Synthesis of Symmetrical and Unsymmetrical 9,10-Diarylanthracene Derivatives via Bis-Suzuki–Miyaura Cross-Coupling Reaction

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Abstract: Synthesis of various 9,10-diarylanthracene derivatives via bis-Suzuki–Miyaura cross-coupling reaction as a key step is described. Availability of the 9,10-dithienylanthracenes derivatives where the thiophene unit is present in the molecule (e. g. 11, 12, 14) may provide an easy access to novel polymer and/or dendrimer preparation. In addition, we have synthesized unsymmetrical 9,10-diarylanthracene derivatives 20–25 by the Suzuki–Miyaura cross-coupling reaction, which are difficult to prepare by other transition metal-catalyzed cross-coupling reactions.

Key words: arenes, boron, coupling, palladium, polymers

Donor-acceptor compounds show various interesting properties such as electron transfer,12 photosynthetic reaction center,3,4 basic materials for nonlinear optics,5–7 photoelectrochemical reaction8,9 and photo optical devices.10 Ferrocene containing 9,10-diarylanthracene derivative is known to be an excellent electron donor. Wagner et al. have synthesized several ferrocene derivatives11 via cross-coupling reaction as a key step using palladium acetate. Various polycyclic hydrocarbons have been studied extensively with regard to fluorescence,12–14 electrochemiluminescence,15–17 enhanced chemiluminescence,18,19 photoconductivity20 and photooxidation21 properties. Recent approach towards the synthesis of heterocyclic rubicene analogs via the ring-closer of 9,10-diheteroarylanthracenes with Pd-catalyst is much simpler and gives good yield.22 In connection with the synthesis of unusual α-amino acid (AAA) derivatives, we needed a simple and useful methodology for the preparation of various 9,10-diarylanthracene derivatives.23 In this respect, a perusal of literature24–27 disclosed that 9,10-diarylanthracenes preparation involve Grignard reaction or aryllithium reagent as a key step. One shortcoming of the cross-coupling reaction with Grignard reagents is that the aryl (or alkyl) magnesium compounds used is so nucleophilic that they attack the reactive functionality present in the starting material(s) or product(s). An attempt to effect the cross-coupling of 9,10-dihaloanthracene such as 3 with Grignard reagents gave polymer under PdCl 2·dppb catalysis conditions. However, using NiCl 2·dppp catalyst, 9,10-diarylanthracene derivative was prepared using Grignard coupling reaction as a key step.28 Another useful method for the preparation 9,10-diarylanthracene derivatives involve acid-catalyzed condensation of veretrol with aromatic aldehyde.29 Recently, water soluble 9,10-dialkylanthracene derivatives have been reported via palladium catalyzed (Heck reaction) cross-coupling reaction of 9,10-dibromoanthracene with different alkenes.30

Recently, Pei et al. have synthesized thiophene-based conjugated polymer31 by a five-step sequence starting from 3-hexylthiophene. Such a kind of thiophene-derived polymer behaves like a light-emitting diode and was found to be useful as devices which also exhibit best electroluminescence performance.32,33 Meijer et al. have synthesized blue-light-emitting conjugated polymer with 9,10-diphenylanthracene unit.34 In this regard, 9,10-bis(4-formylphenyl)anthracene derivative was prepared by a four-step sequence and the monomer dialdehyde was polymerized by reductive coupling35–37 with TiCl 4/Zn. Recently, several poly aromatic hydrocarbons38 such as double-spiro anthracene 1, benzothiophene substituted anthracene 2 and various thiophene substituted anthracene derivatives are reported in the patent literature which are used as excellent electroluminescent devices (Figure 1).39 In spite of several applications of 9,10-diarylanthracenes for polymer synthesis and material science, the scope of these reactions has never been extended beyond simple 9,10-diarylanthracene derivatives.

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Figure 1 Some anthracene derivatives used as electroluminescent devices
Although various methods are available for the synthesis of biaryl derivatives via metal catalyzed cross-coupling reaction, in recent times palladium-catalyzed Suzuki-Miyaura (SM)\(^ {40-47}\) coupling reaction has been found to be one of the most efficient methods for the construction of carbon–carbon bonds in general and more specifically aryl–aryl bonds. On several instances, this methodology has been applied to generate a library of compounds for structure-activity relationships. More recently, Chen et al. has extended the SM cross-coupling methodology to prepare tert-butylated diphenylanthracene derivatives that are useful as a organic light emitting diode devices.\(^ {48}\) Herein, we would like to report the full details of our methodology towards the synthesis of various symmetrical and unsymmetrical 9,10-diarylanthracene derivatives from the inexpensive 9,10-dibromoanthracene (3)\(^ {49}\) using the Suzuki–Miyaura cross-coupling reaction as a key step (Scheme 1).

