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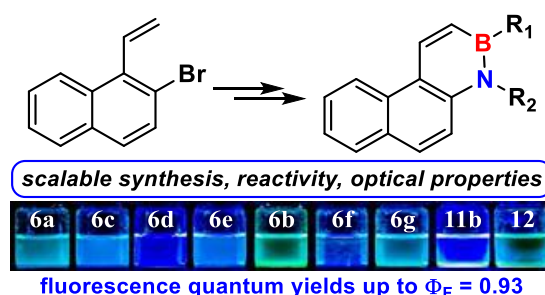
# Synthesis, Functionalization and Optical Properties of 1,2-Dihydro-1-aza-2-boraphenanthrene and Several Highly Fluorescent Derivatives

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*Supporting Information Placeholder*



**ABSTRACT:** Previously unknown 1,2-dihydro-1-aza-2-boraphenanthrene has been synthesized in only three steps from 2-bromo-1-vinylnaphthalene. The reactivity of this new BN-phenanthrene, and of several substituted derivatives, has been tested against bromine and organolithium compounds. Bromination proceeded with complete regioselectivity, affording bromo-substituted compounds suitable for further functionalization via cross coupling reactions. This new family of BN-phenanthrenes exhibits a substantial increase in the quantum yield (up to  $\Phi_F = 0.93$ ) with respect to phenanthrene.

Formal replacement of a C=C bond in an aromatic ring by an isoelectronic B–N bond leads to BN-aromatic compounds.<sup>1</sup> This polarized BN unit in the structure enables the modulation of their properties and provides a great opportunity for the design and production of new materials.<sup>2</sup> Thus, BN-polycyclic aromatic hydrocarbons (BN-PAHs) have been explored as promising components for improved optoelectronic devices.<sup>3</sup> Moreover, the azaborine unit has also recently been investigated in the development of new ligands for transition-metal-based catalysis<sup>4</sup> and as a new pharmacophore in medicinal chemistry.<sup>5</sup>

Significant advances have been made in the field of BN-PAHs in the last decade.<sup>6</sup> Despite this, these compounds are still hampered by the lack of general and mild methodologies for preparing them in sufficient quantities and the need for a better understanding of the effects that replacement of a C=C bond by a B–N bond have on the properties of BN-aromatic compounds. As such, the basic knowledge obtained from the simplest systems is highly valuable, as

shown in a recent comparative analysis of different BN isosteres of naphthalene.<sup>7</sup>

With regard to phenanthrene **1**, another simple polycyclic aromatic hydrocarbon, four BN-isosteres, namely **2**,<sup>8</sup> **3**,<sup>8a</sup> **4**<sup>9</sup> and **5**,<sup>10</sup> have been described and the reactivity of **5** with activated electrophiles and organolithium compounds studied.<sup>10a,11</sup> Their optical properties, which differ markedly depending on the position of the B–N bond, have also been evaluated. For instance, the fluorescence emission maxima and quantum efficiency are highly influenced by this structural difference (Figure 1).

As the reasons for these experimental findings remain unclear, a systematic investigation into how the position and orientation of the BN bond pair affects the reactivity and optical properties of these BN-phenanthrene analogs would be desirable. A study of this nature is not yet possible, however, due to the lack of available synthetic meth-

ods to access various permutations of this substitution pattern. In this context, herein we report an efficient synthesis of an unknown BN-phenanthrene, namely 1,2-dihydro-1-aza-2-boraphenanthrene (**6**), as well as an examination of its reactivity and a study of its main optical properties.

