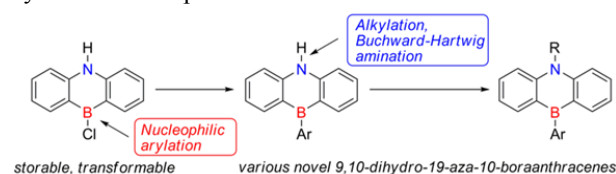


# Chlorine-Substituted 9,10-Dihydro-9-aza-10-boraanthracene as a Precursor for Various Boron- and Nitrogen-Containing $\pi$ -Conjugated Compounds

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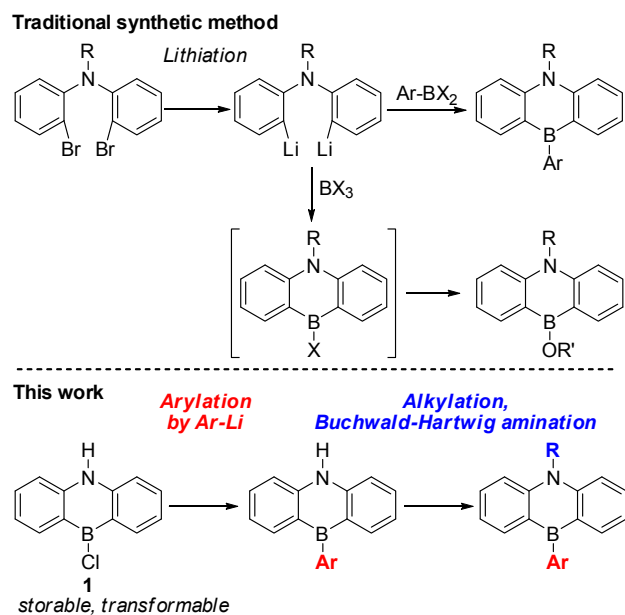


**ABSTRACT:** Chlorine-substituted 9,10-dihydro-9-aza-10-boraanthracene was synthesized. Derivatization of this compound by taking advantage of transformable B-Cl moiety gave 9,10-dihydro-9-aza-10-boraanthracene derivatives with various aryl-substituents. In addition, further functionalization on NH groups by alkylation and Buchwald-Hartwig amination was demonstrated. Photophysical properties of the resulting 9,10-dihydro-9-aza-10-boraanthracene derivatives were also discussed.

Incorporation of boron and nitrogen into a  $\pi$ -conjugated framework is unique strategy to construct functional organic materials because photoelectronic features can be tuned by boron and nitrogen atoms.<sup>1</sup> Recently, a variety of boron- and nitrogen-containing polyaromatic hydrocarbons (PAHs) have been reported and were applied as organic electronic materials such as organic light-emitting diodes, field effect transistors, solar cells.<sup>2,3</sup> Boron- and nitrogen-containing 9,10-dihydroanthracenes (BN-DAs) have been known as  $\pi$ -conjugated compounds bearing interaction between boron and nitrogen atoms after the first synthesis by Maitlis at 1961.<sup>4</sup> By taking advantages of unique photoelectronic properties, such as high emission quantum yield, these compounds were applied as chemical sensors and OLED.<sup>5</sup> In addition to the photoelectronic properties, the catalytic reactivity of azaboroanthracene has been reported.<sup>6</sup> Thus, the BN-DAs would be useful class of compounds, however, the synthetic methodology for BN-DAs has been limited. Typically, BN-DAs were synthesized by a late-stage introduction of boron atom bearing bulky aryl substituents, such as Mes (2,4,6-trimethylphenyl) and Tip (2,4,6-triisopropylphenyl).<sup>4-7</sup> A few examples of functionalization of BN-DAs were reported. Kawashima reported deprotection of MOM group on the nitrogen atom BN-DAs, followed by Pd-catalyzed arylation of the nitrogen.<sup>8</sup> Hydrolysis of B-N bond in *B*-amino-BN-DA were also reported to give hydroxy-substituted BN-DA.<sup>5c,7a</sup> Although the reactive BCl moiety may be promising precursor for various BN-DAs, there is no report on isolation of chlorine-substituted BN-DA.<sup>9</sup> Here, we report the synthesis and isolation of *B*-chlorinated 9,10-

