Synthetic Methods

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Regio- and Stereoselective 1,2-Carboboration of Ynamides with Aryldichloroboranes

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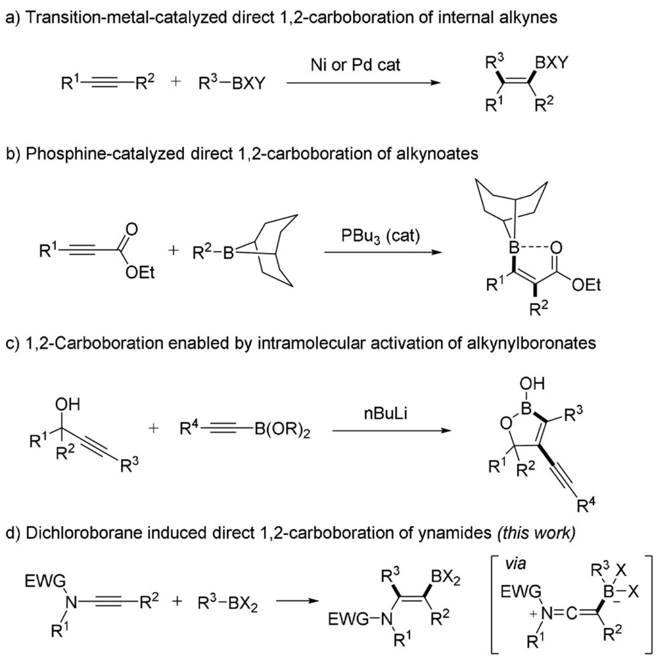
In memory of Klaus Hafner

Abstract: *Catalyst-free 1,2-carboboration of ynamides is presented. Readily available aryldichloroboranes react with alkyl- or aryl-substituted ynamides in high yields with complete regio- and stereoselectivity to valuable β-boryl-β-alkyl/aryl α-aryl substituted enamides which belong to the class of trisubstituted alkenylboronates. The 1,2-carboboration reaction is experimentally easy to conduct, shows high functional group tolerance and broad substrate scope. Gram-scale reactions and diverse synthetic transformations convincingly demonstrate the synthetic potential of this method. The reaction can also be used to access 1-boraphenalenes, a class of boron-doped polycyclic aromatic hydrocarbons.*

Organoboron compounds are versatile reagents in organic synthesis that also play an important role in materials science and medicinal chemistry. Particularly, alkenylboronates are highly useful building blocks in organic synthesis because of their broad application as substrates in the Suzuki–Miyaura cross-coupling,[1] conjugate additions,[2] Zweifel olefination[3] and other interesting transformations that proceed via their alkenylboronate complexes.[4] To date, many methods for the preparation of alkenylboronates have been developed; however, regio- and stereoselective construction of α,β,β-trisubstituted alkenylboronates, which can be used as precursors in the stereoselective synthesis of tetrasubstituted alkenes, is challenging.[5] The carboboration of internal alkynes with organoboron compounds, in which a C−C and a C−B bond are formed, offers a straightforward approach towards α,β,β-trisubstituted alkenylboronates. Along these lines, metal-catalyzed[6] (Scheme 1 a) and phosphine-catalyzed[7] (Scheme 1 b) 1,2-carboboration of internal alkynes have been disclosed. Recently, atom economic environmentally benign catalyst-free direct carboboration, which offers an alternative pathway to α,β,β-trisubstituted alkenylboronates, has received growing attention. For example, Uchiyama and Hirano reported a 1,2-alkynylboration of alkynes enabled by intramolecular activation of alkynylboronates by propargylic alcohols (Scheme 1 c).[8] Highly electrophilic boranes can directly be used for alkyne carboboration. However, in contrast to the well-studied 1,1-carboboration, the "Wrackmeyer" reaction,[9] only a few reports on catalyst-free direct 1,2-carboboration have appeared to date, and these procedures suffer from specific boron species or low yields, which limits their applicability in organic synthesis.[10,11] Therefore, the development of an efficient and practical catalyst-free direct 1,2-carboboration with readily available boron



Scheme 1. Synthesis of α,β,β-trisubstituted alkenylboronates via direct 1,2-carboboration of internal alkynes (EWG = electron withdrawing group).

