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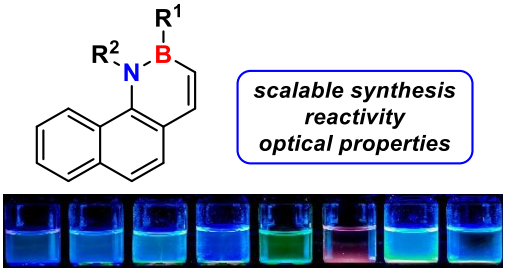
A new member of the BN-phenanthrene family: understanding the role of the B–N bond position

Alberto Abengózar,[†] David Sucunza,[†,*] Patricia García-García,[†] Diego Sampedro,[‡] Adrián Pérez-Redondo[†] and Juan J. Vaquero[†,*]

[†] Departamento de Química Orgánica y Química Inorgánica, Instituto de Investigación Química "Andrés M. del Río" (IQAR), Universidad de Alcalá, 28805-Alcalá de Henares, Spain

[‡] Departamento de Química, Centro de Investigación en Síntesis Química (CISQ), Universidad de La Rioja, Madre de Dios 53, 26006-Logroño, Spain



ABSTRACT: 3,4-Dihydro-4-aza-3-boraphenanthrene, which shows the highest fluorescence quantum yield of all non-substituted BN-phenanthrenes reported to date (ϕ_F = 0.61), has been synthesized in only three steps (76% overall yield) from easily accessible 1-bromo-2-vinylnaphthalene, along with several substituted derivatives. The reactivity of these previously unknown BN-aromatic compounds towards organolithium compounds and bromine has been studied. This latter reaction affords bromo-substituted compounds that are suitable for further functionalization via Suzuki and Sonogashira couplings, with complete regioselectivity. The optical properties and excited state deactivation mechanisms of selected compounds were studied using computational methods.

INTRODUCTION

BN-polycyclic aromatic hydrocarbons (BN-PAHs)[1] have emerged as good candidates for the development of novel materials.[2] The replacement of a C=C bond in an aromatic ring by an isoelectronic B–N bond leads to these new compounds, which retain aromaticity and are structurally analogous to their all-carbon counterparts but have different properties as a result of the presence of a dipole in the molecule. Thus, the azaborine unit has been explored in the design of promising components for enhanced optoelectronic devices,[3] as well as in the search for new ligands for transition metal-based catalysis.[4] Moreover, the possibilities of BN-aromatic compounds as isosteres of phenyl and naphthyl groups in medicinal chemistry has also been reported.[5]

Although BN-PAHs have received great interest in recent years,[6] this field is still limited by the lack of general and mild synthetic methodologies for synthesizing these compounds in sufficiently large quantities.[7] In addition, the effects that replacement of a C=C bond by a B–N bond have on the properties of BN-aromatic compounds are still not fully understood and, consequently, at times are difficult to predict. As such, the information obtained from the simplest systems is still highly valuable.

With regard to the above, a comparison of different BN isosteres of naphthalene has been published recently.[8] BN-isosteres **2**,[9] **3**,[9a] **4**,[10] **5**[11] and **6**[12] of the simple polycyclic aromatic hydrocarbon phenanthrene (**1**) have been described and their optical properties studied, as has the reactivity of **5** and **6** with activated electrophiles and organolithium compounds.[11a,12,13] This study showed that fluorescence emission maxima and quantum efficiencies are strongly affected by the position of the B–N bond (Figure 1). However, as the reasons for these experimental findings remain unclear, a systematic study into how this structural difference influences the reactivity and optical properties of these BN-phenanthrene analogs would be worthwhile. Unfortunately, the lack of available synthetic methods to access various permutations of this substitution pattern currently precludes a study of this nature.

In this context, herein we describe an efficient synthesis of a previously unknown BN-phenanthrene, namely 3,4-dihydro-4-aza-3-boraphenanthrene (**7**), and several substituted derivatives thereof, as well as an examination of their reactivity. Moreover, we report an experimental and theoretical investigation of their main optical properties in comparison with those of phenanthrene and other known isomers of BN-phenanthrene.

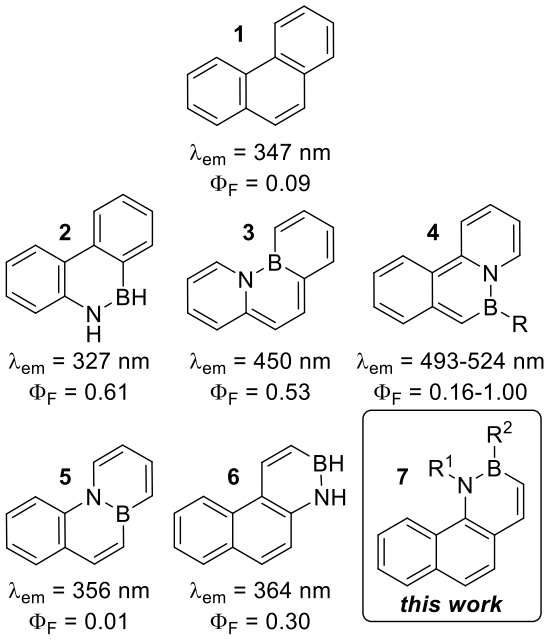


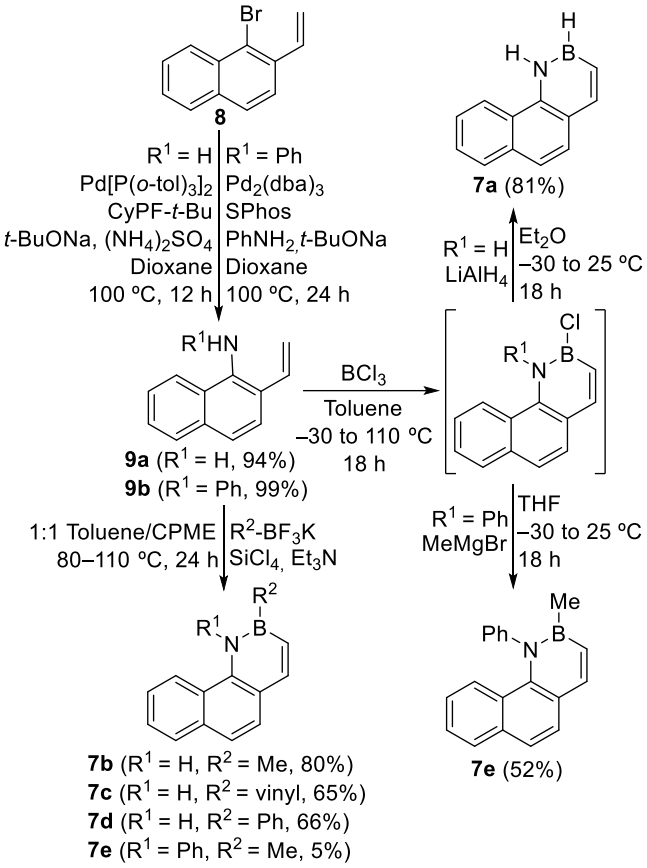
Figure 1. Previously reported BN-phenanthrenes and their fluorescence properties.

RESULTS AND DISCUSSION

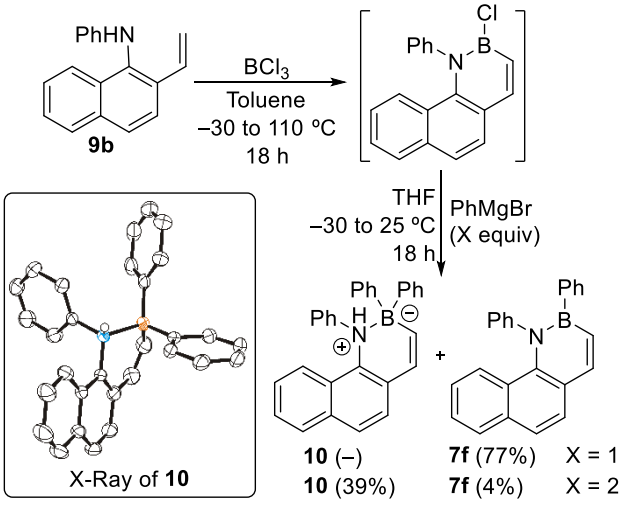
The parent BN-phenanthrene compound **7a** was prepared from easily accessible 1-bromo-2-vinylnaphthalene (**8**)[14] in an overall yield of 76% (Scheme 1). The three steps involved were: a Buchwald–Hartwig amination using ammonium sulfate as an ammonia surrogate and Pd[P(*o*-tol)$_3$]$_2$ and CyPF-*t*Bu as catalytic system,[15] treatment of intermediate **9a** with boron trichloride to force a borylative cyclization, and subsequent treatment with lithium aluminium hydride.[16] Naphthalenamine (**9a**) was used to synthesize boron-substituted derivatives **7b**-**7d** by way of an efficient annulation/aromatization process using potassium organotrifluoroborates.[17]

Synthesis of the nitrogen-substituted derivatives proved more arduous. The first step again involved a Buchwald–Hartwig amination, this time using aniline, Pd$_2$(dba)$_3$ and SPhos,[18] to prepare naphthalenamine **9b** in excellent yield. However, treatment of this intermediate with potassium methyltrifluoroborate, $SiCl_4$ and Et_3N yielded BN-phenanthrene **7e** in a maximum yield of only 5%, therefore this compound had to be synthesized via a two-step sequence: addition of boron trichloride and subsequent treatment with two equivalents of methylmagnesium bromide.[19]

Scheme 1. Synthesis of BN-phenanthrenes 7a-7e



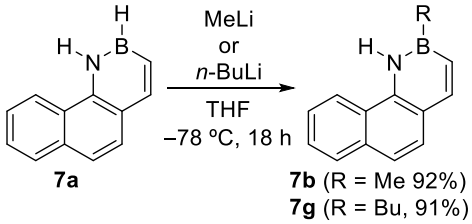
Scheme 2. Synthesis of BN-phenanthrenes 7f and 10



The same synthetic methodology was followed with phenylmagnesium bromide to give the expected compound **7f** in good yield when one equivalent of this Grignard reagent was added to the previously formed chloro-substituted intermediate (Scheme 2). When two equivalents were added, the main product of the reaction was