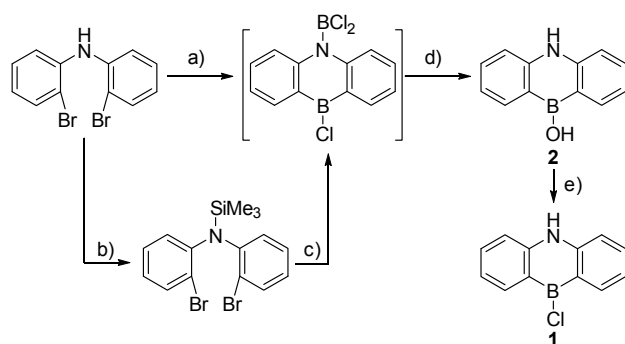
dihydro-9-aza-10-boraanthracene **1** as a common synthetic intermediate for further derivatization with various substituents on the boron atom. The NH moiety of the resulting *B*-arylated compound underwent  $S_N2$ -type alkylation and Pd-catalyzed arylation.

**Scheme 1. Reported method for the synthesis of BN-DAs and this work**



Chlorine-substituted BN-DA **1** was synthesized by two-pot reactions shown in Scheme 2. Treatment of bis(2-bromophenyl)amine with <sup>t</sup>BuLi followed by a reaction with BCl<sub>3</sub> and aqueous quenching gave hydroxyl-substituted BN-DA **2** in 21% isolated yield probably through an intermediate possessing N–BCl<sub>2</sub> bond. BN-DA **2** could also be prepared in 70% yield from bis(2-bromophenyl)amine via bis(2-bromophenyl)trimethylsilylamine. The hydroxy group on the boron atom in **2** could be converted to more reactive chloride by a reaction with one equivalent of BCl<sub>3</sub> with NH group remaining intact. Compound **1** was sensitive toward air and moisture, but storable under inert atmosphere.<sup>10</sup> The structures of **1** and **2** were determined by NMR spectroscopy, mass spectrometry, as well as X-ray crystallography.

**Scheme 2. Synthesis of 1.**

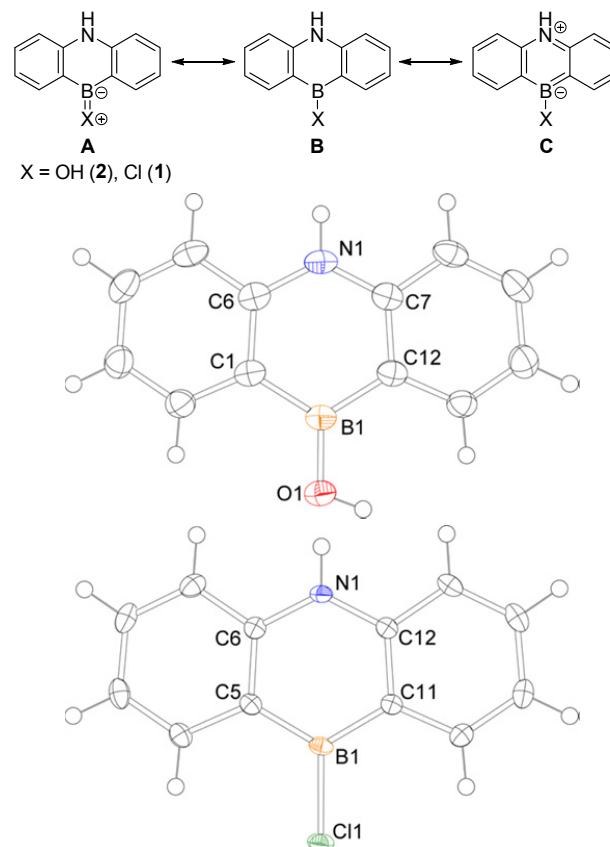


a) 1) 3.5 eq <sup>t</sup>BuLi in hexane, 2) 3.5 eq BCl<sub>3</sub> in heptane; b) 1) 2 eq KH, 2) 1.2 eq Me<sub>3</sub>SiCl, THF, 95%; c) 1) 2.1 eq <sup>t</sup>BuLi in hexane, 2) 2 eq BCl<sub>3</sub> in heptane; d) K<sub>2</sub>CO<sub>3</sub> aq., 21% from bis(2-bromophenyl)amine, 74% from bis(2-bromophenyl)trimethylsilylamine; e) 1 eq BCl<sub>3</sub> in heptane, CH<sub>2</sub>Cl<sub>2</sub>, 89%.

