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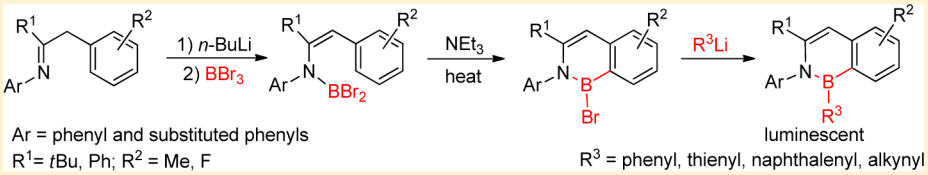
Synthesis of 1,2-Borazaronaphthalenes from Imines by Base-Promoted Borylation of C−H bond

Xinwang Liu, Pengbo Wu, Jianfeng Li, and Chunming Cui*

State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Cooperative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300071, People's Republic of China

Supporting Information



ABSTRACT: A new route from benzylic imines permits the synthesis of 1,2-borazaronaphthalenes in good yields. The reaction involves formation of the enamidyl dibromoborane, which undergoes base-promoted borylation of the nearby aromatic C−H bond. Electrophilic attack of the boron species onto the benzylic arene is supported by the slow borylation of arenes substituted with electron-withdrawing groups. The resultant boron bromides can be easily substituted with lithium reagents to provide a range of products. The electronic properties of these 1,2-borazaronaphthalene derivatives have been investigated by UV−vis and fluorescence spectroscopy.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are an important class of organic compounds that have received significant attention in organic electronics, dyes, sensors, and liquid crystal displays.[1] Replacement of a C=C bond in PAHs with a B−N bond leads to analogous BN aromatic systems because of the isoelectronic relationship of the B−N with a C=C bond. Despite their similarities, they also showed dramatically different reactions and optical and electronic properties due to the polarized B−N bond.[2] As early as 1958, Dewar reported the first synthesis of the singly BN-substituted aromatic compound.[3] Since then, a number of BN aromatic compounds and conjugated systems have been reported. With the increasing demands of new molecular materials in recent years, Piers, Ashe, Liu, and others have carried out extensive efforts in this area.[4−7]

Borazaronaphthalene is isosteric with naphthalene, which represents one of the smallest PAHs with many distinct features from benzene. Because of the BN unit in the molecule, there exist a number of isomers depending on the positions of the B and N atoms. Three of the isomers are shown in Figure 1. Theoretical calculations and experimental studies revealed that these isomers may display different stability, reactivity, and optical properties.[4b,6p,8] The synthesis and properties of isomers **A**, **B**, and their derivatives have been extensively studied, while isomer **C** has not been reported so far.[5e,i,j,7e,9]

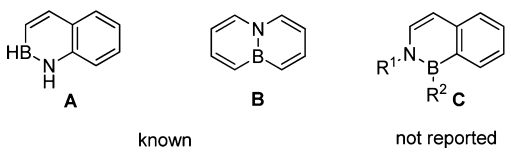


Figure 1. Structures of three borazaronaphthalene isomers.

Although a few effective approaches for the synthesis of 1,2-azaborines have been developed, they generally required either metal catalysts or multiple steps.[6d,10] In some cases, the starting materials are not easily available and the 1,2-azaborine products are difficult to functionalize.[4a,5a] Herein, we report the synthesis of 1,2-borazaronaphthalene derivatives starting with C-benzyl-substituted imines through two steps. The reaction involved a base-promoted C−H borylation of the benzyl rings with a B−Br bond, thus establishing a convenient synthetic route to various substituted BN naphthalene derivatives.

RESULTS AND DISCUSSION

Deprotonation of imine **1a** with *n*-BuLi and subsequent treatment with BBr_3 resulted in the formation of **1b**. No reaction was observed upon heating of **1b** at 80 °C for 1 h in C_6D_6 as disclosed by NMR analysis (see Figure S1 in the Supporting Information). However, addition of 1 equiv of NEt_3 in the reaction media and subsequent heating in toluene at 80 °C for 1 h led to the formation of a new species in 67% yield, whose ^{11}B NMR exhibited a singlet at δ 37.1 ppm, corresponding to a three-coordinate boron species. The NMR data indicated the formation of the 1,2-borazaronaphthalene **1** (Scheme 1).

This finding prompted us to extend this methodology to the investigation of the scope of the reaction and the factors that have pronounced effects on the reaction rate. The key step in this reaction is the C−H borylation of the benzyl ring of the

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Scheme 1. Synthesis of 1,2-Borazaronaphthalene 1

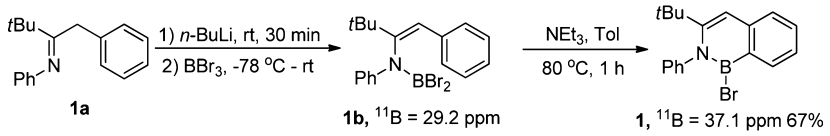
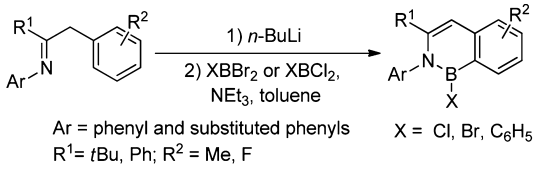
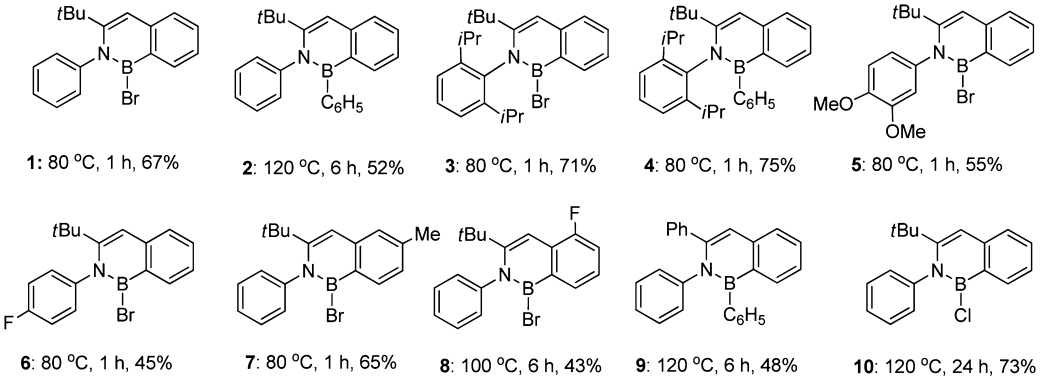


Table 1. Synthesis of Various Substituted BN Naphthalene Derivatives by Base-Mediated Borylation from Imines[a,b]





[a]Reaction conditions: imines (3 mmol), *n*-BuLi (3.0 mmol) in toluene for step 1; NEt_3 (3.0 mmol), $XBBr_2$, or BCl_3 (3.0 mmol), reaction temperatures and times listed for step 2. [b]Isolated yields.

imine. The closely related borylation has been reported to be promoted by Lewis acids such as $AlCl_3$ at high temperatures in a Friedel–Crafts cyclization pattern.[3,7b] The present base-promoted reaction did not require any metal additive under relatively mild conditions; thus, it might be useful for the synthesis of boron-containing conjugated rings. The same reactions with $PhBBr_2$ or BCl_3, instead of BBr_3, also led to the formation of the corresponding BN naphthalenes **2** and **10**. However, the formation of **2** and **10** required more harsh conditions and a longer reaction time, indicating the Lewis acidity of boron halides and the strength of B–X bonds have pronounced effects on the reaction rates (Table 1).

