Supporting Information for

Rhodium-Catalyzed Oxidative Annulation of (2-Arylphenyl)boronic Acids with Alkynes: Selective Synthesis of Phenanthrene Derivatives

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Contents

I. General Information 2
II. Materials 2
III. Experimental Details for KIE Measurement 3
IV. Spectroscopic Data 5
V. ¹H and ¹³C NMR Spectra 10
VI. References 26
I. General Information

Nuclear magnetic resonance spectra were measured with Bruker AVANCEIII-400 spectrometer operating at 400 MHz (\(^1\)H NMR), at 100 MHz (\(^{13}\)C NMR), and at 376 MHz (\(^{19}\)F NMR) in 5 mm NMR tubes. All \(^1\)H NMR chemical shifts were reported in ppm relative to the resonance in TMS at \(\delta 0.00\). All \(^{13}\)C NMR chemical shifts were reported in ppm relative to carbon resonance in chloroform-\(d_1\) at \(\delta 77.16\). Melting points were measured with Mettler Toledo MP90. High resolution mass spectra (HRMS-TOF) were recorded on Bruker micrOTOF II-H3. GC spectra were recorded on Shimadzu GC-8A with Shimadzu silicon OV-17 column (2.6 mm × 1.5 m). GC-MS spectra were recorded on Shimadzu GC-2010 Plus and GCMS-QP2010 SE with Shimadzu CBP-1 column (0.5 mm × 25 m). Silica gel column chromatography was performed using Wakosil® C-200 (64—210 µm).

II. Materials

DMF and toluene were dried and deoxygenated by Grubbs column (Glass Counter Solvent Dispanding System, Nikko Hansen & Co., Ltd.). The rhodium complex [Cp*RhCl\(_2\)]\(_2\) were prepared according to the literature procedure.\(^1\)

- Preparation of (2-arylphenyl)boronic acids,
  To a solution of the corresponding aryl bromide (1.0 mmol in 3.0 mL THF), tBuLi (1.1 mmol as 1.6 mol/L hexane solution) was added dropwise at -78°C and stirred for 0.5 h. After the addition of B(OMe)_3 (1.3 mmol), the resulting mixture was allowed to warm to room temperature and stirred for another 1 h. Diluted aqueous hydrogen chloride (1.0 mol/L, 7.0 mL) was added. The residue was extracted with DCM three times and combined organic layers were dried over Na\(_2\)SO\(_4\). After removal of the solvent, further purification was carried out as follows:

  1b (CAS Reg. No. 1061350-97-7): wash with hexane (60% yield)
  1c (CAS Reg. No. 943341-68-2): column chromatography with hexane/ethyl acetate (75:25, v/v) as eluent (38% yield)
  1d (CAS Reg. No. 219540-53-1): wash with hot hexane (44% yield)
  1e (CAS Reg. No. 1265312-61-5): column chromatography with hexane/ethyl acetate (75:25, v/v) and recrystallization from hexane (36% yield)

All other reagents were purchased from commercial resources and used without further purification.
III. Deuterium-labeling experiments

• H–D Exchange experiment (Scheme 3A)

The deuterated boronic ester 1a–d₅ (0.25 mmol) was treated with alkyne 2a (0.25 mmol) in the presence of [Cp*RhCl₂]₂ (2.0 mol%) and Cu(OAc)₂•H₂O (10 mol%) at 100 °C in DMF (3 mL) for 3 min. under air. The reaction mixture was then poured into water and extracted with DCM for three times. The combined organic layers were dried over Na₂SO₄. After removal of the solvent in vacuo, the residue was subjected to silica gel column chromatography (eluent: hexane to hexane/EtOAc = 3/1) to give 3aa–d₄ along with recovered 1a–d₅ in 25% yield and 75% yield, respectively.

• KIE measurement for a competition reaction

A 1:1 mixture of 1a (0.125 mmol) and 1a–d₅ (0.125 mmol) was treated with alkyne 2a (0.25 mmol) in the presence of [Cp*RhCl₂]₂ (2.0 mol%) and Cu(OAc)₂•H₂O (10 mol%) at 100 °C in DMF (3 mL) for 3 min. under air. The reaction mixture was then poured into water and extracted with DCM for three times. The combined organic layers were dried over Na₂SO₄. After removal of the solvent in vacuo, the residue was subjected to silica gel column chromatography with hexane as eluent to give a mixture of 3aa and 3aa–d₄, of which ratio (3aa:3aa–d₄ = 49:51) was determined by the integration value for aromatic protons in ¹H NMR analysis.

