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Allylboronates from Vinyl Triflates and α-Chloroboronates by Reductive Nickel Catalysis

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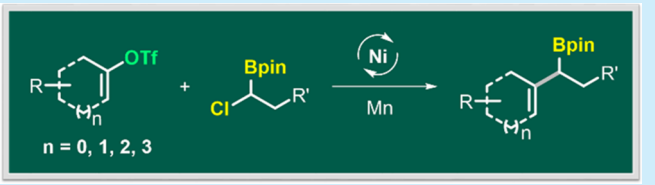
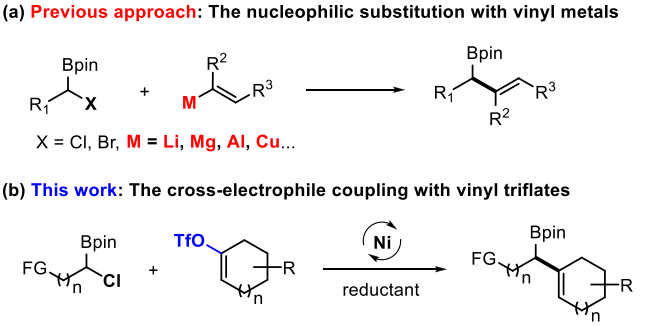
ABSTRACT: Allylboronates are unique building blocks widely used in organic synthesis, but the construction of cyclic allylboranates remains a challenging subject. We demonstrate here a mild and efficient access to this type of compound through the cross-electrophile coupling of vinyl triflates and α-chloroboronates. The reaction proceeded with a good substrate scope and good functional group compatibility. The ready availability of vinyl triflates from ketones, as well as the rich chemistry of allylboranates, makes our method suitable for the divergent modification of biologically active compounds. Preliminary mechanistic studies revealed that α-chloroboronates were activated via a radical process.



Allylboronates are essential building blocks frequently used in the synthesis of natural compounds and pharmaceuticals.[1] They have widely served as coupling partners in the Suzuki−Miyaura reaction for the precise installation of an allyl group.[2] They are also used as nucleophiles for additions to aldehydes and imines to afford homoallylic alcohols and amines.[1] Therefore, the synthesis of allylboronates has received considerable attention over the past years.[3] Approaches to these compounds typically include,[4] but are not limited to, (1) the boration reactions of allylic substrates such as allyl nucleophiles,[5] electrophiles (e.g., halides, acetates, alcohols),[6] and C−H bonds,[7] (2) the hydroboration or diboration reactions of 1,3-dienes,[8] and (3) the hydroboration reactions of allenes.[9] Despite these promising advances, these processes are generally effective for the synthesis of acyclic allylboronates. To date, a method for the construction of cyclic allylboronates, with the structure shown in Scheme 1b, remains to be developed.

Scheme 1. Synthesis of Allylboronates from α-Haloboronates



One strategy that could be used to overcome this limitation would be the reaction of well-defined vinyl species with α-haloboronates (Scheme 1).[10] In this context, the nucleophilic substitution reactions using vinyl metallic species (e.g., vinyl−M, M = Li, Mg, Al, Cu) represent the current state-of-the-art (Scheme 1a). However, partially because of the difficulty in accessing cyclic vinyl metals, these reactions have rarely been investigated for the synthesis of cyclic allylboronates. The use of vinyl electrophiles instead of vinyl metals is advantageous in availability, and it would provide access to a complementary scope of synthetically useful products. However, to our knowledge, there has been no report on the reaction between vinyl electrophiles and α-haloboronates.

The cross-electrophile coupling has recently emerged as a powerful tool for forging C−C bonds between electrophiles.[11] Among the various coupling partners, the amphoteric reagents such as α-haloboronates and α-halosilanes are particularly attractive.[12] These reagents possess nucleophilic and electrophilic sites, thus offering a versatile platform for chemoselective transformations. Recent elegant work by the Martin group has demonstrated the possibility of chemoselective arylation and alkylation of α-haloboronates with aryl bromides and alkenes, respectively.[12b] However, the cross-electrophile vinylation reaction is still unknown. As part of our ongoing interest in reductive vinylation reactions,[13] here we demonstrate a cross-electrophile coupling of vinyl triflates[14] with α-haloboronates (Scheme 1b). This method provides a mild and efficient

