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Method for Accessing Nitrogen-Containing, *B*-Heteroaryl-Substituted 2,1-Borazaronaphthalenes

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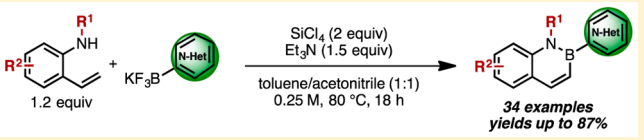
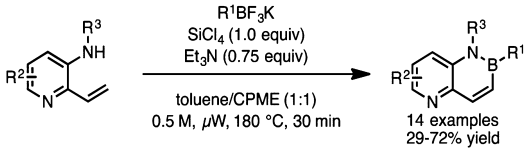
Supporting Information

ABSTRACT: The azaborine motif provides a mimic of aromatic systems through replacement of a C=C bond with a B−N bond. In particular, 2,1-borazaronaphthalenes, accessible through robust methods of synthesis and subsequent functionalization, afford an ideal platform to use for a variety of applications. However, the scope of substructures for this archetype has been limited by the lack of nitrogen-containing heteroaryls that can be incorporated within them. In this study, modified reaction conditions were developed to provide access to a wider range of substructures.



INTRODUCTION

With the well-documented value of isosteric replacements in biological and material applications, the capacity to access complementary systems that advance into new chemical space would be beneficial.[1] The azaborine motif, wherein a C−C double bond is exchanged with a B−N bond, provides a class of compound that mimics traditional aromatic systems both structurally and electronically.[2] Recently, the 2,1-borazaronaphthalene variant has been demonstrated to be a competent bioisostere in direct comparison to all-carbon analogues of propranolol,[3a] a well-known *β*-blocker, and phosphodiesterase 10A inhibitors.[3b] This specific class of azaborines has been investigated for their utility mainly because of the simple and robust method for their synthesis, which begins with a highly versatile condensation between 2-aminostyrenes and potassium organotrifluoroborates.[4] Furthermore, the myriad recent methods for functionalizing this core extends the potential for additional applications of the 2,1-borazaronaphthalene substructure.[5] However, one deficiency within the initial synthetic scope for accessing the 2,1-borazaronaphthalene core was the lack of nitrogen-containing heterocyclic functional units, particularly substituted off of boron.[4] Azaborine subunits containing *N*-heterocyclic scaffolds at this position would be of particular value, especially considering the diverse use of heterocycles and their recognition as "privileged structures" for modulation of biological systems.[6] A recent solution to address this problem was reported by Rombouts et al. using microwave (*μ*W) conditions (eq 1), which allowed the annulation of



(1)

pyridyl styrenes in high yields.[7] Furthermore, they reported select examples of pyridyltrifluoroborates being successful in the annulation under their conditions. Despite this recent advance, we were interested in finding a widely applicable set of conditions that would allow the incorporation of a variety of nitrogen-containing heterocyclic substructures. Herein we report conditions that enable the annulation of various nitrogen heterocyclic trifluoroborates to prepare a range of 2,1-borazaronaphthalene scaffold bearing having *B*-substituted *N*-heterocycles.

RESULTS AND DISCUSSION

Using the standard reaction conditions previously developed by our group for accessing the 2,1-borazaronaphthalene core,[4] initial attempts to condense nitrogen-containing trifluoroborates with *o*-aminostyrene derivatives were met with no success. To understand what caused nitrogen heterocyclic trifluoroborates to be incompatible with the reported conditions, pyridine was added in increasing amounts to the reaction of 2-aminostyrene (**1**) with phenyltrifluoroborate (**2**) (Table 1). As is evident from the results presented, pyridine has a marked inhibitory effect on the reaction, which intensifies with increasing amounts of this additive. With evidence in hand of the direct inhibition caused by added pyridine in the formation of 2-phenyl-2,1-borazaronaphthalene (**3**), we surmised that the effect of Lewis basic sites in the nitrogen-containing, heterocyclic trifluoroborates explained the previous lack of success observed in using them as partners for azaborine synthesis.[8] It was therefore anticipated that increasing the loading of $SiCl_4$ would allow the reaction to proceed in the case of heteroaryl-containing trifluoroborates.

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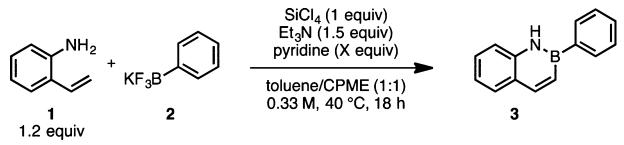
Table 1. Effect of Pyridine on the Synthesis of 2,1-Borazaronaphthalene

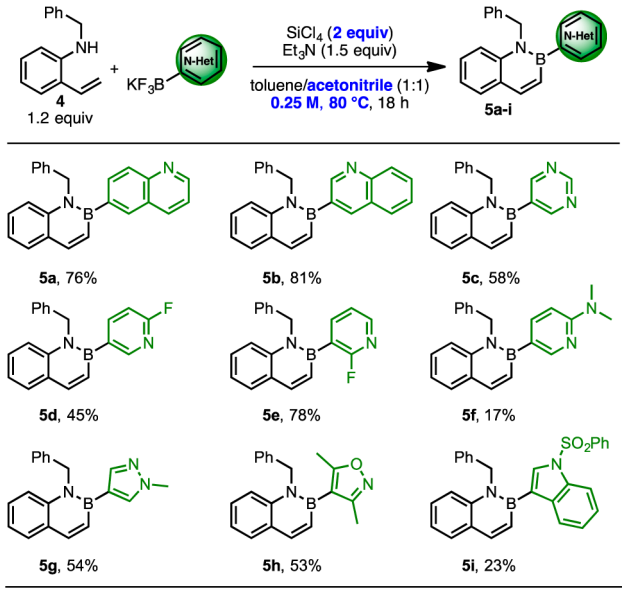


added pyridine	prod:SM[a]
0	full conversion
0.5	66:34
1.0	8:92
2.0	**no reaction**

[a]Ratios determined by GCMS.

By adjusting the reaction conditions (Table 2, in bold), using two equivalents of $SiCl_4$, exchanging cyclopentyl methyl ether (CPME) for acetonitrile, and increasing both the dilution and temperature to improve solubility, the substrate scope was explored. In early condition development, it was observed that some of the heteroaromatic 2,1-borazaronaphthalene cores were observed to have poor solubility, most probably because of the high tendency toward π stacking noticed in extended aromatic systems.[9] To mitigate this, substitutions off the styrenyl nitrogen helped facilitate both the reaction progress and purification by increasing the solubility of the resulting compounds. Upon reaction completion, purification of products was routinely done by initial filtration of solid byproducts followed by column chromatography. With this viable set of conditions to access isolatable products, we started investigating the tolerability of scope for the *N*-benzyl-2-aminostyrene precursor.

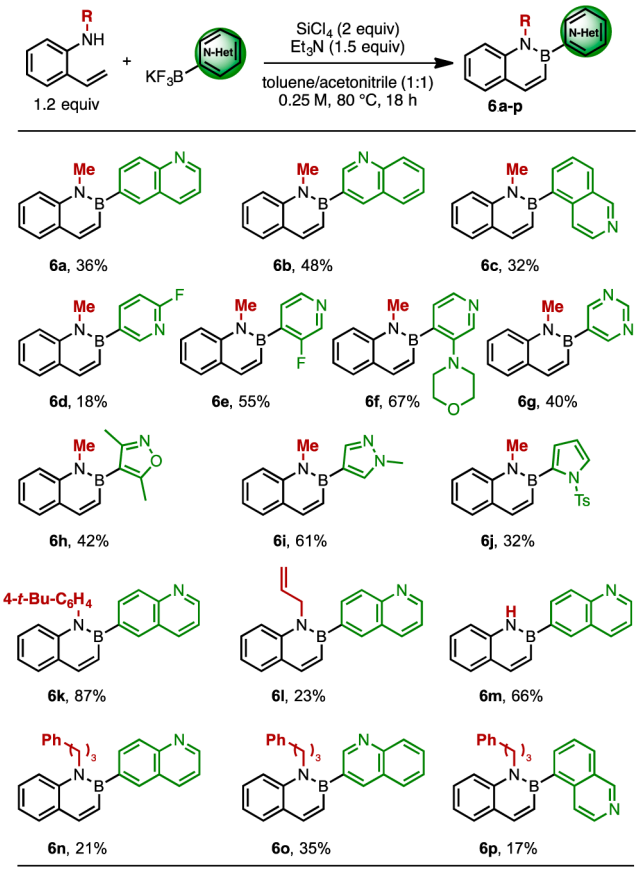
Table 2. Nitrogen-Containing *B*-Heterocyclic 2,1-Borazaronaphthalenes from *N*-Benzyl-2-aminostyrene



Under these conditions, quinolinyl- (**5a,b**), pyrimidinyl- (**5c**), and substituted pyridinyl- (**5d–f**) trifluoroborates were all tolerated in the cyclization process, as well as pyrazolyl- (**5g**), isoxazolyl- (**5h**), and indolyl- (**5i**) derivatives. It was observed that the substitution pattern of pyridine had an effect on yield (**5d** compared to **5e**), presumably caused by a combination of electronic effects.

