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Boron-Containing Enamine and Enamide Linchpins in the Synthesis of Nitrogen Heterocycles

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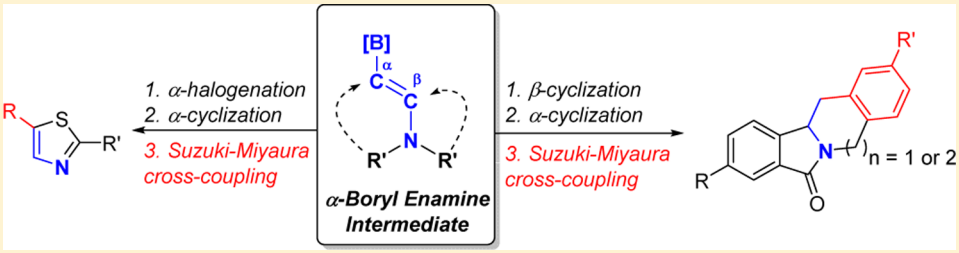
Supporting Information



ABSTRACT: The use of α-boryl enamine and enamide linchpins in the synthesis of nitrogen heterocycles has been demonstrated. Boryl enamines provide ready access to the corresponding α-halo aldehydes, which undergo regioselective annulation to form borylated thiazoles. A condensation/amidation sequence converts α-boryl aldehydes into stable α-boryl enamides without concomitant C → N migration. We also show that palladium-catalyzed cyclization of α-boryl enamides leads to synthetically versatile isoindolones. These molecules can be subsequently used to access polycyclic scaffolds.

INTRODUCTION

Innovative approaches to new synthetic transformations are likely to emerge by thorough consideration of underutilized combinations of functional groups in reaction substrates.[1] In this regard, advances in catalysis directed toward chemical synthesis would benefit from the rational deployment of novel metal- and metalloid-containing intermediates. Our recent explorations in the area of kinetically amphoteric molecules have led to α-boryl aldehydes,[2] which have opened doors to several other amphoteric species.[3] As part of this investigation, we reported the first example of C−B fragment migration driven by the Curtius rearrangement.[4] Since then, we have pursued the application of densely functionalized boron-containing building blocks with the goal of exploiting uncommon intermediates toward the synthesis of nitrogen-containing heterocycles. A particularly intriguing possibility has been to explore the synthesis and application of B−C−C−N motifs as synthetic linchpins (Figure 1). This would help realize one of our long-standing objectives in the area of amphoteric reactivity: engagement of both nucleophilic and electrophilic reactivity nodes in the same sequence.

When it comes to carbon−carbon bond formation, organoboron reagents are among the pillars of organic synthesis. Notably, α-boryl carbonyl species (*C*-bound boron enolates) have rarely been described, which is due to their inherent instability and favorable tautomerization to the *O*-bound boron enolates.[3] In 2011, we reported the preparation of kinetically stable amphoteric α-boryl aldehydes (*C*-bound boryl carbonyl species) and systematically explored aldehyde functionalization

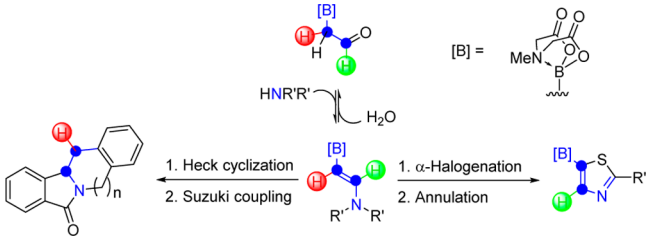


Figure 1. B−C−C−N motifs in nitrogen heterocycle synthesis.

reactions that proceeded without premature engagement of the C−B bond.[2] The use of the *N*-methyliminodiacetyl (MIDA) ligand enforces sp^3-hybridization at boron, shielding it from external Lewis bases,[5] which has allowed us to gain access to a range of novel intermediates.[6] We now demonstrate that α-boryl enamines are useful in the synthesis of α-halogenated boryl aldehydes. These products are amenable to annulation to form 2,5-disubstituted boryl thiazoles. Moreover, we show that α-boryl enamides act as linchpin reagents in intramolecular Suzuki−Miyaura cross-coupling (SMCC) and Heck coupling at the β C−H bond (Figure 1).