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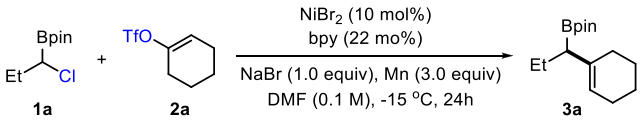
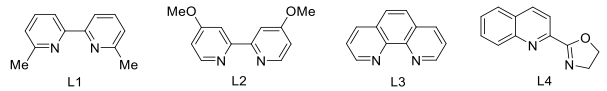
approach to cyclic allylboronates that can be otherwise difficult to access. It thus serves as a good complementary to the existing methodologies for the construction of allylboronates.

We began our investigations by studying the reaction of α-chloroboronate **1a** with vinyl triflate **2a** (Table 1). After screening a range of reaction conditions (see Tables S1−S7), we found that the combination of $NiBr_2$ (10 mol %), bpy (22 mol %), NaBr (1.0 equiv), and Mn (3.0 equiv) in DMF at −15 °C gave the best result, affording **3a** in 84% isolated yield (entry 1). Compatible results were obtained when $NiCl_2$ or NiI_2 was used, whereas the reactions with Ni(dme)Cl_2 or Ni(glyme)Br_2 gave decreased yields (entries 2−5). The inferior results were obtained when other nitrogen ligands were used (entries 6−9). The presence of NaBr has a positive effect on the yield, in which the formation of a vinyl dimer byproduct was partly inhibited (entry 10). It is possible that the in situ halide exchange of NaBr with α-chloroboronate generates α-bromoboronate, which is more reactive and may couple to vinyl triflate more efficiently. The reaction at room temperature afforded a significant amount of vinyl dimer, leading to a decreased yield (entry 11). The reaction with Zn as a reductant was highly ineffective (entry 12). In the absence of a nickel catalyst or reductant, no desired product was observed (entry 13).

Table 1. Optimization of Reaction Conditions[a]



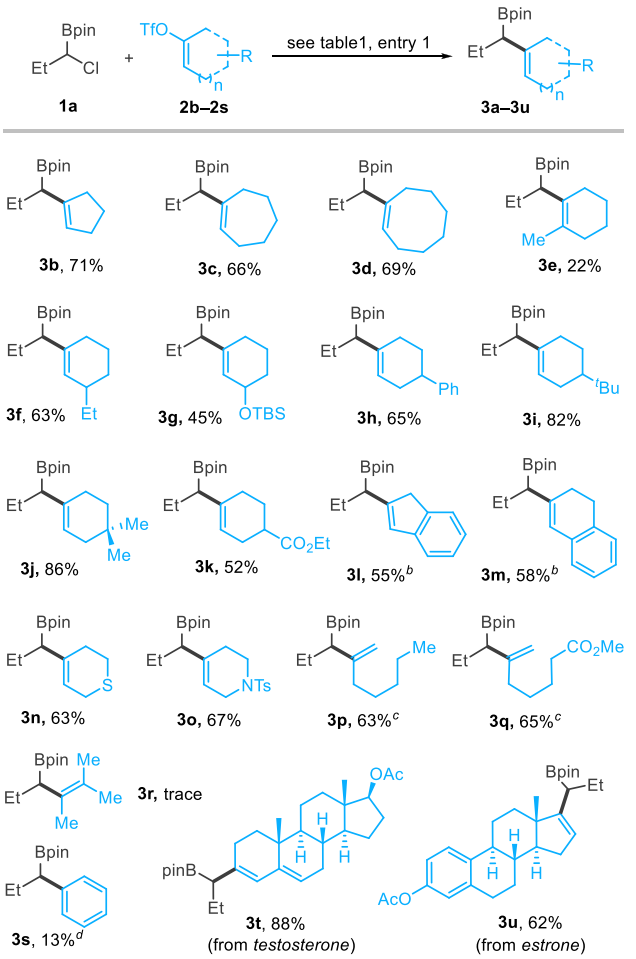
entry	change of conditions	3a (%)
1	none	86 (84)[b]
2	$NiCl_2$	80
3	NiI_2	82
4	Ni(dme)Cl_2	74
5	Ni(diglyme)Br_2	77
6	**L1** instead of bpy	61
7	**L2** instead of bpy	4
8	**L3** instead of bpy	71
9	**L4** instead of bpy	35
10	no NaBr	78
11	r.t. instead of −15 °C	61
12	Zn instead of Mn	22
13	no Ni or Mn	0



[a]**1a** (0.18 mmol) and **2a** (0.1 mmol) were used. The yields were determined by GC using dodecane as an internal standard. [b]**1a** (0.36 mmol) and **2a** (0.2 mmol) were used. Isolated yield.