Various other *N*-substituted 2-aminostyrenes could also be used in the annulation (Table 3). *N*-Methylated 2,1-borazaronaphthalenes could be synthesized (**6a–i**), but were consistently lower yielding compared to *N*-benzyl systems. Examples that had substituents more likely to disrupt $\pi-\pi$ interactions more effectively, such as morpholine (**6f**) or *N*-methylated pyrazole (**6i**), demonstrated higher product isolation. As previously mentioned, there was a consistent effect of the substitution pattern off of pyridine when comparing **6d** and **6e** to the corresponding benzylated compounds **5d** and **5e**. Isoquinoline variants (**6c,p**) could also be formed in modest yield using various *N*-alkylated 2-aminostyrenes partners. Other substituents tolerated off of the styrenyl nitrogen included 4-*t*-Bu-phenyl (**6k**), allyl (**6l**), arylated alkyl (**6n–p**) as well as unsubstituted N–H (**6m**).

Table 3. 2,1-Borazaronaphthalene Annulation with Nitrogen-Modified 2-Aminostyrene



In addition, preinstalled functional groups could be employed on the aminostyrene to develop more elaborated cores (Table 4). Fluorinated motifs (**7a–c**), including trifluoromethyl (**7a**) and trifluoromethyl ether (**7b**) were tolerated, as well as isopropyl (**7d**) and nitrile (**7e**) substituents. Typically those substrates incorporating substituents with more sp^3 character tended to be isolated in higher yield, continuing to suggest the influence of π interactions on the effectiveness of the reaction or isolation process. Aminopyridyl styrenes, similar to those previously reported,[6] were also amenable to these conditions (**7f–i**).

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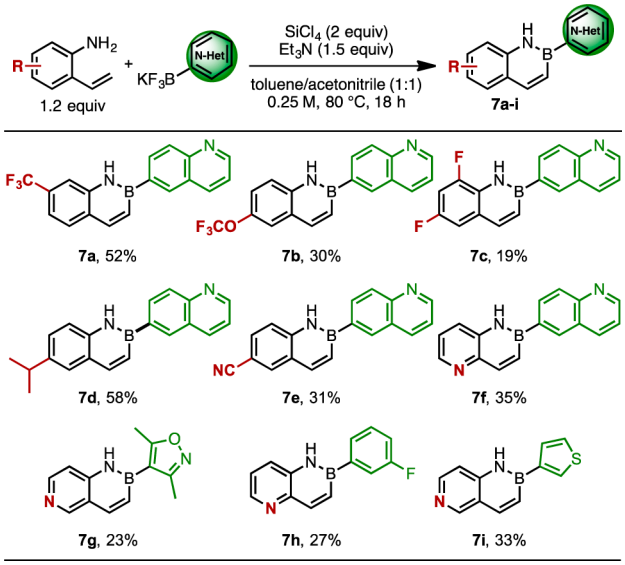
Table 4. Substituted 2-Aminostyrene Derivatives for *B*-Heterocyclic 2,1-Borazaronaphthalenes



CONCLUSION

The development of a new set of reaction conditions has enabled a broad advance of substrate classes available for the 2,1-borazaronaphthalene core isostere. Considering that the conditions were not optimized for each individual substrate, the capacity to access such diversity affords a reliable method to gain entry to versatile 2,1-borazaronaphthalene compounds. It is important to note that many of these substructures, even though quite simple, have no comparable analogues in the all-carbon naphthalene isosteres, speaking volumes about the ability of the method described to allow access to new chemical space. The power to access nitrogen heterocyclic-substituted azaborines thus allows the synthesis of more biologically relevant core structures that can continue to propagate the value of this class of isosteres.

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. MeCN was purchased dry and used as received. Et_3N was distilled prior to use and stored over activated molecular sieves. All reagents were purchased commercially and used as received, unless otherwise noted. Column chromatography was performed by Combiflash(R) using RediSep Rf Gold Normal-Phase Silica(R) columns or Alumina Basic columns. Melting points (°C) are uncorrected. Mass spectra (ESI- or CI-TOF) were recorded using CH_2Cl_2, MeCN, or MeOH as the solvent. IR spectra were recorded using FTIR-ATR of the neat oil or solid products. NMR spectra (^1H, ^{13}C $\{^1H\}$, ^{11}B, ^{19}F $\{^1H\}$) were performed at 298 K. ^1H (500.4 MHz) and ^{13}C $\{^1H\}$ (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 $\{^1H\}$ NMR spectra is due to ^{13}C–^{19}F coupling. ^{11}B (128.4 MHz) and ^{19}F $\{^1H\}$ 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.

Procedure for Synthesis of 2-Aminostyrene Derivatives. Previously unreported 2-aminostyene derivatives were synthesized using known procedures established for the Buchwald–Hartwig amination of 2-bromostyrene (**P1**)[4] or Suzuki cross-coupling of 2-bromoanilines (**P2**).[10]

*N-(4-(tert-Butyl)phenyl)-2-vinylaniline (**6k** Starting Material).* Synthesized following procedure **P1**. Obtained as a brown solid (2.31 g, 92%, 10.0 mmol scale); mp: 65–66 °C; ^1H NMR ($CDCl_3$, 500.4 MHz): δ 7.45–7.43 (dd, J = 7.7, 1.6 Hz, 1H), 7.31–7.21 (m, 3H), 7.19–7.16 (dt, J = 8.0, 1.6 Hz, 1H), 6.98–6.95 (t, J = 7.5 Hz, 1H), 6.94–6.91 (m, 2H), 6.91–6.85 (dd, J = 17.5, 11.0 Hz, 1H), 5.70–5.66 (dd, J = 17.4, 1.5 Hz, 1H), 5.48 (br s, 1H), 5.33–5.30 (dd, J = 11.0, 1.5 Hz, 1H), 1.31 (s, 9H) ppm; ^{13}C $\{^1H\}$ NMR ($CDCl_3$, 125.8 MHz): δ 143.7, 141.1, 140.7, 132.9, 129.1, 128.5, 127.2, 126.1, 121.7, 118.8, 117.6, 116.2, 34.1, 31.5 ppm; IR: ν = 3392, 2957, 1612, 1515, 1455, 1300, 1267, 824, 757, 738 cm^{-1}; HRMS (ESI) m/z calc. for $C_{18}H_{22}N$ $[M + H]^+$ 252.1752, found 252.1756.

*N-(3-Phenylpropyl)-2-vinylaniline (**6n,o,p** Starting Material).* Synthesized following procedure **P1**. Obtained as a yellow liquid (1.00 g, 66%, 6.4 mmol scale); ^1H NMR ($CDCl_3$, 500.4 MHz): δ 7.30–7.27 (td, J = 7.7, 2.0 Hz, 2H), 7.24–7.18 (m, 4H), 7.17–7.13 (td, J = 7.7, 1.4 Hz, 1H), 6.71–6.65 (m, 2H), 6.60–6.59 (d, J = 8.1 Hz, 1H), 5.60–5.56 (dd, J = 17.3, 1.6 Hz, 1H), 5.30–5.27 (dd, J = 11, 1.6 Hz, 1H), 3.76 (br s, 1H), 3.19–3.16 (t, J = 6.9 Hz, 2H), 2.77–2.73 (t, J = 7.4 Hz, 2H), 2.02–1.96 (m, 2H) ppm; ^{13}C $\{^1H\}$ NMR ($CDCl_3$, 125.8 MHz): δ 145.3, 141.6, 133.0, 128.9, 128.5, 128.4, 127.4, 126.0, 124.1, 117.1, 116.1, 110.6, 43.4, 33.5, 31.0 ppm; IR: ν = 3430, 3025, 2934, 2856, 1622, 1601, 1576, 1506, 1455, 1258, 908, 742, 698 cm^{-1}; HRMS (ESI) m/z calc. for $C_{17}H_{20}N$ $[M + H]^+$ 238.1596, found 238.1596.

*4-(Trifluoromethoxy)-2-vinylaniline (**7b** Starting Material).* Synthesized following procedure **P2**. Obtained as a yellow liquid (1.49 g, 73%, 10 mmol scale); ^1H NMR ($CDCl_3$, 500.4 MHz): δ 7.13 (s, 1H), 6.94–6.92 (d, J = 8.7 Hz, 1H), 6.69–6.64 (dd, J = 11.1, 17.4 Hz, 1H), 6.60–6.58 (d, J = 8.7 Hz, 1H), 5.63–5.60 (dd, J = 17.4, 1.2 Hz, 1H), 5.36–5.34 (dd, J = 11.1, 1.1 Hz, 1H), 3.74 (br s, 2H) ppm; ^{13}C $\{^1H\}$ NMR ($CDCl_3$, 125.8 MHz): δ 142.4, 141.5, 131.6, 124.7, 121.6, 120.71 (q, J = 255.8 Hz), 120.0, 117.0, 116.5 ppm; ^{19}F $\{^1H\}$ NMR ($CDCl_3$, 470.8 MHz): δ −58.3 ppm; IR: ν = 3352, 2984, 1780, 1496, 1435, 1247, 1221, 1203, 1046, 917, 873, 820 cm^{-1}; HRMS (ESI) m/z calc. for $C_9H_9NOF_3$ $[M + H]^+$ 204.0636, found 204.0623.

