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Accessing Molecularly Complex Azaborines: Palladium-Catalyzed Suzuki–Miyaura Cross-Couplings of Brominated 2,1-Borazaronaphthalenes and Potassium Organotrifluoroborates

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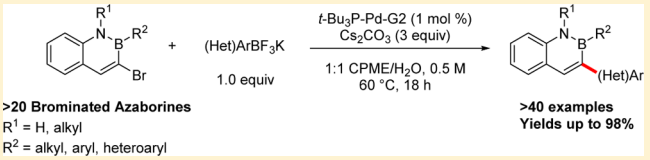
Supporting Information

ABSTRACT: Despite their potential applications in both medicinal chemistry and materials science, there have been limited reports on the functionalization of 2,1-borazaronaphthalenes since their discovery in 1959. To access new chemical space and build molecular complexity, the Suzuki–Miyaura cross-coupling of brominated 2,1-borazaronaphthalenes has been investigated. The palladium-catalyzed cross-coupling proceeds with an array of potassium (hetero)aryltrifluoroborates in high yield with low catalyst loadings under mild reaction conditions. By the use of a high-yielding bromination of various 2,1-borazaronaphthalenes to generate electrophilic azaborine species, a library of 3-(hetero)aryl and 3,6-diaryl-2,1-borazaronaphthalenes has been synthesized.

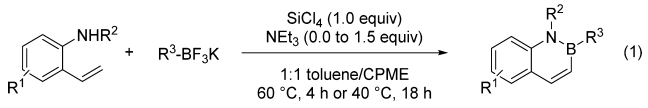


INTRODUCTION

The replacement of a C=C bond with a B–N bond in an aromatic system results in azaborines, heterocycles that retain most of the aromatic character and thermal stability associated with their C=C analogues.[1] Installation of the B–N bond desymmetrizes the heterocycle, allowing functionalization at various positions around the ring with complete regiochemical control. This permits access to elaborate azaborines, the corresponding carbon analogues of which cannot easily be prepared. Because B–N bonds are isoelectronic with C=C double bonds, azaborines have been examined as isosteres for all-carbon aromatics in medicinal chemistry.[2] Azaborines have demonstrated antifungal activity against several different fungi[2g] in addition to exhibiting antibacterial activity against Gram-negative bacteria.[2c,d] Furthermore, the azaborine derivatives of ethylbenzene can bind the hydrophobic pocket of the L99A mutant of the T4 lysozyme as well as inhibit the ethylbenzene dehydrogenase (EbDH) enzyme.[2a,b] Therefore, the synthesis of complex azaborines can provide access to novel drug candidates, thereby aiding the exploration of novel chemical space.[3]

Additionally, the replacement of a C=C bond with a B–N bond in a polycyclic aromatic hydrocarbon (PAH) decreases the HOMO–LUMO gap of the material, which often results in chemiluminescent materials.[4] Thus, in addition to their applications in medicinal chemistry, the isosteric replacement of C=C with B–N has led to the synthesis of classes of compounds that serve as organic light-emitting diodes (OLEDs)[4d] and organic field-effect transistors (OFETs).[4c] Consequently, functionalization of azaborine cores is anticipated to provide access to new classes of compounds with potentially different and impactful photophysical properties.

The promise of azaborines in these fields led us to develop a method to synthesize the core of 2,1-borazaronaphthalene, the B–N analogue of naphthalene (eq 1).[5] 2,1-Borazaronaphthalenes



synthesized through this route are stable toward both strong acid (pH 2 at 37 °C) and base (Cs_2CO_3/H_2O at 60 °C), thus demonstrating their aromatic nature. However, the synthesis of an azaborine core is only the starting point because further functionalization of these molecules allows facile access to novel, increasingly complex molecules.

The method developed for accessing the core of 2,1-borazaronaphthalenes permitted the synthesis of a library of over 50 compounds with various substitutions.[5] This convergent, modular route utilized simple starting materials under mild reaction conditions to afford a highly functionalized azaborine core, allowing selective substitution around the 2,1-borazaronaphthalene system by starting from an *N*- or aryl-substituted 2-aminostyrene to synthesize 1-, 2-, 5-, 6-, 7-, or 8-substituted 2,1-borazaronaphthalenes. However, it was not possible to access 3-substituted-2,1-borazaronaphthalenes through this method, as the reaction between potassium phenyltrifluoroborate and (*E*)-2-styrylaniline did not provide any of the desired product (eq 2).

An alternative method was therefore required for substitution at the 3-position of these azaborines, and thus, a different

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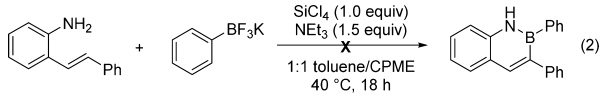
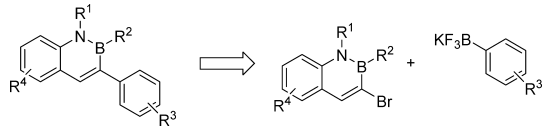


(2)

retrosynthetic disconnection was envisioned (Scheme 1). A Suzuki–Miyaura cross-coupling[6] between brominated 2,1-borazaronaphthalenes and potassium (hetero)aryltrifluoroborates[7] was proposed to elaborate the 2,1-borazaronaphthalenes. Through such a protocol, a library of (hetero)arylated azaborines could be synthesized easily from a brominated starting material, thereby building substantial molecular complexity over two short steps. Only two isolated examples of the cross-coupling of halogenated azaborines and aryl nucleophiles have been previously reported.[8]

Scheme 1. Retrosynthetic Disconnection To Access 3-Aryl-2,1-borazaronaphthalenes



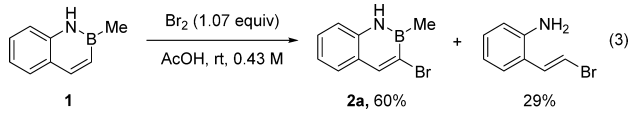
Boronic acids and many boronic acid surrogates are capable of undergoing transmetalation in cross-coupling reactions because an activated palladium complex interacts with a vacant orbital on the boron.[9] Because of the B–N bond, the empty p orbital on boron within the azaborine is occupied by electron donation from the nitrogen. This feature contributes to the azaborine's aromatic stability but was anticipated to reduce its ability to participate in transmetalation. Therefore, we expected selectivity in transmetalation such that the cross-coupling would proceed with the external organoboron nucleophile, leaving the B–C bond of the azaborine intact.

Reported herein is the cross-coupling of 3-bromo-2,1-borazaronaphthalenes with an array of potassium (hetero)-aryltrifluoroborates, providing access to 3-(hetero)aryl-2,1-borazaronaphthalenes. This cross-coupling represents the first reported cross-coupling between an electrophilic brominated azaborine and a nucleophilic organometallic reagent. In this work, 26 2,1-borazaronaphthalenes with various substitutions on boron and nitrogen were brominated, and 43 different cross-coupled 2,1-borazaronaphthalenes were obtained utilizing a palladium-catalyzed Suzuki–Miyaura cross-coupling reaction. The method was then extended to show a second site-selective bromination and subsequent cross-coupling to access diarylated products. The methods developed herein demonstrate that the unique site-selective emplacement of groups about the azaborine core allows more diverse and precise elaboration of these systems with far greater ease and higher selectivities than with naphthalene itself.

RESULTS AND DISCUSSION

2,1-Borazaronaphthalenes exhibit reactivity toward electrophilic aromatic substitution that is complementary to that of their C=C counterparts because the B–N bond desymmetrizes the molecule, with different positions being activated relative to those in naphthalene. Because azaborines are generally less aromatic than their C=C analogues,[1] 2,1-borazaronaphthalenes are also activated toward electrophilic aromatic substitution, and in general such reactions take place under milder reaction conditions. Therefore, initial efforts were focused on the bromination of 2,1-borazaronaphthalenes through an electrophilic aromatic substitution to generate the required electrophilic partner.

The bromination and chlorination of 2-methyl-2,1-borazaronaphthalene (**1**) were first reported by Dewar in 1961 (eq 3).[10]



(3)

To this day, these two halogenated 2,1-borazaronaphthalenes remain the only 3-substituted-2,1-borazaronaphthalenes reported in the literature. The addition of bromine to a solution of **1** in acetic acid resulted in a 60% isolated yield of the desired product. A major halogenated, deboronated side product was generated in 29% yield as a result of the harsh reaction conditions. More recently, the bromination of 1,2-dihydro-1,2-azaborine, the B–N isostere of benzene, was reported to provide the desired product in 91% yield under milder reaction conditions.[11] Utilizing these modified conditions for the bromination of 2,1-borazaronaphthalene by changing the solvent from acetic acid to dichloromethane and cooling the reaction to 0 °C enabled the desired 3-bromo-2,1-borazaronaphthalenes to be easily synthesized. The rate of addition of bromine was vital to the success of the reaction: a rate of ∼1 mmol/h resulted in a high yield for many 2,1-borazaronaphthalenes, while more rapid addition of bromine caused the reaction to exotherm, resulting in decomposition of the 2,1-borazaronaphthalene. Brominations could also be carried out in a shorter period of time by conducting the reaction at −78 °C.

The bromination conditions were applied to an array of 2,1-borazaronaphthalenes to access 3-bromo-2,1-borazaronaphthalenes in high yield (Table 1). Free *N*-H 2,1-borazaronaphthalenes with alkyl substituents on boron were brominated in yields of up to 99% (entries 1–5). Bromination of 2-aryl-2,1-borazaronaphthalenes with either electron-withdrawing or electron-donating groups on the arene afforded the desired products in yields of 81–99% (entries 8–10, 13–17, and 19). Brominated heteroaryl-containing 2,1-borazaronaphthalenes were obtained in variable yields (entries 11, 12, and 18). Substitution on nitrogen did not interfere with the bromination, and the desired products were obtained in modest to excellent yields (entries 6, 7, and 13–19). The brominated products **2r** and **2t** were synthesized in lower yield as a result of the formation of side products resulting from multiple additions of bromine. Interestingly, good to excellent yields of the brominated borazines were achieved even in the presence of what might be considered to be activated arenes (entries 9, 12, 14, and 19). The extraordinary reactivity of the 2,1-borazaronaphthalene toward electrophilic aromatic substitution was further demonstrated in the cases of substrates **2g**, **2m**, **2n**, and **2t**, where the azaborine core was brominated in preference to either an allyl group[12] on nitrogen or an alkyne[13] on boron (entries 7, 13, 14, 20).

Attempts to synthesize 2,1-borazaronaphthalenes from electron-poor 2-aminostyrenes (i.e., 2-amino-5-trifluoromethylstyrene) were unsuccessful under our developed conditions. However, *N*-substituted 2-aminostyrenes are suitable substrates for the synthesis of azaborines. Substitution of the all-carbon ring of the 2,1-borazaronaphthalene does not affect the bromination because the corresponding products were isolated in good yields (entries 21 and 22).

The desired 3-bromo-2,1-borazaronaphthalenes were synthesized with aryl, heteroaryl, alkynyl, and alkyl substituents on boron. However, the presence of an alkene on boron resulted in dibromination of the alkene as the major product (eq 4).

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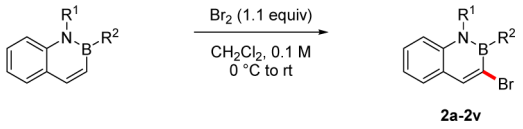
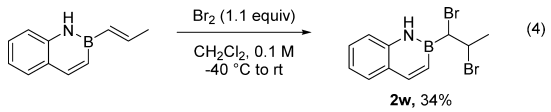
Table 1. Scope of the Bromination of 2,1-Borazaronaphthalenes



2a-2v

entry	product	entry	product	entry	product	entry	product
1	**2a**, 99%	7	**2g**, 98%	13	**2m**, 53%	19	**2s**, 81%[a]
2	**2b**, 96%	8	**2h**, 99%	14	**2n**, 46%[a]	20	**2t**, 29%[a]
3	**2c**, 98%	9	**2i**, 52%	15	**2o**, 95%	21	**2u**, 77%
4	**2d**, 93%	10	**2j**, 91%	16	**2p**, 48%	22	**2v**, 64%
5	**2e**, 97%	11	**2k**, 53%	17	**2q**, 49%[a]		
6	**2f**, 95%	12	**2l**, 89%	18	**2r**, 25%		

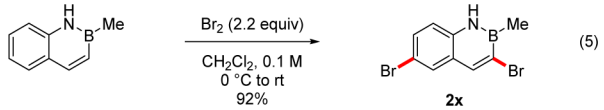
Reaction conditions (unless otherwise noted): 1.0 equiv of 2,1-borazaronaphthalene, 1.1 equiv of Br_2, CH_2Cl_2, 0 °C to rt. [a]The reaction was performed at −40 °C to rt.



2w, 34% (4)

The same result was evident in the bromination of an alkenyl-substituted arene, where addition of bromine resulted in dibromination of the alkene followed by bromination of the arene.[14]

The addition of a second equivalent of bromine to the 2,1-borazaronaphthalene resulted in site-selective dibromination at the 3- and 6-positions of the 2,1-borazaronaphthalene (eq 5),

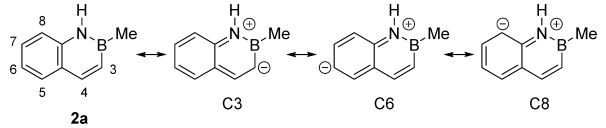


2x (5)

providing the desired product in excellent yield and again demonstrating extraordinary complementarity to naphthalene systems in terms of both selectivity and structural diversity.

As noted previously, the isosteric replacement of C=C with B−N effectively desymmetrizes the molecule and selectively activates the system for electrophilic aromatic substitution to such an extent that both the mono- and dibromination reactions proceed with complete regiochemical control. Resonance structures can be used to rationalize activation of C3 and C6, but such an analysis indicates that C8 should also be activated (Scheme 2).

Scheme 2. Resonance Forms of 2,1-Borazaronaphthalenes



This observed selectivity of electrophilic aromatic substitution at C3 and C6 was reinforced and refined by a rudimentary DFT calculation[15] analyzing the HOMO of the 2,1-borazaronaphthalene. This calculation, completed at the B3LYP/6-31G(d) level of theory, detailed the electron density of the HOMO of 2,1-borazaronaphthalene (Figure 1). The increased electron density at the fused carbons (C4a and C8a) suggests that C4a should be nucleophilic. However, addition of an electrophile at C4a would break the aromaticity in both rings of the azaborine, resulting in a higher energy barrier for reaction,

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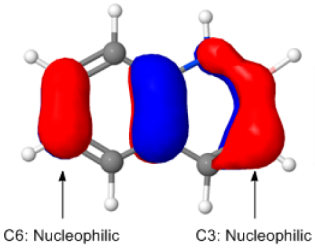


Position	Electron Density of HOMO
C3	0.342764
C6	0.325411
C8	0.024459

Figure 1. DFT-calculated HOMO of 2,1-borazaronaphthalene [calculated at the B3LYP/6-31G(d) level of theory].

thereby disfavoring addition at this carbon. The carbon with the highest electron density in the HOMO is C3, with an electron density of 0.342, whereas C6 is a close second with an electron density of 0.325. The electron density of C8 is only 0.024, showing the lack of nucleophilicity of this carbon relative to C3 and C6. Similar calculations for substrates with substitution around the azaborine (i.e., **2u** and **2v**) show a similar trend, confirming the high reactivity at the 3-position.

Computational studies of brominated intermediates are equally informative in rationalizing the site selectivity observed.[15] A series of calculations at the B3LYP/6-31G(d) level of theory evaluated the relative energies of the intermediates formed after addition of bromine to 2-methyl-2,1-borazaronaphthalene **1** (Figure 2). The relative energy of the intermediate

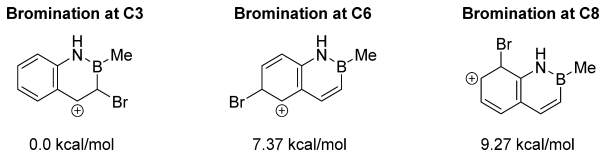


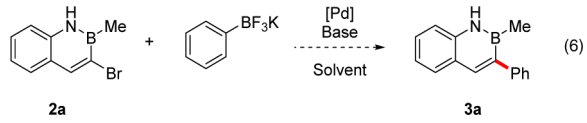
Figure 2. Relative energies for the addition of bromine to 2-methyl-2,1-borazaronaphthalene intermediates [calculated at the B3LYP/6-31G(d) level of theory].

for the bromination at C3 is much lower than those at C6 and C8, explaining the first bromination at the 3-position. This calculation confirms that addition occurs first on the B−N ring because it is both less aromatic and less thermally stable than a C═C ring, which in turn increases its reactivity.[16] Addition of a second equivalent of bromine results in addition to the C═C ring of the 2,1-borazaronaphthalene, specifically at the 6-position, because the intermediate derived from addition at that site is ∼2 kcal/mol lower in energy than that of the C8-brominated intermediate.