A series of imines with different substituents have been synthesized for the generation of the corresponding BN naphthalene derivatives (Table 1). The imines shown in Table 1 were synthesized by the reactions of *N*-phenyl-pivalimidoyl chlorides with benzylmagnesium chlorides in THF. The *N*-aryl and C-phenyl/*t*-Bu-substituted imines worked well to yield the expected BN naphthalenes in modest yields while *N*-*n*-Bu substituted imine **8a** led to a sluggish borylation reaction, and many attempts to isolate the desired product were unsuccessful to date. The bulky substituents on the N=C moiety of the imines apparently accelerate the reaction (**2** vs **4**). The electronic factors on the benzyl ring have significant effects on the reaction rate. Introduction of a fluorine atom in the benzyl ring apparently slowed down the reaction (**8** vs **1**). The imine with a 3-methyl-substituted benzyl group led to the isolation of only one isomer **7** possibly due to the steric effect of the methyl group. To further simplify the synthetic process, one-pot reactions of the imines with BBr_3NEt_3 in the presence of various bases at high temperatures have been investigated. However, the reactions proved to be sluggish, and no expected cyclic products can be observed by NMR analysis.

Compounds **1**–**10** have been fully characterized by multiple nuclear NMR spectroscopy and HRMS. The ^{11}B NMR spectra of **1**–**10** display similar resonances in the very narrow range of δ 36.2–40.0 ppm. Compounds containing a B–X (X = Cl or Br) bond are sensitive to moisture, but the B–Ph-substituted compounds proved to be stable at least for 5 h in dilute acidic (1.0 M HCl) and basic aqueous (1.0 M NaOH) solutions.

To confirm the molecular structures of these species, X-ray single-crystal analysis has been conducted for compound **3** and **4** (for the crystal structure of **4**, see Figure S3 in the Support Information). The colorless crystals of **3** suitable for X-ray analysis were obtained from *n*-hexane.

The structure shown in Figure 2 indicates the planar fused bicyclic six-membered ring contains a BN unit. The B–N bond length of 1.430(4) Å is comparable to analogous distances

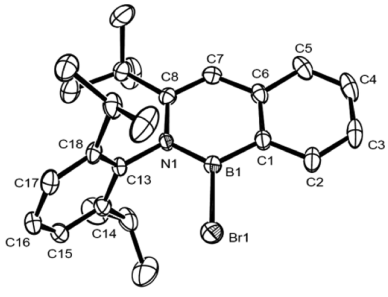


Figure 2. ORTEP illustration of **3** with ellipsoids drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

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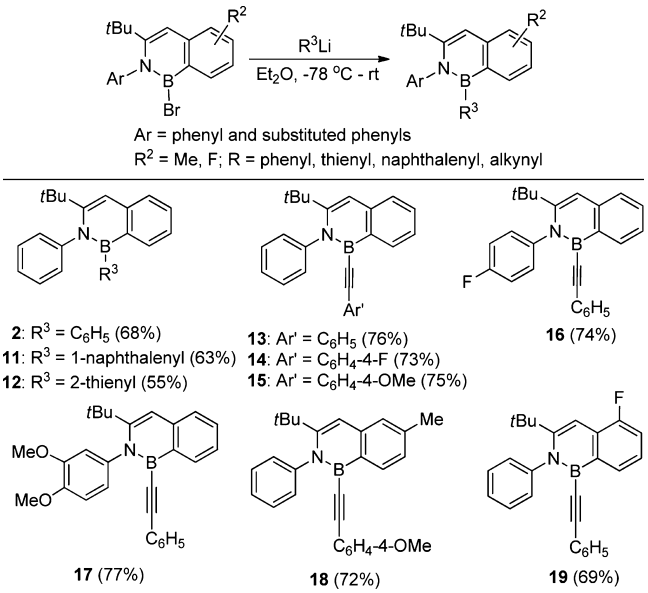
reported for 2,1-borazaronaphthalenes 1.424(5) Å.[7e] The N1−B1−C1−C2 skeleton is planar within experimental error.

The successful synthesis of compounds **1**, **3**, and **5**−**8** containing a B−Br bond allowed us to investigate the substitution reactions with various organolithium compounds for the synthesis of different B-substituted derivatives.[6a,9a] The results are summarized in Table 2. The bromide ligand can be easily substituted by phenyl, naphthalenyl, thienyl, and alkynyl groups to give compounds **2** and **11**−**19** in good yields under mild conditions. However, reactions of **1** with MeLi or 1-propenylmagnesium bromide under the same conditions led to the formation of a mixture that cannot be separated and identified definitely.

Table 2. Synthesis of B-Substituted Derivatives by Substituent Reaction[a,b]

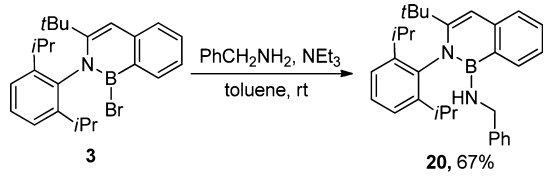


[a]Reaction conditions: 1,2-borazaronaphthalenes bromide (3 mmol), R^3Li (3 mmol) in Et_2O from −78 °C to rt. [b]Isolated yields.

Compounds **2** and **11**−**19** were obtained as white crystalline materials. Crystals of **12** are stable in air for several days while the other crystalline compounds are stable in air for several months. These materials were found to be stable enough for the purification by chromatography on silica gel. It is noted that the substitution reaction can be performed in situ without the isolation of the BN naphthalene boron bromides.

Reaction of **3** with amine $PhCH_2NH_2$ in toluene at room temperature led to the formation of the B−$NHCH_2Ph$ substituted BN cycle **20** as an air-stable white solid in 67% yield (Scheme 2), indicating that the bromide can be easily substituted by a nucleophile. However, reactions of **3** with MeOH and water under similar conditions were sluggish as indicated by NMR analysis, and the resulting products have not been isolated so far.

