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A Convergent, Modular Approach to Functionalized 2,1-Borazaronaphthalenes from 2-Aminostyrenes and Potassium Organotrifluoroborates

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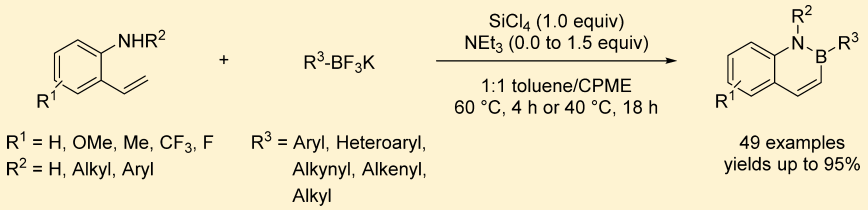
Supporting Information



ABSTRACT: Azaborines are an important class of compounds with applications in both medicinal chemistry and materials science. The first borazaronaphthalene, 2-chloro-2,1-borazaronaphthalene, was reported in 1959; however, access to more highly functionalized substructures has been limited because of the harsh reaction conditions required to displace the chloride on boron. A convergent approach has been developed to synthesize disubstituted 2,1-borazaronaphthalenes from *N*-substituted 2-aminostyrenes and potassium organotrifluoroborates, where the potassium organotrifluoroborate is converted to the active R–BX_2 species (X = Cl or F) in situ by addition of a fluorophile. Starting from aryl-, heteroaryl-, alkynyl-, alkenyl-, and alkyltrifluoroborates, a library of highly functionalized 2,1-borazaronaphthalenes were synthesized in one step under mild, transition-metal-free conditions.

INTRODUCTION

The isosteric replacement of C=C with B–N within the context of aromatic systems leads to azaborines, a class of compounds whose synthesis and reactivity have attracted much attention over the past few years.[1] Theoretical calculations as well as experimental data have shown that 1,2-azaborines are stable aromatic molecules whose aromaticity and thermal stability are slightly lower than those of the corresponding C=C aromatic systems.[2]

Isosteric replacement has become a powerful strategy in many diverse areas, including the pharmaceutical and agrochemical fields,[3] where there is increasing interest in the use of 1,2-azaborine substructures to increase structural diversity.[4] For example, Liu and Heider have demonstrated that the BN isosteres of ethylbenzene can bind the hydrophobic pocket of the L99A mutant of T4 lysozyme,[4a] and these azaborines also act as inhibitors of the enzyme ethylbenzene dehydrogenase (EbDH).[4b] Methods to access functionalized 1,2-azaborines in a straightforward, efficient manner could have an impact on the discovery of new bioactive compounds, leading to novel drug candidates that might overcome the limited range of chemical space in current sample collections.[5]

In addition to their medicinal chemistry applications, 1,2-azaborines have made a significant impact in materials science because of their photophysical properties.[6] Replacing one or more of the carbon atoms in a polycyclic aromatic hydrocarbon (PAH) with boron decreases the HOMO–LUMO gap of the material, providing access to molecules with chemiluminescent properties. Azaborines have been shown to function as organic light-emitting diodes (OLEDs)[6a] and organic field-effect transistors (OFETs).[6c] Therefore, the synthesis of functionalized 1,2-azaborines could provide access to new classes of chemiluminescent compounds as well.

Currently there exist a limited number of approaches to 2,1-borazaronaphthalenes. In 1959, Dewar and Dietz published the synthesis of the first 2,1-borazaronaphthalene via an annulation reaction between 2-aminostyrene and BCl_3 (Scheme 1, **I**).[7] It was later shown that functionalization at nitrogen could be achieved through deprotonation with MeLi and reaction with an alkyl or acyl electrophile.[8] Dewar expanded the scope of these systems by showing that substitution on boron could be achieved by refluxing in Et_2O with an aryl Grignard reagent (Scheme 1, **III**).[3,9] Paetzold synthesized 2,1-borazaronaphthalenes via a three-component reaction employing aniline, an aryldichloroborane, and phenylacetylene (Scheme 1, **IIA**).[10a] As mentioned above, in early syntheses of *N*-substituted 2,1-borazaronaphthalenes, functionalization at nitrogen took place subsequent to ring formation in a second process under strongly basic reaction conditions.[8] However, Paetzold developed a different set of conditions for the synthesis of *N*-substituted 2,1-borazaronaphthalenes (Scheme 1, **IIB**).[10b] An

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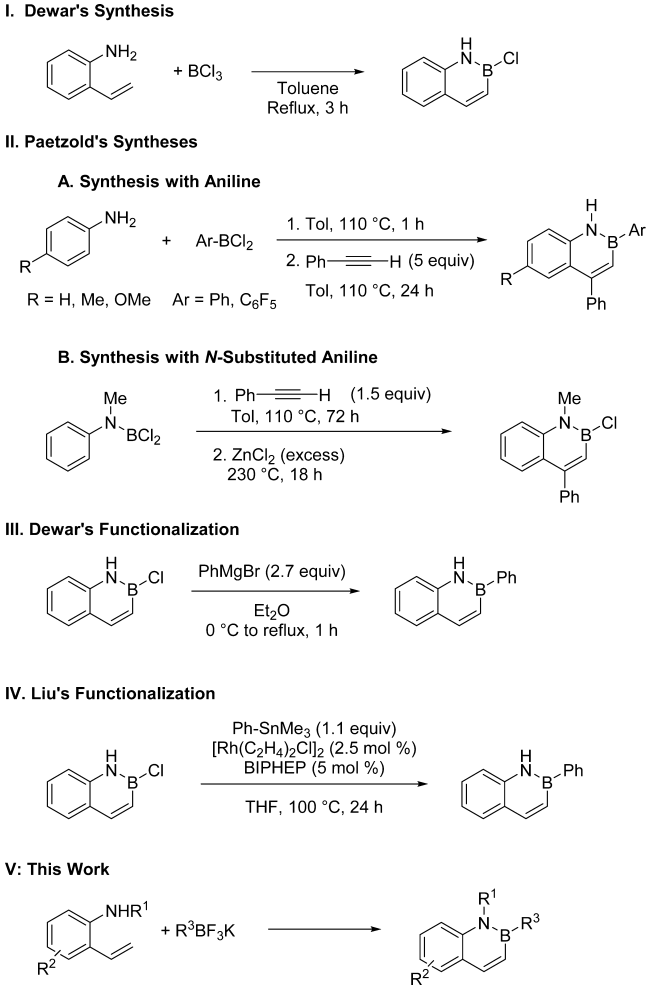
Scheme 1. Synthesis and Functionalization of 2,1-Borazaronaphthalenes



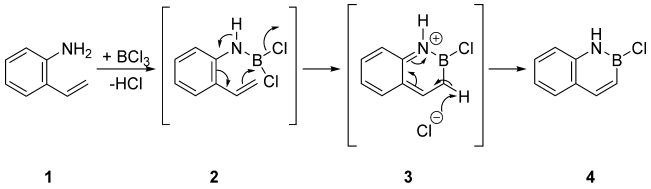
N-substituted aniline starting material was employed, which was first reacted with boron trichloride. The resulting product was then heated to reflux with phenylacetylene, purified, and heated with $ZnCl_2$. Finally, Liu recently published the Rh-catalyzed synthesis of *B*-substituted 1,2-dihydro-1,2-azaborines by reacting 1,2-dihydro-1,2-(chloro)azaborine with trimethylarylstannanes in THF at 100 °C.[11] In a single example, Liu demonstrated the reaction with 2-chloro-2,1-borazaronaphthalene, providing the cross-coupled product in 71% yield (Scheme 1, **IV**).

Although these methods are effective for synthesizing and functionalizing 2,1-borazaronaphthalenes, they are not without limitations. BCl_3 is not an ideal reagent for the transformation because of its strength as a Lewis acid and inherent reactivity. The use of aryl Grignard or organolithium reagents involves strongly nucleophilic reaction conditions that limit the functional group tolerance. Paetzold's method suffers from the use of a superstoichiometric amount of $ZnCl_2$ in addition to the high temperature and long reaction times needed to synthesize the desired product. Liu greatly improved the substrate scope by coupling cyano- and carbonyl-containing arylstannanes in yields of 41 to 81%.[11] However, this method is limited by the use of an expensive rhodium catalyst, toxic and atom-inefficient arylstannane reagents, and a reaction temperature much greater than the boiling point of the solvent.

There are currently no reported examples of the one-step synthesis of 1,2-disubstituted 2,1-borazaronaphthalenes. Previously reported methods require further functionalization at nitrogen and/or boron. The only reported examples of aryl substitution on boron in monosubstituted 2,1-borazaronaphthalenes are phenyl,[7] 2-pyridinyl,[6d] or pentafluorophenyl[10a] rings, where the desired products were synthesized in yields of 43−69%, 13%, and 78−89%, respectively.

To alleviate these limitations, we sought to develop a versatile, concise, metal-free synthesis of *B*- and *N*-substituted 2,1-borazaronaphthalenes under mild reaction conditions using inexpensive materials. The approach is loosely based on the original Dewar synthesis of 2-chloro-2,1-borazaronaphthalene. A plausible mechanism for that approach to 2-chloro-2,1-borazaronaphthalene from boron trichloride and 2-aminostyrene is outlined in Scheme 2. The first step consists of a

Scheme 2. Plausible Mechanism for the Synthesis of 2-Chloro-2,1-borazaronaphthalene



known reaction between a primary amine and BCl_3, which results in the formation of a N−B bond with loss of HCl to form **2**.[12] Nucleophilic attack of the terminal alkene, stabilized by resonance from the amine, results in cyclization with loss of Cl^- to form the iminium intermediate **3**. Elimination of HCl and aromatization of this complex provides 2-chloro-2,1-borazaronaphthalene (**4**).

The potential versatility of this approach can be highlighted by noting that one N−H bond remains intact throughout the transformation. Thus, substitution on nitrogen could easily be achieved by starting with a secondary amine derivative of 2-aminostyrene, providing the corresponding *N*-substituted 2,1-borazaronaphthalene in one step. Furthermore, two of the chlorides in BCl_3 are lost as HCl, with the third being incorporated into the final product. Therefore, to synthesize *B*-substituted 2,1-borazaronaphthalenes, one would utilize an R−BX_2 species (X = halide). Dewar confirmed this possibility by employing commercially available phenyldichloroborane to synthesize 2-phenyl-2,1-borazaronaphthalene.[7] However, only a limited number of organodichloroboranes (<10) are commercially available. Furthermore, the conventional synthesis of aryldihaloboranes, in particular, is an onerous process, beginning with the conversion of a minimally functionalized aryl halide to the corresponding aryl Grignard or aryllithium reagent. This intermediate then undergoes transmetalation to an arylstannane, which is quenched with BCl_3 to form the aryldihaloborane (Scheme 3, **I**).[13] Aside from the excess waste generated from the series of transmetalations, sensitive functional groups cannot be tolerated because of the use of highly reactive organometallic reagents. A second common approach to aryldihaloboranes is the Friedel−Crafts-type addition of BCl_3 to arenes in the presence of $AlCl_3$ (Scheme 3, **II**).[14] However, the regioselectivity in the addition of boron is difficult to control, and the high reactivity of these Lewis acids again limits the functional group tolerance.

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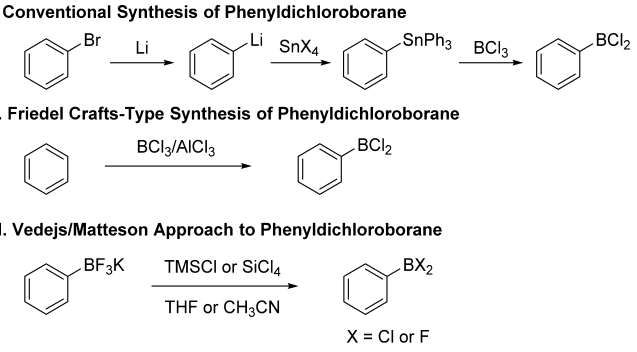
Scheme 3. Methods for Synthesizing Phenyldichloroborane



A more general, convenient approach to organodihaloboranes was first reported by Vedejs, who generated organodichloroboranes in situ by the addition of fluorophiles to potassium organotrifluoroborates (nearly 500 structurally diverse samples of which are commercially available) in THF or acetonitrile (Scheme 3, **III**).[15] Adapting this protocol would allow the use of air- and moisture-stable organotrifluoroborates in the borazine synthesis,[16] which was expected to expand the range of functional groups and subunits that could be incorporated. Thus, aryl- as well as alkyl-, alkenyl-, and alkynyltrifluoroborate substrates were envisioned as suitable precursors. Therefore, a mild synthesis of highly functionalized 2,1-borazaronaphthalenes utilizing *N*-substituted 2-aminostyrenes and potassium organotrifluoroborates was envisioned.

Reported herein is the Lewis acid-promoted annulation/aromatization reaction of substituted 2-aminostyrenes and potassium organotrifluoroborates to provide functionalized 2,1-borazaronaphthalenes. By formation of the required R–BX_2 species in situ via conversion of the organotrifluoroborate with $SiCl_4$, an array of 2,1-borazaronaphthalenes have been prepared. The use of aryl-, heteroaryl-, alkynyl-, alkenyl-, and alkyltrifluoroborates opens an effective and straightforward route to novel 2,1-borazaronaphthalenes.

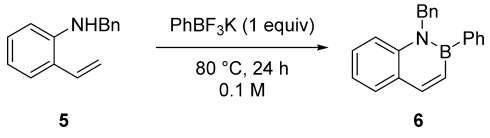
RESULTS AND DISCUSSION

N-Benzyl-2-aminostyrene (**5**) and potassium phenyltrifluoroborate were chosen as model substrates for the synthesis of 1-benzyl-2-phenyl-2,1-borazaronaphthalene (**6**) (Table 1). An array of solvents was tested in reactions at 80 °C for 24 h. On the basis of Matteson's adaptation of the Vedejs protocol,[17] $SiCl_4$ was first used as a fluorophile to generate the required $PhBCl_2$. Any R–BX_2 species (X = Br, Cl, F) should be practicable in the reaction, and therefore, several other fluorophiles were employed as well (entries 6–10). However, $SiCl_4$ provided the desired product in the highest yield. The addition of cyclopentyl methyl ether (CPME), a coordinating solvent, led to an increase in yield compared with toluene (entries 1–5). A 1:1 toluene/CPME mixture was found to be more effective than other solvent combinations. Therefore, after optimization of the solvent and fluorophile, the best conditions were found to be 1 equiv of $SiCl_4$ in 1:1 toluene/CPME at 80 °C for 24 h, which provided the desired product in 60% isolated yield (entry 5).

