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Azaborininones: Synthesis and Structural Analysis of a Carbonyl-Containing Class of Azaborines

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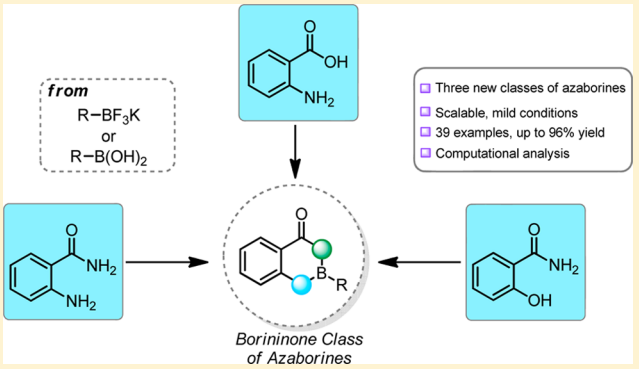
Supporting Information

ABSTRACT: An approach to access azaborininones (carbonyl-containing, boron-based heterocyclic scaffolds) using simple reagents and conditions from both organotrifluoroborates and boronic acids is described. An inexpensive, common reagent, SiO_2, was found to serve as both a fluorophile and desiccant to facilitate the annulation process across three different azaborininone platforms. Computational analysis of some of the cores synthesized in this study was undertaken to compare the azaborininones with the analogous carbon-based heterocyclic systems. Computationally derived pK_a values, NICS aromaticity calculations, and electrostatic potential surfaces revealed a unique isoelectronic/isostructural relationship between these azaborines and their carbon isosteres that changed based on boron connectivity. Correlation to experimentally derived data supports the computational findings.



INTRODUCTION

The preparation of boron-based heteroaromatic species has long fascinated synthetic chemists. Such ring systems greatly expand the library of heterocyclic structures and redefine the reactivity profile of these conjugated systems.[1] Although historically studied as a means to understand aromaticity,[2] boron-based aromatic systems have been recognized as viable, emerging platforms for expanding molecular diversity.[3] Particularly privileged among these boron-based cores is the azaborine scaffold, in which a B−N bond is integrated into the aromatic system.[4] The B−N bond serves as a surrogate for a C═C bond in arenes or heteroarenes, providing structural mimicry with unique electronic properties (and hence chemical reactivity). The unique disconnections, wholly unavailable in the corresponding carbon analogues, provide opportunities for dissonant synthetic routes to bicyclic systems. Additionally, the interchange between B−N and C═C bonds is particularly attractive for drug discovery, as it greatly enhances available structural diversity, and the trivalent nature of boron provides alternative electrostatic contacts for enzymatic targets.[5] Taken together, not only could this enhance potency of existing scaffolds, but it could also lead to new pharmacons. Indeed, oxaboroles[6] and benzodiazaborines[7] have been shown to have unique modes of bioactivity, and recent studies on 2,1-borazaronaphthalenes indicate a strong correlation to known bioactive compounds.[4d,8] Thus, methods to construct new or unexplored boron heterocyclic species would dramatically improve the quality of drug discovery libraries.

Recently, our group has engaged in highly successful programs to access azaborinyl cores from potassium organotrifluoroborates (R-BF_3Ks) *via in situ* generated dihaloboranes, resulting in rapid access to both the 2,1-borazaronaphthalene[9a] and 1,3,2-benzodiazaborole[9b] scaffolds. Although exploration of methods to functionalize these unique cores is being continued,[10] it is also of interest to expand into new polyheteroatom-based azaborinyl systems. Of particular interest was the azaborininone family (Figure 1). These underexplored, carbonyl-bearing, boron-heterocyclic scaffolds chelate a boron atom between a carboxylate or an amide and a secondary point (either an aryl hydroxyl or amino group), thus establishing a 6,6-bicyclic ring system. The three resulting classes of azaborininones have been very sporadically explored[11] and have shown applications as boron protecting/directing groups

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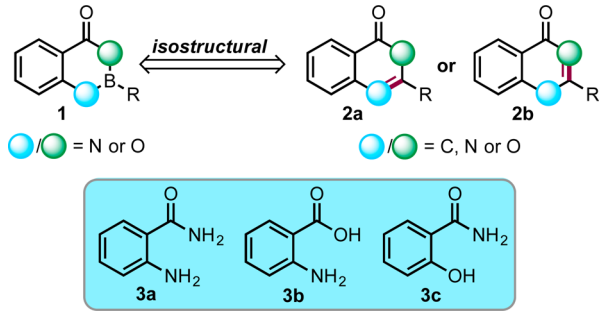


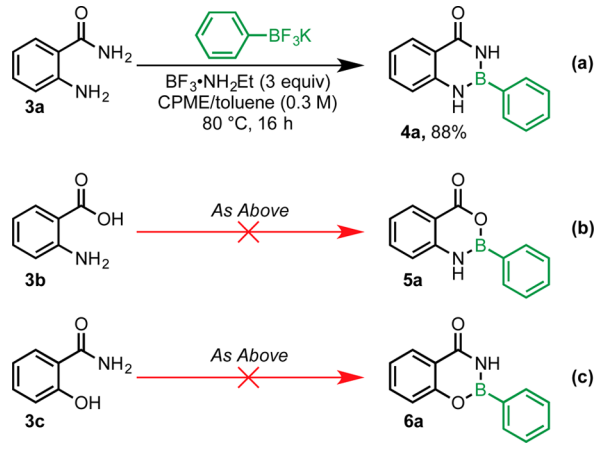
Figure 1. Azaborininones, their possible isosteric counterparts, and their requisite starting points.

for C−H activation,[11e−g] as well as potential promise as therapeutics given their known abilities as insect chemosterilants.[11h] Development of a concise, robust synthetic method applicable to the entire family of azaborininones would be highly attractive. In addition to overcoming a synthetic challenge, the three core systems provide future opportunities to explore the reactivity of an entirely new library of boron-containing compounds. In parallel to these synthetic studies, a computational investigation of the azaborininone family would provide further understanding as to how the substitution of O−B and N−B affect the structural and electronic properties.

RESULTS AND DISCUSSION

Early synthetic efforts centered on accessing 1,3,2-benzodiazaborininones derived from anthranilamide **3a**. Using the conditions established from the prior work with the similar 3,1,2-benzodiazaboroles,[9b] the defluorinative annulation with phenyltrifluoroborate was met with success (Scheme 1a).

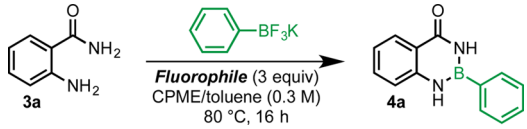
Scheme 1. Attempts at Preparing Various Azaborininones *via* Defluorinative Annulation: (a) Success with 1,3,2-Benzodiazaborininones; (b and c) Failed Attempts at Extension to the Mixed N,O-Azaborininone Classes



Unfortunately, the fluorophile used (BF_3·NH_2Et) to facilitate the cyclization proved unsuccessful in reactions with anthranilic acid, **3b**, or salicylamide, **3c** (Scheme 1b and 1c), likely because the strong Lewis acidity of BF_3 diminished the already weak nucleophilicity of these systems. Thus, although the boron trifluoride based approach would grant access to one core, alternative conditions were required to access the remaining two cores reliably. Given the known affinity of SiO_2 for fluoride in the context of organotrifluoroborates,[12] this reagent was considered as an alternative to BF_3·NH_2Et in enabling mild, defluorinative annulation. Not only would this mitigate the requirement of an excess of a harsh, boron trifluoride-based reagent, but it would also employ an extraordinarily inexpensive, readily available reagent already found in virtually any organic laboratory.

A brief screen of alternative additives in conjunction with **3a** and potassium phenyltrifluoroborate revealed SiO_2 to be the optimal fluorophile (Table 1). Importantly, these same conditions could be extended to both anthranilic acid and salicylamide without modification. Upon further study of SiO_2 as a fluorophile, oven-dried SiO_2 was determined to be more effective and allowed the reaction temperature to be lowered to 60 °C. In addition to being a fluorophilic species, SiO_2 can further convert organotrifluoroborates to their corresponding boronic acids,[12] suggesting a potential reaction intermediate. Exposure of phenylboronic acid in place of phenyltrifluoroborate (Scheme 2) to the optimized conditions resulted in the near-identical yield of **4a** (conditions b, Table 2). This finding also explains the benefit observed with dried SiO_2, as this improved the ability for the SiO_2 to act as a desiccant in the annulation (whose byproduct is H_2O). This indicates two viable mechanisms: one proceeding through a difluoroorganoborane and the other via a SiO_2-mediated boronate species. Both may be operative under SiO_2-mediated annulation, but only the former is possible when using the anhydrous BF_3·NH_2Et conditions.

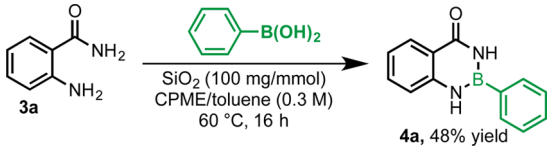
Table 1. Fluorophilic Reagent Optimization



entry	fluorophile	% Conversion[a]
1	BF_3•NH_2Et	100%
2	hexamethyldisilazane (HMDS)	8%
3	SiO_2	100%
4	Florisil	84%
5	alumina (basic)	40%
6	lithium silicate	26%

[a]Conversion determined by ^{1}H NMR spectroscopy.

Scheme 2. Successful Annulation Using a Boronic Acid Mediated by SiO_2



Substrate Scope. With two complementary conditions in hand, the scope of each approach was assessed. In the case of the 1,3,2-benzodiazaborininones (Table 2), derived from anthranilamide and the corresponding potassium organotrifluoroborates, a variety of annulated products could be accessed using either protocol. Typically, the BF_3·NH_2Et conditions outperformed SiO_2-mediated cyclizations (compare yields for **4a**, **4b**, **4e**, **4f**, **4p**−**4r**). Various functional groups were amenable to the annulation process, including ethers (**4f**, **4m**), amines (**4h**), esters (**4i**), and cyano groups (**4j**).

