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Accessing 2,1-Borazaronaphthols: Self-Arylation of 1-Alkyl-2-aryl-3-bromo-2,1-borazaronaphthalenes

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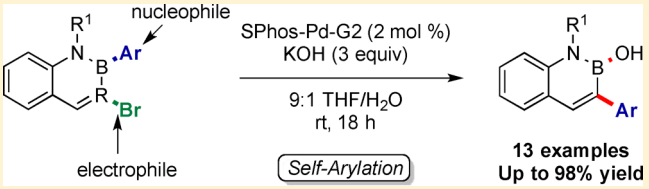
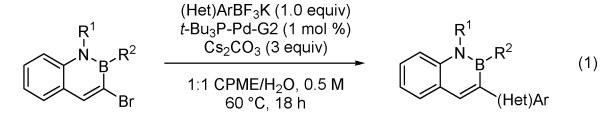
Supporting Information

ABSTRACT: Unlike their *B*-alkyl counterparts, brominated *N*-alkyl *B*-aryl 2,1-borazaronaphthalenes undergo a self-arylation reaction in the presence of a catalytic amount of palladium and base, in which the azaborine serves as both the electrophile and the nucleophile. The products of the self-arylation are air- and moisture-stable 2,1-borazaronaphthols, previously only observed in basic alcoholic solvents. The steric encumbrance of the azaborine appears to prevent formation of the corresponding boron acid anhydride, allowing access to a family of 2,1-borazaronaphthol derivatives.



INTRODUCTION

Upon developing a rapid and efficient synthesis of 2,1-borazaronaphthalenes starting from simple, readily available starting materials,[1] we subsequently developed the Suzuki–Miyaura cross-coupling of brominated 2,1-borazaronaphthalenes with potassium (hetero)aryltrifluoroborates.[2] These studies demonstrated the stability of these azaborines[3] to transition metal catalysis and allowed access to functionalized molecules that could have applications in medicinal chemistry[4] and/or materials science.[5] During the course of this latter study, we first developed conditions for the cross-coupling of *N*-H and *N*-alkyl 3-bromo-*B*-***alkyl***-2,1-borazaronaphthalenes (eq 1).



(1)

R^1 = H, R^2 = Alkyl
R^1 = H, R^2 = Aryl
R^1 = Alkyl, R^2 = Alkyl

At the same time, we investigated the cross-coupling of *B*-***aryl*** 2,1-borazaronaphthalenes with potassium (hetero)-aryltrifluoroborates (eq 1), which was perceived at the outset to present a challenge. In this cross-coupling, both the azaborine and the aryltrifluoroborate would appear to have the potential to serve as a nucleophilic component in cross-coupling reactions, unlike the cross-coupling of the *B*-***alkyl*** 2,1-borazaronaphthalenes, where the aryltrifluoroborate was expected to react preferentially on the basis of a more facile, rate-determining transmetalation.[6] Thus, during cross-coupling events, aryltrifluoroborates are slowly converted to the corresponding tricoordinate boronic acids, which are believed to be the active transmetalation species[7] and are capable of undergoing transmetalation by interacting with an oxo-palladium species to form a tetracoordinate "ate" complex.[8] Similarly, the boron of the 2,1-borazaronaphthalene is also formally tricoordinate, although in this instance contribution of electron density from the nitrogen lone-pair would render the boron less Lewis acidic, in consonance with the aromaticity of the borazine substructure.

In fact, attempts to cross-couple an *N*-substituted 3-bromo-2-***aryl***-2,1-borazaronaphthalene with potassium phenyltrifluoroborate resulted in complete conversion to a side product under the standard reaction conditions. Upon lowering the reaction temperature to room temperature, a mixture of the desired product and the same unknown side product was observed. After removing the nucleophilic component of the reaction (i.e., the potassium phenyltrifluoroborate), unreacted starting material and the same unknown side product were evident after 24 h, demonstrating that the phenyltrifluoroborate was not directly involved in this reaction.

Paetzold previously reported that the aryl group of 2-pentafluorophenyl-2,1-borazaronaphthalene could be displaced upon heating in KOH/MeOH, forming the corresponding 2-methoxy-2,1-borazaronaphthalene.[9] On the basis of the chemical shift in the ^{11}B NMR of our cross-coupling reactions, formation of a 2,1-borazaronaphthalene product containing a B-OR bond appeared possible; however, stability tests, in addition to the successful cross-coupling of other brominated azaborines, demonstrated the inherent stability of the brominated 2,1-borazaronaphthalenes to the basic conditions of the cross-coupling. These results suggested that the process observed was palladium mediated.

By realizing that the brominated 2,1-borazaronaphthalene can serve as both the nucleophile and electrophile in a cross-coupling reaction, a "self-arylation" process became evident. After oxidative addition of the C–Br bond to the palladium

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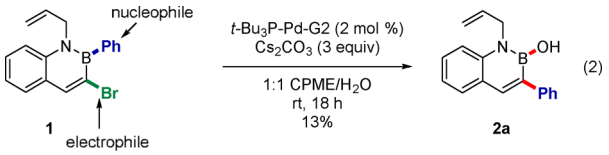
catalyst, transmetalation of the aryl group on boron of the borazine would lead to C−C bond formation and result in formation of a B−OH bond. This self-arylation proceeded in low yield under the initial conditions, providing the product in only 13% yield (eq 2). On the basis of this initial result, we



sought to determine if this transformation could be developed into a viable synthetic protocol for the construction of 3-aryl-2,1-borazaronaphthols

RESULTS AND DISCUSSION

Optimization of the self-arylation of **1** was conducted with the aid of high-throughput experimentation (HTE).[10] A 24-well plate was designed to test the ligand, base, and ratio of solvent to water in the self-arylation. The results were analyzed by HPLC after addition of an internal standard. The product-to-internal standard (P/IS) ratios were calculated to determine the relative amount of product formed in each microscale reaction (10 μmol). The results of this screen are displayed in Figure 1.

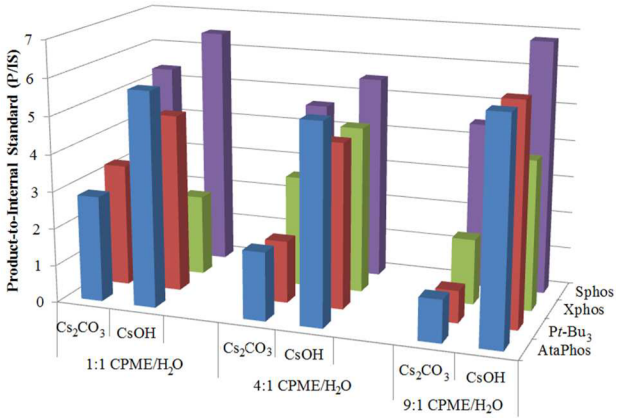


Figure 1. Graphical summary of screen 1. Reaction conditions: 1 mol % aminobiphenyl Pd μ-Cl dimer, 2 mol % ligand, 1.0 equiv of 1-allyl-3-bromo-2-phenyl-2,1-borazaronaphthalene, 3.0 equiv of base, rt, 18 h.

During the transmetalation step of a cross-coupling involving organoborons, an oxo-palladium complex interacts with the vacant orbital on boron. Because the Lewis acidity of the boron center in 2,1-borazaronaphthalenes is attenuated by electron donation from nitrogen, transmetalation is more difficult. Jutand[8a,b] and Hartwig[8c] have both reported that hydroxide bases provide the best conversion to product for cross-couplings in which the rate-determining step is the transmetalation. Hydroxide bases increase the formation of the more reactive ArPd(OH)L complex, which undergoes transmetalation at a faster rate relative to the corresponding ArPd(X)L complex. Utilizing this information, CsOH was employed as a base in the screen, providing the largest increase in conversion across the board when compared with results using Cs_2CO_3.

Of the ligands tested, SPhos provided the highest P/IS ratio with a solvent system of 9:1 cyclopentyl methyl ether (CPME)/H_2O. Further optimization showed that switching the solvent from CPME to THF resulted in higher conversion to the desired product, and switching the base from CsOH to KOH had no major effect on the reaction. The (SPhos)-(aminobiphenyl) palladium chloride precatalyst (commercially available SPhos-Pd-G2, Figure 2) was employed as the palladium source when the self-arylation was scaled from the HTE screen.

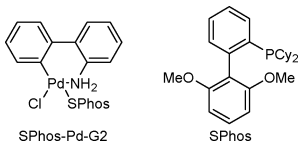
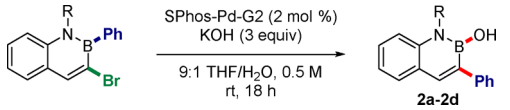
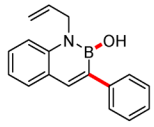
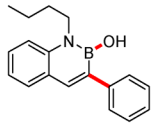
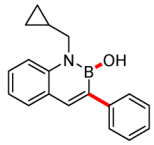
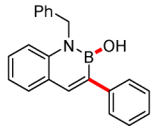


Figure 2. Structures of SPhos-Pd-G2 and SPhos.

