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Regioselective Diversification of 2,1-Borazaronaphthalenes: Unlocking Isosteric Space via C−H Activation

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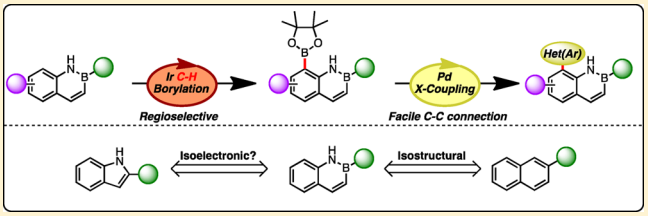
Supporting Information

ABSTRACT: Methods for the regioselective C−H borylation and subsequent cross-coupling of the 2,1-borazaronaphthalene core are reported. Azaborines are dependent on B−N/C═C isosterism when employed in strategies for developing diverse heterocyclic scaffolds. Although 2,1-borazaronaphthalene is closely related to naphthalene in terms of structure, the argument is made that the former has electronic similarities to indole. Based on that premise, iridium-mediated C−H activation has enabled facile installation of a versatile, nucleophilic coupling handle at a previously inaccessible site of 2,1-borazaronaphthalenes. A variety of substituted 2,1-borazaronaphthalene cores can be successfully borylated and further cross-coupled in a facile manner to yield diverse C(8)-substituted 2,1-borazaronaphthalenes.



INTRODUCTION

Isosteres provide versatile molecular scaffolds to optimize chemical space for biological and materials applications.[1] By providing a diverse array of exchangeable, electronically and sterically related chemical motifs, isosteres allow molecules to be fine-tuned for specific needs. Azaborines exemplify one such class of valuable compounds.[2] Capitalizing on the ability of the B−N bond to mimic a C═C bond, numerous aromatic and heteroaromatic systems have been successfully imitated with prospects for rapid diversification patterns not available in the parent system. The 2,1-borazaronaphthalene core is one of the most prominent azaborine systems, highlighted by robust synthetic methods and several strategies for derivatization.[3] Furthermore, the potential bioisosteric viability of this specific system has been recently demonstrated in comparisons with a β-blocker[4a] and phosphodiesterase 10A inhibitors.[4b]

The versatility of 2,1-borazaronaphthalenes arises from the desymmetrization of the heterocyclic core, providing several modes of functionalization (Figure 1). Our group reported accessing these substructures from *o*-aminostyrene and trifluoroborate derivatives, providing diverse substituents off both boron and nitrogen.[3a] Additionally, diversification off boron can be established by nucleophilic substitution and cross-coupling strategies.[3c,d] Based on the electronics of the system, selective bromination occurs at the C(3)-position, followed by secondary bromination at C(6). Recently, halogenation at C(4) has been reported when accessing the 2,1-borazaronaphthalene from the corresponding 2-alkynyl-anilines with dichloroboranes.[3g] The brominated cores can be functionalized by traditional cross-coupling,[3b,g] reductive-coupling,[3e] and even sp^2−sp^3 photoredox cross-coupling,[3f] to install myriad functional groups. Employing an iterative process, this protocol has been successfully applied to the sequential 3,6-difunctionalization of 2,1-borazaronaphthalene cores.[3b] However, access to the remaining positions of substitution has continued to be challenging, limiting the viability of the system as a whole. This is exemplified in the synthesis of 2,1-borazaronaphthalene mimetics of propranolol,[4a] where C(5) and C(8) ethereally substituted 2,1-borazaronaphthalene derivatives required pre-installation of the oxygen functional unit, followed by protection, deprotection, and two subsequent modification steps to introduce the desired side chain. Although such a synthesis might be tolerated from an exploratory, chemical

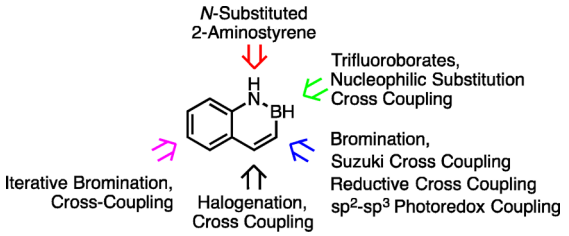


Figure 1. Diversification of the 2,1-borazaronaphthalene core.

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design viewpoint, this strategy would be inefficient for a more expansive molecular diversity study, costing significant time, effort, and material.

Reaction Design and Optimization. When considering ways to expand the 2,1-borazaronaphthalene motif, installing a *nucleophilic* coupling handle directly on the azaborine core would be beneficial. This would present an alternative approach to those employing an *electrophilic*, brominated core, opening up a wide array of complementary transformations.[5] One major drawback to most classical methods for installing nucleophilic coupling partners is that they are often derived from the corresponding halides, effectively passing through the electrophilic coupling partner in an inefficient synthetic pathway. A direct C−H borylation would circumvent that limitation and would lead directly to a readily diversifiable handle on the azaborine core.[6] Inspired by the report of the borylation of 1,2-dihydro-1,2-azaborine,[7] along with the diversity of methods for bicyclic systems, it was envisioned that iridium-catalyzed C−H borylation would provide a versatile platform capable of high regioselectivity.

Structurally, the 2,1-borazaronaphthalene is isosteric to naphthalene, which diborylates as a mixture of 2,6- or 2,7-disubstituted isomers (Figure 2A),[8] owing to a lack of inherent

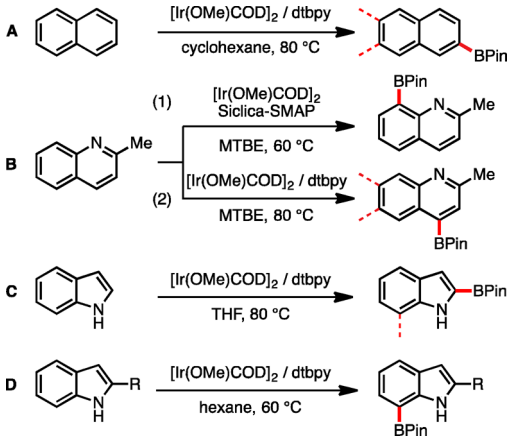

Figure 2. Iridium-catalyzed C−H borylation of bicyclic systems. The first site of borylation depicted in bold; second sites of borylation are depicted depicted by dotted line.

directing effects. Quinolines, which have a similar atomic placement, undergo C(8)-borylation using silica-supported phosphine ligands (Figure 2B1).[9] With traditional amine ligands, borylation of quinoline is predominantly favored at the C(4)-position (Figure 2B2), with subsequent addition at either the C(6)- or C(7)-positions.[10] Indoles, which possess an aromatic N−H functional unit with a geometric trade-off to a 6,5-ring system, typically borylate at the C(2)-position.[11] However, introducing substitution at the C(2)-position of indole, which is consonant with *B*-substitution on 2,1-borazaronaphthalenes, causes exclusive borylation at the C(7)-position (Figure 2D).[12] Furthermore, it is interesting to note the similarity between the electrophilic bromination patterns of 2-phenylindole and 2-phenyl-2,1-borazaronaphthalene, as both brominate at the 3-position (Figure 3).[3b,13]

Considering these three representative bicyclic models for 2,1-borazaronaphthalene, computationally derived electrostatic potential maps were compared to determine their surface electronic similarities (Figure 4). Cursory observation validates

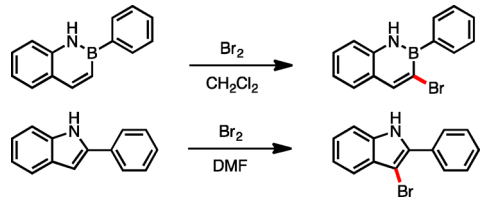

Figure 3. Electrophilic bromination of 2-phenyl 2,1-borazaronaphthalene and 2-phenylindole.

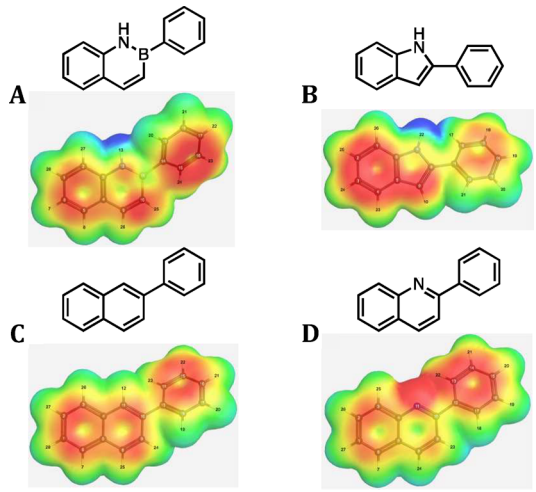

Figure 4. Electrostatic potentials (from +31.38 kcal/mol to −15.69 kcal/mol) for bicyclic systems. Calculations performed at B3LYP/6-31G(d) level of theory[14] using Gaussian 09[15] visualized via WebMO.[16]

the archetypal resemblance of the 2-phenyl-2,1-borazaronaphthalene (Figure 4A) to 2-phenylnaphthalene (Figure 4C). However, with our interest in leveraging the desymmetrization of the azaborine core, a deeper look into the distribution of electron density across the surface of the molecules yields a clear likeness to 2-phenylindole (Figure 4B). In both the azaborine and indole electrostatic potential maps, a significant density of electrons resides around the N−H bond, not seen in either of the other structures (Figure 4C,D). Also, there appears to be a distinct similarity in the asymmetric distribution of the partially electron-deficient region within the bicyclic cores. Encouraged by the congruence of the electrostatic potentials and the comparable reactivity profile for electrophilic bromination, indole could be considered electronically comparable and potentially useful in providing a foundation to predict the selectivity of C−H borylation.

The iridium-catalyzed borylation of 2-substituted indoles and similarly structured aniline scaffolds have been extensively studied by Smith and co-workers, with the anilines proposed to go through a mechanism in which outer-sphere hydrogen-bond coordination of the nitrogen occurs to direct the C−H functionalization.[12,17] The nitrogen of indole is suggested to be incorporated in the mechanism, providing selectivity for the C(7)-position. Computational elucidation of the iridium-catalyzed C−H borylation of several aromatic systems indicates that the transition state for C−H activation, which is predictive of the regioselectivity, contains "significant proton-transfer character".[18] It was surmised that the relative anionic stability of the different C−H centers of the 2,1-borazaronaphthalene core, a trait of proton-transfer processes, could generally predict the site of C−H borylation in these systems. This method is

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analogous to Liu's use of theoretically derived pK_a values in justifying the site selectivity for iridium C−H borylation of 1,2-dihydro-1,2-azaborine.[7]

To validate this approach, computational comparisons of the anion stability at various positions around 2-phenylindole were used as a representative system (see Supporting Information for complete anionic stability studies). Surprisingly, both the C(3)-position and the *ortho*-site of the external phenyl ring were more anionically stabilizing than the known C(7)-borylation site (Figure 5). However, it is well documented that those sites

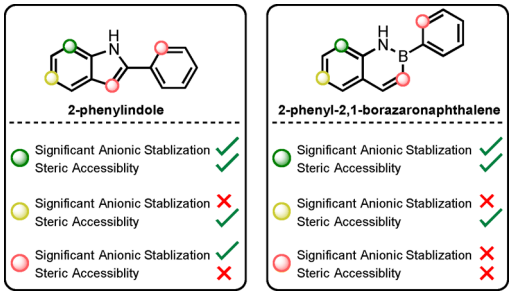
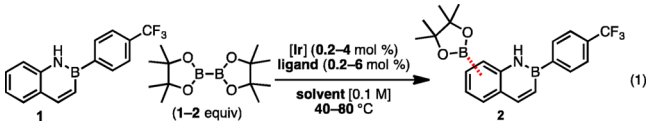


Figure 5. Regioselective analysis for iridium C−H activation for 2-phenyl indole and 2-phenyl-2,1-borazaraonaphthalene.

are inaccessible based on steric factors, considering the steric bulk of the iridium catalyst.[19] Anionic stability only accounts for the electronic factors of the C−H activation event, thus steric constraints must also be entertained. Removing these two nonviable sites, the theoretical method correctly predicted the C(7)-site for borylation. Applying this method to 2-phenyl-2,1-borazaronaphthalene, the C(8)-position appeared to be significantly more amenable to anionic charge stabilization that any other position. Considering this predicted site of borylation in the azaborine has no foreseeable steric constraints, this functionalization method was anticipated to provide access to a previously unattainable position of the 2,1-borazaronaphthalene.

Excited by the potential regioselectivity of the C−H activation strategy, high-throughput experimentation (HTE) was leveraged to survey the various reported C−H borylation conditions for optimal regioselectivity for the 2,1-borazaronaphthalene system (eq 1).[6f] In total, close to 450 conditions



(see Supporting Information) were screened to assess variables such as iridium sources, ligands, solvents, and relative ratios of these components. Bipyridine- and phenanthroline-based ligands proved to be superior to other nitrogen-containing homobidentate ligands, with reaction incorporating those ligands going to full conversion. In contrast, diphosphine ligands showed minimal conversion.[6g] It was further found that catalyst loading was optimal at 4 mol % with a 1:1.25 metal-to-ligand ratio. A slight excess (1.05 equiv) of B_2Pin_2 was required for the reaction to go to completion. However, significant excess led to an increase of diborylated product. As previously observed, solvent played an important role in controlling selectivity, with nonpolar solvents such as hexane and methylcyclohexane proving optimal.

Upon validation of these conditions on benchtop scale, it was observed that higher reaction concentration coincided with increased diborylation. Temperature also played a significant role in sequestering an N-borylated byproduct and preventing significant diborylation. However, given that the solubility of some of the substrates in methylcyclohexane was very low at room temperature, those less soluble substrates required elevated temperatures (40 °C vs 80 °C) for the reaction to proceed. NMR analysis of the isolated, monoborylated compound indicated exclusive borylation at the previously predicted (C)8-position, and this was later confirmed via single crystal X-ray diffraction analysis (Figure 6).

