Supporting Information
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Supporting information for:

Novel palladium free synthesis of a key Quinazolinap precursor

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General methods

CH₂Cl₂ was dried on a PureSolv solvent purification systems from Innovative Technology. Other solvents and reactants were used directly as received from Sigma-Aldrich. Reactions were monitored by thin-layer chromatography with pre-coated silica gel 60 F254 aluminum plates (Merck KGaA, Darmstadt). Flash chromatography was performed on silica gel purchased from Apollo Scientific (Zeoprep 60/40-63m iorons). ¹H, ¹³C and 2D NMR experiments were recorded on a Varian NMR System 500MHz Spectrometer; ¹⁹F NMR experiments were recorded on a Varian NMR System 300 MHz Spectrometer. Proton shifts are reported in ppm relative to residual CHCl₃ (δ=7.26). Multiplicities are given as: s (singlet), d (dublet), dd (doublet of doublets), ddd (doublet of doublets of doublets), t (triplet), m (multiplet). ¹³C chemical shifts are reported relative to residual CHCl₃ (δ=77.00). ¹⁹F chemical shifts are reported relative to trifluoroacetic acid (δ=-76.55). Infrared spectra were recorded on a Varian 3100 FT-IR Excalibur series spectrometer. HR-mass spectra were recorded on a Micromass/Waters Corp. USA liquid chromatography time-of-flight (LCT) mass spectrometer when ESI could be used, or on a gas chromatography time-of-flight (GCT) premier equipped with an electron impact probe otherwise. Melting points were recorded using a Barnsted Electrothermal 9300 apparatus.
Synthesis of 4-chloro-2-(trifluoromethyl)quinazoline (8i)

A solution of trifluoroacetic anhydride (5.10 mL, 1 equiv.) in CH₂Cl₂ (50 mL) was added dropwise over 1h with vigorous stirring to a suspension of anthranilamide (5 g, 1 equiv.) and triethylamine (6.1 mL, 1.2 equiv.) in CH₂Cl₂ (100 mL) at 0°C. The reaction mixture was stirred overnight at room temperature and evaporated under reduced pressure. The crude 2-trifluoroacetamidobenzamide was added to ethanol (150 mL) and 10M NaOH (50 mL) solution and the mixture was heated to reflux for 3.5 h. The reaction was then cooled at 0°C, neutralized to pH = 7 using hydrochloric acid and the volatiles were removed under reduced pressure. The solid residue was filtered, washed with water and dried under high vacuum.

The crude 2-(trifluoromethyl)quinazolin-4-ol was refluxed with N,N-diethylaniline (7.01 mL, 1.2 equiv.) and toluene (150 mL) for 30 min in a Dean Stark apparatus. Phosphorus oxychloride (2.35 mL, 0.7 equiv.) was added by syringe and the resultant solution was refluxed for 6 h. The dark red solution was cooled to room temperature and filtered. The filtrate was sequentially washed with ice-cooled 2M NaOH solution (50 mL), ice cooled water (50 mL), ice cooled 1M hydrochloric acid solution (50 mL), water (50 mL) and brine (50 mL). The organic layer was dried over MgSO₄, filtered and evaporated under reduced pressure. The crude product was then recrystallised from pentane to give 6.34g of 8i (74% over the three steps) as a slightly yellow powder.

8i: ¹H NMR (500 MHz, CDCl₃): 8.38 (1H, d, J = 8.46 Hz), 8.24 (1H, d, J= 8.44 Hz), 8.10 (1H, ddd, J = 8.40, 7.10, 1.06Hz), 7.90 (1H, ddd, J = 8.43, 7.17; 1.04 Hz); ¹³C NMR (125 MHz, CDCl₃): 164.31, 150.63, 136.29, 131.31, 129.77, 126.21, 123.89, 2 missing because of J_FC splitting; ¹⁹F NMR (282 MHz, CDCl₃ with trifluoroacetic acid as reference): -69.94 ; IR (neat, cm⁻¹): 3431.8, 3059.7, 1645.9, 1615.0, 1559.6, 1487.6, 1396.5, 1355.0, 1264.7, 1250.4, 1192.7, 1173.4, 1113.6, 994.1, 880.4, 850.4, 780.0, 758.2, 691.6, 629.8; HR-MS (EI): C₉H₄ClF₃N₂ [M]+ m/z: calc. 232.0015, found 232.0012; mp: 91-92°C.

