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Synthesis of Functionalized 1,3,2-Benzodiazaborole Cores Using Bench-Stable Components

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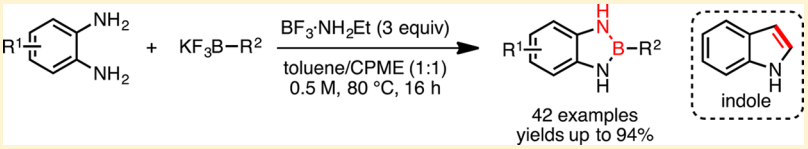
Supporting Information



ABSTRACT: The azaborine motif provides a unique opportunity to develop core isosteres by inserting B–N units in place of C=C bonds within aromatic scaffolds, creating new pseudoaromatic building blocks that retain comparable structural features. Previous synthetic routes to the 1,3,2-benzodiazaborole core have used organoboron dichlorides and boronic acids as the boron precursors. The transformation developed herein utilizes entirely bench stable starting materials, including organotrifluoroborates, enabling a wider array of substrate analogues under facile reaction conditions. Furthermore, physical, structural, and electronic properties of these compounds were explored computationally to understand the influence of the B–N replacement on the structure, aromaticity, and isosteric viability of these analogues.

INTRODUCTION

The ability to create isosteric compounds that alter both the bioavailability and reactivity of molecules without significantly modifying the geometrical shape (isostructural) or the electronic distribution (isoelectronic) of that within the parent structure molecule provides a great advantage for drug development[1] and other chemistry-oriented applications.[2] To that end, B–N isosterism for a carbon–carbon double bond (Figure 1) affords an opportunity to create new core isosteric

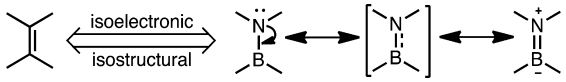


Figure 1. B–N isosterism for C=C bonds.

building blocks for aromatic systems (azaborines). Since the initial synthesis of borazine, a completely inorganic isostere of benzene and the first member of the azaborine class,[3] a whole range of azaborines have been prepared.[4a,b] Further analysis of these cores revealed their unique spectroscopic[4c] and medicinal properties.[4d–f]

The indole structural motif has a demonstrated prominence in biological targets,[5] and therefore accessing isosteric species would be of value for both academic and pharmaceutical applications. Currently, there are two known azaborine isosteres of indole: (i) the 1,3,2-benzodiazaborole (**1**), where the 2–3 carbon–carbon double bond is replaced by a B–N bond,[6] and (ii) the "fused" B–N indole[7] (**2**), in which the adjacent bond in the bicycle is exchanged (Figure 2). The indole-azaborine **1** is particularly valuable because it provides access to an indole isostere in one step via chelation of a boron

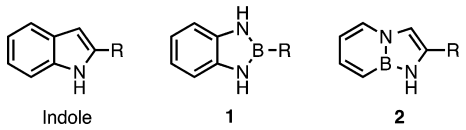


Figure 2. Indole isosteres.

species between the amino groups of *o*-phenylenediamine.[8] Literature reports have revealed the incorporation of different substituents on boron through the use of alkyl-,[8a] trialkyl-,[8b] and dichloroboranes[9a] and, in later contributions, condensation reactions with boronic acids[9b–e] or electron-deficient boronate esters.[9f] The major limitation of the currently available methods is the required use of air- and/or moisture-sensitive boron precursors that limit the diversity within these indole isosteres.

Recently, our group reported the ability to employ bench-stable organotrifluoroborates[10] as precursors for the synthesis of closely related 2,1-borazaronaphthalene cores.[11] This straightforward method enabled access to a library of molecules through activation of the organotrifluoroborate precursors using a fluorophile (e.g., chlorosilane reagents)[12] and subsequent reaction with *o*-aminostyrene derivatives. Application of this strategy to the indole azaborines was envisioned to provide an easily accessible, robust route toward the 1,3,2-benzodiazaborole core in a similar fashion.

RESULTS AND DISCUSSION

Synthetic Method. Initial reaction condition screening, using *o*-phenylenediamine **3a** and phenyltrifluoroborate **4a**,

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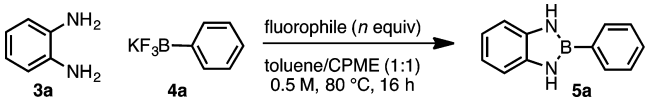
J. Org. Chem. XXXX, XXX, XXX–XXX

indicated that the system established for the 2,1-borazaronaphthalenes[11] could be applied almost directly to the synthesis of 1,3,2-benzodiazaboroles (Table 1). As previously observed, silicon tetrachloride could be used to activate a potassium organotrifluoroborate, generating a highly reactive dichloroborane species,[12] providing good conversion to **5a** (Table 1, entry 1). In exploring more user-friendly fluorophiles, which have recently been shown to activate organotrifluoroborates,[13] we noticed that trivalent, electron-poor boron species could also promote the reaction (Table 1, entries 3−11) but had better effectiveness when used in excess. With boron fluorophiles, initial organotrifluoroborate deprotection generates a difluoroborane species that has significantly poorer reactivity in comparison to the dichloroborane intermediates,[14] thereby requiring excess boron reagent to abstract both of the remaining fluorides. The best results were obtained when using 3 equiv of boron trifluoride ethylamine complex as the fluorophile (Table 1, entry 9), a particularly appealing reagent because it was the sole reagent tested that was a bench-stable solid.

These modified reaction conditions were then applied to prepare 1,3,2-benzodiazaborole analogues using various potassium aryltrifluoroborates (Table 2). In addition to alkyl groups (**5b−d**) and halogens (**5e−g**), the relatively mild reaction conditions enabled vinyl (**5h**), ether (**5i−l,n**) and ester (**5m**) functional groups to be tolerated. Whereas steric hindrance at either the ortho position of the aryltrifluoroborate (**5b,c,e,i,l**) or

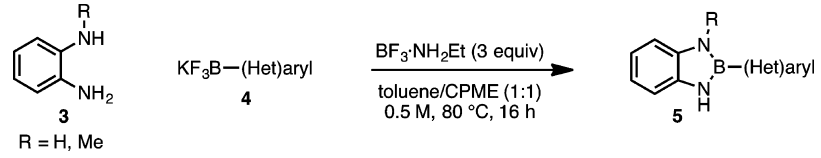
Table 1. Optimization of Fluorophile for Reaction Conditions

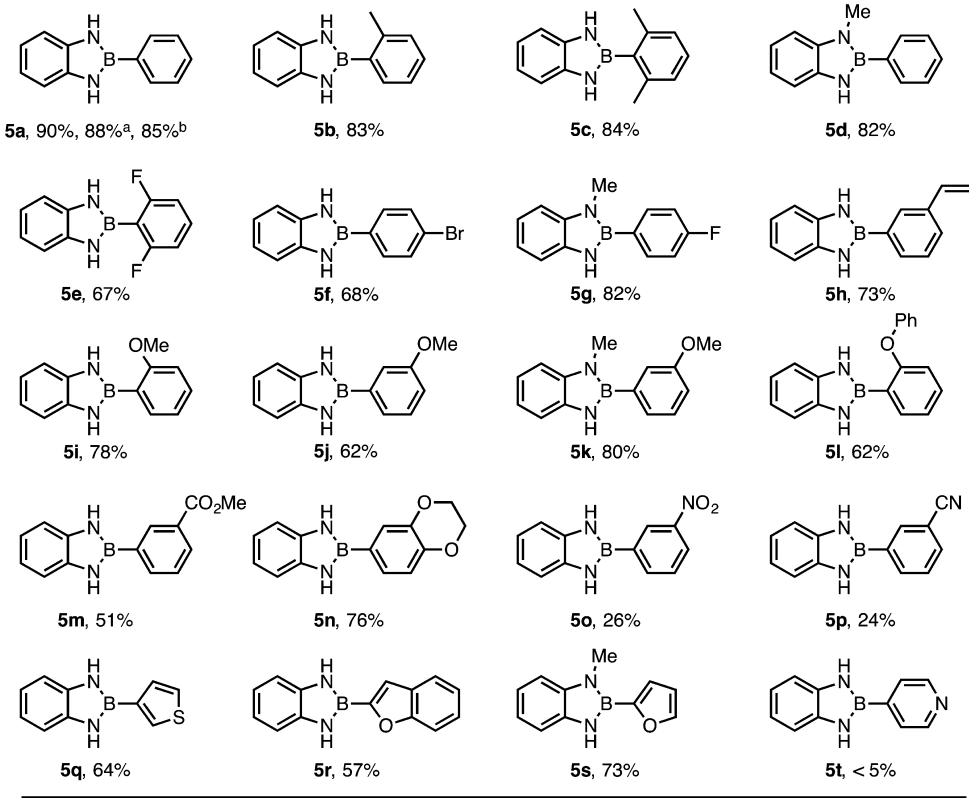


entry	fluorophile	amt, equiv	P:IS[a]
1	$SiCl_4$	1	4.60
2	TMSCl	1	2.49
3	BCl_3 (1.5 M in hexane)	3	4.21
4	$BH_3{\cdot}SMe_2$	3	1.21
5	$BF_3{\cdot}CH_3CN$	3	1.85
6	$BF_3{\cdot}SMe_2$	3	1.60
7	$BF_3{\cdot}THF$	3	0.42
8	$BF_3{\cdot}OEt_2$	3	0.43
9	**$BF_3{\cdot}NH_2Et$**	**3**	**6.85**
10	$BF_3{\cdot}NH_2Et$	2	5.55
11	$BF_3{\cdot}NH_2Et$	1	3.80

[a]Product (P) to internal standard (IS) ratios determined by GCMS using 4,4′-di-*tert*-butylbiphenyl as internal standard.