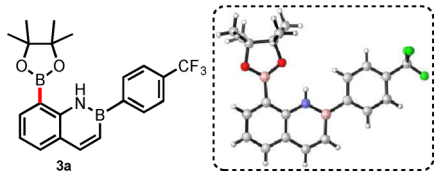


Figure 6. X-ray crystal structure of C(8)-borylated 2,1-borazaronaphthalene.

C−H Borylation Substrate Scope. With conditions for C−H borylation at the (C)8-position of 2,1-borazaronaphthalene established, the applicability to various substrates was considered, starting with substitution off of the boron of the borazine (Table 1). A variety of different *B*-aryl-2,1-borazaronaphthalene substructures (**3a**−**k**) were tolerated with various levels of success. Electronic diversification off the aryl substituent seemed to have little impact on the reaction outcome (compare **3a**,**d**,**h**). However, the substitution pattern off the *B*-aryl subunit did influence the effectiveness of the reaction, with *para*-substitution being preferred over either *meta*- or *ortho*-substitution (compare **3e** to **3f** and **3h**−**j**). Furan substitution (**3m**) was tolerated, albeit modestly, as it presents a competing site for C−H borylation.[20] Alkyl-substituted 2,1-borazaronaphthalenes (**3o**−**r**) were typically well behaved, presumably because of the increased solubility in the reaction solvent. In almost all cases, the mass balance for the reaction consisted exclusively of starting material, product, and various amounts of a single diborylated byproduct, suggesting that reoptimization for a specific substrate would provide a high return of product.

More elaborate 2,1-borazaronaphthalenes were next explored and found to be competent in the selective C−H borylation process (Table 2). 3-Bromo-2,1-borazaronaphthalenes (**4a**,**b**) and the 3,6-dibrominated core (**4c**) reacted reasonably efficiently, as did a substrate with aryl substitution at the 3-position (**4d**), a cross-coupled product of **4a**.[3b] 7-Fluoro-2,1-borazaronaphthalene was also suitable in the selective reaction, providing **4e** in modest yield. However, no other substituent at the 7-positions (e.g., *i*-Pr, Me) allowed productive borylation. Presumably, the steric constraints imparted by substitution at this position prevent accessibility by the sterically congested catalyst. Functionalization at the 6-position was well tolerated, including substrates containing cyano, (**4f**), trifluoromethyl (**4g**), isopropyl (**4h**), and trifluoromethoxy (**4i**) groups. Compounds with electrophilic coupling handles, either installed off the boron subunit (**3g**−**k**) or the brominated borazaronaphthalene core (**4a**−**c**), provide potential lynchpins for rapid core diversification. One such avenue could be photoredox cross-coupling, which has demonstrated tolerance of aryl

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Table 1. Borylation Scope of Boron-Substituted 2,1-Borazaronaphthalenes

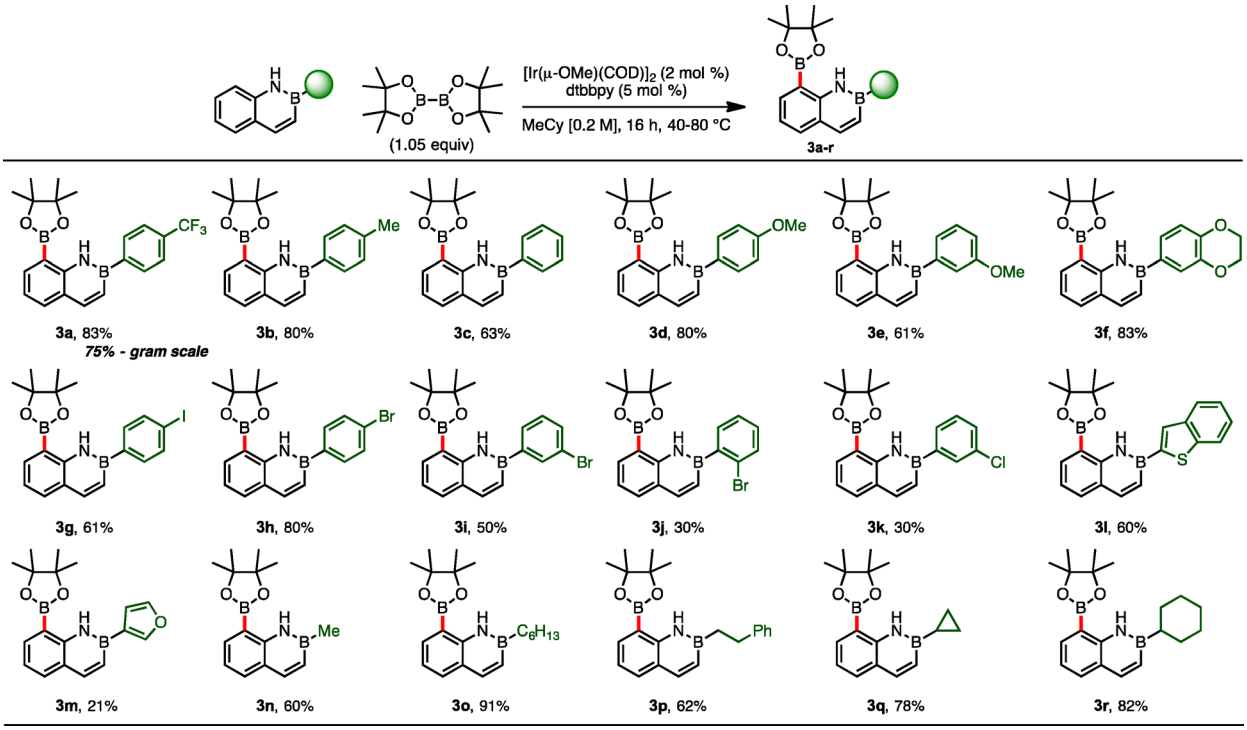
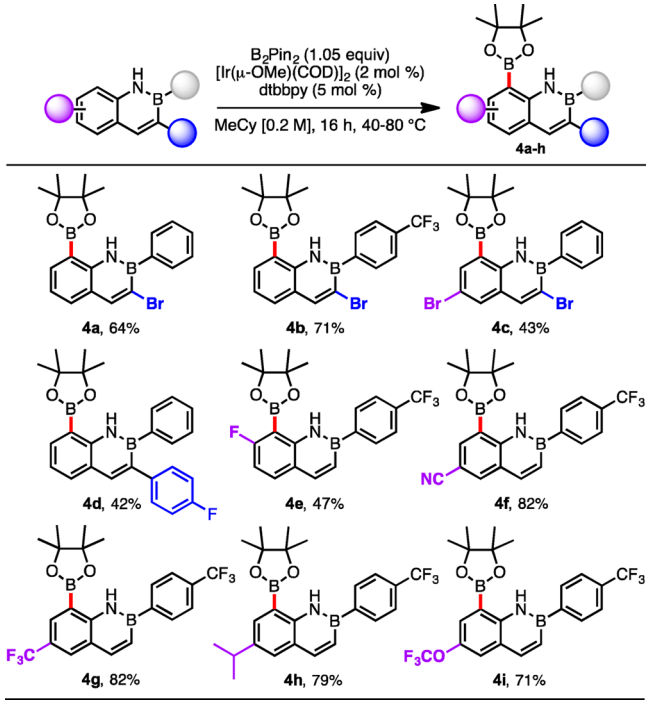


Table 2. Borylation of Elaborated 2,1-Borazaronaphthtalene Scaffolds



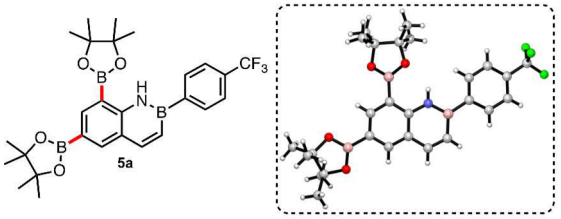
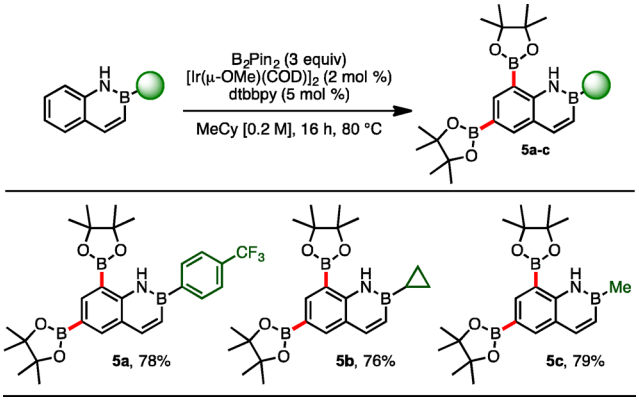


Figure 7. X-ray validation of 6,8-diborylated 2,1-borazaronaphthalene.

Table 3. Diborylation of 2,1-Borazaronaphthalene Cores



borinates[21] and has already been applied with great success to azaborines.[3f]

As previously mentioned, the exclusive byproduct affecting yields came from diborylation. Fortuitously, the second C−H borylation event *again* occurrs regioselectively, this time at the C(6)-position (Figure 7). When increasing the amount of B_2Pin_2 in the reaction, this product can be purposely formed (Table 3). These diborylated cores (**5a−c**) might be further elaborated in divergent functionalization, capitalizing on the stereoelectronic disparities between the sites of borylation, similar to prior work of selective cross-coupling of polyborylated molecules.[22]

While screening the borylation of the 2,1-borazaronaphthalenes, one observed phenomenon was the formation of the N-borylation product. Although only observed in trace amounts at elevated temperatures and lower ligand to metal ratio, similar products have been previously noted and used as an *in situ*

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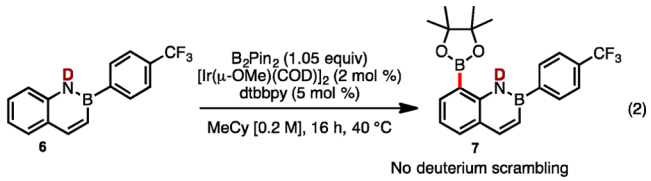
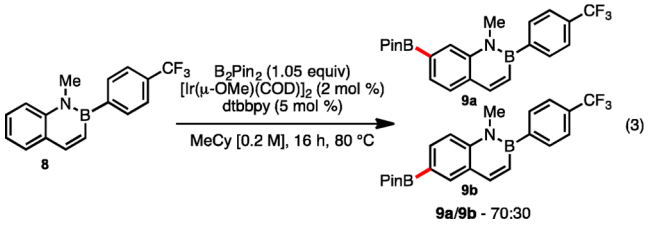
"traceless" directing group for the C(3) borylation of indoles.[17a] To probe whether this byproduct was an intermediate of the reaction pathway, the N-deuterated 2,1-borazaronaphthalene **6** was synthesized and subjected to the borylation conditions (eq 2). No scrambling of the deuterium was observed in the crude



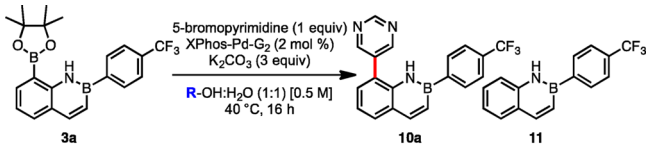


reaction mixture. The C(8)-borylated, N-deuterated product **7** could be isolated, suggesting that the N−H insertion, required to obtain the N-borylated product, is not part of the mechanistic pathway for borylation at the C(8)-position. However, it does appear that the N−H is intrinsically valuable for the regiospecificity of the borylation. When the *N*-methyl-2,1-borazaronaphthalene **8** was subjected to the borylation reaction, complete conversion was observed to an inseparable mixture of two regioisomeric products (eq 3). Analysis by 2D NMR suggests that none of the C(8)-borylated product was obtained. Rather, the isomers obtained were the C(7)-borylated **9a** and C(6)-borylated **9b** 2,1-borazaronaphthalenes, with the major product being the C(7)-borylated isomer. The relative ratio of observed products concurs with the computational model as the C(7)-position has greater favorable anionic charge stabilization compared to the C(6)-positions. It is interesting to note that while C(7) is the second most favorable point of anionic stabilization, C(6) ranks fifth, behind both C(5) and C(4). The lack of observed borylation at those sites could be explained by a peri-interaction,[23] marginally disfavoring those sites. This further suggests that the N−H could play a fundamental role in enabling the C(8)-borylation event, consistent with the outer-sphere, hydrogen-bond coordination model used to explain the *ortho*-C−H borylation for similarly structured anilines.[17b]

Cross-Coupling of 8-Borylated 2,1-Borazaronaphthalenes. With a diverse array of borylated compounds in hand, the viability of the subsequent Suzuki−Miyaura cross-coupling reaction was studied. Taking from conditions previously established for the inverted coupling of brominated 2,1-borazaronaphthalene with organotrifluoborates,[3b] with only minor modification to the solvent and ligand choice, the reaction worked exceedingly well. It was observed that alcoholic solvent mixtures with water were highly effective (Table 4) and that sterically bulky alcohols produced the best results (entries **3** and **4**), avoiding proto-deborylation.