The developed conditions were applied to an array of 1-***alkyl***-3-bromo-2-phenyl-2,1-borazaronaphthalenes. Varying the group on nitrogen does not affect the self-arylation as the corresponding products are obtained in yields up to 98% (Table 1). The scalable nature of the coupling was illustrated by

Table 1. Scope of the Self-Arylation of 1-Alkyl-3-bromo-2-phenyl-2,1-borazaronaphthalenes[b]



entry	product		yield
1		**2a**	94% (96%)[a]
2		**2b**	96%
3		**2c**	98%
4		**2d**	97%

[a]Reaction performed on a 2.5 mmol scale with 1 mol % SPhos-Pd-G2
[b]Reaction conditions (unless otherwise noted): 1.0 equiv of 1-alkyl-3-bromo-2-phenyl-2,1-borazaronaphthalene, 2 mol % SPhos-Pd-G2, 3.0 equiv of base, 9:1 THF/H_2O, rt, 18 h.

performing the reaction on 2.5 mmol, which afforded the self-arylated product in 96% yield while at the same time allowing half of the palladium loading (1 mol %) used in smaller scale reactions.

The isolation of 2,1-borazaronaphthols has not been reported in the literature. In fact, until this study, 2,1-borazaronaphthol was only shown to exist in basic ethanol solution, forming the corresponding anhydride in the solid state (eq 3).[11] In the current study, steric encumbrance provided by substitution of the azaborine at the 1 and 3 positions apparently

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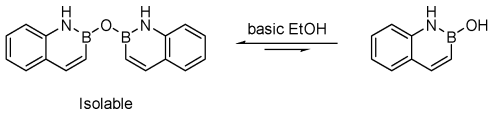


(3)

inhibits anhydride formation, allowing the corresponding 2,1-borazaronaphthols to be isolated in high yield.

Although 2,1-borazaronaphthols were found to decompose on silica gel, surprisingly, they can be converted to their respective anhydrides (to various extents) upon column chromatography with Florisil. The formation of the anhydride was confirmed by passing **2d** through Florisil and obtaining an X-ray structure of the product (Figure 3).

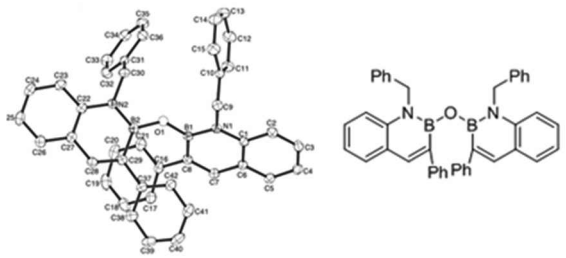
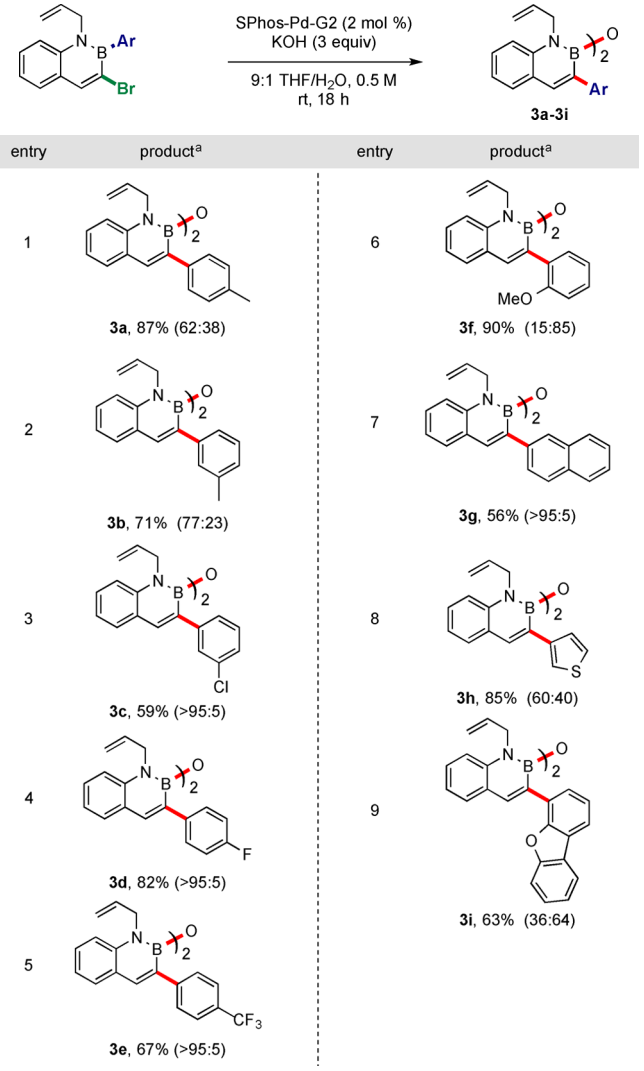


Figure 3. X-ray structure of bis(1-benzyl-3-phenyl-2,1-borazaro-2-naphthyl) ether.

An array of 1-allyl-2-***(hetero)aryl***-3-bromo-2,1-borazaronaphthalenes was subsequently subjected to the standard conditions to ascertain the scope of this novel process (Table 2). After purification with Florisil, many of the products were isolated as mixtures of the anhydride and the monomer. Fortunately, it was discovered that subjecting the anhydride to basic aqueous THF (3 equiv KOH in THF/H_2O) converted the anhydride to the corresponding 2,1-borazaronaphthol. Aryl groups with both electron-donating (entries 1, 2, and 6) and electron-withdrawing groups (entries 3–5) underwent self-arylation in yields up to 90%. The aryl group can be substituted *ortho-* (entry 6), *meta-* (entries 2–3), and *para-* (entries 1, 4–5) to afford the desired products in high yield. The enhanced reactivity of the azaborinyl bromide relative to an aryl halide is evident through self-arylation of the 3-bromo-2,1-borazaronaphthalene that has an embedded aryl chloride (entry 3). Further, heteroaryl groups, specifically thienyl and dibenzofuryl, can be transferred to the 3-position in yields of 85% and 63%, respectively (entries 8–9).

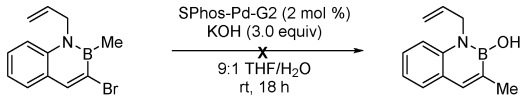
To probe the mechanism of the self-arylation, a crossover experiment was conducted with two brominated azaborines possessing similar substitution patterns. Subjecting both azaborines to the same reaction conditions resulted in complete conversion of both starting materials. HPLC analysis showed formation of all four possible arylated products (self-arylated and cross-arylated) in approximately equal amounts, confirming that the self-arylation observed is an intermolecular process (eq 4).

Table 2. Scope of the Self-Arylation of 1-Allyl-2-aryl-3-bromo-2,1-borazaronaphthalenes[b]

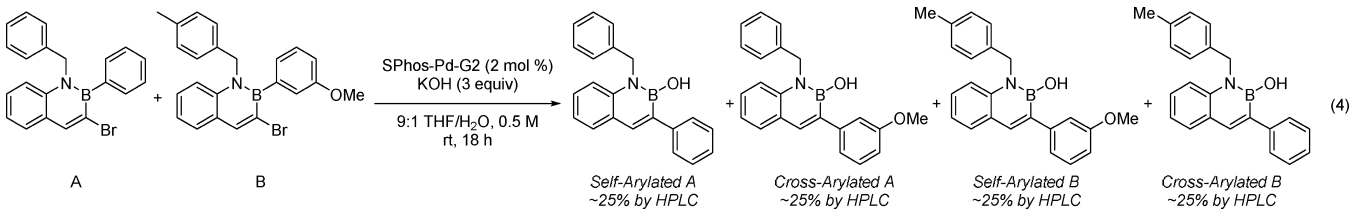


[a]Reported as the ratio of anhydride:monomer [b]Reaction conditions (unless otherwise noted): 1.0 equiv of 1-allyl-2-aryl-3-bromo-2,1-borazaronaphthalene, 2 mol % SPhos-Pd-G2, 3.0 equiv of base, 9:1 THF/H_2O, rt, 18 h.

An *N*-substituted *B-**alkyl*** 3-bromo-2,1-borazaronaphthalene was subjected to the developed self-arylation conditions. Because the C_{alkyl}–B bond is stronger than the C_{aryl}–B bond,[12] transmetalation is more challenging. As expected, the azaborine did not undergo self-alkylation, and only unreacted starting material was observed after 18 h (eq 5).



(5)



(4)

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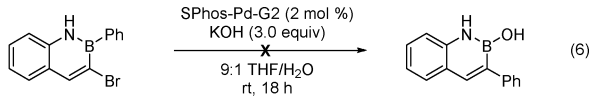
Further, subjecting the free *N*-H 3-bromo-2-phenyl-2,1-borazaronaphthalene to the reaction conditions did not produce the self-arylated product (eq 6). The starting material was consumed in the reaction but an array of products was observed by crude NMR.