• KIE measurement for a set of parallel reactions

The boronic acid 1a (0.25 mmol) or 1a–d₅ (0.25 mmol) was treated with alkyne 2a (0.25 mmol) in the presence of [Cp*RhCl₂]₂ (2.0 mol%) and Cu(OAc)₂•H₂O (10 mol%) at 100 °C in DMF (3 mL). The reaction progress was monitored by GC measurement.
B(OH)$_2$ + \( ^{\text{nPr}}\text{nPr} \) + [Cp*RhCl$_2$]$_2$ (2.0 mol%) \[ \text{Cu(OAc)}_2 \cdot \text{H}_2\text{O} \ (10 \text{ mol%}) \] DMF, 100 °C, air

\[ \text{yield} \ (\%): y = 3.86x + 2.58 \quad R^2 = 0.9831 \]

\[ \text{GC yield [\%]} \quad \text{time [min.]} \]

1a – d$_5$ + \( ^{\text{nPr}}\text{nPr} \) + [Cp*RhCl$_2$]$_2$ (2.0 mol%) \[ \text{Cu(OAc)}_2 \cdot \text{H}_2\text{O} \ (10 \text{ mol%}) \] DMF, 100 °C, air

\[ \text{yield} \ (\%): y = 3.465x + 2.13 \quad R^2 = 0.9802 \]
IV. Spectroscopic Data

9,10-diphenylphenanthrene (3ab)
[CAS Reg. No. 602-15-3]

\[
\begin{array}{c}
\text{Ph} & \text{Ph} \\
\end{array}
\]

Purified by column chromatography with hexane/toluene (91:9, v/v) as eluent (66.3 mg, 81%); white solid; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.13-7.27 (m, 10H), 7.49 (ddd, \(J = 8.1, 7.0, 1.1\) Hz, 2H), 7.56 (dd, \(J = 8.3, 1.3\) Hz, 2H), 7.67 (ddd, \(J = 8.3, 6.8, 1.4\) Hz, 2H), 8.81 (d, \(J = 8.3\) Hz, 2H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 122.6, 126.5, 126.6, 126.8, 127.7, 128.0, 130.1, 131.2, 132.0, 137.3, 139.7; HRMS \(m/z\) calcd for C\(_{26}\)H\(_{19}\) (M\(^+\)) 331.1481, found 331.1471.

9,10-bis(4-methoxyphenyl)phenanthrene (3ac)
[CAS Reg. No. 103162-61-4]

\[
\begin{array}{c}
\text{MeO} & \text{OMe} \\
\end{array}
\]

Purified by recrystallization from toluene and preparative GPC (63.5 mg, 65%); white solid; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 3.81 (s, 6H), 6.78-6.83 (m, 4H), 7.04-7.09 (m, 4H), 7.48 (ddd, \(J = 8.0, 7.1, 0.9\) Hz, 2H), 7.59 (d, \(J = 7.6\) Hz, 2H), 7.65 (ddd, \(J = 8.2, 6.9, 1.3\) Hz, 2H), 8.80 (d, \(J = 8.2\) Hz, 2H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 55.3, 113.3, 122.6, 126.4, 126.7, 128.0, 130.1, 132.15, 132.19, 132.5, 137.3, 158.1; HRMS \(m/z\) calcd for C\(_{28}\)H\(_{23}\)O\(_2\) (M+H\(^+\)) 391.1693, found 391.1683.