Synthesis of 1-(2-(trifluoromethyl)quinazolin-4-yl)naphthalen-2-ol (9i)

2-Naphthol 3 (144.2 mg, 1 equiv.), 4-chloro-2-(trifluoromethyl)quinazoline 8i (232.6 mg, 1 equiv.) and aluminium chloride (400,0 mg, 3 equiv.) were suspended in 1,2-dichloroethane (3 mL) in a Schlenk tube under a nitrogen atmosphere. The mixture was heated at 80 °C for 3.5 h and then diluted in CH₂Cl₂ (15 mL). The mixture was washed with 1M NaOH solution (15 mL), saturated NH₄Cl solution (15 mL), water (15 mL), brine (15 mL), dried over MgSO₄, filtered and evaporated under reduced pressure. The crude product was then crystallised from pentane to give 8.34g of 9i in quantitative yield.

9i: ¹H NMR (500 MHz, CDCl₃): 8.37 (1H, broad s, OH), 8.30 (1H, d, J= 8.49 Hz), 8.03 (1H, ddd, J = 8.41, 7.15, 1.05 Hz), 7.97 (1H, d, J= 8.90 Hz), 7.87 (1H, d, J = 8.09 Hz), 7.72 (1H, d, J = 8.41 Hz), 7.59 (1H, ddd, J = 8.17, 7.15, 0.82 Hz), 7.38 (1H, ddd, J = 8.00, 7.03, 0.73 Hz), 7.34 (1H, d, J = 8.99 Hz), 7.29 (1H, ddd, J = 8.20, 7.01, 0.73 Hz), 7.17 (1H, d, J = 8.38 Hz); ¹³C NMR (125 MHz, CDCl₃): 167.76, 154.36, 150.85, 135.52, 133.32, 132.35, 129.68, 129.51, 128.87, 128.50, 128.25, 127.22, 124.44, 124.07. 119.01, 114.11, 2 missing because of J_FC splitting; ¹⁹F NMR (282 MHz, CDCl₃ with trifluoroacetic acid as reference): -70.40 ; IR (neat, cm⁻¹): 3446.6, 1631.3, 1571.2, 1517.2, 1493.9, 1440.5, 1389.6, 1355.2, 1299.5, 1280.7, 1247.6, 1204.0, 1176.1, 1130.3, 1107.3, 1064.0, 1017.0, 986.9, 967.3, 886.3, 813.2, 771.7; HR-MS (ESI): C₁₉H₁₂F₃N₂O [MH]+ m/z: calc. 341.0902, found 341.0886; mp: 202-204°C.
Synthesis of 1N-benzyl-1-(2-phenylquinazolin-4-yl)naphthalen-2-amine (13b)

N-benzyl naphthalen-2-amine 12b (233.3 mg, 1 equiv.), 4-chloro-2-phenylquinazoline 8g (240.7 mg, 1 equiv.) and aluminium chloride (400.2 mg, 3 equiv.) were suspended in 1,2-dichloroethane (3 mL) in a Schlenk tube under a nitrogen atmosphere. The mixture was heated at 80 °C for 3.5 h and then diluted in CH₂Cl₂ (15 mL). The mixture was washed with 1M NaOH solution (15 mL), saturated NH₄Cl solution (15 mL), water (15 mL), brine (15 mL), dried over MgSO₄, filtered and evaporated under reduced pressure. The solid was purified by column chromatography in Pentane/CH₂Cl₂ 1:3, to afford a brown solid in 67% yield (293.1 mg).