Scheme 2. Aminolysis of the B−Br Bond



These new compounds have been characterized by ^1H, ^{13}C, and ^{11}B NMR spectroscopy and HRMS. The crystal structure of **18** has been established by X-ray single-crystal analysis (Figure 3). Compound **18** was obtained by reaction of **7** with the alkynyllithium LiCC−C_6H_4−OMe. The X-ray analysis confirmed the methyl group in the benzyl ring lies in the para position of the boron atom. The N-substituted phenyl ring is approximately perpendicular to the central BN borazaronaphthalene ring with a dihedral angle of 86.65(13)°. The B−C≡C−C unit is almost linear. The small dihedral angle of 22.04(12)° between the two aromatic rings attached to the C≡C triple bond indicates some degree of π−π interactions between the two rings through the triple bond.[61]

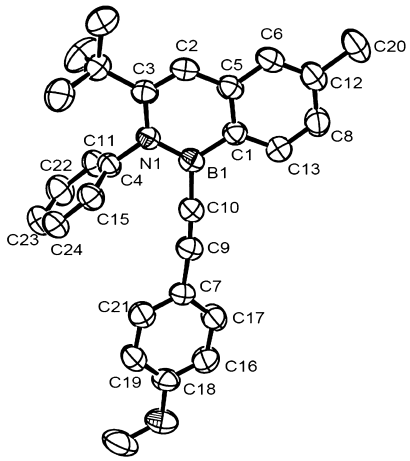


Figure 3. ORTEP illustration of **18** with ellipsoids drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

BN aromatic compounds have been studied as luminescent materials. Having these novel BN naphthalene derivatives in hand, we are interested in the investigation of their electronic structures by UV−vis and fluorescence spectroscopy (Figures 4 and 5 and Table 3).

The UV−vis spectra of the B-alkynyl-substituted derivatives in CH_2Cl_2 exhibited the absorption maxima in the range of 349−352 nm, somewhat red-shifted compared with the other 1,2-borazaronaphthalenes with an aromatic ring on the boron atom. These B-phenyl 1,2-borazaronaphthalenes exhibited a similar absorption maxima with known 2,1-borazaronaphtha-

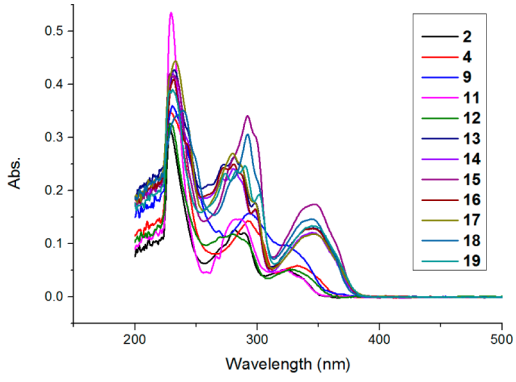


Figure 4. UV−vis spectra of selected 1,2-borazaronaphthalenes. All tests were performed in CH_2Cl_2 solution at 10^{-5} M.

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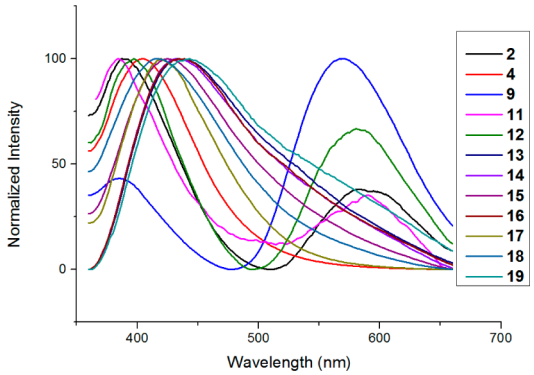


Figure 5. Normalized fluorescence emission spectra of selected 1,2-borazaronaphthalenes. All tests were performed in *n*-hexane solution at 10^{-5} M and λ_{ex} = 340 nm.

Table 3. Fluorescence Data for Selected Compounds[a]

compd	λ_{em} (nm)	Φ_F[b]	compd	λ_{em} (nm)	Φ_F[b]
2	388, 582		**14**	432	
4	405	0.14	**15**	424	0.11
9	385, 570		**16**	435	0.11
11	384, 590		**17**	420	
12	397, 580	0.15	**18**	416	
13	433		**19**	443	

[a]All experiments were performed in *n*-hexane solution at 10^{-5} M, λex =340 nm. [b]Absolute quantum yields were determined by a calibrated integrating sphere system.

lene derivatives (ca. 320 nm, type **A** in Figure 1) in the UV−vis spectra.[9a,b]

Compounds **2**, **9**, **11**, and **12** with two neighboring aromatic rings on the BN rings have similar fluorescence emission patters, in which two emission bands were observed. The emission maxima at 388, 384, and 397 nm for **2**, **11**, and **12** are more intense than those in the low energy region. In contrast, the emission maximum at 385 nm for **9** is only slightly weaker than the one at 570 nm. Compound **4** with the bulky 2,6-*i*-$Pr_2C_6H_3$ group on the nitrogen atom only shows one strong emission maximum at 405 nm. This suggests that the high wavelength emission bands (582, 570, 590, 580 nm) for **2**, **9**, **11**, and **12** are relevant to the $\pi-\pi$ interaction between the neighboring aromatic rings on the BN ring. The steric hindrance in **4** due to the bulky Ar group led to unfavorable $\pi-\pi$ overlap between the Ar and phenyl rings and, thus, the disappearance of the emission band. Compound **9** displays the relatively strong emission arising from the phenyl−phenyl interactions, probably due to the more efficient $\pi-\pi$ overlap as a result of the less hindered environment.

Compounds **13**−**19** with an alkynyl group on the boron atom only show one emission maximum ranging from 416 to 443 nm, which can be regarded as the emissions due to the BN naphthalene core. These emission maxima are red-shifted in comparison to those (the high energy emissions) observed in **2**, **9**, **11**, and **12**, indicating the more pronounced interaction of the alkynyl π system with the BN naphthalene unit than the aromatic rings on the boron atom in **2** and **9**, **11**, and **12**. The absolute quantum yields for the selected compounds **4**, **12**, **15**, and **16** are given in Table 3.

CONCLUSION

In conclusion, we have established a convenient and reliable base-promoted borylation route to novel 1,2-borazaronaphthalenes starting from easily available imines under mild conditions. This method allowed the synthesis of various substituted BN naphthalene derivatives. The ease of the generation of the ring system with a B−Br bond is especially important for the modification of the electronic structures of this class of the BN aromatic system as observed in the conjugation enlargement by a C≡C triple bond. This luminescent BN system encouraged us to employ this route to synthesize large π systems, which will be reported in due course.

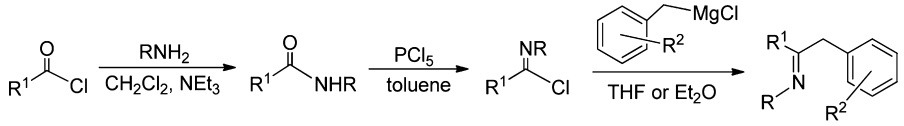
EXPERIMENTAL SECTION

General Considerations. All operations involving air- and moisture-sensitive compounds were carried out under an atmosphere of dry argon by using a modified Schlenk line and glovebox techniques. All solvents were freshly distilled from Na. The ^{1}H, ^{13}C, ^{11}B, and ^{19}F NMR spectra were recorded on a 400 MHz NMR spectrometer. Chemical shifts are referenced against external Me_4Si (^{1}H, ^{13}C), $BF_3\cdot Et_2O$ (^{11}B), and $CFCl_3$ (^{19}F). High-resolution mass spectra (HRMS) were obtained on a Q-Tof spectrometer. Imines were synthesized by a modified method (Scheme 3).[11]