The impact of the site-selective bromination can be demonstrated by comparison with the bromination of naphthalene. Unlike 2,1-borazaronaphthalenes, which undergo electrophilic aromatic substitution selectively at the 3-position, the natural site for electrophilic aromatic substitution of naphthalene is the 1-position.[17] In fact, the bromination of 2-methylnaphthalene to form 1-bromo-2-methylnaphthalene proceeds in 87% yield[18] whereas the bromination of the corresponding azaborine **1** yields 3-bromo-2-methyl-2,1-borazaronaphthalene (**2a**) in 99% yield, demonstrating complementary electrophilic aromatic substitutions of the C═C and B−N analogues to access molecules with different substitution patterns.

Furthermore, to install a halogen at the 3-position of naphthalene requires either a directing group under harsh reaction conditions[19] or a gold-catalyzed cyclization in the presence of NIS.[20] The corresponding bromination of 2,1-borazaronaphthalene is a one-step process resulting in the addition of bromine to a highly functionalized molecule.

Upon the synthesis of the brominated 2,1-borazaronaphthalenes, investigations of the Suzuki−Miyaura cross-coupling reaction were conducted. 3-Bromo-2-methyl-2,1-borazaronaphthalene **2a** and potassium phenyltrifluoroborate were chosen as model substrates in the reaction to synthesize 2-methyl-3-phenyl-2,1-borazaronaphthalene (**3a**) (eq 6).



Initially, stability tests were performed to ensure that 2,1-borazaronaphthalenes would be stable in basic media at the elevated temperatures required for the cross-coupling. Heating of the 2,1-borazaronaphthalenes at 60 °C in a 1:1 THF/H_2O solvent system with 3 equiv of Cs_2CO_3 resulted in complete recovery of the 2,1-borazaronaphthalenes. Initial reaction conditions for the cross-coupling of phenyltrifluoroborate with the brominated azaborine **2a** were determined through a limited screening process. Of the palladium sources and ligands tested in this initial screen, the (t-Bu_3P)(aminobiphenyl) palladium chloride precatalyst (commercially available t-Bu_3P-Pd-G2; Figure 3) was chosen for future study as it contained a

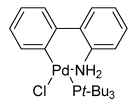
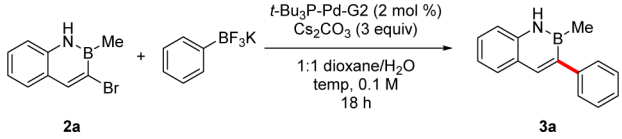


Figure 3. Structure of t-Bu_3P-Pd-G2.

relatively inexpensive phosphine ligand and demonstrated high conversion of the starting material.

Optimization continued by variation of the temperature, solvent, and catalyst loading with Cs_2CO_3 as the base (Table 2). With a solvent system of 1:1 dioxane/H_2O, a reaction temperature of 40 °C resulted in incomplete conversion after 18 h

Table 2. Optimization of the Cross-Coupling of 3-Bromo-2-methyl-2,1-borazaronaphthalene with Potassium Phenyltrifluoroborate



entry	variation from above conditions	product-to-internal standard ratio[a]
1	40 °C reaction temperature	1.11
2	60 °C reaction temperature	2.04
3	1:1 CPME/H_2O as solvent, 60 °C	2.08
4	1:1 toluene/H_2O as solvent, 60 °C	1.36
5	1:1 THF/H_2O as solvent, 60 °C	1.73
6	1 mol % [Pd][b]	1.99
7	0.5 mol % [Pd][b]	1.67
8	0.25 M concentration[b]	2.00
9	0.5 M concentration[b]	2.02

[a]Determined by HPLC with the addition of 10 mol % 4,4′-di-*tert*-butylbiphenyl as an internal standard. Entries 2, 3, 6, 8, and 9 resulted in complete conversion of the starting material. [b]Reaction completed at 60 °C with 1:1 CPME/H_2O as the solvent.

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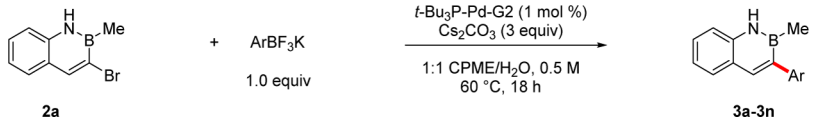
(entry 1); however, increasing the temperature to 60 °C provided complete conversion to the desired product in 18 h (entry 2). Various solvents were then screened in this reaction. No side products were observed with any solvent, meaning the solvent affected only the rate of the reaction. Both cyclopentyl methyl ether (CPME) and dioxane afforded complete conversion to the desired product, whereas toluene and THF did not (entries 3–5). CPME was chosen as the cosolvent in the reaction because of its more favorable properties relative to dioxane. Optimization then continued with a solvent system of 1:1 CPME/H_2O. Because of the increased temperature, decreasing the palladium loading to 1 mol % resulted in complete conversion (entry 6), but when the catalyst loading was further decreased to 0.5 mol %, starting material remained after 18 h (entry 7). The concentration of the reaction was also screened, and complete conversion was achieved with a concentration of 0.5 M (entries 8 and 9). Therefore, 1 mol % *t*-Bu_3P-Pd-G2, 3 equiv of Cs_2CO_3, and 1:1 CPME/H_2O at 60 °C for 18 h were used as the standard cross-coupling conditions.

The general reaction conditions were applied to a representative set of potassium aryltrifluoroborates with 3-bromo-2-methyl-2,1-borazaronaphthalene as the electrophilic partner in the cross-coupling reaction (Table 3). To investigate the method fully, both electron-rich (entries 1–8) and electron-poor (entries 10–13) aryltrifluoroborates were examined. All of the aryltrifluoroborates utilized were successfully cross-coupled without employing an excess of the organotrifluoroborate, providing the desired 3-aryl-2,1-borazaronaphthalenes in yields of 53–98%. Aryltrifluoroborates with *ortho* (entry 3), *meta* (entries 2, 8–12, 14), and *para* (entries 4, 5, and 13) substitution afforded the desired products in high yield. Both 1- and 2-naphthyltrifluoroborate were successful nucleophiles in this reaction, and the products were obtained in yields of 93% and 95%, respectively (entries 6 and 7). When a disubstituted aryltrifluoroborate was subjected to the reaction, the product was synthesized in 73% yield (entry 9). The scalable nature of the cross-coupling was demonstrated by performing the reaction on a 4.5 mmol scale with 0.5 mol % *t*-Bu_3P-Pd-G2, which provided the desired products in high yield (entries 1 and 2).

To expand the range of nucleophiles, 3-bromo-2-methyl-2,1-borazaronaphthalene was coupled with a variety of potassium heteroaryltrifluoroborates (Table 4). The thienyltrifluoroborates were successfully cross-coupled, affording the desired products in yields of 84% and 86% (entries 2 and 3). Other heteroaryltrifluoroborates, including furyl and isoxazolyl, were successfully coupled, and the corresponding 3-heteroaryl-2,1-borazaronaphthalenes were synthesized in yields up to 72%

Table 3. Scope of the Cross-Coupling with Potassium Aryltrifluoroborates



2a 3a-3n

entry	product	entry	product	entry	product	entry	product
1	**3a**, 98% (93%[b])	5	**3e**, 89%	9	**3i**, 73%	12	**3l**, 90%
2	**3b**, 95% (98%[b])	6	**3f**, 93%	10	**3j**, 53%	13	**3m**, 88%
3	**3c**, 94%	7	**3g**, 95%	11	**3k**, 88%	14	**3n**, 79%
4	**3d**, 67%[a]	8	**3h**, 71%				

Reaction conditions (unless otherwise noted): 1.0 equiv of 3-bromo-2-methyl-2,1-borazaronaphthalene, 1.0 equiv of potassium aryltrifluoroborate, 1 mol % *t*-Bu_3P-Pd-G2, 3.0 equiv of base, 1:1 CPME/H_2O, 60 °C, 18 h. [a]Reaction concentration of 0.1 M. [b]Reaction completed on a 4.5 mmol scale with 0.5 mol % *t*-Bu_3P-Pd-G2.

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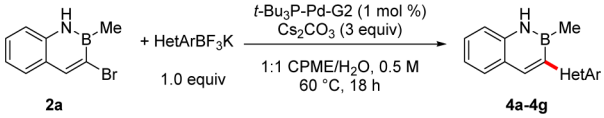
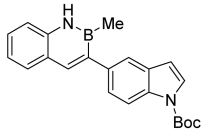
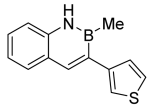
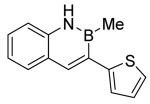
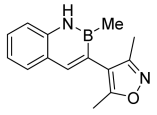
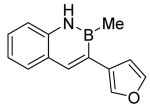
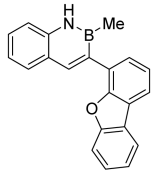
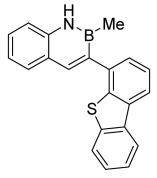
Table 4. Scope of the Cross-Coupling with Potassium Heteroaryltrifluoroborates



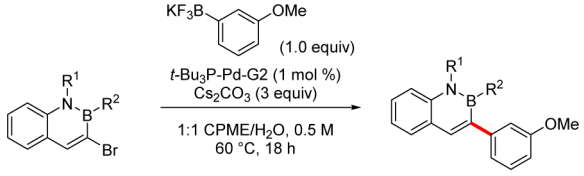
entry	product		yield
1		**4a**	56%
2		**4b**	86%
3		**4c**	84%
4		**4d**	51%
5		**4e**	72%
6		**4f**	54%[a]
7		**4g**	52%[a]

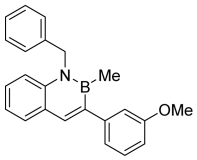
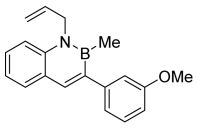
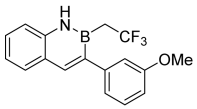
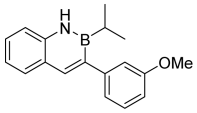
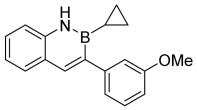
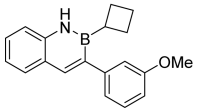
Reaction conditions (unless otherwise noted): 1.0 equiv of 3-bromo-2-methyl-2,1-borazaronaphthalene, 1.0 equiv of potassium heteroaryltrifluoroborate, 1 mol % *t*-Bu_3P-Pd-G2, 3.0 equiv of base, 1:1 CPME/H_2O, 60 °C, 18 h. [a]Reaction concentration of 0.1 M.

(entries 4 and 5). Larger heteroaryltrifluoroborates, such as 4-dibenzofuranyl- and 4-dibenzothienyltrifluoroborate, were efficient as nucleophiles in the coupling, furnishing the products in yields of 54% and 52%, respectively, after the concentration of the reaction was lowered to 0.1 M (entries 6 and 7).

To demonstrate the versatility of this method, other 3-bromo-2-alkyl-2,1-borazaronaphthalenes were synthesized and subjected to the standard cross-coupling conditions with potassium 3-methoxyphenyltrifluoroborate as the nucleophilic partner (Table 5). All six brominated 2,1-borazaronaphthalenes provided the desired products in good to excellent yields. Brominated *N*-substituted *B*-alkyl 2,1-borazaronaphthalenes were successful electrophiles in this cross-coupling reaction. Benzyl and allyl substituents on nitrogen did not affect the cross-coupling, providing the desired products in yields of 93%, and 83%, respectively (entries 1 and 2). The product from the

Table 5. Scope of Cross-Coupling of 3-Bromo-2-alkyl-2,1-borazaronaphthalenes



entry	product		yield
1		**5a**	93%
2		**5b**	83%
3		**5c**	67%
4		**5d**	77%
5		**5e**	84%
6		**5f**	70%

Reaction conditions: 1.0 equiv of 3-bromo-2-alkyl-2,1-borazaronaphthalene, 1.0 equiv of potassium 3-methoxyphenyltrifluoroborate, 1 mol % *t*-Bu_3P-Pd-G2, 3.0 equiv of base, 1:1 CPME/H_2O, 60 °C, 18 h.

cross-coupling of 3-bromo-2-(*β*,*β*,*β*-trifluoroethyl)-2,1-borazaronaphthalene was obtained in 67% yield, providing access to fluorinated 2,1-borazaronaphthalenes (entry 3). Secondary cyclic (cyclobutyl and cyclopropyl) and noncyclic (isopropyl) substituents on boron afforded the corresponding cross-coupled product in yields of 70%, 84%, and 77%, respectively (entries 4–6).

After viable reaction conditions for the coupling of 3-bromo-2-*alkyl*-2,1-borazaronaphthalenes were determined, the coupling of the corresponding 3-bromo-2-*aryl*-2,1-borazaronaphthalenes was investigated. Although transmetalation of the *B*-alkyl systems would likely never compete with those of the arylboron nucleophiles, aryl groups are much more easily transferred. Therefore, there was concern that 3-bromo-2-aryl-2,1-borazaronaphthalenes would not be stable in the cross-coupling reaction, with the potential that the *B*-aryl group of the azaborine could compete with the nucleophilic aryltrifluoroborate in the reaction, resulting in a mixture of products. Fortunately, subjecting 3-bromo-2-phenyl-2,1-borazaronaphthalene (**2h**) to the reaction conditions with 1 equiv of either potassium phenyltrifluoroborate or phenylboronic acid resulted in the desired cross-coupled product **11a** in a yield of 77% or 54%, respectively (Table 6, entry 1). On the basis of these

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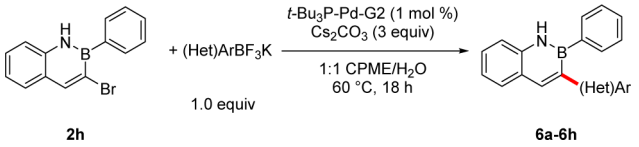
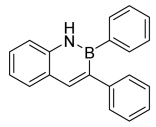
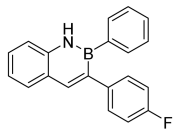
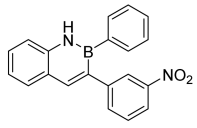
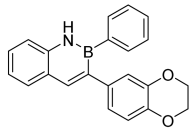
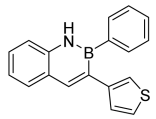
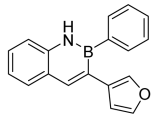
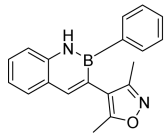
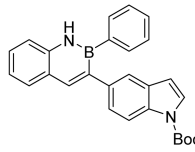
Table 6. Scope of the Cross-Coupling with Various Potassium (Hetero)aryltrifluoroborates



2h **6a-6h**

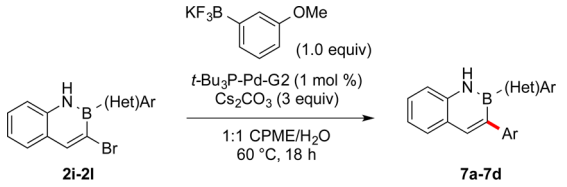
entry	product		yield
1		**6a**	77% (54%[a])
2		**6b**	71%
3		**6c**	32%
4		**6d**	52%
5		**6e**	70%
6		**6f**	80%
7		**6g**	88%
8		**6h**	75%

Reaction conditions (unless otherwise noted): 1.0 equiv of 3-bromo-2-phenyl-2,1-borazaronaphthalene, 1.0 equiv of potassium (hetero)-aryltrifluoroborate, 1 mol % t-Bu_3P-Pd-G2, 3.0 equiv of base, 1:1 CPME/H_2O, 60 °C, 18 h. [a]Phenylboronic acid was utilized as the nucleophile.