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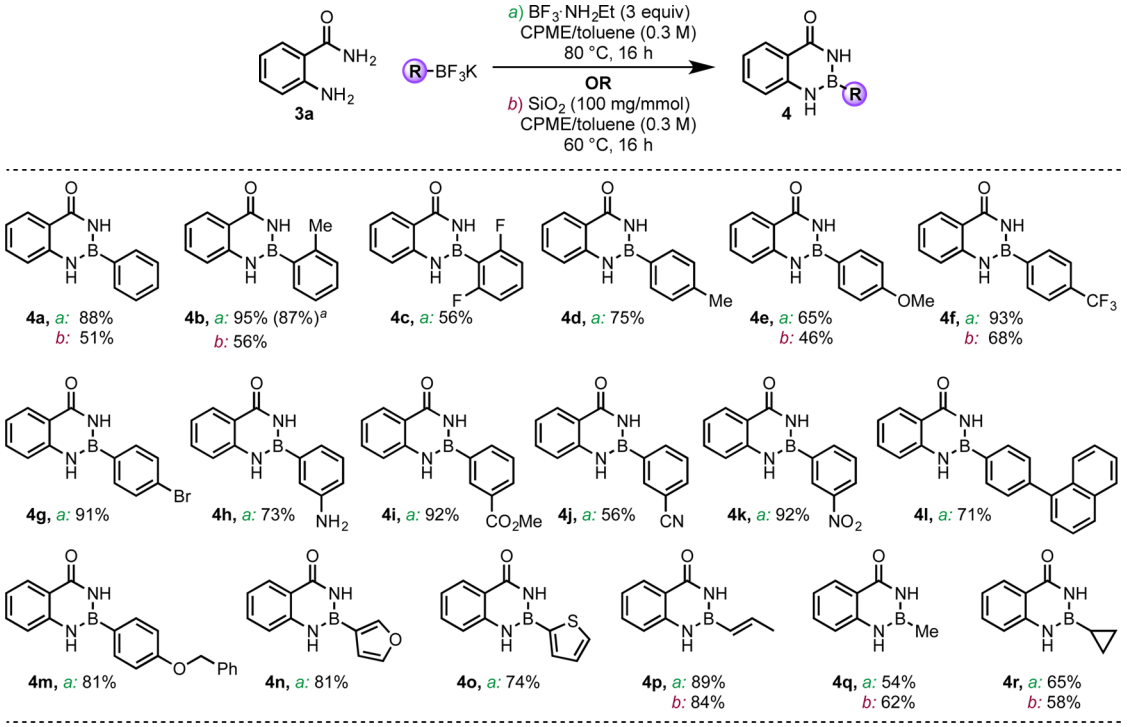
Table 2. Synthesis of 1,3,2-Benzodiazaborininones *via* Defluorinative Annulation

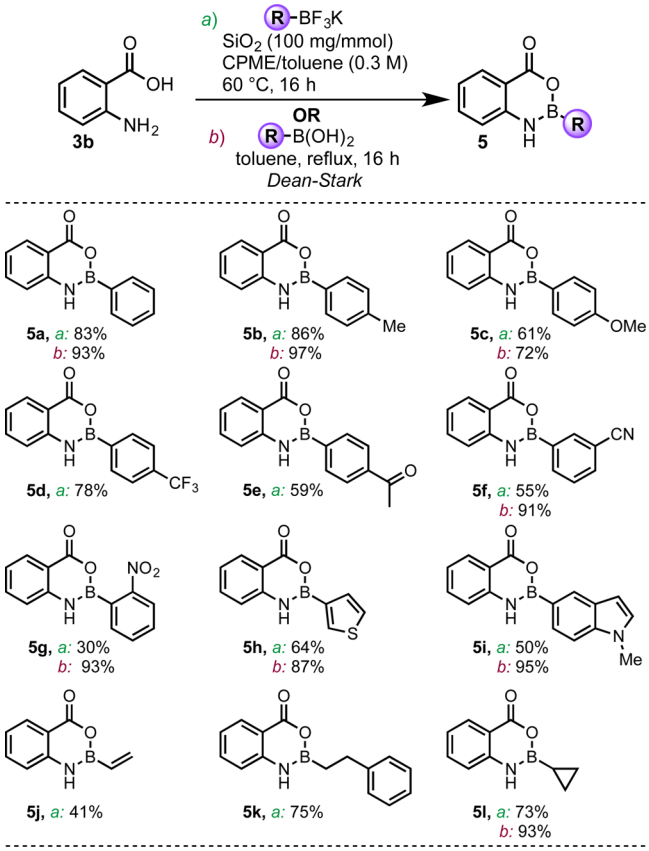


[a]Yield on 7 mmol scale (see Experimental Section for full reaction conditions).

Furthermore, polycyclic (**4l**) and multiple heterocyclic (**4n**, **4o**) species could be accessed, as well as nonaryl organotrifluoroborates (**4p**–**4r**). Finally, the $BF_3{\cdot}NH_2Et$ conditions were readily scalable to furnish gram quantities of **4b**. Stability studies of **4a** indicate that it is quite sensitive to an aqueous base, but is rather insensitive to aqueous acid or neutral pH solutions. Little to no hydrolysis was observed even after 18 h in aqueous DMSO (see Supporting Information for aqueous stability studies).

Utilization of the SiO_2-based conditions enabled initial entry to the mixed N,O-azaborininone classes. Starting from anthranilic acid (**3b**), a variety of 1,3,2-benzoxazaborininones could be synthesized (Table 3). A range of potassium organotrifluoroborates were quite competent in the synthesis of this class of oxazaborininone, and functional group tolerance remained high. In addition to retaining the functional group tolerance seen with 1,3,2-benzodiazaborininones, additional substrates containing ketones (**5e**) and indoles (**5i**) were demonstrated to be amenable to cyclization. Alkenyl- (**5j**) and alkyl-3,1,2-benzoxazaborinine substrates (**5k**, **5l**) could also readily be prepared. One difficulty encountered was inconsistent conversion observed upon isolation of the products. Oftentimes, **3b** would remain even after purification by silica plug, suggestive of a reversible process (via hydrolysis). Using ^1H NMR spectroscopy, these compounds were determined to be very intolerant to water and rapidly hydrolyzed to the corresponding boronic acid and **3b** in a quantifiable manner (see Supporting Information for stability studies).[11e,13] However, apart from hydrolysis, these systems were found to be stable in organic solutions even at elevated temperatures. With this in mind, supplementary conditions involving boronic acids were considered, capitalizing on azeotropic water removal to drive cyclization.[11e,14] These conditions (denoted conditions *b*) provide an alternative route that in many cases gives equal to superior yields, likely because of the now nonreversible annulation. Although not the focus of this study, considering

Table 3. Synthesis of 3,1,2-Benzoxazaborininones *via* Defluorinative Annulation



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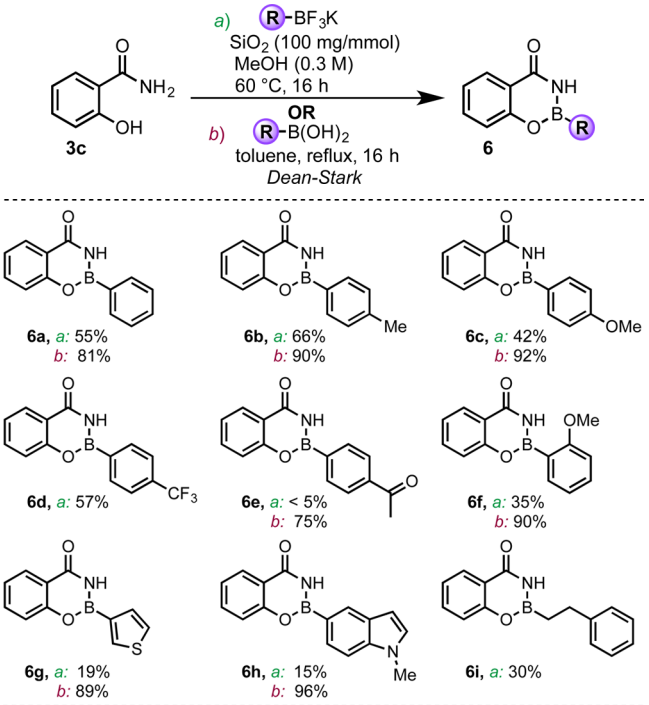
the practical benefits of trifluoroborates,[15] this approach was useful for systems prone to hydrolysis (**5a**–**5c**, **5f**–**5i**, **5l**).

The isomeric 1,3,2-benzoxaborininones (Table 4) could also be accessed from salicylamide (**3c**). These substrates were

Table 4. Synthesis of 1,3,2-Benzoxazaborininones *via* Defluorinative Annulation



typically the lowest-yielding members of the azaborininone family. This can be attributed to the diminished nucleophilicity of the amidyl nitrogen relative to aniline, combined with the lability of *O*-borylated phenols. In this case, a significant difference in yield exists between the SiO_2 conditions (*a*) and the Dean–Stark condensation (*b*). This likely relates to the unique electronics of this azaborininone class, which is more prone to degradation via hydrolysis. Similar to **5a**, **6a** underwent rapid hydrolysis in aqueous DMSO to give **3c** and phenylboronic acid. Despite this sensitivity, many, if not all, of the boryl substitution patterns tolerated with other members of the azaborininone family could be accessed with this more sensitive core. Not surprisingly, the azeotropic protocol fared far better with these systems. Indeed, in some cases, such as the acetophenone derivative **6e**, azeotropic condensation was the only way to effect annulation.

■ COMPUTATIONAL EVALUATION

In parallel to developing a user-friendly synthesis of this underexplored azaborine class, we sought to evaluate their electronic properties. More specifically, we hoped to discern what, if any, isostructural (or isoelectronic) character these systems possessed. Indeed, many possible isosteres were envisioned, such as isochromones for 3,1,2-benzoxazaborininones or isoquinolinones for 1,3,2-benzodiazaborole. The compounds compared were considered on an isostructural basis, focusing on the structural similarities, comparing B–N/C=C and the analogous B–O/C=N. Given the prior successes in analyzing the 1,3,2-benzodiazaborole core using quantum mechanical calculations,[9b] computational modeling was used to glean insight. All calculations were carried out using Gaussian 09,[16] and the structures were visualized via WebMO.[17] Geometry optimizations were performed in the gas phase at the B3LYP/6-311+G(2d,p) level of theory.[18] The method used for calculations involving thermochemical values (e.g., computed pK_a) of the various systems involved (i) geometry optimization and vibrational frequency calculations in the gas phase at the B3LYP/6-311+G(2d,p) level of theory and (ii) geometry optimization and vibrational frequency calculations in implicit water (H_2O) using PCM[19] at the B3LYP/6-311+G(2d,p) level of theory. Stationary points were characterized by frequency analysis at 298.15 K, with structures at energy minima showing no imaginary frequencies. To probe the ring current in these systems, nuclear independent chemical shift (NICS) values were determined at the GIAO-B3LYP/6-311+G(2d,p) level of theory at distances of 0.0 Å [A(0) and B(0)] and 1 Å [A(1) and B(1)] from each ring system as well as from the center of the bicyclic systems [Center(1)] in the perpendicular direction.[20]

Initial computational investigations focused on the truncated cores (i.e., without functionalization on boron) to explore the structural and electronic features in comparison to isostructural compounds (Table 5). Looking at the 1,3,2-benzodiazaborininones, isoquinolinone **10** and quinolinone **11** were identified as likely isosteres. A pictorial comparison of the electrostatic potential maps of these isosteres with the truncated 1,3,2-benzodiazaborininone **7** seemed to indicate that this system was a hybrid of both structures, with **7** having comparable A ring electrostatic potential to **11** and B ring similarity to **10**. This is not altogether surprising given that nitrogen is well-known to participate in electron donation to boron. Indeed, the B–N bond lengths in the 1,3,2-benzodiazaborininone are quite uniform despite the nitrogen atoms being in vastly different electronic environments. This is corroborated in the slight contraction seen in the C=O bond as compared to isoquinolinone (**10**), indicating diminished nitrogen participation in the carbonyl π system. NICS calculations, which provide a quantitative correlation for electron delocalization using "theoretical nuclei" at the center of a π-system to probe electron shielding, were used for further elucidations.[21] Specifically, NICS(1) values were highlighted based on their improved ability to observe a π-delocalized aromatic ring current. NICS studies indicated that, relative to its isosteres, 1,3,2-benzodiazaborininone **7** has less aromatic character in its B ring. This finding is in agreement with prior work by our group and others, wherein boryl-based aromatic systems display diminished aromatic character when compared to their indole counterparts.[9b,20a] This effect is less pronounced in the adjoined carbon ring but is still observed. NICS values between the two possible isosteres of this system are relatively similar, with **11** having slightly less aromatic character in its B ring and thus more similarity to **7**. Because of the aforementioned inherent stability issues of these systems, experimentally derived pK_a values were unobtainable, and thus theoretical values were pursued.[21] The computed pK_a's of **7** are quite uniform, indicative of a strong electron donation to boron by both nitrogen atoms. The pK_a's are notably higher than their isosteres, a consequence of the competitive donation by both nitrogen atoms into boron and the lack of complete resonance stabilization around the B ring to delocalize negative charge.