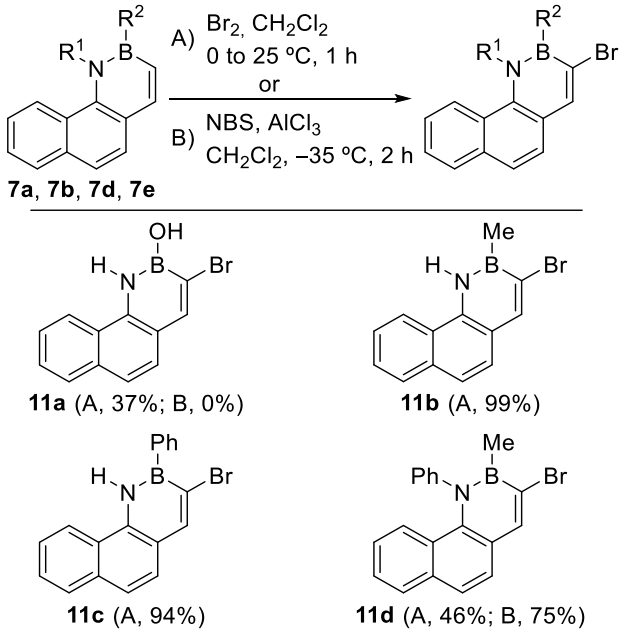
the zwitterionic derivative **10**, with **7f** being isolated in very poor yield. The crystal structure of **10** was determined by X-ray diffraction analysis (Figure S1),[20] thus confirming this double addition to the boron atom, which has been previously reported in similar BN-aromatic compounds by Dewar et al.[21]

Scheme 3. Reactivity with organolithium compounds



In order to gain a more in-depth understanding of the properties of this new family of BN-phenanthrenes, and to extend the possibilities for obtaining functionalized derivatives, their reactivity was investigated. We started by exploring the addition of organolithium compounds to BN-phenanthrene **7a** (Scheme 3) and found that addition of two equivalents of MeLi or *n*BuLi afforded the formation of **7b** or **7g** in excellent yields via a nucleophilic aromatic substitution in which the hydride on boron acts as a leaving group.[19]

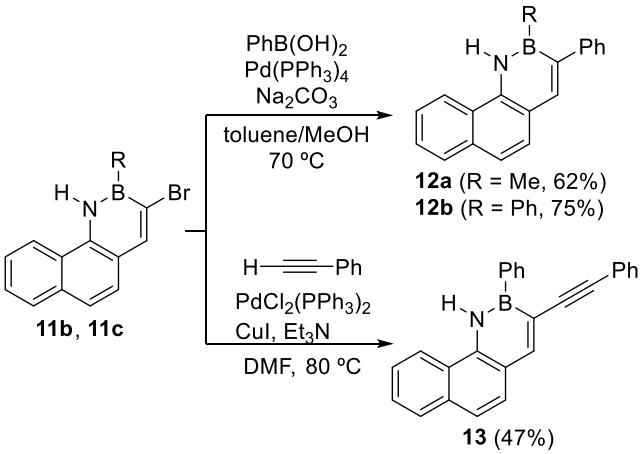
Scheme 4. Regioselective bromination of 7a, 7b, 7d, 7e



Electrophilic aromatic substitution[22] and, in particular, halogenation, generally followed by cross-coupling reactions,[11a,23] has proven to be a useful tool for the functionalization of BN-aromatic compounds. As such, the bromination of four different 3,4-dihydro-4-aza-3-boraphenanthrenes (**7a**, **7b**, **7d** and **7e**) by treatment with bromine in CH_2Cl_2 or *N*-bromosuccinimide (NBS) in the presence of $AlCl_3$ was studied (Scheme 4). All reactions occurred with complete regioselectivity at C2 under both conditions, as confirmed by X-ray diffraction analysis of a single crystal of **11d** (Figure S2).[20] This result was expected as this position next to the boron has been reported to be the most reactive in related BN-aromatics for electrophilic attacks.[11a,23d] However, compounds **11a-11c** were isolated in better yields when bromine was used as electrophile, and **11d** after addition of NBS and $AlCl_3$. The comparatively low yield of **11a** is due to the instability of **7a** under these reaction conditions and the difficulty of purifying it. Indeed, the hydrogen connected to the boron was replaced by a hydroxy group during this process.

As these bromo-substituted derivatives can be used for further functionalization, various palladium-catalyzed cross-coupling reactions were tested with **11b** and **11c** (Scheme 5). In this manner, **12a** and **12b** were formed in good yields under standard Suzuki coupling conditions, and alkynyl-BN-phenanthrene **13** isolated in moderate yield after the Sonogashira coupling of **11c**. Nevertheless, the Buchwald–Hartwig reaction did not work under any of the reaction conditions tested.

Scheme 5. Cross-coupling reactions



To explore the photophysics of these previously unknown BN-phenanthrenes, the UV and fluorescence spectra of the parent compound **7a** and some of its substituted derivatives (**7b**-**7f**, **12b** and **13**) were measured (Table 1, Figure 2). When compared with phenanthrene (λ_{em} = 347 nm, ϕ_F = 0.09), the emission spectrum of **7a** underwent a slight bathochromic shift (λ_{em} = 371 nm), along with a substantial increase in the quantum yield (ϕ_F = 0.61). It is worth noting that this new BN-phenanthrene, together with the previously known isomer **2**, shows the highest fluorescence quantum yield of all non-substituted BN isosteres of phenanthrene reported to date.[9a,10,11a,12]

Table 1. UV/Vis and fluorescence data for BN-phenanthrenes 7a-7f, 12b and 13[a]

compound	ε ($M^{-1}cm^{-1}$)	$\lambda_{abs\ max}$ (λ_{exc}) (nm)	λ_{em} (nm)	ϕ_F [b]
7a	9149	351 (335)	371	0.61
7b	6995	352 (335)	373	0.70
7c	9746	355 (339)	387	0.42
7d	10685	360 (343)	383	0.57
7e	5454	359 (342)	387	0.04
7f	6200	364 (347)	392	0.04
12b	15049	365 (348)	396	0.51
13	7294	387 (368)	416	0.72

[a] All experiments were performed using cyclohexane solutions. [b] Quantum yields reported relative to 9,10-diphenylanthracene (ϕ_F = 0.93)

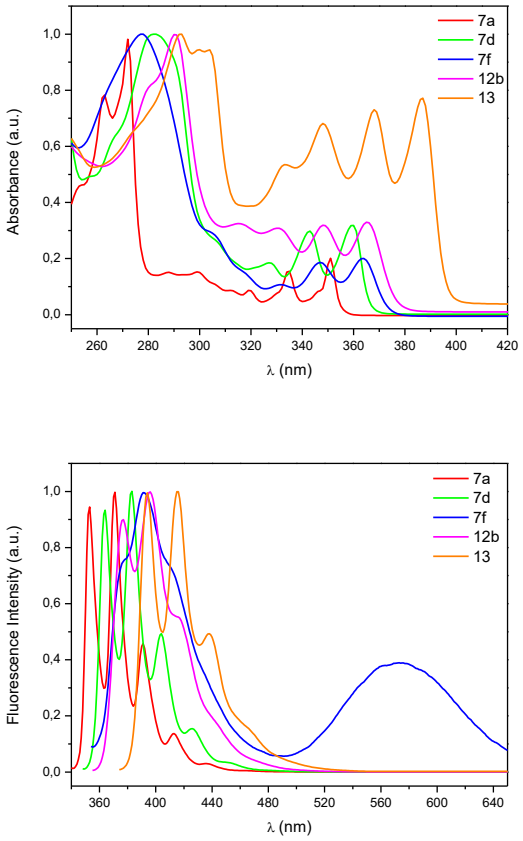


Figure 2. UV/Vis absorption (top) and emission (bottom) spectra for selected BN-phenanthrenes **7a**, **7d**, **7f**, **12b** and **13** in cyclohexane

The alkyl- and aryl-substituted derivatives **7b**-**7f** exhibited similar slightly red-shifted emission maxima with respect to phenanthrene but diverged significantly as regards the fluorescence quantum yield. Thus, while non-nitrogen substituted species **7b**-**7d** displayed a similar value to that of the parent compound (**7a**), the quantum yield of nitrogen-substituted derivatives **7e** and **7f** was notably lower. Interestingly, in addition to the common emission at around 400 nm found for other derivatives, **7f** shows another emission band located at ca. 560 nm. This additional band could be explained by computational means (see SI). The steric hindrance caused by the two neighboring aromatic rings allows for the presence of two different minima of comparable energy in the excited state. Emission from one of them (more planar and analog to other compounds) implies the emission at 397 nm, while the other minimum (more distorted) implies the emission at 498 nm. These low quantum yields could be due to excimer formation, as it has been reported for related compounds.[24] This was checked by measuring the fluorescence dependence on concentration of **7f** (see SI), but no significant differences were found. As an alternative deactivation channel, the phenyl rings placed on the nitrogen atom could rotate through the single bond to allow the excited state decay. Finally, **12b** and **13**, which contain an additional phenyl or alkynyl group at C2, maintained a high quantum yield but showed a larger bathochromic shift (λ_{em} for **13** of 416 nm).