9,10-bis(4-(trifluoromethyl)phenyl)phenanthrene (3ad)
[CAS Reg. No. 1628571-65-2]

\[
\begin{array}{c}
\text{CF}_3 & \text{CF}_3 \\
\end{array}
\]

Purified by column chromatography with hexane as eluent and preparative GPC (69.0 mg, 59%); white solid; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.28 (d, \(J = 7.9\) Hz, 4H), 7.44 (dd, \(J = 8.3, 1.0\) Hz, 2H),
7.50-7.57 (m, 6H), 7.72 (ddd, J = 8.3, 7.8, 1.4 Hz, 2H), 8.84 (d, J = 8.3 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 122.9, 124.2 (q, J = 270.5 Hz), 125.0 (q, J = 4.7 Hz), 127.2, 127.6, 129.3 (q, J = 32.4 Hz), 130.3, 131.2, 131.4, 136.1, 143.1; HRMS m/z calcld for C$_{28}$H$_{17}$F$_6$ (M+H$^+$) 467.1229, found 467.1252.

diethyl-4,4'-(phenanthrene-9,10-diyl)dibenzoate (3ae)

CAS Reg. No. 1246739-17-2

Concentration in vacuo and subsequent trituration with hexane afforded a white precipitation, which was collected by filtration (85.4 mg, 72%); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.40 (t, J = 7.2 Hz, 6H), 4.37 (q, J = 7.2 Hz, 4H), 7.22-7.26 (m, 4H), 7.43-7.54 (m, 4H), 7.70 (ddd, J = 8.3, 6.7, 1.6 Hz, 2H), 7.91-7.97 (m, 4H), 8.83 (d, J = 8.3 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 14.5, 61.2, 122.8, 127.0, 127.1, 129.1, 129.2, 130.3, 131.2, 131.3, 136.4, 144.3, 166.6; HRMS m/z calcld for C$_{32}$H$_{27}$O$_4$ (M+H$^+$) 475.1904, found 475.1880.

9,10-bis(methoxymethyl)phenanthrene (3af)

CAS Reg. No. 13935-65-4

Purified by column chromatography with hexane/toluene (83:17, v/v) as eluent (38.1 mg, 57%); yellow solid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.56 (s, 6H), 5.08 (s, 4H), 7.62-7.70 (m, 4H), 8.23-8.30 (m, 2H), 8.68-8.75 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 58.5, 68.2, 122.9, 125.8, 126.9, 127.1, 131.0, 131.1, 131.8; HRMS m/z calcld for C$_{18}$H$_{16}$O$_2$ (M$^+$) 266.1307, found 266.1303.

diethyl phenanthrene-9,10-dicarboxylate (3ag)

CAS Reg. No. 1436427-31-4

Purified by column chromatography with hexane/toluene (83:17, v/v) as eluent and preparative GPC (15.0 mg, 19%); white solid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.46 (t, J = 7.2 Hz, 6H), 4.52 (q, J = 7.2
Hz, 4H), 7.64-7.70 (m, 2H), 7.71-7.78 (m, 2H), 8.17 (dd, J = 8.2, 1.0 Hz, 2H), 8.72 (d, J = 8.3 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 14.3, 62.1, 123.0, 126.9, 127.3, 127.7, 128.5, 130.0, 131.1, 168.1; HRMS m/z calcd for C$_{20}$H$_{19}$O$_4$ (M+H$^+$) 323.1278, found 323.1248.

diethyl 2-([1,1'-biphenyl]-2-yl)maleate (3ag')

![diethyl 2-([1,1'-biphenyl]-2-yl)maleate](image)

Purified by column chromatography with hexane/toluene (83:17, v/v) as eluent and preparative GPC (14.1 mg, 17%); yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 1.13 (t, J = 7.2 Hz, 3H), 1.24 (t, J = 7.2 Hz, 3H), 3.97 (q, J = 7.2 Hz, 2H), 4.15 (q, J = 7.2 Hz, 2H), 5.92 (s, 1H), 7.29-7.49 (m, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 13.8, 14.2, 61.0, 61.6, 125.1, 127.5, 127.6, 128.3, 129.61, 129.63, 129.83, 131.0, 134.4, 140.3, 141.7, 147.0, 165.0, 167.1; HRMS m/z calcd for C$_{20}$H$_{20}$O$_4$ (M$^+$) 324.1362, found 324.1357.

ethyl 10-phenylphenanthrene-9-carboxylate (3ah)

![ethyl 10-phenylphenanthrene-9-carboxylate](image)