Scheme 1

Towards our goal to prepare 9,10-diarylanthracene derivatives, the 9,10-dibromoanthracene (3) was treated with phenylboronic acid in the presence of palladium(0) catalyst, Pd(PPh\(_3\))\(_4\) (7 mol\%) under aqueous base and THF–toluene solvent conditions to deliver the 9,10-diphenylanthracene (4) in 96\% yield (Scheme 2).\(^ {27}\) Later on, the Suzuki–Miyaura cross-coupling reaction was attempted with other substituted phenylboronic acids using (PPh\(_3\))\(_4\)Pd (5–10 mol\%) catalyst and the outcome of these results are shown in Table 1. Typically, 70–99\% yields of the coupling products were obtained. All the coupling products 4–10 were characterised by appropriate spectral data (UV, \(^1\)H NMR, \(^13\)C NMR, HRMS).

Scheme 2

Having prepared 9,10-diarylanthracene derivatives 4–10, next we tried to introduce heteroaryl groups in the 9,10-positions of the anthracene moiety. In this regard, we explored the SM cross-coupling reaction of 9,10-dibromoanthracene (3) with 2-thienylboronic acid using Pd(PPh\(_3\))\(_4\) (10 mol\%) as a catalyst. The coupling product 11\(^ {22b}\) (mp 242–243 °C) was obtained in 56\% yield (Table 2) and was identified by \(^1\)H NMR spectrum. Along the similar lines, other heteroaryl boronic acids were reacted with 9,10-dibromoanthracene (3), to give the corresponding 9,10-diheteroarylanthracene derivatives 11–14 and the outcome of these results are shown in Table 2.

Next goal involving stepwise Suzuki coupling reaction directed our efforts towards the preparation of unsymmetrical 9,10-diarylanthracene derivatives. In this respect, we treated the 9,10-dibromoanthracene (3) with 1.5 equivalents of 2-thienylboronic acid under the same reaction conditions and 9-bromo-10-(2-thienyl)anthracene derivative 15 (mp 175 °C) was isolated in 79\% yield (Scheme 3). Later on, a selective SM cross-coupling reaction was attempted with other heteroaryl boronic acids such as 3-thiophenecarboxylic acid, 2-furanboronic acid, 5-acetylthiopheneboronic acid, 2-benzothiopheneboronic acid using the (PPh\(_3\))\(_4\)Pd catalyst and the outcome of these results are shown in Table 3. Typically, 61–90\% yields of the coupling products were obtained. All the mono-coupling products 15–19 were characterized by appropriate spectral data (UV, \(^1\)H NMR, \(^13\)C NMR, HRMS).

Scheme 3

Towards the synthesis of unsymmetrical 9,10-diarylanthracene derivatives, initially the monobromo derivative 15 was reacted with 4-methylphenylboronic acid in the presence of Pd(PPh\(_3\))\(_4\) (10 mol\%) catalyst to give 9,10-diarylanthracene derivative 20 in 64\% yield (Scheme 4).

Scheme 4

Later on, various aryloboronic acids were reacted with 16 to generate the corresponding unsymmetrical 9,10-diarylanthracene derivatives 21–25 and the results are summarized in Table 4.

We have shown that highly functionalized 9,10-diarylanthracenes can be efficiently prepared in one-step procedure using the Suzuki–Miyaura cross-coupling reaction from the commercially available 9,10-dibromoanthracene 3. It is worth mentioning that some of the commercially available 9,10-diarylanthracenes derivatives\(^ {50}\) are very
expensive and this methodology provides an easy access to several 9,10-diarylanthracene derivatives. In addition, stepwise procedure also delivers unsymmetrical 9,10-diarylanthracene derivatives. The advantages of this approach reside in good yields, short synthetic sequence and simple operating conditions. Moreover, all the final products obtained in the present study are crystalline solids and show blue fluorescence (on TLC) in short wave length (254 nm). It may be pertinent to mention that the substrate listed in Table 1 has been prepared by a four-step sequence involving Grignard coupling reaction as a key step. Moreover, the aldehyde functionality present in 7 can be used for further synthetic manipulation. Since polycyclic anthracene derivative posses useful application in fluorescence, electrochemiluminescence and nonlinear optical materials preparation, the methodology reported here may find useful applications in material science and polymer synthesis.