*2,4-Difluoro-6-vinylaniline (**7c** Starting Material).* Synthesized following procedure **P2**. Obtained as a yellow liquid (0.60 g, 39%, 10.0 mmol scale); ^1H NMR ($CDCl_3$, 500.4 MHz): δ 6.85–6.82 (dt, J = 9.4, 2.1 Hz, 1H), 6.75–6.69 (m, 2H), 5.68–5.64 (dd, J = 17.4, 0.9 Hz, 1H), 5.41–5.39 (dd, J = 11.0 Hz, 1H), 3.64 (br s, 2H) ppm; ^{13}C $\{^1H\}$ NMR ($CDCl_3$, 125.8 MHz): δ 155.0 (dd, J = 238.1, 12.6 Hz), 151.4 (dd, J = 240.4, 12.5 Hz), 130.9 (dd, J = 3.7, 2.5 Hz), 128.3 (dd, J = 13.2, 2.9 Hz), 126.4 (dd, J = 13.2, 4.8 Hz), 117.5, ppm, 108.3 (dd, J = 22.5, 3.3 Hz), 102.8 (dd, J = 27.0, 23.4 Hz); ^{19}F $\{^1H\}$ NMR ($CDCl_3$, 470.8 MHz): δ −124.3, −130.7 ppm; IR: ν = 3462, 3376, 3087, 1586, 1482, 1294, 1111, 978, 919, 859, 587 cm^{-1}; HRMS (ESI) m/z calc. for $C_8H_8NF_2$ $[M + H]^+$ 156.0625, found 156.0633.

*4-Amino-3-vinylbenzonitrile (**7e** Starting Material).* Synthesized following procedure **P2**. Obtained as a yellow solid (0.61 g, 43%, 10.0 mmol scale); mp: 77–78 °C; ^1H NMR ($CDCl_3$, 500.4 MHz): δ 7.48 (d, J = 1.8 Hz, 1H), 7.31–7.29 (dd, J = 8.4, 1.9 Hz, 1H), 6.67–6.61 (m, 2H), 5.65–5.61 (dd, J = 17.4, 1.0 Hz, 1H), 5.42–5.40 (dd, J = 11.0, 0.9 Hz, 1H), 2.04 (s, 2H) ppm; ^{13}C $\{^1H\}$ NMR ($CDCl_3$, 125.8 MHz): δ 147.7, 132.3, 131.5, 130.7, 123.6, 120.0, 117.9, 115.3, 100.1 ppm; IR: ν = 3465, 3369, 2215, 1631, 1599, 1558, 1499, 1425, 1307, 1282, 890, 815, cm^{-1}; HRMS (ESI) m/z calc. for $C_9H_9N_2$ $[M + H]^+$ 145.0766, found 145.0773.

General Procedure for Synthesis of Nitrogen-Containing Heteroaryl-2,1-borazaronaphthalenes. Potassium heteroaryltrifluoroborate (1.0 equiv) was introduced into a microwave vial with a stir bar. The vial was sealed with a Teflon-coated septum cap, then evacuated and purged with N_2 four times. An MeCN/toluene mixture (0.25 M, 1:1, v/v) and 2-aminostyrene (1.2 equiv) were introduced via syringe, followed by NEt_3 (1.5 equiv) and $SiCl_4$ (2.0 equiv). The resulting suspension was heated to 80 °C under vigorous stirring for 18 h. The vial was then cooled to rt, and the reaction mixture was neutralized by using saturated $NaHCO_3$ aqueous solution. The

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resulting solid was filtered off and the remaining solution was extracted with EtOAc/H_2O, dried ($MgSO_4$), and concentrated under vacuum. The crude material was purified through a short plug of silica and flushed with hexanes/EtOAc mixture (20 times solvent volume, 4:1, *v*/*v*). Solvents were removed *in vacuo* to obtain a crude material that was further purified by automated column chromatography on silica gel or basic alumina, eluting with a gradient method of CH_2Cl_2 and hexanes, starting at 100% hexanes to 10:90 hexanes/CH_2Cl_2.

1-Benzyl-2-(quinolin-6-yl)-2,1-borazaronaphthalene (**5a**). Purified on silica gel and obtained as a white solid (131.0 mg, 76%, 0.5 mmol scale); mp: 105−106 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 8.89−8.90 (m, 1H), 8.17−8.20 (d, J = 11.3 Hz, 1H), 8.02−8.06 (m, 2 H), 7.95 (s, 1H), 7.86−7.88 (d, J = 8.4 Hz, 1H), 7.74−7.75 (d, J = 7.6 Hz, 1H), 7.30−7.39 (m, 5H), 7.22−7.26 (m, 2H), 7.10−7.15 (m, 3H), 5.46 (s, 2H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 150.4, 148.1, 145.7, 141.1, 139.0, 136.2, 133.4, 132.4, 130.4, 128.8, 128.8, 128.3, 127.8, 127.4, 127.0, 125.7, 121.3, 121.0, 117.0, 52.6 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 36.7 ppm; IR: ν = 1605, 1588, 1547, 1492, 1455, 1410, 1353, 1229, 1181, 1143, 1118, 982, 840, 814, 798, 765, 748, 698, 476, 465 cm^{-1}; HRMS (ESI) m/z calc. for $C_{24}H_{19}BN_2Na$ [M + Na]$^+$ 369.1539, found 369.1547.

1-Benzyl-2-(quinolin-3-yl)-2,1-borazaronaphthalene (**5b**). Purified on silica gel and obtained as a white solid (140.8 mg, 81%, 0.5 mmol scale); mp: 94−95 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 9.07 (s, 1 H), 8.27 (s, 1H), 8.20−8.22 (d, J = 11.3 Hz, 1H), 8.07−8.09 (d, J = 8.5 Hz, 1H), 7.75−7.76 (d, J = 7.6 Hz, 1H), 7.68−7.70 (m, 2H), 7.48−7.51 (t, J = 8 Hz, 1H), 7.39−7.40 (m, 2H), 7.32−7.29 (m, 2H), 7.26−7.23 (m, 2H), 7.15−7.12 (m, 3H), 5.48 (s, 2H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 153.7, 147.7, 146.0, 141.2, 140.7, 138.7, 130.5, 129.5, 129.2, 128.9 (2 × C), 128.0, 127.7, 127.4, 127.1, 126.4, 125.6, 121.5, 117.0, 52.6 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 36.1 ppm; IR: ν = 1608, 1593, 1550, 1491, 1452, 1415, 1347, 1282, 1226, 943, 913, 856, 812, 789, 761, 731, 695, 477 cm^{-1}; HRMS (ESI) m/z calc. for $C_{24}H_{19}BN_2Na$ [M + Na]$^+$ 369.1539, found 369.1534.

1-Benzyl-2-(pyrimidin-5-yl)-2,1-borazaronaphthalene (**5c**). Purified on silica gel and obtained as a brown solid (86.2 mg, 58%, 0.5 mmol scale); mp: 123−124 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 9.18 (s, 1H), 8.82 (s, 2H), 8.21−8.23 (d, J = 11.3 Hz, 1H), 7.75−7.76 (d, J = 7.5 Hz, 1H), 7.40 (m, 2H), 7.24−7.31 (m, 4H), 7.08−7.09 (d, J = 7.5 Hz, 2H), 7.03−7.05 (d, J = 11.3 Hz, 1H), 5.40 (s, 2H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 160.1, 158.2, 146.6, 140.9, 138.0, 130.6, 129.2, 129.0, 127.4, 127.3, 125.3, 121.8, 116.9, 52.5 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 34.9 ppm; IR: ν = 1611, 1592, 1568, 1543, 1493, 1452, 1403, 1354, 1280, 1251, 1218, 1138, 962, 810, 762, 725, 695, 638, 482, 463 cm^{-1}; HRMS (ESI) m/z calc. for $C_{19}H_{17}BN_3$ [M + H]$^+$ 298.1516, found 298.1508.

1-Benzyl-2-(6-fluoropyridin-3-yl)-2,1-borazaronaphthalene (**5d**). Purified on silica gel and obtained as a brown solid (70.3 g, 45%, 0.5 mmol scale); mp: 93−94 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 8.34 (d, J = 1.85 Hz, 1H), 8.17−8.15 (d, J = 11.3 Hz, 1H), 7.88−7.84 (td, J = 8.5, 2.1 Hz, 1H), 7.73−7.72 (d, J = 7.6 Hz, 1H), 7.37−7.36 (m, 2H), 7.31−7.28 (t, J = 7.2 Hz, 2H), 7.25−7.21 (m, 2H), 7.09−7.08 (d, J = 7.3 Hz, 2H), 7.02−7.00 (d, J = 11.3 Hz, 1H), 6.87−6.85 (dd, J = 8.2, 2.3 Hz, 1H), 5.38 (s, 2H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 163.8 (d, J = 239.7 Hz), 151.3 (d, J = 13.5 Hz), 146.1, 145.2 (d, J = 7.3 Hz), 141.0, 138.4, 130.4, 129.0 (2 x C), 127.3, 127.1, 125.4, 121.5, 116.9, 108.8 (d, J = 35.3 Hz), 52.4 ppm; ^{19}F {^{1}H} NMR ($CDCl_3$, 470.8 MHz): δ −68.5 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 35.6 ppm; IR: ν = 1611, 1575, 1550, 1482, 1451, 1412, 1346, 1277, 1233, 1146, 1056, 964, 834, 805, 761, 727, 695, 645, 478, 463 cm^{-1}; HRMS (ESI) m/z calc. for $C_{20}H_{17}BN_2F$ [M + H]$^+$ 315.1469, found 315.1458.