This result suggested that substitution on nitrogen is required for the self-arylation to proceed smoothly, creating an environment suitable for self-arylation. Several lines of investigation were carried out in an attempt to rationalize this phenomenon. One contributing factor in these systems was postulated to be the difference in strength of the B−C_{aryl} bond in the *N*-H versus the *N*-substituted azaborines. To clarify this hypothesis, a series of calculations, conducted at the B3LYP/6-31G(d,p) level of theory, were completed to determine the relative bond order of the B−C_{aryl} bonds (Figure 4). The

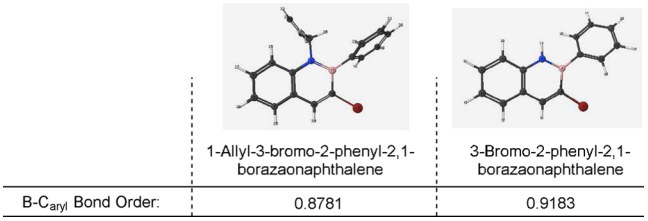


Figure 4. Optimized geometry and bond orders for *N*-allyl and *N*-H 2,1-borazaronaphthalenes (calculated at the B3LYP/6-31G(d,p) level of theory).

calculations revealed that the B−C_{aryl} bond was weaker in the case of the *N*-allyl 2,1-borazaronaphthalene. Thus, the substituent on nitrogen in this system causes the arene to rotate such that it is no longer in plane with the azaborine, thereby decreasing molecular orbital overlap between the empty p orbital on boron of the azaborine and the arene, weakening the B−C_{aryl} bond. In comparison, the free *N*-H 2,1-borazaronaphthalene is nearly planar, resulting in better orbital overlap and a stronger B−C_{aryl} bond. (Figure 4).

Another factor postulated was the ability of the boron to interact with an oxo-palladium species to facilitate the transmetalation process. Transmetalation in the Suzuki−Miyaura cross-coupling reaction has been postulated to proceed via the formation of a tetracoordinate "ate" complex, in which the vacant orbital on boron interacts with an oxo-palladium complex.[8] Formation of the "ate" complex can be viewed as an interaction between a Lewis acidic boron source and the Lewis basic oxo-palladium species. Increasing the Lewis acidity of the boron will favor formation of the "ate" complex, thereby facilitating transmetalation. The relative Lewis acidities of the *N*-allyl and *N*-H 2,1-borazaronaphthalenes were therefore calculated as a means to determine the suitability of these entities to participate in the requisite Lewis acid−base complex formation. Because substitution on nitrogen rotates the arene out of the plane of the 2,1-borazaronaphthalene, the loss in molecular orbital overlap results in a relative charge on the boron atom of the 1-allyl-2-phenyl-2,1-borazaronaphthalene of 0.652, which is significantly greater than that of the free N−H 2-phenyl-2,1-borazaronaphthalene (0.568). In further calculations, the increased Lewis acidity of the *N*-allyl 2,1-borazaronaphthalene was also determined to favor the required "ate" complex formation by ∼2 kcal/mol over that of the N−H congener (Figure 5). This series of calculations, conducted at

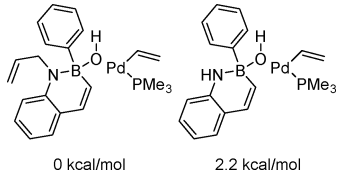
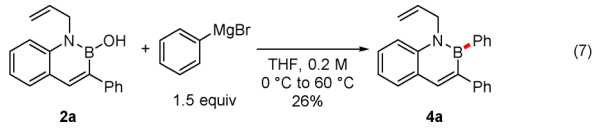


Figure 5. Relative energies of formation of Pd-'ate' complexes (calculated at the B3LYP/LANL2DZ level of theory).

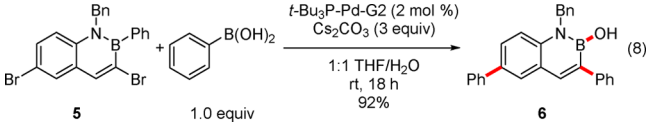
the B3LYP/LANL2DZ level of theory, used PMe_3 as a generic ligand on palladium and a vinyl group as a generic coupling partner. Although the calculations do not provide information about the mechanism of the transmetalation, they do suggest that there is an increased stability of the "ate" complex for the *N*-allyl 2,1-borazaronaphthalene relative to that of the free N−H 2,1-borazaronaphthalene.

Given that the aryl group in *N*-alkyl-*B*-aryl-3-bromo-2,1-borazaronaphthalenes was subject to competitive reaction in Suzuki-type reactions, investigations were carried out to determine how these systems could be otherwise manipulated in synthetically useful ways. Although attempts to access 1,2,3-trisubstituted-2,1-borazaronaphthalenes via cross-coupling of **1** with an external trifluoroborate were unsuccessful because mixtures of cross-coupled and self-arylated products were observed, the product of the self-arylation could be reacted with a Grignard reagent at elevated temperature to form the desired trisubstituted azaborine in low yield (eq 7).



In more successful efforts, Kumada coupling between an aryl Grignard reagent and a brominated 2,1-borazaronaphthalene afforded the 1,2,3-trisubstituted-2,1-borazaronaphthalenes in high yield with 1 mol % of the (t-Bu_3P)(aminobiphenyl) palladium chloride precatalyst (commercially available t-Bu_3P-Pd-G2, Table 3). *ortho*-, *meta*-, and *para*-Substituted aryl Grignard reagents proved to be successful nucleophiles in the reaction, and the desired products were obtained in yields up to 89% (entries 2−4). Further, the substituent on nitrogen could be changed without loss of yield (entry 5).

The next reaction investigated was the coupling of 1-benzyl-3,6-dibromo-2-phenyl-2,1-borazaronaphthalene with 1 equiv of $PhB(OH)_2$ under slightly modified conditions (eq 8). The



dibrominated azaborine underwent self-arylation in addition to a second cross-coupling with the phenylboronic acid, affording the desired product in 92% yield. The product of this dual cross-coupling was a 1,3,6-trisubstituted-2,1-borazaronaphthol, building molecular complexity by functionalizing three different borazine positions through a single operation. Attempts to

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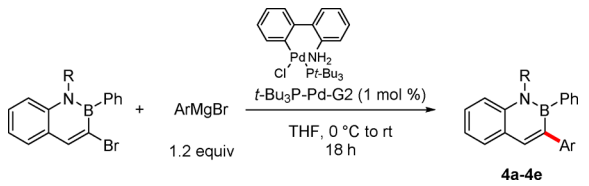
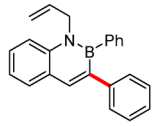
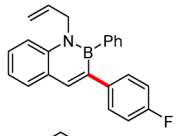
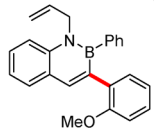
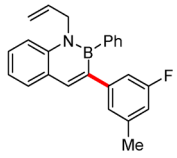
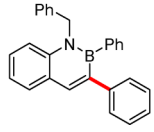
Table 3. Scope of the Kumada Coupling with Aryl Grignard Reagents[a]



entry	product		yield
1		**4a**	84%
2		**4b**	89%
3		**4c**	73%
4		**4d**	79%
5		**4e**	85%

[a]Reaction conditions (unless otherwise noted): 1.0 equiv of 1-allyl-3-bromo-2-phenyl-2,1-borazaronaphthalene, 1.2 equiv of ArMgBr, 1 mol % *t*-Bu_3P-Pd-G2, THF, 0 °C to rt, 18 h.

employ arylboronic acids that were structurally different from the B-aryl group embedded within the borazaronaphthalene resulted in a mixture of cross-coupled products because no site-selectivity could be achieved in reactions of the two incorporated bromides.

To confirm that the dibrominated azaborine underwent a dual cross-coupling, a crystal structure was obtained for **6** (Figure 6). Interestingly, the X-ray structure also reveals that looking at the molecule with a 90° rotation such that it is lying horizontal, the B−N ring of the 2,1-borazaronaphthalene is not completely planar, with the boron atom being located approximately 0.15 Å or ∼3.5° out of plane.

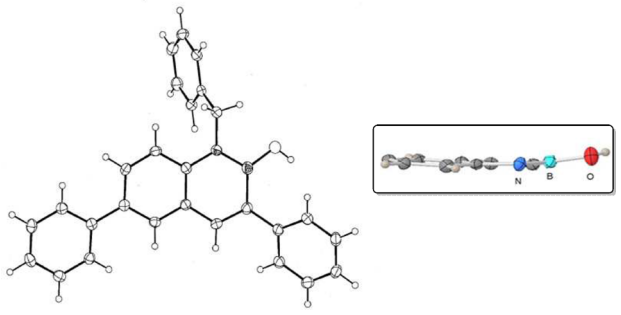


Figure 6. X-ray structure of 1-benzyl-3,6-diphenyl-2,1-borazaronaphthol (left). Rotated to show the nonplanarity of the B−N ring without substituents at 1, 3, and 6-positions (right).