General Procedure for the Synthesis of Imines. *N-(3,3-Dimethyl-1-phenylbutan-2-ylidene)aniline (**1a**).* To *N*-phenylpivalimidoyl chloride (9.8 g, 50 mmol) in 50 mL of THF was slowly added benzylmagnesium chloride in THF (2.0 M, 25 mL, 50 mmol) at 0 °C. After the reaction was stirred at 0 °C for 12 h, 30 mL of water was added to quench the reaction. The mixture was extracted with Et_2O (30 mL × 3). The extract was dried over $MgSO_4$. Removal of the solvent and reduced pressure distillation gave **1a** as a pale yellow oil (9.5 g, 76%). Bp: 82 °C (1.0 mmHg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32−7.13 (m, 5H), 7.05 (d, J = 7.3 Hz, 2H), 6.98 (t, J = 7.4 Hz, 1H), 6.71 (d, J = 7.4 Hz, 2H), 3.78 (s, 2H), 1.28 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 176.8, 150.3, 136.2, 127.6, 127.4, 127.2, 124.8, 121.4, 117.7, 39.9, 34.2, 27.8. HRMS (ESI): m/z calcd for $C_{18}H_{22}N$ $[M + H]^+$ 252.1747, found 252.1743

*N-(3,3-Dimethyl-1-phenylbutan-2-ylidene)-4-fluoroaniline (**2a**).* Obtained as a colorless oil (10.9 g, yield 81%). Bp: 85 °C (1.0 mmHg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25−7.11 (m, 3H), 7.00−6.94 (m, 2H), 6.92−6.84 (m, 2H), 6.62−6.54 (m, 2H), 3.75 (s, 2H), 1.25 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 179.2, 158.9 (d, J =

Scheme 3. Synthesis of Benzylic Imines 1a−8a



1a: R = C_6H_5, R^1 = *t*Bu, R^2 = H
2a R = 4-FC_6H_4, R^1 = *t*Bu, R^2 = H
3a: R = 3,4-$(MeO)_2C_6H_3$, R^1 = *t*Bu, R^2 = H
4a: R = 2,6-*i*$Pr_2C_6H_3$, R^1 = *t*Bu, R^2 = H
5a: R = C_6H_5, R^1 = *t*Bu, R^2 = 3-Me
6a: R = C_6H_5, R^1 = *t*Bu, R^2 = 2-F
7a: R = C_6H_5, R^1 = C_6H_5; R^2 = H
8a: R = *n*Bu, R^1 = *t*Bu, R^2 = H

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241.4 Hz), 147.4, 137.1, 128.5, 128.3, 126.0, 120.0 (d, J = 8.1 Hz), 115.3 (d, J = 22.2 Hz), 41.0, 35.1, 28.7. ^{19}F NMR (376 MHz, $CDCl_3$): δ −122.2. HRMS (ESI): m/z calcd for $C_{18}H_{21}FN$ $[M + H]^+$ 270.1653, found 270.1652

*N-(3,3-Dimethyl-1-phenylbutan-2-ylidene)-3,4-dimethoxyaniline (**3a**).* Obtained as a sticky pale yellow oil (9.6 g 62%). Bp: 165 °C (1.0 mmHg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23−7.06 (m, 3H), 6.98 (d, J = 7.4 Hz, 2H), 6.71 (d, J = 8.3 Hz, 1H), 6.19 (d, J = 8.4 Hz, 1H), 6.14 (s, 1H), 3.80 (s, 3H), 3.74 (s, 2H), 3.67 (s, 3H), 1.24 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 178.7, 149.0, 145.2, 144.6, 137.6, 128.5, 128.2, 125.9, 111.6, 109.6, 103.7, 56.1, 55.6, 40.9, 35.3, 28.8. HRMS (ESI): m/z calcd for $C_{20}H_{26}NO_2$ $[M + H]^+$ 312.1958, found 312.1953

*N-(3,3-Dimethyl-1-phenylbutan-2-ylidene)-2,6-diisopropylaniline (**4a**).* Obtained as a sticky pale yellow oil (13.2 g, 79%). Bp: 171 °C (1.0 mmHg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16−7.06 (m, 3H), 7.05−6.94 (m, 3H), 6.87−6.79 (m, 2H), 3.55 (s, 2H), 2.63 (hept, J = 6.8 Hz, 2H), 1.33 (s, 9H), 1.16 (d, J = 6.9 Hz, 6H), 1.11 (d, J = 6.7 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 174.9, 146.0, 136.8, 135.1, 129.4, 128.0, 125.8, 122.6, 122.3, 41.5, 36.5, 29.0, 28.2, 23.5, 21.2. HRMS (ESI): m/z calcd for $C_{24}H_{34}N$ $[M + H]^+$ 336.2686, found 336.2683.

*N-(3,3-Dimethyl-1-(m-tolyl)butan-2-ylidene)aniline (**5a**).* The reaction of Grignard reagent with imidoyl chloride was performed in Et_2O. Compound **5a** was obtained as a pale yellow oil (9.5 g, 72%). Bp: 91 °C (1.0 mmHg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.14−7.07 (m, 2H), 7.00 (t, J = 7.6 Hz, 1H), 6.88−6.81 (m, 2H), 6.76−6.66 (m, 2H), 6.57 (dd, J = 8.4, 1.1 Hz, 2H), 3.61 (s, 2H), 2.18 (s, 3H), 1.14 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 177.9, 151.4, 137.7, 137.1, 129.5, 128.7, 128.0, 126.6, 125.4, 122.4, 118.8, 40.9, 35.2, 28.9, 21.3. HRMS (ESI): m/z calcd for $C_{19}H_{24}N$ $[M + H]^+$ 266.1903, found 266.1901

*N-(1-(2-Fluorophenyl)-3,3-dimethylbutan-2-ylidene)aniline (**6a**).* The reaction of Grignard reagent with imidoyl chloride was performed in Et_2O. Compound **6a** was obtained as a pale yellow oil (8.8 g, 65%). Bp: 93 °C (1.0 mmHg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20 (t, J = 7.8 Hz, 2H), 7.17−7.10 (m, 1H), 7.07−6.98 (m, 2H), 6.98−6.87 (m, 2H), 6.67 (dd, J = 8.3, 0.9 Hz, 2H), 3.75 (s, 2H), 1.26 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 177.0, 160.3 (d, J = 245.5 Hz), 151.1, 130.2 (d, J = 4.0 Hz), 128.7, 127.8 (d, J = 8.1 Hz), 124.3 (d, J = 16.2 Hz), 123.7 (d, J = 4.0 Hz), 122.6, 118.6, 115.1 (d, J = 22.2 Hz), 41.0, 28.6, 27.8 (d, J = 3.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ −116.5. HRMS (ESI): m/z calcd for $C_{18}H_{21}FN$ $[M + H]^+$ 270.1653, found 270.1649

*N-(1,2-Diphenylethylidene)aniline (**7a**).*[12] Obtained as a yellow solid (8.5 g, 63%) by recrystallization from Et_2O. ^{1}H spectral data were the same with the reported data.