Table 2. Scope of Reaction with (Hetero)aryltrifluoroborates[c]





[a]Reaction run under ambient atmosphere. [b]Reaction run on 30 mmol scale. [c]Reaction conditions: 1.0 equiv of diamine, 1.0 equiv of potassium organotrifluoroborates, 3.0 equiv of $BF_3{\cdot}NH_2Et$, 1/1 toluene/CPME (0.5 M), 80 °C, 18 h.

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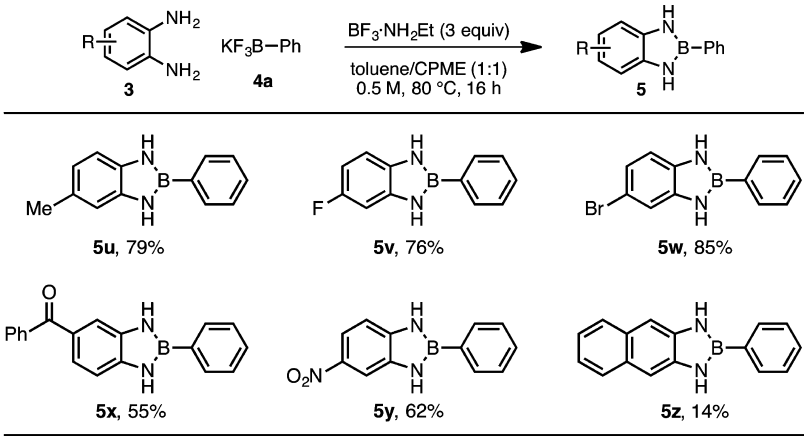
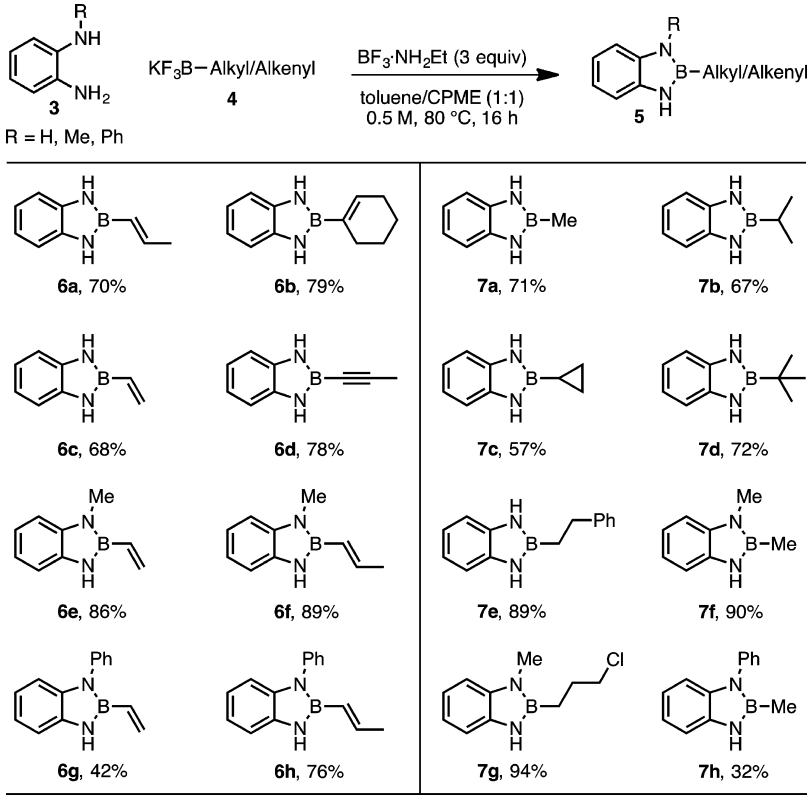
Table 3. Scope of Reaction with Substituted *o*-Phenylenediamines[a]



[a]Reaction conditions: 1.0 equiv of diamine, 1.0 equiv of trifluoroborates, 3.0 equiv of $BF_3{\cdot}NH_2Et$, 1/1 toluene/CPME (0.5 M), 80 °C, 18 h.

Table 4. Scope of Reactions of Alkyl- and Alkenyltrifluoroborates[a]



[a]Reaction conditions: 1.0 equiv of diamine, 1.0 equiv of organotrifluoroborates, 3.0 equiv of $BF_3{\cdot}NH_2Et$, 1/1 toluene/CPME (0.5 M), 80 °C, 18 h.

on one of the diamine nitrogen atoms (**5d**,**g**,**s**) did not deeply affect the reaction, the presence of some electron-withdrawing substituents such as nitro (**5o**) or cyano (**5p**) groups resulted in lower yields. Heteroaryltrifluoroborates containing sulfur (**5q**) or oxygen (**5r**,**s**) atoms were well tolerated. Unfortunately, the method could not be extended to nitrogen-containing heteroaryls such as pyridyl subunits (**5t**).

The utility of this protocol, using all air-stable starting materials, consequently allowed the reaction to proceed even in the absence of an argon purge of the reaction vessel or solvents (88% under air versus 90% under argon for **5a**). It is of note that, for several of the reactions, the only purification required was a basic aqueous (saturated $NaHCO_3$) workup followed by extraction with ethyl acetate, highlighting the ease of access toward these cores. In most remaining cases, the only additional purification required was passage through a flash plug of silica gel.

Desymmetrization of the starting phenylenediamine enabled the synthesis of unsymmetrical azaborine cores (Table 3). Use of functionalized phenylenediamines allowed the facile introduction of versatile synthetic handles such as bromo (**5w**), carbonyl (**5x**), and nitro (**5y**) groups. Some difficulty was encountered when using 2,3-naphthalenediamine (**5z**), presumably because of the heterogeneity of the reaction mixture under these reaction conditions.

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J. Org. Chem. XXXX, XXX, XXX−XXX

The scope of the method was further advanced to other C_{sp^2}-hybridized as well as C_{sp^3}-hybridized groups on the boron atom (Table 4). Alkenyltrifluoroborates were well tolerated under these conditions (Table 4, left), affording the corresponding azaborines in good yields (**6a−c**). An alkynyltrifluoroborate was also utilized to exhibit that the procedure could be extended to sp-hybridized centers (**6d**). *N*-Methylation of the diamine did not affect the reaction (**6e**,**f**), and the presence of a bulky *N*-phenyl group was tolerated when using sterically small organotrifluoroborates (**6g**,**h**). However, only starting diamine was observed when attempting to cyclize such substrates with larger aliphatic or aryl substituents on the organoboron precursors.

Substituted azaborine compounds with C_{sp^3}-hybridized units on the boron (Table 4, right) were found to be less stable than their C_{sp^2}-hybridized counterparts. The *B*-alkyl compounds, when subjected to the standard workup, readily decomposed in the presence of water. This problem was overcome by foregoing the aqueous workup and directly subjecting the reaction mixture to a flash plug of silica, allowing access to pure material in moderate (**7c**) to good yields (**7g**). Once isolated and stored as solids on the benchtop, no degradation of the products were observed. Using this modified workup procedure, primary (**7a**,**e−h**), secondary (**7b**,**c**), and tertiary (**7d**) alkyl substituted azaborines were isolated. *N*-Alkylated diamines could be used as reaction partners, affording the corresponding azaborines, often in very good yields (**7f−h**).

Physical Properties and Computationally Derived Results. With the primary objective of the project achieved (development of a straightforward method of synthesis of the 1,3,2-benzodiazaborole core involving only bench-stable partners), attention was next focused on understanding the potential value and versatility of these indole isosteres. Initially, the pK_a value of the azaborine N−H was determined via bracketing experiments (see the Supporting Information), and a pK_a of roughly 18.2 (in DMSO) was found for the monoalkylated derivative **5d**. This value falls slightly lower than the pK_a for indole (20.9)[15] and significantly below that of the "fused" B−N indole (around 30).[7] Considering the pK_a for aniline (30.6) or phenylacetamide (21.5), the lower pK_a suggests that the 1,3,2-benzodiazaborole anion is better at inductively stabilizing the negative charge generated on deprotonation.

Computational models were further studied as a means of assessing the structural and electronic correlation between azaborine cores and indole. Liu,[16] and more recently Northrop,[9e] previously looked at various computational methods for analyzing the core of the indole-azaborine systems, but we were primarily interested in the effect caused by substitution around the core. All calculations were carried out using Gaussian 09,[17] and the structures were visualized via WebMO.[18] Geometry optimizations were performed in the gas phase at the B3LYP/6-311+G(2d,p) level of theory.[19] Stationary points were characterized by frequency analysis at 298 K. To probe the ring current in these systems, 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 from the center of the bicyclic systems [Center(1)] in the perpendicular direction (Figure 3).