13b: ¹H NMR (500 MHz, CDCl₃): 8.59 (1H, dd, J = 4.30, 2.97 Hz), 8.23 (1H, d, J = 8.14 Hz), 8.08 (1H, d, J = 8.27 Hz), 7.90 (1H, t, J = 7.43 Hz), 7.67-7.60 (2H, m), 7.57 (1H, d, J = 8.14 Hz), 7.55-7.45 (4H, m), 4.42 (2H, s), 4.16 (1H, broad s, NH); ¹³C NMR (125 MHz, CDCl₃): 145.78, 139.18, 136.72, 135.19, 134.78, 131.13, 129.04, 128.95, 128.93, 128.75, 128.68, 128.65, 128.48, 128.23, 128.20, 127.63, 127.60, 127.32, 126.31, 125.99, 125.83, 125.30, 122.49, 122.04, 117.83, 104.68, 48.38; IR (neat, cm⁻¹): 3419.6, 1629.9, 1566.7, 1552.9, 1480.0, 1477.3, 1347.4, 1335.4, 1319.5, 1247.6, 1158.3, 1077.0, 1028.7, 981.9, 844.6, 769.5, 733.6, 701.7, 692.4, 659.6; HR-MS (ESI): C₃₁H₂₃N₃[MH]⁺ m/z: calc. 438.1970, found 438.1957; mp: 180°C (decomposition).

Synthesis of 1-(2-phenylquinazolin-4-yl)naphthalen-2-amine (13a)

Methanol (50 mL) was poured on 1N-benzyl-1-(2-phenylquinazolin-4-yl)naphthalen-2-amine 13b (500 mg, 1 equiv.) and 5% palladium on charcoal (243.2 mg, 0.1 equiv.) under a hydrogen atmosphere. The suspension was stirred overnight at room temperature. The reaction was filtered over celite, then evaporated under reduced pressure. The product was purified by column chromatography in CH₂Cl₂ to afford 345.2 mg of 13a as a beige powder (87%).

13a: ¹H NMR (500 MHz, CDCl₃): 8.56 (1H, dd, J = 7.09, 2.02 Hz), 7.82 (1H, dd, J= 6.05, 3.35 Hz), 7.78 (1H, d, J = 8.79 Hz), 7.67 (1H, dd, J= 5.95, 3.23 Hz), 7.61 (1H, d, J = 2.02 Hz), 7.57 (1H, ddd, J = 8.26, 7.04, 1.10 Hz), 7.52-7.45 (4H, m), 7.30-7.24 (2H, m), 7.22 (1H, s, NH₂); ¹³C NMR (125 MHz, CDCl₃): 139.18, 134.78, 131.13, 129.04, 128.95, 128.93, 128.75, 128.68, 128.65, 128.23, 128.20, 127.63, 127.60, 127.32, 126.31, 125.99, 125.83, 125.30, 122.49, 122.04, 117.83, 104.68; IR (cm⁻¹): 3427.8, 1629.9, 1566.7, 1552.9, 1480.0, 1477.3, 1347.4, 1335.4, 1319.5, 1247.6, 1158.3, 1077.0, 1028.7, 981.9, 844.6, 769.5, 733.6, 701.7, 692.4, 659.6; HR-MS (ESI): C₂₄H₂₃N₃[MH]⁺ m/z: calc. 348.1501, found 348.1500; mp: 193°C (decomposition).
$^1$H NMR
$^{13}$C NMR
8i HMBC NMR
$^{19}$F NMR
$9i$ $^1$H NMR
$^{13}$C NMR
$^{19}\text{F NMR}$
$^{13}$C NMR – Magnified
13a $^1$H NMR
Supporting Information
Palladium-catalyzed intramolecular C-H activation: a synthetic approach towards polycyclic aromatic hydrocarbons

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B. Spectral (1H, 13C and IR) and analytical data for compounds(3a-3p), 4 and (5a-5p) S2-S13

A. General remarks

All reactions were carried out using oven-dried glassware. Commercial grade reagents were used without further purification. Solvents were dried and distilled following usual protocols prior to use. All yields
Refer to isolated yields after column purification. Column chromatography was carried out using Silica gel (60-120 mesh) purchased from Rankem, India. TLC was performed on aluminium-backed plates coated with Silica gel 60 with F254 indicator (Merck).

