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

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Abstract

Azaborines are an important class of compounds with applications in both medicinal chemistry and materials science. 2-Chloro-2,1-borazonaphthalene was the first borazonaphthalene 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-borazonaphthalenes from *N*-substituted 2-aminostyrenes and potassium organotrifluoroborates, where the potassium organotrifluoroborate is converted to the active R-BX_2 species ($\text{X} = \text{Cl}$ or F) *in situ* by addition of a fluorophile. Starting from aryl-, heteroaryl-, alkynyl-, alkenyl-, and alkyltrifluoroborates, a library of highly functionalized 2,1-borazonaphthalenes are synthesized in one step under mild, transition-metal free conditions.

INTRODUCTION

The isosteric replacement of $\text{C}=\text{C}$ with B-N within the context of aromatic systems leads to azaborines, a class of compounds whose synthesis and reactivity has attracted much attention over the last 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 the corresponding $\text{C}=\text{C}$ aromatic system.²

Isosteric replacement has become a powerful strategy in many diverse areas, including the pharmaceutical and agrochemical fields³ 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 ethylbenzene dehydrogenase (EbdH) enzyme.^{4b} Methods to access functionalized 1,2-azaborines in a straightforward, efficient manner could have an impact in the discovery of

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Copies of ¹H, ¹³C, and ¹¹B NMR spectra for all compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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 owing to 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 BCl₃ (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 Et₂O 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 1,2-borazaronaphthalenes (Scheme 1, **IIB**).^{10b} Thus, an *N*-substituted aniline starting material was employed, which was first reacted with boron trichloride. This product was then heated to reflux with phenylacetylene, purified, and heated with ZnCl₂. 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 trimethylarylstannes 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 70% yield (Scheme 1, **IV**).

Although these methods are effective for synthesizing and functionalizing 2,1-borazaronaphthalenes, they are not without limitations. BCl₃ 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 functional group tolerability. Paetzold's method suffers from the use of a superstoichiometric amount of ZnCl₂, 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 for 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 43–69%, 13%, and 78–89% yields, 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 2,1-borazaronaphthalene. A plausible mechanism for that approach to 2,1-borazaronaphthalene from boron trichloride and 2-aminostyrene is outlined in Scheme 2. The first step consists of a known reaction between a primary amine and BCl_3 , which results in the formation of an N-B bond with loss of HCl to form **2**.¹² Nucleophilic attack of the terminal alkene, stabilized by resonance from the amine, cyclizes 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, and 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-borazaronaphthalenes in one step. Further, 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 ($\text{X} = \text{halide}$). Dewar confirmed this possibility by employing the 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 owing to 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, regioselectivity in the addition of boron is difficult to control, and the high reactivity of these Lewis acids again limits functional group tolerability.

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 organotri-fluoroborates 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, by utilizing *N*-substituted 2-aminostyrenes and potassium organotrifluoroborates, a mild synthesis of highly functionalized 2,1-borazaronaphthalenes was envisioned.

Reported herein is the Lewis acid promoted annulation/aromatization reaction of substituted 2-aminostyrenes and potassium organotrifluoroborates, providing functionalized 2,1-borazaronaphthalenes. By forming the required R-BX_2 species *in situ* via conversion of the organotri-fluoroborate with SiCl_4 , an array of 2,1-borazaronaphthalenes has been prepared. The use of aryl, heteroaryl, alkynyl, alkenyl, and alkyltrifluoroborates allows an effective and straightforward route to novel 2,1-borazaronaphthalenes.

RESULTS AND DISCUSSION

N-Benzyl-2-aminostyrene and potassium phenyltrifluoroborate were chosen as model substrates for the synthesis of 1-benzyl-2-phenyl-2,1-borazaronaphthalene (Table 1). An array of solvents was tested in reactions at 80 °C for 24 h. Based on Matteson's adaptation of the Vedejs protocol,¹⁷ SiCl_4 was first used as a fluorophile to generate the required PhBCl_2 .