*N-(3,3-Dimethyl-1-phenylbutan-2-ylidene)butan-1-amine (**8a**).* Obtained as a colorless liquid (8.8 g, yield 76%). Bp: 66 °C (1.0 mmHg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34−7.26 (m, 2H), 7.22 (q, J = 7.1 Hz, 1H), 7.09 (d, J = 7.3 Hz, 2H), 3.76 (s, 2H), 3.28 (t, J = 7.0 Hz, 2H), 1.66−1.49 (m, 2H), 1.40−1.26 (m, 2H), 1.16 (s, 9H), 0.91 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 128.5, 128.0, 126.0, 51.7, 40.8, 33.4, 33.2, 28.3, 20.6, 14.1. HRMS (ESI): m/z calcd for $C_{16}H_{26}N$ $[M + H]^+$ 232.2060, found 232.2063.

Synthesis of 1b. To imine **1a** (3.0 mmol) in 30 mL of toluene was added *n*-BuLi (2.4 M, 1.3 mL, 3.0 mmol) at room temperature, and the mixture was stirred at room temperature for 30 min. The resulting suspension was cooled to −78 °C, and neat BBr_3 (3.0 mmol) was added. The reaction was slowly warmed to room temperature and stirred overnight. After filtration, the solvents were removed under reduced pressure to give **1b** as a colorless liquid (1.1 g, 88%). This compound cannot be further purified by distillation but can be directly used for the further reaction. ^{1}H NMR (400 MHz, C_6D_6): δ 7.56 (m, 2H), 7.35 (m, 2H), 6.88−7.13 (m, 6H), 6.50 (s, 1H, *t*-BuC=C*H*), 1.03 (s, 9H, *t*-Bu). ^{11}B NMR (128 MHz, C_6D_6): δ 29.2. HRMS (EI): m/z calcd for $C_{18}H_{20}BBr_2N$ $[M]^+$ 419.0050, found 419.0048

General Procedure for the Synthesis of 1,2-Borazaronaphthalene. *n*-BuLi (2.4 M, 1.3 mL, 3 mmol) was added to imine (3.0 mmol) in 30 mL of toluene, and the reaction was stirred at room temperature for 30 min. The resulted lithium salt suspension was cooled to −78 °C, and $PhBBr_2$ or BBr_3 (3 mmol) was added. The reaction was slowly warmed to room temperature and stirred overnight. After filtration, NEt_3 (3 mmol, 0.42 mL) was added to the filtrate, and the reaction was heated at 80 or 120 °C for several hours depending on the substrates. After filtration to remove NEt_3·HBr, the solvent was removed under reduced pressure to give crude product. The crude product was purified by crystallization from *n*-hexane or toluene at −40 °C.

*1-Bromo-2-phenyl-3-tert-butyl-1,2-dihydrobenzo[c][1,2]-azaborinine (**1**).* The reaction was heated at 80 °C for 1 h. Compound **1** was obtained as a white solid (0.68 g, 67%). Mp: 98 °C. ^{1}H NMR (400 MHz, C_6D_6): δ 8.62 (d, J = 7.7 Hz, 1H), 7.51−7.41 (m, 2H), 7.38−7.25 (m, 1H), 7.06−6.99 (m, 3H), 6.99−6.93 (m, 2H), 6.90 (s, 1H), 1.06 (s, 9H). ^{13}C NMR (101 MHz, C_6D_6): δ 151.9, 146.0, 141.6, 136.0, 132.0, 131.8, 127.6, 126.9, 125.7, 110.4, 37.7, 32.3, the resonance for the carbon atom adjacent to the boron could not be observed. ^{11}B NMR (128 MHz, C_6D_6): δ 37.1. HRMS (EI): m/z calcd for $C_{18}H_{19}BBrN$ $[M]^+$ 339.0789, found 339.0795.

*3-tert-Butyl-1,2-diphenyl-1,2-dihydrobenzo[c][1,2]azaborinine (**2**).* $PhBBr_2$ was used, and the reaction was performed at 120 °C for 6 h. Compound **2** was obtained as a white solid by crystallization from toluene (0.53 g, 52%). Mp: 128−129 °C. ^{1}H NMR (400 MHz, C_6D_6): δ 7.98 (d, J = 7.7 Hz, 1H), 7.65 (d, J = 7.9 Hz, 1H), 7.53 (t, J = 7.0 Hz, 1H), 7.25 (t, J = 7.3 Hz, 1H), 7.19 (s, 2H), 7.13−7.01 (m, 4H), 7.01−6.92 (m, 2H), 6.85−6.76 (m, 3H), 1.22 (s, 9H). ^{13}C NMR (101 MHz, C_6D_6): δ 151.1, 145.8, 142.1, 136.7, 132.6, 131.8, 131.1, 127.1, 126.8, 126.7, 126.6, 126.3, 124.8, 110.4, 37.8, 32.6, the resonances for the carbon atoms adjacent to the boron could not be observed. ^{11}B NMR (128 MHz, C_6D_6): δ 39.3. HRMS (ESI): m/z calcd for $C_{24}H_{25}BN$ $[M + H]^+$ 338.2075, found 338.2069

*1-Bromo-3-tert-butyl-2-(2,6-diisopropylphenyl)-1,2-dihydrobenzo[c][1,2]azaborinine (**3**).* Obtained as a white solid (0.90 g, 71%). Single crystals of **3** suitable for X-ray diffraction were obtained by cooling a solution of **3** in *n*-hexane. Mp: 115−116 °C. ^{1}H NMR (400 MHz, C_6D_6): δ 8.63 (d, J = 7.7 Hz, 1H), 7.47−7.38 (m, 2H), 7.29−7.19 (m, 2H), 7.09−7.03 (m, 3H), 2.64 (hept, J = 6.8 Hz, 2H), 1.17 (d, J = 6.7 Hz, 6H), 1.15−1.11 (m, 15H). ^{13}C NMR (101 MHz, C_6D_6): δ 152.8, 145.7, 142.9, 141.9, 136.4, 132.2, 128.8, 126.6, 125.5, 124.3, 113.6, 39.2, 34.1, 28.6, 25.2, 23.9, the resonance for the carbon atom adjacent to the boron could not be observed. ^{11}B NMR (128 MHz, C_6D_6): δ 36.5. HRMS (EI): m/z calcd for $C_{24}H_{31}BBrN$ $[M]^+$ 423.1728, found 423.1731

*3-tert-Butyl-2-(2,6-diisopropylphenyl)-1-phenyl-1,2-dihydrobenzo[c][1,2]azaborinine (**4**).* Obtained as a white solid by recrystallization from toluene (0.95 g, 75%). Single crystals of **4** suitable for X-ray diffraction were obtained by cooling a solution of **4** in toluene. Mp: 188−189 °C. ^{1}H NMR (400 MHz, C_6D_6): δ 8.11 (d, J = 7.8 Hz, 1H), 7.59 (d, J = 7.9 Hz, 1H), 7.51−7.44 (m, 1H), 7.23−7.17 (m, 3H), 7.07 (dd, J = 5.2, 1.8 Hz, 3H), 7.01 (dd, J = 6.9, 2.7 Hz, 2H), 6.96 (d, J = 7.7 Hz, 2H), 2.88−2.70 (m, 2H), 1.22 (s, 9H), 1.13 (d, J = 6.8 Hz, 6H), 0.49 (d, J = 6.7 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.2, 145.6, 142.1, 141.5, 136.9, 135.3, 130.6, 127.8, 127.0, 126.5, 125.8, 123.8, 123.6, 112.4, 39.2, 33.9, 28.0, 24.2, 23.9, the resonances for the carbon atoms adjacent to the boron could not be observed. ^{11}B NMR (128 MHz, C_6D_6): δ 40.0. HRMS (ESI): m/z calcd for $C_{30}H_{37}BN$ $[M + H]^+$ 422.3014, found 422.3016

