Dihydroaromatic Boronic Esters as Building Blocks for the Synthesis of Phenanthrenes and Phenanthridines

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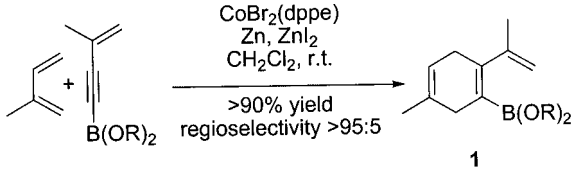
Alkenyl-substituted dihydroaromatic boronic esters, generated by neutral cobalt(I)-catalysed Diels–Alder reactions, reacted under palladium catalysis conditions with diiodobenzene, bromoiodobenzene and iodoaniline derivatives for the synthesis of regioselectively substituted phenanthrene and phenanthridine derivatives.

Introduction

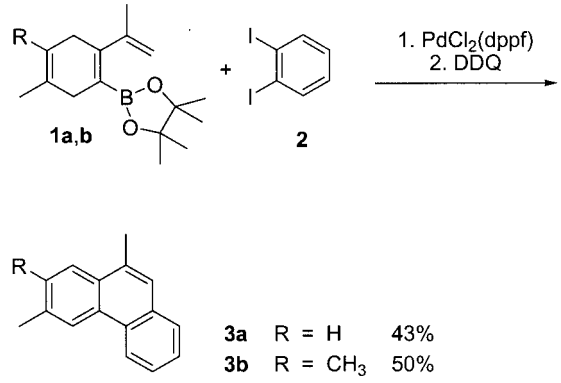
An increasing number of reports describe the use of boronic esters and their derivatives as nontoxic and easily handled building blocks in organic synthesis.[1,2b] Subsequent transition metal-catalysed reactions, such as the Suzuki coupling reaction, generate a wide variety of products in good yields and with defined regiochemistry.[2] We have reported the successful application of alkynyl boronic esters as dienophiles in the cobalt(I)-catalysed Diels–Alder reaction for the synthesis of dihydroaromatic boronic esters of type **1** (Scheme 1). These compounds can be used in Suzuki coupling reactions for the synthesis of a wide variety of biaryl, styrene and phenylacetylene derivatives and tricyclic products.[3] Accordingly, diversity oriented synthetic approaches[4] for the synthesis of structurally more complex products from simple starting materials can be envisaged. By this strategy, the generation of regioselectively substituted biaryl, phenanthrene and phenanthridine derivatives,[5] which are substructures in biologically active compounds,[6] seems possible.



Scheme 1.

Results and Discussion

We envisioned that the synthesis of other aromatic compounds such as phenanthrenes and phenanthridines should also be possible through the use of dihydroaromatic boronic ester **1** as starting material, so **1** was treated with *ortho*-dihaloarenes under palladium(0) catalysis conditions. Accordingly, the dihydroaromatic pinacol boronic esters **1a** and **1b** (Scheme 2) and 1,2-diiodobenzene (**2**) were used in a domino Suzuki coupling/Heck reaction sequence with subsequent DDQ oxidation. This procedure gave rise to the desired compounds **3a** and **3b** in acceptable nonoptimised yields, thus verifying our approach in principle.



Scheme 2. Reaction conditions: 1) $PdCl_2(dppf)$ 10 mol%, THF, aq. NaOH, 12 h, room temp. → 60 °C. 2) DDQ 1.2 equiv., toluene, room temp., 0.5 h.

Surprisingly, under identical reaction conditions, the corresponding aromatic boronic ester **4** gave a 2:1 adduct (isolated in 84% yield), the NMR spectroscopic data of which suggest the formation of compound **5** (Scheme 3). Product **5** is presumably formed by the expected Suzuki reaction between **4** and **2** and the insertion of the double bond as expected in the Heck reaction. The β-hydride elimination necessary for the completion of the Heck reaction of a palladium–phenanthrene species seems to be slower than a second Suzuki reaction of a palladium–fluorene species.[7] Therefore, another molecule of **4** is incorporated and compound **5** is obtained.[8]

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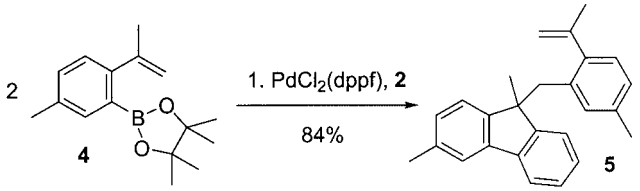
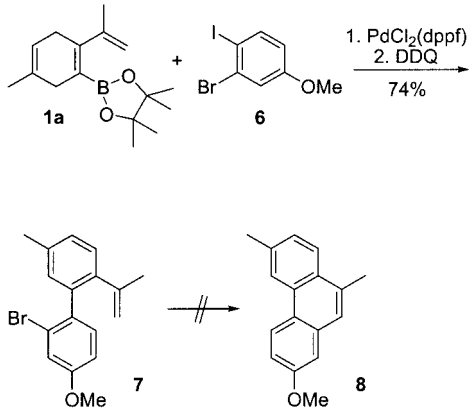


Scheme 3. Reaction conditions: $PdCl_2(dppf)$ 10 mol%, THF, aq. NaOH, 12 h, room temp. → 60 °C.

The use of the less reactive dihydroaromatic boronic ester **1a** is advantageous, since the Suzuki coupling reaction is slower and allows the β-hydride elimination of the Heck intermediate, thus significantly reducing the amount of the 2:1 adduct **5**.

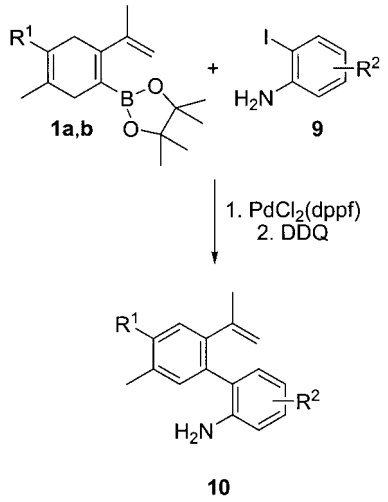
A general problem in this synthetic approach to substituted phenanthrene derivatives is that substituted *ortho*-diiodobenzene derivatives are relatively unstable, not commercially available and quite tedious to synthesise. Besides these disadvantages, regioselective coupling reactions with substituted diiodobenzene derivatives such as 1,2-diiodo-4-methylbenzene seem to be nontrivial to achieve. We therefore focused our attention on the use of 1-bromo-2-iodobenzene derivative **6**, which should allow chemoselective carbon-carbon bond formations in a domino process. Suzuki coupling with the more reactive iodo functionality of **6** should generate **7**, and subsequent Heck-type carbon-carbon bond formation with the less reactive bromo functionality should yield the desired tricyclic compound **8** (Scheme 4).



Scheme 4. Reaction conditions: 1) $PdCl_2(dppf)$ 10 mol%, THF, aq. NaOH, 12 h, room temp. → 60 °C. 2) DDQ 1.2 equiv., toluene, room temp., 0.5 h.

