Organic LETTERS

Letter

pubs.acs.org/OrgLett

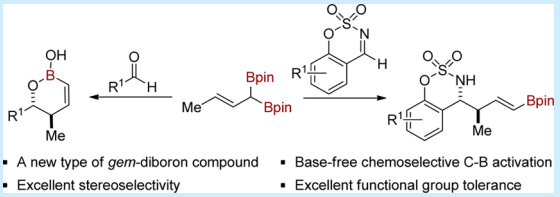
Chemo- and Stereoselective Crotylation of Aldehydes and Cyclic Aldimines with Allylic *gem*-Diboronate Ester

Jinyoung Park,[†] Seoyoung Choi,[†] Yeosan Lee, and Seung Hwan Cho*

Department of Chemistry, Pohang University of Science and Technology (POSTECH), Pohang 37673, Republic of Korea

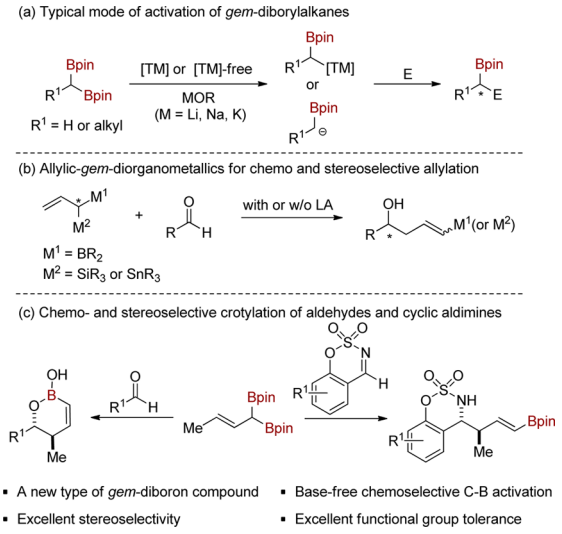
Supporting Information

ABSTRACT: We report a highly chemo- and stereoselective crotylation of aldehydes and cyclic aldimines with allylic-*gem*-diboronate ester as a new type of organoboron reagent. The allylic-*gem*-diboronate ester undergoes the crotylation with aldehydes and cyclic aldimines in excellent stereoselectivity, forming *anti*-5,6-disubstituted oxaborinin-2-ols or (*E*)-*δ*-boryl-*anti*-homoallylic amines in high efficiency. The reaction shows a wide range of substrate scope and excellent functional group tolerance. The synthetic applications of the obtained products, including stereospecific C−C, C−O, and C−Cl bond formation, are also demonstrated.



The preparation of new types of organoboron compounds is especially important owing to their stability and ability to undergo a wide range of organic transformations.[1,2] In recent years, *gem*-diborylalkanes have emerged as attractive synthetic intermediates for synthesizing organoborons via transition-metal-catalyzed or transition-metal-free chemo- and stereoselective transformations with suitable electrophiles.[3,4] Although considerable advances have been made in recent years, most of the methods developed employed alkyl-substituted *gem*-diboron reagents, the use of which necessitates strong base (MOH or MO-*t*-Bu, M = Li, Na, K) to activate one of the pinacolato boron (Bpin) units of the *gem*-diborylalkane chemoselectively through the formation of an *α*-borylalkylmetal[3] species or *α*-borylcarbanion[5] (Scheme 1a). This leads to a lack of functional group compatibility and limits the synthetic application of these reagents. Therefore, the development of new types of *gem*-diboron compounds that exhibit new reactivity and selectivity is highly desirable.

