Supporting Information

Preparation of phenanthrenes from ortho-amino-biphenyls and alkynes via base-promoted homolytic aromatic substitution

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General

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**General:** All reactions involving air- or moisture-sensitive reagents or intermediates were carried out in pre-heated glassware under an argon atmosphere using standard Schlenk techniques. Acetonitrile (MeCN), dioxane and benzotrifluoride (BTF) were used as extra dry over molecular sieve. All other solvents and reagents were purified according to standard procedures or were used as received from *Aldrich, Fluka, Acros* or *ABCR*. IR spectra were recorded on a *Digilab FTS 4000* with a *Specac MKII Golden Gate Single Reflection ART System*. $^1$H NMR and $^{13}$C NMR spectra were recorded on a *DPX 300, AV 400 or DD2 600* at 300 K. Spectra were calibrated relative to solvent’s residual proton and carbon chemical shift: CHCl$_3$ ($\delta = 7.26$ for $^1$H NMR and $\delta = 77.0$ for $^{13}$C NMR). TLC was performed using Merck silica gel 60 F-254 plates, detection of compounds with UV light or dipping into a solution of KMnO$_4$ (1.5 g in 400 mL H$_2$O, 5 g NaHCO$_3$), followed by heating. Flash column chromatography (FC) was performed using Merck or Fluka silica gel 60 (40-63 μm) applying a pressure of about 0.2 – 0.4 bar. Mass spectra were recorded on a *Finnigan MAT 4200S*, a *Bruker Daltonics Micro Tof*, a *Waters-Micromass Quatro LCZ* (ESI) or *Orbitrap LTQ XL* (APCI); peaks are given in m/z (% of basis peak).

**General procedure for the synthesis of ortho-amino-biaryls (GP1)**

In a Schlenk-tube, 2-bromo-4-methylaniline (467 mg, 2.50 mmol, 1.0 equiv), boronic acid (3.00 mmol, 1.2 equiv.), K$_2$CO$_3$ (1.55 g, 11.3 mmol, 4.5 equiv.) were dissolved in a 1:1 mixture of H$_2$O/DME and stirred at room temperature for 30 min. Then Pd(PPh$_3$)$_2$Cl (35 mg, 0.05 mmol, 2 mol%) was added and the resulting mixture was stirred at 80 °C for 20 h. After cooling to room temperature the reaction mixture was extracted with EtOAc three times, the combined organic layers were dried over MgSO$_4$ and concentrated *in vacuo*. Crude product was purified by flash chromatography on silica gel.

**General procedure for the base-promoted homolytic aromatic substitution (GP2)**

The reactions were carried out under argon atmosphere. A flame-dried Schlek-tube containing ortho-amino-biphenyl (0.25 mmol, 1.0 equiv.), phenyl acetylene (256 mg, 2.50 mmol, 10.0 equiv.), isoamyl nitrite (44.0 mg, 0.375 mmol, 1.5 equiv.) and Bu$_4$NI (9.0 mg, 0.025 mmol, 10 mol%) in BTF (0.125M) was heated to 70 °C and stirred for 24h. After cooling to room temperature most of the solvent was removed *in vacuo* and the residue was adsorbed on silica gel and afterwards purified by flash chromatography on silica gel.
General procedure for the base-promoted homolytic aromatic substitution (GP3)

The reactions were carried out under argon atmosphere. A flame-dried Schlenk-tube containing 5-methyl-[1,1'-biphenyl]-2-amine (46 mg, 0.25 mmol, 1.0 equiv.), alkyne (2.5 mmol, 10 equiv.), isoamyl nitrite (44.0 mg, 0.375 mmol, 1.5 equiv.) and Bu₄NI (9.0 mg, 0.025 mmol, 10 mol%) in BTF (0.125 M) was heated to 70 °C and stirred for 24 h. After cooling to room temperature most of the solvent was removed in vacuo and the residue was adsorbed on silica gel and afterwards purified by flash chromatography on silica gel.
5-Methyl-[1,1'-biphenyl]-2-amine (1a)

According to GP1 with phenylboronic acid (366 mg, 3.00 mmol, 1.2 eq.). The crude mixture was purified by flash chromatography on silica gel using a 80:1 mixture of pentane/EtOAc as eluent to provide analytically pure product 1a as pale yellow solid (375 mg, 2.46 mmol, 82%).

$^1$H NMR (300 MHz, CDCl$_3$, 300 K): $\delta = 7.47 – 7.40$ (m, 4H, CH$_{arom}$), 7.40 – 7.29 (m, 1H, CH$_{arom}$), 6.98 ($d, J = 8.1$ Hz, 2H, CH$_{arom}$), 6.71 ($d, J = 7.8$ Hz, 1H, CH$_{arom}$), 3.00 (s, 2H, NH$_2$), 2.29 (s, 3H, CH$_3$). $^{13}$C NMR (75 MHz, CDCl$_3$, 300 K): $\delta = 140.8$ (C), 139.7 (C), 131.0 (CH), 129.1 (2 × CH), 129.0 (CH), 128.8 (2 × CH), 128.0 (C), 127.9 (C), 127.1 (CH), 115.9 (CH), 20.4 (CH$_3$). HRMS (ESI) exact mass calculated for C$_{13}$H$_{13}$NH: 184.1121, found: 184.1128 ([M+H]$^+$). Analytical data are in accordance with the literature values.$^{[1]}$

4',5-Dimethyl-[1,1'-biphenyl]-2-amine (1c)

According to GP1 with p-tolylboronic acid (408 mg, 3.00 mmol, 1.2 equiv). The crude mixture was purified by flash chromatography on silica gel using a 80:1 mixture of pentane/EtOAc as eluent to provide analytically pure product 1c as pale yellow oil (355 mg, 1.80 mmol, 72%).

$^1$H NMR (300 MHz, CDCl$_3$, 300 K): $\delta = 7.44 – 7.37$ (m, 2H, CH$_{arom}$), 7.31 ($dd, J = 8.4$, 0.8 Hz, 2H, CH$_{arom}$), 7.07 – 7.01 (m, 2H, CH$_{arom}$), 6.79 – 6.70 (m, 1H, CH$_{arom}$), 3.66 (s, 2H, NH$_2$), 2.46 (s, 3H, CH$_3$), 2.34 (s, 3H, CH$_3$). $^{13}$C NMR (75 MHz, CDCl$_3$, 300 K): $\delta = 141.0$ (C), 136.8 (C), 136.8 (C), 131.1 (CH), 129.5 (2 × CH), 129.1 (2 × CH), 128.9 (CH), 128.1 (C), 128.0 (C), 116.0 (CH), 21.3 (CH$_3$), 20.6 (CH$_3$). HRMS (ESI) exact mass calculated for C$_{14}$H$_{15}$NH: 198.1277, found: 198.1276 ([M+H]$^+$). IR (neat): 3456 w, 3363 w, 3019 w, 2919 w, 2861 w, 1619 m, 1500 s, 1454 w, 1399 w, 1296 m, 1153 w, 1110 w, 1039 w, 884 w, 821 s.
4'-(*tert*-butyl)-5-Methyl-[1,1'-biphenyl]-2-amine (1d)

According to **GP1** with (4-(*tert*-butyl)phenyl)boronic acid (534 mg, 3.00 mmol, 1.2 equiv.). The crude mixture was purified by flash chromatography on silica gel using a 5:1 mixture of pentane/EtOAc as eluent to provide analytically pure product 1d as white solid (413 mg, 1.73 mmol, 69%). **¹H NMR** (300 MHz, CDCl₃, 300 K): δ = 7.52 – 7.44 (m, 2H, CH₆arom), 7.43 – 7.37 (m, 2H, CH₆arom), 7.03 – 6.93 (m, 2H, CH₆arom), 6.73 (d, J = 8.6 Hz, 1H, CH₆arom), 3.63 (s, 2H, NH₂), 2.29 (s, 3H, CH₃), 1.38 (s, 9H, 3 × CH₃). **¹³C NMR** (75 MHz, CDCl₃, 300 K): δ = 150.1 (C), 140.8 (C), 136.7 (C), 131.2 (CH), 128.9 (CH), 128.8 (2 × CH), 128.2 (C), 128.1 (C), 125.8 (2 × CH), 116.1 (CH), 34.7 (C), 31.5 (3 × CH₃), 20.6 (CH₃). **HRMS** (ESI) exact mass calculated for C₁₇H₂₁N: 240.1747, found: 240.1747 ([M+H]⁺). **IR** (neat): 3455w, 3368w, 3023w, 2961s, 2866m, 1620m, 1499s, 1462m, 1394m, 1363m, 1272m, 1201w, 1153w, 1112w, 1018w, 884w, 840m. **MP**: 93 °C.

5-Methyl-4’-(trimethylsilyl)-[1,1'-biphenyl]-2-amine (1e)

According to **GP1** with (4-(trimethylsilyl)phenyl)boronic acid (582 mg, 3.00 mmol, 1.2 equiv.). The crude mixture was purified by flash chromatography on silica gel using a 100:1 mixture of pentane/EtOAc as eluent to provide analytically pure product 1e as yellow oil (485 mg, 1.90 mmol, 76%). **¹H NMR** (300 MHz, CDCl₃, 300 K): δ = 7.63 – 7.58 (m, 2H, CH₆arom), 7.46 (d, J = 8.2 Hz, 2H, CH₆arom), 7.02 – 6.96 (m, 2H, CH₆arom), 6.76 – 6.71 (m, 1H, CH₆arom), 3.64 (s, 3H, CH₃), 2.30 (s, 2H, NH₂), 0.32 (s, 9H, 3 × CH₃). **¹³C NMR** (75 MHz, CDCl₃, 300 K): δ = 140.7 (C), 140.1 (C), 139.3 (C), 133.9 (2 × CH), 131.1 (CH), 129.2 (CH), 128.5 (2 × CH), 128.3 (C), 128.1 (C), 116.2 (CH), 20.6 (CH₃), -0.9 (3 × CH₃). **HRMS** (ESI) exact mass calculated for C₁₆H₂₁NSiH: 256.1516, found: 256.1505 ([M+H]⁺). **IR** (neat): 3454w, 3368w, 3015w, 2954m, 2920w, 1620m, 1504m, 1381w, 1294w, 1249m, 1153w, 1113m, 842s.
4'-Methoxy-5-methyl-[1,1'-biphenyl]-2-amine (1f)

According to GP1 with (4-methoxyphenyl)boronic acid (457 mg, 3.00 mmol, 1.2 equiv.). The crude mixture was purified by flash chromatography on silica gel using a 5:1 mixture of pentane/EtOAc as eluent to provide analytically pure product 1f as brown solid (432 mg, 2.03 mmol, 81%). \(^1\)H NMR (300 MHz, CDCl\(_3\), 300 K): \(\delta = 7.43 - 7.35\) (m, 2H, CH\(_{arom}\)), 7.04 – 6.90 (m, 4H, CH\(_{arom}\)), 6.71 (dd, \(J = 7.5, 0.9\) Hz, 1H, CH\(_{arom}\)), 3.86 (s, 3H, OCH\(_3\)), 3.62 (s, 2H, NH\(_2\)), 2.29 (s, 3H, CH\(_3\)). \(^{13}\)C NMR (75 MHz, CDCl\(_3\), 300 K): \(\delta = 158.9\) (C), 140.9 (C), 132.0 (C), 131.1 (CH), 130.3 (2 × CH), 128.8 (CH), 128.2 (C), 127.8 (C), 116.1 (CH), 114.3 (2 × CH), 55.4 (OCH\(_3\)), 20.6 (CH\(_3\)). HRMS (ESI) exact mass calculated for C\(_{14}\)H\(_{15}\)NOH: 214.1226, found: 214.1223 ([M+H\(^+\)]. IR (neat): 3449\(^w\), 3365\(^w\), 3006\(^w\), 2931\(^w\), 2836\(^w\), 1609\(m\), 1500\(s\), 1462\(^m\), 1297\(^m\), 1244\(^s\), 1178\(^m\), 1106\(^w\), 1029\(^m\), 836\(^m\). MP: 41 °C.