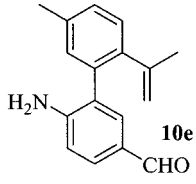
While the Suzuki reaction to provide **7** with the Pd(dppf) catalyst proceeded in good yield,[7] however, the desired Heck cyclisation to afford the phenanthrene derivative **8** unfortunately could not be achieved. Several Pd^0 catalysts[9] tested under standard conditions described in the literature or even under harsher reaction conditions yielded only traces of the desired phenanthrene derivative. GCMS analysis shows the reduced product formed by hydrodebromination (Br → H in **7**) as main product in these cases.

To circumvent this limitation, we now focused our attention on an alternative reaction pathway involving iodoaniline derivatives. Better molecular diversity should be obtainable in this approach if the intermediate biarylamine derivatives **10** are used as a synthetic platform. Compounds **10** can be used as a precursors for the synthesis either of phenanthrene derivatives (by diazotisation) or of phenanthridines (by hydroamination). The synthesis of phenanthrenes involves iodoanilines (**9** in Scheme 5), which can easily be synthesised from the corresponding anilines.[10] The palladium-catalysed coupling reaction proceeds without any difficulty to deliver the desired biphenylamine products **10**,



Scheme 5. Reaction conditions: 1) $PdCl_2(dppf)$ 10 mol%, THF, aq. NaOH, 12 h, room temp. → 60 °C. 2) DDQ 1.2 equiv., toluene, room temp., 0.5 h.

Table 1. Suzuki coupling reaction of dihydroaromatic boronic esters with iodoaniline derivatives.

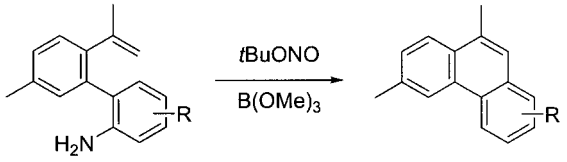
No.	R^1	R^2 (**9**)	Product (**10**)	Yield
1	H	H	**10a**	66%
2	CH_3	H	**10b**	72%
3	H	5-F	**10c**	67%
4	H	4-CO_2Me	**10d**	51%
5	H	4-CH_3	 **10e**	24%[a]
6	H	5-CH_3	**10f**	74%

[a] Besides **10e**, about 20% of the originally desired dehydrated product 2-(2-isopropenyl-5-methylphenyl)-4-methylaniline were also found. This latter product, however, could not be obtained in analytically pure form.

which can be isolated in good yields after DDQ oxidation (Table 1).

The oxidation of the *para*-toluidine derivative (Table 1; No. 5) afforded the oxidised product in a single synthetic step. Besides the desired dehydrogenation of the dihydroaromatic ring, the methyl group in a *para* relationship to the amine was also oxidised to provide the corresponding aldehyde functionality, while the other methyl groups present in the molecule were untouched.[11]

Intermediates **10** can be converted into the initially desired phenanthrene derivatives **11** by diazotisation with nitrite esters and prolonged heating (3–5 d) in the presence of borate esters (Scheme 6, Table 2).[12]



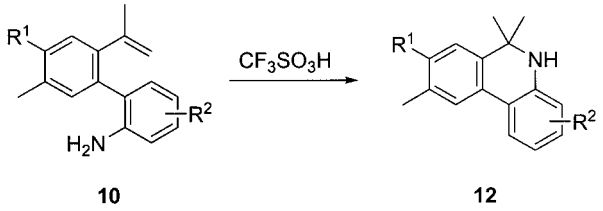
Scheme 6. Reaction conditions: *t*BuONO 2.0 equiv., $B(OMe)_3$ 2.0 equiv., toluene, 150 °C, sealed tube, 3–5 d.

Table 2. Synthesis of phenanthrenes by diazotisation of vinyl-substituted biarylamine compounds.

No.	R in biphenylamine (**10**)	Product	Yield
1	H	**11a**	85%
2	5-F	**11b**	71%
3	4-CO_2Me	**11c**	69%

Use of BF_3·Et_2O as a stronger Lewis acid resulted in the formation of a fluorinated biaryl side product by a Schiemann-type reaction.[13]

The synthetic value of the intermediates of type **10** is exemplified by the use of the aniline derivatives in an intramolecular hydroamination reaction for the synthesis of regioselectively substituted phenanthridine derivatives of type **12**. This interconversion can easily be accomplished by an acid-catalysed intramolecular hydroamination of the olefinic double bond (Scheme 7, Table 3).[14]



Scheme 7. Reaction conditions: 0.2 equiv. CF_3SO_3H, toluene, 12 h, 100 °C.

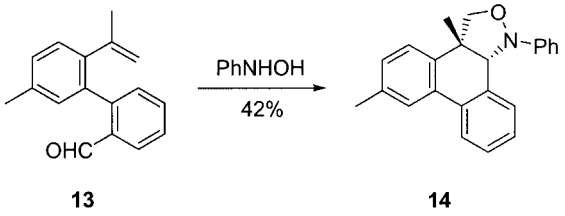
In a control experiment, aniline and α-methylstyrene were allowed to react under identical reaction conditions, only trace amounts of the desired hydroamination product being obtained in this case. However, the corresponding intramolecular reaction produced the phenanthridine derivatives in acceptable to good yields.

Table 3. Intramolecular hydroamination for the synthesis of phenanthridines.

No.	R^1, R^2 in biphenylamine (10)	Product	Yield
1	R^1 = CH_3 R^2 = H	**12a**	72%
2	R^1 = H R^2 = 5-F	**12b**	96%
3	R^1 = H R^2 = 5-CH_3	**12c**	44%

In addition to the described synthetic approaches to tricyclic phenanthrene derivatives, we also envisioned dihydroaromatic boronic ester **1** as a starting point for another short synthesis of polycyclic compounds.

Treatment of **1** with 2-iodobenzaldehyde and subsequent DDQ oxidation provided the biphenyl aldehyde **13** (Scheme 8). Transformation of **13** into the corresponding nitrone with phenyl hydroxylamine set the stage for an intramolecular 1,3-dipolar cycloaddition (Huisgen reaction). The nitrone was not isolated but cyclised directly under the reaction conditions to afford the desired tetracyclic derivative **14**.[15]



Scheme 8. Reaction conditions: PhNHOH 3.0 equiv., Et_2O, 48 h, room temp.

Conclusions

In summary, we have shown that dihydroaromatic alkenyl-substituted boronic esters of type **1** can serve as a platform for the synthesis of various classes of polycyclic compounds. The broadest synthetic use was achieved with easily prepared iodoaniline derivatives, which could be used as building blocks for the synthesis of a variety of substituted phenanthrene and phenanthridine derivatives in short reaction sequences.

Experimental Section

General Information: ^{1}H NMR, ^{13}C NMR and ^{19}F NMR: Bruker ARX 200, ARX 300 or ARX 400 spectrometers. Chemical shifts for ^{1}H NMR and ^{13}C NMR are reported in ppm relative to tetramethylsilane (TMS, δ = 0.0 ppm) or residual deuterated solvents as internal standard. Chemical shifts for ^{19}F NMR are reported in ppm relative to BF_3·OEt_2 as external standard. GC/MS spectra were recorded on an Agilent 6890 GC system with an Agilent 5973 Mass Selective Detector. Low resolution and high resolution mass spectra were recorded on a Varian MAT CH7a, a Finnigan MAT 95S, a Micromass VG 7070 or a Micromass VG AutoSpec spectrometer. Thin layer chromatography was performed on pre-

coated sheets obtained from Merck (60, F_{254}). IR spectra were recorded on a Bruker IFS Interferometer as KBr pellets. Column chromatography was performed on Merck silica grade 60 (40–63 μm, 230–400 mesh). Commercially available chemicals were used as purchased. Solvents were freshly distilled from drying agents prior to use.

