired products were obtained with both high yields and regioselectivity, providing a practical approach for producing internal alkenyl boronate compounds which have well-established synthetic utility in organic chemistry.



Scheme 3 Scope of Cu-catalyzed selective protonation of 1,2-alkenyl bis(boronates). *Reagents and conditions*: 1,2-alkenyl bis(boronates) (0.20 mmol), CuI·2LiCl (0.04 M in THF, 1 mL), LiOMe (0.50 mmol), isopropanol (0.26 mmol), r.t, 16 h. Percentage yield in parentheses represents the isolated yield of the α-products. Regioselectivity was determined by ^{1}H NMR spectroscopy of the purified product.



Scheme 4 Scope of tandem diboration–protonation of terminal alkenes. *Reagents and conditions*: terminal alkyne (1.05 mmol), 3% Au/TiO_2 (5 μmol), $B_2(pin)_2$ (1.00 mmol), toluene (1 M, 1 mL), 80 °C, 24 h; then CuI·2LiCl (0.04 M in THF, 5 mL), LiOMe (2.50 mmol), isopropanol (1.30 mmol), r.t, 16 h. Regioselectivity was determined by ^{1}H NMR spectroscopy of the crude mixture. Percentage yield in parentheses represents the isolated yield of the α-products.

Conflict of Interest

The authors declare no conflict of interest.

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0043-1774906.

References and Notes

(1) (a) Miyaura, N.; Yamada, K.; Suzuki, A. *Tetrahedron Lett.* **1979**, *20*, 3437. (b) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457. (c) Lennox, A. J. J.; Lloyd-Jones, G. C. *Chem. Soc. Rev.* **2014**, *43*, 412. (d) Suzuki, A. *Chem. Commun.* **2005**, 4759.

(2) For review of hydroboration of alkyne, see: (a) Beletskaya, I.; Pelter, A. *Tetrahedron* **1997**, *53*, 4957. (b) Barbeyron, R.; Benedetti, E.; Cossy, J.; Vasseur, J.-J.; Arseniyadis, S.; Smietana, M. *Tetrahedron* **2014**, *70*, 8431. (c) Yoshida, H. *ACS Catal.* **2016**, *6*, 1799. (d) Geier, S. J.; Vogels, C. M.; Melanson, J. A.; Westcott, S. A. *Chem. Soc. Rev.* **2022**, *51*, 8877.

(3) Selective examples of transition-metal-catalyzed β-selective hydroboration: (a) Tucker, C. E.; Davidson, J.; Knochel, P. *J. Org. Chem.* **1992**, *57*, 3482. (b) Pereira, S.; Srebnik, M. *Tetrahedron Lett.* **1996**, *37*, 3283. (c) Ohmura, T.; Yamamoto, Y.; Miyaura, N. *J. Am. Chem. Soc.* **2000**, *122*, 4990. (d) Gunanathan, C.; Hölscher, M.; Pan, F.; Leitner, W. *J. Am. Chem. Soc.* **2012**, *134*, 14349. (e) Obligacion, J. V.; Neely, J. M.; Yazdani, A. N.; Pappas, I.; Chirik, P. J. *J. Am. Chem. Soc.* **2015**, *137*, 5855.

(4) Morrill, C.; Funk, T. W.; Grubbs, R. H. *Tetrahedron Lett.* **2004**, *45*, 7733.

(5) (a) Kou, T.; Jun, T.; Tatsuo, I.; Norio, M. *Chem. Lett.* **2000**, *29*, 126. (b) Takagi, J.; Takahashi, K.; Ishiyama, T.; Miyaura, N. *J. Am. Chem. Soc.* **2002**, *124*, 8001.

(6) Gao, F.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2010**, *132*, 10961.

(7) (a) Jang, H.; Zhugralin, A. R.; Lee, Y.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2011**, *133*, 7859. For an alternate Cu-catalyzed synthesis of 2-boryl-1-alkenes from propargylic alcohols, see: (b) Mao, L.; Bertermann, R.; Emmert, K.; Szabó, K.; Marder, T. B. *Org. Lett.* **2017**, *19*, 6586.