RESULTS AND DISCUSSION

Pyrrolidine-Catalyzed Route to Boryl Enamines and Their α-Halogenation. As part of our effort in exploiting the

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chemistry of B−C−C−N motifs, we have pursued the parent (or unsubstituted) α-MIDA boryl aldehyde **1** (Figure 2).

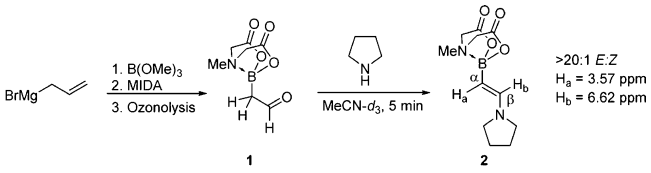
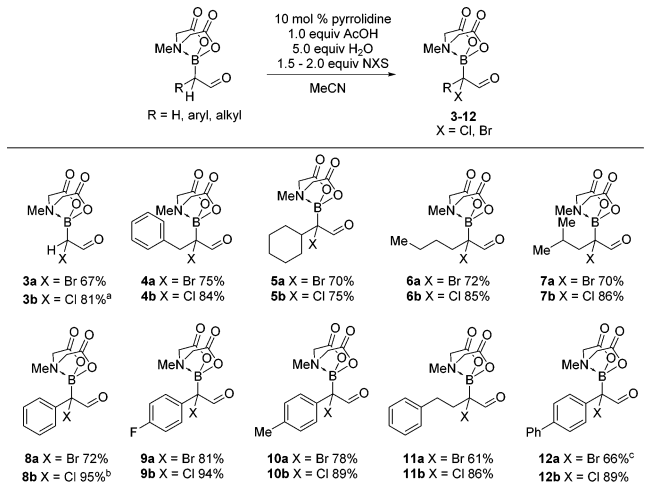


Figure 2. Synthesis of **1** and quantitative formation of boryl-enamine **2**.

Ozonolysis of allyl MIDA boronate on multigram scale provided an efficient means for the preparation of the parent α-boryl aldehyde **1**, which was isolated as a white solid. With this aldehyde in hand, we sought to investigate the formation of α-boryl enamine **2** via condensation of α-boryl aldehyde **1** with pyrrolidine. Pyrrolidine was selected for its nucleophilicity and relatively unhindered nature compared to other aliphatic amines.[7] A condensation reaction between equimolar amounts of **1** and pyrrolidine in acetonitrile-d_3 was monitored by ^{1}H NMR. Complete consumption of the aldehyde **1** was accompanied by quantitative formation of the parent boryl enamine **2** (>20:1 *E*:*Z*) within 5 min of mixing (Figure 2).[8] It was also found that 10 mol % pyrrolidine cleanly delivers a 9:1 aldehyde:enamine ratio in solution. This data led us to evaluate the reactivity of boryl enamines as nucleophilic intermediates in α-substitution chemistry, particularly in α-halogenation.[9]

We subjected the parent α-boryl aldehyde **1** to electrophilic bromination conditions using *N*-bromosuccinimide (NBS) at room temperature in the presence of 10 mol % pyrrolidine. This resulted in the full consumption of the starting aldehyde within 4 h; however, a mixture of mono- and dibrominated species was obtained. Cooling the reaction mixture to 0 °C and adding NBS slowly over 1 h afforded the monobrominated boryl aldehyde in 67% yield (Scheme 1, **3a**).[10] The use of acetic acid and water was found to be optimal for pyrrolidine turnover and reduced reaction times.