General Procedure for the Cobalt(I)-Catalysed Diels–Alder Reaction (GP A): The alkynyl boronate (1.0 equiv.) and the diene (1.0–2.0 equiv.) were added under argon to a suspension of zinc iodide (30 mol%), zinc powder (30 mol%) and $CoBr_2$(dppe) (10 mol%) in anhydrous dichloromethane (2.0–12.0 mL) and the mixture was stirred for 3 h at room temperature. The solvent was removed under vacuum, pentane was added, and the mixture was filtered through a plug of silica. The filtrate was collected and freed from solvent under vacuum. The crude product was purified by silica gel chromatography (eluent: MTBE/pentane).

General Procedure for the Palladium(0)-Catalysed Suzuki Cross-Coupling Reaction (GP B): An oxygen-free solution of tetrahydrofuran (4.0–20.0 mL) and aqueous NaOH (10%, 1.6–8.0 mL) was prepared and the dihydroaromatic boronic ester and the iodoarene were added, together with $PdCl_2$(dppf) (10 mol%). The resulting mixture was stirred overnight. Diethyl ether was added, and the organic phase was separated. The aqueous phase was extracted twice with diethyl ether. The organic phases were combined and dried over anhydrous $MgSO_4$, and the solvent was removed under vacuum. The crude product was purified by silica gel chromatography (eluent: MTBE/pentane).

General Procedure for the Synthesis of Phenanthrene Derivatives by Diazotisation (GP C): The biarylamine (1.0 equiv.), *tert*-butyl nitrite (1.5–2.0 equiv.) and trimethylborate (2.0 equiv.) were heated in toluene (2.5–3.0 mL) in a pressure-stable Pyrex tube at 100–150 °C for 3–5 d. The solvent was removed under vacuum and the crude product was purified by silica gel chromatography (eluent: MTBE/pentane).

2-(2-Isopropenyl-5-methyl-1,4-cyclohexadien-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1a): This compound was prepared as described in GP A; 4,4,5,5-tetramethyl-2-(3-methylbut-3-en-1-ynyl)[1,3,2]dioxoborolane (2.00 g, 10.4 mmol), isoprene (1.3 mL, 13 mmol, 1.3 equiv.), $CoBr_2$(dppe) (617 mg, 1.0 mmol, 10 mol%), zinc powder (195 mg, 3.0 mmol, 30 mol%) and zinc iodide (957 mg, 3.0 mmol, 30 mol%) in CH_2Cl_2 (12.0 mL) were stirred for 3 h at room temperature. Purification by FC (MTBE/pentane, 1:99, R_f = 0.41) afforded **1a** (2.10 g, 79%) as a colourless liquid. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.23 (s, 12 H, 4×CH_3), 1.65 (s, 3 H, CH_3), 1.85 (s, 3 H, CH_3), 2.58–2.77 (m, 4 H, 2×CH_2), 4.71–4.76 (m, 2 H, CH_2), 5.36–5.39 (m, 1 H, CH) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.7, 22.9, 24.6 (4 C), 30.7, 33.7, 82.9, 111.9, 117.8, 131.0, 147.9, 148.8 ppm. The carbon atom beside the boron atom is not resolved. MS (EI, 70 eV): *m*/*z* (%) = 260 (25) [*M*]$^+$, 245 (10), 159 (29), 145 (42), 132 (100), 117 (25), 101 (16), 84 (58). HRMS: calcd. for $C_{16}H_{25}BO_2$: 260.1948; found 260.1939.

2-(2-Isopropenyl-4,5-dimethyl-1,4-cyclohexadien-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1b): This compound was prepared as described in GP A; 4,4,5,5-tetramethyl-2-(3-methylbut-3-en-1-ynyl)-1,3,2-dioxoborolane (1.00 g, 5.2 mmol), 2,3-dimethyl-1,3-butadiene (425 mg, 5.2 mmol, 1.0 equiv.), $CoBr_2$(dppe) (309 mg, 0.5 mmol, 10 mol%), zinc powder (98 mg, 1.5 mmol, 30 mol%) and zinc iodide (478 mg, 1.5 mmol, 30 mol%) in CH_2Cl_2 (6.0 mL) were stirred for 3 h at room temperature. Purification by FC (MTBE/pentane 1:99, R_f = 0.40) afforded **1b** (767 mg, 54%) as a pale yellow liquid. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.16 (s, 12 H, 4×CH_3), 1.56 (s, 6 H, 2×CH_3), 1.81 (s, 3 H, CH_3), 2.48–2.72 (m, 4 H, 2×CH_2), 4.58–4.72 (m, 2 H, 2×CH) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 18.0, 18.4, 21.7, 24.6 (4 C), 36.1, 36.5, 82.8 (2 C), 111.8, 122.3, 123.0, 148.4, 148.6 ppm. The carbon atom beside the boron atom is not resolved. MS (EI, 70 eV): *m*/*z* (%) = 274 (5) [*M*]$^+$, 259 (9), 173 (27), 159 (44), 146 (100), 133 (25), 119 (13), 101 (21), 84 (58). HRMS: calcd. for $C_{17}H_{27}BO_2$: 274.2104; found 274.2123.

3,10-Dimethylphenanthrene (3a): This compound was prepared as described in GP B; dihydroaromatic boronic ester **1a** (100 mg, 0.38 mmol) was stirred with 1,2-diiodobenzene (125 mg, 0.38 mmol, 1.0 equiv.) and $PdCl_2$(dppf) (27 mg, 38 μmol, 10 mol%) in a mixture of THF (4.0 mL) and 10% aqueous NaOH (1.60 mL, 4.0 mmol, 10.5 equiv.) for 12 h. Oxidation of the crude dihydroaromatic product was performed with DDQ (104 mg, 0.46 mmol, 1.2 equiv.). Purification by FC (pentane, R_f = 0.23) afforded **3a** (20 mg, 96 μmol, 25%) as a colourless solid, m.p. 60–61 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.61 (s, 3 H, CH_3), 2.72 (s, 3 H, CH_3), 7.40 (d, *J* = 8.1 Hz, 1 H, H_{ar}), 7.55 (s, 1 H, H_{ar}), 7.62–7.66 (m, 2 H, H_{ar}), 7.70 (d, *J* = 8.1 Hz, 2 H, H_{ar}), 8.02–8.06 (m, 1 H, H_{ar}), 8.45 (s, 1 H, H_{ar}), 8.69–8.74 (1 H, H_{ar}) ppm. ^{13}C NMR (75 MHz, C_6D_6): δ = 19.9, 22.0, 122.8, 123.4, 125.0, 126.2, 126.6, 127.1, 128.1, 128.5, 130.4, 130.6, 130.8, 131.6, 132.8, 135.5 ppm. MS (EI, 70 eV): *m*/*z* (%) = 206 (100) [*M*]$^+$, 191 (56), 176 (7), 101 (8), 89 (15), 76 (7). HRMS calcd. for $C_{16}H_{14}$: 206.1096; found 206.1094.