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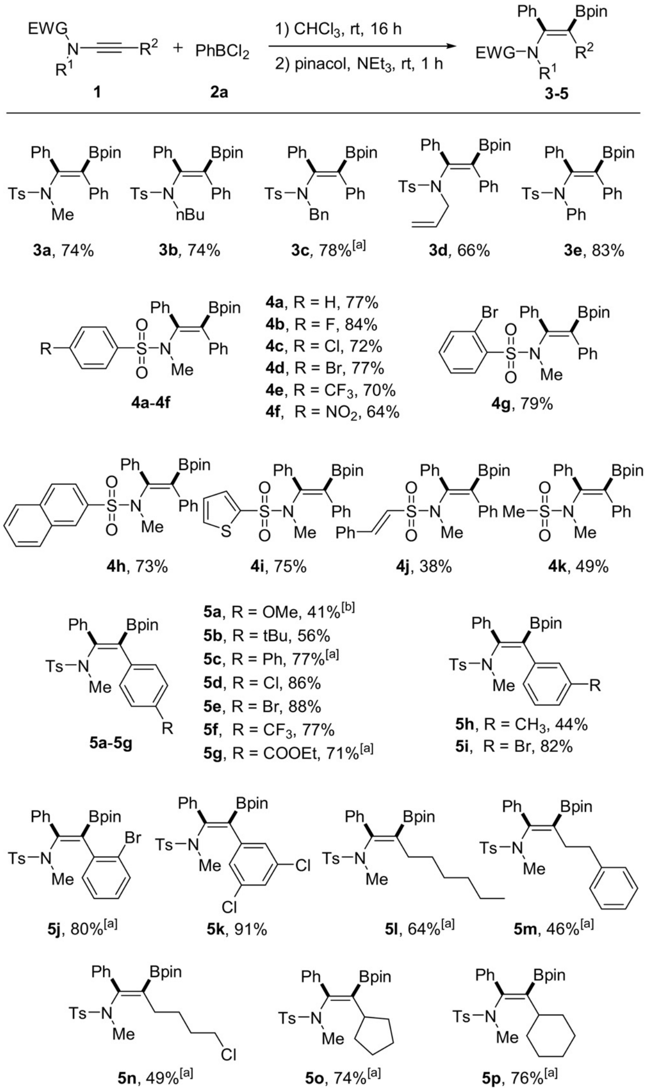
reagents, which would expand the scope and the synthetic utility of boron-mediated organic transformations, is highly desirable.

Encouraged by our recent work on catalyst-free boration,[12] we decided to study the electrophilic 1,2-carboboration of ynamides, that are versatile N-containing alkyne synthons in organic synthesis,[13] with readily available boron reagents for the preparation of highly substituted β-boryl-enamides. Such enamides are valuable in organic chemistry as they can be readily further transformed to various highly substituted enamides. Moreover, they can also serve as substrates for the preparation of boron-doped polycyclic aromatic hydrocarbons. On the basis of the inherent nature of the polarized ynamide triple bond,[13] we assumed that ionic 1,2-carboboration would be feasible with readily available boron reagents in the absence of any catalyst (Scheme 1 d). Thus, reaction of an electrophilic boron reagent with an ynamide should generate the corresponding keteniminium-type zwitterion, which upon stereoselective intramolecular 1,3-migration of the R^3-substituent of the boron ate complex moiety from boron to carbon would deliver the targeted α,β,β-trisubstituted alkenylboron derivative with complete regio- and stereoselectivity.

We first explored the reaction of the ynamide **1a** with various readily available phenylboronic acid derivatives that differ in electrophilicity at ambient temperature in CH_2Cl_2. To our delight, commercially available dichlorophenylborane **2a** (3 equiv) gave after treatment of the crude product with pinacol the targeted trisubstituted alkenylpinacol boronate **3a** in good yield (76% NMR yield; for the structure of **3a**, see Scheme 2).[14] Other common boron reagents, including phenyl boronic acid (**2b**), phenyl pinacol boronic ester (**2c**), phenyl catechol boronic ester (**2d**), and triphenylboroxine (**2e**) did not engage in the 1,2-carboboration, because their boron Lewis acidity is too low for the initial electrophilic borylation step (see the Supporting Information, SI). Solvent screening revealed $CHCl_3$ to be superior to all other solvents tested. Decreasing the amount of boron reagent **2a** from 3 to 1.5 equivalents did not influence reaction outcome to a large extent and the best result was obtained with 2 equivalents of **2a** (74% isolated yield, see SI for details on the optimization study).

