Isomerization

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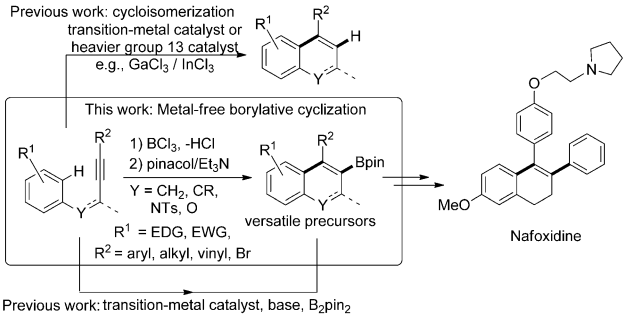
Formation of C(sp^2)–Boronate Esters by Borylative Cyclization of Alkynes Using BCl_3

*Andrew J. Warner, James R. Lawson, Valerio Fasano, and Michael J. Ingleson**

Abstract: *BCl_3 is an inexpensive electrophile which induces the borylative cyclization of a wide range of substituted alkynes to regioselectively form polycycles containing synthetically versatile C(sp^2)–boronate esters. It proceeds rapidly, with good yields and is compatible with a range of functional groups and substitution patterns. Intermolecular 1,2-carboboration of alkynes is also achieved using BCl_3 to generate trisubstituted vinyl boronate esters.*

C(sp^2)–boronic acid and ester derivatives are ubiquitous in modern synthetic chemistry because of their good ambient stability, low toxicity, utility in C–C bond formations, and facile transformation into other important functional groups.[1] Classic synthetic approaches to forming C(sp^2)–B bonds require Grignard or organolithium reagents, and thus have issues with functional-group compatibility, and often require C(sp^2)–halide precursors and cryogenic temperatures.[1b] Simple methods which are functional-group tolerant for forming C(sp^2)–B bonds are highly desirable, particularly reactions that proceed directly from hydrocarbon precursors. The most notable recent breakthrough in this area is iridium-catalyzed direct C–H borylation.[2] Whilst this reaction has developed into a truly powerful transformation, the discovery of new routes, particularly transition-metal-free methods, to efficiently generate C(sp^2)–boronate esters, which are challenging to access by iridium catalysis, remains desirable. Recent advances in transition-metal-free borylation include benzannulations,[3] radical mediated borylation,[4] electrophilic borylation,[5] and carbanion-mediated borylation.[6]

One underexplored approach to metal-free C(sp^2)–B bond formation proceeding from simple hydrocarbon precursors is the borylative cyclization of alkynes, wherein a boron electrophile activates an alkyne for intramolecular electrophilic cyclization with a second π-system. This approach represents a step-economical reaction which would simultaneously create new C(sp^2)–B and C–C bonds to generate new polycyclic frameworks such as borylated dihydroquinolines, dihydronaphthalenes, and phenanthrenes, which are prevalent in (or are key precursors to) biologically active molecules, pharmaceuticals (e.g. Nafoxidine; Scheme 1) and/or organic materials.[7] Alkyne cyclization with concomitant functional-group installation has been principally limited to chalcogen and halogen electrophiles,[8] and to the best of our knowledge, to date, the borylative cyclization of alkynes to form polycyclic structures containing C(sp^2)–boronate esters requires transition-metal catalysis.[9] Metal-free borylative cyclization to form polycyclic C(sp^2)–$B(OR)_2$ species is not documented. Furthermore, metal-free borylative cyclization is distinct from the reactivity of transition metals and heavier group 13 electrophiles (e.g., $GaCl_3$), which catalyze the cycloisomerization of alkynes without concomitant functional-group installation (Scheme 1).[10]



Scheme 1. BCl_3-induced alkyne borylative cyclization. EDG = electron-donating group, EWG = electron-withdrawing group.