4'-Chloro-5-methyl-[1,1'-biphenyl]-2-amine (1g)

According to GP1 with (4-chlorophenyl)boronic acid (469 mg, 3.00 mmol, 1.2 equiv.). The crude mixture was purified by flash chromatography on silica gel using a 30:1 mixture of pentane/EtOAc as eluent to provide analytically pure product 1g as yellow oil (407 mg, 1.88 mmol, 75%). \(^1\)H NMR (300 MHz, CDCl\(_3\), 300 K): \(\delta = 7.41\) (s, 4H, CH\(_{arom}\)), 7.00 (ddd, \(J = 8.1, 2.1, 0.7\) Hz, 1H, CH\(_{arom}\)), 6.96 – 6.90 (m, 1H, CH\(_{arom}\)), 6.71 (d, \(J = 8.0\) Hz, 1H, CH\(_{arom}\)), 3.61 (s, 2H, NH\(_2\)), 2.29 (s, 3H, CH\(_3\)). \(^{13}\)C NMR (75 MHz, CDCl\(_3\), 300 K): \(\delta = 140.7\) (C), 138.2 (C), 133.2 (C), 130.9 (CH), 130.6 (2 × CH), 129.5 (CH), 129.0 (2 × CH), 128.3 (C), 126.7 (C), 116.2 (CH), 20.5 (CH\(_3\)). HRMS (ESI) exact mass calculated for C\(_{13}\)H\(_{12}\)NClH: 218.0731, found: 218.0730 ([M+H\(^+\)]. IR (neat): 3456\(^w\), 3378\(^w\), 3043\(^w\), 2921\(^w\), 2361\(^w\), 2158\(^w\), 2087\(^w\), 1620\(m\), 1503\(s\), 1413\(^w\), 1284\(^w\), 1284\(^w\), 843\(^s\).
4'-Fluoro-5-methyl-[1,1'-biphenyl]-2-amine (1h)

According to GPI with (4-fluorophenyl)boronic acid (420 mg, 3.00 mmol, 1.2 equiv.). The crude mixture was purified by flash chromatography on silica gel using a 50:1 mixture of pentane/EtOAc as eluent to provide analytically pure product 1h as brown solid (387 mg, 1.93 mmol, 77%).

$^1$H NMR (300 MHz, CDCl$_3$, 300 K): $\delta = 7.48 - 7.32$ (m, 2H, CH$_{arom}$), 7.19 - 7.07 (m, 2H, CH$_{arom}$), 7.05 - 6.94 (m, 1H, CH$_{arom}$), 6.97 - 6.90 (m, 1H, CH$_{arom}$), 6.72 (d, $J = 8.0$ Hz, 1H, CH$_{arom}$), 3.63 (s, 2H, NH$_2$), 2.29 (s, 3H, CH$_3$).

$^{13}$C NMR (75 MHz, CDCl$_3$, 300 K): $\delta = 162.1$ (d, $J = 248.3$ Hz, C), 140.6 (C), 135.6 (d, $J = 3.3$ Hz, C), 131.1 (CH), 130.9 (d, $J = 8.0$ Hz, 2 × CH), 129.3 (CH), 128.4 (C), 127.1 (C), 116.2 (CH), 115.8 (d, $J = 21.3$ Hz, 2 × CH), 20.5 (CH$_3$). HRMS (ESI) exact mass calculated for C$_{13}$H$_{12}$NFH: 202.1207, found: 202.1205 ([M+H]$^+$).

IR (neat): 3454 w, 3367 w, 3016 w, 2920 w, 2862 w, 1621 m, 1500 s, 1395 w, 1296 w, 1223 m, 1157 m, 1093 w, 883 w, 841 m. MP: 57 °C.

1-(2'-Amino-5'-methyl-[1,1'-biphenyl]-4-yl)ethan-1-one (1i)

According to GPI with (4-acetylphenyl)boronic acid (492 mg, 3.00 mmol, 1.2 equiv.). The crude mixture was purified by flash chromatography on silica gel using a 9:1 mixture of pentane/EtOAc as eluent to provide analytically pure product 1i as yellow solid (400 mg, 1.78 mmol, 71%).

$^1$H NMR (300 MHz, CDCl$_3$, 300 K): $\delta = 7.94$ (d, $J = 8.5$ Hz, 2H, CH$_{arom}$), 7.51 (d, $J = 0.6$ Hz, 2H, CH$_{arom}$), 6.97 (ddd, $J = 8.1$, 2.1, 0.7 Hz, 1H, CH$_{arom}$), 6.92 - 6.90 (m, 1H, CH$_{arom}$), 6.73 (d, $J = 8.0$ Hz, 1H, CH$_{arom}$), 2.53 (s, 3H, CH$_3$), 2.23 (s, 3H, CH$_3$).

$^{13}$C NMR (75 MHz, CDCl$_3$, 300 K): $\delta = 197.8$ (C), 144.4 (C), 136.1 (C), 131.0 (CH), 123.0 (CH), 129.5 (2 × CH), 129.2 (C), 129.0 (2 × CH), 127.9 (C), 127.6 (C), 117.5 (CH), 26.7 (CH$_3$), 20.6 (CH$_3$). HRMS (ESI) exact mass calculated for C$_{15}$H$_{15}$NOH: 226.1226, found: 226.1229 ([M+H]$^+$). IR (neat): 3451 w, 2255 w, 1681 m, 1604 m, 1499 w, 1360 w, 1269 m, 905 s. MP: 105 °C.
Methyl 2'-amino-5'-methyl-[1,1'-biphenyl]-4-carboxylate (1j)

According to GP1 with (4-(methoxycarbonyl)phenyl)boronic acid (540 mg, 3.00 mmol, 1.2 equiv.). The crude mixture was purified by flash chromatography on silica gel using a 10:1 mixture of pentane/EtOAc as eluent to provide analytically pure product 1j as yellow solid (452 mg, 1.88 mmol, 75%). $^1$H NMR (300 MHz, CDCl$_3$, 300 K): δ = 8.22 - 7.98 (m, 2H, CH$_{arom}$), 7.65 - 7.45 (m, 2H, CH$_{arom}$), 7.01 (ddd, J = 8.0, 2.1, 0.7 Hz, 1H, CH$_{arom}$), 6.97 – 6.95 (m, 1H, CH$_{arom}$), 6.72 (d, J = 8.0 Hz, 1H, CH$_{arom}$), 3.94 (s, 3H, CO$_2$CH$_3$), 3.65 (s, 2H, NH$_2$), 2.29 (s, 3H, CH$_3$). $^{13}$C NMR (75 MHz, CDCl$_3$, 300 K): δ = 166.9 (C), 144.5 (C), 140.5 (C), 130.7 (CH), 130.0 (2 × CH), 129.7 (CH), 129.1 (2 × CH), 128.8 (C), 128.3 (C), 126.7 (C), 116.3 (CH), 52.1 (CO$_2$CH$_3$), 20.4 (CH$_3$). HRMS (ESI) exact mass calculated for C$_{15}$H$_{15}$NO$_2$H: 242.1176, found: 242.1173 ([M+H]$^+$). IR (neat): 3448 w, 3371 w, 3017 w, 2950 w, 1718 s, 1609 m, 1499 m, 1435 m, 1397 w, 1191 m, 1113 m, 1018 w, 966 w, 818 w, 862 w. MP: 104 °C.

5-Methyl-4'-(trifluoromethyl)-[1,1'-biphenyl]-2-amine (1k)

According to GP1 with (4-(trifluoromethyl)phenyl)boronic acid (570 mg, 3.00 mmol, 1.2 equiv.). The crude mixture was purified by flash chromatography on silica gel using a 25:1 mixture of pentane/EtOAc as eluent to provide analytically pure product 1k as pale yellow solid (452 mg, 1.80 mmol, 72%). $^1$H NMR (300 MHz, CDCl$_3$, 300 K): δ = 7.75 - 7.66 (m, 2H, CH$_{arom}$), 7.60 (dt, J = 7.8, 0.8 Hz, 2H, CH$_{arom}$), 7.03 (ddd, J = 8.0, 2.1, 0.8 Hz, 1H, CH$_{arom}$), 6.99 – 6.92 (m, 1H, CH$_{arom}$), 6.73 (d, J = 8.0 Hz, 1H, CH$_{arom}$), 3.68 (s, 2H, NH$_2$), 2.30 (s, 3H, CH$_3$). $^{13}$C NMR (75 MHz, CDCl$_3$, 300 K): δ = 143.6 (C), 140.7 (C), 130.9 (CH), 129.9 (CH), 129.6 (2 × CH), 128.5 (C), 126.5 (C), 125.8 (q, J = 3.7 Hz, 2 × CH), 122.5 (q, J = 272.0 Hz, CF$_3$), 119.0 (CH), 20.5 (CH$_3$). Quaternary carbon next to CF$_3$ could not be detected. HRMS (ESI) exact mass calculated for C$_{14}$H$_{12}$NF$_3$H: 252.0995, found: 252.0991 ([M+H]$^+$). IR (neat): 3460 w, 3369 w, 3018 w, 2924 w, 1619 m, 1502 m, 1398 w, 1325 s, 1166 m, 1124 m, 1069 m, 1018 w, 909 w, 848 m, 816 w. MP: 91 °C.
4-Methyl-2-(naphthalen-1-yl)aniline (1l)

According to GP1 with naphthalen-1-ylboronic acid (516 mg, 3.00 mmol, 1.2 equiv.). The crude mixture was purified by flash chromatography on silica gel using a 30:1 mixture of pentane/EtOAc as eluent to provide analytically pure product 1l as red oil (379 mg, 1.63 mmol, 65%).