2,3,10-Trimethylphenanthrene (3b): This compound was prepared as described in GP B; dihydroaromatic boronic ester **1b** (125 mg, 0.46 mmol) was stirred with 1,2-diiodobenzene (150 mg, 0.46 mmol, 1.0 equiv.) and $PdCl_2$(dppf) (27 mg, 38 μmol, 8 mol%) in a mixture of THF (4.0 mL) and 10% aqueous NaOH (1.60 mL, 4.0 mmol, 10.5 equiv.) for 12 h. Oxidation of the crude dihydroaromatic product was performed with DDQ (124 mg, 0.55 mmol, 1.2 equiv.). Purification by FC (pentane, R_f = 0.21) afforded **3b** (40 mg, 0.18 mmol, 40%) as a colourless solid, m.p. 113–114 °C. ^{1}H NMR (200 MHz, C_6D_6): δ = 2.30 (s, 3 H, CH_3), 2.34 (s, 3 H, CH_3), 2.57 (d, *J* = 1.0 Hz, 3 H, CH_3), 7.42–7.63 (m, 4 H, H_{ar}), 7.90–8.02 (m, 1 H, H_{ar}), 8.42 (s, 1 H, H_{ar}), 8.61–8.71 (m, 1 H, H_{ar}) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 19.9, 20.0, 20.4, 123.3, 123.4, 125.0, 126.2 (2 C), 126.8, 128.3, 128.8, 130.8, 131.2, 131.5, 132.4, 135.0, 135.8 ppm. IR (KBr): $\tilde{\nu}$ = 3080, 3012, 2961, 1604, 1448, 1027, 888, 749 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 220 (100) [*M*]$^+$, 205 (17). HRMS calcd. for $C_{17}H_{16}$: 220.1252; found 220.1252.

2-(2-Isopropenyl-5-methylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4): The dihydroaromatic boronic ester **1a** (1.29 g, 5.0 mmol) in toluene (20.0 mL) was treated with DDQ (1.32 g, 6.0 mmol, 1.2 equiv.) and stirred for one hour at room temperature. The reaction mixture was washed twice with an aqueous solution of 10% NaOH/10% $Na_2S_2O_3$, the organic phase was dried over $MgSO_4$, and the solvent was removed under vacuum. Purification by FC (MTBE/pentane, 1:99, R_f = 0.39) afforded **4** (922 mg, 3.57 mmol, 72%) as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.32 (s, 12 H, 4×CH_3), 2.09–2.13 (m, 3 H, CH_3), 2.31–2.34 (m, 3 H, CH_3), 4.83–4.88 (m, 1 H, =CH_2), 5.01–5.05 (m, 1 H, =CH_2), 7.09–7.45 (m, 3 H, H_{ar}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.9, 24.6, 24.7 (4 C), 83.6 (2 C), 113.8, 127.1, 128.3, 130.6, 134.9, 135.6, 146.8, 147.4 ppm. MS (EI, 70 eV): *m*/*z* (%) = 258 (36) [*M*]$^+$, 200 (15), 185 (10), 175 (39), 158 (100), 142 (87), 131 (23), 115 (22). HRMS: calcd. for $C_{16}H_{14}$: 258.1791; found 258.1802.

9-(2-Isopropenyl-5-methylbenzyl)-3,9-dimethyl-9*H*-fluorene (5): This compound was prepared as described in GP B; dihydroaromatic boronic ester **4** (98 mg, 0.38 mmol) was stirred with 1,2-diiodobenzene (125 mg, 0.38 mmol, 1.0 equiv.) and $PdCl_2$(dppf) (27 mg, 38 μmol, 10 mol%) in a mixture of THF (4.0 mL) and 10% aqueous NaOH (1.60 mL, 4.0 mmol, 10.5 equiv.) for 12 h. The reaction

mixture was extracted with diethyl ether, the organic phase was dried over $MgSO_4$, and the solvent was removed under vacuum. Purification by FC (MTBE/pentane, 1:9, R_f = 0.40) afforded **5** (54 mg, 0.16 mmol, 84%) as a colourless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.52 (s, 3 H, CH_3), 1.72–1.77 (m, 3 H, CH_3), 2.16 (s, 3 H, CH_3), 2.41 (s, 3 H, CH_3), 3.18 (s, 2 H, CH_2), 4.43–4.49 (m, 1 H, =CH_2), 4.97–5.04 (m, 1 H, =CH_2), 6.68 (s, 1 H, H_{ar}), 6.99–6.91 (m, 2 H, H_{ar}), 7.02–7.05 (m, 2 H, H_{ar}), 7.06–7.34 (m, 4 H, H_{ar}), 7.48 (s, 1 H, H_{ar}), 7.61–7.67 (m, 1 H, H_{ar}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.0, 21.5, 25.3, 25.9, 41.5, 51.0, 115.4, 119.6, 120.3, 123.6, 123.9, 126.6 (2 C), 126.8, 127.6, 127.7, 131.3, 134.8, 135.0, 136.5, 139.7, 139.8, 141.8, 145.2, 149.2, 152.3 ppm. MS (EI, 70 eV): *m*/*z* (%) = 338 (5) $[M]^+$, 323 (6), 193 (100), 178 (34), 145 (25).

2-Bromo-2′-isopropenyl-4-methoxy-5′-methyl-1,1′-biphenyl (7): This compound was prepared as described in GP B; dihydroaromatic boronic ester **1a** (1.27 g, 4.88 mmol) was stirred with 2-bromo-1-iodo-4-methoxybenzene (1.56 g, 4.98 mmol, 1.0 equiv.) and $PdCl_2$(dppf) (350 mg, 0.5 mmol, 10 mol%) in a mixture of THF (10.0 mL) and 10% aqueous NaOH (5.0 mL, 12.5 mmol, 2.5 equiv.) for 36 h. The reaction mixture was extracted with diethyl ether, the organic phase was dried over $MgSO_4$, and the solvent was removed under vacuum. The crude product was dissolved in toluene (40 mL) and stirred with DDQ (1.36 g, 6.0 mmol, 1.2 equiv.) for 2 h. Diethyl ether was added, the organic phase was separated, washed twice with an aqueous solution of 10% NaOH/10% $Na_2S_2O_3$ and dried over $MgSO_4$, and the solvent was removed under vacuum. Purification by FC (MTBE/pentane, 1:99, R_f = 0.10) afforded **7** (1.15 g, 3.61 mmol, 74%) as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.78 (s, 3 H, CH_3), 2.38 (s, 3 H, CH_3), 3.83 (s, 3 H, OCH_3), 4.81–4.84 (m, 1 H, =CH_2), 4.96–4.99 (m, 1 H, =CH_2), 6.86 (dd, *J* = 8.5, 2.7 Hz, H_{ar}), 7.04 (br. s, 1 H, H_{ar}), 7.11–7.28 (m, 4 H, H_{ar}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.0, 23.5, 55.4, 113.0, 115.7, 117.5, 123.8, 128.1, 128.3, 131.5, 131.9, 135.1, 136.1, 138.4, 140.3, 145.0, 159.0 ppm. MS (EI, 70 eV): *m*/*z* (%) = 316 (1) $[M]^+$, 301 (1), 237 (100), 222 (89), 207 (14), 193 (9), 178 (33), 152 (11), 111 (7). HRMS: calcd. for $C_{16}H_{14}$: 316.0463; found 316.0466.