We first evaluated the electrostatic potentials of indole azaborines and their carbon analogues (Figure 4). A pictorial comparison of the electrostatic potential maps for both the 1,3,2-benzodiazaborole core and the "fused" B−N indole core

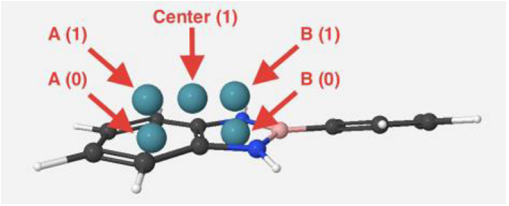

Figure 3. NICS values calculated.

explored by Liu[7] to similar 6−5 aromatic ring systems indicated that they most closely resemble the indole framework. It is thus visually apparent that both azaborines present a greater likeness to indole [compare 2-methylindole (**8a**) and 2-methylbenzimidazole (**9**) to their azaborine analogues **7a** and **2a**], supporting the notion that the B−N bond displays some of the electronic properties of a C=C bond. An even stronger likeness can be seen on comparison of *N*-alkylated azaborines **8b**,**c** to **7f** and **2b**, respectively. The strong similarity between the electrostatic potential maps in these isosteric systems presumably results from enhanced electron availability from the methylated nitrogen within the five-membered ring. In the case of **7f**, although this would enhance electron density, it would also reduce competitive conjugation of the lone pairs of the now desymmetrized nitrogen atoms. Quantitatively, this is observed by a slight lengthening of the MeN−B bond (1.439 Å) in comparison to the HN−B bond (1.435 Å). This factor is also noticed in the indole and "fused" B−N indole, though to lesser extents (see the Supporting Information for a full bond length table). When taken together, these factors lead to an electronic hybrid between **8c** and **8b** where the dimethylated 1,3,2-benzodiazaborole core closely resembles the A ring of **8b** while having a B ring more similar to that of **8c**.

Nuclear independent chemical shift (NICS) calculations[20] were performed to assess the relative aromatic character of each ring (Table 5). NICS calculations provide quantitative correlations for aromaticity using "theoretical nuclei" at the center of a ring system to probe electron shielding.[20] A more negative NICS value indicates greater electron shielding via a stronger ring current and thus more π-electron delocalization. Enhanced delocalization is indicative of greater aromatic character. Because of ring current effects, only rings of similar size can be compared.[21] Across a selection of several molecules (Table 5), a few preliminary trends for the indole-azaborines can be ascertained. Initially, an increase in aromaticity in the A ring from *o*-phenylenediamine **3** to the cyclized azaborine products was observed, presumably caused by the nitrogen lone pairs becoming locked in plane with the rest of the π cloud upon annulation. Furthermore, the A rings of the 1,3,2-benzodiazaborole **7a** share values similar to those for the corresponding indole **8a** and benzimidazole **9**. However, on examination of the B ring, there is a lower electron shielding effect for the azaborine, presumably caused by incomplete π delocalization with the B−N bond. This is confirmed by the NICS calculation for "fused" B−N indole **2a**, where lower electron shielding occurs in both rings caused by the conjoined B−N bond. Similar values for related compounds have been observed by Liu.[16] Furthermore, B-ring deshielding is perturbed by the hybridization of groups bound to boron (**5a−7a**, **6d**), presumably caused by orbital overlap or the electron-donating character of these functional groups. This hybridization effect has been previously observed within the benzene-azaborine

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J. Org. Chem. XXXX, XXX, XXX−XXX

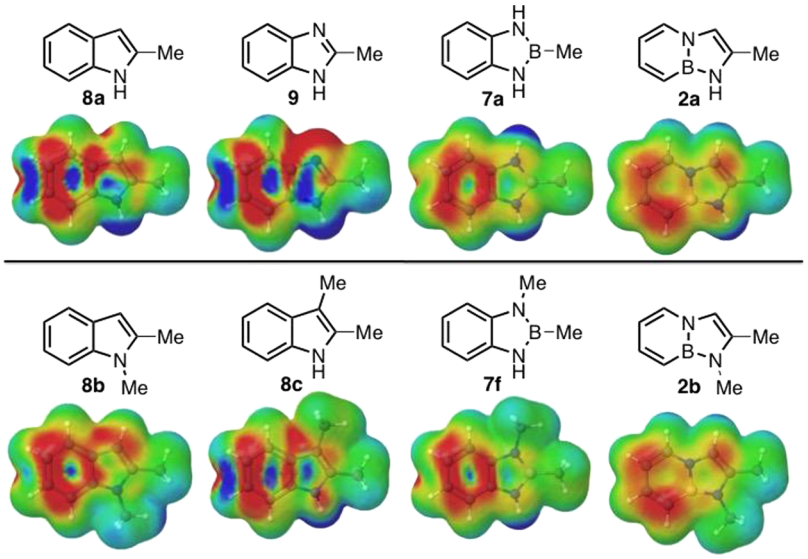
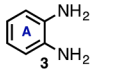
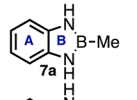
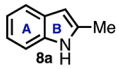
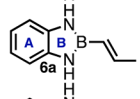
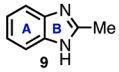
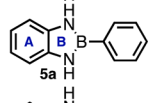
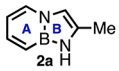
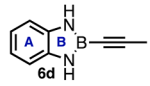


Figure 4. Electrostatic potentials (from +31.38 to −31.38 kcal/mol) of the 1,3,2-benzodiazaborole in comparison to indole.

Table 5. NICS Comparisons (ppm) of 1,3,2-Benzodiazaborole and Its Relative Carbon Isosteres[a]

	NICS(0) A Ring	NICS(1) A Ring	NICS(0) B Ring	NICS(1) B Ring	NICS(1) Center		NICS(0) A Ring	NICS(1) A Ring	NICS(0) B Ring	NICS(1) B Ring	NICS(1) Center
 3	-8.57	-8.73	-	-	-	 7a	-9.60	-10.20	-6.86	-5.61	-14.30
 8a	-9.20	-10.46	-10.57	-8.96	-16.22	 6a	-9.42	-10.09	-6.93	-5.60	-14.21
 9	-9.82	-10.83	-9.23	-9.06	-16.16	 5a	-9.34	-9.96	-6.32	-5.30	-14.02
 2a	-6.21	-7.65	-9.31	-7.41	-13.08	 6d	-9.55	-10.27	-7.80	-6.05	-14.48

[a]All structures are fully optimized to local minima (B3LYP/6-311+G(2d,p)).

scaffold,[22] where sp-hybridized groups generally induce shielding relative to its phenyl counterpart.

CONCLUSIONS

The synthetic approach to the 1,3,2-benzodiazaboroles described highlights the ability to synthesize these azaborine cores via bench-stable reagents in a facile procedure, tolerant to atmospheric conditions. Furthermore, the simple workup and purification conditions employed enable rapid access to molecules with valuable isosteric potential. The physical and computational data suggest that this class of azaborine compounds demonstrates some aromatic tendencies, which could be leveraged for potential application of this core isostere of indole.

EXPERIMENTAL SECTION

General Considerations. All reactions were carried out under an inert atmosphere of argon in oven-dried glassware, unless otherwise noted. Toluene and cyclopentyl methyl ether (CPME) were dried using a J. C. Meyer solvent system. *o*-Phenylenediamine (99%) was recrystallized from toluene. Standard flash chromatography procedures were followed using 32−63 μm silica gel. Column chromatography was performed by Combiflash using RediSep Rf Gold Normal-Phase Silica columns. Melting points (°C) are uncorrected. HRMS data were obtained by either ESI or CI using a TOF mass spectrometer in CH_2Cl_2 or MeCN as the solvent. NMR spectra (^1H, ^{13}C, ^{11}B, ^{19}F) were performed at 298 K. ^1H (500.4 MHz) and ^{13}C (125.8 MHz) NMR chemical shifts are reported relative to internal TMS (δ 0.00 ppm) or to residual protiated solvent. ^{11}B (128.4 MHz) and ^{19}F NMR (282.4 MHz) chemical shifts were referenced to external $BF_3{\cdot}Et_2O$ (0.0 ppm) and $CFCl_3$ (0.0 ppm), respectively. Data are presented as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, m = multiplet), coupling constant *J* (Hz), and integration.

General Procedure for Synthesis of Aryl 1,3,2-Benzodiazaboroles 5a−z. Diamine (1 equiv, 1 mmol), organotrifluoroborate (1 equiv, 1 mmol), and $BF_3{\cdot}NH_2Et$ (3 equiv, 3 mmol) were added to an oven-dried Biotage microwave vial with a stir bar. The vial was sealed with a cap, which was lined with a disposable Teflon septum, and the reaction vessel was subsequently evacuated and purged three times with argon. A 1/1 mixture of CPME (1 mL) and toluene (1 mL) was added, and the reaction mixture was heated to 80 °C. After it was stirred overnight, the reaction mixture was diluted with 5 mL of saturated $NaHCO_3$ and extracted with EtOAc (2 × 5 mL). The organic phase was washed with brine and dried ($MgSO_4$), before being condensed under vacuum to afford the azaborine.

