Brønsted Acid-Catalysed Hydroarylation of Unactivated Alkynes in Fluoroalcohol–Hydrocarbon Biphasic System: Construction of Phenanthrene Frameworks

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1. General Statement

$^1$H NMR, $^{13}$C NMR, and $^{19}$F NMR spectra were recorded on a Bruker Avance 500 spectrometer at 500 MHz ($^1$H NMR), at 126 MHz ($^{13}$C NMR), and 470 MHz ($^{19}$F NMR). Chemical shift values are given in ppm relative to internal Me$_4$Si (for $^1$H NMR: $\delta = 0.00$ ppm), CDCl$_3$ (for $^{13}$C NMR: $\delta = 77.0$ ppm), and C$_6$F$_6$ (for $^{19}$F NMR: $\delta = 0.00$ ppm). IR spectra were recorded on a Horiba FT-300S spectrometer by the attenuated total reflectance (ATR) method. Mass spectra were measured on a JEOL JMS-T100GCV spectrometer.

Gel permeation chromatography (GPC) was performed on a Japan Analytical Industry LC-908 apparatus equipped with a JAIGEL-1H and -2H assembly. Column chromatography was conducted on silica gel (Silica Gel 60 N, Kanto Chemical Co., Inc.). Toluene, dichloromethane, and tetrahydrofuran (THF) were purified by a solvent-purification system (GlassContour) equipped with columns of activated alumina and supported-copper catalyst (Q-5) before use. 1,1,1,3,3,3-Hexafluoropropan-2-ol (HFIP) was distilled and stored over activated molecular sieves 4A. Cyclohexane was distilled from MgSO$_4$ and stored over activated molecular sieves 4A.

1-Bromo-2-(2-phenylethynyl)benzene, 1-[2-(phenylethynyl)phenyl]boronic acid, 1-bromonaphthalen-2-yl trifluoromethanesulfonate, 2-[2,2'-binaphthalen]-1-yl trifluoromethanesulfonate, 2-[(4-methylphenyl)ethynyl]-1,1'-biphenyl (1r), 2-[(4-methoxyphenyl)ethynyl]-1,1'-biphenyl (1s), 2-[(4-chlorophenyl)ethynyl]-1,1'-biphenyl (1t), and 2-[(4-bromophenyl)ethynyl]-1,1'-biphenyl (1u) were prepared according to the literature procedures. Unless otherwise noted, materials were obtained from commercial sources and used directly without further purifications.

2. Preparation of 2-(Phenylethynyl)biaryls

[Procedure A]

A toluene (3.0 mL), ethanol (1.5 mL), and H$_2$O (1.5 mL) solution of 1-bromo-2-(phenylethynyl)benzene (1.2 mmol) was degassed by using the freeze-pump-thaw method three times. To the mixture were added PdCl$_2$(PPh$_3$)$_2$ (5–7 mol%), Na$_2$CO$_3$ (1.2–1.7 equiv), and an arylboronic acid (1.2–1.3 equiv). After stirring at 70 °C for 2–6 h under nitrogen, the reaction was quenched with an aqueous NH$_4$Cl solution. Organic materials were extracted with ethyl acetate three times. The combined extracts were washed with brine and dried over Na$_2$SO$_4$. After the solvent was removed under reduced pressure, the residue was purified by silica gel column chromatography to give the corresponding 2-(phenylethynyl)biaryl 1.
[Procedure B]

A toluene (3.0 mL), ethanol (1.5 mL), and H2O (1.5 mL) solution of an aryl halide (1.5 mmol) was degassed by using the freeze-pump-thaw method three times. To the mixture was added PdCl2(PPh3)2 (5 mol%), Na2CO3 (1.5 equiv), and [2-(phenylethynyl)phenyl]boronic acid (1.2 equiv). After stirring at 80 °C for 2–6 h under nitrogen, the reaction was quenched with an aqueous NH4Cl solution. Organic materials were extracted with ethyl acetate three times. The combined extracts were washed with brine and dried over Na2SO4. After the solvent was removed under reduced pressure, the residue was purified by silica gel column chromatography to give the corresponding 2-(phenylethynyl)biaryl 1.

2-(Phenylethynyl)-1,1'-biphenyl (1a)

Compound 1a was prepared according to Procedure A using 1-bromo-2-(phenylethynyl)benzene (316 mg, 1.23 mmol), PdCl2(PPh3)2 (43 mg, 61 µmol), Na2CO3 (162 mg, 1.5 mmol), and phenylboronic acid (176 mg, 1.4 mmol) at 70 °C for 2 h. Purification by silica gel column chromatography (hexane) gave 1a (235 mg, 75%) as a pale yellow oil.

1H NMR (500 MHz, CDCl3): δ 7.27–7.29 (m, 3H), 7.32–7.35 (m, 3H), 7.38–7.48 (m, 5H), 7.64–7.68 (m, 3H). 13C NMR (126 MHz, CDCl3): δ 89.7, 92.6, 121.9, 123.8, 127.4, 127.8, 128.2, 128.4, 128.6, 128.9, 129.7, 129.8, 131.7, 133.2, 140.9, 144.3.

Spectral data for this compound showed good agreement with literature data.7

2-Methyl-2'(phenylethynyl)-1,1'-biphenyl (1b)

Compound 1b was prepared according to Procedure A using 1-bromo-2-(phenylethynyl)benzene
(312 mg, 1.21 mmol), PdCl$_2$(PPh$_3$)$_2$ (43 mg, 61 µmol), Na$_2$CO$_3$ (160 mg, 1.5 mmol), and (2-methylphenyl)boronic acid (201 mg, 1.48 mmol) at 70 °C for 6 h. Purification by silica gel column chromatography (hexane/chloroform = 100/3) gave 1b (182 mg, 56%) as a pale yellow oil.

$^1$H NMR (500 MHz, CDCl$_3$): δ 2.20 (s, 3H), 7.11–7.13 (m, 2H), 7.15–7.17 (m, 3H), 7.22–7.33 (m, 7H), 7.58–7.60 (m, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$): δ 20.0, 88.9, 92.3, 122.8, 123.3, 125.2, 127.0, 127.5, 127.9, 128.06, 128.10, 129.4, 129.6, 129.8, 131.3, 131.6, 136.2, 140.7, 144.7. IR (neat): ν 3059, 3020, 1491, 1442, 752, 746, 687 cm$^{-1}$. HRMS (EI): m/z Calcd. for C$_{21}$H$_{16}$ [M$^+$]: 268.1247; Found: 268.1247.

3',5'-Dimethyl-2-(phenylethynyl)-1,1'-biphenyl (1c)

Compound 1c was prepared according to Procedure A using 1-bromo-2-(phenylethynyl)benzene (312 mg, 1.21 mmol), PdCl$_2$(PPh$_3$)$_2$ (47 mg, 66 µmol), Na$_2$CO$_3$ (177 mg, 1.7 mmol), and (3,5-dimethylphenyl)boronic acid (228 mg, 1.52 mmol) at 70 °C for 6 h. Purification by silica gel column chromatography (hexane) gave 1c (219 mg, 64%) as a pale yellow oil.

$^1$H NMR (500 MHz, CDCl$_3$): δ 2.39 (s, 6H), 7.04 (s, 1H), 7.28–7.29 (m, 3H), 7.30–7.31 (m, 3H), 7.32–7.35 (m, 2H), 7.38 (ddd, $J$ = 7.5, 7.5, 1.2 Hz, 1H), 7.42 (dd, $J$ = 7.5, 1.2 Hz, 1H), 7.63 (dd, $J$ = 7.5, 0.9 Hz, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$): δ 21.4, 89.6, 92.2, 121.4, 123.6, 126.8, 127.2, 128.0, 128.2, 128.4, 129.1, 129.4, 131.3, 132.8, 137.3, 140.4, 144.0. IR (neat): ν 3059, 3032, 3022, 2916, 1603, 1493, 850, 750, 687 cm$^{-1}$. HRMS (EI): m/z Calcd. for C$_{22}$H$_{18}$ [M$^+$]: 282.1403; Found: 282.1411.

4'-Methyl-2-(phenylethynyl)-1,1'-biphenyl (1d)

Compound 1d was prepared according to Procedure A using 1-bromo-2-(phenylethynyl)benzene (312 mg, 1.21 mmol), PdCl$_2$(PPh$_3$)$_2$ (43 mg, 61 µmol), Na$_2$CO$_3$ (163 mg, 1.5 mmol), and (4-methylphenyl)boronic acid (210 mg, 1.54 mmol) at 70 °C for 6 h. Purification by silica gel column chromatography (hexane) gave 1d (232 mg, 71%) as a pale yellow oil.