The structures of BN-DAs **1** and **2** are shown in Figure 1. Both **1** and **2** adopt planar geometry in the solid state, being similar to previously reported BN-DAs. Structural parameters of **2**, such as planarity, bond lengths and angles, are compara-

ble to those of the previously reported BN-DA bearing B–O group on the boron atom.<sup>7a</sup> On the other hand, the bond lengths between boron and carbon atoms [B1–C5 = 1.512(2) Å, B1–C11 = 1.515(2) Å] in **1** are shorter than those of **2** [B–C: 1.537(3)–1.545(3) Å]. The shorter B–C bonds in **1** would be explained by the contribution of the resonance structure **C** in BN-DA (Scheme 3), which have interaction between boron and nitrogen atoms through the formation of B=C and N=C double bond in **1**, while **2** has strong interaction between boron and oxygen atoms, preventing the contribution of the resonance structure **C** (Scheme 3, **A**).

**Scheme 3. Resonance structures of 1 and 2.**

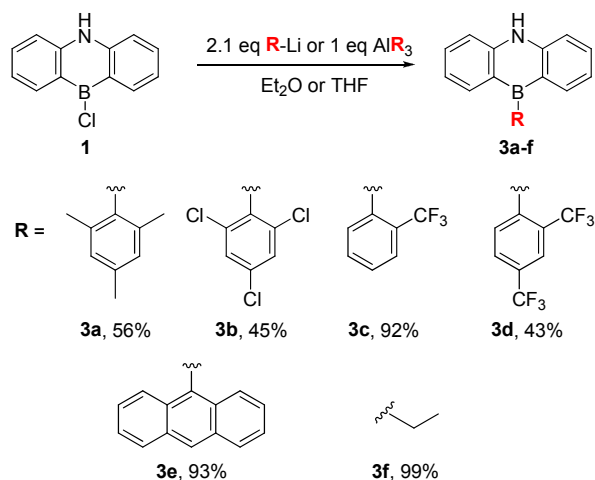


**Figure 1.** Molecular structures of **2** (top) and **1** (bottom) determined by X-ray crystallography (drawn at 50% ellipsoid probability). For **2**, one of the three crystallographically independent molecules is shown.

The various BN-DAs were synthesized by sequential deprotonation/nucleophilic substitution on the boron atom of **2** by aryllithium reagents (Scheme 4). The reaction of **1** with 2.1 equivalents of MesLi gave Mes-substituted BN-DA **3a** in 56% yield. Haloaryl groups, such as 2,4,6-trichlorophenyl, 2-(trifluoromethyl)phenyl, and 2,4-bis(trifluoromethyl)phenyl groups, could be introduced into the boron atom to give **3b–3d**. Moreover, anthryl-substituted BN-DA **3e** was synthesized in a similar manner. These compounds were characterized by NMR and HRMS. Additionally, structures of **3a,b** were determined by X-ray crystallography. Due to the steric hindrance around a vacant p-orbital of the boron atom derived from these aryl substituents, **3a–e** were stable under air and able to be purified by silica gel column chromatography. By utilization of reactivity of **1**, *B*-alkyl BN-DA could be synthesized. The

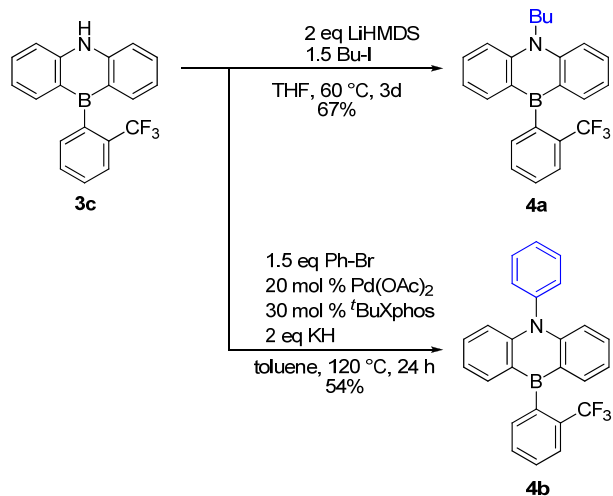
reaction of EtMgBr with **1** afforded *B*-ethyl BN-DA **3f** in low yield (26%). Using AlEt<sub>3</sub> instead of Grignard reagent, **3f** was obtained in 99% yield.