Moving to 3,1,2-benzoxazaborininone **8** and 1,3,2-benzoxazaborininones **9**, similar trends were observed. As a whole these mixed N,O systems displayed less electron delocalization and

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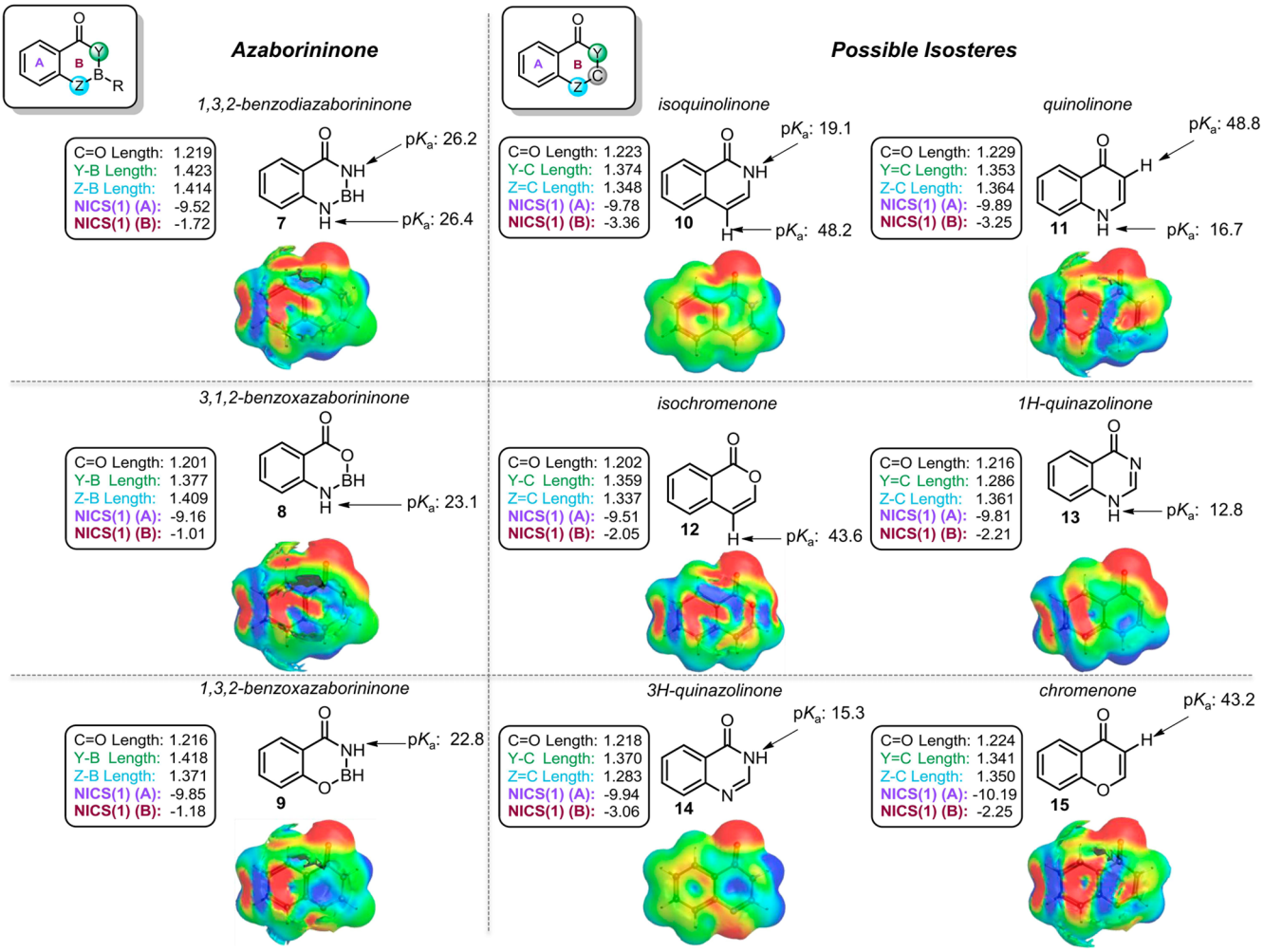
Table 5. Comparison of the Azaborininone Family with Their Probable Isosteres[a]



[a]All distances given in angstroms (Å), and the electrostatic potentials range from +31.38 to −31.38 kcal mol^{-1}. NICS(1) values are given in ppm where a more negative NICS value indicates greater electron shielding via a stronger ring current and more π-electron delocalization (thus greater aromatic character).

were more acidic. This increased acidity can be attributed to diminished π-orbital overlap with boron by the secondary heteroatom (in this case oxygen). The lower participation of electron donation by oxygen likely also relates to the observed, less negative, NICS values for the B rings of these systems. However, the isosteric character of these two systems was not as uniform. Using electrostatic potentials, **8** more closely resembles isochromone **12**, whereas **9** appears to be more of a hybrid of **14** and **15**. These trends are also borne out in the NICS analysis of the B rings of **8** and **9**, wherein **9** has slightly more aromatic character than **8**, indicating more oxygen participation in the ring system and thus provides further plausibility to B−O/C═N mimicry.[22] Additionally, the C═N resonance contribution of amides renders the system more aromatic. The relatively longer B−N bond seen in **9** also is in line with enhanced oxygen participation. However, the NICS value for the B ring of **9** more closely aligns with the B ring of **15**. The exact opposite is true for the A ring, thus supporting the notion that **9** is a hybrid of the two systems.

To probe the role of electronics in these systems further, substitution on boron was next explored (Table 6). Four representative *B*-aryl groups were selected that not only provided a range of electronic environments but also were prepared during the synthetic studies to allow correlative studies. In general, adding a *B*-aryl group led to diminished aromatic character in both the A and B rings for all members of the azaborininone family, as the boron is in favorable π-orbital overlap with the external ring. In particular, the 1,3,2-benzoxazaborininones showed the most significant disparity in the NICS values of the B ring from its truncated system. Ultimately, this increase may relate to their observed experimental instability. Electronically, the 1,3,2-benzodiazaborininones were the least sensitive to electronic changes, suggesting the overriding participation of both nitrogen atoms in this core. The 3,1,2-benzoxazaborininones seemed to be most influenced by electronic changes and appeared to gain aromatic character in both the A and B rings with more electron-deficient *B*-arenes.

As a means of correlating some of the observed computational trends with experimental data, NICS calculations were compared with some possible values that could be experimentally derived. Although pK_a's would have been ideal, the instability of these systems to strongly basic environments prohibited such a correlative study. Instead, IR and NMR spectroscopy were used as a means of quantitatively comparing calculations to experiment. Initially, the computed

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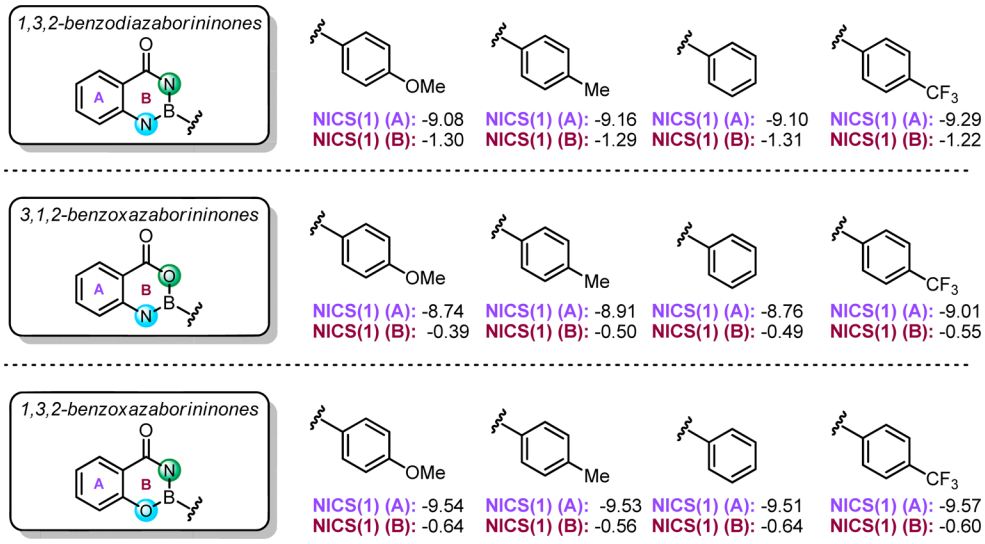
Table 6. NICS Analysis of Electronically Disparate Azaborininones Divided by Class



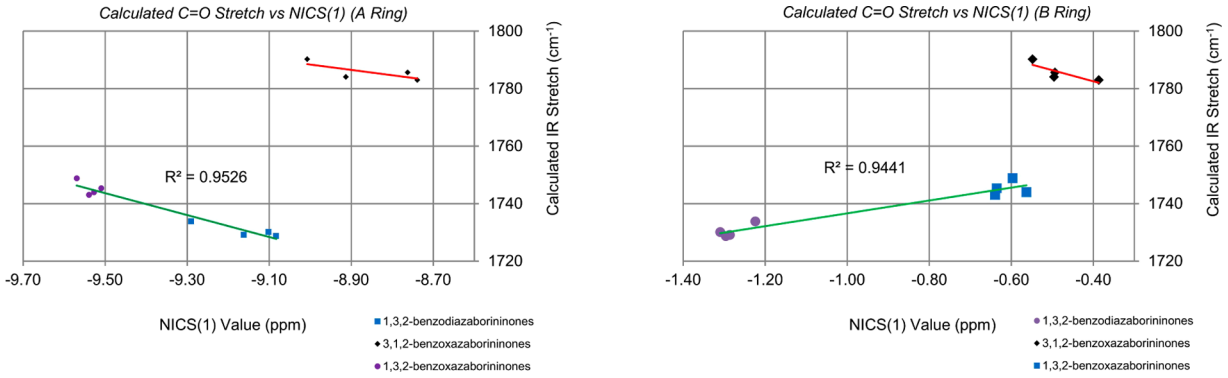


Figure 2. Plots of computed C═O IR stretch vs NICS values for both the A and B rings of various azaborininones.

IR values were compared against the NICS values for both rings, to determine if the double bond character of the carbonyl would be influenced by the aromatic character of the rings and the relative electron-donation propensity of the adjacent heteroatom with boron. It was observed that, whereas the amide-containing 1,3,2-benzoxazaborininones and 1,3,2-benzodiazaborininones were readily comparable, the 3,1,2-benzoxazaborininones did not trend with the other members of the azaborininone class (Figure 2). This is not altogether that surprising given the pseudo-α,β-unsaturated character of the structures (via B−N/C═C isosterism) possible with the former two systems that are not possible in the latter. This trend is also in agreement with the findings of the truncated systems. Whereas the amide-based systems usually are hybrid structures and very much electronically related, the ester-like 3,1,2-benzoxazaborininones are more like their isochromenone isosteres. Comparison of the experimental values for these systems provided some level of correlation, but because of their complex IR spectrum, the correlations were less than ideal (see Supporting Information for details). For a more precise correlation, ^{13}C NMR was used, which would be quite sensitive to electronic changes. Experimental NMR values correlated well with NICS(1) values in both rings, indicating the electronic shielding trends observed computationally may indeed occur in these systems experimentally (Figure 3). In general, the distribution of these values was self-consistent within each structural class (i.e., bimodal for the two classes plotted). Moreover, although the B rings show aromatic character, the values observed for the A ring are more analogous to aromatic systems [NICS(1) value of benzene is −10.20].[20b] This is similarly reflected in these studies, with the A ring showing a stronger correlation than the B ring. Thus, this provides some level of experimental validation of the trends observed in the NICS studies.

