

# Benzyltriboronates: Building Blocks for Diastereoselective Carbon–Carbon Bond Formation

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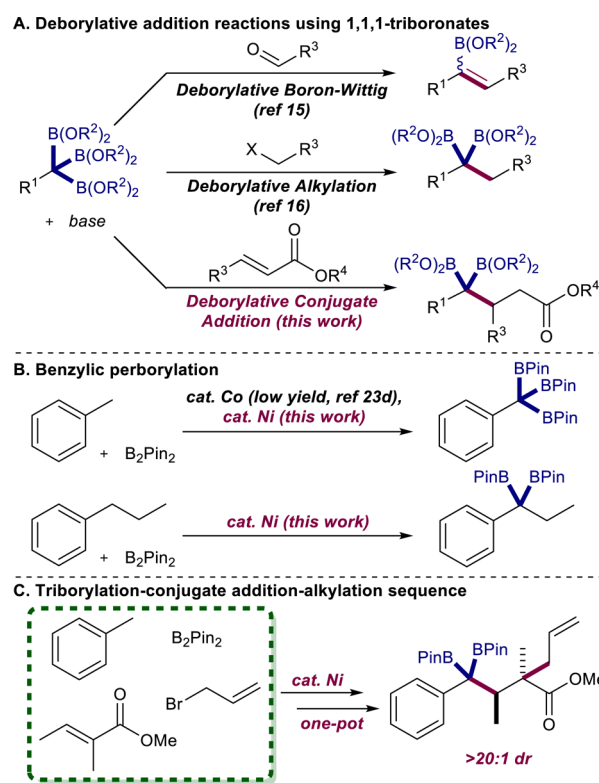
**S** Supporting Information

**ABSTRACT:** A highly diastereoselective carbon–carbon bond-forming reaction involving the tandem coupling of benzyltriboronates, enoates, and alkyl halides is described. This method was enabled by the discovery of  $\alpha$ -diimine nickel catalysts that promote the chemoselective triborylation of benzylic C(sp<sup>3</sup>)–H bonds using B<sub>2</sub>Pin<sub>2</sub> (Pin = pinacolate). The C–H functionalization method is effective with methylarenes and for the diborylation of secondary benzylic C–H bonds, providing direct access to polyboron building blocks from readily available hydrocarbons. Combination of the benzylic perborylation with a new deborylative conjugate addition–alkylation method enables a one-pot procedure in which multiple simple precursors are combined to generate diastereopure products containing quaternary stereocenters.

Organoboron compounds are versatile reagents for carbon–carbon and carbon–heteroatom bond formation.<sup>1</sup> Arylboronates are the most widely used nucleophilic partner in Suzuki–Miyaura cross couplings<sup>2,3</sup> and the most commonly deployed in the pharmaceutical industry due to their ease of handling, synthetic accessibility, and reliability.<sup>4</sup> Alkylboronates, typically synthesized by alkene hydroboration<sup>5</sup> or Miyaura-type borylation of alkyl halides,<sup>6</sup> are likewise valuable reagents for C–C bond formation whose utility will continue to grow as methods for C(sp<sup>3</sup>)–C(sp<sup>3</sup>) cross coupling mature.<sup>7</sup> Polyboron compounds such as *gem*-diboronates are beginning to emerge as useful reagents for C–C bond formation as well and have been applied to alkylation reactions,<sup>8</sup> boron–Wittig olefinations,<sup>9</sup> 1,2-additions to carbonyls<sup>10</sup> and imines,<sup>11</sup> addition to pyridine-*N*-oxides,<sup>12</sup> allylic substitution,<sup>13</sup> and enantioselective cross couplings.<sup>14</sup> The use of 1,1,1-alkyltriboronates for C–C bond formation offers similar, if not greater, potential but is less explored and limited to deborylative boron–Wittig olefination<sup>15</sup> or deborylative alkylation (Scheme 1A).<sup>16</sup>

The full synthetic potential of geminal alkylpolyboronates has yet to be realized principally due to the paucity of straightforward methods for their preparation. The direct, metal-catalyzed polyborylation of C(sp<sup>3</sup>)–H bonds offers a potentially transformative route as readily available, minimally functionalized hydrocarbons may be used as starting materials. Although C–H borylation is one of the most widely used C–H functionalization methods, most precious<sup>17</sup> and base metal catalysts<sup>18</sup> favor C(sp<sup>2</sup>)–H sites, a result of established kinetic preference for oxidative addition.<sup>19</sup> Metal-catalyzed methods for alkane borylation have been reported<sup>17,20</sup> including recent notable