$^1$H NMR (300 MHz, CDCl$_3$, 300 K): $\delta = 7.95 - 7.82$ (m, 2H, CH$_{arom}$), 7.68 – 7.62 (m, 1H, CH$_{arom}$), 7.57 – 7.39 (m, 4H, CH$_{arom}$), 7.14 – 7.04 (m, 1H, CH$_{arom}$), 7.00 (d, $J = 2.2$ Hz, 1H, CH$_{arom}$), 6.81 (d, $J = 8.0$ Hz, 1H, CH$_{arom}$), 3.39 (s, 2H, NH$_2$), 2.32 (s, 3H, CH$_3$).

$^{13}$C NMR (75 MHz, CDCl$_3$, 300 K): $\delta =$ 170.6 (C), 167.4 (C), 143.9 (C), 134.0 (2 × C), 131.9 (2 × CH), 129.5 (CH), 128.5 (CH), 128.1 (CH), 127.8 (CH), 126.4 (CH), 126.2 (CH), 126.1 (CH), 125.9 (CH), 116.3 (CH), 20.7 (CH$_3$). HRMS (ESI) exact mass calculated for C$_{17}$H$_{15}$NH: 234.1277, found: 234.1279 ([M+H]$^+$). IR (neat): 3453 w, 3367 w, 3017 w, 2919 w, 2859 w, 2362 w, 1620 m, 1485 s, 1391 m, 1294 m, 1190 w, 1153 m, 1091 m, 1014 m, 880 m, 834 s.

2'-Fluoro-5-methyl-[1,1'-biphenyl]-2-amine (1m)

According to GP1 with (2-fluorophenyl)boronic acid (420 mg, 3.00 mmol, 1.2 equiv.). The crude mixture was purified by flash chromatography on silica gel using a 50:1 to 25.1 mixture of pentane/EtOAc as eluent to provide analytically pure product 1m as brown solid (397 mg, 1.97 mmol, 79%).

$^1$H NMR (300 MHz, CDCl$_3$, 300 K): $\delta = 7.41 - 7.29$ (m, 2H, CH$_{arom}$), 7.24 – 7.13 (m, 2H, CH$_{arom}$), 7.03 (ddd, $J = 8.1$, 2.1, 0.8 Hz, 1H, CH$_{arom}$), 6.98 – 6.93 (m, 1H), 6.74 (d, $J = 8.1$ Hz, 1H, CH$_{arom}$), 3.29 (s, 2H, NH$_2$), 2.29 (s, 3H, CH$_3$). $^{13}$C NMR (75 MHz, CDCl$_3$, 300 K): $\delta =$ 160.0 ($d$, $J = 244.6$ Hz, C), 141.6 (C), 132.1 ($d$, $J = 3.7$ Hz, CH), 131.6 (CH), 129.9 (CH), 129.4 ($d$, $J = 8.0$ Hz, CH), 128.0 (C), 127.0 ($d$, $J = 16.4$ Hz, C), 124.6 ($d$, $J = 3.6$ Hz, CH), 121.9 (C), 116.2 (CH), 116.1 ($d$, $J = 22.4$ Hz, CH), 20.53 (CH$_3$). HRMS (ESI) exact mass calculated for C$_{13}$H$_{12}$NFH: 202.1207, found: 202.1207 ([M+H]$^+$). IR (neat): 3462 w, 3374 w, 3018 w, 2919 w, 2859 w, 1622 m, 1486 s, 1447 m, 1285 m, 1213 s, 1153 m, 1105 m, 1040 w, 988 w, 944 w, 886 w, 812 s. MP: 49 °C.
3'-Fluoro-5-methyl-[1,1'-biphenyl]-2-amine (1n)

According to GP1 with (3-fluorophenyl)boronic acid (420 mg, 3.00 mmol, 1.2 equiv.). The crude mixture was purified by flash chromatography on silica gel using a 50:1 mixture of pentane/EtOAc as eluent to provide analytically pure product 1n as pale yellow oil (385 mg, 1.93 mmol, 77%).

\( ^1H \) NMR (300 MHz, CDCl\(_3\), 300 K): \( \delta = 7.39 \ (td, J = 7.9, 6.0 \text{ Hz}, 1H, \text{ CH}_{\text{arom}}), 7.25 - 7.22 \ (m, 1H, \text{ CH}_{\text{arom}}), 7.18 \ (ddd, J = 9.9, 2.6, 1.6 \text{ Hz}, 1H, \text{ CH}_{\text{arom}}), 7.07 - 6.97 \ (m, 2H, \text{ CH}_{\text{arom}}), 6.95 \ (d, J = 2.0 \text{ Hz}, 1H, \text{ CH}_{\text{arom}}), 6.74 \ (d, J = 8.0 \text{ Hz}, 1H, \text{ CH}_{\text{arom}}), 3.81 \ (s, 2H, \text{ NH}_2), 2.29 \ (s, 3H, \text{ CH}_3) \). 

\( ^13C \) NMR (75 MHz, CDCl\(_3\), 300 K): \( \delta = 163.2 \ (d, J = 246.0 \text{ Hz}, \text{ C}), 141.9 \ (d, J = 7.7 \text{ Hz}, \text{ C}), 140.3 \ (\text{ C}), 131.0 \ (\text{ CH}), 130.4 \ (d, J = 8.5 \text{ Hz}, \text{ CH}), 129.6 \ (\text{ CH}), 128.7 \ (\text{ C}), 127.0 \ (d, J = 1.9 \text{ Hz}, \text{ C}), 125.0 \ (d, J = 2.9 \text{ Hz}, \text{ CH}), 116.5 \ (\text{ CH}), 116.2 \ (d, J = 21.3 \text{ Hz}, \text{ CH}), 114.2 \ (d, J = 21.0 \text{ Hz}, \text{ CH}), 20.6 \ (\text{ CH}_3). \)

HRMS (ESI) exact mass calculated for C\(_{13}\)H\(_{12}\)NFH: 202.1207, found: 202.1207 ([M+H]\(^+\)]. IR (neat): 3460\(w\), 3371\(w\), 3018\(w\), 2920\(w\), 2860\(w\), 1612\(s\), 1581\(s\), 1505\(s\), 1433\(m\), 1300\(m\), 1266\(m\), 1211\(m\), 115\(m\), 1078\(w\), 1041\(w\), 926\(m\), 875\(m\).
3-Methyl-9-phenylphenanthrene (2a)

According to GP2 with 5-methyl-[1,1'-biphenyl]-2-amine (1a, 46 mg, 0.25 mmol, 1.0 equiv.). Crude product was purified by flash column chromatography on silica gel using a 20:1 mixture of pentane/DCM as eluent to provide analytically pure product 2a as yellow oil (52 mg, 0.20 mmol, 78%).

$^1$H NMR (300 MHz, CDCl$_3$, 300 K): $\delta = 8.80$ (d, $J = 8.3$ Hz, 1H, CH$_{arom}$), 8.54 (s, 1H, CH$_{arom}$), 7.94 (dd, $J = 8.3, 1.4$ Hz, 1H, CH$_{arom}$), 7.81 (d, $J = 8.1$ Hz, 1H, CH$_{arom}$), 7.70 – 7.64 (m, 2H, CH$_{arom}$), 7.60 – 7.45 (m, 7H, CH$_{arom}$), 2.67 (s, 3H, CH$_3$).

$^{13}$C NMR (75 MHz, CDCl$_3$, 300 K): $\delta =$ 141.1 (C), 138.0 (C), 136.4 (C), 131.4 (C), 130.5 (C), 130.2 (2 × CH), 130.2 (C), 129.7 (C), 128.7 (CH), 128.7 (CH), 128.4 (2 × CH), 127.5 (CH), 127.4 (CH), 127.0 (CH), 126.5 (CH), 126.3 (CH), 123.0 (CH), 122.4 (CH), 22.3 (CH$_3$).

HRMS (APCI) exact mass calculated for C$_{21}$H$_{16}$: 268.1246, found: 268.1246 [M$^+$.]

Analytical data are in accordance with the literature values.$^{[2]}$

9-Phenylphenanthrene (2b)

According to GP2 with [1,1'-biphenyl]-2-amine (1b, 42 mg, 0.25 mmol, 1.0 equiv.). Crude product was purified by flash column chromatography on silica gel using a 20:1 mixture of pentane/DCM as eluent to provide analytically pure product 2b as white solid (46 mg, 0.18 mmol, 72%).

$^1$H NMR (300 MHz, C$_6$D$_6$, 300 K): $\delta =$ 8.59 – 8.47 (m, 2H, CH$_{arom}$), 8.01 (dd, $J = 8.2, 1.1$ Hz, 1H, CH$_{arom}$), 7.69 – 7.62 (m, 1H, CH$_{arom}$), 7.55 (s, 1H, CH$_{arom}$), 7.48 – 7.35 (m, 5H, CH$_{arom}$), 7.35 – 7.21 (m, 4H, CH$_{arom}$).