■ CONCLUSIONS

In summary, a modular approach to the synthesis of the underexplored azaborininone family of azaborines is presented. A set of simple conditions enables various organotrifluoroborates to undergo facile defluorinative annulation facilitated by two inexpensive fluorophiles. Alternatively, boronic acids also succumb to annulation via a more classical condensation route. Three classes, 1,3,2-benzodiazaborininones, 1,3,2-benzoxazaborininones, and 3,1,2-benzoxazaborininones, can be prepared using these varying approaches. These classes were further studied using computational methods, revealing some similarities to possible carbon isosteres. Whereas 1,3,2-benzodiazaborininones and 3,1,2-benzoxazaborininones appear to represent a hybrid between their plausible isosteres, the 1,3,2-benzoxazaborininones seem to align closely with isochromenones. Correlations between computed NICS values and experimentally derived trends provide support for these computed trends.

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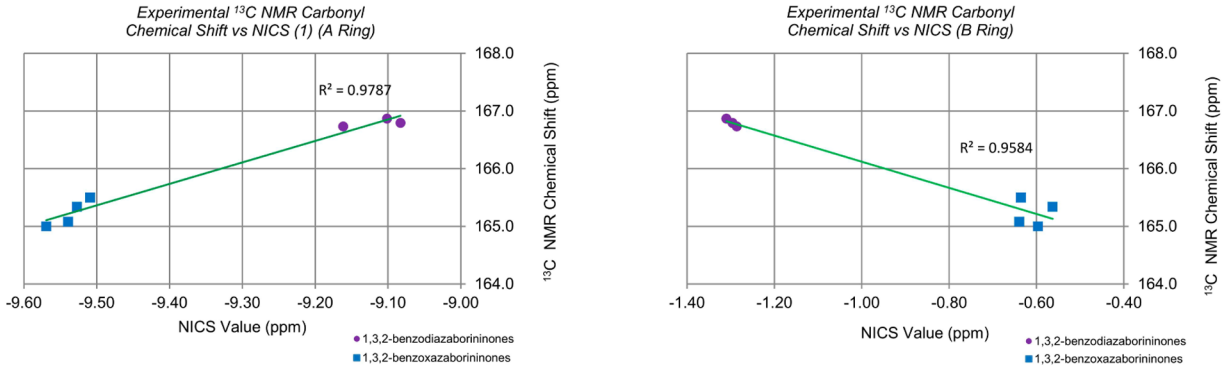

Figure 3. Plots of experimental ^{13}C NMR values vs computed NICS values for both the A and B rings of various 1,3,2-benzoxazaborininones and 1,3,2-benzodiazaborininones.

EXPERIMENTAL SECTION

General Considerations. All reactions were carried out under an inert atmosphere of nitrogen or argon in oven-dried glassware, unless otherwise noted. Toluene and cyclopentyl methyl ether (CPME) were dried using a J. C. Meyer solvent system. SiO_2 was dried in a laboratory oven at 160 °C. All reagents were purchased commercially and used as received, unless otherwise noted. Melting points (°C) are uncorrected. Mass spectra (ESI- or EI-TOF) were recorded using CH_2Cl_2 or MeCN as the solvent. IR spectra were recorded using FTIR-ATR of the neat oil or solid products. NMR spectra (^1H, ^{13}C $\{^1H\}$, ^{11}B, ^{19}F $\{^1H\}$) were performed at 298 K. ^1H (500.4 MHz) and ^{13}C $\{^1H\}$ (125.8 MHz) NMR chemical shifts are reported relative to internal TMS (δ = 0.00 ppm) or to residual protonated solvent. Any observed splitting in the ^{13}C $\{^1H\}$ NMR spectra is due to $^{13}C-^{19}F$ coupling. ^{11}B (128.4 MHz) chemical shifts were referenced to external $BF_3{\cdot}Et_2O$ (0.0 ppm). Data are presented as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, m = multiplet, br = broad), coupling constant J (Hz), and integration.

Procedure A: Cyclization of Potassium Organotrifluoroborates Activated with $BF_3{\cdot}EtNH_2$ To Form 1,3,2-Benzodiazaborininones. To a microwave vial with a stir bar were added anthranilamide (1.0 equiv) and the appropriate potassium organotrifluoroborate (1.05 equiv) along with $BF_3{\cdot}EtNH_2$ (3.0 equiv). The reaction vessel was capped and purged with argon, upon which CPME and toluene were added in a 1:1 mixture (3 mL/mmol). The reaction was then heated at 80 °C for 16 h. Upon cooling to rt, the reaction mixture was washed with an aqueous solution of $NaHCO_3$, extracted with EtOAc, and dried ($MgSO_4$), before being concentrated to afford the azaborininone product. If needed, the product was further purified by passage of the crude matter through a short pad of silica, using a 9:1 mixture of hexane/EtOAc as eluent.

Procedure B-1: Cyclization of Potassium Organotrifluoroborates Activated with SiO_2 To Form Azaborininones. To a microwave vial with a stir bar were added anthranilamide, anthranilic acid, or salicylamide (1.0 equiv) and potassium organotrifluoroborates (1.05 equiv) along with oven-dried SiO_2 (100 mg/mmol). The reaction vessel was capped and purged with argon, upon which CPME and toluene were added in a 1:1 mixture (3 mL/mmol). The reaction was then heated at 60 °C for 16 h. Upon cooling to rt, the reaction mixture was filtered through a short pad of Celite and flushed with MeOH, before being concentrated. If needed, the solid was further washed with EtOAc for purification to afford the azaborininone product.

*2-Phenyl-1,3,2-benzodiazaborininone (**4a**).* Obtained as a white solid by procedure A (195 mg, 88%, 1.0 mmol scale) and procedure B-1 (113 mg, 51%, 1.0 mmol scale); mp: 206–208 °C; ^1H NMR ($CDCl_3$, 500.4 MHz): δ 8.27 (d, J = 7.9 Hz, 1H), 7.70 (d, J = 7.5 Hz, 2H), 7.61–7.44 (m, 5H), 7.18 (t, J = 7.6 Hz, 1H), 7.12 (d, J = 8.1 Hz, 1H), 6.81 (s, 1H) ppm; ^{13}C $\{^1H\}$ NMR ($CDCl_3$, 125.8 MHz): δ 166.9, 144.4, 134.1, 132.0, 131.2, 129.4, 128.7, 122.1, 119.1, 117.8 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 29.4 ppm; IR: ν = 3347, 3245, 1635, 1612, 1526, 1484, 1270, 747, 686 cm^{-1}; HRMS (CI) m/z calcd for $C_{13}H_{12}BN_2O$ $[M + H]^+$ 223.1043, found 223.1043.

*2-(o-Tolyl)-1,3,2-benzodiazaborininone (**4b**).* Obtained as a white solid by procedure A after recrystallization from EtOAc (1.43 g, 87%, 7.0 mmol scale) and procedure B-1 (132 mg, 56%, 1.0 mmol scale); mp: 168–169 °C; ^1H NMR ($CDCl_3$, 500.4 MHz): δ 8.25 (d, J = 7.9 Hz, 1H), 7.55 (t, J = 7.6 Hz, 1H), 7.45 (d, J = 7.2 Hz, 1H), 7.34 (t, J = 7.5 Hz, 1H), 7.30 (s, 1H), 7.23 (d, J = 6.1 Hz, 2H), 7.18 (t, J = 7.6 Hz, 1H), 7.07 (d, J = 8.1 Hz, 1H), 6.72 (s, 1H), 2.48 (s, 3H) ppm; ^{13}C $\{^1H\}$ NMR ($CDCl_3$, 125.8 MHz): δ 166.5, 144.4, 140.9, 134.0, 132.7, 130.1, 130.1, 129.3, 125.6, 122.1, 119.0, 117.7, 22.6 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 30.7 ppm; IR: ν = 3385, 3210, 1614, 1516, 1484, 1455, 745, 723 cm^{-1}; HRMS (ES+) m/z calcd for $C_{14}H_{14}BN_2O$ $[M + H]^+$ 237.1199, found 237.1193.

*2-(2,6-Fluorophenyl)-1,3,2-benzodiazaborininone (**4c**).* Obtained as a beige solid by procedure A after recrystallization from EtOAc (150 mg, 58%, 1.0 mmol scale); mp: 164–165 °C; ^1H NMR (acetone-d_6, 500.4 MHz): δ 8.59 (s, 1H), 8.55 (s, 1H), 8.15 (d, J = 7.9 Hz, 1H), 7.64–7.50 (m, 2H), 7.42 (d, J = 8.1 Hz, 1H), 7.18 (t, J = 7.5 Hz, 1H), 7.05 (t, J = 7.8 Hz, 2H) ppm; ^{13}C $\{^1H\}$ NMR (DMSO-d_6, 125.8 MHz): δ 165.9, 164.8 (dd, J = 244.6, 13.7 Hz), 145.4, 133.9, 133.1 (t, J = 10.1 Hz), 128.4, 121.8, 119.4, 118.5, 111.6 (dd, J = 22.7, 5.3 Hz) ppm; ^{19}F $\{^1H\}$ NMR (acetone-d_6, 470.8 MHz): δ −103.6 ppm; ^{11}B NMR (acetone-d_6, 128.4 MHz): δ 28.0 ppm; IR: ν = 3438, 3362, 1666, 1616, 1454, 982, 762, 750, 720 cm^{-1}; HRMS (ES+) m/z calcd for $C_{13}H_{10}BN_2OF_2$ $[M + H]^+$ 259.0854, found 259.0862.

*2-(p-Tolyl)-1,3,2-benzodiazaborininone (**4d**).* Obtained as a white solid by procedure A (177 mg, 75%, 1.0 mmol scale); mp: 255–256 °C; ^1H NMR ($CDCl_3$, 500.4 MHz): δ 8.26 (d, J = 7.8 Hz, 1H), 7.61 (d, J = 7.8 Hz, 2H), 7.56 (t, J = 7.7 Hz, 1H), 7.51 (s, 1H), 7.31 (d, J = 7.6 Hz, 2H), 7.18 (t, J = 7.6 Hz, 1H), 7.11 (d, J = 8.1 Hz, 1H), 6.76 (s, 1H), 2.43 (s, 3H) ppm; ^{13}C $\{^1H\}$ NMR ($CDCl_3$, 125.8 MHz): δ 166.7, 144.5, 141.6, 134.0, 132.0, 129.6, 129.4, 122.0, 119.1, 117.7, 21.8 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 29.5 ppm; IR: ν = 3321, 3247, 1635, 1615, 1486, 1364, 1342, 1272, 752, 719, 477 cm^{-1}; HRMS (EI) m/z calcd for $C_{14}H_{13}BN_2O$ $[M]^+$ 236.1121, found 236.1136.

*2-(4-Methoxyphenyl)-1,3,2-benzodiazaborininone (**4e**).* Obtained as a white solid by procedure A (82 mg, 65%, 0.5 mmol scale) and procedure B-1 (58 mg, 68%, 0.5 mmol scale); mp: 215–217 °C; ^1H NMR ($CDCl_3$, 500.4 MHz): δ 8.26 (d, J = 7.9 Hz, 1H), 7.65 (d, J = 8.5 Hz, 2H), 7.56 (dt, J = 7.8, 1.5 Hz, 1H), 7.52 (s, 1H), 7.17 (t, J = 7.6 Hz, 1H), 7.10 (d, J = 8.1 Hz, 1H), 7.02 (d, J = 8.5 Hz, 2H), 6.73 (s, 1H), 3.88 (s, 3H) ppm; ^{13}C $\{^1H\}$ NMR ($CDCl_3$, 125.8 MHz): δ 166.8, 162.2, 144.6, 134.0, 133.7, 129.4, 121.9, 119.0, 117.6, 114.4, 55.4 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 29.2 ppm; IR: ν = 3352, 3290, 1640, 1602, 1507, 1487, 1242, 1179, 753 cm^{-1}; HRMS (ES+) m/z calcd for $C_{14}H_{14}{}^{10}BN_2O_2$ $[M + H]^+$ 252.1185, found 252.1187.