With the optimized reaction conditions in hand, we studied the reaction with respect to the scope of vinyl triflates (Table 2). The cyclic vinyl triflates, ranging from five- to eight-membered rings, coupled to **1a** efficiently to afford the desired products in moderate to good yields (**3a**−**d**). Whereas the 2-substituted vinyl triflate resulted in a low yield of product **3e**, substitution at the 3- and 4-position was tolerated (**3f**−**k**). The moderate yields of coupling products were obtained when indenyl triflate (**3l**) and 3,4-dihydronaphthalenyl triflate (**3m**) were used. Nonaromatic heterocycles are essential structural motifs found in various pharmaceuticals.[15] Our method provides an efficient approach to produce heterocyclic allylboronates, including those bearing 3,6-dihydro-2*H*-thiopyran (**3n**) and 3-piperideine (**3o**) heterocycles. Reactions with acyclic vinyl substrates were less effective under the standard conditions. By changing the ligand to 4,7-diphenyl-1,10-phenanthroline, the reactions with **1a** afforded the desired products in moderate yields (**3p**, **3q**). Only a trace of product was observed when all-substituted acyclic vinyl triflate was used (**3r**). The use of phenyl triflate afforded the desired product in 13% yield (**3s**). The abundance of ketones in nature prompted us to investigate the potential of our method for the functionalization of biologically active molecules. Testosterone- and estrone-derived vinyl triflates coupled to **1a** efficiently, and allylboronate **3t** and **3u** were produced in moderate to good yield.

Table 2. Substrate Scope of Vinyl Triflates[a]



[a]**1a** (0.36 mmol) and vinyl triflates (0.2 mmol) were used. Isolated yields. [b]NMR yield was used because of the difficulty in purification with the dechloro byproduct of α-chloroboronates. [c]4,7-Diphenyl-1,10-phenanthroline was used instead of 2,2′-bipyridine. [d]Phenyl triflate (0.2 mmol) was used.

The substrate scope of α-chloroboronates is shown in Table 3. α-Chloroboronates with different chain lengths of the alkyl group were tolerated (**3v**, **3w**, **3x**). The reactions with sterically hindered substrates were less effective (**3y**, **3z**). The presence of an aryl group, bearing either electron-rich or electron-poor substituents, at the alkyl chain was tolerated (**3aa**−**ad**). The reaction has shown good functional group compatibility. α-

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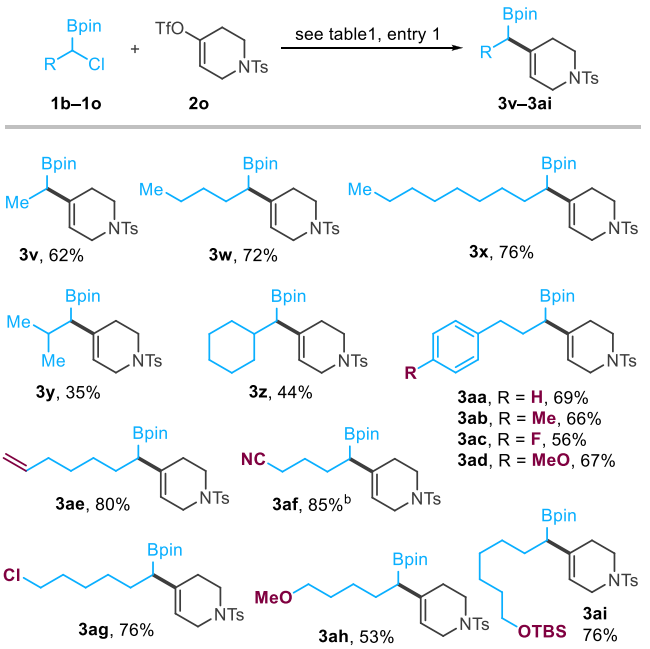
Table 3. Substrate Scope of α-Chloroboronates[a]