Analytical TLC was performed on (10 × 5 cm) glass plate coated with Acme’s silica gel G or GF 254 (containing 13% CaSO4 as a binder). Visualization of the spot on TLC plate was achieved either by exposure to I2 vapor, or UV light. Flash chromatography was performed using Acme’s silica gel (100–200 mesh) and the column was usually eluted with EtOAc and petroleum ether (bp 60–80°C) mixture. Melting points are uncorrected. FT-IR spectra were recorded as KBr pellets unless otherwise mentioned. UV spectra were taken in CHCl3 solvent. MeCN and CCl4 were distilled over P2O5. Anhyd THF and Et2O were obtained by distillation over sodium-benzophenone ketyl. For all the reactions, anhyd MgSO4 was used as drying agent after workup. 9,10-Dibromoanthracene was purchased from Lancaster Chemical Co (UK). 4-Fluorophenylboronic acid, 4-cyanophenylboronic acid, 3-(trifluoromethyl)phenylboronic acid were obtained from Optima Chemical Groups, LLC, USA. Catalysts (PPh3)4Pd was prepared according to literature proce-

<table>
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<th>Entry</th>
<th>Boronic Acid</th>
<th>Coupling Product</th>
<th>Yield (%)</th>
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<td>2</td>
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Phenylboronic acid, 4-methylphenylboronic acid, 2-furylboronic acid, 2-thienylboronic acid were prepared according to literature procedure and the remaining other boronic acids were purchased from Lancaster Chemical Co (UK) and Aldrich Chemical Co (USA). $^1$H and $^{13}$C NMR samples were prepared in CDCl$_3$ and chemical shifts are reported in $\delta$ scale using tetramethylsilane as the internal standard. 60 MHz $^1$H NMR spectra were recorded on EM-300 spectrometer. 300 MHz $^1$H and 75.4 MHz $^{13}$C NMR spectra were recorded on Bruker spectrometer. Coupling constant ($J$) are in Hertz.

9,10-Diarylanthracene Derivatives via the Suzuki–Miyaura Cross-Coupling Reaction; General Procedure

A mixture of 9,10-dibromoanthracene (3; 1 equiv), arylboronic acid (3–5 equiv), (PPh$_3$)$_4$Pd (ca. 5–10 mol%), Na$_2$CO$_3$ (4 equiv) in H$_2$O and solvent (THF and toluene, 1:1) was heated at 80 °C under N$_2$. Typically, the coupling reaction required 4–8 h for completion. At the conclusion of the reaction (TLC monitoring), the mixture was worked up according to the general procedure. The crude product was purified by a silica gel column chromatography. Elution of the column with petroleum ether gave the desired cross-coupling product.

9,10-Diphenylanthracene (4)

A mixture of 3 (32 mg, 0.1 mmol), phenylboronic acid (51.7 mg, 0.38 mmol), [Pd(PPh$_3$)$_4$] (7.5 mg, 7 mol%), Na$_2$CO$_3$ (40 mg, 0.38 mmol) in H$_2$O (1 mL) and solvent [THF (3 mL) and toluene (3 mL)] was heated at 85 °C under N$_2$ for 6 h. At the conclusion of the reaction (TLC monitoring), the mixture was worked up according to the general procedure. The crude product was purified by a silica gel column chromatography. Elution of the column with petroleum ether gave the desired cross-coupling product 4 (30 mg, 96%) as a white crystalline solid; mp 248–250 °C (Lit. $^2$ mp 245–248 °C); $R_f$ 0.7 (petroleum ether).

$^1$H NMR (300 MHz, CDCl$_3$): $\delta = 7.29–7.46$ (m, 4 H, ArH), 7.47–7.66 (m, 10 H, ArH), 7.67–7.72 (m, 4 H, ArH).