Any R-BX₂ species (X = Br, Cl, F) should be practicable in the reaction, and therefore several other fluorophiles were employed in the reaction (entries 6–10). However, SiCl₄ provided the desired product in the highest yield. The addition of cyclopentyl methyl ether (CPME), a coordinating solvent, led to an increase in yield when compared to toluene (entries 1–5). A 1:1 mixture of toluene/CPME was found to be more effective than other solvent combinations. Therefore, after optimization of solvent and fluorophile, the best conditions were 1 equivalent of SiCl₄ in 1:1 toluene/CPME at 80 °C for 24 h, providing 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 increasing the concentration to 0.5 M, but then yields decreased at 1 M (entries 1–4). Interestingly, the reaction was complete after 30 min at 80 °C, and lowering the temperature to 60 °C resulted in the desired product 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 SiCl₄ to 0.75 equivalents resulted in a lower yield (entry 8). Employing the conditions from entry 6 but lowering the reaction temperature to 40 °C resulted in the desired product obtained in 78% yield, but with a longer reaction time of 18 h (entry 9).

In addition to varying these parameters, several additives were screened in the reaction. Utilization of one or two equivalents of K₂CO₃, which was added to quench the HCl generated in the reaction, did not change the yield of the reaction. Addition of one or two equivalents of NaOt Bu or NEt₃ resulted in no product formation. Use of KBr, which was added to form the R-BBr₂ species *in situ*, also did not change the yield of the reaction.¹⁸ Therefore the preferred conditions for the synthesis of 1-phenyl-2-benzyl-borazonaphthalene were determined to be 1.5 equiv of amine, 1.0 equiv of organotrifluoroborate, 1.0 equiv of SiCl₄ in a 1:1 mixture of toluene/CPME at 60 °C for 4 h.

These standard conditions were applied to a variety of functionalized potassium aryl- and heteroaryltrifluoroborates, providing the corresponding 2,1-borazonaphthalenes in yields up to 79% (Table 3). Sixteen different potassium aryl- and heteroaryltrifluoroborates afforded the corresponding disubstituted 2,1-borazonaphthalenes in moderate to good yields. Electron-donating aryltrifluoroborates with *para* or *meta* substitution provided the desired product in good yield (entries 2–5, 7). When the aryltrifluoroborates contained electron-withdrawing groups substituted *meta* or *para*, or for disubstituted derivatives, the corresponding 2,1-borazonaphthalenes were synthesized with yields up to 70% (entries 8–13). The mild conditions of this method allowed ester, nitrile, and nitro functional groups on the aryltrifluoroborates (entries 8–10), which would not be possible from approaches using Grignard reagents. 3-Thienyl-, 4-dibenzofuranyl-, and 4-dibenzothienyltrifluoroborates provided the desired products in moderate yields after lowering the reaction temperature to 40 °C (entries 14–16). Because of steric factors imposed on substituting the 2,1-borazonaphthalene at the 1 and 2 positions, sterically encumbered organotrifluoroborates provided the corresponding products in lower yield, as evident in the use of 1- and 2-naphthyltrifluoroborate, where the less sterically hindered 2-naphthyltrifluoroborate results in a higher 69% yield of the product (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-borazonaphthalenes, we sought to extend this method to alkenyl- and alkynyltrifluoroborates, providing access to novel systems (Table 4). There are no previously reported examples with alkenyl or alkynyl

substituents on 2,1-borazaronaphthalenes. By lowering 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 1–2). A phenyl-substituted alkenyltrifluoroborate provided the desired product in 51% yield (entry 3). An alkynyl 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} These materials were all 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 the use of diverse, readily available, primary and secondary alkyltrifluoroborates 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 -trifluoroethyltrifluoroborate¹⁹ was effectively used in the reaction, resulting in 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 product in good yields (entries 5–7). Scaling up the reaction with potassium methyltrifluoroborate provided a similar yield on a 5 mmol scale (entry 1).

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 2,1-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 corresponding 2,1-borazaronaphthalenes were synthesized in yields of 61% and 55%, respectively (entries 2–3). 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 substituting the azaborine in the 1 and 2 positions is evident as the yield decreased to 40% when an aryl group was substituted on nitrogen, and no desired product was obtained when a diphenylmethyl group was substituted on nitrogen (entries 5–6).