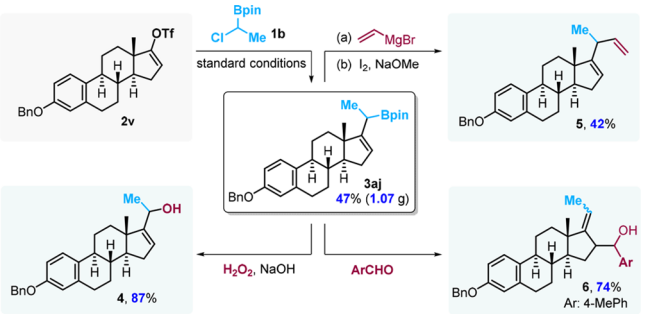


[a]**2o** (0.20 mmol) and α-chloroboronates (0.36 mmol) were used. Isolated yields. [b]Reactions for 36 h.

Chloroboronates with functionalities, such as alkene (**3ae**), nitrile (**3af**), alkyl chloride (**3ag**), ether (**3ah**), and silyl ether (**3ai**), could be selectively vinylated to afford the products in moderate to good yields.

The modification of biologically active compounds represents a promising approach to alter their pharmacological profiles. Our method offers the opportunity for the divergent modification of these compounds. For example, estrone-derived vinyl triflates could be functionalized with **1b** on the gram scale to afford allylboronate **3aj** (Scheme 2). Because of

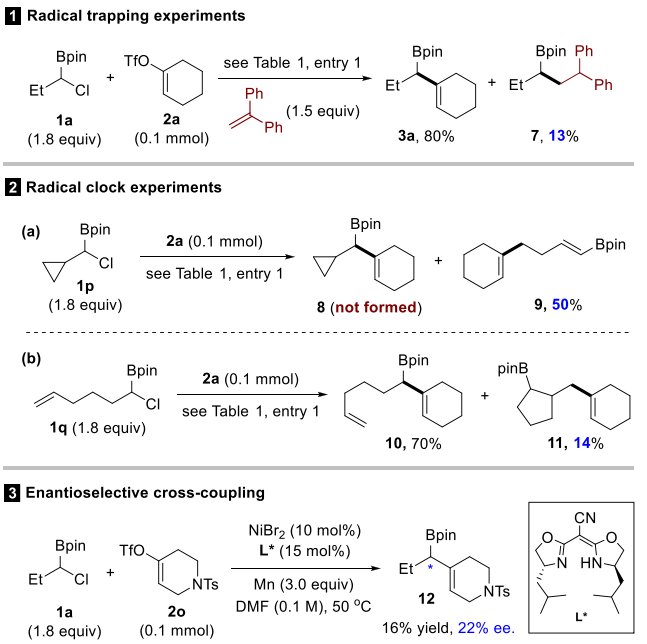
Scheme 2. Synthetic Application



the rich chemistry of allylboronate, compound **3aj** could undergo divergent transformation to provide the hydration product **4**, the vinylation product **5**, and the addition product **6**.

In the presence of 1,1-diphenylethylene, the reaction of **1a** with **2a** afforded **3a** in 80% yield, along with 13% of alkene trapping product **7** (Scheme 3 (1)). This result suggests that α-chloroboronates might be activated via a radical mechanism. To confirm this hypothesis, several control experiments were performed. (1) The reaction of cyclopropyl substrate **1p** with **2a** exclusively produced the ring-opening product (Scheme 3

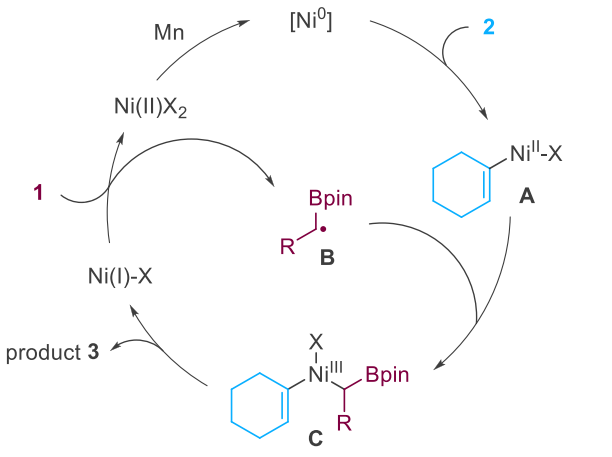
Scheme 3. Mechanistic Studies



(2a)).[16] (2) Under the standard conditions, the reaction of alkene substrate **1q** with **2a** afforded the cyclized product **11** in 14% yield (Scheme 3 (2b)). (3) The reaction of racemic **1a** afforded allylboronate **12** in 22% ee when chiral ligand **L*** was used (Scheme 3 (3)). These results are consistent with a pathway in which a radical process might be involved in the activation of α-chloroboronates.

