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# Zirconium-Catalyzed Synthesis of Alkenylaminoboranes: From a Reliable Preparation of Alkenylboronates to a Direct Stereodivergent Access to Alkenyl Bromides

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Cite This: https://dx.doi.org/10.1021/acs.orglett.0c00908 Read Online

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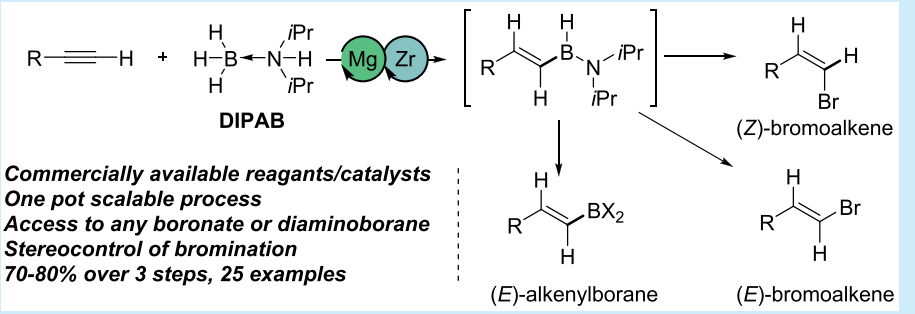
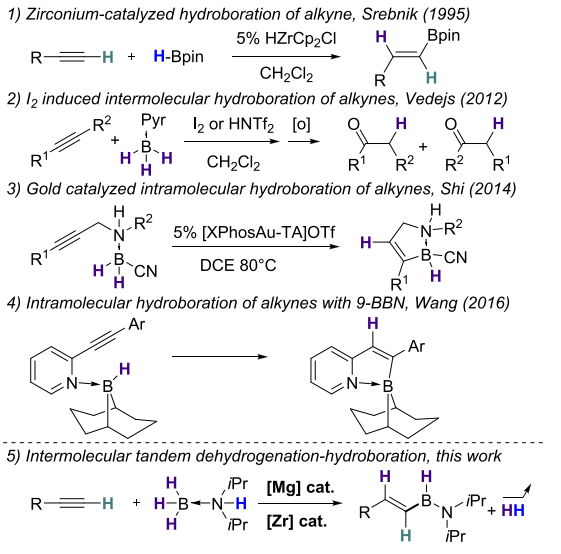



**ABSTRACT:** A simple procedure has been optimized for the preparation of alkenylaminoborane from alkynes using diisopropylaminoborane and $HZrCp_2Cl$. Coupled with a magnesium-catalyzed dehydrogenation, it allowed for the use of air- and moisture-stable diisopropylamine. This synthesis has been extended to a one-pot sequence leading directly to bromoalkenes with controlled stereochemistry. As such, it provides an easy, scalable, cheap process to access alkenylboronates and both (*E*)- and (*Z*)-bromoalkenes from commercially available alkynes.



Alkenylboron derivatives are versatile building blocks[1] traditionally used in Suzuki−Miyaura[2] or Chan−Lam−Evans cross-coupling reactions. Recently, they have been elegantly used in metal-free halide-mediated carbon−carbon bond formation.[3] Similarly to most arylboron derivatives, alkenylboronates can be obtained by the addition of the corresponding Grignard or lithiated compounds to trialkoxyboranes or other boron-centered electrophiles. However, the difficult preparation of vinylmetal and the low stability of the carbon−boron bond as borate usually lead to significantly lower yields than for the corresponding aromatic derivatives. Alternatively, transition-metal-catalyzed borylation of alkenylhalides or triflates is more efficient but somehow limited by the accessibility of starting materials, prepared in one or two steps from commercially available reagents. The reaction scope could nonetheless be widened by using dehydrogenative coupling of alkenes with boranes, which is often easier on styrenyl derivatives. Hence, alkyne hydroboration remains the most reliable, high-yielding, and robust access to alkenylboranes.[4] Over the last 50 years, many boranes have been used in this reaction, mostly, 9-BBN, $(ipc)_2BH$, $Cy_2BH$, pinacolborane, and catecholborane.[5] Depending on the substrates, the reaction can be sluggish and unselective, which led to the development of catalysts based on transition metal complexes of Rh,[6−8] Ir,[9,10] Ru,[11−13] Co,[14−16] Al,[17,18] Fe,[19−22] Cu,[23,24] Mg,[25,26] or Zr (Scheme 1-1).[27] The resulting product function

