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# Selective Borylation of [4]Helicene

David Nečas,* [a] Reinhard P. Kaiser,[a] and Jan Ulč [a]

**Abstract:** Ir-catalyzed borylation of [4]helicene under different reaction conditions was studied for the first time. The obtained results indicate that monoborylation proceeded to give a mixture of 2- and 3-borylated product in good yields (up to 74% isolated yield). It was possible to shift selectivity in favor of the 3-borylated product by using sterically demanding ligands. The monoborylated [4]helicenes were further arylated by using Suzuki-Miyaura cross-coupling or oxidized to the corresponding phenols in very good yields.

## Introduction

Helicenes represent a unique class of polycyclic aromatic hydrocarbons where the benzene rings are *ortho*-fused, fully conjugated, and with a non-planar topology. They have attracted much interest owing to their unrivalled structural features[1–3] and have also been shown to be effective in the development of materials with chiroptical properties, which are useful for molecular-based electronic applications.[4–6] Of importance, these properties can be addressed by introducing the substituents at the periphery of the helical core. From the synthetic point of view such modifications are not trivial, therefore the selectively substituted helicenes are usually made from pre-functionalized substrates.[1,2] These methods are usually not general enough to produce a large library of congeners. This can be explained by the lack of compatibility of some functional groups or their deactivation effects on the key reaction for producing helicenes. Although a post-functionalization of helicenes appears attractive and would greatly accelerate the development of new functional molecules it has been underdeveloped in the history of helicene chemistry.[7,8]

We speculated that helicenes could be selectively functionalized by an iridium catalyzed, sterically driven C-H activation/borylation process. According to the best of our knowledge such an endeavor, i.e. borylation of helical polyaromatics, has not been reported yet.[9] Because of the avoidance of borylation of C-H bonds *ortho* to ring junction we speculated that, by using standard conditions, helicenes would be nearly equally borylated at the accessible positions 2 and 3. Since the position 3 is more distant from the other end of the molecule and thus less sterically hindered, the appropriate choice of catalytic system and the third dimension (nonplanarity) of the molecule would contrive additional level of regioselectivity to distinguish between these two positions.

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Supporting information for this article is given via a link at the end of the document.

## Results and Discussion

Since the bay-region torsion-angle in phenanthrene (the shortest [n]helicene) is close to 0°, we chose benzo[c]phenanthrene ([4]helicene, the shortest [n]helicene that is non-planar in its lowest energy conformation, torsion-angle 19°,[1] Figure 1) as a substrate to prove the aforementioned idea.

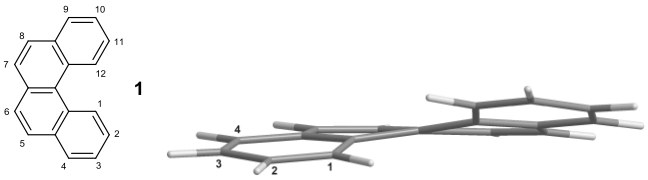
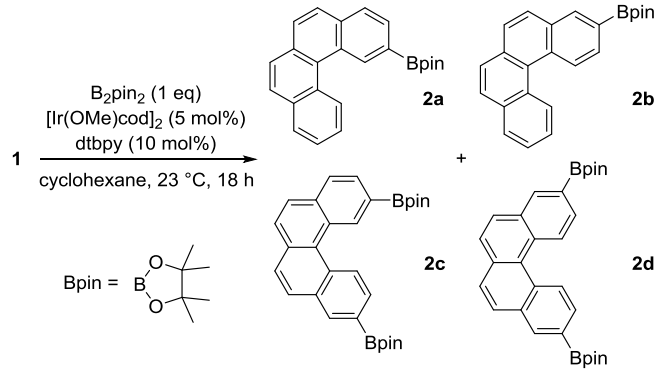



**Figure 1.** Molecular structure of [4]helicene.

Based on the preceding studies of iridium-catalyzed borylation of arenes[10–15] and fused polyarenes[9,16–26] we subjected [4]helicene **1** to mild borylation conditions. Equimolar quantities of the substrate and $B_2pin_2$ and a catalytic amount of $[Ir(OMe)(cod)]_2$ (5 mol% Ir) and dtbpy (10 mol%) were reacted in cyclohexane at 23 °C for 18 h. Removal of the volatiles and subsequent column chromatography on silica gel (hexane/DCM from 100:0 to 0:100) resulted in three colorless fractions, unreacted **1** (39%), a mixture of monoborylated [4]helicenes (51%) and the last small fraction containing a mixture of bisborylated [4]helicenes (<8%). The subsequent separation of the second fraction by non-aqueous reverse phase chromatography (NARP) afforded two regioisomers, 2-borylated [4]helicene **2a** (27%) and 3-borylated [4]helicene **2b** (22%). The structure of the products **2a** and **2b** was unequivocally confirmed by a single-crystal X-ray diffraction analysis (Figure 2). Separation of the third fraction provided two analytically pure compounds showing that the second borylation could take place on the other terminal ring of [4]helicene in positions 10 and 11 giving rise to symmetrical 3,10-bisborylated [4]helicene **2d** and unsymmetrical 2,10-bisborylated [4]helicene **2c**. Formation of symetrically bisborylated 2,11-bisborylated [4]helicene was not observed.




**Scheme 1.** Ir-catalyzed borylation of [4]helicene.

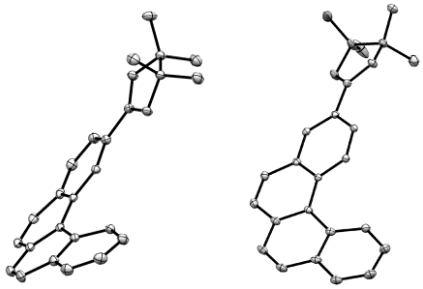
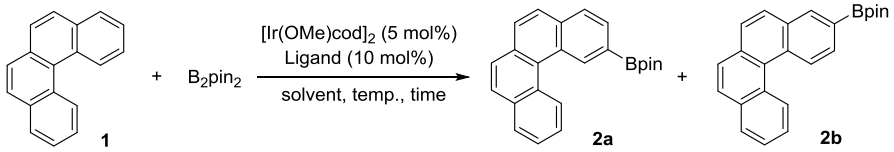