Upon synthesizing 1,2-disubstituted 2,1-borazaronaphthalenes with various substituents on nitrogen and boron, we sought to extend the method to aryl substituted 2-aminostyrenes, because 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* a Wittig olefination and Buchwald-Hartwig amination to provide access to the requisite 2-aminostyrenes.²¹ The substituents on the aminostyrene can be placed at various positions about the arene to provide the corresponding 2,1-borazaronaphthalenes in yields up to 75% (Table 7). Electron withdrawing substituents such as fluorine and trifluoromethyl groups provide the desired product in yields of 73% and 64%, respectively (entries 1–2). Substitution of electron donating substituents, such as methyl and methoxy groups, about the aromatic ring result in the corresponding 2,1-borazaronaphthalenes being synthesized in good yield (entries 3–4). The nature of the process insures that complete control of 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-borazonaphthalenes^{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-borazonaphthalene, 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-borazonaphthalene in almost all cases, demonstrating the stability of these azaborines. To achieve the synthesis of N-H 2,1-borazonaphthalenes, 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-borazonaphthalenes were prepared in yields up to 66%. However, addition of 1.5 equiv of NEt₃, which served to quench HCl formed during the reaction, led to increased yields, providing the desired products in yields up to 95% (Table 8). Cyclic and acyclic alkyltrifluoroborates provide the desired product in high yield (entries 1–2). The mild reaction conditions allow installation of an alkyl iodide and bromide on the 2,1-borazonaphthalene, providing the desired products in 69% and 80% yield, respectively. Alkenyl and alkynyltrifluoroborates can be employed, providing the desired products in good yield (entries 5–6). Electron-donating, electron-withdrawing, and electron-neutral aryltrifluoroborates are effective in the reaction, as the 2,1-borazonaphthalenes are synthesized in yields up to 95% (entries 7–9). Three heterocyclic trifluoroborates were used in the reaction to provide the desired product in yields up to 92% (entries 10–12).

1-Alkyl-2-aryl-, 1,2-dialkyl-, and 1,2-diaryl-2,1-borazonaphthalenes 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 the 1-aryl-2-alkyl-2,1-borazonaphthalene **13** (eq 1).

(1)

The overall impact of this method can be demonstrated by comparing the current synthesis of 2,1-borazonaphthalenes with those of the isosteric, substituted naphthalenes. Whereas the synthesis of 1-alkyl-2-aryl- and 1,2-dialkyl-2,1-borazonaphthalenes (**7a–7p** and **9a–9g**) proceeds under mild reaction conditions, the synthesis of the corresponding disubstituted naphthalenes employs alkyl- and aryl- Grignard reagents to substitute 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 tolerability, the synthesis of the electrophilic naphthalene in these systems requires several steps and harsh reaction conditions. By contrast, the synthesis of the 2,1-borazonaphthalenes (**7a–7p** and **10d**) is a transition metal-free route that does not require a multi-step synthesis of starting materials. The synthesis of 1-aryl-2-alkyl-naphthalenes requires only one step;²⁴ however, only a few examples are 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** is synthesized in similar yield. The synthesis of 1-substituted-2-alkynyl- and 1-substituted-2-alkenylnaphthalenes can be envisioned to proceed through a similar cross coupling as the 1,2-diarylnaphthalene.²⁵ More importantly, in comparison with **11a–11d**, 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-eight *N*- and *B*-substituted 2,1-borazaronaphthalenes were synthesized *via* an annulation/aromatization reaction of potassium organotrifluoroborates and substituted 2-aminostyrenes. By utilizing the *in situ* conversion of organotrifluoroborates to the active organodihaloboranes with SiCl₄, 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 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 all previous studies over the past 50+ years combined.

Further, 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 regioselectivity and substituents about both aromatic rings. Investigations toward the reactivity of these compounds and applications of this approach to other borazine cores are currently underway.