## Scheme 1. Utility of Alkyltriboronates in C–C Bond Formation, Synthesis of Benzylpolyboronates by C–H Borylation, and Combination of These Methods To Provide a Diastereoselective Tandem Coupling Sequence



examples of iridium- and rhodium-catalyzed borylation of methane at high pressures,<sup>21</sup> but chemoselective C(sp<sup>3</sup>)–H borylation in the presence of C(sp<sup>2</sup>)–H bonds is far less common and more challenging. Strategies to overcome this selectivity bias rely primarily on the use of directing groups,<sup>22</sup> while a handful of nondirected methods selectively functionalize benzylic C–H bonds.<sup>23</sup> In most of these examples, only one C–H bond is converted to a C–B bond.<sup>24</sup> New catalytic methods that convert multiple C–H bonds on the same carbon to boron functional groups would be valuable and enable exploration of the full synthetic potential of alkyl polyboronates.

Our laboratory previously reported  $\alpha$ -diimine cobalt dialkyl and bis(carboxylate) compounds that are active for the catalytic

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borylation of C(sp<sup>3</sup>)-H bonds of methylarenes with B<sub>2</sub>Pin<sub>2</sub> as the boron source.<sup>23d</sup> The 1,1-diboronates were the major products but, with toluene as the substrate, a small amount (18% yield) of the 1,1,1-triboronate product was isolated when excess boron reagent and high cobalt loadings of 50 mol% were used. The forcing conditions, low yield, and difficulty in product isolation precluded reactivity studies of this interesting benzylpolyboronate and inspired development of a synthetically useful catalytic method. Here we describe  $\alpha$ -diimine nickel dialkyl and bis(carboxylate) complexes that enable the selective preparation of benzyltriboronates via perborylation of benzylic C-H bonds (Scheme 1B). Combination of the Ni-catalyzed perborylation method with a new deborylative conjugate addition protocol (Scheme 1A) provides a convenient one-pot, tandem procedure for the diastereoselective synthesis of value-added products from simple, abundant precursors (Scheme 1C).

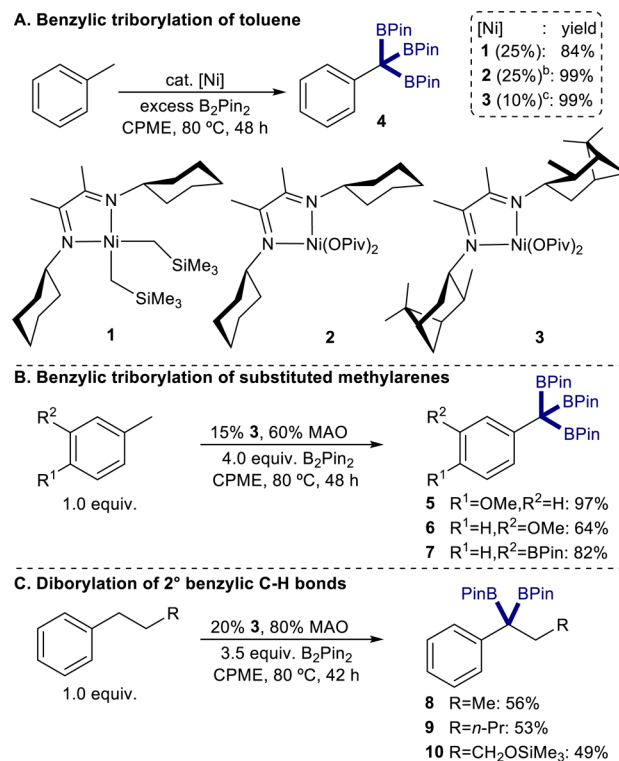
Inspired by the observation of benzylboronate products by Tobisu, Chatani, and co-workers in Ni catalysis<sup>18f</sup> and our own success with *N*-alkyl-substituted  $\alpha$ -diimine (RADI) cobalt dialkyl complexes,<sup>23d</sup> the analogous Ni(II) dialkyl complexes were targeted for evaluation in catalytic C-H borylation. (CyADI)Ni(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub> (1) was isolated as a teal, diamagnetic solid in 79% yield following pyridine displacement by addition of the free  $\alpha$ -diimine to (py)<sub>2</sub>Ni(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub> (py = pyridine).<sup>25</sup> The solid-state structure of 1 established a distorted square planar geometry (see Supporting Information (SI), Figure S2). Because both cobalt and nickel bis(carboxylate) compounds have proven to be readily synthesized, bench-stable precursors for a host of catalytic reactions,<sup>18e,23d,26</sup> (CyADI)Ni(OPiv)<sub>2</sub> (2) (Piv = pivaloyl) was also prepared by addition of the free  $\alpha$ -diimine to a well-defined Ni(II) pivalate precursor, [(NEt<sub>3</sub>)Ni(OPiv)<sub>2</sub>]<sub>2</sub>, a compound first reported by Eremenko and co-workers.<sup>27</sup>