Scheme 1. Chemo- and Stereoselective Transformation of *gem*-Diorganometallic Reagents



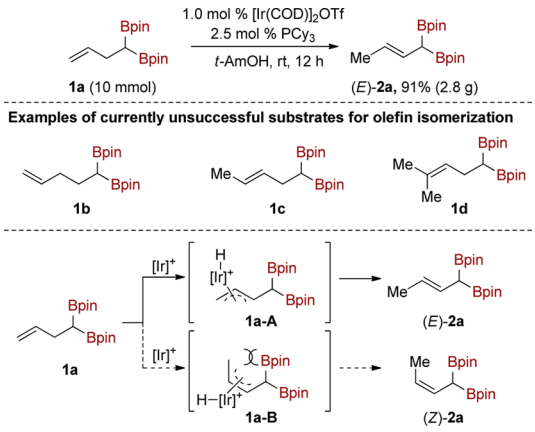
The stereoselective addition of allylorganometallics to aldehydes and imines was of central importance in synthetic chemistry because it could be used to form homoallylic alcohols or amines, which constitute prevalent motifs in many pharmaceuticals and natural products.[5,6] In recent decades, research in this field has focused on accessing and increasing the scope of allylorganometallics while achieving high stereoselectivity. Although these systems were still considered powerful and reliable tools in organic synthesis, the vast majority of them employed allylic-mono-organometallic species, and the use of allylic-*gem*-diorganometallics has been barely studied (Scheme 1b).[7,8] As a rare example, the reaction of aldehydes with *δ*-silyl allylboronate esters was reported to afford (*Z*)-*δ*-silyl homoallylic alcohols or (*E*)-*δ*-boryl homoallylic alcohols with moderate to high diastereoselectivity in the presence of an appropriate Lewis acid under harsh reaction conditions.[7a,b] Furthermore, the chemo- and enantioselective allylboration of aldehydes with *α*-stannylallylboranes was reported to provide enantioenriched (*E*)-*α*-stannyl homoallylic alcohols at very low temperature (−78 °C).[7c−f] However, this reaction required the use of relatively unstable and toxic tin reagents, thus limiting its synthetic utility. Consequently, the development of a systematic and predictable method employing readily accessible, nontoxic, and benchtop-stable allylic-*gem*-diorganometallics remains an important challenge. Herein, we report the design and synthesis of (*E*)-allylic-*gem*-diboronate esters and their utilization in chemo- and stereoselective crotylation of aldehydes and cyclic aldimines (Scheme 1c).

Received: June 15, 2017

DOI: 10.1021/acs.orglett.7b01821
Org. Lett. XXXX, XXX, XXX−XXX

As part of our continuing efforts to develop chemo- and stereoselective transformations of *gem*-diborylalkanes,[3k,m,4b−d] we attempted to prepare allylic-*gem*-diboron compounds that bear two identical boron units at the allylic position. The preparation of these proposed reagents was expected to allow the chemo- and stereoselective allylboration of aldehydes and imines to form homoallylic alcohols and amines that contain the other boron unit at the terminal alkene position. To achieve our desired goal, we designed a strategy to synthesize allylic-*gem*-diboron compounds by the metal-catalyzed olefin isomerization of homoallylic *gem*-diboronate ester **1**, which could be easily prepared by an S_N2 reaction between diborylmethane and allyl bromide using lithium diisopropylamide (LDA) as a base. Inspired by several precedents,[9] we investigated the viability of the proposed strategy employing a range of transition-metal catalysts with **1a** as a model substrate.[10] When **1a** was employed as a substrate in the presence of a cationic iridium catalyst having SbF_6 as a counteranion with a tricyclohexylphosphine ligand in 1,2-DCE at room temperature, the starting material was recovered. Interestingly, the effect of the counteranion in the iridium catalyst was dramatic, and when a catalyst bearing BAr^F [BAr^F = tetrakis(3,5-bis(trifluoromethyl)phenyl)borate] or PF_6 as a counteranion was used, the corresponding allylic-*gem*-diboronate ester **2a** was obtained in 70% and 76% conversion, respectively, with excellent (*E*)-selectivity. The high conversion (87%) was achieved when Ir[(COD)]$_2$OTf was used as a catalyst in 1,2-DCE. Further solvent screening revealed that *tert*-amyl alcohol was the most effective solvent, and the desired allylic-*gem*-diboronate ester **2a** was obtained in a nearly quantitative yield (Scheme 2).[10] It should be noted that the reaction was