These optimized conditions were then tested on a variety of the borylated 2,1-borazaronaphthalene cores, focusing on adding heterocyclic diversity to a variety of substituted azaborine substrates (Table 5). Across the board, the yields were generally excellent, with several of the reactions

Table 4. Solvent Optimization of Cross-Coupling[a]



	Alcohol	**3a** : IS	**10a** : IS	**11** : IS
1	MeOH	0.07	1.93	0.02
2	EtOH	0.08	2.18	0.18
3	*i*-PrOH	0.07	2.54	0
4	*t*-BuOH	0.03	2.62	0
5	phenol	0.00	0.30	1.40
6	cyclohexanol	0.00	1.63	1.53

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

proceeding nearly quantitatively (**10a,c−e,h,i,o**). Indeed, for reactions that went to full conversion, oftentimes the only purification required was simple aqueous workup followed by rapid purification through a plug of silica to remove the palladium catalyst. In most cases, yield losses corresponded to the required use of column chromatography, owing to incomplete reaction. 5-Bromopyrimidine cross-coupled well with various 8-borylated 2,1-borazaronaphthalene analogues (**10a−c**). Pyridine (**10d**), quinoline (**10e**), and thiophene (**10f,g**) substrates also worked well. Although highly functionalized cores such as caffeine could easily be installed with little difficulty (**10h,i**), substitution on the all-carbon ring of the azaborine core seemed to hinder the reaction (**10j,k**). Standard aryl bromides could also be cross-coupled in high yields (**10n−q**), including challenging electron-rich *N,N*-dimethylamino derivatives (**10p,q**). Unusual substuctures were synthesized using both nucleophilic and electrophilic 2,1-borazaronaphthalene derivatives that could be conjoined to generate heterodimeric-azaborines (**10l,m**).

CONCLUSIONS

In summary, a protocol for the selective C−H borylation and subsequent cross-coupling of 2,1-borazaronaphthalenes has been developed, allowing late-stage functionalization of a previously inaccessible position (Figure 8). Furthermore, an isoelectronic correlation of 2,1-borazaronaphthalene to indole is presented for the first time. Computational methods to account for the electronic factors of proton-transfer-like C−H activation were applied to identify the potential site of borylation. High-throughput experimentation was utilized for rapid identification of viable reaction conditions that were applicable across a wide array of substrates. Subjecting the reaction to excess B_2Pin_2 resulted in the exclusive formation of a diborylated adduct, providing an unprecedented opportunity for chemoselective functionalization in the all-carbon ring. Furthermore, it was demonstrated that the N−H is imperative for selectivity, although the reaction is most probably not going through a productive N−H insertion pathway. The resulting borylated substrates could be further cross-coupled using mild Suzuki−Miyaura conditions to provide highly elaborated azaborine scaffolds. These developed methods open up new opportunities for the diversification of 2,1-borazaronaphthalene and thus entries into unexplored isosteric space wholly inaccessible to the all-carbon naphthalene core itself.

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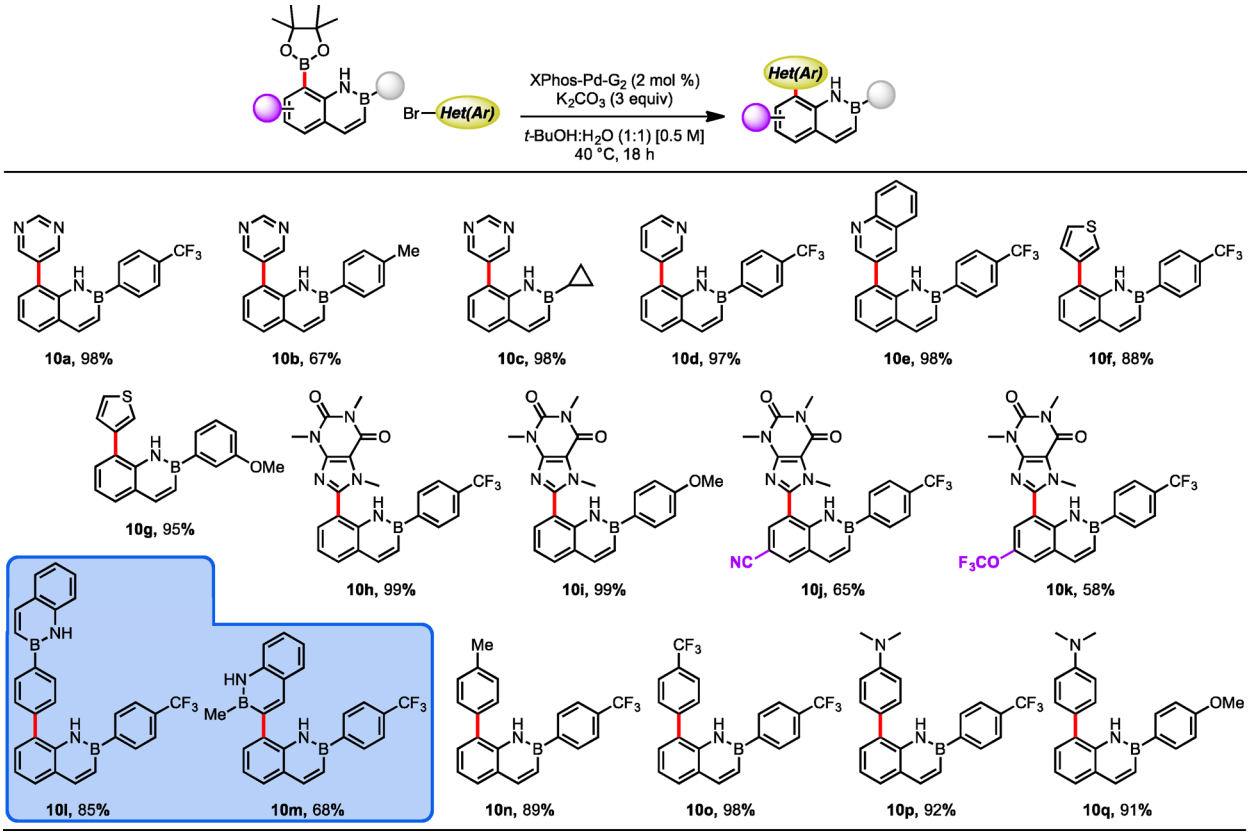
Table 5. Cross-Coupling of (Hetero)aryl Bromides with 8-Borylated 2,1-Borazaronaphthalene Cores



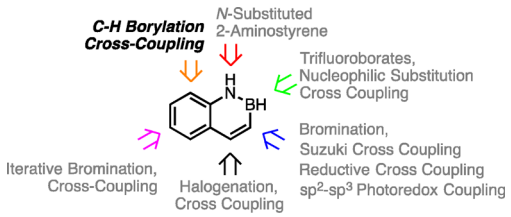


Figure 8. Methods of diversification for 2,1-borazaronaphthalene.

EXPERIMENTAL SECTION

General Considerations. All reactions were carried out under an inert atmosphere of nitrogen or argon in oven-dried glassware, unless otherwise noted. Toluene was dried using a J. C. Meyer solvent system. Methylcyclohexane was degassed under a stream of argon. All reagents were purchased commercially and used as received, unless otherwise noted. Column chromatography was performed by Combiflash using RediSep Rf Gold Normal-Phase Silica columns. Melting points (°C) are uncorrected. Mass spectra (ESI- or EI-TOF) were recorded using CH_2Cl_2 or MeCN as the solvent. IR spectra were recorded using FTIR-ATR of the neat oil or solid products. NMR spectra (^{1}H, ^{13}C {^{1}H}, ^{11}B, ^{19}F {^{1}H}) were performed at 298 K. ^{1}H (500.4 MHz) and ^{13}C {^{1}H} (125.8 MHz) NMR chemical shifts are reported relative to internal TMS (δ = 0.00 ppm) or to residual protiated solvent. Any observed splitting in the ^{13}C {^{1}H} NMR spectra is due to ^{13}C–^{19}F coupling. ^{11}B (128.4 MHz) and ^{19}F {^{1}H} NMR (470.8 MHz) chemical shifts were referenced to external $BF_3{\cdot}Et_2O$ (0.0 ppm) and $CFCl_3$ (0.0 ppm), respectively. Data are presented as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, m = multiplet, br = broad), coupling constant J (Hz), and integration.

Unreported 2,1-Borazaronaphthalene Scaffolds. 2,1-Borazaronaphthalene structures were synthesized by conditions as previously reported.[3a] In cases where the *o*-aminostyrene was not available, *o*-bromoaniline derivatives (1.0 equiv) were cross-coupled with vinyltrifluoroborate (1.1 equiv) using $PdCl_2{\cdot}$dppf (10 mol %) and Cs_2CO_3 (2.5 equiv) in THF/H_2O (9:1–0.1 M) mixture at 70 °C for 16 h. After consumption of the bromoaniline, the reaction was quenched with H_2O, extracted with Et_2O, dried ($MgSO_4$), and concentrated *in vacuo*. The resulting solids were subject to a flash plug of silica, eluting with a 1:1 mixture of hexane/EtOAc, and then concentrated *in vacuo*. The resulting crude *o*-aminostyrenes were then subjected to the azaborine cyclization reaction with *p*-(trifluoromethyl)phenyl-trifluoroborate (1.05 equiv) using $SiCl_4$ (1.0 equiv) and Et_3N (1.5 equiv) in CPME/toluene (1:1–0.25 M) at 60 °C for 16 h. The reactions were then subjected to a silica gel plug and flushed with 9:1 mixture of hexane/EtOAc and further purified by automated column chromatography if required.

*7-Fluoro-2-(4-(trifluoromethyl)phenyl)-2,1-borazaronaphthalene (Starting Material **4e**).* Obtained as a light brown solid (235.3 mg, 32%, 2.5 mmol scale); mp: 114–115 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 8.15 (d, J = 11.4 Hz, 2H), 7.99 (d, J = 7.7 Hz, 2H), 7.73 (d, J = 7.7 Hz, 2H), 7.66 (dd, J = 8.4, 6.3 Hz, 1H), 7.21 (d, J = 11.5 Hz, 1H), 7.08 (dd, J = 9.9, 2.6 Hz, 1H), 6.99 (td, J = 8.5, 2.3 Hz, 1H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 162.7 (d, J = 247.8 Hz), 145.6, 141.0 (d, J = 10.9 Hz), 132.8, 131.5 (q, J = 31.3 Hz), 131.2 (d, J = 9.9 Hz), 124.8 (q, J = 4.0 Hz), 124.2 (q, J = 271.9 Hz), 122.5, 110.0 (d, J = 23.1 Hz), 104.2 (d, J = 24.0 Hz) ppm; ^{19}F {^{1}H} NMR ($CDCl_3$, 470.8 MHz): δ −62.8, −111.3 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 35.0 ppm; IR: ν = 3394, 1569, 1326, 1215, 1165, 1119, 1106, 1067, 829, 700 cm^{-1}; HRMS (EI) m/z calcd for $C_{15}H_{10}BNF_4$ $[M]^+$ 291.0842, found 291.0869.

*6-(Cyano)-2-(4-(trifluoromethyl)phenyl)-2,1-borazaronaphthalene (Starting Material **4f**).* Starting from pure 5-cyano-2-aminostyrene, the product was obtained as light yellow solid (202 mg, 85%, 0.5 mmol scale); mp: 163–165 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 8.35 (s, 1H), 8.17 (d, J = 11.6 Hz, 1H), 8.06–8.00 (m, 3H), 7.75 (d, J = 7.8 Hz, 2H), 7.71 (dd, J = 8.4, 1.7 Hz, 1H), 7.47 (d, J = 8.4 Hz, 1H), 7.40 (dd, J = 11.6, 1.7 Hz, 1H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 145.1, 142.4, 134.5, 133.0, 131.9 (q, J = 32.5 Hz), 130.9,

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125.6, 124.9 (q, J = 3.9 Hz), 124.1 (q, J = 272.2 Hz), 119.3, 119.0, 104.9 ppm; ^{19}F {^{1}H} NMR ($CDCl_3$, 470.8 MHz): δ −62.9; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 34.6; IR: ν = 3307, 2231, 1614, 1574, 1324, 1104, 1066, 834, 800 cm^{-1}; HRMS (EI) m/z calcd for $C_{16}H_{10}BF_3N_2$ [M]$^+$ 298.0889, found 298.0890.

*6-(Trifluoromethyl)-2-(4-(trifluoromethyl)phenyl)-2,1-borazaronaphthalene (Starting Material **4g**).* Obtained as a light brown solid (471.6 mg, 55%, 2.5 mmol scale); mp: 109−110 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 8.26 (s, 1H), 8.19 (d, J = 11.5 Hz, 1H), 8.05−7.94 (m, 3H), 7.75 (d, J = 7.8 Hz, 2H), 7.70 (dd, J = 8.5, 1.9 Hz, 1H), 7.45 (d, J = 8.5 Hz, 1H), 7.36 (dd, J = 11.5, 1.9 Hz, 1H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 145.8, 141.7, 132.9, 131.7 (q, J = 32.4 Hz), 127.0 (q, J = 3.9 Hz), 125.0, 124.9 (q, J = 3.7 Hz), 124.8 (q, J = 3.9 Hz), 124.3 (q, J = 271.5 Hz), 124.2 (q, J = 271.8 Hz), 123.7 (q, J = 32.6 Hz), 118.8 ppm; ^{19}F {^{1}H} NMR ($CDCl_3$, 470.8 MHz): δ −61.4, −62.8 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 35.5 ppm; IR: ν = 3398, 1627, 1573, 1318, 1172, 1119, 1105, 1065, 806 cm^{-1}; HRMS (EI) m/z calcd for $C_{16}H_{10}BNF_6$ [M]$^+$ 341.0810, found 341.0829.

*6-Isopropyl-2-(4-(trifluoromethyl)phenyl)-2,1-borazaronaphthalene (Starting Material **4h**).* Starting from pure 5-isopropyl-2-aminostyrene. Obtained as a white solid (145.1 mg, 79%, 0.5 mmol scale); mp: 200−203 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 8.22−8.11 (m, 2H), 8.00 (d, J = 7.7 Hz, 2H), 7.73 (d, J = 7.8 Hz, 2H), 7.54 (s, 1H), 7.40 (dd, J = 8.6, 1.6 Hz, 1H), 7.33 (d, J = 8.3 Hz, 1H), 7.25 (dd, J = 11.6, 1.6 Hz, 1H), 3.05 (sept, J = 7.0 Hz, 1H), 1.35 (d, J = 6.9 Hz, 6H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 146.1, 142.0, 138.1, 132.7, 131.1 (q, J = 32.1 Hz), 127.5, 126.5, 125.7, 124.7 (q, J = 3.4 Hz), 124.3 (q, J = 272.0 Hz), 118.2, 33.6, 24.1 ppm; ^{19}F {^{1}H} NMR ($CDCl_3$, 470.8 MHz): δ −62.7 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 32.9 ppm; IR: ν = 3357, 1571, 1332, 1162, 1134, 1120, 1104, 1066, 789 cm^{-1}; HRMS (EI) m/z calcd for $C_{18}H_{17}BNF_3$ [M]$^+$ 315.1406, found 315.1424.