With excess (4.0 equiv.) B<sub>2</sub>Pin<sub>2</sub> and 25 mol% of 1, the catalytic borylation of toluene in cyclopentylmethyl ether (CPME) at 80 °C resulted in isolation of the benzyltriboronate 4 in 84% yield (Scheme 2A). Repeating this procedure with 25 mol% of 2 in combination with 100 mol% of methylaluminoxane (MAO) activator provided a quantitative yield of 4. Notably, the yields of 4 using 1 and 2 were significantly higher with lower precatalyst loadings and temperatures than with cobalt, highlighting the advantage of the nickel-catalyzed method.

Nickel sources,  $\alpha$ -diimine ligands, and catalytic conditions were evaluated to lower the amount of Ni required (see SI, Table S1). Because formation of bis(chelate) nickel complexes was believed to be a deactivation pathway (see SI, Scheme S1), the nickel bis(pivalate) complex bearing a bulkier diimine ligand was synthesized. Pale green (Piv<sup>c</sup>ADI)Ni(OPiv)<sub>2</sub> (3, Scheme 2A) was isolated in 89% yield and was active for the triborylation of toluene. With only 10 mol% of 3 in combination with 40 mol% MAO, quantitative formation of 4 was obtained. This reaction was also successfully scaled; starting with 2.17 mmol of toluene, 1.00 g (99% yield) of 4 was isolated.

With the improved performance of 3, the generality of benzylic triborylation was examined with a series of methylarenes (Scheme 2B). High yields of the benzyltriboronate products derived from 3-methylanisole, 4-methylanisole, and *m*-tolylboronic acid pinacol ester were obtained. Although these products were isolated following acidic aqueous workup with no additional purification, the benzyltriboronates underwent protodeborylation to mono- or diboronates upon prolonged exposure to aqueous conditions or by attempted purification by column chromatography. Extended exposure to air also resulted in decomposition, likely by autoxidation.

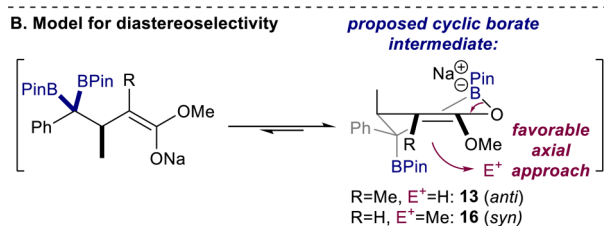
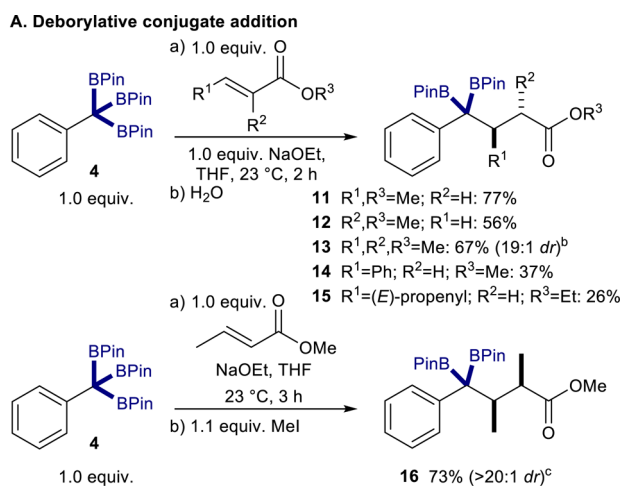
## Scheme 2. Benzylic Perborylation of Substituted Methylarenes and Linear Alkylarenes Using $\alpha$ -Diimine Nickel Dialkyl and Bis(pivalate) Precatalysts<sup>a</sup>



<sup>a</sup>Isolated yields. Reactions conducted with 0.55 mmol methylarene or alkylarene in 0.55 mL of CPME at 80 °C. See SI for experimental details. <sup>b</sup>100 mol% MAO as catalyst activator. 4 was isolated with 13% impurity of remaining B<sub>2</sub>Pin<sub>2</sub>. <sup>c</sup>40 mol% MAO activator used.