*1-Bromo-3-tert-butyl-2-(3,4-dimethoxyphenyl)-1,2-dihydrobenzo[c][1,2]azaborinine (**5**).* Obtained as a white solid by recrystallization from Et_2O (0.60 g, 55%). Mp: 112−114 °C. ^{1}H NMR (400 MHz, C_6D_6): δ 8.66 (d, J = 7.7 Hz, 1H), 7.47 (q, J = 7.7 Hz, 2H), 7.30 (t, J = 7.2 Hz, 1H), 6.95 (s, 1H), 6.61 (d, J = 8.4 Hz, 1H), 6.56 (s, 1H), 6.42 (d, J = 8.4 Hz, 1H), 3.33 (s, 3H), 3.28 (s, 3H), 1.16 (s, 9H). ^{13}C NMR (101 MHz, C_6D_6): δ 152.2, 149.1, 148.9, 141.4, 138.4, 135.8, 131.7, 126.7, 125.5, 123.5, 115.9, 110.2, 110.1, 55.2, 55.0, 37.6, 32.3, the resonance for the carbon atom adjacent to the boron could not be observed. ^{11}B NMR (128 MHz, C_6D_6): δ 37.2. HRMS (EI): m/z calcd for $C_{20}H_{23}BBrNO_2$ $[M]^+$ 399.1000, found 399.0994

*1-Bromo-3-tert-butyl-2-(4-fluorophenyl)-1,2-dihydrobenzo[c][1,2]azaborinine (**6**).* White solid (0.48 g, 45%). Mp: 94−96 °C. ^{1}H NMR (400 MHz, C_6D_6): δ 8.59 (d, J = 7.7 Hz, 1H), 7.49−7.40 (m,

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2H), 7.34−7.24 (m, 1H), 6.86 (s, 1H), 6.72−6.58 (m, 4H), 1.00 (s, 9H). ^{13}C NMR (101 MHz, C_6D_6): δ 162.0 (d, J = 247.4 Mz), 151.7, 141.9, 141.5, 136.0, 133.2 (d, J = 8.1 Hz), 132.1, 126.9, 125.8, 114.8 (d, J = 22.2 Hz), 110.5, 37.5, 32.2, the resonance for the carbon atom adjacent to the boron could not be observed. ^{11}B NMR (128 MHz, C_6D_6): δ 36.6. ^{19}F NMR (376 MHz, C_6D_6): δ −113.9. HRMS (EI): m/z calcd for $C_{18}H_{18}BBrFN$ $[M]^+$ 357.0695, found 357.0697

*1-Bromo-3-tert-butyl-6-methyl-2-phenyl-1,2-dihydrobenzo[c][1,2]azaborinine (**7**).* White solid (0.69 g, 65%). Mp: 109 °C. ^{1}H NMR (400 MHz, C_6D_6): δ 8.55 (d, J = 7.9 Hz, 1H), 7.25 (s, 1H), 7.13 (s, 1H), 7.06−6.94 (m, 5H), 6.88 (s, 1H), 2.22 (s, 3H), 1.09 (s, 9H). ^{13}C NMR (101 MHz, C_6D_6): δ 151.7, 145.9, 141.8, 141.7, 135.8, 131.6, 127.3, 127.2, 126.6, 110.0, 37.5, 32.1, 21.5, the resonance for the carbon atom adjacent to the boron could not be observed. ^{11}B NMR (128 MHz, C_6D_6): δ 36.6. HRMS (EI): m/z calcd for $C_{19}H_{21}BBrN$ $[M]^+$ 353.0945, found 353.0949

*1-Bromo-3-tert-butyl-5-fluoro-2-phenyl-1,2-dihydrobenzo[c][1,2]azaborinine (**8**).* The reaction was performed at 100 °C for 6 h. Compound **8** was obtained as a white solid (0.46 g, 43%). Mp: 93−94 °C. ^{1}H NMR (400 MHz, C_6D_6): δ 8.29 (d, J = 7.6 Hz, 1H), 7.39 (s, 1H), 7.13−6.97 (m, 5H), 6.95−6.86 (m, 2H), 1.01 (s, 9H). ^{13}C NMR (101 MHz, C_6D_6): δ 158.5 (d, J = 250.5 Hz), 152.8, 145.5, 131.5, 131.4 (d, J = 4.0 Hz), 129.9 (d, J = 7.1 Hz), 127.7, 127.5, 125.9 (d, J = 7.1 Hz), 116.2 (d, J = 19.2 Hz), 101.6 (d, J = 6.1 Hz), 37.9, 32.0, the resonance for the carbon atom adjacent to the boron could not be observed. ^{11}B NMR (128 MHz, C_6D_6): δ 36.6. ^{19}F NMR (376 MHz, C_6D_6): δ −124.5. HRMS (EI): m/z calcd for $C_{18}H_{18}BBrFN$ $[M]^+$ 357.0695, found 357.0701

*1,2,3-Triphenyl-1,2-dihydrobenzo[c][1,2]azaborinine (**9**).* $PhBBr_2$ was used, and the reaction was performed at 120 °C for 6 h. Compound **9** was obtained as a white solid (0.51 g, 52%) by chromatography on silica gel with *n*-hexane as elute. Mp: 123−124 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, J = 7.7 Hz, 1H), 7.68 (dt, J = 14.7, 7.2 Hz, 2H), 7.37 (dd, J = 10.6, 3.9 Hz, 1H), 7.25−7.11 (m, 10H), 7.00−6.79 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 144.9, 144.7, 141.2, 138.9, 136.6, 133.2, 131.1, 129.8, 129.7, 127.5, 127.4, 127.0, 126.8, 126.7, 126.2, 125.6, 124.7, 113.7, the resonances for the carbon atoms adjacent to the boron could not be observed. ^{11}B NMR (128 MHz, $CDCl_3$): δ 39.0. HRMS (ESI): m/z calcd for $C_{26}H_{21}BN$ $[M + H]^+$ 358.1762, found 358.1758

*3-tert-Butyl-1-chloro-2-phenyl-1,2-dihydrobenzo[c][1,2]-azaborinine (**10**).* BCl_3 was used, and the reaction was performed at 120 °C for 24 h. Compound **10** was obtained as a white solid by recrystallization from *n*-hexane (0.65 g, 73%). Mp: 95 °C. ^{1}H NMR (400 MHz, C_6D_6): δ 8.52 (d, J = 7.7 Hz, 1H), 7.45 (tt, J = 7.9, 4.2 Hz, 2H), 7.28 (ddd, J = 8.0, 6.4, 1.9 Hz, 1H), 7.08−6.92 (m, 5H), 6.85 (s, 1H), 1.06 (s, 9H). ^{13}C NMR (101 MHz, C_6D_6): δ 151.3, 144.5, 141.9, 134.0, 131.7, 131.3, 127.7, 127.2, 126.6, 125.2, 109.4, 37.4, 32.0. ^{11}B NMR (128 MHz, C_6D_6): δ 36.2. HRMS (EI): m/z calcd for $C_{18}H_{19}BClN$ $[M]^+$ 295.1294, found 295.1296