*2-(4-(Trifluoromethyl)phenyl)-1,3,2-benzodiazaborininone (**4f**).* Obtained as a white solid by procedure A (270 mg, 93%, 1.0 mmol scale) and procedure B-1 (197 mg, 68%, 1.0 mmol scale); mp: >260 °C; ^1H NMR (DMSO-d_6, 500.4 MHz): δ 9.80 (s, 1H), 9.45 (s, 1H), 8.23 (d, J = 7.5 Hz, 2H), 8.04 (d, J = 7.7 Hz, 1H), 7.77 (d, J = 7.6 Hz,

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2H), 7.57 (t, J = 7.4 Hz, 1H), 7.43 (d, J = 7.9 Hz, 1H), 7.11 (t, J = 7.7 Hz, 1H) ppm; ^{13}C {^{1}H} NMR (DMSO-d_6, 125.8 MHz): δ 166.7, 145.6, 134.3, 133.8, 130.9 (q, J = 31.7 Hz), 128.3, 124.6 (q, J = 272.2 Hz), 124.6 (q, J = 3.4 Hz), 121.5, 119.3, 118.6 ppm; ^{19}F {^{1}H} NMR (DMSO-d_6, 470.8 MHz): δ −63.1 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 28.5 ppm; IR: ν = 3333, 3245, 1630, 1616, 1316, 1110, 1066, 763, 526 cm^{-1}; HRMS (ES+) m/z calcd for $C_{14}H_{11}BN_2OF_3$ $[M + H]^+$ 291.0917, found 291.0916.

*2-(4-Bromophenyl)-1,3,2-benzodiazaborininone (**4g**).* Obtained as a white solid by modification to procedure A, as **4g** was not particularly soluble in EtOAc. As a result, some product could be collected as a precipitate from the aqueous workup (273 mg, 91%, 1.0 mmol scale); mp: >260 °C; ^{1}H NMR (DMSO-d_6, 500.4 MHz): δ 9.73 (s, 1H), 9.36 (s, 1H), 8.04−7.95 (m, 3H), 7.65 (d, J = 8.3 Hz, 2H), 7.60−7.53 (m, 1H), 7.40 (d, J = 8.0 Hz, 1H), 7.10 (t, J = 7.3 Hz, 1H) ppm; ^{13}C {^{1}H} NMR (DMSO-d_6, 125.8 MHz): δ 166.6, 145.7, 135.8, 133.8, 131.1, 128.3, 125.0, 121.3, 119.2, 118.5 ppm; ^{11}B NMR (THF, 128.4 MHz): δ 29.4 ppm; IR: ν = 3331, 3240, 1615, 1486, 1269, 753, 717, 528 cm^{-1}; HRMS (ES+) m/z calcd for $C_{13}H_{11}BN_2OBr$ $[M + H]^+$ 301.0148, found 301.0157.

*2-(3-Aminophenyl)-1,3,2-benzodiazaborininone (**4h**).* Obtained as a tan solid by modification to procedure A, as **4h** was minimally soluble in EtOAc. As a result, the product could be collected directly as a precipitate from the aqueous workup (173 mg, 73%, 1.0 mmol scale); mp: 210−213 °C; ^{1}H NMR (DMSO-d_6, 500.4 MHz): δ 9.38 (s, 1H), 9.17 (s, 1H), 7.99 (d, J = 7.9 Hz, 1H), 7.61−7.50 (m, 1H), 7.42 (d, J = 8.2 Hz, 1H), 7.19−7.12 (m, 2H), 7.12−7.04 (m, 2H), 6.70 (d, J = 7.7 Hz, 1H), 4.92 (s, 2H) ppm; ^{13}C {^{1}H} NMR (DMSO-d_6, 125.8 MHz): δ 166.6, 148.3, 146.0, 133.6, 128.7, 128.2, 121.5, 121.0, 119.1, 118.5, 116.6, 99.9 ppm; ^{11}B NMR (MeCN, 128.4 MHz): δ 30.1 ppm; IR: ν = 3395, 3292, 3211, 1657, 1608, 1526, 1484, 757, 509 cm^{-1}; HRMS (ES+) m/z calcd for $C_{13}H_{12}BN_3ONa$ $[M + Na]^+$ 260.0971, found 260.0984.

*2-(3-(Methoxycarbonyl)phenyl)-1,3,2-benzodiazaborininone (**4i**).* Obtained as a white solid by modification to procedure A, as **4i** was not particularly soluble in EtOAc. As a result some product was also collected as a precipitate from the aqueous workup (258 mg, 92%, 1.0 mmol scale); mp: 234−235 °C; ^{1}H NMR (DMSO-d_6, 500.4 MHz): δ 9.82 (s, 1H), 9.48 (s, 1H), 8.63 (s, 1H), 8.27 (d, J = 7.4 Hz, 1H), 8.05 (d, J = 7.8 Hz, 1H), 8.01 (d, J = 7.8 Hz, 1H), 7.63−7.54 (m, 2H), 7.44 (d, J = 8.1 Hz, 1H), 7.10 (t, J = 7.5 Hz, 1H), 3.89 (s, 3H) ppm; ^{13}C {^{1}H} NMR (DMSO-d_6, 125.8 MHz): δ 166.9, 166.6, 145.8, 138.5, 134.5, 133.8, 131.4, 129.7, 128.6, 128.3, 121.3, 119.3, 118.6, 52.5 ppm; ^{11}B NMR (THF, 128.4 MHz): δ 29.5 ppm; IR: ν = 3320, 3226, 2951, 1716, 1623, 1487, 1289, 749, 690 cm^{-1}; HRMS (ES+) m/z calcd for $C_{15}H_{14}BN_2O_3$ $[M + H]^+$ 281.1097, found 281.1092.

*2-(3-Cyanophenyl)-1,3,2-benzodiazaborininone (**4j**).* Obtained as a white solid by procedure A after purifying via plug of silica gel with EtOAc/hexane (1:1) as eluent (138 mg, 56%, 1.0 mmol scale); mp: >260 °C; ^{1}H NMR (DMSO-d_6, 500.4 MHz): δ 9.84 (s, 1H), 9.47 (s, 1H), 8.48 (s, 1H), 8.35 (t, J = 6.6 Hz, 1H), 8.01 (d, J = 7.5 Hz, 1H), 7.93 (d, J = 6.9 Hz, 1H), 7.66 (t, J = 7.5 Hz, 1H), 7.58 (d, J = 7.1 Hz, 1H), 7.40 (d, J = 7.1 Hz, 1H), 7.16−7.03 (m, 1H) ppm; ^{13}C {^{1}H} NMR (DMSO-d_6, 125.8 MHz): δ 166.6, 145.6, 138.2, 137.3, 134.1, 133.9, 129.2, 128.3, 121.5, 119.4, 119.3, 118.6, 111.6 ppm; ^{11}B NMR (THF, 128.4 MHz): δ 29.3 ppm; IR: ν = 3365, 3197, 2230, 1651, 1619, 1485, 760, 699, 687 cm^{-1}; HRMS (ES+) m/z calcd for $C_{14}H_{11}BN_3O$ $[M + H]^+$ 248.0995, found 248.0991.

*2-(3-Nitrophenyl)-1,3,2-benzodiazaborininone (**4k**).* Obtained as a beige solid by procedure A (123 mg, 92%, 0.5 mmol scale); mp: >260 °C; ^{1}H NMR (DMSO-d_6, 500.4 MHz): δ 9.97 (s, 1H), 9.62 (s, 1H), 8.92 (s, 1H), 8.46 (d, J = 7.4 Hz, 1H), 8.31 (dd, J = 8.2, 1.4 Hz, 1H), 8.02 (d, J = 7.9 Hz, 1H), 7.74 (t, J = 7.8 Hz, 1H), 7.63−7.55 (m, 1H), 7.44 (d, J = 8.1 Hz, 1H), 7.13 (t, J = 7.5 Hz, 1H) ppm; ^{13}C {^{1}H} NMR (DMSO-d_6, 125.8 MHz): δ 166.6, 148.1, 145.6, 140.3, 140.3, 133.9, 129.7, 128.3, 125.4, 121.6, 119.3, 118.6 ppm; ^{11}B NMR (THF, 128.4 MHz): δ 29.1 ppm; IR: ν = 3325, 1614, 1515, 1484, 1345, 1269, 763, 679 cm^{-1}; HRMS (ES-) m/z calcd for $C_{13}H_9BN_3O_3$ $[M - H]^-$ 266.0737, found 266.0747.

*2-(4-(Naphthalen-1-yl)phenyl)-1,3,2-benzodiazaborininone (**4l**).* Obtained as a beige solid by procedure A (247 mg, 71%, 1.0 mmol scale); mp: 255−256 °C; ^{1}H NMR (DMSO-d_6, 500.4 MHz): δ 9.76 (s, 1H), 9.42 (s, 1H), 8.20 (d, J = 7.8 Hz, 2H), 8.01 (t, J = 8.7 Hz, 2H), 7.96 (d, J = 8.2 Hz, 1H), 7.82 (d, J = 8.3 Hz, 1H), 7.61−7.52 (m, 5H), 7.52−7.43 (m, 3H), 7.10 (t, J = 7.4 Hz, 1H) ppm; ^{13}C {^{1}H} NMR (DMSO-d_6, 125.8 MHz): δ 166.8, 146.0, 142.5, 139.7, 133.9, 133.8, 133.8, 131.1, 129.6, 128.8, 128.3, 128.2, 127.3, 126.8, 126.3, 125.9, 125.5, 121.2, 119.2, 118.6 ppm; ^{11}B NMR (THF, 128.4 MHz): δ 29.9 ppm; IR: ν = 3320, 1657, 1316, 1533, 1511, 1485, 1358, 798, 774, 760, 716 cm^{-1}; HRMS (ES-) m/z calcd for $C_{23}H_{16}BN_2O$ $[M - H]^-$ 347.1356, found 347.1357.

*2-(4-(Benzyloxy)phenyl)-1,3,2-benzodiazaborininone (**4m**).* Obtained as a white solid by procedure A (265 mg, 81%, 1.0 mmol scale); mp: 249−251 °C; ^{1}H NMR (DMSO-d_6, 500.4 MHz): δ 9.57 (s, 1H), 9.20 (s, 1H), 8.07−7.94 (m, 3H), 7.54 (t, J = 7.6 Hz, 1H), 7.46 (d, J = 7.7 Hz, 2H), 7.43−7.37 (m, 3H), 7.33 (t, J = 7.3 Hz, 1H), 7.11−7.03 (m, 3H), 5.17 (s, 2H) ppm; ^{13}C {^{1}H} NMR (DMSO-d_6, 125.8 MHz): δ 166.7, 160.8, 146.0, 137.3, 135.5, 133.7, 128.8, 128.3, 128.2, 128.0, 120.9, 118.9, 118.4, 114.7, 69.4 ppm; ^{11}B NMR (THF, 128.4 MHz): δ 29.6 ppm; IR: ν = 3404, 3302, 1645, 1622, 1604, 1486, 1214, 996, 759, 721 cm^{-1}; HRMS (ES+) m/z calcd for $C_{20}H_{18}BN_2O_2$ $[M + H]^+$ 329.1461, found 329.1458.