*6-(Trifluoromethoxy)-2-(4-(trifluoromethyl)phenyl)-2,1-borazaronaphthalene (Starting Material **4i**).* Starting from pure 5-trifluoromethoxy-2-aminostyrene. Obtained as a white solid (637 mg, 59%, 3.0 mmol scale); mp: 81−82 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 8.20 (s, 1H), 8.14 (d, J = 11.5 Hz, 1H), 7.99 (d, J = 7.8 Hz, 2H), 7.74 (d, J = 7.8 Hz, 2H), 7.56 (s, 1H), 7.42−7.30 (m, 3H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 145.3, 143.2, 138.2, 132.8, 131.5 (q, J = 32.2 Hz), 126.0, 125.0 (q, J = 3.8 Hz), 124.2 (q, J = 272.1 Hz), 122.0, 121.1, 120.6 (q, J = 256.6 Hz), 119.4 ppm; ^{19}F {^{1}H} NMR ($CDCl_3$, 470.8 MHz): δ −58.1, −62.8 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 33.7 ppm; IR: ν = 3407, 1565, 1333, 1260, 1209, 1153, 1115, 1102795, 713 cm^{-1}; HRMS (EI) m/z calcd for $C_{16}H_{10}BNOF_6$ [M]$^+$ 357.0760, found 357.0778.

*N-Methyl-2-(4-(trifluoromethyl)phenyl)-2,1-borazaronaphthalene (**8**).* Starting from pure *N*-methyl-2-aminostyrene. Obtained as a light brown solid (658 mg, 57%, 4.0 mmol scale); mp: 120−122 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 8.12 (d, J = 11.3 Hz, 1H), 7.76 (d, J = 7.9 Hz, 1H), 7.74 (d, J = 8.6 Hz, 2H), 7.72 (d, J = 8.2 Hz, 2H), 7.69−7.60 (m, 2H), 7.34 (t, J = 7.2 Hz, 1H), 6.94 (d, J = 11.3 Hz, 1H), 3.73 (s, 3H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 145.2, 142.0, 133.1, 130.3, 129.6 (q, J = 32.1 Hz), 128.9, 126.8, 124.4 (q, J = 272.0 Hz), 124.2 (q, J = 3.7 Hz), 121.2, 115.1, 36.7 ppm; ^{19}F {^{1}H} NMR ($CDCl_3$, 470.8 MHz): δ −62.6 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 35.8 ppm; IR: ν = 3020, 1589, 1552, 1325, 1159, 1112, 1101, 1067, 805, 762 cm^{-1}; HRMS (EI) m/z calcd for $C_{16}H_{13}BNF_3$ [M]$^+$ 287.1093, found 287.1083.

*Deuteration of 2,1-borazaronaphthalene N-Deuterio-2-(4-(trifluoromethyl)phenyl)-2,1-borazaronaphthalene (**6**).* To a microwave vial with a stir bar, 2-(4-(trifluoromethyl)phenyl)-2,1-borazaronaphthalene (273 mg, 1 mmol, 1 equiv) was added. The vial was capped and purged with argon. Et_2O (3 mL) was added followed by KHMDS (2 mL of a 1 M solution in THF, 2 equiv). The reaction was stirred for 20 min at rt, at which time D_2O (3 mL) was added dropwise and stirred for an additional 30 min. The reaction mixture was then extracted with EtOAc (5 mL) and dried ($MgSO_4$). Removal of the solvent afforded 218 mg (80%) of a yellow solid; mp: 149−150 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 8.19 (d, J = 11.5 Hz, 1H), 8.00 (d, J = 7.7 Hz, 2H), 7.71 (d, J = 7.8 Hz, 2H), 7.69 (d, J = 7.9 Hz, 1H), 7.48 (t, J = 7.2 Hz, 1H), 7.37 (d, J = 8.1 Hz, 1H), 7.30−7.19 (m, 2H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 146.1, 139.7, 132.8, 131.2 (q, J = 32.1 Hz), 129.5, 128.6, 125.7, 124.7 (q, J = 3.7 Hz), 124.3 (q, J = 272.0 Hz), 121.4, 118.2 ppm; ^{19}F {^{1}H} NMR ($CDCl_3$, 470.8 MHz): δ −62.7 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 33.0 ppm; IR: ν = 2923, 2502, 1612, 1325, 1118, 1108, 1071, 812, 762, 643 cm^{-1}; HRMS (EI) m/z calcd for $C_{15}H_{10}DBNF_3$ [M]$^+$ 274.0999, found 274.1018.

Experimental Procedure for Iridium-Catalyzed C−H Borylation of 2,1-Borazaronaphthalenes. In a microwave vial with stir bar, 2,1-borazaronaphthalene (0.5 mmol, 1.0 equiv) and B_2Pin_2 (133.3 mg, 0.53 mmol, 1.05 equiv) were added. The reaction vessel was capped and purged with argon followed by the addition of 1 mL of degassed methylcyclohexane. In a separate vial, [Ir(μ-OMe)(COD)]$_2$ (6.6 mg, 0.01 mmol, 2 mol %) and di-*t*-Bu-bipyridine (6.7 mg, 0.025 mmol, 5 mol %) were precomplexed under an inert atmosphere in 1 mL degassed methylcyclohexane, stirring 30 min at rt as the mixture turned magenta. The catalyst mixture was then added to the reaction mixture via syringe. The reaction was then heated and run for 16 h while being monitored by HPLC for completion. Upon cooling, the reaction mixture was condensed and adhered to silica, which was directly subjected to purification by automated silica gel column chromatography with a gradient solution of hexane/EtOAc as the mobile phase.

*8-(4,4,5,5-Tetramethyl-1,3,2-dioxaboryl)-2-(4-(trifluoromethyl)-phenyl)-2,1-borazaronaphthalene (**3a**).* Reaction was run at 40 °C, and the product was obtained as a white solid (166 mg, 83%, 0.5 mmol scale); mp: 135−137 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 10.61 (s, 1H), 8.21 (d, J = 11.4 Hz, 1H), 8.12 (d, J = 7.7 Hz, 2H), 8.05 (d, J = 7.2 Hz, 1H), 7.82 (d, J = 7.8 Hz, 1H), 7.78 (d, J = 7.6 Hz, 2H), 7.32 (d, J = 11.5 Hz, 1H), 7.29−7.23 (m, 1H), 1.51 (s, 12H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 146.3, 145.6, 137.0, 133.4, 133.0, 131.1 (q, J = 32.0 Hz), 125.3, 124.7 (q, J = 4.0 Hz), 124.4 (q, J = 272.1 Hz), 120.6, 84.3, 25.0 ppm; ^{19}F {^{1}H} NMR ($CDCl_3$, 470.8 MHz): δ −62.7 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 30.8 (br, 2B) ppm; IR: ν = 3355, 2984, 1600, 1321, 1307, 1127, 1104, 786 cm^{-1}; HRMS (EI) m/z calcd for $C_{21}H_{22}B_2NO_2F_3$ [M]$^+$ 399.1789, found 399.1798.

*2-(p-Tolyl)-8-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-2,1-borazaronaphthalene (**3b**).* Reaction was run at 80 °C for 24 h, and the product was obtained as a white solid (552 mg, 80%, 2.0 mmol scale); mp: 105−108 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 10.46 (s, 1H), 8.12 (d, J = 11.5 Hz, 1H), 7.97 (dd, J = 7.2, 1.4 Hz, 1H), 7.92 (d, J = 7.8 Hz, 2H), 7.76 (d, J = 7.6 Hz, 1H), 7.38−7.30 (m, 3H), 7.18 (t, J = 7.4 Hz, 1H), 2.44 (s, 3H), 1.47 (s, 12H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 145.9, 145.5, 139.4, 136.6, 133.3, 132.9, 132.6, 128.9, 119.9, 84.1, 25.0, 21.5 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 33.2, 30.5 ppm; IR: ν = 3351, 2973, 1599, 1565, 1355, 1307, 1138, 775 cm^{-1}; HRMS (EI) m/z calcd for $C_{21}H_{25}B_2NO_2$ [M]$^+$ 345.2071, found 345.2077.

*2-Phenyl-8-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-2,1-borazaronaphthalene (**3c**).* Reaction was run at 40 °C, and the product was obtained as a white solid (104 mg, 63%, 0.5 mmol scale); mp: 131−133 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 10.58 (s, 1H), 8.20 (d, J = 11.5 Hz, 1H), 8.09 (d, J = 7.4 Hz, 2H), 8.06 (d, J = 7.2 Hz, 1H), 7.83 (d, J = 7.8 Hz, 1H), 7.62−7.51 (m, 3H), 7.38 (dd, J = 11.5, 1.9 Hz, 1H), 7.26 (t, J = 7.4 Hz, 1H), 1.53 (s, 12H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 145.9, 145.7, 136.8, 133.4, 132.9, 129.5, 128.2, 125.3, 120.2, 84.2, 25.0 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 30.8 (br, 2B) ppm; IR: ν = 3348, 2981, 1599, 1354, 1305, 1138, 1125, 793, 746 cm^{-1}; HRMS (EI) m/z calcd for $C_{20}H_{23}B_2NO_2$ [M]$^+$ 331.1915, found 331.1921.

*2-(4-Methoxyphenyl)-8-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-2,1-borazaronaphthalene (**3d**).* Reaction was run at 40 °C, and the product was obtained as an off-white solid (144 mg, 80%, 0.5 mmol scale); mp: 95−98 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 10.40 (s, 1H), 8.11 (d, J = 11.5 Hz, 1H), 8.01−7.95 (m, 3H), 7.76 (dd, J = 7.9, 1.6 Hz, 1H), 7.27 (s, 1H), 7.18 (t, J = 7.4 Hz, 1H), 7.06 (d, J = 8.3 Hz, 2H), 3.91 (s, 3H), 1.49 (s, 12H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 160.9, 146.0, 145.3, 136.6, 134.4, 133.3, 125.1, 119.9, 113.7, 84.1, 55.1, 25.0 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 31.4 (br, 2B)

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ppm; IR: ν = 3354, 2975, 1597, 1355, 1308, 1252, 1178, 1138, 1125, 800, 788 cm^{-1}; HRMS (ESI) m/z calcd for $C_{21}H_{26}B_2NO_3$ $[M + H]^+$ 362.2099, found 362.2109.

*2-(3-Methoxyphenyl)-8-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-2,1-borazaronaphthalene (**3e**).* Reaction was run at 80 °C, and the product was obtained as a white solid (91 mg, 61%, 0.41 mmol scale); mp: 96−98 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 10.48 (s, 1H), 8.17 (dd, J = 11.6, 9.1 Hz, 1H), 8.02 (t, J = 7.1 Hz, 1H), 7.84−7.75 (m, 1H), 7.63 (d, J = 7.4 Hz, 1H), 7.57 (t, J = 4.4 Hz, 1H), 7.46 (t, J = 7.8 Hz, 1H), 7.35−7.28 (m, 1H), 7.22 (dd, J = 14.8, 7.4 Hz, 1H), 7.05 (dd, J = 8.3, 2.8 Hz, 1H), 3.95 (s, 3H), 1.49 (s, 12H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 159.5, 145.8, 145.7, 136.8, 133.4, 129.2, 125.3 (2 x C), 120.2, 117.9, 115.2, 84.1, 55.1, 25.0 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 31.0 (br, 2B) ppm; IR: ν = 3355, 2965, 1603, 1462, 1358, 1303, 1265, 1142, 1126, 774 cm^{-1}; HRMS (ESI) m/z calcd for $C_{21}H_{26}B_2NO_3$ $[M + H]^+$ 362.2099, found 362.2092.

*2-(2,3-Dihydrobenzo[1,4]dioxine)-8-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-2,1-borazaronaphthalene (**3f**).* Reaction was run at 40 °C, and the product was obtained as a yellow oil (162 mg, 83%, 0.5 mmol scale); ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 10.46 (s, 1H), 8.14 (d, J = 11.6 Hz, 1H), 8.01 (dd, J = 7.2, 1.6 Hz, 1H), 7.79 (dd, J = 7.7, 1.6 Hz, 1H), 7.58 (d, J = 1.6 Hz, 1H), 7.56 (dd, J = 7.9, 1.6 Hz, 1H), 7.29 (dd, J = 11.7, 1.9 Hz, 1H), 7.21 (t, J = 7.4 Hz, 1H), 7.05 (d, J = 7.9 Hz, 1H), 4.35 (s, 4H), 1.52 (s, 12H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 146.0, 145.4, 145.1, 143.6, 136.6, 133.3, 126.2, 125.1, 121.7, 112.0, 117.2, 84.2, 64.6, 64.3, 25.0 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 30.5 (br, 2B) ppm; IR: ν = 3347, 2981, 1598, 1309, 1281, 1126, 1066, 801, 795 cm^{-1}; HRMS (ESI) m/z calcd for $C_{22}H_{25}B_2NO_4$ $[M]^+$ 389.1970, found 389.1987.