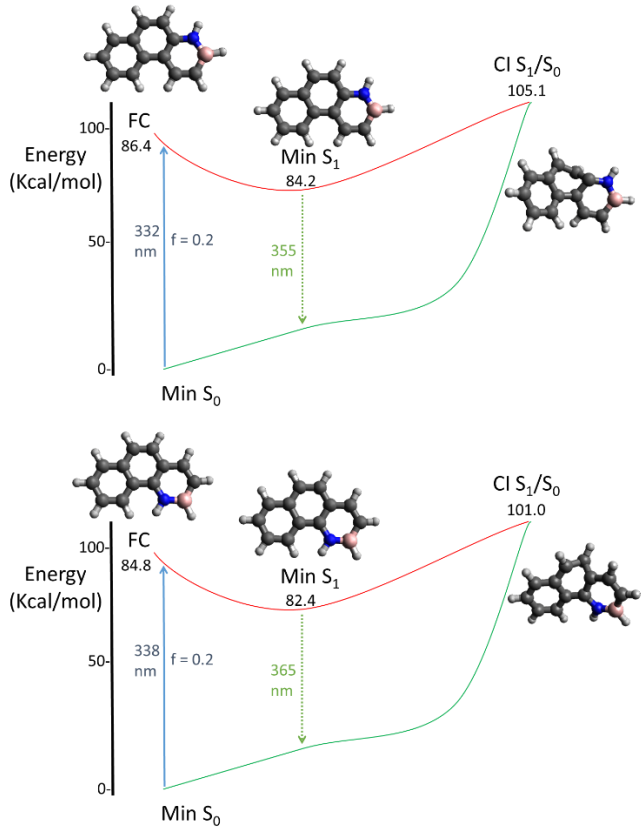


Figure 3. Computed critical points along the potential energy surface for **6** (top) and **7a**

A computational study was carried out to gain a deeper insight into the photophysics of these BN-phenanthrenes, with **7a** being selected as the core structure for this new family of compounds. For the sake of comparison, we also performed calculations for **6**. We first computed the ab-

sorption spectra for both compounds using the qualitative TD-DFT methodology (see Computational Details). A good agreement between the experimental and computational data was obtained when using the B3LYP functional together with the 6-31+G** basis set; cyclohexane was included as solvent using the PCM method. For **6**, S_1 was found to be a bright state (325 nm, f = 0.24), with an emission from the excited state at 356 nm. For **7a**, an absorption with maximum at 326 nm (f = 0.12) and an emission at 331 nm were computed. The HOMO-LUMO transition is mainly responsible for the absorption in both compounds (see SI).

The radiationless deactivation of the excited state requires the presence of an accessible funnel to the ground state, such as a conical intersection (CI) point. Indeed, several CIs were found for **6** and **7a** using CASSCF (see SI). While structurally related to phenanthrene, the presence of the B-N moiety implies an asymmetry in the chromophore. As such, the different CIs found feature the typical kink found in PAHs located in different parts of the structure.[25] In any case, the B-N bond does not take part in the geometrical deformation. In this sense, substitution of the carbon atoms also results in a modification of the deactivation mechanisms in addition to the optical properties.

To obtain a more quantitative overview of the properties of **6** and **7a**, the critical points along the potential energy surface (PES) were computed for both compounds at the CASPT2//CASSCF level of theory using a (14,13) active space and the ANO-L-VDZ basis set (see Computational Details). The results are shown in Figure 3.

Both **6** and **7a** share a similar shape of the PES, with a planar minimum in the first excited state, which accounts for the emission and the relatively small Stokes shift (see Table 1). In both cases, the lower energy conical intersection point is located well above the energy of the S_1 minimum. This allows for a radiative deactivation of the excited state, in agreement with the relatively high fluorescence quantum yields measured. If the energy barrier in S_1 is exceeded, the ground state could be recovered by a competitive non-radiative mechanism. A detailed analysis of the CIs is provided in the SI.

The energy profile for **6a** and **7** is very similar to the one already described in related BN-PAHs (see Figure 1).[11a] The inclusion of the B-N moiety in the hydrocarbon backbone modifies not only the absorption but also the availability of competing deactivation channels. When a CI point of low energy is available (as in **5**,[11a] Figure 1), these compounds will feature an emission of low intensity. In contrast, high-energy CIs are related with strongly emissive compounds (as in **2**,[11a] **6** and **7a**). This allows for the rationalization of the optical properties of the BN-phenanthrenes in which the BN moiety is located in different positions. In turn, this should help in the design of new BN-PAHs with controlled properties.

CONCLUSIONS

An efficient preparation of the previously unknown BN-phenanthrene **7a** (three steps from 2-bromo-1-vinylnaphthalene **8**; overall yield: 76%), along with several substituted derivatives, has been reported. This methodology could potentially be used to synthesise more complex BN-PAHs by careful selection of the starting materials. Moreover, the reactivity of this new family of BN-aromatic species with organolithium compounds and bromine has been evaluated. This latter reaction afforded bromo-substituted compounds with complete regioselectivity at C2, which are appropriate for further functionalization via Suzuki and Sonogashira couplings. A study of the photophysics of these new BN-phenanthrenes confirmed the previously observed dramatic effect of the B–N unit. Indeed, the parent compound **7a** underwent a slight bathochromic shift along with a substantial increase in the quantum yield (ϕ_F = 0.61) when compared with phenanthrene. The optical properties of these compounds were rationalized by means of theoretical calculations. Competitive radiative and non-radiative deactivation mechanisms account for the experimental data. In addition, a planar minimum in the excited state is responsible for the emission, whereas a kink in any of the non-substituted rings allows for the non-emissive deactivation. This discovery suggests new possibilities for obtaining functionalized BN-aromatics with modulated properties, thus providing a further option for tuning the emissive properties of phenanthrene-based materials.

EXPERIMENTAL SECTION

General Methods. Reagents were acquired from commercial sources and used without further purification. When required, solvents were dried using an MBRAUN MB-SPS-800 apparatus. In general, reactions were carried out under an argon atmosphere using oven-dried glassware with magnetic stirring and dry solvents. Reactions were monitored using analytical TLC plates (Merck; silica gel 60 F254, 0.25 mm), and compounds were visualized with UV radiation. Silica gel grade 60 (70–230 mesh, Merck) was used for column chromatography. All melting points were determined in open capillary tubes using a Stuart Scientific SMP3 melting point apparatus (uncorrected). IR spectra were obtained using a Perkin-Elmer FTIR spectrum 2000 spectrophotometer. ^{1}H, ^{13}C{^{1}H} and ^{11}B{^{1}H} NMR spectra were recorded using either a Varian Mercury VX-300, Varian Unity 300 or Varian Unity 500 MHz spectrometer at room temperature. Chemical shifts are given in ppm (δ) downfield from TMS, with calibration with respect to the residual protonated solvent used (δ_H = 7.24 ppm and δ_C = 77.0 ppm for $CDCl_3$). ^{11}B{^{1}H} NMR spectra were referenced externally to $BF_3{\cdot}OEt_2$ (δ_B = 0 ppm). Coupling constants (J) are in Hertz (Hz) and signals are described as follows: s, singlet; d, doublet; t, triplet; q, quadruplet; m, multiplet; br, broad; ap, apparent. High-resolution analysis (HRMS) was performed using an Agilent 6210 time of-flight LC/MS. Absorption spectra were recorded using a Uvikon 941 (Kontron Instruments) UV-Vis spectrophotometer. Steady-state fluorescence

measurements were carried out using a PTI Quanta Master spectrofluorimeter equipped with a Xenon flash lamp as a light source, single concave grating monochromators and Glan-Thompson polarizers in the excitation and emission paths. Detection was allowed by a photomultiplier cooled by a Peltier system. Slit widths were selected at 6 nm for both excitation and emission paths and polarizers were fixed at the "magic angle" condition. Right angle geometry and rectangular 10 mm path cells were used for the fluorescence measurements. The starting material 1-Bromo-2-naphthaldehyde was purchased from Sigma-Aldrich and was used without further purification.

1-Bromo-2-vinylnaphthalene (8). $MePPh_3Br$ (1.93 g, 5.30 mmol, 1.3 equiv.) and *t*BuOK (701 mg, 6.12 mmol, 1.5 equiv.) were dissolved in THF (20 mL), and the resulting yellow suspension was stirred at room temperature for 2 h. The reaction mixture was then cooled to 0 °C and a solution of 1-bromo-2-naphthaldehyde (1.00 g, 4.08 mmol, 1.0 equiv.) in THF (2 mL) added dropwise. After removing the cooling bath, the mixture was stirred at room temperature for 3 h. Silica gel was then added and the solvents removed under reduced pressure. Purification by flash column chromatography (Hexane) gave **8** (869 mg, 3.73 mmol, 91%) as a colorless oil, which solidified upon cooling. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 8.34 (dd, *J* = 8.4, 1.2 Hz, 1H, H-8), 7.80–7.76 (m, 1H, H-5), 7.75 (d, *J* = 8.6 Hz, 1H, H-4) 7.65 (d, *J* = 8.6 Hz, 1H, H-3), 7.57 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H, H-7), 7.48 (ddd, *J* = 8.0, 6.9, 1.2 Hz, 1H, H-6), 7.38 (dd, J_{trans} = 17.5 Hz, J_{cis} = 11.0 Hz, 1H, H-9), 5.82 (dd, J_{trans} = 17.5 Hz, J_{gem} = 0.8 Hz, 1H, H-10), 5.47 (dd, J_{cis} = 11.0 Hz, J_{gem} = 0.8 Hz, 1H, H-10). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ (ppm) 136.8 (C-9), 134.9 (C-2), 134.0 (C-8a), 132.5 (C-4a), 128.0 (C-5), 127.74 (C-4), 127.70 (C-7), 127.5 (C-8), 126.6 (C-6), 123.9 (C-3), 123.7 (C-1), 117.4 (C-10). Spectral data were in accordance with those in literature.[14]

2-Vinylnaphthalen-1-amine (9a). $Pd[P(o\text{-}tol)_3]_2$ (18.2 mg, 0.025 mmol, 5.0 mol%) and CyPF-*t*Bu (14.3 mg, 0.025 mmol, 5.0 mol%) were dissolved in dioxane (1 mL) in a Schlenk flask and mixed for 5 min. An oven-dried Biotage microwave vial equipped with a stir bar was charged with aryl halide **8** (117 mg, 0.50 mmol, 1.0 equiv.), ammonium sulfate (100 mg, 0.75 mmol, 1.5 equiv.) and sodium *tert*-butoxide (223 mg, 2.25 mmol, 4.5 equiv.). The vial was sealed with a cap lined with a disposable Teflon septum, evacuated under vacuum and purged with argon three times. Dioxane (5 mL) was added, followed by the solution of the catalyst. The reaction was stirred at 100 °C for 12 h, then the reaction mixture was diluted with EtOAc (10 mL) and filtered through a pad of Celite. The filtrate was concentrated under reduced pressure and the remaining residue purified by flash column chromatography (10% EtOAc/Hexane) to give **9a** (79 mg, 0.47 mmol, 94%) as an orange solid. M.p.: 56–58 °C. IR (KBr) $\tilde{\upsilon}_{max}$ (cm^{-1}) 3350 (NH_2), 3059, 1622, 1565, 1510, 1400, 1084, 989, 902, 800, 743. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.82–7.79 (m, 1H, H-8), 7.78–7.76 (m, 1H, H-5), 7.47 (d, *J* = 8.6 Hz, 1H, H-3), 7.46–7.43 (m, 2H, H-6, H-7), 7.30 (d, *J* = 8.6 Hz, 1H, H-4), 6.97 (dd, J_{trans} = 17.4 Hz, J_{cis} = 11.1 Hz, 1H, H-9), 5.73 (dd, J_{trans} = 17.4 Hz, J_{gem} = 1.3 Hz, 1H, H-10), 5.41 (dd, J_{cis} = 11.1 Hz, J_{gem} = 1.3 Hz, 1H, H-10), 4.33 (br s, 1H, NH_2). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ (ppm) 138.7 (C-1), 133.8 (C-4a), 132.7 (C-9), 128.5 (C-5), 125.8 (C-6), 125.2 (C-7), 125.0 (C-3), 123.7 (C-8a), 120.8 (C-8), 118.7 (C-4), 117.8 (C-2), 115.4 (C-10). HRMS (APCI) *m/z* calculated for $C_{12}H_{12}N$ $[M+H]^+$: 170.0964. Found $[M+H]^+$: 170.0973.