$^1$H NMR (500 MHz, CDCl$_3$): δ 2.43 (s, 3H), 7.25–7.32 (m, 6H), 7.35–7.42 (m, 4H), 7.58 (d, $J$ = 8.1 Hz, 2H), 7.63–7.65 (m, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$): δ 21.2, 89.5, 92.1, 121.4, 123.5, 126.8, 128.0, 128.2, 128.5, 128.6, 129.2, 129.4, 131.3, 133.0, 137.2, 137.6, 143.7.
Spectral data for this compound showed good agreement with the literature data.\(^7\)

4\(^\prime\)-(tert-Butyl)-2-(phenylethynyl)-1,1\(^\prime\)-biphenyl (1e)

![Chemical Structure](image)

Compound 1e was prepared according to Procedure A using 1-bromo-2-(phenylethynyl)benzene (310 mg, 1.20 mmol), PdCl\(_2\)(PPh\(_3\))\(_2\) (44 mg, 62 \(\mu\)mol), Na\(_2\)CO\(_3\) (168 mg, 1.6 mmol), and [4-(tert-butyl)phenyl]boronic acid (262 mg, 1.47 mmol) at 70 °C for 6 h. Purification by silica gel column chromatography (hexane) gave 1e (279 mg, 75%) as a pale yellow oil.

\(^1\)H NMR (500 MHz, CDCl\(_3\)): δ 1.38 (s, 9H), 7.24–7.27 (m, 3H), 7.28–7.32 (m, 3H), 7.35 (ddd, \(J = 7.6, 7.6, 1.4\) Hz, 1H), 7.42 (dd, \(J = 7.6, 1.3\) Hz, 1H), 7.47 (d, \(J = 8.4\) Hz, 2H), 7.60–7.63 (m, 3H).

\(^{13}\)C NMR (126 MHz, CDCl\(_3\)): δ 31.4, 34.6, 89.7, 92.2, 121.6, 123.6, 124.8, 126.8, 128.0, 128.2, 128.4, 129.0, 129.3, 131.3, 132.7, 137.6, 143.9, 150.3. IR (neat): ν 3057, 2962, 2902, 2866, 1493, 1475, 833, 750, 733, 688 cm\(^{-1}\). HRMS (EI): \(m/z\) Calcd. for C\(_{24}\)H\(_{22}\) [M]+: 310.1716; Found: 310.1716.

2\(^\prime\)-(Phenylethynyl)-[1,1\(^\prime\)-biphenyl]-4-ol (1f)

![Chemical Structure](image)

Compound 1f was prepared according to Procedure B using 4-bromophenol (262 mg, 1.52 mmol), PdCl\(_2\)(PPh\(_3\))\(_2\) (56 mg, 80 \(\mu\)mol), Na\(_2\)CO\(_3\) (292 mg, 2.75 mmol), and [2-(phenylethynyl)phenyl]boronic acid (403 mg, 1.82 mmol) at 80 °C for 6 h. Purification by silica gel column chromatography (hexane/ethyl acetate = 5/1) and GPC (chloroform) gave 1f (74 mg, 18%) as a red oil.

\(^1\)H NMR (500 MHz, CDCl\(_3\)): δ 5.61 (br s, 1H), 6.90 (d, \(J = 8.5\) Hz, 2H), 7.24–7.28 (m, 4H), 7.31–7.36 (m, 4H), 7.54 (d, \(J = 8.5\) Hz, 2H), 7.61 (d, \(J = 7.6\) Hz, 1H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)): δ 89.5, 92.1, 114.8, 121.3, 123.4, 126.6, 128.1, 128.2, 128.5, 129.3, 130.7, 131.3, 132.9, 133.2, 143.3, 155.0. IR (neat): ν 3355, 3059, 3022, 1610, 1516, 1491, 1250, 1215, 1173, 748, 688 cm\(^{-1}\). HRMS (EI): \(m/z\) Calcd. for C\(_{20}\)H\(_{14}\)O [M]+: 270.1039; Found: 270.1040.
4'-Fluoro-2-(phenylethynyl)-1,1'-biphenyl (1g)

![Structure of 1g]

Compound 1g was prepared according to Procedure A using 1-bromo-2-(phenylethynyl)benzene (315 mg, 1.22 mmol), PdCl$_2$(PPh$_3$)$_2$ (57 mg, 80 µmol), Na$_2$CO$_3$ (178 mg, 1.7 mmol), and (4-fluorophenyl)boronic acid (213 mg, 1.52 mmol) at 70 °C for 6 h. Purification by silica gel column chromatography (hexane) gave 1g (244 mg, 73%) as a pale yellow oil.

$^1$H NMR (500 MHz, CDCl$_3$): δ 7.12–7.17 (m, 2H), 7.28–7.32 (m, 3H), 7.32–7.36 (m, 3H), 7.38–7.40 (m, 2H), 7.61–7.65 (m, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$): δ 89.1, 92.4, 114.8 (d, $J_{CF}$ = 21 Hz), 121.6, 123.3, 127.2, 128.2, 128.3, 128.6, 129.4, 131.0 (d, $J_{CF}$ = 8 Hz), 131.3, 132.9, 136.6 (d, $J_{CF}$ = 3 Hz), 142.8, 162.4 (d, $J_{CF}$ = 247 Hz). $^{19}$F NMR (470 MHz, CDCl$_3$): δ 46.5–46.6 (m).

Spectral data for this compound showed good agreement with literature data.7

4'-Chloro-2-(phenylethynyl)-1,1'-biphenyl (1h)

![Structure of 1h]

Compound 1h was prepared according to Procedure A using 1-bromo-2-(phenylethynyl)benzene (313 mg, 1.22 mmol), PdCl$_2$(PPh$_3$)$_2$ (44 mg, 63 µmol), Na$_2$CO$_3$ (164 mg, 1.5 mmol), and (4-chlorophenyl)boronic acid (231 mg, 1.48 mmol) at 70 °C for 6 h. Purification by silica gel column chromatography (hexane) gave 1h (256 mg, 73%) as a pale yellow solid.

$^1$H NMR (500 MHz, CDCl$_3$): δ 7.23–7.29 (m, 4H), 7.31–7.33 (m, 4H), 7.38 (d, $J$ = 8.4 Hz, 2H), 7.56 (d, $J$ = 8.4 Hz, 2H), 7.61 (d, $J$ = 7.3 Hz, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$): δ 89.0, 92.5, 121.4, 123.1, 127.3, 128.0, 128.2, 128.3, 128.5, 129.2, 130.6, 131.3, 133.0, 133.5, 138.9, 142.4. IR (neat): ν 3059, 1489, 1471, 1088, 827, 750, 687 cm$^{-1}$. HRMS (EI): $m/z$ Calcd. for C$_{20}$H$_{13}$Cl [M]$^+$: 288.0700; Found: 288.0695.

1-{[2‘-(Phenylethynyl)-[1,1'-biphenyl]-4-yl]ethan-1-one (1i)

![Structure of 1i]

Compound 1i was prepared according to Procedure B using 4'-bromoacetophenone (302 mg,
1.52 mmol), PdCl₂(PPh₃)_2 (62 mg, 88 μmol), Na₂CO₃ (290 mg, 2.74 mmol), and [2-( phenylethynyl)phenyl]boronic acid (406 mg, 1.83 mmol) at 80 °C for 6 h. Purification by silica gel column chromatography (hexane/ethyl acetate = 10/1) gave 11 (402 mg, 89%) as an orange oil. 

¹H NMR (500 MHz, CDCl₃): δ 2.54 (s, 3H), 7.20–7.22 (m, 3H), 7.25–7.34 (m, 5H), 7.61 (d, J = 7.2 Hz, 1H), 7.69 (d, J = 8.5 Hz, 2H), 7.97 (d, J = 8.5 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃): δ 26.3, 88.6, 92.5, 121.2, 122.8, 127.5, 127.7, 128.07, 128.07, 128.4, 128.9, 129.1, 129.3, 131.0, 132.8, 135.6, 142.1, 144.9, 197.4.

Spectral data for this compound showed good agreement with literature data.