*2-(4-Iodophenyl)-8-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-2,1-borazaronaphthalene (**3g**).* Reaction was run at 40 °C, and the product was obtained as an off-while solid (139 mg, 61%, 0.5 mmol scale); mp: 114−115 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 10.48 (s, 1H), 8.15 (d, J = 11.5 Hz, 1H), 7.99 (dd, J = 7.1, 1.6 Hz, 1H), 7.85 (d, J = 8.0 Hz, 2H), 7.78 (dd, J = 7.7, 1.5 Hz, 1H), 7.72 (d, J = 8.0 Hz, 2H), 7.25 (dd, J = 11.5, 1.9 Hz, 1H), 7.21 (t, J = 7.4 Hz, 1H), 1.47 (s, 12H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 146.0, 145.7, 137.2, 136.9, 134.5, 133.4, 125.2, 120.3, 96.4, 84.2, 25.0 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 31.3 (br, 2B) ppm; IR: ν = 3347, 2984, 1600, 1352, 1306, 1124, 792, 775 cm^{-1}; HRMS (EI) m/z calcd for $C_{20}H_{22}B_2NO_2I$ $[M + Na]^+$ 457.0881, found 457.0906.

*2-(4-Bromophenyl)-8-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-2,1-borazaronaphthalene (**3h**).* Reaction was run at 40 °C, and the product was obtained as a white solid (164 mg, 80%, 0.5 mmol scale); mp: 132−135 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 10.53 (s, 1H), 8.18 (d, J = 11.5 Hz, 1H), 8.04 (dd, J = 7.2, 1.6 Hz, 1H), 7.89 (d, J = 8.0 Hz, 2H), 7.81 (dd, J = 7.8, 1.5 Hz, 1H), 7.68 (d, J = 8.0 Hz, 2H), 7.33−7.21 (m, 2H), 1.51 (s, 12H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 146.0, 145.7, 136.9, 134.4, 133.4, 131.3, 125.3, 124.2, 120.4, 84.2, 25.0 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 30.4 (br, 2B) ppm; IR: ν = 3340, 2976, 1601, 1353, 1307, 1138, 1125, 794, 777 cm^{-1}; HRMS (ESI) m/z calcd for $C_{20}H_{23}B_2NO_2Br$ $[M + H]^+$ 410.1098, found 410.1092.

*2-(3-Bromophenyl)-8-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-2,1-borazaronaphthalene (**3i**).* Reaction was run at 40 °C, and the product was obtained as a white solid (102 mg, 50%, 0.5 mmol scale); mp: 211−213 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 10.62 (s, 1H), 8.24−8.15 (m, 2H), 8.03 (d, J = 6.5 Hz, 1H), 7.96 (d, J = 7.0 Hz, 1H), 7.81 (d, J = 7.7 Hz, 1H), 7.61 (d, J = 8.2 Hz, 1H), 7.39 (t, J = 7.5 Hz, 1H), 7.33−7.20 (m, 2H), 1.52 (s, 12H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 146.1, 145.7, 136.9, 135.4, 133.4, 132.2, 131.6, 129.9, 125.3, 123.1, 120.4, 84.3, 25.0 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 31.3 (br, 2B) ppm; IR: ν = 3354, 2964, 1602, 1358, 1307, 1125, 776 cm^{-1}; HRMS (ESI) m/z calcd for $C_{20}H_{23}B_2NO_2Br$ $[M + H]^+$ 410.1098, found 410.1086.

*2-(2-Bromophenyl)-8-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-2,1-borazaronaphthalene (**3j**).* Reaction was run at 40 °C, and the product was obtained as a yellow solid (62 mg, 30%, 0.5 mmol scale); mp: 89−90 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 10.42 (s, 1H), 8.16 (d, J = 11.5 Hz, 1H), 8.02 (d, J = 6.5 Hz, 1H), 7.81 (d, J = 7.7 Hz, 1H), 7.67 (dd, J = 11.5, 7.3 Hz, 2H), 7.40 (t, J = 7.6 Hz, 1H), 7.29−7.21 (m, 3H), 1.42 (s, 12H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 145.3, 145.1, 136.9, 135.9, 133.4, 132.6, 129.9, 127.5, 126.6, 125.0, 120.5, 84.2, 24.9 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 31.8 (br, 2B) ppm; IR: ν = 3338, 2991, 1597, 1354, 1141, 1126, 819, 757 cm^{-1}; HRMS (ESI) m/z calcd for $C_{20}H_{23}B_2NO_2Br$ $[M + H]^+$ 410.1098, found 410.1085.

*2-(3-Chlorophenyl)-8-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-2,1-borazaronaphthalene (**3k**).* Reaction was run at 80 °C, and the product was obtained as a white solid (56 mg, 30%, 0.33 mmol scale); mp: 118−120 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 10.60 (s, 1H), 8.18 (d, J = 11.6 Hz, 1H), 8.05−7.95 (m, 2H), 7.92−7.86 (m, 1H), 7.80 (d, J = 7.8 Hz, 1H), 7.47−7.41 (m, 2H), 7.30−7.27 (m, 1H), 7.23 (t, J = 7.5 Hz, 1H), 1.50 (s, 12H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 146.1, 145.7, 136.8, 134.5, 133.3, 132.5, 131.0, 129.5, 129.3, 125.2, 120.4, 84.3, 25.0 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 30.9 (br, 2B) ppm; IR: ν = 3352, 2971, 1602, 1359, 1307, 1141, 1125, 778, 760 cm^{-1}; HRMS (ESI) m/z calcd for $C_{20}H_{23}B_2NO_2Cl$ $[M + H]^+$ 366.1603, found 366.1608.

*2-(Benzothiophen-2-yl)-8-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-2,1-borazaronaphthalene (**3l**).* Reaction was run at 80 °C, and the product was obtained as a white solid (117 mg, 60%, 0.5 mmol scale); mp: 163−164 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 10.52 (s, 1H), 8.16 (d, J = 11.5 Hz, 1H), 8.03−7.96 (m, 3H), 7.95−7.90 (m, 1H), 7.79 (d, J = 7.4 Hz, 1H), 7.43−7.36 (m, 2H), 7.30 (dd, J = 11.5, 1.9 Hz, 1H), 7.23 (t, J = 7.4 Hz, 1H), 1.53 (s, 12H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 145.8, 145.7, 143.1, 141.5, 136.9, 133.4, 131.0, 125.4, 124.6, 124.0, 123.9, 122.5, 120.4, 84.3, 25.0 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 30.5 (br, 2B) ppm; IR: ν = 3335, 2976, 1597, 1353, 1307, 1137, 798 cm^{-1}; HRMS (ESI) m/z calcd for $C_{22}H_{24}B_2NO_2S$ $[M + H]^+$ 388.1714, found 388.1715.

*2-(Furan-3-yl)-8-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-2,1-borazaronaphthalene (**3m**).* Reaction was run at 80 °C, and the product was obtained as a white solid (33 mg, 21%, 0.5 mmol scale); mp: 195−197 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 10.44 (s, 1H), 8.13 (d, J = 11.4 Hz, 1H), 7.80 (s, 1H), 7.66 (d, J = 7.8 Hz, 1H), 7.45 (t, J = 7.6 Hz, 1H), 7.30 (d, J = 8.1 Hz, 1H), 7.24−7.14 (m, 2H), 7.03 (s, 1H), 1.51 (s, 12H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 147.1, 145.0, 140.5, 129.3, 128.1, 125.5, 120.5, 118.0, 116.0, 84.8, 24.9 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 27.4 (br, 2B) ppm; IR: ν = 3348, 2971, 1574, 1560, 1451, 1303, 1138, 778 cm^{-1}; HRMS (ESI) m/z calcd for $C_{18}H_{22}B_2NO_3$ $[M + H]^+$ 322.1786, found 322.1793.

*2-Methyl-8-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-2,1-borazaronaphthalene (**3n**).* Reaction was run at 80 °C, and the product was obtained as a thick yellow oil (80 mg, 60%, 0.5 mmol scale); ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 9.68 (s, 1H), 7.92 (d, J = 9.5 Hz, 2H), 7.70 (d, J = 7.8 Hz, 1H), 7.13 (t, J = 7.7 Hz, 1H), 6.80 (d, J = 11.4 Hz, 1H), 1.44 (s, 12H), 0.79 (s, 3H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 145.8, 144.1, 136.3, 133.2, 124.6, 119.5, 83.9, 24.9 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 36.5, 30.0 ppm; IR: ν = 3358, 2984, 1601, 1354, 1311, 1136, 1101, 760 cm^{-1}; HRMS (ESI) m/z calcd for $C_{15}H_{22}B_2NO_2$ $[M + H]^+$ 270.1837, found 270.1827.

*2-Hexyl-8-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-2,1-borazaronaphthalene (**3o**).* Reaction was run at 40 °C, and the product was obtained as a white solid (65 mg, 91%, 0.21 mmol scale); mp: 127−130 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 9.85 (s, 1H), 7.98−7.92 (m, 2H), 7.76−7.68 (m, 1H), 7.15 (t, J = 7.4 Hz, 1H), 6.82 (d, J = 11.4 Hz, 1H), 1.73−1.65 (m, 2H), 1.48−1.43 (m, 14H), 1.42−1.33 (m, 6H), 0.95 (t, J = 6.7 Hz, 3H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 145.9, 144.0, 136.2, 133.2, 124.8, 119.6, 83.9, 32.3, 32.0, 25.4, 24.9, 22.6, 14.1 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 37.5, 29.8 ppm; IR: ν = 3354, 2921, 1600, 1354, 1303, 1137, 762 cm^{-1}; HRMS (ESI) m/z calcd for $C_{20}H_{32}B_2NO_2$ $[M + H]^+$ 340.2623, found 340.2630.

*2-Phenethyl-8-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-2,1-borazaronaphthalene (**3p**).* Reaction was run at 40 °C, and the product was obtained as a white solid (111 mg, 62%, 0.5 mmol scale); mp: 58−60 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 9.91 (s, 1H), 8.00−7.91 (m, 2H), 7.72 (d, J = 7.7 Hz, 1H), 7.36−7.29 (m, 4H), 7.23−7.11 (m, 2H), 6.84 (dd, J = 11.5, 1.9 Hz, 1H), 3.01 (t, J = 8.3 Hz, 2H), 1.71 (t, J

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= 8.3 Hz, 2H), 1.43 (s, 12H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 145.7, 145.2, 144.4, 136.4, 133.3, 128.2, 128.0, 127.9, 125.3, 124.8, 119.8, 84.0, 31.5, 24.9 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ37.8, 31.5 ppm; IR: ν = 3349, 2978, 1598, 1355, 1311, 1137, 1127, 759 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{22}H_{28}B_2NO_2$ $[M + H]^+$ 360.2306, found 360.2305.

*2-Cyclopropyl-8-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-2,1-borazaronaphthalene (**3q**).* Reaction was run at 80 °C, and the product was obtained as a white solid (115 mg, 78%, 0.5 mmol scale); mp: 75−76 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 9.61 (s, 1H), 8.04−7.84 (m, 2H), 7.69 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.13 (t, *J* = 7.4 Hz, 1H), 6.62 (dd, *J* = 11.6, 1.9 Hz, 1H), 1.45 (s, 12H), 0.97−0.80 (m, 2H), 0.72−0.57 (m, 2H), 0.37 (tt, *J* = 8.8, 6.0 Hz, 1H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 145.9, 144.5, 136.4, 133.2, 124.7, 119.4, 83.9, 24.9, 6.3 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 37.3, 30.0 ppm; IR: ν = 3356, 2979, 1598, 1353, 1297, 1135, 1109, 794, 774 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{17}H_{24}B_2NO_2$ $[M + H]^+$ 296.1993, found 296.1990.

*2-Cyclohexyl-8-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-2,1-borazaronaphthalene (**3r**).* Reaction was run at 40 °C, and the product was obtained as a yellow solid (138 mg, 82%, 0.5 mmol scale); mp: 69−70 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 9.94 (s, 1H), 8.07−7.87 (m, 2H), 7.72 (d, *J* = 7.3 Hz, 1H), 7.15 (t, *J* = 7.4 Hz, 1H), 6.88 (dd, *J* = 11.5, 1.9 Hz, 1H), 2.08−1.97 (m, 2H), 1.85−1.71 (m, 3H), 1.54−1.38 (m, 18H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 145.7, 144.4, 136.2, 133.2, 124.8, 119.6, 83.9, 29.6, 27.7, 27.2, 24.9 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 40.2, 31.8 ppm; IR: ν = 3356, 2917, 1599, 1356, 1309, 1137, 1124, 800 cm^{-1}; HRMS (EI) *m/z* calcd for $C_{20}H_{29}B_2NO_2$ $[M + Na]^+$ 337.2384, found 337.2386.

*3-Bromo-2-phenyl-8-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-2,1-borazaronaphthalene (**4a**).* Reaction was run at 80 °C, and the product was obtained as a white solid (130 mg, 64%, 0.5 mmol scale); mp: 72−74 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 10.48 (s, 1H), 8.49 (s, 1H), 8.22−8.14 (m, 2H), 8.06 (dd, *J* = 7.1, 1.5 Hz, 1H), 7.75 (d, *J* = 7.8 Hz, 1H), 7.64−7.50 (m, 3H), 7.27 (t, *J* = 7.5 Hz, 1H), 1.47 (s, 12H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 147.1, 144.9, 137.1, 133.6, 132.5, 129.3, 127.8, 124.7, 121.0, 84.4, 25.0 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 30.6 (br, 2B) ppm; IR: ν = 3338, 2974, 1597, 1373, 1344, 1309, 1132, 698 cm^{-1}; HRMS (EI) *m/z* calcd for $C_{20}H_{22}B_2NO_2Br$ $[M]^+$ 409.1020, found 409.1041.