***N*-Phenyl-2-vinylnaphthalen-1-amine (9b).** An oven-dried Biotage microwave vial equipped with a stir bar was charged with $Pd_2(dba)_3{\cdot}CHCl_3$ (31 mg, 0.030 mmol, 2.0 mol%), SPhos (30 mg, 0.072 mmol, 4.8 mol%), sodium *tert*-butoxide (223 mg, 2.25 mmol, 1.5 equiv.) and aryl bromide **8** (350 mg, 1.50 mmol, 1.0 equiv.). The vial was sealed with a cap lined with a disposable Teflon septum, evacuated under vacuum, and purged with argon three times. Dioxane (15 mL) was added, followed by aniline (171 µL, 1.80 mmol, 1.2 equiv.). The reaction mixture was stirred at 100 °C for 24 h, then diluted with Et_2O (15 mL) and filtered through a pad of Celite. The filtrate was removed under reduced pressure and the remaining residue was purified by flash column chromatography (5% EtOAc/Hexane) to give **9b** (366 mg, 1.49 mmol, 99%) as a white solid. M.p.: 86–88 °C. IR (KBr) $\tilde{\upsilon}_{max}$ (cm^{-1}) 3392 (NH), 3061, 3038, 1602, 1498, 1416, 1377, 1308, 1254, 922, 820, 747, 691. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.06–8.04 (m, 1H, H-8), 7.91 (dd, *J* = 8.1, 1.4 Hz, 1H, H-5), 7.84 (d, *J* = 8.7 Hz, 1H, H-3), 7.81 (d, *J* = 8.7 Hz, 1H, H-4), 7.52 (ddd, *J* = 8.1, 6.8, 1.3 Hz, 1H, H-6), 7.47 (ddd, *J* = 8.2, 6.8, 1.4 Hz, 1H, H-7), 7.24–7.21 (m, 2H, H-11, H-13), 7.20 (dd, J_{trans} = 17.6 Hz, J_{cis} = 11.1 Hz, 1H, H-15), 6.85 (tt, *J* = 7.4, 1.1 Hz, 1H, H-12), 6.65–6.62 (m, 2H, H-10, H-14), 5.92 (dd, J_{trans} = 17.6 Hz, J_{gem} = 1.1 Hz, 1H, H-16), 5.59 (br s, 1H, N*H*), 5.41 (dd, J_{cis} = 11.1 Hz, J_{gem} = 1.1 Hz, 1H, H-16). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ (ppm) 147.2 (C-9), 134.2 (C-4a), 133.8 (C-1), 133.0 (C-15), 132.1 (C-2), 131.5 (C-8a), 129.2 (2C, C-11, C-13), 128.1 (C-5), 126.48 (C-4), 126.47 (C-7), 126.1 (C-6), 123.9 (C-8), 123.4 (C-3), 118.4 (C-12), 115.8 (C-16), 113.8 (2C, C-10, C-14). HRMS (APCI) *m/z* calculated for $C_{18}H_{16}N$ $[M+H]^+$: 246.1277. Found $[M+H]^+$: 246.1270.

General procedure for borylative cyclization with boron trichloride. The corresponding amine (1.0 equiv.) was dissolved in anhydrous toluene (0.05 M) in a Schlenk flask, and the resulting solution was cooled to –30 °C. Cold boron trichloride solution (1.0 M in hexanes; 2.0 equiv.) was added dropwise to the vigorously stirring cold solution of amine in toluene using a syringe. Upon conclusion of the addition, the reaction mixture was allowed to warm to room temperature over one hour, then heated at reflux for 18 hours. At the end of the reaction, the mixture was concentrated under reduced pressure to afford the corresponding B–Cl intermediate as an air- and moisture-sensitive solid, which was used in the next step without further purification.

3-Chloro-3,4-dihydro-4-aza-3-boraphenanthrene. Following the general procedure, amine **9a** (470 mg, 2.78 mmol) was dissolved in toluene (56 mL) followed by addition of boron trichloride solution (5.6 mL, 5.55 mmol) to give 3-chloro-3,4-dihydro-4-aza-3-boraphenanthrene (589 mg, 2.76 mmol, 99%) as a red solid. ^{1}H NMR (500 MHz,

$CDCl_3$) δ (ppm) 8.81 (br s, 1H, N*H*), 8.18 (d, *J* = 8.3 Hz, 1H, H-10), 8.15 (d, *J* = 11.6 Hz, 1H, H-4), 7.91 (d, *J* = 7.7 Hz, 1H, H-7), 7.65–7.62 (m, 1H, H-9), 7.62 (d, *J* = 8.8 Hz, 1H, H-5), 7.61–7.58 (m, 1H, H-8), 7.58 (d, *J* = 8.8 Hz, 1H, H-6), 6.89 (dd, *J* = 11.6, 1.9 Hz, 1H, H-3). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ (ppm) 148.0 (C-4), 135.7 (C-10b), 133.6 (C-6a), 128.9 (C-7), 127.2 (C-5), 127.1 (C-8), 127.0 (C-3*), 126.3 (C-9), 123.3 (C-10a), 121.9 (C-6), 120.7 (C-4a), 119.6 (C-10). *Carbon not observed in $^{13}C\{^1H\}$ NMR, assigned by gHSQC. $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$) δ (ppm) 32.70.

3-Chloro-4-phenyl-3,4-dihydro-4-aza-3-boraphenanthrene. Following the general procedure, amine **9b** (491 mg, 2.00 mmol) was dissolved in toluene (40 mL) followed by addition of boron trichloride solution (4.0 mL, 4.00 mmol) to give 3-chloro-4-phenyl-3,4-dihydro-4-aza-3-boraphenanthrene (573 mg, 1.98 mmol, 99%) as a pale-green solid. ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.14 (d, *J* = 11.5 Hz, 1H, H-4), 7.81 (dd, *J* = 8.0, 1.5 Hz, 1H, H-7), 7.65 (ap s, 2H, H-5, H-6), 7.49–7.42 (m, 3H, H-13, H-14, H-15), 7.35 (ddd, *J* = 8.0, 6.8, 1.0 Hz, 1H, H-8), 7.29–7.25 (m, 3H, H-10, H-12, H-16), 7.01 (d, *J* = 11.5 Hz, 1H, H-3), 6.99 (ddd, *J* = 9.0, 6.8, 1.5 Hz, 1H, H-9). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ (ppm) 148.1 (C-4), 146.0 (C-11), 138.7 (C-10b), 135.5 (C-6a), 129.3 (2C, C-13, C-15), 128.8 (2C, C-12, C-16), 128.6 (C-7), 128.5 (C-3*), 127.8 (C-5), 127.2 (C-14), 126.2 (C-10), 125.9 (C-8), 125.4 (C-10a), 124.4 (C-9), 124.0 (C-6), 123.9 (C-4a). *Carbon not observed in $^{13}C\{^1H\}$ NMR, assigned by gHSQC. $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$) δ (ppm) 34.41.

3,4-Dihydro-4-aza-3-boraphenanthrene (7a). In a Schlenk flask, 3-chloro-3,4-dihydro-4-aza-3-boraphenanthrene (589 mg, 2.76 mmol, 1.0 equiv.) was dissolved in anhydrous Et_2O (55 mL), and the resulting solution cooled to –30 °C. Cold lithium aluminum hydride solution (1.0 M in Et_2O; 5.5 mL, 5.52 mmol, 2.0 equiv.) was added dropwise using a syringe, and the reaction mixture was allowed to warm to room temperature and stirred for 18 hours. A hydrochloric acid solution (2.0 M in Et_2O; 3.0 mL, 6.07 mmol, 2.2 equiv.) was then added and the resulting mixture filtered through a silica gel plug. The filtrate was concentrated under reduced pressure to afford parental BN-phenanthrene **7a** (404 mg, 2.26 mmol, 81%) as a pale-red solid without further purification. M.p.: 78–80 °C. IR (KBr) $\tilde{\upsilon}_{max}$ (cm^{-1}) 3410 (NH), 2963, 2541, 2470 (BH), 1586, 1562, 1442, 1428, 1261, 1100, 884, 796, 771, 666. ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 9.28 (br s, 1H, N*H*), 8.27 (dd, *J* = 8.4, 1.2 Hz, 1H, H-10), 8.21 (dd, *J* = 11.3, 1.2 Hz, 1H, H-4), 7.93–7.91 (m, 1H, H-7), 7.67 (d, *J* = 8.6 Hz, 1H, H-5), 7.64 (ddd, *J* = 8.4, 6.9, 1.5 Hz, 1H, H-9), 7.59 (d, *J* = 8.6 Hz, 1H, H-6), 7.59 (ddd, *J* = 8.0, 6.9, 1.2 Hz, 1H, H-8), 7.16 (ddd, *J* = 11.3, 2.5, 1.7 Hz, 1H, H-3), 5.73–4.78 (br s, 1H, B*H*). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ (ppm) 145.7 (C-4), 135.9 (C-10b), 133.4 (C-6a), 130.9 (C-3*), 128.9 (C-7), 127.7 (C-5), 126.7 (C-8), 126.0 (C-9), 124.0 (C-10a), 121.8 (C-4a), 121.5 (C-6), 119.7 (C-10). *Carbon not observed in $^{13}C\{^1H\}$ NMR, assigned by gHSQC. $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$) δ (ppm) 31.95. HRMS (APCI) *m/z* calculated for $C_{12}H_{11}BN$ $[M+H]^+$: 180.0979. Found $[M+H]^+$: 180.0977.