With the optimized conditions in hand, we first tested the scope with respect to the ynamide (Scheme 2). The relative configuration in selected examples were unambiguously assigned by NMR spectroscopy (see SI). Various N-tosyl ynamides bearing different R^1-N-substituents such as n-butyl (**3b**), benzyl (**3c**) and allyl (**3d**) were subjected to the 1,2-carboboration. The desired α,β,β-trisubstituted alkenylboronates were isolated in good yields (66–78%). Aromatic N-substituents are also tolerated, as shown by the 1,2-carboboration of the N-phenyl-tosyl ynamide **1e** which gave **3e** in a high yield. The N-sulfonyl protecting group can also be varied. Electronic effects exerted by the aryl group are not that pronounced, as arylsulfonyl groups bearing halides (**4b**–**4d**), trifluoromethyl (**4e**) and nitro (**4f**) all gave good yields (64–84%). Sterically more crowded ynamides also furnished the corresponding products **4g** and **4h** in good yields and the thienyl moiety was compatible with the electrophilic B-reagent (see **4i**). β-Styrenylsulfonyl and methanesulfonyl protected ynamides engaged in the carboboration, albeit with moderate yields (**4j** and **4k**). Next, N-tosylated N-methyl-ynamides bearing different R^2-substituents were tested in the reaction with **2a** (**5a**–**5p**). Surprisingly, for aryl substituted ynamides with electron donating groups at the para position, lower reactivity was noted as compared to the less nucleophilic systems bearing electron-withdrawing para-substituents (see **5a**–**5g**). Aryl-substituted ynamides with meta- and ortho-substitution at the aryl moiety were tolerated as well (**5h**–**5j**). Again, for the electron-poorer halo-substituted congeners, higher yields were obtained. Furthermore, alkyl-substituted ynamides could be employed in this 1,2-carboboration and the corresponding α,β,β-trisubstituted alkenylboronates **5l**–**5p** were obtained in moderate to good yields. Of note, the β-branched alkyl substituted alkynes **1o**

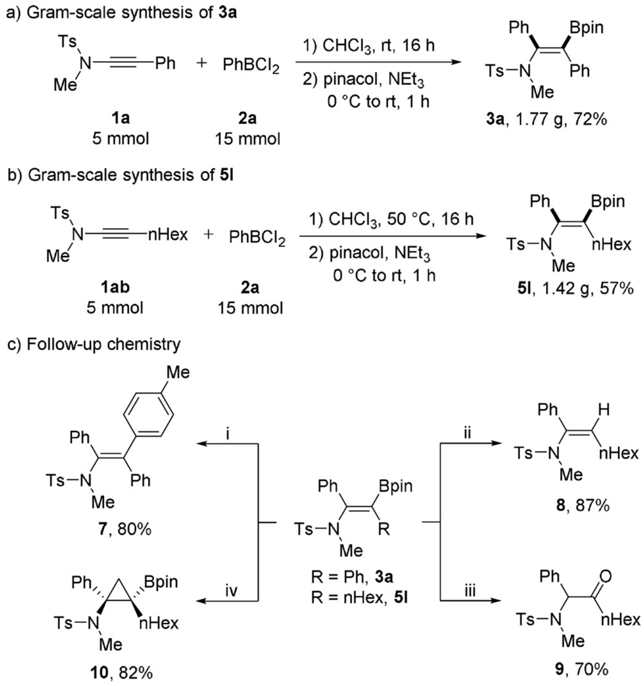


Scheme 2. 1,2-Carboboration of various ynamides. Reaction conditions: **1** (0.20 mmol), **2a** (0.40 mmol) in $CHCl_3$ (2 mL), rt, 16 h, under Ar; pinacol (1.0 mmol), NEt_3 (1.0 mL), 1 h, isolated yields. [a] **2a** (0.60 mmol), 50 °C. [b] **2a** (0.24 mmol), 1 h.

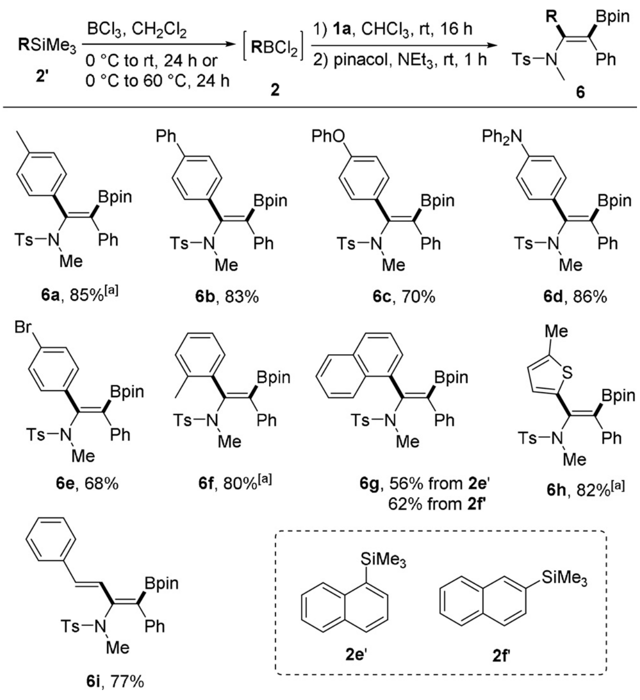
and **1p** provided higher yields as compared to the primary alkyl substituted ynamides (see **5l**–**5m**).