*3-Bromo-8-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-2-(4-(trifluoromethyl)phenyl)-2,1-borazaronaphthalene (**4b**).* Reaction was run at 80 °C, and the product was obtained as an off-white solid (169 mg, 71%, 0.5 mmol scale); mp: 122−124 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 10.50 (s, 1H), 8.46 (s, 1H), 8.20 (d, *J* = 7.4 Hz, 2H), 8.08 (d, *J* = 7.0 Hz, 1H), 7.79 (d, *J* = 7.5 Hz, 2H), 7.73 (d, *J* = 7.6 Hz, 1H), 7.28 (t, *J* = 7.1 Hz, 1H), 1.47 (s, 12H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 147.4, 144.6, 137.4, 133.7, 132.5, 131.0 (q, *J* = 32.1 Hz), 124.8, 124.4 (q, *J* = 271.8 Hz), 124.3 (q, *J* = 3.9 Hz), 121.4, 84.5, 24.9 ppm; ^{19}F {^{1}H} NMR ($CDCl_3$, 470.8 MHz): δ −62.6 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 32.0 (br, 2B) ppm; IR: ν = 3340, 2980, 1598, 1558, 1320, 1120, 1068, 761 cm^{-1}; HRMS (EI) *m/z* calcd for $C_{21}H_{21}B_2NO_2F_3Br$ $[M]^+$ 477.0894, found 477.0891.

*3,6-Dibromo-2-phenyl-8-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-2,1-borazaronaphthalene (**4c**).* Reaction was run at 80 °C, and the product was obtained as a white solid (52 mg, 43%, 0.25 mmol scale); mp: 136−138 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 10.34 (s, 1H), 8.35 (s, 1H), 8.13−8.03 (m, 3H), 7.82 (s, 1H), 7.54−7.47 (m, 3H), 1.44 (s, 12H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 145.8, 143.4, 139.2, 134.0, 133.5, 129.5, 127.8, 126.3, 113.8, 84.8, 24.9 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 32.7, 30.7 ppm; IR: ν = 3550, 2975, 1593, 1555, 1416, 1370, 1312, 1141, 848, 793 cm^{-1}; HRMS (EI) *m/z* calcd for $C_{20}H_{21}B_2NO_2Br_2$ $[M]^+$ 487.0125, found 487.0122.

*3-(4-Fluorophenyl)-2-phenyl-8-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-2,1-borazaronaphthalene (**4d**).* Reaction was run at 60 °C, and the product was obtained as a light brown solid (45 mg, 42%, 0.25 mmol scale); mp: 164−165 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 10.39 (s, 1H), 8.03−7.96 (m, 2H), 7.83 (d, *J* = 7.1 Hz, 1H), 7.57 (d, *J* = 7.9 Hz, 2H), 7.39−7.29 (m, 5H), 7.24 (t, *J* = 7.4 Hz, 1H), 7.03 (t, *J* = 8.8 Hz, 2H), 1.46 (s, 12H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 161.7 (d, *J* = 244.2 Hz), 145.2, 143.7, 140.5, 136.7, 133.6, 133.4, 130.1 (d, *J* = 7.8 Hz), 128.6, 127.7, 124.7, 120.6, 114.7 (d, *J* = 21.1 Hz), 84.2, 24.9 ppm; ^{19}F {^{1}H} NMR ($CDCl_3$, 470.8 MHz): δ −111.7 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 34.0, 31.2 ppm; IR: ν = 3348, 2970, 2915, 1600, 1446, 1346, 1310, 1131, 760 cm^{-1}; HRMS (EI) *m/z* calcd for $C_{26}H_{26}B_2NO_2F$ $[M]^+$ 425.2134, found 425.2144.

*7-Fluoro-8-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-2-(4-(trifluoromethyl)phenyl)-2,1-borazaronaphthalene (**4e**).* Reaction was run at 80 °C, and the product was obtained as brown cystals (98 mg, 47%, 0.5 mmol scale); mp: 132−135 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 10.80 (s, 1H), 8.15 (d, *J* = 11.5 Hz, 1H), 8.08 (d, *J* = 7.8 Hz, 2H), 7.79−7.70 (m, 3H), 7.23 (dd, *J* = 11.5, 1.4 Hz, 1H), 6.95 (t, *J* = 9.0 Hz, 1H), 1.51 (s, 12H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 168.6 (d, *J* = 254.2 Hz), 146.6 (d, *J* = 11.2 Hz), 145.9, 135.14 (d, *J* = 11.7 Hz), 132.9, 131.2 (q, *J* = 32.2 Hz), 124.7 (q, *J* = 3.7 Hz), 124.3 (q, *J* = 272.2 Hz), 122.2, 109.5 (d, *J* = 26.8 Hz), 84.1, 24.9 ppm; ^{19}F {^{1}H} NMR ($CDCl_3$, 470.8 MHz): δ −62.7, −97.1 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 33.6, 30.2 ppm; IR: ν = 3345, 2982, 1599, 1320, 1208, 1162, 1138, 1119, 1066, 802 cm^{-1}; HRMS (EI) *m/z* calcd for $C_{21}H_{21}B_2NO_2F_4$ $[M]^+$ 417.1695, found 417.1695.

*6-Cyano-8-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-2-(4-(trifluoromethyl)phenyl)-2,1-borazaronaphthalene (**4f**).* Reaction was run at 80 °C for 24 h, and the product was obtained as a white solid (202 mg, 93%, 1.0 mmol scale); mp: 195−196 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 10.66 (s, 1H), 8.22 (d, *J* = 1.6 Hz, 1H), 8.15 (d, *J* = 11.6 Hz, 1H), 8.12−8.05 (m, 3H), 7.76 (d, *J* = 7.9 Hz, 2H), 7.41 (dd, *J* = 11.7, 1.2 Hz, 1H), 1.49 (s, 12H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 147.7, 145.4, 139.2, 137.3, 133.1, 131.8 (q, *J* = 32.0 Hz), 125.2, 124.9 (q, *J* = 3.7 Hz), 124.1 (q, *J* = 271.4, Hz), 119.0, 104.2, 85.0, 25.0 ppm; ^{19}F {^{1}H} NMR ($CDCl_3$, 470.8 MHz): δ −62.9 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 33.7, 30.3 ppm; IR: ν = 3346, 2985, 2928, 1719, 1608, 1395, 1317, 1135, 1118, 792 cm^{-1}; HRMS (EI) *m/z* calcd for $C_{22}H_{21}B_2N_2O_2F_3$ $[M]^+$ 424.1741, found 424.1750.

*8-(4,4,5,5-Tetramethyl-1,3,2-dioxaboryl)-6-(trifluoromethyl)-2-(4-trifluoromethyl)phenyl)-2,1-borazaronaphthalene (**4g**).* Reaction was run at 80 °C, and the product was obtained as a white solid (140 mg, 82%, 0.5 mmol scale); mp: 160−162 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 10.66 (s, 1H), 8.23 (d, *J* = 1.3 Hz, 1H), 8.20 (d, *J* = 11.6 Hz, 1H), 8.09 (d, *J* = 7.8 Hz, 2H), 8.05 (s, 1H), 7.77 (d, *J* = 7.8 Hz, 2H), 7.39 (dd, *J* = 11.6, 1.5 Hz, 1H), 1.51 (s, 12H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 147.3, 146.0, 133.0, 133.0 (q, *J* = 3.7 Hz), 131.5 (q, *J* = 32.1 Hz), 130.3 (q, *J* = 3.8 Hz), 124.8 (q, *J* = 3.8 Hz), 124.7, 124.4 (q, *J* = 272.2 Hz), 124.2 (q, *J* = 271.8 Hz), 122.8 (q, *J* = 32.7 Hz), 84.8, 25.0 ppm; ^{19}F {^{1}H} NMR ($CDCl_3$, 470.8 MHz): δ −61.3, −62.8 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 33.5, 31.0 ppm; IR: ν = 3350, 2985, 1618, 1581, 1319, 1142, 1113, 1067, 793 cm^{-1}; HRMS (EI) *m/z* calcd for $C_{22}H_{21}B_2NO_2F_6$ $[M]^+$ 467.1663, found 467.1652.

*6-Isopropyl-8-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-2-(4-(trifluoromethyl)phenyl)-2,1-borazaronaphthalene (**4h**).* Reaction was run at 80 °C, and the product was obtained as a white solid (174 mg, 79%, 0.5 mmol scale); mp: 198−202 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 10.54 (s, 1H), 8.18 (d, *J* = 11.5 Hz, 1H), 8.09 (d, *J* = 8.0 Hz, 2H), 7.90 (d, *J* = 2.1 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.65 (d, *J* = 2.0 Hz, 1H), 7.28 (dd, *J* = 11.4, 2.1 Hz, 1H), 3.06 (sept, *J* = 6.9 Hz, 1H), 1.49 (s, 12H), 1.35 (d, *J* = 6.9 Hz, 6H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 146.2, 144.0, 140.9, 135.9, 132.9, 130.9 (q, *J* = 32.2 Hz), 130.5, 125.4, 124.7 (q, *J* = 3.8 Hz), 124.4 (q, *J* = 272.1 Hz), 84.2, 33.5, 25.0, 24.2 ppm; ^{19}F {^{1}H} NMR ($CDCl_3$, 470.8 MHz): δ −62.7 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 30.5 (br, 2B) ppm; IR: ν = 3350, 2954, 1572, 1332, 1163, 1120, 1067, 789 cm^{-1}; HRMS (EI) *m/z* calcd for $C_{24}H_{28}B_2NO_2F_3$ $[M]^+$ 441.2285, found 441.2253.

*8-(4,4,5,5-Tetramethyl-1,3,2-dioxaboryl)-6-(trifluoromethoxy)-2-(4-(trifluoromethyl)phenyl)-2,1-borazaronaphthalene (**4i**).* Reaction was run at 80 °C, and the product was obtained as a white solid (171 mg, 71%, 0.5 mmol scale); mp: 117−119 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 10.57 (s, 1H), 8.15 (d, *J* = 11.6 Hz, 1H), 8.08 (d, *J* = 7.8 Hz, 2H), 7.85 (d, *J* = 2.4 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.64 (d, *J* = 2.0 Hz, 1H), 7.37 (dd, *J* = 11.6, 1.8 Hz, 1H), 1.49 (s, 12H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 145.5, 144.0, 142.5, 132.9, 131.3 (q, *J* = 32.2 Hz), 129.6, 126.0, 124.8, 124.8 (q, *J* = 3.8 Hz), 124.2 (q, *J* = 271.0

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Hz), 120.5 (q, J = 256.2 Hz), 84.7, 25.0 (q, J = 79.7 Hz) ppm; ^{19}F {^{1}H} NMR ($CDCl_3$, 470.8 MHz): δ −58.0, −62.8 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 30.0 (br, 2B) ppm; IR: ν = 3353, 2981, 1574, 1315, 1259, 1155, 1140, 1106, 1067, 774 cm^{-1}; HRMS (EI) m/z calcd for $C_{22}H_{21}B_2NO_3F_6$ [M]$^+$ 483.1612, found 483.1620.

*6,8-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-2-(4-(trifluoromethyl)phenyl)-2,1-borazaronaphthalene (**5a**).* Reaction was run at 80 °C with 3.0 equiv of B_2Pin_2 (381 mg, 1.5 mmol), and the product was obtained as a white solid (203 mg, 78%, 0.5 mmol scale); mp: 220−222 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 10.69 (s, 1H), 8.49 (s, 1H), 8.34 (s, 1H), 8.24 (dd, J = 11.6, 2.9 Hz, 1H), 8.12 (d, J = 6.3 Hz, 2H), 7.77 (d, J = 6.5 Hz, 2H), 7.30 (d, J = 11.6 Hz, 1H), 1.50 (s, 12H), 1.43 (s, 12H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 147.8, 146.7, 143.2, 141.0, 133.0 (2 x C), 131.2 (q, J = 31.9 Hz), 124.7 (q, J = 3.1 Hz), 124.4 (q, J = 272.3 Hz), 84.2, 83.7, 25.0, 24.8 ppm; ^{19}F {^{1}H} NMR ($CDCl_3$, 470.8 MHz): δ −62.6 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 30.3 (br, 3B) ppm; IR: ν = 3352, 2981, 1605, 1345, 1321, 1164, 1138 cm^{-1}; HRMS (ESI) m/z calcd for $C_{27}H_{34}B_3NO_4F_3$ [M + H]$^+$ 526.2719, found 526.2724.

2-Cyclopropyl-6,8-bis(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-2,1-borazaronaphthalene (5b). Reaction was run at 80 °C with 3.0 equiv of B_2Pin_2 (381 mg, 1.5 mmol), and the product was obtained as a white solid (160 mg, 76%, 0.5 mmol scale); mp: 120−124 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 9.66 (s, 1H), 8.33 (s, 1H), 8.15 (s, 1H), 7.92 (d, J = 11.7 Hz, 1H), 6.57 (d, J = 11.9 Hz, 1H), 1.42 (s, 12H), 1.37 (s, 12H), 0.90−0.87 (m, 2H), 0.63 (dd, J = 6.0, 2.2 Hz, 2H), 0.40−0.28 (m, 1H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 148.1, 144.8, 142.6, 140.7, 124.1, 83.9, 83.5, 24.9, 24.8, 14.0, 6.3, 6.0 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 38.0, 30.2 (br, 2B) ppm; IR: ν = 3358, 2978, 1605, 1360, 1342, 1313, 1138, 851, 774 cm^{-1}; HRMS (ESI) m/z calcd for $C_{23}H_{35}B_3NO_4$ [M + H]$^+$ 422.2845, found 422.2849.

2-Methyl-6,8-bis(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-2,1-borazaronaphthalene (5c). Reaction was run at 80 °C with 3.0 equiv of B_2Pin_2 (381 mg, 1.5 mmol), and the product was obtained as a white solid (156 mg, 79%, 0.5 mmol scale); mp: 167−170 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 9.80 (s, 1H), 8.38 (s, 1H), 8.21 (s, 1H), 7.97 (d, J = 11.5 Hz, 1H), 6.80 (d, J = 12.5 Hz, 1H), 1.44 (s, 12H), 1.39 (s, 12H), 0.81 (s, 3H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 148.1, 144.5, 142.6, 140.8, 124.1, 83.9, 83.5, 24.9, 24.8 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 37.6, 30.5 (br, 2B) ppm; IR: ν = 3354, 2981, 1605, 1340, 1313, 1270, 1139, 758 cm^{-1}; HRMS (ESI) m/z calcd for $C_{21}H_{33}B_3NO_4$ [M + H]$^+$ 396.2689, found 396.2693.