General procedure for borylative cyclization with potassium organotrifluoroborates. An oven-dried Biotage microwave vial equipped with a stir bar was charged with the corresponding potassium organotrifluoroborate (1.0 equiv.). The vial was sealed with a cap lined with a disposable Teflon septum, evacuated under vacuum, and purged with argon three times. CMPE (0.5 M) and toluene (0.5 M) were then added, followed by the corresponding amine (1.2 equiv.), $SiCl_4$ (1.0 equiv.) and Et_3N (1.5 equiv.) under argon. The reaction mixture was stirred at 80 or 110 °C for 24 h, then at the end of the reaction, the mixture was cooled to room temperature, diluted with Et_2O and filtered through a silica gel plug. The filtrate was concentrated under reduced pressure and the remaining residue was purified by flash column chromatography (using the eluent indicated in each case) to afford the corresponding 3,4-dihydro-4-aza-3-boraphenanthrenes.

*3-Methyl-3,4-dihydro-4-aza-3-boraphenanthrene (**7b**).* Following the general procedure, potassium methyltrifluoroborate (122 mg, 1.00 mmol) was dissolved in CPME (2.0 mL) and toluene (2.0 mL), followed by addition of amine **9a** (203 mg, 1.20 mmol), $SiCl_4$ (116 μL, 1.00 mmol) and Et_3N (209 μL, 1.50 mmol). After heating at 80 °C, purification by flash column chromatography (5% EtOAc/Hexane) gave **7b** (154 mg, 0.80 mmol, 80%) as a white solid. M.p.: 84–86 °C. IR (KBr) $\tilde{\upsilon}_{max}$ (cm^{-1}) 3400 (NH), 3011, 2927, 1591, 1561, 1449, 1128, 883, 833, 794, 745, 679. ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.69 (br s, 1H, N*H*), 8.23 (d, *J* = 8.5 Hz, 1H, H-10), 8.08 (d, *J* = 11.3 Hz, 1H, H-4), 7.92–7.91 (m, 1H, H-7), 7.64 (d, *J* = 8.5 Hz, 1H, H-5), 7.61 (ddd, *J* = 8.5, 7.0, 1.7 Hz, 1H, H-9), 7.59–7.56 (m, 1H, H-8), 7.54 (d, *J* = 8.5 Hz, 1H, H-6), 6.98 (dd, *J* = 11.3, 1.8 Hz, 1H, H-3), 0.92 (s, 3H, H-11). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ (ppm) 144.8 (C-4), 135.9 (C-10b), 133.3 (C-6a), 131.0 (C-3*), 128.8 (C-7), 127.6 (C-5), 126.3 (C-8), 125.7 (C-9), 123.7 (C-10a), 120.7 (C-4a), 120.6 (C-6), 119.6 (C-10), 2.7 (C-11*). *Carbon not observed in $^{13}C\{^1H\}$ NMR, assigned by gHSQC. $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$) δ (ppm) 37.55. HRMS (APCI) *m/z* calculated for $C_{13}H_{13}BN$ $[M+H]^+$: 194.1136. Found $[M+H]^+$: 194.1130.

*3-Vinyl-3,4-dihydro-4-aza-3-boraphenanthrene (**7c**).* Following the general procedure, potassium vinyltrifluoroborate (56 mg, 0.40 mmol) was dissolved in CPME (0.8 mL) and toluene (0.8 mL), followed by addition of amine **9a** (81 mg, 0.48 mmol), $SiCl_4$ (46 μL, 0.40 mmol) and Et_3N (84 μL, 0.60 mmol). After heating at 80 °C, purification by flash column chromatography (5% EtOAc/Hexane) gave **7c** (53 mg, 0.26 mmol, 65%) as a white solid. M.p.: 92–94 °C. IR (KBr) $\tilde{\upsilon}_{max}$ (cm^{-1}) 3399 (NH), 3064, 2977, 1590, 1451, 1133, 1014, 944, 836, 754, 717, 643. ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.80 (br s, 1H, N*H*), 8.25 (d, *J* = 8.3 Hz, 1H, H-10), 8.16 (d, *J* = 11.4 Hz, 1H, H-4), 7.92–7.90 (m, 1H, H-7), 7.64 (d, *J* = 8.5 Hz, 1H, H-5), 7.62 (ddd, *J* = 8.3, 6.9, 1.5 Hz, 1H, H-9), 7.57 (ddd, *J* = 7.8, 6.9, 1.3 Hz, 1H, H-8), 7.55 (d, *J* = 8.5 Hz, 1H, H-6), 7.20 (dd, *J* = 11.4, 1.8 Hz, 1H, H-3), 6.64 (dd, J_{trans} = 19.6 Hz, J_{cis} = 13.3 Hz, 1H, H-11), 6.31 (dd, J_{trans} = 19.6 Hz, J_{gem} = 3.5 Hz, 1H, H-12), 6.10 (dd, J_{cis} = 13.3 Hz, J_{gem}

= 3.5 Hz, 1H, H-12). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ (ppm) 145.7 (C-4), 137.9 (C-11*), 135.7 (C-10b), 133.5 (C-6a), 132.0 (C-12), 128.9 (C-7), 128.0 (C-3*), 127.5 (C-5), 126.5 (C-8), 125.8 (C-9), 123.9 (C-10a), 121.5 (C-4a), 121.1 (C-6), 119.6 (C-10). *Carbon not observed in $^{13}C\{^1H\}$ NMR, assigned by gHSQC. $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$) δ (ppm) 32.62. HRMS (APCI) *m/z* calculated for $C_{14}H_{13}BN$ $[M+H]^+$: 206.1136. Found $[M+H]^+$: 206.1128.

*3-Phenyl-3,4-dihydro-4-aza-3-boraphenanthrene (**7d**).* Following the general procedure, potassium phenyltrifluoroborate (572 mg, 2.95 mmol) was dissolved in CPME (5.9 mL) and toluene (5.9 mL), followed by addition of amine **9a** (600 mg, 3.55 mmol), $SiCl_4$ (341 μL, 2.95 mmol) and Et_3N (617 μL, 4.43 mmol). After heating at 80 °C, purification by flash column chromatography (5% EtOAc/Hexane) gave **7d** (500 mg, 1.96 mmol, 66%) as a white solid. M.p.: 94–96 °C. IR (KBr) $\tilde{\upsilon}_{max}$ (cm^{-1}) 3415 (NH), 2917, 1591, 1560, 1446, 1428, 1225, 1149, 791. ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 9.21 (br s, 1H, N*H*), 8.34 (d, *J* = 8.3 Hz, 1H, H-10), 8.27 (d, *J* = 11.4 Hz, 1H, H-4), 8.03–8.01 (m, 2H, H-12, H-16), 7.95–7.93 (m, 1H, H-7), 7.70 (d, *J* = 8.7 Hz, 1H, H-5), 7.66 (ddd, *J* = 8.3, 6.9, 1.4 Hz, 1H, H-9), 7.60 (ddd, *J* = 8.0, 6.9, 1.2 Hz, 1H, H-8), 7.59 (d, *J* = 8.7 Hz, 1H, H-6), 7.56–7.48 (m, 3H, H-13, H-14, H-15), 7.42 (dd, *J* = 11.4, 1.9 Hz, 1H, H-3). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ (ppm) 146.3 (C-4), 138.4 (C-11**), 135.9 (C-10b), 133.6 (C-6a), 132.6 (2C, C-12, C-16), 129.6 (C-14), 129.0 (C-7), 128.7 (C-3*), 128.3 (2C, C-13, C-15), 127.5 (C-5), 126.6 (C-8), 126.0 (C-9), 124.0 (C-10a), 121.5 (C-4a), 121.3 (C-6), 119.5 (C-10). *Carbon not observed in $^{13}C\{^1H\}$ NMR, assigned by gHSQC. **Carbon not observed in $^{13}C\{^1H\}$ NMR, assigned by gHMBC. $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$) δ (ppm) 34.07. HRMS (APCI) *m/z* calculated for $C_{18}H_{15}BN$ $[M+H]^+$: 256.1292. Found $[M+H]^+$: 256.1284.

*3-Methyl-4-phenyl-3,4-dihydro-4-aza-3-boraphenanthrene (**7e**).* Following the general procedure, potassium methyltrifluoroborate (120 mg, 0.98 mmol) was dissolved in CPME (2.0 mL) and toluene (2.0 mL), followed by addition of amine **9b** (288 mg, 1.18 mmol), $SiCl_4$ (113 μL, 0.98 mmol) and Et_3N (205 μL, 1.47 mmol). After heating at 110 °C, purification by flash column chromatography (Hexane) gave **7e** (13 mg, 0.049 mmol, 5%) as a white solid. M.p.: 94–96 °C. IR (KBr) $\tilde{\upsilon}_{max}$ (cm^{-1}) 3004, 2924, 1588, 1489, 1428, 1330, 1308, 1228, 1133, 827, 732, 698, 689. ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.05 (d, *J* = 11.2 Hz, 1H, H-4), 7.78 (dd, *J* = 8.2, 1.5 Hz, 1H, H-7), 7.64 (d, *J* = 8.4 Hz, 1H, H-5), 7.57 (d, *J* = 8.4 Hz, 1H, H-6), 7.45–7.41 (m, 2H, H-13, H-15), 7.37 (tt, *J* = 7.4, 1.3 Hz, 1H, H-14), 7.32–7.30 (m, 1H, H-10), 7.30 (ddd, *J* = 8.2, 6.8, 0.9 Hz, 1H, H-8), 7.20–7.17 (m, 2H, H-12, H-16), 7.00 (d, *J* = 11.2 Hz, 1H, H-3), 6.94 (ddd, *J* = 8.5, 6.8, 1.5 Hz, 1H, H-9), 0.60 (s, 3H, H-17). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ (ppm) 148.4 (C-11), 145.3 (C-4), 138.6 (C-10b), 135.3 (C-6a), 131.3 (C-3*), 129.4 (2C, C-13, C-15), 128.5 (C-7), 128.3 (2C, C-12, C-16), 128.1 (C-5), 126.43 (C-14), 126.38 (C-8), 125.6 (C-10a), 125.3 (C-10), 123.9 (C-4a), 123.8 (C-9), 122.8 (C-6), 5.1 (C-17*). *Carbon not observed in $^{13}C\{^1H\}$ NMR, assigned by gHSQC. $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$) δ (ppm) 39.66. HRMS (APCI) *m/z* calculated for $C_{19}H_{17}BN$ $[M+H]^+$: 270.1449. Found $[M+H]^+$: 270.1439.