EXPERIMENTAL SECTION

General Considerations

JohnPhos, NaOt-Bu, 2-bromostyrene, and SiCl₄ were purchased and used as received. Amines were distilled prior to use. Toluene and CPME were dried using a J.C. Meyer solvent system. Standard benchtop techniques were employed for handling air-sensitive reagents. Melting points (°C) are uncorrected. NMR spectra were recorded on a 500 or 400 MHz spectrometer. ¹⁹F NMR chemical shifts were referenced to external CFCl₃ (0.0 ppm). ¹¹B NMR spectra were obtained on a spectrometer equipped with the appropriate decoupling accessories. All ¹¹B NMR chemical shifts were referenced to an external BF₃·OEt₂ (0.0 ppm) with a negative sign indicating an upfield shift. Data are presented as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad), coupling constant *J* (Hz) and 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 ultraviolet light. HRMS data was 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 calc. for $\text{C}_2\text{H}_2\text{BF}_6 [\text{M}-\text{K}]^-$ 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 calc. for $\text{C}_3\text{H}_6\text{BF}_3\text{Br} [\text{M}-\text{K}]^-$ 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 calc. for $\text{C}_3\text{H}_6\text{BF}_3\text{I} [\text{M}-\text{K}]^-$ 236.9559, found 236.9577. Anal. Calcd. for $\text{C}_3\text{H}_6\text{BF}_3\text{IK}$: 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 calc. for $\text{C}_{12}\text{H}_7\text{BF}_3\text{S} [\text{M}-\text{K}]^-$ 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 was added Pd μ -Cl dimer (0.02 mmol, 0.5 mol %), JohnPhos (0.04 mmol, 1 mol %), and NaOt-Bu (5.6 mmol, 1.4 equiv). The vial was sealed with a cap lined with a disposable Teflon septum then 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). After cooling to rt, the reaction mixture was diluted with Et₂O (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 mixture of EtOAc/hexanes as the eluent. The eluent for most of the amines is 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, CDCl₃) 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 calc. for $\text{C}_{16}\text{H}_{18}\text{NO}$ $[\text{M}+\text{H}]^+$ 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 calc. for $\text{C}_{11}\text{H}_{14}\text{N}$ $[\text{M}+\text{H}]^+$ 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, $J = 17.4$ Hz, 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, $J = 10.9$ Hz, 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, 62.8. IR (neat) 3423, 3062, 2844, 1735, 1500, 907, 742 cm^{-1} . HRMS (ESI) m/z calc. for $\text{C}_{21}\text{H}_{20}\text{N}$ $[\text{M}+\text{H}]^+$ 286.1596, found 286.1597.

General Procedure for the Wittig Olefination and Buchwald-Hartwig Amination For Synthesis of Substituted 2-Aminostyrenes

To an oven dried 25 mL round bottom flask with stir bar was added MePh_3PBr (6 mmol, 1.2 equiv). The flask was sealed with a septum and evacuated and purged three times with Ar. The flask was cooled to -78 °C and $n\text{-BuLi}$ (1.6 M in hexanes, 6 mmol, 1.2 equiv) was

added dropwise, keeping the reaction temperature below -70°C . The reaction was stirred at -78°C for 1 h and allowed to warm to rt. The reaction 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 was allowed to warm slowly to rt and stirred 18 h. The reaction was quenched at 0°C by addition of sat. aq NH_4Cl , 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 confirming the product by NMR. To an oven-dried Biotage microwave vial equipped with a stir bar was added Pd $\mu\text{-Cl}$ dimer (0.02 mmol, 0.5 mol %), JohnPhos (0.04 mmol, 1 mol %), and NaOt-Bu (5.6 mmol, 1.4 equiv). The vial was sealed with a cap lined with a disposable Teflon septum then 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). After cooling to rt, the reaction mixture was 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)

Completed on 2 mmol scale. 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, $J = 17.4$ Hz, 11.0 Hz, 1H), 6.65 (d, $J = 8.6$ Hz, 1H), 5.71 (dd, $J = 17.1$ Hz, 1.2 Hz, 1H), 5.44 (dd, $J = 11.0$ Hz, 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 calc. for $\text{C}_{16}\text{H}_{15}\text{NF}_3$ $[\text{M}+\text{H}]^+$ 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, $J = 18.0$ Hz, 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 calc. for $\text{C}_{16}\text{H}_{18}\text{N}$ $[\text{M}+\text{H}]^+$ 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, $J = 17.4$ Hz, 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 calc. for $\text{C}_{16}\text{H}_{18}\text{N}$ $[\text{M}+\text{H}]^+$ 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, $J = 17.1$ Hz, 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 calc. for $\text{C}_{17}\text{H}_{20}\text{NO}_2$ $[\text{M}+\text{H}]^+$ 270.1494, found 270.1488.

General Procedure for the Synthesis of 2-Aminostyrene

(2-aminostyrene was synthesized according to the literature).³¹ To a 100 mL round bottom flask with stir bar was added 2-amino-phenethyl 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 colorless oil.

2-Vinylaniline (12-amine).³¹

Obtained 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, then 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) and SiCl_4 (0.5 mmol, 1 equiv) 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. After cooling to rt, the reaction mixture was diluted with hexanes (2 mL). The reaction mixture was filtered over a two-inch 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 calc. for $\text{C}_{21}\text{H}_{18}\text{BN}$ $[\text{M}]^+$ 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 calc. for $\text{C}_{25}\text{H}_{26}\text{BN}$ $[\text{M}]^+$ 351.2158, found 351.2167.