$^{13}$C NMR (75 MHz, CDCl$_3$, 300 K): $\delta =$ 140.9 (C), 138.9 (C), 131.7 (C), 131.2 (C), 130.7 (C), 130.1 (2 × CH), 130.1 (C), 128.7 (C), 128.4 (2 × CH), 127.6 (CH), 127.4 (CH), 127.0 (CH), 126.9 (CH), 126.6 (CH), 126.6 (CH), 126.5 (CH), 126.5 (CH), 123.0 (CH), 122.6 (CH). HRMS (APCI) exact mass calculated for C$_{20}$H$_{14}$: 254.1090, found: 254.1079 [M$^+$.]. Analytical data are in accordance with the literature values.$^{[3]}$
2,6-Dimethyl-10-phenylphenanthrene (2c)

According to GP2 with 4',5-dimethyl-[1,1'-biphenyl]-2-amine (1c, 49 mg, 0.25 mmol, 1.0 equiv.). Crude product was purified by flash column chromatography on silica gel using pentane as eluent to provide analytically pure product 2c as yellowish solid (60 mg, 0.18 mmol, 72%). $^1$H NMR (300 MHz, CDCl$_3$, 300 K): δ = 8.68 (d, $J = 8.4$ Hz, 1H, CH$_{arom}$), 8.58 – 8.47 (m, 1H, CH$_{arom}$), 7.81 (s, 1H, CH$_{arom}$), 7.72 (dt, $J = 1.7$, 0.8 Hz, 1H, CH$_{arom}$), 7.65 (s, 1H, CH$_{arom}$), 7.62 – 7.41 (m, 7H, CH$_{arom}$), 2.67 (s, 3H, CH$_3$), 2.50 (s, 3H, CH$_3$). $^{13}$C NMR (75 MHz, CDCl$_3$, 300 K): δ = 141.3 (C), 137.7 (C), 136.3 (2 × C), 136.2 (2 × C), 131.5 (C), 130.2 (2 × CH), 129.3 (C), 128.6 (CH), 128.4 (2 × CH), 128.3 (CH), 128.1 (CH), 127.6 (CH), 127.3 (CH), 126.5 (CH), 123.0 (CH), 122.2 (CH), 22.3 (CH$_3$), 21.8 (CH$_3$). HRMS (APCI) exact mass calculated for C$_{22}$H$_{18}$: 283.1470, found: 283.1470 [M$^+$]. IR (neat): 3024 w, 2918 m, 1620 w, 1496 s, 1443 m, 1370 w, 1147 w, 1032 w, 892 m, 817 m, 779 m, 702 s, 587 s. MP: 173 °C.

2-(tert-Butyl)-6-Methyl-10-phenylphenanthrene (2d)

According to GP2 with 4’-(tert-butyl)-5-methyl-[1,1'-biphenyl]-2-amine (1d, 60 mg, 0.25 mmol, 1.0 equiv.). Crude product was purified by flash column chromatography on silica gel using pentane as eluent to provide analytically pure product 2d as yellowish solid (69 mg, 0.21 mmol, 85%). $^1$H NMR (300 MHz, CDCl$_3$, 300 K): δ = 8.76 – 8.70 (m, 1H, CH$_{arom}$), 8.55 – 8.49 (m, 1H, CH$_{arom}$), 7.98 (d, $J = 2.1$ Hz, 1H, CH$_{arom}$), 7.85 - 7.72 (m, 2H, CH$_{arom}$), 7.71 – 7.41 (m, 7H, CH$_{arom}$), 2.67 (s, 3H, CH$_3$), 1.39 (s, 9H, 3 × CH$_3$). $^{13}$C NMR (75 MHz, CDCl$_3$, 300 K): δ = 149.3 (C), 141.3 (C), 138.1 (C), 136.3 (C), 131.1 (C), 130.2 (2 × CH), 130.1 (C), 129.5 (C), 128.6 (CH), 128.4 (2 × CH), 128.4 (C), 128.3 (CH), 127.5 (CH), 127.3 (CH), 124.5 (CH), 122.8 (2 × CH), 122.3 (CH), 35.1 (C), 31.5 (3 × CH), 22.3 (CH$_3$). HRMS (APCI) exact mass calculated for C$_{25}$H$_{24}$: 324.1870, found: 324.1873 [M$^+$]. IR (neat): 2964w, 1616w, 1372w, 1268w, 906s, 828w, 730s, 650w. MP: 132 °C.
Trimethyl(6-methyl-10-phenylphenanthren-2-yl)silane (2e)

According to GP2 with 5-methyl-4’-(trimethylsilyl)-[1,1’-biphenyl]-2-amine (1e, 64 mg, 0.25 mmol, 1.0 equiv.). Crude product was purified by flash column chromatography on silica gel using pentane as eluent to provide analytically pure product 2e as yellow oil (59 mg, 0.18 mmol, 70%). $^1$H NMR (300 MHz, CDCl$_3$, 300 K): $\delta$ = 8.76 ($dd$, $J$ = 8.2, 0.6 Hz, 1H, CH$_{arom}$), 8.59 – 8.50 ($m$, 1H, CH$_{arom}$), 8.15 ($dd$, $J$ = 1.3, 0.6 Hz, 1H, CH$_{arom}$), 7.81 ($dd$, $J$ = 8.2, 1.5 Hz, 2H, CH$_{arom}$), 7.68 (s, 1H, CH$_{arom}$), 7.65 – 7.41 ($m$, 6H, CH$_{arom}$), 2.67 (s, 3H, CH$_3$), 0.30 (s, 9H, 3 × CH$_3$). $^{13}$C NMR (75 MHz, CDCl$_3$, 300 K): $\delta$ = 141.1 (C), 138.4 (C), 138.1 (C), 136.4 (C), 132.5 (CH), 130.8 (C), 130.7 (CH), 130.5 (C), 130.3 (2 × CH), 130.1 (C), 129.9 (C), 128.8 (CH), 128.6 (CH), 128.3 (2 × CH), 127.5 (CH), 127.4 (CH), 122.5 (CH), 122.1 (CH), 22.3 (CH$_3$), -0.98 (3 × CH$_3$). HRMS (APCI) exact mass calculated for C$_{24}$H$_{24}$Si: 340.1639, found: 340.1642 [M$^+$]. IR (neat): 3026 w, 2953 m, 1599 w, 1492 w, 1444 w, 1364 w, 1248 s, 1124 m, 892 w, 852 s, 753 m, 701 m, 664 w, 587 m.

2-Methoxy-6-methyl-10-phenylphenanthrene (2f)

According to GP2 with 4’-methoxy-5-methyl-[1,1’-biphenyl]-2-amine (1f, 53 mg, 0.25 mmol, 1.0 equiv.). Crude product was purified by flash column chromatography on silica gel using a 100:1 mixture of pentane/DCM as eluent to provide analytically pure product 2f as yellow solid (57 mg, 0.19 mmol, 76%). $^1$H NMR (300 MHz, CDCl$_3$, 300 K): $\delta$ = 8.68 ($d$, $J$ = 8.9 Hz, 1H, CH$_{arom}$), 8.46 – 8.38 ($m$, 1H, CH$_{arom}$), 7.77 ($d$, $J$ = 8.1 Hz, 1H, CH$_{arom}$), 7.65 (s, 1H, CH$_{arom}$), 7.62 – 7.45 ($m$, 5H, CH$_{arom}$), 7.39 ($dd$, $J$ = 7.9, 1.5 Hz, 1H, CH$_{arom}$), 7.37 – 7.27 ($m$, 2H, CH$_{arom}$). $^{13}$C NMR (75 MHz, CDCl$_3$, 300 K): $\delta$ = 158.3 (C), 141.2 (C), 137.4 (C), 136.5 (C), 132.8 (C), 130.3 (C), 130.1 (2 × CH), 128.7 (C), 128.7 (CH), 128.5 (2 × CH), 128.1 (CH), 127.8 (CH), 127.4 (CH), 124.9 (C), 124.6 (CH), 121.9 (CH), 116.3 (CH), 108.0 (CH), 55.4 (CH$_3$), 22.3 (CH$_3$). HRMS (APCI) exact mass calculated for C$_{22}$H$_{18}$O: 299.1419, found: 299.1419 [M$^+$]. IR (neat): 2935 w, 2362 w, 2250 w, 1614 m, 1498 m, 1462 m, 1259 m, 1221 m, 1097 w, 1045 m, 905 s, 822 w, 729 s, 649 m, 587 m. MP: 104 °C.
2-Chloro-6-methyl-10-phenylphenanthrene (2g)

According to GP2 with 4’-chloro-5-methyl-[1,1’-biphenyl]-2-amine (1g, 54 mg, 0.25 mmol, 1.0 equiv.). Crude product was purified by flash column chromatography on silica gel using pentane as eluent to provide analytically pure product 2g as white solid (50 mg, 0.17 mmol, 67%). 

$^1$H NMR (300 MHz, CDCl$_3$, 300 K): $\delta = 8.67$ ($d$, $J = 8.9$ Hz, 1H, CH$_{arom}$), 8.45 – 8.41 ($m$, 1H, CH$_{arom}$), 7.89 ($d$, $J = 2.2$ Hz, 1H, CH$_{arom}$), 7.79 ($d$, $J = 8.1$ Hz, 1H, CH$_{arom}$), 7.68 ($s$, 1H, CH$_{arom}$), 7.59 ($dd$, $J = 8.9$, 2.3 Hz, 1H, CH$_{arom}$), 7.56 – 7.44 ($m$, 6H, CH$_{arom}$), 2.65 ($s$, 3H, CH$_3$). 

13C NMR (75 MHz, CDCl$_3$, 300 K): $\delta = 140.3$ (C), 137.0 (C), 136.8 (C), 132.5 (C), 132.5 (C), 130.0 ($2 \times$ CH), 129.6 (C), 129.4 (C), 128.9 (CH), 128.7 (C), 128.6 (CH), 128.5 (CH), 128.5 ($2 \times$ CH), 127.6 (CH), 126.7 (CH), 126.0 (CH), 124.5 (CH), 122.2 (CH), 22.2 (CH$_3$). HRMS (APCI) exact mass calculated for C$_{21}$H$_{15}$Cl: 302.0855, found: 302.0857 [M$^+$.].

IR (neat): 3042 w, 2257 w, 2064 w, 1598 m, 1493 m, 1438 m, 902 s, 820 s, 722 m, 730 s, 649 w, 582 m.

MP: 118 °C.

2-Fluoro-6-methyl-10-phenylphenanthrene (2h)

According to GP2 with 4’-fluoro-5-methyl-[1,1’-biphenyl]-2-amine (1h, 50 mg, 0.25 mmol, 1.0 equiv.). Crude product was purified by flash column chromatography on silica gel using a 100:1 mixture of pentane/DCM as eluent to provide analytically pure product 2h as white solid (50 mg, 0.18 mmol, 70%). 

$^1$H NMR (300 MHz, CDCl$_3$, 300 K): $\delta = 8.74$ ($dd$, $J = 9.2$, 5.7 Hz, 1H, CH$_{arom}$), 8.43 ($s$, 1H, CH$_{arom}$), 7.79 ($d$, $J = 8.1$ Hz, 1H, CH$_{arom}$), 7.69 ($s$, 1H, CH$_{arom}$), 7.62 – 7.34 ($m$, 8H, CH$_{arom}$), 2.65 ($s$, 3H, CH$_3$). 