Final refinement of the reaction conditions required various temperatures, concentrations, and ratios of reagents to be examined (Table 2). At 80 °C, the reaction provided more desired product when the concentration was increased to 0.5 M, but then the yield decreased at 1 M (entries 1–4). Interestingly, the reaction was complete after 30 min at 80 °C, and when the temperature was lowered to 60 °C, the desired product was isolated in the same yield in 4 h (entry 5). Increasing the amount of amine increased the yield by 20% (entry 6); however, increasing the amount of phenyltrifluoroborate did not change the yield of the reaction (entry 7). Decreasing the amount of $SiCl_4$ to 0.75 equiv resulted in a lower yield (entry 8). Employing the conditions from entry 6 but lowering the reaction temperature to 40 °C afforded the desired product in 78% yield, but with a longer reaction time of 18 h (entry 9).

In addition to the variation of these parameters, several additives were screened in the reaction. Utilization of 1 or 2 equiv of K_2CO_3, which was added to quench the HCl generated in the reaction, did not change the yield of the reaction. Addition of 1 or 2 equiv of NaO*t*-Bu or NEt_3 resulted in no product formation. The use of KBr, which was added to form the R–BBr_2 species in situ, also did not change the yield of the reaction.[18] Therefore, the preferred conditions for the synthesis of 1-benzyl-2-phenyl-2,1-borazaronaphthalene were determined to be 1.5 equiv of amine, 1.0 equiv of organotrifluoroborate, and 1.0 equiv of $SiCl_4$ in a 1:1 toluene/CPME mixture at 60 °C for 4 h.

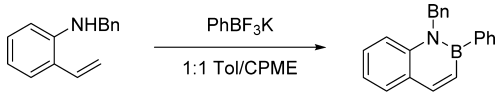
Table 1. Initial Reaction Conditions for the Synthesis of 2,1-Borazaronaphthalenes



5 6

entry	solvent	fluorophile (1 equiv)	yield (%)
1	toluene	$SiCl_4$	58
2	1:1 toluene/DME	$SiCl_4$	36
3	1:1 toluene/THF	$SiCl_4$	18
4	1:1 toluene/TBME	$SiCl_4$	16
5	**1:1 toluene/CPME**	**$SiCl_4$**	**60**
6	1:1 toluene/CPME	(*p*-tol)$SiCl_3$	47
7	1:1 toluene/CPME	$SiBr_4$	42
8	1:1 toluene/CPME	TMSCl	41
9	1:1 toluene/CPME	$BF_3{\cdot}OEt_2$	0
10	1:1 toluene/CPME	$BF_3{\cdot}SMe_2$	5

Table 2. Final Reaction Refinement of the Synthesis of 2,1-Borazaronaphthalenes



5 6

entry	amine:BF_3K:$SiCl_4$ (equiv)	conc. (M)	temp (°C), time	yield (%)
1	1.0:1.0:1.0	0.1	80, 30 min	58
2	1.0:1.0:1.0	0.25	80, 30 min	60
3	1.0:1.0:1.0	0.5	80, 30 min	65
4	1.0:1.0:1.0	1	80, 30 min	42
5	1.0:1.0:1.0	0.5	60, 4 h	65
6	**1.5:1.0:1.0**	**0.5**	**60, 4 h**	**79**
7	1.0:2.0:1.0	0.5	60, 4 h	65
8	1.0:1.0:0.75	0.5	60, 4 h	73
9	1.5:1.0:1.0	0.5	40, 18 h	78

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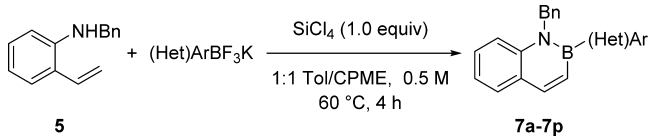
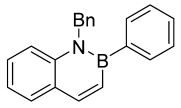
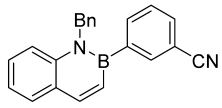
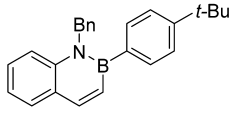
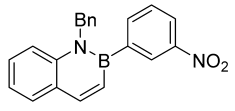
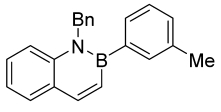
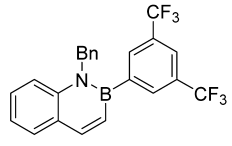
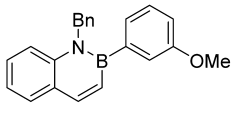
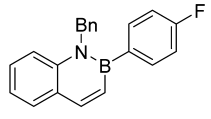
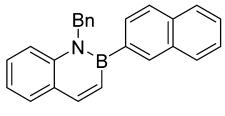
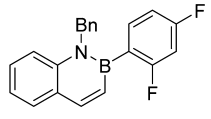
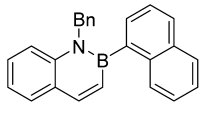
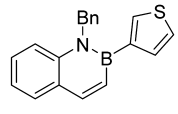
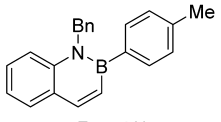
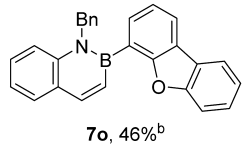
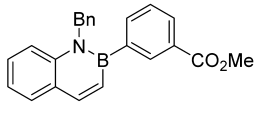
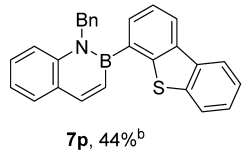
Table 3. Scope of the Reaction with Potassium (Hetero)aryltrifluoroborates



5 **7a-7p**

entry	product	entry	product
1	 **7a**, 79% (78%[a])	9	 **7i**, 50%
2	 **7b**, 44%	10	 **7j**, 49%
3	 **7c**, 57%	11	 **7k**, 50%
4	 **7d**, 64%	12	 **7l**, 70%
5	 **7e**, 69%	13	 **7m**, 13%
6	 **7f**, 15%	14	 **7n**, 56%[b]
7	 **7g**, 72%	15	 **7o**, 46%[b]
8	 **7h**, 65%	16	 **7p**, 44%[b]

Reaction conditions (unless otherwise noted): 1.5 equiv of amine, 1.0 equiv of (hetero)aryltrifluoroborate, 1.0 equiv of $SiCl_4$, 1:1 toluene/CPME, 60 °C, 4 h. [a]Reaction completed on a 5 mmol scale. [b]Reaction temperature of 40 °C, 18 h.

These standard conditions were applied to a variety of functionalized potassium aryl- and heteroaryltrifluoroborates, which reacted with **5** to provide the corresponding 1-benzyl-2,1-borazaronaphthalenes in yields up to 79% (Table 3). Sixteen different potassium aryl- and heteroaryltrifluoroborates afforded the corresponding disubstituted 2,1-borazaronaphthalenes in moderate to good yields. Electron-donating aryltrifluoroborates with *para* or *meta* substitution provided the desired products in good yield (entries 2–5 and 7). When the aryltrifluoroborates contained electron-withdrawing groups substituted *meta* or *para*, or for disubstituted derivatives, the corresponding 2,1-borazaronaphthalenes were synthesized in yields up to 70% (entries 8–13). The mild conditions of this method allowed ester, nitrile, and nitro functional groups on the aryltrifluoroborate (entries 8–10), which would not be possible in approaches using Grignard reagents. 3-Thienyl-, 4-

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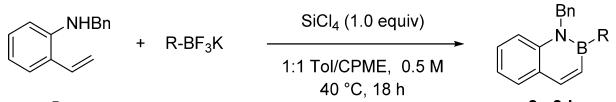
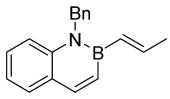
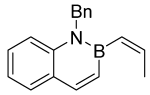
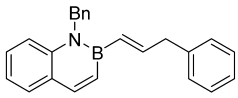
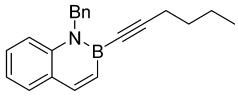
dibenzofuranyl-, and 4-dibenzothienyltrifluoroborate provided the desired products in moderate yields after the reaction temperature was lowered to 40 °C (entries 14−16). Because of steric factors imposed by substituting the 2,1-borazaronaphthalene at the 1 and 2 positions, sterically encumbered organotrifluoroborates provided the corresponding products in lower yields, as is evident in the use of 1- and 2-naphthyltrifluoroborate, where the less sterically hindered 2-naphthyltrifluoroborate results in a higher product yield of 69% (entries 5 and 6). The scalability of the reaction conditions was illustrated by conducting the reaction on a 5 mmol scale without loss of yield (entry 1).

After synthesizing aryl- and heteroaryl-containing 2,1-borazaronaphthalenes, we sought to extend this method to alkenyl- and alkynyltrifluoroborates, providing access to novel systems (Table 4). There are no previously reported examples

Table 4. Scope of the Reaction with Potassium Alkenyl- and Alkynyltrifluoroborates



5 8a-8d

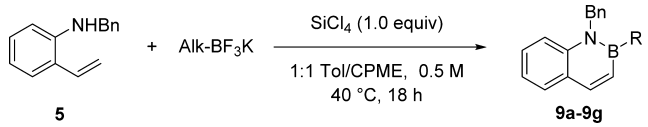
entry	product		yield (%)
1		**8a**	54
2		**8b**	57[a]
3		**8c**	51
4		**8d**	47

Reaction conditions: 1.2 equiv of amine, 1.0 equiv of alkyltrifluoroborate, 1.0 equiv of $SiCl_4$, 1:1 toluene/CPME, 40 °C, 18 h. [a]A 95:5 *cis:trans* ratio of R−BF_3K was employed in the reaction.

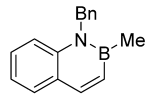
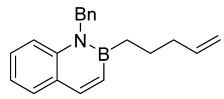
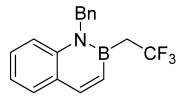
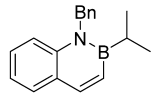
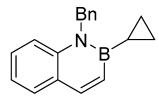
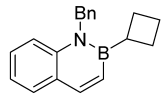
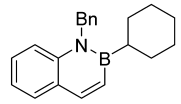
of 2,1-borazaronaphthalenes with alkenyl or alkynyl substituents. With a decrease in the reaction temperature to 40 °C, four different azaborines of this type were synthesized in yields up to 57%. It is important to note that both *cis*- and *trans*-propenyltrifluoroborate were used in the reaction, and complete retention of stereochemistry of the olefin was achieved (entries 1 and 2). A phenyl-substituted alkenyltrifluoroborate provided the desired product in 51% yield (entry 3). A 2-alkynyl-substituted 2,1-borazaronaphthalene was synthesized in good yield starting from 1-hexynyltrifluoroborate (entry 4).

Previously reported *B*-alkyl-substituted 2,1-borazaronaphthalenes have been limited to simple aliphatic derivatives, including methyl, ethyl, isopropyl, and *tert*-butyl systems, which were synthesized in yields of 43%, 54%, 8%, and 25%, respectively.[7,10b] All of these materials were generated via addition of an alkylmetallic reagent to the B−Cl derivative in a second step after assembly of the aromatic core. The approach described herein allows diverse, readily available primary and secondary alkyltrifluoroborates to be employed in a direct, straightforward, one-step synthesis of 2-alkyl-2,1-borazaronaphthalenes with yields up to 58% (Table 5). For example, *β*,*β*,*β*-trifluoroethyltrifluoroborate[19] was effectively used in the reaction, affording the corresponding product in 40% yield (entry 3). An acyclic secondary trifluoroborate was successfully utilized, and the desired product was obtained in 58% yield (entry 4). Cyclic secondary trifluoroborates such as cyclopropyl, cyclobutyl, and cyclohexyl derivatives provided the desired products in good yields (entries 5−7). Scaling up the reaction with potassium methyltrifluoroborate provided a similar yield on a 5 mmol scale (entry 1).

Table 5. Scope of the Reaction with Potassium Alkyltrifluoroborates



5 9a-9g

entry	product		yield (%)
1		**9a**	48(51[a])
2		**9b**	50
3		**9c**	40
4		**9d**	58
5		**9e**	49
6		**9f**	51
7		**9g**	42

Reaction conditions (unless otherwise noted): 1.5 equiv of amine, 1.0 equiv of alkyltrifluoroborate, 1.0 equiv of $SiCl_4$, 1:1 toluene/CPME, 40 °C, 18 h. [a]Reaction completed on a 5 mmol scale.

After synthesizing an array of 2,1-borazaronaphthalenes with varying groups on boron, the method was extended by reacting diverse nitrogen-substituted 2-aminostyrenes with phenyltrifluoroborate to provide the corresponding 2-phenyl-2,1-borazaronaphthalenes (Table 6). This convergent approach allows disubstituted 2,1-borazaronaphthalenes to be easily synthesized. The requisite starting materials for this method were synthesized via a Buchwald−Hartwig amination of commercially available 2-bromostyrene.[20] Different groups were installed on nitrogen, such as PMB and allyl, and the

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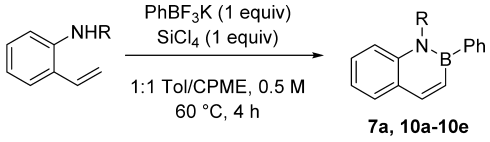
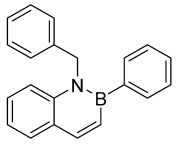
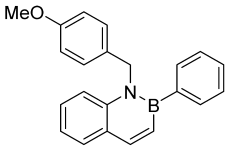
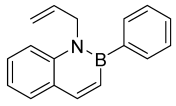
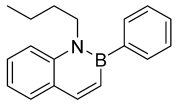
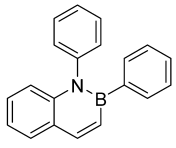
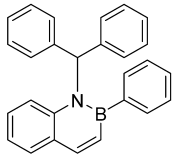
Table 6. Scope of the Reaction with *N*-Substituted 2-Aminostyrenes



7a, 10a-10e

entry	product	yield (%)
1		**7a** 79
2		**10a** 61
3		**10b** 55[a]
4		**10c** 71
5		**10d** 40
6		**10e** 0

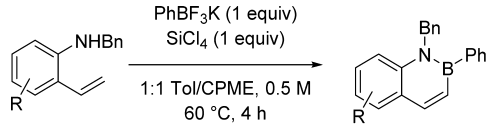
Reaction conditions (unless otherwise noted): 1.5 equiv of amine, 1.0 equiv of aryltrifluoroborate, 1.0 equiv of $SiCl_4$, 1:1 toluene/CPME, 60 °C, 4 h. [a]Reaction temperature of 40 °C, 18 h.

corresponding 2,1-borazaronaphthalenes were synthesized in yields of 61% and 55%, respectively (entries 2 and 3). A straight-chain alkylamine was also synthesized and employed in the reaction to provide the desired product in 71% yield (entry 4).