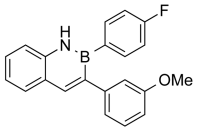
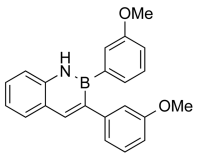
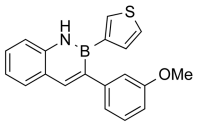
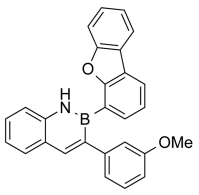
results, the scope of the cross-coupling was analyzed with an array of potassium (hetero)aryltrifluoroborates (Table 6). Aryltrifluoroborates with either *para* or *meta* substitution provided the desired product in yields of 71% and 32%, respectively (entries 2 and 3). Several heteroaryltrifluoroborates were successful nucleophiles in this coupling, such as thienyl, furyl, and isoxazolyl, affording the cross-coupled products in yields of 70%, 80%, and 88%, respectively (entries 5−7). The desired cross-coupled product was obtained in 75% yield when an *N*-Boc-indolyltrifluoroborate was employed as the nucleophile in the reaction (entry 8).

To demonstrate the versatility of this method, other 3-bromo-2-(hetero)aryl-2,1-borazaronaphthalenes were synthesized and subjected to the standard cross-coupling conditions with potassium 3-methoxyphenyltrifluoroborate as the nucleophilic partner (Table 7). Two additional 3-bromo-2-aryl-2,1-

Table 7. Scope of Cross-Coupling of 3-Bromo-2-(hetero)aryl-2,1-borazaronaphthalenes



2i-2l **7a-7d**

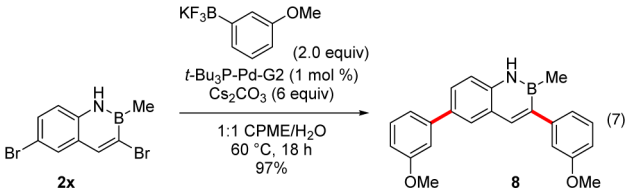
entry	product		yield
1		**7a**	62%
2		**7b**	50%
3		**7c**	24%
4		**7d**	32%

Reaction conditions: 1.0 equiv of 3-bromo-2-(hetero)aryl-2,1-borazaronaphthalene, 1.0 equiv of potassium 3-methoxyphenyltrifluoroborate, 1 mol % t-Bu_3P-Pd-G2, 3.0 equiv of base, 1:1 CPME/H_2O, 60 °C, 18 h.

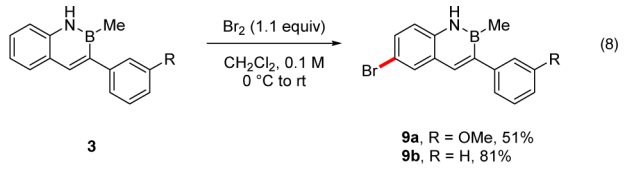
borazaronaphthalenes were subjected to the cross-coupling reaction, and the corresponding products were isolated in yields of 62% and 50% (entries 1 and 2). Heteroaryl-containing 2,1-borazaronaphthalenes were also successful electrophiles for the coupling. When the electrophile was 3-bromo-2-(3-thienyl)-2,1-borazaronaphthalene, the desired product was obtained in 24% yield (entry 3). Steric hindrance of the 2,1-borazaronaphthalene can affect the success of the coupling reaction. For example, 3-bromo-2-(4-dibenzofuranyl)-2,1-borazaronaphthalene could serve as the electrophilic partner in this reaction but afforded the desired product in only 32% yield (entry 4).

After the analysis of the scope of the cross-coupling to include both *B*-alkyl- and *B*-aryl-2,1-borazaronaphthalenes, studies were directed toward accessing doubly cross-coupled products. Addition of 2 equiv of 3-methoxyphenyltrifluoroborate to 3,6-dibromo-2-methyl-2,1-borazaronaphthalene (**2v**) provided the desired product in 97% isolated yield (eq 7).

dx.doi.org/10.1021/jo5011894 | J. Org. Chem. 2014, 79, 6663−6678



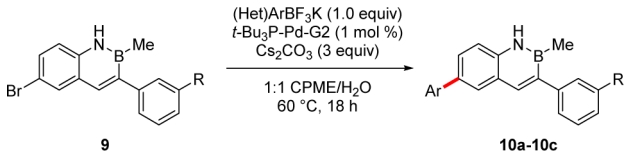
Unfortunately, the cross-coupling was not selective upon addition of 1 equiv of potassium aryltrifluoroborate. Therefore, to access doubly cross-coupled products utilizing different potassium (hetero)aryltrifluoroborates, the product of one cross-coupling had to be subjected to a second site-selective bromination. In the case of cross-coupling products **3a** and **3b**, the second bromination proceeded at the 6-position to yield 6-bromo-3-(3-methoxyphenyl)-2-methyl-2,1-borazaronaphthalene (**9a**) and 6-bromo-3-phenyl-2-methyl-2,1-borazaronaphthalene (**9b**), respectively, in moderate to good yields (eq 8).

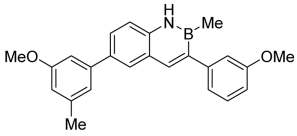
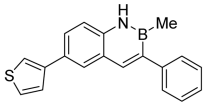
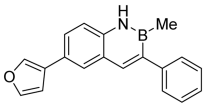


Rather remarkably, the borazine was brominated effectively at its second most reactive site in the presence of the electron-rich methoxy-substituted arene.

These brominated 2,1-borazaronaphthalenes reacted with an array of potassium (hetero)aryltrifluoroborates to provide access to highly substituted 2,1-borazaronaphthalenes (Table 8).

Table 8. Scope of the Cross-Coupling with Various Potassium Organotrifluoroborates



entry	product		yield
1		**10a**	86%
2		**10b**	84%
3		**10c**	69%

Reaction conditions: 1.0 equiv of 6-bromo-3-aryl-2-methyl-2,1-borazaronaphthalene, 1.0 equiv of potassium (hetero)aryltrifluoroborate, 1 mol % *t*-Bu_3P-Pd-G2, 3.0 equiv of base, 1:1 CPME/H_2O, 60 °C, 18 h.

A 3,5-disubstituted aryltrifluoroborate reacted with **9a** to provide the cross-coupled product **10a** in 86% isolated yield (entry 1). Heteroaryltrifluoroborates were also efficient nucleophiles for this reaction, as 3-thienyltrifluoroborate and 3-furyltrifluoroborate reacted with **9b** to afford the desired products in 84% and 69% yield, respectively (entries 2 and 3).

The overall impact of the approaches to borazine synthesis described herein can be appreciated by comparing these tactics to those utilized for the construction of various substituted naphthalenes. For example, the most convenient synthesis of 2,3-disubstituted naphthalenes provides the symmetrical products in good to excellent yields,[21] but unsymmetrical naphthalenes would result in a mixture of products. The cross-coupling route described herein allows direct and site-specific installation of a (hetero)aryl unit at the C3 position, thus alleviating the limitation of obtaining regioisomeric products.

In a similar scenario, the products of the cross-coupling of brominated *N*-substituted 2,1-borazaronaphthalenes are isosteric to 1,2,3-trisubstituted naphthalenes, whose synthesis often results in mixtures of regioisomers.[22,23] In the case of the 2,1-borazaronaphthalenes, bromination and subsequent cross-coupling allow a library of (hetero)arylated azaborines to be synthesized with complete regiocontrol.

Lastly, the products obtained using the 3,6-diaryl-2,1-borazaronaphthalenes are isosteres of 2,3,6-trisubstituted naphthalenes. There are currently no examples of naphthalenes with this substitution pattern,[24] whereas the corresponding cross-couplings described herein allow the ready synthesis of such site-specific polysubstituted 2,1-borazaronaphthalenes in high yield.

CONCLUSIONS

The first general method for the Suzuki–Miyaura cross-coupling of a halogenated azaborine has been reported. 2,1-Borazaronaphthalenes undergo site-selective bromination at the 3-position, whereupon addition of a second equivalent of bromine allows access to 3,6-dibromo-2,1-borazaronaphthalenes. In this work, 26 different brominated 2,1-borazaronaphthalenes were synthesized in high yield. These brominated 2,1-borazaronaphthalenes are suitable electrophiles in the Suzuki–Miyaura cross-coupling reaction with an array of potassium (hetero)aryltrifluoroborates.

Furthermore, this cross-coupling easily builds molecular complexity within this family of azaborines. Most of the research conducted on azaborines has primarily focused on their synthesis, with limited studies of their reactivity as isosteres of the all-carbon analogues. Before this study, bromine and chlorine were the only two substituents reported at the 3-position of 2,1-borazaronaphthalene, and they were synthesized in low to moderate yields in the early 1960s. The methods described herein expand the substitution at the C3 position to include aryl and heteroaryl substituents. Most importantly, however, the protocols developed demonstrate that 2,1-borazaronaphthalenes are stable toward palladium catalysis, thereby allowing access to highly functionalized molecules and opening the door to the exploration of azaborines in other transition-metal-catalyzed reactions.

EXPERIMENTAL SECTION

General Considerations. *t*-Bu_3P-Pd-G2 was synthesized according to the literature.[25] CPME was dried using a J. C. Meyer solvent system. Standard benchtop techniques for handling air-sensitive reagents were employed. Melting points (°C) are uncorrected. NMR spectra were recorded on a 400 or 500 MHz spectrometer. ^{19}F NMR chemical shifts were referenced to external $CFCl_3$ (0.0 ppm). ^{11}B NMR spectra were obtained on a spectrometer equipped with the appropriate decoupling accessories. All of the ^{11}B NMR chemical shifts were referenced to external $BF_3{\cdot}OEt_2$ (0.0 ppm), with a negative sign

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indicating an upfield shift. Data are presented as follows: chemical shift (multiplicity, coupling constant, integration). Chemical shifts (δ) are reported in parts per million and coupling constants (J) in hertz. Multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad. Analytical thin-layer chromatography (TLC) was performed on TLC silica gel plates (0.25 mm) precoated with a fluorescent indicator. Standard flash chromatography procedures were followed using 32−63 μm silica gel. Visualization was effected with ultraviolet light. HRMS data were obtained by either ESI or CI using a TOF mass spectrometer

Synthesis of Potassium Organotrifluoroborates. 3-Vinylphenylboronic acid, 4-naphthalene-1-ylphenylboronic acid, and 3-methoxy-5-methylphenylboronic are commercially available. They were converted to the corresponding potassium trifluoroborates upon treatment with sat. aq. KHF_2.[26]

Potassium 3-Vinylphenyltrifluoroborate. White solid. Mp >250 °C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.46 (br s, 1H), 7.3 (d, J = 6.8 Hz, 1H), 7.18 (d, J = 7.1 Hz, 1H), 7.13−7.10 (m, 1H), 6.72−6.67 (m, 1H), 5.70 (d, J = 17.9 Hz, 1H), 5.14 (d, J = 10.8 Hz, 1H). ^{13}C NMR (125.8 MHz, DMSO-d_6) δ 138.7, 135.2, 131.8, 129.9, 126.9, 123.5, 112.2. ^{11}B NMR (128.38 MHz, DMSO-d_6) δ 3.4. ^{19}F NMR (338.8 MHz, DMSO-d_6) δ −139.6. IR (neat) 1322, 1260, 1056, 957, 794, 662 cm^{-1}. HRMS (ESI) m/z calcd for $C_8H_7BF_3$ $[M - K]^-$ 171.0593, found 171.0586.

Potassium 4-Naphthalen-1-ylphenyltrifluoroborate. White solid. Mp >250 °C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.96−7.94 (m, 2H), 7.89−7.86 (m, 1H), 7.63−7.60 (m, 2H), 7.55−7.40 (m, 4H), 7.30−7.27 (m, 2H). ^{13}C NMR (125.8 MHz, DMSO-d_6) δ 141.3, 137.2, 133.9, 131.9, 131.5, 128.6, 128.3, 127.3, 127.0, 126.3, 126.1, 126.0, 125.9. ^{11}B NMR (128.38 MHz, DMSO-d_6) δ 3.7. ^{19}F NMR (338.8 MHz, DMSO-d_6) δ −139.0. IR (neat) 3058, 2920, 1647, 1394, 1217, 773 cm^{-1}. HRMS (ESI) m/z calcd for $C_{16}H_{11}BF_3$ $[M - K]^-$ 271.0906, found 271.0906.

Potassium 3-Methoxy-5-methylphenyltrifluoroborate. White solid. Mp >250 °C. ^{1}H NMR (500 MHz, acetone-d_6) δ 6.94 (s, 1H), 6.89 (s, 1H), 6.48 (s, 1H), 3.69 (s, 3H), 2.22 (s, 3H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 158.8, 136.3, 124.8, 113.5, 112.1, 54.0, 20.7. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 4.3. ^{19}F NMR (338.8 MHz, acetone-d_6) δ −142.1. IR (neat) 2918, 1588, 1321, 1287, 1021, 956, 850, 803 cm^{-1}. HRMS (ESI) m/z calcd for $C_8H_9BOF_3$ $[M - K]^-$ 189.0694, found 189.0693.

Synthesis of 2,1-Borazaronaphthalanes. 2,1-Borazaronaphthalenes were synthesized according to the literature procedure.[5]

2-(β,β,β-Trifluoroethyl)-2,1-borazaronaphthalene. Obtained as an off-white solid (130 mg, 21%, 3 mmol scale). Mp 59−61 °C. ^{1}H NMR (500 MHz, acetone-d_6) δ 9.74 (br s, 1H), 8.13 (d, J = 11.2 Hz, 1H), 7.70 (d, J = 7.7 Hz, 1H), 7.56−7.52 (m, 1H), 7.47−7.43 (m, 1H), 7.23−7.18 (m, 1H), 6.94−6.90 (m, 1H), 2.42−2.30 (m, 2H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 145.3, 140.3, 129.2, 128.4, 127.3 (q, J = 278 Hz), 125.3, 121.1, 118.3. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 33.8. IR (neat) 3361, 2970, 1563, 1278, 1236, 1102, 1032, 768 cm^{-1}. HRMS (CI) m/z calcd for $C_{10}H_9BNF_3$ $[M]^+$ 211.0780, found 211.0778.

2-Isopropyl-2,1-borazaronaphthalene. Obtained as an off-white solid (650 mg, 76%, 5 mmol scale). Mp 59−61 °C. ^{1}H NMR (500 MHz, acetone-d_6) δ 9.06 (br s, 1H), 8.01 (d, J = 11.5 Hz, 1H), 7.6 (d, J = 7.6 Hz, 1H), 7.53−7.49 (m, 1H), 7.40−7.35 (m, 1H), 7.13−7.09 (m, 1H), 6.87−6.82 (m, 1H), 1.56−1.48 (m, 1H), 1.18−1.11 (m, 6H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 144.5, 140.7, 128.9, 127.8, 125.2, 120.2, 118.2, 19.6. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 37.9. IR (neat) 3361, 2940, 1560, 1438, 1056, 1035, 761 cm^{-1}. HRMS (CI) m/z calcd for $C_{11}H_{14}BN$ $[M]^+$ 171.1219, found 171.1223.

2-Cyclobutyl-2,1-borazaronaphthalene. Obtained as an off-white solid (379 mg, 69%, 3 mmol scale). Mp 63−64 °C. ^{1}H NMR (500 MHz, acetone-d_6) δ 9.09 (br s, 1H), 8.02 (d, J = 11.5 Hz, 1H), 7.61 (d, J = 7.8 Hz, 1H), 7.51−7.48 (m, 1H), 7.39−7.35 (m, 1H), 7.14−7.09 (m, 1H), 6.90−6.85 (m, 1H), 2.47−2.40 (m, 1H), 2.27−2.11 (m, 5H), 2.07−2.00 (m, 1H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 144.5, 140.7, 128.9, 127.8, 125.2, 120.2, 118.0, 25.5, 22.1. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 37.7. IR (neat) 3363, 2960, 2934, 2858, 1560, 1438, 760 cm^{-1}. HRMS (CI) m/z calcd for $C_{12}H_{14}BN$ $[M]^+$ 183.1219, found 183.1212.

2-(3-Methoxyphenyl)-2,1-borazaronaphthalene. Obtained as an off-white solid (834 mg, 71%, 5 mmol scale). Mp 80−82 °C. ^{1}H NMR (500 MHz, acetone-d_6) δ 9.77 (br s, 1H), 8.18 (d, J = 11.5 Hz, 1H), 7.70−7.66 (m, 2H), 7.63−7.60 (m, 2H), 7.46−7.42 (m, 1H), 7.39−7.35 (m, 1H), 7.31−7.27 (m, 1H), 7.21−7.17 (m, 1H), 7.00−6.97 (m, 1H), 3.85 (s, 3H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 159.6, 145.4, 141.0, 129.0, 129.0, 128.2, 125.6, 125.4, 120.7, 118.5, 118.1, 114.9, 54.4. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 34.0. IR (neat) 3368, 3051, 2406, 1566, 1250, 1039, 763 cm^{-1}. HRMS (CI) m/z calcd for $C_{15}H_{14}BNO$ $[M]^+$ 235.1168, found 235.1177.