**Figure 2.** ORTEP drawings of **2a** (left) and **2b** (right) with 30% thermal ellipsoids.

This positive result prompted us to look for conditions that enable to control regioselectvity of borylation as well as to increase yields of mono-borylated products. Easy recovery and recycling of the unreacted helicene allowed us to use 2 equivalents of **1** to reduce the amount of the formed bisborylated products **2c** and **2d** when screening the reaction conditions (Table 1). Excess of **1**, temperature increased to 50 °C, and a shorter reaction time resulted in the same conversion of **1** with a slightly better yield of the **2a** and **2b** (Entry 1). Additional increase of the reaction temperature to 80 °C gave 56:44 mixture of **2a** and **2b** in 74% isolated yield (based on 1 eq. of **1**) in 3 hours (Entry 2). The reaction did not proceed at 23 °C in polar solvents such as 1,4-dioxane, THF or ethyl acetate (Entries 3-5). When a less polar MTBE was used at 23 °C the reaction took place with a low conversion of 13% (Entry 6). Increasing the reaction temperature to 80 °C did not bring any considerable improvement in the yield (entry 7), and the use of microwave conditions[27,28] resulted in lower selectivity affording a complex mixture of products in which the presence of tri-borylated [4]helicenes was observed by EI/MS (entry 8). Change of the ligand to 3,4,7,8-tetramethyl-1,10-phenanthroline, which often overperforms dtbpy,[29] did not provide any improvement and resulted in a low conversion at 80 °C either MTBE or cyclohexane (entries 9, 10). (See the SI for the complete list of conditions tested.)

**Table 1**. Ir-catalyzed borylation of **1** under various conditions.

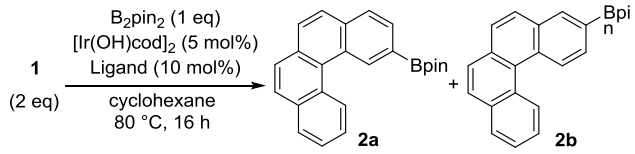



| Entry | Ligand[a] | Solvent[b] | Temp. [°C] | Time [h] | Conversion[c] | Yield **2a** + **2b**[d] |
|---|---|---|---|---|---|---|
| 1 | dtbpy | cyclohexane | 50 | 12 | 59 | 54 |
| 2 | dtbpy | cyclohexane | 80 | 3 | 82 | 74 |
| 3 | dtbpy | dioxane | 23 | 18 | 0 | 0 |
| 4 | dtbpy | THF | 23 | 18 | 0 | 0 |
| 5 | dtbpy | EtOAc | 23 | 18 | 0 | 0 |
| 6 | dtbpy | MTBE | 23 | 18 | 13 | 13 |
| 7 | dtbpy | MTBE | 80 | 3 | 20 | 18 |
| 8 | dtbpy | MTBE | 80[e] | 1 | 50 | n.d. |
| 9 | tmphen | cyclohexane | 80 | 3 | 3 | n.d. |
| 10 | tmphen | MTBE | 80 | 3 | 30 | n.d. |

[a] dtbpy - 4,4´-Di-*tert*-butyl-2,2´-dipyridyl; tmphen - 3,4,7,8-Tetramethyl-1,10-phenanthroline. [b] MTBE – Methyl *tert*-butyl ether. [c] Conversion based on 1 eq. of **1**. [d] Isolated combined yield of **2a**+**2b** based on 1 eq. of **1** (ratio **2a**/**2b** 1/0.8). [e] Microwave irradiation.

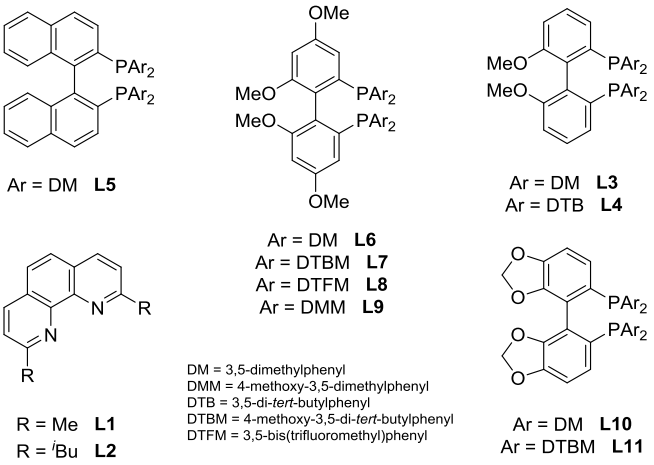
In order to take advantage of the shape of the molecule **1** and affect the regioisomer ratio we followed the idea of Itami and coworkers for *para*-substitution of benzene derivatives, based on the steric difference of active catalysts possessing bipyridyl or bisphosphine type ligands.[30] The ratio of products **2a** and **2b** ranged from 1:1 to 1:3 depending on the ligand used (Table 2). Whereas the standard dtbpy ligand afforded **2a** and **2b** in almost 1:1 ratio, more rigid and sterically demanding ligands preferred position 3, which is sterically less shielded by the other terminal benzene ring of the molecule. Bipyridine type ligands such as 2,9-di-*iso*-butyl-1,10-phenanthroline **L2** and neocuproine **L1** combined with $[Ir(cod)OH]_2$ afforded the products **2a** and **2b** in 1:1.3 and 1:1.6 ratio, respectively (Entries 1 and 2). A sterically demanding diphosphine ligand, DM-MeO-BIPHEP **L3**, reported as the best one for *para*-substitution provided 1:1.9 mixture of **2a** and **2b** in 48% combined yield (Entry 3). By further screening of other ligands, we found that DM-Segphos **L10** (Entry 10) or DM-Garphos **L6** (Entry 6) provided the products in a good combined isolated yields of 65% and 52% and better regioselectivity with the **2a:2b** ratios of 1:2.8 and 1:2.7, respectively.