[Purified by column chromatography with hexane/toluene (91:9, v/v) as eluent and preparative GPC (21.6 mg, 26%); white solid; $^1$H NMR (400 MHz, CDCl$_3$) δ 0.97 (t, J = 7.2 Hz, 3H), 4.11 (q, J = 7.2 Hz, 2H), 7.41-7.55 (m, 6H), 7.62-7.75 (m, 4H), 7.90-7.96 (m, 1H), 8.77 (d, J = 8.4 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 13.9, 61.3, 122.8, 123.0, 126.0, 127.0, 127.2, 127.57, 127.59, 127.9, 128.1, 128.2, 130.1, 130.5, 130.8, 130.8, 131.0, 136.6, 138.3, 169.4; HRMS m/z calcd for C$_{23}$H$_{19}$O$_2$ (M$^+$) 327.1380, found 327.1363.]

5,6-dipropyltetraphene (3ba)

![5,6-dipropyltetraphene](image)

Purified by column chromatography with hexane/toluene (91:9, v/v) as eluent (52.8 mg, 68%); white solid; $^1$H NMR (400 MHz, CDCl$_3$) δ 1.20 (t, J = 7.3 Hz, 3H), 1.24 (t, J = 7.3 Hz, 3H), 1.73-1.92 (m, 4H), 3.09-3.19 (m, 2H), 3.19-3.30 (m, 2H), 7.50-7.58 (m, 2H), 7.60-7.68 (m, 2H), 8.04-8.15 (m, 3H),
8.55 (s, 1H), 8.85-8.92 (m, 1H), 9.20 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 15.0, 15.0, 24.0, 24.0, 32.0, 32.0, 121.7, 123.3, 123.3, 125.0, 125.6, 125.7, 125.9, 127.2, 128.2, 128.3, 128.9, 130.3, 130.3, 131.2, 131.8, 132.2, 133.8, 133.8; HRMS m/z calcd for C$_{24}$H$_{25}$ (M+H$^+$) 313.1951, found 313.1967.

2-methyl-9,10-dipropylphenanthrene (3ca)
[CAS Reg. No. 1628571-72-1]

Purified by column chromatography with hexane as eluent and preparative GPC (55.8 mg, 81%); white solid; $^1$H NMR (400 MHz, CDCl$_3$) δ 1.13-1.20 (m, 6H), 1.69-1.81 (m, 4H), 2.59 (s, 3H), 3.08-3.16 (m, 4H), 7.42 (dd, $J = 8.4$, 1.5 Hz, 1H), 7.54-7.61 (m, 2H), 7.86 (s, 1H), 8.05-8.11 (m, 1H), 8.60 (d, $J = 8.5$ Hz, 1H), 8.65-8.71 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 15.0, 22.2, 24.1, 24.2, 31.6, 31.7, 122.9, 123.0, 124.5, 124.8, 125.4, 126.2, 127.2, 127.8, 130.0, 131.1, 131.6, 133.7, 134.0, 136.2; HRMS m/z calcd for C$_{21}$H$_{25}$ (M+H$^+$) 277.1951, found 277.1939.

2-methoxy-9,10-dipropylphenanthrene (3da)
[CAS Reg. No. 1628571-78-7]

Purified by column chromatography with hexane/ethyl acetate (95:5, v/v) as eluent (71.5 mg, 98%); white solid; $^1$H NMR (400 MHz, CDCl$_3$) δ 1.167 (t, $J = 7.4$ Hz, 3H), 1.170 (t, $J = 7.4$ Hz, 3H), 1.70-1.82 (m, 4H), 3.06-3.17 (m, 4H), 3.99 (s, 3H), 7.25 (dd, $J = 9.0$, 2.6 Hz, 1H), 7.49 (d, $J = 2.6$ Hz, 1H), 7.52-7.60 (m, 2H), 8.04-8.11 (m, 1H), 8.57-8.67 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 15.0, 15.0, 23.8, 24.2, 31.8, 31.8, 55.5, 106.6, 114.8, 122.6, 124.3, 124.7, 124.9, 125.6, 125.7, 130.1, 130.4, 132.9, 133.4, 134.7, 158.4; HRMS m/z calcd for C$_{21}$H$_{25}$O (M+H$^+$) 293.1900, found 293.1910.