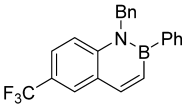
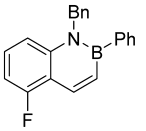
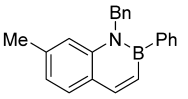
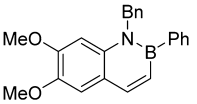
As with the 1-naphthyltrifluoroborate, steric restrictions on substitution of the azaborine at the 1 and 2 positions were evident, as the yield decreased to 40% when an aryl group was substituted on nitrogen (entry 5), and no desired product was obtained when a diphenylmethyl group was substituted on nitrogen (entry 6).

Having synthesized 1,2-disubstituted 2,1-borazaronaphthalenes with various substituents on nitrogen and boron, we sought to extend the method to aryl-substituted 2-aminostyrenes, as aryl-functionalized 2-aminostyrenes have not previously been employed in the synthesis of 2,1-borazaronaphthalenes. To access the requisite substrates, substituted 2-bromobenzaldehydes were converted in a two-step process via Wittig olefination and Buchwald–Hartwig amination to provide access to the requisite 2-aminostyrenes with substituents placed at various positions about the arene.[21] These aminostyrenes provided the corresponding 2,1-borazaronaphthalenes in yields up to 75% (Table 7). Electron-withdrawing substituents such as

Table 7. Scope of the Reaction with Substituted 2-Aminostyrenes



5 **11a-11d**

entry	product	yield (%)
1		**11a** 64
2		**11b** 73
3		**11c** 75
4		**11d** 59

Reaction conditions: 1.5 equiv of amine, 1.0 equiv of aryltrifluoroborate, 1.0 equiv of $SiCl_4$, 1:1 toluene/CPME, 60 °C, 4 h.

fluorine and trifluoromethyl groups provided the desired product in yields of 73% and 64%, respectively (entries 1 and 2). Substitution of electron-donating methyl and methoxy groups about the aromatic ring gave the corresponding 2,1-borazaronaphthalenes in good yields (entries 3 and 4). The nature of the process ensures that complete control of the regiochemistry can be achieved in the placement of substituents about both rings, an advantage enjoyed over many syntheses of substituted naphthalenes themselves.

One potential route to obtain monosubstituted N–H 2,1-borazaronaphthalenes[7,10a] would employ the synthesis of an *N*-protected azaborine that could later be deprotected. It was for this reason that *N*-benzyl-2-aminostyrene was chosen for optimization. However, because of the aromatic character of the 2,1-borazaronaphthalene, the N–C bond of the benzyl group acts more like a C–C bond. Attempts to remove this protecting group, as well as the PMB and allyl protecting groups, were unsuccessful, resulting in recovery of the starting 2,1-borazaronaphthalene in almost all cases, demonstrating the stability of these azaborines. To achieve the synthesis of N–H 2,1-borazaronaphthalenes, the two-component annulation/aromatization reactions were carried out with 2-aminostyrene. After lowering the concentration of the standard reaction conditions to 0.25 M, the monosubstituted 2,1-borazaronaph-

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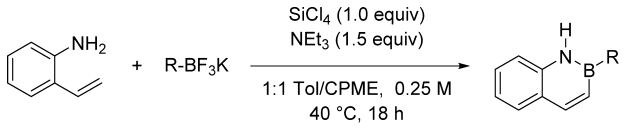
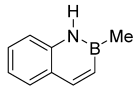
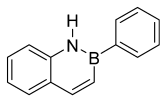
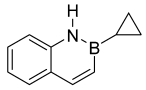
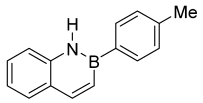
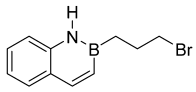
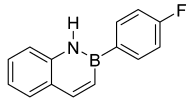
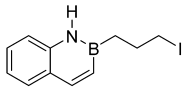
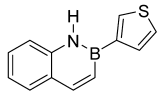
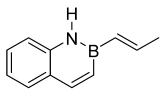
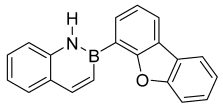
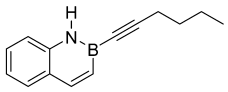
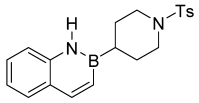
thalenes were prepared in yields up to 66%. However, addition of 1.5 equiv of NEt_3, which served to quench the HCl formed during the reaction, led to increased yields, providing the desired products in yields up to 95% (Table 8). Cyclic and

Table 8. Scope of the Reaction with 2-Aminostyrene



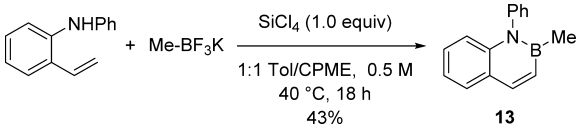
1 **12a-12k**

entry	product	entry	product
1	 **12a**, 55%	7	 **12g**, 95%
2	 **12b,** 52%	8	 **12h**, 93%
3	 **12c**, 80%	9	 **12i**, 86%
4	 **12d**, 69%	10	 **12j**, 92%
5	 **12e**, 52%	11	 **12k**, 82%
6	 **12f**, 73%	12	 **12l**, 17%[a]

Reaction conditions (unless otherwise noted): 1.2 equiv of amine, 1.0 equiv of organotrifluoroborate, 1.0 equiv of $SiCl_4$, 1.5 equiv of NEt_3, 1:1 toluene/CPME, 40 °C, 18 h. [a]Without 1.5 equiv of NEt_3.

acyclic alkyltrifluoroborates provided the desired products in high yields (entries 1 and 2). The mild reaction conditions allowed the installation of an alkyl iodide and bromide on the 2,1-borazaronaphthalene, providing the desired products in 69% and 80% yield, respectively (entries 3 and 4). Alkenyl and alkynyltrifluoroborates could be employed, providing the desired products in good yield (entries 5 and 6). Electron-donating, electron-withdrawing, and electron-neutral aryltrifluoroborates were effective in the reaction, as the 2,1-borazaronaphthalenes were synthesized in yields up to 95% (entries 7–9). Three heterocyclic trifluoroborates were used in the reaction, providing the desired products in yields up to 92% (entries 10–12).

1-Alkyl-2-aryl-, 1,2-dialkyl, and 1,2-diaryl-2,1-borazaronaphthalenes have been synthesized in yields up to 95%. To demonstrate that the fourth complementary substitution pattern was accessible, an aryl-substituted 2-aminostyrene was reacted with potassium methyltrifluoroborate, providing access to 1-aryl-2-alkyl-2,1-borazaronaphthalene **13** (eq 1).



13 (1)

The overall impact of this method can be demonstrated by comparing the current synthesis of 2,1-borazaronaphthalenes with those of the isosteric substituted naphthalenes. Whereas the syntheses of 1-alkyl-2-aryl- and 1,2-dialkyl-2,1-borazaronaphthalenes (**7a–p** and **9a–g**, respectively) proceed under mild reaction conditions, the syntheses of the corresponding disubstituted naphthalenes employ alkyl and aryl Grignard reagents for substitution at the 2-position of the naphthalene followed by a high temperature oxidation.[22] The use of these Grignard reagents severely restricts the types of functional groups that can be incorporated. The synthesis of 1-alkyl-2-aryl- and 1,2-diarylnaphthalenes requires a palladium-catalyzed borylation and/or cross-coupling.[23] Although effective in providing a range of products with high functional group tolerance, the synthesis of the electrophilic naphthalene in these systems requires several steps and harsh reaction conditions. By contrast, the synthesis of the 2,1-borazaronaphthalenes (**7a–p** and **10d**) is a transition-metal-free route that does not require a multistep synthesis of starting materials. The synthesis of 1-aryl-2-alkylnaphthalenes requires only one step;[24] however, only a few examples have been reported, and these are void of any functional groups. In fact, only straight-chain alkyl substituents were present on the alkyne in this gallium-catalyzed reaction. The success in utilizing highly elaborated potassium alkyltrifluoroborates alleviates the problem of synthesizing functionalized alkynes, and the corresponding 2,1-borazaronaphthalene **13** was synthesized in similar yield. The synthesis of 1-substituted-2-alkynyl- and 1-substituted-2-alkenylnaphthalenes can be envisioned to proceed through a cross-coupling similar to that for the 1,2-diarylnaphthalenes.[25] More importantly, in comparison with **11a–d**, there are only a few examples of the synthesis of 1,2-disubstituted naphthalenes with further substitution on the naphthyl ring. For example, there are no reported examples of the naphthalenes analogous to the fluorinated and trifluoromethylated 2,1-borazaronaphthalenes **11a** and **11b**.[26] The corresponding 2,1-borazaronaphthalenes are synthesized in a convergent manner by reacting an aryl- or *N*-substituted 2-aminostyrene with an organotrifluoroborate to provide access to highly functionalized products with complete control of regioselectivity that would be virtually impossible to replicate easily in the naphthalenes themselves.

■ CONCLUSIONS

Forty-nine *N*- and *B*-substituted 2,1-borazaronaphthalenes were synthesized via an annulation/aromatization reaction of potassium organotrifluoroborates and substituted 2-aminostyrenes. By utilization of the in situ conversion of organotrifluoroborates to the active organodihaloboranes with $SiCl_4$, the use of harsh reaction conditions was avoided, allowing the synthesis of highly functionalized azaborines in a straightforward, efficient manner. Alkyl, alkenyl, aryl, and heteroaryl substituents at the 2-position of 2,1-borazaronaphthalenes can be prepared from the same synthetic precursor, allowing a

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library of highly functionalized and substituted 2,1-borazaronaphthalenes to be synthesized easily. In fact, more diversity has been introduced into the 2,1-borazaronaphthalene platform as a result of this study than in all previous studies over the past 50+ years combined.

Furthermore, whereas the synthesis of the isosteric 1,2-disubstituted naphthalenes requires the use of strongly nucleophilic organometallic reagents that limit the types of functional groups that can be tolerated, the synthesis of disubstituted 2,1-borazaronaphthalenes described herein proceeds under mild reaction conditions. The reactions also transpire without the need for preactivation of the rings or expensive transition-metal catalysts in a convergent, modular manner that permits complete control of the regioselectivity and substituents about both aromatic rings. Investigations of the reactivity of these compounds and applications of this approach to other borazine cores are currently underway.

EXPERIMENTAL SECTION

General Considerations. JohnPhos, NaO*t*-Bu, 2-bromostyrene, and $SiCl_4$ were purchased and used as received. Amines were distilled prior to use. Toluene and CPME were dried using a JC Meyer solvent system. Standard benchtop techniques were employed to handle air-sensitive reagents. Melting points (°C) are uncorrected. NMR spectra were recorded on a 500 or 400 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 ^{11}B NMR chemical shifts were referenced to external $BF_3{\cdot}OEt_2$ (0.0 ppm), with a negative sign indicating an upfield shift. Chemical shifts (δ) are given in parts per million. Multiplicities are denoted as follows: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad. Coupling constants (J) are given in hertz. ^1H NMR data are presented as follows: chemical shift (multiplicity, coupling constant, integration). 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 UV light. HRMS data were obtained by either ESI or CI using a TOF mass spectrometer.

Potassium β,β,β-Trifluoroethyltrifluoroborate.[19] White solid. Mp: >250 °C. ^1H NMR (500 MHz, acetone-d_6): δ 1.08 (br s, 2H). ^{13}C NMR (125.8 MHz, acetone-d_6): δ 131.9 (J = 280 Hz), 25.2 (br). ^{11}B NMR (128.38 MHz, acetone-d_6): δ 3.75. ^{19}F NMR (338.8 MHz, acetone-d_6): δ −56.6, −139.6. IR (neat): 1322, 1260, 1056, 957, 794, 662 cm^{-1}. HRMS (ESI) m/z: calcd for $C_2H_2BF_6$ $[M - K]^-$ 151.0154, found 151.0148.

Potassium 3-Bromopropyltrifluoroborate.[27] White solid. Mp: >250 °C. ^1H NMR (500 MHz, acetone-d_6): δ 3.41−3.36 (m, 2H), 1.82−1.77 (m, 2H), 0.24−0.21 (m, 2H). ^{13}C NMR (125.8 MHz, acetone-d_6): δ 38.2, 29.8, 18.2 (br). ^{11}B NMR (128.38 MHz, acetone-d_6): δ 6.03. ^{19}F NMR (338.8 MHz, acetone-d_6): δ −141.1. IR (neat): 2912, 1437, 1267, 1080, 1009, 920, 868, 832 cm^{-1}. HRMS (ESI) m/z: calcd for $C_3H_6BF_3Br$ $[M - K]^-$ 188.9698, found 188.9704.

Potassium 3-Iodopropyltrifluoroborate.[27] White solid. Mp: >250 °C. ^1H NMR (500 MHz, acetone-d_6): δ 3.20 (t, J = 7.6 Hz, 2H), 1.83−1.77 (m, 2H), 0.25−0.18 (m, 2H). ^{13}C NMR (125.8 MHz, acetone-d_6): δ 30.9, 20.3 (br), 13.1. ^{11}B NMR (128.38 MHz, acetone-d_6): δ 5.80. ^{19}F NMR (338.8 MHz, acetone-d_6): δ −141.0. IR (neat): 2918, 1267, 1215, 1084, 992, 918, 859 cm^{-1}. HRMS (ESI) m/z: calcd for $C_3H_6BF_3I$ $[M - K]^-$ 236.9559, found 236.9577. Anal. Calcd for $C_3H_6BF_3IK$: C, 13.06; H, 2.19; F, 20.66. Found: C, 12.78; H, 1.92; F, 20.06.

Potassium Dibenzo[*b*,*d*]thiophen-4-yltrifluoroborate. White solid. Mp: >250 °C. ^1H NMR (500 MHz, acetone-d_6): δ 8.20−8.16 (m, 1H), 8.03 (d, J = 7.6 Hz, 1H), 7.85−7.81 (m, 1H), 7.62 (d, J = 6.7 Hz, 1H), 7.39−7.36 (m, 2H), 7.31−7.27 (m, 1H). ^{13}C NMR (125.8 MHz, acetone-d_6): δ 142.9, 140.6, 136.0, 133.8, 130.3, 130.3, 125.7, 123.4, 122.2, 121.0, 119.3. ^{11}B NMR (128.38 MHz, acetone-d_6): δ 4.28. ^{19}F NMR (338.8 MHz, acetone-d_6): δ −141.3. IR (neat): 3064, 2357, 1374, 959, 798, 748 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{12}H_7BF_3S$ $[M - K]^-$ 251.0316, found 251.0314.