1-Benzyl-2-(3-methylphenyl)-2,1-borazonaphthalene (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 calc. for $\text{C}_{22}\text{H}_{20}\text{BN}$ $[\text{M}]^+$ 309.1689, found 309.1700.

1-Benzyl-2-(3-methoxyphenyl)-2,1-borazonaphthalene (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} . HRMS (ESI) m/z calc. for $\text{C}_{22}\text{H}_{21}\text{BNO}$ $[\text{M}+\text{H}]^+$ 326.1716, found 326.1721.

1-Benzyl-2-(2-naphthyl)-2,1-borazonaphthalene (7e)

Obtained as a tan solid (119 mg, 69%). mp: 146–148 °C. ^1H 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 calc. for $\text{C}_{25}\text{H}_{20}\text{BN}$ $[\text{M}]^+$ 345.1689, found 345.1700.

1-Benzyl-2-(1-naphthyl)-2,1-borazonaphthalene (7f)

Obtained as a yellow oil that crystallized in the refrigerator (26 mg, 15%). mp: 144–146 °C. ^1H 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 calc. for $\text{C}_{25}\text{H}_{20}\text{BN}$ $[\text{M}]^+$ 345.1689, found 345.1689.

1-Benzyl-2-(4-methylphenyl)-2,1-borazonaphthalene (7g)

Obtained as a white solid (111 mg, 72%). mp: 96–98 °C. ^1H 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 calc. for $\text{C}_{22}\text{H}_{20}\text{BN}$ $[\text{M}]^+$ 309.1689, found 309.1688.

Methyl-3-(2-benzyl-2,1-borazonaphthyl)benzoate (7h)

Obtained as a tan solid (115 mg, 65%). mp: 91–93 °C. ^1H 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 calc. for $\text{C}_{23}\text{H}_{21}\text{BNO}_2$ $[\text{M}+\text{H}]^+$ 354.1665, found 354.1657.

3-(2-Benzyl-2,1-borazonaphthyl)benzonitrile (7i)

Obtained as a yellow oil that crystallized in the refrigerator (80 mg, 50%). mp: 117–119 °C. ^1H 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 calc. for $\text{C}_{22}\text{H}_{17}\text{BFN}_2$ $[\text{M}+\text{F}]^-$ 339.1469, found 339.1471.

1-Benzyl-2-(3-nitrophenyl)-2,1-borazonaphthalene (7j)

Obtained as a tan solid (84 mg, 49%). mp: 114–117 °C. ^1H 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 calc. for $\text{C}_{21}\text{H}_{17}\text{BN}_2\text{NaO}_2$ $[\text{M}+\text{Na}]^+$ 363.1281, found 363.1270.

1-Benzyl-2-(3,5-bis(trifluoromethyl)phenyl)-2,1-borazonaphthalene (7k)

Obtained as a tan solid (109 mg, 50%). mp: 88–92 °C. ^1H 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 calc. for $\text{C}_{23}\text{H}_{16}\text{BF}_7\text{N}$ $[\text{M}+\text{F}]^-$ 450.1264, found 450.1265.

1-Benzyl-2-(4-fluorophenyl)-2,1-borazonaphthalene (7l)

Obtained as a tan solid (110 mg, 70%). mp: 112–114 °C. ^1H 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 calc. for $\text{C}_{22}\text{H}_{20}\text{BFNO}$ $[\text{M}+\text{OCH}_3]^-$ 344.1622, found 344.1627.

1-Benzyl-2-(2,4-difluorophenyl)-2,1-borazonaphthalene (7m)

Obtained as a tan solid (22 mg, 13%). mp: 107–110 °C. ^1H 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 calc. for $\text{C}_{21}\text{H}_{16}\text{BF}_3\text{N}$ $[\text{M}+\text{F}]^-$ 350.1328, found 350.1330.

1-Benzyl-2-(3-thienyl)-2,1-borazonaphthalene (7n)

Obtained as an off-white solid (84 mg, 56%). mp: 108–110 $^\circ\text{C}$. ^1H 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 calc. for $\text{C}_{19}\text{H}_{17}\text{BNS}$ $[\text{M}+\text{H}]^+$ 302.1175, found 302.1183.