**Scheme 1. Relevant Precedent Examples in the Literature**



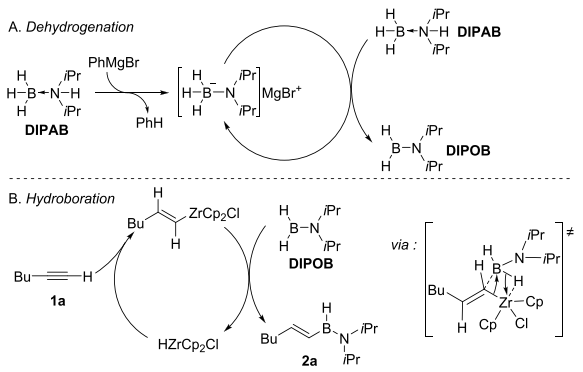

**Received:** March 11, 2020

solely depends on the hydroboration reagent nature and often requires a tricky selective postfunctionalization to be used in the next synthetic steps.

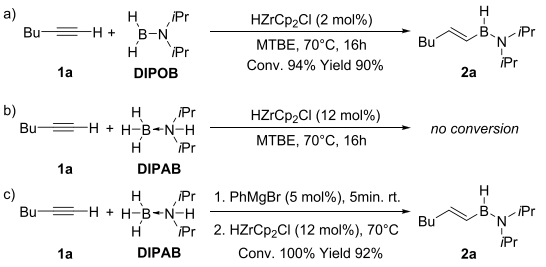
Aminoorganoboranes, on the other hand, are likely to be easily transformed in most common boronic acid derivatives using simple workup procedures and represent a more versatile synthon family.[28,29] Access to these compounds has widely been described.[28,30−36] For alkenyl analogues, only palladium-catalyzed borylation of vinyltriflates and vinyl halides[37] has been reported. Indeed, diisopropylaminoborane is unreactive in direct hydroboration of alkenes or alkynes, due to its poor Lewis acidity. This reagent is isoelectronic from diisopropylethene and one of the few aminoboranes that exists under monomeric form in solution.[38] So far, hydroboration of alkyne using aminoborane has only been described with 40% yield using unstable pyrroloborane.[39] Amine borane complexes and alkynes can react intramolecularly (Scheme 1-4)[40] using gold catalysts (Scheme 1-3)[41] or using borenium intermediates[42] generated with stoichiometric $I_2$ or $HNTf_2$ (Scheme 1-2).[43] In most cases, using organometallic catalysis with the alkyne/amine borane combination usually leads to hydrogen release, which is directly used in the semihydrogenation of the alkyne.[44,45] As zirconocenes have been shown to dehydrogenate amine borane complexes leading to poly(aminoborane) or poly(iminoborane),[46] an extra challenge was determining conditions under which the alkyne would react faster with zirconium hydride than the borane.

Mechanistically, we hypothesized that hydrozirconation of alkyne followed by reaction with di-*iso*-propylaminoborane (DIPOB) would lead to alkenylaminoborohydride via $\sigma$-bond metathesis or intermolecular addition followed by direct hydride transfer (Scheme 2B). The addition of organozirconium reagents has been found to proceed only on chloroboranes only using Pd and Ni complexes.[47−50] In this reaction, despite the high Lewis acidity of the chloroborane, no direct addition of organozirconium was observed.[47] However, initial tests showed that vinylzirconium was reacting quite efficiently on DIPOB, and the resulting compound was a mixture of the vinylaminoborane and Schwartz reagent. The putative intermediate alkenylaminoborohydride was not observed to strengthen the $\sigma$-bond metathesis pathway, and the zirconium hydride was regenerated completely. As a result, it triggered the possibility of a catalytic version of the reaction, assuming the reaction conditions would be compatible with the hydrozirconation of alkyne. Indeed using 1.1 equiv of DIPOB and 12 mol % of $ZrCp_2HCl$, the hydroboration of hexyne proceeded at 70 °C with 100% conversion in MTBE (Scheme 3a). The reaction was also quite efficient in THF and MTBE (Supporting Information Table 1, entries 1−3), as the reaction was complete after 16 h. In MTBE, either the reaction time or the catalyst loading could be reduced without a significant loss in conversion and yield (Supporting Information Table 1, entries 6−13).