**Ethyl 2’-(phenylethynyl)-[1,1’-biphenyl]-4-carboxylate (1j)**

![Chemical structure](https://example.com/structure.png)

Compound 1j was prepared according to Procedure B using ethyl 4-bromobenzoate (344 mg, 1.50 mmol), PdCl₂(PPh₃)_2 (59 mg, 84 μmol), Na₂CO₃ (283 mg, 2.67 mmol), and [2-( phenylethynyl)phenyl]boronic acid (407 mg, 1.83 mmol) at 80 °C for 6 h. Purification by silica gel column chromatography (hexane/ethyl acetate = 30/1) gave 1j (429 mg, 87%) as a yellow solid. 

¹H NMR (500 MHz, CDCl₃): δ 1.45 (t, J = 7.2 Hz, 3H), 4.45 (q, J = 7.2 Hz, 2H), 7.31–7.33 (m, 3H), 7.35–7.44 (m, 5H), 7.71 (d, J = 7.5 Hz, 1H), 7.80 (d, J = 8.0 Hz, 2H), 8.22 (d, J = 8.0 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃): δ 14.1, 60.7, 88.7, 92.5, 121.3, 122.9, 127.5, 128.06, 128.08, 128.4, 128.9, 129.1, 129.2, 131.1, 132.8, 142.3, 144.8, 166.2. IR (neat): ν 3059, 2981, 1711, 1269, 1109, 1097, 752, 687 cm⁻¹. HRMS (EI): m/z Calcd. for C₂₅H₁₈O₂ [M⁺]: 326.1301; Found: 326.1304.

**2’-(Phenylethynyl)-[1,1’-biphenyl]-4-carbonitrile (1k)**

![Chemical structure](https://example.com/structure.png)

Compound 1k was prepared according to Procedure B using 4-bromobenzonitrile (275 mg, 1.51 mmol), PdCl₂(PPh₃)_2 (55 mg, 78 μmol), Na₂CO₃ (253 mg, 2.38 mmol), and [2-( phenylethynyl)phenyl]boronic acid (401 mg, 1.80 mmol) at 80 °C for 6 h. Purification by silica gel column chromatography (hexane/ethyl acetate = 15/1) gave 1k (412 mg, 98%) as a yellow solid. 

¹H NMR (500 MHz, CDCl₃): δ 7.26–7.30 (m, 5H), 7.31–7.37 (m, 3H), 7.62 (d, J = 7.0 Hz, 1H), 7.65 (d, J = 8.2 Hz, 2H), 7.69 (d, J = 8.2 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃): δ 88.2, 92.8, 110.9, 118.7, 121.2, 122.6, 128.0, 128.2, 128.3, 128.5, 129.0, 129.8, 131.0, 131.4, 132.9, 141.4, 144.8. IR (neat): ν 3059, 3020, 2227, 1493, 837, 837, 750, 725, 688 cm⁻¹. HRMS (EI): m/z Calcd. for C₂₁H₁₃N
\[ [M]^+ : 279.1043; \text{Found: } 279.1041. \]

**4'-Nitro-2-(phenylethynyl)-1,1'-biphenyl (1l)**

![Structure](image)

Compound 1l was prepared according to Procedure B using 1-iodo-4-nitrobenzene (377 mg, 1.51 mmol), \( \text{PdCl}_2(\text{PPh}_3)_2 \) (53 mg, 75 \( \mu \)mol), \( \text{Na}_2\text{CO}_3 \) (326 mg, 3.07 mmol), and [2-(phenylethynyl)phenyl]boronic acid (408 mg, 1.84 mmol) at 80 °C for 6 h. Purification by silica gel column chromatography (hexane/ethyl acetate = 50/1) gave 1l (398 mg, 88%) as a yellow solid.

\[^1\text{H} \text{NMR (500 MHz, CDCl}_3) : \delta 7.33–7.35 (m, 3H), 7.37–7.44 (m, 5H), 7.71 (ddd, \( J = 6.2, 1.7, 1.7 \) Hz, 1H), 7.83 (d, \( J = 8.8 \) Hz, 2H), 8.31 (d, \( J = 8.8 \) Hz, 2H). \[^1\text{C} \text{NMR (126 MHz, CDCl}_3) : \delta 88.2, 93.0, 121.4, 122.6, 122.9, 128.22, 128.24, 128.4, 128.6, 129.1, 130.0, 131.1, 133.1, 141.0, 146.8, 146.9. \]

Spectral data for this compound showed good agreement with literature data.\(^8\)

**2-(Phenylethynyl)-4'-((trifluoromethyl)-1,1'-biphenyl (1m)**

![Structure](image)

Compound 1m was prepared according to Procedure A using 1-bromo-2-(phenylethynyl)benzene (314 mg, 1.22 mmol), \( \text{PdCl}_2(\text{PPh}_3)_2 \) (61 mg, 86 \( \mu \)mol), \( \text{Na}_2\text{CO}_3 \) (217 mg, 2.05 mmol), and [4-(trifluoromethyl)phenyl]boronic acid (285 mg, 1.50 mmol) at 70 °C for 6 h. Purification by silica gel column chromatography (hexane/dichloromethane = 25/1) gave 1m (260 mg, 66%) as a white solid.

\[^1\text{H} \text{NMR (500 MHz, CDCl}_3) : \delta 7.28–7.31 (m, 3H), 7.35–7.38 (m, 1H), 7.39–7.41 (m, 2H), 7.66 (d, \( J = 7.6 \) Hz, 1H), 7.70 (d, \( J = 8.1 \) Hz, 2H), 7.76 (d, \( J = 8.1 \) Hz, 2H). \[^1\text{C} \text{NMR (126 MHz, CDCl}_3) : \delta 88.7, 92.8, 121.7, 123.0, 124.3 (q, \( J_{CF} = 272 \) Hz), 124.8 (q, \( J_{CF} = 4 \) Hz), 127.8, 128.3, 128.4, 128.6, 129.3, 129.5 (q, \( J_{CF} = 33 \) Hz), 129.7, 131.3, 133.0, 142.3, 144.2. \[^1\text{F} \text{NMR (470 MHz, CDCl}_3) : \delta 99.6 (s). \]

IR (neat): \( \nu 3060, 1321, 1165, 1119, 1109, 1066, 839, 750, 733 \text{ cm}^{-1}. \)

HRMS (EI): \( m/z \) Calcd. for \( \text{C}_{21}\text{H}_{13}\text{F}_3 [M]^+ : 322.0964; \text{Found: } 322.0963. \)
2-[2-(Phenylethynyl)phenyl]naphtalene (1n)

Compound 1n was prepared according to Procedure A using 1-bromo-2-(phenylethynyl)benzene (313 mg, 1.22 mmol), PdCl$_2$(PPh$_3$)$_2$ (45 mg, 64 µmol), Na$_2$CO$_3$ (164 mg, 1.55 mmol), and naphthalen-2-ylboronic acid (252 mg, 1.47 mmol) at 70 °C for 6 h. Purification by silica gel column chromatography (hexane) gave 1n (281 mg, 76%) as a yellow oil.

$^1$H NMR (500 MHz, CDCl$_3$): δ 7.20–7.21 (m, 3H), 7.27–7.29 (m, 2H), 7.33 (dd, $J = 7.6$ Hz, 1H), 7.40 (dd, $J = 7.6$, 7.6 Hz, 1H), 7.47–7.49 (m, 2H), 7.51 (d, $J = 7.6$ Hz, 1H), 7.68 (d, $J = 7.6$ Hz, 1H), 7.82–7.91 (m, 4H), 8.12 (s, 1H).

$^{13}$C NMR (126 MHz, CDCl$_3$): δ 89.4, 92.4, 121.7, 123.3, 126.0, 126.1, 127.1, 127.2, 127.6, 127.7, 128.1, 128.19, 128.19, 128.3, 128.6, 129.8, 131.3, 132.7, 133.0, 133.2, 138.0, 143.7.

Spectral data for this compound showed good agreement with literature data.$^6$

2-[2-(Phenylethynyl)phenyl]benzo[b]thiophene (1o)

Compound 1o was prepared according to Procedure A using 1-bromo-2-(phenylethynyl)benzene (315 mg, 1.22 mmol), PdCl$_2$(PPh$_3$)$_2$ (45 mg, 65 µmol), Na$_2$CO$_3$ (165 mg, 1.6 mmol), and benzo[b]thiophen-2-ylboronic acid (266 mg, 1.49 mmol) at 70 °C for 6 h. Purification by silica gel column chromatography (hexane) gave 1o (313 mg, 82%) as a yellow oil.