#### Scheme 4. Introduction of aryl and alkyl groups into **1**.



The N-H group in **3** is also transformable by typical organic reactions, such as nucleophilic alkylation and Buchwald-Hartwig amination (Scheme 5). In practice, the alkylation of **3c** by 1-iodobutane in the presence of LiHMDS gave *N*-butylated BN-DA **4a** in 67% yield. On the other hand, the arylation of **3c** by Buchwald-Hartwig amination with PhBr in the presence of Pd catalyst afforded phenylated BN-DA **4b** in 54% yield.

#### Scheme 5. Functionalization on the nitrogen atom of **3c**.



The BN-DAs are known as emissive compounds.<sup>5,7b-e</sup> Thus, we investigated the photophysical properties of the present BN-DAs **3b-3e** and **4a,b** (Table 1). *B*-Phenyl derivatives **3b-3d** having NH moiety showed an absorption around 386-389 nm and strong emission around 401-413 nm with emission quantum yield of 0.79-0.90. On the other hand, anthryl-substituted BN-DA **3e** showed a slightly different photophysical properties, such as longer-wavelength shifted (absorption and) emission with a significantly lower quantum yield.<sup>11</sup> DFT calculations suggested that the HOMO and LUMO of **3b-3d** are localized around BN-DA moieties (See SI),<sup>12</sup> being reasonable to  $\pi$ - $\pi^*$  transitions. In the case of **3e**, the HOMO is localized on the anthryl substituent, while the LUMO is  $\pi$ -

orbital of BN-DA moiety (See SI). Thus, the electronic transition of **3e** would have charge-transfer type character between anthryl- and BN-DA moieties. In agreement with charge-transfer type character, the emission peak was blue-shifted to 419 nm in non-polar solvent, benzene.

Table 1. Photophysical properties of **1-4**.

compounds	$\lambda_{\text{abs}} / \text{nm}$	$\lambda_{\text{em}} / \text{nm}$	$\Phi_{\text{em}}$
<b>2</b>	366	377	0.03
<b>1</b>	366	379	<sup>b</sup>
<b>3b</b>	396	413	0.82
<b>3c</b>	386	401	0.85
<b>3d</b>	388	407	0.90
<b>3e</b>	394 (394) <sup>c</sup>	424 (419) <sup>c</sup>	0.19
<b>3f</b>	381	394	<sup>b</sup>
<b>4a</b>	386	401	0.90
<b>4b</b>	389	404	0.79

<sup>a</sup>Absorption and emission spectra were recorded in CH<sub>2</sub>Cl<sub>2</sub> solution at ambient temperature. <sup>b</sup>Due to the instability toward air and moisture, emission quantum yield was not determined. <sup>c</sup>in benzene.

The chlorine-substituted BN-DA **1** was synthesized and isolated for the first time. The chloride on the boron atom was substituted with aryl group by using aryllithium reagents. The subsequent functionalization on the nitrogen atom of arylated BN-DA by alkylation and Buchwald-Hartwig amination was also investigated to give six BN-DAs, exhibiting high emission quantum yield or CT-type emission. These results indicate that **1** is useful precursor for a variety of BN-DA derivatives. Further investigations toward BN-DA derivatives were currently underway.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Details of experiments, X-ray crystallography, NMR and UV-vis spectra, and DFT calculations (PDF)  
 Crystallographic information files (CIF)  
 Cartesian coordination of optimized structures (XYZ)

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### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENT

This work was supported by Grants-in-Aid for Scientific Research from JSPS (KAKENHI 17H01191, 17K19128). Financial Support was furthermore received from CREST 14529307 from JST. We thank Prof. T. Hiyama (Chuo University) for providing us with

access to an X-ray diffractometer. We also thank Prof. H. Shinokubo (Nagoya University) for APCI-MS measurements and Profs. S. Yamaguchi and A. Fukazawa (Nagoya University) for emission quantum yield measurements. We thank Profs. Y. Shoji and T. Fukushima (Tokyo Institute of Technology) for emission lifetime measurement under the Cooperative Research Program of "Network Joint Research Center for Materials and Devices".