CONCLUSIONS

The self-arylation of N-substituted 3-bromo-2,1-borazaronaphthalenes has been reported to proceed in high yield under mild reaction conditions. The products of the self-arylation are air- and moisture-stable 2,1-borazaronaphthols, the first isolable examples of this class of azaborine. To the best of our knowledge, this self-arylation is the first report demonstrating the ability of brominated azaborines to serve as both the nucleophile and electrophile in cross-coupling reactions. The 2,1-borazaronaphthols are converted to their corresponding anhydrides upon purification with Florisil, but they can be hydrolyzed back to the 2,1-borazaronaphthols by subjecting the anhydride to basic aqueous THF. The corresponding 1,2,3-trisubstituted-2,1-borazaronaphthalenes can be afforded by performing a Kumada coupling with an aryl Grignard reagent. The overall value of the synthetic method described herein can be highlighted by comparison with the synthesis of isosteric naphthalene derivatives. Accessing 3-arylnaphth-2-ols through cross-coupling at the 3-position requires protection and deprotection of the alcohol,[13] whereas the self-arylation alleviates the need for protecting group manipulation to afford the isosteric azaborine in a single step.

EXPERIMENTAL SECTION

General Considerations. *t*-Bu_3P-Pd-G2 and SPhos-Pd-G2 were synthesized according to the literature.[14] THF was dried using a J. C. Meyer solvent system with passage through two columns of activated alumina. Standard benchtop techniques were employed for handling air-sensitive reagents. Melting points (°C) are uncorrected. NMR spectra were recorded on a 400 or 500 MHz spectrometer. ^{19}F NMR chemical shifts were referenced to external $CFCl_3$ (0.0 ppm). ^{11}B NMR spectra were obtained on a spectrometer equipped with the appropriate decoupling accessories. All ^{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. 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. Visualization of the TLC plates was effected with ultraviolet light. Standard flash chromatography[15] procedures were followed using 100−200 mesh Florisil. HRMS data were obtained by either ESI or CI using a TOF mass spectrometer. For HRMS of most anhydrides, ionization of the sample resulted in dissociation to the monomer, which was found within 5 ppm.

Synthesis of 1-Alkyl-2-aryl-3-bromo-2,1-borazaronaphthalenes. The 1-alkyl-2-aryl-3-bromo-2,1-borazaronaphthalenes were prepared according to the literature.[1,2]

1-Allyl-3-bromo-2-(4-methylphenyl)-2,1-borazaronaphthalene. Obtained as an off-white solid (0.4 mmol scale, 100 mg, 74%). Mp: 86−88 °C. ^{1}H NMR (500 MHz, acetone-d_6) δ 8.49 (s, 1H), 7.77−7.73 (m, 1H), 7.62−7.54 (m, 2H), 7.38 (d, J = 6.3 Hz, 2H), 7.30−7.20 (m, 3H), 6.03−5.94 (m, 1H), 5.13 (d, J = 10.3 Hz, 1H), 4.91 (d, J = 17.3 Hz, 1H), 4.73−4.71 (m, 2H), 2.36 (s, 3H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 146.0, 140.1, 137.3, 135.2, 131.6, 129.6, 128.9, 128.1, 126.4, 121.8, 117.1, 115.2, 51.4, 20.6. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 37.2. IR (neat) 3013, 2920, 1607, 1367, 918, 764 cm^{-1}. HRMS (CI) m/z calc. for $C_{18}H_{18}BBrN$ $[M + H]^+$ 338.0716, found 338.0712.

1-Allyl-3-bromo-2-(4-fluorophenyl)-2,1-borazaronaphthalene. Obtained as an off-white solid (0.74 mmol scale, 141 mg, 56%). Mp: 63−65 °C. ^{1}H NMR (500 MHz, acetone-d_6) δ 8.50 (s, 1H), 7.77 (d, J

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= 7.8 Hz, 1H), 7.63−7.50 (m, 4H), 7.32−7.28 (m, 1H), 7.21−7.16 (m, 2H), 6.04−5.97 (m, 1H), 5.14 (dd, J = 10.5, 1.2 Hz, 1H), 4.91 (dd, J = 17.4, 1.2 Hz, 1H), 4.71−4.69 (m, 2H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 162.8 (d, J = 244 Hz), 146.2, 140.0, 135.0, 133.7 (d, J = 8.8 Hz), 129.7, 129.0, 126.4, 122.0, 117.1, 115.3, 114.3 (d, J = 20.1 Hz), 51.4. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 36.3. IR (neat) 3066, 1595, 1370, 920, 764 cm^{-1}. HRMS (CI) m/z calc. for $C_{17}H_{14}BBrFN$ $[M]^+$ 341.0387, found 341.0380.

1-Allyl-3-bromo-2-(4-trifluoromethylphenyl)-2,1-borazaronaphthalene. Obtained as a yellow oil (1.7 mmol scale, 230 mg, 35%). ^{1}H NMR (500 MHz, acetone-d_6) δ 8.49 (s, 1H), 7.77−7.73 (m, 3H), 7.70−7.67 (m, 2H), 7.62−7.56 (m, 2H), 7.32−7.27 (m, 1H), 6.00−5.95 (m, 1H), 5.13 (d, J = 10.5 Hz, 1H), 4.90 (d, J = 17.4 Hz, 1H), 4.66−4.64 (m, 2H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 146.5, 139.8, 134.7, 132.1, 129.8, 129.4 (q, J = 32 Hz), 129.2, 126.5, 124.6 (q, J = 271 Hz), 124.0 (q, J = 3.8 Hz), 122.2, 117.0, 115.6, 51.5. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 35.8. IR (neat) 2959, 1323, 1123, 1071, 832, 764 cm^{-1}. HRMS (CI) m/z calc. for $C_{18}H_{14}BBrF_3N$ $[M]^+$ 391.0355, found 391.0345.

1-Allyl-3-bromo-2-(3-methylphenyl)-2,1-borazaronaphthalene. Obtained as a yellow oil (1.7 mmol scale, 505 mg, 88%). ^{1}H NMR (500 MHz, acetone-d_6) δ 8.48 (s, 1H), 7.74 (d, J = 7.8 Hz, 1H), 7.59−7.53 (m, 2H), 7.32−7.26 (m, 4H), 7.19 (d, J = 6.6 Hz, 1H), 6.00−5.94 (m, 1H), 5.12 (dd, J = 10.5, 1.2 Hz, 1H), 4.90 (dd, J = 17.4, 1.2 Hz, 1H), 4.70−4.68 (m, 2H), 2.35 (s, 3H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 146.1, 140.0, 136.4, 135.1, 132.0, 129.6, 129.0, 128.5, 128.5, 127.4, 126.4, 121.8, 117.0, 115.3, 51.4, 20.9. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 37.5. IR (neat) 2980, 1546, 1367, 763, 744 cm^{-1}. HRMS (CI) m/z calc. for $C_{18}H_{17}BBrN$ $[M]^+$ 337.0637, found 337.0636.

1-Allyl-3-bromo-2-(3-chlorophenyl)-2,1-borazaronaphthalene. Obtained as a yellow oil (1.14 mmol scale, 300 mg, 74%). ^{1}H NMR (500 MHz, acetone-d_6) δ 8.51 (s, 1H), 7.78 (dd, J = 7.8, 1 Hz, 1H), 7.63−7.56 (m, 2H), 7.50 (s, 1H), 7.42−7.39 (m, 3H), 7.33−7.29 (m, 1H), 6.03−5.98 (m, 1H), 5.15 (dd, J = 10.8, 1.2 Hz, 1H), 4.91 (dd, J = 17.4, 1.2 Hz, 1H), 4.70−4.67 (m, 2H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 146.4, 139.8, 134.8, 133.3, 131.0, 129.8, 129.7, 129.4, 129.2, 127.8, 126.5, 122.1, 117.1, 115.5, 51.5. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 35.9. IR (neat) 3058, 1545, 1366, 1242, 764 cm^{-1}. HRMS (CI) m/z calc. for $C_{17}H_{14}BNClBr$ $[M]^+$ 357.0091, found 357.0098.

1-Allyl-3-bromo-2-(2-methoxyphenyl)-2,1-borazaronaphthalene. Obtained as a yellow oil (0.6 mmol scale, 142 mg, 67%). ^{1}H NMR (500 MHz, acetone-d_6) δ 8.45 (s, 1H), 7.75 (d, J = 7.6 Hz, 1H), 7.63−7.60 (m, 1H), 7.57−7.53 (m, 1H), 7.39−7.34 (m, 1H), 7.29−7.25 (m, 2H), 7.02−6.98 (m, 2H), 5.95−5.89 (m, 1H), 5.09 (d, J = 10.5 Hz, 1H), 4.96 (d, J = 17.4 Hz, 1H), 4.77−4.69 (m, 1H), 4.65−4.58 (m, 1H), 3.72 (s, 3H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 160.8, 145.2, 140.0, 135.0, 132.0, 129.6, 129.5, 128.7, 126.5, 121.7, 120.3, 116.8, 115.4, 109.9, 54.7, 51.6. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 37.1. IR (neat) 2948, 1596, 1366, 1235, 762 cm^{-1}. HRMS (CI) m/z calc. for $C_{18}H_{17}BBrNO$ $[M]^+$ 353.0587, found 353.0598.