13C NMR (75 MHz, CDCl$_3$, 300 K): $\delta = 161.4$ ($d$, $J = 244.6$ Hz, C), 140.6 (C), 137.4 ($d$, $J = 3.9$ Hz, C), 136.9 (C), 133.1 ($d$, $J = 8.9$ Hz, C), 130.1 ($2 \times$ CH), 129.9 (C), 129.2 (C), 128.8 (CH), 128.6 ($3 \times$ CH), 128.6 (CH), 127.7 (CH), 127.1 ($d$, $J = 1.9$ Hz, C), 125.4 ($d$, $J = 9.0$ Hz, CH), 122.2 (CH), 115.4 ($d$, $J = 23.6$ Hz, CH), 111.6 ($d$, $J = 21.5$ Hz, CH), 22.3 (CH$_3$). HRMS (APCI) exact mass calculated for C$_{21}$H$_{15}$F: 286.1152, found: 286.1146 [M$^+$.]. IR (neat): 3042 w, 2257 w, 2064 w, 1598 m, 1493 m, 1438 m, 902 s, 820 s, 722 m, 730 s, 649 w, 582 m. MP: 82 °C.
1-(6-Methyl-10-phenylphenanthren-2-yl)ethan-1-one (2i)

According to GP2 with 1-(2'-amino-5'-methyl-[1,1'-biphenyl]-4-yl)ethan-1-one (1i, 56 mg, 0.25 mmol, 1.0 equiv.). Crude product was purified by flash column chromatography on silica gel using pentane as eluent to provide analytically pure product 2i as white solid (62 mg, 0.20 mmol, 82%). 

\[ ^1H\text{ NMR} (300\text{ MHz, } \text{CDCl}_3, \text{ 300 K}): \delta = 8.81 \text{ (d, } J = 8.7 \text{ Hz, 1H, CH}_\text{arom}), \ 8.68 - 8.49 \text{ (m, 2H, CH}_\text{arom}), \ 8.20 \text{ (dd, } J = 8.7, 1.9 \text{ Hz, 1H, CH}_\text{arom}), \ 7.82 \text{ (d, } J = 8.1 \text{ Hz, 1H, CH}_\text{arom}), \ 7.72 \text{ (s, 1H, CH}_\text{arom}), \ 7.63 - 7.46 \text{ (m, 6H, CH}_\text{arom}), \ 2.66 \text{ (s, 3H, CH}_3), \ 2.59 \text{ (s, 3H, CH}_3) \text{.} \]

\[ ^13\text{C NMR} (75\text{ MHz, } \text{CDCl}_3, \text{ 300 K}): \delta = 198.1 \text{ (C), 140.2 (C), 138.3 (C), 136.9 (C), 134.8 (C), 133.5 (C), 130.7 (C), 130.5 (C), 130.0 (2 \times \text{ CH}), 129.8 (\text{CH}), 129.4 (C), 128.7 (\text{CH}), 128.5 (2 \times \text{ CH}), 128.3 (\text{CH}), 128.3 (\text{CH}), 127.7 (\text{CH}), 124.7 (\text{CH}), 123.4 (\text{CH}), 122.9 (\text{CH}), 26.6 (\text{CH}_3), 22.2 (\text{CH}_3). \]

HRMS (APCI) exact mass calculated for C_{23}H_{18}O: 310.1350, found: 310.1352 [M+]^+. IR (neat): 2920v, 1680s, 1602m, 1495w, 1417w, 1372w, 1268s, 1149w, 899w, 829w, 767w, 703m, 595w. MP: 133 °C.

Methyl 6-methyl-10-phenylphenanthrene-2-carboxylate (2j)

According to GP2 with methyl 2'-amino-5'-methyl-[1,1'-biphenyl]-4-carboxylate (1j, 60 mg, 0.25 mmol, 1.0 equiv.). Crude product was purified by flash column chromatography on silica gel using a 50:1 mixture of pentane/EtO as eluent to provide analytically pure product 2j as yellow solid (54 mg, 0.17 mmol, 66%). 

\[ ^1H\text{ NMR} (300\text{ MHz, } \text{CDCl}_3, \text{ 300 K}): \delta = 8.80 \text{ (d, } J = 8.7 \text{ Hz, 1H, CH}_\text{arom}), \ 8.66 \text{ (d, } J = 1.8 \text{ Hz, 1H, CH}_\text{arom}), \ 8.62 - 8.50 \text{ (m, 1H, CH}_\text{arom}), \ 8.25 \text{ (dd, } J = 8.7, 1.8 \text{ Hz, 1H, CH}_\text{arom}), \ 7.81 \text{ (d, } J = 8.1 \text{ Hz, 1H, CH}_\text{arom}), \ 7.70 \text{ (s, 1H, CH}_\text{arom}), \ 7.59 - 7.45 \text{ (m, 6H, CH}_\text{arom}), \ 3.92 \text{ (s, 3H, CH}_3), \ 2.66 \text{ (s, 3H, CH}_3). \]

\[ ^13\text{C NMR} (75\text{ MHz, } \text{CDCl}_3, \text{ 300 K}): \delta = 167.3 \text{ (C), 140.3 (C), 138.2 (C), 136.8 (C), 133.5 (C), 130.7 (C), 130.4 (C), 130.1 (2 \times \text{ CH}), 129.7 (\text{CH}), 129.4 (\text{C}), 129.1 (\text{CH}), 128.6 (\text{CH}), 128.5 (2 \times \text{ CH}), 128.2 (\text{CH}), 127.8 (\text{C}), 127.6 (\text{CH}), 126.1 (\text{CH}), 123.1 (\text{CH}), 122.9 (\text{CH}), 52.2 (\text{CH}_3), 22.2 (\text{CH}_3). \]

HRMS (ESI) exact mass calculated for C_{23}H_{19}O_2Na: 349.1199, found: 349.1203 ([M+Na]⁺). IR (neat): 30324w, 2950v, 1717s, 1616w, 1496w, 1435m, 1370w, 1273s, 1240m, 1118m, 996w, 909w, 809w, 763m, 585w. MP: 174 °C.
6-Methyl-10-phenyl-2-(trifluoromethyl)phenanthrene (2k)

According to GP2 with 5-methyl-4’-(trifluoromethyl)-[1,1’-biphenyl]-2-amine (1k, 63 mg, 0.25 mmol, 1.0 equiv.). Crude product was purified by flash column chromatography on silica gel using pentane as eluent to provide analytically pure product 2k as yellowish solid (60 mg, 0.18 mmol, 72%). $^1$H NMR (300 MHz, CDCl$_3$, 300 K): $\delta$ = 8.90 – 8.78 (m, 1H, CH$_{arom}$), 8.55 – 8.49 (m, 1H, CH$_{arom}$), 8.23 (dt, $J$ = 1.9, 0.9 Hz, 1H, CH$_{arom}$), 7.89 – 7.79 (m, 2H, CH$_{arom}$), 7.75 (s, 1H, CH$_{arom}$), 7.63 – 7.46 (m, 6H, CH$_{arom}$), 2.67 (s, 3H, CH$_3$). $^{13}$C NMR (75 MHz, CDCl$_3$, 300 K): $\delta$ = 140.1 (C), 137.9 (C), 137.1 (C), 132.6 (C), 130.9 (C), 130.4 (C), 130.1 (2 × CH), 129.8 (CH), 129.4 (C), 128.9 (CH), 128.7 (CH), 128.4 (q, $J$ = 32.2 Hz, C) 127.9 (2 × CH), 124.3 (q, $J$ = 4.4 Hz, CH), 123.9 (CH), 122.8 (CH), 122.7 (q, $J$ = 272.5 Hz, CF$_3$), 122.2 (q, $J$ = 4.4 Hz, CH), 22.3 (CH$_3$). HRMS (APCI) exact mass calculated for C$_{22}$H$_{15}$F$_3$: 336.1116, found: 336.91120 [M$^+$]. IR (neat): 2253w, 1374w, 1325m, 1127m, 903s, 723s, 649m. MP: 127°C.

5-Fluoro-3-methyl-9-phenylphenanthrene (2m)

According to GP2 with 2'-fluoro-5-methyl-[1,1'-biphenyl]-2-amine (1m, 50 mg, 0.25 mmol, 1.0 equiv.). Crude product was purified by flash column chromatography on silica gel using a 100:1 mixture of pentane/DCM as eluent to provide analytically pure product 2m as colorless oil (25 mg, 90 µmol, 35%). $^1$H NMR (300 MHz, CDCl$_3$, 300 K): $\delta$ = 8.98 (dt, $J$ = 1.8, 0.9 Hz, 1H, CH$_{arom}$), 7.81 (d, $J$ = 8.1 Hz, 1H, CH$_{arom}$), 7.75 – 7.67 (m, 2H, CH$_{arom}$), 7.59 - 7.32 (m, 8H, CH$_{arom}$), 2.66 (s, 3H, CH$_3$). $^{13}$C NMR (75 MHz, CDCl$_3$, 300 K): $\delta$ = 161.7 (d, $J$ = 252.1 Hz, C), 140.9 (C), 137.3 (d, $J$ = 3.0 Hz, C), 136.9 (d, $J$ = 2.5 Hz, C), 134.2 (d, $J$ = 4.5 Hz, C), 130.1 (2 × CH), 130.0 (C), 128.8 (d, $J$ = 1.4 Hz, CH), 128.7 (d, $J$ = 2.2 Hz, CH), 128.4 (CH), 128.3 (2 × CH), 128.1 (d, $J$ = 5.4 Hz, CH), 127.4 (CH), 127.4 (d, $J$ = 25.4 Hz, CH), 126.3 (d, $J$ = 10.3 Hz, CH), 122.9 (d, $J$ = 3.5 Hz, CH), 119.8 (d, $J$ = 8.9 Hz, C), 113.2 (d, $J$ = 25.4 Hz, CH), 22.2 (CH$_3$). HRMS (APCI) exact mass calculated for C$_{21}$H$_{15}$F: 286.1152, found: 286.1146 [M$^+$]. IR (neat): 2919w, 2371w, 1617w, 1568w, 1492w, 1447s, 1384w, 1324w, 1221m, 896m, 809m, 766s, 702s.
6-Fluoro-3-methyl-9-phenylphenanthrene (2n) and 1-fluoro-6-methyl-10-phenylphenanthrene (2n')

According to GP2 with 3'-fluoro-5-methyl-[1,1'-biphenyl]-2-amine (1n, 50 mg, 0.25 mmol, 1.0 equiv.). Crude product was purified by flash column chromatography on silica gel using a 100:1 mixture of pentane/DCM as eluent to provide the analytically pure product 2n (20 mg, 70 μmol, 28%) along with 2n' (35 mg, 0.12 mmol, 49%).

