



Practical, efficient, and broadly applicable synthesis of readily differentiable vicinal diboronate compounds by catalytic three-component reactions



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ABSTRACT

A practical, efficient and broadly applicable catalytic method for synthesis of easily differentiable vicinal diboronate compounds is presented. Reactions are promoted by a combination of PCy_3 or PPh_3 , CuCl and LiOt-Bu and may be performed with readily accessible alkenyl boronate substrates. Through the use of an alkenyl-B(pin) (pin = pinacolato) or alkenyl-B(dan) (dan = naphthalene-1,8-diaminato) starting material and commercially available (pin)B-B(dan) or $\text{B}_2(\text{pin})_2$ as the reagent, a range of vicinal diboronates, including those that contain a B-substituted quaternary carbon center, may be prepared in up to 91% yield and with >98% site selectivity. High enantioselectivities can be obtained (up to 96:4 er) through the use of commercially available chiral bis-phosphine ligands for reactions that afford mixed diboronate products.

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1. Introduction

Organoboron compounds that contain vicinal C–B(pin) (pin = pinacolato) bonds are of considerable value in chemical synthesis and may be accessed through diboron additions to alkenes catalyzed by Pd- or Pt-based complexes,¹ metal alkoxides² or carbohydrate-based diboron species.³ A primary C–B bond may be induced to undergo cross-coupling reactions site selectively because of activation provided by the neighboring, more substituted C–B(pin) unit.⁴ In 2009 we showed that vicinal diboronate compounds may be synthesized through exceptionally site-selective (<2% geminal diboronate) and stereoselective (*syn*) Cu–B(pin) addition to alkenyl–B(pin) moiety; the resulting Cu–C bond was then reacted with deuterio-methanol *in situ*, affording **ii** with complete diastereoselectivity (>98% retention of stereochemistry; Scheme 1a).⁵ More recently, we envisioned that three-component fusion of an alkenyl–B(pin) with (dan)B–B(pin) (dan = naphthalene-1,8-diaminato)⁶ and an allyl electrophile (in place of MeOH) might deliver, through site-selective Cu–B(dan) addition/allylic substitution,⁷ valuable easy-to-differentiate vicinal diboronate products (e.g., **viii**, Scheme 1b). Specifically, we surmised that the intermediate copper-

alkoxide (**iii**, Scheme 1b) should favor interaction with the more Lewis acidic B(pin) unit (**iv**), which would afford a Cu–B(dan) complex (**v**) along with products containing a terminal B(dan) and an internal B(pin) group (**vi**). Differentiation of a B(pin) and a B(dan) moiety would be easier [vs two B(pin) groups]; as a result, the method would offer a distinct advantage, especially when selective functionalization at the typically less reactive secondary C–B bond is desired [e.g., internal B(pin) and a terminal B(dan) group]. Alternatively, a sequence involving an alkenyl–B(dan) substrate and $\text{B}_2(\text{pin})_2$ would furnish the complementary diboron isomer [i.e., primary C–B(pin) and secondary C–B(dan)]. Herein, we disclose the realization of these objectives.

2. Results and discussion

We first probed the possibility of a three-component process with vinyl–B(pin), allylphosphate and (dan)B–B(pin) (Table 1).⁸ With NaOt-Bu as the base but without a ligand there was near complete (~95%) disappearance of the limiting reagent [(vinyl–B(pin))] but **1a** was obtained in 39% yield (entry 1). Efficiency improved substantially with the addition of 11.0 mol % PPh_3 , as vicinal diboronate **1a** was isolated in 78% yield (entry 2). Evaluation of other alkali metal alkoxides (entries 3–4) and several mono- and bidentate phosphines with distinct steric and electronic attributes (entries 5–9) indicated that the combination of PCy_3 and LiOt-Bu is

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The C–B(pin) bond of the bis-boronate products can be site selectively oxidized to afford the corresponding alcohol products (e.g., **7** and **8**, Scheme 3). The remaining C–B(dan) bond can then be converted to a C–C bond,¹¹ as the examples in Scheme 3 illustrate,

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