1-Benzyl-2-(4-dibenzofuryl)-2,1-borazonaphthalene (7o)

Obtained as a white solid (89 mg, 46%). mp: 106–107 $^\circ\text{C}$. ^1H 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 calc. for $\text{C}_{27}\text{H}_{20}\text{BNO}$ $[\text{M}]^+$ 385.1638, found 385.1626.

1-Benzyl-2-(4-dibenzothieryl)-2,1-borazonaphthalene (7p)

Obtained as a white solid (88 mg, 44%). mp: 116–117 $^\circ\text{C}$. ^1H 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 calc. for $\text{C}_{27}\text{H}_{21}\text{BNS}$ $[\text{M}+\text{H}]^+$ 402.1488, found 402.1477.

1-Benzyl-2-((E)-1-propen-1-yl)-2,1-borazonaphthalene (8a)

Obtained as a yellow oil that crystallized in the refrigerator (68 mg, 53%). mp: 70–72 $^\circ\text{C}$. ^1H 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), 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, 155, 1358, 1218, 982, 758 cm^{-1} . HRMS (CI) m/z calc. for $\text{C}_{18}\text{H}_{18}\text{BN}$ $[\text{M}]^+$ 259.1532, found 259.1539.

1-Benzyl-2-((Z)-1-propen-1-yl)-2,1-borazonaphthalene (8b)

Obtained as a yellow oil that crystallized in the refrigerator overnight (74 mg, 57%). mp: 70–72 $^\circ\text{C}$. ^1H 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 calc. for $\text{C}_{18}\text{H}_{18}\text{BN}$ $[\text{M}]^+$ 259.1532, found 259.1527.

1-Benzyl-2-((E)-3-phenyl-1-propen-1-yl)-2,1-borazonaphthalene (8c)

Obtained as a yellow oil that crystallized in the refrigerator (85 mg, 52%). mp: 75–77 °C. ^1H 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 calc. for $\text{C}_{24}\text{H}_{23}\text{BN}$ $[\text{M}+\text{H}]^+$ 336.1924, found 336.1926.

1-Benzyl-2-(1-butynyl)-2,1-borazonaphthalene (8d)

Obtained as a yellow oil that crystallized upon standing (78 mg, 52%). mp: 46–47 °C. ^1H 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 calc. for $\text{C}_{21}\text{H}_{22}\text{BN}$ $[\text{M}]^+$ 299.1845, found 299.1841.

1-Benzyl-2-methyl-2,1-borazonaphthalene (9a)

Obtained as a tan solid (56 mg, 48%). mp: 56–60 °C. ^1H 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 calc. for $\text{C}_{16}\text{H}_{16}\text{BN}$ $[\text{M}]^+$ 233.1376, found 233.1374.

1-Benzyl-2-(4-penten-1-yl)-2,1-borazonaphthalene (9b)

Obtained as a yellow oil (72 mg, 50%). ^1H 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 calc. for $\text{C}_{20}\text{H}_{22}\text{BN}$ $[\text{M}]^+$ 287.1845, found 287.1841.

2-Benzyl-1-trifluoroethyl-2,1-borazonaphthalene (9c)

Obtained as an off white solid (60 mg, 40%). mp: 76–78 °C. ^1H 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 calc. for $\text{C}_{17}\text{H}_{15}\text{BNF}_3$ $[\text{M}]^+$ 301.1250, found 301.1245.

1-Benzyl-2-isopropyl-2,1-borazonaphthalene (9d)

Obtained as a yellow oil that crystallized upon standing (76 mg, 58%). mp: 67–69 °C. ^1H 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 calc. for $\text{C}_{18}\text{H}_{20}\text{BN}$ $[\text{M}]^+$ 261.1689, found 261.1688.

1-Benzyl-2-cyclopropyl-2,1-borazonaphthalene (9e)

Obtained as a yellow oil that crystallized in the refrigerator (64 mg, 49%). mp: 41–43 °C. ^1H 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 calc. for $\text{C}_{18}\text{H}_{18}\text{BN}$ $[\text{M}]^+$ 259.1532, found 259.1534.

1-Benzyl-2-cyclobutyl-2,1-borazonaphthalene (9f)

Obtained as a yellow oil that crystallized in the refrigerator (69 mg, 51%). mp: 44–47 °C. ^1H 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 calc. for $\text{C}_{19}\text{H}_{20}\text{BN}$ $[\text{M}]^+$ 273.1689, found 273.1692.