1-Benzyl-2-(2-fluoropyridin-3-yl)-2,1-borazaronaphthalene (**5e**). Purified on silica gel and obtained as a yellow solid (122.3 mg, 78%, 0.5 mmol scale); mp: 108−109 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 8.18−8.19 (dd, J = 4.5, 2.0 Hz, 1H), 8.15−8.13 (d, J = 11.3 Hz, 1H), 7.76−7.70 (m, 2H), 7.39−7.33 (m, 2H), 7.24−7.17 (m, 4H), 7.10−7.07 (m, 1H), 7.04−7.03 (d, J = 7.7 Hz, 2H), 7.00−6.98 (d, J = 11.3 Hz, 1H), 5.33 (s, 2H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 164.5 (d, J = 235.2 Hz), 147.7 (d, J = 14.5 Hz), 145.9, 144.7 (d, J = 8.5 Hz), 140.8, 138.2, 130.4, 128.8, 128.7, 127.4, 127.0, 125.5, 121.5, 121.0 (d, J = 3.8 Hz), 117.0, 52.6 ppm; ^{19}F {^{1}H} NMR ($CDCl_3$, 470.8 MHz): δ −58.1 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 35.1 ppm; IR: ν = 1609, 1592, 1549, 1494, 1416, 1400, 1367, 1350, 1286, 1244, 1219, 1192, 962, 804, 764, 750, 744, 734, 706, 696 cm^{-1}; HRMS (ESI) m/z calc. for $C_{20}H_{16}BN_2FNa$ [M + Na]$^+$ 337.1288, found 337.1285.

1-Benzyl-2-(4-(N,N-dimethylamino)pyridin-5-yl)-2,1-borazaronaphthalene (**5f**). Purified on silica gel and obtained as a pale yellow solid (28.9 mg, 17%, 0.5 mmol scale); mp: 139−140 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 8.43 (m, 1H), 8.09−8.07 (d, J = 11.4 Hz, 1H), 7.67−7.65 (d, J = 8.4 Hz, 1H), 7.62−7.60 (dd, J = 8.6, 2.2 Hz, 1H), 7.31−7.27 (m, 4H), 7.23−7.20 (m, 1H), 7.17−7.14 (m, 3H), 7.09−7.07 (d, J = 11.4 Hz, 1H), 6.48−6.46 (dd, J = 8.6, 0.7 Hz, 1H), 5.47 (s, 2H), 3.07 (s, 6H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 159.0, 152.8, 145.0, 142.2, 141.5, 139.2, 130.2, 128.9, 128.4, 127.3, 126.9, 125.7, 120.8, 116.9, 105.4, 52.5, 37.9 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 34.0 ppm; IR: ν = 1588, 1549, 1510, 1495, 1453, 1412, 1385, 1344, 1272, 1242, 1223, 1145, 953, 805, 765, 759, 737, 730, 694, 478 cm^{-1}; HRMS (ESI) m/z calc. for $C_{22}H_{23}BN_3$ [M + H]$^+$ 340.1985, found 340.1989.

1-Benzyl-2-(1-methyl-1H-pyrazol-4-yl)-2,1-borazaronaphthalene (**5g**). Purified on silica gel and obtained as a yellow solid (80.7 mg, 54%, 0.5 mmol scale); mp: 116−117 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 8.05−8.03 (d, J = 11.5 Hz, 1H), 7.69 (s, 1H), 7.65−7.64 (d, J = 7.5 Hz, 1H), 7.46 (s, 1H), 7.33−7.30 (m, 4H), 7.26−7.24 (m, 1H), 7.20−7.19 (d, J = 7.5 Hz, 2H), 7.17−7.11 (m, 2H), 5.51 (s, 2H), 3.88 (s, 3H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 145.0, 144.8, 141.9, 138.6, 135.4, 130.1, 129.0, 128.5, 127.0, 127.0, 125.8, 120.7, 116.2, 52.6, 38.6 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 33.4 ppm; IR: ν = 1604, 1591, 1548, 1533, 1487, 1460, 1411, 1376, 1347, 1327, 1299, 1218, 1177, 934, 896, 808, 761, 730, 696, 674 cm^{-1}; HRMS (ESI) m/z calc. for $C_{19}H_{18}BN_3Na$ [M + Na]$^+$ 322.1491, found 322.1470.

1-Benzyl-2-(3,5-dimethylisoxazole-4-yl)-2,1-borazaronaphthalene (**5h**). Purified on silica gel and obtained as a pale yellow solid (83.0 mg, 53%, 0.5 mmol scale); mp: 110−111 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 8.14−8.12 (d, J = 11.3 Hz, 1H), 7.73−7.71 (d, J = 7.7 Hz, 1H), 7.45−7.35 (m, 2H), 7.23−7.20 (m, 3H), 7.18−7.15 (m, 1H), 6.97−6.96 (d, J = 7.4 Hz, 2H), 6.93−6.91 (d, J = 11.3 Hz, 1H), 5.36 (s, 2H), 2.20 (s, 3H), 2.15 (s, 3H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 169.8, 162.0, 145.8, 141.1, 138.1, 130.4, 128.7, 128.6, 127.4, 127.0, 125.6, 121.5, 117.0, 52.2, 12.8, 12.2 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 34.6 ppm; IR: ν = 1589, 1547, 1492, 1415, 1402, 1356, 1288, 1259, 1209, 1133, 1055, 1028, 958, 896, 818, 769, 733, 697, 481, 468 cm^{-1}; HRMS (ESI) m/z calc. for $C_{20}H_{20}BN_2O$ [M + H]$^+$ 315.1669, found 315.1674.

1-Benzyl-2-(1-(phenylsulfonyl)-1H-indol-3-yl)-2,1-borazaronaphthalene (**5i**). Purified on silica gel and obtained as a white solid (53.4 mg, 23%, 0.5 mmol scale); mp: 74−75 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 8.15−8.13 (d, J = 11.4 Hz, 1H), 8.03−8.01 (d, J = 8.3 Hz, 1H), 7.74−7.69 (m, 3H), 7.58−7.57 (d, J = 7.9 Hz, 1H), 7.49−7.46 (td, J = 7.5, 1.0 Hz, 1H), 7.41−7.38 (m, 3H), 7.35−7.32 (m, 5H), 7.30−7.27 (m, 1H), 7.24−7.20 (m, 2H), 7.14−7.11 (d, J = 11.3 Hz, 1H), 7.10−7.08 (d, J = 7.35 Hz, 2H), 5.41 (s, 2H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 145.4, 141.6, 138.9, 138.3, 135.6, 134.5, 133.6, 130.4, 129.1, 128.9, 128.9, 128.7, 127.3, 127.1, 126.7, 125.6, 124.4, 123.3, 122.4, 121.3, 116.9, 113.5, 52.7 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 34.0 ppm; IR: ν = 1609, 1592, 1551, 1445, 1412, 1368, 1175, 1130, 1087, 1021, 984, 809, 765, 746, 726, 686, 596, 587, 569, 551 cm^{-1}; HRMS (ESI) m/z calc. for $C_{29}H_{24}BN_2O_2S$ [M + H]$^+$ 475.1652, found 475.1645.

1-Methyl-2-(quinolin-6-yl)-2,1-borazaronaphthalene (**6a**). Purified by basic alumina column and obtained as a pale yellow oil (48.0 mg, 36%, 0.5 mmol scale); ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 9.30 (s, 1H), 8.44−8.43 (d, J = 5.9 Hz, 1H), 8.13−8.11 (d, J = 11.3 Hz, 1H), 7.99−7.98 (d, J = 8.2 Hz, 1H), 7.79−7.77 (t, J = 6.2 Hz, 2H), 7.68−7.60 (m, 3H), 7.48−7.47 (d, J = 5.8 Hz, 1H), 7.35−7.32 (t, J = 7.6 Hz, 1H), 6.96−6.94 (d, J = 11.3 Hz, 1H), 3.54 (s, 3H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 153.1, 145.0, 142.8, 142.2, 137.7, 134.4, 130.4, 128.9, 128.4, 127.2, 127.0, 126.8, 121.7, 121.4, 115.1, 37.1 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 36.6 ppm; IR: ν = 1608, 1590,

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1549, 1455, 1409, 1336, 1289, 1266, 1238, 1215, 1174, 1135, 1101, 1044, 830, 805, 760, 734, 674, 480 cm^{-1}; HRMS (ESI) m/z calc. for $C_{18}H_{16}BN_2$ $[M + H]^+$ 271.1407, found 271.1400.