General Procedure for the Synthesis of 2-Aminostyrenes. To an oven-dried Biotage microwave vial equipped with a stir bar were added Pd(μ-Cl) dimer (0.02 mmol, 0.5 mol %), JohnPhos (0.04 mmol, 1 mol %), and NaO*t*-Bu (5.6 mmol, 1.4 equiv). The vial was sealed with a cap lined with a disposable Teflon septum, evacuated under vacuum, and purged with Ar three times. Toluene (8 mL) was added, followed by 2-bromostyrene (4 mmol, 1 equiv) and the corresponding amine (4.8 mmol, 1.2 equiv). The resulting mixture was heated to 80 °C and stirred until full consumption of 2-bromostyrene was observed by HPLC (~24 h). The reaction mixture was cooled to rt, diluted with Et_2O (16 mL), and filtered over Celite. The solvent was removed in vacuo, and the product was purified by flash column chromatography on silica gel with an EtOAc/hexanes mixture as the eluent. The eluent for most of the amines was hexanes to 2% EtOAc/hexanes.

*N-Benzyl-2-vinylaniline (**7a-amine**).*[28] The reaction was conducted using 27 mmol of 2-bromostyrene, and the catalyst loading was reduced to 0.25 mol % Pd(μ-Cl) dimer and 0.5 mol % JohnPhos. The product was obtained as a yellow oil (4.44 g, 78%). ^1H NMR (500 MHz, $CDCl_3$): δ 7.41−7.33 (m, 4H), 7.31−7.26 (m, 2H), 7.18−7.12 (m, 1H), 6.82−6.71 (m, 2H), 6.64 (d, J = 8.1 Hz, 1H), 5.62 (dd, J = 1.6, 17.3 Hz, 1H), 5.31 (dd, J = 1.6, 11.0 Hz, 1H), 4.36 (d, J = 5.3 Hz, 2H), 4.17 (br s, 1H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 145.2, 139.4, 133.1, 129.1, 128.8, 127.6, 127.5, 127.4, 124.4, 117.7, 116.5, 111.1, 48.5.

*N-(4-Methoxybenzyl)-2-vinylaniline (**10a-amine**).* The reaction was conducted using 7 mmol of 2-bromostyrene, and the catalyst loading was reduced to 0.25 mol % Pd(μ-Cl) dimer and 0.5 mol % JohnPhos. The product was obtained as a yellow oil (1.12 g, 69%). ^1H NMR (500 MHz, $CDCl_3$): δ 7.33−7.26 (m, 3H), 7.19−7.12 (m, 1H), 6.92−6.86 (m, 2H), 6.80−6.70 (m, 2H), 6.65 (d, J = 8.2 Hz, 1H), 5.61 (dd, J = 1.6, 17.4 Hz, 1H), 5.29 (dd, J = 1.6, 11.0 Hz, 1H), 4.28 (s, 2H), 4.08 (br s, 1H), 3.81 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 159.1, 145.3, 133.1, 131.4, 129.1, 129.0, 127.5, 124.4, 117.6, 116.4, 114.2, 111.1, 55.4, 48.0. IR (neat): 3436, 2840, 1602, 1509, 1246, 747 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{16}H_{18}NO$ $[M + H]^+$ 240.1388, found 240.1378.

*N-Allyl-2-vinylaniline (**10b-amine**).* Obtained as a yellow oil (643 mg, 81%). ^1H NMR (500 MHz, $CDCl_3$): δ 7.31 (dd, J = 7.6 Hz, 1.0 Hz, 1H), 7.23−7.20 (m, 1H), 6.85−6.78 (m, 2H), 6.68 (d, J = 8.1 Hz, 1H), 6.07−5.99 (m, 1H), 5.66 (dd, J = 17.4 Hz, 1.7 Hz, 1H), 5.38−5.32 (m, 2H), 5.23 (dd, J = 10.3 Hz, 1.2 Hz, 1H), 3.99 (br s, 1H), 3.85−3.83 (m, 2H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 144.9, 135.3, 132.9, 128.8, 127.4, 124.3, 117.4, 116.3, 116.2, 111.0, 46.5. IR (neat): 3436, 3082, 1601, 1507, 131, 913, 746 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{11}H_{14}N$ $[M + H]^+$ 160.1126, found 160.1131.

*N-Butyl-2-vinylaniline (**10c-amine**).*[29] Obtained as a yellow oil (502 mg, 72%). ^1H NMR (500 MHz, $CDCl_3$): δ 7.26−7.23 (m, 1H), 7.19−7.14 (m, 1H), 6.77−6.67 (m, 2H), 6.63 (d, J = 8.2 Hz, 1H), 5.60 (dd, J = 1.6, 17.3 Hz, 1H), 5.30 (dd, J = 1.6, 11.0 Hz, 1H), 3.74 (br s, 1H), 3.15−3.11 (m, 2H), 1.68−1.60 (m, 2H), 1.49−1.40 (m, 2H), 0.97 (t, J = 7.4 Hz, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 145.7, 133.2, 129.1, 127.6, 124.2, 117.1, 116.2, 110.7, 43.9, 31.8, 20.5, 14.1.

*N-Phenyl-2-vinylaniline (**10d-amine**).*[30] Obtained as a yellow oil (661 mg, 85%). ^1H NMR (500 MHz, $CDCl_3$): δ 7.48 (dd, J = 1.4, 7.7 Hz, 1H), 7.28−7.18 (m, 4H), 7.04−6.99 (m, 1H), 6.96−6.85 (m, 4H), 5.69 (dd, J = 1.4, 17.5 Hz, 1H), 5.53 (br s, 1H), 5.32 (dd, J = 1.4, 11.0 Hz, 1H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 144.2, 140.2, 133.0, 130.2, 129.5, 128.7, 127.3, 122.7, 120.6, 120.2, 117.4, 116.4.

*N-Benzhydryl-2-vinylaniline (**10e-amine**).* Obtained as a yellow solid (821 mg, 72%). Mp: 76−78 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 7.41−7.35 (m, 8H), 7.32−7.27 (m, 3H), 7.09−7.05 (m, 1H), 6.84 (dd, J = 17.4, 11.0 Hz, 1H), 6.76−6.72 (m, 1H), 6.48 (d, J = 7.8 Hz, 1H), 5.67 (d, J = 17.4 Hz, 1H), 5.58 (br s, 1H), 5.33 (dd, J = 10.9, 1.3 Hz, 1H), 4.41 (br s, 1H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 144.1, 142.8, 136.6, 132.9, 128.7, 127.3, 127.2, 124.3, 117.6, 116.4, 112.1, 109.5,

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62.8. IR (neat): 3423, 3062, 2844, 1735, 1500, 907, 742 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{21}H_{20}N$ $[M + H]^+$ 286.1596, found 286.1597.

General Procedure for the Wittig Olefination and Buchwald–Hartwig Amination for the Synthesis of Substituted 2-Aminostyrenes. To an oven-dried 25 mL round-bottom flask with a stir bar was added $MePh_3PBr$ (6 mmol, 1.2 equiv). The flask was sealed with a septum, evacuated, and purged three times with Ar. The flask was cooled to −78 °C, and *n*-BuLi (1.6 M in hexanes, 6 mmol, 1.2 equiv) was added dropwise, keeping the reaction temperature below −70 °C. The reaction mixture was stirred at −78 °C for 1 h and allowed to warm to rt. The mixture was cooled to −78 °C, and the corresponding aldehyde (4 mmol, 1 equiv) was added dropwise (or in small portions if solid) over the course of 10 min. The reaction mixture was allowed to warm slowly to rt and was stirred for 18 h. The reaction was quenched at 0 °C by addition of sat. aq NH_4Cl, and the mixture was extracted with EtOAc, dried ($MgSO_4$), and concentrated. Ph_3PO was removed by addition of Et_2O, cooling to 0 °C, and filtering over a small plug of silica. The crude product was taken directly to the next step after the product was confirmed by NMR analysis. To an oven-dried Biotage microwave vial equipped with a stir bar was added Pd(μ-Cl) dimer (0.02 mmol, 0.5 mol %), JohnPhos (0.04 mmol, 1 mol %), and NaO*t*-Bu (5.6 mmol, 1.4 equiv). The vial was sealed with a cap lined with a disposable Teflon septum, evacuated under vacuum, and purged with Ar three times. Toluene (8 mL) was added, followed by the substituted-2-bromostyrene (4 mmol, 1 equiv) and benzylamine (4.8 mmol, 1.2 equiv). The resulting mixture was heated to 80 °C and stirred until full consumption of 2-bromostyrene was observed by HPLC (~24 h). The reaction mixture was cooled to rt, diluted with Et_2O (16 mL), and filtered over Celite. The solvent was removed in vacuo, and the product was purified by flash column chromatography on silica gel with hexanes as the eluent.

N-Benzyl-5-trifluoromethyl-2-vinylaniline (***11a-amine***). The reaction was completed on a 2 mmol scale, and the product was obtained as a yellow oil (160 mg, 29%). ^1H NMR (500 MHz, $CDCl_3$): δ 7.51 (d, *J* = 1.5 Hz, 1H), 7.41–7.37 (m, 5H), 7.35–7.32 (m, 1H), 6.76 (dd, *J* = 17.4, 11.0 Hz, 1H), 6.65 (d, *J* = 8.6 Hz, 1H), 5.71 (dd, *J* = 17.1, 1.2 Hz, 1H), 5.44 (dd, *J* = 11.0, 1.2 Hz, 1H), 4.54 (br s, 1H), 4.43 (s, 2H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 147.3, 138.2, 131.8, 128.8, 127.5, 127.3, 126.3 (q, *J* = 212 Hz), 125.9 (q, *J* = 3.7 Hz), 124.52 (q, *J* = 3.7 Hz), 123.8, 119.0 (q, *J* = 32 Hz), 118.17, 109.9, 47.9. IR (neat): 3446, 3031, 2857, 1615, 1523, 1328, 1290, 1109 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{16}H_{15}NF_3$ $[M + H]^+$ 278.1157, found 278.1165.

N-Benzyl-3-fluoro-2-vinylaniline (***11b-amine***). Obtained as a yellow oil (390 mg, 43%). ^1H NMR (500 MHz, $CDCl_3$): δ 7.39–7.35 (m, 4H), 7.31 (d, *J* = 4.2 Hz, 1H), 7.06–7.04 (m, 1H), 6.60 (dd, *J* = 18.0, 11.6 Hz, 1H), 6.51–6.45 (m, 1H), 6.42 (d, *J* = 8.3 Hz, 1H), 5.74 (d, *J* = 18.1 Hz, 1H), 5.62 (d, *J* = 11.7 Hz, 1H), 4.58 (br s, 1H), 4.37–4.36 (m, 2H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 161.1 (d, *J* = 244 Hz), 147.0 (d, *J* = 6.3 Hz), 139.0, 129.2 (d, *J* = 11.3 Hz), 128.9, 127.5, 127.4, 127.0 (d, *J* = 3.8 Hz), 120.7 (d, *J* = 3.8 Hz), 111.5 (d, *J* = 16.5 Hz), 106.5 (d, *J* = 3 Hz), 104.4 (d, *J* = 23 Hz), 48.52. IR (neat): 3428, 3029, 2917, 2849, 1470, 1120, 735, 698 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{16}H_{18}N$ $[M + H]^+$ 224.1439, found 224.1442.

N-Benzyl-5-methyl-2-vinylaniline (***11c-amine***). Obtained as a yellow oil (473 mg, 53%). ^1H NMR (500 MHz, $CDCl_3$): δ 7.45–7.39 (m, 4H), 7.36–7.33 (m, 1H), 7.24 (d, *J* = 7.8 Hz, 1H), 6.80 (dd, *J* = 17.4, 11.5 Hz, 1H), 6.62 (d, *J* = 7.8 Hz, 1H), 6.54 (s, 1H), 5.64 (d, *J* = 17.4 Hz, 1H), 5.30 (d, *J* = 11.0 Hz, 1H), 4.39 (s, 2H), 4.17 (br s, 1H), 2.33 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 145.0, 139.3, 138.9, 132.7, 128.6, 127.6, 127.3, 127.2, 121.5, 118.4, 115.4, 111.6, 48.4, 21.7. IR (neat): 3435, 3027, 2858, 1611, 1514, 1453, 908, 806, 697 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{16}H_{18}N$ $[M + H]^+$ 224.1439, found 224.1442.

N-Benzyl-4,5-dimethoxy-2-vinylaniline (***11d-amine***). Obtained as a yellow oil (430 mg, 40%). ^1H NMR (500 MHz, $CDCl_3$): δ 7.43–7.36 (m, 4H), 7.32–7.29 (m, 1H), 6.93 (s, 1H), 6.77 (dd, *J* = 17.1, 11.0 Hz, 1H), 6.29 (s, 1H), 5.56 (d, *J* = 17.4 Hz, 1H), 5.24 (d, *J* = 11.0 Hz, 1H), 4.36 (s, 2H), 4.01–3.65 (br s, 1H), 3.86 (s, 3H), 3.80 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 150.0, 141.3, 140.1, 139.3, 132.1, 128.6, 127.5, 127.3, 115.8, 113.8, 111.6, 97.4, 56.7, 55.8, 49.2. IR (neat): 3430, 2921, 2851, 1612, 1515, 1218, 732 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{17}H_{20}NO_2$ $[M + H]^+$ 270.1494, found 270.1488.

2-Aminostyrene (2-Vinylaniline, 12-amine). 2-Aminostyrene was synthesized according to a literature procedure.[31] To a 100 mL round-bottom flask with stir bar were added 2-aminophenethyl alcohol (20 g, 146 mmol) and potassium hydroxide (8.2 g, 146 mmol). The flask was connected to a vacuum distillation apparatus and heated to 180 °C under vacuum (0.05 Torr). The product was distilled over 4 h and collected as a colorless oil (13.15 g, 75%). ^1H NMR (500 MHz, acetone-d_6): δ 7.28 (d, *J* = 7.6 Hz, 1H), 7.00 (dd, *J* = 7.6, 7.6 Hz, 1H), 6.89 (dd, *J* = 17.4, 11.2 Hz, 1H), 6.72–6.69 (m, 1H), 6.64–6.57 (m, 1H), 5.59 (d, *J* = 17.4 Hz, 1H), 5.18 (d, *J* = 11.0 Hz, 1H), 4.60 (br s, 2H). ^{13}C NMR (125.8 MHz, acetone-d_6): δ 145.3, 133.0, 128.5, 126.2, 122.6, 117.2, 115.6, 112.9.