2-Phenyl-2,3-dihydro-1H-1,3,2-benzodiazaborole[9d] ***(5a)***. Thirty millimole scale reaction in a 200 mL round-bottom flask. Obtained as a tan solid (4.949 g, 85%). Mp: 198−200 °C. ^1H NMR (500.4 MHz, $CDCl_3$): δ 7.76−7.74 (m, 2H), 7.49−7.41 (m, 3H), 7.14 (dd, *J* = 5.3, 3.4 Hz, 2H), 6.99 (ddd *J* = 5.6, 3.3 Hz, 0.9 Hz, 2H), 6.79 (s, 2H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 136.4, 133.2, 129.9, 128.3, 119.5, 111.3.

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J. Org. Chem. XXXX, XXX, XXX−XXX

^{11}B NMR (128.4 MHz, MeCN): δ 28.5. IR (neat): 3441, 3418, 1421, 746, 699, 597 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{12}H_{12}BN_2$ $[M + H]^+$ 195.1094, found 195.1100.

2-(o-Tolyl)-2,3-dihydro-1H-1,3,2-benzodiazaborole[23] ***(5b)***. Obtained as a tan solid (173 mg, 83%). Mp: 107−110 °C. ^{1}H NMR (500.4 MHz, $CDCl_3$): δ 7.65 (d, J = 7.3 Hz, 1H), 7.36 (t, J = 7.3 Hz, 1H), 7.28 (d, J = 7.3 Hz, 2H), 716 (dd, J = 5.6, 3.4 Hz, 2H), 7.02 (dd, J = 5.6, 3.4 Hz, 2H), 6.73 (s, 2H), 2.59 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 142.0, 136.2, 134.4, 130.0, 129.6, 125.4, 119.5, 111.2, 23.1. ^{11}B NMR (128.4 MHz, MeCN): δ 28.6. IR (neat): 3457, 3423, 1605, 1416, 1351, 740, 612 cm^{-1}. HRMS (CI) m/z: calcd for $C_{13}H_{14}BN_2$ $[M + H]^+$ 209.1250, found 209.1242.

2-(2,6-Dimethylphenyl)-2,3-dihydro-1H-1,3,2-benzodiazaborole ***(5c)***. Obtained as a tan solid (186 mg, 84%). Mp: 124−126 °C. ^{1}H NMR (500.4 MHz, $CDCl_3$): δ 7.24 (t, J = 7.7 Hz, 1H), 7.15 (dd, 5.4, 3.6 Hz, 2H), 7. 08 (d, J = 7.7 Hz, 2H), 7.01 (dd, J = 5.4, 3.4 Hz, 2H), 6.54 (s, 2H), 2.33 (s, 6H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 141.8, 136.2, 128.9, 126.4, 119.3, 111.2, 23,2. ^{11}B NMR (128.4 MHz, MeCN): δ 29.5. IR (neat): 3421, 3054, 2925, 1440, 1352, 739, 617 cm^{-1}. HRMS (CI) m/z: calcd for $C_{14}H_{14}BN_2$ $[M - H]^-$ 221.1250, found 221.1257.

1-Methyl-2-phenyl-2,3-dihydro-1H-1,3,2-benzodiazaborole[9c] ***(5d)***. Three mmol scale reaction in a 20 mL microwave vial. Obtained as a dark red solid (171 mg, 82%). Mp: 84−88 °C. ^{1}H NMR (500.4 MHz, $CDCl_3$): δ 7.74−7.70 (m, 2H), 7.47−7.44 (m, 3H), 7.18−7.07 (m, 3H), 7.03 (td, J = 7.6, 1.3 Hz, 1H), 6.66 (s, 1H), 3.52 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 139.1, 135.9, 133.8, 129.2, 128.2, 119.3, 119.3, 110.1, 106.8, 30.0. ^{11}B NMR (128.4 MHz, MeCN): δ 28.8. IR (neat): 3431, 3054, 3045, 1409, 736, 703, 587 cm^{-1}. HRMS (CI) m/z: calcd for $C_{13}H_{13}BN_2$ $[M]^+$ 208.1172, found 208.1172.

2-(2,6-Difluorophenyl)-2,3-dihydro-1H-1,3,2-benzodiazaborole ***(5e)***. Product further purified via a plug of silica with hexane/EtOAc (4:1) as eluent. Obtained as a tan solid (154 mg, 67%). Mp: 148−151 °C. ^{1}H NMR (500.4 MHz, DMSO-d_6): δ 9.01 (s, 2H), 7.54 (tt, J = 8.2, 6.9 Hz, 1H), 7.18 (dd, J = 5.7, 3.3 Hz, 2H), 7.16−7.12 (m, 2H), 6.96−6.74 (m, 2H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 167.0 (dd, J = 247.5, 13.4 Hz), 135.7, 132.2 (t, J = 11.3 Hz), 119.7, 111.5, 111.4 (dd, J = 23.1, 5.6 Hz). ^{11}B NMR (128.4 MHz, MeCN): δ 24.6. ^{19}F NMR (282.4 MHz, $CDCl_3$): δ −103.0. IR (neat): 3450, 3054, 1624, 1453, 979, 779, 735, 590 cm^{-1}. HRMS (CI) m/z: calcd for $C_{12}H_9BN_2F_2$ $[M]^+$ 230.0827, found 230.0827.

2-(4-Bromophenyl)-2,3-dihydro-1H-1,3,2-benzodiazaborole[9c] ***(5f)***. Obtained as a tan solid (184 mg, 68%), Mp: 216−218 °C. ^{1}H NMR (500.4 MHz, $CDCl_3$): δ 7.61−7.54 (m, 4H), 7.12 (dd, J = 5.4, 3.3 Hz, 2H), 6.99 (dd, J = 5.3, 4.4 Hz, 2H), 6.76 (s, 2H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 136.3, 134.8, 131.5, 124.5, 119.7, 111.4. ^{11}B NMR (128.4 MHz, MeCN): δ 28.2. IR (neat): 3418, 1584, 1427, 1275, 751, 599 cm^{-1}. HRMS (CI) m/z: calcd for $C_{12}H_{10}BN_2Br$ $[M]^+$ 272.0120, found 272.0133.

2-(4-Fluorophenyl)-1-methyl-2,3-dihydro-1H-1,3,2-benzodiazaborole ***(5g)***. Obtained as a brown solid (185 mg, 82%). Mp: 114−115 °C. ^{1}H NMR (500.4 MHz, $CDCl_3$): δ 7.68 (dd, J = 8.8, 5.7 Hz, 2H), 7.19−7.12 (m, 2H), 7.12−7.03 (m, 3H), 7.00 (t, J = 6.8 Hz, 1H), 6.61 (s, 1H), 3.48 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 163.8 (d, J = 248.4 Hz), 139.0, 135.8, 135.6 (d, J = 7.9 Hz), 119.4, 119.4, 115.4 (d, J = 19.9 Hz), 110.9, 108.9, 30.0. ^{11}B NMR (128.4 MHz, MeCN): δ 28.0. ^{19}F NMR (282.4 MHz, $CDCl_3$): δ −112.5. IR (neat): 3437, 3054, 2910, 1596, 1397, 1217, 830, 738, 576 cm^{-1}. HMRS (CI) m/z: calcd for $C_{13}H_{12}BN_2F$ $[M]^+$ 226.1078, found 226.1080.

2-(3-Vinylphenyl)-2,3-dihydro-1H-1,3,2-benzodiazaborole ***(5h)***. Obtained as a light brown solid (162 mg, 73%). Mp: 119−121 °C. ^{1}H NMR (500.4 MHz, DMSO-d_6): δ 9.16 (s, 2H), 8.05 (s, 1H), 7.80 (d, J = 7.2 Hz, 1H), 7.48 (d, J = 7.7 Hz, 1H), 7.40 (t, J = 7.5 Hz, 1H), 7.09−7.02 (m, 2H), 6.84−6.81 (m, 2H), 6.77 (dd, J = 17.5, 10.8 Hz, 1H), 5.92 (d, J = 17.6 Hz, 1H), 5.31 (d, J = 10.9 Hz, 1H). ^{13}C NMR (125.8 MHz, DMSO-d_6): δ 137.1, 136.9, 136.5, 133.0, 131.1, 128.2, 127.3, 118.3, 114.1, 110.8. ^{11}B NMR (128.4 MHz, MeCN): δ 28.5. IR (neat): 3445, 3425, 3054, 1353, 904, 746, 688, 564 cm^{-1}. HMRS (CI) m/z: calcd for $C_{14}H_{14}BN_2$ $[M + H]^+$ 221.1250, found 221.1244.

2-(2-Methoxyphenyl)-2,3-dihydro-1H-1,3,2-benzodiazaborole[24] ***(5i)***. Obtained as a tan solid (175 mg, 78%). Mp: 123−124 °C. ^{1}H NMR (500.4 MHz, DMSO-d_6): δ 8.77 (s, 2H), 7.86 (d, J = 7.2 Hz, 1H), 7.39 (t, J = 7.7 Hz, 1H), 7.11 (dd, J = 5.7, 3.3 Hz, 2H), 7.05−6.95 (m, 2H), 6.81 (dd, J = 5.8, 3.2 Hz, 2H), 3.89 (s, 3H). ^{13}C NMR (125.8 MHz, DMSO-d_6): δ 163.2, 136.9, 135.3, 131.0, 120.1, 118.0, 110.7, 110.4, 55.0. ^{11}B NMR (128.4 MHz, MeCN): δ 27.4. IR (neat): 3460, 3423, 1598, 1418, 1243, 743, 619 cm^{-1}. HMRS (CI) m/z: calcd for $C_{13}H_{14}BN_2O$ $[M + H]^+$ 225.1199, found 225.1201.