*1-Methyl-2-(quinolin-3-yl)-2,1-borazaronaphthalene (**6b**).* Purified by basic alumina column and obtained as a yellow solid (65.1 mg, 48%, 0.5 mmol scale); mp: 101−102 °C; ^1H NMR ($CDCl_3$, 500.4 MHz): δ 9.16 (s, 1H), 8.39 (s, 1H), 8.17−8.11 (m, 2H), 7.87−7.85 (d, J = 8.1 Hz, 1H), 7.75−7.72 (m, 2H), 7.67−7.62 (m, 1H), 7.22−7.65 (m, 2H), 7.33−7.30 (m, 1H), 7.04−7.01 (d, J = 11.3 Hz, 1H), 3.78 (s, 3H) ppm; ^{13}C $\{^1H\}$ NMR ($CDCl_3$, 125.8 MHz): δ 154.2, 147.6, 145.3, 142.2, 141.1, 130.3, 129.4, 129.2, 128.9, 127.9, 127.8, 126.9, 126.4, 121.3, 115.1, 36.9 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 35.4 ppm; IR: ν = 1608, 1590, 1549, 1483, 1409, 1343, 1316, 1288, 1215, 1190, 1141, 1120, 1023, 947, 912, 807, 788, 753, 693, 484 cm^{-1}; HRMS (ESI) m/z calc. for $C_{18}H_{16}BN_2$ $[M + H]^+$ 271.1407, found 271.1409.

*2-(Isoquinolin-5-yl)-1-methyl-2,1-borazaronaphthalene (**6c**).* Purified by basic alumina column and obtained as a yellow oil (43.1 mg, 32%, 0.5 mmol scale); ^1H NMR ($CDCl_3$, 500.4 MHz): δ 9.30 (s, 1H), 8.44−8.43 (d, J = 5.8 Hz, 1H), 8.14−8.11 (d, J = 11.3 Hz, 1H), 8.00−7.98 (d, J = 8.2 Hz, 1H), 7.79−7.77 (t, J = 5.6 Hz, 2H), 7.68−7.60 (m, 3H), 7.48−7.47 (d, J = 5.9 Hz, 1H), 7.35−7.32 (t, J = 7.0 Hz, 1H), 6.96−6.94 (d, J = 11.3 Hz, 1H), 3.55 (s, 3H) ppm; ^{13}C $\{^1H\}$ NMR ($CDCl_3$, 125.8 MHz): δ 153.1, 145.0, 142.7, 142.2, 137.7, 134.4, 130.4, 128.9, 128.4, 127.2, 127.1, 126.8, 121.6, 121.4, 115.1, 37.1 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 36.5 ppm; IR: ν = 1608, 1590, 1550, 1455, 1445, 1424, 1409, 1336, 1289, 1238, 1215, 1174, 1135, 1101, 1044, 830, 805, 760, 739, 674 cm^{-1}; HRMS (ESI) m/z calc. for $C_{18}H_{16}BN_2$ $[M + H]^+$ 271.1407, found 271.1389.

*2-(6-Fluoropyridin-3-yl)-1-methyl-2,1-borazaronaphthalene (**6d**).* Purified by basic alumina column and obtained as a brown oil (21.5 g, 18%, 0.5 mmol scale); ^1H NMR ($CDCl_3$, 500.4 MHz): δ 8.43 (s, 1H), 8.10−8.08 (d, J = 11.3 Hz, 1H), 8.02−7.08 (td, J = 8.4, 2.1 Hz, 1H), 7.74−7.72 (d, J = 7.7 Hz, 1H), 7.65−7.58 (m, 2H), 7.32−7.29 (td, J = 7.8, 1.2 Hz, 1H), 7.02−7.00 (dd, J = 8.2, 2.6 Hz, 1H), 6.92−6.90 (d, J = 11.3 Hz, 1H), 3.72 (s, 3H) ppm; ^{13}C $\{^1H\}$ NMR ($CDCl_3$, 125.8 MHz): δ 163.7 (d, J = 239.3 Hz), 151.7 (d, J = 13.3 Hz), 145.9 (d, J = 7.1 Hz), 145.4, 142.1, 130.4, 129.0, 126.9, 121.4, 115.2, 108.9 (d, J = 35.3 Hz), 36.7 ppm; ^{19}F $\{^1H\}$ NMR ($CDCl_3$, 470.8 MHz): δ −68.9 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 35.0 ppm; IR: ν = 1608, 1581, 1552, 1482, 1470, 1444, 1412, 1342, 1289, 1241, 1213, 1123, 984, 853, 830, 802, 763, 740, 633, 486 cm^{-1}; HRMS (ESI) m/z calc. for $C_{14}H_{13}BN_2F$ $[M + H]^+$ 239.1156, found 239.1161.

*2-(3-Fluoropyridin-4-yl)-1-methyl-2,1-borazaronaphthalene (**6e**).* Purified by basic alumina column and obtained as a brown solid (65.1 mg, 55%, 0.5 mmol scale); mp: 97−98 °C; ^1H NMR ($CDCl_3$, 500.4 MHz): δ 8.49 (s, 1H), 8.47−8.46 (dd, J = 4.6, 2.3 Hz, 1H), 8.12−8.10 (d, J = 11.3 Hz, 1H), 7.75−7.73 (dd, J = 7.7, 1.2 Hz, 1H), 7.66−7.64 (d, J = 8.4 Hz, 1H), 7.62−7.59 (td, J = 6.9, 1.4 Hz, 1H), 7.39−7.37 (t, J = 4.8 Hz, 1H), 7.33−7.30 (td, J = 7.8, 0.8 Hz, 1H), 6.90−6.87 (d, J = 11.3 Hz, 1H), 3.63 (s, 3H) ppm; ^{13}C $\{^1H\}$ NMR ($CDCl_3$, 125.8 MHz): δ 160.7 (d, J = 250.6 Hz), 145.7, 144.9 (d, J = 3.0 Hz), 141.8, 137.5 (d, J = 27.1 Hz), 130.4, 129.1, 128.3 (d, J = 5.6 Hz), 127.0, 121.6, 115.1, 37.1 ppm; ^{19}F $\{^1H\}$ NMR ($CDCl_3$, 470.8 MHz): δ −118.8 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 33.2 ppm; IR: ν = 1611, 1586, 1552, 1442, 1410, 1346, 1282, 1237, 1202, 1054, 1001, 842, 798, 755, 664, 586, 574, 548, 525, 482 cm^{-1}; HRMS (ESI) m/z calc. for $C_{14}H_{13}BN_2F$ $[M + H]^+$ 239.1156, found 239.1166.

*1-Methyl-2-(2-(morpholino)pyridin-3-yl)-2,1-borazaronaphthalene (**6f**).* Purified by basic alumina column and obtained as a colorless oil (102.1 mg, 67%, 0.5 mmol scale); ^1H NMR ($CDCl_3$, 500.4 MHz): δ 8.28−8.27 (dd, J = 4.9 2.0 Hz, 1H), 8.05−8.03 (d, J = 11.3 Hz, 1H), 7.70−7.69 (dd, J = 7.7, 1.2 Hz, 1H), 7.61−7.55 (m, 3H), 7.29−7.25 (td, J = 7.8, 1.3 Hz, 1H), 6.94−6.92 (d, J = 11.3 Hz, 1H), 6.85−6.83 (dd, J = 7.1, 5.0 Hz, 1H), 3.60 (s, 7H), 3.27 (s, 4H) ppm; ^{13}C $\{^1H\}$ NMR ($CDCl_3$, 125.8 MHz): δ 156.3, 140.2, 138.3, 135.7, 135.1, 123.2, 121.8, 119.7, 114.1, 108.4, 107.9, 60.0, 42.9, 29.7 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 34.7 ppm; IR: ν = 1609, 1590, 1572, 1551, 1455, 1408, 1364, 1335, 1286, 1231, 1217, 1116, 980, 941, 925, 908, 808, 785, 762, 728 cm^{-1}; HRMS (ESI) m/z calc. for $C_{18}H_{21}BN_3O$ $[M + H]^+$ 306.1778, found 306.1771.

*1-Methyl-2-(pyrimidin-5-yl)-2,1-borazaronaphthalene (**6g**).* Purified by basic alumina column and obtained as a brown solid (44.5 mg, 40%, 0.5 mmol scale); mp: 109−110 °C; ^1H NMR ($CDCl_3$, 500.4 MHz): δ 9.25 (s, 1H), 8.94 (s, 2H), 8.15−8.12 (d, J = 11.3 Hz, 1H), 7.76−7.74 (d, J = 7.8 Hz, 1H), 7.70−7.62 (m, 2H), 7.35−7.32 (t, J = 6.8 Hz, 1H), 6.95−6.92 (d, J = 11.3 Hz, 1H), 3.75 (s, 3H) ppm; ^{13}C $\{^1H\}$ NMR ($CDCl_3$, 125.8 MHz): δ 160.6, 157.9, 145.9, 141.9, 130.5, 129.2, 127.0, 121.7, 115.2, 36.8 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 34.3 ppm; IR: ν = 1610, 1591, 1571, 1547, 1459, 1408, 1351, 1340, 1291, 1215, 1188, 1137, 1106, 980, 801, 754, 728, 647, 637, 484 cm^{-1}; HRMS (ESI) m/z calc. for $C_{13}H_{13}BN_3$ $[M + H]^+$ 222.1203, found 222.1201.