Scheme 1. Substrate Scope of α-Boryl Aldehyde Halogenation



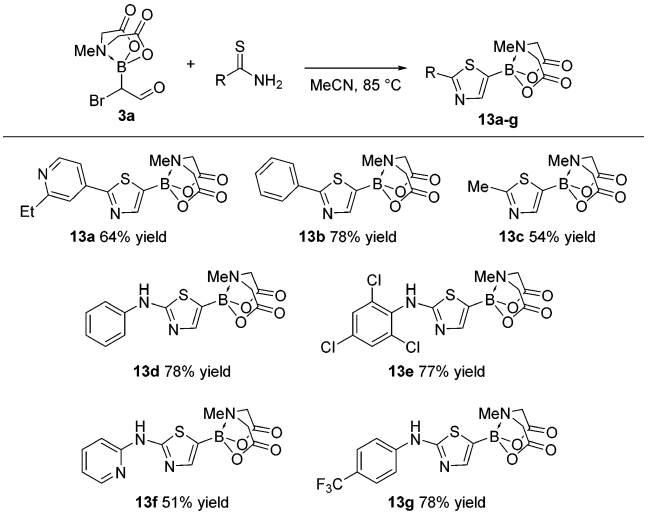
[a] Formation of the mono-chlorinated product required modification of the standard reaction conditions: parent aldehyde **1** (1.0 equiv), pyrrolidine (2.0 equiv), AcOH (1.0 equiv), H_2O (5.0 equiv), NCS (1.0 equiv) in MeCN (0.1 M) RT, 5 h. [b] 49% ee when 50 mol% L-proline is used in place of pyrrolidine [c] contaminated with succinimide by-product

Application of the bromination protocol to a variety of substituted α-boryl aldehydes was then explored (Scheme 1). Both electron-rich and electron-poor aryl substrates as well as alkyl derivatives were smoothly converted to the α-brominated products in good yields. The corresponding chlorinated compounds were readily obtained by substituting NCS for NBS and increasing the reaction temperature to 45 °C.[11] Crucially, there was no evidence for premature cleavage of the carbon−boron bond under these oxidative conditions.[12]

Condensation-Based Access to Boryl Thiazoles. The synthesis of boryl heterocycles is commonly accomplished with organometallic reagents under cryogenic conditions and is effective for simple and/or highly biased heteroaromatic substrates.[13] Extension of this chemistry to functionally richer molecules has been problematic due to functional group tolerance and regioselectivity issues.[14] To demonstrate the utility of α-halogenated boryl aldehydes in the preparation of borylated heterocycles, we set out to investigate the feasibility of a one-pot aldehyde condensation/bromide displacement annulation process.

Thioamides are known to undergo annulation with α-halogenated aldehydes.[15] α-Bromo boryl aldehyde **3a** was subjected to cyclization conditions with a variety of primary thioamides, which resulted in the corresponding 2,5-disubstituted boryl thiazoles as single regioisomers (Scheme 2, **13a**−**c**). Importantly, there was no evidence of premature C−B bond scission under these conditions. Thioureas also participated in the condensation reaction with **3a** to produce a variety of 2-amino-5-borylthiazoles in good yields (**13d**−**g**). The 2,5-series of boryl thiazoles can now be accessed from **3a**, whereas the 2,4-regioisomers can be obtained from our previously reported α-bromo acyl boronate building blocks.[6a] A swap in the oxidation states of adjacent carbons in these two building blocks (bromo boryl aldehyde vs bromo acyl boronate) provides the basis for regioselectivity.