9,10-Dibenzoxyphenylanthracene (5)

A mixture of 3 (40 mg, 0.12 mmol), 4-methoxyphenylboronic acid (58 mg, 0.39 mmol), [Pd(PPh$_3$)$_4$] (10 mg, 7 mol%), Na$_2$CO$_3$ (32 mg, 0.39 mmol) in H$_2$O (1 mL) and solvent [THF (3 mL) and toluene (3 mL)] was heated at 85 °C under N$_2$ for 6 h. At the conclusion of the reaction (TLC monitoring), the mixture was worked up according to the general procedure. The crude product was purified by a silica gel column chromatography. Elution of the column with petroleum ether gave the desired cross-coupling product 5 (40 mg, 79%) as a white crystalline solid; mp 260–264 °C (Lit. $^3$ mp 260–264 °C); $R_f$ 0.7 (petroleum ether).

$^1$H NMR (300 MHz, CDCl$_3$): $\delta = 7.29–7.46$ (m, 4 H, ArH), 7.47–7.66 (m, 10 H, ArH), 7.67–7.72 (m, 4 H, ArH).
Table 4  Unsymmetrical 9,10-Diarylanthracene Derivatives 21–25
Obtained via the SM Cross-Coupling Reaction with 9-Bromo-10-(thien-3-yl)anthracene (16)

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<th>Entry</th>
<th>Boronic Acid</th>
<th>Coupling Product</th>
<th>Yield (%)</th>
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</table>

A mixture of 3 (105 mg, 0.31 mmol), 4-formylphenylboronic acid (34 mg, 0.23 mmol), [Pd(PPh3)4] (10 mg, 10 mol%), Na2CO3 (23 mg, 0.21 mmol) in H2O (1 mL) and solvent [THF (3 mL) and toluene (3 mL)] was heated at 85 °C under N2 for 7 h. At the conclusion of the reaction (TLC monitoring), the mixture was worked up according to the general procedure. The crude product was purified by a silica gel column chromatography. Elution of the column with petroleum ether gave the desired cross-coupling product 6 (109 mg, 99%) as a white crystalline solid; mp 280–281 °C; Rf 0.5 (petroleum ether).

1H NMR (300 MHz, CDCl3): δ = 2.54 (s, 6 H, ArCH3), 7.28–7.42 (m, 12 H, ArH), 7.69–7.75 (m, 4 H, ArH).

13C NMR (75.43 MHz, CDCl3): δ = 21.6 (ArCH3), 123.6, 125.0, 127.2, 129.3, 130.2, 131.4, 136.2, 137.2.

HRMS (EI): m/z calcd for C29H22: 358.1721; found: 358.1718.


9,10-Bis(4-fluorophenyl)anthracene (9)

A mixture of 3 (505 mg, 1.5 mmol), 4-fluorophenylboronic acid (767 mg, 5.95 mmol), [Pd(PPh3)4] (171 mg, 10 mol%), Na2CO3 (630 mg) and solvent [THF (10 mL), toluene (10 mL) and H2O (4 mL)] was heated at 85 °C under N2 for 10 h. At the conclusion of the reaction (TLC monitoring), the mixture was worked up according to the general procedure. The crude product was purified by a silica gel column chromatography. Elution of the column with 4% EtOAc–petroleum ether gave the desired cross-coupling product 9 (58 mg, 85%) as a white crystalline solid; mp 226–228 °C (dec.); Rf 0.2 (10% EtOAc–petroleum ether).

IR (KBr): 1700 (CHO) cm⁻¹.

1H NMR (300 MHz, CDCl3): δ = 7.37 (dd, J = 6.8, 3.2 Hz, 4 H, ArH), 7.39 (dd, J = 6.8, 3.2 Hz, 4 H, ArH), 7.67 (d, J = 8.2 Hz, 4 H, ArH), 8.15 (d, J = 8.2 Hz, 4 H, ArH), 10.21 (s, 2 H, ArCHO).

13C NMR (75.43 MHz, CDCl3): δ = 125.6, 126.5, 129.3, 129.8, 132.0, 135.7, 136.1, 145.7, 191.9 (CHO).

HRMS (EI): m/z calcd for C29H18O2: 386.1304; found: 386.1299.

UV (CHCl3): λmax (ε) = 267 (16023), 379 (6780), 396 nm (6813).