General Procedure for the Substitution of the Bromide by Lithium Salts. *Synthesis of 3-tert-Butyl-1,2-diphenyl-1,2-dihydrobenzo[c][1,2]azaborinine (**2**).* To **1** (1.02 g, 3 mmol) in 15 mL of Et_2O was added 3 mmol of PhLi (generated in situ) at −78 °C. The mixture was slowly warmed to room temperature and stirred overnight. To this solution was added 20 mL of water to quench the reaction. The mixture was extracted by Et_2O (30 mL × 3). The extract was dried over $MgSO_4$, and the solvent was removed under vacuum. Compound **2** was obtained as a white solid by recrystallization from Et_2O (0.69 g, 68%).

Compounds **11**−**19** were prepared similarly as described for **2**. Only spectroscopic data are given below.

*3-tert-Butyl-1-(naphthalen-1-yl)-2-phenyl-1,2-dihydrobenzo[c][1,2]azaborinine (**11**).* White solid (0.73 g, 63%). Mp: 168−169 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82−7.72 (m, 2H), 7.69−7.62 (m, 2H), 7.58 (d, J = 8.3 Hz, 1H), 7.42−7.36 (m, 2H), 7.32−7.24 (m, 3H), 7.19 (dd, J = 12.8, 6.4 Hz, 2H), 7.10 (td, J = 7.8, 1.3 Hz, 2H), 7.01 (d, J = 7.9 Hz, 1H), 6.94 (t, J = 7.4 Hz, 1H), 6.75 (td, J = 7.8, 1.2 Hz, 1H), 1.34 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 151.8, 145.7, 141.2, 136.2, 135.7, 132.5, 131.5, 131.1, 130.2, 130.1, 129.8, 128.1, 126.9, 126.5, 126.4, 126.3, 126.3, 124.7, 124.6, 124.5, 124.5, 110.1, 37.9, 32.7. ^{11}B NMR (128 MHz, $CDCl_3$): δ 41.1. HRMS (ESI): m/z calcd for $C_{28}H_{27}BN$ $[M + H]^+$ 388.2231, found 388.2226

*3-tert-Butyl-2-phenyl-1-(thiophene-2-yl)-1,2-dihydrobenzo[c][1,2]azaborinine (**12**).* White solid (0.57 g, 55%). Mp: 134−136 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, J = 7.8 Hz, 1H), 7.66 (q, J = 8.1 Hz, 2H), 7.40 (d, J = 4.7 Hz, 1H), 7.35 (t, J = 7.2 Hz, 1H), 7.27−7.19 (m, 5H), 7.04−6.99 (m, 2H), 6.86 (d, J = 3.3 Hz, 1H), 1.27 (s, 9H). ^{13}C NMR (101 MHz, C_6D_6): δ 151.2, 145.6, 141.9, 136.4, 132.9, 131.8, 131.0, 128.5, 127.2, 126.8, 126.6, 126.4, 124.7, 110.5, 37.5, 32.4, the resonances for the carbon atoms adjacent to the boron could not be observed. ^{11}B NMR (128 MHz, $CDCl_3$): δ 37.8. HRMS (ESI): m/z calcd for $C_{22}H_{23}BNS$ $[M + H]^+$ 344.1639, found 344.1636

*3-tert-Butyl-2-phenyl-1-(phenylethynyl)-1,2-dihydrobenzo[c][1,2]azaborinine (**13**).* Purified by chromatography on silica gel with EtOAc/*n*-hexane (1/10, v/v) as the eluent. White solid (0.82 g, 76%). Mp: 157 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.41 (d, J = 7.4 Hz, 1H), 7.75−7.63 (m, 2H), 7.54−7.37 (m, 6H), 7.32−7.25 (m, 3H), 7.24−7.16 (m, 2H), 6.95 (s, 1H), 1.31 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 151.9, 147.4, 141.2, 135.1, 132.2, 131.3, 131.2, 128.3, 128.0, 127.5, 127.0, 126.4, 124.6, 123.7, 110.4, 109.4, 37.7, 32.4, the resonances for the carbon atoms adjacent to the boron could not be observed. ^{11}B NMR (128 MHz, C_6D_6): δ 31.1. HRMS (ESI): m/z calcd for $C_{26}H_{25}BN$ $[M + H]^+$ 362.2075, found 362.2081

*3-tert-Butyl-1-((4-fluorophenyl)ethynyl)-2-phenyl-1,2-dihydrobenzo[c][1,2]azaborinine (**14**).* White solid (0.83 g, 73%). Mp: 137−138 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.37 (d, J = 7.6 Hz, 1H), 7.72−7.63 (m, 2H), 7.52−7.36 (m, 6H), 7.20−7.12 (m, 2H), 6.99−6.90 (m, 3H), 1.30 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.6 (d, J = 251.5 Hz), 151.9, 147.4, 141.2, 135.0, 134.2 (d, J = 8.1 Hz), 131.4, 131.2, 127.6, 126.9, 126.4, 124.7, 119.8 (d, J = 3.0 Hz), 115.4 (d, J = 22.2 Hz), 109.5, 109.2, 37.7, 32.4, the resonances for the carbon atoms adjacent to the boron could not be observed. ^{11}B NMR (128 MHz, $CDCl_3$): δ 30.7. ^{19}F NMR (376 MHz, $CDCl_3$): δ −110.6. HRMS (ESI): m/z calcd for $C_{26}H_{24}BFN$ $[M + H]^+$ 380.1980, found 380.1982

*3-tert-Butyl-1-((4-methoxyphenyl)ethynyl)-2-phenyl-1,2-dihydrobenzo[c][1,2]azaborinine (**15**).* White solid (0.88 g, 75%). Mp: 167−168 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.39 (d, J = 7.5 Hz, 1H), 7.71−7.61 (m, 2H), 7.51−7.37 (m, 6H), 7.13 (d, J = 8.6 Hz, 2H), 6.91 (s, 1H), 6.79 (d, J = 8.6 Hz, 2H), 3.82 (s, 3H), 1.29 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.7, 151.8, 147.5, 141.1, 135.1, 133.8, 131.4, 131.1, 127.5, 126.8, 126.3, 124.5, 115.8, 113.7, 110.6, 109.2, 55.2 37.7, 32.4, the resonances for the carbon atoms adjacent to the boron could not be observed. ^{11}B NMR (128 MHz, $CDCl_3$): δ 30.7. HRMS (ESI): m/z calcd for $C_{27}H_{27}BNO$ $[M + H]^+$ 392.2180, found 392.2175