**Table 2**. Effect of the ligand on the regioselectivity of Ir-catalyzed C-H borylation of [4]helicene **1**.

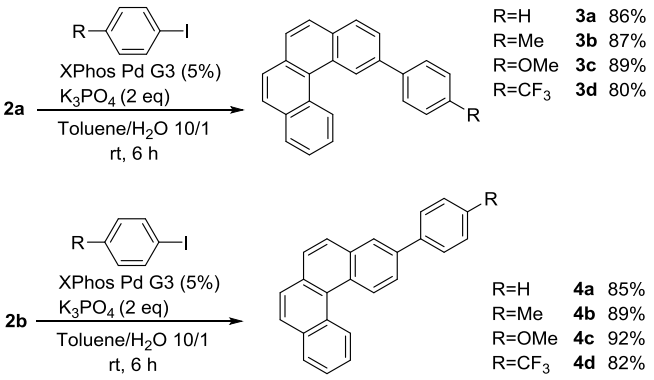



| Entry | Ligand | Yield **2a** + **2b** [%][a] | Ratio **2a**/**2b**[b] |
|---|---|---|---|
| 1 | **L1** | 42 | 1/1.6 |
| 2 | **L2** | 34 | 1/1.3 |
| 3 | **L3** | 48 | 1/1.9 |
| 4 | **L4** | 31 | 1/2.1 |
| 5 | **L5** | 51 | 1/2.4 |
| 6 | **L6** | 52 | 1/2.7 |
| 7 | **L7** | 34 | 1/2.4 |
| 8 | **L8** | 31 | 1/1.9 |
| 9 | **L9** | 23 | 1/1.9 |
| 10 | **L10** | 65 | 1/2.8 |
| 11 | **L11** | 54 | 1/2.3 |

[a] Isolated combined yield of **2a**+**2b** based on 1 eq. of **1**. [b] Ratio determined by $^1$H NMR.

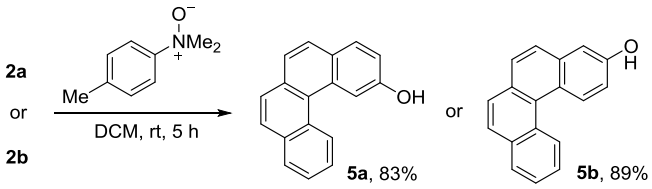



To demonstrate the synthetic utility of the products **2a** and **2b**, Suzuki-Miyaura cross-coupling reactions of both isomers with selected aryl iodides were carried out (Scheme 2). Both monoborylated helicenes showed a good reactivity and the respective arylated products **3a**-**3d** and **4a**-**4d** were obtained in good isolated yields (80-92%)




**Scheme 2.** Pd-catalyzed coupling reactions of **2a** and **2b**

In addition, transformation of the prepared boronates **2** to the corresponding phenols **5** was attempted.[31] Gratifyingly, the reactions of boronates **2a** and **2b** with *N,N*-dimethyl-4-toluidine *N*-oxide in DCM proceeded uneventfully giving rise to the corresponding hydroxy derivatives **5a** and **5b** in 83% and 89% isolated yields, respectively (Scheme 3).




**Scheme 3.** Hydroxylations of boronate esters **2a** and **2b**.

## Conclusions

In summary, we have shown that [4]helicene could be selectively monoborylated by using Ir-catalyzed borylation process to produce, predominantly, two regioisomers of [4]helicene-mono(boronate) esters. In addition, by using different ligands the regioselectivity of the monoborylation could be improved. Both prepared Bpin helicenes show good stability and reactivity for Suzuki-Miyaura coupling reactions. Application of this chemistry and extension for higher helicenes are underway in our laboratory.

## Experimental Section

**General methods:** Catalysts, reagents and solvents were obtained from commercial suppliers (Aldrich, TCI, Alfa Aesar, Strem Chemicals, Penta) and were used without further purification. Solvents for column chromatography were distilled prior to use. Argon was used as an inert gas. Silica gel 60 (0.035–0.070 mm) (Acros Organics) was used for column chromatography. TLC was performed on aluminum sheets with layer of Silica gel 60 $F_{254}$ purchased from MERCK. Spots on TLC plates were detected by using UV lamp ($\lambda$ = 254 nm) or basic permanganate solution. PTLC was performed on glass sheets with layer of Silica gel GF (Analtech). NMR spectra were recorded on Varian VNMRS 300 ($\nu(^1H)$ = 299.94 MHz, $\nu(^{13}C)$ = 75.43 MHz), on Bruker Avance III (400 MHz) ($\nu(^1H)$ = 400.13 MHz, $\nu(^{13}C)$ = 100.61 MHz), or on Bruker Avance III (600 MHz) ($\nu(^1H)$ = 600.17 MHz, $\nu(^{13}C)$ = 150.04 MHz) in deuterated solvents and referenced to residual solvent peak ($CDCl_3$ $^1H$: 7.26 ppm, $^{13}C$: 77 ppm). Chemical shifts are given in $\delta$-scale, coupling constants *J* are given in Hz. Mass spectra were recorded on VG-Analytical ZAB-SEQ. Infrared spectra were recorded in KBr and measured on spectrometer Thermo Nicolet AVATAR 370 FT-IR. All melting points are uncorrected and were determined on Kofler apparatus. HPLC separations were performed on a Gilson 321 H2 pumps with 25x250 mm preparative column (Labio, Czech Republic), filled with BIOSPHER PSI 120 C18 sorbent (7µm mesh). $[Ir(OH)cod]_2$ was prepared according to the reported procedure[32] [4]Helicene was prepared according to the reported procedure,[33] and recrystallized before use.

CCDC 1487957 (**2a**) and CCDC 1487958 (**2b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**Borylation of [4]helicene (First experiment and separation of products)**: A flame dried 10 ml thick-wallet crimp reaction vial was charged with $[Ir(OMe)cod]_2$ (3.3 mg, 0.005 mmol), dtbpy (2.7 mg, 0.01 mmol), $B_2pin_2$ (25 mg, 0.1 mmol), and [4]helicene (23 mg, 0.1 mmol). Then cyclohexane (0.8 mL) was added and argon was bubbled through the reaction mixture to remove $O_2$ and reduce the volume to 0.5 mL and the vessel was crimp-sealed with a septum cap under the flow of argon. Afterwards, the reaction mixture was stirred at 23 °C for 18 h. DCM (2 mL) was added and the solution was filtered through a short pad of silica gel (washed with DCM 5 mL). Volatiles were removed under reduced pressure and column chromatography of the residue (hexane/DCM from 100/0 to 0/100) afforded recovered [4]helicene (the first fraction, 9 mg, 39%), a mixture of **2a** and **2b** (the second fraction, 18.1 mg, 51%), and a mixture of **2c** and **2d** (the third fraction, 3.7 mg, <8%). The second and third fractions were subsequently separated by preparative nonaqueous reversed-phase HPLC (NARP). Separation of the second fraction (MeOH/DCM 99/1) afforded 9.6 mg of **2a** (27%) and 7.8 mg of **2b** (22%). Separation of the third fraction (MeOH/DCM 97/3) afforded **2c** (~1.5 mg, ~3%) and **2d** (~1.5 mg, ~3%).