9,10-Bis(4-cyanophenyl)anthracene (8)

A mixture of 3 (60 mg, 0.18 mmol), 4-cyanophenylboronic acid (79 mg, 0.55 mmol), [Pd(PPh3)4] (15 mg, 7 mol%), Na2CO3 (0.5 mL, 2 mol%) and solvent [THF (3 mL) and toluene (3 mL)] was heated at 85 °C under N2 for 12 h. At the conclusion of the reaction (TLC monitoring), the mixture was worked up according to the general procedure. The crude product was purified by a silica gel column chromatography. Elution of the column with 2% EtOAc–petroleum ether gave the desired cross-coupling product 8 (58 mg, 85%) as a white crystalline solid; mp 266–228 °C (dec.); Rf 0.2 (10% EtOAc–petroleum ether).

IR (KBr): 2229 (CN=) cm⁻¹.

1H NMR (300 MHz, CDCl3): δ = 7.36–7.42 (m, 4 H, ArH), 7.51–7.58 (m, 4 H, ArH), 7.60 (d, J = 8.2 Hz, 4 H, ArH), 7.92 (d, J = 8.2 Hz, 4 H, ArH).

13C NMR (75.43 MHz, CDCl3): δ = 111.7 (CN), 118.7, 125.8, 126.2, 129.2, 132.0, 132.3, 135.5, 143.9.

HRMS (EI): m/z calcd for C29H16N2: 380.1313; found: 380.1313.

UV (CHCl3): λmax (ε) = 263 (13287), 377 (8588), 394 nm (8175).

9,10-Bis(4-formylphenyl)anthracene (7)

A mixture of 3 (30 mg, 0.09 mmol), 4-formylphenylboronic acid (34 mg, 0.23 mmol), [Pd(PPh3)4] (10 mg, 10 mol%), Na2CO3 (23 mg, 0.21 mmol) in H2O (1 mL) and solvent [THF (3 mL) and toluene (3 mL)] was heated at 85 °C under N2 for 8 h. At the conclusion of the reaction (TLC monitoring), the mixture was worked up according to the general procedure. The crude product was purified by a silica gel column chromatography. Elution of the column with 4% EtOAc–petroleum ether gave the desired cross-coupling product 7 (24 mg, 70%) as a white crystalline solid; mp 272–273 °C (dec.) (Lit.52 mp >300 °C); Rf 0.4 (40% EtOAc–petroleum ether).

IR (KBr): 1700 (CHO) cm⁻¹.

1H NMR (300 MHz, CDCl3): δ = 7.38 (dd, J = 6.8, 3.2 Hz, 4 H, ArH), 7.39 (dd, J = 6.8, 3.2 Hz, 4 H, ArH), 7.67 (d, J = 8.2 Hz, 4 H, ArH), 8.15 (d, J = 8.2 Hz, 4 H, ArH), 10.21 (s, 2 H, ArCHO).

13C NMR (75.43 MHz, CDCl3): δ = 125.6, 126.5, 129.3, 129.8, 132.0, 135.7, 136.1, 145.7, 191.9 (CHO).

HRMS (EI): m/z calcd for C29H18O2: 386.1304; found: 386.1299.

UV (CHCl3): λmax (ε) = 267 (16023), 379 (6780), 396 nm (6813).

9,10-Bis(4,3-cyano-phenyl)anthracene (8)

A mixture of 3 (505 mg, 1.5 mmol), 4-cyanophenylboronic acid (767 mg, 5.95 mmol), [Pd(PPh3)4] (171 mg, 10 mol%), Na2CO3 (630 mg) and solvent [THF (10 mL), toluene (10 mL) and H2O (4 mL)] was heated at 85 °C under N2 for 10 h. At the conclusion of the reaction (TLC monitoring), the mixture was worked up according to the general procedure. The crude product was purified by a silica gel column chromatography. Elution of the column with 2% EtOAc–petroleum ether gave the desired cross-coupling product 8 (58 mg, 85%) as a white crystalline solid; mp 226–228 °C (dec.); Rf 0.2 (10% EtOAc–petroleum ether).

IR (KBr): 2229 (CN=) cm⁻¹.

1H NMR (300 MHz, CDCl3): δ = 7.36–7.42 (m, 4 H, ArH), 7.51–7.58 (m, 4 H, ArH), 7.60 (d, J = 8.2 Hz, 4 H, ArH), 7.92 (d, J = 8.2 Hz, 4 H, ArH).