(8) (a) Lavallo, V.; Canac, Y.; Präsang, C.; Donnadieu, B.; Bertrand, G. *Angew. Chem. Int. Ed.* **2005**, *44*, 5705. (b) Gao, Y.; Yazdani, S.; Kendrick IV, A.; Junor, G. P.; Kang, T.; Grotjahn, D. B.; Bertrand, G.; Jazzar, R.; Engle, K. M. *Angew. Chem. Int. Ed.* **2021**, *60*, 19871.

(9) For a recent review on site-selective functionalization of vicinal bis(boronates), see: (a) Viso, A.; Fernández de la Pradilla, R.; Tortosa, M. *ACS Catal.* **2022**, *12*, 10603. For selected examples of site-selective functionalization, see: (b) Miller, S. P.; Morgan, J. B.; Nepveux, F. J.; Morken, J. P. *Org. Lett.* **2004**, *6*, 131. (c) Mlynarski, S. N.; Schuster, C. H.; Morken, J. P. *Nature* **2014**, *505*, 386. (d) Lee, J.; Radomkit, S.; Torker, S.; del Pozo, J.; Hoveyda, A. H. *Nat. Chem.* **2018**, *10*, 99. (e) Blaisdell, T. P.; Caya, T. C.; Zhang, L.; Sanz-Marco, A.; Morken, J. P. *J. Am. Chem. Soc.* **2014**, *136*, 9264. (f) Nóvoa, L.; Trulli, L.; Parra, A.; Tortosa, M. *Angew. Chem. Int. Ed.* **2021**, *60*, 11763. (g) Xu, N.; Kong, Z.; Wang, J. Z.; Lovinger, G. J.; Morken, J. P. *J. Am. Chem. Soc.* **2022**, *144*, 17815. (h) Teresa, J.; Velado, M.; Fernández de la Pradilla, R.; Viso, A.; Lozano, B.; Tortosa, M. *Chem. Sci.* **2023**, *14*, 1575. (i) Zhang, M.; Lee, P. S.; Allais, C.; Singer, R. A.; Morken, J. P. *J. Am. Chem. Soc.* **2023**, *145*, 8308. (j) Kong, Z.; Hu, W.; Morken, J. P. *ACS Catal.* **2023**, 11522.

(10) (a) Ishiyama, T.; Matsuda, N.; Miyaura, N.; Suzuki, A. *J. Am. Chem. Soc.* **1993**, *115*, 11018. (b) Prokopcová, H.; Ramírez, J.; Fernández, E.; Kappe, C. O. *Tetrahedron Lett.* **2008**, *49*, 4831. (c) Chen, Q.; Zhao, J.; Ishikawa, Y.; Asao, N.; Yamamoto, Y.; Jin, T. *Org. Lett.* **2013**, *15*, 5766.

(11) Zhao, F.; Jia, X.; Li, P.; Zhao, J.; Zhou, Y.; Wang, J.; Liu, H. *Org. Chem. Front.* **2017**, *4*, 2235.

(12) (a) Lesley, G.; Nguyen, P.; Taylor, N. J.; Marder, T. B.; Scott, A. J.; Clegg, W.; Norman, N. C. *Organometallics* **1996**, *15*, 5137. (b) Iverson, C. N.; Smith, M. R. *Organometallics* **1996**, *15*, 5155. (c) Cui, Q.; Musaev, D. G.; Morokuma, K. *Organometallics* **1997**, *16*, 1355. (d) Cui, Q.; Musaev, D. G.; Morokuma, K. *Organometallics* **1998**, *17*, 1383. (e) Ali, H. A.; El Aziz Al Quntar, A.; Goldberg, I.; Srebnik, M. *Organometallics* **2002**, *21*, 4533.

(13) Thomas, R. Ll.; Souza, F. E. S.; Marder, T. B. *J. Chem. Soc., Dalton Trans.* **2001**, 1650.

(14) (a) Toshima, N.; Yonezawa, T. *New J. Chem.* **1998**, *22*, 1179. (b) Narayan, N.; Meiyazhagan, A.; Vajtai, R. *Materials* **2019**, *12*, 3602. (c) Astruc, D. *Chem. Rev.* **2020**, *120*, 461.