**Scheme 2. Proposed Catalytic Cycles**




**Scheme 3. Hydroboration Using Various Borane Sources**




One of the downsides of DIPOB is related to its relative instability toward air and moisture, requiring distillation prior to use. These limitations could be bypassed by inducing *in situ* dehydrogenation of the corresponding diisopropylaminoborane complex (DIPAB). Direct reaction with DIPAB was unsuccessful (Scheme 3b). However, as described previously,[28] DIPAB dehydrogenation could be performed at room temperature using as little as 5 mol % of PhMgBr, among other Mg complexes (Scheme 2A).[51−53] We, therefore, attempted to sequentially add PhMgBr and, after 5 min, Schwartz reagent (Scheme 3c). Solvent and catalyst loading variation were performed (Supporting Information Table 2). The quantity of Schwartz reagent should be greater than the one required for dehydrogenation. Hence if 5% of PhMgBr is used, 10 to 12% of $HZrCp_2Cl$ would ensure reproducible results, and the product was isolated in 92% yield. Noticeably, amine borane complexes have been known to participate in transition-metal-catalyzed reaction with multiple carbon−carbon bonds, but usually as hydrogen sources, leading to alkanes,[54,55] not hydroboration reagents.

If the reaction could be run using *in situ* dehydrogenation followed by the hydroboration itself, remaining Grignard has led during the scoping study to side reactions and generally lower yields than those obtained with pure DIPOB. The study was therefore pursued using the aminoborane, keeping in mind that careful optimization of stoichiometry between PhMgBr and $HZrCp_2Cl$ could prevent side reactions to occur on some trickier substrates. An example will be given of this in the last part of this study with the *in situ* bromination.

After having checked that conversions were complete on most simple substrates (Scheme 4), we found that the reaction worked equally well on 1-methylbutynol provided that 2 equiv of DIPOB was used. Only aniline and methylester were found to be incompatible with the reaction conditions (Scheme 4). As some substrates were less reactive, a 4 h reaction time was kept as a standard. The versatility of the reaction was proven using classical workup procedures on a few substrates in order to obtain the various boron derivatives (29 examples, Scheme 5), which could easily be accessed from alkenylaminoboranes: 1,5-diazaborolanes using 1,8-diaminonaphthalene (Scheme 5A) and boronic esters using pinacol (Scheme 5B) or neopentyl glycol (Scheme 5C). In the case of Bdan, the purification over silica gel led to yield diminution. However,


https://dx.doi.org/10.1021/acs.orglett.0c00908
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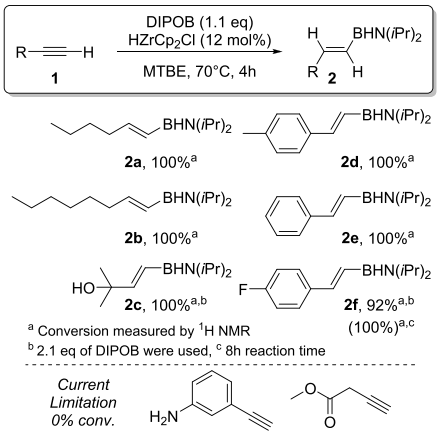
**Scheme 4. Synthesis of Alkenylaminoboranes**