General Procedure for the Synthesis of 2,1-Borazaronaphthalenes. To an oven-dried Biotage microwave vial equipped with a stir bar was added the potassium organotrifluoroborate (0.5 mmol, 1 equiv). The vial was sealed with a cap lined with a disposable Teflon septum, evacuated under vacuum, and purged with Ar three times. CPME (0.5 mL) and toluene (0.5 mL) were added, followed by the 2-vinylaniline (0.75 mmol, 1.5 equiv or 0.60 mmol, 1.2 equiv), $SiCl_4$ (0.5 mmol, 1 equiv), and NEt_3 (0.75 equiv, if required) under Ar. The resulting mixture was heated either to 60 °C for 4 h or to 40 °C for 18 h, depending on the substrate, and then cooled to rt and diluted with hexanes (2 mL). The reaction mixture was filtered over a 2 in. plug of silica and flushed with 20% CH_2Cl_2/hexanes (10 mL). The solvent was removed in vacuo to provide the desired product. A few *B*-alkyl 2,1-borazaronaphthalenes required purification via flash column chromatography with 30% CH_2Cl_2/hexanes as the eluent.

1-Benzyl-2-phenyl-2,1-borazaronaphthalene (***7a***). Obtained as a tan solid (117 mg, 79%). Mp: 95–98 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 8.13 (d, *J* = 11.4 Hz, 1H), 7.70 (d, *J* = 7.6 Hz, 1H), 7.57–7.48 (m, 2H), 7.36–7.27 (m, 7H), 7.24–7.17 (m, 2H), 7.13 (d, *J* = 7.1 Hz, 2H), 7.05 (d, *J* = 11.4 Hz, 1H), 5.44 (s, 2H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 145.5, 141.3, 139.4, 132.7, 130.4, 128.9, 128.7, 128.1, 127.9, 127.5, 127.0, 125.9, 121.2, 117.2, 52.6. ^{11}B NMR (128.38 MHz, $CDCl_3$): δ 37.04. IR (neat): 3026, 1609, 1548, 1241, 966, 814, 701 cm^{-1}. HRMS (CI) m/z: calcd for $C_{21}H_{18}BN$ $[M]^+$ 295.1532, found 295.1521.

1-Benzyl-2-(4-tert-butylphenyl)-2,1-borazaronaphthalene (***7b***). Obtained as a tan solid (78 mg, 44%). Mp: 134–136 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 8.11 (d, *J* = 11.4 Hz, 1H), 7.69 (d, *J* = 7.6 Hz, 1H), 7.51 (d, *J* = 8.1 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.34–7.28 (m, 4H), 7.26–7.21 (m, 1H), 7.20–7.13 (m, 3H), 7.08 (d, *J* = 11.3 Hz, 1H), 5.48 (br s, 2H), 1.32 (s, 9H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 151.1, 145.3, 141.4, 139.7, 132.9, 130.4, 128.9, 128.6, 127.5, 126.9, 125.9, 124.8, 121.1, 117.2, 52.7, 34.8, 31.5. ^{11}B NMR (128.38 MHz, $CDCl_3$): δ 37.17. IR (neat): 2966, 1610, 1553, 1239, 805, 764 cm^{-1}. HRMS (CI) m/z: calcd for $C_{25}H_{26}BN$ $[M]^+$ 351.2158, found 351.2167.

1-Benzyl-2-(3-methylphenyl)-2,1-borazaronaphthalene (***7c***). Obtained as a yellow oil that crystallized in the refrigerator (89 mg, 57%). Mp: 97–99 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 8.10 (d, *J* = 11.4 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.38–7.25 (m, 6H), 7.23–7.09 (m, 6H), 7.04 (d, *J* = 11.4 Hz, 1H), 5.43 (s, 2H), 2.29 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 145.4, 141.3, 139.5, 137.1, 133.6, 130.4, 129.5, 128.9, 128.8, 128.7, 127.8, 127.5, 126.9, 125.9, 121.1, 117.2, 52.6, 21.7. ^{11}B NMR (128.38 MHz, $CDCl_3$): δ 37.38. IR (neat): 3026, 1610, 1549, 1412, 762 cm^{-1}. HRMS (CI) m/z: calcd for $C_{22}H_{20}BN$ $[M]^+$ 309.1689, found 309.1700.

1-Benzyl-2-(3-methoxyphenyl)-2,1-borazaronaphthalene (***7d***). Obtained as a tan solid (105 mg, 64%). Mp: 97–100 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 8.11 (d, *J* = 11.4 Hz, 1H), 7.69 (d, *J* = 7.7 Hz, 1H), 7.36–7.31 (m, 2H), 7.30–7.23 (m, 3H), 7.22–7.15 (m, 2H), 7.13–7.09 (m, 3H), 7.07–7.01 (m, 2H), 6.88–6.84 (m, 1H), 5.42 (s, 2H), 3.57 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 158.9, 145.6, 141.4, 139.5, 130.4, 129.1, 128.9, 128.8, 127.5, 126.9, 125.9, 125.0, 121.2, 117.2, 117.1, 114.2, 54.9, 52.7. ^{11}B NMR (128.38 MHz, $CDCl_3$): δ 36.77. IR (neat): 3032, 1589, 1547, 1417, 1226, 764 cm^{-1}.

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HRMS (ESI) m/z: calcd for $C_{22}H_{21}BNO$ $[M + H]^+$ 326.1716, found 326.1721.

*1-Benzyl-2-(2-naphthyl)-2,1-borazaronaphthalene (**7e**).* Obtained as a tan solid (119 mg, 69%). Mp: 146−148 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.16 (d, J = 11.4 Hz, 1H), 8.00 (s, 1H), 7.82−7.77 (m, 2H), 7.75−7.70 (m, 2H), 7.62 (dd, J = 1.1, 8.2 Hz, 1H), 7.47−7.41 (m, 2H), 7.39−7.34 (m, 2H), 7.32−7.28 (m, 2H), 7.26−7.19 (m, 2H), 7.16−7.10 (m, 3H), 5.48 (s, 2H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 145.6, 141.4, 139.4, 133.2, 133.1, 132.8, 130.5, 129.9, 128.9, 128.8, 128.3, 127.8, 127.5, 127.0, 127.0, 126.1, 125.9, 125.9, 121.2, 117.2, 52.7. ^{11}B NMR (128.38 MHz, $CDCl_3$): δ 36.66. IR (neat): 3051, 1608, 1546, 1227, 804 cm^{-1}. HRMS (CI) m/z: calcd for $C_{25}H_{20}BN$ $[M]^+$ 345.1689, found 345.1700.

*1-Benzyl-2-(1-naphthyl)-2,1-borazaronaphthalene (**7f**).* Obtained as a yellow oil that crystallized in the refrigerator (26 mg, 15%). Mp: 144−146 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.15 (d, J = 11.3 Hz, 1H), 7.86 (d, J = 7.9 Hz, 1H), 7.80 (d, J = 8.2 Hz, 1H), 7.77−7.74 (m, 2H), 7.49 (d, J = 6.6 Hz, 1H), 7.47−7.43 (m, 1H), 7.42−7.34 (m, 4H), 7.24−7.18 (m, 3H), 7.16−7.12 (m, 1H), 7.07−7.01 (m, 3H), 5.30 (s, 2H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 145.2, 141.3, 139.0, 135.3, 133.3, 130.5, 129.4, 129.1, 128.9, 128.7, 128.6, 128.6, 127.8, 127.6, 126.8, 125.9, 125.6, 125.5, 121.3, 117.3, 52.9. ^{11}B NMR (128.38 MHz, $CDCl_3$): δ 30.03. IR (neat): 3026, 1592, 1549, 946, 762 cm^{-1}. HRMS (CI) m/z: calcd for $C_{25}H_{20}BN$ $[M]^+$ 345.1689, found 345.1689.

*1-Benzyl-2-(4-methylphenyl)-2,1-borazaronaphthalene (**7g**).* Obtained as a white solid (111 mg, 72%). Mp: 96−98 °C. ^{1}H NMR (500 MHz, acetone-d_6): δ 8.17 (d, J = 11.2 Hz, 1H), 7.76 (d, J = 7.6 Hz, 1H), 7.46−7.40 (m, 3H), 7.37−7.34 (m, 1H), 7.30−7.27 (m, 2H), 7.22−7.18 (m, 2H), 7.14 (d, J = 7.6 Hz, 4H), 7.01 (d, J = 11.2 Hz, 1H), 5.50 (s, 2H), 2.30 (s, 3H). ^{13}C NMR (125.8 MHz, acetone-d_6): δ 145.3, 141.1, 139.4, 137.4, 130.2, 132.5, 128.6, 128.5, 128.4, 127.3, 126.7, 125.6, 121.0, 117.0, 51.8, 20.4. ^{11}B NMR (128.38 MHz, acetone-d_6): δ 37.99. IR (neat): 2919, 1606, 1410, 1243, 803, 767 cm^{-1}. HRMS (CI) m/z: calcd for $C_{22}H_{20}BN$ $[M]^+$ 309.1689, found 309.1688.

*Methyl-3-(2-benzyl-2,1-borazaronaphthyl)benzoate (**7h**).* Obtained as a tan solid (115 mg, 65%). Mp: 91−93 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.26−8.21 (m, 1H), 8.15 (d, J = 11.4 Hz, 1H), 8.00 (td, J = 1.5, 7.9 Hz, 1H), 7.72 (d, J = 7.6 Hz, 1H), 7.68 (td, J = 1.3, 7.4 Hz, 1H), 7.41−7.35 (m, 3H), 7.32−7.27 (m, 2H), 7.26−7.19 (m, 2H), 7.11 (d, J = 7.1 Hz, 2H), 7.04 (d, J = 11.4 Hz, 1H), 5.40 (s, 2H), 3.85 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 167.6, 145.9, 141.2, 139.1, 136.9, 134.0, 130.5, 129.5, 129.2, 128.9, 128.9, 127.9, 127.5, 127.0, 125.8, 121.4, 117.2, 52.6, 52.1. ^{11}B NMR (128.38 MHz, $CDCl_3$): δ 36.78. IR (neat): 3026, 1714, 1548, 1233, 1107, 752 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{23}H_{21}BNO_2$ $[M + H]^+$ 354.1665, found 354.1657.

*3-(2-Benzyl-2,1-borazaronaphthyl)benzonitrile (**7i**).* Obtained as a yellow oil that crystallized in the refrigerator (80 mg, 50%). Mp: 117−119 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.17 (d, J = 11.4 Hz, 1H), 7.79 (s, 1H), 7.75−7.71 (m, 1H), 7.69 (td, J = 1.3, 7.6 Hz, 1H), 7.60 (td, J = 1.4, 7.8 Hz, 1H), 7.41−7.35 (m, 3H), 7.32−7.28 (m, 2H), 7.26−7.21 (m, 2H), 7.08 (d, J = 7.2 Hz, 2H), 6.97 (d, J = 11.3 Hz, 1H), 5.35 (s, 2H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 146.5, 141.1, 138.7, 136.6, 136.2, 131.6, 130.7, 129.2, 129.2, 128.5, 127.6, 127.4, 125.7, 121.7, 119.5, 117.2, 112.1, 52.6. ^{11}B NMR (128.38 MHz, $CDCl_3$): δ 36.03. IR (neat): 3030, 2227, 1610, 1550, 1414, 763 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{22}H_{17}BFN_2$ $[M + F]^-$ 339.1469, found 339.1471.

*1-Benzyl-2-(3-nitrophenyl)-2,1-borazaronaphthalene (**7j**).* Obtained as a tan solid (84 mg, 49%). Mp: 114−117 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.41−8.36 (m, 1H), 8.23−8.14 (m, 2H), 7.80−7.73 (m, 2H), 7.49−7.45 (m, 1H), 7.41−7.38 (m, 2H), 7.34−7.28 (m, 2H), 7.27−7.22 (m, 2H), 7.09 (d, J = 7.2 Hz, 2H), 7.01 (d, J = 11.3 Hz, 1H), 5.38 (s, 2H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 148.0, 146.5, 141.1, 138.6, 138.4, 130.7, 129.2, 129.1, 128.8, 127.5, 127.4, 127.3, 125.7, 123.0, 121.7, 117.2, 52.6. ^{11}B NMR (128.38 MHz, $CDCl_3$): δ 35.70. IR (neat): 3030, 1609, 1528, 1342, 808, 730 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{21}H_{17}BN_2NaO_2$ $[M + Na]^+$ 363.1281, found 363.1270.

*1-Benzyl-2-(3,5-bis(trifluoromethyl)phenyl)-2,1-borazaronaphthalene (**7k**).* Obtained as a tan solid (109 mg, 50%). Mp: 88−92 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.21 (d, J = 11.4 Hz, 1H), 7.90 (s, 2H), 7.82 (s, 1H), 7.76 (d, J = 8.0 Hz, 1H), 7.46−7.41 (m, 2H), 7.33−7.22 (m, 4H), 7.07 (d, J = 7.4 Hz, 2H), 7.01−6.97 (m, 1H), 5.34 (s, 2H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 146.8, 141.2, 138.5, 132.5, 132.4, 130.8 (q, J = 46.3 Hz), 130.7, 129.4, 129.1, 127.5, 127.4, 125.6, 123.7 (q, J = 273.4 Hz), 121.9, 117.1, 52.7. ^{11}B NMR (128.38 MHz, $CDCl_3$): δ 36.09. IR (neat): 2921, 1611, 1350, 1277, 1126, 764 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{23}H_{16}BF_7N$ $[M + F]^-$ 450.1264, found 450.1265.

*1-Benzyl-2-(4-fluorophenyl)-2,1-borazaronaphthalene (**7l**).* Obtained as a tan solid (110 mg, 70%). Mp: 112−114 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.13 (d, J = 11.3 Hz, 1H), 7.73−7.69 (m, 1H), 7.52−7.46 (m, 2H), 7.38−7.28 (m, 4H), 7.24−7.17 (m, 2H), 7.12 (d, J = 7.1 Hz, 2H), 7.05−6.99 (m, 3H), 5.41 (s, 2H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 163.2 (d, J = 252.5 Hz), 145.7, 141.3, 139.3, 134.6 (d, J = 8.2 Hz), 130.5, 129.0, 128.8, 127.5, 127.1, 125.8, 121.3, 117.2 (d, J = 20.0 Hz), 114.9, 52.6. ^{11}B NMR (128.38 MHz, $CDCl_3$): δ 35.99. IR (neat): 2913, 1594, 1216, 812 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{22}H_{20}BFNO$ $[M + OCH_3]^-$ 344.1622, found 344.1627.