*1-Methyl-2-(3,5-dimethylisoxazole-4-yl)-2,1-borazaronaphthalene (**6h**).* Purified by basic alumina column and obtained as a white solid (49.5 mg, 42%, 0.5 mmol scale); mp: 86−87 °C; ^1H NMR ($CDCl_3$, 500.4 MHz): δ 8.06−8.04 (d, J = 11.3 Hz, 1H), 7.73−7.72 (d, J = 7.7 Hz, 1H), 7.64−7.57 (m, 2H), 7.32−7.25 (td, J = 7.0, 1.2 Hz, 1H), 6.87−6.84 (d, J = 11.3 Hz, 1H), 3.65 (s, 3H), 2.37 (s, 3H), 2.26 (s, 3H) ppm; ^{13}C $\{^1H\}$ NMR ($CDCl_3$, 125.8 MHz): δ 170.3, 162.2, 145.0, 142.3, 130.3, 128.8, 126.9, 121.4, 115.1, 36.8, 12.9, 12.2 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 33.7 ppm; IR: ν = 1591, 1551, 1463, 1444, 1415, 1404, 1360, 1336, 1291, 1279, 1253, 1217, 1207, 1131, 972, 891, 813, 767, 738, 485 cm^{-1}; HRMS (ESI) m/z calc. for $C_{14}H_{16}BN_2O$ $[M + H]^+$ 239.1356, found 239.1354.

*1-Methyl-2-(1-methyl-1H-pyrazol-4-yl)-2,1-borazaronaphthalene (**6i**).* Purified by basic alumina column and obtained as a brown solid (67.4 mg, 61%, 0.5 mmol scale); mp: 82−83 °C; ^1H NMR ($CDCl_3$, 500.4 MHz): δ 7.94−7.92 (d, J = 11.3 Hz, 1H), 7.84 (s, 1H), 7.64−7.61 (m, 2H), 7.54−7.48 (m, 2H), 7.23−7.18 (m, 1H), 6.98−6.95 (d, J = 11.4 Hz, 1H), 3.96 (s, 3H), 3.79 (s, 3H) ppm; ^{13}C $\{^1H\}$ NMR ($CDCl_3$, 125.8 MHz): δ 144.7, 144.1, 142.6, 135.6, 129.9, 128.4, 126.5, 120.5, 114.7, 38.5, 36.5 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 31.9 ppm; IR: ν = 1608, 1590, 1552, 1531, 1495, 1460, 1438, 1409, 1361, 1342, 1322, 1214, 1176, 1148, 1118, 940, 801, 757, 688, 677 cm^{-1}; HRMS (ESI) m/z calc. for $C_{13}H_{15}BN_3$ $[M + H]^+$ 224.1359, found 224.1370.

*1-Methyl-2-(1-tosyl-1H-pyrrol-2-yl)-2,1-borazaronaphthalene (**6j**).* Purified by basic alumina column and obtained as a white solid (57.9 mg, 32%, 0.5 mmol scale); mp: 122−123 °C; ^1H NMR ($CDCl_3$, 500.4 MHz): δ 8.00−7.98 (d, J = 11.3 Hz, 1H), 7.71−7.69 (d, J = 7.6 Hz, 1H), 7.59−7.54 (m, 2H), 7.51−7.50 (d, J = 8.4 Hz, 2H), 7.46−7.45 (dd, J = 3.1, 1.4 Hz, 1H), 7.28−7.25 (m, 1H), 7.17−7.15 (d, J = 8.4 Hz, 2H), 6.69−6.67 (d, J = 11.3 Hz, 1H), 6.40−6.38 (t, J = 3.2 Hz, 1H), 6.30−6.29 (q, J = 1.5 Hz, 1H), 3.49 (s, 3H), 2.35 (s, 3H) ppm; ^{13}C $\{^1H\}$ NMR ($CDCl_3$, 125.8 MHz): δ 144.5, 144.0, 142.1, 136.3, 130.1, 129.5, 128.6, 127.0, 126.9, 123.8, 121.0, 120.2, 115.1, 113.7, 37.3, 21.5 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 32.8 ppm; IR: ν = 1612, 1594, 1554, 1456, 1411, 1359, 1293, 1168, 1058, 1034, 951, 807, 756, 727, 701, 672, 588, 539, 489 cm^{-1}; HRMS (ESI) m/z calc. for $C_{20}H_{20}BN_2O_2S$ $[M + H]^+$ 363.1339, found 363.1335.

*1-(4-(tert-Butyl)phenyl)-2-(quinolin-6-yl)-2,1-borazaronaphthalene (**6k**).* Purified by basic alumina column and obtained as a brown solid (167.8 mg, 87%, 0.5 mmol scale); mp: 157−158 °C; ^1H NMR ($CDCl_3$, 500.4 MHz): δ 8.83 (s, 1H), 8.23−8.21 (d, J = 11.3 Hz, 1H), 7.93−7.92 (d, J = 7.9 Hz, 1H), 7.83−7.81 (d, J = 8.3 Hz, 1H), 7.75−7.73 (d, J = 7.5 Hz, 1H), 7.67 (s, 1H), 7.51−7.50 (d, J = 8.3 Hz, 1H), 7.41−7.34 (m, 3H), 7.29−7.22 (m, 3H), 7.11−7.08 (m, 3H), 1.34 (s, 9H) ppm; ^{13}C $\{^1H\}$ NMR ($CDCl_3$, 125.8 MHz): δ 150.5, 150.4, 147.9, 145.5, 142.8, 140.8, 136.2, 134.6, 134.4, 129.7, 128.8, 128.3, 127.6, 127.3, 126.3, 126.1, 121.3, 120.6, 117.8, 34.6, 31.4 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 34.1 ppm; IR: ν = 1604, 1594, 1545, 1506, 1486, 1410, 1321, 1291, 1281, 1258, 1170, 1150, 894, 837, 807, 794, 770, 758, 581, 550 cm^{-1}; HRMS (ESI) m/z calc. for $C_{27}H_{26}BN_2$ $[M + H]^+$ 389.2189, found 389.2201.

*1-Allyl-2-(quinolin-6-yl)-2,1-borazaronaphthalene (**6l**).* Purified by basic alumina column and obtained as a yellow solid (33.6 mg, 23%, 0.5 mmol scale); mp: 85−86 °C; ^1H NMR ($CDCl_3$, 500.4 MHz): δ 9.28 (s, 1H), 8.41−8.40 (d, J = 5.7 Hz, 1H), 8.14−8.11 (d, J

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= 11.3 Hz, 1H), 7.98−7.96 (d, J = 7.9 Hz, 1H), 7.77−7.76 (d, J = 6.8 Hz, 2H), 7.64−7.58 (m, 2H), 7.55−7.52 (t, J = 7.0 Hz, 1H), 7.49−7.48 (d, J = 5.9 Hz, 1H), 7.31−7.28 (t, J = 7.6 Hz, 1H), 6.95−6.93 (d, J = 11.3 Hz, 1H), 5.93−5.86 (m, 1H), 5.11−5.09 (d, J = 10.6 Hz, 1H), 4.91−4.88 (d, J = 17.3 Hz, 1H), 4.71−4.67 (dd, J = 15.2, 2.0 Hz, 1H), 4.58−4.54 (dd, J = 17.2, 2.1 Hz, 1H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 153.0, 145.2, 142.6, 141.1, 137.6, 134.9, 133.5, 130.5, 128.6, 128.4, 127.3, 127.1, 126.7, 121.7, 121.3, 116.6, 116.2, 51.0 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 37.1 ppm; IR: ν = 1608, 1590, 1547, 1455, 1409, 1358, 1333, 1283, 1245, 1219, 1174, 1134, 1049, 937, 918, 833, 809, 761, 675, 473 cm^{-1}; HRMS (ESI) m/z calc. for $C_{20}H_{18}BN_2$ [M + H]$^+$ 297.1563, found 297.1566.

*2-(Quinolin-6-yl)-2,1-borazaronaphthalene (**6m**).* Purified by basic alumina column and obtained as a white solid (84.6 mg, 66%, 0.5 mmol scale); mp: 226−227 °C; ^{1}H NMR (DMSO-d_6, 500.4 MHz): δ 10.7 (s, 1H), 8.94 (s, 1H), 8.69 (s, 1H), 8.48−8.44 (m, 2H), 8.24−8.22 (d, J = 11.3 Hz, 1H), 8.12−8.10 (d, J = 8.2 Hz, 1H), 7.80−7.73 (m, 2H), 7.59−7.51 (m, 2H), 7.42−7.40 (d, J = 11.1 Hz, 1H), 7.22−7.21 (m, 1H) ppm; ^{13}C {^{1}H} NMR (DMSO-d_6, 125.8 MHz): δ 150.9, 148.5, 145.5, 140.9, 136.4, 134.3, 135.6, 129.1, 128.5, 128.0, 127.7, 125.2, 121.5, 120.8, 118.7 ppm; ^{11}B NMR (Acetone-d_6, 128.4 MHz): δ 32.7 ppm; IR: ν = 1615, 1597, 1568, 1496, 1456, 1448, 1346, 1320, 1288, 1268, 1219, 1178, 1159, 872, 828, 802, 791, 765, 753 cm^{-1}; HRMS (ESI) m/z calc. for $C_{17}H_{14}BN_2$ [M + H]$^+$ 257.1250, found 257.1245.