2-(3-Methoxyphenyl)-2,3-dihydro-1H-1,3,2-benzodiazaborole[24] ***(5j)***. Product further purified via recrystallization from boiling toluene. Obtained as a brown solid (139 mg, 62%). Mp: 150−152 °C. ^{1}H NMR (500.4 MHz, DMSO-d_6): 9.11 (s, 2H), 7.51 (s, 1H), 7.47 (d, J = 7.1 Hz, 1H), 7.33 (td, J = 7.7, 2.1 Hz, 1H), 7.06 (dt, J = 5.6, 2.6 Hz, 2H), 6.96 (d, J = 8.1 Hz, 1H), 6.82 (dt, J = 5.6, 2.7 Hz, 2H), 3.81 (s, 3H). ^{13}C NMR (125.8 MHz, DMSO-d_6): δ 156.9, 137.1, 129.0, 125.6, 118.5, 118.3, 115.0, 110.7, 54.9. ^{11}B NMR (128.4 MHz, MeCN): δ 28.4. IR (neat): 3414, 1425, 750, 698, 634 cm^{-1}. HMRS (CI) m/z: calcd for $C_{13}H_{14}BN_2O$ $[M + H]^+$ 225.1199, found 225.1201.

2-(3-Methoxyphenyl)-1-methyl-2,3-dihydro-1H-1,3,2-benzodiazaborole ***(5k)***. Obtained as a dark brown solid (191 mg, 80%). Mp: 86−88 °C. ^{1}H NMR (500.4 MHz, $CDCl_3$): δ 7.40 (t, J = 7.4 Hz, 1H), 7.30 (d, J = 7.4 Hz, 1H), 7.25 (s, 1H), 7.14−7.04 (m, 3H), 7.03−6.97 (m, 2H), 6.66 (s, 1H), 3.87 (s, 3H), 3.51 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 159.4, 139.0, 135.8, 129.5, 126.1, 119.32, 199.31, 119.2, 114.5, 110.9, 108.9, 55.3, 30.0. ^{11}B NMR (128.4 MHz, MeCN): δ 28.4. IR (neat): 3427, 1575, 1402, 1254, 749, 702, 608 cm^{-1}. HMRS (CI) m/z: calcd for $C_{14}H_{16}BN_2O$ $[M + H]^+$ 239.1356, found 239.1359.

2-(2-Phenoxyphenyl)-2,3-dihydro-1H-1,3,2-benzodiazaborole ***(5l)***. Product further purified via a plug of silica with hexane/EtOAc (4/1) as eluent. Obtained as a brown solid (178 mg, 62%). Mp: 81−83 °C. ^{1}H NMR (500.4 MHz, $CDCl_3$): δ 7.79−7.75 (m, 1H), 7.41−7.32 (m, 3H), 7.17 (dt, J = 11.4, 7.3 Hz, 2H), 7.12−7.07 (m, 4H), 7.03 (s, 2H), 6.96 (d, J = 3.2 Hz, 1H), 6.95 (d, J = 3.3 Hz, 1H), 6.89−6.86 (m, 1H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 161.8, 157.2, 136.3, 135.1, 131.4, 130.1, 123.8, 123.3, 119.6, 119.4, 118.1, 111.2. ^{11}B NMR (128.4 MHz, $CDCl_3$): δ 27.1. IR (neat): 3431, 3186, 2946, 2865, 1458, 1274, 738, 575 cm^{-1}. HMRS (CI) m/z: calcd for $C_{18}H_{15}BN_2ONa$ $[M + Na]^+$ 309.1175, found 309.1181.

2-(4-(Methoxycarbonyl)phenyl)-2,3-dihydro-1H-1,3,2-benzodiazaborole ***(5m)***. Obtained as a tan solid (130 mg, 51%). Mp: 171−172 °C. ^{1}H NMR (500.4 MHz, DMSO-d_6): δ 9.33 (s, 2H), 8.54 (s, 1H), 8.16 (d, J = 7.9 Hz, 1H), 7.99 (dt, J = 8.1, 1.7 Hz, 1H), 7.58 (td, J = 7.6, 1.7 Hz, 1H), 7.16−7.02 (m, 2H), 6.83 (dt, J = 5.6, 2.5 Hz, 2H), 3.90 (s, 3H). ^{13}C NMR (125.8 MHz, DMSO-d_6): δ 166.6, 138.1, 137.1, 134.0, 130.0, 129.3, 128.3, 118.4, 111.0, 52.1. ^{11}B NMR (128.4 MHz, MeCN): δ 28.0. IR (neat): 3424, 3404, 2950, 1701, 1431, 1282, 1263, 741, 690 cm^{-1}. HMRS (CI) m/z: calcd for $C_{14}H_{14}BN_2O_2$ $[M + H]^+$ 253.1148, found 253.1137.

2-(2,3-Dihydrobenzo[b][1,4]dioxin-6-yl)-2,3-dihydro-1H-1,3,2-benzodiazaborole ***(5n)***. Obtained as a tan solid (191 mg, 76%). Mp: 199−201 °C. ^{1}H NMR (500.4 MHz, $CDCl_3$): δ 7.24−7.20 (m, 2H), 7.10 (dd, J = 5.3, 3.4 Hz, 2H), 6.98−6.93 (m, 3H), 6.68 (s, 2H), 4.30 (s, 4H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 145.3, 143.6, 136.5, 126.5, 121.9, 119.4, 117.4, 111.1, 64.7, 64.5. ^{11}B NMR (128.4 MHz, MeCN): δ 28.5. IR (neat): 3446, 3416, 2995, 2940, 2875, 1575, 1245, 1126, 745, 547 cm^{-1}. HMRS (CI) m/z: calcd for $C_{14}H_{14}BN_2O_2$ $[M + H]^+$ 253.1148, found 253.1157.

2-(3-Nitrophenyl)-2,3-dihydro-1H-1,3,2-benzodiazaborole[9c] ***(5o)***. Product further purified via a plug of silica with hexane/EtOAc (4/1) as eluent. Obtained as a tan solid (62 mg, 26%). Mp: 210−211 °C. ^{1}H NMR (500.4 MHz, DMSO-d_6): δ 9.46 (s, 2H), 8.79 (s, 1H), 8.32 (d, J = 7.1 Hz, 1H), 8.25 (d, J = 7.7 Hz, 1H), 7.74 (t, J = 7.7 Hz, 1H), 7.09 (dd, J = 5.8, 3.1 Hz, 2H), 6.86 (dt, J = 5.7, 3.1 Hz, 2H). ^{13}C NMR (125.8 MHz, DMSO-d_6): δ 147.6, 139.7, 136.9, 129.5, 127.5, 123.9, 118.7, 111.1. ^{11}B NMR (128.4 MHz, MeCN): δ 27.7. IR (neat): 3397, 1620, 1429, 1346, 1270, 737, 687 cm^{-1}. HMRS (CI) m/z: calcd for $C_{12}H_{11}BN_3O_2$ $[M + H]^+$ 240.0944, found 240.0937.

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J. Org. Chem. XXXX, XXX, XXX−XXX

*2-(3-Cyanophenyl)-2,3-dihydro-1H-1,3,2-benzodiazaborole (**5p**).* Obtained as a tan solid (53 mg, 24%). Mp: 195−196 °C. ^{1}H NMR (500.4 MHz, $CDCl_3$): δ 8.01 (s, 1H), 7.94 (dt, *J* = 7.5, 1.3 Hz, 1H), 7.71 (dt, *J* = 7.8, 1.5 Hz, 1H), 7.54 (td, *J* = 7.6, 0.7 Hz, 1H), 7.19−7.13 (m, 2H), 7.01 (dd, *J* = 5.7, 3.1 Hz, 2H), 6.86 (s, 2H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 137.2, 136.7, 136.1, 133.0, 129.0, 120.1, 119.1, 112.7, 111.7. ^{11}B NMR (128.4 MHz, $CDCl_3$): δ 27.6. IR (neat): 3415, 3378, 3065, 2232, 1434, 1273, 745, 693, 561 cm^{-1}. HMRS (CI) *m*/*z*: calcd for $C_{13}H_{11}BN_3$ $[M + H]^+$ 220.1046, found 220.1048.