*1-Benzyl-2-(2,4-difluorophenyl)-2,1-borazaronaphthalene (**7m**).* Obtained as a tan solid (22 mg, 13%). Mp: 107−110 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.13 (d, J = 11.3 Hz, 1H), 7.74−7.70 (m, 1H), 7.39−7.33 (m, 2H), 7.32−7.26 (m, 2H), 7.24−7.17 (m, 3H), 7.06 (d, J = 7.2 Hz, 2H), 6.99 (d, J = 11.3 Hz, 1H), 6.86−6.77 (m, 2H), 5.35 (s, 2H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 165.0 (dd, J = 115.3, 12.7 Hz), 163.1 (dd, J = 122.6, 10.9 Hz), 145.7, 141.1, 138.8, 134.6 (dd, J = 11.8, 9.1 Hz), 130.5, 128.8, 128.8, 127.7, 127.0, 125.9, 121.5, 117.3, 111.4 (dd, J = 20.0, 2.7 Hz), 103.6 (dd, J = 29.1, 24.5 Hz), 52.8. ^{11}B NMR (128.38 MHz, $CDCl_3$): δ 35.50. IR (neat): 2923, 1606, 1241, 973, 808 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{21}H_{16}BF_3N$ $[M + F]^-$ 350.1328, found 350.1330.

*1-Benzyl-2-(3-thienyl)-2,1-borazaronaphthalene (**7n**).* Obtained as an off-white solid (84 mg, 56%). Mp: 108−110 °C. ^{1}H NMR (500 MHz, acetone-d_6): δ 8.17 (d, J = 11.5 Hz, 1H), 7.76 (d, J = 7.8 Hz, 1H), 7.65 (s, 1H), 7.49 (dd, J = 4.6, 2.7 Hz, 1H), 7.43−7.37 (m, 1H), 7.35−7.31 (m, 4H), 7.30−7.20 (m, 4H), 7.11 (d, J = 11.2 Hz, 1H), 5.57 (s, 2H). ^{13}C NMR (125.8 MHz, acetone-d_6): δ 145.2, 141.3, 139.2, 131.7, 131.1, 130.1, 128.8, 128.5, 127.3, 126.8, 125.6, 125.3, 121.0, 116.8, 52.0. ^{11}B NMR (128.38 MHz, acetone-d_6): δ 35.47. IR (neat): 2922, 1551, 2523, 1232, 764 cm^{-1}. HRMS (CI) m/z: calcd for $C_{19}H_{17}BNS$ $[M + H]^+$ 302.1175, found 302.1183.

*1-Benzyl-2-(4-dibenzofuryl)-2,1-borazaronaphthalene (**7o**).* Obtained as a white solid (89 mg, 46%). Mp: 106−107 °C. ^{1}H NMR (500 MHz, acetone-d_6): δ 8.28 (d, J = 11.2 Hz, 1H), 8.11−8.07 (m, 2H), 7.85 (d, J = 7.8 Hz, 1H), 7.59 (d, J = 7.3 Hz, 1H), 7.55 (d, J = 8.6 Hz, 1H), 7.45−7.33 (m, 5H), 7.28−7.22 (m, 3H), 7.17−7.12 (m, 4H), 5.52 (s, 2H). ^{13}C NMR (125.8 MHz, acetone-d_6): δ 158.0, 155.9, 145.5, 143.9, 140.1, 138.9, 131.0, 130.3, 128.6, 128.3, 127.6, 127.0, 126.6, 125.8, 124.1, 122.8, 122.6, 121.3, 120.7, 120.6, 117.2, 111.4, 111.3, 52.4. ^{11}B NMR (128.38 MHz, acetone-d_6): δ 37.20. IR (neat): 3027, 2923, 1712, 1550, 1186, 757, 737 cm^{-1}. HRMS (CI) m/z: calcd for $C_{27}H_{20}BNO$ $[M]^+$ 385.1638, found 385.1626.

*1-Benzyl-2-(4-dibenzothienyl)-2,1-borazaronaphthalene (**7p**).* Obtained as a white solid (88 mg, 44%). Mp: 116−117 °C. ^{1}H NMR (500 MHz, acetone-d_6): δ 8.30−8.28 (m, 2H), 8.24 (d, J = 8.1 Hz, 1H), 7.90−7.88 (m, 1H), 7.83 (d, J = 7.8 Hz, 1H), 7.57−7.55 (m, 2H), 7.49−7.39 (m, 4H), 7.25 (dd, J = 9.5, 7.3 Hz, 1H), 7.21−7.12 (m, 6H), 5.49 (s, 2H). ^{13}C NMR (125.8 MHz, acetone-d_6): δ 146.6, 143.4, 141.4, 139.8, 139.3, 136.1, 135.1, 130.9, 130.2, 129.1, 128.9, 128.1, 127.2, 127.1, 126.2, 124.8, 124.7, 123.0, 122.2, 121.9, 121.7, 117.8, 52.6. ^{11}B NMR (128.38 MHz, acetone-d_6): δ 37.20. IR (neat): 3028, 1711, 1548, 1371, 1220, 752 cm^{-1}. HRMS (CI) m/z: calcd for $C_{27}H_{21}BNS$ $[M + H]^+$ 402.1488, found 402.1477.

*1-Benzyl-2-((E)-1-propen-1-yl)-2,1-borazaronaphthalene (**8a**).* Obtained as a yellow oil that crystallized in the refrigerator (70 mg, 54%). Mp: 70−72 °C. ^{1}H NMR (500 MHz, acetone-d_6): δ 8.02 (d, J = 11.5 Hz, 1H), 7.66−7.64 (m, 1H), 7.41 (d, J = 8.6 Hz, 1H), 7.33−7.27 (m, 3H), 7.23−7.16 (m, 3H), 7.13−7.08 (m, 2H), 6.87−6.82 (m, 1H),

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6.26 (d, J = 17.5 Hz, 1H), 5.42 (s, 2H), 1.92−1.89 (m, 3H). ^{13}C NMR (125.8 MHz, acetone-d_6): δ 146.2, 144.3, 141.5, 139.0, 130.0, 128.5, 128.2, 127.0, 126.8, 125.8, 120.5, 116.0, 50.2, 21.5. ^{11}B NMR (128.38 MHz, acetone-d_6): δ 37.27. IR (neat): 3010, 1713, 1608, 1552, 1358, 1218, 982, 758 cm^{-1}. HRMS (CI) m/z: calcd for $C_{18}H_{18}BN$ $[M]^+$ 259.1532, found 259.1539.

*1-Benzyl-2-((Z)-1-propen-1-yl)-2,1-borazaronaphthalene (**8b**).* Obtained as a yellow oil that crystallized in the refrigerator overnight (74 mg, 57%). Mp: 70−72 °C. ^{1}H NMR (500 MHz, acetone-d_6): δ 8.08 (d, J = 11.2 Hz, 1H), 7.70 (d, J = 7.8 Hz, 1H), 7.43 (d, J = 8.6 Hz, 1H), 7.35−7.31 (m, 1H), 7.29−7.25 (m, 2H), 7.21−7.13 (m, 4H), 7.02−6.99 (m, 1H), 6.33−6.27 (m, 1H), 6.08 (d, J = 13.7 Hz, 1H), 5.40 (s, 2H), 1.86 (d, J = 6.8 Hz, 3H). ^{13}C NMR (125.8 MHz, acetone-d_6): δ 144.4, 141.4, 138.8, 138.7, 130.1, 128.5, 128.2, 127.0, 126.7, 125.8, 120.7, 116.2, 51.1, 17.7. ^{11}B NMR (128.38 MHz, acetone-d_6): δ 36.46. IR (neat): 3010, 1713, 1608, 1218, 982, 807, 758 cm^{-1}. HRMS (CI) m/z: calcd for $C_{18}H_{18}BN$ $[M]^+$ 259.1532, found 259.1527.

*1-Benzyl-2-((E)-3-phenyl-1-propen-1-yl)-2,1-borazaronaphthalene (**8c**).* Obtained as a yellow oil that crystallized in the refrigerator (85 mg, 51%). Mp: 75−77 °C. ^{1}H NMR (500 MHz, acetone-d_6): δ 8.02 (d, J = 11.5 Hz, 1H), 7.67−7.64 (m, 1H), 7.44 (d, J = 8.6 Hz, 1H), 7.35−7.10 (m, 13H), 6.94−6.88 (m, 1H), 6.37 (d, J = 17.4 Hz, 1H), 5.48 (s, 2H), 3.59 (d, J = 6.6 Hz, 2H). ^{13}C NMR (125.8 MHz, acetone-d_6): δ 149.9, 144.9, 141.9, 139.4, 130.4, 129.2, 129.0, 128.9, 128.8, 128.7, 127.5, 127.2, 126.4, 126.3, 121.0, 116.5, 50.8, 43.0. ^{11}B NMR (128.38 MHz, acetone-d_6): δ 35.32. IR (neat): 3026, 1608, 1416, 1218, 990, 763, 748, 700 cm^{-1}. HRMS (CI) m/z: calcd for $C_{24}H_{23}BN$ $[M + H]^+$ 336.1924, found 336.1926.

*1-Benzyl-2-(1-butynyl)-2,1-borazaronaphthalene (**8d**).* Obtained as a yellow oil that crystallized upon standing (71 mg, 47%). Mp: 46−47 °C. ^{1}H NMR (500 MHz, acetone-d_6): δ 8.53 (d, J = 11.2 Hz, 1H), 8.16 (d, J = 7.8 Hz, 1H), 7.93 (d, J = 8.6 Hz, 1H), 7.84−7.79 (m, 1H), 7.77−7.58 (m, 7H), 7.37 (d, J = 11.2 Hz, 1H), 6.15 (s, 2H), 2.83 (dd, J = 8.5, 7.0 Hz, 2H), 1.98−1.93 (m, 2H), 1.87−1.82 (m, 2H), 1.32−1.27 (m, 2H). ^{13}C NMR (125.8 MHz, acetone-d_6): δ 145.5, 141.4, 139.3, 130.6, 129.0, 128.8, 127.3, 127.2, 126.6, 121.4, 116.9, 111.0, 53.3, 31.0, 21.0, 19.6, 13.3. ^{11}B NMR (128.38 MHz, acetone-d_6): δ 29.01. IR (neat): 3029, 2956, 2930, 2185, 1549, 1412, 1228, 806, 762 cm^{-1}. HRMS (CI) m/z: calcd for $C_{21}H_{22}BN$ $[M]^+$ 299.1845, found 299.1841.

*1-Benzyl-2-methyl-2,1-borazaronaphthalene (**9a**).* Obtained as a tan solid (56 mg, 48%). Mp: 56−60 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.93 (d, J = 11.4 Hz, 1H), 7.61 (d, J = 7.6 Hz, 1H), 7.30−7.25 (m, 4H), 7.23−7.18 (m, 1H), 7.13−7.08 (m, 3H), 6.87 (d, J = 11.4 Hz, 1H), 5.30 (s, 2H), 0.84 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 144.3, 141.9, 138.7, 130.3, 128.8, 128.4, 127.0, 126.7, 126.0, 120.5, 116.0, 51.1. ^{11}B NMR (128.38 MHz, $CDCl_3$): δ 38.99. IR (neat): 2966, 1608, 1355, 1221, 761 cm^{-1}. HRMS (CI) m/z: calcd for $C_{16}H_{16}BN$ $[M]^+$ 233.1376, found 233.1374.

*1-Benzyl-2-(4-penten-1-yl)-2,1-borazaronaphthalene (**9b**).* Obtained as a yellow oil (72 mg, 50%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.00−7.94 (m, 1H), 7.60 (d, J = 7.5 Hz, 1H), 7.29−7.22 (m, 4H), 7.21−7.16 (m, 1H), 7.12−7.05 (m, 3H), 6.95 (dd, J = 2.1, 11.5 Hz, 1H), 5.88−5.77 (m, 1H), 5.28 (s, 2H), 5.02−4.89 (m, 2H), 2.11 (q, J = 7.0 Hz, 2H), 1.78−1.70 (m, 2H), 1.34−1.28 (m, 2H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 144.7, 141.7, 139.4, 138.7, 130.3, 128.8, 128.4, 127.0, 126.9, 125.9, 120.5, 116.1, 114.4, 50.6, 37.0, 26.0. ^{11}B NMR (128.38 MHz, $CDCl_3$): δ 38.94. IR (neat): 2921, 1610, 1415, 759 cm^{-1}. HRMS (CI) m/z: calcd for $C_{20}H_{22}BN$ $[M]^+$ 287.1845, found 287.1841.

*2-Benzyl-1-trifluoroethyl-2,1-borazaronaphthalene (**9c**).* Obtained as an off-white solid (60 mg, 40%). Mp: 76−78 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.98 (d, J = 11.60 Hz, 1H), 7.57 (d, J = 7.63 Hz, 1H), 7.24 (d, J = 3.97 Hz, 2H), 7.21−7.15 (m, 2H), 7.13 (d, J = 7.02 Hz, 1H), 7.11−7.07 (m, 2H), 7.03−6.98 (m, 1H), 6.95 (d, J = 7.63 Hz, 1H), 5.17 (s, 2H), 2.20 (q, J = 13.4 Hz, 2H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 145.9, 141.4, 137.5, 130.6, 129.1, 129.0, 128.9 (q, J = 274 Hz), 127.5, 127.2, 125.6, 121.6, 116.3, 50.1. ^{11}B NMR (128.38 MHz, $CDCl_3$): δ 38.94. IR (neat): 3033, 2956, 2924, 2853, 1249, 1088, 1048, 762 cm^{-1}. HRMS (CI) m/z: calcd for $C_{17}H_{15}BNF_3$ $[M]^+$ 301.1250, found 301.1245.