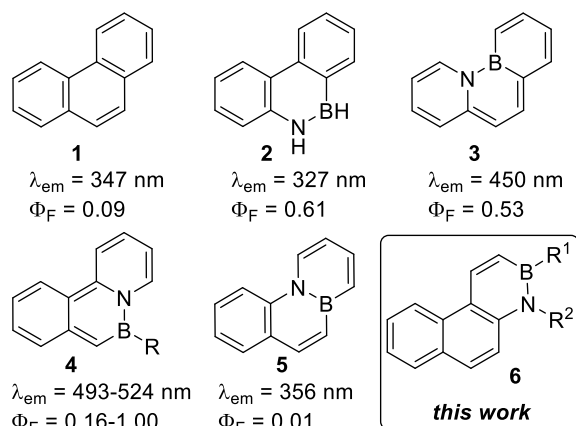
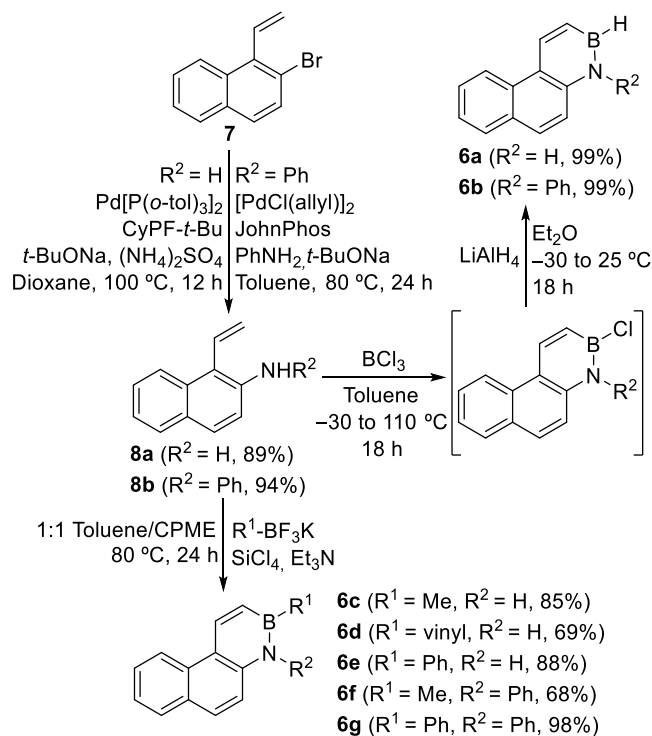


Figure 1. Known BN-phenanthrenes and their fluorescence properties.

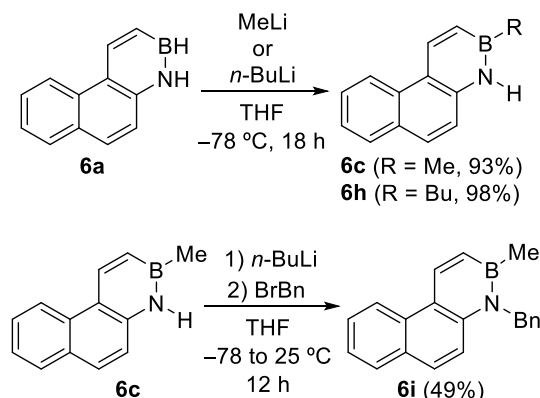
### Scheme 1. Synthesis of BN-phenanthrenes 6a-6g



Our first aim was the preparation of BN-phenanthrene **6a** and its substituted derivatives **6b-6g** (Scheme 1). Both non-boron substituted compounds **6a** and **6b** were synthesized in three steps from easily accessible 2-bromo-1-vinylnaphthalene (**7**).<sup>12</sup> The first step involved a Buchwald–Hartwig amination using either ammonium sulfate as an ammonia surrogate and Pd[P(o-tol)<sub>3</sub>]<sub>2</sub> and CyPF-*t*-Bu as

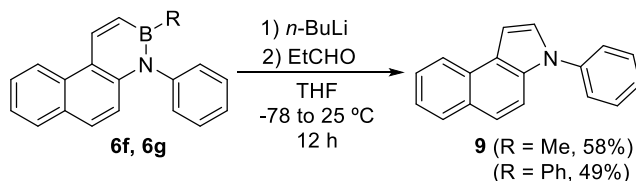
catalytic system<sup>13</sup> to produce **8a**, or aniline, [PdCl(allyl)]<sub>2</sub> and JohnPhos<sup>14</sup> to give **8b**. After treatment of these intermediates with boron trichloride to force a borylative cyclization and a subsequent reaction with lithium aluminum hydride,<sup>15</sup> BN-phenanthrene **6a** and **6b** were isolated in excellent overall yields. Intermediates **8a** and **8b** were also used to synthesize boron-substituted derivatives **6c-6g**, this time via a highly efficient annulation/aromatization process using potassium organotrifluoroborates.<sup>14</sup>

### Scheme 2. Reactivity with organolithium compounds



In order to gain insight into the properties of this new family of BN-phenanthrenes, their reactivity was evaluated. We began our investigation by exploring the addition of organolithium compounds and electrophiles to BN-phenanthrene **6a** (Scheme 2). Addition of two equivalents of MeLi or *n*BuLi led to the formation of **6c** or **6h** in excellent yields via a nucleophilic aromatic substitution in which the hydride on boron acts as a leaving group.<sup>16</sup> The same products were achieved when an electrophile such as iodomethane or benzyl bromide was also added to the reaction medium; substitution at nitrogen was never observed. This kind of reaction only took place when a boron-substituted derivative (**6c**) was directly used as starting material, although total conversion was not achieved and reaction yields never exceeded the 49% found for **6i**. The use of sodium hydride and DMF instead of *n*BuLi and THF did not improve this result.