*2-(Furan-3-yl)-1,3,2-benzodiazaborininone (**4m**).* Obtained as a light brown solid by procedure A (172 mg, 81%, 1.0 mmol scale); mp: 190−192 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 8.25 (d, J = 7.9 Hz, 1H), 8.00 (s, 1H), 7.90 (s, 1H), 7.60 (s, 1H), 7.55 (t, J = 8.2 Hz, 1H), 7.27 (s, 1H), 7.17 (t, J = 7.5 Hz, 1H), 7.09 (d, J = 8.1 Hz, 1H), 6.68 (s, 1H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 167.0, 148.6, 144.5, 144.1, 134.0, 129.3, 121.9, 119.1, 117.5, 111.7 ppm; ^{11}B NMR (EtOAc, 128.4 MHz): δ 28.2 ppm; IR: ν = 3347, 3250, 1636, 1610, 1516, 1487, 1150, 754, 732, 668, 527 cm^{-1}; HRMS (ES+) m/z calcd for $C_{11}H_{10}BN_2O_2$ $[M + H]^+$ 213.0835, found 213.0836

*2-(Thiophen-2-yl)-1,3,2-benzodiazaborininone (**4n**).* Obtained as a white solid by procedure A (169 mg, 74%, 1.0 mmol scale); mp: 211−213 °C; ^{1}H NMR (DMSO-d_6, 500.4 MHz): δ 9.71 (s, 1H), 9.26 (s, 1H), 7.99 (dd, J = 11.2, 2.5 Hz, 2H), 7.92 (d, J = 4.6 Hz, 1H), 7.55 (td, J = 7.8, 1.5 Hz, 1H), 7.41 (d, J = 8.1 Hz, 1H), 7.29 (dd, J = 4.6, 3.5 Hz, 1H), 7.09 (t, J = 7.5 Hz, 1H) ppm; ^{13}C {^{1}H} NMR (DMSO-d_6, 125.8 MHz): δ 166.4, 145.8, 136.7, 133.8, 132.8, 129.0, 128.3, 121.2, 119.2, 118.5 ppm; ^{11}B NMR (EtOAc, 128.4 MHz): δ 27.7 ppm; IR: ν = 3315, 3240, 1614, 1530, 1486, 1264, 1025, 753, 698, 687, 474 cm^{-1}; HRMS (ES+) m/z calcd for $C_{11}H_{10}BN_2OS$ $[M + H]^+$ 229.0607, found 229.0618.

*(E)-2-(Prop-1-en-1-yl)-1,3,2-benzodiazaborininone (**4o**).* Obtained as an off-white solid by procedure A (166 mg, 89%, 1.0 mmol scale) and procedure B-1 (156 mg, 84%, 1.0 mmol scale); mp: 142−143 °C; ^{1}H NMR (DMSO-d_6, 500.4 MHz): δ 9.25 (s, 1H), 8.91 (s, 1H), 7.93 (d, J = 7.8 Hz, 1H), 7.55−7.45 (m, 1H), 7.22 (d, J = 8.2 Hz, 1H), 7.02 (t, J = 7.5 Hz, 1H), 6.77 (dq, J = 18.7, 6.3 Hz, 1H), 5.69 (dd, J = 17.9, 1.7 Hz, 1H), 1.86 (d, J = 6.3 Hz, 3H) ppm; ^{13}C {^{1}H} NMR (DMSO-d_6, 125.8 MHz): δ 166.4, 145.9, 145.7, 133.5, 128.3, 120.7, 119.1, 118.1, 22.1 ppm; ^{11}B NMR (EtOAc, 128.4 MHz,): δ 28.4 ppm; IR: ν = 3315, 3201, 1608, 1517, 1485, 1362, 986, 754 cm^{-1}; HRMS (ES+) m/z calcd for $C_{10}H_{12}BN_2O$ $[M + H]^+$ 187.1043, found 187.1048.

*2-Methyl-1,3,2-benzodiazaborininone (**4p**).* Obtained as a white solid by procedure A after purifying via a plug of silica gel with EtOAc/hexane (1:1) as eluent (86 mg, 54%, 1.0 mmol scale) and procedure B-1 (86 mg, 62%, 1.0 mmol scale); mp: 181−182 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 8.20 (d, J = 6.8 Hz, 1H), 7.50 (t, J = 6.8 Hz, 1H), 7.12 (t, J = 7.2 Hz, 2H), 6.98 (d, J = 7.3 Hz, 1H), 6.40 (s, 1H), 0.59 (s, 3H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 166.5, 144.4, 133.8, 129.2, 121.6, 118.7, 117.2 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 32.3 ppm; IR: ν = 3267, 3190, 1609, 1519, 1486, 1364, 909, 749 cm^{-1}; HRMS (CI) m/z calcd for $C_8H_9BN_2O$ $[M]^+$ 160.0808, found 160.0808.

*2-Cyclopropyl-1,3,2-benzodiazaborininone (**4q**).* Obtained as a white solid by procedure A (121 mg, 65%, 1.0 mmol scale) and procedure B-1 (108 mg, 58%, 1.0 mmol scale); mp: 186−188 °C; ^{1}H NMR (DMSO-d_6, 500.4 MHz): δ 8.98 (s, 1H), 8.50 (s, 1H), 7.90 (dd,

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J = 7.9, 1.4 Hz, 1H), 7.47 (td, J = 7.8, 1.6 Hz, 1H), 7.17 (d, J = 8.0 Hz, 1H), 6.99 (t, J = 7.5 Hz, 1H), 0.68 (dt, J = 9.2, 2.5 Hz, 2H), 0.65−0.59 (m, 2H), 0.05 (ddd, J = 9.2, 6.5, 2.9 Hz, 1H) ppm; ^{13}C {^{1}H} NMR (DMSO-d_6, 125.8 MHz): δ 166.2, 145.8, 133.4, 128.2, 120.4, 118.7, 117.8, 5.4 ppm; ^{11}B NMR (EtOAc, 128.4 MHz): δ 30.4 ppm; IR: ν = 3380, 3308, 3189, 1615, 1557, 1488, 1393, 1254, 752 cm^{-1}; HRMS (ES+) m/z calcd for $C_{10}H_{12}BN_2O$ $[M + H]^+$ 187.1043, found 187.1048.

Procedure C: Condensation of Boronic Acids To Form Oxazaborininones. To a round-bottomed flask with a stir bar were added the appropriate boronic acid (1 equiv) and either anthranilic acid or salicylamide (1 equiv) followed by toluene (4 mL/mmol). The flask was equipped with a Dean−Stark trap, and the reaction was heated to reflux. The reaction was stirred at this temperature overnight. After this time, the solvent was removed *in vacuo* by rotary evaporation, giving a crude solid. The resulting solid was further purified by washing with hexane/EtOAc (1:1), affording the desired, pure oxazaborininone.

*2-Phenyl-3,1,2-benzoxazaborininone (**5a**).* Obtained as a white solid by procedure B-1 (367 mg, 83%, 2.0 mmol scale) and procedure C (650 mg, 93%, 3.0 mmol scale); mp: 211−212 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 8.21 (d, J = 7.8 Hz, 1H), 7.95 (d, J = 6.9 Hz, 2H), 7.64−7.59 (m, 1H), 7.58−7.53 (m, 1H), 7.48 (t, J = 7.4 Hz, 2H), 7.20 (t, J = 7.5 Hz, 1H), 7.09 (d, J = 8.1 Hz, 1H), 6.89 (s, 1H) ppm; ^{13}C {^{1}H} NMR (DMSO-d_6, 125.8 MHz): δ 161.8, 146.1, 135.8, 133.8, 131.8, 130.1, 128.3, 122.2, 118.1, 114.9 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 28.9 ppm; IR: ν = 3315, 1685, 1613, 1484, 1431, 1271, 1227, 750, 692 cm^{-1}; HRMS (ES+) m/z calcd for $C_{13}H_{11}BNO_2$ $[M + H]^+$ 224.0883, found 224.0904.

*2-(p-Tolyl)-3,1,2-benzoxazaborininone (**5b**).* Obtained as an off-white solid by procedure B-1 (408 mg, 86%, 2.0 mmol scale) and procedure C (230 mg, 97%, 2.0 mmol scale); mp: 220−221 °C; ^{1}H NMR (DMSO-d_6, 500.4 MHz): δ 9.66 (s, 1H), 7.94 (d, J = 7.9 Hz, 1H), 7.88 (d, J = 7.8 Hz, 2H), 7.67−7.62 (m, 1H), 7.33 (d, J = 8.1 Hz, 1H), 7.29 (d, J = 7.6 Hz, 2H), 7.13 (t, J = 7.6 Hz, 1H), 2.35 (s, 3H) ppm; ^{13}C {^{1}H} NMR (DMSO-d_6, 125.8 MHz): δ 161.4, 145.7, 141.3, 135.5, 133.6, 129.7, 128.7, 121.8, 117.7, 114.4, 21.3 ppm; ^{11}B NMR (MeCN, 128.4 MHz): δ 29.2 ppm; IR: ν = 3307, 1701, 1613, 1485, 1280, 756, 695, 626 cm^{-1}; HRMS (ES+) m/z calcd for $C_{14}H_{13}BNO_2$ $[M + H]^+$ 238.1039, found 238.1033.

*2-(4-Methoxyphenyl)-3,1,2-benzoxazaborininone (**5c**).* Obtained as a white solid by procedure B-1 (154 mg, 61%, 1.0 mmol scale) and procedure C after an additional wash with *t*-BuOH (364 mg, 72%, 2.0 mmol scale); mp: 205−206 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 8.18 (d, J = 7.8 Hz, 1H), 7.88 (d, J = 8.5 Hz, 2H), 7.61−7.54 (m, 1H), 7.16 (t, J = 7.5 Hz, 1H), 7.04 (d, J = 8.1 Hz, 1H), 6.99 (d, J = 8.6 Hz, 2H), 6.75 (s, 1H), 3.87 (s, 3H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 162.5, 161.8, 146.2, 135.9, 135.8, 130.1, 122.1, 118.0, 114.7, 114.1, 55.5 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 28.6 ppm; IR: ν = 3340, 1698, 1599, 1428, 1281, 1251, 1224, 1180, 753, 693 cm^{-1}; HRMS (ES+) m/z calcd for $C_{14}H_{13}BNO_3$ $[M + H]^+$ 254.0988, found 254.0984.

*2-(4-(Trifluoromethyl)phenyl)-3,1,2-benzoxazaborininone (**5d**).* Obtained as a white solid by procedure B-1 (226 mg, 78%, 1.0 mmol scale); mp: >260 °C; ^{1}H NMR (DMSO-d_6, 500.4 MHz): δ 9.50 (s, 1H), 8.12 (d, J = 7.8 Hz, 2H), 7.93 (d, J = 7.7 Hz, 1H), 7.81 (d, J = 7.9 Hz, 2H), 7.62 (t, J = 7.4 Hz, 1H), 7.28 (d, J = 8.1 Hz, 1H), 7.09 (t, J = 7.5 Hz, 1H) ppm; ^{13}C NMR (DMSO-d_6, 126 MHz): δ 162.1, 146.7, 136.0, 134.5, 131.4 (q, J = 31.4 Hz), 130.4, 124.9 (q, J = 272 Hz), 125.0 (q, J = 3.5 Hz), 122.0, 118.2, 115.0 ppm; ^{19}F {^{1}H} NMR (DMSO-d_6, 470.8 MHz): δ −61.3 ppm; ^{11}B NMR (EtOAc, 128.4 MHz): δ 28.8 ppm; IR: ν = 3307, 1686, 1615, 1326, 1265, 1149, 1108, 1071, 759, 635 cm^{-1}; HRMS (ES+) m/z calcd for $C_{14}H_{10}BNO_2F_3$ $[M + H]^+$ 292.0757, found 292.0753.