2-(3-Methoxyphenyl)-1-(4-methylbenzyl)-2,1-borazaronaphthalene. Obtained as an off-white solid (569 mg, 56%, 3 mmol scale). Mp 113−115 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (d, J = 11.2 Hz, 1H), 7.73 (d, J = 7.6 Hz, 1H), 7.40−7.36 (m, 2H), 7.31−7.28 (m, 1H), 7.23−7.20 (m, 1H), 7.17−7.11 (m, 3H), 7.09−7.01 (m, 4H), 6.92−6.88 (m, 1H), 5.43 (br s, 2H), 3.66 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 162.2, 158.8, 145.3, 141.2, 136.6, 130.2, 129.3, 128.8, 128.5, 127.2, 125.6, 124.8, 120.9, 117.2, 117.0, 113.9, 54.8, 52.3, 21.0. ^{11}B NMR (128.38 MHz, $CDCl_3$) δ 37.3. IR (neat) 2995, 1548, 1415, 1255, 1225, 1028, 766 cm^{-1}. HRMS (CI) m/z calcd for $C_{23}H_{22}BNO$ $[M]^+$ 339.1794, found 339.1781.

1-Allyl-2-methyl-2,1-borazaronaphthalene. Obtained as a yellow oil (285 mg, 52%, 3 mmol scale). ^{1}H NMR (500 MHz, acetone-d_6) δ 7.91 (d, J = 11.2 Hz, 1H), 7.64 (d, J = 7.8 Hz, 1H), 7.52−7.59 (m, 1H), 7.46−7.42 (m, 1H), 7.17−7.14 (m, 1H), 6.81−6.78 (m, 1H), 6.08−6.02 (m, 1H), 5.09 (d, J = 10.5 Hz, 1H), 4.91 (d, J = 17.4 Hz, 1H), 4.70−4.68 (m, 2H), 0.81 (s, 3H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 144.0, 141.5, 134.7, 130.0, 128.1, 126.6, 120.2, 115.5, 114.6, 48.9. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 39.2. IR (neat) 3008, 1609, 1551, 1412, 1353, 1219, 757 cm^{-1}. HRMS (ESI) m/z calcd for $C_{12}H_{14}BN$ $[M]^+$ 183.1219, found 183.1215.

1-Allyl-2-(3-methoxyphenyl)-2,1-borazaronaphthalene. Obtained as a yellow oil (486 mg, 59%, 3 mmol scale). ^{1}H NMR (500 MHz, acetone-d_6) δ 8.13 (d, J = 11.2 Hz, 1H), 7.76 (d, J = 7.8 Hz, 1H), 7.64−7.61 (m, 1H), 7.56−7.51 (m, 1H), 7.35−7.31 (m, 1H), 7.28−7.23 (m, 1H), 7.18−7.14 (m, 2H), 6.95−6.89 (m, 2H), 6.18−6.11 (m, 1H), 5.22−5.17 (m, 1H), 4.99−4.93 (m, 1H), 4.85−4.82 (m, 2H), 3.81 (s, 3H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 159.1, 145.2, 141.0, 136.1, 130.1, 128.7, 128.5, 127.0, 124.3, 121.0, 117.3, 116.7, 114.9, 113.3, 54.3, 50.3. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 37.2. IR (neat) 3009, 2939, 2830, 1549, 1413, 1281, 1049, 764 cm^{-1}. HRMS (ESI) m/z calcd for $C_{18}H_{19}BNO$ $[M + H]^+$ 276.1560, found 276.1564.

1-Benzyl-2-(4-trifluoromethylphenyl)-2,1-borazaronaphthalene. Obtained as a white solid (585 mg, 54%, 3 mmol scale). Mp 84−86 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33−8.30 (m, 1H), 7.89−7.72 (m, 5H), 7.55−7.35 (m, 6H), 7.28−7.19 (m, 3H), 5.53 (s, 2H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 146.3, 141.3, 139.2, 132.9, 132.5 (q, J = 226 Hz), 130.8, 130.2 (d, J = 32 Hz), 129.2, 127.8, 127.4, 125.9, 124.6 (d, J = 3 Hz), 123.8, 121.8, 117.4, 52.8. ^{11}B NMR (128.38 MHz, $CDCl_3$) δ 37.1. IR (neat) 2923, 1551, 1233, 859, 762, 682, 632 cm^{-1}. HRMS (CI) m/z calcd for $C_{22}H_{17}BNF_3$ $[M]^+$ 363.1406, found 363.1403.

2-(4-Fluorophenyl)-1-(4-methoxybenzyl)-2,1-borazaronaphthalene. Obtained as a white solid (700 mg, 68%, 3 mmol scale). Mp 95−97 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (d, J = 11.5 Hz, 1H), 7.77 (d, J = 7.3 Hz, 1H), 7.60−7.57 (m, 2H), 7.46−7.41 (m, 2H), 7.28−7.25 (m, 1H), 7.11−7.09 (m, 5H), 6.92−6.90 (m, 2H), 5.43 (s, 2H), 3.83 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 163.1 (d, J = 245 Hz), 158.5, 145.5, 141.2, 134.5 (d, J = 7 Hz), 131.02, 130.3, 128.6, 127.3, 126.7, 121.1, 117.1, 114.7 (d, J = 20 Hz), 114.3, 55.2, 51.8. ^{11}B NMR (128.38 MHz, $CDCl_3$) δ 37.2. IR (neat) 3027, 1550, 1414, 1234, 787, 761, 731 cm^{-1}. HRMS (CI) m/z calcd for $C_{22}H_{19}BNOF$ $[M]^+$ 343.1544, found 343.1540.

General Procedure for the Bromination of 2,1-Borazaronaphthalenes. To a flame-dried 100 mL round-bottom flask with a stir bar was added the corresponding 2,1-borazaronaphthalene (2.0 mmol). The flask was sealed with a rubber septum, evacuated under vacuum, and purged with Ar three times. Anhydrous CH_2Cl_2

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(10 mL) was added, and the flask was cooled to 0 °C. Bromine (352 mg, 2.2 mmol, 1.1 equiv) in CH_2Cl_2 (10 mL) was added under Ar at a rate of 1.1 mmol/h. After the addition, the reaction mixture was slowly warmed to rt. The reaction was monitored by TLC, and when it was complete (usually after warming to rt), the reaction mixture was concentrated in vacuo. The crude 2,1-borazaronaphthalene was purified by flash column chromatography with 0−30% CH_2Cl_2/hexane as the eluent to provide the desired 3-bromo-2,1-borazaronaphthalene.

3-Bromo-2-methyl-2,1-borazaronaphthalene (**2a**). Obtained as an off-white solid (1969 mg, 99%, 9 mmol scale). Mp 115−117 °C. ^{1}H NMR (500 MHz, acetone-d_6) δ 9.63 (br s, 1H), 8.29 (s, 1H), 7.62 (d, J = 7.8 Hz, 1H), 7.47−7.42 (m, 2H), 7.17−7.14 (m, 1H), 0.79 (s, 3H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 144.3, 140.2, 128.6, 128.55, 124.9, 121.2, 118.2. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 39.2. IR (neat) 3361, 2940, 1560, 1438, 1056, 1035, 761 cm^{-1}. HRMS (CI) m/z calcd for C_9H_9BrBN $[M]^+$ 221.0011, found 221.0019.

3-Bromo-2-(β,β,β-trifluoroethyl)-2,1-borazaronaphthalene (**2b**). Obtained as an off-white solid (138 mg, 96%, 0.5 mmol scale). Mp 61−63 °C. ^{1}H NMR (500 MHz, acetone-d_6) δ 9.87 (br s, 1H), 8.44 (s, 1H), 7.71−7.64 (m, 2H), 7.53−7.49 (m, 1H), 7.26−7.23 (m, 1H), 2.55−5.49 (m, 2H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 146.2, 139.5, 129.3, 128.8, 128.7 (q, J = 274 Hz), 125.2, 122.3, 118.8. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 33.4. IR (neat) 3361, 2970, 1563, 1278, 1236, 1102, 1032, 768 cm^{-1}. HRMS (CI) m/z calcd for $C_{10}H_8BrBNF_3$ $[M]^+$ 288.9885, found 288.9884.

3-Bromo-2-isopropyl-2,1-borazaronaphthalene (**2c**). Obtained as an off-white solid (488 mg, 98%, 2 mmol scale). Mp 57−69 °C. ^{1}H NMR (500 MHz, acetone-d_6) δ 9.26 (br s, 1H), 8.33 (s, 1H), 7.65−7.57 (m, 2H), 7.45−7.41 (m, 1H), 7.20−7.15 (m, 1H), 1.85−1.80 (m, 1H), 1.19−1.15 (m, 6H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 145.5, 140.1, 128.6, 128.5, 125.0, 121.4, 118.5, 18.6. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 38.0. IR (neat) 3373, 2956, 2852, 1610, 1558, 1424, 1137, 849, 757 cm^{-1}. HRMS (CI) m/z calcd for $C_{11}H_{13}BrBN$ $[M]^+$ 249.0324, found 249.0330.

3-Bromo-2-cyclopropyl-2,1-borazaronaphthalene (**2d**). Obtained as an off-white solid (689 mg, 93%, 3 mmol scale). Mp 83−85 °C. ^{1}H NMR (500 MHz, acetone-d_6) δ 8.87 (br s, 1H), 8.28 (s, 1H), 7.61−7.58 (m, 1H), 7.46−7.42 (m, 1H), 7.41−7.38 (m, 1H), 7.14−7.10 (m, 1H), 0.88−0.86 (m, 2H), 0.85−0.82 (m, 2H), 0.77−0.73 (m, 1H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 144.6, 140.3, 128.6, 128.5, 124.7, 121.0, 118.1, 6.1. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 37.2. IR (neat) 3374, 2954, 1557, 1428, 1105, 925, 848, 748 cm^{-1}. HRMS (CI) m/z calcd for $C_{11}H_{11}BrBN$ $[M]^+$ 247.0168, found 247.0159.

3-Bromo-2-cyclobutyl-2,1-borazaronaphthalene (**2e**). Obtained as an off-white solid (506 mg, 97%, 2 mmol scale). Mp 84−86 °C. ^{1}H NMR (500 MHz, acetone-d_6) δ 9.33 (br s, 1H), 8.28 (s, 1H), 7.64−7.60 (m, 2H), 7.46−7.42 (m, 1H), 7.19−7.15 (m, 1H), 2.65−2.61 (m, 1H), 2.26−2.15 (m, 5H), 1.97−1.93 (m, 1H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 145.0, 140.0, 128.6, 128.5, 125.0, 121.4, 118.5, 25.0, 21.8. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 37.1. IR (neat) 3353, 2979, 1612, 1557, 1428, 1205, 927, 757 cm^{-1}. HRMS (CI) m/z calcd for $C_{12}H_{13}BrBN$ $[M]^+$ 261.0324, found 261.0330.

3-Bromo-2-benzyl-2-methyl-2,1-borazaronaphthalene (**2f**). Obtained as an off-white solid (886 mg, 95%, 3 mmol scale). Mp 75−77 °C. ^{1}H NMR (500 MHz, acetone-d_6) δ 8.34 (s, 1H), 7.65−7.63 (m, 1H), 7.40−7.33 (m, 2H), 7.23−7.12 (m, 6H), 5.38 (s, 2H), 0.97 (s, 3H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 144.8, 140.6, 138.0, 129.5, 128.8, 128.6, 127.0, 126.0, 125.7, 121.3, 116.3, 51.6. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 37.3. IR (neat) 2917, 1608, 1359, 1028, 753, 735, 722, 697 cm^{-1}. HRMS (CI) m/z calcd for $C_{16}H_{15}BrBN$ $[M]^+$ 311.0481, found 311.0490.

1-Allyl-3-bromo-2-methyl-2,1-borazaronaphthalene (**2g**). Obtained as a yellow oil (781 mg, 98%, 3 mmol scale). ^{1}H NMR (500 MHz, acetone-d_6) δ 8.25 (s, 1H), 7.62 (d, J = 7.8 Hz, 1H), 7.48 (d, J = 3.4 Hz, 2H), 7.20−7.16 (m, 1H), 6.08−6.00 (m, 1H), 5.13−5.08 (m, 1H), 4.94−4.90 (m, 1H), 4.74−4.72 (m, 2H), 0.92 (s, 3H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 144.5, 140.5, 134.1, 129.5, 128.7, 125.8, 121.1, 115.9, 115.0, 50.0. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 38.9. IR (neat) 3031, 1607, 1362, 1216, 913, 760, 741 cm^{-1}. HRMS (CI) m/z calcd for $C_{12}H_{13}BBrN$ $[M]^+$ 261.0324, found 261.0330.

3-Bromo-2-phenyl-2,1-borazaronaphthalene (**2h**). Obtained as an off-white solid (840 mg, 99%, 3 mmol scale). Mp 84−86 °C. ^{1}H NMR (500 MHz, acetone-d_6) δ 9.90 (br s, 1H), 8.54 (s, 1H), 7.95−7.92 (m, 2H), 7.75−7.71 (m, 2H), 7.54−7.51 (m, 1H), 7.45−7.40 (m, 3H), 7.27−7.23 (m, 1H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 146.7, 140.1, 133.5, 128.9, 128.8, 128.5, 127.4, 124.9, 121.6, 118.6. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 34.0. IR (neat) 3371, 3052, 1552, 1420, 1009, 761, 748, 702 cm^{-1}. HRMS (CI) m/z calcd for $C_{14}H_{11}BrBN$ $[M]^+$ 283.0168, found 283.0174.

3-Bromo-2-(3-methoxyphenyl)-2,1-borazaronaphthalene (**2i**). Obtained as an off-white solid (325 mg, 52%, 2 mmol scale). Mp 107−109 °C. ^{1}H NMR (500 MHz, acetone-d_6) δ 9.87 (br s, 1H), 8.54 (s, 1H), 7.72−7.69 (m, 2H), 7.53−7.48 (m, 3H), 7.37−7.34 (m, 1H), 7.26−7.23 (m, 1H), 7.01−6.97 (m, 1H), 3.84 (s, 3H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 159.0, 146.8, 140.1, 128.9, 128.6, 128.5, 125.8, 124.9, 121.7, 119.0, 118.6, 114.4, 54.5. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 37.8. IR (neat) 3323, 2970, 2933, 1557, 1427, 1252, 1047, 791 cm^{-1}. HRMS (CI) m/z calcd for $C_{15}H_{14}BBrNO$ $[M + H]^+$ 314.0352, found 314.0341.

3-Bromo-2-(4-fluorophenyl)-2,1-borazaronaphthalene (**2j**). Obtained as an off-white solid (274 mg, 91%, 2 mmol scale). Mp 114−116 °C. ^{1}H NMR (500 MHz, acetone-d_6) δ 9.89 (br s, 1H), 8.50 (s, 1H), 7.99−7.96 (m, 2H), 7.69−7.66 (m, 2H), 7.52−7.49 (m, 1H), 7.24−7.18 (m, 3H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 163.6 (d, J = 246 Hz), 146.8, 140.1, 135.9 (d, J = 7.5 Hz), 128.9, 128.5, 124.9, 121.7, 118.6, 114.3 (d, J = 20.2 Hz). ^{11}B NMR (128.38 MHz, acetone-d_6) δ 33.1. IR (neat) 3376, 3055, 1615, 1593, 1425, 1214, 800, 757 cm^{-1}. HRMS (CI) m/z calcd for $C_{14}H_{10}BBrFN$ $[M]^+$ 301.0074, found 301.0080.

3-Bromo-2-(3-thienyl)-2,1-borazaronaphthalene (**2k**). Obtained as a light-brown solid (305 mg, 53%, 2 mmol scale). Mp 66−68 °C. ^{1}H NMR (500 MHz, acetone-d_6) δ 9.91 (br s, 1H), 8.52 (s, 1H), 8.35−8.32 (m, 1H), 7.83 (d, J = 4.9 Hz, 1H), 7.70 (d, J = 8.1 Hz, 1H), 7.66 (d, J = 8.1 Hz, 1H), 7.57−7.54 (m, 1H), 7.53−7.48 (m, 1H), 7.25−7.20 (m, 1H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 146.8, 140.0, 133.7, 132.0, 128.9, 128.5, 124.8, 124.7, 121.5, 118.4. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 30.9. IR (neat) 3749, 2977, 2349, 1557, 758 cm^{-1}. HRMS (CI) m/z calcd for $C_{12}H_{10}BBrNS$ $[M + H]^+$ 289.9810, found 289.9810.