General procedure for the Grignard Reaction. In a Schlenk flask, 3-chloro-4-phenyl-3,4-dihydro-4-aza-3-boraphenanthrene (58 mg, 0.20 mmol, 1.0 equiv.) was dissolved in anhydrous THF (4.0 mL), and the resulting solution was cooled to –30 °C. The corresponding organomagnesium bromide solution (1.0 or 2.0 equiv.) was added dropwise using a syringe, then the reaction mixture was allowed to warm to room temperature and stirred for 18 hours. At the end of the reaction, the mixture was concentrated under reduced pressure and the remaining residue was purified by flash column chromatography (0–10% CH_2Cl_2/Hexane) to afford the corresponding 3-substituted-3,4-dihydro-4-aza-3-boraphenanthrenes.

*3-Methyl-4-phenyl-3,4-dihydro-4-aza-3-boraphenanthrene (**7e**).* Following the general procedure, 3-chloro-4-phenyl-3,4-dihydro-4-aza-3-boraphenanthrene (58 mg, 0.20 mmol) and methylmagnesium bromide solution (1.0 M in DBE; 400 μL, 0.40 mmol) gave **7e** (28 mg, 0.104 mmol, 52%) as a white solid.

*3,4-Diphenyl-3,4-dihydro-4-aza-3-boraphenanthrene (**7f**).* Following the general procedure, 3-chloro-4-phenyl-3,4-dihydro-4-aza-3-boraphenanthrene (58 mg, 0.20 mmol) and phenylmagnesium bromide solution (1.0 M in THF; 200 μL, 0.20 mmol) gave **7f** (51 mg, 0.154 mmol, 77%) as a white solid. M.p.: 181–183 °C. IR (KBr) $\tilde{\upsilon}_{max}$ (cm^{-1}) 3051, 2918, 1584, 1490, 1431, 1328, 1276, 1246, 831, 737. ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.21 (d, *J* = 11.2 Hz, 1H, H-4), 7.82–7.81 (m, 1H, H-7), 7.70 (d, *J* = 8.5 Hz, 1H, H-5), 7.65 (d, *J* = 8.5 Hz, 1H, H-6), 7.33 (ddd, *J* = 8.0, 6.8, 1.0 Hz, 1H, H-8), 7.32–7.29 (m, 1H, H-10), 7.26–7.22 (m, 3H, H-13, H-14, H-15), 7.17–7.12 (m, 4H, H-3, H-19, H-20, H-21), 7.08–7.06 (m, 2H, H-12, H-16), 7.05–7.03 (m, 2H, H-18, H-22), 6.94 (ddd, *J* = 8.9, 6.8, 1.5 Hz, 1H, H-9). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ (ppm) 147.2 (C-11), 146.2 (C-4), 142.3 (C-17**), 137.9 (C-10b), 135.6 (C-6a), 133.0 (2C, C-18, C-22), 132.7 (C-3*), 129.1 (2C, C-12, C-16), 129.0 (2C, C-13, C-15), 128.5 (C-7), 127.9 (C-5), 126.92 (2C, C-19, C-21), 126.87 (C-10), 126.8 (C-8), 126.5 (C-14), 125.6 (C-10a), 125.5 (C-20), 124.5 (C-4a), 123.8 (C-9), 123.6 (C-6). *Carbon not observed in $^{13}C\{^1H\}$ NMR, assigned by gHSQC. **Carbon not observed in $^{13}C\{^1H\}$ NMR, assigned by gHMBC. $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$) δ (ppm) 36.66. HRMS (EI) *m/z* calculated for $C_{24}H_{18}BN$ $[M]^+$: 331.1527. Found $[M]^+$: 331.1533.

*3,3,4-Triphenyl-4H-3,4-dihydro-4-aza-3-boraphenanthrene (**10**).* Following the general procedure, 3-chloro-4-phenyl-3,4-dihydro-4-aza-3-boraphenanthrene (58 mg, 0.20 mmol) and phenylmagnesium bromide solution (1.0 M in THF; 400 μL, 0.40 mmol) gave **7f** (3.0 mg, 0.009 mmol, 4%) and **10** (32 mg, 0.078 mmol, 39%) as a white solid. M.p.: 174–176 °C. IR (KBr) $\tilde{\upsilon}_{max}$ (cm^{-1}) 3045, 2998, 1495, 1431, 1371, 1274, 1190, 1149, 836, 732, 702. ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.81 (dd, *J* = 8.3, 0.7 Hz 1H, H-10), 7.78–7.76 (m, 1H, H-6, H-7), 7.54 (br s, 1H, N*H*), 7.52 (ddd, *J* = 8.3, 7.1, 1.0 Hz, 1H, H-9), 7.42–7.39 (m, 2H, H-5, H-8), 7.30–7.22 (m, 2H, H-18, H-18')†, 7.20 (d, *J* = 12.3 Hz, 1H, H-

3), 7.06 (d, *J* = 12.3 Hz, 1H, H-4), 7.06–6.96 (m, 8H, H-16, H-16', H-17, H-17')†, 6.96–6.95 (m, 3H, H-13, H-14), 6.83–6.79 (m, 2H, H-12). †Proton signal appears as a broad singlet probably due to restricted rotation of these phenyl rings. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ (ppm) 151.4 (2C, C-15**, C-15'**), 141.2 (C-11), 133.4 (C-6a), 133.0 (C-4a), 130.2 (C-3*), 129.9 (C-4), 129.3 (C-7), 129.2 (C-6), 128.8 (C-10b), 128.4 (2C, C-13), 128.0 (C-9), 127.5 (C-10a), 127.1 (C-5), 126.4 (C-14), 125.4 (C-8), 122.2 (2C, C-12), 118.8 (C-10). *Carbon not observed in $^{13}C\{^1H\}$ NMR, assigned by gHSQC. **Carbon not observed in $^{13}C\{^1H\}$ NMR, assigned by gHMBC. C-16, C-16', C-17, C-17', C-18 and C-18' are not observed in $^{13}C\{^1H\}$ NMR probably due to broadening of the signal caused by restricted rotation of these rings; no cross peaks were observed in the gHSQC or gHMBC spectra. $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$) δ (ppm) 1.44. HRMS (EI) *m/z* calculated for $C_{30}H_{24}BN$ $[M]^+$: 409.2002. Found $[M]^+$: 409.2016.

General procedure for the reaction with organolithium compounds. In a Schlenk flask, 3,4-dihydro-4-aza-3-boraphenanthrene **7a** (1.0 equiv.) was dissolved in anhydrous THF (0.1 M), and the resulting solution was cooled to −78 °C. At this temperature the solution was treated with the corresponding organolithium compound (2.0 equiv.). The reaction mixture was stirred at low temperature for 2 h, then cold hydrochloric acid (2.0 M in Et_2O; 2.0 equiv.) was slowly added to the reaction mixture at −78 °C. The mixture was allowed to stand at −78 °C for 1 h, then warmed to room temperature and allowed to stir for 12 hours. At the conclusion of the reaction, the mixture was quenched with saturated NH_4Cl solution, and the aqueous layer was extracted with Et_2O. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure. The remaining residue was purified by flash column chromatography (using the eluent indicated in each case) to afford the corresponding B-substituted products.

*3-Methyl-3,4-dihydro-4-aza-3-boraphenanthrene (**7b**).* Following the general procedure, compound **7a** (54 mg, 0.30 mmol) was dissolved in THF (3.0 mL). The solution was treated with methyllithium solution (1.6 M in Et_2O; 375 μL, 0.60 mmol) followed by addition of hydrochloric acid (300 μL, 0.60 mmol). Purification by flash column chromatography (5% EtOAc/Hexane) gave **7b** (53 mg, 0.27 mmol, 92%) as a white solid.

*3-Butyl-3,4-dihydro-4-aza-3-boraphenanthrene (**7g**).* Following the general procedure, compound **7a** (27 mg, 0.15 mmol) was dissolved in THF (1.5 mL). The solution was treated with *n*-butyllithium solution (1.6 M in hexanes; 188 μL, 0.30 mmol) followed by addition of hydrochloric acid (150 μL, 0.30 mmol). Purification by flash column chromatography (Hexane) gave **7g** (32 mg, 0.14 mmol, 91%) as a light-yellow oil. IR (NaCl) $\tilde{\upsilon}_{max}$ (cm^{-1}) 3411 (NH), 2955, 2923, 1592, 1559, 1447, 1329, 1123, 827, 736. ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.70 (br s, 1H, N*H*), 8.25 (d, *J* = 8.4 Hz, 1H, H-10), 8.07 (d, *J* = 11.4 Hz, 1H, H-4), 7.90 (dd, *J* = 8.0, 0.8 Hz, 1H, H-7), 7.62 (d, *J* = 8.5 Hz, 1H, H-5), 7.62–7.60 (m, 1H, H-9), 7.56 (ddd, *J* = 8.0, 6.9, 1.1 Hz, 1H, H-8), 7.52 (d, *J* = 8.5 Hz, 1H, H-6), 6.96 (dd, *J* = 11.4, 1.8 Hz, 1H, H-3), 1.70–1.64 (m, 2H, H-12), 1.49–1.41 (m, 2H, H-13), 1.39 (t, *J* = 8.0 Hz, 2H, H-11), 0.97 (t, *J* = 7.3 Hz, 3H, H-14). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ (ppm) 144.9 (C-4), 135.9 (C-10b), 133.4 (C-6a), 130.2 (C-3*), 128.9 (C-7), 127.6 (C-5), 126.4 (C-8), 125.8 (C-9), 123.8 (C-10a), 120.9 (C-4a), 120.7 (C-6), 119.6 (C-10), 28.4 (C-12), 25.8 (C-13), 18.8 (C-11*), 14.2 (C-14). *Carbon not observed in $^{13}C\{^1H\}$ NMR, assigned by gHSQC. $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$) δ (ppm) 38.19. HRMS (APCI) *m/z* calculated for $C_{16}H_{19}BN$ $[M+H]^+$: 236.1605. Found $[M+H]^+$: 236.1600.