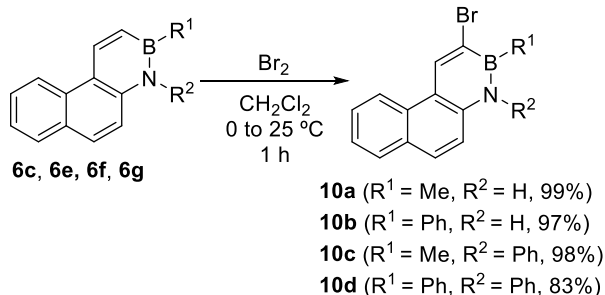
### Scheme 3. Formation of indole 9



Very recently, our group has described the regioselective C–H functionalization of BN-aromatics via coordination of the organolithium to the boron atom followed by the addition of a carbonyl compound.<sup>17</sup> We tested the same reaction conditions used in this previous work (2 equiv. of *n*BuLi

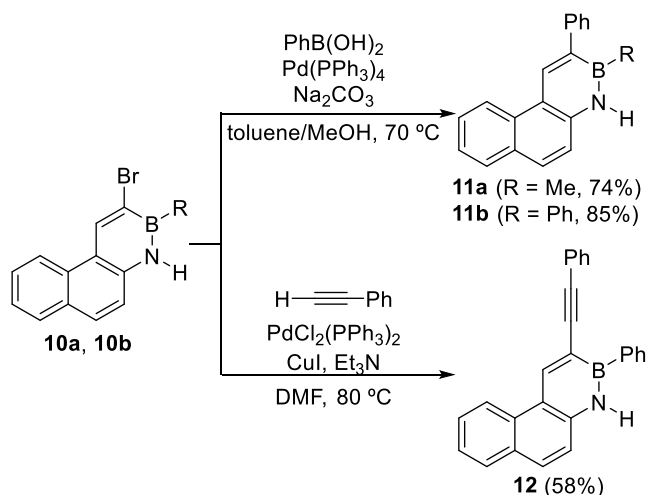
and an excess of propanal) with boron- and nitrogen-substituted BN-phenanthrenes **6f** and **6g** but did not achieve the same reactivity. Indole **9** was the only reaction product obtained in these experiments, together with varying amounts of starting material (Scheme 3). A resembling result has recently been described in a similar substrate, albeit under oxidation reaction conditions.<sup>17</sup>

#### Scheme 4. Regioselective bromination of **6c**, **6e-6g**



Electrophilic aromatic substitution has proven to be a useful tool for the functionalization of BN-aromatic compounds.<sup>18</sup> In particular, several halogenations, generally followed by cross-coupling reactions, have been reported.<sup>10a,19</sup> In this sense, bromination of four different 1,2-dihydro-1-aza-2-boraphenanthrene derivatives (**6c**, **6e**, **6f** and **6g**) by treatment with 1.1 equivalents of bromine in  $\text{CH}_2\text{Cl}_2$  has been tested (Scheme 4). Under these conditions, all the reactions occurred with complete regioselectivity at C3, as confirmed by X-ray diffraction analysis of a single crystal of **10b** (see SI),<sup>20</sup> no traces of other regioisomers or dibrominated products were observed, and compounds **10a-10d** were isolated in excellent yields. It is worthy to note that this position next to the boron has been reported in related BN-aromatics as the most negative and, therefore, the expected position for electrophilic attacks.<sup>10a,19d</sup> Moreover, X-ray analysis of **10b** provides other interesting data on its solid state structure, as the short length of the bond C9-C10, 1.358 Å, which is in accord with a localized double bond in this position, in the manner that it also occurs with phenanthrene.<sup>21</sup>

#### Scheme 5. Cross-coupling reactions



Interestingly, these bromo-substituted derivatives are suitable for further functionalization by different palladium-catalyzed cross-coupling reactions (Scheme 5). Thus, treatment of **10a** and **10b** under standard Suzuki coupling conditions afforded **11a** and **11b** in good yields. Sonogashira coupling also worked efficiently for **10b**, with alkynyl-BN-phenanthrene **12** being isolated in moderate yield. This was not the case, however, for the Buchwald-Hartwig reaction, as we were unable to achieve the expected aminated products under any of the reaction conditions tested.