We continued the studies by varying the R-substituent at the dichloroborane **2** with the ynamide **1a** as the substrate (Scheme 3). Considering the limited stability of dichloroboranes, we developed a highly practical one-pot, two-step process utilizing bench-stable trimethyl(aryl)silanes as starting materials. Dichloroboranes **2** were readily generated in situ through the reaction of the corresponding trimethyl-(aryl)silanes with BCl_3 in CH_2Cl_2 (volatiles were then removed in vacuo).[15] Then, a $CHCl_3$ solution of **1a** was added to the dichloroborane and the mixture was stirred at room temperature for 16 h. Functional groups, such as methyl (**6a**), phenyl (**6b**), phenoxy (**6c**), diphenylamino (**6d**) and halide (**6e**) at the para position of the phenyl group were compatible with this sequence and the corresponding alkenyl boronates were isolated in 68–86% overall yields. The sterically more hindered ortho-tolyldichloroborane also reacted well (**6f**). Naphthyl- and thienyl-based boron reagents engaged in the 1,2-carboboration of **1a** (**6g**–**6i**). Interestingly, dichloro(naphthalen-1-yl)borane (from **2e′**) and dichloro(naphthalen-2-yl)borane (from **2f′**) led to the same product **6g** (see SI for detailed discussion).[16] Notably, the reaction of the dichloroalkenylborane with **1a** proceeded efficiently and the α,β,β-trisubstituted alkenylboronate **6i** was isolated in high yield. However, reaction of cyclohexyldichloroborane with **1a** provided the carboboration product in traces only (not shown).

To demonstrate the synthetic value of the carboboration, two gram-scale reactions and four follow-up transformations



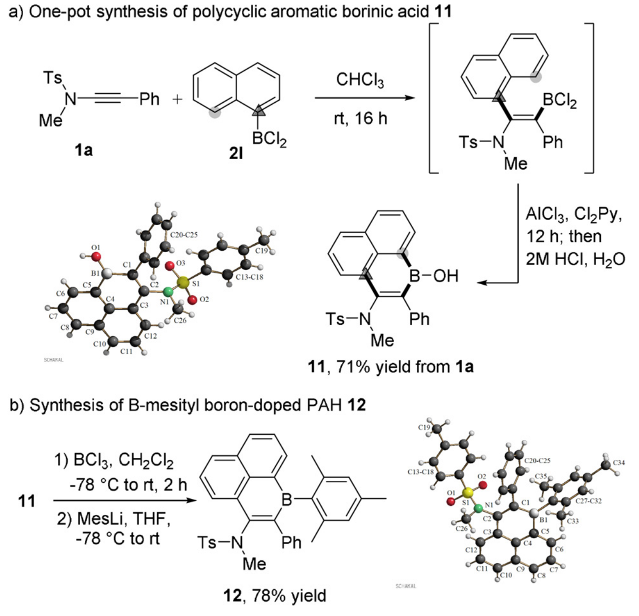
Scheme 4. Gram-scale reactions and follow-up chemistry. Reaction conditions: (i) **3a**, 4-MeC_6H_4I, $Pd(dppf)Cl_2$, Cs_2CO_3, 1,4-dioxane, H_2O, 70 °C, 12 h; (ii) **5l**, $AgNO_3$, NEt_3, EtOH, H_2O, 80 °C, 3 h; (iii) **5l**, $NaBO_3{\cdot}4H_2O$, THF, H_2O, r.t. 4 h; (iv) **5l**, $ZnEt_2$, CF_3COOH, CH_2I_2, CH_2Cl_2, 0 °C to r.t., overnight.