$^1$H NMR (500 MHz, CDCl$_3$): δ 7.28–7.37 (m, 7H), 7.48–7.50 (m, 2H), 7.65 (dd, $J = 6.9$, 6.9 Hz, 2H), 7.79 (d, $J = 7.5$ Hz, 1H), 7.84 (d, $J = 7.8$ Hz, 1H), 7.93 (s, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$): δ 89.3, 93.9, 121.2, 122.1, 123.3, 123.6, 123.7, 124.3, 124.4, 127.7, 128.37, 128.37, 128.6, 129.5, 131.4, 133.7, 135.8, 140.0, 140.2, 142.2. IR (neat): ν 3055, 1491, 1441, 1425, 748, 737, 721, 687, 667 cm$^{-1}$. HRMS (EI): $m/z$ Calcd. for C$_{22}$H$_{14}$S $[M]^{+}$: 310.0811; Found: 310.0810.
1-Phenyl-2-(phenylethynyl)naphthalene (1p)

A toluene (15 mL) solution of 1-bromonaphthalen-2-yl trifluoromethanesulfonate (1.18 g, 3.31 mmol) was degassed by using the freeze-pump-thaw method three times. To the solution were added Pd(OAc)$_2$ (295 mg, 1.32 mmol), PCy$_3$ (743 mg, 2.65 mmol), K$_3$PO$_4$ (3.03 g, 14.3 mmol), and phenylboronic acid (806 mg, 6.61 mmol). After stirring at 40 °C for 72 h, the reaction was quenched with an aqueous NH$_4$Cl solution. Organic materials were extracted with ethyl acetate three times. The combined extracts were washed with brine and dried over Na$_2$SO$_4$. After the solvent was removed under reduced pressure, the residue was purified by silica gel column chromatography (hexane/chloroform = 100/3–25/2) to give 1-phenynaphthalen-2-yl trifluoromethanesulfonate (906 mg, 78%) as a colourless liquid.

$^1$H NMR (500 MHz, CDCl$_3$): δ 7.39–7.41 (m, 2H), 7.46–7.58 (m, 6H), 7.64 (d, J = 8.5 Hz, 1H), 7.93 (d, J = 7.4 Hz, 1H), 7.95 (d, J = 8.9 Hz, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$): δ 118.3 (q, $J_{CF}$ = 321 Hz), 119.4, 126.8, 126.9, 127.4, 128.1, 128.4, 128.5, 129.9, 130.7, 132.5, 132.6, 133.0, 133.3, 144.1. $^{19}$F NMR (470 MHz, CDCl$_3$): δ 87.4 (s). IR (neat): ν 3060, 1419, 1201, 1136, 943, 831, 808, 750 cm$^{-1}$. HRMS (EI): m/z Calcd. for C$_{17}$H$_{11}$F$_3$O$_3$S [M]$^+$: 352.0376; Found: 352.0362.

To a THF (15 mL) solution of phenylacetylene (0.43 mL, 4.0 mmol) was added n-BuLi (1.6 M in hexane, 2.5 mL, 4.0 mmol) at 0 °C. After stirring at 0 °C for 1 h, a THF (15 mL) solution of 1-phenynaphthalen-2-yl trifluoromethanesulfonate (702 mg, 1.99 mmol) was added to the reaction mixture. After being refluxed for 3 h, the reaction was quenched with an aqueous NaHCO$_3$ solution. Organic materials were extracted with ethyl acetate three times. The combined extracts were washed with brine and dried over Na$_2$SO$_4$. After the solvent was removed under reduced pressure, the residue was purified by silica gel column chromatography (hexane/chloroform = 20/1) to give 1p (293 mg, 48%) as a colourless hard oil.

$^1$H NMR (500 MHz, CDCl$_3$): δ 7.33–7.41 (m, 5H), 7.53 (ddd, J = 8.4, 6.8, 1.4 Hz, 1H), 7.60 (ddd, J = 8.1, 6.8, 1.2 Hz, 1H), 7.62–7.65 (m, 1H), 7.66–7.69 (m, 4H), 7.85 (d, J = 8.5 Hz, 2H), 7.94 (d, J = 8.4 Hz, 1H), 7.98 (d, J = 8.1 Hz, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$): δ 90.0, 93.2, 120.1, 123.4, 126.3, 126.4, 126.6, 127.41, 127.43, 127.89, 127.94, 128.1, 128.2, 130.6, 131.3, 132.1, 133.0, 138.9, 143.0. IR (neat): ν 3057, 818, 744, 731, 696, 688, 679 cm$^{-1}$. HRMS (EI): m/z Calcd. for C$_{24}$H$_{16}$ [M]$^+$: 304.1247; Found: 304.1246.
1-(Phenylethynyl)-2,2'-binaphthalene (1q)

A DMF (7.5 mL) and Et$_3$N (7.5 mL) solution of [2,2'-binaphthalen]-1-yl trifluoromethanesulfonate (1.23 g, 3.05 mmol), PdCl$_2$(PPh$_3$)$_2$ (527 mg, 0.751 mmol), and CuI (190 mg, 1.0 mmol) was degassed by using the freeze-pump-thaw method three times. To the mixture was added phenylacetylene (0.49 mL, 4.5 mmol). After stirring at 80 °C for 9 h, the reaction was quenched with aqueous NaHCO$_3$ solution. Organic materials were extracted with ethyl acetate three times. The combined extracts were washed with brine and dried over Na$_2$SO$_4$. After the solvent was removed under reduced pressure, the residue was purified by silica gel column chromatography (hexane/chloroform = 20/1–10:1) to give 1q (902 mg, 83%) as a pale yellow hard oil.

$^1$H NMR (500 MHz, CDCl$_3$): δ 7.50–7.53 (m, 3H), 7.75–7.82 (m, 5H), 7.91 (d, $J$ = 8.5 Hz, 1H), 7.95–7.98 (m, 1H), 8.06 (d, $J$ = 8.4 Hz, 1H), 8.10 (d, $J$ = 8.1 Hz, 1H), 8.17–8.19 (m, 2H), 8.21 (d, $J$ = 8.5 Hz, 1H), 8.29 (dd, $J$ = 8.5, 1.8 Hz, 1H), 8.57 (d, $J$ = 1.3 Hz, 1H), 9.06 (d, $J$ = 8.5 Hz, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$): δ 87.6, 97.8, 118.4, 123.4, 125.99, 125.99, 126.2, 126.6, 127.1, 127.2, 127.56, 127.56, 128.0, 128.06, 128.06, 128.15, 128.15, 128.6, 128.8, 131.2, 132.1, 132.6, 133.1, 133.6, 138.4, 142.1. IR (neat): ν 3055, 1489, 904, 814, 808, 725, 646 cm$^{-1}$. HRMS (APCI+): m/z Calcd. for C$_{28}$H$_{19}$ [M + H]$^+$: 355.1481; Found: 355.1488.

3. Synthesis of Phenacenes 2

[Procedure C]

To a cyclohexane (3.0 mL) solution of a 2-(phenylethynyl)biaryl 1 (0.3 mmol) was added HFIP (0.8 mL). To the reaction mixture was added a HFIP (0.7 mL) solution of TsOH·H$_2$O (5.7 mg, 30 µmol). After stirring vigorously at room temperature for 9 h under air, dichloromethane (5 mL) was added and the resulting mixture was filtered through a pad of NaHCO$_3$ (dichloromethane). After the solvent was removed under reduced pressure, the residue was purified by silica gel column chromatography to give the corresponding phenacene 2.
9-Phenylphenanthrene (2a)

Compound 2a was synthesised according to Procedure C using 1a (76 mg, 0.30 mmol), TsOH·H₂O (6.1 mg, 32 µmol), cyclohexane (3.0 mL), and HFIP (1.5 mL). Purification by silica gel column chromatography (hexane/chloroform = 100/3) gave 2a (58 mg, 77%) as a white solid.