2′-Isopropenyl-5′-methyl-1,1′-biphenyl-2-amine (10a): This compound was prepared as described in GP B; dihydroaromatic boronic ester **1a** (500 mg, 1.9 mmol) was stirred with 2-iodoaniline (416 mg, 1.9 mmol, 1.0 equiv.) and $PdCl_2$(dppf) (135 mg, 0.19 mmol, 10 mol%) in a mixture of THF (20.0 mL) and 10% aqueous NaOH (8.0 mL, 20 mmol, 10.5 equiv.) for 36 h. The reaction mixture was extracted with diethyl ether, the organic phase was filtered through silica gel, and the solvent was removed under vacuum. The crude product was dissolved in toluene (20 mL) and stirred with DDQ (517 mg, 2.28 mmol, 1.2 equiv.) for 2 h. Diethyl ether was added, the organic phase was separated, washed twice with an aqueous solution of 10% NaOH/10% $Na_2S_2O_3$ and dried over $MgSO_4$, and the solvent was removed under vacuum. Purification by FC (MTBE/pentane 4:1, R_f = 0.40) afforded **10a** (280 mg, 1.26 mmol, 66%) as a pale yellow oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.72 (m, 3 H, CH_3), 2.35 (s, 3 H, CH_3), 3.54 (br. s, 2 H, NH_2), 4.87–4.91 (m, 1 H, =CH_2), 4.94–4.98 (m, 1 H, =CH_2), 6.69–6.89 (m, 2 H, H_{ar}), 6.99–7.04 (m, 1 H, H_{ar}), 7.05–7.17 (m, 3 H, H_{ar}), 7.21–7.27 (m, 1 H, H_{ar}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.0, 23.2, 115.2, 115.3, 118.2, 127.9, 128.2, 128.3, 129.0, 130.6, 131.4, 136.6, 137.1, 140.6, 143.6, 145.9 ppm. IR (KBr): $\tilde{\nu}$ = 3470, 3379, 3022, 2968, 2917, 1614, 1483, 1453, 1298, 896, 826, 749 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 223 (18) $[M]^+$, 208 (100), 193 (32), 178 (6), 165 (11), 96 (9). HRMS: calcd. for $C_{16}H_{17}N$: 223.1361; found 223.1355.

2′-Isopropenyl-4′,5′-dimethyl-1,1′-biphenyl-2-amine (10b): This compound was prepared as described in GP B; dihydroaromatic boronic ester **1b** (300 mg, 1.09 mmol) was stirred with 2-iodoaniline (249 mg, 1.14 mmol, 1.05 equiv.) and $PdCl_2$(dppf) (81 mg, 0.11 mmol, 10 mol%) in a mixture of THF (12.0 mL) and 10% aqueous NaOH (4.8 mL, 12 mmol, 10.5 equiv.) for 12 h. The reaction mixture was extracted with diethyl ether, the organic phase was filtered through silica gel, and the solvent was removed under vacuum. The crude product was dissolved in toluene (20 mL) and stirred with DDQ (324 mg, 1.4 mmol, 1.2 equiv.) for 2 h. Diethyl ether was added, the organic phase was separated, washed twice with an aqueous solution of 10% NaOH/10% $Na_2S_2O_3$ and dried over $MgSO_4$, and the solvent was removed under vacuum. Purification by FC (MTBE/pentane, 4:1) afforded **10b** (187 mg, 0.79 mmol, 72%) as a yellow oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.74 (m, 3 H, CH_3), 2.28 (s, 3 H, CH_3), 2.31 (s, 3 H, CH_3), 3.48 (br. s, 2 H, NH_2), 4.89–4.93 (m, 1 H, =CH_2), 4.95–5.00 (m, 1 H, =CH_2), 6.69–6.82 (m, 2 H, H_{ar}), 7.00–7.10 (m, 2 H, H_{ar}), 7.12–7.18 (m, 2 H, H_{ar}) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 19.3, 19.4, 23.3, 115.0, 115.2, 118.2, 127.8, 128.1, 130.2, 130.7, 131.8, 134.1, 135.7, 135.8, 141.0, 143.7, 145.9 ppm. IR (KBr): $\tilde{\nu}$ = 3469, 3378, 3014, 2968, 2918, 1614, 1485, 1451, 1297, 889, 749 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 237 (6) $[M]^+$, 222 (100), 204 (4), 191 (2), 178 (3), 165 (7), 152 (4). HRMS calcd. for $C_{17}H_{19}N$: 237.1517; found 237.1515.

5-Fluoro-2′-isopropenyl-5′-methyl-1,1′-biphenyl-2-amine (10c): This compound was prepared as described in GP B; dihydroaromatic boronic ester **1a** (100 mg, 0.38 mmol) was stirred with 5-fluoro-2-iodoaniline (90 mg, 0.38 mmol, 1.0 equiv.) and $PdCl_2$(dppf) (27 mg, 40 μmol, 10 mol%) in a mixture of THF (4.0 mL) and 10% aqueous NaOH (1.60 mL, 4.0 mmol, 10.5 equiv.) for 12 h. The reaction mixture was extracted with diethyl ether, the organic phase was filtered through silica gel, and the solvent was removed under vacuum. The crude product was dissolved in toluene (20.0 mL) and stirred with DDQ (104 mg, 0.46 mmol, 1.2 equiv.) for 2 h. Diethyl ether was added, the organic phase was separated, washed twice with an aqueous solution of 10% NaOH/10% $Na_2S_2O_3$ and dried over $MgSO_4$, and the solvent was removed under vacuum. Purification by FC (MTBE/pentane, 4:1) afforded **10c** (62 mg, 0.26 mmol, 67%) as a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.75 (s, 3 H, CH_3), 2.37 (s, 3 H, CH_3), 3.68 (br. s, 2 H, NH_2), 4.88–4.93 (m, 1 H, =CH_2), 4.97–5.02 (m, 1 H, =CH_2), 6.93–6.51 (m, 2 H, H_{ar}), 6.96 (dd, *J* = 8.3, 6.3 Hz, 1 H), 7.04–7.09 (m, 1 H, H_{ar}), 7.12–7.19 (m, 2 H, H_{ar}), 7.26 (d, *J* = 7.8 Hz, 1 H, H_{ar}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.1, 23.2, 101.6 (d, *J* = 24.3 Hz), 104.6 (d, *J* = 21.5 Hz), 115.3, 123.6 (d, *J* = 2.8 Hz), 128.5, 129.0, 131.4, 131.6 (d, *J* = 21 Hz), 135.6, 137.1, 140.9, 145.2 (d, *J* = 10.7 Hz), 146.7, 163.0 (d, *J* = 243.0 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 3479, 3389, 2969, 2920, 1709, 1618, 1508, 974, 827 cm^{-1}. ^{19}F NMR (188 MHz, $CDCl_3$): δ = –115.4 ppm. MS (EI, 70 eV): *m*/*z* (%) = 242 (100) $[M + H]^+$, 228 (78), 211 (34), 198 (23), 185 (19). HRMS (ESI) calcd. for $C_{16}H_{17}FN$ ($[M + H]^+$): 242.1345; found 242.1352.