Scheme 3. 1,2-Carboboration with various dichloroboranes. Reaction conditions: $RSiMe_3$ (0.60 mmol), BCl_3 (1.20 mmol, 1 M in CH_2Cl_2), 0 °C to rt or to 60 °C, 24 h, under Ar; then **1a** (0.20 mmol) in $CHCl_3$ (1 mL), rt, 16 h, under Ar; pinacol (1.0 mmol), NEt_3 (1.0 mL), 1 h, isolated yields. [a] The dichloroborane was prepared in advance.

were conducted (Scheme 4). First, gram-scale reaction of **1a** and **1ab** with $PhBCl_2$ (**2a**) under standard conditions afforded the desired products **3a** and **5l** in 72% and 57% yield, demonstrating the practicality (Scheme 4a,b). The triaryl substituted enamide **7** was obtained by Suzuki–Miyaura cross-coupling of **3a** with 4-MeC_6H_4I in 80% yield (Scheme 4c).[17] $AgNO_3$-catalyzed protodeboration of **5l** gave stereospecifically the disubstituted enamide **8** (87%).[18] Treatment of **5l** with $NaBO_3$ provided the ketone **9** in a good yield and **5l** was successfully converted into the fully substituted cyclopropylboronate **10** using $ZnEt_2/CH_2I_2$ (82%).[19]

Recently, boron-doped polycyclic aromatic hydrocarbons (B-PAHs) have attracted increasing attention because of their interesting materials properties.[20] Among them, a 1-boraphenalene scaffold is one of the minimal substructures of B-PAHs, to which several synthetic accesses have been reported.[21] We found that our ynamide 1,2-carboboration can also be applied to the preparation of 1-boraphenalenes that furnish amino groups at the 3-position (Scheme 5). Thus, a one-pot synthesis of boraphenalene **11** was achieved via a sequence comprising the 1,2-carboboration of **1a** with dichloro(naphthalen-1-yl)borane followed by an intramolecular boron-Friedel–Crafts arylation and subsequent hydrolysis. The stable hydroxy-substituted boraphenalene **11** was obtained in 71% overall yield (Scheme 5a). Upon treatment with BCl_3 in CH_2Cl_2,[22] the boraphenalene **11** was further converted into the corresponding chloride. Removal of the solvent and reaction with mesityllithium in THF eventually provided mesityl-substituted boraphenalene **12** (78%, Scheme 5b).



Scheme 5. Synthesis of 1-boraphenalenes.

Boraphenalenes **11** and **12** are both air and moisture stable at room temperature, and crystals suitable for X-ray crystallography were obtained from their solutions in ethyl acetate/pentane.[23] The structural analysis of **12** revealed that not only the mesityl and phenyl groups, but also the amino plane are oriented in an orthogonal fashion against the boraphenalenyl plane (Scheme 5b). In UV-vis absorption spectrum in $CHCl_3$, boraphenalene **12** exhibited two broad absorption bands with the lowest energy absorption maximum (λ_{abs}) of 399 nm. In the same solvent, **12** exhibited a broad emission band with the maximum (λ_{em}) of 524 nm with a large Stokes shift of 5979 cm^{-1} (Figure S1), where the fluorescence quantum yield (Φ_F) was 0.22. These values are comparable to those of the hitherto-known boraphenalenes.[21d,f] Notably, the fact that both the λ_{abs} and λ_{em} values showed only subtle dependence on the solvent polarities (Table S1) suggests that the amino group does not work as an electron-donating group in this scaffold, consistent with its orthogonal orientation. The time-dependent (TD)-DFT calculation at the B3LYP/6–31 + G(d) level of theory suggested that the lowest-energy absorption band can be attributed to the mixture of two electronic transitions from HOMO to LUMO and from HOMO–1 to LUMO (Table S2, Figure S3). While LUMO is delocalized over the boraphenalene skeleton, HOMO and HOMO–1 are located on the mesityl moiety or the phenylboraphenalene skeleton without contribution of the amino group. In the solid state, the fluorescence quantum yield was increased to $\Phi_F = 0.41$, while retaining the emission spectrum almost identical to that in solution (Figure S2). Its nonplanar molecular skeleton likely plays a role in preventing an intermolecular interaction.

In summary, we have described an efficient method for the preparation of β-boryl-β-alkyl/aryl α-aryl substituted enamides from ynamides via catalyst-free direct 1,2-carboboration. Readily available dichloroboranes react with ynamides to afford the corresponding valuable α,β,β-trisubstituted alkenylboronates in good yields with complete regio- and stereoselectivity under very mild conditions. The reaction is operationally easy to conduct and features broad substrate scope and high functional group tolerance. The value of current methodology was documented by successful follow-up reactions and the synthesis of B-PAHs.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: 1,2-carboboration · catalyst-free reaction · synthetic methods · trisubstituted alkenylboronates · ynamides

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