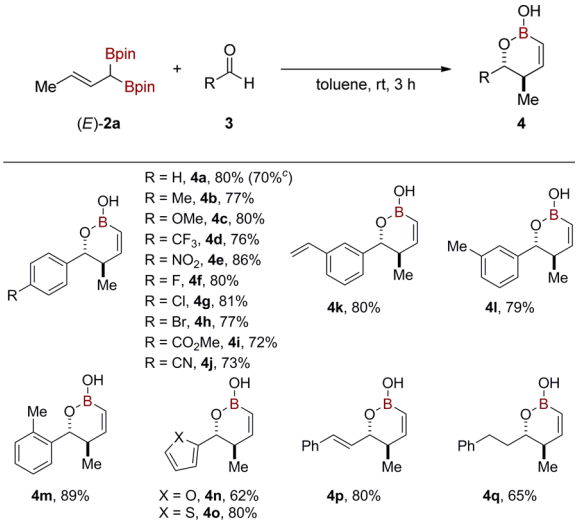
Scheme 2. Synthesis of Allylic *gem*-Diboronate Ester and the Proposed Model for Iridium-Catalyzed Olefin Isomerization



efficiently scaled to 10 mmol without difficulty, and the desired allylic-*gem*-diboronate ester (*E*)-**2a** was isolated in 91% yield (2.8 g) by recrystallization from *n*-hexane at −78 °C. We assumed that the olefin isomerization proceeded via a cationic π-allyl intermediate, and the intermediate **1a-A** is expected to be more favorable than **1a-B** mainly due to steric hindrance between the methyl group and the Bpin group in **1a-B**. Indeed, when we monitored the olefin isomerization by ^{1}H NMR, (*E*)-**2a** was observed exclusively over time.[10] Unfortunately, attempts to prepare other substituted allylic-*gem*-diboron compounds were unsuccessful under the reaction conditions, and only starting materials were recovered.[11]

After establishing efficient conditions to prepare the allylic-*gem*-diboronate ester (*E*)-**2a**, we investigated the chemo- and

Scheme 3. Substrate Scope of Aldehydes for Chemo- and Stereoselective Crotylation Reactions[a,b]



[a]Reaction conditions: (*E*)-**2a** (1.1 equiv), aldehyde (**3**, 0.20 mmol), and toluene (2.0 mL) at room temperature for 3 h. [b]Isolated yields are provided. [c]Isolated yield on a 1.0 mmol scale.

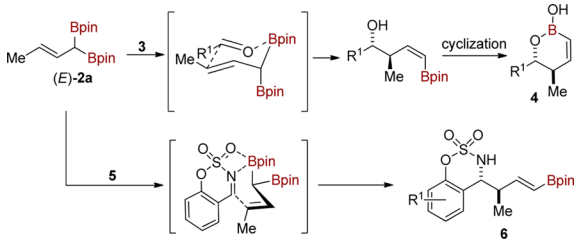
stereoselective crotylation of aldehyde **3** with (*E*)-**2a** at room temperature (Scheme 3). Interestingly, when benzaldehyde and (*E*)-**2a** were subjected in toluene at room temperature, the corresponding *anti*-oxaborinin-2-ol **4a** was obtained in 80% yield. The *anti*- and (*Z*)-selectivity observed clearly indicated that the reaction proceeded via a chair-like transition state with subsequent cyclization, affording the corresponding product **4** (vide infra). Different *para*-substituted benzaldehydes bearing electron-donating (**4b** and **4c**) or electron-withdrawing substituents (**4d** and **4e**) on the aromatic ring underwent the crotylation reaction in good to excellent yields (76−86%). Benzaldehydes bearing fluoro, chloro, and bromo substituents were compatible with the crotylation conditions, affording **4f−h** in good yields. The reactions exhibited excellent functional group tolerance, and benzaldehydes containing ester (**4i**), cyano (**4j**), and alkene (**4k**) substituents underwent crotylation with good efficiency. Substrates having substituents at the *meta*- and *ortho*-position participated in crotylation without difficulty, forming **4k−m** in good yields. The reaction of heteroaryl aldehydes resulted in the formation of the corresponding products **4n** and **4o** in 62% and 80% yields, respectively. Cinnamyl and aliphatic aldehydes were also proceeded to form products **4p** and **4q** in good yields.