*2-(4-Acetylphenyl)-3,1,2-benzoxazaborininone (**5e**).* Obtained as a white solid by procedure B-1 (313 mg, 59%, 2.0 mmol scale); mp: 252−253 °C; ^{1}H NMR (DMSO-d_6, 500.4 MHz): δ 9.64 (s, 1H), 8.09 (d, J = 7.9 Hz, 2H), 8.03 (d, J = 7.9 Hz, 2H), 7.96 (d, J = 7.8 Hz, 1H), 7.65 (t, J = 7.5 Hz, 1H), 7.32 (d, J = 8.1 Hz, 1H), 7.13 (t, J = 7.5 Hz, 1H), 2.62 (s, 3H) ppm; ^{13}C {^{1}H} NMR (DMSO-d_6, 125.8 MHz): δ 198.7, 162.0, 146.5, 139.2, 136.1, 134.1, 130.3, 128.0, 122.3, 118.3, 115.1, 27.5 ppm; ^{11}B NMR (acetone-d_6, 128 MHz): δ 27.6 ppm; IR: ν = 3308, 1668, 1614, 1484, 1399, 1261, 1233, 760, 628 cm^{-1}; HRMS (ES+) m/z calcd for $C_{15}H_{13}BNO_3$ $[M + H]^+$ 266.0988, found 266.0983.

*2-(3-Cyanophenyl)-3,1,2-benzoxazaborininone (**5f**).* Obtained as an off-white solid by procedure B-1 (136 mg, 55%, 1.0 mmol scale) and procedure C (677 mg, 91%, 3.0 mmol scale); mp: >260 °C; ^{1}H NMR (DMSO-d_6, 500.4 MHz): δ 9.33 (s, 1H), 8.26 (s, 1H), 8.15 (d, J = 7.5 Hz, 1H), 7.90 (d, J = 7.6 Hz, 2H), 7.64 (t, J = 7.6 Hz, 1H), 7.59 (t, J = 7.5 Hz, 1H), 7.21 (d, J = 8.1 Hz, 1H), 7.06 (t, J = 7.5 Hz, 1H) ppm; ^{13}C {^{1}H} NMR (DMSO-d_6, 125.8 MHz): δ 162.1, 146.8, 138.1, 137.2, 136.0, 134.5, 130.4, 129.6, 121.8, 119.5, 118.1, 114.8, 111.8 ppm; ^{11}B NMR (acetone-d_6, 128 MHz): δ 27.1 ppm; IR: ν = 3313, 2235, 1694, 1621, 1526, 1483, 1279, 753, 688, 524 cm^{-1}; HRMS (ES+) m/z calcd for $C_{14}H_{10}BN_2O_2$ $[M + H]^+$ 249.0835, found 249.0836.

*2-(2-Nitrophenyl)-3,1,2-benzoxazaborininone (**5g**).* Obtained as a light yellow solid by procedure B-1 (81 mg, 30%, 1.0 mmol scale) and procedure C (498 mg, 93%, 2.0 mmol scale); mp: 210−211 °C; ^{1}H NMR (DMSO-d_6, 500.4 MHz): δ 9.43 (s, 1H), 8.25 (d, J = 8.2 Hz, 1H), 7.98 (d, J = 7.8 Hz, 1H), 7.92−7.85 (m, 2H), 7.76 (t, J = 7.3 Hz, 1H), 7.65 (t, J = 7.5 Hz, 1H), 7.19−7.13 (m, 2H) ppm; ^{13}C {^{1}H} NMR (DMSO-d_6, 125.8 MHz): δ 161.8, 151.3, 146.5, 136.3, 135.1, 134.3, 131.6, 130.4, 123.8, 122.5, 118.2, 114.8 ppm; ^{11}B NMR (methanol-d_4, 128 MHz): δ 27.0 ppm; IR: ν = 3348, 1698, 1510, 1484, 1342, 1266, 756, 724, 695 cm^{-1}; HRMS (ES+) m/z calcd for $C_{13}H_{10}BN_2O_4$ $[M + H]^+$ 269.0734, found 269.0741.

*2-(Thiophen-3-yl)-3,1,2-benzoxazaborininone (**5h**).* Obtained as an off-white solid by procedure B-1 (147 mg, 64%, 1.0 mmol scale) and procedure C after washing with *t*-BuOH (400 mg, 87%, 3.0 mmol scale); mp: 227−229 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 8.19 (d, J = 7.9 Hz, 1H), 8.13 (s, 1H), 7.60 (t, J = 7.7 Hz, 1H), 7.53 (d, J = 4.8 Hz, 1H), 7.49−7.43 (m, 1H), 7.19 (t, J = 7.6 Hz, 1H), 7.07 (d, J = 8.1 Hz, 1H), 6.77 (s, 1H) ppm; ^{13}C {^{1}H} NMR (DMSO-d_6, 125.8 MHz): δ 161.7, 146.1, 136.7, 135.9, 131.6, 130.1, 127.0, 122.2, 118.0, 114.9 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 27.0 ppm; IR: ν = 3295, 1694, 1619, 1524, 1483, 1273, 1096, 695, 658, 521 cm^{-1}; HRMS (ES+) m/z calcd for $C_{11}H_9BNO_2S$ $[M + H]^+$ 230.0447, found 230.0445.

*2-(1-Methyl-1H-indol-5-yl)-3,1,2-benzoxazaborininone (**5i**).* Obtained as a white solid by procedure B-1 (138 mg, 50%, 1.0 mmol scale) and procedure C (524 mg, 95%, 2.0 mmol scale); mp: >260 °C; ^{1}H NMR (DMSO-d_6, 500.4 MHz): δ 9.65 (s, 1H), 8.28 (s, 1H), 7.95 (d, J = 7.8 Hz, 1H), 7.79 (d, J = 8.3 Hz, 1H), 7.64 (t, J = 8.3 Hz, 1H), 7.53 (d, J = 8.3 Hz, 1H), 7.38−7.34 (m, 2H), 7.12 (t, J = 7.5 Hz, 1H), 6.53 (d, J = 2.8 Hz, 1H), 3.81 (s, 3H) ppm; ^{13}C {^{1}H} NMR (DMSO-d_6, 125.8 MHz): δ 161.9, 146.4, 138.8, 135.8, 130.6, 130.1, 128.3, 127.6, 126.4, 122.0, 118.0, 114.7, 109.8, 101.5, 32.9 ppm; ^{11}B NMR (acetone-d_6, 128 MHz): δ 28.7 ppm; IR: ν = 3285, 1693, 1612, 1520, 1485, 1293, 1268, 1175, 753, 717, 697 cm^{-1}; HRMS (ES+) m/z calcd for $C_{16}H_{14}BN_2O_2$ $[M + H]^+$ 277.1148, found 277.1147.

*2-Vinyl-3,1,2-benzoxazaborininone (**5j**).* Obtained as an off-white solid by procedure B-1 (142 mg, 41%, 2.0 mmol scale); mp: 140−141 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): 8.14 (d, J = 8.6 Hz, 1H), 7.55 (td, J = 7.7, 1.5 Hz, 1H), 7.15 (t, J = 7.6 Hz, 1H), 6.98 (d, J = 8.1 Hz, 1H), 6.51 (s, 1H), 6.41 (dd, J = 19.1, 3.6 Hz, 1H), 6.16 (dd, J = 13.6, 3.4 Hz, 1H), 6.07 (dd, J = 19.1, 13.6 Hz, 1H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 161.8, 144.2, 137.2, 135.5, 131.1, 122.9, 117.1, 115.6 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 27.6 ppm; IR: ν = 3265, 1706, 1618, 1516, 1486, 1351, 1283, 1175. 755, 694 cm^{-1}; HRMS (ES+) m/z calcd for $C_9H_9BNO_2$ $[M + H]^+$ 174.0726, found 174.0730.

*2-Phenethyl-3,1,2-benzoxazaborininone (**5k**).* Obtained as a yellow solid by procedure B-1 (377 mg, 75%, 2.0 mmol scale); mp: 100−102 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 8.12 (d, J = 7.9 Hz, 1H), 7.52 (td, J = 8.2, 1.5 Hz, 1H), 7.30 (t, J = 7.5 Hz, 2H), 7.26−7.23 (m, 2H), 7.22−7.17 (m, 1H), 7.13 (t, J = 7.6 Hz, 1H), 6.84 (d, J = 8.0 Hz, 1H), 6.23 (s, 1H), 2.91 (t, J = 8.0 Hz, 2H), 1.50 (t, J = 8.0 Hz, 2H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 161.9, 144.1, 143.6, 135.5, 131.0, 128.7, 128.1, 126.1, 122.8, 116.8, 115.2, 29.8 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 32.7 ppm; IR: ν = 3118, 1689, 1619,

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1520, 1489, 1276, 1131, 757, 693 cm^{-1}; HRMS (ES+) m/z calcd for $C_{15}H_{15}BNO_2$ $[M + H]^+$ 252.1196, found 252.1196.

*2-Cyclopropyl-3,1,2-benzoxazaborininone (**5l**).* Obtained as a beige solid by procedure B-1 after washing with 5:1 hexane/EtOAc instead of straight EtOAc (137 mg, 73%, 1.0 mmol scale) and procedure C (516 mg, 92%, 3.0 mmol scale); mp: 155−156 °C; ^1H NMR ($CDCl_3$, 500.4 MHz): δ 8.07 (d, J = 7.8 Hz, 1H), 7.52 (t, J = 7.7 Hz, 1H), 7.08 (t, J = 7.6 Hz, 1H), 6.94 (d, J = 8.1 Hz, 1H), 6.58 (s, 1H), 0.82−0.71 (m, 4H), 0.02 (tt, J = 8.7, 6.6 Hz, 1H) ppm; ^{13}C $\{^1H\}$ NMR ($CDCl_3$, 125.8 MHz): δ 162.1, 144.4, 135.3, 130.7, 122.0, 116.5, 114.8, 5.0 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 32.3 ppm; IR: ν = 3270, 1699, 1615, 1515, 1486, 1442, 1163, 755 cm^{-1}; HRMS (ES+) m/z calcd for $C_{10}H_{11}{}^{10}BNO_2$ $[M + H]^+$ 187.0919, found 187.0925.

Procedure B-2: Cyclization of Potassium Trifluoroborates Activated with Silica Gel To Form 1,3,2-Benzoxazaborininones. To a microwave vial with a stir bar were added salicylamide (1.0 equiv) and the appropriate potassium organotrifluoroborates (1.05 equiv) along with oven-dried silica gel (100 mg/mmol). The reaction vessel was capped and purged with argon, and subsequently dry MeOH was added (3 mL/mmol). The reaction was then heated at 60 °C for 16 h. Upon cooling to rt, the reaction mixture was filtered through a short pad Celite and flushed with additional MeOH. Removal of the solvent *in vacuo* afforded the desired 1,3,2-benzoxazaborininone product.

*2-Phenyl-1,3,2-benzoxazaborininone (**6a**).* Obtained as a white solid by procedure B-2 after recrystallization from $CHCl_3$ (123 mg, 55%, 1.0 mmol scale) and procedure C (2.75 g, 81%, 10.0 mmol scale); mp: 195−196 °C; ^1H NMR ($CDCl_3$, 500.4 MHz): δ 8.25 (s, 1H), 8.22 (dd, J = 7.8, 1.6 Hz, 1H), 8.01 (d, J = 6.8 Hz, 2H), 7.70−7.64 (m, 1H), 7.61−7.56 (m, 1H), 7.52 (t, J = 7.3 Hz, 2H), 7.41 (d, J = 8.2 Hz, 1H), 7.32 (t, J = 7.5 Hz, 1H) ppm; ^{13}C $\{^1H\}$ NMR ($CDCl_3$, 125.8 MHz): δ 165.3, 155.8, 134.8, 133.3, 132.1, 128.4, 128.3, 123.7, 119.5, 119.1 ppm; ^{11}B NMR (128.4 MHz, $CDCl_3$): δ 32.2 ppm; IR: ν = 3202, 3101, 1688, 1471, 11373, 1276, 1245, 758, 629 cm^{-1}; HRMS (ES+) m/z calcd for $C_{13}H_{11}BNO_2$ $[M + H]^+$ 224.0883, found 224.0880.