13C NMR (75.43 MHz, CDCl3): δ = 111.7 (CN), 118.7, 125.8, 126.2, 129.2, 132.0, 132.3, 135.5, 143.9.

HRMS (EI): m/z calcd for C29H16N2: 380.1313; found: 380.1313.

UV (CHCl3): λmax (ε) = 263 (13287), 377 (8588), 394 nm (8175).
silica gel column chromatography. Elution of the column with petroleum ether gave the desired cross-coupling product 9 (544 mg, 99%) as a white crystalline solid; mp >300 °C; Rf 0.6 (petroleum ether).

1H NMR (300 MHz, CDCl₃): δ = 7.26–7.38 (m, 8 H, ArH), 7.40–7.46 (m, 4 H, ArH), 7.63–7.69 (m, 4 H, ArH).

13C NMR (75.43 MHz, CDCl₃): δ = 115.4 (21.2), 125.1, 126.6, 129.8, 132.7 (7.7), 134.5 (3.4), 136.0, 162.2 (245.9). Values in parentheses are c13C, 19F couplings in Hertz.

HRMS (EI): m/z calcd for C₂₂H₁₄F₂ (M⁺): 366.1220; found: 366.1220.

UV (CHCl₃): λ max (ε) = 263 (10769), 375 (5929), 394 nm (5406).

9.10-Bis(3-trifluoromethyl)phenyl)anthracene (10)
A mixture of 3 (50 mg, 0.15 mmol), 3-trifluoromethylphenylboronic acid (107 mg, 0.6 mmol), [Pd(PPh₃)₄] (10 mg, 6 mol%), Na₂CO₃ (1 mL, 2 M) and solvent [THF (3 mL) and toluene (3 mL)] was heated at 85 °C under N₂ for 11 h. At the conclusion of the reaction (TLC monitoring), the mixture was worked up according to the general procedure. The crude product was purified by a silica gel column chromatography. Elution of the column with petroleum ether gave the desired cross-coupling product 10 (71 mg, 99%) as a white crystalline solid; mp 251–252 °C; Rf 0.6 (petroleum ether).

1H NMR (300 MHz, CDCl₃): δ = 7.35–7.41 (m, 4 H, ArH), 7.57–7.63. (m, 4 H, ArH), 7.63–7.86 (m, 8 H, ArH).

13C NMR (75.43 MHz, CDCl₃): δ = 124.4, 124.5, 125.5, 126.4, 127.8, 127.84, 127.88, 128.95, 129.88, 129.9, 131.0, 134.5, 135.7, 139.6.

HRMS (EI): m/z calcd for C₂₆H₇₃F₆ (M⁺): 466.1156; found: 466.1156.

UV (CHCl₃): λ max (ε) = 262 (16375), 374 (7633), 393 nm (6963).

9.10-Bis(2-thienyl)anthracene (11)
A mixture of 3 (25 mg, 0.07 mmol), 2-thienylboronic acid (47 mg, 0.37 mmol), [Pd(PPh₃)₄] (10 mg, 6 mol%), Na₂CO₃ (39 mg, 0.37 mmol) in H₂O (1 mL) and solvent [THF (3 mL) and toluene (3 mL)] was heated at 85 °C under N₂ for 12 h. At the conclusion of the reaction (TLC monitoring), the mixture was worked up according to the general procedure. The crude product was purified by a silica gel column chromatography. Elution of the column with petroleum ether gave the desired cross-coupling product 11 (15 mg, 56%) as a yellow crystalline solid; mp 175 °C; Rf 0.8 (petroleum ether).

1H NMR (300 MHz, CDCl₃): δ = 7.21–7.22 (m, 2 H, thiophene-H), 7.31 (dd, J = 5.1, 3.4 Hz, 2 H, thiophene-H), 7.38–7.42 (m, 4 H, ArH). 7.62 (dd, J = 5.1, 3.4 Hz, 2 H, thiophene-H), 7.84–7.88 (m, 4 H, ArH).

13C NMR (75.43 MHz, CDCl₃): δ = 112.1, 123.7, 124.4, 125.9, 126.4, 130.3, 131.0, 140.1, 141.3.

HRMS (EI): m/z calcd for C₃₀H₁₈S₂ (M⁺): 442.0849; found: 442.0851.