1-Allyl-3-bromo-2-(2-naphthyl)-2,1-borazaronaphthalene. Obtained as a yellow oil (0.56 mmol scale, 86 mg, 41%). ^{1}H NMR (500 MHz, acetone-d_6) δ 8.55 (s, 1H), 8.02 (s, 1H), 7.94−7.89 (m, 3H), 7.8 (dd, J = 7.9, 1.3 Hz, 1H), 7.65−7.57 (m, 3H), 7.53−7.49 (m, 2H), 7.34−7.30 (m, 1H), 6.04−5.97 (m, 1H), 5.15 (dd, J = 10.5, 1.2 Hz, 1H), 4.94 (dd, J = 17.4, 1.2 Hz, 1H), 4.75−4.73 (m, 2H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 146.2, 140.0, 135.1, 133.2. 133.0, 131.3, 129.7, 129.1, 128.9, 128.0, 127.6, 126.6, 126.5, 125.9, 125.8, 122.0, 117.1, 115.3, 51.5. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 36.8. IR (neat) 3054, 1545, 1370, 1226, 819, 764, 748 cm^{-1}. HRMS (CI) m/z calc. for $C_{21}H_{17}BBrN$ $[M]^+$ 373.0637, found 373.0644.

1-Allyl-3-bromo-2-(3-thienyl)-2,1-borazaronaphthalene. Obtained as an off-white solid (1.7 mmol, 210 mg, 37%). Mp: 69−71 °C. ^{1}H NMR (500 MHz, acetone-d_6) δ 8.46 (s, 1H), 7.76−7.70 (m, 1H), 7.64−7.50 (m, 4H), 7.37−7.26 (m, 2H), 6.08−6.02 (m, 1H), 5.16 (d, J = 10.3 Hz, 1H), 4.92 (d, J = 17.4 Hz, 1H), 4.75−4.71 (m, 2H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 146.0, 140.2, 135.4, 131.2, 129.6, 129.5, 129.0, 126.3, 124.7, 121.9, 117.0, 115.3, 51.5. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 36.0. IR (neat) 3066, 1545, 1365, 1237, 763, 707 cm^{-1}. HRMS (ESI) m/z calc. for $C_{15}H_{14}BBrNS$ $[M + H]^+$ 330.0123, found 330.0117.

1-Allyl-3-bromo-2-(4-dibenzofuryl)-2,1-borazaronaphthalene. Obtained as an off-white solid (0.64 mmol scale, 230 mg, 87%). Mp: 48−50 °C. ^{1}H NMR (500 MHz, acetone-d_6) δ 8.57 (s, 1H), 8.15−8.10 (m, 2H), 7.84 (d, J = 7.8 Hz, 1H), 7.69−7.67 (m, 1H), 7.62−7.60 (m, 1H), 7.56 (d, J = 7.1 Hz, 1H), 7.53−7.51 (m, 1H), 7.47−7.43 (m, 2H), 7.38−7.33 (m, 2H), 5.98−5.90 (m, 1H), 5.06 (dd, J = 10.5, 1.2 Hz, 1H), 4.94 (dd, J = 17.4, 1.2 Hz, 1H), 4.84−4.79 (m, 1H), 4.72−4.68 (m, 1H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 157.5, 156.0, 146.1, 140.0, 134.7, 130.3, 129.8, 129.1, 127.1, 126.7, 124.2, 122.9, 122.7, 122.7, 122.2, 120.8, 120.8, 117.0, 115.6, 111.4, 51.9. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 37.2. IR (neat) 3055, 2910, 1368, 1187, 757 cm^{-1}. HRMS (CI) m/z calc. for $C_{23}H_{17}BBrNO$ $[M]^+$ 413.0587, found 413.0570.

3-Bromo-1-butyl-2-phenyl-2,1-borazaronaphthalene. Obtained as an off-white solid (1 mmol scale, 242 mg, 71%,). Mp: 55−57 °C. ^{1}H NMR (500 MHz, acetone-d_6) δ 8.45 (s, 1H), 7.78−7.71 (m, 2H), 7.64−7.58 (m, 1H), 7.50−7.35 (m, 5H), 7.33−7.27 (m, 1H), 4.09−4.04 (m, 2H), 1.72−1.66 (m, 2H), 1.23−1.17 (m, 2H), 0.77−0.73 (m, 3H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 145.7, 139.9, 131.4, 129.9, 129.1, 127.5, 127.4, 126.6, 121.7, 116.0, 48.6, 31.9, 19.6, 12.9. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 37.4. IR (neat) 3066, 3032, 1596, 1223, 765 cm^{-1}. HRMS (CI) m/z calc. for $C_{18}H_{19}BrBN$ $[M]^+$ 339.0794, found 339.0807.

3-Bromo-1-cyclopropylmethyl-2-phenyl-2,1-borazaronaphthalene. Obtained as an off-white solid (3 mmol scale, 371 mg, 37%). Mp: 73−75 °C. ^{1}H NMR (500 MHz, acetone-d_6) δ 8.45 (s, 1H), 7.87 (d, J = 8.8 Hz, 1H), 7.78−7.75 (m, 1H), 7.65−7.61 (m, 1H), 7.48−7.30 (m, 6H), 4.05 (d, J = 6.4 Hz, 2H), 1.24−1.20 (m, 1H), 0.37−0.33 (m, 2H), $^-$0.02-$^-$0.05 (m, 2H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 145.8, 140.2, 132.0, 129.8, 129.1, 127.6, 127.4, 126.6, 121.8, 116.6, 52.4, 11.0, 4.0. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 37.2. IR (neat) 3008, 1546, 1363, 764, 704 cm^{-1}. HRMS (CI) m/z calc. for $C_{18}H_{18}BBrN$ $[M + H]^+$ 338.0716, found 338.0714.

1-Benzyl-3,6-dibromo-2-phenyl-2,1-borazaronaphthalene. Obtained as an off-white solid (710 mg, 95%, 2 mmol scale). Mp: 156−158 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.79 (s, 1H), 7.47−7.42 (m, 3H), 7.38−7.35 (m, 3H), 7.32−7.20 (m, 4H), 7.05−7.02 (m, 2H), 5.32 (s, 2H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 145.1, 138.9, 137.8, 131.5, 131.4, 128.8, 128.2, 128.1, 127.6, 127.1, 125.5, 123.7, 119.1, 114.7, 53.6. ^{11}B NMR (128.38 MHz, $CDCl_3$) δ 34.4. IR (neat) 3065, 3029, 2920, 1536, 1367, 1355, 1242, 816 cm^{-1}. HRMS (CI) m/z calc. for $C_{21}H_{16}BBr_2N$ $[M]^+$ 450.9743, found 450.9748.

General Procedure for the Self-Arylation of 1-Alkyl-2-aryl-3-bromo-2,1-borazaronaphthalenes. To a Biotage microwave vial equipped with a stir bar was successively introduced SPhos-Pd-G2 (7.2 mg, 10 μmol, 2 mol %), KOH (84 mg, 1.5 mmol, 3 equiv), and 3-bromo-2-aryl-2,1-borazaronaphthalene (0.50 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. Anhydr. degassed THF (0.9 mL) and degassed H_2O (0.1 mL) were added under Ar, and the vial was stirred at rt for 18 h. The reaction was diluted with H_2O (2 mL), extracted with EtOAc (3 × 2 mL), and dried ($MgSO_4$). The solvent was removed *in vacuo*, and the product was purified by flash column chromatography on Florisil using a 0 to 40% CH_2Cl_2/hexane as the eluent to yield the anhydride. The column was flushed successively with 100% CH_2Cl_2 and 100% EtOAc to yield the 2,1-borazaronaphthol. For reactions that went to completion without side-product formation, crude reaction mixtures were passed through a plug of Florisil to afford the desired product. Characterization of monomer and/or anhydride is provided for each self-arylated product. For those compounds in which complete separation was achieved, both the monomer and anhydride were characterized.

*1-Allyl-3-phenyl-2,1-borazaronaphthol (**2a**).* Obtained as a yellow oil (123 mg, 94%). ^{1}H NMR (500 MHz, acetone-d_6) δ 7.80 (s, 1H), 7.61 (d, J = 7.8 Hz, 1H), 7.49−7.45 (m, 2H), 7.42−7.33 (m, 4H), 7.30−7.26 (m, 1H), 7.08−7.04 (m, 1H), 6.64 (br s, 1H), 6.07−6.00

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(m, 1H), 5.12−5.07 (m, 2H), 4.75−4.70 (m, 2H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 143.2, 142.7, 141.6, 135.4, 130.0, 128.4, 128.2, 127.7, 126.2, 124.3, 119.2, 114.6, 114.5, 44.7. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 28.5. IR (neat) 3629, 3066, 2980, 1384, 759 cm^{-1}. HRMS (ESI) m/z calc. for $C_{17}H_{17}BNO$ $[M + H]^+$ 262.1403, found 262.1408.