*2-(p-Tolyl)-1,3,2-benzoxazaborininone (**6b**).* Obtained as a white solid by procedure B-2 after recrystallization from $CHCl_3$ (156 mg, 66%, 1.0 mmol scale) and procedure C (1.32 g, 90%, 5.0 mmol scale); mp: 200−202 °C; ^1H NMR ($CDCl_3$, 500.4 MHz): δ 8.20 (dd, J = 7.8, 1.7 Hz, 1H), 7.97 (s, 1H), 7.87 (d, J = 7.9 Hz, 2H), 7.66 (td, J = 7.8, 1.7 Hz, 1H), 7.39 (d, J = 8.3 Hz, 1H), 7.34−7.28 (m, 3H), 2.44 (s, 3H) ppm; ^{13}C $\{^1H\}$ NMR ($CDCl_3$, 125.8 MHz): δ 165.1, 155.9, 142.6, 134.8, 133.3, 129.1, 128.3, 123.6, 119.4, 119.1, 21.7 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 30.7 ppm; IR: ν = 3210, 3098, 1667, 1609, 1454, 1372, 1276, 860, 760 cm^{-1}; HRMS (ES+) m/z calcd for $C_{14}H_{13}BNO_2$ $[M + H]^+$ 238.1039, found 238.1031.

*2-(4-Methoxyphenyl)-1,3,2-benzoxazaborininone (**6c**).* Obtained as a white solid by procedure B-2 after recrystallization from $CHCl_3$ (106 mg, 42%, 1.0 mmol scale) and procedure C (466 mg, 92%, 2.0 mmol scale); mp: 231−233 °C; ^1H NMR ($CDCl_3$, 500.4 MHz): δ 8.19 (d, J = 8.2 Hz, 1H), 7.89 (d, J = 8.3 Hz, 2H), 7.66 (t, J = 7.7 Hz, 1H), 7.58 (s, 1H), 7.38 (d, J = 8.3 Hz, 1H), 7.30 (t, J = 7.3 Hz, 1H), 7.03 (d, J = 8.3 Hz, 2H), 3.90 (s, 3H) ppm; ^{13}C $\{^1H\}$ NMR ($CDCl_3$, 125.8 MHz): δ 164.8, 162.9, 155.9, 135.1, 134.8, 128.4, 123.5, 119.3, 119.0, 113.9, 55.1 ppm; ^{11}B NMR (THF, 128.4 MHz): δ 31.2 ppm; IR: ν = 3203, 1680, 1471, 1454, 1373, 1334, 1247, 756, 708 cm^{-1}; HRMS (ES+) m/z calcd for $C_{14}H_{13}BNO_3$ $[M + H]^+$ 254.0991, found 254.0991.

*2-(4-(Trifluoromethyl)phenyl)-1,3,2-benzoxazaborininone (**6d**).* Obtained as a white solid by procedure B-2 after recrystallization from $CHCl_3$ (167 mg, 57%, 1.0 mmol scale); mp: 245−246 °C; ^1H NMR ($CDCl_3$, 500.4 MHz): δ 8.21 (dd, J = 7.8, 1.6 Hz, 1H), 8.08 (d, J = 8.0 Hz, 2H), 7.97 (s, 1H), 7.76 (d, J = 8.2 Hz, 2H), 7.69 (td, J = 7.6, 1.5 Hz, 1H), 7.42 (d, J = 8.3 Hz, 1H), 7.34 (t, J = 7.6 Hz, 1H) ppm; ^{13}C $\{^1H\}$ NMR ($CDCl_3$, 125.8 MHz): δ 165.0, 155.8, 135.4, 134.0 (q, J = 32.5 Hz), 133.8, 128.7, 125.2 (q, J = 3.7 Hz), 124.3, 124.0 (d, J = 272.5 Hz), 119.7, 119.4 ppm; ^{19}F $\{^1H\}$ NMR ($CDCl_3$, 470.8 MHz): δ −63.2 ppm; ^{11}B NMR (MeCN, 128.4 MHz): δ 31.6 ppm; IR: ν = 3172, 3100, 1683, 1614, 1323, 1108, 1097, 1069, 865, 835, 755, 636 cm^{-1}; HRMS (ES+) m/z calcd for $C_{14}H_{10}BNO_2F_3$ $[M + H]^+$ 292.0757, found 292.0750.

*2-(4-Acetylphenyl)-1,3,2-benzoxazaborininone (**6e**).* Obtained as a white solid by procedure C (398 mg, 75%, 2.0 mmol scale); mp: 236−238 °C; ^1H NMR ($CDCl_3$, 500.4 MHz): δ 8.21 (dd, J = 7.8, 1.7 Hz, 1H), 8.06 (dd, J = 10.3, 8.5 Hz, 4H), 7.91 (s, 1H), 7.69 (td, J = 7.8, 1.7 Hz, 1H), 7.42 (d, J = 8.2 Hz, 1H), 7.34 (t, J = 7.5 Hz, 1H), 2.67 (s, 3H) ppm; ^{13}C $\{^1H\}$ NMR ($CDCl_3$, 125.8 MHz): δ 197.9, 164.7, 155.6, 139.7, 135.1, 133.5, 128.5, 127.8, 124.0, 119.4, 119.1, 26.7 ppm; ^{11}B NMR (THF, 128.4 MHz): δ 31.4 ppm; IR: ν = 3158, 3100, 2985, 1687, 1673, 1402, 1258, 864, 753, 619 cm^{-1}; HRMS (ES+) m/z calcd for $C_{15}H_{13}BNO_3$ $[M + H]^+$ 266.0988 found 266.0990.

*2-(2-Methoxyphenyl)-1,3,2-benzoxazaborininone (**6f**).* Obtained as a white solid by procedure B-2 after further washing with acetone (89 mg, 35%, 1.0 mmol scale) and procedure C (454 mg, 90%, 2.0 mmol scale); mp: 169−171 °C; ^1H NMR (THF-d_8, 500.4 MHz): δ 8.59 (s, 1H), 8.12 (dd, J = 7.8, 1.6 Hz, 1H), 8.06 (dd, J = 7.4, 1.6 Hz, 1H), 7.67−7.62 (m, 1H), 7.56−7.46 (m, 1H), 7.38 (dd, J = 8.3, 0.6 Hz, 1H), 7.27 (t, J = 7.5 Hz, 1H), 7.06 (t, J = 7.4 Hz, 2H), 3.97 (s, 3H) ppm; ^{13}C $\{^1H\}$ NMR (THF-d_8, 125.8 MHz): δ 165.2, 163.0, 155.9, 135.6, 134.0, 133.4, 127.9, 123.0, 120.2, 118.6, 110.2, 54.6 ppm; ^{11}B NMR (THF-d_8, 128.4 MHz): δ 31.4 ppm; IR: ν = 3397, 1694, 1598, 1468, 1420, 1365, 1243, 767, 752 cm^{-1}; HRMS (ES+) m/z calcd for $C_{14}H_{13}BNO_3$ $[M + H]^+$ 254.0988, found 254.0981.

*2-(Thiophen-3-yl)-1,3,2-benzoxazaborininone (**6g**).* Obtained as a white solid by procedure B-2 after further washing with acetone (44 mg, 19%, 1.0 mmol scale) and procedure C (408 mg, 89%, 2.0 mmol scale); mp: 215−217 °C; ^1H NMR ($CDCl_3$, 500.4 MHz): δ 8.24−8.18 (m, 2H), 8.11 (s, 1H), 7.70−7.63 (m, 1H), 7.60 (dd, J = 4.8, 0.9 Hz, 1H), 7.50 (dd, J = 4.8, 2.7 Hz, 1H), 7.38 (d, J = 8.3 Hz, 1H), 7.31 (t, J = 7.5 Hz, 1H) ppm; ^{13}C $\{^1H\}$ NMR ($CDCl_3$, 125.8 MHz): δ 165.3, 155.9, 136.5, 134.9, 130.7, 128.4, 126.4, 123.6, 119.4, 119.0 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 29.7 ppm; IR: ν = 3163, 3102, 1679, 1469, 1385, 1263, 1244, 760, 662 cm^{-1}; HRMS (ES+) m/z calcd for $C_{11}H_9BNO_2S$ $[M + H]^+$ 230.0447, found 230.0463.

*2-(1-Methyl-1H-indol-5-yl)-1,3,2-benzoxazaborininone (**6h**).* Obtained as a beige solid by procedure B-2 after recrystallization from $CHCl_3$ (41 mg, 15%, 1.0 mmol scale) and procedure C (528 mg, 95%, 2.0 mmol scale); mp: 244−246 °C; ^1H NMR ($CDCl_3$, 500.4 MHz): δ 8.27 (s, 1H), 8.19 (dd, J = 7.8, 1.7 Hz, 1H), 7.75 (d, J = 8.3 Hz, 1H), 7.70−7.62 (m, 2H), 7.43 (dd, J = 12.4, 8.3 Hz, 2H), 7.28 (t, J = 7.5 Hz, 1H), 7.12 (d, J = 3.1 Hz, 1H), 6.61 (s, 1H), 3.85 (s, 3H) ppm; ^{13}C $\{^1H\}$ NMR ($CDCl_3$, 125.8 MHz): δ 165.0, 156.1, 139.0, 134.7, 129.5, 128.5, 128.3, 127.4, 125.8, 123.3, 119.4, 119.0, 109.2, 101.9, 32.8 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 29.9 ppm; IR: ν = 3210, 2185, 3097, 1680, 1601, 1372, 1242, 1184, 1177, 759, 622, 598 cm^{-1}; HRMS (ES+) m/z calcd for $C_{16}H_{14}BN_2O_2$ $[M + H]^+$ 277.1148, found 277.1157.

*2-Phenethyl-1,3,2-benzoxazaborininone (**6i**).* Obtained as a white solid by procedure B-2 after further washing with acetone (75 mg, 30%, 1.0 mmol scale); mp: 115−116 °C; ^1H NMR ($CDCl_3$, 500.4 MHz): δ 8.13 (dd, J = 7.8, 1.6 Hz, 1H), 7.65−7.59 (m, 1H), 7.40 (s, 1H), 7.33−7.25 (m, 6H), 7.21 (t, J = 7.2 Hz, 1H), 2.93 (t, J = 8.1 Hz, 2H), 1.53 (t, J = 8.1 Hz, 2H) ppm; ^{13}C $\{^1H\}$ NMR ($CDCl_3$, 125.8 MHz): δ 164.6, 155.7, 143.2, 134.7, 128.4, 128.3, 127.8, 125.9, 123.5, 119.3, 118.8, 29.4 ppm; ^{11}B NMR (acetonitrile, 128.4 MHz): δ 32.7 ppm; IR: ν = 3105, 2928, 1688, 1468, 1373, 1348, 752, 731, 699 cm^{-1}; HRMS (CI) m/z calcd for $C_{15}H_{15}BNO_2$ $[M + H]^+$ 252.1196, found 252.1194.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.7b00747.

Aqueous stability studies, computed properties for azaborininones and isosteres, methods and data for computational pK_a evaluation, geometry optimized Cartesian coordinates for computed molecules, along

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with ^{1}H, ^{13}C, ^{19}F, and ^{11}B NMR spectra for all compounds (PDF)

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Notes

The authors declare no competing financial interest.

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