General procedure for the bromination of 3,4-dihydro-4-aza-3-boraphenanthrenes. ***Method A:*** the corresponding 3,4-dihydro-4-aza-3-boraphenanthrene (1.0 equiv.) was loaded into a Schlenk flask under argon. Anhydrous CH_2Cl_2 (0.1 M) was then added, and the resulting solution was cooled to 0 °C. A recently prepared bromine solution (0.2 M in CH_2Cl_2; 1.1 equiv.) was added under argon at a rate of 1.1 mmol/h. After addition, the reaction mixture was slowly warmed to room temperature. The reaction was monitored by TLC and, when complete (usually after stirring at r.t. for 1 hour), the mixture was concentrated under reduced pressure. The remaining residue was purified by flash column chromatography (using the eluent indicated in each case) to provide the desired 2-bromo-3,4-dihydro-4-aza-3-boraphenanthrene. ***Method B:*** aluminum chloride (1.5 equiv.) and *N*-bromosuccinimide (1.5 equiv.) were loaded into a Schlenk flask under argon. Anhydrous CH_2Cl_2 (0.02 M) was added, and the resulting suspension was stirred at r.t. for 30 min. The mixture was then cooled to −35 °C and treated with a solution of the corresponding 3,4-dihydro-4-aza-3-boraphenanthrene (1.0 equiv.) in CH_2Cl_2. This reaction mixture was stirred at −35 °C for 2 h. After solvent removal, hexane was added, and the mixture was filtered to remove any solids. The filtrate was further concentrated under reduced pressure and the remaining residue purified by flash column chromatography (using the eluent indicated in each case) to provide the desired 2-bromo-3,4-dihydro-4-aza-3-boraphenanthrene.

*2-Bromo-3-hydroxy-3,4-dihydro-4-aza-3-boraphenanthrene (**11a**).* Following general procedure **A**, compound **7a** (18 mg, 0.10 mmol) was dissolved in CH_2Cl_2 (1.0 mL), followed by addition of bromine solution (550 μL, 0.11 mmol). Purification by flash column chromatography (20% EtOAc/Hexane) gave **11a** (10 mg, 0.037 mmol, 37%) as a white solid. M.p.: 248–250 °C. IR (KBr) $\tilde{\upsilon}_{max}$ (cm^{-1}) 3584 (OH), 3400 (NH), 2918, 1590, 1560, 1456, 895, 797, 735, 688. ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.24 (s, 1H, H-4), 8.07 (dd, *J* = 8.1, 1.5 Hz, 1H, H-10), 7.95 (br s, 1H, N*H*), 7.87–7.85 (m, 1H, H-7), 7.58 (ddd, *J* = 8.1, 6.9, 1.7 Hz, 1H, H-9), 7.56 (ddd, *J* = 7.7, 6.9, 1.5 Hz, 1H, H-8), 7.46 (ap s, 2H, H-5, H-6), 4.53 (s, 1H, O*H*). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ (ppm) 147.1 (C-4), 135.8 (C-10b), 133.6 (C-6a), 128.9 (C-7), 126.8 (C-8), 126.4 (C-5), 126.1 (C-9), 123.4 (C-10a), 120.7 (C-6), 120.3 (C-3**), 119.7 (C-10), 118.4 (C-4a). **Carbon not observed in $^{13}C\{^1H\}$ NMR, assigned by gHMBC. $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$) δ (ppm) 27.31.

HRMS (APCI) *m/z* calculated for $C_{12}H_{10}BBrNO$ $[M+H]^+$: 274.0033. Found $[M+H]^+$: 274.0030.

*2-Bromo-3-methyl-3,4-dihydro-4-aza-3-boraphenanthrene (**11b**).* Following general procedure **A**, compound **7b** (19 mg, 0.10 mmol) was dissolved in CH_2Cl_2 (1.0 mL), followed by addition of bromine solution (550 μL, 0.11 mmol). Purification by flash column chromatography (2% EtOAc/Hexane) gave **11b** (27 mg, 0.099 mmol, 99%) as a white solid. M.p.: 108–110 °C. IR (KBr) $\tilde{\upsilon}_{max}$ (cm^{-1}) 3400 (NH), 2917, 1588, 1558, 1454, 1426, 1144, 1009, 911, 797, 737, 688. ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.71 (br s, 1H, N*H*), 8.31 (s, 1H, H-4), 8.20 (d, *J* = 8.3 Hz, 1H, H-10), 7.89 (dd, *J* = 7.9, 1.6 Hz, 1H, H-7), 7.62 (ddd, *J* = 8.3, 6.9, 1.6 Hz, 1H, H-9), 7.58 (ddd, *J* = 7.9, 6.9, 1.2 Hz, 1H, H-8), 7.53 (d, *J* = 8.7 Hz, 1H, H-6), 7.51 (d, *J* = 8.7 Hz, 1H, H-5), 0.96 (s, 3H, H-11). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ (ppm) 145.1 (C-4), 135.1 (C-10b), 133.3 (C-6a), 130.3 (C-3**), 129.0 (C-7), 126.8 (C-8), 126.5 (C-5), 126.2 (C-9), 123.5 (C-10a), 121.7 (C-6), 120.8 (C-4a), 119.5 (C-10), 2.6 (C-11*). *Carbon not observed in $^{13}C\{^1H\}$ NMR, assigned by gHSQC. **Carbon not observed in $^{13}C\{^1H\}$ NMR, assigned by gHMBC. $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$) δ (ppm) 37.16. HRMS (EI) *m/z* calculated for $C_{13}H_{11}BBrN$ $[M]^+$: 271.0162. Found $[M]^+$: 271.0172.

*2-Bromo-3-phenyl-3,4-dihydro-4-aza-3-boraphenanthrene (**11c**).* Following general procedure **A**, compound **7d** (255 mg, 1.00 mmol) was dissolved in CH_2Cl_2 (10 mL), followed by addition of bromine solution (5.5 mL, 1.10 mmol). Purification by flash column chromatography (5% EtOAc/Hexane) gave **11c** (315 mg, 0.94 mmol, 94%) as a white solid. M.p.: 93–95 °C. IR (KBr) $\tilde{\upsilon}_{max}$ (cm^{-1}) 3402 (NH), 3049, 1586, 1558, 1425, 1409, 1226, 1022, 847, 805, 739, 701. ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 9.04 (br s, 1H, N*H*), 8.55 (s, 1H, H-4), 8.24–8.22 (m, 1H, H-10), 7.99–7.98 (m, 2H, H-12, H-16), 7.93–7.91 (m, 1H, H-7), 7.64 (ddd, *J* = 8.1, 6.9, 1.6 Hz, 1H, H-9), 7.63–7.60 (m, 1H, H-8), 7.60 (ap s, 2H, H-5, H-6), 7.54–7.49 (m, 3H, H-13, H-14, H-15). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ (ppm) 147.6 (C-4), 138.1 (C-11**), 135.3 (C-10b), 133.5 (C-6a), 133.3 (2C, C-12, C-16), 129.4 (C-14), 129.1 (C-7), 128.0 (2C, C-13, C-15), 127.8 (C-3**), 127.1 (C-8), 126.5 (C-9), 126.4 (C-5), 123.6 (C-10a), 122.4 (C-6), 121.2 (C-4a), 119.5 (C-10). **Carbon not observed in $^{13}C\{^1H\}$ NMR, assigned by gHMBC. $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$) δ (ppm) 33.60. HRMS (EI) *m/z* calculated for $C_{18}H_{13}BBrN$ $[M]^+$: 333.0319. Found $[M]^+$: 333.0329.

*2-Bromo-3-methyl-4-phenyl-3,4-dihydro-4-aza-3-boraphenanthrene (**11d**).* Following general procedure **B**, $AlCl_3$ (20 mg, 0.15 mmol) and NBS (27 mg, 0.15 mmol) were dissolved in CH_2Cl_2 (5 mL). The resulting suspension was treated with a solution of compound **7e** (27 mg, 0.10 mmol) in CH_2Cl_2 (2 mL). Purification by flash column chromatography (Hexane) gave **11d** (26 mg, 0.075 mmol, 75%) as a white solid. M.p.: 134–136 °C. IR (KBr) $\tilde{\upsilon}_{max}$ (cm^{-1}) 3053, 2919, 1582, 1489, 1401, 1328, 1231, 916, 747, 691. ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.36 (s, 1H, H-4), 7.77 (dd, *J* = 8.1, 1.5 Hz, 1H, H-7), 7.58 (d, *J* = 8.5 Hz, 1H, H-6), 7.54 (d, *J* = 8.5 Hz, 1H, H-5), 7.46–7.42 (m, 2H, H-13, H-15), 7.40 (tt, *J* = 7.3, 1.2 Hz, 1H, H-14), 7.32 (ddd, *J* = 8.1, 6.9, 0.7 Hz, 1H, H-8), 7.20 (d, *J* = 8.7 Hz, 1H, H-10), 7.18–7.15 (m, 2H, H-12, H-16), 6.93 (ddd, *J* = 8.7, 6.9, 1.5 Hz, 1H, H-9), 0.72 (s, 3H, H-17). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ (ppm) 148.2 (C-11), 145.9 (C-4), 137.9 (C-10b), 135.3 (C-6a), 130.5 (C-3**), 129.6 (2C, C-13, C-15), 128.7 (C-7), 128.3 (2C, C-12, C-16), 127.2 (C-5), 127.0 (C-14), 126.1 (C-10), 125.7 (C-8), 125.4 (C-10a), 124.3 (C-9), 123.8 (C-6), 123.3 (C-4a), 4.9 (C-17*). *Carbon not observed in $^{13}C\{^1H\}$ NMR, assigned by gHSQC. **Carbon not observed in $^{13}C\{^1H\}$ NMR, assigned by gHMBC. $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$) δ (ppm) 39.44. HRMS (EI) *m/z* calculated for $C_{19}H_{15}BBrN$ $[M]^+$: 347.0475. Found $[M]^+$: 347.0471.