\[ \text{\unexpanded{\delta}} 7.40-7.44 (m, 1H), 7.46-7.53 (m, 5H), 7.55-7.58 (m, 1H), 7.60-7.63 (m, 2H), 7.65 (s, 1H), 7.84 (dd, } J = 7.7, 1.0 \text{ Hz, 1H}), 7.90 (dd, } J = 8.2, 0.9 \text{ Hz, 1H}), 8.67 (d, } J = 8.2 \text{ Hz, 1H)} \]

\[ \text{\unexpanded{\delta}} 122.5, 122.9, 126.4, 126.46, 126.54, 126.8, 126.9, 127.3, 127.5, 128.3, 128.6, 129.9, 130.0, 130.6, 131.1, 131.5, 138.7, 140.8. \]

Spectral data for this compound showed good agreement with literature data.\(^7\)

4-Methyl-10-phenylphenanthrene (2b)

Compound 2b was synthesised according to Procedure C using 1b (81 mg, 0.30 mmol), TsOH·H₂O (5.9 mg, 31 µmol), cyclohexane (3.0 mL), and HFIP (1.5 mL). Purification by silica gel column chromatography (hexane/chloroform = 20/1) and GPC (chloroform) gave 2b (67 mg, 82%) as a colourless oil.

\[ \text{\unexpanded{\delta}} 3.15 (s, 3H), 7.36-7.39 (m, 1H), 7.40-7.43 (m, 1H), 7.45-7.50 (m, 5H), 7.55-7.62 (m, 2H), 7.63 (s, 1H), 7.77 (d, } J = 8.2 \text{ Hz, 1H}), 7.87 (dd, } J = 7.5, 1.6 \text{ Hz, 1H}), 8.87 (d, } J = 8.1 \text{ Hz, 1H}) \]

\[ \text{\unexpanded{\delta}} 27.6, 125.4, 125.59, 125.62, 126.1, 127.2, 127.5, 127.9, 128.2, 128.7, 130.1, 130.6, 131.10, 131.10, 132.84, 132.84, 135.5, 139.2, 141.5. \]

IR (neat): ν 3057, 2960, 1597, 1489, 1450, 1390, 1215, 891, 808, 744, 723, 698 cm⁻¹. HRMS (EI): \text{m/z} \text{Calcd. for } C_{21}H_{16} [M]^+: 268.1247; \text{Found: } 268.1250.

1,3-Dimethyl-10-phenylphenanthrene (2c)

Compound 2c was synthesised according to Procedure C using 1c (86 mg, 0.30 mmol), TsOH·H₂O (6.1 mg, 32 µmol), cyclohexane (3.0 mL), and HFIP (1.5 mL). Purification by silica gel
column chromatography (hexane/chloroform = 20/1) gave 2c (69 mg, 80%) as a pale yellow solid. 

$^1$H NMR (500 MHz, CDCl$_3$): δ 1.93 (s, 3H), 2.47 (s, 3H), 7.10 (s, 1H), 7.28–7.31 (m, 5H), 7.43 (s, 1H), 7.44–7.47 (m, 1H), 7.49–7.53 (m, 1H), 7.70 (dd, $J = 7.8$, 1.1 Hz, 1H), 8.40 (s, 1H), 8.60 (d, $J = 8.3$ Hz, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$): δ 21.6, 25.2, 121.1, 122.9, 126.3, 126.6, 126.7, 127.7, 128.0, 128.1, 129.1, 129.3, 130.1, 130.9, 131.9, 132.5, 135.6, 135.9, 138.6, 145.4.

Spectral data for this compound showed good agreement with literature data.

2-Methyl-10-phenylphenanthrene (2d)

Compound 2d was synthesised according to Procedure C using 1d (82 mg, 0.30 mmol), TsOH·H$_2$O (6.1 mg, 32 µmol), cyclohexane (3.0 mL), and HFIP (1.5 mL). Purification by silica gel column chromatography (hexane/chloroform = 20/1) gave 2d (76 mg, 93%) as a pale yellow oil.

$^1$H NMR (500 MHz, CDCl$_3$): δ 2.43 (s, 3H), 7.43–7.55 (m, 7H), 7.58–7.61 (m, 1H), 7.62 (s, 1H), 7.67 (s, 1H), 7.82 (d, $J = 7.8$ Hz, 1H), 8.61 (d, $J = 8.7$ Hz, 1H), 8.62 (d, $J = 9.2$ Hz, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$): δ 21.7, 122.3, 122.8, 124.6, 126.36, 126.44, 127.3, 127.6, 128.2, 128.3, 128.4, 128.6, 129.98, 130.02, 131.16, 131.19, 136.2, 138.5, 141.0.

Spectral data for this compound showed good agreement with literature data.

2-(tert-Butyl)-10-phenylphenanthrene (2e)

Compound 2e was synthesised according to Procedure C using 1e (94 mg, 0.30 mmol), TsOH·H$_2$O (5.7 mg, 30 µmol), cyclohexane (3.0 mL), and HFIP (1.5 mL). Purification by silica gel column chromatography (hexane/chloroform = 20/1) gave 2e (84 mg, 90%) as a white solid.

$^1$H NMR (500 MHz, CDCl$_3$): δ 1.32 (s, 9H), 7.41–7.45 (m, 1H), 7.48–7.62 (m, 6H), 7.65 (s, 1H), 7.71 (dd, $J = 8.7$, 2.0 Hz, 1H), 7.84 (d, $J = 7.8$ Hz, 1H), 7.94 (d, $J = 2.0$ Hz, 1H), 8.65 (d, $J = 8.8$ Hz, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$): δ 31.3, 34.9, 122.4, 122.6, 122.7, 124.6, 126.39, 126.44, 127.3, 127.5, 128.2, 128.4, 129.0, 130.0, 130.8, 131.3, 138.9, 140.9, 149.2. IR (neat): ν 3057, 2962, 2902, 1614, 1485, 1454, 1373, 1269, 1215, 897, 827, 787, 744, 700, 592 cm$^{-1}$. HRMS (EI): $m/z$ Calcd. for C$_{24}$H$_{22}$ [M$^+$]: 310.1716; Found: 310.1718.

Spectral data for this compound showed good agreement with literature data.
10-Phenylphenanthren-2-ol (2f)

![Structure of 2f]

Compound 2f was synthesised according to Procedure C using 1f (66 mg, 0.24 mmol), TsOH·H₂O (4.6 mg, 24 µmol), cyclohexane (2.4 mL), and HFIP (1.2 mL). Purification by silica gel column chromatography (hexane/chloroform/ethyl acetate = 10/1/1) gave 2f (34 mg, 52%) as a pale yellow solid.

¹H NMR (500 MHz, CDCl₃): δ 5.07 (s, 1H), 7.20–7.23 (m, 2H), 7.42–7.44 (m, 1H), 7.47–7.55 (m, 5H), 7.61–7.64 (m, 2H), 7.84 (d, J = 7.8 Hz, 1H), 8.58 (d, J = 8.3 Hz, 1H), 8.64 (d, J = 8.6 Hz, 1H).

¹³C NMR (126 MHz, CDCl₃): δ 110.5, 116.4, 122.0, 124.9, 125.0, 125.9, 126.7, 127.4, 128.2, 128.4, 128.7, 129.9, 130.0, 130.5, 132.7, 137.8, 140.7, 154.1. IR (neat): ν 3511, 3354, 3057, 3024, 1614, 1454, 1214, 744, 698, 590 cm⁻¹. HRMS (APCI+): m/z Calcd. for C₂₀H₁₄O [M]+: 270.1039; Found: 270.1046.

2-Fluoro-10-phenylphenanthrene (2g)

![Structure of 2g]

Compound 2g was synthesised according to Procedure C using 1g (82 mg, 0.30 mmol), TsOH·H₂O (5.7 mg, 30 µmol), cyclohexane (3.0 mL), and HFIP (1.5 mL). Purification by silica gel column chromatography (hexane/chloroform = 20/1) gave 2g (74 mg, 91%) as a white solid.

¹H NMR (500 MHz, CDCl₃): δ 7.33–7.37 (m, 1H), 7.42–7.46 (m, 1H), 7.48–7.49 (m, 2H), 7.53–7.58 (m, 2H), 7.60–7.64 (m, 1H), 7.68 (s, 1H), 7.84 (dd, J = 7.8, 1.1 Hz, 1H), 8.57 (d, J = 8.3 Hz, 1H), 8.66–8.69 (m, 1H).