![Chemical Structure of 2n]

**2n** Minor regioisomer (white solid): $^1$H NMR (300 MHz, CDCl₃, 300 K): $\delta = 8.40 – 8.32$ (m, 2H, CH$_{arom}$), 7.89 (dd, $J = 9.1, 6.0$ Hz, 1H, CH$_{arom}$), 7.79 ($d, J = 8.1$ Hz, 1H, CH$_{arom}$), 7.60 ($s$, 1H, CH$_{arom}$), 7.57 – 7.43 (m, 6H, CH$_{arom}$), 7.30 – 7.21 (m, 1H, CH$_{arom}$), 2.65 ($s$, 3H, CH$_3$). $^{13}$C NMR (75 MHz, CDCl$_3$, 300 K): $\delta = 161.6$ (d, $J = 245.6$ Hz, C), 140.9 (C), 137.6 (C), 136.6 (C), 123.2 ($d, J = 8.5$ Hz, C), 130.2 (CH), 130.1 ($d, J = 8.5$ Hz, CH), 129.6 ($d, J = 8.1$ Hz, C), 129.4 (CH), 129.3 ($d, J = 8.1$ Hz, CH), 128.7 (CH), 128.5 (2 × CH), 128.2 ($d, J = 1.5$ Hz, C), 127.6 (CH), 126.7 ($d, J = 2.3$ Hz, CH), 122.6 (CH), 115.3 ($d, J = 23.5$ Hz, CH), 108.1 ($d, J = 23.5$ Hz, CH), 22.3 (CH$_3$). IR (neat): 3014w, 2362s, 1601m, 1524m, 1439m, 1273w, 1201m, 948w, 863w, 823w, 767w, 701m, 513s. HRMS (APCI) exact mass calculated for C$_{21}$H$_{15}$F: 286.1152, found: 286.1154 [M$^+$]. MP: 93 °C.

![Chemical Structure of 2n']

**2n'** Major regioisomer (colorless oil): $^1$H NMR (300 MHz, CDCl$_3$, 300 K): $\delta = 8.58$ (ddd, $J = 8.5, 1.1$ Hz, 1H, CH$_{arom}$), 8.52 – 8.45 (m, 1H, CH$_{arom}$), 7.77 ($d, J = 8.1$ Hz, 1H, CH$_{arom}$), 7.64 – 7.52 (m, 2H, CH$_{arom}$), 7.54 – 7.38 (m, 6H, CH$_{arom}$), 7.20 (ddd, $J = 12.5, 7.8, 1.1$ Hz, 1H, CH$_{arom}$), 2.66 ($s$, 3H, CH$_3$). $^{13}$C NMR (75 MHz, CDCl$_3$, 300 K): $\delta = 159.7$ (d, $J = 256.8$ Hz, C), 143.6 ($d, J = 3.5$ Hz, C), 136.9 (C), 134.0 (C), 132.9 ($d, J = 3.2$ Hz, C), 130.0 (CH), 129.5 (C), 129.3 (C), 129.2 (CH), 128.8 (CH), 128.8 (CH), 128.5 (CH), 127.5 (2 × CH), 126.7 (CH), 126.5 ($d, J = 9.2$ Hz, C), 122.7 (CH), 120.6 ($d, J = 8.9$ Hz, C), 118.9 ($d, J = 3.9$ Hz, CH), 112.7 ($d, J = 23.0$ Hz, CH), 22.2 (CH$_3$). HRMS (APCI) exact mass calculated for C$_{21}$H$_{15}$F: 286.1152, found: 286.1145 [M$^+$]. IR (neat): 3055m, 2919w, 1599m, 1519w, 1456s, 1369m, 1241s, 1143m, 895m, 810s, 752s, 701s.
9-(4-Chlorophenyl)-3-methylphenanthrene (2o)

According to GP3 with 1-chloro-4-ethynylbenzene (344 mg, 2.50 mmol, 10.0 equiv.). Crude product was purified by flash column chromatography on silica gel using a 20:1 mixture of pentane/DCM as eluent to provide analytically pure product 2o as yellowish solid (56 mg, 0.19 mmol, 74%). 1H NMR (300 MHz, CDCl3, 300 K): δ = 8.88 - 8.66 (m, 1H, CHarom), 8.61 - 8.42 (m, 1H, CHarom), 7.88 - 7.77 (m, 2H, CHarom), 7.70 – 7.59 (m, 2H, CHarom), 7.56 – 7.40 (m, 6H, CHarom), 2.65 (s, 3H, CH3). 13C NMR (75 MHz, CDCl3, 300 K): δ = 139.4 (C), 136.6 (C), 136.5 (C), 133.3 (C), 131.4 (2 × CH), 131.0 (C), 130.4 (C), 130.1 (C), 129.4 (C), 128.7 (CH), 128.5 (CH), 128.5 (2 × CH), 127.5 (CH), 126.5 (CH), 126.5 (CH), 126.4 (CH), 123.0 (CH), 122.3 (CH), 22.2 (CH3). HRMS (APCI) exact mass calculated for C21H15Cl: 302.0857, found: 302.0850 [M+]. IR (neat): 3064 w, 2919 w, 1606 w, 1489 s, 1448 w, 1400 w, 1149 w, 1091 s, 1015 m, 949 w, 894 m, 834 s. MP: 88 °C.

9-(4-Bromophenyl)-3-methylphenanthrene (2p)

According to GP3 with 1-bromo-4-ethynylbenzene (453 mg, 2.50 mmol, 10.0 equiv.). Crude product was purified by flash column chromatography on silica gel using a 20:1 mixture of pentane/DCM as eluent to provide analytically pure product 2p as yellow solid (60 mg, 0.17 mmol, 69%). 1H NMR (300 MHz, CDCl3, 300 K): δ = 8.70 – 8.63 (m, 1H, CHarom), 8.42 (s, 1H, CHarom), 7.78 – 7.67 (m, 2H, CHarom), 7.60 – 7.50 (m, 4H, CHarom), 7.50 – 7.37 (m, 1H, CHarom), 7.38 – 7.30 (m, 3H, CHarom), 2.56 (s, 3H, CH3). 13C NMR (75 MHz, CDCl3, 300 K): δ = 140.0 (C), 136.7 (C), 136.6 (C), 131.9 (2 × CH), 131.6 (2 × CH), 131.1 (C), 130.5 (C), 130.3 (C), 129.5 (C), 128.8 (CH), 128.7 (CH), 127.6 (CH), 126.7 (CH), 126.6 (CH), 126.5 (CH), 123.1 (CH), 122.5 (CH), 121.6 (CH), 22.4 (CH3). HRMS (APCI) exact mass calculated for C21H15Br: 346.0352, found: 346.0346 [M+]. IR (neat): 2254w, 1067w, 1488m, 1387w, 1170w, 1074w, 1011m, 904s, 833m. MP: 100 °C.
3-Methyl-9-(4-(trifluoromethyl)phenyl)phenanthrene (2q)

According to GP3 with 1-ethyl-4-(trifluoromethyl)benzene (426 mg, 2.50 mmol, 10.0 equiv.). Crude product was purified by flash column chromatography on silica gel using a 50:1 mixture of pentane/DCM as eluent to provide analytically pure product 2q as yellowish solid (61 mg, 0.18 mmol, 73%).

$^1$H NMR (300 MHz, CDCl$_3$, 300 K): δ = 8.79 (dd, J = 8.4, 1.1 Hz, 1H, CH$_{arom}$), 8.53 (s, 1H, CH$_{arom}$), 7.85 – 7.75 (m, 4H, CH$_{arom}$), 7.73 – 7.62 (m, 4H, CH$_{arom}$), 7.57 – 7.50 (m, 1H, CH$_{arom}$), 7.48 (dd, J = 8.1, 1.6 Hz, 1H, CH$_{arom}$), 2.67 (s, 3H, CH$_3$).

$^{13}$C NMR (75 MHz, CDCl$_3$, 300 K): δ = 144.9 (C), 137.0 (C), 136.5 (C), 130.9 (C), 130.6 (2 × CH), 130.6 (C), 130.4 (C), 129.7 (q, J = 32.7 Hz, C), 129.4 (C), 128.9 (CH), 128.8 (CH), 127.8 (CH), 126.8 (CH), 126.6 (CH), 126.5 (CH), 125.4 (q, J = 3.9 Hz, 2 × CH), 124.5 (q, J = 271.2 Hz, CF$_3$) 123.2 (CH), 122.5 (CH), 22.4 (CH$_3$).

HRMS (APCI) exact mass calculated for C$_{22}$H$_{15}$F$_3$: 336.1120, found: 336.1114 [M$^+$.]. IR (neat): 3071w, 2923w, 16116w, 1504w, 1450w, 1410w, 1323s, 1164m, 1123s, 1066m, 1019w, 957w, 895w, 847m. MP: 92 °C.

9-(4-Methoxyphenyl)-3-methylphenanthrene (2r)

According to GP3 with 1-ethyl-4-methoxybenzene (330 mg, 2.50 mmol, 10.0 equiv.). Crude product was purified by flash column chromatography on silica gel using a 100:1 mixture of pentane/Et$_2$O as eluent to provide analytically pure product 2r as yellow foam (60 mg, 0.20 mmol, 80%).

$^1$H NMR (300 MHz, CDCl$_3$, 300 K): δ = 8.81 - 8.73 (m, 1H, CH$_{arom}$), 8.52 (d, J = 1.6 Hz, 1H, CH$_{arom}$), 7.95 (dd, J = 8.2, 1.4 Hz, 1H, CH$_{arom}$), 7.79 (d, J = 8.1 Hz, 1H, CH$_{arom}$), 7.70 – 7.62 (m, 2H, CH$_{arom}$), 7.58 – 7.40 (m, 4H, CH$_{arom}$), 7.06 (d, J = 8.6 Hz, 2H, CH$_{arom}$), 3.92 (s, 3H, OCH$_3$), 2.66 (s, 3H, CH$_3$).

$^{13}$C NMR (75 MHz, CDCl$_3$, 300 K): δ = 159.0 (C), 137.4 (C), 136.1 (C), 133.3 (C), 131.6 (C), 131.2 (2 × CH), 130.4 (C), 129.9 (C), 129.6 (C), 128.5 (CH), 128.4 (CH), 127.3 (CH), 126.9 (CH), 126.3 (CH), 126.1 (CH), 122.9 (CH), 122.3 (CH), 113.8 (2 × CH), 55.4 (OCH$_3$), 22.2 (CH$_3$).