*1-(3-Phenylpropyl)-2-(quinolin-6-yl)-2,1-borazaronaphthalene (**6n**).* Purified by basic alumina column and obtained as a yellow oil (39.1 mg, 21%, 0.5 mmol scale); ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 9.29 (s, 1H), 8.41−8.40 (d, J = 5.9 Hz, 1H), 8.10−8.07 (d, J = 11.2 Hz, 1H), 7.98−7.96 (d, J = 8.1 Hz, 1H), 7.76−7.71 (m, 2H), 7.64−7.61 (t, J = 7.0 Hz, 1H), 7.53−7.50 (t, J = 7.1 Hz, 1H), 7.46−7.42 (m, 2H), 7.30−7.27 (t, J = 7.5 Hz, 1H), 7.13−7.09 (m, 3H), 6.89−6.86 (m, 3H), 4.10−4.04 (m, 1H), 3.90−3.84 (m, 1H), 2.40−2.37 (t, J = 7.4 Hz, 2H), 2.03−1.94 (m, 2H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 153.0, 145.1, 142.5, 140.8, 140.7, 137.5, 133.6, 130.8, 128.7, 128.4, 128.2, 128.0, 127.5, 127.0, 126.8, 125.9, 121.6, 121.2, 115.4, 47.9, 33.0, 31.3 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 37.0 ppm; IR: ν = 1608, 1590, 1549, 1494, 1453, 1411, 1353, 1279, 1259, 1216, 1171, 1043, 1030, 830, 806, 763, 741, 698, 674, 475 cm^{-1}; HRMS (ESI) m/z calc. for $C_{26}H_{24}BN_2$ [M + H]$^+$ 375.2033, found 375.2031.

*1-(3-Phenylpropyl)-2-(quinolin-3-yl)-2,1-borazaronaphthalene (**6o**).* Purified by basic alumina column and obtained as a colorless oil (65.3 mg, 35%, 0.5 mmol scale); ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 9.10−9.09 (d, J = 1.3 Hz, 1H), 8.26 (s, 1H), 8.17−8.15 (d, J = 8.4 Hz, 1H), 8.09−8.07 (d, J = 11.3 Hz, 1H), 7.82−7.80 (d, J = 8.1 Hz, 1H), 7.76−7.71 (m, 2H), 7.58−7.55 (t, J = 7.6 Hz, 1H), 7.52−7.49 (t, J = 7.3 Hz, 1H), 7.46−7.44 (d, J = 8.5 Hz, 1H), 7.27−7.23 (m, 1H), 7.12−7.09 (m, 2H), 7.06−7.05 (d, J = 7.1 Hz, 1H), 7.02−7.01 (d, J = 7.3 Hz, 2H), 6.95−6.93 (d, J = 11.2 Hz, 1H), 4.21−4.18 (m, 2H), 2.57−2.54 (t, J = 7.4 Hz, 2H), 2.16−2.10 (m, 2H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 153.3, 147.5, 145.4, 140.7, 140.6, 140.0, 130.7, 129.3, 129.3, 128.8, 128.3, 128.1, 127.9, 127.9, 127.4, 126.4, 126.0, 121.2, 115.4, 47.5, 33.0, 31.5 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 34.9 ppm; IR: ν = 1608, 1591, 1549, 1486, 1453, 1412, 1347, 1280, 1217, 1189, 1125, 1026, 949, 910, 808, 788, 763, 749, 698, 477 cm^{-1}; HRMS (ESI) m/z calc. for $C_{26}H_{24}BN_2$ [M + H]$^+$ 375.2033, found 375.2045.

*2-(Isoquinolin-5-yl)-1-(3-phenylpropyl)-2,1-borazaronaphthalene (**6p**).* Purified by basic alumina column and obtained as a colorless oil (29.3 mg, 17%, 0.5 mmol scale); ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 9.29 (s, 1H), 8.41−8.40 (d, J = 5.8 Hz, 1H), 8.10−8.07 (d, J = 11.3 Hz, 1H), 7.98−7.96 (d, J = 8.1 Hz, 1H), 7.76−7.71 (m, 2H), 7.64−7.61 (t, J = 8.1 Hz, 1H), 7.53−7.50 (td, J = 8.5, 1.5 Hz, 1H), 7.46−7.41 (m, 2H), 7.30−7.27 (t, J = 7.1 Hz, 1H), 7.13−7.09 (m, 3H), 6.89−6.86 (m, 3H), 4.10−4.04 (m, 1H), 3.90−3.84 (m, 1H), 2.41−2.38 (t, J = 7.4 Hz, 2H), 2.04−1.94 (m, 2H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 153.1, 145.1, 142.6, 140.8, 140.7, 137.5, 133.6, 130.8, 128.8, 128.5, 128.2, 128.0, 127.5, 127.0, 126.8, 125.9, 121.6, 121.2, 115.4, 48.0, 33.3, 31.3 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 36.6 ppm; IR: ν = 1608, 1590, 1548, 1453, 1411, 1352, 1259, 1216, 1171, 1134, 1106, 1042, 1030, 829, 805, 762, 740, 698, 675, 474 cm^{-1}; HRMS (ESI) m/z calc. for $C_{26}H_{24}BN_2$ [M + H]$^+$ 375.2033, found 375.2025.

*2-(Quinolin-6-yl)-7-(trifluoromethyl)-2,1-borazaronaphthalene (**7a**).* Purified by basic alumina column and obtained as a white solid (83.8 mg, 52%, 0.5 mmol scale); mp: 173−174 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 8.96−8.95 (dd, J = 4.2, 1.7 Hz, 1H), 8.43 (br s, 1H), 8.38 (s, 1H), 8.24−8.19 (m, 4H), 7.79−7.77 (d, J = 8.1 Hz, 1H), 7.68 (s, 1H), 7.52−7.42 (m, 3H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 151.1, 149.2, 145.1, 139.6, 136.5, 133.7, 132.6, 130.4, 130.2, 129.1, 128.1, 127.8, 121.4, 117.6, 115.5 ppm; ^{19}F {^{1}H} NMR ($CDCl_3$, 470.8 MHz): δ −62.2 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 32.7 ppm; IR: ν = 1619, 1571, 1459, 1358, 1329, 1249, 1219, 1167, 1150, 1123, 1070, 924, 835, 772 cm^{-1}; HRMS (ESI) m/z calc. for $C_{18}H_{13}BN_2F_3$ [M + H]$^+$ 325.1124, found 325.1121.

*2-(Quinolin-6-yl)-6-(trifluoromethoxy)-2,1-borazaronaphthalene (**7b**).* Purified by basic alumina column and obtained as a white solid (51.4 mg, 30%, 0.5 mmol scale); mp: 204−205 °C; ^{1}H NMR (DMSO-d_6, 500.4 MHz): δ 10.9 (s, 1H), 8.97−8.96 (m, 1H), 8.71 (s, 1H), 8.48−8.45 (t, J = 8.0 Hz, 2H), 8.30−8.27 (d, J = 11.6 Hz, 1H), 8.14−8.12 (d, J = 8.5 Hz, 1H), 7.91−7.89 (d, J = 8.9 Hz, 1H), 7.81 (s, 1H), 7.60−7.51 (m, 3H) ppm; ^{13}C {^{1}H} NMR (DMSO-d_6, 125.8 MHz): δ 151.0, 148.6, 144.8, 141.9, 139.7, 136.4, 134.5, 133.5, 128.1, 127.7, 125.5, 121.8, 121.6, 120.7, 120.3 ppm; ^{19}F {^{1}H} NMR ($CDCl_3$, 470.8 MHz): δ −57.0 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 32.2 ppm; IR: ν = 1572, 1457, 1251, 1225, 1205, 1177, 1156, 1123, 996, 975, 942, 899, 876, 832, 801, 767, 754, 740, 478, 463 cm^{-1}; HRMS (ESI) m/z calc. for $C_{18}H_{13}BN_2OF_3$ [M + H]$^+$ 341.1073, found 341.1062.