*2-(Thiophen-3-yl)-2,3-dihydro-1H-1,3,2-benzodiazaborole (**5q**).* Obtained as a tan solid (128 mg, 64%). Mp: 221−222 °C. ^{1}H NMR (500.4 MHz, $CDCl_3$): δ 7.75−7.73 (m, 1H), 7.45 (dd, *J* = 4.7, 2.6 Hz, 1H), 7.42 (d, *J* = 4.6 Hz, 1H), 7.11 (dd, *J* = 7.5, 3.8 Hz, 2H), 6.97 (dd, *J* = 5.7, 3.3 Hz, 2H), 6.70 (s, 2H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 136.3, 131.9, 131.2, 126.1, 119.5, 111.2. ^{11}B NMR (128.4 MHz, MeCN): δ 26.4. IR (neat): 3427, 1431, 740, 662, 600 cm^{-1}. HMRS (CI) *m*/*z*: calcd for $C_{10}H_9BN_2S$ $[M]^+$ 200.0580, found 200.0601.

*2-(2-Benzofuranyl)-2,3-dihydro-1H-1,3,2-benzodiazaborole (**5r**).* Obtained as a tan solid (132 mg, 57%). Mp: 220−222 °C. ^{1}H NMR (500.4 MHz, $CDCl_3$): δ 7.66 (d, *J* = 7.9 Hz, 1H), 7.56 (d, *J* = 8.2 Hz, 1H), 7.39−7.32 (m, 1H), 7.29−7.23 (m, 2H), 7.16 (dd, *J* = 7.4, 3.7 Hz, 2H), 7.01 (dd, *J* = 5.8, 3.2 Hz, 2H), 6.96 (s, 2H). ^{13}C NMR (125.8 MHz, DMSO-d_6): δ 156.5, 136.7, 128.0, 125.0, 122.7, 121.5, 118.7, 115.5, 111.2, 111.1. ^{11}B NMR (128.4 MHz, MeCN): δ 24.8. IR (neat): 3436, 1569, 1411, 1337, 735, 602 cm^{-1}. HMRS (CI) *m*/*z*: calcd for $C_{14}H_{12}BN_2O$ $[M + H]^+$ 235.1043, found 235.1053.

*2-(Furan-2-yl)-1-methyl-2,3-dihydro-1H-1,3,2-benzodiazaborole (**5s**).* Product further purified via a plug of silica with hexane/EtOAc (4/1) as eluent. Obtained as a brown solid (144 mg, 73%). Mp: 73−75 °C. ^{1}H NMR (500.4 MHz, $CDCl_3$): δ 7.75 (s, 1H), 7.60 (d, *J* = 1.4 Hz, 1H), 7.06−7.03 (m, 3H) 6.99 (dt, *J* = 7.4, 1.4 Hz, 1H), 6.66 (s, 1H), 6.57 (s, 1H) 3.49 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 147.4, 143.2, 138.9, 119.2, 119.1, 113.2, 110.8, 108.6, 30.0. ^{11}B NMR (128.4 MHz, MeCN): δ 26.4. IR (neat): 3431, 3054, 2947, 1478, 1345, 733, 541 cm^{-1}. HMRS (CI) *m*/*z*: calcd for $C_{11}H_{11}BN_2O$ $[M]^+$ 198.0964, found 198.0965.

5-Methyl-2-phenyl-2,3-dihydro-1H-1,3,2-benzodiazaborole[9c] *(**5u**).* Obtained as a tan solid (164 mg, 79%). Mp: 212−214 °C. ^{1}H NMR (500.4 MHz, $CDCl_3$ with 1% TMS): δ 7.74−7.71 (m, 2H), 7.44−7.41 (m, 3H), 7.00 (dd, *J* = 7.9, 3.4 Hz, 1H), 6.94 (s, 1H), 6.79 (d, *J* = 7.9 Hz, 1H), 6.69 (s, 2H), 2.40 (d, *J* = 3.4 Hz, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$ with 1% TMS): δ 136.6, 134.2, 133.1, 129.8, 129.0, 128.3, 120.1, 112.0, 110.8, 21.5. ^{11}B NMR (128.4 MHz, MeCN): δ 28.6. IR (neat): 3440, 3054, 2915, 1603, 1419, 805, 695, 569 cm^{-1}. HMRS (CI) *m*/*z*: calcd for $C_{13}H_{14}BN_2$ $[M + H]^+$ 209.1250, found 209.1247.

*5-Fluoro-2-phenyl-2,3-dihydro-1H-1,3,2-benzodiazaborole (**5v**).* Obtained as a brown solid (160 mg, 76%). Mp: 186−188 °C. ^{1}H NMR (500.4 MHz, $CDCl_3$): δ 7.73−7.70 (m, 2H), 7.47−7.41 (m, 3H), 6.98 (dd, *J* = 8.4, 4.9 Hz, 1H), 6.85 (dd, *J* = 9.3, 2.5 Hz, 1H), 6.78 (s, 1H), 6.71−6.66 (m, 2H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 157.9 (d, *J* = 233.9 Hz), 136.9 (d, *J* = 11.9 Hz), 133.1, 132.6, 130.0, 128.4, 110.7 (d, *J* = 9.9 Hz), 105.8 (d, *J* = 24.1 Hz), 99.0 (d, *J* = 26.8 Hz). ^{11}B NMR (128.4 MHz, MeCN): δ 29.2. ^{19}F NMR (282.4 MHz, $CDCl_3$): δ −124.9. IR (neat): 3441, 1424, 1365, 1255, 1139, 700, 587 cm^{-1}. HMRS (CI) *m*/*z*: calcd for $C_{12}H_{11}BN_2F$ $[M + H]^+$ 213.0999, found 213.1000.

*5-Bromo-2-phenyl-2,3-dihydro-1H-1,3,2-benzodiazaborole (**5w**).* Eight millimole scale reaction in a 20 mL microwave vial. Obtained as a brown solid (1.64 g, 76%). Mp: 157−159 °C. ^{1}H NMR (500.4 MHz, $CDCl_3$): δ 7.77−7.63 (m, 2H), 7.45 (d, *J* = 6.0 Hz, 3H), 7.24 (s, 1H), 7.12−7.05 (m, 1H), 6.97 (d, *J* = 7.9 Hz, 1H), 6.77 (s, 2H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 137.8, 135.5, 133.2, 130.2, 128.4, 122.2, 114.3, 112.2, 112.0. ^{11}B NMR (128.4 MHz, MeCN): δ 28.8. IR (neat): 3435, 1599, 1420, 803, 697, 566 cm^{-1}. HMRS (CI) *m*/*z*: calcd for $C_{12}H_{10}BBrN_2$ $[M]^+$ 272.0120, found 272.0127.

*5-Phenylcarbonyl-2-phenyl-2,3-dihydro-1H-1,3,2-benzodiazaborole (**5x**).* Eight millimole scale reaction in a 20 mL microwave vial. Product further purified via recrystallization from boiling toluene. Obtained as a burnt orange solid (1.31 g, 55%). Mp: 186−187 °C. ^{1}H NMR (500.4 MHz, DMSO-d_6): δ 9.68 (s, 1H), 9.44 (s, 1H), 7.96−7.85 (m, 2H), 7.74−7.66 (m, 2H), 7.66−7.59 (m, 1H), 7.58−7.51 (m, 3H), 7.45 (t, *J* = 4.6 Hz, 3H), 7.39 (dd, *J* = 8.1, 2.5 Hz, 1H), 7.19 (dd, *J* = 8.4, 2.8 Hz, 1H). ^{13}C NMR (125.8 MHz, DMSO-d_6): δ 195.4, 142.0, 139.0, 137.0, 133.5, 131.3, 129.8, 128.2, 128.0, 127.5, 122.7, 112.6, 110.3. ^{11}B NMR (128.4 MHz, MeCN): δ 30.2. IR (neat): 3460, 3372, 1603, 1428, 1287, 707, 630 cm^{-1}. HMRS (CI) *m*/*z*: calcd for $C_{19}H_{16}BN_2O$ $[M + H]^+$ 299.1356, found 299.1348.

5-Nitro-2-phenyl-2,3-dihydro-1H-1,3,2-benzodiazaborole[9c] *(**5y**).* Product further purified via recrystallization from boiling toluene. Obtained as an orange solid (148 mg, 62%). Mp: 195−196 °C. ^{1}H NMR (500.4 MHz, DMSO-d_6): δ 9.97 (s, 1H), 9.70 (s, 1H), 7.94−7.86 (m, 4H), 7.50−7.45 (m, 3H), 7.20 (d, *J* = 8.5 Hz, 1H). ^{13}C NMR (125.8 MHz, DMSO-d_6): δ 143.7, 139.8, 137.1, 133.6, 130.2, 128.1, 116.0, 110.1, 105.9. ^{11}B NMR (128.4 MHz, MeCN): δ 31.0. IR (neat): 3435, 3415, 3380, 1610, 1435, 1303, 695, 631 cm^{-1}. HMRS (ESI-) *m*/*z*: calcd for $C_{12}H_9BN_3O_2$ $[M - H]^-$ 238.0788, found 238.0788.