Next, we wondered whether allylic-*gem*-diboronate ester (*E*)-**2a** could be exploited in the chemo- and stereoselective crotylation reactions with imines. Because crotylation of imines could form homoallylic amines, core scaffolds in many pharmaceuticals,[5a−c,12] the development of efficient and selective methods to access homoallylic amines containing the Bpin group at the terminal alkene position would be intriguing. To assess the viability of the crotylation of imines with (*E*)-**2a**, we subjected a range of *N*-protected imines to the crotylation conditions of aldehydes; but no desired products were obtained. Extensive screening revealed that the benzo[1,2,3]oxathiazine 2,2-dioxide (**5a**) was a viable electrophile, and the desired δ-boryl-homoallylic amine **6a** was obtained in 1,2-DCE at 90 °C with excellent *anti*- and (*E*)-selectivity in 84% isolated yield.[10] This result suggested that the *cis* configuration between the *N*-

DOI: 10.1021/acs.orglett.7b01821
Org. Lett. XXXX, XXX, XXX−XXX

protecting group and the aromatic ring was a crucial factor in the reaction, presumably because the *trans* configuration of the *N*-protected imines suffered from steric hindrance between the *N*-protecting group and the boron unit of the allylic-*gem*-diboronate ester when forming the closed transition state. The obtained product **6a** was crystalline, and the stereoselectivity of its formation was confirmed by single-crystal X-ray diffraction.[10] Because the product displayed complete *anti*- and (*E*)-selectivity, we assumed the reaction proceeded via half-chair-like transition state (Scheme 4). When one of the boron units in (*E*)-**2a** bound

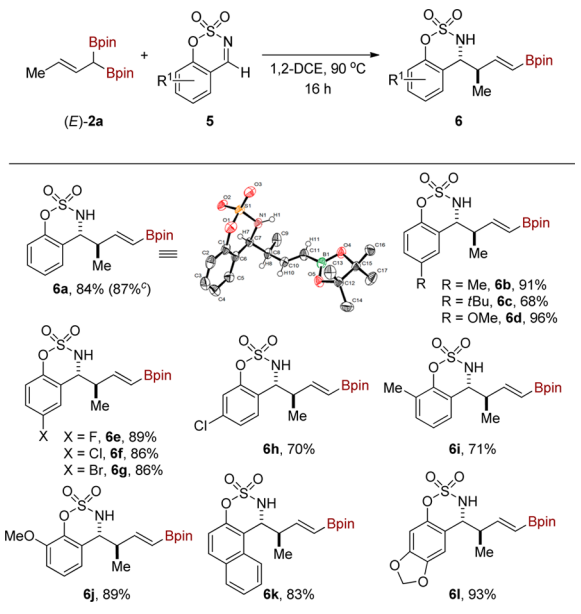
Scheme 4. Proposed Model for the Crotylation of (*E*)-2a with Aldehydes and Cyclic Aldimines



to the nitrogen atom of the substrate, the corresponding half-chair-like transition state was formed, and subsequent allyl group transfer led to the desired homoallylic amine with excellent *anti*- and (*E*)-selectivity.