*1-Butyl-3-phenyl-2,1-borazaronaphthol (**2b**).* Obtained as a yellow oil (133 mg, 96%). ^{1}H NMR (500 MHz, acetone-d_6) δ 7.78 (s, 1H), 7.63−7.60 (m, 1H), 7.49−7.38 (m, 6H), 7.29−7.25 (m, 1H), 7.10−7.05 (m, 1H), 6.54 (s, 1H), 4.11−4.05 (m, 2H), 1.74−1.70 (m, 2H), 1.53−1.43 (m, 2H), 1.00−0.93 (m, 3H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 143.0, 142.9, 141.6, 130.3, 128.5, 128.4, 127.8, 126.2, 124.4, 119.0, 113.8, 42.2, 31.2, 20.1, 13.4. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 29.2. IR (neat) 3635, 2957, 2870, 1387, 760 cm^{-1}. HRMS (CI) m/z calc. for $C_{18}H_{20}BNO$ $[M]^+$ 277.1638, found 277.1636.

*1-Cyclopropylmethyl-3-phenyl-2,1-borazaronaphthol (**2c**).* Obtained as a yellow oil (135 mg, 98%). ^{1}H NMR (500 MHz, acetone-d_6) δ 7.78 (s, 1H), 7.64−7.55 (m, 2H), 7.48−7.45 (m, 3H), 7.42−7.37 (m, 2H), 7.30−7.26 (m, 1H), 7.09−7.06 (m, 1H), 6.48 (s, 1H), 4.02−3.98 (m, 2H), 1.38−1.32 (m, 1H), 0.51−0.45 (m, 4H).^{13}C NMR (125.8 MHz, acetone-d_6) δ 143.2, 142.9, 141.9, 130.3, 128.5, 128.4, 127.7, 126.2, 124.3, 119.0, 114.2, 46.1, 10.8, 3.5. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 29.2. IR (neat) 3627, 3019, 2916, 1381, 759 cm^{-1}. HRMS (CI) m/z calc. for $C_{18}H_{18}BNO$ $[M]^+$ 275.1481, found 275.1493.

*1-Benzyl-3-phenyl-2,1-borazaronaphthol (**2d**).* Obtained as a yellow oil (151 mg, 97%). ^{1}H NMR (500 MHz, acetone-d_6) δ 7.86 (s, 1H), 7.63 (d, J = 7.8 Hz, 1H), 7.55 (d, J = 7.3 Hz, 2H), 7.44−7.40 (m, 2H), 7.32−7.20 (m, 8H), 7.04−7.01 (m, 1H), 6.85 (s, 1H), 5.35 (s, 2H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 143.4, 142.7, 141.7, 139.4, 130.1, 128.6, 128.5, 128.4, 127.8, 126.5, 126.3, 126.3, 124.5, 119.4, 115.0, 46.3. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 29.4. IR (neat) 3632, 3030, 2924, 1387, 760 cm^{-1}. HRMS (CI) m/z calc. for $C_{21}H_{18}BNO$ $[M]^+$ 311.1481, found 311.1477.

*1-Allyl-3-(4-methylphenyl)-2,1-borazaronaphthol (**3a**-Monomer).* Obtained as a yellow oil (0.26 mmol scale, 62 mg, 87%, 62:38 monomer:anhydride). ^{1}H NMR (500 MHz, acetone-d_6) δ 7.77 (s, 1H), 7.61−7.58 (m, 1H), 7.41−7.33 (m, 4H), 7.22−7.18 (m, 2H), 7.08−7.03 (m, 1H), 6.56 (s, 1H), 6.07−6.00 (m, 1H), 5.12−5.06 (m, 2H), 4.72−4.70 (m, 2H), 2.35 (s, 3H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 142.8, 141.5, 139.8, 135.6, 135.4, 129.9, 129.1, 128.0, 127.6, 124.3, 119.1, 114.6, 114.5, 44.7, 20.1. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 28.5. IR (neat) 3607, 3062, 2979, 1384, 1353, 750 cm^{-1}. HRMS (CI) m/z calc. for $C_{18}H_{18}BNO$ $[M]^+$ 275.1481, found 275.1477.

*Bis(1-allyl-3-(4-methylphenyl)-2,1-borazaro-2-naphthyl) Ether (**3a**-Anhydride).* Obtained as a yellow oil (0.26 mmol scale, 62 mg, 87%, 62:38 monomer:anhydride). ^{1}H NMR (500 MHz, acetone-d_6) δ 7.67 (s, 2H), 7.58 (d, J = 7.6 Hz, 2H), 7.40−7.36 (m, 4H), 7.10−7.05 (m, 6H), 6.89 (d, J = 7.8 Hz, 4H), 6.05−5.97 (m, 2H), 5.13 (dd, J = 10.4, 1.3 Hz, 2H), 5.04 (dd, J = 17.5, 1.3 Hz, 2H), 4.72−4.69 (m, 4H), 2.12 (s, 6H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 142.8, 141.1, 139.2, 135.2, 135.0, 129.8, 128.2, 127.9, 127.9, 124.7, 119.6, 115.0, 114.9, 45.6, 20.0. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 29.4. IR (neat) 2980, 2890, 1384, 1353, 748 cm^{-1}. HRMS (ESI) m/z calc. for $C_{18}H_{18}BNO$ $[M - C_{18}H_{16}BNO]^+$ 275.1481, found 275.1478. HRMS found for $[monomer]^+$.

*1-Allyl-3-(3-methylphenyl)-2,1-borazaronaphthol (**3b**-Monomer).* Obtained as a yellow oil (0.5 mmol scale, 98 mg, 71%, 77:23 monomer:anhydride). ^{1}H NMR (500 MHz, acetone-d_6) δ 7.78 (s, 1H), 7.61 (d, J = 7.6 Hz, 1H), 7.41−7.34 (m, 2H), 7.29−7.25 (m, 3H), 7.11−7.04 (m, 2H), 6.61 (s, 1H), 6.07−6.01 (m, 1H), 5.12−5.07 (m, 2H), 4.72−4.70 (m, 2H), 2.36 (s, 3H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 143.0, 142.6, 141.6, 137.8, 135.4, 130.5, 130.0, 128.4, 128.1, 127.0, 124.7, 124.3, 119.1, 114.6, 114.5, 44.7, 20.6. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 28.6. IR (neat) 3623, 2977, 2922, 1608, 1383, 761 cm^{-1}. HRMS (ESI) m/z calc. for $C_{18}H_{17}BNO$ $[M - H]^+$ 274.1403, found 274.1404.

*Bis(1-allyl-3-(3-methylphenyl)-2,1-borazaro-2-naphthyl) Ether (**3b**-Anhydride).* Obtained as a yellow oil (0.5 mmol scale, 98 mg, 71%, 77:23 monomer:anhydride). ^{1}H NMR (500 MHz, acetone-d_6) δ 7.61 (s, 2H), 7.56 (d, J = 7.6 Hz, 2H), 7.40−7.36 (m, 4H), 7.08 (d, J = 5.9 Hz, 2H), 6.94−6.88 (m, 6H), 6.79 (d, J = 6.8 Hz, 2H), 6.11−6.06 (m, 2H), 5.18−5.12 (m, 4H), 4.87−4.83 (m, 2H), 4.75−4.72 (m, 2H), 2.04 (s, 6H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 142.9, 141.8, 141.2, 136.8, 135.2, 129.9, 128.7, 128.1, 127.4, 126.5, 125.2, 124.6, 119.6, 115.1, 114.9, 45.7, 20.3. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 29.1. IR (neat) 3034, 2982, 1605, 1384, 1352, 760 cm^{-1}. HRMS (ESI) m/z calc. for $C_{18}H_{17}BNO$ $[M - C_{18}H_{17}BNO]^+$ 274.1403, found 274.1410. HRMS found for $[monomer-H]^+$.

*Bis(1-allyl-3-(3-chlorophenyl)-2,1-borazaro-2-naphthyl) Ether (**3c**-Anhydride).* Obtained as a yellow oil (0.45 mmol scale, 76 mg, 59%, >95:5 monomer:anhydride).^{1}H NMR (500 MHz, acetone-d_6) δ 7.66 (s, 2H), 7.58 (d, J = 7.3 Hz, 2H), 7.47−7.39 (m, 4H), 7.12−7.08 (m, 2H), 7.05−6.97 (m, 8H), 6.17−6.10 (m, 2H), 5.21−5.12 (m, 4H), 4.87−4.79 (m, 4H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 147.9, 141.4, 136.4, 134.8, 132.6, 131.4, 131.3, 131.2, 130.1, 130.7, 129.4, 128.0, 123.6, 118.6, 117.0, 51.5. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 28.8. IR (neat) 3063, 2974, 1384, 1352, 1187, 749 cm^{-1}. HRMS (ESI) m/z calc. for $C_{31}H_{24}B_2Cl_2N_2O$ $[M - C_3H_4]^+$ 532.1452, found 532.1424. HRMS found for $[M\text{-allyl}]^+$.