**General procedure for the Table 1 and Table SI-1:** A flame dried 10 ml thick-wallet crimp reaction vial was charged with $[Ir(OMe)cod]_2$ (3.3 mg, 0.005 mmol), ligand (0.01 mmol), $B_2pin_2$ (25 mg, 0.1 mmol), and [4]helicene (46 mg, 0.2 mmol). Then cyclohexane (0.8 mL) was added and argon was bubbled through the reaction mixture to remove $O_2$ and reduce the volume to 0.5 mL and the vessel was crimp-sealed with a septum cap under the flow of argon. Afterwards, the reaction mixture was stirred and heated (optional) in an aluminum heating block at appropriate temperature for desired time. (Entry 8, microwave reactor was used). After cooling (optional), DCM (2 mL) was added and the solution was filtered through a short pad of silica gel (washed with DCM 5 mL). Volatiles were removed under reduced pressure and column chromatography of the residue (hexane/DCM 2:1) afforded recovered [4]helicene (the first fraction) and a mixture of **2a** and **2b** (the second fraction). The ratio of **2a**:**2b** was calculated by integration of aromatic region of $^1H$ NMR spectra of second fraction, solitary singlet at $\delta$ = 9.63 ppm belongs to **2a** and solitary singlet at $\delta$ = 8.54 ppm belongs to **2b**. (See the Supporting Information file for a detailed discussion about the determination of regioisomers ratios.)

**General procedure for the Table 2:** A flame dried 10 ml thick-wallet crimp reaction vial was charged with $[Ir(OH)cod]_2$ (3.2 mg, 0.005 mmol), ligand (0.01 mmol), $B_2pin_2$ (25 mg, 0.1 mmol), and [4]helicene (46 mg, 0.2 mmol). Then cyclohexane (0.8 mL) was added and argon was bubbled through the reaction mixture to remove $O_2$ and reduce the volume to 0.5 mL and the vessel was crimp-sealed with a septum cap under the flow of argon. Afterwards, the reaction mixture was stirred and heated in an aluminum heating block at 80 °C for 16 h. After cooling, DCM (2 mL) was added and the solution was filtered through a short pad of silica gel (washed with DCM 5 mL). Volatiles were removed under reduced pressure and column chromatography of the residue (hexane/DCM 2:1) afforded recovered [4]helicene (first fraction) and mixture of **2a** and **2b** (second fraction). The ratio of **2a**:**2b** was calculated by integration of aromatic region of $^1H$ NMR spectra of second fraction, solitary singlet at $\delta$ = 9.63 ppm belongs to **2a** and solitary singlet at $\delta$ = 8.54 ppm belongs to **2b**. (See the Supporting Information file for a detailed discussion about the determination of regioisomers ratios.)

**2-(Benzo[*c*]phenanthren-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2a).** Colorless crystals: m.p. 161.2 °C (DCM/MeOH); $^1H$ NMR (600 MHz, Chloroform-*d*) $\delta$ 9.63 (s, 1H), 9.20 (d, *J* = 8.5 Hz, 1H), 8.05 – 8.02 (m, 3H), 7.92 – 7.82 (m, 4H), 7.76 (ddd, *J* = 8.4, 6.9, 1.5 Hz, 1H), 7.65 (ddd, *J* = 7.9, 6.8, 1.1 Hz, 1H), 1.42 (s, 12H); $^{13}C$ NMR (151 MHz, Chloroform-*d*) $\delta$ 135.61, 135.26, 133.55, 130.92, 130.87, 130.30, 129.65, 128.40, 128.29, 127.92, 127.84, 127.60, 127.42, 127.26, 126.69, 126.30, 125.85, 83.91 (2C), 24.95 (4C); IR (DRIFT, KBr) 2977, 1608, 1388, 1338, 1304, 1139, 860, 756, 661 $cm^{-1}$; EI-MS m/z (%) 354 (100), 269 (10), 254 (88); HRMS (ESI) calcd for $C_{24}H_{24}O_2B$ 355.18639, found 355.18655.

**2-(Benzo[*c*]phenanthren-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2b).** Colorless crystals: m.p. 168.6 °C (DCM/MeOH); $^1$H NMR (600 MHz, Chloroform-*d*) δ 9.17 – 9.10 (m, 2H), 8.54 (s, 1H), 8.07 (dd, *J* = 8.4, 1.3 Hz, 1H), 8.03 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.98 – 7.90 (m, 2H), 7.86 – 7.81 (m, 2H), 7.70 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.66 – 7.60 (m, 1H), 1.44 (s, 12H); $^{13}$C NMR (151 MHz, Chloroform-*d*) δ 136.36, 133.43, 132.73, 132.14, 131.69, 131.12, 130.41, 128.52, 127.96, 127.89, 127.86, 127.16, 126.96, 126.80, 126.76, 126.22, 125.85, 84.01 (2C), 24.96 (4C); IR (DRIFT, KBr) 2980, 1606, 1457, 1366, 1308, 1139, 967, 850, 751, 695 cm$^{-1}$; EI-MS m/z (%) 354 (100), 268 (17), 254 (30), 226 (16); HRMS (ESI) calcd for $C_{24}H_{24}O_2B$ 355.18639, found 355.18652.