Once we had developed a useful method for the synthesis of various functionalized BN-phenanthrenes **6**, and had studied their reactivity, we focused on studying their main photophysical properties. The absorption and emission data for the parent compound **6a** and a selection of its substituted derivatives (**6b-6g**, **11b** and **12**) in cyclohexane are summarized in table 1.

**Table 1. UV/Vis and fluorescence data for BN-phenanthrenes **6a-6g**, **11b** and **12**.**<sup>[a]</sup>

compound	$\epsilon$ ( $\text{M}^{-1}\text{cm}^{-1}$ )	$\lambda_{\text{abs max}}$ ( $\lambda_{\text{exc}}$ ) (nm)	$\lambda_{\text{em}}$ (nm)	$\Phi_{\text{F}}$ <sup>[b]</sup>
<b>6a</b>	14450	345 (329)	364	0.30
<b>6b</b>	10160	349 (333)	369	0.48
<b>6c</b>	9250	346 (331)	366	0.35
<b>6d</b>	14330	351 (335)	379	0.70
<b>6e</b>	13510	355 (339)	377	0.93
<b>6f</b>	10060	350 (334)	370	0.37
<b>6g</b>	9880	354 (339)	378	0.29
<b>11b</b>	18090	362 (346)	395	0.82
<b>12</b>	8570	388 (370)	416	0.88

[a] All experiments were performed in cyclohexane solution. [b] Quantum yields reported relative to 9,10-diphenylanthracene ( $\Phi_{\text{F}} = 0.93$ ).

With respect to phenanthrene ( $\lambda_{\text{em}} = 347 \text{ nm}$ ,  $\Phi_{\text{F}} = 0.09$ ), the emission spectrum of **6a** was observed to undergo a

slight bathochromic shift, along with a substantial increase in the quantum yield ( $\phi_F = 0.30$ ). This is in accordance with a general trend observed in all isomers of BN-phenanthrene studied previously, except in **5**, with the introduction of a BN unit leading to increased fluorescence quantum yields with regard to the all-carbon analogue.<sup>8a,9,10a</sup> The alkyl- and aryl-substituted species **6b-6g** displayed similar slightly red-shifted emission maxima with respect to phenanthrene but differed significantly in their fluorescence quantum yield. Thus, while nitrogen-substituted derivatives **6b**, **6f** and **6g** showed a value comparable to that of the parent (**6a**), non-nitrogen substituted derivatives **6d** and **6e**, in which boron was substituted by a vinyl or phenyl group, exhibited remarkably higher quantum yields.

Due to the excellent fluorescence properties of **6e** ( $\lambda_{em} = 377$  nm,  $\phi_F = 0.93$  in cyclohexane), we also evaluated **11b** and **12**, which additionally contain a phenyl or an alkynyl group at C3. Both compounds maintained a high quantum yield but exhibited a larger bathochromic shift, with **12** having an emission maximum at 416 nm. Moreover, the emission of **6e** in different solvents was evaluated in order to explore in greater depth the effect that solvent has on the fluorescence: a quantum yield of 64% was found in  $CH_2Cl_2$ , 68% in THF, 68% in  $CH_3CN$  and 90% in DMSO.

In order to get a deeper insight into the photophysical properties of the BN-phenantrenes, we performed a series of theoretical calculations at the B3LYP/6-31+G\*\* level on all the compounds **1-6** shown in Figure 1. We focused on the absorption and emission properties together with the orbitals involved (see Table 2). Further data could be found in the SI. While a detailed computational study is far from the scope of this paper, some qualitative conclusions could be drawn. The relevant absorption bands imply in all cases a  $\pi \rightarrow \pi^*$  transition. The inclusion of the BN moiety in the phenanthrene scaffold causes the breaking of the symmetry. This is clearly shown in the orbitals involved in the relevant transitions (see SI). For **2**, **3**, **4** and **6**, BN substitution implies a strengthening of the absorption bands while only in **5** a decrease in the oscillator strength value was observed. Regarding, the band maxima, a bathochromic shift of varying intensity for **2-6** was computed in agreement with the experimental data. This is especially relevant for **4** (computed band maximum 413 nm). This is due to a destabilization of the HOMO and a stabilization of the LUMO compared to phenanthrene, in agreement with the general rules recently reported for BN-tetracenes.<sup>22</sup> Upon light absorption, **1-6** evolve in the excited state to reach a planar minimum (see SI) from which emission can take place. The computed Stokes shift is 38 nm for **1** and vary from 24 nm (**2**) to 90 nm (**4**) for the BN-substituted compounds. The computed emission is in good agreement with the experimental data. Interestingly, the emission of this type of compounds could be shifted to both longer and shorter wavelengths with respect to the parent **1**. The different shape of the potential energy surface and the availability of non-radiative deactivation channels should affect the fluorescence quantum yield. These effects have been discussed