Although the detailed mechanism for this reaction requires further investigation, on the basis of the above results and on reports presented by other investigators,[17] we tentatively proposed a catalytic cycle, as shown in Scheme 4. The

Scheme 4. Proposed Mechanism



oxidative addition of vinyl triflate to Ni(0) would afford vinyl–Ni(II) (**A**), which may trap an alkyl radical to afford complex **C**.[17a] The reductive elimination of compound **C** would give the desired product **3** and generate Ni(I). Alkyl radical **B** might be generated via the single-electron reaction of α-chloroboronates **1** with Ni(I).[17c]

In summary, we have demonstrated the cross-electrophile coupling of vinyl triflates with α-chloroboronates. This

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reaction offers a mild and efficient approach for the synthesis of cyclic allylboronates, which are difficult to access otherwise. The synthetic utility of this method was demonstrated by its application to the divergent modification of biologically active molecules. Preliminary mechanistic experiments revealed that a radical process was involved in the activation of α-chloroboronates. Further studies on the reductive vinylation reactions are ongoing in our laboratories.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c01683.

Detailed optimization of reaction conditions, part of the mechanistic studies, detailed experimental procedures, characterization data, and copies of ^{1}H and ^{13}C NMR spectra for new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) For selected reviews, see: (a) Denmark, S. E.; Fu, J. Catalytic Enantioselective Addition of Allylic Organometallic Reagents to Aldehydes and Ketones. *Chem. Rev.* **2003**, *103*, 2763. (b) Ramachandran, P. V.; Burghardt, T. E. Recent developments in the chiral synthesis of homoallylic amines via organoboranes. *Pure Appl. Chem.* **2006**, *78*, 1397. (c) Hall, D. G.; Lachance, H. *Allylboration of Carbonyl Compounds*; Wiley: Hoboken, NJ, 2012. (d) Yus, M.; González-Gómez, J. C.; Foubelo, F. Diastereoselective Allylation of Carbonyl Compounds and Imines: Application to the Synthesis of Natural Products. *Chem. Rev.* **2013**, *113*, 5595.

(2) Selected references: (a) Sebelius, S.; Olsson, V. J.; Wallner, O. A.; Szabo, K. J. Palladium-Catalyzed Coupling of Allylboronic Acids with Iodobenzenes. Selective Formation of the Branched Allylic Product in the Absence of Directing Groups. *J. Am. Chem. Soc.* **2006**, *128*, 8150. (b) Glasspoole, B. W.; Ghozati, K.; Moir, J. W.; Crudden, C. M. Suzuki-Miyaura cross-couplings of secondary allylic boronic esters. *Chem. Commun.* **2012**, *48*, 1230. (c) Yang, Y.; Buchwald, S. L. Ligand-Controlled Palladium-Catalyzed Regiodivergent Suzuki-Miyaura Cross-Coupling of Allylboronates and Aryl Halides. *J. Am. Chem. Soc.* **2013**, *135*, 10642.

(3) An elegant review: Diner, C.; Szabo, K. J. Recent Advances in the Preparation and Application of Allylboron Species in Organic Synthesis. *J. Am. Chem. Soc.* **2017**, *139*, 2.