Scheme 2. Condensation/Bromide Displacement with Thioamides and Thioureas



We note that 2,5-disubstituted thiazoles are sporadically utilized motifs in medicinal chemistry, despite the well-recognized value of the thiazole core. This is evident upon examination of the PDB database: only 7 crystallographically characterized structures incorporate the 2,5-regioisomer heterocycle motif, whereas 52 contain the 2,4-variant.[16] We sought to

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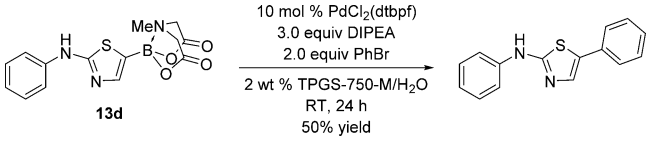
demonstrate the application of our novel boryl thiazoles in cross-coupling reactions. After an extensive screen of conditions, we found that the use of Lipshutz's surfactant TPGS-750-M in water was essential in the SMCC transformation (Scheme 3).[17] Our condensation-driven access to the

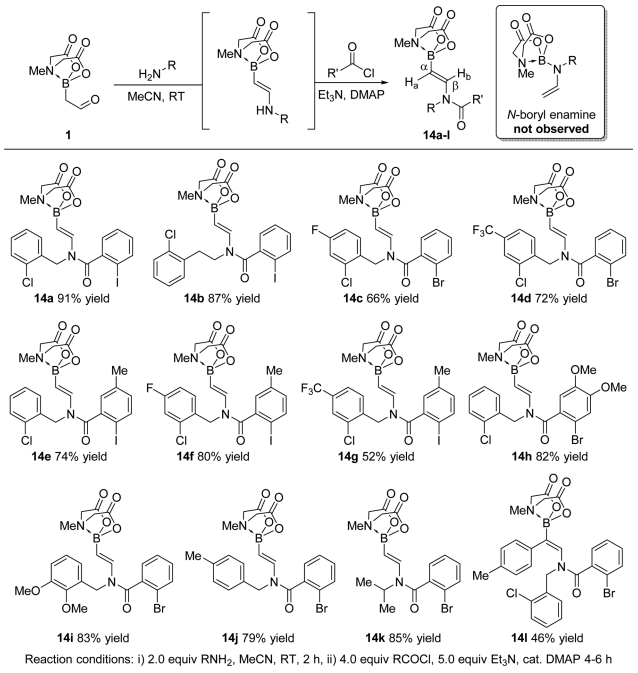
Scheme 3. SMCC of 2,5-Disubstituted Boryl Thiazoles



2,5-disubstituted boryl thiazole core and successful SMCC of **13d** extends the repertoire of options for medicinal chemistry[18] and materials science.[19]

Mitigation of C → N Boryl Migration Captures Novel Boryl Enamides and Enables Their Application in the Synthesis of Heterocycles. The condensative synthesis of boryl thiazoles proceeds through an equilibrating *N*-acyl imine/enamide intermediate. Involvement of the enamide component encouraged us to investigate boron's influence on the enamide functionality, in particular on the attenuation of nitrogen's nucleophilicity using boron substitution. This led us to pursue the preparation of α-boryl enamide scaffolds for downstream applications toward nitrogen-containing heterocycles.[20] We previously established that the addition of primary amines to α-boryl aldehydes triggered C → N migration of the B[MIDA] group, affording the undesired *N*-boryl enamines.[21] Fortunately, we have now identified a way to prevent this migratory process and trap the *C*-boryl enamine species using acyl chlorides. Thus, in the presence of Et_3N and DMAP, we were able to isolate the corresponding *C*-boryl enamides as white solids after purification (Scheme 4) with no evidence of rearrangement.[22]

Scheme 4. Trapping of α-Boryl Enamine Intermediates with Acyl Chlorides Affords α-Boryl Enamides



Reaction conditions: i) 2.0 equiv RNH_2, MeCN, RT, 2 h, ii) 4.0 equiv RCOCl, 5.0 equiv Et_3N, cat. DMAP 4-6 h