Given the ubiquity of alkyne functionalization using boron electrophiles (e.g., hydroboration) the cyclization of unactivated[11] alkynes induced by any boron electrophile is relatively scarce. Noteworthy exceptions use $B(C_6F_5)_3$ to initiate cyclization, thus generating a variety of borylated polycyclic structures.[12] Whilst notable, these reactions use the expensive (relative to BCl_3) electrophile $B(C_6F_5)_3$, which can concomitantly install a C_6F_5 group, and more significantly, precludes formation of the desirable boronic acid derivatives.[12] Herein, we report borylative cyclization, using BCl_3, as a method which is functional-group tolerant and rapidly generates polycyclic structures containing C(sp^2)–boronate esters. The reaction features concomitant C–C and C–B bond formation under mild reaction conditions from simple starting materials.

Our studies into borylative cyclization started with 1,4-diphenylbut-1-ynes (e.g., **1a**; Scheme 2), thus targeting borylated dihydronaphthalenes because of their importance in pharmaceuticals.[7] BCl_3 was utilized as it is inexpensive and more electrophilic than BF_3, with Et_2O-BF_3 previously shown

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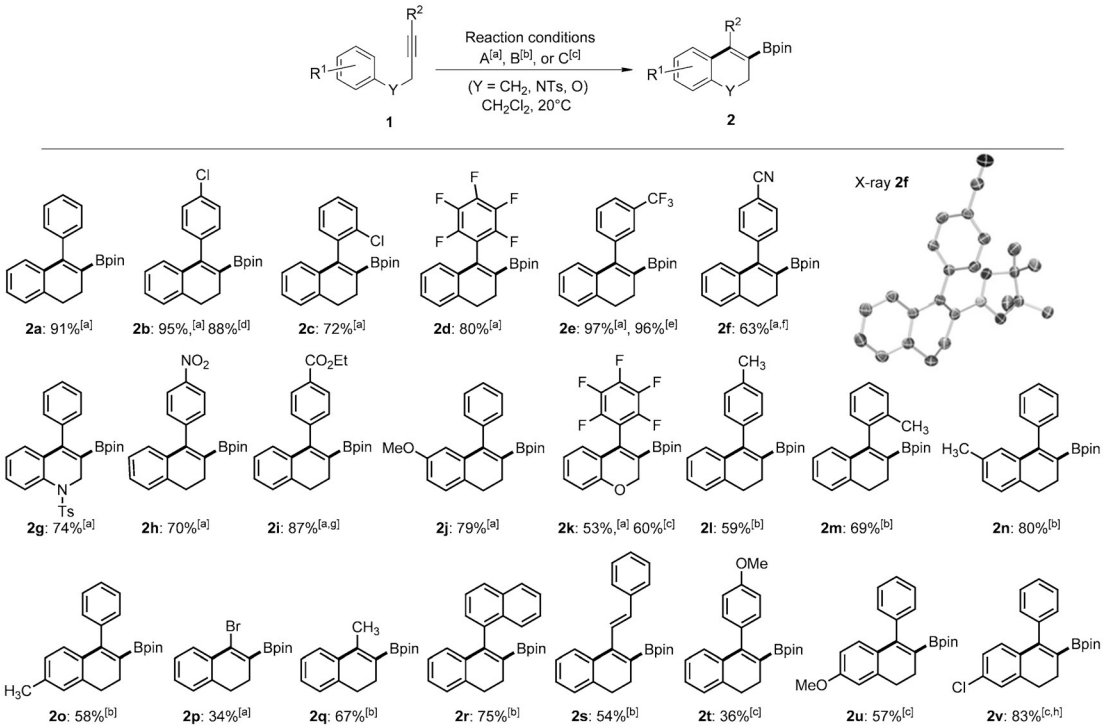