(15) Ishiyama, T.; Kitano, T.; Miyaura, N. *Tetrahedron Lett.* **1998**, *39*, 2357.

(16) Khan, A.; Asiri, A. M.; Kosa, S. A.; Garcia, H.; Grirrane, A. *J. Catal.* **2015**, *329*, 401.

(17) **(*E*)-2,2′-(3-Phenylprop-1-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)**
In a dry box, an oven-dried 2-dram vial was charged with prop-2-yn-1-ylbenzene (122 mg, 1.05 mmol, 1.05 equiv), $B_2(pin)_2$ (254 mg, 1.00 mmol, 1.00 equiv), and 3% Au/TiO_2 (98 mg, 5.00 μmol, 0.05 equiv). The mixture was dissolved in toluene (1.00 mL). The reaction mixture was sealed with a PTFE-lined closed cap, brought out of the dry box and stirred at 80 °C for 24 h. At the completion of the reaction, the crude mixture was passed through a short pad of Celite using diethyl ether as solvent. The filtrate was concentrated and purified by column chromatography (silica gel, 0–1% ethyl acetate/hexane, stained with $KMnO_4$) to give the desired product as a white solid (296 mg, 82%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.24 (m, 2 H), 7.18–7.13 (m, 3 H), 5.79 (s, 1 H), 3.55 (d, *J* = 1.9 Hz, 2 H), 1.26 (s, 12 H), 1.19 (s, 12 H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 139.4, 129.8, 128.3, 126.1, 83.8, 83.5, 45.7, 25.0, 24.9. HRMS (DART): *m/z* [M + H]$^+$ calcd 371.2560; found: 371.2571. The reaction could also be conducted without a dry box using Schlenk techniques.

(18) Hitosugi, S.; Tanimoto, D.; Nakanishi, W.; Isobe, H. *Chem. Lett.* **2012**, *41*, 972.

(19) (a) Miura, H.; Hachiya, Y.; Nishio, H.; Fukuta, Y.; Toyomasu, T.; Kobayashi, K.; Masaki, Y.; Shishido, T. *ACS Catal.* **2021**, *11*, 758. (b) Oka, N.; Yamada, T.; Sajiki, H.; Akai, S.; Ikawa, T. *Org. Lett.* **2022**, *24*, 3510. (c) Ito, M.; Yamazaki, H.; Ito, A.; Oda, R.; Komiya, M.; Higuchi, K.; Sugiyama, S. *Eur. J. Org. Chem.* **2023**, *26*, e202300458.

(20) **4,4,5,5-Tetramethyl-2-(3-phenylprop-1-en-2-yl)-1,3,2-dioxaborolane**
In a dry box, an oven-dried 2-dram vial was charged with (*E*)-2,2′-(3-phenylprop-1-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (74.0 mg, 0.20 mmol, 1.00 equiv) and

lithium methoxide (19.0 mg, 0.50 mmol, 2.5 equiv). The mixture was dissolved in a freshly prepared solution of CuI·2LiCl (0.40 M Cu in THF, 1.00 mL). Isopropanol (solvent grade; 15.6 mg, 0.26 mmol, 1.30 equiv) was then added. The reaction mixture was sealed with a PTFE-lined closed cap, brought out of the dry box, and stirred at rt for 16 h. At the completion of the reaction, the crude mixture was passed through a short pad of silica using diethyl ether as solvent. The filtrate was concentrated and purified by column chromatography (silica gel, 0–2% ethyl acetate/hexane, stained with $KMnO_4$) to give the desired product as a colorless oil (39 mg, 80%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.26 (m, 2 H), 7.22–7.14 (m, 3 H), 5.84 (d, *J* = 3.3 Hz, 1 H), 5.54 (s, 1 H), 3.49 (s, 2 H), 1.22 (s, 12 H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 140.8, 129.9, 129.3, 128.2, 125.8, 83.6, 41.5, 24.8. HRMS (DART): *m/z* $[M + H]^+$ calcd 245.1707; found: 245.1712.