*1-Benzyl-2-isopropyl-2,1-borazaronaphthalene (**9d**).* Obtained as a yellow oil that crystallized upon standing (76 mg, 58%). Mp: 67−69 °C. ^{1}H NMR (500 MHz, acetone-d_6): δ 8.08 (d, J = 11.5 Hz, 1H), 7.67 (dd, J = 7.6, 1.5 Hz, 1H), 7.41−7.38 (m, 1H), 7.34−7.27 (m, 3H), 7.21 (d, J = 7.3 Hz, 1H), 7.16−7.12 (m, 3H), 6.99 (d, J = 11.7 Hz, 1H), 5.44 (s, 2H), 1.69−1.62 (m, 1H), 1.15−1.11 (m, 6H). ^{13}C NMR (125.8 MHz, acetone-d_6): δ 145.2, 141.2, 139.1, 139.0, 128.5, 128.2, 126.8, 126.7, 125.6, 120.5, 116.4, 49.7, 20.0. ^{11}B NMR (128.38 MHz, acetone-d_6): δ 41.05. IR (neat): 2950, 2917, 1558, 1440, 1134, 764 cm^{-1}. HRMS (CI) m/z: calcd for $C_{18}H_{20}BN$ $[M]^+$ 261.1689, found 261.1688.

*1-Benzyl-2-cyclopropyl-2,1-borazaronaphthalene (**9e**).* Obtained as a yellow oil that crystallized in the refrigerator (64 mg, 49%). Mp: 41−43 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.90 (d, J = 11.6 Hz, 1H), 7.56 (d, J = 7.9 Hz, 1H), 7.32−7.26 (m, 4H), 7.25−7.19 (m, 3H), 7.12−7.06 (m, 1H), 6.41 (d, J = 11.6 Hz, 1H), 5.48 (s, 2H), 0.87−0.81 (m, 2H), 0.70−0.64 (m, 2H), 0.36−0.26 (m, 1H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 145.0, 141.8, 139.1, 130.2, 128.8, 128.4, 127.0, 126.6, 126.2, 120.4, 115.8, 51.1, 6.4. ^{11}B NMR (128.38 MHz, $CDCl_3$): δ 38.54. IR (neat): 3000, 1610, 1416, 761 cm^{-1}. HRMS (CI) m/z: calcd for $C_{18}H_{18}BN$ $[M]^+$ 259.1532, found 259.1534.

*1-Benzyl-2-cyclobutyl-2,1-borazaronaphthalene (**9f**).* Obtained as a yellow oil that crystallized in the refrigerator (69 mg, 51%). Mp: 44−47 °C. ^{1}H NMR (500 MHz, acetone-d_6): δ 8.11 (d, J = 11.5 Hz, 1H), 7.68 (dd, J = 7.7, 1.3 Hz, 1H), 7.36−7.24 (m, 4H), 7.20−7.07 (m, 5H), 5.28 (s, 2H), 2.53−2.51 (m, 1H), 2.22−2.12 (m, 5H), 1.96−1.91 (m, 1H). ^{13}C NMR (125.8 MHz, acetone-d_6): δ 145.2, 141.4, 138.9, 130.0, 128.4, 128.2, 126.8, 126.6, 125.6, 120.4, 116.1, 50.1, 25.8, 22.0. ^{11}B NMR (128.38 MHz, acetone-d_6): δ 39.92. IR (neat): 3027, 2962, 2858, 1551, 1414, 1217, 760 cm^{-1}. HRMS (CI) m/z: calcd for $C_{19}H_{20}BN$ $[M]^+$ 273.1689, found 273.1692.

*1-Benzyl-2-cyclohexyl-2,1-borazaronaphthalene (**9g**).* Obtained as a yellow oil that crystallized in the refrigerator (63 mg, 42%). Mp: 48−51 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.03 (d, J = 11.60 Hz, 1H), 7.62 (d, J = 7.63 Hz, 1H), 7.33−7.27 (m, 4H), 7.25−7.21 (m, 1H), 7.15−7.11 (m, 3H), 7.05−7.00 (m, 1H), 5.39 (s, 2H), 1.82−1.69 (m, 5H), 1.60−1.23 (m, 6H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 145.0, 139.0, 130.0, 128.6, 128.5, 128.1, 127.8, 126.2, 125.7, 120.4, 116.4, 50.3, 30.3, 27.8, 27.0. ^{11}B NMR (128.38 MHz, $CDCl_3$): δ 39.34. IR (neat): 3029, 2917, 2846, 1552, 1418, 802, 761 cm^{-1}. HRMS (CI) m/z: calcd for $C_{21}H_{24}BN$ $[M]^+$ 301.2002, found 301.2008.

*1-(4-Methoxybenzyl)-2-phenyl-2,1-borazaronaphthalene (**10a**).* Obtained as a white solid (100 mg, 61%). Mp: 134−136 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.11 (d, J = 11.3 Hz, 1H), 7.69 (d, J = 7.7 Hz, 1H), 7.56−7.51 (m, 2H), 7.36−7.30 (m, 5H), 7.20−7.15 (m, 1H), 7.06−7.01 (m, 3H), 6.82 (d, J = 8.6 Hz, 2H), 5.37 (s, 2H), 3.75 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 158.6, 145.5, 141.3, 132.7, 131.4, 130.4, 128.7, 128.1, 127.8, 127.5, 126.9, 121.1, 117.2, 114.3, 55.3, 52.0. ^{11}B NMR (128.38 MHz, $CDCl_3$): δ 37.19. IR (neat): 2998, 1609, 1509, 1246, 759 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{22}H_{20}BNNaO$ $[M + Na]^+$ 348.1536, found 348.1547.

*1-Allyl-2-phenyl-2,1-borazaronaphthalene (**10b**).* Obtained as a yellow oil that crystallized in the refrigerator (325 mg, 55%). Mp: 44−46 °C. ^{1}H NMR (500 MHz, acetone-d_6): δ 8.13 (d, J = 11.2 Hz, 1H), 7.77−7.74 (m, 1H), 7.64−7.60 (m, 3H), 7.54−7.51 (m, 1H), 7.42−7.35 (m, 3H), 7.25 (dd, J = 8.5, 7.5 Hz, 1H), 6.91 (d, J = 11.2 Hz, 1H), 6.15−6.09 (m, 1H), 5.18 (dd, J = 10.6, 1.3 Hz, 1H), 4.95 (dd, J = 17.4, 1.2 Hz, 1H), 4.84−4.82 (m, 2H). ^{13}C NMR (125.8 MHz, acetone-d_6): δ 145.2, 141.1, 136.0, 132.2, 130.2, 128.5, 127.8, 127.5, 127.1, 121.0, 116.7, 115.0, 50.2. ^{11}B NMR (128.38 MHz, acetone-d_6): δ 37.19. IR (neat): 3029, 2917, 2846, 1552, 1418, 802, 761 cm^{-1}. HRMS (CI) m/z: calcd for $C_{17}H_{16}BN$ $[M]^+$ 245.1376, found 245.1382.

*1-Butyl-2-phenyl-2,1-borazaronaphthalene (**10c**).* Obtained as a yellow oil (93 mg, 71%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.02 (d, J = 11.3 Hz, 1H), 7.70 (dd, J = 7.7, 1.5 Hz, 1H), 7.63−7.59 (m, 1H), 7.57−7.51 (m, 3H), 7.45−7.40 (m, 2H), 7.39−7.34 (m, 1H), 7.26−7.21 (m, 1H), 6.89 (d, J = 11.3 Hz, 1H), 4.18−4.12 (m, 2H), 1.82−1.72 (m, 2H), 1.33−1.23 (m, 2H), 0.84 (t, J = 7.4 Hz, 3H). ^{13}C NMR

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(126 MHz, $CDCl_3$): δ 144.8, 141.1, 132.4, 130.7, 128.6, 127.8, 127.5, 127.4, 120.8, 115.7, 47.8, 32.4, 20.3, 13.9. ^{11}B NMR (128 MHz, $CDCl_3$): δ 36.35. IR (neat): 2957, 1609, 1551, 1411, 751 cm^{-1}. HRMS (CI) *m/z*: calcd for $C_{18}H_{20}BN$ $[M]^+$ 261.1689, found 261.1680.

*1,2-Diphenyl-2,1-borazaronaphthalene (**10d**).* Obtained as a tan solid (56 mg, 40%). Mp: 111−115 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 8.19 (d, *J* = 11.4 Hz, 1H), 7.74 (dd, *J* = 1.4, 7.8 Hz, 1H), 7.45−7.40 (m, 2H), 7.39−7.31 (m, 2H), 7.26−7.23 (m, 3H), 7.22−7.14 (m, 6H), 6.97 (d, *J* = 8.5 Hz, 1H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 145.4, 144.0, 142.9, 134.0, 129.9, 129.6, 129.5, 128.4, 127.7, 127.3, 127.2, 126.2, 121.3, 117.8. ^{11}B NMR (128.38 MHz, $CDCl_3$): δ 35.38. IR (neat): 2921, 1595, 1293, 702 cm^{-1}. HRMS (ESI) *m/z*: calcd for $C_{20}H_{17}BN$ $[M + H]^+$ 282.1454, found 282.1455.

*1-Benzyl-2-phenyl-6-trifluoromethyl-2,1-borazaronaphthalene (**11a**).* Obtained as a white solid (116 mg, 64%). Mp: 110−112 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 8.34 (d, *J* = 11.2 Hz, 1H), 8.18 (s, 1H), 7.69−7.64 (m, 2H), 7.57 (dd, *J* = 6.2, 3.1 Hz, 2H), 7.36−7.30 (m, 5H), 7.26−7.22 (m, 1H), 7.17−7.14 (m, 3H), 5.58 (s, 2H). ^{13}C NMR (125.8 MHz, acetone-d_6): δ 145.2, 138.6, 132.2, 128.7, 128.2, 128.1, 127.7, 127.4 (q, *J* = 24 Hz), 127.0, 126.9, 126.5 (q, *J* = 251 Hz), 125.6, 125.5, 124.5 (q, *J* = 4 Hz), 118.1, 52.0. ^{11}B NMR (128.38 MHz, acetone-d_6): δ 38.76. IR (neat): 3026, 2925, 2851, 1623, 1326, 1120, 902, 704 cm^{-1}. HRMS (CI) *m/z*: calcd for $C_{22}H_{17}BNF_3$ $[M]^+$ 363.1406, found 363.1397.

*1-Benzyl-2-phenyl-5-fluoro-2,1-borazaronaphthalene (**11b**).* Obtained as a white solid (117 mg, 73%). Mp: 126−127 °C. ^1H NMR (500 MHz, acetone-d_6): δ 8.43 (d, *J* = 11.5 Hz, 1H), 7.56 (dd, *J* = 6.5, 3.1 Hz, 2H), 7.38−7.33 (m, 4H), 7.31−7.26 (m, 3H), 7.23−7.20 (m, 1H), 7.15 (d, *J* = 7.6 Hz, 2H), 7.09 (d, *J* = 11.7 Hz, 1H), 6.98 (dd, *J* = 9.7, 8.2 Hz, 1H), 5.51 (s, 2H). ^{13}C NMR (125.8 MHz, acetone-d_6): δ 159.8 (d, *J* = 246 Hz), 142.3 (d, *J* = 6.3 Hz), 138.9, 136.0 (d, *J* = 7.5 Hz), 132.2, 128.7, 128.5 (d, *J* = 10 Hz), 128.1, 127.7, 126.9, 125.6, 116.4 (d, *J* = 16 Hz), 113.3 (d, *J* = 4 Hz), 106.3 (d, *J* = 21 Hz), 52.3. ^{11}B NMR (128.38 MHz, acetone-d_6): δ 38.00. IR (neat): 3016, 2926, 1590, 1405, 1234, 974, 783, 728 cm^{-1}. HRMS (CI) *m/z*: calcd for $C_{21}H_{17}BNF$ $[M]^+$ 313.1438, found 313.1431.

*1-Benzyl-2-phenyl-7-methyl-2,1-borazaronaphthalene (**11c**).* Obtained as a white solid (116 mg, 75%). Mp: 91−93 °C. ^1H NMR (500 MHz, acetone-d_6): δ 8.14 (d, *J* = 11.2 Hz, 1H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.54 (dd, *J* = 6.5, 3.1 Hz, 2H), 7.32−7.27 (m, 6H), 7.22−7.19 (m, 1H), 7.15 (d, *J* = 7.3 Hz, 2H), 7.04 (d, *J* = 7.8 Hz, 1H), 6.92 (d, *J* = 11.2 Hz, 1H), 5.47 (s, 2H), 2.28 (s, 3H). ^{13}C NMR (125.8 MHz, acetone-d_6): δ 145.2, 141.1, 139.4, 138.6, 132.2, 130.1, 128.6, 127.7, 127.6, 126.7, 125.6, 125.2, 122.4, 117.2, 51.7, 21.2. ^{11}B NMR (128.38 MHz, acetone-d_6): δ 37.99. IR (neat): 3055, 3023, 3005, 2921, 1599, 1349, 963, 830, 699 cm^{-1}. HRMS (CI) *m/z*: calcd for $C_{22}H_{20}BN$ $[M]^+$ 309.1689, found 309.1675.

*1-Benzyl-2-phenyl-6,7-dimethoxy-2,1-borazaronaphthalene (**11d**).* Obtained as a white solid (104 mg, 59%). Mp: 112−115 °C. ^1H NMR (500 MHz, acetone-d_6): δ 8.09 (d, *J* = 11.29 Hz, 1H), 7.60−7.51 (m, 2H), 7.38−7.28 (m, 6H), 7.25−7.17 (m, 3H), 6.95 (s, 1H), 6.83 (d, *J* = 11.29 Hz, 1H), 5.49 (s, 2H), 3.84 (s, 3H), 3.60 (m, 3H). ^{13}C NMR (125.8 MHz, acetone-d_6): δ 150.9, 145.0, 144.8, 139.7, 136.3, 132.5, 128.8, 127.8, 127.7, 127.0, 126.1, 121.2, 111.5, 101.0, 55.5, 55.1, 52.4. ^{11}B NMR (128.38 MHz, acetone-d_6): δ 38.12. IR (neat): 3029, 3004, 2965, 2871, 1546, 1261, 1226, 762, 737 cm^{-1}. HRMS (CI) *m/z*: calcd for $C_{23}H_{23}BNO_2$ $[M]^+$ 356.1822, found 356.1820.

*2-Methyl-2,1-borazaronaphthalene (**12a**).*[9] Obtained as a white solid (39 mg, 55%). Mp: 70−71 °C. ^1H NMR (500 MHz, acetone-d_6): δ 9.26 (br s, 1H), 7.94 (d, *J* = 11.2 Hz, 1H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.46−7.42 (m, 1H), 7.38−7.34 (m, 1H), 7.10 (dd, *J* = 7.3, 7.0 Hz, 1H), 6.74 (d, *J* = 11.5 Hz, 1H), 0.69 (s, 3H). ^{13}C NMR (125.8 MHz, acetone-d_6): δ 143.8, 141.0, 128.9, 127.7, 125.0, 120.0, 117.8. ^{11}B NMR (128.38 MHz, acetone-d_6): δ 37.72. IR (neat): 3363, 2931, 1560, 1438, 764, 752 cm^{-1}. HRMS (CI) *m/z*: calcd for $C_9H_{10}BN$ $[M]^+$ 143.0906, found 143.0895.