(4) For other represented approaches, see: (a) Yamamoto, Y.; Takahashi, M.; Miyaura, N. Synthesis of Pinacol Allylic Boronic Esters via Olefin Cross-Metathesis between Pinacol Allylboronate and Terminal or Internal Alkenes. *Synlett* **2002**, *1*, 128. (b) Althaus, M.; Mahmood, A.; Suárez, J. R.; Thomas, S. P.; Aggarwal, V. K. Application of the Lithiation-Borylation Reaction to the Preparation of Enantioenriched Allylic Boron Reagents and Subsequent In Situ Conversion into 1,2,4-Trisubstituted Homoallylic Alcohols with Complete Control over All Elements of Stereochemistry. *J. Am. Chem. Soc.* **2010**, *132*, 4025. (c) Potter, B.; Edelstein, E. K.; Morken, J. P. Modular, Catalytic Enantioselective Construction of Quaternary Carbon Stereocenters by Sequential Cross-Coupling Reactions. *Org. Lett.* **2016**, *18*, 3286. (d) Edelstein, E. K.; Namirembe, S.; Morken, J. P. Enantioselective Conjunctive Cross-Coupling of Bis(alkenyl) Borates: A General Synthesis of Chiral Allylboron Reagents. *J. Am. Chem. Soc.* **2017**, *139*, 5027.

(5) (a) Roush, W. R.; Ando, K.; Powers, D. B.; Palkowitz, A. D.; Halterman, R. L. Asymmetric Synthesis Using Diisopropyl Tartrate Modified (E)- and (Z)-Crotylboronates: Preparation of the Chiral Crotylboronates and Reactions with Achiral Aldehydes. *J. Am. Chem. Soc.* **1990**, *112*, 6339. (b) Beckmann, E.; Hoppe, D. Synthesis of an Enantioenriched a-Carbamoyloxy-crotylboronate and Its Homoaldol Reaction with Aldehydes. *Synthesis* **2005**, 217.

(6) Selected recent references, see: (a) Guzman-Martinez, A.; Hoveyda, A. H. Enantioselective Synthesis of Allylboronates Bearing a Tertiary or Quaternary B-Substituted Stereogenic Carbon by NHC-Cu-Catalyzed Substitution Reactions. *J. Am. Chem. Soc.* **2010**, *132*, 10634. (b) Park, J. K.; Lackey, H. H.; Ondrusek, B. A.; McQuade, D. T. Stereoconvergent Synthesis of Chiral Allylboronates from an E/Z Mixture of Allylic Aryl Ethers Using a 6-NHC-Cu(I) Catalyst. *J. Am. Chem. Soc.* **2011**, *133*, 2410. (c) Zhou, Q.; Srinivas, H. D.; Zhang, S.; Watson, M. P. Accessing Both Retention and Inversion Pathways in Stereospecific, Nickel-Catalyzed Miyaura Borylations of Allylic Pivalates. *J. Am. Chem. Soc.* **2016**, *138*, 11989. (d) Miralles, N.; Gómez, J. E.; Kleij, A. W.; Fernández, E. Copper-Mediated SN2'Allyl-Alkyl and Allyl-Boryl Couplings of Vinyl Cyclic Carbonates. *Org. Lett.* **2017**, *19*, 6096. (e) Zhou, Y.; Wang, H.; Liu, Y.; Zhao, Y.; Zhang, C.; Qu, J. Iron-catalyzed boration of allylic esters: an efficient approach to allylic boronates. *Org. Chem. Front.* **2017**, *4*, 1580. (f) Chen, P.-P.; Zhang, H.; Cheng, B.; Chen, X.; Cheng, F.; Zhang, S.-Q.; Lu, Z.; Meng, F.; Hong, X. How Solvents Control the Stereospecificity of Ni-Catalyzed Miyaura Borylation of Allylic Pivalates. *ACS Catal.* **2019**, *9*, 9589. (g) Ge, Y.; Cui, X.-Y.; Tan, S. M.; Jiang, H.; Ren, J.; Lee, N.; Lee, R.; Tan, C.-H. Guanidine-Copper Complex Catalyzed Allylic Borylation for the Enantioconvergent Synthesis of Tertiary Cyclic Allylboronates. *Angew. Chem., Int. Ed.* **2019**, *58*, 2382.

(7) (a) Deng, H.-P.; Eriksson, L.; Szabó, K. J. Allylic sp3 C-H borylation of alkenes via allyl-Pd intermediates: an efficient route to allylboronates. *Chem. Commun.* **2014**, *50*, 9207. (b) Tao, Z.-L.; Li, X.-H.; Han, Z.-Y.; Gong, L.-Z. Diastereoselective Carbonyl Allylation with Simple Olefins Enabled by Palladium Complex-Catalyzed C-H Oxidative Borylation. *J. Am. Chem. Soc.* **2015**, *137*, 4054. (c) Mao, L.;

https://dx.doi.org/10.1021/acs.orglett.0c01683
Org. Lett. XXXX, XXX, XXX−XXX

Bertermann, R.; Rachor, S. G.; Szabó, K. J.; Marder, T. B. Palladium-Catalyzed Oxidative Borylation of Allylic C-H Bonds in Alkenes. *Org. Lett.* **2017**, *19* (24), 6590.