3-Bromo-2-(4-dibenzofuranyl)-2,1-borazaronaphthalene (**2l**). Obtained as an off-white solid (663 mg, 89%, 2 mmol scale). Mp 132−134 °C. ^{1}H NMR (500 MHz, acetone-d_6) δ 10.33 (br s, 1H), 8.66 (s, 1H), 8.18−8.13 (m, 2H), 7.96 (d, J = 7.3 Hz, 1H), 7.82 (d, J = 7.9 Hz, 1H), 7.78−7.76 (m, 1H), 7.63−7.57 (m, 2H), 7.53−7.47 (m, 2H), 7.41−7.38 (m, 1H), 7.34−7.31 (m, 1H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 159.0, 156.0, 147.0, 140.0, 133.2, 129.3, 128.9, 127.3, 125.3, 124.3, 123.2, 123.0, 122.6, 122.2, 121.8, 120.9, 119.0, 111.8. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 33.5. IR (neat) 3382, 3036, 1567, 1185, 748, 726 cm^{-1}. HRMS (CI) m/z calcd for $C_{20}H_{13}BBrNO$ $[M]^+$ 373.0274, found 373.0276.

1-Allyl-3-bromo-2-phenyl-2,1-borazaronaphthalene (**2m**). Obtained as a white solid (513 mg, 53%, 3 mmol scale). Mp 109−111 °C. ^{1}H NMR (500 MHz, acetone-d_6) δ 8.51 (s, 1H), 7.78−7.74 (m, 1H), 7.63−7.56 (m, 2H), 7.50−7.47 (m, 2H), 7.43−7.37 (m, 3H), 7.33−7.28 (m, 1H), 6.03−5.96 (m, 1H), 5.13 (d, J = 10.5 Hz, 1H), 4.94−4.90 (m, 1H), 4.73−4.71 (m, 2H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 146.1, 140.0, 135.0, 131.4, 129.6, 129.0, 127.8, 127.4, 126.4, 121.9, 117.1, 115.3, 51.4. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 39.3. IR (neat) 2979, 1607, 1586, 1544, 1368, 1245, 965, 701 cm^{-1}. HRMS (ESI) m/z calcd for $C_{17}H_{15}BrBN$ $[M]^+$ 323.0481, found 323.0494.

1-Allyl-3-bromo-2-(3-methoxyphenyl)-2,1-borazaronaphthalene (**2n**). Obtained as a yellow oil (324 mg, 46%, 2 mmol scale). ^{1}H NMR (500 MHz, acetone-d_6) δ 8.52 (s, 1H), 7.80−7.78 (m, 1H), 7.64−7.55 (m, 2H), 7.34−7.30 (m, 2H), 7.06−6.94 (m, 2H), 6.96−6.93 (m, 1H), 6.05−6.00 (m, 1H), 5.17−5.13 (m, 1H), 4.95−4.92 (m, 1H), 4.76−4.73 (m, 2H), 3.80 (s, 3H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 158.9, 146.1, 140.0, 135.2, 129.6, 129.0, 128.7, 126.4, 123.5, 121.9,

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117.0, 116.8, 115.2, 113.2, 54.3, 51.4. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 36.5. IR (neat) 2953, 1644, 1545, 1366, 1282, 1048, 763 cm^{-1}. HRMS (ESI) m/z calcd for $C_{18}H_{18}BrBNO$ $[M + H]^+$ 354.0665, found 354.0657.

*1-Benzyl-3-bromo-2-phenyl-2,1-borazaronaphthalene (**2o**).* Obtained as an off-white solid (710 mg, 95%, 2 mmol scale). Mp 121−124 °C. ^{1}H NMR (500 MHz, acetone-d_6) δ 8.58 (br s, 1H), 7.79 (d, J = 7.6 Hz, 1H), 7.49−7.41 (m, 4H), 7.36−7.30 (m, 3H), 7.28−7.23 (m, 3H), 7.20−7.17 (m, 1H), 7.14−7.09 (m, 2H), 5.39 (s, 2H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 146.4, 140.0, 138.4, 131.5, 129.7, 129.0, 128.6, 127.9, 127.5, 126.8, 126.7, 125.5, 122.0, 117.5, 53.0. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 37.3. IR (neat) 3025, 1606, 1545, 1367, 1355, 1243, 971, 763, 723, 703 cm^{-1}. HRMS (CI) m/z calcd for $C_{21}H_{17}BrBN$ $[M]^+$ 373.0637, found 373.0638.

*1-Benzyl-3-bromo-2-(4-trifluoromethylphenyl)-2,1-borazaronaphthalene (**2p**).* Obtained as an off-white solid (211 mg, 48%, 1 mmol scale). Mp 55−57 °C. ^{1}H NMR (500 MHz, acetone-d_6) δ 8.61 (s, 1H), 7.81 (d, J = 7.9 Hz, 1H), 7.71−7.67 (m, 4H), 7.46−7.42 (m, 2H), 7.29−7.25 (m, 3H), 7.21−7.18 (m, 1H), 7.13−7.11 (m, 2H), 5.36 (s, 2H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 147.0, 140.1, 138.3, 132.3, 130.1, 129.8, 129.5 (q, J = 4 Hz), 128.9, 128.0, 127.3, 127.1, 127.0 (q, J = 272 Hz), 125.8, 122.5, 117.7, 53.4. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 36.5. IR (neat) 3029, 1546, 1323, 1122, 834, 725 cm^{-1}. HRMS (CI) m/z calcd for $C_{22}H_{16}BrBF_3N$ $[M]^+$ 441.0511, found 441.0511.

*3-Bromo-2-(4-fluorophenyl)-1-(4-methoxybenzyl)-2,1-borazaronaphthalene (**2q**).* Obtained as an off-white solid (207 mg, 49%, 1 mmol scale). Mp 68−70 °C. ^{1}H NMR (500 MHz, acetone-d_6) δ 8.56 (s, 1H), 7.78 (d, J = 7.8 Hz, 1H), 7.53−7.41 (m, 4H), 7.27−7.24 (m, 1H), 7.13−7.10 (m, 2H), 7.04−7.00 (m, 2H), 6.87−6.85 (m, 2H), 5.31 (s, 2H), 3.71 (s, 3H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 162.8 (d, J = 245 Hz), 158.8, 146.4, 140.0, 133.7 (d, J = 8 Hz), 130.0, 129.7, 129.0, 126.7, 126.6, 122.0, 117.5, 114.3 (d, J = 20 Hz), 114.0, 54.5, 52.4. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 37.5. IR (neat) 2971, 1550, 1414, 1234, 762, 625 cm^{-1}. HRMS (CI) m/z calcd for $C_{22}H_{18}BrBNOF$ $[M]^+$ 421.0649, found 421.0654.

*1-Benzyl-3-bromo-2-(3-thienyl)-2,1-borazaronaphthalene (**2r**).* Obtained as an off-white solid (237 mg, 25%, 2.5 mmol scale). Mp 66−68 °C. ^{1}H NMR (500 MHz, acetone-d_6) δ 8.56 (s, 1H), 7.81−7.80 (m, 1H), 7.56−7.54 (m, 1H), 7.50−7.48 (m, 1H), 7.46−7.41 (m, 2H), 7.32−7.29 (m, 2H), 7.27−7.21 (m, 3H), 7.16−7.14 (m, 2H), 5.44 (s, 2H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 146.3, 138.6, 131.7, 131.0, 129.7, 129.6, 129.0, 128.7, 126.9, 126.6, 125.5, 124.8, 122.0, 117.4, 53.2. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 36.3. IR (neat) 2958, 1733, 1540, 758, 719 cm^{-1}. HRMS (CI) m/z calcd for $C_{19}H_{15}BrBNS$ $[M]^+$ 379.0202, found 379.0208.

*3-Bromo-2-(3-methoxyphenyl)-1-(4-methylbenzyl)-2,1-borazaronaphthalene (**2s**).* Obtained as an off-white solid (337 mg, 81%, 1 mmol scale). Mp 116−118 °C. ^{1}H NMR (500 MHz, acetone-d_6) δ 8.57 (s, 1H), 7.79 (d, J = 7.8 Hz, 1H), 7.47−7.42 (m, 2H), 7.29−7.26 (m, 2H), 7.10−7.05 (m, 2H), 7.03−7.00 (m, 4H), 6.90−6.87 (m, 1H), 5.35 (s, 2H), 3.66 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 158.9, 146.4, 140.0, 136.3, 135.5, 129.6, 129.2, 129.0, 128.7, 126.7, 125.5, 123.5, 121.9, 117.5, 116.7, 113.4, 54.2, 52.8, 20.0. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 37.0. IR (neat) 3048, 1406, 1336, 1313, 1094, 875, 792, 704 cm^{-1}. HRMS (CI) m/z calcd for $C_{23}H_{21}BrBNO$ $[M]^+$ 417.0900, found 417.0913.

*3-Bromo-2-(hex-1-yn-1-yl)-2,1-borazaronaphthalene (**2t**).* Obtained as a yellow oil (83 mg, 29%, 1 mmol scale). ^{1}H NMR (500 MHz, acetone-d_6) δ 9.96 (br s, 1H), 8.40 (s, 1H), 7.66 (d, J = 8.1 Hz, 1H), 7.59−7.57 (m, 1H), 7.50−7.47 (m, 1H), 7.22−7.19 (m, 1H), 2.40 (t, J = 6.8 Hz, 2H), 1.59−1.49 (m, 4H), 0.95−0.90 (m, 3H). ^{13}C NMR (500 MHz, acetone-d_6) δ 145.1, 139.6, 128.8, 128.5, 124.7, 121.6, 118.1, 109.5, 30.5, 21.5, 19.1, 12.9. ^{11}B NMR (500 MHz, acetone-d_6) δ 26.4. IR (neat) 3649, 2956, 2931, 1613, 1556, 997, 799, 759 cm^{-1}. HRMS (CI) m/z calcd for $C_{14}H_{15}BNBr$ $[M]^+$ 287.0481, found 287.0481.

*1-Benzyl-3-bromo-2,7-dimethyl-2,1-borazaronaphthalene (**2u**).* Obtained as a white solid (50 mg, 77%, 0.2 mmol scale). Mp 85−87 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (s, 1H), 7.47−7.44 (m, 1H), 7.34−7.31 (m, 2H), 7.28−7.25 (m, 1H), 7.14−7.10 (m, 3H), 7.00−6.97 (m, 1H), 5.35 (s, 2H), 2.34 (s, 3H), 1.00 (s, 3H). ^{13}C NMR (500 MHz, $CDCl_3$) δ 144.5, 140.8, 138.9, 137.8, 129.2, 128.7, 127.0, 125.7, 123.9, 122.6, 116.2, 51.9, 22.1. ^{11}B NMR (500 MHz, $CDCl_3$) δ 38.1. IR (neat) 2926, 1590, 1452, 1364, 809, 685 cm^{-1}. HRMS (CI) m/z calcd for $C_{17}H_{17}BNBr$ $[M]^+$ 325.0637, found 325.0647.

*1-Benzyl-3-bromo-6,7-dimethoxy-2-methyl-2,1-borazaronaphthalene (**2v**).* Obtained as a white solid (24 mg, 64%, 0.1 mmol scale). Mp 96−98 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.31−7.22 (m, 3H), 7.15−7.11 (m, 2H), 6.93 (s, 1H), 6.73 (s, 1H), 5.31 (s, 2H), 3.89 (s, 3H), 3.67 (s, 3H), 1.01 (s, 3H). ^{13}C NMR (500 MHz, $CDCl_3$) 150.3, 144.4, 140.1, 138.1, 136.2, 129.1, 127.5, 126.0, 119.7, 110.0, 55.2, 55.9, 52.9. ^{11}B NMR (500 MHz, $CDCl_3$) δ 37.9. IR (neat) 2924, 1258, 1029, 823, 810, 751, 687, 609 cm^{-1}. HRMS (CI) m/z calcd for $C_{18}H_{19}BNO_2Br$ $[M]^+$ 371.0692, found 371.0683.

*2-(1,2-Dibromopropyl)-2,1-borazaronaphthalene (**2w**).* Obtained as an off-white solid (221 mg, 34%, 2 mmol scale). Mp 91−93 °C. ^{1}H NMR (500 MHz, acetone-d_6) δ 9.60 (br s, 1H), 8.13 (d, J = 11.6 Hz, 1H), 7.69−7.67 (m, 1H), 7.51−7.43 (m, 2H), 7.21−7.17 (m, 1H), 6.93−6.91 (m, 1H), 4.91−4.85 (m, 1H), 4.23 (d, J = 10.7 Hz, 1H), 1.98 (d, J = 6.4 Hz, 3H). ^{13}C NMR (500 MHz, acetone-d_6) δ 145.9, 139.7, 129.2, 128.4, 125.5, 121.2, 118.4, 50.5, 25.4. ^{11}B NMR (500 MHz, acetone-d_6) δ 34.0. IR (neat) 3360, 2978, 1614, 1562, 1441, 760 cm^{-1}. HRMS (CI) m/z calcd for $C_{11}H_{13}BBr_2N$ $[M + H]^+$ 327.9508, found 327.9509.

*6-Bromo-3-(3-methoxyphenyl)-2-methyl-2,1-borazaronaphthalene (**9a**).* Obtained as an off-white solid (167 mg, 51%, 1 mmol scale). Mp 100−102 °C. ^{1}H NMR (500 MHz, acetone-d_6) δ 9.47 (br s, 1H), 7.72 (s, 1H), 7.66 (d, J = 7.6 Hz, 1H), 7.55−7.51 (m, 2H), 7.44−7.41 (m, 1H), 7.17−7.14 (m, 1H), 6.90−6.87 (m, 1H), 6.82−6.80 (m, 1H), 3.80 (s, 3H), 0.65 (s, 3H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 159.3, 147.1, 141.6, 140.8, 133.0, 129.5, 128.5, 124.6, 120.8, 117.9, 115.7, 113.7, 113.4, 55.1. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 37.4. IR (neat) 3382, 2987, 1616, 1457, 1345, 122, 1014, 759 cm^{-1}. HRMS (CI) m/z calcd for $C_{16}H_{16}BBrNO$ $[M + H]^+$ 328.0508, found 328.0518.

*6-Bromo-3-phenyl-2-methyl-2,1-borazaronaphthalene (**9b**).* Obtained as an off-white solid (240 mg, 81%, 1 mmol scale). Mp 96−98 °C. ^{1}H NMR (500 MHz, acetone-d_6) 9.58 (br s, 1H), 7.86−7.83 (m, 2H), 7.51−7.48 (m, 1H), 7.44−7.38 (m, 5H), 7.30−7.28 (m, 1H), 0.88 (s, 3H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 144.6, 140.1, 139.4, 131.3, 130.6, 128.3, 128.2, 126.8, 126.3, 119.7, 112.6. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 37.6. IR (neat) 3350, 2961, 1606, 1439, 1313, 821, 702 cm^{-1}. HRMS (CI) m/z calcd for $C_{15}H_{13}BBrN$ $[M]^+$ 297.0324, found 297.0330.

General Procedure for the Dibromination of 2,1-Borazaronaphthalenes. To a flame-dried 100 mL round-bottom flask with a stir bar was added the corresponding 2,1-borazaronaphthalene (2.0 mmol). The flask was sealed with a rubber septum, evacuated under vacuum, and purged with Ar three times. Anhydrous CH_2Cl_2 was added (10 mL), and the flask was cooled to 0 °C. Bromine (703 mg, 4.4 mmol, 2.2 equiv) in CH_2Cl_2 (10 mL) was added under Ar at a rate of 1.1 mmol/h. After the addition, the reaction mixture was slowly warmed to rt. The reaction was monitored by TLC, and when it was complete (usually after warming to rt), the reaction mixture was concentrated in vacuo. The crude 2,1-borazaronaphthalene was purified by flash column chromatography with 0−30% CH_2Cl_2/hexane as the eluent to provide the desired 3,6-dibromo-2,1-borazaronaphthalene.