General procedure for the Suzuki reaction. In an oven-dried Biotage microwave vial equipped with a stir bar, the corresponding aryl bromide (0.15 mmol, 1.0 equiv.) and phenylboronic acid (27 mg, 0.21 mmol, 1.4 equiv.) were dissolved in toluene (0.6 mL) and methanol (0.2 mL). The resulting solution was treated with a suspension of sodium carbonate (375 mg) in distilled water (1.5 mL) before addition of $Pd(PPh_3)_4$ (8.8 mg, 0.0075 mmol, 5.0 mol%). The vial was sealed with a cap lined with a disposable Teflon septum and the reaction mixture stirred at 70 °C for 12 hours. At the end of the reaction, the mixture was quenched with saturated NaCl solution (5 mL) and the aqueous layer extracted with EtOAc (3 x 5 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure. The remaining residue was purified by flash column chromatography (2–5% EtOAc/Hexane) to afford the corresponding coupled products.

*3-Methyl-2-phenyl-3,4-dihydro-4-aza-3-boraphenanthrene (**12a**).* Following the general procedure, aryl bromide **11b** (41 mg, 0.15 mmol) gave **12a** (25 mg, 0.093 mmol, 62%) as a white solid. M.p.: 126–128 °C. IR (KBr) $\tilde{\upsilon}_{max}$ (cm^{-1}) 3414 (NH), 2930, 1590, 1564, 1452, 1418, 1308, 1205, 1121, 807, 730, 703. ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.80 (br s, 1H, N*H*), 8.27 (d, *J* = 8.3 Hz, 1H, H-10), 8.01 (s, 1H, H-4), 7.91 (d, *J* = 8.0 Hz, 1H, H-7), 7.67 (d, *J* = 8.5 Hz, 1H, H-5), 7.65–7.62 (m, 1H, H-9), 7.59–7.55 (m, 2H, H-6, H-8), 7.50–7.48 (m, 2H, H-13, H-17), 7.45–7.42 (m, 2H, H-14, H-16), 7.32–7.29 (m, 1H, H-15), 0.97 (s, 3H, H-11). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ (ppm) 144.8 (C-12), 144.1 (C-3**), 142.3 (C-4), 135.3 (C-10b), 133.4 (C-6a), 128.9 (C-7), 128.24 (2C, C-14, C-16), 128.23 (2C, C-13, C-17), 127.7 (C-5), 126.4 (C-8), 126.0 (C-15), 125.9 (C-9), 123.5 (C-10a), 121.1 (C-6), 120.8 (C-4a), 119.7 (C-10), 2.9 (C-11*). *Carbon not observed in $^{13}C\{^1H\}$ NMR, assigned by gHSQC. **Carbon not observed in $^{13}C\{^1H\}$ NMR, assigned by gHMBC. $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$) δ (ppm) 38.03. HRMS (EI) *m/z* calculated for $C_{19}H_{16}BN$ $[M]^+$: 269.1370. Found $[M]^+$: 269.1376.

*2,3-Diphenyl-3,4-dihydro-4-aza-3-boraphenanthrene (**12b**).* Following the general procedure, aryl bromide **11c** (50 mg, 0.15 mmol) gave **12b** (37 mg, 0.11 mmol, 75%) as a white solid. M.p.: 172–174 °C. IR (KBr) $\tilde{\upsilon}_{max}$ (cm^{-1}) 3408 (NH), 3051, 3021, 1585, 1563, 1443, 1417, 809, 738, 700. ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 9.08 (br s, 1H, N*H*), 8.29 (d, *J* = 8.2 Hz, 1H, H-10), 8.18 (s, 1H, H-4), 7.94 (d, *J* = 7.9 Hz, 1H,

H-7), 7.74 (d, *J* = 8.6 Hz, 1H, H-5), 7.66–7.63 (m, 1H, H-9), 7.62 (d, *J* = 8.6 Hz, 1H, H-6), 7.61–7.58 (m, 1H, H-8), 7.58 (dd, *J* = 7.8, 1.8 Hz, 2H, H-12, H-16), 7.40–7.35 (m, 5H, H-13, H-14, H-15, H-18, H-22), 7.33–7.30 (m, 2H, H-19, H-21), 7.28–7.24 (m, 1H, H-20). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ (ppm) 144.4 (C-4), 144.1 (C-17), 143.2 (C-3**), 140.2 (C-11**), 135.4 (C-10b), 133.5 (C-6a), 133.3 (2C, C-12, C-16), 129.0 (C-7), 128.8 (2C, C-18, C-22), 128.6 (C-14), 128.1 (2C, C-19, C-21), 127.9 (2C, C-13, C-15), 127.6 (C-5), 126.7 (C-8), 126.13 (C-20), 126.08 (C-9), 123.7 (C-10a), 121.8 (C-6), 121.3 (C-4a), 119.7 (C-10). **Carbon not observed in $^{13}C\{^1H\}$ NMR, assigned by gHMBC. $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$) δ (ppm) 35.05. HRMS (EI) *m/z* calculated for $C_{24}H_{18}BN$ $[M]^+$: 331.1527. Found $[M]^+$: 331.1517.

3-Phenyl-2-(phenylethynyl)-3,4-dihydro-4-aza-3-boraphenanthrene (13). An oven-dried Biotage microwave vial equipped with a stir bar was charged with $PdCl_2(PPh_3)_2$ (5.3 mg, 0.0075 mmol, 5.0 mol%), CuI (1.4 mg, 0.0075 mmol, 5.0 mol%) and aryl bromide **11c** (50 mg, 0.15 mmol, 1.0 equiv.). The vial was sealed with a cap lined with a disposable Teflon septum, evacuated under vacuum, and purged with argon three times. Anhydrous DMF (1.5 mL) was added, followed by phenylacetylene (50 μL, 0.45 mmol, 3.0 equiv.) and Et_3N (63 μL, 0.45 mmol, 3.0 equiv.) under argon. The reaction mixture was then stirred at 80 ºC for 24 h. At the end of the reaction, the mixture was quenched with saturated NaCl solution (10 mL) and the aqueous layer extracted with EtOAc (3 x 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure. The remaining residue was purified by flash column chromatography (20% CH_2Cl_2/Hexane) to afford **13** (25 mg, 0.070 mmol, 47%) as a brown solid. M.p.: 131–133 ºC. IR (KBr) $\tilde{\upsilon}_{max}$ (cm^{-1}) 3408 (NH), 2914, 2850, 2185 (C≡C), 1559, 1488, 1418, 1222, 803, 755, 703, 671. ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 9.20 (br s, 1H, N*H*), 8.48 (s, 1H, H-4), 8.29 (d, *J* = 8.3 Hz, 1H, H-10), 8.24–8.22 (m, 2H, H-12, H-16), 7.93 (d, *J* = 7.9 Hz, 1H, H-7), 7.68–7.65 (m, 2H, H-5, H-9), 7.63–7.60 (m, 2H, H-6, H-8), 7.57–7.54 (m, 2H, H-13, H-15), 7.53–7.50 (m, 3H, H-14, H-20, H-24), 7.35–7.32 (m, 2H, H-21, H-23), 7.31–7.27 (m, 1H, H-22). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ (ppm) 149.6 (C-4), 138.3 (C-11**), 135.9 (C-10b), 133.9 (C-6a), 133.4 (2C, C-12, C-16), 131.4 (2C, C-20, C-24), 129.5 (C-14), 129.1 (C-7), 128.3 (2C, C-21, C-23), 128.1 (2C, C-13, C-15), 127.7 (C-22), 127.2 (C-5), 127.1 (C-8), 126.4 (C-9), 124.4 (C-19), 123.7 (C-10a), 122.4 (C-3**), 122.1 (C-6), 120.9 (C-4a), 119.8 (C-10), 94.5 (C-18), 93.2 (C-17). **Carbon not observed in $^{13}C\{^1H\}$ NMR, assigned by gHMBC. $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$) δ (ppm) 34.53. HRMS (EI) *m/z* calculated for $C_{26}H_{18}BN$ $[M]^+$: 355.1527. Found $[M]^+$: 355.1537.

Computational details. The ground state minima of **6** and **7a** were computed at the DFT level of theory and the vertical transitions at the TD-DFT level of theory. The solvent (cyclohexane) effect was taken into account using the polarizable continuum model (PCM).[26] CAM-B3LYP[27] and B3LYP[28] functionals were tested using the 6-31+G** basis set. The excitation and emission energies calculated using the B3LYP functional are closer to the experimental values.

The computational photochemical study was performed using the Multi-State Complete Active Space Perturbation to Second Order with a Complete Active Space Self Consistent Field reference wavefunction (MS-CASPT2//SA-CASSCF) methodology.[29] In this case, the State Averaged-Complete Active Space Self Consistent Field (SA-CASSCF) method was used to compute the critical points along the potential energy surface. For both **6** and **7a**, the active space chosen includes the complete set of π and π* orbitals and the nitrogen atom lone pair (14 electrons in 13 orbitals). The minima in S_1 were calculated from the Franck–Condon structure by using the steepest descent algorithm. The electronic states crossings were optimized at the CASSCF level and the two non-adiabatic coupling vectors defining the branching plane (gradient difference and derivative coupling) were computed. The dynamic correlation for the critical points was included at the MS-CASPT2 level of theory. CASSCF calculations were performed using the Gaussian 16 software[30] while MOLCAS 8.2 was used to calculate the CASPT2 single point energy corrections.[31] Both CASSCF and CASPT2 calculations were performed with the ANO-L-VDZ basis set.

ASSOCIATED CONTENT

Supporting Information

Computational data, X-ray crystallographic data for **10** and **11d**, 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.

AUTHOR INFORMATION

Corresponding Author

* david.sucunza@uah.es; juanjose.vaquero@uah.es

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