**2,2'-(Benzo[*c*]phenanthrene-2,10-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2c).** A colorless amorphous solid: m.p. 133.5 °C; $^1$H NMR (400 MHz, Chloroform-*d*) δ 9.62 (s, 1H), 9.18 (d, *J* = 8.5 Hz, 1H), 8.54 (s, 1H), 8.12 (dd, *J* = 8.5, 1.2 Hz, 1H), 8.01 (s, 2H), 7.97 – 7.80 (m, 4H), 1.45 (s, 12H), 1.41 (s, 12H); $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 136.27, 135.57, 135.20, 132.80, 132.17, 131.60, 131.21, 130.98, 129.74, 127.94, 127.89, 127.75, 127.65, 127.59, 127.44, 126.68, 84.04 (2C), 83.91 (2C), 24.97 (4C), 24.95 (4C); IR (DRIFT, KBr) 2978, 2929, 1609, 1444, 1386, 1364, 1344, 1302, 1143, 1099, 967, 850, 686, cm$^{-1}$; EI-MS m/z (%) 480 (100), 394 (5), 380 (6), 294 (8), 280 (17); HRMS (ESI) calcd for $C_{30}H_{35}O_4B_2$ 481.27160, found 481.27174.

**3,10-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[*c*]phenanthrene (2d).** Colorless crystals: m.p. 273.5 °C (DCM/MeOH); $^1$H NMR (400 MHz, Chloroform-*d*) δ 9.11 (d, *J* = 8.5 Hz, 2H), 8.52 (d, *J* = 1.0 Hz, 2H), 8.07 (dd, *J* = 8.5, 1.2 Hz, 2H), 7.96 (d, *J* = 8.5 Hz, 2H), 7.82 (d, *J* = 8.5 Hz, 2H), 1.43 (s, 24H).); $^{13}$C NMR (151 MHz, Chloroform-*d*) δ 136.37 (2C), 132.75 (2C), 132.45 (2C), 132.32 (2C), 131.31 (2C), 128.46 (2C), 127.09 (2C), 127.05 (2C), 126.81 (2C), 84.09 (4C), 25.03 (8C); IR (DRIFT, KBr) 2978, 2932, 1612, 1449, 1367, 1320, 1302, 1145, 1092, 968, 845, 701, cm$^{-1}$; EI-MS m/z (%) 480 (100), 394 (6), 381 (8), 294 (10), 280 (20); HRMS (ESI) calcd for $C_{30}H_{35}O_4B_2$ 481.27160, found 481.27178.

**Cross-coupling reactions of 2a or 2b with aryl iodides:** To a solution of **2a** or **2b** (35.4 mg, 0.1 mmol) in toluene/$H_2O$ (10/1, 2 mL) was added XPhos-Pd-G3 (4.3 mg, 5 mol%), $K_3PO_4$ (42.5 mg, 200 mol%) and an aryl iodide (0.12 mmol) and the reaction mixture was stirred at 23 °C for 6h. All volatiles were evaporated, the residue redissolved in DCM and separated by preparative TLC (hexane/DCM 10:1) to give the corresponding product **3** or **4**.

**2-Phenylbenzo[*c*]phenanthrene (3a).** Yield 26.2 mg (86%); colorless crystals: m.p. 141.8 °C (DCM/MeOH); $^1$H NMR (600 MHz, Chloroform-*d*) δ 9.36 (bs, 1H), 9.19 (d, *J* = 8.4 Hz, 1H), 8.10 (d, *J* = 8.2 Hz, 1H), 8.04 (d, *J* = 7.5 Hz, 1H), 7.95 – 7.88 (m, 3H), 7.86 – 7.83 (m, 2H), 7.82 – 7.79 (m, 2H), 7.71 (ddd, *J* = 8.4, 7.0, 1.3 Hz, 1H), 7.66 – 7.62 (m, 1H), 7.56 – 7.51 (m, 2H), 7.44 – 7.40 (m, 1H); $^{13}$C NMR (151 MHz, Chloroform-*d*) δ 141.53, 138.88, 133.56, 132.61, 131.30, 130.61, 130.35, 128.99, 128.99 (2C), 128.61, 127.80, 127.60, 127.58 (2C), 127.55, 127.35, 127.10, 126.96, 126.86, 126.29 (2C), 125.88, 125.32; IR (DRIFT, KBr) 3093, 3052, 1599, 1485, 1447, 1226, 846, 763, 702, 679 cm$^{-1}$; EI-MS m/z (%) 304 (100), 226 (55), 78 (28); HRMS (EI) calcd for $C_{24}H_{16}$ 304.1252, found 304.1255. The spectral characteristics of **3a** were in agreement with the previously published data.[34]

**2-(*p*-Tolyl)benzo[*c*]phenanthrene (3b).** Yield 27.7 mg (87%); colorless crystals: m.p. 139.7 °C (DCM/MeOH); $^1$H NMR (600 MHz, Chloroform-*d*) δ 9.34 (s, 1H), 9.19 (d, *J* = 8.5 Hz, 1H), 8.09 (d, *J* = 8.3 Hz, 1H), 8.04 (dd, *J* = 7.8, 0.7 Hz, 1H), 7.94 – 7.91 (m, 2H), 7.88 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.86 – 7.82 (m, 2H), 7.72 – 7.68 (m, 3H), 7.66 – 7.62 (m, 1H), 7.40 – 7.31 (m, 2H), 2.46 (s, 3H); $^{13}$C NMR (151 MHz, Chloroform-*d*) δ 138.81, 138.62, 137.19, 133.53, 132.46, 131.29, 130.62, 130.37, 129.71 (2C), 128.93, 128.59, 127.81, 127.54, 127.51, 127.40 (2C), 127.10, 126.87, 126.78, 126.24, 125.97, 125.83, 125.24, 21.15; IR (DRIFT, KBr) 3039, 1602, 1499, 845, 829, 815, 787, 746, 676 cm$^{-1}$; EI-MS m/z (%) 318 (100), 302 (10), 226 (60), 92 (33); HRMS (EI) calcd for $C_{25}H_{18}$ 318.1409, found 318.1405.