*3,6-Dibromo-2-methyl-2,1-borazaronaphthalene (**2x**).* Obtained as an off-white solid (822 mg, 92%, 3 mmol scale). Mp 80−82 °C. ^{1}H NMR (500 MHz, acetone-d_6) δ 9.70 (br s, 1H), 8.26−8.22 (m, 1H), 7.77 (s, 1H), 7.52−7.50 (m, 1H), 7.40−7.38 (m, 1H), 0.78 (s, 3H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 143.2, 139.1, 131.2, 130.5, 126.4, 120.2, 113.1. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 37.5. IR (neat) 3350, 2961, 1554, 1423, 1195, 911, 861, 811 cm^{-1}. HRMS (CI) m/z calcd for $C_9H_8Br_2BN$ $[M]^+$ 298.9117, found 298.9125.

General Procedure for the Cross-Coupling of 3-Bromo-2,1-Borazaronaphthalenes. In a Biotage microwave vial equipped with a stir bar were successively introduced t-Bu_3P-Pd-G2 (3.8 mg, 7.5 μmol, 1 mol %), potassium (hetero)aryltrifluoroborate (0.75 mmol, 1 equiv), 3-bromo-2-methyl-2,1-borazaronaphthalene (167 mg,

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0.75 mmol, 1 equiv), and Cs_2CO_3 (731 mg, 2.25 mmol, 3 equiv). The vial was sealed with a cap lined with a disposable Teflon septum, evacuated under vacuum, and purged with Ar three times. Degassed CPME (0.75 mL) and degassed H_2O (0.75 mL) were added under Ar. The resulting mixture was heated at 60 °C and stirred for 18 h. After cooling to rt, the vial was uncapped, and the reaction mixture was diluted with EtOAc (3 mL) and H_2O (3 mL). The reaction mixture was extracted with EtOAc (3 × 3 mL) and dried ($MgSO_4$). The solvent was removed in vacuo, and the product was purified by *rapid* flash column chromatography on silica gel or neutral alumina using 0 to 20% CH_2Cl_2/hexane as the eluent for most 2,1-borazaronaphthalenes. Several heteroaryl 2,1-borazaronaphthalenes required 20−80% CH_2Cl_2/hexane as the eluent. The cross-couplings for Tables 5−8 were completed on a 0.5 mmol scale.

*3-Phenyl-2-methyl-2,1-borazaronaphthalene (**3a**).* Obtained as a yellow oil (161 mg, 98%). ^{1}H NMR (500 MHz, acetone-d_6) δ 9.41 (br s, 1H), 7.91 (s, 1H), 7.69 (d, J = 7.69 Hz, 1H), 7.51−7.45 (m, 3H), 7.43−7.40 (m, 3H), 7.30−7.27 (m, 1H), 7.17−7.14 (m, 1H), 0.84 (s, 3H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 145.0, 141.2, 140.3, 129.3, 128.1, 128.0, 127.9, 125.8, 125.0, 120.5, 117.5. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 37.3. IR (neat) 3373, 3054, 1613, 1563, 1454, 1421, 756, 700 cm^{-1}. HRMS (CI) m/z calcd for $C_{15}H_{14}BN$ $[M]^+$ 219.1219, found 219.1223.

*3-(3-Methoxyphenyl)-2-methyl-2,1-borazaronaphthalene (**3b**).* Obtained as a yellow oil (177 mg, 95%). ^{1}H NMR (500 MHz, acetone-d_6) 9.43 (br s, 1H), 7.93 (s, 1H), 7.69 (d, J = 7.6 Hz, 1H), 7.49 (d, J = 8.3 Hz, 1H), 7.42−7.38 (m, 1H), 7.34−7.30 (m, 1H), 7.17−7.13 (m, 1H), 7.04−7.00 (m, 2H), 6.88−6.85 (m, 1H), 3.83 (s, 3H), 0.81 (s, 3H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 159.7, 146.5, 141.1, 140.3, 129.3, 129.0, 127.9, 124.9, 120.5, 120.5, 117.5, 113.7, 111.3, 54.5. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 37.4. IR (neat) 3346, 3001, 1573, 1461, 1225, 1019, 753 cm^{-1}. HRMS (CI) m/z calcd for $C_{16}H_{16}BNO$ $[M]^+$ 249.1325, found 249.1325.

*3-(2-Methoxyphenyl)-2-methyl-2,1-borazaronaphthalene (**3c**).* Obtained as a yellow oil (176 mg, 94%). ^{1}H NMR (500 MHz, acetone-d_6) δ 9.28 (br s, 1H), 7.76 (s, 1H), 7.64 (d, J = 7.6 Hz, 1H), 7.48 (d, J = 8.3 Hz, 1H), 7.40−7.37 (m, 1H), 7.29−7.26 (m, 1H), 7.21−7.19 (m, 1H), 7.14−7.11 (m, 1H), 7.01−6.98 (m, 2H), 3.74 (s, 3H), 0.62 (s, 3H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 156.5, 141.0, 140.3, 134.4, 129.5, 129.0, 127.6, 127.5, 125.0, 120.4, 120.3, 117.5, 110.4, 54.5. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 37.6. IR (neat) 3372, 2997, 2939, 2832, 1596, 1458, 1417, 1220, 759, 750, 702 cm^{-1}. HRMS (CI) m/z calcd for $C_{16}H_{16}BNO$ $[M]^+$ 249.1325, found 249.1317.

*3-(4-Naphthalen-1-ylphenyl)-2-methyl-2,1-borazaronaphthalene (**3d**).* Reaction performed with a concentration of 0.1 M. Obtained as an off-white solid (173 mg, 67%). Mp 73−75 °C. ^{1}H NMR (500 MHz, acetone-d_6) δ 9.49 (br s, 1H), 8.03−8.01 (m, 2H), 8.00−7.98 (m, 1H), 7.97−7.95 (m, 1H), 7.73−7.71 (m, 1H), 7.60−7.57 (m, 2H), 7.53−7.45 (m, 8H), 7.17−7.15 (m, 1H), 0.91 (s, 3H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 144.1, 141.4, 140.4, 140.1, 138.2, 134.0, 131.6, 129.8, 129.7, 129.3, 128.3, 128.1, 128.0, 127.5, 126.8, 126.0, 125.7, 125.6, 125.4, 125.0, 120.6, 117.5. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 37.4. IR (neat) 3375, 3051, 1614, 1565, 1425, 1220, 844, 800, 777, 759 cm^{-1}. HRMS (CI) m/z calcd for $C_{25}H_{20}BN$ $[M]^+$ 345.1689, found 345.1690.

*3-(4-Methylphenyl)-2-methyl-2,1-borazaronaphthalene (**3e**).* Obtained as an off-white solid (156 mg, 89%). Mp 53−55 °C. ^{1}H NMR (500 MHz, acetone-d_6) δ 9.41 (br s, 1H), 7.88 (s, 1H), 7.67 (d, J = 7.8 Hz, 1H), 7.48 (d, J = 7.48 Hz, 1H), 7.40−7.37 (m, 1H), 7.35−7.33 (m, 2H), 7.21−7.19 (m, 2H), 7.15−7.12 (m, 1H), 2.35 (s, 3H), 0.81 (s, 3H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 142.0, 140.7, 140.2, 135.1, 129.2, 128.7, 127.9, 127.7, 125.0, 120.5, 117.5, 20.2. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 37.5. IR (neat) 3383, 3022, 2938, 1613, 1566, 1454, 1425, 879, 822, 759, 749 cm^{-1}. HRMS (CI) m/z calcd for $C_{16}H_{16}BN$ $[M]^+$ 233.1376, found 233.1374.

*3-(1-Naphthyl)-2-methyl-2,1-borazaronaphthalene (**3f**).* Obtained as a yellow oil (187 mg, 93%). Mp 58−60 °C. ^{1}H NMR (500 MHz, acetone-d_6) δ 9.55 (br s, 1H), 7.93 (d, J = 8.1 Hz, 1H), 7.87 (s, 1H), 7.84−7.82 (m, 1H), 7.78 (d, J = 8.6 Hz, 1H), 7.70−7.76 (m, 1H), 7.59−7.55 (m, 1H), 7.54−7.51 (m, 1H), 7.49−7.44 (m, 2H), 7.41−7.37 (m, 1H), 7.34−7.31 (m, 1H), 7.20−7.16 (m, 1H), 0.49 (s, 3H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 143.4, 142.3, 140.6, 133.8, 131.8, 129.2, 128.1, 128.0, 127.7, 136.4, 126.3, 125.7, 125.5, 125.4, 125.3, 124.8, 120.6, 117.7. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 37.6. IR (neat) 3369, 3053, 2980, 1613, 1566, 1421, 777, 759 cm^{-1}. HRMS (CI) m/z calcd for $C_{19}H_{16}BN$ $[M]^+$ 269.1376, found 269.1368.

*3-(2-Naphthyl)-2-methyl-2,1-borazaronaphthalene (**3g**).* Obtained as a colorless solid (192 mg, 95%). Mp 87−89 °C. ^{1}H NMR (500 MHz, acetone-d_6) δ 9.50 (br s, 1H), 8.04 (s, 1H), 7.95−7.85 (m, 4H), 7.74−7.71 (m, 1H), 7.67−7.64 (m, 1H), 7.54−7.51 (m, 1H), 7.50−7.41 (m, 3H), 7.19−7.16 (m, 1H), 0.81 (s, 3H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 142.7, 141.6, 140.4, 133.8, 132.1, 129.3, 128.0, 127.8, 127.7, 127.5, 127.3, 126.1, 125.9, 125.7, 125.2, 125.0, 120.1, 117.6. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 37.3. IR (neat) 3366, 3053, 2979, 1561, 1308, 758, 744 cm^{-1}. HRMS (CI) m/z calcd for $C_{19}H_{16}BN$ $[M]^+$ 269.1376, found 269.1372.

*3-(3-Vinylphenyl)-2-methyl-2,1-borazaronaphthalene (**3h**).* Obtained as a yellow oil (128 mg, 71%). ^{1}H NMR (500 MHz, acetone-d_6) δ 9.45 (br s, 1H), 7.93 (s, 1H), 7.73−7.69 (m, 1H), 7.56−7.47 (m, 2H), 7.44−7.34 (m, 4H), 7.17−7.13 (m, 1H), 6.86−6.80 (m, 1H), 5.86 (d, J = 17.4 Hz, 1H), 5.25 (d, J = 10.8 Hz, 1H), 0.81 (s, 3H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 145.3, 141.2, 140.3, 137.4, 137.2, 129.2, 128.2, 127.9, 127.7, 125.9, 124.9, 123.6, 120.5, 117.5, 113.0. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 37.4. IR (neat) 2917, 2848, 1596, 1422, 1161, 1036, 761 cm^{-1}. HRMS (CI) m/z calcd for $C_{16}H_{16}BNO$ $[M]^+$ 249.1325, found 249.1325.

*3-(3-Methoxy-5-trifluoromethylphenyl)-2-methyl-2,1-borazaronaphthalene (**3i**).* Obtained as a yellow oil (174 mg, 73%). ^{1}H NMR (500 MHz, acetone-d_6) δ 9.53 (br s, 1H), 8.00 (s, 1H), 7.72 (d, J = 7.6 Hz, 1H), 7.51−7.48 (m, 1H), 7.46−7.42 (m, 1H), 7.34 (s, 1H), 7.26 (s, 1H), 7.19−7.15 (m, 2H), 3.93 (s, 3H), 0.81 (s, 3H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 160.0, 147.7, 142.0, 140.1, 130.9 (q, J = 32 Hz), 129.5, 128.4, 126.6 (q, J = 260 Hz), 124.6, 120.6, 117.6, 117.4, 116.8 (q, J = 3.7 Hz), 107.9 (q, J = 3.7 Hz), 55.0. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 37.4. IR (neat) 3378, 2940, 2842, 1598, 1354, 1121, 1057, 759, 692 cm^{-1}. HRMS (CI) m/z calcd for $C_{17}H_{15}BNOF_3$ $[M]^+$ 317.1199, found 317.1207.

*3-(3-Nitrophenyl)-2-methyl-2,1-borazaronaphthalene (**3j**).* Obtained as an off-white solid (105 mg, 53%). Mp 135−137 °C. ^{1}H NMR (500 MHz, acetone-d_6) δ 9.56 (br s, 1H), 8.26 (s, 1H), 8.13 (d, J = 7.8 Hz, 1H), 8.00 (s, 1H), 7.85 (d, J = 7.6 Hz, 1H), 7.72 (d, J = 7.8 Hz, 1H), 7.67−7.64 (m, 1H), 7.51−7.48 (m, 1H), 7.47−7.42 (m, 1H), 7.18−7.15 (m, 1H), 0.80 (s, 3H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 148.4, 146.7, 142.5, 140.6, 134.4, 129.6, 129.3, 128.6, 124.5, 122.3, 120.7, 120.5, 117.6. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 37.5. IR (neat) 3376, 3054, 2967, 1609, 1579, 1417, 1253, 879, 759, 749, 698 cm^{-1}. HRMS (CI) m/z calcd for $C_{15}H_{13}BN_2O_2$ $[M]^+$ 264.1070, found 264.1080.

*3-(3-Methoxycarbonylphenyl)-2-methyl-2,1-borazaronaphthalene (**3k**).* Obtained as a yellow oil (182 mg, 88%). ^{1}H NMR (500 MHz, acetone-d_6) δ 9.45 (br s, 1H), 8.18 (s, 1H), 7.93 (s, 2H), 7.73−7.69 (m, 2H), 7.52−7.47 (m, 2H), 7.44−7.42 (m, 1H), 7.17−7.13 (m, 1H), 3.90 (s, 3H), 0.80 (s, 3H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 166.6, 145.3, 141.7, 140.5, 132.6, 130.2, 129.4, 128.9, 128.3, 128.2, 126.7, 124.8, 120.6, 117.6, 51.4. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 37.4. IR (neat) 3354, 3051, 2949, 1711, 1567, 1436, 1306, 756 cm^{-1}. HRMS (ESI) m/z calcd for $C_{17}H_{17}BNO_2$ $[M + H]^+$ 278.1352, found 278.1342.

*3-(3-Fluorophenyl)-2-methyl-2,1-borazaronaphthalene (**3l**).* Obtained as a yellow oil (160 mg, 90%). ^{1}H NMR (500 MHz, acetone-d_6) δ 9.48 (br s, 1H), 7.93 (s, 1H), 7.69 (d, J = 7.6 Hz, 1H), 7.49 (d, J = 8.1 Hz, 1H), 7.43−7.40 (m, 2H), 7.27−7.24 (m, 1H), 7.20−7.13 (m, 2H), 7.05−7.02 (m, 1H), 0.81 (s, 3H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 163.8 (d, J = 248 Hz), 147.6 (d, J = 7.6 Hz), 141.7, 140.5, 129.70 (d, J = 8.8 Hz), 129.3, 128.2, 124.7, 120.1 (d, J = 2.5 Hz), 120.6, 117.6, 116.5 (d, J = 20.1 Hz), 112.3 (d, J = 11.2 Hz). ^{11}B NMR (128.38 MHz, acetone-d_6) δ 37.0. IR (neat) 3376, 3054, 2967, 1609, 1579, 1417, 1253, 879, 759, 749, 698 cm^{-1}. HRMS (CI) m/z calcd for $C_{15}H_{13}BNF$ $[M]^+$ 237.1125, found 237.1120.

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*3-(4-Trifluoromethylphenyl)-2-methyl-2,1-borazaronaphthalene (**3m**).* Obtained as an off-white solid (156 mg, 88%). Mp 116−118 °C. ^{1}H NMR (500 MHz, acetone-d_6) 9.54 (br s, 1H), 7.95 (s, 1H), 7.73−7.69 (m, 3H), 7.63−7.61 (m, 2H), 7.52−7.49 (m, 1H), 7.45−7.42 (m, 1H), 7.17−7.14 (m, 1H), 0.80 (s, 3H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 149.2, 142.2, 140.6, 129.5, 128.6, 128.5, 127.3 (q, J = 32 Hz), 124.8 (q, J = 276 Hz), 124.9 (q, J = 3.8 Hz), 123.7, 120.7, 117.6. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 37.1. IR (neat) 3346, 3030, 1614, 1334, 1325, 110, 1071, 762, 755 cm^{-1}. HRMS (CI) m/z calcd for $C_{16}H_{13}BNF_3$ $[M]^+$ 287.1093, found 287.1093.