## REFERENCES

- (1) For reviews, see: (a) Liu, Z.; Marder, T. B. B-N versus C-C: How Similar Are They? *Angew. Chem. Int. Ed.* **2008**, *47*, 242-244. (b) Bosdet, M. J. D.; Piers, W. E. B-N as a C-C substitute in aromatic systems. *Can. J. Chem.* **2009**, *87*, 8-29. (c) Campbell, P. G.; Marwitz, A. J. V.; Liu, S.-Y. Recent Advances in Azaborine Chemistry. *Angew. Chem. Int. Ed.* **2012**, *51*, 6074-6092. (d) Wang, X. Y.; Wang, J. Y.; Pei, J. BN Heterosuperbenzenes: Synthesis and Properties. *Chem.-Eur. J.* **2015**, *21*, 3528-3539. (e) Helten, H. B=N Units as Part of Extended  $\pi$ -Conjugated Oligomers and Polymers. *Chem.-Eur. J.* **2016**, *22*, 12972-12982. (f) Bélanger-Chabot, G.; Braunschweig, H.; Roy, D. K. Recent Developments in Azaborine Chemistry. *Eur. J. Inorg. Chem.* **2017**, *2017*, 4353-4368. (g) Giustra, Z. X.; Liu, S.-Y. The State of the Art in Azaborine Chemistry: New Synthetic Methods and Applications. *J. Am. Chem. Soc.* **2018**, *140*, 1184-1194.
- (2) (a) Bosdet, M. J. D.; Jaska, C. A.; Piers, W. E.; Sorensen, T. S.; Parvez, M. Blue Fluorescent 4a-Aza-4b-boraphenanthrenes. *Org. Lett.* **2007**, *9*, 1395-1398. (b) Bosdet, M. J. D.; Piers, W. E.; Sorensen, T. S.; Parvez, M. 10a-Aza-10b-borapyrenes: Heterocyclic Analogues of Pyrene with Internalized BN Moieties. *Angew. Chem., Int. Ed.* **2007**, *46*, 4940-4943. (c) Jaska, C. A.; Emslie, D. J. H.; Bosdet, M. J. D.; Piers, W. E.; Sorensen, T. S.; Parvez, M. Triphenylene Analogues with B<sub>2</sub>N<sub>2</sub>C<sub>2</sub> Cores: Synthesis, Structure, Redox Behavior, and Photophysical Properties. *J. Am. Chem. Soc.* **2006**, *128*, 10885-10896. (d) Jaska, C. A.; Piers, W. E.; McDonald, R.; Parvez, M. Synthesis, Characterization, and Fluorescence Behavior of Twisted and Planar B<sub>2</sub>N<sub>2</sub>-Quaterphenyl Analogues. *J. Org. Chem.* **2007**, *72*, 5234-5243. (e) Bosdet, M. J. D.; Piers, W. E.; Sorensen, T. S.; Parvez, M. 5b,7b-Diaza-3b,9b-diborabenz[ghi]perylene. *Can. J. Chem.* **2010**, *88*, 426-433. (f) Neue, B.; Araneda, J. F.; Piers, W. E.; Parvez, M. BN-Dibenz[*a,o*]picenes: Analogues of an Unknown Polycyclic Aromatic Hydrocarbon. *Angew. Chem., Int. Ed.* **2013**, *52*, 9966-9969.
- (3) (a) Hatakeyama, T.; Hashimoto, S.; Seki, S.; Nakamura, M. Synthesis of BN-Fused Polycyclic Aromatics via Tandem Intramolecular Electrophilic Arene Borylation. *J. Am. Chem. Soc.* **2011**, *133*, 18614-18617. (b) Hatakeyama, T.; Hashimoto, S.; Oba, T.; Nakamura, M. Azaboradibenzo[6]helicene: Carrier Inversion Induced by Helical Homochirality. *J. Am. Chem. Soc.* **2012**, *134*, 19600-19603. (c) Wang, X.-Y.; Lin, H.-R.; Lei, T.; Yang, D.-C.; Zhuang, F.-D.; Wang, J.-Y.; Yuan, S.-C.; Pei, J. Azaborine Compounds for Organic Field-Effect Transistors: Efficient Synthesis, Remarkable Stability, and BN Dipole Interactions. *Angew. Chem., Int. Ed.* **2013**, *52*, 3117-3120. (d) Wang, X.-Y.; Zhuang, F.-D.; Wang, R.-B.; Wang, X.-C.; Cao, X.-Y.; Wang, J.-Y.; Pei, J. A Straightforward Strategy toward Large BN-Embedded  $\pi$ -Systems: Synthesis, Structure, and Optoelectronic Properties of Extended BN Heterosuperbenzenes. *J. Am. Chem. Soc.* **2014**, *136*, 3764-3767. (e) Zhong, Z.; Wang, X.-Y.; Zhuang, F.-D.; Ai, N.; Wang, J.; Wang, J.