HRMS (APCI) exact mass calculated for C$_{22}$H$_{18}$O: 298.1352, found: 298.1346 [M$^+$.]. IR (neat): 3017w, 2923w, 2930w, 2835w, 1609m, 1507s, 1459m, 1377w, 1284w, 1245s, 1175m, 1107w, 1034m, 905m, 836m. MP: 103 °C.
3-Methyl-9-(m-tolyl)phenanthrene (2s)

According to GP3 with 1-ethynyl-3-methylbenzene (290 mg, 2.50 mmol, 10.0 equiv.). Crude product was purified by flash column chromatography on silica gel using a 20:1 mixture of pentane/DCM as eluent to provide analytically pure product 2s as yellowish oil (52 mg, 0.19 mmol, 74%). \[^1^H\,\text{NMR}\, (300\,\text{MHz, CDCl}_3, \,300\,\text{K}): \delta = 8.77 \,(dd, J = 8.3, \,1.2 \,Hz, \,1H, \,CH\text{arom}), \,8.52 \,(d, J = 1.6 \,Hz, \,1H, \,CH\text{arom}), \,7.93 \,(dd, J = 8.3, \,1.4 \,Hz, \,1H, \,CH\text{arom}), \,7.80 \,(d, J = 8.0 \,Hz, \,1H, \,CH\text{arom}), \,7.69 \,-\,7.61 \,(m, \,2H, \,CH\text{arom}), \,7.53 \,(ddd, J = 8.2, \,6.9, \,1.3 \,Hz, \,1H, \,CH\text{arom}), \,7.49 \,-\,7.33 \,(m, \,4H, \,CH\text{arom}), \,7.31 \,-\,7.25 \,(m, \,1H, \,CH\text{arom}), \,7.26 \,(s, \,3H, \,CH_3), \,2.66 \,(s, \,3H, \,CH_3). \,^{13}\text{C\,NMR}\,(75\,\text{MHz, CDCl}_3, \,300\,\text{K}): \delta = 140.9 \,(C), \,138.0 \,(C), \,137.9 \,(C), \,136.2 \,(C), \,131.4 \,(C), \,130.8 \,(CH), \,130.4 \,(C), \,130.0 \,(C), \,129.6 \,(C), \,128.6 \,(CH), \,128.5 \,(CH), \,128.1 \,(CH), \,128.0 \,(CH), \,127.2 \,(CH), \,127.2 \,(CH), \,127.0 \,(CH), \,126.3 \,(CH), \,126.2 \,(CH), \,122.8 \,(CH), \,122.3 \,(CH), \,22.2 \,(CH_3), \,21.5 \,(CH_3). \,\text{HRMS (APCI)}\,\text{exact mass calculated for C}_{22}\text{H}_{18}: \,282.1403, \,\text{found:} \,282.1396 \,[M^+]. \,\text{IR (neat):} \,3020\,\text{m}, \,2918\,\text{m}, \,2858\,\text{w}, \,1600\,\text{s}, \,1503\,\text{m}, \,1449\,\text{s}, \,1377\,\text{m}, \,1168\,\text{w}, \,1199\,\text{w}, \,1091\,\text{w}, \,1043\,\text{m}, \,954\,\text{w}, \,891\,\text{s}.\n
3-Methyl-9-(2-(trifluoromethyl)phenyl)phenanthrene (2t)

According to GP3 with 1-ethynyl-2-(trifluoromethyl)benzene (425 mg, 2.50 mmol, 10.0 equiv.). Crude product was purified by flash column chromatography on silica gel using pentane as eluent to provide analytically product 2t as brown oil (68 mg, 0.20 mmol, 81%). \[^1^H\,\text{NMR}\, (300\,\text{MHz, CDCl}_3, \,300\,\text{K}): \delta = 8.78 \,(dd, J = 8.4, \,1.2 \,Hz, \,1H, \,CH\text{arom}), \,8.62 \,-\,8.46 \,(m, \,1H, \,CH\text{arom}), \,7.89 \,(dd, J = 7.6, \,1.6 \,Hz, \,1H, \,CH\text{arom}), \,7.81 \,(d, J = 8.1 \,Hz, \,1H, \,CH\text{arom}), \,7.70 \,-\,7.57 \,(m, \,4H, \,CH\text{arom}), \,7.51 \,-\,7.35 \,(m, \,4H, \,CH\text{arom}), \,2.68 \,(s, \,3H, \,CH_3). \,^{13}\text{C\,NMR}\,(75\,\text{MHz, CDCl}_3, \,300\,\text{K}): \delta = 139.5 \,(C), \,136.7 \,(C), \,134.4 \,(C), \,132.9 \,(CH), \,132.0 \,(C), \,131.2 \,(CH), \,130.3 \,(C), \,130.1 \,(q, \,J = 29.9 \,Hz, \,C), \,130.0 \,(C), \,129.0 \,(C), \,128.7 \,(CH), \,128.6 \,(CH), \,127.7 \,(CH), \,127.7 \,(CH), \,127.0 \,(CH), \,126.4 \,(CH), \,126.2 \,(2 \times \,CH), \,124.1 \,(q, \,J = 271.2 \,Hz, \,CF_3), \,122.7 \,(CH), \,122.4 \,(CH), \,22.2 \,(CH_3). \,\text{HRMS (APCI)}\,\text{exact mass calculated for C}_{22}\text{H}_{15}\text{F}_{3}: \,336.1120, \,\text{found:} \,336.1114 \,[M^+]. \,\text{IR (neat):} \,3068\,\text{w}, \,2922\,\text{w}, \,1602\,\text{w}, \,1503\,\text{w}, \,1451\,\text{w}, \,1314\,s, \,1264\,w, \,1168\,m, \,1126s, \,1035m, \,899w.\n
3-Methyl-9-(naphthalen-1-yl)phenanthrene (2u)

According to GP3 with 1-ethynlnaphthalene (381 mg, 2.50 mmol, 10.0 equiv.). Crude product was purified by flash column chromatography on silica gel using a 20:1 mixture of pentane/DCM as eluent to provide analytically pure product 2u as white solid (68 mg, 0.21 mmol, 85%) along with small amounts of another unidentified isomer. 

\(^{1}\text{H}\) NMR (300 MHz, CDCl\(_3\), 300 K): \(\delta = 8.81 (d, J = 8.2 \text{ Hz}, 1\text{H}, \text{CH}_{\text{arom}}), 8.60 (s, 1\text{H}, \text{CH}_{\text{arom}}), 8.00 - 7.94 (m, 2\text{H}, \text{CH}_{\text{arom}}), 7.81 (d, J = 8.0 \text{ Hz}, 1\text{H}, \text{CH}_{\text{arom}}), 7.75 (s, 1\text{H}, \text{CH}_{\text{arom}}), 7.66 - 7.30 (m, 9\text{H}, \text{CH}_{\text{arom}}), 2.70 (s, 3\text{H}, \text{CH}_{3})\).

\(^{13}\text{C}\) NMR (75 MHz, CDCl\(_3\), 300 K): \(\delta = 138.8 (\text{C}), 136.6 (\text{C}), 136.2 (\text{C}), 133.7 (\text{C}), 133.2 (\text{C}), 132.5 (\text{C}), 130.5 (\text{C}), 130.2 (\text{C}), 129.7 (\text{C}), 128.8 (\text{CH}), 128.7 (\text{CH}), 128.4 (\text{CH}), 128.3 (\text{CH}), 128.1 (\text{CH}), 128.0 (\text{CH}), 127.6 (\text{CH}), 126.8 (\text{CH}), 126.6 (\text{CH}), 126.4 (\text{CH}), 126.1 (\text{CH}), 126.0 (\text{CH}), 125.6 (\text{CH}), 122.9 (\text{CH}), 122.5 (\text{CH}), 22.4 (\text{CH}_3)\).

HRMS (APCI) exact mass calculated for C\(_{25}\)H\(_{18}\): 318.1403, found: 318.1394 [M+].

IR (neat): 3058 \text{m}, 2165 \text{w}, 1920 \text{w}, 1591 \text{m}, 1504 \text{s}, 1449 \text{m}, 1378 \text{m}, 1038 \text{w}, 906 \text{s}.

MP: 82 °C.

2-(3-Methylphenanthren-9-yl)pyridine (2v)

According to GP3 with 2-ethynylpyridine (258 mg, 2.50 mmol, 10.0 equiv.) Crude product was purified by flash column chromatography on silica gel using a 10:1 mixture of pentane/Et\(_2\)O as eluent to provide analytically pure product 2v as green oil (44 mg, 0.17 mmol, 66%). 

\(^{1}\text{H}\) NMR (300 MHz, CDCl\(_3\), 300 K): \(\delta = 8.84 (d, J = 4.9 \text{ Hz}, 1\text{H}, \text{CH}_{\text{arom}}), 8.77 (dd, J = 8.3, 1.3 \text{ Hz}, 1\text{H}, \text{CH}_{\text{arom}}), 8.56 - 8.50 (m, 1\text{H}, \text{CH}_{\text{arom}}), 8.08 (dd, J = 8.2, 1.4 \text{ Hz}, 1\text{H}, \text{CH}_{\text{arom}}), 7.88 - 7.82 (m, 3\text{H}, \text{CH}_{\text{arom}}), 7.72 - 7.62 (m, 2\text{H}, \text{CH}_{\text{arom}}), 7.59 - 7.53 (m, 1\text{H}, \text{CH}_{\text{arom}}), 7.46 (dd, J = 8.1, 1.6 \text{ Hz}, 1\text{H}, \text{CH}_{\text{arom}}), 7.40 - 7.34 (m, 1\text{H}, \text{CH}_{\text{arom}}), 2.65 (s, 3\text{H}, \text{CH}_3)\).

\(^{13}\text{C}\) NMR (75 MHz, CDCl\(_3\), 300 K): \(\delta = 159.5 (\text{C}), 149.5 (\text{CH}), 137.0 (2 \times \text{C}), 136.7 (\text{CH}), 136.1 (\text{C}), 130.7 (\text{C}), 130.5 (\text{C}), 129.4 (\text{C}), 129.0 (\text{CH}), 128.7 (\text{CH}), 128.6 (\text{CH}), 126.7 (\text{CH}), 126.5 (\text{CH}), 125.3 (\text{CH}), 123.0 (\text{CH}), 122.5 (\text{CH}), 122.2 (\text{CH}), 22.4 (\text{CH}_3)\).

HRMS (ESI) exact mass calculated for C\(_{20}\)H\(_{15}\)NH: 270.1227, found: 270.1282 ([M+H]\(^+\)).

IR (neat): 3051\text{w}, 2918\text{w}, 1584\text{s}, 1521\text{w}, 1468\text{s}, 1450\text{m}, 1382\text{w}, 1254\text{w}, 1150\text{m}, 1046\text{m}, 933\text{m}, 895\text{m}, 786\text{s}, 763\text{s}, 725\text{s}, 586\text{m}.
9-(Cyclohex-1-en-1-yl)-3-methylphenanthrene (2w)

According to GP3 with 1-ethynylcyclohex-1-ene (256 mg, 2.50 mmol, 10.0 equiv.). Crude product was purified by flash column chromatography on silica gel using pentane as eluent to provide analytically pure product 2w as colorless oil (31 mg, 0.12 mmol, 46%).