UV (CHCl₃): λ max (ε) = 254 (15288), 394 nm (7251).

Anal. Calcd for C₂₂H₁₄O₂: C, 85.13; H, 4.5; Found: C, 84.77; H, 4.65.

9.10-Bis(benzo[b]2-thienyl)anthracene (14)
A mixture of 3 (30 mg, 0.09 mmol), benzo[b]thiophene-2-boronic acid (79 mg, 0.45 mmol), [Pd(PPh₃)₄] (10 mg, 10 mol%), Na₂CO₃ (37 mg, 0.35 mmol) in H₂O (1 mL) and solvent [THF (3 mL) and toluene (3 mL)] was heated at 85 °C under N₂ for 14 h. At the conclusion of the reaction (TLC monitoring), the mixture was worked up according to the general procedure. The crude product was purified by a silica gel column chromatography. Elution of the column with petroleum ether gave the desired cross-coupling product 14 (25 mg, 64%) as a yellow crystalline solid; mp >300 °C; Rf 0.6 (petroleum ether).

1H NMR (300 MHz, CDCl₃): δ = 7.31–7.52 (m, 10 H, ArH), 7.92–8.00 (m, 8 H, ArH).

13C NMR (75.43 MHz, CDCl₃): δ = 112.1, 122.1, 123.7, 124.4, 124.6, 125.9, 126.4, 130.3, 131.0, 140.1, 141.3.

HRMS (EI): m/z calcd for C₃₉H₁₈S₂ (442.08, M⁺): 442.0849; found: 442.0851.

UV (CHCl₃): λ max (ε) = 254 (21850), 382 (5782), 401 nm (5098).

Anal. Calcd for C₃₀H₁₈S₂: C, 81.43; H, 4.10; Found: C, 81.34; H, 4.49.

9-Bromo-10-(thien-2-yl)anthracene (15)
A mixture of 3 (35 mg, 0.10 mmol), 2-thienyloboronic acid (26 mg, 0.20 mmol), [Pd(PPh₃)₄] (12 mg, 10 mol%), Na₂CO₃ (2 M, 0.5 mL) and solvent [THF (3 mL) and toluene (3 mL)] was heated at 85 °C under N₂ for 8 h. At the conclusion of the reaction (TLC monitoring), the mixture was worked up according to the general procedure. The crude product was purified by a silica gel column chromatography. Elution of the column with petroleum ether gave the recovered starting material 3 (15 mg) and the desired cross-coupling product 15 (16 mg, 79%, based on the recovered starting material 3) as a yellow crystalline solid; mp 175 °C; Rf 0.8 (petroleum ether).
A mixture of 3 (400 mg, 0.19 mmol), 3-thienylboronic acid (304 mg, 2.38 mmol), [Pd(PPh₃)₄] (75 mg, 0.55 mol%), Na₂CO₃ (2 M, 5 mL) and solvent [THF (20 mL) and toluene (20 mL)] was heated at 85 °C under N₂ for 10 h. At the conclusion of the reaction (TLC monitoring), the mixture was worked up according to the general procedure. The crude product was purified by a silica gel column chromatography. Elution of the column with petroleum ether gave the recovered starting material 3 (190 mg) and the desired cross-coupling product 16 (210 mg, 90%, based on the recovered starting material 3) as a yellow crystalline solid; mp 159–161 °C; Rₖ 0.35 (petroleum ether).

HRMS (EI): \( m/z \) calcd for C₁₈H₁₁BrS: 337.9764; found: 337.9761.

UV (CHCl₃): \( \lambda_{\text{max}} (\varepsilon) = 255 \) (14451), 381 (7482), 400 nm (7122).

9-Bromo-10-thien-3-ylanthracene (16) A mixture of 3 (35 mg, 0.10 mmol), 2-furfurylboronic acid (23 mg, 0.20 mmol), [Pd(PPh₃)₄] (10 mg, 8 mol%), Na₂CO₃ (2 M, 0.5 mL) and solvent [THF (3 mL) and toluene (3 mL)] was heated at 85 °C under N₂ for 9 h. At the conclusion of the reaction (TLC monitoring), the mixture was worked up according to the general procedure. The crude product was purified by a silica gel column chromatography. Elution of the column with petroleum ether gave the recovered starting material 3 (7 mg) and the desired cross-coupling product 17 (11.5 mg, 65%, based on the recovered starting material 3) as a yellow crystalline solid; mp 159–161 °C; Rₖ 0.35 (petroleum ether).