(8) (a) Wu, J. Y.; Moreau, B.; Ritter, T. Iron-Catalyzed 1,4-Hydroboration of 1,3-Dienes. *J. Am. Chem. Soc.* **2009**, *131*, 12915. (b) Ely, R. J.; Morken, J. P. Regio- and Stereoselective Ni-Catalyzed 1,4-Hydroboration of 1,3-Dienes: Access to Stereodefined (Z)-Allylboron Reagents and Derived Allylic Alcohols. *J. Am. Chem. Soc.* **2010**, *132*, 2534. (c) Peng, S.; Yang, J.; Liu, G.; Huang, Z. Ligand controlled cobalt catalyzed regiodivergent 1,2-hydroboration of 1,3-dienes. *Sci. China: Chem.* **2019**, *62*, 336. (d) Wang, M.; Gao, S.; Chen, M. Stereoselective Syntheses of (E)-γ,δ-Bisboryl-Substituted syn-Homoallylic Alcohols via Chemoselective Aldehyde Allylboration. *Org. Lett.* **2019**, *21*, 2151.

(9) Yuan, W.; Song, L.; Ma, S. Copper-Catalyzed Borylcupration of Allenylsilanes. *Angew. Chem., Int. Ed.* **2016**, *55*, 3140.

(10) (a) Brown, H. C.; De Lue, N. R.; Yamamoto, Y.; Maruyama, K.; Kasahara, T.; Murahashi, S.; Sonoda, A. Organoboranes. 23. Reaction of Organolithium and Grignard Reagents with α-Bromoalkylboronate Esters. A Convenient, Essentially Quantitative Procedure for the Synthesis of Tertiary Alkyl-, Benzyl-, Propargyl-, and Stereospecific Allylboranes. *J. Org. Chem.* **1977**, *42*, 4088. (b) Matteson, D. S.; Majumdar, D. α-Chloro Boronic Esters from Homologation of Boronic Esters. *J. Am. Chem. Soc.* **1980**, *102*, 7588. (c) Nyzam, V.; Belaud, C.; Villiéras, J. Preparation of (2-methoxycarbonyl)-allylboronates from (ol-methoxycarbonyl)vinylalanate. *Tetrahedron Lett.* **1993**, *34*, 6899. (d) Kennedy, J. W. J.; Hall, D. G. Novel Isomerically Pure Tetrasubstituted Allylboronates: Stereocontrolled Synthesis of r-Exomethylene γ-Lactones as Aldol-Like Adducts with a Stereogenic Quaternary Carbon Center. *J. Am. Chem. Soc.* **2002**, *124*, 898.

(11) For recent reviews of the cross-electrophile reactions, see: (a) Knappke, C. E. I.; Grupe, S.; Gärtner, D.; Corpet, M.; Gosmini, C.; Jacobi von Wangelin, A. Reductive Cross-Coupling Reactions between Two Electrophiles. *Chem. - Eur. J.* **2014**, *20*, 6828. (b) Moragas, T.; Correa, A.; Martin, R. Metal-Catalyzed Reductive Coupling Reactions of Organic Halides with Carbonyl Type Compounds. *Chem. - Eur. J.* **2014**, *20*, 8242. (c) Weix, D. J. Methods and Mechanisms for Cross-Electrophile Coupling of Csp^2 Halides with Alkyl Electrophiles. *Acc. Chem. Res.* **2015**, *48*, 1767. (d) Gu, J.; Wang, X.; Xue, W.; Gong, H. Nickel-catalyzed Reductive Coupling of Alkyl Halides with Other Electrophiles: Concept and Mechanistic Considerations. *Org. Chem. Front.* **2015**, *2*, 1411. (e) Lucas, E. L.; Jarvo, E. R. Stereospecific and Stereoconvergent Cross-couplings between Alkyl Electrophiles. *Nat. Rev. Chem.* **2017**, *1*, 0065. (f) Richmond, E.; Moran, J. Recent Advances in Nickel Catalysis Enabled by Stoichiometric Metallic Reducing Agents. *Synthesis* **2018**, *50*, 499.