-Y.; Pei, J.; Peng, J.; Cao, Y. Curved BN-embedded nanographene for application in organic solar cells. *J. Mater. Chem. A*, **2016**, *4*, 15420-15425. (f) Hashimoto, S.; Ikuta, T.; Shiren, K.; Nakatsuka, S.; Ni, J.; Nakamura, M.; Hatakeyama, T. Triplet-Energy Control of Polycyclic Aromatic Hydrocarbons by BN Replacement: Development of Ambipolar Host Materials for Phosphorescent Organic Light-Emitting Diodes. *Chem. Mater.* **2014**, *26*, 6265-6271. (g) Wang, X.-Y.; Zhuang, F.-D.; Zhou, X.; Yang, D.-C.; Wang, J.-Y.; Pei, J. Influence of alkyl chain length on the solid-state properties and transistor performance of BN-substituted tetrathienonaphthalenes. *J. Mater. Chem. C*, **2014**, *2*, 8152-8161. (h) Matsui, K.; Oda, S.; Yoshiura, K.; Nakajima, K.; Yasuda, N.; Hatakeyama, T. One-Shot Multiple Borylation toward BN-Doped Nanographenes. *J. Am. Chem. Soc.* **2018**, *140*, 1195-1198. (i) Nakatsuka, S.; Gotoh, H.; Kinoshita, K.; Yasuda, N.; Hatakeyama, T. Divergent Synthesis of Heteroatom-Centered 4,8,12-Triazatriangulenes. *Angew. Chem., Int. Ed.* **2017**, *56*, 5087-5090. (j) Hatakeyama, T.; Shiren, K.; Nakajima, K.; Nomura, S.; Nakatsuka, S.; Kinoshita, K.; Ni, J.; Ono, Y.; Ikuta, T. Ultrapur Blue Thermally Activated Delayed Fluorescence Molecules: Efficient HOMO-LUMO Separation by the Multiple Resonance Effect. *Adv. Mater.* **2016**, *28*, 2777-2781. (k) Wang, X.-Y.; Zhuang, F.-D.; Wang, J.-Y.; Pei, J., Incorporation of polycyclic azaborine compounds into polythiophene-type conjugated polymers for organic field-effect transistors. *Chem. Commun.* **2015**, *51*, 17532-17535.
- (4) Maitlis, P. M. 75. New heteroaromatic compounds. Part IX. Some 10,9-borazaroanthracenes. *J. Chem. Soc.* **1961**, 425-429.
- (5) (a) Agou, T.; Sekine, M.; Kobayashi, J.; Kawashima, T. Multi-step detection of cyanide ion by a bis(dimesitylboryl) dibenzoazaborine. *J. Organomet. Chem.* **2009**, *694*, 3833-3836. (b) Agou, T.; Sekine, M.; Kobayashi, J.; Kawashima, T. Detection of Biologically Important Anions in Aqueous Media by Dicationic Azaborines Bearing Ammonio or Phosphonio Groups. *Chem.-Eur. J.* **2009**, *15*, 5056-5062. (c) Agou, T.; Sekine, M.; Kobayashi, J.; Kawashima, T. Synthesis and reactivity of a bis(dimesitylboryl)azaborine and its fluoride sensing ability. *Chem. Commun.* **2009**, 1894-1896. (d) Park, I. S.; Numata, M.; Adachi, C.; Yasuda, T. A Phenazaborin-Based High-Efficiency Blue Delayed Fluorescence Material. *Bull. Chem. Soc. Jpn.* **2016**, *89*, 375-377. (e) Bell, B. M.; Clark, T. P.; De Vries, T. S.; Lai, Y.; Laiter, D. S.; Gallagher, T. J.; Jeon, J.-H.; Kearns, K. L.; McIntire, T.; Mukhopadhyay, S.; Na, H.-Y.; Paine, T. D.; Rachford, A. A. Boron-based TADF emitters with improved OLED device efficiency roll-off and long lifetime. *Dyes Pigment.* **2017**, *141*, 83-92. (f) Park, I. S.; Matsuo, K.; Aizawa, N.; Yasuda, T., High-Performance Dibenzoheteroborin-Based Thermally Activated Delayed Fluorescence Emitters: Molecular Architectonics for Concurrently Achieving Narrowband Emission and Efficient Triplet-Singlet Spin Conversion. *Adv. Funct. Mater.* **2018**, *28*, 1802031. (g) Stanoppi, M.; Lorbach, A. Boron-based donor-spiro-acceptor compounds exhibiting thermally activated delayed fluorescence (TADF). *Dalton Trans.* **2018**, *47*, 10394-10398.