Having established the optimal conditions, we investigated the substrate scope for cyclic aldimines **5** with (*E*)-**2a**, and the results are summarized in Scheme 5. In all cases, the obtained products were obtained by recrystallization from a mixture of Et_2O and *n*-hexane at −20 °C. Benzo[1,2,3]oxathiazine-2,2-dioxides having electron-donating substituents (**6b−d**) underwent chemo- and stereoselective crotylation in moderate to excellent yields. The reactions of cyclic aldimines bearing halides such as fluoro,

Scheme 5. Substrate Scope of Cyclic Aldimines for Chemo- and Stereoselective Crotylation Reactions[a,b]

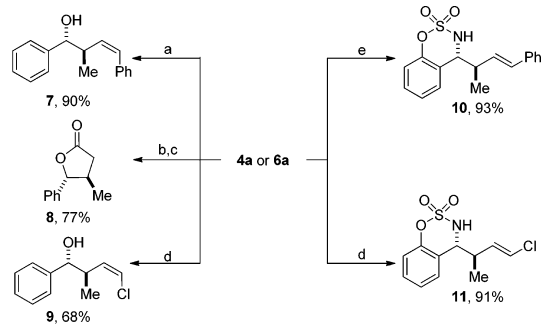


[a]Reaction conditions: (*E*)-**2a** (1.5 equiv), cyclic aldimine (**5**, 0.20 mmol), and 1,2-DCE (0.4 mL) at 90 °C for 16 h. [b]Isolated yields are provided. [c]Isolated yield on a 1.0 mmol scale.

chloro, and bromo groups were compatible with the reaction conditions, affording the corresponding products **6e−h** in good yields. Cyclic aldimines that have substituents at the *ortho*-position on the aromatic ring gave the corresponding products **6i** and **6j** in good yields. Naphthyl-substituted and dioxole-containing cyclic aldimines reacted efficiently, affording **6k** and **6l** in 83% and 93% yield, respectively. Note that all the reaction products obtained in this study exhibited complete *anti*- and (*E*)-selectivity.

To underscore the synthetic utility of the products obtained in this study, we sought to identify conditions for Pd-catalyzed cross-coupling with aryl iodides (Scheme 6). When the resulting

Scheme 6. Further Transformations of 4a and 6a[a]



[a]Reaction conditions: (a) cat. $Pd(PPh_3)_4$, PhI, CsF, THF/H_2O, 50 °C, 16 h; (b) $NaBO_3{\cdot}4H_2O$, THF/H_2O, rt, 3 h; (c) PCC, NaOAc, CH_2Cl_2, rt, 12 h; (d) $CuCl_2$, CH_2Cl_2, rt, 6 h; (e) cat. $Pd[P(t\text{-}Bu)_3]_2$, PhI, KOH, THF/H_2O, rt, 3 h.

4a was treated with $Pd(PPh_3)_4$ in the presence of 2 equiv of CsF as a base in a mixture of 1,4-dioxane and H_2O at 50 °C, the corresponding coupled product **7** was obtained in 90% yield with retention of (*Z*)-configuration. The boron unit of **4a** was oxidized in the presence of sodium perborate to form a 1:1.7 diastereomeric mixture of hemiacetal, and subsequent PCC oxidation gave the corresponding γ-butyrolactone **8** in 77% in two steps. A chlorine atom could be introduced at the boron functionality of **4a** in the presence of 2 equiv of copper(II) chloride, forming the corresponding (*Z*)-alkenyl chloride **9** in 68% yield. The obtained product **6a** could also be achieved for a C−C bond-forming reaction, and the corresponding product **10** was obtained in the presence of a catalytic amount of $Pd[P(t\text{-}Bu)_3]_2$ and 3 M aq KOH as a base at room temperature in THF in 93% yield. Treatment of **6a** with $CuCl_2$ resulted in the formation of (*E*)-δ-chloro-*anti*-homoallylic amine **11** in 91% yield.