(12) (a) Hofstra, J. L.; Cherney, A. H.; Ordner, C. M.; Reisman, S. E. Synthesis of Enantioenriched Allylic Silanes via Nickel-Catalyzed Reductive Cross-Coupling. *J. Am. Chem. Soc.* **2018**, *140*, 139. (b) Sun, S.-Z.; Martin, R. Nickel-Catalyzed Umpolung Arylation of Ambiphilic α-Bromoalkyl Boronic Esters. *Angew. Chem., Int. Ed.* **2018**, *57*, 3622. (c) Sun, S.-Z.; Börjesson, M.; Martin-Montero, R. M.; Martin, R. Site-Selective Ni-Catalyzed Reductive Coupling of α-Haloboraneswith Unactivated Olefins. *J. Am. Chem. Soc.* **2018**, *140*, 12765.

(13) (a) Tian, Z.-X.; Qiao, J.-B.; Xu, G.-L.; Pang, X.; Qi, L.; Ma, W.-Y.; Zhao, Z.-Z.; Duan, J.; Du, Y.-F.; Su, P.; Liu, X.-Y.; Shu, X.-Z. Highly Enantioselective Cross-Electrophile Aryl-Alkenylation of Unactivated Alkenes. *J. Am. Chem. Soc.* **2019**, *141*, 7637. (b) Pan, F.-F.; Guo, P.; Li, C.-L.; Su, P.; Shu, X.-Z. Enones from Acid Fluorides and Vinyl Triflates by Reductive Nickel Catalysis. *Org. Lett.* **2019**, *21*, 3701. (c) He, R.-D.; Li, C.-L.; Pan, Q.-Q.; Guo, P.; Liu, X.-Y.; Shu, X.-Z. Reductive Coupling between C-N and C-OElectrophiles. *J. Am. Chem. Soc.* **2019**, *141*, 12481. (d) Duan, J.; Du, Y.-F.; Pang, X.; Shu, X.-Z. Ni-catalyzed cross-electrophile coupling betweenvinyl/aryl and alkyl sulfonates: synthesis of cycloalkenes and modification of peptides. *Chem. Sci.* **2019**, *10*, 8706.

(14) (a) Busacca, C. A.; Eriksson, M. C.; Fiaschi, R. Cross Coupling of Vinyl Triflates and Aikyl Grignard Reagents Catalyzed by Nickel(0)-Complexes. *Tetrahedron Lett.* **1999**, *40*, 3101. (b) Cho, E. J.; Buchwald, S. L. The Palladium-Catalyzed Trifluoromethylation of Vinyl Sulfonates. *Org. Lett.* **2011**, *13*, 6552. (c) Liao, L.; Jana, R.; Urkalan, K. B.; Sigman, M. S. A Palladium-Catalyzed Three-Component Cross-Coupling of Conjugated Dienes or Terminal Alkenes with Vinyl Triflates and Boronic Acids. *J. Am. Chem. Soc.* **2011**, *133*, 5784. (d) Chen, H.; Sun, S.; Liao, X. Nickel-Catalyzed Decarboxylative Alkenylation of Anhydrides with Vinyl Triflates or Halides. *Org. Lett.* **2019**, *21*, 3625.

(15) Ferles, M.; Pliml, J. *Adv. Heterocycl. Chem.* **1970**, *12*, 43−101.

(16) Stevenson, J. P.; Jackson, W. F.; Tanko, J. M. Cyclopropylcarbinyl-Type Ring Openings. Reconciling the Chemistry of Neutral Radicals and Radical Anions. *J. Am. Chem. Soc.* **2002**, *124*, 4271.

(17) (a) Biswas, S.; Weix, D. J. Mechanism and Selectivity in Nickel-Catalyzed Cross-Electrophile Coupling of Aryl Halides with Alkyl Halides. *J. Am. Chem. Soc.* **2013**, *135*, 16192. (b) Everson, D. A.; Weix, D. J. Cross-Electrophile Coupling: Principles of Reactivity and Selectivity. *J. Org. Chem.* **2014**, *79*, 4793. (c) Diccianni, J. B.; Diao, T. Mechanisms of Nickel-Catalyzed Cross-Coupling Reactions. *Trends in Chemistry* **2019**, *1*, 830.

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