1-Benzyl-2-cyclohexyl-2,1-borazonaphthalene (9g)

Obtained as a yellow oil that crystallized in the refrigerator (63 mg, 42%). mp: 48–51 °C. ^1H 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 calc. for $\text{C}_{21}\text{H}_{24}\text{BN}$ $[\text{M}]^+$ 301.2002, found 301.2008.

1-(4-Methoxybenzyl)-2-phenyl-2,1-borazonaphthalene (10a)

Obtained as a white solid (100 mg, 61%). mp: 134–136 °C. ^1H 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 calc. for $\text{C}_{22}\text{H}_{20}\text{BNNaO}$ $[\text{M}+\text{Na}]^+$ 348.1536, found 348.1547.

1-Allyl-2-phenyl-2,1-borazonaphthalene (10b)

Obtained as a yellow oil that crystallized in the refrigerator (325 mg, 55%). mp: 44–46 °C. ^1H 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 calc. for $\text{C}_{17}\text{H}_{16}\text{BN} [\text{M}]^+$ 245.1376, found 245.1382.

1-Butyl-2-phenyl-2,1-borazaronaphthalene (10c)

Obtained as a yellow oil (93 mg, 71%). ^1H 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 (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 calc. for $\text{C}_{18}\text{H}_{20}\text{BN} [\text{M}]^+$ 261.1689, found 261.1680.

1,2-Diphenyl-2,1-borazaronaphthalene (10d)

Obtained as a tan solid (34 mg, 24%). mp: 111–115 $^{\circ}\text{C}$. ^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 calc. for $\text{C}_{20}\text{H}_{17}\text{BN} [\text{M}+\text{H}]^+$ 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 $^{\circ}\text{C}$. ^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 calc. for $\text{C}_{22}\text{H}_{17}\text{BNF}_3 [\text{M}]^+$ 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 $^{\circ}\text{C}$. ^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 calc. for $\text{C}_{21}\text{H}_{17}\text{BNF} [\text{M}]^+$ 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 $^{\circ}\text{C}$. ^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 calc. for $\text{C}_{22}\text{H}_{20}\text{BN} [\text{M}]^+$ 309.1689, found 309.1675.

1-Benzyl-2-phenyl-6,7-dimethoxy-2,1-borazonaphthalene (11d)

Obtained as a white solid (104 mg, 55%). 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 calc. for $\text{C}_{23}\text{H}_{23}\text{BNO}_2$ $[\text{M}]^+$ 356.1822, found 356.1820.

2-Methyl-2,1-borazonaphthalene (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 calc. for $\text{C}_9\text{H}_{10}\text{BN}$ $[\text{M}]^+$ 143.0906, found 143.0895.

2-Cyclopropyl-2,1-borazonaphthalene (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 calc. for $\text{C}_{11}\text{H}_{12}\text{BN}$ $[\text{M}]^+$ 169.1063, found 169.1069.

2-(3-Bromopropyl)-2,1-borazonaphthalene (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 calc. for $\text{C}_{11}\text{H}_{13}\text{BNBr}$ $[\text{M}]^+$ 249.0324, found 249.0317.

2-(3-Iodopropyl)-2,1-borazonaphthalene (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 calc. for $\text{C}_{11}\text{H}_{13}\text{BNI}$ $[\text{M}]^+$ 297.0186, found 297.0174.

2-((E)-1-Propen-1-yl)-2,1-borazonaphthalene (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 calc. for $\text{C}_{11}\text{H}_{13}\text{BN}$ $[\text{M}+\text{H}]^+$ 170.1141, found 170.1142.

2-(1-Butynyl)-2,1-borazonaphthalene (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 calc. for $\text{C}_{14}\text{H}_{17}\text{BN}$ $[\text{M}+\text{H}]^+$ 210.1454, found 210.1462.

2-Phenyl-2,1-borazonaphthalene (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 calc. for $\text{C}_{14}\text{H}_{12}\text{BN}$ $[\text{M}]^+$ 205.1063, found 205.1065.

2-(4-Methylphenyl)-2,1-borazonaphthalene (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 calc. for $\text{C}_{15}\text{H}_{15}\text{BN}$ $[\text{M}+\text{H}]^+$ 220.1298, found 220.1302.

2-(4-Fluorophenyl)-2,1-borazonaphthalene (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 = 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 calc. for $\text{C}_{14}\text{H}_{12}\text{BFN}$ $[\text{M}+\text{H}]^+$ 224.1047, found 224.1050.