In comparison to *N*-benzyl-*N*-propenyl benzamide, the boryl enamide **14k** possesses a relatively electron-rich α-carbon. In addition, boron substitution results in enhanced electrophilicity of the β-carbon as indicated by the 0.9 ppm downfield shift of the H_b (^1H NMR) signal relative to the reported alkyl counterpart.[23] The unusual electronic nature of boryl enamides was confirmed using single crystal X-ray analysis of **14l** (Figure 3). The enamide functionality features an *abcd* torsion angle of

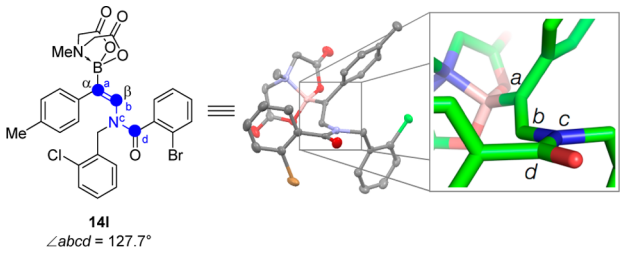
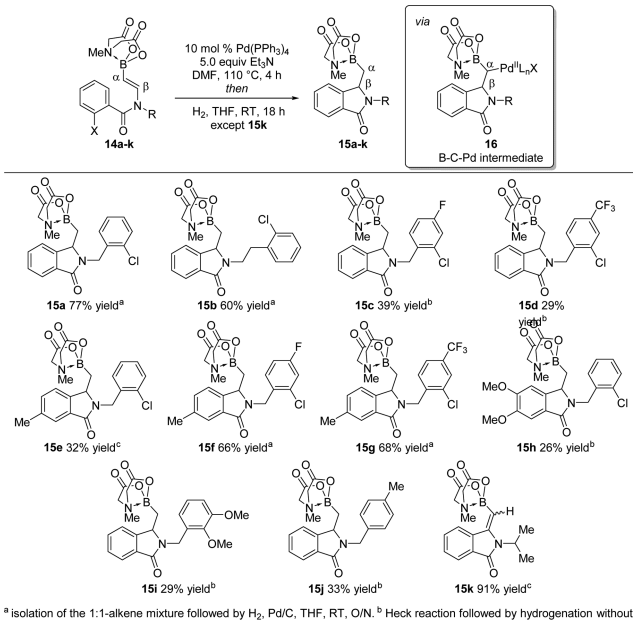


Figure 3. X-ray structure of **14l**. Hydrogen atoms are omitted for clarity. Inset: zoom-in of enamide geometry.

127.7°, which stands in contrast to the value of 180°, typically seen in other crystal structures of enamides.[24] The atypical torsion angle recorded for **14l** results in the electronic isolation of both amide and alkene functional groups. We became interested in exploring the polarized electronic character of α-boryl enamides in intramolecular transformations with the goal of gaining access to a range of nitrogen-containing heterocycles. We note that β-metalloenamides have been used or implicated in synthesis only on a few occasions.[25]

To probe the possibility of α-boryl enamide cyclization, we turned to the Heck reaction as electron-rich alkene substrates are known to facilitate the migratory insertion process.[26] When **14a** was subjected to Heck reaction conditions with $Pd(PPh_3)_4$, exclusive formation of the 3-methyleneisoindolone derived from a 5-*exo-trig* cyclization was observed.[27] The product was formed as a mixture of *E*/*Z* alkene isomers (Scheme 5, **15k**). A

Scheme 5. Borylmethyl-Isoindolones via 5-*exo-trig* Cyclization of α-Boryl Enamides



[a] isolation of the 1:1-alkene mixture followed by H_2, Pd/C, THF, RT, O/N. [b] Heck reaction followed by hydrogenation without purification. [c] isolated as the 1:1 mixture of geometric isomers