before for **5**.<sup>10a</sup> Beyond the involved transitions, the computed frontier orbitals can also provide a qualitative explanation of the regioselective addition of  $Br_2$  (Scheme 4). A careful look at the computed HOMO reveals a large coefficient in C3 (see SI), which would suggest a preference for the bromination at this position.

**Table 2. Computed absorption and emission data for phenanthrene **1** and BN-analogues **2-6**.<sup>[a]</sup>**

compound	$\lambda_{abs\ max}$ (nm)	$f$	$\lambda_{em}$ (nm)
<b>1</b>	298	0.14	336
<b>2</b>	301	0.22	325
<b>3</b>	402	0.32	458
<b>4</b>	413	0.30	503
<b>5</b>	314	0.06	354
<b>6</b>	325	0.24	356

[a] Computed at the B3LYP 6-31+G\*\* level, using PCM (cyclohexane).

In conclusion, the synthesis of a new family of BN-phenantrenes has been reported. We have achieved a remarkably efficient preparation of the parent compound **6a**, in three steps, from easily accessible 2-bromo-1-vinylnaphthalene **7** (88% overall yield), along with several substituted derivatives. Moreover, this synthetic strategy could potentially be applied for the synthesis of more complex BN-PAHs by selecting appropriate starting materials. The reactivity of this new family of BN-phenantrenes with an activated electrophile (bromine) and organolithium compounds was evaluated in order to gain an insight into their properties. Of particular interest is the introduction of a bromo substituent, which allows straightforward derivatization based on palladium-catalyzed cross-coupling reactions. Bromination of four different derivatives showed that this reaction proceeds with complete regioselectivity at C3, and subsequent Suzuki and Sonogashira reactions that these compounds are suitable for further functionalization. These findings generate new possibilities for obtaining functionalized BN-aromatics with modulated properties. Evaluation of the optical properties of this new family of BN-phenantrenes confirmed the previously observed dramatic effect of the B-N unit. Indeed, the parent compound **6a** was observed to undergo a slight bathochromic shift along with a substantial increase in the quantum yield ( $\phi_F = 0.30$ ) with respect to phenanthrene. Non-nitrogen substituted derivatives **6e**, **11b** and **12** exhibited remarkably higher quantum yields ( $\phi_F = 0.82-0.93$ ), thus showing that this strategy of isoelectronic BN incorporation might provide an alternative method for tuning the emissive properties of phenanthrene-based materials.

## ASSOCIATED CONTENT

### Supporting Information

Experimental details, computational data, X-ray crystallographic data for **10b**, UV/Vis absorption and emission spectra and NMR spectra for all new compounds (PDF).