2-(3-Thiophenyl)-2,1-borazonaphthalene (12j)

Obtained as a white solid (97 mg, 92%). mp: 154–155 °C. ^1H 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 Hz, 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 calc. for $\text{C}_{12}\text{H}_9\text{BNS}$ $[\text{M}+\text{H}]^+$ 212.0705, found 212.0710.

2-(4-Dibenzofuryl)-2,1-borazonaphthalene (12k)

Obtained as a white solid (126 mg, 82%). mp: 144–146 °C. ^1H 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 calc. for $\text{C}_{20}\text{H}_{14}\text{BNO}$ $[\text{M}]^+$ 295.1168, found 295.1165.

2-[*p*-Toluenesulfonyl-4-piperidinyl]-2,1-borazonaphthalene (12l)

Obtained as a white solid (31 mg, 17%). mp: 72–73 °C. ^1H 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 calc. for $\text{C}_{20}\text{H}_{24}\text{BN}_2\text{O}_2\text{S}$ $[\text{M}]^+$ 367.1652, found 367.1647.

1-Phenyl-2-methyl-2,1-borazonaphthalene (13)

Obtained as a white solid (47 mg, 43%). mp: 59–61 °C. ^1H 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 calc. for $\text{C}_{15}\text{H}_{14}\text{BN}$ $[\text{M}]^+$ 219.1219, found 219.1219.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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I. Dewar's Synthesis

II. Paetzold's Syntheses

A. Synthesis with Aniline

B. Synthesis with *N*-Substituted Aniline

III. Dewar's Functionalization

IV. Liu's Functionalization

V: This Work

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

Scheme 2.

Plausible Mechanism for the Synthesis of 2,1-Borazonaphthalene.

I. Conventional Synthesis of Phenylchloroborane **II. Friedel Crafts-Type Synthesis of Phenylchloroborane** **III. Vedejs/Matteson Approach to Phenylchloroborane**

Scheme 3.
Methods For Synthesizing Phenylchloroborane.

Table 1

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

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	<i>p</i> -tolSiCl ₃	47
7	1:1 Toluene/CPME	SiBr_4	42
8	1:1 Toluene/CPME	TMSCl	41
9	1:1 Toluene/CPME	$\text{BF}_3 \cdot \text{OEt}_2$	0
10	1:1 Toluene/CPME	$\text{BF}_3 \cdot \text{SMe}_2$	5

Table 2

Final Reaction Refinement on the Synthesis of 2,1-Borazaronaphthalene.

entry	amine : BF ₃ K : 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

Table 3

Scope of the Reaction with Potassium (Hetero)aryltrifluoroborates.

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

entry	product	entry	product
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 SiCl₄, 1:1 Tol/CPME, 60 °C, 4 h.

^aReaction completed on 5 mmol scale.

^bReaction temperature of 40 °C, 18 h.

Table 4

Scope of the Reaction with Potassium Alkynyl- and Alkenyltrifluoroborates.

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

Reaction conditions (unless otherwise noted): 1.2 equiv of amine, 1.0 equiv of alkyltrifluoroborate, 1.0 equiv of SiCl_4 , 1:1 Tol/CPME, 40 °C, 18 h.

^a 95:5 *cis:trans* ratio of $\text{R-BF}_3\text{K}$ employed in reaction.

Table 5

Scope of the Reaction with Potassium Alkyltrifluoroborates.

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 SiCl₄, 1:1 Tol/CPME, 40 °C, 18 h.^a Reaction completed on 5 mmol scale.

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

entry	product	yield (%)
1		79
2		61
3		55 ^a
4		71
5		40
6		0

Reaction conditions (unless otherwise noted): 1.5 equiv of amine, 1.0 equiv of aryltrifluoroborate, 1.0 equiv of SiCl₄, 1:1 Tol/CPME, 60 °C, 4 h.

^a Reaction temperature of 40 °C, 18 h.

Table 7

Scope of the Reaction with Substituted 2-Aminostyrenes.

entry	product	yield (%)
1		64
2		73
3		75
4		59

Reaction conditions (unless otherwise noted): 1.5 equiv of amine, 1.0 equiv of aryltrifluoroborate, 1.0 equiv of SiCl_4 , 1:1 Tol/CPME, 60 $^\circ\text{C}$, 4 h.

Table 8

Scope of the Reaction with 2-Aminostyrene.

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% ^b

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 Tol/CPME, 40 °C, 18 h.

^b Without 1.5 equiv of NEt_3