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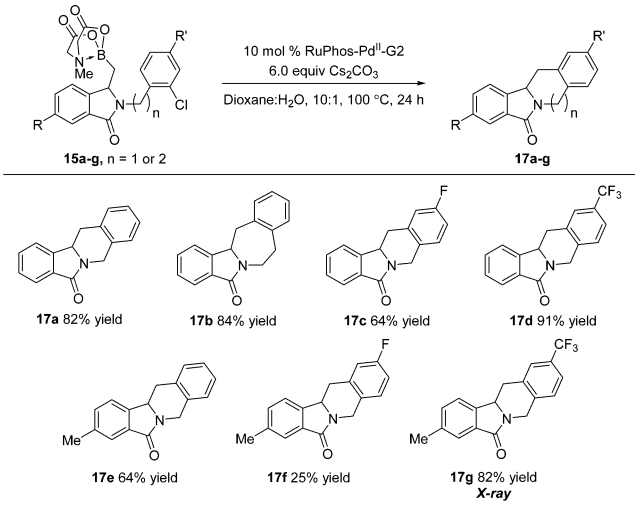
number of other boryl enamides were subjected to cyclization conditions, delivering similar results. As a consequence of the regioselective migratory insertion, the Pd^{II}-center attached to the α-carbon forms the *gem*-bis-metallo $sp^3B-C-Pd$ intermediate **16**. The electron-rich sp^3-boronate is proposed to destabilize **16** due to the lack of Pd/boron interaction, thereby promoting rapid β-hydride elimination. This stands in contrast to reports by Hall[28] and Shibata[29] where no β-hydride elimination with $sp^2B-C-Pd$ intermediates was observed in the SMCC of 1,1-diborylalkanes and aryl halides. The crude methyleneisoindolones were then subjected to hydrogenation in the presence of Pd/C to afford the novel borylmethyl-isoindolones after column chromatography.[30] This sequence not only demonstrates the relative stability of the C−B bond under our conditions, but also suggests the downstream potential for asymmetric hydrogenation to access enantioenriched borylmethyl-isoindolones.

We are interested in the synthetic transformation of the sp^3C-B bond of borylmethyl-isoindolones **15a−g** through SMCC.[31] A comprehensive literature search revealed only two examples of 6-membered ring synthesis[32] via intramolecular SMCC of alkyl boronates and no examples of 7-membered ring formation.[33] This lack of precedent for the intramolecular SMCC of sp^3C-B bonds can be attributed to the challenges associated with transmetalation to form the medium ring palladacycles. Fortunately, alkyl-MIDA boronates **15a−g** were readily converted into the corresponding tetracyclic lactams **17a−g** in good yields (Scheme 6), which exemplifies the utility

Scheme 6. Intramolecular SMCC Process



of SMCC for the formation of 6- and 7-membered rings. This cyclization protocol enables access to the biologically relevant class of tetracyclic scaffolds seen in natural products such as lennoxamine.[34]

SUMMARY

In summary, we have explored the B−C−C−N motifs in the synthesis of nitrogen-containing heterocycles. Mild α-halogenation, catalyzed by pyrrolidine, proceeds through the intermediacy of boryl enamines. The halogenated products can be used in the regioselective synthesis of a new class of 2,5-disubstituted boryl thiazoles. α-Boryl aldehydes also undergo quantitative condensation/amidation sequence, which affords stable α-boryl enamides without concomitant C → N migration. Heck cyclization of the enamides provides the privileged isoindolone scaffold equipped with boron. The stability to reductive conditions suggests that borylated enamides may find utility in asymmetric hydrogenation. The application of the Heck products through SMCC engagement of the C−B bond enables convenient access to biologically relevant tetracyclic scaffolds and affords novel retrosynthetic opportunities for the construction of polycyclic scaffolds. Overall, our chemistry realizes the synthetic potential of α-boryl enamine and α-boryl enamide linchpins for production of nitrogen heterocycles and offers a rich repertoire of tools for the construction of heterocycles through the use of intermediates containing B−C−C−N linkages.

ASSOCIATED CONTENT

Supporting Information

Detailed procedures, spectral data (^1H, ^{13}C, ^{11}B NMR and HRMS) for all new compounds and X-ray data tables are available on the Internet. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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