*2-Cyclopropyl-2,1-borazaronaphthalene (**12b**).* Obtained as a white solid (41 mg, 52%). Mp: 67−68 °C. ^1H NMR (500 MHz, acetone-d_6): δ 9.16 (br s, 1H), 7.91 (d, *J* = 11.5 Hz, 1H), 7.57−7.55 (m, 1H), 7.43−7.40 (m, 1H), 7.36−7.32 (m, 1H), 7.09−7.05 (m, 1H), 6.44 (d, *J* = 11.5 Hz, 1H), 0.80−0.75 (m, 2H), 0.57−0.55 (m, 2H), 0.32−0.28 (m, 1H). ^{13}C NMR (125.8 MHz, acetone-d_6): δ 144.3, 140.1, 128.9, 127.8, 125.0, 119.9, 117.7, 5.4. ^{11}B NMR (128.38 MHz, acetone-d_6): δ 38.06. IR (neat): 3380, 3076, 2998, 1561, 1137, 748 cm^{-1}. HRMS (CI) *m/z*: calcd for $C_{11}H_{12}BN$ $[M]^+$ 169.1063, found 169.1069.

*2-(3-Bromopropyl)-2,1-borazaronaphthalene (**12c**).* Obtained as a white solid (99 mg, 80%). Mp: 65−67 °C. ^1H NMR (500 MHz, acetone-d_6): δ 9.31 (br s, 1H), 8.01 (d, *J* = 11.5 Hz, 1H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.50−7.47 (m, 1H), 7.41−7.37 (m, 1H), 7.14−7.10 (m, 1H), 6.8 (d, *J* = 11.7 Hz, 1H), 3.54−3.51 (m, 2H), 2.18−2.12 (m, 2H), 1.40−1.35 (m, 2H). ^{13}C NMR (125.8 MHz, acetone-d_6): δ 144.4, 140.8, 129.0, 127.9, 125.2, 120.3, 118.0, 36.7, 29.7. ^{11}B NMR (128.38 MHz, acetone-d_6): δ 37.91. IR (neat): 3362, 3006, 2958, 1559, 809, 760 cm^{-1}. HRMS (CI) *m/z*: calcd for $C_{11}H_{13}BNBr$ $[M]^+$ 249.0324, found 249.0317.

*2-(3-Iodopropyl)-2,1-borazaronaphthalene (**12d**).* Obtained as a white solid (103 mg, 69%). Mp: 61−63 °C. ^1H NMR (500 MHz, acetone-d_6): δ 9.3 (br s, 1H), 8.0 (d, *J* = 11.5 Hz, 1H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.48 (d, *J* = 8.1 Hz, 1H), 7.41−7.37 (m, 1H), 7.14−7.10 (m, 1H), 6.79 (d, *J* = 11.5 Hz, 1H), 3.33 (dd, *J* = 8.0, 7.1 Hz, 2H), 2.15−2.09 (m, 2H), 1.37−1.34 (m, 2H). ^{13}C NMR (125.8 MHz, acetone-d_6): δ 144.4, 140.8, 129.0, 127.9, 125.2, 120.3, 118.0, 30.6, 10.6. ^{11}B NMR (128.38 MHz, acetone-d_6): δ 37.78. IR (neat): 3363, 2950, 2917, 1558, 1440, 763 cm^{-1}. HRMS (CI) *m/z*: calcd for $C_{11}H_{13}BNI$ $[M]^+$ 297.0186, found 297.0174.

*2-((E)-1-Propen-1-yl)-2,1-borazaronaphthalene (**12e**).* Obtained as a white solid (44 mg, 52%). Mp: 56−57 °C. ^1H NMR (500 MHz, acetone-d_6): δ 9.23 (br s, 1H), 7.99 (d, *J* = 11.5 Hz, 1H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.46−7.43 (m, 1H), 7.39−7.35 (m, 1H), 7.10 (dd, *J* = 8.3, 7.5 Hz, 1H), 6.98 (d, *J* = 11.6 Hz, 1H), 6.78−6.71 (m, 1H), 6.09 (d, *J* = 17.6 Hz, 1H), 1.91−1.90 (m, 3H). ^{13}C NMR (125.8 MHz, acetone-d_6): δ 144.1, 143.6, 141.0, 129.0, 127.9, 125.5, 120.2, 118.0, 21.1. ^{11}B NMR (128.38 MHz, acetone-d_6): δ 32.98. IR (neat): 3370, 2846, 1612, 1438, 986, 816, 751 cm^{-1}. HRMS (CI) *m/z*: calcd for $C_{11}H_{13}BN$ $[M + H]^+$ 170.1141, found 170.1142.

*2-(1-Butynyl)-2,1-borazaronaphthalene (**12f**).* Obtained as a yellow oil that crystallized in the refrigerator (76 mg, 73%). Mp: 42−44 °C. ^1H NMR (500 MHz, acetone-d_6): δ 9.65 (br s, 1H), 8.05 (d, *J* = 11.2 Hz, 1H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.56 (d, *J* = 8.1 Hz, 1H), 7.43 (dd, *J* = 8.8, 7.7 Hz, 1H), 7.16 (dd, *J* = 8.0, 7.3 Hz, 1H), 6.79 (d, *J* = 11.5 Hz, 1H), 2.36 (dd, *J* = 10.0, 7.0 Hz, 2H), 1.57−1.53 (m, 2H), 1.52−1.44 (m, 2H), 0.94−0.87 (m, 3H). ^{13}C NMR (125.8 MHz, acetone-d_6): δ 144.7, 140.6, 129.0, 128.3, 125.1, 120.8, 118.1, 30.7, 21.6, 19.1, 12.9. ^{11}B NMR (128.38 MHz, acetone-d_6): δ 26.72. IR (neat): 3385, 2931, 2187, 1560, 1174, 808, 760 cm^{-1}. HRMS (CI) *m/z*: calcd for $C_{14}H_{17}BN$ $[M + H]^+$ 210.1454, found 210.1462.

*2-Phenyl-2,1-borazaronaphthalene (**12g**).*[7a] Obtained as a white solid (96 mg, 95%). Mp: 136−138 °C. ^1H NMR (500 MHz, acetone-d_6): δ 9.76 (br s, 1H), 8.18 (d, *J* = 11.7 Hz, 1H), 8.06 (d, *J* = 7.1 Hz, 2H), 7.70−7.66 (m, 2H), 7.47−7.41 (m, 4H), 7.30 (d, *J* = 11.6, 1H), 7.18 (dd, *J* = 10.8, 7.8 Hz, 1H). ^{13}C NMR (125.8 MHz, acetone-d_6): δ 145.4, 141.0, 133.0, 129.3, 129.1, 128.2, 127.9, 125.6, 120.7, 118.5. ^{11}B NMR (128.38 MHz, acetone-d_6): δ 34.23. IR (neat): 3380, 2925, 1560, 1440, 1212, 815, 752 cm^{-1}. HRMS (CI) *m/z*: calcd for $C_{14}H_{12}BN$ $[M]^+$ 205.1063, found 205.1065.

*2-(4-Methylphenyl)-2,1-borazaronaphthalene (**12h**).* Obtained as a white solid (102 mg, 93%). Mp: 131−132 °C. ^1H NMR (500 MHz, acetone-d_6): δ 9.69 (br s, 1H), 8.15 (d, *J* = 11.5 Hz, 1H), 7.95 (d, *J* = 7.8 Hz, 2H), 7.67 (dd, *J* = 8.8, 7.2 Hz, 2H), 7.45−7.42 (m, 1H), 7.29−7.25 (m, 3H), 7.17 (dd, *J* = 8.8, 7.5 Hz, 1H), 2.36 (s, 3H). ^{13}C NMR (125.8 MHz, acetone-d_6): δ 145.1, 141.0, 139.1, 133.1, 129.1, 128.6, 128.2, 125.6, 120.6, 118.5, 20.6. ^{11}B NMR (128.38 MHz, acetone-d_6): δ 34.20. IR (neat): 3380, 3012, 1713, 1561, 1438, 802, 753 cm^{-1}. HRMS (CI) *m/z*: calcd for $C_{15}H_{15}BN$ $[M + H]^+$ 220.1298, found 220.1302.

*2-(4-Fluorophenyl)-2,1-borazaronaphthalene (**12i**).* Obtained as a white solid (96 mg, 86%). Mp: 131−132 °C. ^1H NMR (500 MHz, acetone-d_6): δ 9.79 (br s, 1H), 8.18 (d, *J* = 11.5 Hz, 1H), 8.10−8.07 (m, 2H), 7.69 (d, *J* = 7.8 Hz, 1H), 7.65 (d, *J* = 8.3 Hz, 1H), 7.45 (dd, *J*

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= 8.8, 7.6 Hz, 1H), 7.27 (d, J = 11.5 Hz, 1H), 7.21−7.17 (m, 3H). ^{13}C NMR (125.8 MHz, acetone-d_6): δ 164.0 (d, J = 246 Hz), 145.5, 141.0, 135.2 (d, J = 7.5 Hz), 129.1, 128.3, 125.5, 120.7, 118.5, 114.65 (d, J = 20 Hz). ^{11}B NMR (128.38 MHz, acetone-d_6): δ 33.86. IR (neat): 3381, 3064, 2924, 1593, 1205, 813, 758 cm^{-1}. HRMS (CI) m/z: calcd for $C_{14}H_{12}BFN$ [M + H]$^+$ 224.1047, found 224.1050.

2-(3-Thiophenyl)-2,1-borazaronaphthalene (12j). Obtained as a white solid (97 mg, 92%). Mp: 154−155 °C. ^{1}H NMR (500 MHz, acetone-d_6): δ 9.73 (br s, 1H), 8.16−8.12 (m, 2H), 7.75 (d, J = 4.6 Hz, 1H), 7.66 (d, J = 7.8 Hz, 1H), 7.58 (d, J = 8.3 Hz, 1H), 7.53 (dd, J = 4.4, 2.4 Hz, 1H), 7.43 (dd, J = 8.8, 7.3 Hz, 1H), 7.24 (d, J = 11.5 Hz, 1H), 7.16 (dd, J = 9.0, 7.5 Hz, 1H). ^{13}C NMR (125.8 MHz, acetone-d_6): δ 145.2, 141.0, 132.6, 131.2, 129.1, 128.2, 125.5, 125.4, 120.6, 118.3. ^{11}B NMR (128.38 MHz, acetone-d_6): δ 31.77. IR (neat): 3379, 2925, 1563, 1058, 1031, 756 cm^{-1}. HRMS (CI) m/z: calcd for $C_{12}H_{11}BNS$ [M + H]$^+$ 212.0705, found 212.0710.

2-(4-Dibenzofuryl)-2,1-borazaronaphthalene (12k). Obtained as a white solid (126 mg, 82%). Mp: 144−146 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.53 (br s, 1H), 8.23 (d, J = 11.5 Hz, 1H), 8.16 (d, J = 7.1 Hz, 1H), 8.03 (dd, J = 14.9, 7.6 Hz, 2H), 7.73 (d, J = 7.8 Hz, 2H), 7.55−7.47 (m, 5H), 7.43−7.40 (m, 1H), 7.28−7.25 (m, 1H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 160.2, 155.8, 145.4, 140.2, 133.8, 129.4, 128.3, 127.0, 125.7, 124.0, 123.3, 123.0, 122.8, 122.2, 121.0, 120.7, 118.7, 115.5. ^{11}B NMR (128.38 MHz, $CDCl_3$): δ 33.59. IR (neat): 3392, 2923, 1561, 116, 754, 736, 721 cm^{-1}. HRMS (CI) m/z: calcd for $C_{20}H_{14}BNO$ [M]$^+$ 295.1168, found 295.1165.

2-(N-Toluenesulfonylpiperidin-4-yl)-2,1-borazaronaphthalene (12l). Obtained as a white solid (31 mg, 17%). Mp: 72−73 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.00 (d, J = 11.5 Hz, 1H), 7.69 (d, J = 8.1 Hz, 1H), 7.66 (s, 1H), 7.60 (d, J = 7.8 Hz, 2H), 7.42−7.40 (m, 1H), 7.35 (d, J = 8.1 Hz, 2H), 7.26−7.24 (m, 1H), 7.17 (dd, J = 8.3, 7.5 Hz, 2H), 6.78 (d, J = 11.5 Hz, 1H), 3.87 (d, J = 11.2 Hz, 2H), 2.46 (s, 3H), 2.34 (dd, J = 12.3, 11.0 Hz, 2H), 1.98−1.90 (m, 2H), 1.79−1.70 (m, 2H), 1.24−1.17 (m, 1H). ^{13}C NMR (125.8 MHz, acetone-d_6): δ 145.1, 143.2, 139.7, 133.3, 129.5, 129.3, 128.2, 127.7, 125.3, 121.0, 117.9, 47.6, 28.2, 21.4. ^{11}B NMR (128.38 MHz, acetone-d_6): δ 36.96. IR (neat): 3343, 2915, 1597, 1455, 1108, 1057, 1034, 613 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{20}H_{24}BN_2O_2S$ [M]$^+$ 367.1652, found 367.1647.

1-Phenyl-2-methyl-2,1-borazaronaphthalene (13). Obtained as a white solid (47 mg, 43%). Mp: 59−61 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.99 (d, J = 11.6 Hz, 1H), 7.65 (dd, J = 7.6, 1.2 Hz, 1H), 7.55−7.51 (m, 2H), 7.45−7.43 (m, 1H), 7.26−7.24 (m, 1H), 7.18−7.14 (m, 3H), 6.90 (d, J = 11.3 Hz, 1H), 6.77 (d, J = 8.5 Hz, 1H), 0.48 (s, 3H). ^{13}C NMR (125.8 MHz, acetone-d_6): δ 144.3, 144.0, 143.0, 129.7, 129.5, 128.3, 127.9, 127.1, 125.6, 120.5, 116.8. ^{11}B NMR (128.38 MHz, acetone-d_6): δ 36.21. IR (neat): 3002, 2929, 1592, 1490, 1307, 762 cm^{-1}. HRMS (CI) m/z: calcd for $C_{15}H_{14}BN$ [M]$^+$ 219.1219, found 219.1219.

■ ASSOCIATED CONTENT

Supporting Information

Copies of ^{1}H, ^{13}C, and ^{11}B NMR spectra for all compounds. 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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