*3-tert-Butyl-2-(4-fluorophenyl)-1-(phenylethynyl)-1,2-dihydrobenzo[c][1,2]azaborinine (**16**).* White solid (0.84 g, 74%). Mp: 167−169 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36 (d, J = 7.6 Hz, 1H), 7.65 (q, J = 8.1 Hz, 2H), 7.44 (t, J = 7.0 Hz, 1H), 7.35 (dd, J = 8.5, 5.0 Hz, 2H), 7.31−7.26 (m, 3H), 7.25−7.18 (m, 2H), 7.13 (t, J = 8.5 Hz, 2H), 6.91 (s, 1H), 1.28 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 161.6 (d, J = 247.5 Hz), 151.7, 143.4, 141.1, 135.1, 132.7 (d, J = 8.0 Hz), 132.1, 131.3, 128.5, 128.2, 126.5, 124.8, 123.5, 114.3 (d, J = 23.2 Hz), 110.7, 109.6, 37.6, 32.4, the resonances for the carbon atoms adjacent to the boron could not be observed. ^{11}B NMR (128 MHz, $CDCl_3$): δ 32.0. ^{19}F NMR (376 MHz, $CDCl_3$): δ −115.5. HRMS (ESI): m/z calcd for $C_{26}H_{24}BFN$ $[M + H]^+$ 380.1980, found 380.1978

*3-tert-Butyl-2-(3,4-dimethoxyphenyl)-1-(phenylethynyl)-1,2-dihydrobenzo[c][1,2]azaborinine (**17**).* White solid (0.97 g, 77%). Mp: 132−133 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38 (d, J = 7.6 Hz, 1H), 7.73−7.59 (m, 2H), 7.51−7.40 (m, 1H), 7.31−7.21 (m, 5H), 7.04−6.83 (m, 4H), 3.99 (s, 3H), 3.87 (s, 3H), 1.32 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.1, 147.9, 147.8, 141.2, 140.3, 135.0, 132.1, 131.2, 128.3, 128.1, 126.3, 124.6, 123.7, 123.2, 115.3, 110.0, 109.6, 109.5, 56.1, 37.8, 32.5, the resonances for the carbon atoms adjacent to the boron could not be observed. ^{11}B NMR (128 MHz, $CDCl_3$): δ

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32.6. HRMS (ESI): m/z calcd for $C_{28}H_{29}BNO_2$ $[M + H]^+$ 422.2286, found 422.2284

*3-tert-Butyl-1-((4-methoxyphenyl)ethynyl)-6-methyl-2-phenyl-1,2-dihydrobenzo[c][1,2]azaborinine (**18**).* White solid (0.87 g, 72%). Mp: 128−129 °C. Crystals of **18** suitable for X-ray diffraction were obtained by cooling a solution of **18** in Et_2O. ^1H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, J = 7.7 Hz, 1H), 7.37−7.26 (m, 6H), 7.17 (s, 1H), 7.00 (d, J = 8.7 Hz, 2H), 6.73 (s, 1H), 6.67 (d, J = 8.7 Hz, 2H), 3.70 (s, 3H), 2.42 (s, 3H), 1.16 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.6, 151.9, 147.6, 141.4, 141.2, 135.1, 133.8, 131.4, 127.4, 126.8, 126.3, 126.1, 115.9, 113.6, 110.3, 108.9, 55.2, 37.7, 32.4, 22.0, the resonances for the carbon atoms adjacent to the boron could not be observed. ^{11}B NMR (128 MHz, $CDCl_3$): δ 32.4. HRMS (ESI): m/z calcd for $C_{28}H_{29}BNO$ $[M + H]^+$ 406.2337, found 406.2330

*3-Butyl-5-fluoro-2-phenyl-1-(phenylethynyl)-1,2-dihydrobenzo-[c][1,2]azaborinine (**19**).* White solid (0.78 g, 69%). Mp: 143−145 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, J = 7.3 Hz, 1H), 7.50−7.43 (m, 3H), 7.42−7.31 (m, 4H), 7.31−7.21 (m, 3H), 7.21−7.13 (m, 3H), 1.29 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.5 (d, J = 252.5 Hz), 152.8, 147.1, 132.2, 131.2, 130.7, 129.7 (d, J = 8.0 Hz), 128.5, 128.1, 127.6, 127.2, 125.0, 123.4, 115.6 (d, J = 20.2 Hz), 110.8, 101.0, 100.9, 38.1, 32.4, the resonances for the carbon atoms adjacent to the boron could not be observed. ^{11}B NMR (128 MHz, $CDCl_3$): δ 30.6. ^{19}F NMR (376 MHz, $CDCl_3$): δ −124.9. HRMS (ESI): m/z calcd for $C_{26}H_{24}BFN$ $[M + H]^+$ 380.1980, found 380.1983

*Synthesis of N-Benzyl-3-tert-butyl-2-(2,6-diisopropylphenyl)-benzo[c][1,2]azaborinin-1(2H)-amine (**20**).* To a mixture of **3** (1.0 mmol, 0.42 g) and NEt_3 (0.14 mL, 1.0 mmol) in 15 mL of toluene was added $PhCH_2NH_2$ (0.11 mL, 1 mmol). The mixture was stirred at room temperature for 6 h. After removal of solvents, the residual was extracted with 15 mL of Et_2O. The solution was concentrated and stored at −40 °C for 8 h to give **20** as a white solid (0.30 g, 67%). Mp: 121 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, J = 7.5 Hz, 1H), 7.58 (dt, J = 23.4, 7.3 Hz, 2H), 7.48−7.20 (m, 9H), 6.64 (s, 1H), 3.90 (s, 2H), 2.85 (m, 2H), 1.28 (d, J = 6.8 Hz, 6H), 1.19 (s, 9H), 1.10 (d, J = 6.7 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.1, 146.6, 141.9, 136.9, 130.7, 129.8, 127.7, 127.5, 126.4, 126.1, 125.8, 124.8, 123.4, 122.9, 105.7, 45.5, 37.1, 31.8, 27.5, 24.8, 21.8. ^{11}B NMR (128 MHz, $CDCl_3$): δ 28.7. HRMS (ESI): m/z calcd for $C_{31}H_{40}BN_2$ $[M + H]^+$ 451.3279, found 451.3284.

*Reactions of **1** with MeLi or 1-Propenylmagnesium Bromide.* Reactions of **1** with MeLi or 1-propenylmagnesium bromide in Et_2O from −78 °C to room temperature led to the formation of a complicated mixture from which the desired substitution products cannot be isolated in pure form.

Reaction of 3 with MeOH. The reaction of **3** with MeOH was performed in Et_2O. The corresponding product can be observed by NMR but cannot be obtained in pure form.

Stability of 4 in Aqueous Solution. At room temperature, 0.10 g of **4** was added to 20 mL of 1.0 M HCl and NaOH aqueous solutions, respectively. The mixtures were stirred at room temperature for 5 h. Extraction of the aqueous solutions with Et_2O (20 mL × 2) resulted in the recovery of **4** in 90% and 92% yields, respectively.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

NMR experiments for the effects of NEt_3 on the borylation reaction, crystallographic data, and selected bond parameters for compounds **3**, **4**, and **18** and ^1H, ^{11}B, and ^{13}C spectra of the 1,2-borazaronaphthalene derivatives reported in this paper. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: cmcui@nankai.edu.cn.

Notes

The authors declare no competing financial interest.

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