**2-(4-Methoxyphenyl)benzo[*c*]phenanthrene (3c).** Yield 29.8 mg (89%); a colorless amorphous solid: m.p. 116.2 °C; $^1$H NMR (600 MHz, Chloroform-*d*) δ 9.31 (bs, 1H), 9.20 (d, *J* = 8.6 Hz, 1H), 8.07 (d, *J* = 8.2 Hz, 1H), 8.04 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.93 – 7.91 (m, 2H), 7.88 – 7.80 (m, 3H), 7.76 – 7.68 (m, 3H), 7.64 (ddd, *J* = 7.9, 6.8, 1.1 Hz, 1H), 7.10 – 7.05 (m, 2H), 3.90 (s, 3H); $^{13}$C NMR (151 MHz, Chloroform-*d*) δ 159.25, 138.48, 133.97, 133.52, 132.24, 131.29, 130.64, 130.37, 128.92, 128.59, 128.56 (2C), 127.78, 127.51, 127.45, 127.10, 126.87, 126.64, 126.22, 125.80, 125.60, 125.07, 114.44 (2C), 55.40; IR (DRIFT, KBr) 3046, 3005, 2931, 2833, 1608, 1510, 1499, 1284, 1247, 1180, 1038, 1028, 847, 834, 791, 752 cm$^{-1}$; EI-MS m/z (%) 334 (100), 319 (25), 289 (23), 276 (16), 263 (11), 226 (45), 108 (18); HRMS (APCI) calcd for $C_{25}H_{18}O$ 334.13522, found 334.13535.

**2-(4-(Trifluoromethyl)phenyl)benzo[*c*]phenanthrene (3d).** Yield 29.8 mg (80%); colorless crystals: m.p. 160.6 °C (DCM/MeOH); $^1$H NMR (600 MHz, Chloroform-*d*) δ 9.35 (s, 1H), 9.13 (d, *J* = 8.4 Hz, 1H), 8.12 (d, *J* = 8.3 Hz, 1H), 8.06 (d, *J* = 7.9 Hz, 1H), 7.94 (d, *J* = 8.5 Hz, 2H), 7.91 – 7.84 (m, 5H), 7.78 (d, *J* = 8.1 Hz, 2H), 7.71 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.66 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1H); $^{13}$C NMR (151 MHz, Chloroform-*d*) δ 145.05, 137.28, 133.60, 133.03, 131.37, 130.55, 130.22, 129.37 (q, *J* = 30.4 Hz), 129.27, 128.71, 127.81, 127.77 (3C), 127.61, 127.50 (2C), 127.01, 126.83, 126.71, 126.41, 126.03, 125.91 (q, *J* = 3.7 Hz), 124.99, 124.32 (q, *J* = 271.9 Hz); IR (DRIFT, KBr) 3050, 1614, 1326, 1164, 1111, 1071, 847, 831, 787, 750 cm$^{-1}$; EI-MS m/z (%) 372 (100), 331 (9), 302 (17), 226 (35), 145 (15); HRMS (EI) calcd for $C_{25}H_{15}F_3$ 372.1126, found 372.1123.

**3-Phenylbenzo[*c*]phenanthrene (4a).** Yield 25.9 mg (85%); colorless crystals: m.p. 145.1 °C (DCM/MeOH) (Lit.[35] 138-139 °C, HOAc); $^1$H NMR (400 MHz, Chloroform-*d*) δ 9.23 – 9.16 (m, 2H), 8.24 (d, *J* = 2.0 Hz, 1H), 8.04 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.99 – 7.82 (m, 7H), 7.72 (ddd, *J* = 8.5, 6.9, 1.5 Hz, 1H), 7.65 (ddd, *J* = 7.5, 7.0, 1.2 Hz, 1H), 7.57 – 7.51 (m, 2H), 7.45 – 7.40 (m, 1H); $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 140.61, 138.33, 133.86, 133.55, 131.07, 130.31, 129.48, 128.94 (2C), 128.58, 128.43, 127.85, 127.70, 127.50, 127.48, 127.36 (2C), 127.29, 127.27, 126.86, 126.34, 126.19, 125.92, 125.37; IR (DRIFT, KBr) 3050, 2923, 1597, 1486, 1422, 1230, 884, 835, 749, 696 cm$^{-1}$; EI-MS m/z (%) 304 (100), 226 (19), 77 (20); HRMS (EI) calcd for $C_{24}H_{16}$ 304.1252, found 304.1249.

**3-(*p*-Tolyl)benzo[*c*]phenanthrene (4b).** Yield 28.3 mg (89%); colorless crystals: m.p. 138.8 °C (DCM/MeOH); $^1$H NMR (400 MHz, Chloroform-*d*) δ 9.22 – 9.14 (m, 2H), 8.22 (d, *J* = 2.0 Hz, 1H), 8.04 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.98 – 7.83 (m, 5H), 7.75 – 7.69 (m, 3H), 7.64 (ddd, *J* = 7.9, 7.0, 1.1 Hz, 1H), 7.37 – 7.33 (m, 2H), 2.45 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 138.27, 137.69, 137.34, 133.89, 133.55, 130.99, 130.31, 129.68 (2C), 129.31, 128.56, 128.38, 127.86, 127.69, 127.39, 127.29, 127.22, 127.18 (2C), 126.87, 126.15, 125.99, 125.88, 125.29, 21.18; IR (DRIFT, KBr) 3045, 2917, 2854 1514, 1497, 1487, 884, 833, 815, 789, 740, 677 cm$^{-1}$; EI-MS m/z (%) 318 (100), 302 (10), 226 (14), 91 (10); HRMS (EI) calcd for $C_{25}H_{18}$ 318.1409, found 318.1407.

**3-(4-Methoxyphenyl)benzo[*c*]phenanthrene (4c).** Yield 30.8 mg (92%); colorless crystals: m.p. 151.2 °C (DCM/MeOH); $^1$H NMR (600 MHz, Chloroform-*d*) δ 9.18 (d, *J* = 6.6 Hz, 1H), 9.17 (d, *J* = 7.0 Hz, 1H), 8.18 (d, *J* = 2.1 Hz, 1H), 8.04 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.96 – 7.90 (m, 3H), 7.85

(d, *J* = 6.3 Hz, 1H), 7.84 (d, *J* = 6.3 Hz, 1H), 7.78 – 7.75 (m, 2H), 7.71 (ddd, *J* = 8.5, 6.9, 1.5 Hz, 1H), 7.65 (ddd, *J* = 7.9, 6.8, 1.1 Hz, 1H), 7.09 – 7.06 (m, 2H), 3.90 (s, 3H); $^{13}$C NMR (151 MHz, Chloroform-*d*) δ 159.36, 137.93, 133.92, 133.54, 133.07, 130.92, 130.29, 129.07, 128.55, 128.38, 128.35 (2C), 127.85, 127.64, 127.32, 127.30, 127.22, 126.87, 126.12, 125.87, 125.60, 125.12, 114.40 (2C), 55.39; IR (DRIFT, KBr) 3046, 3003, 2837, 1606, 1510, 1500, 1286, 1252, 1233, 1024, 836, 819, 792, 757, 677, 644 cm$^{-1}$; EI-MS m/z (%) 334 (100), 319 (27), 289 (31), 226 (16); HRMS (APCI) calcd for $C_{25}H_{18}O$ 334.13522, found 334.13524.