In summary, we successfully developed a highly efficient chemo- and stereoselective crotylation system for aldehydes and cyclic aldimines using an allylic-*gem*-diboronate ester as a new type of organoboron compound.[13] The reaction showed broad substrate scope with respect to aldehydes or cyclic aldimines, forming the *anti*-5,6-disubstituted oxaborinin-2-ols or (*E*)-δ-boryl-substituted *anti*-homoallylic amines in high yields. The stereoselectivity obtained indicated that the reaction of the allylic-*gem*-diboronate ester with aldehydes proceeds via a chair-like transition state, whereas that with cyclic aldimines proceeds via a half-chair-like transition state. The further synthetic applications of the reaction products were demonstrated by stereoselective Pd-catalyzed cross-coupling and C−O and C−Cl bond-forming reactions. Further studies to expand the scope of the crotylation reactions and develop an asymmetric version of this transformation are ongoing in our laboratory.[14]

DOI: 10.1021/acs.orglett.7b01821
Org. Lett. XXXX, XXX, XXX−XXX

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b01821.

Experimental procedures, characterization of all new compounds, and crystallographic data (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: seunghwan@postech.ac.kr.

ORCID

Seung Hwan Cho: 0000-0001-5803-4922

Author Contributions

†J.P. and S.C. contributed equally to this work.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT & Future Planning (NRF-2015R1C1A1A02036326). J.P. thanks the National Research Foundation of Korea (NRF) for the global Ph.D. fellowship (NRF-2016H1A2A1908616).

■ REFERENCES

(1) (a) Crudden, C. M.; Edwards, D. *Eur. J. Org. Chem.* **2003**, *2003*, 4695. (b) Scott, H. K.; Aggarwal, V. K. *Chem. - Eur. J.* **2011**, *17*, 13124.

(2) (a) Molander, G. A.; Sandrock, D. L. *Curr. Opin. Drug Discov. Devel.* **2009**, *12*, 811. (b) Cuenca, A. B.; Shishido, R.; Ito, H.; Fernández, E. *Chem. Soc. Rev.* **2017**, *46*, 415.

(3) (a) Endo, K.; Ohkubo, T.; Hirokami, M.; Shibata, T. *J. Am. Chem. Soc.* **2010**, *132*, 11033. (b) Endo, K.; Ohkubo, T.; Shibata, T. *Org. Lett.* **2011**, *13*, 3368. (c) Endo, K.; Ohkubo, T.; Ishioka, T.; Shibata, T. *J. Org. Chem.* **2012**, *77*, 4826. (d) Hong, K.; Liu, X.; Morken, J. P. *J. Am. Chem. Soc.* **2014**, *136*, 10581. (e) Li, H.; Zhang, Z.; Shangguan, X.; Huang, S.; Chen, J.; Zhang, Y.; Wang, J. *Angew. Chem., Int. Ed.* **2014**, *53*, 11921. (f) Potter, B.; Szymaniak, A. A.; Edelstein, E. K.; Morken, J. P. *J. Am. Chem. Soc.* **2014**, *136*, 17918. (g) Sun, C.; Potter, B.; Morken, J. P. *J. Am. Chem. Soc.* **2014**, *136*, 6534. (h) Joannou, M. V.; Moyer, B. S.; Goldfogel, M. J.; Meek, S. J. *Angew. Chem., Int. Ed.* **2015**, *54*, 14141. (i) Joannou, M. V.; Moyer, B. S.; Meek, S. J. *J. Am. Chem. Soc.* **2015**, *137*, 6176. (j) Ebrahim-Alkhalil, A.; Zhang, Z.-Q.; Gong, T.-J.; Su, W.; Lu, X.-Y.; Xiao, B.; Fu, Y. *Chem. Commun.* **2016**, *52*, 4891. (k) Kim, J.; Park, S.; Park, J.; Cho, S. H. *Angew. Chem., Int. Ed.* **2016**, *55*, 1498. (l) Murray, S. A.; Green, J. C.; Tailor, S. B.; Meek, S. J. *Angew. Chem., Int. Ed.* **2016**, *55*, 9065. (m) Park, J.; Lee, Y.; Kim, J.; Cho, S. H. *Org. Lett.* **2016**, *18*, 1210. (n) Shi, Y.; Hoveyda, A. H. *Angew. Chem., Int. Ed.* **2016**, *55*, 3455. (o) Zhang, Z.-Q.; Zhang, B.; Lu, X.; Liu, J.-H.; Lu, X.-Y.; Xiao, B.; Fu, Y. *Org. Lett.* **2016**, *18*, 952.