HRMS (EI): \( m/z \) calcd for C₂₀H₁₃BrO (379.98, M⁺): 379.9870; found: 379.9870.

UV (CHCl₃): \( \lambda_{\text{max}} (\varepsilon) = 257 \) (11465), 380 (7476), 400 nm (6949).

9-Bromo-10-(thien-2-yl)anthracene (17) A mixture of 3 (30 mg, 0.09 mmol), 5-acetylthiophene-2-boronic acid (20 mg, 0.146 mmol), [Pd(PPh₃)₄] (8 mg, 9 mol%), Na₂CO₃ (2 M, 0.5 mL) and solvent [THF (2 mL) and toluene (2 mL)] was heated at 85 °C under N₂ for 18 h. At the conclusion of the reaction (TLC monitoring), the mixture was worked up according to the general procedure. The crude product was purified by a silica gel column chromatography. Elution of the column with petroleum ether gave the recovered starting material 3 (18 mg) and the desired cross-coupling product 19 (9 mg, 61%, based on the recovered starting material 3) as a semi-solid; Rₖ 0.6 (20% EtOAc–petroleum ether).

IR (KBr): 1661 cm⁻¹.

UV (CHCl₃): \( \lambda_{\text{max}} (\varepsilon) = 260 \) (71106), 382 (892), 400 nm (869).

9-(4-Methylphenyl)-10-(thien-2-yl)anthracene (20) A mixture of 15 (15 mg, 0.04 mmol), 4-methylphenylboronic acid (11.5 mg, 0.08 mmol), [Pd(PPh₃)₄] (5 mg, 10 mol%), Na₂CO₃ (2 M, 0.5 mL) and solvent [THF (2 mL) and toluene (2 mL)] was heated at 85 °C under N₂ for 8 h. At the conclusion of the reaction (TLC monitoring), the mixture was worked up according to the general procedure. The crude product was purified by a silica gel column chromatography. Elution of the column with petroleum ether gave the desired cross-coupling product 20 (10 mg, 64%) as a white crystalline solid; mp 184–186 °C; Rₖ 0.75 (petroleum ether).

HRMS (EI): \( m/z \) calcd for C₂₅H₂₁S (M⁺): 350.1129; found: 350.1124.

UV (CHCl₃): \( \lambda_{\text{max}} (\varepsilon) = 265 \) (12562), 378 (9650), 396 nm (9091).

9-(4-Methylphenyl)-10-(thien-3-yl)anthracene (21) A mixture of 16 (25 mg, 0.07 mmol), 4-methylphenylboronic acid (20 mg, 0.146 mmol), [Pd(PPh₃)₄] (8 mg, 9 mol%), Na₂CO₃ (2 M, 0.5 mL) and solvent [THF (3 mL) and toluene (3 mL)] was heated at 85 °C under N₂ for 11.5 h. At the conclusion of the reaction (TLC monitoring), the mixture was worked up according to the general procedure. The crude product was purified by a silica gel column chromatography. Elution of the column with petroleum ether gave the desired cross-coupling product 21 (22 mg, 85%) as a white crystalline solid; mp 196–197 °C; Rₖ 0.75 (petroleum ether).

HRMS (EI): \( m/z \) calcd for C₂₅H₂₁O₃ (M⁺): 378.9921; found: 378.9913.

UV (CHCl₃): \( \lambda_{\text{max}} (\varepsilon) = 260 \) (6676), 382 (895), 402 nm (869).
A mixture of 16 (25 mg, 0.07 mmol), 4-fluorophenylboronic acid (22 mg, 0.15 mmol), [Pd(PPh3)4] (8 mg, 9 mol%) and Na2CO3 (2 M, 0.5 mL) was heated at 85 °C under N2 for 9 h. At the conclusion of the reaction (TLC monitoring), the mixture was worked up according to the general procedure. The crude product was purified by a silica gel column chromatography. Elution of the column with petroleum ether gave the desired cross-coupling product 23 (23.5 mg, 99%) as a white crystalline solid; mp 256–257 °C; Rf 0.4 (30% EtOAc–petroleum ether).

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