*3-(3-Cyanophenyl)-2-methyl-2,1-borazaronaphthalene (**3n**).* Obtained as an off-white solid (145 mg, 79%). Mp 61−63 °C. ^{1}H NMR (500 MHz, acetone-d_6) δ 9.59 (br s, 1H), 8.00 (s, 1H), 7.81 (s, 1H), 7.78−7.73 (m, 2H), 7.70−7.67 (m, 1H), 7.65−7.60 (m, 1H), 7.52−7.49 (m, 1H), 7.46−7.43 (m, 1H), 7.17−7.14 (m, 1H), 0.79 (s, 3H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 146.3, 142.3, 140.6, 132.7, 131.3, 129.5, 129.3, 129.2, 128.5, 124.6, 120.7, 118.7, 117.6, 112.1. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 37.5. IR (neat) 3338, 2980, 1558, 1260, 1088, 945, 793 cm^{-1}. HRMS (CI) m/z calcd for $C_{16}H_{13}BN_2$ $[M]^+$ 244.1172, found 244.1174.

*3-(N-Boc-indol-5-yl)-2-methyl-2,1-borazaronaphthalene (**4a**).* Obtained as an off-white solid (150 mg, 56%). Mp 80−82 °C. ^{1}H NMR (500 MHz, acetone-d_6) δ 9.42 (br s, 1H), 8.20 (d, J = 8.3 Hz, 1H), 7.94 (s, 1H), 7.70−7.67 (m, 1H), 7.66−7.64 (m, 2H), 7.50−7.48 (m, 1H), 7.44−7.38 (m, 2H), 7.16−7.13 (m, 1H), 6.69−6.67 (m, 1H), 1.69 (s, 9H), 0.83 (s, 3H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 149.4, 141.0, 140.2, 139.7, 133.8, 130.8, 129.1, 127.7, 126.0, 125.0, 124.8, 120.5, 120.0, 117.5, 114.5, 107.4, 83.3, 27.3. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 37.5. IR (neat) 3375, 2976, 1730, 1370, 1160, 1134, 759, 749, 727 cm^{-1}. HRMS (CI) m/z calcd for $C_{22}H_{23}BN_2O_2$ $[M]^+$ 358.1853, found 358.1856.

*3-(3-Thienyl)-2-methyl-2,1-borazaronaphthalene (**4b**).* Obtained as an off-white solid (145 mg, 86%). Mp 62−64 °C. ^{1}H NMR (500 MHz, acetone-d_6) δ 9.41 (br s, 1H), 8.10 (s, 1H), 7.67−7.64 (m, 1H), 7.47−7.44 (m, 2H), 7.40−7.37 (m, 3H), 7.16−7.13 (m, 1H), 0.90 (s, 3H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 145.8, 140.41, 140.4, 129.4, 128.1, 128.0, 128.0, 125.2, 120.8, 120.8, 117.9. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 37.2. IR (neat) 3372, 3052, 2938, 1612, 1563, 1426, 878, 777, 758, 748 cm^{-1}. HRMS (CI) m/z calcd for $C_{13}H_{12}BNS$ $[M]^+$ 225.0784, found 225.0789.

*3-(2-Thienyl)-2-methyl-2,1-borazaronaphthalene (**4c**).* Obtained as a yellow oil (142 mg, 84%). ^{1}H NMR (500 MHz, acetone-d_6) δ 9.50 (br s, 1H), 8.13 (s, 1H), 7.68 (d, J = 7.8 Hz, 1H), 7.47−7.44 (m, 1H), 7.42−7.39 (m, 1H), 7.36−7.34 (m, 1H), 7.28−7.25 (m, 1H), 7.16−7.13 (m, 1H), 7.11−7.08 (m, 1H), 0.95 (s, 3H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 147.7, 140.1, 139.8, 129.1, 128.0, 127.6, 124.6, 124.5, 123.9, 120.8, 117.5. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 37.0. IR (neat) 3371, 3056, 2945, 1612, 1560, 1426, 1336, 877, 757, 693 cm^{-1}. HRMS (CI) m/z calcd for $C_{13}H_{12}BNS$ $[M]^+$ 225.0784, found 225.0784.

*3-(3,5-Dimethylisoxazol-4-yl)-2-methyl-2,1-borazaronaphthalene (**4d**).* Obtained as an off-white solid (91 mg, 51%). Mp 69−71 °C. ^{1}H NMR (500 MHz, acetone-d_6) δ 9.58 (br s, 1H), 8.27 (s, 1H), 7.6 (d, J = 7.3 Hz, 1H), 7.47−7.41 (m, 2H), 7.16−7.13 (m, 1H), 1.58 (s, 3H), 1.39 (s, 3H), 0.81 (s, 3H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 163.1, 158.3, 144.1, 140.6, 129.1, 128.3, 124.5, 120.5, 118.3, 117.7, 10.5, 9.7. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 38.1. IR (neat) 3372, 3052, 2967, 1613, 1566, 1449, 1187, 777, 749 cm^{-1}. HRMS (CI) m/z calcd for $C_{14}H_{15}BN_2O$ $[M]^+$ 238.1277, found 238.1283.

*3-(3-Furanyl)-2-methyl-2,1-borazaronaphthalene (**4e**).* Obtained as a yellow oil (113 mg, 72%). ^{1}H NMR (500 MHz, acetone-d_6) δ 9.41 (br s, 1H), 8.09 (s, 1H), 7.79 (s, 1H), 7.67−7.65 (m, 1H), 7.61−7.58 (m, 1H), 7.47−7.43 (m, 1H), 7.38−7.35 (m, 1H), 7.14−7.11 (m, 1H), 6.87−6.89 (m, 1H), 0.89 (s, 3H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 142.9, 139.9, 139.7, 138.8, 128.9, 128.6, 127.5, 124.9, 120.5, 117.4, 109.4. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 37.5. IR (neat) 3362, 2932, 1614, 1426, 1031, 872, 760 cm^{-1}. HRMS (CI) m/z calcd for $C_{13}H_{12}BNO$ $[M]^+$ 209.1012, found 209.1006.

*3-(4-Dibenzofuranyl)-2-methyl-2,1-borazaronaphthalene (**4f**).* Reaction performed with a concentration of 0.1 M. Obtained as an off-white solid (125 mg, 54%). Mp 63−65 °C. ^{1}H NMR (500 MHz, acetone-d_6) δ 9.56 (br s, 1H), 8.13 (s, 1H), 8.09 (d, J = 7.6 Hz, 1H), 8.00 (dd, J = 7.1 Hz, 1.5 Hz, 1H), 7.74−7.71 (m, 1H), 7.59−7.54 (m, 2H), 7.49−7.41 (m, 4H), 7.38−7.34 (m, 1H), 7.19−7.17 (m, 1H), 0.73 (s, 3H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 155.9, 153.5, 142.8, 140.6, 129.8, 129.4, 128.3, 127.6, 127.0, 124.7, 124.4, 123.9, 123.0, 122.7, 120.7, 120.6, 118.6, 117.7, 111.4. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 37.6. IR (neat) 3374, 3052, 2968, 1614, 1566, 1425, 1187, 777, 749 cm^{-1}. HRMS (CI) m/z calcd for $C_{21}H_{16}BNO$ $[M]^+$ 309.1325, found 309.1313.

*3-(4-Dibenzothienyl)-2-methyl-2,1-borazaronaphthalene (**4g**).* Reaction performed with a concentration of 0.1 M. Obtained as an off-white solid (127 mg, 52%). Mp 62−64 °C. ^{1}H NMR (500 MHz, acetone-d_6) δ 9.63 (br s, 1H), 8.31 (d, J = 7.8 Hz, 1H), 8.22 (d, J = 7.8 Hz, 1H), 8.10 (s, 1H), 7.90−7.88 (m, 1H), 7.72−7.70 (m, 1H), 7.59−7.54 (m, 2H), 7.50−7.45 (m, 3H), 7.38−7.35 (m, 1H), 7.21−7.18 (m, 1H), 0.66 (s, 3H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 142.1, 140.8, 140.2, 139.5, 138.6, 136.1, 135.5, 129.4, 128.5, 126.6, 126.4, 124.8, 124.4, 124.3, 122.5, 121.8, 120.7, 119.3, 117.7. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 38.2. IR (neat) 3366, 3056, 2980, 1707, 1567, 1440, 1021, 749 cm^{-1}. HRMS (CI) m/z calcd for $C_{21}H_{16}BNS$ $[M]^+$ 325.1097, found 325.1086.

*3-(3-Methoxyphenyl)-2-methyl-1-benzyl-2,1-borazaronaphthalene (**5a**).* Obtained as a yellow oil (157 mg, 93%). ^{1}H NMR (500 MHz, acetone-d_6) 7.92 (s, 1H), 7.74 (d, J = 7.6 Hz, 1H), 7.42 (d, J = 8.3 Hz, 1H), 7.35−7.27 (m, 4H), 7.23−7.21 (m, 1H), 7.20−7.16 (m, 3H), 7.01−6.98 (m, 2H), 6.90−6.87 (m, 1H), 5.44 (s, 2H), 3.83 (s, 3H), 0.86 (s, 3H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 159.6, 146.8, 141.8, 141.0, 138.5, 130.3, 128.9, 128.6, 128.3, 126.7, 126.1, 125.7, 120.9, 120.8, 115.8, 114.1, 111.3, 54.5, 50.9. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 39.5. IR (neat) 3027, 1734, 1604, 1368, 1046, 727 cm^{-1}. HRMS (CI) m/z calcd for $C_{23}H_{22}BNO$ $[M]^+$ 339.1794, found 339.1786.

*3-(3-Methoxyphenyl)-2-methyl-1-allyl-2,1-borazaronaphthalene (**5b**).* Obtained as a yellow oil (120 mg, 83%). ^{1}H NMR (500 MHz, acetone-d_6) 7.85 (s, 1H), 7.72 (d, J = 7.3 Hz, 1H), 7.56−7.53 (m, 1H), 7.49−7.45 (m, 1H), 7.33−7.28 (m, 1H), 7.21−7.17 (m, 1H), 6.95−6.93 (m, 2H), 6.88−6.84 (m, 1H), 6.14−6.07 (m, 1H), 5.13 (d, J = 10.5 Hz, 1H), 4.97 (d, J = 17.4 Hz, 1H), 4.81−4.79 (m, 2H), 3.83 (s, 3H), 0.84 (s, 3H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 159.6, 146.8, 141.5, 140.8, 134.7, 130.3, 128.9, 128.2, 125.9, 120.8, 120.6, 115.4, 114.7, 114.0, 111.2, 54.5, 49.3. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 39.3. IR (neat) 3648, 2979, 1734, 1367, 1047, 761 cm^{-1}. HRMS (CI) m/z calcd for $C_{19}H_{20}BNO$ $[M]^+$ 289.1638, found 289.1649.

*3-(3-Methoxyphenyl)-2-(β,β,β-trifluoroethyl)-2,1-borazaronaphthalene (**5c**).* Obtained as a yellow oil (71 mg, 67%). ^{1}H NMR (500 MHz, acetone-d_6) δ 9.66 (br s, 1H), 8.03 (s, 1H), 7.77 (d, J = 7.8 Hz, 1H), 7.70 (d, J = 8.1 Hz, 1H), 7.51−7.48 (m, 1H), 7.37−7.33 (m, 1H), 7.28−7.24 (m, 1H), 6.98−6.96 (m, 2H), 6.91−6.88 (m, 1H), 3.84 (s, 3H), 2.48 (q, J = 14.2 Hz, 2H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 159.9, 145.6, 143.0, 139.7, 129.4, 129.2, 128.9 (q, J = 272 Hz), 128.5, 125.0, 121.6, 120.5, 118.2, 113.7, 111.6, 54.5. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 33.6. IR (neat) 3408, 2961, 1699, 1596, 1240, 1038, 760 cm^{-1}. HRMS (ESI) m/z calcd for $C_{17}H_{14}BNOF_3$ $[M - H]^-$ 316.1121, found 316.1120.

*3-(3-Methoxyphenyl)-2-isopropyl-2,1-borazaronaphthalene (**5d**).* Obtained as a yellow oil (107 mg, 77%). ^{1}H NMR (500 MHz, acetone-d_6) δ 9.12 (br s, 1H), 7.87 (s, 1H), 7.67 (d, J = 7.6 Hz, 1H), 7.61 (d, J = 8.1 Hz, 1H), 7.42−7.39 (m, 1H), 7.33−7.30 (m, 1H), 7.17−7.14 (m, 1H), 6.98−6.96 (m, 2H), 6.88−6.86 (m, 1H), 3.83 (s, 3H), 1.93−1.90 (m, 1H), 1.10−1.07 (m, 6H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 159.6, 146.9, 142.1, 140.3, 129.1, 128.9, 127.9, 124.7, 120.7, 120.4, 117.9, 113.7, 111.1, 54.5, 19.3. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 38.5. IR (neat) 3380, 2938, 1732, 1574, 1461, 1280, 760 cm^{-1}. HRMS (CI) m/z calcd for $C_{18}H_{20}BNO$ $[M]^+$ 277.1638, found 277.1637.

*3-(3-Methoxyphenyl)-2-cyclopropyl-2,1-borazaronaphthalene (**5e**).* Obtained as yellow oil (115 mg, 84%). ^{1}H NMR (500 MHz, acetone-d_6) δ 8.64 (br s, 1H), 7.88 (s, 1H), 7.66 (d, J = 7.8 Hz, 1H),

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7.48 (d, J = 8.3 Hz, 1H), 7.37−7.31 (m, 2H), 7.15−7.10 (m, 3H), 6.68−6.65 (m, 1H), 3.83 (s, 3H), 0.83−0.80 (m, 2H), 0.75−0.72 (m, 2H), 0.54−0.50 (m, 1H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 159.6, 146.3, 141.0, 140.4, 129.2, 128.9, 127.9, 124.7, 120.7, 120.4, 117.6, 113.9, 111.3, 54.5, 6.4. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 37.6. IR (neat) 3382, 2993, 1597, 1464, 1258, 1046, 760 cm^{-1}. HRMS (CI) m/z calcd for $C_{18}H_{18}BNO$ $[M]^+$ 275.1481, found 275.1476.

*3-(3-Methoxyphenyl)-2-cyclobutyl-2,1-borazaronaphthalene (**5f**).* Obtained as yellow oil (101 mg, 70%). ^{1}H NMR (500 MHz, acetone-d_6) δ 9.18 (br s, 1H), 7.88 (s, 1H), 7.68 (d, J = 7.6 Hz, 1H), 7.63 (d, J = 7.8 Hz, 1H), 7.43−7.40 (m, 1H), 7.30−7.27 (m, 1H), 7.17−7.14 (m, 1H), 6.96−6.92 (m, 2H), 6.86−6.83 (m, 1H), 3.82 (s, 3H), 2.75−2.70 (m, 1H), 2.12−2.04 (m, 5H), 1.93−1.85 (m, 1H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 159.6, 146.5, 141.6, 140.2, 129.2, 128.8, 127.9, 124.9, 120.7, 120.3, 117.8, 113.4, 111.2, 54.5, 25.6, 21.5. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 37.4. IR (neat) 3381, 2962, 1596, 1461, 1046, 758, 703 cm^{-1}. HRMS (CI) m/z calcd for $C_{19}H_{20}BNO$ $[M]^+$ 289.1638, found 289.1635.

*2,3-Diphenyl-2,1-borazaronaphthalene (**6a**).* Obtained as a white solid (108 mg, 77%). Mp 106−108 °C. ^{1}H NMR (500 MHz, acetone-d_6) δ 9.70 (br s, 1H), 8.07 (s, 1H), 7.79 (d, J = 7.8 Hz, 1H), 7.73−7.70 (m, 1H), 7.50−7.45 (m, 3H), 7.31−7.22 (m, 9H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 144.6, 143.3, 140.4, 133.5, 129.3, 128.6, 128.3, 128.1, 127.8, 127.3, 125.8, 125.2, 121.1, 118.2. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 35.3. IR (neat) 3371, 3051, 2923, 1560, 1420, 1307, 756 cm^{-1}. HRMS (CI) m/z calcd for $C_{20}H_{16}BN$ $[M]^+$ 281.1376, found 281.1371.

*3-(4-Fluorophenyl)-2-phenyl-2,1-borazaronaphthalene (**6b**).* Obtained as a yellow oil (106 mg, 71%). ^{1}H NMR (500 MHz, acetone-d_6) δ 9.70 (br s, 1H), 8.06 (s, 1H), 7.77−7.75 (m, 1H), 7.71 (d, J = 8.1 Hz, 1H), 7.48−7.45 (m, 3H), 7.31−7.24 (m, 6H), 7.06−7.01 (m, 2H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 161.6 (d, J = 243 Hz), 143.4, 140.8 (d, J = 2.5 Hz), 140.4, 133.4, 130.3 (d, J = 7.5 Hz), 129.4, 128.4, 128.2, 127.4, 125.1, 121.1, 118.2, 114.5 (d, J = 21 Hz). ^{11}B NMR (128.38 MHz, acetone-d_6) δ 34.8. IR (neat) 3381, 3050, 2979, 2348, 1698, 1218, 834, 753 cm^{-1}. HRMS (CI) m/z calcd for $C_{20}H_{15}BFN$ $[M]^+$ 299.1282, found 299.1280.