Methyl 6-Amino-2′-isopropenyl-5′-methyl-1,1′-biphenyl-3-carboxylate (10d): This compound was prepared as described in GP B; dihydroaromatic boronic ester **1a** (100 mg, 0.38 mmol) was stirred with methyl 4-amino-3-iodobenzoate (105 mg, 0.38 mmol, 1.0 equiv.) and $PdCl_2$(dppf) (27 mg, 40 μmol, 10 mol%) in a mixture of THF (4.0 mL) and 10% aqueous NaOH (1.60 mL, 4.0 mmol, 10.5 equiv.) for 12 h. The reaction mixture was extracted with diethyl ether, the organic phase was filtered through silica gel, and the solvent was removed under vacuum. The crude product was dissolved in toluene (20 mL) and stirred with DDQ (104 mg, 0.46 mmol, 1.2 equiv.) for 2 h. Diethyl ether was added, the organic phase was separated, washed twice with an aqueous solution of

10% NaOH/10% $Na_2S_2O_3$ and dried over $MgSO_4$, and the solvent was removed under vacuum. Purification by FC (MTBE/pentane, 2:3, R_f = 0.32) afforded **10d** (55 mg, 0.19 mmol, 51%) as a pale yellow solid. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.75 (s, 3 H, CH_3), 2.35 (s, 3 H, CH_3), 3.83 (s, 3 H, OCH_3), 4.02 (br. s, 2 H, NH_2), 4.84–4.89 (m, 1 H, =CH_2), 4.93–4.98 (m, 1 H, =CH_2), 6.66 (d, J = 8.3 Hz, 1 H, H_{ar}), 7.05 (br. s, 1 H, H_{ar}), 7.10–7.19 (m, 1 H, H_{ar}), 7.22–7.27 (d, J = 8.0 Hz, 1 H, H_{ar}), 7.75 (d, J = 8.0 Hz, 1 H, H_{ar}), 7.82 (dd, J = 8.2, 2.0 Hz, 1 H, H_{ar}) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 20.9, 23.4, 51.5, 113.9, 115.5, 119.2, 126.7, 128.6, 128.9, 130.3, 131.3, 132.5, 135.3, 137.2, 140.6, 145.1, 148.2, 167.3 ppm. IR (KBr): $\tilde{\nu}$ = 3484, 3382, 2948, 2917, 1699, 1620, 1440 cm^{-1}. MS (EI, 70 eV): m/z (%) = 282 (100) [M + H]$^+$, 268 (49), 251 (30), 236 (42), 224 (52), 208 (41), 194 (44), 180 (19), 167 (23), 152 (11), 128 (11), 115 (14). HRMS calcd. for $C_{18}H_{19}NO_2$: 281.1416; found 281.1397.

6-Amino-2′-isopropenyl-5′-methyl-1,1′-biphenyl-3-carbaldehyde (10e): This compound was prepared as described in GP B; dihydroaromatic boronic ester **1a** (100 mg, 0.38 mmol) was stirred with 2-iodotoluidine (89 mg, 0.38 mmol, 1.0 equiv.) and $PdCl_2$(dppf) (27 mg, 40 μmol, 10 mol%) in a mixture of THF (4.0 mL) and 10% aqueous NaOH (1.60 mL, 4.0 mmol, 10.5 equiv.) for 12 h. The reaction mixture was extracted with diethyl ether, the organic phase was filtered through silica gel, and the solvent was removed under vacuum. The crude product was dissolved in toluene (20 mL) and stirred with DDQ (104 mg, 0.46 mmol, 1.2 equiv.) for 2 h. Diethyl ether was added, the organic phase was separated, washed twice with an aqueous solution of 10% NaOH/10% $Na_2S_2O_3$ and dried over $MgSO_4$, and the solvent was removed under vacuum. Purification by FC (MTBE/pentane, 3:7, R_f = 0.30) afforded **10e** (18 mg, 80 μmol, 20%) as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.75 (s, 3 H, CH_3), 2.36 (s, 3H, CH_3), 4.20 (br. s, 2 H, NH_2), 4.84–4.89 (m, 1 H, CHH), 4.94–4.99 (m, 1 H, CHH), 6.73 (d, J = 8.5 Hz, 1 H, H_{ar}), 6.99–7.40 (m, 3 H, H_{ar}), 7.53 (d, J = 2.0 Hz, 2 H, H_{ar}), 7.67 (dd, J = 8.3, 2.0 Hz, 1 H, H_{ar}) 9.73 (s, 1 H, CHO) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.9, 23.4, 114.3, 115.8, 127.0, 127.3, 128.9, 129.1, 130.6, 131.2, 133.7, 134.8, 137.4, 140.7, 145.0, 149.9, 190.6 ppm. IR (KBr): $\tilde{\nu}$ = 3475, 3360, 2918, 1672, 1617, 1614, 825 cm^{-1}. MS (EI, 70 eV): m/z (%) = 251 (21) [M]$^+$, 236 (100), 207 (65), 193 (18), 165 (11), 96 (7), 77 (4). HRMS (ESI) calcd. for $C_{18}H_{17}NO$ ([M + H]$^+$): 252.1388; found 252.1388.

2-(2-Isopropenyl-5-methylphenyl)-5-methylaniline (10f): This compound was prepared as described in GP B; dihydroaromatic boronic ester **1a** (200 mg, 0.76 mmol) was stirred with 2-iodo-5-methylaniline (178 mg, 0.76 mmol, 1.0 equiv.) and $PdCl_2$(dppf) (54 mg, 80 μmol, 10 mol%) in a mixture of THF (8.0 mL) and 10% aqueous NaOH (3.20 mL, 8.0 mmol, 10.5 equiv.) for 12 h. The reaction mixture was extracted with diethyl ether, the organic phase was filtered through silica gel, and the solvent was removed under vacuum. The crude product was dissolved in toluene (40 mL) and stirred with DDQ (204 mg, 0.9 mmol, 1.2 equiv.) for 3 h. Diethyl ether was added, the organic phase was separated, washed twice with an aqueous solution of 10% NaOH/10% $Na_2S_2O_3$ and dried over $MgSO_4$, and the solvent was removed under vacuum. Purification by FC (MTBE/pentane, 1:10) afforded **10f** (193 mg, 0.81 mmol, 74%) as a yellow oil. R_f = 0.30 (MTBE/pentane, 1:2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.19 (d, J = 7.8 Hz, 1 H, H_{Ar}), 7.09 (dd, J = 7.8, 1.2 Hz, 1 H, H_{Ar}), 6.96–6.91 (m, 2 H, H_{Ar}), 6.59–6.52 (m, 2 H, H_{Ar}), 4.92 (m, 1 H, =CH_2), 4.83 (m, 1 H, =CH_2), 3.36 (br. s, 2 H, NH_2), 2.34 (s, 3 H, CH_3), 2.04 (s, 3 H, CH_3), 1.55 (s, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.3, 21.0, 23.3, 112.5, 115.1, 116.6, 127.4, 128.4, 130.8, 131.5, 132.8, 136.2, 136.7, 139.3, 140.6, 144.7, 146.3 ppm. IR (film): $\tilde{\nu}$ = 3465, 3377, 3008, 2916, 1623, 1506, 1479, 1306, 1245, 893, 828, 813 cm^{-1}. MS (EI, 70 eV): m/z (%) = 237 (40) [M]$^+$, 222 (100) [M – CH_3]$^+$, 207 (88), 189 (7), 178 (7), 165 (7), 152 (5), 103 (9). HRMS (EI) calcd. for $C_{17}H_{19}N$: 237.1517; found 237.1512.