*6,8-Difluoro-2-(quinolin-6-yl)-2,1-borazaronaphthalene (**7c**).* Purified by basic alumina column and obtained as a white solid (27.2 mg, 19%, 0.5 mmol scale); mp: 243−244 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 8.95−8.94 (dd, J = 4.2, 1.7 Hz, 1H), 8.42 (br s, 1H), 8.34 (s, 1H), 8.23−8.18 (m, 3H), 8.07−8.05 (d, J = 11.6 Hz, 1H), 7.48−7.45 (d, J = 11.6 Hz, 1H), 7.43−7.40 (dd, J = 8.3, 4.3 Hz, 1H), 7.15−7.14 (d, J = 8.8 Hz, 1H), 7.08−7.03 (td, J = 8.4, 2.6 Hz, 1H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 155.9 (dd, J = 241.8, 11.7 Hz), 151.4 (dd, J = 246.3, 13.1 Hz), 151.1, 149.2, 144.2 (t, J = 3.7, 3.1 Hz), 136.5, 133.6, 132.6, 129.1, 128.1, 126.9 (dd, J = 9.5, 4.5 Hz), 125.8 (d, J = 12.9 Hz), 121.3, 109.3 (dd, J = 21.5, 3.8 Hz), 103.1 (dd, J = 28.3, 22.3 Hz) ppm; ^{19}F {^{1}H} NMR ($CDCl_3$, 470.8 MHz): δ −119.8, −133.0 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 32.0 ppm; IR: ν = 1567, 1455, 1438, 1403, 1289, 1242, 1177, 1111, 1040, 978, 890, 829, 794, 769, 741, 707, 682, 647, 617, 594 cm^{-1}; HRMS (ESI) m/z calc. for $C_{17}H_{12}BN_2F_2$ [M + H]$^+$ 293.1062, found 293.1051.

*6-Isopropyl-2-(quinolin-6-yl)-2,1-borazaronaphthalene (**7d**).* Purified by basic alumina column and obtained as a white solid (85.3 mg, 58%, 0.5 mmol scale); mp: 148−149 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 8.92−8.91 (dd, J = 4.1, 1.7 Hz, 1H), 8.33 (m, 2H), 8.18−8.14 (m, 4H), 7.50 (s, 1H), 7.39−7.30 (m, 4H), 3.05−2.97 (m, 1H), 1.32 (s, 3H), 1.31 (s, 3H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 150.7, 149.0, 145.8, 141.8, 138.4, 136.4, 133.2, 132.9, 128.8, 128.1, 127.4, 126.5, 125.7, 121.1, 118.2, 33.6, 24.2 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 32.2 ppm; IR: ν = 1568, 1453, 1441, 1422, 1287, 1235, 1223, 1187, 1176, 1123, 838, 830, 822, 810, 803, 777, 755, 725, 707, 464 cm^{-1}; HRMS (ESI) m/z calc. for $C_{20}H_{20}BN_2$ [M + H]$^+$ 299.1720, found 299.1723.

*2-(Quinolin-6-yl)-6-carbonitrile-2,1-borazaronaphthalene (**7e**).* Purified by basic alumina column and obtained as a white solid (43.0 mg, 31%, 0.5 mmol scale); mp: 150−151 °C; ^{1}H NMR (DMSO-d_6, 500.4 MHz): δ 11.0 (s, 1 H), 8.97 (s,1H), 8.73 (s, 1H), 8.47−8.46 (d, J = 7.5 Hz, 2H), 8.32 (s, 1H), 8.29−8.26 (d, J = 11.6 Hz, 1H), 8.14−8.12 (d, J = 8.3 Hz, 1H), 7.93−7.86 (q, J = 23.6, 8.3 Hz, 2H), 7.60−7.54 (m, 2H) ppm; ^{13}C {^{1}H} NMR (DMSO-d_6, 125.8 MHz): δ 151.2, 148.7, 144.7, 143.7, 136.5, 134.9, 134.4, 133.5, 130.7, 128.2, 127.7, 125.1, 121.6, 119.9, 119.4, 102.9 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 33.2 ppm; IR: ν = 2221, 1613, 1597, 1576, 1461, 1343, 1321, 1298, 1244, 1212, 1180, 1171, 900, 877, 868, 832, 797, 770, 744, 574 cm^{-1}; HRMS (ESI) m/z calc. for $C_{18}H_{13}BN_3$ [M + H]$^+$ 282.1203, found 282.1206.

*2-(Quinolin-6-yl)-6,5-borazaroquinoline (**7f**).* Purified by basic alumina column and obtained as a white solid (45.1 mg, 35%, 0.5

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mmol scale); mp: 176−177 °C; ^{1}H NMR (DMSO-d_6, 500.4 MHz): δ 10.8 (br s, 1H), 8.95 (s, 1H), 8.72 (s, 1H), 8.54−8.46 (m, 3H), 8.33−8.30 (d, J = 11.2 Hz, 1H), 8.16−8.11 (dd, J = 16.6, 7.3 Hz, 2H), 7.71−7.69 (d, J = 10.8 Hz, 1H), 7.59−7.53 (m, 2H) ppm; ^{13}C {^{1}H} NMR (DMSO-d_6, 125.8 MHz): δ 151.1, 148.6, 146.6, 143.6, 142.3, 136.8, 136.5, 134.6, 133.5, 128.1, 127.7, 126.2, 123.3, 121.6 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 32.6 ppm; IR: ν = 1598, 1567, 1460, 1445, 1374, 1353, 1321, 1264, 1240, 1219, 1194, 1182, 1116, 826, 791, 767, 741, 622, 588, 478 cm^{-1}; HRMS (ESI) m/z calc. for $C_{16}H_{13}BN_3$ $[M + H]^+$ 258.1203, found 258.1198.

*2-(3,5-Dimethylisoxazole-4yl)-6,5-borazaroisoquinoline (**7g**).* Purified by basic alumina column and obtained as a white solid (25.7 mg, 23%, 0.5 mmol scale); mp: 200−2017 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 8.90 (s, 1H), 8.50 (d, J = 5.7 Hz, 1H), 8.14 (d, J = 11.6 Hz, 1H), 8.06 (br s, 1H), 7.22 (d, J = 5.7 Hz, 1H), 7.15 (d, J = 11.7 Hz, 1H), 2.60 (s, 3H), 2.46 (s, 3H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 174.0, 162.1, 151.8, 147.7, 144.6, 143.5, 121.4, 112.7 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 31.7 ppm; IR: ν = 3368, 3276, 2930, 1630, 1518, 1399, 1083, 967, 823, 798 cm^{-1}; HRMS (ESI) m/z calc. for $C_{12}H_{13}BN_3O$ $[M + H]^+$ 226.1152, found 226.1150.

*2-(3-Fluorophenyl)-6,5-borazaroquinoline (**7h**).* Purified by basic alumina column and obtained as a white solid (30.9 mg, 27%, 0.5 mmol scale); mp: 246−247 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 8.61−8.59 (dd, J = 4.4, 1.4 Hz, 1H), 8.39−8.37 (d, J = 11.8 Hz, 1H), 8.07 (br s, 1H), 7.70−7.67 (td, J = 7.9, 0.7 Hz, 2H), 7.59−7.58 (dd, J = 9.6, 2.5 Hz, 1H), 7.53−7.51 (dd, J = 11.9, 2.2 Hz, 1H), 7.48−7.44 (m, 1H), 7.41−7.38 (dd, J = 8.2, 4.4 Hz, 1H), 7.18−7.14 (m, 1H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 163.0 (d, J = 245.1 Hz), 147.1, 144.0, 143.1, 135.8, 130.0 (d, J = 6.9 Hz), 128.3 (d, J = 3.2 Hz), 125.9, 123.0, 119.0 (d, J = 18.8 Hz), 116.8 (d, J = 20.3 Hz). ^{19}F {^{1}H} NMR ($CDCl_3$, 470.8 MHz): δ −113.5 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 31.7 ppm; IR: ν = 1596, 1568, 1445, 1418, 1377, 1323, 1289, 1261, 1236, 1226, 1198, 1164, 880, 868, 825, 799, 786, 753, 746, 689 cm^{-1}; HRMS (ESI) m/z calc. for $C_{13}H_{11}BN_2F$ $[M + H]^+$ 225.0999, found 225.1009.

*2-(Thiophen-3-yl)-6,5-borazaroisoquinoline (**7i**).* Purified by basic alumina column and obtained as a white solid (34.9 mg, 33%, 0.5 mmol scale); mp: 165−166 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 8.87 (s, 1H), 8.50−8.48 (d, J = 5.7 Hz, 1H), 8.13−8.06 (m, 2H), 7.99 (dd, J = 2.5, 1.0 Hz, 1H), 7.58−7.57 (dd, J = 4.8, 1.0 Hz, 1H), 7.50−7.49 (dd, J = 4.8, 2.7 Hz, 1H), 7.31−7.29 (dd, J = 11.6, 1.7 Hz, 1H), 7.21−7.20 (d, J = 5.7 Hz, 1H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 151.6, 147.5, 144.9, 143.3, 133.7, 130.3, 126.4, 121.9, 112.6 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 31.1 ppm; IR: ν = 1623, 1568, 1516, 1465, 1426, 1385, 1325, 1204, 1172, 1129, 1077, 1043, 976, 939, 911, 827.8, 786, 755, 693, 557 cm^{-1}; HRMS (ESI) m/z calc. for $C_{11}H_{10}BN_2S$ $[M + H]^+$ 213.0658, found 213.0656.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b02574.

Copies of ^{1}H, ^{13}C, ^{11}B, and ^{19}F NMR spectra for all compounds (PDF)

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Notes

The authors declare no competing financial interest.

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