**3-(4-(Trifluoromethyl)phenyl)benzo[*c*]phenanthrene (4d).** Yield 30.5 mg (82%); colorless crystals: m.p. 178.4 °C (DCM/MeOH); $^1$H NMR (600 MHz, Chloroform-*d*) δ 9.22 (d, *J* = 8.8 Hz, 1H), 9.15 (d, *J* = 8.4 Hz, 1H), 8.24 (d, *J* = 1.9 Hz, 1H), 8.05 (d, *J* = 7.9 Hz, 1H), 7.98 – 7.84 (m, 7H), 7.81 – 7.75 (m, 2H), 7.73 (ddd, *J* = 8.4, 7.0, 1.3 Hz, 1H), 7.69 – 7.64 (m, 1H); $^{13}$C NMR (151 MHz, Chloroform-*d*) δ 144.11, 136.71, 133.75, 133.58, 131.31, 130.24, 129.98, 129.47 (q, *J* = 32.5 Hz), 128.69, 128.65, 127.81, 127.75, 127.61 (2C), 127.57 (2C), 127.17, 126.81, 126.74, 126.32, 126.05, 125.86 (q, *J* = 3.7 Hz), 125.04, 124.33 (q, *J* = 271.9 Hz); IR (DRIFT, KBr) 3047, 1614, 1412, 1330, 1157, 1128, 1110, 1071, 836 cm$^{-1}$; EI-MS m/z (%) 372 (100), 302 (10), 226 (26), 145 (12); HRMS (EI) calcd for $C_{25}H_{15}F_3$ 372.1126, found 372.1121.

**Hydroxylation of 2a and 2b:** Hydroxylation of boronate esters **2a** and **2b** was carried out according to the previously reported procedure.[31] To a solution of *N,N*-dimethyl-4-toluidine *N*-oxide (22.6 mg, 0.15 mmol) in DCM (1.5 mL) was added boronate ester **2** (35.4 mg, 0.1 mmol) and the reaction mixture was stirred at 23 °C for 5h. All volatiles were evaporated and the residue was purified by preparative TLC (ethyl acetate/hexane 1:4) to give the corresponding product **5**.

**Benzo[*c*]phenanthren-2-ol (5a).** Yield 20.3 mg (83%); a yellowish amorphous solid; $^1$H NMR (400 MHz, Chloroform-*d*) δ 9.13 (d, *J* = 8.5 Hz, 1H), 8.56 (d, *J* = 2.3 Hz, 1H), 8.01 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.95 – 7.78 (m, 4H), 7.71 – 7.58 (m, 3H), 7.23 (dd, *J* = 8.7, 2.4 Hz, 1H), 5.16 (s, 1H); $^{13}$C NMR (151 MHz, Chloroform-*d*) δ 154.12, 133.29, 131.67, 131.58, 130.49, 130.36, 128.59, 128.56, 127.61, 127.23 (2C), 126.93, 126.25, 126.11, 125.67, 124.65, 116.29, 111.59; IR (DRIFT, KBr) 3333, 3048, 1604, 1524, 1506, 1203, 839, 750, 622, 538 cm$^{-1}$; EI-MS m/z (%) 244 (100), 226 (16), 213 (26), 189 (39); HRMS (EI) calcd for $C_{18}H_{12}O$ 244.0888, found 244.0889.

**Benzo[*c*]phenanthren-3-ol (5b).** Yield 21.7 mg (89%); a yellowish amorphous solid; $^1$H NMR (600 MHz, Chloroform-*d*) δ 9.06 (d, *J* = 8.4 Hz, 1H), 9.04 (d, *J* = 9.2 Hz, 1H), 8.01 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.86 – 7.74 (m, 4H), 7.67 (ddd, *J* = 8.4, 6.8, 1.5 Hz, 1H), 7.62 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1H), 7.36 (d, *J* = 2.8 Hz, 1H), 7.27 (dd, *J* = 9.3, 2.8 Hz, 1H), 5.16 (s, 1H); $^{13}$C NMR (151 MHz, Chloroform-*d*) δ 153.34, 135.12, 133.59, 130.00, 129.84, 129.71, 128.51, 127.79, 127.63 (2C), 126.84, 126.54, 126.37, 125.96, 125.83, 125.16, 116.54, 111.23; IR (DRIFT, KBr) 3354, 3049, 1626, 1612, 1525, 1502, 1420, 1232, 866, 833, 749, 671, 572, 418 cm$^{-1}$; EI-MS m/z (%) 244 (100), 226 (12), 215 (45), 189 (36); HRMS (EI) calcd for $C_{18}H_{12}O$ 244.0888, found 244.0889. The spectral characteristics of **5b** were in agreement with the previously published data.[36]

**Supporting Information** (see footnote on the first page of this article): Crystallographic data of compounds **2a** and **2b**, $^1$H and $^{13}$CNMR spectra of all described compounds.