3,10-Dimethylphenanthrene (3a/11a): This compound was prepared as described in GP C; **10a** (25 mg, 0.11 mmol), *tert*-butyl nitrite (20 μL, 0.17 mmol, 1.5 equiv.) and trimethylborate (24 μL, 0.22 mmol, 2.0 equiv.) were stirred in toluene (3.0 mL) at 100 °C for 5 d. According to GCMS analysis the desired product was achieved in quantitative yield. Workup of the reaction afforded **11a** in 85% yield. For detailed work-up procedure and the spectroscopic data see under **3a**.

3-Fluoro-6,9-dimethylphenanthrene (11b): This compound was prepared as described in GP C; **10c** (62 mg, 0.26 mmol), *tert*-butyl nitrite (59 μL, 0.5 mmol, 2.0 equiv.) and trimethylborate (55 μL, 0.5 mmol, 2.0 equiv.) in toluene (2.5 mL) were stirred at 150 °C for 3 d. Purification by FC (MTBE/pentane, 1:4, R_f = 0.30) afforded **11b** (41 mg, 0.18 mmol, 71%) as a pale yellow solid, m.p. 61–62 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.62 (s, 3 H, CH_3), 2.70 (d, J = 1.0 Hz, 3 H, CH_3), 7.25–7.50 (m, 4 H, H_{ar}), 7.93 (d, J = 8.6 Hz, 1 H, H_{ar}), 8.41 (s, 1 H, H_{ar}), 8.60 (dd, J = 9.3, 5.6 Hz, 1 H, H_{ar}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.0, 21.9, 111.7 (d, J = 20.3 Hz), 114.4 (d, J = 23.7 Hz), 122.6, 124.7, 124.8, 125.0 (d, J = 3.4 Hz), 126 (d, J = 1.7 Hz) 128.0, 129.5 (d, J = 1.3 Hz), 130.2, 133.5 (d, J = 8.8 Hz), 133.9, 136.2, 160.8 (J = 245.5 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 1619, 1504, 870, 815, 762 cm^{-1}. ^{19}F NMR (188 MHz, $CDCl_3$): δ = –116.1 ppm. MS (EI, 70 eV): m/z (%) = 224 (100) [M]$^+$, 209 (48), 196 (6), 183 (7), 98 (9). HRMS (ESI) calcd. for $C_{16}H_{13}F$ ([M + H]$^+$): 224.1001; found 224.1007.

Methyl 6,9-Dimethyl-3-phenanthrenecarboxylate (11c): This compound was prepared as described in GP C; **10d** (62 mg, 0.22 mmol), *tert*-butyl nitrite (59 μL, 0.5 mmol, 2.0 equiv.) and trimethylborate (55 μL, 0.5 mmol, 2.0 equiv.) in toluene (3.0 mL) were stirred at 150 °C for 3 d. Purification by FC (MTBE/pentane, 1:4) afforded **11c** (40 mg, 0.15 mmol, 69%) as a pale yellow solid, m.p. 111–112 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.64 (s, 3 H, CH_3), 2.71 (s, 3 H, CH_3), 4.02 (s, 3 H, OCH_3), 7.47–7.52 (m, 2 H, H_{ar}), 7.79 (d, J = 8.3 Hz, 1 H, H_{ar}), 7.94 (d, J = 8.3 Hz, 1 H, H_{ar}), 7.14 (dd, J = 8.3, 1.5 Hz, 1 H, H_{ar}), 8.58 (s, 1 H, H_{ar}), 9.35 (m, 1 H, H_{ar}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.1, 21.9, 52.2, 123.0, 124.6, 125.0, 125.3, 126.4, 126.8, 127.8, 128.7, 128.8, 130.1, 130.6, 135.1, 135.5, 136.7, 167.6 ppm. IR (KBr): $\tilde{\nu}$ = 2948, 1709, 1616, 1262, 806, 763 cm^{-1}. MS (EI, 70 eV): m/z (%) = 264 (100) [M]$^+$, 233 (56), 202 (16), 189 (41), 116 (12), 101 (14). HRMS (ESI) calcd. for $C_{18}H_{17}O_2$ ([M + H]$^+$): 265.1229; found 265.1229.

General Procedure for the Synthesis of Phenanthridine Derivatives (GP D): The (2-isopropenyl-1,1′-biphenyl-2′-yl)amine was stirred in a Pyrex tube in toluene with trifluoromethanesulfonic acid at 100 °C for 12 h. After evaporation of the solvent under vacuum the crude product was purified by chromatography on silica (eluent: MTBE/pentane).

6,6,8,9-Tetramethyl-5,6-dihydrophenanthridine (12a): This compound was prepared as described in GP D; **10b** (50 mg, 0.21 mmol) and trifluoromethanesulfonic acid (4.0 μL, 45 μmol, 0.2 equiv.) were stirred in toluene (2.0 mL) at 100 °C for 12 h. After evaporation of the solvent under vacuum, purification by FC (MTBE/pentane, 1:4, R_f = 0.48) afforded **12a** (36 mg, 0.14 mmol, 72%) as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.52 (s, 6 H, $C(CH_3)_2$), 2.32 (s, 3 H, CH_3), 2.33 (s, 3 H, CH_3), 3.76 (br. s, 1 H, NH), 6.32–7.20 (m, 4 H, H_{ar}), 7.55 (s, 1 H, H_{ar}), 7.71 (dd, J = 7.8, 1.3 Hz, 1 H, H_{ar}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.6, 19.7, 29.8 (2 C), 53.3, 115.1, 118.6, 122.9, 123.8, 124.5, 128.2, 129.3,

135.0, 135.7, 138.5, 139.0, 143.3 ppm. IR (KBr): $\tilde{\nu}$ = 3357, 1607, 1312, 1262, 872, 746, 726 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 237 (7) [*M*]$^+$, 222 (100), 204 (5), 165 (7), 103 (7). HRMS: calcd. for $C_{17}H_{19}N$: 237.1517; found 237.1511.