*3-(3-Nitrophenyl)-2-phenyl-2,1-borazaronaphthalene (**6c**).* Obtained as an off-white solid (52 mg, 32%). Mp 140−142 °C. ^{1}H NMR (500 MHz, acetone-d_6) δ 9.83 (br s, 1H), 8.25 (s, 1H), 8.22 (s, 1H), 8.13−8.08 (m, 1H), 7.84 (d, J = 7.8 Hz, 1H), 7.75−7.72 (m, 1H), 7.68−7.65 (m, 1H), 7.54−7.50 (m, 2H), 7.46−7.43 (m, 2H), 7.33−7.24 (m, 4H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 148.2, 146.4, 144.5, 140.7, 135.1, 133.3, 129.7, 129.0, 128.9, 128.3, 127.5, 124.9, 122.9, 121.4, 120.5, 118.3. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 35.4. IR (neat) 3371, 3051, 2780, 1560, 1286, 1264, 756, 699 cm^{-1}. HRMS (ESI) m/z calcd for $C_{20}H_{15}BN_2O_2Na$ $[M + Na]^+$ 349.1124, found 349.1125.

*3-(2,3-Dihydrobenzo[b][1,4]dioxin-6-yl)-2-phenyl-2,1-borazaronaphthalene (**6d**).* Obtained as an off-white solid (88 mg, 52%). Mp 55−57 °C. ^{1}H NMR (500 MHz, acetone-d_6) δ 9.61 (br s, 1H), 8.04 (s, 1H), 7.76 (d, J = 7.8 Hz, 1H), 7.70−7.68 (m, 1H), 7.53−7.51 (m, 2H), 7.47−7.43 (m, 1H), 7.33−7.27 (m, 3H), 7.23−7.20 (m, 1H), 6.82 (s, 1H), 6.74−6.72 (m, 2H), 4.25−4.20 (m, 4H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 143.3, 142.7, 142.3, 140.2, 137.8, 133.3, 129.2, 128.1, 128.0, 127.3, 125.2, 121.7, 121.1, 118.1, 117.0, 116.4, 65.2, 64.1. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 37.8. IR (neat) 3355, 2980, 1560, 1506, 1412, 1307, 1281, 1244, 754 cm^{-1}. HRMS (CI) m/z calcd for $C_{22}H_{19}BNO_2$ $[M + H]^+$ 340.1509, found 340.1516.

*2-Phenyl-3-(3-thienyl)-2,1-borazaronaphthalene (**6e**).* Obtained as an off-white solid (100 mg, 70%). Mp 72−74 °C. ^{1}H NMR (500 MHz, acetone-d_6) δ 9.63 (br s, 1H), 8.22 (s, 1H), 7.75 (d, J = 7.8 Hz, 1H), 7.70−7.67 (m, 1H), 7.56−7.52 (m, 2H), 7.47−7.43 (m, 1H), 7.36−7.29 (m, 4H), 7.23−7.20 (m, 1H), 7.16−7.14 (m, 1H), 7.08−7.06 (m, 1H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 145.1, 142.3, 140.2, 133.1, 129.2, 128.4, 128.2, 128.1, 127.4, 125.2, 124.6, 121.2, 120.8, 118.2. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 35.0. IR (neat) 3372, 2979, 2919, 1613, 1559, 1423, 754 cm^{-1}. HRMS (CI) m/z calcd for $C_{18}H_{14}BNS$ $[M]^+$ 287.0940, found 287.0939.

*3-(3-Furanyl)-2-phenyl-2,1-borazaronaphthalene (**6f**).* Obtained as a dark-yellow oil (104 mg, 80%). ^{1}H NMR (500 MHz, acetone-d_6) δ 9.61 (br s, 1H), 8.24 (s, 1H), 7.75 (d, J = 7.8 Hz, 1H), 7.66−7.64 (m, 1H), 7.60−7.57 (m, 2H), 7.49−7.43 (m, 2H), 7.39−7.37 (m, 3H), 7.23−7.21 (m, 2H), 6.85 (s, 1H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 142.6, 140.8, 140.0, 139.8, 132.6, 129.0, 128.2, 128.0, 127.9, 127.5, 125.2, 121.2, 118.1, 109.9. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 35.3. IR (neat) 3353, 2979, 1706, 1506, 1318, 951, 815, 703 cm^{-1}. HRMS (CI) m/z calcd for $C_{18}H_{14}BNO$ $[M]^+$ 271.1168 found 271.1156.

*3-(3,5-Dimethylisoxazol-4-yl)-2-phenyl-2,1-borazaronaphthalene (**6g**).* Obtained as a white solid (132 mg, 88%). Mp 80−82 °C. ^{1}H NMR (500 MHz, acetone-d_6) δ 9.84 (br s, 1H), 8.04 (s, 1H), 7.78−7.74 (m, 2H), 7.54−7.50 (m, 3H), 7.34−7.29 (m, 3H), 7.26−7.23 (m, 1H), 2.11 (s, 3H), 1.86 (s, 3H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 163.4, 158.5, 146.0, 140.7, 132.8, 129.2, 128.7, 128.5, 127.6, 124.8, 121.2, 118.4, 118.3, 10.5, 9.8. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 34.5. IR (neat) 3378, 1615, 1423, 1156, 756, 709 cm^{-1}. HRMS (ESI) m/z calcd for $C_{19}H_{18}BN_2O$ $[M + H]^+$ 301.1512, found 301.1521.

*3-(N-Boc-indol-5-yl)-2-phenyl-2,1-borazaronaphthalene (**6h**).* Obtained as an off-white solid (168 mg, 75%). Mp 96−98 °C. ^{1}H NMR (500 MHz, acetone-d_6) δ 9.65 (br s, 1H), 8.11 (s, 1H), 8.07−8.04 (m, 1H), 7.79−7.77 (m, 1H), 7.73−7.71 (m, 1H), 7.63−7.62 (m, 1H), 7.53−7.47 (m, 4H), 7.29−7.21 (m, 5H), 6.57−6.56 (m, 1H), 1.67 (s, 9H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 149.4, 143.4, 140.3, 139.4, 133.5, 130.7, 129.2, 128.1, 128.0, 127.3, 125.9, 125.5, 125.3, 121.1, 120.5, 118.2, 114.2, 107.3, 83.3, 59.6, 27.4. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 35.1. IR (neat) 3371, 2975, 1731, 1370, 1162, 1135, 764, 752 cm^{-1}. HRMS (ESI) m/z calcd for $C_{27}H_{25}BN_2O_2Na$ $[M + Na]^+$ 443.1907, found 443.1902.

*2-(4-Fluorophenyl)-3-(3-methoxyphenyl)-2,1-borazaronaphthalene (**7a**).* Obtained as an off-white solid (102 mg, 62%). Mp 74−76 °C. ^{1}H NMR (500 MHz, acetone-d_6) δ 9.73 (br s, 1H), 8.08 (s, 1H), 7.77 (d, J = 7.8 Hz, 1H), 7.69 (d, J = 8.3 Hz, 1H), 7.53−7.44 (m, 3H), 7.25−7.18 (m, 2H), 7.05−7.00 (m, 2H), 6.87−6.80 (m, 3H), 3.67 (s, 3H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 163.2 (d, J = 250 Hz), 159.5, 145.9, 143.3, 140.4, 135.7, 135.6, 129.4, 128.9, 128.4, 125.1, 121.2, 120.9, 118.2, 114.1 (d, J = 20.5 Hz), 111.6, 54.3. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 34.6. IR (neat) 3371, 2928, 1595, 1570, 1417, 1277, 1161, 760 cm^{-1}. HRMS (CI) m/z calcd for $C_{21}H_{18}BNOF$ $[M + H]^+$ 330.1465, found 330.1466.

*2,3-Bis(3-Methoxyphenyl)-2,1-borazaronaphthalene (**7b**).* Obtained as an off-white solid (185 mg, 50%). Mp 85−87 °C. ^{1}H NMR (500 MHz, acetone-d_6) δ 9.68 (br s, 1H), 8.10 (s, 1H), 7.79−7.77 (m, 1H), 7.72−7.70 (m, 1H), 7.49−7.46 (m, 1H), 7.24−7.18 (m, 3H), 7.09−7.05 (m, 2H), 6.90−6.86 (m, 3H), 6.81−6.79 (m, 1H), 3.67 (s, 3H), 3.65 (s, 3H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 159.4, 158.9, 146.0, 143.1, 140.4, 129.3, 128.7, 128.4, 128.3, 125.6, 125.1, 121.2, 120.9, 118.6, 118.2, 114.2, 113.9, 115.6, 54.3, 54.1. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 34.8. IR (neat) 3344, 3006, 2938, 1597, 1223, 1037, 786, 703 cm^{-1}. HRMS (ESI) m/z calcd for $C_{22}H_{21}BNO_2$ $[M + H]^+$ 342.1665, found 342.1650.

*3-(3-Methoxyphenyl)-2-(3-thienyl)-2,1-borazaronaphthalene (**7c**).* Obtained as a yellow oil (39 mg, 24%). ^{1}H NMR (500 MHz, acetone-d_6) δ 9.74 (br s, 1H), 8.01 (s, 1H), 7.75 (d, J = 8.1 Hz, 1H), 7.66 (d, J = 8.1 Hz, 1H), 7.57−7.55 (m, 1H), 7.48−7.45 (m, 1H), 7.39−7.36 (m, 1H), 7.27−7.18 (m, 3H), 6.93−6.84 (m, 3H), 3.73 (s, 3H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 159.4, 146.5, 143.1, 140.3, 132.0, 131.9, 129.3, 128.8, 128.3, 124.9, 124.3, 121.0, 120.8, 118.0, 114.0, 111.7, 54.3. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 32.2. IR (neat) 3374, 2924, 1562, 1261, 852, 761, 685 cm^{-1}. HRMS (CI) m/z calcd for $C_{19}H_{17}BNOS$ $[M + H]^+$ 318.1124, found 318.1109.

*2-(4-Dibenzofuranyl)-3-(3-methoxyphenyl)-2,1-borazaronaphthalene (**7d**).* Obtained as a white solid (64 mg, 32%). Mp 71−73 °C. ^{1}H NMR (500 MHz, acetone-d_6) δ 10.11 (br s, 1H), 8.24 (s, 1H), 8.08−8.04 (m, 2H), 7.87 (d, J = 7.8 Hz, 1H), 7.78−7.76 (m, 1H), 7.55−7.41 (m, 4H), 7.37−7.34 (m, 1H), 7.31−7.25 (m, 2H), 7.13−7.10 (m, 1H), 6.94−6.92 (m, 1H), 6.91−6.90 (m, 1H), 6.71−6.68 (m, 1H), 3.53 (s, 3H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 159.4, 158.9, 155.8, 145.9, 143.1, 140.0, 132.8, 129.5, 128.7, 128.4, 126.9, 125.3, 124.1, 122.8, 122.5, 122.3, 121.4, 120.7, 120.6, 120.5, 118.3, 113.6,

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111.7, 111.4, 54.2. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 33.9. IR (neat) 3390, 3051, 2929, 1564, 1450, 1165, 756 cm^{-1}. HRMS (ESI) m/z calcd for $C_{27}H_{21}BNO_2$ $[M + H]^+$ 402.1665, found 402.1673.

*3,6-Bis(3-Methoxyphenyl)-2-methyl-2,1-borazaronaphthalene (**8**).* Obtained as a yellow oil (172 mg, 97%). ^{1}H NMR (500 MHz, acetone-d_6) δ 9.50 (br s, 1H), 8.04−8.01 (m, 2H), 7.75−7.71 (m, 1H), 7.57−7.55 (m, 1H), 7.39−7.27 (m, 4H), 7.03−7.01 (m, 2H), 6.90−6.86 (m, 2H), 3.86 (s, 3H), 3.84 (s, 3H), 0.85 (s, 3H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 160.3, 159.7, 146.4, 142.2, 141.3, 139.9, 133.3, 129.7, 129.0, 127.4, 126.9, 125.1, 120.5, 118.9, 118.0, 113.7, 112.2, 112.1, 111.4, 54.6, 54.5. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 38.6. IR (neat) 3366, 2954, 1733, 1576, 1038, 933, 776, 699 cm^{-1}. HRMS (CI) m/z calcd for $C_{23}H_{23}BNO_2$ $[M + H]^+$ 356.1822, found 356.1829.

*6-(3-Methoxy-5-methylphenyl)-3-(3-methoxyphenyl)-2-methyl-2,1-borazaronaphthalene (**10a**).* Obtained as an off-white solid (158 mg, 86%). Mp 143−145 °C. ^{1}H NMR (500 MHz, acetone-d_6) δ 9.10 (br s, 1H), 7.82 (s, 1H), 7.63−7.61 (m, 1H), 7.40−7.35 (m, 3H), 7.12−7.10 (m, 1H), 6.96−6.94 (m, 1H), 6.72 (s, 1H), 6.53 (s, 1H), 6.52−6.50 (m, 2H), 3.85 (s, 3H), 3.43 (s, 3H), 2.16 (s, 3H), 0.21 (s, 3H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 158.9, 158.8, 145.1, 143.0, 141.6, 140.2, 138.2, 132.6, 130.6, 128.9, 127.6, 124.9, 123.0, 120.3, 117.4, 115.0, 112.9, 112.5, 111.8, 54.6, 54.0, 20.6. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 37.9. IR (neat) 3390, 3052, 2932, 1595, 1451, 1164, 758 cm^{-1}. HRMS (ESI) m/z calcd for $C_{24}H_{25}BNO_2$ $[M + H]^+$ 370.1978, found 370.1960.

*3-Phenyl-6-(3-thienyl)-2-methyl-2,1-borazaronaphthalene (**10b**).* Obtained as a white solid (126 mg, 84%). Mp 72−74 °C. ^{1}H NMR (500 MHz, acetone-d_6) δ 9.49 (br s, 1H), 8.04 (s, 1H), 7.95 (s, 1H), 7.78−7.78 (m, 1H), 7.68−7.66 (m, 1H), 7.58−7.56 (m, 1H), 7.53−7.51 (m, 2H), 7.47−7.45 (m, 2H), 7.43−7.40 (m, 2H), 7.30−7.27 (m, 1H), 0.81 (s, 3H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 144.9, 142.0, 141.2, 139.6, 128.5, 128.1, 128.0, 126.5, 126.4, 126.2, 126.1, 125.8, 125.2, 119.1, 118.0. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 37.9. IR (neat) 3366, 3058, 2931, 1596, 1450, 1220, 750, 700 cm^{-1}. HRMS (CI) m/z calcd for $C_{19}H_{16}BNS$ $[M]^+$ 301.1097, found 301.1099.

*6-(3-Furanyl)-3-phenyl-2-methyl-2,1-borazaronaphthalene (**10c**).* Obtained as a dark-yellow oil (98 mg, 69%). ^{1}H NMR (500 MHz, acetone-d_6) δ 9.50 (br s, 1H), 8.01 (s, 1H), 7.94−7.92 (m, 2H), 7.68−7.66 (m, 2H), 7.63 (s, 1H), 7.51−7.48 (m, 1H), 7.47−7.44 (m, 2H), 7.42−7.38 (m, 2H), 7.30−7.27 (m, 1H), 0.79 (s, 3H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 144.9, 143.8, 141.0, 139.4, 138.2, 128.0, 128.0, 126.3, 125.9, 125.9, 125.8, 125.2, 125.0, 118.0, 108.6. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 37.7. IR (neat) 3366, 3058, 2929, 1596, 1450, 1220, 1163, 750, 760 cm^{-1}. HRMS (CI) m/z calcd for $C_{19}H_{16}BNO$ $[M]^+$ 285.1325, found 285.1318.

Computational Study. Calculations were performed using the Gaussian 09 software package.[27] The geometries were optimized at the B3LYP/6-311G(d) level, and molecular orbitals and molecular energies were calculated at the same level.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Copies of ^{1}H, ^{13}C, and ^{11}B NMR spectra for all compounds as well as atom coordinates and total energies for the DFT calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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