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

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## REFERENCES

- (1) (a) 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. (b) Wang, X.-Y.; Wang, J.-Y.; Pei, J. BN Heterosuperbenzenes: Synthesis and Properties. *Chem. Eur. J.* **2015**, *21*, 3528–3539. (c) Campbell, P. G.; Marwitz, A. J. V.; Liu, S.-Y. Recent Advances in Azaborine Chemistry. *Angew. Chem. Int. Ed.* **2012**, *51*, 6074–6092.
- (2) (a) Bosdet, M. J. D.; Piers, W. E. B–N as a C–C Substitute in Aromatic Systems. *Can. J. Chem.* **2009**, *87*, 8–29. (b) Liu, Z.; Marder, T. B. B–N versus C–C: How Similar Are They? *Angew. Chem. Int. Ed.* **2008**, *47*, 242–244.
- (3) For a review, see: Wang, J.-Y.; Pei, J. BN-embedded aromatics for optoelectronic applications. *Chin. Chem. Lett.* **2016**, *27*, 1139–1146.
- (4) (a) McConnell, C. R.; Campbell, P. G.; Fristoe, C. R.; Memmel, P.; Zakharov, L. N.; Li, B.; Darrigan, C.; Chrostowska, A.; Liu S.-Y. Synthesis and Characterization of 1,2-Azaborine-Containing Phosphine Ligands: A Comparative Electronic Structure Analysis. *Eur. J. Inorg. Chem.* **2017**, 2207–2210. (b) Sun, F.; Huang, M.; Zhoub, Z.; Fang X. 4a,8a-Azaboranaphthalene-4-yl phosphine Ligands: Synthesis and Electronic Modulation in Suzuki–Miyaura Coupling Reactions. *RSC Adv.* **2015**, *5*, 75607–75611.
- (5) (a) Vlasceanu, A.; Jessing, M.; Kilburn, J. P. BN/CC Isosterism in Borazaronaphthalenes towards Phosphodiesterase 10A (PDE10A) Inhibitors. *Bioorg. Med. Chem.* **2015**, *23*, 4453–4461. (b) Rombouts, F. J. R.; Tovar, F.; Austin, N.; Tresadern, G.; Trabanco, A. A. Benzazaborinines as Novel Bioisosteric Replacements of Naphthalene: Propranolol as an Example. *J. Med. Chem.* **2015**, *58*, 9287–9295. (c) Knack, D. H.; Marshall, J. L.; Harlow, G. P.; Dudzik, A.; Szaleniec, M.; Liu, S.-Y.; Heider, J. BN/CC Isosteric Compounds as Enzyme Inhibitors: N- and B-Ethyl-1,2-azaborine Inhibit Ethylbenzene Hydroxylation as Nonconvertible Substrate Analogues. *Angew. Chem. Int. Ed.* **2013**, *52*, 2599–2601. (d) Liu, L.; Marwitz, A. J. V.; Matthews, B. W.; Liu, S.-Y. Boron Mimetics: 1,2-Dihydro-1,2-azaborines Bind inside a Nonpolar Cavity of T4 Lysozyme. *Angew. Chem. Int. Ed.* **2009**, *48*, 6817–6819.
- (6) (a) Bélanger-Chabot, G.; Braunschweig, H.; Roy D. K. Recent Developments in Azaborinine Chemistry. *Eur. J. Inorg. Chem.* **2017**, 4353–4368. (b) Morgan, M. M.; Piers, W. E. Efficient synthetic methods for the installation of boron–nitrogen bonds in conjugated organic molecules. *Dalton Trans.* **2016**, *45*, 5920–5924.
- (7) Liu, Z.; Ishibashi, J. S. A.; Darrigan, C.; Dargelos, A.; Chrostowska, A.; Li, B.; Vasiliu, M.; Dixon, D. A.; Liu, S.-Y. The Least Stable Isomer of BN Naphthalene: Toward Predictive Trends for the Optoelectronic Properties of BN Acenes. *J. Am. Chem. Soc.* **2017**, *139*, 6082–6085.
- (8) (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) Dewar, M. J. S.; Kubba, V. P.; Pettit, R. New Heteroaromatic Compounds. Part I. 9-Axa-10-boraphenanthrene. *J. Chem. Soc.* **1958**, 3073–3075.
- (9) Lu, J.-S.; Ko, S.-B.; Walters, N. R.; Kang, Y.; Sauriol, F.; Wang, S. Formation of Azaborines by Photoelimination of B,N-Heterocyclic Compounds. *Angew. Chem. Int. Ed.* **2013**, *52*, 4544–4548.