(4) (a) Coombs, J. R.; Zhang, L.; Morken, J. P. *J. Am. Chem. Soc.* **2014**, *136*, 16140. (b) Jo, W.; Kim, J.; Choi, S.; Cho, S. H. *Angew. Chem., Int. Ed.* **2016**, *55*, 9690. (c) Kim, J.; Cho, S. H. *Synlett* **2016**, *27*, 2525. (d) Lee, Y.; Baek, S.-Y.; Park, J.; Kim, S.-T.; Tussupbayev, S.; Kim, J.; Baik, M.-H.; Cho, S. H. *J. Am. Chem. Soc.* **2017**, *139*, 976. (e) Hwang, C.; Jo, W.; Cho, S. H. *Chem. Commun.* **2017**, *53*, 7573.

(5) For recent reviews, see: (a) Yus, M.; González-Gómez, J. C.; Foubelo, F. *Chem. Rev.* **2011**, *111*, 7774. (b) Diner, C.; Szabó, K. J. *J. Am. Chem. Soc.* **2017**, *139*, 2. For selected examples, see: (c) Rauniyar, V.; Hall, D. G. *J. Am. Chem. Soc.* **2004**, *126*, 4518. (d) Burgos, C. H.; Canales, E.; Matos, K.; Soderquist, J. A. *J. Am. Chem. Soc.* **2005**, *127*, 8044. (e) Lou, S.; Moquist, P. N.; Schaus, S. E. *J. Am. Chem. Soc.* **2006**, *128*, 12660. (f) Wooten, A. J.; Kim, J. G.; Walsh, P. J. *Org. Lett.* **2007**, *9*, 381. (g) Chen, J. L. Y.; Scott, H. K.; Hesse, M. J.; Willis, C. L.; Aggarwal, V. K. *J. Am. Chem. Soc.* **2013**, *135*, 5316. (h) Jain, P.; Antilla, J. C. *J. Am. Chem. Soc.* **2010**, *132*, 11884. (i) Chen, J. L. Y.; Aggarwal, V. K. *Angew. Chem., Int. Ed.* **2014**, *53*, 10992. (j) Robbins, D. W.; Lee, K.; Silverio, D. L.; Volkov, A.; Torker, S.; Hoveyda, A. H. *Angew. Chem., Int. Ed.* **2016**, *55*, 9610.

(6) (a) Yamamoto, Y.; Miyairi, T.; Ohmura, T.; Miyaura, N. *J. Org. Chem.* **1999**, *64*, 296. (b) Shimizu, H.; Igarashi, T.; Miura, T.; Murakami, M. *Angew. Chem., Int. Ed.* **2011**, *50*, 11465. (c) Miura, T.; Nishida, Y.; Murakami, M. *J. Am. Chem. Soc.* **2014**, *136*, 6223. (d) Miura, T.; Nishida, Y.; Morimoto, M.; Murakami, M. *J. Am. Chem. Soc.* **2013**, *135*, 11497. (e) Weber, F.; Ballmann, M.; Kohlmeyer, C.; Hilt, G. *Org. Lett.* **2016**, *18*, 548. (f) Trost, B. M.; Cregg, J. J.; Quach, N. *J. Am. Chem. Soc.* **2017**, *139*, 5133.

(7) (a) Shimizu, M.; Kitagawa, H.; Kurahashi, T.; Hiyama, T. *Angew. Chem., Int. Ed.* **2001**, *40*, 4283. (b) Carosi, L.; Lachance, H.; Hall, D. G. *Tetrahedron Lett.* **2005**, *46*, 8981. (c) Chen, M.; Roush, W. R. *J. Am. Chem. Soc.* **2011**, *133*, 5744. (d) Stewart, P. S.; Chen, M.; Roush, W. R.; Ess, D. H. *Org. Lett.* **2011**, *13*, 1478. (e) Chen, M.; Roush, W. R. *Org. Lett.* **2012**, *14*, 1880. (f) Chen, M.; Roush, W. R. *J. Am. Chem. Soc.* **2012**, *134*, 3925.