¹³C NMR (126 MHz, CDCl₃): δ 111.3 (d, J_CF = 22 Hz), 115.3 (d, J_CF = 24 Hz), 122.3, 125.2 (d, J_CF = 9 Hz), 126.6, 126.9, 127.21, 127.22, 128.5, 128.6, 128.8, 129.6, 129.9, 131.0, 132.7 (d, J_CF = 8 Hz), 138.1 (d, J_CF = 4 Hz), 140.2, 161.4 (d, J_CF = 246 Hz). ¹⁹F NMR (470 MHz, CDCl₃): δ 47.5–47.6 (m).

Spectral data for this compound showed good agreement with literature data.⁷,¹⁰

2-Chloro-10-phenylphenanthrene (2h)

![Structure of 2h]

Compound 2h was synthesised according to Procedure C using 1h (87 mg, 0.30 mmol), TsOH·H₂O (6.0 mg, 32 µmol), cyclohexane (3.0 mL), and HFIP (1.5 mL). Purification by silica gel
column chromatography (hexane/chloroform = 20/1) gave 2h (77 mg, 89%) as a pale yellow solid.

\[ ^1H \text{ NMR (500 MHz, CDCl}_3\text{): } \delta 7.41–7.50 \text{ (m, 5H), } 7.52 \text{ (dd, } J = 8.9, 2.2 \text{ Hz, 1H), } 7.54–7.61 \text{ (m, 2H), } 7.64 \text{ (s, 1H), } 7.81 \text{ (dd, } J = 7.7, 0.9 \text{ Hz, 1H), } 7.85 \text{ (d, } J = 2.2 \text{ Hz, 1H), } 8.54 \text{ (d, } J = 8.1 \text{ Hz, 1H), } 8.57 \text{ (d, } J = 8.9 \text{ Hz, 1H). } \]

\[ ^{13}C \text{ NMR (126 MHz, CDCl}_3\text{): } \delta 122.4, 124.5, 125.9, 126.8, 126.9, 127.1, 127.6, 128.5, 128.6, 128.7, 128.9, 129.4, 129.9, 131.3, 132.2, 132.5, 137.8, 140.0. \]

Spectral data for this compound showed good agreement with literature data.\(^{10}\)

1-(10-Phenylphenanthren-2-yl)ethan-1-one (2i)

\[
\begin{align*}
&\text{Compounds 2i was synthesised according to Procedure C using 1i (91 mg, 0.31 mmol),} \\
&\text{TsOH-H}_2\text{O (6.1 mg, 32 µmol), cyclohexane (3.0 mL), and HFIP (1.5 mL). Purification by silica gel} \\
&\text{column chromatography (hexane/chloroform/ethyl acetate = 10/1/1) gave 2i (71 mg, 78%) as a} \\
&\text{yellow oil.} \\
&\end{align*}
\]

\[ ^1H \text{ NMR (500 MHz, CDCl}_3\text{): } \delta 2.59 \text{ (s, 3H), } 4.42 \text{ (q, } J = 7.1 \text{ Hz, 2H), } 7.49–7.56 \text{ (m, 5H), } 7.66–7.70 \text{ (m, 2H), } 7.74 \text{ (s, 1H),} \\
&7.89–7.91 \text{ (m, 1H), } 8.20 \text{ (dd, } J = 8.7, 1.7 \text{ Hz, 1H), } 8.56 \text{ (d, } J = 1.7 \text{ Hz, 1H), } 8.69–8.71 \text{ (m, 1H), } 8.77 \text{ (d, } J = 8.7 \text{ Hz, 1H).} \\
&^{13}C \text{ NMR (126 MHz, CDCl}_3\text{): } \delta 26.5, 123.1, 123.3, 126.2, 126.8, 127.6, 128.2, 128.3, 128.5, 128.7, 128.9, 130.4, 132.4, 133.7, 134.7, 139.1, 139.9, 197.9. \]

Spectral data for this compound showed good agreement with literature data.\(^{11}\)

Ethyl 10-phenylphenanthrene-2-carboxylate (2j)

\[
\begin{align*}
&\text{Compound 2j was synthesised according to Procedure C using 1j (98 mg, 0.30 mmol),} \\
&\text{TsOH-H}_2\text{O (6.0 mg, 32 µmol), cyclohexane (3.0 mL), and HFIP (1.5 mL). Purification by silica gel} \\
&\text{column chromatography (hexane/chloroform/ethyl acetate = 15/1/1) gave 2j (77 mg, 79%) as a} \\
&\text{white solid.} \\
&\end{align*}
\]

\[ ^1H \text{ NMR (500 MHz, CDCl}_3\text{): } \delta 1.42 \text{ (t, } J = 7.1 \text{ Hz, 3H), } 4.42 \text{ (q, } J = 7.1 \text{ Hz, 2H), } 7.50–7.60 \text{ (m, 5H),} \\
&7.65–7.70 \text{ (m, 2H), } 7.75 \text{ (s, 1H), } 7.90–7.92 \text{ (m, 1H), } 8.29 \text{ (dd, } J = 8.6, 1.5 \text{ Hz, 1H), } 8.71–8.74 \text{ (m,} \\
&2H), 8.78 \text{ (d, } J = 8.2 \text{ Hz, 1H).} \]

\[ ^{13}C \text{ NMR (126 MHz, CDCl}_3\text{): } \delta 14.2, 61.0, 123.0, 123.1, 126.2, 126.8, 127.6, 127.8, 128.16, 128.23, 128.4, 128.7, 129.1, 129.2, 130.0, 130.5, 132.3, 133.5, 139.1, 140.0, 166.6. \text{ IR (neat): v 3053, 2978, 1716, 1371, 1275, 1238, 1120, 1024, 742, 700 cm}^{-1}. \text{ HRMS (EI): } \\
m/z \text{ Calcd. for C}_{23}\text{H}_{18}\text{O}_2 [M]^{+}: 326.1301; \text{ Found: 326.1304.} \]
10-Phenylphenanthrene-2-carbonitrile (2k)

Compound 2k was synthesised according to Procedure C using 1k (84 mg, 0.30 mmol), TfOH (4.8 mg, 32 µmol), cyclohexane (3.0 mL), and HFIP (1.5 mL). Purification by silica gel column chromatography (hexane/chloroform/ethyl acetate = 20/2/1) gave 2k (60 mg, 72%) as a white solid.

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.48–7.57 (m, 5H), 7.69–7.75 (m, 2H), 7.78 (s, 1H), 7.81 (dd, $J = 8.6, 1.2$ Hz, 1H), 7.91–7.93 (m, 1H), 8.25 (d, $J = 1.6$ Hz, 1H), 8.68 (d, $J = 9.0$ Hz, 1H), 8.79 (d, $J = 8.6$ Hz, 1H).

$^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 109.8, 119.3, 123.0, 124.0, 127.3, 127.7, 128.0, 128.5, 128.7, 128.86, 128.88, 129.2, 129.9, 130.8, 132.2, 132.4, 133.1, 138.0, 139.2.

Spectral data for this compound showed good agreement with literature data.$^{10,12}$

2-Nitro-10-phenylphenanthrene (2l)

Compound 2l was synthesised according to Procedure C using 1l (90 mg, 0.30 mmol), TfOH (5.1 mg, 34 µmol), cyclohexane (3.0 mL), and HFIP (1.5 mL). Purification by silica gel column chromatography (hexane/chloroform/ethyl acetate = 20/4/1) gave 2l (72 mg, 80%) as a yellow solid.

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.51–7.54 (m, 3H), 7.56–7.59 (m, 2H), 7.72–7.76 (m, 2H), 7.82 (s, 1H), 7.94–7.95 (m, 1H), 8.41 (dd, $J = 9.1, 2.4$ Hz, 1H), 8.70–8.72 (m, 1H), 8.83 (d, $J = 2.4$ Hz, 1H), 8.85 (d, $J = 10.0$ Hz, 1H).

$^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 120.1, 122.8, 123.4, 124.3, 127.3, 127.5, 128.1, 128.76, 128.81, 129.0, 129.6, 129.9, 130.8, 132.8, 134.6, 139.0, 139.2, 145.9.

Spectral data for this compound showed good agreement with literature data.$^{12}$

10-Phenyl-2-(trifluoromethyl)phenanthrene (2m)

Compound 2m was synthesised according to Procedure C using 1m (97 mg, 0.30 mmol), TsOH·H$_2$O (6.0 mg, 32 µmol), cyclohexane (3.0 mL), and HFIP (1.5 mL). Purification by silica gel column chromatography (hexane/chloroform = 20/1) gave 2m (91 mg, 94%) as a pale yellow solid.