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**Keywords:** Borylation • C-H activation • Helicene • Homogeneous catalysis • Iridium

[1] M. Gingras, *Chem. Soc. Rev.* **2013**, *42*, 968–1006.
[2] M. Gingras, G. Félix, R. Peresutti, *Chem. Soc. Rev.* **2013**, *42*, 1007–1050.
[3] M. Gingras, *Chem. Soc. Rev.* **2013**, *42*, 1051–1095.
[4] Y. Yang, R. C. da Costa, M. J. Fuchter, A. J. Campbell, *Nat. Photonics* **2013**, *7*, 634–638.
[5] Y. Yang, R. C. da Costa, D.-M. Smilgies, A. J. Campbell, M. J. Fuchter, *Adv. Mater.* **2013**, *25*, 2624–2628.
[6] J. Storch, J. Zadny, T. Strasak, M. Kubala, J. Sykora, M. Dusek, V. Cirkva, P. Matejka, M. Krbal, J. Vacek, *Chem. – Eur. J.* **2015**, *21*, 2343–2347.
[7] P. M. op den Brouw, W. H. Laarhoven, *Recl. Trav. Chim. Pays-Bas* **1978**, *97*, 265–268.
[8] J. W. Diesveld, J. H. Borkent, W. H. Laarhoven, *Recl. Trav. Chim. Pays-Bas* **1980**, *99*, 391–394.
[9] G. Zhang, F. Rominger, M. Mastalerz, *Chem. – Eur. J.* **2016**, *22*, 3084–3093.
[10] T. Ishiyama, Y. Nobuta, J. F. Hartwig, N. Miyaura, *Chem. Commun.* **2003**, 2924–2925.
[11] T. Ishiyama, J. Takagi, K. Ishida, N. Miyaura, N. R. Anastasi, J. F. Hartwig, *J. Am. Chem. Soc.* **2002**, *124*, 390–391.
[12] J.-Y. Cho, M. K. Tse, D. Holmes, R. E. Maleczka, M. R. Smith, *Science* **2002**, *295*, 305–308.
[13] J. F. Hartwig, *Chem. Soc. Rev.* **2011**, *40*, 1992–2002.
[14] I. A. I. Mkhalid, J. H. Barnard, T. B. Marder, J. M. Murphy, J. F. Hartwig, *Chem. Rev.* **2010**, *110*, 890–931.
[15] T. Ishiyama, N. Miyaura, *Pure Appl. Chem.* **2006**, *78*, DOI 10.1351/pac200678071369.
[16] D. N. Coventry, A. S. Batsanov, A. E. Goeta, J. A. K. Howard, T. B. Marder, R. N. Perutz, *Chem. Commun.* **2005**, 2172–2174.
[17] R. Ozawa, K. Yoza, K. Kobayashi, *Chem. Lett.* **2011**, *40*, 941–943.
[18] T. Kimoto, K. Tanaka, Y. Sakai, A. Ohno, K. Yoza, K. Kobayashi, *Org. Lett.* **2009**, *11*, 3658–3661.
[19] M. N. Eliseeva, L. T. Scott, *J. Am. Chem. Soc.* **2012**, *134*, 15169–15172.
[20] S. D. Ros, A. Linden, K. K. Baldridge, J. S. Siegel, *Org. Chem. Front.* **2015**, *2*, 626–633.
[21] A. G. Crawford, Z. Liu, I. A. I. Mkhalid, M.-H. Thibault, N. Schwarz, G. Alcaraz, A. Steffen, J. C. Collings, A. S. Batsanov, J. A. K. Howard, et al., *Chem. – Eur. J.* **2012**, *18*, 5022–5035.
[22] Z. Liu, Y. Wang, Y. Chen, J. Liu, Q. Fang, C. Kleeberg, T. B. Marder, *J. Org. Chem.* **2012**, *77*, 7124–7128.
[23] S. Hitosugi, Y. Nakamura, T. Matsuno, W. Nakanishi, H. Isobe, *Tetrahedron Lett.* **2012**, *53*, 1180–1182.
[24] L. Ji, K. Fucke, S. K. Bose, T. B. Marder, *J. Org. Chem.* **2015**, *80*, 661–665.
[25] H. Shinokubo, *Proc. Jpn. Acad. Ser. B* **2014**, *90*, 1–11.
[26] Y. Koyama, S. Hiroto, H. Shinokubo, *Angew. Chem. Int. Ed.* **2013**, *52*, 5740–5743.
[27] P. Harrisson, J. Morris, T. B. Marder, P. G. Steel, *Org. Lett.* **2009**, *11*, 3586–3589.
[28] L. Zeqing, L. Zhibin, W. Yuqiang, Y. Pei, *Res. Chem. Intermed.* **2012**, *39*, 1917–1926.
[29] S. M. Preshlock, B. Ghaffari, P. E. Maligres, S. W. Krska, R. E. Maleczka, M. R. Smith, *J. Am. Chem. Soc.* **2013**, *135*, 7572–7582.
[30] Y. Saito, Y. Segawa, K. Itami, *J. Am. Chem. Soc.* **2015**, *137*, 5193–5198.
[31] C. Zhu, R. Wang, J. R. Falck, *Org. Lett.* **2012**, *14*, 3494–3497.
[32] L. M. Green, D. W. Meek, *Organometallics* **1989**, *8*, 659–666.
[33] M. Scholz, M. Mühlstädt, F. Dietz, *Tetrahedron Lett.* **1967**, *8*, 665–668.
[34] L. Peng, L. T. Scott, *J. Am. Chem. Soc.* **2005**, *127*, 16518–16521.
[35] J. Szmuszkovicz, E. J. Modest, *J. Am. Chem. Soc.* **1950**, *72*, 566–570.
[36] J. Carreras, M. Patil, W. Thiel, M. Alcarazo, *J. Am. Chem. Soc.* **2012**, *134*, 16753–16758.

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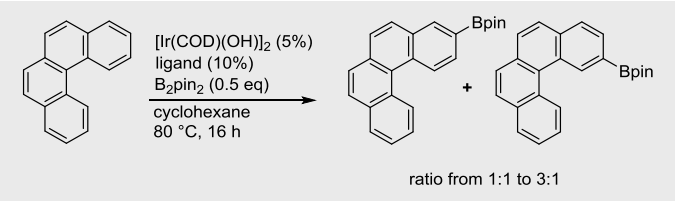


Ir-catalyzed borylation of [4]helicene has been studied. The results indicate that monoborylation proceeded to give a mixture of 2- and 3-borylated product in good yields. The use of sterically demanding ligands favored formation of the 3-borylated product. The monoborylated [4]helicenes were further arylated by using Suzuki-Miyaura cross-coupling or oxidized to the corresponding phenols in very good yields.

**C-H Activation**

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***Page No. – Page No.***

**Selective Borylation of [4]Helicene**