2-Phenyl-2,3-dihydro-1H-1,3,2-naphthodiazaborole[9c] *(**5z**).* Product further purified via recrystallization from boiling toluene. Obtained as a tan solid (33.5 mg, 14%). Mp: > 250 °C. ^{1}H NMR (500.4 MHz, DMSO-d_6): δ 9.30 (s, 2H), 8.00−7.95 (m, 2H), 7.77 (dd, *J* = 6.6, 3.3 Hz, 2H), 7.48−7.44 (m, 3H), 7.42 (s, 2H), 7.22 (dd, *J* = 6.9, 3.1 Hz, 2H). ^{13}C NMR (125.8 MHz, DMSO-d_6): δ 139.0, 133.7, 129.9, 128.6, 128.0, 126.4, 122.0, 105.4. ^{11}B NMR (128.4 MHz, MeCN): δ 30.8. IR (neat): 3429, 1435, 862, 695, 588 cm^{-1}. HMRS (CI) *m*/*z*: calcd for $C_{16}H_{14}BN_2$ $[M + H]^+$ 245.1250, found 245.1252.

General Procedure for Synthesis of Alkyl and Alkenyl 1,3,2-Benzodiazaboroles 6a−h and 7a−h. Diamine (1 equiv, 1 mmol), organotrifluoroborate (1 equiv, 1 mmol), and $BF_3{\cdot}NH_2Et$ (3 equiv, 3 mmol) were placed in an oven-dried Biotage microwave vial with a stir bar. The vial was sealed with a cap, which was lined with a disposable Teflon septum. The reaction vessel was subsequently evacuated and purged three times with argon. A 1/1 mixture of CPME (1 mL) and toluene (1 mL) was added, and the reaction mixture was heated to 80 °C. After it was stirred overnight, the reaction mixture was diluted with 2 mL of hexane and run though a 2 in. silica plug, with 10% EtOAc in hexane as eluent. The reaction mixture was then condensed under vacuum to afford the azaborine compound.

*(E)-2-(Prop-1-en-1-yl)-2,3-dihydro-1H-1,3,2-benzodiazaborole (**6a**).* Obtained as a brown solid (110 mg, 70%). Mp: 72−74 °C. ^{1}H NMR (500.4 MHz, $CDCl_3$): δ 7.05 (dd, *J* = 5.7, 3.3 Hz, 2H), 6.94 (dd, *J* = 5.8, 3.2 Hz, 2H), 6.60−6.33 (m, 3H), 5.90 (d, *J* = 17.7 Hz, 1H), 1.95 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 143.8, 136.3, 119.1, 110.9, 22.1. ^{11}B NMR (128.4 MHz, $CDCl_3$): δ 27.0. IR (neat): 3385, 3185, 1500, 1272, 743 cm^{-1}. HMRS (CI) *m*/*z*: calcd for $C_9H_{12}BN_2$ $[M + H]^+$ 159.1094, found 159.1100.

*2-(Cyclohex-1-en-1-yl)-2,3-dihydro-1H-1,3,2-benzodiazaborole (**6b**).* Obtained as a brown solid (156 mg, 79%). Mp: 123−125 °C. ^{1}H NMR (500.4 MHz, $CDCl_3$): δ 7.03 (dd, *J* = 5.6, 3.2 Hz, 2H), 6.92 (dd, *J* = 5.6, 3.2 Hz, 2H), 6.41 (s, 3H), 2.29−2.25 (m, 2H), 2.21−2.16 (m, 2H), 1.74−1.67 (m, 4H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 138.0, 136.3, 119.0, 110.8, 27.3, 26.7, 22.8, 22.4. ^{11}B NMR (128.4 MHz, $CDCl_3$): δ 27.9. IR (neat): 3430, 2923, 2852, 1627, 1431, 738, 594 cm^{-1}. HMRS (CI) *m*/*z*: calcd for $C_{12}H_{16}BN_2$ $[M + H]^+$ 199.1407, found 199.1411.

*2-Vinyl-2,3-dihydro-1H-1,3,2-benzodiazaborole (**6c**).* Product further purified via a plug of silica with hexane/EtOAc (4/1) as eluent. Obtained as a tan solid (97 mg, 68%). Mp: 106−108 °C. ^{1}H NMR (500.4 MHz, $CDCl_3$): δ 7.05 (dt, *J* = 7.3, 3.6 Hz, 2H), 6.94 (dd, *J* = 5.7, 3.2 Hz, 2H), 6.52 (s, 2H), 6.31 (dd, J_{trans} = 20.0, J_{cis} = 13.7 Hz, 1H), 6.08−5.85 (m, 2H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 136.1, 131.8, 119.4, 111.1. ^{11}B NMR (128.4 MHz, MeCN): δ 27.5. IR (neat): 3415, 3054, 1615, 1407, 1270, 954, 750, 631 cm^{-1}. HMRS (CI) *m*/*z*: calcd for $C_8H_9BN_2$ $[M]^+$ 144.0859, found 144.0849.

*2-(1-Propynyl)-2,3-dihydro-1H-1,3,2-benzodiazaborole (**6d**).* Obtained as a white solid (122 mg, 78%). Mp: 130−131 °C. ^{1}H NMR (500.4 MHz, $CDCl_3$): δ 7.06−7.03 (m, 2H), 6.96 (dd, *J* = 5.7, 3.2 Hz, 2H), 6.59 (s, 2H), 2.02 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 135.5, 119.7, 111.2, 5.0. ^{11}B NMR (128.4 MHz, MeCN): δ 20.2. IR

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J. Org. Chem. XXXX, XXX, XXX−XXX

(neat): 3422, 3057, 2204, 1418, 1352, 1266, 729, 624 cm^{-1}. HMRS (CI) *m/z*: calcd for $C_9H_9BN_2$ $[M]^+$ 156.0859, found 156.0844.

*1-Methyl-2-vinyl-2,3-dihydro-1H-1,3,2-benzodiazaborole (**6e**).* Obtained as a dark red oil (136 mg, 86%). ^1H NMR (500.4 MHz, $CDCl_3$): δ 7.05 (d, J = 7.4 Hz, 1H), 7.02−6.99 (m, 2H), 6.96 (dt, J = 7.1, 2.7 Hz, 1H), 6.50 (s, 1H), 6.41 (dd, J = 18.6, 15.5 Hz, 1H), 5.98 (d, J = 18.6 Hz, 2H), 3.40, (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 135.8, 131.8, 119.2, 119.1, 110.7, 108.5, 29.5. ^{11}B NMR (128.4 MHz, MeCN): δ 26.71. IR (neat): 3428, 3054, 2930, 1614, 1443, 1399, 1010, 733 cm^{-1}. HMRS (CI) *m/z*: calcd for $C_9H_{12}BN_2$ $[M + H]^+$ 159.1094, found 159.1090.

*(E)-1-Methyl-2-(prop-1-en-1-yl)-2,3-dihydro-1H-1,3,2-benzodiazaborole (**6f**).* Obtained as a dark brown solid (153 mg, 89%). Mp: 81−85 °C. ^1H NMR (500.4 MHz, $CDCl_3$): δ 7.02 (d, J = 7.5 Hz, 1H), 6.99 (d, J = 3.4 Hz, 2H), 6.94 (dd, J = 7.0, 4.3 Hz, 1H), 6.49−6.42 (dd, J = 18.0, 6.0 Hz, 1H), 6.40 (s, 1H), 5.98 (dd, J = 18.0, 1.8 Hz, 1H), 3.37 (s, 3H), 1.96 (dd, J = 6.0, 1.8 Hz, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 143.7, 138.9, 136.0, 118.9, 118.8, 110.4, 108.2, 29.4, 22.3. ^{11}B NMR (128.4 MHz, MeCN): δ 27.0. IR (neat): 3424, 2905, 1645, 1412, 1240, 984, 733 cm^{-1}. HMRS (CI) *m/z*: calcd for $C_{10}H_{14}BN_2$ $[M + H]^+$ 173.1250, found 173.1254.

*1-Phenyl-2-vinyl-2,3-dihydro-1H-1,3,2-benzodiazaborole (**6g**).* Ten millimole scale reaction in a 50 mL round-bottom flask. Product was further purified via combiflash with hexane/EtOAc as solvents. Obtained as a deep red oil (0.93 g, 42%). ^1H NMR (500.4 MHz, $CDCl_3$): δ 7.47 (t, J = 7.1 Hz, 2H), 7.40−7.29 (m, 3H), 7.13 (d, J = 7.7 Hz, 1H), 7.07 (d, J = 7.9 Hz, 1H), 7.01 (t, J = 7.4 Hz, 1H), 6.94 (t, J = 7.6 Hz, 1H), 6.70 (s, 1H), 6.25 (dd, J_{trans} = 20.1, J_{cis} = 13.9 Hz, 1H), 5.99−5.84 (m, 2H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 140.6, 137.8, 135.7, 132.4, 129.4, 126.9, 120.1, 119.3, 111.3, 110.1. ^{11}B NMR (128.4 MHz, MeCN): δ 26.7. IR (neat): 3430, 3054, 1596, 1396, 1269, 736, 696 cm^{-1}. HMRS (CI) *m/z*: calcd for $C_{14}H_{14}BN_2$ $[M + H]^+$ 221.1250, found 221.1254.