*N-Deuterio-8-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-2-(4-(trifluoromethyl)phenyl)-2,1-borazaronaphthalene (**7**).* Reaction was run at 40 °C, and the product was obtained as a white solid (81.4 mg, 41%, 0.5 mmol scale); mp: 139−140 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 8.20 (d, J = 11.5 Hz, 1H), 8.10 (d, J = 7.8 Hz, 2H), 8.02 (d, J = 7.1 Hz, 1H), 7.81 (d, J = 7.7 Hz, 1H), 7.75 (d, J = 7.9 Hz, 2H), 7.30 (d, J = 11.5 Hz, 1H), 7.24 (t, J = 7.4 Hz, 1H), 1.49 (s, 12H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 146.2, 145.5, 137.0, 133.4, 132.9, 131.0 (q, J = 32.2 Hz), 125.3, 124.7 (q, J = 3.7 Hz), 124.3 (q, J = 272.1 Hz), 120.5, 84.2, 25.0 ppm; ^{19}F {^{1}H} NMR ($CDCl_3$, 470.8 MHz): δ −62.7 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 33.0 (br, 2B) ppm; IR: ν = 2983, 1603, 1555, 1374, 1323, 1305, 1163, 1109, 1067, 761 cm^{-1}; HRMS (EI) m/z calcd for $C_{21}H_{21}DB_2NO_2F_3$ [M]$^+$ 400.1852, found 400.1877.

Experimental Procedure for Palladium-Catalyzed Cross-Coupling of 8-Borylated 2,1-Borazaronaphthalenes. To a microwave vial with a stir bar were added borylated 2,1-borazaronaphthalene (1.0 equiv), solid aryl bromide (1.1 equiv), K_2CO_3 (3.0 equiv), and XPhos-Pd-G2 catalyst (2 mol %). The reaction vial was then capped and purged with argon. A solvent mixture of degassed t-BuOH/H_2O (1:1−2 mL/mmol) was added followed by any liquid aryl bromides (1.1 equiv). The reaction vessel was then heated at 40 °C for 18 h. Upon cooling, the solution was washed with H_2O, extracted with CH_2Cl_2, further washed with saturated NH_4Cl, dried (Na_2SO_4), and concentrated *in vacuo*. If required, the product was further purified by automated column chromatography with silica gel and hexane/EtOAc as eluent to yield 8-substituted 2,1-borazaronaphthalenes.

*8-(Pyrimidin-5-yl)-2-(4-(trifluoromethyl)phenyl)-2,1-borazaronaphthalene (**10a**).* Obtained as a light brown solid (172 mg, 98%, 0.5 mmol scale); mp: 97−99 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 9.39 (s, 1H), 8.99 (s, 2H), 8.27 (d, J = 11.5 Hz, 1H), 8.19 (s, 1H), 7.84−7.80 (m, 3H), 7.66 (d, J = 7.9 Hz, 2H), 7.42 (dd, J = 7.2, 1.1 Hz, 1H), 7.37 (t, J = 7.6 Hz, 1H), 7.33 (dd, J = 11.6, 1.6 Hz, 1H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 158.7, 158.6, 157.5, 146.6, 137.2, 132.9, 132.2, 131.8 (q, J = 32.4 Hz), 131.2, 130.4, 126.5, 125.1 (q, J = 3.6 Hz), 124.3 (q, J = 272.2 Hz), 123.6, 121.8 ppm; ^{19}F {^{1}H} NMR ($CDCl_3$, 470.8 MHz): δ −62.9 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 33.4 ppm; IR: ν = 3409, 3285, 2980, 1568, 1323, 1162, 1117, 1065, 827, 757 cm^{-1}; HRMS (ES+) m/z calcd for $C_{19}H_{14}BF_3N_3$ [M + H]$^+$ 352.1223, found 352.1222.

*8-(Pyrimidin-5-yl)-2-(p-tolyl)-2,1-borazaronaphthalene (**10b**).* Obtained as a white solid (100.3 mg, 67%, 0.5 mmol scale); mp: 102−104 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 9.39 (s, 1H), 8.99 (s, 2H), 8.19 (d, J = 11.6 Hz, 1H), 8.13 (s, 1H), 7.77 (dd, J = 7.8, 1.5 Hz, 1H), 7.67−7.61 (m, 2H), 7.41−7.28 (m, 3H), 7.24 (d, J = 7.6 Hz, 2H), 2.39 (s, 3H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 158.5, 157.5, 145.8, 140.3, 137.5, 132.8, 132.5, 131.0, 130.0, 129.3, 126.4, 123.3, 121.2, 21.7 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 32.3 ppm; IR: ν = 3403, 3031, 1597, 1549, 1436, 1401, 1191, 760, 726, 721, 692 cm^{-1}; HRMS (EI) m/z calcd for $C_{19}H_{16}BN_3$ [M]$^+$ 297.1437, found 297.1453.

*2-Cyclopropyl-8-(pyrimidin-5-yl)-2,1-borazaronaphthalene (**10c**).* Obtained as a beige solid (60.6 mg, 98%, 0.25 mmol scale); mp: 135−137 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 9.34 (s, 1H), 8.92 (s, 2H), 7.95 (d, J = 11.5 Hz, 1H), 7.66 (d, J = 7.5 Hz, 1H), 7.59 (s, 1H), 7.29 (dd, J = 7.3, 1.5 Hz, 1H), 7.22 (t, J = 7.5 Hz, 1H), 6.49 (dd, J = 11.7, 1.6 Hz, 1H), 0.83 (m, 2H), 0.55 (m, 2H), 0.11(m, 1H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 158.3, 157.5, 144.9, 137.4, 132.7, 130.9, 129.7, 125.9, 122.6, 120.6, 6.3 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 36.7 ppm; IR: ν = 3277, 3023, 2995, 1605, 1565, 1453, 1411, 1356, 827, 768 cm^{-1}; HRMS (EI) m/z calcd for $C_{15}H_{14}BN_3$ [M]$^+$ 247.1281, found 247.1306.

*8-(Pyridin-3-yl)-2-(4-(trifluoromethyl)phenyl)-2,1-borazaronaphthalene (**10d**).* Obtained as a yellow solid (170 mg, 97%, 0.5 mmol scale); mp: 55−56 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 8.86 (d, J = 1.6 Hz, 1H), 8.79 (dd, J = 4.8, 1.5 Hz, 1H), 8.37 (s, 1H), 8.26 (d, J = 11.5 Hz, 1H), 7.90 (dt, J = 7.7, 1.8 Hz, 1H), 7.81 (d, J = 7.8 Hz, 2H), 7.77 (d, J = 7.8 Hz, 1H), 7.65 (d, J = 7.8 Hz, 2H), 7.54 (dd, J = 7.5, 5.0 Hz, 1H), 7.44 (dd, J = 7.3, 1.2 Hz, 1H), 7.34 (t, J = 7.6 Hz, 1H), 7.30 (dd, J = 11.6, 1.8 Hz, 1H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 150.5, 149.8, 146.7, 137.2, 137.1, 133.9, 132.9, 131.5 (q, J = 32.3 Hz), 130.3, 130.1, 127.4, 126.3, 125.0 (q, J = 4.0 Hz), 124.2, 123.3 (q, J = 270.9 Hz), 121.6 ppm; ^{19}F {^{1}H} NMR ($CDCl_3$, 470.8 MHz): δ −62.8 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 33.3 ppm; IR: ν = 3398, 3029, 2970, 2931, 1601, 1567, 1320, 1119, 1104, 1065 cm^{-1}; HRMS (ES+) m/z calcd for $C_{20}H_{15}BF_3N_2$ [M + H]$^+$ 351.1280, found 351.1301.

*8-(Quinolin-3-yl)-2-(4-(trifluoromethyl)phenyl)-2,1-borazaronaphthalene (**10e**).* Obtained as a white solid (197 mg, 98%, 0.5 mmol scale); mp: 138−140 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 9.15 (d, J = 2.1 Hz, 1H), 8.49 (s, 1H), 8.38 (d, J = 1.7 Hz, 1H), 8.29 (dd, J = 13.5, 10.1 Hz, 1H), 7.94 (d, J = 8.1 Hz, 1H), 7.86 (t, J = 7.7 Hz, 1H), 7.83−7.77 (m, 3H), 7.69 (t, J = 7.4 Hz, 1H), 7.61 (d, J = 7.8 Hz, 1H), 7.54 (dd, J = 7.3, 1.1 Hz, 1H), 7.39 (t, J = 7.6 Hz, 1H), 7.33 (dd, J = 11.5, 1.6 Hz, 1H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 151.3, 147.9, 146.7, 137.5, 136.4, 132.9, 131.5 (q, J = 32.2 Hz), 131.1, 130.5, 130.4, 130.4, 129.7, 128.1, 128.1, 127.8, 127.5, 126.4, 125.0 (q, J = 3.6 Hz), 124.4 (q, J = 272.0 Hz), 121.7 ppm; ^{19}F {^{1}H} NMR ($CDCl_3$, 470.8 MHz): δ −62.9 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 31.6 ppm; IR: ν = 3402, 3012, 2969, 2935, 1561, 1319, 1160, 1110, 1065, 821, 751 cm^{-1}; HRMS (ES+) m/z calcd for $C_{24}H_{17}BF_3N_2$ [M + H]$^+$ 401.1437, found 401.1426.

*8-(Thiophen-3-yl)-2-(4-(trifluoromethyl)phenyl)-2,1-borazaronaphthalene (**10f**).* Obtained as a white solid (156.3 mg, 88%, 0.5 mmol scale); mp: 95−96 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 8.79

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(s, 1H), 8.25 (d, J = 11.5 Hz, 1H), 7.87 (d, J = 7.8 Hz, 2H), 7.73−7.66 (m, 3H), 7.63 (dd, J = 4.9, 3.0 Hz, 1H), 7.53−7.49 (m, 2H), 7.36 (dd, J = 4.9, 1.2 Hz, 1H), 7.32−7.27 (m, 2H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 146.4, 138.2, 137.3, 132.7 (2 x C), 131.2 (q, J = 32.2 Hz), 129.4, 129.2, 128.3, 127.5, 125.9, 124.8 (q, J = 3.8 Hz), 124.2 (q, J = 272.0 Hz), 123.6, 121.1 ppm; ^{19}F {^{1}H} NMR ($CDCl_3$, 470.8 MHz): δ −62.7 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 33.0 ppm; IR: ν = 3397, 3096, 3047, 3016, 1600, 1566, 1324, 1102, 1066, 752 cm^{-1}; HRMS (EI) m/z calcd for $C_{19}H_{13}BF_3NS$ [M]$^+$ 355.0814, found 355.0829.

*8-(Thiophen-3-yl)-2-(3-methoxyphenyl)-2,1-borazaronaphthalene (**10g**).* Obtained as a white solid (150 mg, 95%, 0.5 mmol scale); mp: 85−86 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 8.76 (s, 1H), 8.20 (d, J = 11.5 Hz, 1H), 7.67 (d, J = 7.8 Hz, 1H), 7.61 (dd, J = 4.7, 3.0 Hz, 1H), 7.51 (d, J = 2.1 Hz, 1H), 7.48 (dd, J = 7.5, 1.1 Hz, 1H), 7.40−7.34 (m, 3H), 7.33 (d, J = 2.5 Hz, 1H), 7.29 (dd, J = 11.5, 1.7 Hz, 1H), 7.24 (t, J = 7.7 Hz, 1H), 6.98 (dt, J = 7.3, 2.3 Hz, 1H), 3.86 (s, 3H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 159.7, 146.1, 138.6, 137.8, 129.6, 129.4, 129.3, 128.7, 127.5, 126.1, 126.0, 125.1, 123.8, 120.9, 118.2, 115.2, 55.3 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 34.7 ppm; IR: ν = 3384, 2920, 1597, 1565, 1436, 1264, 1255, 755, 720 cm^{-1}; HRMS (ES+) m/z calcd for $C_{19}H_{17}BNOS$ [M + H]$^+$ 318.1124, found 318.1106.

*2-(4-(Trifluoromethyl)phenyl)-8-(1,3,7-trimethyl-2,6-dioxo-2,3,6,7-tetrahydro-1H-purin-8-yl)-2,1-borazaronaphthalene (**10h**).* Obtained as a white solid (233 mg, 99%, 0.5 mmol scale); mp: >260 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 11.04 (s, 1H), 8.26 (d, J = 11.6 Hz, 1H), 8.04 (d, J = 7.7 Hz, 2H), 7.87 (d, J = 7.7 Hz, 1H), 7.70 (d, J = 7.9 Hz, 2H), 7.67 (dd, J = 7.7, 1.2 Hz, 1H), 7.44−7.32 (m, 2H), 4.15 (s, 3H), 3.76 (s, 3H), 3.49 (s, 3H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 155.6, 151.8, 149.6, 148.0, 146.3, 139.3, 133.2, 132.7, 131.8 (q, J = 32.3 Hz), 129.5, 127.2, 125.1 (q, J = 3.4 Hz), 124.4 (q, J = 272.1 Hz), 120.4, 115.0, 108.8, 35.1, 30.1, 28.4 ppm; ^{19}F {^{1}H} NMR ($CDCl_3$, 470.8 MHz): δ −62.8 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 33.0 ppm; IR: ν = 3312, 2950, 1698, 1658, 1539, 1323, 1164, 1108, 1067 cm^{-1}; HRMS (ES+) m/z calcd for $C_{23}H_{20}BF_3N_5O_2$ [M + H]$^+$ 466.1662, found 466.1668.