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.43–7.51 (m, 5H), 7.59–7.64 (m, 2H), 7.70 (s, 1H), 7.78 (d, $J = 8.6$ Hz, 1H), 7.83 (d, $J = 7.8$ Hz, 1H), 8.21 (s, 1H), 8.60 (d, $J = 8.4$ Hz, 1H), 8.73 (d, $J = 8.6$ Hz, 1H).

$^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 122.2 (q, $J_{CF} = 3$ Hz), 122.9, 123.8, 124.1 (q, $J_{CF} = 4$ Hz), 124.4 (q,
$J_{CF} = 273 \text{ Hz}$, 127.1, 127.8, 127.9, 128.2 (q, $J_{CF} = 32 \text{ Hz}$), 128.6, 128.8, 128.9, 129.1, 129.9, 130.5, 132.2, 132.7, 138.6, 139.7. $^{19}$F NMR (470 MHz, CDCl$_3$): $\delta$ 99.9 (s).

Spectral data for this compound showed good agreement with literature data.$^{10,12}$

5-Phenylchrysene (2n)

![Diag3-5-Phenylchrysene.png](image)

Compound 2n was synthesised according to Procedure C using 1n (93 mg, 0.30 mmol), TsOH-H$_2$O (5.9 mg, 31 $\mu$mol), cyclohexane (3.0 mL), and HFIP (1.5 mL). Purification by silica gel column chromatography (hexane/chloroform = 20/1) gave 2n (61 mg, 65%) as a yellow solid.

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.11 (ddd, $J = 8.5$, 7.0, 1.4 Hz, 1H), 7.42–7.47 (m, 6H), 7.62 (dd, $J = 7.8$, 7.0 Hz, 1H), 7.68 (ddd, $J = 8.4$, 6.9, 1.3 Hz, 1H), 7.78 (d, $J = 8.6$ Hz, 1H), 7.83 (s, 1H), 7.90–7.94 (m, 2H), 8.00 (d, $J = 9.0$ Hz, 1H), 8.76 (d, $J = 9.0$ Hz, 2H).

$^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 122.2, 123.1, 124.6, 125.7, 126.67, 126.74, 127.0, 127.4, 128.0, 128.1, 128.4, 128.8, 128.9, 129.0, 129.9, 130.0, 130.6, 130.8, 131.4, 133.3, 138.4, 145.5.

Spectral data for this compound showed good agreement with literature data.$^6$

6-Phenylbenzo[b]naphtho[2,1-d]thiophene (2o)

![Diag3-6-Phenylbenzo[b]naphtho[2,1-d]thiophene.png](image)

Compound 2o was synthesised according to Procedure C using 1o (93 mg, 0.30 mmol), TsOH-H$_2$O (5.9 mg, 31 $\mu$mol), cyclohexane (3.0 mL), and HFIP (1.5 mL). Purification by silica gel column chromatography (hexane/chloroform = 25/1) gave 2o (65 mg, 69%) as a pale yellow solid.

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.09–7.13 (m, 2H), 7.34 (ddd, $J = 7.9$, 6.3, 1.8 Hz, 1H), 7.52–7.62 (m, 7H), 7.65 (s, 1H), 7.91 (dd, $J = 8.0$, 7.4 Hz, 2H), 8.18 (dd, $J = 8.0$, 0.6 Hz, 1H).

$^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 122.7, 123.9, 124.3, 124.8, 125.5, 126.6, 126.7, 126.8, 127.8, 128.1, 128.5, 128.6, 129.3, 130.7, 131.3, 136.6, 137.3, 138.2, 139.2, 141.3.

Spectral data for this compound showed good agreement with literature data.$^{13}$

5-Phenylbenzo[c]phenanthrene (2p)

![Diag3-5-Phenylbenzo[c]phenanthrene.png](image)

S17
Compound 2p was synthesised according to Procedure C using 1p (91 mg, 0.30 mmol), TsOH-H2O (5.9 mg, 31 µmol), cyclohexane (3.0 mL), and HFIP (1.5 mL). Purification by silica gel column chromatography (hexane/chloroform = 20/1) and GPC (chloroform) gave 2p (53 mg, 58%) as a yellow solid.

1H NMR (500 MHz, CDCl3): δ 7.44–7.47 (m, 1H), 7.51–7.55 (m, 3H), 7.57–7.63 (m, 3H), 7.65–7.70 (m, 2H), 7.77 (s, 1H), 7.80 (d, J = 8.5 Hz, 1H), 7.89 (d, J = 8.5 Hz, 1H), 8.00–8.05 (m, 1H), 9.13 (d, J = 8.4 Hz, 1H), 9.17 (d, J = 8.2 Hz, 1H). 13C NMR (126 MHz, CDCl3): δ 125.8, 125.88, 125.92, 126.2, 126.7, 126.8, 126.9, 127.39, 127.39, 127.8, 127.9, 128.2, 128.4, 128.6, 130.05, 130.05, 130.3, 130.7, 132.2, 133.5, 139.1, 140.6.

Spectral data for this compound showed good agreement with literature data.14

13-Phenylpicene (2q)

![13-Phenylpicene (2q)]

Compound 2q was synthesised according to Procedure C using 1q (104 mg, 0.29 mmol), TsOH-H2O (6.0 mg, 32 µmol), cyclohexane (4.0 mL), and HFIP (1.5 mL). Purification by silica gel column chromatography (hexane/chloroform = 20/1) and GPC (chloroform) gave 2q (45 mg, 43%) as a yellow solid.

1H NMR (500 MHz, CDCl3): δ 6.91 (ddd, J = 8.3, 6.9, 1.4 Hz, 1H), 7.17–7.20 (m, 4H), 7.34–7.36 (m, 2H), 7.39 (d, J = 8.5 Hz, 1H), 7.43 (ddd, J = 8.1, 6.9, 1.0 Hz, 1H), 7.61 (ddd, J = 8.5, 6.9, 1.4 Hz, 1H), 7.74 (d, J = 8.3 Hz, 1H), 7.80–7.85 (m, 2H), 7.86–7.89 (m, 2H), 7.90 (d, J = 8.1 Hz, 1H), 8.24 (s, 1H), 8.63 (d, J = 8.5 Hz, 1H). 13C NMR (126 MHz, CDCl3): δ 118.16, 118.22, 124.3, 124.5, 124.7, 125.3, 127.2, 127.82, 127.84, 128.36, 128.38, 128.60, 128.62, 128.7, 129.9, 130.1, 130.7, 133.1, 133.9, 134.7, 135.0, 137.1, 137.7, 137.9, 140.3, 140.6. IR (neat): ν 3051, 2922, 2852, 1585, 1518, 1491, 1444, 1365, 1309, 1215, 1024, 862, 806, 737, 688 cm⁻¹. HRMS (APCI+): m/z Calcd. for C28H19 [M + H]+: 355.1481; Found: 355.1477.

9-(4-Methylphenyl)phenanthrene (2r)

![9-(4-Methylphenyl)phenanthrene (2r)]

Compound 2r was synthesised according to Procedure C using 1r (81 mg, 0.30 mmol), TsOH-H2O (5.7 mg, 30 µmol), cyclohexane (3.0 mL), and HFIP (1.5 mL) at room temperature for 3 h. Purification by silica gel column chromatography (hexane/dichloromethane = 100/1) gave 2r (69 mg, 86%) as a white solid.
\textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): \(\delta\) 2.43 (s, 3H), 7.28 (d, \(J = 7.8\) Hz, 2H), 7.41 (d, \(J = 7.8\) Hz, 2H), 7.49 (dd, \(J = 7.8, 7.6\) Hz, 1H), 7.55 (dd, \(J = 7.5, 6.8\) Hz, 1H), 7.58–7.62 (m, 2H), 7.64 (s, 1H), 7.83 (d, \(J = 7.5\) Hz, 1H), 7.93 (d, \(J = 7.8\) Hz, 1H), 8.66 (d, \(J = 8.2\) Hz, 1H), 8.71 (d, \(J = 8.3\) Hz, 1H). \textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}): \(\delta\) 21.2, 122.5, 122.8, 126.3, 126.40, 126.43, 126.8, 126.9, 127.4, 128.6, 129.0, 129.85, 129.90, 130.6, 131.2, 131.6, 137.0, 137.8, 138.7.