Scheme 2. Cyclization to produce 3-borylated 4-substituted 1,2-dihydronaphthalenes and derivatives.[28] [a] Reaction conditions A: 1) BCl_3 (1.1 equiv); 2) pinacol (1.1 equiv), NEt_3 (15 equiv). [b] Reaction conditions B: 1) BCl_3 (2.1 equiv), TBP (1 equiv); 2) pinacol (1.1 equiv), NEt_3 (15 equiv). [c] Reaction conditions C: 1) $[Cl_2B(2\text{-DMAP})][AlCl_4]$ (1 equiv); 2) pinacol (2.1 equiv), NEt_3 (15 equiv). [d] Using unpurified CH_2Cl_2 and 2 equiv BCl_3 in air. [e] Carried out on a 1.2 gram scale. [f] A reaction time of 12 h. g) 2 equiv of BCl_3. [h] 2.5 h at 60 °C in a sealed vessel. DMAP = 2-(*N*,*N*-dimethylamino)pyridine, Ts = 4-toluenesulfonyl.

not to cyclize aryl-substituted alkynes.[13] The addition of BCl_3 (1.1 equiv) to **1a** at 20 °C in CH_2Cl_2 led to complete consumption of **1a** within 10 minutes (Scheme 2). In the ^{1}H NMR spectrum there was the appearance of a characteristic doublet at $\delta = 6.79$ ppm, which is attributed to the aromatic proton *ortho* to the newly formed carbon–carbon bond. The appearance of a broad resonance at $\delta = 54$ ppm in the ^{11}B NMR spectrum was also consistent with a vinylBCl_2 moiety. In situ formation of the pinacol boronate ester was facile, and **2a** was isolated as the desired cyclized product in 91 % yield. Formation of the borylated dihydronaphthalene presumably proceeds by activation of the alkyne by BCl_3, with the potentially competing haloboration reaction disfavored for internal alkynes and BCl_3.[14] The BCl_3-activated alkyne (as a vinyl cation or a π complex) is sufficiently electrophilic at the carbon center to undergo an intramolecular S_EAr reaction by a 6-*endo*-dig cyclization; no 5-*exo*-dig cyclized products were observed throughout this work. Loss of H^+ as HCl then leads to rearomatization, with no competing protodeboronation of the newly formed vinylBCl_2 moiety, which is subsequently pinacol protected. The borylative cyclization of **1a** with BCl_3 is distinct to the reactivity of transition metals[10] and heavier group 13 Lewis acids (e.g., $GaCl_3$ and $InCl_3$),[15] which catalyze the cycloisomerization of similar alkynes (Scheme 1, top). The disparity observed between BCl_3 and the heavier group 13 analogues presumably arises from the less polar and stronger B–C bond (relative to Ga–C), which makes the borylated compounds more resistant to protodemetallation and thus enables isolation of the desired C(sp^2)–boronate esters. Notably, protodeboronation products are observed as a minor component for a number of substrates (these may also form by HCl initiated cyclization), but performing the reaction with the hindered base 2,4,6-tri-*tert*-butylpyridine (TBP) enables cleaner borylative cyclization (this requires 2 equiv of BCl_3 with 1 equiv consumed by formation of $[(TBP)H][BCl_4]$).

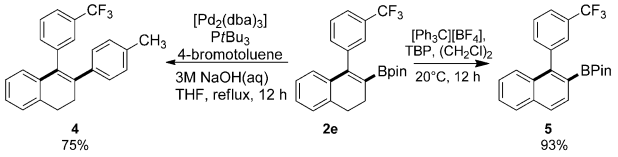
The functional-group tolerance of the BCl_3 borylative cyclization proved to be broad (Scheme 2). Substrates containing halide substituents (**1b–d**) at the *ortho*- and *para*-positions of the aryl alkyne, and the pentafluoro aryl alkyne were all rapidly cyclized (reactions complete within 10 min) and the corresponding pinacol boronate esters were isolated in yields of greater than 70 %. The alkyne **1b** was successfully cyclized open to air and using unpurified CH_2Cl_2, albeit using excess BCl_3 (due to H_2O present in unpurified CH_2Cl_2). Only a 7 % decrease in the yield of the isolated product was noted compared to the reaction under rigorously anhydrous conditions, thus highlighting the robustness of this reaction. Trifluoromethyl groups often undergo C–F activation with strong boron electrophiles, but in this case the CF_3-containing alkyne **1e** was successfully cyclized and isolated in 97 % yield. **2e** was also produced on a gram scale, and isolated in a 96 % yield (1.74 g). The alkyne **1f**, containing a Lewis basic nitrile functionality, reacted rapidly with BCl_3 initially resulting in the formation of two compounds. One compound was consistent with a vinylBCl_2 species and the other with a R–