*Bis(1-allyl-3-(4-fluorophenyl)-2,1-borazaro-2-naphthyl) Ether (**3d**-Anhydride).* Obtained as an off-white solid (0.31 mmol scale, 71 mg, 82%, >95:5 monomer:anhydride). Mp: 120−122 °C. ^{1}H NMR (500 MHz, acetone-d_6) δ 7.66 (s, 2H), 7.58 (d, J = 7.8 Hz, 2H), 7.43−7.39 (m, 4H), 7.17−7.08 (m, 6H), 6.84−6.80 (m, 4H), 6.13−6.04 (m, 2H), 5.18 (d, J = 10.5 Hz, 2H), 5.07 (d, J = 17.1 Hz, 2H), 4.79−4.77 (m, 4H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 161.4 (d, J = 243 Hz), 143.4, 141.1, 138.2 (d, J = 3.9 Hz), 135.0, 130.0, 129.7, 129.7, 128.3, 124.4, 119.8, 115.0 (d, J = 5.0 Hz), 114.2 (d, J = 22 Hz), 45.6. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 29.2. IR (neat) 3063, 2926, 1384, 1352, 749 cm^{-1}. HRMS (CI) m/z calc. for $C_{17}H_{15}BNOF$ $[M - C_{17}H_{13}BNOF]^+$ 279.1231, found 279.1237. HRMS found for $[monomer]^+$.

*Bis(1-allyl-3-(4-trifluoromethylphenyl)-2,1-borazaro-2-naphthyl) Ether (**3e**-Anhydride).* Obtained as an off-white solid (0.5 mmol scale, 110 mg, 67%, >95:5 monomer:anhydride). Mp: 133−135 °C. ^{1}H NMR (500 MHz, acetone-d_6) δ 7.78 (s, 2H), 7.6 (d, J = 7.3 Hz, 2H), 7.48−7.37 (m, 8H), 7.28 (d, J = 7.6 Hz, 4H), 7.13−7.08 (m, 2H), 6.15−6.10 (m, 2H), 5.20 (d, J = 10.5 Hz, 2H), 5.09 (d, J = 17.1 Hz, 2H), 4.83−4.81 (m, 4H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 146.0, 144.5, 141.3, 134.9, 130.4, 128.9, 128.5, 127.5, 126.7 (q, J = 264 Hz), 124.4 (q, J = 5.0 Hz), 124.2, 120.0, 115.2, 115.1, 45.6. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 28.8. IR (neat) 3056, 3 + 36, 2384, 1324, 1110, 761 cm^{-1}. HRMS (CI) m/z calc. for $C_{18}H_{15}BF_3NO$ $[M - C_{18}H_{13}BF_3NO]^+$ 329.1199, found 329.1197. HRMS found for $[monomer]^+$.

*1-Allyl-3-(2-methoxyphenyl)-2,1-borazaronaphthol (**3f**-Monomer).* Obtained as a yellow oil (0.36 mmol scale, 94 mg, 90%, 15:85 monomer:anhydride). ^{1}H NMR (500 MHz, acetone-d_6) δ 7.70 (s, 1H), 7.58 (d, J = 7.6 Hz, 1H), 7.40−7.34 (m, 2H), 7.30−7.25 (m, 2H), 7.05−6.99 (m, 3H), 6.34 (s, 1H), 6.04−5.98 (m, 1H), 5.10 (dd, J = 13.7, 1.7 Hz, 2H), 4.72−4.70 (m, 2H), 3.83 (s, 3H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 156.4, 143.8, 141.7, 135.6, 132.0, 129.9, 129.9, 128.0, 128.0, 124.3, 120.9, 118.9, 114.5, 114.0, 110.9, 54.9, 44.6. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 29.1. IR (neat) 3628, 2980, 1386, 1352, 1187, 750 cm^{-1}. HRMS (ESI) m/z calc. for $C_{18}H_{19}BNO_2$ $[M + H]^+$ 292.1509, found 292.1501.

*Bis(1-allyl-3-(2-naphthyl)-2,1-borazaro-2-naphthyl) Ether (**3g**-Anhydride).* Obtained as an off-white solid (0.20 mmol scale, 35 mg, 56%, >95:5 monomer:anhydride). Mp: 90−92 °C. ^{1}H NMR (500 MHz, acetone-d_6) δ 7.68 (d, J = 6.4 Hz, 2H), 7.59 (s, 2H), 7.55−7.52 (m, 4H), 7.48−7.37 (m, 8H), 7.34−7.30 (m, 4H), 7.23 (d, J = 8.3 Hz, 2H), 7.06−7.01 (m, 2H), 6.19−6.11 (m, 2H), 5.22−5.14 (m, 4H), 4.93−4.83 (m, 4H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 143.6, 141.2, 139.5, 135.2, 133.3, 132.0, 130.0, 128.2, 127.6, 127.2, 126.9, 126.8, 126.3, 125.4, 125.1, 124.5, 119.6, 115.2, 115.0, 45.7. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 29.3. IR (neat) 3057, 2923, 1390, 1354,

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1215, 742 cm^{-1}. HRMS (CI) m/z calc. for $C_{21}H_{18}BNO$ [M − $C_{21}H_{16}BNO$]$^+$ 311.1481, found 311.1472. HRMS found for [monomer]$^+$.

*1-Allyl-3-(3-thienyl)-2,1-borazaronaphthol (**3h**-Monomer).* Obtained as a yellow oil (0.5 mmol scale, 114 mg, 85%, 60:40 monomer:anhydride). ^{1}H NMR (500 MHz, acetone-d_6) δ 7.99 (s, 1H), 7.63−7.58 (m, 2H), 7.49−7.46 (m, 1H), 7.45−7.42 (m, 1H), 7.39−7.32 (m, 2H), 7.08−7.04 (m, 1H), 6.70 (s, 1H), 6.07−5.97 (m, 1H), 5.11−5.04 (m, 2H), 4.72−4.70 (m, 2H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 142.1, 141.9, 141.4, 135.2, 129.9, 128.0, 127.2, 125.3, 124.3, 121.1, 119.3, 114.6, 114.4, 44.8. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 28.9. IR (neat) 3627, 3064, 2932, 1385, 1352, 1187, 750 cm^{-1}. HRMS (ESI) m/z calc. for $C_{15}H_{15}BNOS$ [M + H]$^+$ 268.0967, found 268.0978.

*1-Allyl-3-(4-dibenzofuryl)-2,1-borazaronaphthol (**3i**-Monomer).* Obtained as a yellow oil (0.5 mmol scale, 111 mg, 63%, 36:64 monomer:anhydride). ^{1}H NMR (500 MHz, acetone-d_6) δ 8.13−8.10 (m, 1H), 8.06 (s, 1H), 8.04−8.00 (m, 1H), 7.71−7.67 (m, 1H), 7.66−7.62 (m, 1H), 7.56−7.39 (m, 6H), 7.15−7.11 (m, 1H), 7.02 (m, 1H), 6.14−6.02 (m, 1H), 5.22−5.15 (m, 2H), 4.84−4.82 (m, 2H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 157.0, 154.6, 146.3, 143.1, 136.6, 131.3, 129.7, 128.5, 128.5, 128.2, 125.4, 125.2, 125.0, 124.4, 123.8, 121.8, 120.2, 120.0, 115.8, 115.8, 112.7, 45.9. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 29.0. IR (neat) 3623, 3063, 2928, 1385, 1187, 750 cm^{-1}. HRMS (ESI) m/z calc. for $C_{23}H_{19}BNO_2$ [M + H]$^+$ 352.1509, found 352.1523.

General Procedure for the Hydrolysis of Bis(1-substituted-3-aryl-2,1-borazaro-2-naphthyl) Ethers. To a Biotage microwave vial equipped with stir bar was successively introduced KOH (0.3 mmol, 3 equiv) and bis(1-allyl-3-(3-methylphenyl)-2,1-borazaro-2-naphthyl) ether (0.1 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. Anhydr. degassed THF (0.9 mL) and degassed H_2O (0.1 mL) were added under Ar, and the vial was stirred at rt for 18 h. The reaction was diluted with H_2O (1 mL), extracted with EtOAc (3 × 1 mL), and dried ($MgSO_4$). The solvent was removed *in vacuo* to yield 1-allyl-3-(3-methylphenyl)-2,1-borazaronaphthol (**3b**-monomer).

General Procedure for the Self-Arylation and Cross-Coupling of 1-Benzyl-3,6-dibromo-2-phenyl-2,1-borazaronaphthalenes. To a Biotage microwave vial equipped with a stir bar was successively introduced *t*-Bu_3P-Pd-G2 (2.3 mg, 5 μmol, 2 mol %), Cs_2CO_3 (84 mg, 1.5 mmol, 3 equiv), phenylboronic acid (31 mg, 1.0 equiv) and 1-benzyl-3,6-dibromo-2-phenyl-2,1-borazaronaphthalene (0.25 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. Anhydr degassed THF (0.6 mL) and degassed H_2O (0.6 mL) were added under Ar, and the vial was stirred at rt for 18 h. The reaction was diluted with H_2O (2 mL), extracted with EtOAc (3 × 2 mL), and dried ($MgSO_4$). The solvent was removed *in vacuo*, and the product was purified by passing through a short plug of Florisil.