*2-(4-Methoxyphenyl)-8-(1,3,7-trimethyl-2,6-dioxo-2,3,6,7-tetrahydro-1H-purin-8-yl)-2,1-borazaronaphthalene (**10i**).* Recrystallized from toluene and obtained as a white solid (212 mg, 99%, 0.5 mmol scale); mp: >260 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 10.76 (s, 1H), 8.14 (d, J = 11.6 Hz, 1H), 7.89 (d, J = 8.5 Hz, 2H), 7.79 (d, J = 7.7 Hz, 1H), 7.61 (dd, J = 7.2, 1.0 Hz, 1H), 7.36 (dd, J = 11.5, 1.5 Hz, 1H), 7.29 (t, J = 7.7 Hz, 1H), 7.00 (d, J = 8.5 Hz, 2H), 4.13 (s, 3H), 3.87 (s, 3H), 3.77 (s, 3H), 3.49 (s, 3H). ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 161.3, 155.3, 151.6, 149.7, 147.7, 145.0, 139.5, 134.4, 132.2, 128.9, 126.7, 119.4, 114.3, 113.8, 108.4, 55.1, 34.7, 29.7, 28.3 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 31.6 ppm; IR: ν = 3305, 2939, 1703, 1662, 1598, 1442, 1243, 1179, 1026 cm^{-1}; HRMS (EI) m/z calcd for $C_{23}H_{23}BN_5O_3$ [M + H]$^+$ 428.1894, found 428.1891.

*6-Cyano-2-(4-(trifluoromethyl)phenyl)-8-(1,3,7-trimethyl-2,6-dioxo-2,3,6,7-tetrahydro-1H-purin-8-yl)-2,1-borazaronaphthalene (**10j**).* Obtained as a light yellow solid (79.7 mg, 65%, 0.25 mmol scale); mp: >260 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 11.35 (s, 1H), 8.23 (d, J = 11.6 Hz, 1H), 8.17 (s, 1H), 8.04 (d, J = 7.5 Hz, 2H), 7.88 (d, J = 1.5 Hz, 1H), 7.73 (d, J = 7.8 Hz, 2H), 7.53 (d, J = 11.5 Hz, 1H), 4.20 (s, 3H), 3.75 (s, 3H), 3.49 (s, 3H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 155.5, 151.6, 147.8, 147.1, 145.4, 141.8, 136.4, 133.4, 132.5 (q, J = 32.4 Hz), 131.1, 127.2, 125.2 (q, J = 3.8 Hz), 124.18 (q, J = 118.4 Hz), 116.3, 109.1, 104.1, 35.1, 30.0, 28.4 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 34.0 ppm; ^{19}F {^{1}H} NMR ($CDCl_3$, 470.8 MHz): δ −62.9 ppm; IR: ν = 3308, 2962, 2230, 1712, 1674, 1327, 1166, 1101, 1070, 779 cm^{-1}; HRMS (ES+) m/z calcd for $C_{24}H_{19}BN_6O_2F_3$ [M + H]$^+$ 491.1615, found 491.1636.

*6-(Trifluoromethoxy)-2-(4-(trifluoromethyl)phenyl)-8-(1,3,7-trimethyl-2,6-dioxo-2,3,6,7-tetrahydro-1H-purin-8-yl)-2,1-borazaronaphthalene (**10k**).* Obtained as a white solid (81 mg, 58%, 0.25 mmol scale); mp: 209−210 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 11.13 (s, 1H), 8.21 (d, J = 11.6 Hz, 1H), 8.03 (d, J = 7.8 Hz, 2H), 7.74−7.67 (m, 3H), 7.55 (d, J = 2.3 Hz, 1H), 7.47 (dd, J = 11.6, 1.6 Hz, 1H), 4.17 (s, 3H), 3.75 (s, 3H), 3.48 (s, 3H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 155.5, 151.6, 147.9, 147.8, 145.5, 141.8, 137.9, 133.2, 132.1 (q, J = 32.5 Hz), 127.7, 125.1 (q, J = 3.7 Hz), 124.2, 124.0 (q, J = 274.8 Hz), 122.5, 120.8 (q, J = 257.6 Hz), 116.0, 109.0, 34.9, 30.0, 28.3 ppm; ^{19}F {^{1}H} NMR ($CDCl_3$, 470.8 MHz): δ −58.3, −62.9 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 32.8 ppm; IR: ν = 3302, 3047, 2951, 1702, 1663, 1326, 1267, 1257, 1166, 1106 cm^{-1}; HRMS (ES+) m/z calcd for $C_{24}H_{19}BN_5O_3F_6$ [M + H]$^+$ 550.1485, found 550.1480.

*8-(4-(2,1-Borazaronaphthalen-2-yl)phenyl)-2-(4-(trifluoromethyl)phenyl)-2,1-borazaronaphthalene (**10l**).* Obtained as an off white solid (202 mg, 85%, 0.5 mmol scale); mp: 138−140 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 8.76 (s, 1H), 8.21−8.29 (m, 3H), 8.16 (d, J = 7.6 Hz, 2H), 7.84 (d, J = 7.8 Hz, 2H), 7.73 (t, J = 9.9 Hz, 2H), 7.70 (d, J = 7.7 Hz, 2H), 7.66 (d, J = 7.8 Hz, 2H), 7.52 (d, J = 7.0 Hz, 1H), 7.49 (t, J = 7.2 Hz, 1H), 7.41 (d, J = 8.8 Hz, 1H), 7.39−7.29 (m, 3H), 7.26 (t, J = 7.8 Hz, 1H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ146.7, 146.1, 140.3, 139.3, 137.2, 133.9, 133.0, 131.4 (q, J = 30.9 Hz), 131.2, 129.8, 129.8, 129.5, 129.4, 128.8, 128.1, 126.2, 126.0, 125.0, 125.0 (q, J = 4.6 Hz), 124.5 (q, J = 273.0 Hz), 121.5, 121.4, 118.5 ppm; ^{19}F {^{1}H} NMR ($CDCl_3$, 470.8 MHz): δ −62.8 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 33.8 ppm; IR: ν = 3385, 3397, 2954, 2931, 1598, 1562, 1437, 1322, 1167, 1117, 1066, 808, 757 cm^{-1}; HRMS (EI) m/z calcd for $C_{29}H_{21}B_2F_3N_2$ [M]$^+$ 476.1843, found 476.1857.

*8-(2-Methyl-2,1-borazaronaphthalen-3-yl)-2-(4-(trifluoromethyl)-phenyl)-2,1-borazaronaphthalene (**10m**).* Obtained as a white solid (70 mg, 68%, 0.25 mmol scale); mp: 159−161 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 8.42 (s, 1H), 8.28 (d, J = 11.5 Hz, 1H), 8.04 (s, 1H), 8.01 (s, 1H), 7.81 (d, J = 7.7 Hz, 2H), 7.68 (t, J = 6.1 Hz, 2H), 7.61 (d, J = 7.7 Hz, 2H), 7.52 (t, J = 7.6 Hz, 1H), 7.39−7.33 (m, 2H), 7.33−7.22 (m, 3H), 0.64 (s, 3H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 146.8, 144.6, 140.3, 137.2, 134.0, 132.9, 131.2 (q, J = 32.3 Hz), 129.8, 129.1, 128.9, 128.2, 125.8, 124.9 (q, J = 3.2 Hz), 124.5 (q, J = 272.0 Hz), 121.5, 121.2, 117.9 ppm; ^{19}F {^{1}H} NMR ($CDCl_3$, 470.8 MHz): δ −62.8 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 35.57, 30.9 ppm; IR: ν = 3377, 1559, 1320, 1101, 1063, 759, 752, 717 cm^{-1}; HRMS (EI) m/z calcd for $C_{24}H_{19}B_2N_2F_3$ [M]$^+$ 414.1686, found 414.1686.

*8-(p-Tolyl)-2-(4-(trifluoromethyl)phenyl)-2,1-borazaronaphthalene (**10n**).* Obtained as a white solid (162.1 mg, 89%, 0.5 mmol scale); mp: 92−93 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 8.70 (s, 1H), 8.26 (d, J = 11.5 Hz, 1H), 7.84 (d, J = 7.8 Hz, 2H), 7.71 (d, J = 7.8 Hz, 1H), 7.67 (d, J = 7.9 Hz, 2H), 7.49−7.43 (m, 3H), 7.41 (d, J = 7.9 Hz, 2H), 7.30 (t, J = 7.6 Hz, 2H), 2.51 (s, 3H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 146.4, 138.0, 137.1, 134.8, 132.7, 131.2 (q, J = 32.3 Hz), 131.1, 130.1, 129.5, 129.2, 128.9, 125.9, 124.7 (q, J = 3.8 Hz), 123.2 (q, J = 271.9 Hz), 121.1, 21.2 ppm; ^{19}F {^{1}H} NMR ($CDCl_3$, 470.8 MHz): δ −62.8 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 33.1 ppm; IR: ν = 3403, 3031, 2923, 2856, 1600, 1567, 1322, 1104, 1065, 753 cm^{-1}; HRMS (EI) m/z calcd for $C_{22}H_{17}BF_3N$ [M]$^+$ 363.1406, found 363.1399.

*2,8-Bis(4-(trifluoromethyl)phenyl)-2,1-borazaronaphthalene (**10o**).* Obtained as a white solid (204 mg, 98%, 0.5 mmol scale); mp: 105−106 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 8.47 (s, 1H), 8.27 (d, J = 11.5 Hz, 1H), 7.87 (d, J = 8.1 Hz, 2H), 7.81 (d, J = 7.8 Hz, 2H), 7.76 (d, J = 7.7 Hz, 1H), 7.71 (d, J = 8.0 Hz, 2H), 7.67 (d, J = 7.9 Hz, 2H), 7.44 (dd, J = 7.3, 1.3 Hz, 1H), 7.38−7.27 (m, 2H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.7, 141.9, 136.9, 132.9, 131.4 (q, J = 32.3 Hz), 130.6 (q, J = 32.5 Hz), 130.2, 130.1, 129.9, 129.7, 126.6 (q, J = 3.7 Hz), 126.3, 125.0 (q, J = 3.8 Hz), 124.4 (q, J = 271.9 Hz), 124.2 (q, J = 272.0 Hz), 121.5 ppm; ^{19}F {^{1}H} NMR ($CDCl_3$, 470.8 MHz): δ −62.5, −62.8 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 31.5 ppm; IR: ν = 3405, 3035, 2939, 1566, 1323, 1098, 1067, 1016, 818, 755 cm^{-1}; HRMS (EI) m/z calcd for $C_{22}H_{14}BNF_6$ [M]$^+$ 417.1123, found 417.1129.

*8-(4-(Dimethylamino)phenyl)-2-(4-(trifluoromethyl)phenyl)-2,1-borazaronaphthalene (**10p**).* Obtained as a white solid (180.4 mg, 92%, 0.5 mmol scale); mp: 114−115 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 8.82 (s, 1H), 8.25 (d, J = 11.5 Hz, 1H), 7.86 (d, J = 7.8 Hz,

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2H), 7.68−7.63 (m, 3H), 7.47−7.41 (m, 3H), 7.30−7.22 (m, 2H), 6.93 (d, J = 8.5 Hz, 2H), 3.08 (s, 6H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 150.1, 146.5, 137.3, 132.8, 132.6, 131.4, 131.0 (q, J = 32.2 Hz), 130.1, 129.5, 128.3, 126.4 (q, J = 272.1 Hz), 125.8, 124.7 (q, J = 3.9 Hz), 121.1, 112.9, 40.4 ppm; ^{19}F {^{1}H} NMR ($CDCl_3$, 470.8 MHz): δ 62.8 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 32.9 ppm; IR: ν = 3386, 3045, 2893, 2804, 1601, 1565, 1522, 1321, 1115, 1103, 1064 cm^{-1}; HRMS (ES+) m/z calcd for $C_{23}H_{21}BF_3N_2$ $[M]^+$ 393.1750, found 393.1763.

*8-(4-(Dimethylamino)phenyl)-2-(4-methoxyphenyl)-2,1-borazaronaphthalene (**10q**).* Obtained as a light gray solid (161 mg, 91%, 0.5 mmol scale); mp: 140−142 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 8.71 (s, 1H), 8.18 (d, J = 11.6 Hz, 1H), 7.75 (d, J = 8.5 Hz, 2H), 7.62 (d, J = 7.6 Hz, 1H), 7.47 (d, J = 8.7 Hz, 2H), 7.40 (dd, J = 7.3, 1.4 Hz, 1H), 7.29 (d, J = 11.8 Hz, 1H), 7.23 (t, J = 7.5 Hz, 1H), 6.99 (d, J = 8.5 Hz, 2H), 6.95 (d, J = 8.4 Hz, 1H), 3.86 (s, 3H), 3.09 (s, 6H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 161.1, 150.4, 145.8, 137.9, 134.4, 131.3, 130.4, 129.5, 128.4, 125.8 (d, J = 5.2 Hz), 120.7, 114.0, 113.2, 77.0, 55.3, 40.7 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 33.8 ppm; IR: ν = 3381, 2962, 2927, 2835, 1595, 1558, 1433, 1237, 1179, 819, 759 cm^{-1}; HRMS (ES+) m/z calcd for $C_{23}H_{24}BN_2O$ $[M + H]^+$ 355.1982, found 355.1989.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.7b01331.

Crystallographic data for **3a** (CIF)
Crystallographic data for **5a** (CIF)
Included are copies of ^{1}H, ^{13}C, ^{11}B, and ^{19}F NMR spectra for all compounds along with additional HTE screening data, computational characterization data and 2-D NMR and X-ray crystallographic validation of the regioselective borylation (PDF)

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Notes

The authors declare no competing financial interest.

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