CN→BCl_3 adduct (determined by ^{11}B NMR spectroscopy). After twelve hours the desired cyclized product was the only species observed in the ^{11}B NMR spectrum, with reversible coordination between the nitrile group and BCl_3 only slowing the cyclization and not leading to any observable side products. The structure of **2f** was also confirmed by X-ray crystallography (Scheme 2). Other alkynes possessing oxo-containing functional groups, including a tosyl-protected amine linker (**1g**), nitro (**1h**), and ester (**1i**), were all cyclized and isolated as the pinacol boronate ester in greater than or equal to 70% yields. **1i** required two equivalents of BCl_3 for complete cyclization with one equivalent of BCl_3 coordinating to the ester moiety and the second inducing the cyclization. The ester→BCl_3 adduct was subsequently cleaved on addition of NEt_3 during the esterification step to yield **2i**. The ether-containing substrates **1j** and **1k** were also amenable to cyclization with BCl_3 with minimal ether cleavage observed, presumably because of the rapid nature of the BCl_3-induced cyclization. The cyclization of **1g** and **1k** confirms that this methodology is not limited to forming dihydronaphthalenes, but is also applicable to dihydroquinoline and chromene formation. Tolyl-substituted alkynes (**1l–o**) reacted with BCl_3 to give a mixture of cyclized products attributable to Brønsted acid initiated methyl group migration.[16] This migration was avoided simply by repeating the cyclization in the presence of TBP, which effectively sequesters the HCl by-product, and the alkynes **1l–o** all cleanly cyclized to give the desired product.

Previous work on electrophilic cyclization using iodonium salts only succeeded when the alkyne substituent was capable of electronically stabilizing the vinyl cation intermediate (e.g., *p*-$MeOC_6H_4$-functionalized alkynes).[17] Attempts at borylative cyclization of the terminal alkyne 4-phenyl-1-butyne failed because of preferential haloboration with BCl_3. In contrast, upon addition of BCl_3, the bromo-terminated alkyne **1p** was converted into two products. Post esterification the major product was the dihydronaphthalene, **2p** (Scheme 2) and the minor component was that derived from haloboration of **1p** (by GC-MS). Cyclization of an alkyl terminated alkyne, **1q**, was achieved with BCl_3, but in addition to the borylated dihydronaphthalene product (**2q**) a borylated naphthalene and tetralin were produced, consistent with transfer hydrogenation proceeding under these reaction conditions.[18] When cyclization was repeated with BCl_3 and TBP, **2q** was isolated in a 67% yield, thus confirming that aryl groups for the stabilization of vinyl cations are not essential for BCl_3-induced cyclization. TBP/BCl_3 also enabled the cyclization of alkynes substituted with naphthyl and vinyl groups to form **2r** and **2s**, respectively. In the absence of TBP lower yields were observed.