*1-Benzyl-3,6-diphenyl-22,1-borazaronaphthol (**6**).* Obtained as an off-white solid (89 mg, 92%). Mp: 68−70 °C. ^{1}H NMR (500 MHz, acetone-d_6) δ 7.98−7.94 (m, 2H), 7.67 (d, J = 7.3 Hz, 2H), 7.61−7.55 (m, 3H), 7.45−7.40 (m, 4H), 7.35−7.27 (m, 7H), 7.24−7.20 (m, 1H), 6.97 (br s, 1H), 5.38 (s, 2H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 143.9, 142.9, 141.4, 140.7, 139.6, 132.3, 128.9, 128.7, 128.6, 128.3, 128.0, 127.0, 126.8, 126.7, 126.6, 126.6, 126.6, 125.0, 115.8, 45.6 ^{11}B NMR (128.38 MHz, acetone-d_6) δ 29.8. IR (neat) 3602, 3026, 1387, 763, 698 cm^{-1}. HRMS (ESI) m/z calc. for $C_{27}H_{23}BNO$ [M + H]$^+$ 388.1873, found 388.1874.

General Procedure for the Kumada Coupling of 3-Bromo-2-aryl-2,1-borazaronaphthalenes. To a Biotage microwave vial equipped with a stir bar was successively introduced *t*-Bu_3P-Pd-G2 (1.7 mg, 3.3 μmol, 1 mol %), and 3-bromo-2-aryl-2,1-borazaronaphthalene (0.33 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. Anhydr. degassed THF (0.8 mL) was added under Ar, and the vial was cooled to 0 °C. PhMgBr (1 M in THF, 0.4 mL diluted to 0.8 mL) was added dropwise over 15 min at 0 °C. The reaction was slowly warmed to rt overnight. The reaction was quenched with sat. aq NH_4Cl (0.5 mL), extracted with EtOAc (3 × 2 mL), and dried ($MgSO_4$). The solvent was removed *in vacuo*, and the product was purified by flash column chromatography on silica gel using a 0 to 20% CH_2Cl_2/hexane as the eluent.

*1-Allyl-2,3-diphenyl-2,1-borazaronaphthalene (**4a**).* Obtained as a yellow oil (89 mg, 84%). ^{1}H NMR (500 MHz, acetone-d_6) δ 8.09 (s, 1H), 7.85 (d, J = 7.8 Hz, 1H), 7.66−7.62 (m, 1H), 7.57−7.52 (m, 1H), 7.33−7.23 (m, 6H), 7.14−7.05 (m, 5H), 6.08−6.01 (m, 1H), 5.15 (d, J = 10.5 Hz, 1H), 4.98 (d, J = 17.4 Hz, 1H), 4.76−4.74 (m, 2H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 144.4, 143.0, 140.3, 135.7, 131.7, 130.4, 128.6, 128.5, 127.4, 127.2, 127.0, 126.6, 125.4, 121.3, 116.6, 115.0, 50.1. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 38.0. IR (neat) 3051, 2922, 1370, 763, 700 cm^{-1}. HRMS (CI) m/z calc. for $C_{23}H_{20}BN$ [M]$^+$ 321.1689, found 321.1684.

*1-Allyl-3-(4-fluorophenyl)-2-phenyl-2,1-borazaronaphthalene (**4b**).* Obtained as a yellow oil (101 mg, 89%). ^{1}H NMR (500 MHz, acetone-d_6) δ 8.08 (s, 1H), 7.84 (d, J = 7.6 Hz, 1H), 7.65−7.62 (m, 1H), 7.57−7.52 (m, 1H), 7.33−7.25 (m, 6H), 7.15−7.10 (m, 2H), 6.91−6.85 (m, 2H), 6.07−6.01 (m, 1H), 5.15 (d, J = 10.5 Hz, 1H), 4.97 (d, J = 17.2 Hz, 1H), 4.74−4.72 (m, 2H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 161.5 (d, J = 243 Hz), 143.3, 140.9 (d, J = 4 Hz), 140.6, 135.9, 132.0, 130.7, 130.5 (d, J = 8 Hz), 128.8, 127.5 (d, J = 20 Hz), 126.7, 121.7, 116.9, 115.3, 114.4, 114.3, 51.0. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 37.7. IR (neat) 3068, 1506, 1370, 1220, 832, 766 cm^{-1}. HRMS (CI) m/z calc. for $C_{23}H_{19}BFN$ [M]$^+$ 339.1595, found 339.1604.

*1-Allyl-3-(2-methoxyphenyl)-2-phenyl-2,1-borazaronaphthalene (**4c**).* Obtained as an off-white solid (86 mg, 73%). Mp: 64−66 °C. ^{1}H NMR (500 MHz, acetone-d_6) δ 7.91 (s, 1H), 7.78 (d, J = 7.9 Hz, 1H), 7.63 (d, J = 8.5 Hz, 1H), 7.54−7.50 (m, 1H), 7.29−7.25 (m, 3H), 7.16−7.12 (m, 4H), 7.10−7.06 (m, 1H), 6.86−6.83 (m, 1H), 6.65 (d, J = 8.2 Hz, 1H), 6.10−6.03 (m, 1H), 5.17 (dd, J = 10.5, 1.4 Hz, 1H), 5.01 (dd, J = 17.1, 1.5 Hz, 1H), 4.76−4.74 (m, 2H), 3.33 (s, 3H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 156.3, 142.9, 140.5, 136.2, 134.4, 131.8, 130.3, 129.7, 128.3, 127.6, 127.0, 126.9, 126.7, 121.3, 120.2, 116.8, 115.2, 110.2, 54.3, 50.9. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 37.5. IR (neat) 3006, 2830, 1489, 1370, 1340, 748 cm^{-1}. HRMS (CI) m/z calc. for $C_{24}H_{22}BNO$ [M]$^+$ 351.1794, found 351.1800.

*1-Allyl-3-(3-fluoro-3-methylphenyl)-2-phenyl-2,1-borazaronaphthalene (**4d**).* Obtained as an off-white solid (93 mg, 79%). Mp: 71−73 °C. ^{1}H NMR (500 MHz, acetone-d_6) δ 8.08 (s, 1H), 7.83 (d, J = 7.6 Hz, 1H), 7.63 (d, J = 8.6 Hz, 1H), 7.55−7.51 (m, 1H), 7.34−7.25 (m, 6H), 7.00 (d, J = 6.6 Hz, 1H), 6.93−6.89 (m, 1H), 6.81−6.77 (m, 1H), 6.07−6.01 (m, 1H), 5.15 (d, J = 10.5 Hz, 1H), 4.97 (d, J = 17.4 Hz, 1H), 4.75−4.73 (m, 2H), 2.09 (s, 3H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 159.7 (d, J = 243 Hz), 142.8, 140.3, 135.7, 131.8 (d, J = 5 Hz), 131.7, 130.4, 128.5, 127.7 (d, J = 6 Hz), 127.3, 127.1, 126.5, 123.3, 123.1, 121.4, 116.6, 115.1, 113.7 (d, J = 22 Hz), 50.1, 13.5. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 37.3. IR (neat) 3046, 1498, 1367, 1223, 1118, 766, 704 cm^{-1}. HRMS (CI) m/z calc. for $C_{24}H_{21}BFN$ [M]$^+$ 353.1751, found 353.1761.

*1-Benzyl-2,3-Diphenyl-2,1-borazaronaphthalene (**4e**).* Obtained as an off-white solid (105 mg, 85%). Mp: 90−92 °C. ^{1}H NMR (500 MHz, acetone-d_6) δ 8.16 (s, 1H), 7.86 (d, J = 7.6 Hz, 1H), 7.64 (d, J = 7.3 Hz, 1H), 7.47−7.43 (m, 2H), 7.39−7.35 (m, 1H), 7.31−7.25 (m, 5H), 7.21−7.11 (m, 9H), 5.42 (s, 2H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 144.4, 143.4, 140.3, 139.1, 131.2, 130.5, 128.8, 128.7, 128.5, 128.5, 127.5, 127.3, 126.8, 126.7, 125.6, 125.5, 121.5, 117.1, 52.3. ^{11}B NMR (128.38 MHz, acetone-d_6) δ 34.5. IR (neat) 3064, 2922, 1547, 1376, 767, 702 cm^{-1}. HRMS (CI) m/z calc. for $C_{27}H_{22}BN$ [M]$^+$ 371.1845, found 371.1840.

Computational Study. Calculations were performed using the Gaussian 09 software package.[16] The geometries were optimized at the B3LYP/6-311(d,p) level, and molecular orbitals and molecular energies were calculated at the same level.

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■ ASSOCIATED CONTENT

Supporting Information

Copies of ^{1}H, ^{13}C, and ^{11}B NMR spectra for all compounds as well as X-ray crystallographic data (CIF files), atom coordinates, and total energies for the computational study. 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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