3-Fluoro-6,6,9-trimethyl-5,6-dihydrophenanthridine (12b): This compound was prepared as described in GP D; **10c** (78 mg, 0.32 mmol) and trifluoromethanesulfonic acid (4 μL, 45 μmol, 0.1 equiv.) were stirred in toluene (2.0 mL) at 100 °C for 12 h. After evaporation of the solvent under vacuum and purification by FC (MTBE/pentane, 1:10, R_f = 0.36), **12b** (75 mg, 0.3 mmol, 94%) was isolated as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.60 (s, 6 H, $(CH_3)_2C$), 2.49 (s, 3 H, CH_3), 3.83 (br. s, 1 H, NH), 6.48–6.42 (m, 1 H, H_{ar}), 6.66–6.56 (m, 1 H, H_{ar}), 7.35–7.15 (m, 2 H, H_{ar}), 7.59 (m, 1 H, H_{ar}), 7.75 (m, 1 H, H_{ar}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.2, 29.8, 53.7, 101.7 (d, *J* = 24.3 Hz), 105.54 (d, *J* = 22.0 Hz), 117.5 (d, *J* = 2.3 Hz), 122.9, 123.3, 124.7 (d, *J* = 10.2 Hz), 128.0, 129.7, 136.6, 137.3, 144.9 (d, *J* = 10.7 Hz), 163.4 (d, *J* = 245.3 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 3362, 2958, 1721, 1618, 1499, 1474, 1450, 1294, 1260, 1154, 1109, 1001, 840, 822, 576 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 241 (5) [*M*]$^+$, 226 (100) [*M* – CH_3]$^+$, 211 (4), 183 (6), 170 (3), 113 (5). HRMS (ESI) calcd. for $C_{16}H_{17}FN$ ([*M* + H]$^+$): 242.1345; found 242.1317.

2,6,6,9-Tetramethyl-5,6-dihydrophenanthridine (12c): This compound was prepared as described in GP D; **10f** (37 mg, 0.16 mmol) and trifluoromethanesulfonic acid (4 μL, 45 μmol, 0.3 equiv.) were stirred in toluene (2.0 mL) at 100 °C for 12 h. After evaporation of the solvent under vacuum and purification by FC (MTBE/pentane, 1:25), **12c** (16 mg, 70 μmol, 44%) was isolated as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.59 (s, 6 H, $(CH_3)_2C$), 2.42 (s, 3 H, CH_3), 2.48 (s, 3 H, CH_3), 3.82 (br. s, 1 H, NH), 7.65–6.68 (m, 6 H, H_{ar}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.9, 21.2, 29.4, 53.5, 114.7, 115,5, 123.16, 123.19, 123.7, 128.1, 129.4, 130.0, 136.4, 138.2, 139.0, 140.8 ppm. MS (EI, 70 eV): *m*/*z* (%) = 237 (8) [*M*]$^+$, 222 (100) [*M* – CH_3]$^+$, 165 (7), 111(4), 102 (4). HRMS (ESI) calcd. for $C_{17}H_{20}N$ ([*M* + H]$^+$): 238.1595; found 238.1614.

2′-Isopropenyl-5′-methyl-1,1′-biphenyl-2-carbaldehyde (13): This compound was prepared as described in GP B; dihydroaromatic boronic ester **1a** (100 mg, 0.38 mmol) was stirred with 2-iodobenzaldehyde (88 mg, 0.38 mmol, 1.0 equiv.) and $PdCl_2$(dppf) (27 mg, 40 μmol, 10 mol%) in a mixture of THF (4.0 mL) and 10% aqueous NaOH (1.60 mL, 4.4 mmol, 11.4 equiv.) for 12 h. The reaction mixture was extracted with diethyl ether, the organic phase was filtered through silica gel, and the solvent was removed under vacuum. The crude product was dissolved in toluene (20.0 mL) and stirred with DDQ (324 mg, 1.4 mmol, 1.2 equiv.) for 2 h. Diethyl ether was added, the organic phase was separated, washed twice with an aqueous solution of 10% NaOH/10% $Na_2S_2O_3$ and dried over $MgSO_4$, and the solvent was removed under vacuum. Purification by FC (MTBE/pentane, 1:9, R_f = 0.49) afforded **13** (65 mg, 0.28 mmol, 73%) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.53 (dd, *J* = 1.5, 1.0 Hz, 3 H, CH_3), 2.38 (s, 3 H, CH_3), 4.81–4.88 (m, 1 H, =CH_2), 4.95–5.02 (m, 1 H, =CH_2), 7.02–7.08 (m, 1 H, H_{ar}), 7.17–7.23 (m, 2 H, H_{ar}), 7.33–7.51 (m, 2 H, H_{ar}), 7.59 (td, *J* = 7.5, 1.5 Hz, 1 H, H_{ar}), 7.93–8.02 (m, 1 H, H_{ar}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.5, 23.0, 113.9, 115.3, 126.6, 126.9, 128.5, 128.7, 130.2, 130.7, 133.2, 134.4, 137.0, 140.3, 144.6, 149.4, 190.1 ppm. IR (film): $\tilde{\nu}$ = 3077, 2969, 2920, 2849, 1694, 1598, 900, 825, 775 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 236 (3) [*M*]$^+$, 207 (100), 192 (65), 165 (20), 152 (13). HRMS calcd. for $C_{17}H_{16}O$: 236.1201; found 236.1203.

3a,6-Dimethyl-1-phenyl-1,3,3a,11b-tetrahydrophenanthro[9,10-*c*]isoxazole (14): Biaryl **13** (60 mg, 0.25 mmol) and *N*-phenylhydroxylamine (54 mg, 0.5 mmol, 2.0 equiv.) were stirred in diethyl ether (4.0 mL) at room temperature for 36 h. Another portion of *N*-phenylhydroxylamine (27 mg, 0.25 mmol, 1.0 equiv.) was added and stirring was continued for 12 h. The solvent was removed under vacuum. Purification by FC (MTBE/pentane, 1:9, R_f = 0.41) afforded **14** (35 mg, 0.11 mmol, 42%) as a white solid, m.p. 125–126 °C (decomp.). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.32 (s, 3 H, CH_3), 2.41 (s, 3 H, CH_3), 4.11 (s, 1 H, CH), 4.32 (d, *J* = 7.6 Hz, 1 H, =CH_2), 4.67 (d, *J* = 7.6 Hz, 1 H, =CH_2), 6.92–7.09 (m, 4 H, H_{ar}), 7.15–7.26 (m, 4 H, H_{ar}), 7.33 (d, *J* = 8.0 Hz, 1 H, H_{ar}), 7.43 (td, *J* = 7.6, 1.3 Hz, 1 H, H_{ar}), 7.75 (br. s, 1 H, H_{ar}), 7.91 (d, *J* = 8.0 Hz, 1 H, H_{ar}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.3, 24.0, 50.0, 76.2, 78.8, 119.0 (2 C), 123.9, 123.9, 124.4, 126.4, 127.3, 128.4 (2 C), 129.2, 129.7, 130.4, 131.4, 131.9, 133.3, 136.4, 136.9, 151.2 ppm. IR (film): $\tilde{\nu}$ = 2956, 2918, 1594, 1483, 1449, 1000, 821, 766, 701 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 327 (5) [*M*]$^+$, 206 (100), 192 (33), 178 (7), 165 (6), 93 (11), 77 (5). HRMS calcd. for $C_{23}H_{21}NO$: 327.1623; found 327.1629.

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