In contrast to the borylative cyclization of **1i** and **1k** with BCl_3, it was observed that for other ether-containing substrates (e.g., **1t** and **1u**), BCl_3, with and without TBP, gave extremely low yields of the isolated desired products (Scheme 2). In situ NMR analysis showed that **1t** reacted rapidly with BCl_3 to initially produce the cyclized product and ether-cleavage products ($ArylOBCl_2$ and chloromethane). Previously, we reported that the borocation, $[Cl_2B(2\text{-}DMAP)][AlCl_4]$ (**3**), which can be readily produced and handled in air as a solid for short periods, is reasonably tolerant of methoxy groups during borylation reactions and it does not haloborate internal alkynes.[19] Using **3** led to more selective borylative cyclization reactions, thus enabling isolation of **2t** and **2u** in moderate yields (36 and 57%). The selectivity disparity between BCl_3 and **3** is attributed to the lower nucleophilicity of $[AlCl_4]^-$ versus Cl^- (produced during cyclization with BCl_3), thus suppressing ether cleavage by attack of the anion on the $Me^{\delta+}$ of Ar(Me)O→BCl_3 adducts. The more electrophilic (relative to BCl_3) borocation **3** was also essential for cyclizing substrates containing deactivated internal aromatic nucleophiles. For example, the alkyne **1v** did not react when combined with BCl_3 (at 20°C or at raised temperatures), but using **3** and heating at 60°C for 2.5 hours led to full cyclization. It is noteworthy that **1v** (and **1o** and **1u**) cyclized to produce only one regioisomer, thus borylative cyclization is also highly regioselective. To the best of our knowledge 4-R-1,2-dihydronaphthalenes borylated at the C3-position are currently unknown and represent useful intermediates because of the importance of this structure in pharmaceuticals (e.g., Nafoxidine).

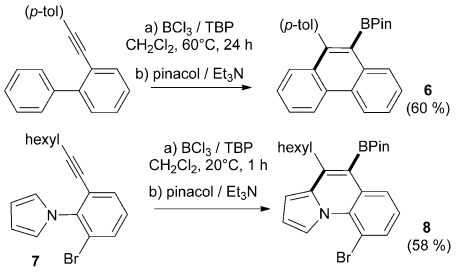
To demonstrate the utility of the borylated products **2e** was coupled with 4-bromotoluene to produce **4** in 75% yield (Scheme 3). This proof-of-principle synthesis of a nafoxidine analogue proceeds in an overall 63% yield over three steps



Scheme 3. Cross-coupling and oxidation of **2e**. dba = dibenzylideneacetone, THF = tetrahydrofuran.

starting from the commercially available terminal alkyne and haloarene precursors. The cross-coupled product **4** can be readily oxidized using $[Ph_3C][BF_4]$ to produce the 1,2-disubstituted naphthalene in good yield upon isolation (75% from **4**; see the Supporting Information). Alternatively, this oxidation procedure was adapted to allow dehydrogenation of **2e**, thus generating the borylated naphthalene **5** in 93% yield (Scheme 3). Regioselectively functionalized naphthalenes are useful in their own right or as precursors to higher acenes.[20] To date the selective formation of 1-substituted-2-borylated-naphthalenes by iridium catalysis requires installation of directing groups at C1,[21] whereas borylative cyclization/oxidation offers more versatility in the nature of the C1 substituent.

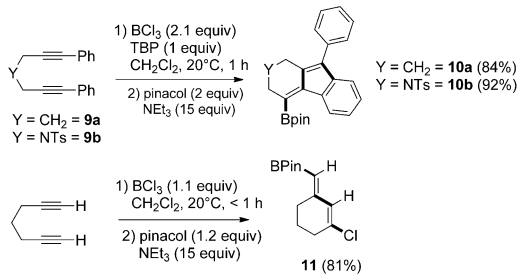
With the functional-group tolerance and utility of the products from 4-aryl-1-alkyne borylative cyclization confirmed, our attention turned to identifying other systems amenable to BCl_3-induced cyclization guided by previously reported metal-catalyzed cycloisomerization reactions. The borylative cyclization of a 2-alkynyl-1,1′-biphenyl was selected as it undergoes cycloisomerization and represents a more rigid analogue of 4-aryl-1-alkynes. 2-(*p*-tolylethynyl)-1,1′-biphenyl underwent borylative cyclization using BCl_3/TBP. Whilst the reaction is slower than dihydronaphthalene