(8) Examples for stereoselective allylboration of allylic−diorganometalic reagents: (a) Barrett, A. G. M.; Braddock, D. C.; de Koning, P. D.; White, A. J. P.; Williams, D. J. *J. Org. Chem.* **2000**, *65*, 375. (b) Peng, Z.-H.; Woerpel, K. A. *Org. Lett.* **2001**, *3*, 675. (c) Flamme, E. M.; Roush, W. R. *J. Am. Chem. Soc.* **2002**, *124*, 13644. (d) Smitrovich, J. H.; Woerpel, K. A. *Synthesis* **2002**, *2002*, 2778. (e) Peng, F.; Hall, D. G. *J. Am. Chem. Soc.* **2007**, *129*, 3070. (f) Chen, M.; Handa, M.; Roush, W. R. *J. Am. Chem. Soc.* **2009**, *131*, 14602.

(9) (a) Vasseur, A.; Bruffaerts, J.; Marek, I. *Nat. Chem.* **2016**, *8*, 209. (b) Li, H.; Mazet, C. *Acc. Chem. Res.* **2016**, *49*, 1232. (c) Kochi, T.; Hamasaki, T.; Aoyama, Y.; Kawasaki, J.; Kakiuchi, F. *J. Am. Chem. Soc.* **2012**, *134*, 16544. (d) Crossley, S. W. M.; Barabé, F.; Shenvi, R. A. *J. Am. Chem. Soc.* **2014**, *136*, 16788. (e) Wang, Z.-X.; Bai, X.-Y.; Yao, H.-C.; Li, B.-J. *J. Am. Chem. Soc.* **2016**, *138*, 14872.

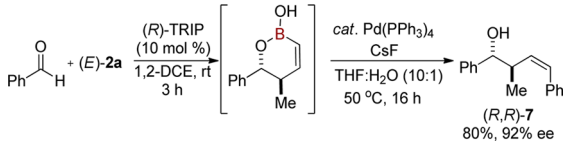
(10) See the Supporting Information for details.

(11) Further studies to expand the scope of allylic-*gem*-diboron compounds are underway in our laboratory.

(12) Examples for the allylboration of imines: (a) Wada, R.; Shibuguchi, T.; Makino, S.; Oisaki, K.; Kanai, M.; Shibasaki, M. *J. Am. Chem. Soc.* **2006**, *128*, 7687. (b) Lou, S.; Moquist, P. N.; Schaus, S. E. *J. Am. Chem. Soc.* **2007**, *129*, 15398. (c) Vieira, E. M.; Snapper, M. L.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2011**, *133*, 3332. (d) Silverio, D. L.; Torker, S.; Pilyugina, T.; Vieira, E. M.; Snapper, M. L.; Haeffner, F.; Hoveyda, A. H. *Nature* **2013**, *494*, 216. (e) van der Mei, F. W.; Miyamoto, H.; Silverio, D. L.; Hoveyda, A. H. *Angew. Chem., Int. Ed.* **2016**, *55*, 4701.

(13) During preparation of this manuscript, a related report for the synthesis of chiral (*E*)-*δ*-boryl-substituted *anti*-homoallylic alcohols using similar types of allylic *gem*-diboron compounds was reported; see: Miura, T.; Nakahashi, J.; Murakami, M. *Angew. Chem., Int. Ed.* **2017**, *56*, 6989.

(14) In our preliminary experiment, the reaction of benzaldehyde with (*E*)-**2a** in the presence of (*R*)-TRIP as a catalyst and subseqeunt Pd-catalyzed cross-coupling afforded the product (*R*,*R*)-**7** in 80% yield with 92% ee. For details, see the Supporting Information.



DOI: 10.1021/acs.orglett.7b01821
Org. Lett. XXXX, XXX, XXX−XXX