Spectral data for this compound showed good agreement with literature data.\textsuperscript{10,11}

\textbf{9-(4-Methoxyphenyl)phenanthrene (2s)}

\begin{center}
\includegraphics[width=0.2\textwidth]{9-4-Methoxyphenylphenanthrene.png}
\end{center}

Compound 2s was synthesised according to Procedure C using 1s (85 mg, 0.30 mmol), TsOH·H\textsubscript{2}O (5.8 mg, 30 \(\mu\)mol), cyclohexane (3.0 mL), and HFIP (1.5 mL) at room temperature for 1 h. Purification by silica gel column chromatography (hexane/dichloromethane = 5/1) gave 2s (82 mg, 96\%) as a white solid.

\textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): \(\delta\) 3.86 (s, 3H), 7.02 (d, \(J = 8.6\) Hz, 2H), 7.45 (d, \(J = 8.6\) Hz, 2H), 7.45 (ddd, \(J = 7.8, 6.8, 1.1\) Hz, 1H), 7.58 (ddd, \(J = 8.2, 7.0, 1.1\) Hz, 1H), 7.61–7.64 (m, 2H), 7.64 (s, 1H), 7.85 (d, \(J = 7.8\) Hz, 1H), 7.94 (d, \(J = 8.2\) Hz, 1H), 8.68 (d, \(J = 8.2\) Hz, 1H), 8.74 (d, \(J = 8.2\) Hz, 1H).

\textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}): \(\delta\) 55.3, 113.7, 122.5, 122.9, 126.3, 126.40, 126.41, 126.8, 126.9, 127.4, 128.5, 129.8, 130.6, 131.1, 131.4, 131.6, 133.1, 138.4, 159.0.

Spectral data for this compound showed good agreement with literature data.\textsuperscript{10,11}

\textbf{9-(4-Chlorophenyl)phenanthrene (2t)}

\begin{center}
\includegraphics[width=0.2\textwidth]{9-4-Chlorophenylphenanthrene.png}
\end{center}

Compound 2t was synthesised according to Procedure C using 1t (87 mg, 0.30 mmol), TsOH·H\textsubscript{2}O (12 mg, 60 \(\mu\)mol), cyclohexane (3.0 mL), and HFIP (1.5 mL) at 60 °C for 3 h. Purification by silica gel column chromatography (hexane/dichloromethane = 100/1) gave 2t (64 mg, 73\%) as a white solid.

\textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): \(\delta\) 7.43 (d, \(J = 8.7\) Hz, 2H), 7.46 (d, \(J = 8.7\) Hz, 2H), 7.51 (ddd, \(J = 8.1, 7.0, 0.6\) Hz, 1H), 7.57–7.66 (m, 4H), 7.83 (d, \(J = 8.1\) Hz, 1H), 7.85 (d, \(J = 7.8\) Hz, 1H), 8.68 (d, \(J = 8.2\) Hz, 1H), 8.74 (d, \(J = 8.2\) Hz, 1H).

\textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}): \(\delta\) 122.5, 123.0, 126.55, 126.57, 126.60, 126.8, 126.9, 127.6, 128.5, 128.6, 130.0, 130.6, 130.8, 131.35, 131.35, 133.4, 137.4, 139.2.

Spectral data for this compound showed good agreement with literature data.\textsuperscript{10,11}
9-(4-Bromophenyl)phenanthrene (2u)

Compound 2u was synthesised according to Procedure C using 1u (99 mg, 0.30 mmol), TsOH·H₂O (11 mg, 60 µmol), cyclohexane (3.0 mL), and HFIP (1.5 mL) at 60 °C for 3 h. Purification by silica gel column chromatography (hexane/dichloromethane = 100/1) gave 2u (71 mg, 71%) as a white solid.

1H NMR (500 MHz, CDCl₃): δ 7.37 (d, J = 8.2 Hz, 2H), 7.51 (dd, J = 7.6, 7.6 Hz, 1H), 7.57–7.66 (m, 6H), 7.83 (d, J = 8.0 Hz, 1H), 7.84 (d, J = 8.2 Hz, 1H), 8.68 (d, J = 8.2 Hz, 1H), 8.73 (d, J = 8.2 Hz, 1H). 13C NMR (126 MHz, CDCl₃): δ 121.5, 122.5, 123.0, 126.5, 126.58, 126.60, 126.8, 126.9, 127.5, 128.6, 130.0, 130.6, 130.7, 131.3, 131.4, 131.7, 137.4, 139.6.

Spectral data for this compound showed good agreement with literature data.¹⁰

4. Recycling of HFIP Solution Containing TsOH for Sequential Hydroarylation

To a cyclohexane (3.0 mL) solution of 1a (76 mg, 0.30 mmol) was added HFIP (0.8 mL). To the reaction mixture was added a HFIP (0.7 mL) solution of TsOH·H₂O (5.7 mg, 30 µmol). After stirring vigorously at room temperature for 9 h under air, the cyclohexane (upper) and HFIP (lower) layers were separated by extracting the cyclohexane layer. The combined extracts were filtered through a pad of silica gel (hexane/chloroform = 20/1). After the solvent was removed under reduced pressure, the yield of 2a was determined by ¹H NMR measurement using CH₂Br₂ as an internal standard. The second cycle was conducted by adding another cyclohexane (3.0 mL) solution of 1a (0.3 mmol) to the remained HFIP solution containing TsOH. Thus, the same experiment was continuously conducted up to the fifth cycle.

5. References
6. $^1$H, $^{13}$C, and $^{19}$F NMR Charts

2-(Phenylethynyl)-1,1'-biphenyl (1a)

![NMR Chart](image)

*ti-14U916-Sonogashira*

![NMR Chart](image)
2-Methyl-2’-(phenylethynyl)-1,1’-biphenyl (1b)
3',5'-Dimethyl-2-(phenylethynyl)-1,1'-biphenyl (1c)
4′-Methyl-2-(phenylethynyl)-1,1′-biphenyl (1d)
4′-(tert-Butyl)-2-(phenylethynyl)-1,1′-biphenyl (1e)
2'-(Phenylethynyl)-[1,1'-biphenyl]-4-ol (1f)
4'-Fluoro-2-(phenylethynyl)-1,1'-biphenyl (1g)
4′-Chloro-2-(phenylethynyl)-1,1′-biphenyl (1h)
1-{2′-(Phenylethynyl)-[1,1'-biphenyl]-4-yl}ethan-1-one (1i)
Ethyl 2'-(phenylethynyl)-[1,1'-biphenyl]-4-carboxylate (1j)
2'-{(Phenylethynyl)-[1,1'-biphenyl]-4-carbonitrile (1k)
4'-Nitro-2-(phenylethynyl)-1,1'-biphenyl (II)
2-(Phenylethynyl)-4'-(trifluoromethyl)-1,1'-biphenyl (1m)
2-\{(2-(Phenylethynyl)phenyl)naphthalene (1n)\}
2-[[2-(Phenylethynyl)phenyl]benzo[b]thiophene (1o)
1-Phenyl-2-(phenylethynyl)naphthalene (1p)
1-(Phenylethynyl)-2,2'-binaphthalene (1q)
9-Phenylphenanthrene (2a)
4-Methyl-10-phenylphenanthrene (2b)
1,3-Dimethyl-10-phenylphenanthrene (2c)
2-Methyl-10-phenylphenanthrene (2d)
2-(tert-Butyl)-10-phenylphenanthrene (2e)
10-Phenylphenanthren-2-ol (2f)
2-Fluoro-10-phenylphenanthrene (2g)
2-Chloro-10-phenylphenanthrene (2h)
1-(10-Phenylphenanthren-2-yl)ethan-1-one (2i)
Ethyl 10-phenylphenanthrene-2-carboxylate (2j)
10-Phenylphenanthrene-2-carbonitrile (2k)
2-Nitro-10-phenylphenanthrene (2I)
10-Phenyl-2-(trifluoromethyl)phenanthrene (2m)
5-Phenylchrysene (2n)
6-Phenylbenzo[b]naphtho[2,1-d]thiophene (2o)
5-Phenylbenzo[c]phenanthrene (2p)
13-Phenylpicene (2q)
9-(4-Methylphenyl)phenanthrene (2r)
9-(4-Methoxyphenyl)phenanthrene (2s)
9-(4-Chlorophenyl)phenanthrene (2t)
9-(4-Bromophenyl)phenanthrene (2u)