Scheme 4. Borylative cyclization of alkyne-functionalized biaryls.

formation, heating for 24 hours led to the isolation of **6** in 60% yield post esterification (Scheme 4). The disparity in reaction outcome between BCl_3 (borylative cyclization) and $GaCl_3$ (cycloisomerization) is again noteworthy.[22] The borylative cyclization of 2-alkynyl-1,1′-biphenyls forms versatile intermediates (e.g., **6**) which can be transformed into desirable materials, such as dibenzochrysenes by established methodologies.[23] The more functionality-rich precursor **7**, containing a heteroaromatic, a bromide, and a hexyl-substituted alkyne, was also amenable to borylative cyclization and delivered **8** in 58% yield. This reactivity indicates the applicability of this reaction to form pharmaceutically desirable borylated heterocycles, such as pyrrolo-[1,2a]-quinolines (e.g., **8**).[24]

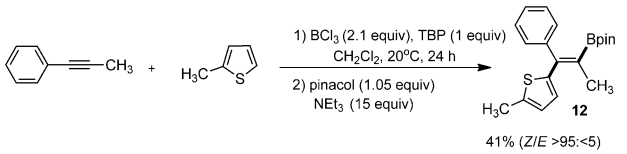
To further demonstrate the utility of borylative cyclization, we explored the cyclization of diynes. Again guided by transition metal catalyzed cycloisomerization[25] we investigated the reactivity of the diynes **9a** and **9b** with BCl_3 (Scheme 5). In the presence of TBP the cyclization proceeded



Scheme 5. Electrophilic borylative cyclization of diynes.

rapidly at 20 °C and produced the boronate esters **10a** and **10b**, which were isolated in 84 and 92% yield, respectively, after pinacol protection. The mild reaction conditions and compatibility with *N*-tosyl suggests a similar functional-group tolerance to that in **2x** formation. The reaction of the terminal diyne, 1,6-heptadiyne, with BCl_3 also proceeded rapidly, and delivered a chlorinated cyclohexene possessing a vinyl BCl_2 moiety *exo* to the newly formed ring. Upon esterification, **11** was isolated in 81% yield and characterized by a combination of one- and two-dimensional NMR spectroscopy, as well as comparison to the product from the reaction of 1,6-heptadiyne and iodosylbenzene.[26]

Finally, we investigated whether a BCl_3-activated alkyne could be intercepted by an external π-nucleophile, similar to the reactivity observed by combining $B(C_6F_5)_3$, phenylacetylene, and *N*-*t*Bu-pyrrole.[27] 1-Phenyl-1-propyne shows no reactivity with 2-methylthiophene or BCl_3 alone, yet when all three were combined in the presence of TBP, the product (**12**) from a *trans*-1,2-carboboration was isolated after esterification in a 41% yield (Scheme 6). Thus BCl_3-induced alkyne carboboration is not limited to intramolecular π-nucleophiles.



Scheme 6. Intermolecular 1,2-carboboration.

In conclusion, BCl_3 is an inexpensive and functional-group-tolerant electrophile for the transition-metal-free borylative cyclization of alkynes. It provides rapid, high-yielding access to hitherto unknown $C(sp^2)$–boronate esters which are versatile synthetic intermediates. This methodology has been exemplified by forming a range of important polycyclic structures. The π-nucleophile is not limited to internal π-systems, as intermolecular nucleophiles are also amenable. These features, combined with the multitude of alkynes which are reported to undergo metal-catalyzed cycloisomerizations, indicates that borylative cyclization is a powerful, transition-metal-free route for accessing polycyclic structures containing $C(sp^2)$–boronate esters.

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[28] CCDC 1408578 (**2 f**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

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