- (10) (a) Abengózar, A.; García-García, P.; Sucunza, D.; Frutos, L. M.; Castaño, O.; Sampedro, D.; Pérez-Redondo, A.; Vaquero, J. J. Synthesis, Optical Properties, and Regioselective Functionalization of 4a-Aza-10a-boraphenanthrene. *Org. Lett.* **2017**, *19*, 3458–3461. (b) Dewar, M. J. S.; Kaneko, C.; Bhattacharjee, M. K. New Heteroaromatic Compounds. XVI. Compounds with Heteroatoms at Bridgeheads. *J. Am. Chem. Soc.* **1962**, *84*, 4884–4887.
- (11) Abengózar, A.; Fernández-González, M. A.; Sucunza, D.; Frutos, L. M.; Salgado, A.; García-García, P.; Vaquero, J. J. C–H Functionalization of BN-Aromatics Promoted by Addition of Organolithium Compounds to the Boron Atom. *Org. Lett.* **2018**, *20*, 4902–4906.
- (12) Grudzien, K.; Zukowska, K.; Malinska, M.; Wozniak, K.; Barbasiewicz, M. Mechanistic Studies of Hoveyda–Grubbs Metathesis Catalysts Bearing S-, Br-, I-, and N-coordinating Naphthalene Ligands. *Chem. Eur. J.* **2014**, *20*, 2819–2828.
- (13) Green, R. A.; Hartwig, J. F. Palladium-Catalyzed Amination of Aryl Chlorides and Bromides with Ammonium Salts. *Org. Lett.* **2014**, *16*, 4388–4391.
- (14) Wisniewski, S. R.; Guenther, C. L.; Argintaru, O. A.; Molander, G. A. A Convergent, Modular Approach to Functionalized 2,1-Borazaronaphthalenes from 2-Aminostyrenes and Potassium Organotrifluoroborates. *J. Org. Chem.* **2014**, *79*, 365–378.
- (15) (a) Ishibashi, J. S. A.; Marshall, J. L.; Mazière, A.; Lovinger, G. J.; Li, B.; Zakharov, L. N.; Dargelos, A.; Graciaa, A.; Chrostowska, A.; Liu, S.-Y. Two BN Isosteres of Anthracene: Synthesis and Characterization. *J. Am. Chem. Soc.* **2014**, *136*, 15414–15421. (b) Dewar, M. J. S.; Dietz, R. New Heteroaromatic Compounds. Part III. 2,1-Borazaronaphthalene (1,2-Dihydro-1-aza-2-boranaphthalene). *J. Chem. Soc.* **1959**, 2728–2730.
- (16) Lamm, A. N.; Garner III, E. B.; Dixon, D. A.; Liu S.-Y. Nucleophilic Aromatic Substitution Reactions of 1,2-Dihydro-1,2-Azaborine. *Angew. Chem. Int. Ed.* **2011**, *50*, 8157–8160.
- (17) van de Wouw, H. L.; Lee, J. Y.; Awuyah, E. C.; Klausen, R. S. A BN Aromatic Ring Strategy for Tunable Hydroxy Content in Polystyrene. *Angew. Chem. Int. Ed.* **2018**, *57*, 1673–1677.
- (18) (a) Zhang, Y.; Dan, W.; Fang X. Metal Nitrate Mediated Regioselective Nitration of BN-Substituted Arenes. *Organometallics* **2017**, *36*, 1677–1680. (b) Zhang, Y.; Sun, F.; Dan, W.; Fang X. Friedel–Crafts Acylation Reactions of BN-Substituted Arenes. *J. Org. Chem.* **2017**, *82*, 12877–12887.
- (19) (a) Abengózar, A.; García-García, P.; Sucunza, D.; Pérez-Redondo, A.; Vaquero, J. J. Synthesis of functionalized helical BNbenzo[c]phenanthrenes. *Chem. Commun.* **2018**, *54*, 2467–2470. (b) Sun, F.; Lv, L.; Huang, M.; Zhou, Z.; Fang, X. Palladium-Catalyzed Cross-Coupling Reactions of 4a,8a-Azaboranaphthalene. *Org. Lett.* **2014**, *16*, 5024–5027. (c) Molander, G. A.; Wisniewski, S. R. Accessing Molecularly Complex Azaborines: Palladium-Cata-

lyzed Suzuki–Miyaura Cross-Couplings of Brominated 2,1-Borazaronaphthalenes and Potassium Organotrifluoroborates. *J. Org. Chem.* **2014**, *79*, 6663–6678 (d) Pan, J.; Kampf, J. W.; Ashe, A. J. Electrophilic Aromatic Substitution Reactions of 1,2-Dihydro-1,2-azaborines. *Org. Lett.* **2007**, *9*, 679–681.

(20) CCDC 1905045 contains the supplementary crystallographic data for this paper. The data can be obtained free of

charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/structures](http://www.ccdc.cam.ac.uk/structures).

(21) Trotter, J. The Crystal and Molecular Structure of Phenanthrene. *Acta Cryst.* **1963**, *16*, 605–608.

(22) Ishibashi, J. S. A.; Dargelos, A.; Darrigan, C.; Chrostowska, A.; Liu, S.-Y. *Organometallics* **2017**, *36*, 2494–2497.