- (6) (a) Dimitrijevic, E.; Taylor, M. S., 9-Hetero-10-boraanthracene-derived borinic acid catalysts for regioselective activation of polyols. *Chem. Sci.* **2013**, *4*, 3298-3303. (b) Pawliczek, M.; Hashimoto, T.; Maruoka, K., Alkylative kinetic resolution of vicinal diols under phase-transfer conditions: a chiral ammonium borinate catalysis. *Chem. Sci.* **2018**, *9*, 1231-1235.
- (7) (a) Kranz, M.; Hampel, F.; Clark, T., N-methyl-B-mesityldibenzo-1,4-azaborinine: the first experimental structure of a 1,4-azaborinine derivative. *J. Chem. Soc., Chem. Commun.* **1992**, 1247-1248. (b) Agou, T.; Kobayashi, J.; Kawashima, T. Tuning of the Optical Properties and Lewis Acidity of Dibenzopnictogenaborins by Modification on Bridging Main Group Elements. *Inorg. Chem.* **2006**, *45*, 9137-9144. (c) Agou, T.; Kobayashi, J.; Kawashima, T., Syntheses, Structure, and Optical Properties of Ladder-Type Fused Azaborines. *Org. Lett.* **2006**, *8*, 2241-2244. (d) Agou, T.; Kobayashi, J.; Kawashima, T., Development of a general route to periphery-functionalized azaborines and ladder-type azaborines by using common intermediates. *Chem. Commun.* **2007**, 3204-3206. (e) Agou, T.; Arai, H.; Kawashima, T. Synthesis, Structure, and Properties of a Dinaphthoazaborine. *Chem. Lett.* **2010**, *39*, 612-613. (f) Igarashi, T.; Tobisu, M.; Chatani, N. Catalytic Double Carbon-Boron Bond Formation for the Synthesis of Cyclic Diarylborinic Acids as Versatile Building Blocks for  $\pi$ -Extended Heteroarenes. *Angew. Chem., Int. Ed.* **2017**, *56*, 2069-2073. (g) Kawai, S.; Nakatsuka, S.; Hatakeyama, T.; Pawlak, R.; Meier, T.; Tracey, J.; Meyer, E.; Foster, A. S., Multiple heteroatom substitution to graphene nanoribbon. *Sci. Adv.* **2018**, *4*, eaar7181.
- (8) Agou, T.; Kojima, T.; Kobayashi, J.; Kawashima, T. Synthesis of  $\pi$ -Conjugated Dendrimers Based on Azaborines. *Org. Lett.* **2009**, *11*, 3534-3537.
- (9) In the 1,2- and 1,4-dehydroazaborine, the synthesis and transformations of B-Cl or B-OMe have been reported. See: (a) Abbey, E. R.; Lamm, A. N.; Baggett, A. W.; Zakharov, L. N.; Liu, S.-Y. Protecting Group-Free Synthesis of 1,2-Azaborines: A Simple Approach to the Construction of BN-Benzenoids. *J. Am. Chem. Soc.* **2013**, *135*, 12908-12913. (b) Liu, X.; Zhang, Y.; Li, B.; Zakharov, L. N.; Vasiliu,

M.; Dixon, D. A.; Liu, S.-Y. A Modular Synthetic Approach to Monocyclic 1,4-Azaborines. *Angew. Chem., Int. Ed.* **2016**, *55*, 8333-8337.  
(c) Xu, S.; Haeffner, F.; Li, B.; Zakharov, L. N.; Liu, S.-Y. Monobenzofused 1,4-Azaborines: Synthesis, Characterization, and Discovery of a Unique Coordination Mode. *Angew. Chem., Int. Ed.* **2014**, *53*, 6795-6799.

(10) Compound **1** was stable in solution even in the presence of NEt<sub>3</sub>. However, slightly more nucleophilic bases, such as pyridine and

quinuclidine, could coordinate to the boron center in **1**, as suggested by high-field shift of <sup>11</sup>B NMR signal to 0-10 ppm.

(11) To confirm the possibility of TADF emission, we measured emission lifetime of **3e** (Figure S15). However, no long lifetime component was observed.

(12) Details of the DFT calculations are described in the Supporting Information.

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