$^1$H NMR (300 MHz, CDCl$_3$, 300 K): $\delta = 8.75 - 8.66 (m, 1H, CH$_{arom}$), 8.46 (s, 1H, CH$_{arom}$), 8.04 (dd, $J = 8.0$, 1.6 Hz, 1H, CH$_{arom}$), 7.75 (d, $J = 8.1$ Hz, 1H, CH$_{arom}$), 7.66 - 7.56 (m, 2H, CH$_{arom}$), 7.51 (s, 1H, CH$_{arom}$), 7.46 - 7.38 (m, 2H, CH$_{arom}$), 5.86 (dt, $J = 3.7$, 1.9 Hz, 1H, C=CH), 2.63 (s, 3H, CH$_3$), 2.48 - 2.40 (m, 2H, CH$_2$), 2.37 - 2.24 (m, 2H, CH$_2$), 1.95 - 1.77 (m, 4H, 2 × CH$_2$).

$^{13}$C NMR (75 MHz, CDCl$_3$, 300 K): $\delta = 140.6$ (C), 138.2 (C), 135.7 (C), 130.3 (C), 129.8 (C), 129.7 (C), 128.7 (C), 128.3 (CH), 128.1 (CH), 126.5 (CH), 126.1 (CH), 125.9 (CH), 125.0 (CH), 122.9 (CH), 122.2 (CH), 31.0 (CH$_2$), 25.6 (CH$_2$), 23.3 (CH$_2$), 22.4 (CH$_3$), 22.1 (CH$_2$). HRMS (APCI) exact mass calculated for C$_{21}$H$_{20}$: 272.1560, found: 272.1553 [M$^+$].

IR (neat): 3066 w, 2924 s, 2855 m, 1602 m, 1502 m, 1446 m, 1378 w, 1342 w, 1133 w, 1042 w, 886 m.

9-Cyclopropyl-3-methylphenanthrene (2x)

According to GP3 with ethynylcyclopropane (165 mg, 2.50 mmol, 10.0 equiv.). Crude product was purified by flash column chromatography on silica gel using pentane as eluent to provide analytically pure product 2x as colorless oil (33 mg, 0.14 mmol, 57%).

$^1$H NMR (300 MHz, CDCl$_3$, 300 K): $\delta = 8.73 (dd, J = 6.3$, 3.3 Hz, 1H, CH$_{arom}$), 8.54 - 8.48 (m, 1H, CH$_{arom}$), 8.48 - 8.44 (m, 1H, CH$_{arom}$), 7.76 - 7.64 (m, 3H, CH$_{arom}$), 7.53 (t, $J = 0.9$ Hz, 1H, CH$_{arom}$), 7.41 (dd, $J = 8.1$, 1.6 Hz, 1H, CH$_{arom}$), 2.63 (s, 3H, CH$_3$), 2.41 - 2.28 (m, 1H, CH), 1.15 - 1.06 (m, 2H, CH$_2$), 0.90 - 0.78 (m, 2H, CH$_2$).

$^{13}$C NMR (75 MHz, CDCl$_3$, 300 K): $\delta = 136.3$ (C), 135.7 (C), 132.9 (C), 130.2 (C), 129.9 (C), 129.7 (C), 128.3 (CH), 128.1 (CH), 126.3 (CH), 126.0 (CH), 125.0 (CH), 124.4 (CH), 122.9 (CH), 122.2 (CH), 22.1 (CH$_3$), 13.8 (CH), 6.2 (2 × CH$_2$). HRMS (APCI) exact mass calculated for C$_{18}$H$_{16}$: 232.1247, found: 232.1237 [M$^+$]. IR (neat): 3077 m, 3007 m, 2917 w, 1610 m, 1504 m, 1433 m, 1327 m, 1221 w, 1164 m, 1124 m, 1022 m, 950 w, 890 s.
Methyl 3-methylphenanthrene-9-carboxylate (2y)

According to GP3 with methyl propiolate (210 mg, 2.50 mmol, 10.0 equiv.). Crude product was purified by flash column chromatography on silica gel using a 50:1 mixture of pentane/EtOAc as eluent to provide analytically pure product 2y as brown oil (30 mg, 0.12 mmol, 48%).

\( ^1H \text{NMR} \) (300 MHz, CDCl\(_3\), 300 K): \( \delta = 9.05 - 8.85 \) (m, 1H, CH\(_{\text{arom}}\)), 8.78 – 8.66 (m, 1H, CH\(_{\text{arom}}\)), 8.49 – 8.43 (m, 2H, CH\(_{\text{arom}}\)), 7.86 (d, \( J = 8.1 \) Hz, 1H, CH\(_{\text{arom}}\)), 7.73 – 7.62 (m, 2H, CH\(_{\text{arom}}\)), 7.47 (dd, \( J = 8.2, 1.6 \) Hz, 1H, CH\(_{\text{arom}}\)), 4.04 (s, 3H, CO\(_2\)CH\(_3\)), 2.64 (s, 3H, CH\(_3\)).

\( ^{13}C \text{NMR} \) (75 MHz, CDCl\(_3\), 300 K): \( \delta = 168.1 \) (C), 139.1 (C), 132.4 (CH), 132.3 (C), 130.4 (C), 129.8 (CH), 129.3 (C), 128.8 (CH), 127.9 (C), 127.3 (CH), 126.7 (CH), 126.6 (CH), 125.1 (C), 122.8 (CH), 122.4 (CH), 52.2 (CO\(_2\)CH\(_3\)), 22.4 (CH\(_3\)). HRMS (ESI) exact mass calculated for \( C_{17}H_{14}O_2Na \): 273.0886, found: 273.0897 ([M+Na]\(^+\)]. IR (neat): 2950 w, 1714 s, 1621 m, 1520 w, 1449 m, 1296 m, 1250 s, 1193 s, 1161 s, 1109 m, 1030 m, 913 w, 874 w.

Trimethyl(3-methylphenanthren-9-yl)silane (2z) and trimethyl(6-methylphenanthren-9-yl)silane (2z’)

According to GP3 with ethynyltrimethylsilane (246 mg, 2.50 mmol, 10.0 equiv). Crude product was purified by flash column chromatography on silica gel using pentane as eluent to provide an inseparable mixture of two isomers as yellow oil (31 mg, 0.12 mmol, 47%).

\( ^1H \text{NMR} \) (300 MHz, CDCl\(_3\), 300 K): \( \delta = 8.79 - 8.66 \) (m, 1H, CH\(_{\text{arom}}\)), 8.51 (m, 1H, CH\(_{\text{arom}}\)), 8.17 – 8.03 (m, 1H, CH\(_{\text{arom}}\)), 7.96 – 7.86 (m, 1H, CH\(_{\text{arom}}\)), 7.79 (m, 1H, CH\(_{\text{arom}}\)), 7.69 – 7.56 (m, 2H, CH\(_{\text{arom}}\)), 7.43 (dd, \( J = 7.9, 1.6 \) Hz, 1H, CH\(_{\text{arom}}\)), 2.64 (s, 3H, CH\(_3\)), 0.53 (s, 9H, 2 \( \times \) CH\(_3\)). For the major isomer: \( ^{13}C \text{NMR} \) (75 MHz, CDCl\(_3\), 300 K): \( \delta = 134.8 \) (CH), 128.6 (CH), 128.4 (CH), 128.0 (CH), 125.7 (CH), 125.4 (CH), 123.0 (CH), 121.9 (CH), 21.9 (CH\(_3\)), 0.0 (3 \( \times \) CH\(_3\)). For the minor isomer: \( ^{13}C \text{NMR} \) (75 MHz, CDCl\(_3\), 300 K): \( \delta = 134.8 \) (CH), 128.6 (CH), 128.4 (CH), 128.0 (CH), 125.7 (CH), 125.4 (CH), 123.0 (CH), 121.9 (CH), 21.9 (CH\(_3\)), 0.0 (3 \( \times \) CH\(_3\)). Other signals cannot be clearly identified. HRMS (APCI) exact mass calculated for \( C_{18}H_{20}Si \): 264.1324, found: 264.1329 [M\(^+\)]. IR (neat): 2932 w, 2311 w, 1289 w, 931 s, 822 m, 750 s, 686 m.
X-ray crystallographic data


X-ray crystal structure analysis of 2c: formula C22H18, M = 282.36, colourless crystal, 0.18 x 0.15 x 0.05 mm, a = 11.2196(4), b = 12.1534(4), c = 11.8670(4) Å, β = 112.497(1)°, V = 1495.0(1) Å³, ρcalc = 1.255 gcm⁻³, μ = 0.532 mm⁻¹, empirical absorption correction (0.911 ≤ T ≤ 0.972), Z = 4, monoclinic, space group P21/c (No. 14), λ = 1.54178 Å, T = 100(2) K, ω and φ scans, 15233 reflections collected (±h, ±k, ±l) to a maximum θ angle of 66.60° (0.84 Å resolution), 2634 independent (Rint = 0.030) and 2283 observed reflections [I>2σ(I)], 201 refined parameters, R = 0.038, wR2 = 0.104, max. (min.) residual electron density 0.32 (-0.31) e.Å⁻³, hydrogen atoms calculated and refined as riding atoms.

X-ray crystal structure analysis of 2g: formula C21H15Cl, M = 302.78, colourless crystal, 0.15 x 0.15 x 0.08 mm, a = 11.2081(2), b = 12.3535(3), c = 11.9376(3) Å, β = 113.383(3)°, V = 1517.1(1) Å³, ρcalc = 1.326 gcm⁻³, μ = 0.245 mm⁻¹, empirical absorption correction (0.964 ≤ T ≤ 0.980), Z = 4, monoclinic, space group P21/c (No. 14), λ = 0.71073 Å, T = 223(2) K, ω and φ scans, 8277 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.66 Å⁻¹, 3609 independent (Rint = 0.039) and 2653 observed reflections [I>2σ(I)], 200 refined parameters, R = 0.061,
$wR^2 = 0.151$, max. (min.) residual electron density $0.22\, (-0.23)\, \text{e.Å}^{-3}$, hydrogen atoms calculated and refined as riding atoms.

Figure 1. Crystal structure of compound 2c.

(Thermals ellipsoids are shown with 50% probability.)

Figure 2. Crystal structure of compound 2g.

(Thermals ellipsoids are shown with 30% probability.)
2v
Literature