The polyborylation of the benzylic positions of linear alkyl arenes was also explored with 3. C(sp<sup>3</sup>)-H borylation of this substrate class has only been achieved previously using silyl directing groups<sup>22d</sup> or vast excess of substrate and long reaction times.<sup>23b,e</sup> Using 20 mol% of 3 and excess (3.5 equiv.) B<sub>2</sub>Pin<sub>2</sub>, the benzylic diborylation of *n*-propylbenzene, *n*-pentylbenzene, and trimethylsilyl-protected 3-phenylpropanol was accomplished to afford 8, 9, and 10, respectively (Scheme 2C). Precatalyst 3 was also effective for the synthesis of benzyltriboronates from methylarenes (see SI, Scheme S2) at superior yields and lower catalyst loadings than previously reported with cobalt.<sup>23d</sup>

The development of a direct method for the preparation of 1,1,1-alkyltriboronates from C(sp<sup>3</sup>)-H functionalization offers a new opportunity to explore the utility of these products in C-C bond-forming reactions. Known deborylative boron-Wittig olefination<sup>15</sup> and deborylative alkylation<sup>16</sup> protocols were demonstrated (see SI, Scheme S3). Further efforts focused on development of new C-C bond-forming transformations. Conjugate addition of  $\alpha$ -boryl nucleophiles to unsaturated carbonyls has previously been reported for  $\alpha$ -boryl radicals<sup>28</sup> and  $\alpha$ -boryl-zirconocenes.<sup>29</sup> Benzylic  $\alpha$ -diboryl anions were postulated to be sufficiently soft nucleophiles to exhibit similar reactivity. To test this, a THF solution of 4 and (*E*)-methylcrotonate was treated with NaOEt at room temperature, providing 11 (Scheme 3A) in 77% yield following aqueous workup. Repeating this procedure with methyl methacrylate and methyl tiglate provided 12 and 13, respectively, in good yield and, in the case of 13, excellent diastereoselectivity (19:1).

Scheme 3. Base-Mediated Deborylative Conjugate Addition Using Isolated Benzyltriboronate 4<sup>a</sup>

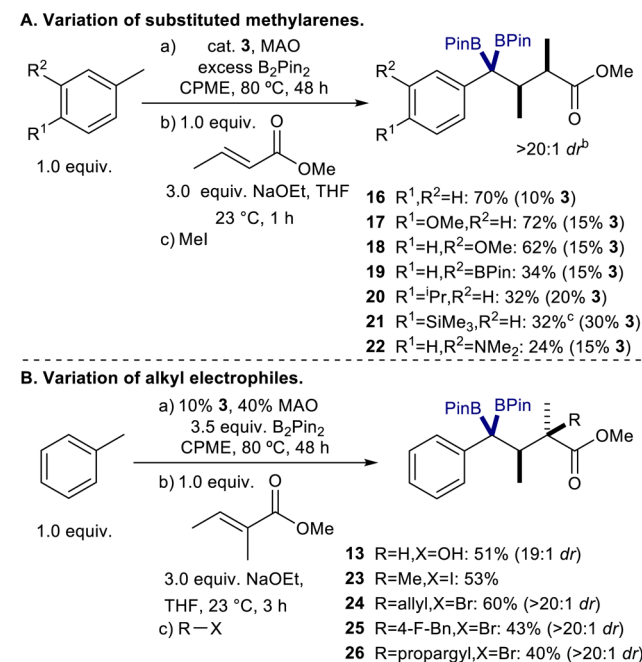
<sup>a</sup>Isolated yields. Reactions conducted with 0.28 mmol of benzyltriboronate in 5.6 mL of THF. See SI for experimental details. Diastereomeric ratios (*dr*) determined by gas chromatography of crude reaction mixtures and confirmed by <sup>1</sup>H NMR spectroscopy of isolated products. <sup>b</sup>Major diastereomer **13** assigned as opposite of that assigned for **16** (minor diastereomer). <sup>c</sup>Diastereomer of **16** determined by X-ray crystallography (see SI, Figure S4).

Notably, products resulting from the deborylative conjugate addition to phenyl-substituted (*E*)-methyl cinnamate (**14**) and the  $\alpha,\beta,\gamma,\delta$ -unsaturated ethyl sorbate (**15**) were also obtained, albeit at reduced yields, predominantly due to competing 1,2-addition to the more electron deficient enoates.