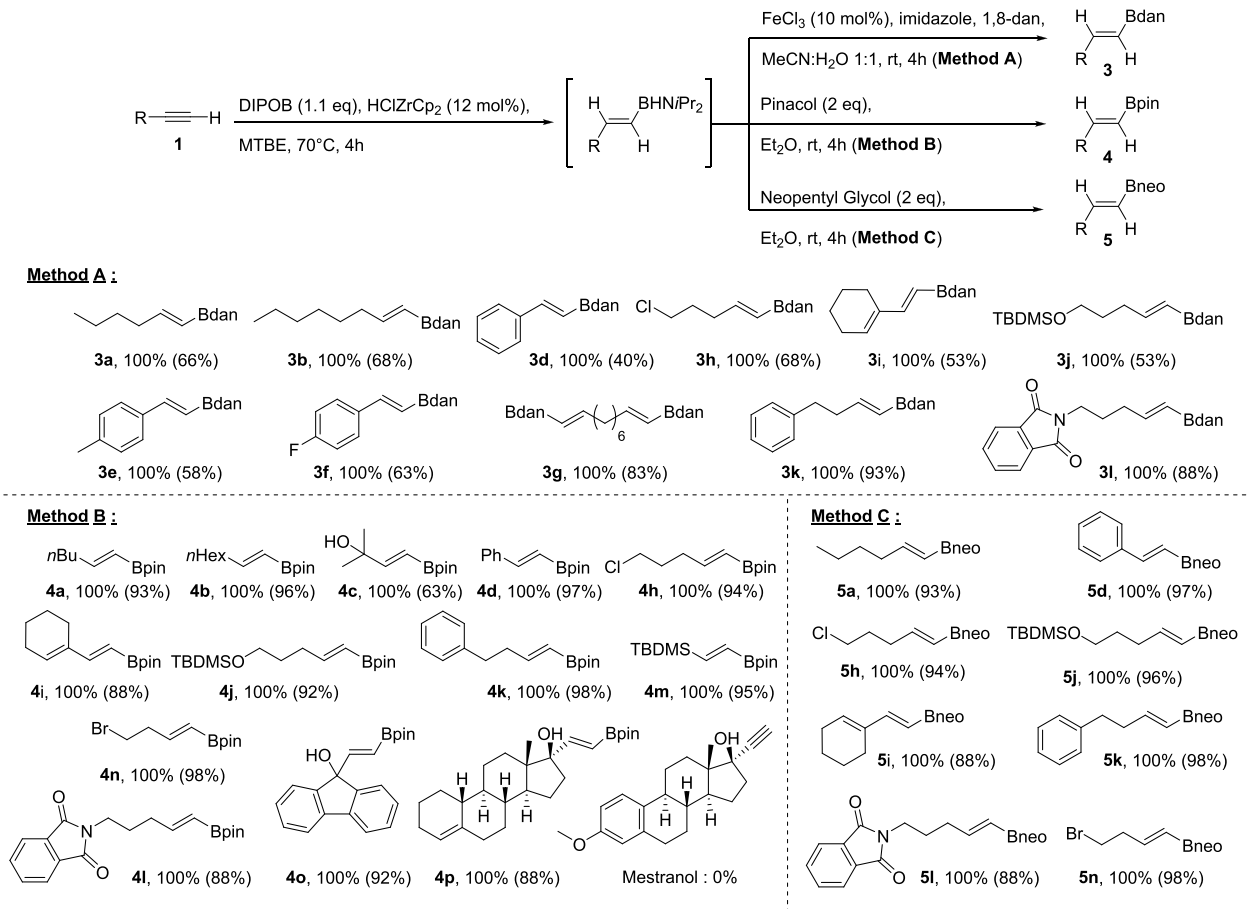



the alkenyldiazaborolane was still isolated in 53−93% yield depending on the starting material. The reaction tolerates chloride (**3h**), substituted phenyl rings (**3d**, **3e**, **3f**), and silylated alcohols (**3j**). Ene-yne is fairly reactive, affording borylated diene in 53% yield. In general, substitution by an alkyl chain led to the best isolated yields (**3a**, **3b**, **3g**, **3h**, **3j**, **3k**, and **3l**). For pinacolboronate and neopentylglycol boronates, yields are generally higher (63−98%) due to the lower propensity of protodeborylation during purification. Group tolerance is very similar, and the reaction is efficient in the presence of alcohols (**4c**, **5n**, **5o**), chlorides (**4h**, **5h**), bromides (**4n**), phthalimide (**4l**, **5l**), silylether (**4j**, **5j**), and silane (**4m**). As witnessed by the reaction on enyne (**4i**, **5i**), the hydroboration of carbon−carbon double bonds was not observed, even on nonconjugated substrates bearing multiple functionalities such as lynestrenol (**4p**). To date, mestranol, despite displaying no potentially problematic functional group, failed to react even using 20 mol % of catalyst at a higher temperature.