*(E)-1-Phenyl-2-(1-propenyl)-2,3-dihydro-1H-1,3,2-benzodiazaborole (**6h**).* Product further purified via a plug of silica with hexane/EtOAc (4/1) as eluent. Obtained as a red solid (178 mg, 76%). Mp: 61−63 °C. ^1H NMR (500.4 MHz, $CDCl_3$): δ 7.53−7.43 (m, 2H), 7.40−7.29 (m, 3H), 7.13−7.08 (m, 1H), 7.08−7.03 (m, 1H), 7.03−6.97 (m, 1H), 6.96−6.90 (m, 1H), 6.59 (s, 1H), 6.49−6.34 (m, 1H), 5.84 (d, J = 18.9 Hz, 1H), 1.91−1.84 (m, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 144.5, 140.8, 138.0, 136.0, 129.3, 127.0, 125.9, 119.9, 119.1, 111.0, 109.8, 22.2. ^{11}B NMR (128.4 MHz, $CDCl_3$): δ 26.8. IR (neat): 3387, 1597, 1495, 1315, 746, 691 cm^{-1}. HMRS (CI) *m/z*: calcd for $C_{14}H_{13}BN_2$ $[(M + H) - CH_3]^+$ 220.1172, found 220.1172.

2-Methyl-2,3-dihydro-1H-1,3,2-benzodiazaborole[8b] *(**7a**).* Product further purified via a plug of silica with hexane/EtOAc (4/1) as eluent. Obtained as a tan solid (94 mg, 71%). Mp: 67−68 °C. ^1H NMR (500.4 MHz, $CDCl_3$): δ 7.00 (dd, J = 5.7, 3.2 Hz, 2H), 6.91 (dd, J = 5.7, 3.2 Hz, 2H), 6.30, (s, 2H), 0.63 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 136.4, 118.9, 110.5. ^{11}B NMR (128.4 MHz, $CDCl_3$): δ 30.3. IR (neat): 3421, 3385, 3054, 2905, 1612, 1263, 739, 600 cm^{-1}. HMRS (CI) *m/z*: calcd for $C_7H_8BN_2$ $[M - H]^-$ 131.0781, found 131.0783.

2-Isopropyl-2,3-dihydro-1H-1,3,2-benzodiazaborole[8a] *(**7b**).* Product further purified via a plug of silica with hexane/EtOAc (4:1) as eluent. Obtained as a tan solid (107 mg, 67%). Mp: 78−79 °C. ^1H NMR (500.4 MHz, $CDCl_3$): δ 7.07−6.97 (m, 2H), 6.94−6.86 (m, 2H), 6.31 (s, 2H), 1.52 (sept, J = 7.4 Hz, 1H), 1.15 (d, J = 6.7 Hz, 6H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 136.2, 119.0, 110.8, 20.1. ^{11}B NMR (128.4 MHz, $CDCl_3$): δ 32.4. IR (neat): 3432, 3385, 3186, 2945, 1458, 1431, 1274, 738, 576 cm^{-1}. HMRS (CI) *m/z*: calcd for $C_9H_{13}BN_2$ $[M]^+$ 160.1172 found 160.1177.

*2-Cyclopropyl-2,3-dihydro-1H-1,3,2-benzodiazaborole (**7c**).* Product further purified via a plug of silica with hexane/EtOAc (4/1) as eluent. Obtained as a dark brown solid (90 mg, 57%). Mp: 64−66 °C. ^1H NMR (500.4 MHz, $CDCl_3$): δ 7.01−6.94 (m, 2H), 6.92−6.86 (m, 2H), 6.15 (s, 2H), 0.82 (dt, J = 9.4, 3.8 Hz, 2H), 0.50 (dd, J = 6.6, 3.8 Hz, 2H), 0.21 (tt, J = 9.4, 6.3 Hz, 1H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 136.3, 118.9, 110.5, 5.6. ^{11}B NMR (128.4 MHz, MeCN): δ 31.2. IR (neat): 3414, 2998, 2925, 1440, 900, 733, 588 cm^{-1}. HMRS (CI) *m/z*: calcd for $C_9H_{11}BN_2$ $[M]^+$ 158.1015, found 158.1008.

2-(tert-Butyl)-2,3-dihydro-1H-1,3,2-benzodiazaborole[8a] *(**7d**).* Half millimole scale reaction. Product further purified via a plug of silica with hexane/EtOAc (4/1) as eluent. Obtained as a tan solid (63 mg, 72%). Mp: 90−91 °C. ^1H NMR (500.4 MHz, $CDCl_3$): δ 7.05−6.99 (m, 2H), 6.95−6.88 (m, 2H), 6.26 (s, 2H), 1.13 (s, 9H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 136.2, 119.1, 110.8, 100.1, 29.1. ^{11}B NMR (128.4 MHz, $CDCl_3$): δ 33.08. IR (neat): 3438, 3390, 3345, 3194, 2939, 1477, 1435, 585, 568 cm^{-1}. HMRS (CI) *m/z*: calcd for $C_{10}H_{15}BN_2$ $[M]^+$ 174.1328, found 174.1328.

2-Phenethyl-2,3-dihydro-1H-1,3,2-benzodiazaborole[25] *(**7e**).* Obtained as a brown solid (198 mg, 89%). Mp: 112−114 °C. ^1H NMR (500.4 MHz, $CDCl_3$): δ 7.31 (t, J = 7.5 Hz, 2H), 7.27 (d, J = 1.4 Hz, 2H), 7.21 (t, J = 7.2 Hz, 1H), 7.00 (dd, J = 5.7, 3.2 Hz, 2H), 6.91 (dd, J = 5.7, 3.2 Hz, 2H), 6.29 (s, 2H), 2.90 (t, J = 8.1 Hz, 2H), 1.59 (t, J = 8.1 Hz, 2H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 144.4, 136.2, 128.6, 128.1, 125.9, 119.0, 110.7, 32.0. ^{11}B NMR (128.4 MHz, MeCN): δ 31.0. IR (neat): 3433, 2925, 1434, 1267, 732, 593 cm^{-1}. HMRS (CI) *m/z*: calcd for $C_{14}H_{15}BN_2$ $[M]^+$ 222.1328, found 222.1328.

*1,2-Dimethyl-2,3-dihydro-1H-1,3,2-benzodiazaborole (**7f**).* Five millimole scale reaction in a 20 mL microwave vial. Obtained as a dark brown solid (0.66 g, 90%). Mp: 80−82 °C. ^1H NMR (500.4 MHz, $CDCl_3$): δ 7.04−6.96 (m, 3H), 6.96−6.90 (m, 1H), 6.29 (s, 1H), 3.31 (s, 3H), 0.65 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 138.8, 136.1, 118.7, 118.5, 110.1, 107.9, 29.2. ^{11}B NMR (128.4 MHz, MeCN): δ 30.3. IR (neat): 3425, 3054, 2910, 1615, 1413, 1368, 1356, 732, 586 cm^{-1}. HMRS (CI) *m/z*: calcd for $C_8H_{11}BN_2$ $[M]^+$ 146.1051, found 146.1021.

*2-(3-Chloropropyl)-1-methyl-2,3-dihydro-1H-1,3,2-benzodiazaborole (**7g**).* Obtained as a brown oil (194 mg, 94%). ^1H NMR (500.4 MHz, $CDCl_3$): δ 7.03−6.87 (m, 3H), 6.93 (dt, J = 6.93, 2.5 Hz, 1H), 6.26 (s, 1H), 3.60 (t, J = 6.7 Hz, 2H), 3.31 (s, 3H), 2.08−1.98 (m, 2H), 1.36 (t, J = 8.0 Hz, 2H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 138.7, 135.9, 119.0, 118.8, 110.4, 108.2, 47.4, 29.3, 29.3. ^{11}B NMR (128.4 MHz, $CDCl_3$): δ 30.6. IR (neat): 3327, 2928, 1617, 1307, 1052, 910, 731 cm^{-1}. HMRS (CI) *m/z*: calcd for $C_{10}H_{14}BN_2Cl$ $[M]^+$ 208.0939, found 208.0939.

*2-Methyl-1-phenyl-2,3-dihydro-1H-1,3,2-benzodiazaborole (**7h**).* Ten millimole scale reaction in a 50 mL round-bottom flask. Product was further purified via Combiflash with hexane/EtOAc as solvents. Obtained as a deep red oil (0.93 g, 32%). ^1H NMR (500.4 MHz, $CDCl_3$): δ 7.46 (t, J = 7.9 Hz, 2H), 7.37−7.28 (m, 3H), 7.06 (dt, J = 10.9, 7.9 Hz, 2H), 6.97 (t, J = 7.7 Hz, 1H), 6.91 (t, J = 7.7 Hz, 1H), 6.48 (s, 1H), 0.64 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 141.0, 137.7, 136.0, 129.3, 126.6, 125.7, 119.6, 118.9, 110.7, 109.6. ^{11}B NMR (128.4 MHz, MeCN): δ 30.6. IR (neat): 3433, 1597, 1409, 1356, 1271, 734, 697 cm^{-1}. HMRS (CI) *m/z*: calcd for $C_{13}H_{14}BN_2$ $[M + H]^+$ 209.1250, found 209.1250.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00435.

pK_a study of 1-methyl-2-phenyl-2,3-dihydro-1*H*-1,3,2-benzodiazaborole (**5d**), calculated bond lengths, geometry optimized Cartesian coordinates for computed molecules, and ^1H, ^{13}C, ^{11}B, and ^{19}F NMR spectra for all compounds (PDF)

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Notes

The authors declare no competing financial interest.

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J. Org. Chem. XXXX, XXX, XXX−XXX

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