Given that the intermediate in the deborylative conjugate addition of **4** to methyl tiglate proceeds through a sodium enolate, the stereocontrol at the  $\alpha$ -position of the ester in **13** likely occurs during protonation when the reaction is quenched. Intramolecular coordination of the enolate to a boronate substituent and subsequent axial approach of an electrophile was hypothesized to explain this phenomenon (Scheme 3B).<sup>30</sup> To test this, the deborylative conjugate addition of **4** and (*E*)-methylcrotonate was carried out, and the reaction was quenched with iodomethane (Scheme 3A). The resulting product, **16**, was isolated in >20:1 *dr* as the *syn* diastereomer opposite that of **13**, consistent with the stereochemical model. These results highlight the unique ability of the boronate groups to act not only as masking groups for soft nucleophilic anions but also elements for substrate-controlled diastereoselectivity.

The possibility of generating these benzyltriboronates *in situ* and directly applying them toward further chemistry was also investigated. This would not only obviate the need for difficult isolation of these sensitive reagents, but it would provide a convenient one-pot method for rapidly building molecular complexity directly from toluene or other simple substituted methylarenes. The synthesis of **16** was conducted directly from toluene,  $\text{B}_2\text{Pin}_2$ , (*E*)-methylcrotonate, and iodomethane without

isolating **4** (Scheme 4A). Following the Ni-catalyzed triborylation of toluene, the crude triboronate product was exposed to

Scheme 4. Diastereoselective, One-Pot Tandem Triborylation–Conjugate Addition–Alkylation<sup>a</sup>

<sup>a</sup>Isolated yields. See SI for experimental details. Diastereomeric ratios (*dr*) determined by gas chromatography of crude reaction mixtures and confirmed by <sup>1</sup>H NMR spectroscopy of isolated products. <sup>b</sup>Diastereomers assigned by analogy to that of **16**. <sup>c</sup>NMR yield; 22% isolated yield.

the conjugate addition–alkylation conditions to provide **16** in 70% yield and >20:1 *dr*. The method was then successfully extended to other substituted methylarenes. Generation of **5**, **6**, and **7** *in situ*, followed by conjugate addition and alkylation, yielded products **17**, **18**, and **19**, respectively, in good to modest yields with high diastereoselectivity (>20:1). The one-pot procedure was also applied using *p*-cymene, 4-tolyltrimethylsilane, and *N,N*-dimethyl-*m*-toluidine, resulting in isolation of **20**, **21**, and **22**, respectively, following column chromatography without the need for purification of the 1,1,1-triboronate intermediates.

The scope of the alkyl electrophile was also explored. Using toluene,  $\text{B}_2\text{Pin}_2$ , methyltiglate, and quenching with water, **13** was isolated (19:1 *dr*) in 51% yield (Scheme 4B). Quenching the reaction with iodomethane provided the methylated product **23** in 53% yield. Further variation of the alkyl electrophile might provide access to diastereomerically enriched products with quaternary stereocenters. This was successfully demonstrated using allyl bromide, 4-fluorobenzyl bromide, and propargyl bromide to give products **24**, **25**, and **26**, respectively, with high degrees (>20:1) of diastereoselectivity. The solid state structure of **25** was confirmed by X-ray crystallography (see SI, Figure S5), verifying the identity of the major diastereomer as that predicted by the stereochemical model in Scheme 3B and allowing for assignment of the diastereomers of **24** and **26** by analogy.

In summary, an  $\alpha$ -diimine nickel catalyst has been developed that is effective for the perborylation of benzylic  $\text{C}(\text{sp}^3)\text{-H}$  bonds of methyl- and alkylarenes. The unique products are useful building blocks for a diastereoselective conjugate addition–

alkylation sequence, highlighting the ability of the multiple boronate groups to act simultaneously as soft carbanion masking groups and intramolecular stereocontrol elements. Combination of the C(sp<sup>3</sup>)-H polyborylation with deborylative C-C bond formation into a one-pot procedure allowed an effective method for rapid elaboration of simple and abundant precursors to complex products poised for further elaboration with remaining C-B bond functionality.<sup>31</sup>

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b12896.

X-ray crystallographic data (CIF)

Complete experimental details, precatalyst optimization studies, and characterization data of nickel complexes and boronate products (PDF)

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### Notes

The authors declare no competing financial interest.

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(31) The geminal diboronate functionality in the conjugate addition products in Schemes 3 and 4 can likely be further elaborated using the methods described in refs 8–14.