As previously mentioned, the reaction can be performed directly on air-stable amine borane complexes. 4-Phenylbut-1-yne was converted to the corresponding boronate in 96% yield on a 10 mmol scale over the course of 4 reactions performed in a single pot (dehydrogenation using PhMgBr, Zr-catalyzed hydroboration, dehydrocoupling with MeOH, and transesterification with the neopentylglycol or pinacol, Scheme 6). On substituted propargyl alcohol (fluorenol and lynestrenol), the reaction works equally well, affording the neopentylglycol boronates in 92% and 88% yield, respectively.

The tandem dehydrogenation−hydroboration process was then extended to the formation of vinyl bromide. These compounds are highly useful building blocks for cross-coupling reactions, and classical preparation methods usually afford configurationally more stable (*E*)-bromoolefins.[56] After optimization (see Supporting Information), we found that a methanolysis followed by a treatment with $CuBr_2$ in a THF:$H_2O$ mixture was leading to the (*E*)-bromoolefin (Scheme 7A), whereas a direct addition of $Br_2$, followed by a basic methanolysis using MeONa, provided mostly the (*Z*)-

**Scheme 5. Synthesis of Alkenyldiazaborolanes**



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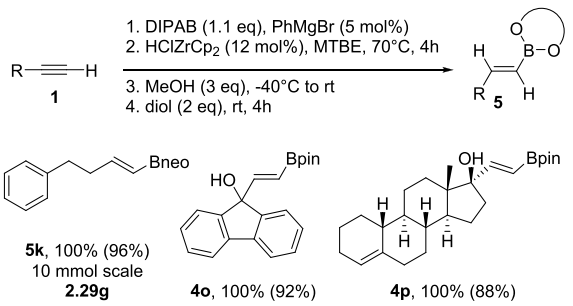
**Scheme 6. Reaction Extension Using *in Situ* Dehydrogenation**




bromoolefin (Scheme 7B). The reaction could also be performed starting from DIPOB and the alkyne, but the *in situ* dehydrogenation usually provided better results by avaoiding the manipulation of sensitive aminoborane. With this stereodivergent method in hand, we prepared 19 different bromoolefins with a very good control of stereochemistry in the case of (*E*)-isomers (*E*:*Z* ratio >94:6) (Scheme 7A). Similarly, when the resulting olefin is not bound to an $sp^2$ carbon, the (*Z*)-isomers were isolated with almost perfect control of the stereochemistry (*Z*:*E* ratio >94:6). For dec-1,9-diyne, both (*E*)-**6g** and (*Z*)-**6g** isomers were isolated in good yields and good stereoselectivity, 56% (*E*:*Z* 98:2) and 84% (*Z*:*E* 96:4), respectively. In most cases, alkyl-derived bromoolefins were obtained in good yields ((*E*)-**6b** and (*Z*)-**6b**; (*E*)-**6h** and (*Z*)-**6h**; and (*E*)-**6k** and (*Z*)-**6k**). The reaction is mostly limited by the product volatility as witnessed by the impracticality of obtaining a pure sample of (*Z*)-bromobutene and (*Z*)-bromohexene (*Z*)-**6a** despite a complete conversion and a >80% NMR yield. The problem was similar to TBDMS-acetylene products ((*E*)-**6m** and (*Z*)-**6m**), for which the selectivity was close to perfect (>99:1), but yields were deceivingly low (41% and 46%, respectively). For enyne products ((*E*)-**6i** and (*Z*)-**6i**), as well as styrenyl bromides ((*E*)-**6d** and (*Z*)-**6d**; (*E*)-**6e** and (*Z*)-**6e**), products were isolated in good yields, but selectively was displaced in favor of the (*E*)-olefin due to further isomerization into the most stable isomer under the reaction conditions.