9,10-dipropyl-2-(trifluoromethyl)phenanthrene (3ea)
[CAS Reg. No. 1628571-76-5]

Purified by column chromatography with hexane as eluent (71.8 mg, 87%); white solid; $^1$H NMR (400 MHz, CDCl$_3$) δ 1.17 (t, $J = 7.4$ Hz, 6H), 1.68-1.82 (m, 4H), 3.10-3.20 (m, 4H), 7.61-7.71 (m,
2H), 7.78 (dd, J = 8.7, 1.5 Hz, 1H), 8.13 (dd, J = 8.0, 1.5 Hz, 1H), 8.35 (s, 1H), 8.72 (dd, J = 8.0, 1.5 Hz, 1H), 8.80 (d, J = 8.7 Hz, 1H); \[^{13}\text{C}\] NMR (100 MHz, CDCl\(_3\)) \(\delta\) 14.8, 14.9, 24.1, 24.2, 31.5, 31.7, 121.3 (q, J = 3.1 Hz), 122.2 (q, J = 4.2 Hz), 123.5, 123.9, 124.9 (q, J = 270.3), 125.1, 126.1, 127.8, 128.3 (q, J = 31.9 Hz), 129.2, 131.0, 132.1, 132.2, 133.9, 135.7; HRMS m/z calcd for \(\text{C}_{21}\text{H}_{22}\text{F}_3\) (M+H\(^+\)) 331.1668, found 331.1662.

2-phenyl-9,10-dipropylphenanthrene (3fa)

![Structure](image)

Purified by column chromatography with hexane as eluent (71.1 mg, 84%); white solid; m.p. 115-116 °C; \(^1\text{H}\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.18 (t, J = 7.3 Hz, 3H), 1.19 (t, J = 7.3 Hz, 3H), 1.71-1.88 (m, 4H), 3.12-3.25 (m, 4H), 7.39-7.45 (m, 1H), 7.50-7.57 (m, 2H), 7.58-7.65 (m, 2H), 7.74-7.81 (m, 2H), 7.85 (dd, J = 8.6, 1.9 Hz, 1H), 8.08-8.15 (m, 1H), 8.30 (d, J = 1.8 Hz, 1H), 8.70-8.76 (m, 1H), 8.78 (d, J = 8.6 Hz, 1H); \[^{13}\text{C}\] NMR (100 MHz, CDCl\(_3\)) \(\delta\) 15.0, 15.0, 24.2, 24.2, 31.6, 31.7, 123.1, 123.2, 123.7, 124.9, 124.9, 125.7, 126.7, 127.4, 127.6, 129.1, 129.1, 129.8, 131.5, 131.8, 134.1, 134.5, 139.3, 141.8; HRMS m/z calcd for \(\text{C}_{26}\text{H}_{27}\) (M+H\(^+\)) 339.2107, found 339.2105.
V. $^1$H and $^{13}$C NMR Spectra

9,10-diphenylphenanthrene (3ab)
9,10-diphenylphenanthrene (3ab)
9,10-bis(4-methoxyphenyl)phenanthrene (3ac)
9,10-bis(4-(trifluoromethyl)phenyl)phenanthrene (3ad)
diethyl-4,4’-(phenanthrene-9,10-diyl)dibenzoate (3ae)
9,10-bis(methoxymethyl)phenanthrene (3af)
diethyl phenanthrene-9,10-dicarboxylate (3ag)
diethyl 2-([1,1'-biphenyl]-2-yl)maleate (3ag’)

\[
\text{EtO}_2\text{C} = \text{CO}_2\text{Et}\n\]

![NMR spectrum](image-url)

![NMR spectrum](image-url)
ethyl 10-phenylphenanthrene-9-carboxylate (3ah)
5,6-dipropyltetraphene (3ba)
2-methyl-9,10-dipropylphenanthrene (3ca)
2-methoxy-9,10-dipropylphenanthrene (3da)
9,10-dipropyl-2-(trifluoromethyl)phenanthrene (3ea)
2-phenyl-9,10-dipropylphenanthrene (3fa)
Dimethyl-9,9'-biphenanthrene (5aa)
10,10'-Diethyl-9,9'-biphenanthrene (5ab)
VI. References