Overall, di-*iso*-propylaminoborane, which is unreactive toward alkene and alkyne, was found to be a good hydroboration reagent when combined with $HClZrCp_2$ used as a catalyst. The reaction was optimized on various substrates, including alcohols and halides, which could be incompatible with classical hydroboration conditions. Depending on the workup conditions, the resulting alkenylaminoboranes could be transformed into the corresponding borinic acid derivatives (diaminoboranes or boronates) but also into bromoolefins by displacement of the boron atom by bromine. The last reaction could, at will, provide both bromoalkene stereoisomers without requiring isolation of the boron intermediate. Finally, as DIPAB is air and moisture stable, this hydroboration reagent could advantageously replace more reactive boranes which are often quite sensitive.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c00908.

Experimental procedure and $^1H$, $^{11}B$, $^{13}C$ NMR and HRMS of compounds (PDF)

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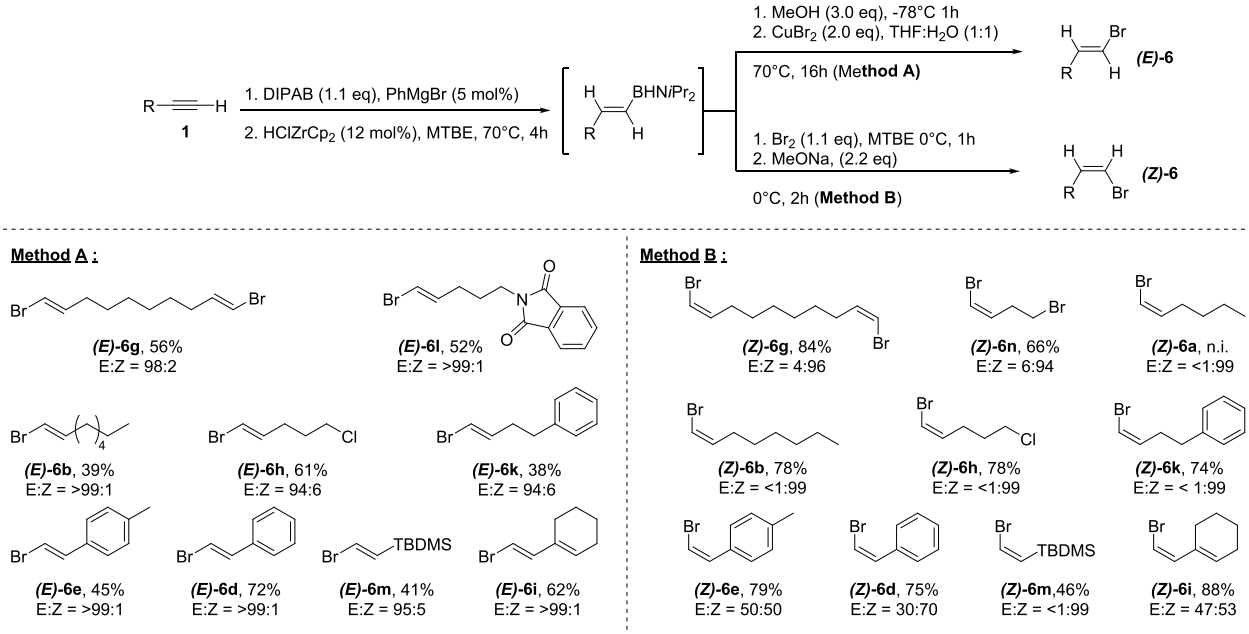
**Scheme 7. Stereodivergent Access to Bromoolefins**






https://dx.doi.org/10.1021/acs.orglett.0c00908
Org. Lett. XXXX, XXX, XXX−XXX

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## Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

## Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

This work was funded by the Université de Bordeaux and the CNRS. M.B. thanks the Ministère de l'Enseignement Supérieur, de la Recherche et de l'Innovation for a fellowship. V.L. thanks AST Innovations for funding.

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