The $^1$H NMR spectra were measured with Bruker-200 (200 MHz) or Bruker-400 (400 MHz) and $^{13}$C NMR spectra were measured with Bruker-200 (50 MHz) or Bruker-400 (100 MHz) using CDCl$_3$. Coupling constants in $^1$H NMR are in Hz. Elemental analyses were carried out in Perkin-Elmer 2400 instrument in the analytical lab of chemistry department, IIT, Kharagpur. IR spectra were recorded on Perkin-Elmer IR7313 spectrophotometer. Melting points were taken in open capillaries and are uncorrected.

**B. Spectral and analytical data for compounds**

1-(1-Bromo-naphthalen-2-yl)-2-phenyl-ethanol (3a)

![Chemical structure of 3a](image)

Colorless semisolid; $R_f$ (10:1 petroleum ether/ethylacetate) 0.24; IR (vmax, in CHCl$_3$): 3350, 812 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 200MHz) 2.76-2.95 (1H, m), 3.26 (1H, dd, $J = 3.2, 13.6$ Hz), 5.61 (1H, dd, $J = 2.8, 9.2$ Hz), 7.19-7.38 (5H, m), 7.49-7.66 (2H, m), 7.69-7.77 (1H, m), 7.83-7.88 (2H, m), 8.36 (1H, d, $J = 8.2$ Hz); $^{13}$C NMR (50 MHz, CDCl$_3$) 44.5, 72.2, 121.5, 124.4, 126.5, 127.4, 127.5, 128.1, 128.3, 129.4 (2 × C), 129.5 (2 × C), 132.2, 134.2, 135.1, 136.4, 141.1; Elemental analysis: Found: C, 66.02; H, 4.65. C$_{18}$H$_{15}$BrO requires C, 66.07; H, 4.62.

1-(1-Bromo-naphthalen-2-yl)-2-p-tolyl-ethanol (3b)

![Chemical structure of 3b](image)

Colorless semisolid; $R_f$ (10:1 petroleum ether/ethylacetate) 0.28; IR (vmax, in CHCl$_3$): 3376, 1508, 1053, 816 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 200MHz) 2.39 (3H, s), 2.78-2.93 (1H, m), 3.24 (1H, dd, $J = 2.8, 13.6$ Hz), 5.58 (1H, dd, $J = 3, 9.4$ Hz), 7.14-7.22 (2H, m), 7.25-7.32 (2H, m), 7.53-7.69 (2H, m), 7.74-7.78 (1H, m), 7.84-7.88 (2H, m), 8.40 (1H, d, $J = 8.4$ Hz); $^{13}$C NMR (50 MHz, CDCl$_3$) 21.2, 43.9, 74.9, 121.5, 124.4, 126.5, 127.4, 127.5, 128.1, 128.3, 129.4 (2 × C), 129.5 (2 × C), 132.2, 134.2, 135.1, 136.4, 141.1; Elemental analysis: Found C, 66.99; H, 5.22. C$_{19}$H$_{17}$BrO requires C, 66.87; H, 5.02.
1-(1-Bromo-4-methyl-naphthalene-2-yl)-2-phenyl-ethanol (3c)

Colorless semisolid; \( R_f \) (10:1 petroleum ether/ethylacetate) 0.25; IR (\( \nu_{\text{max}} \), in \( \text{CHCl}_3 \)): 3320, 1498, 821 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\), 200MHz) 2.71 (3H, s), 2.82-2.89 (1H, m), 3.25 (1H, dd, \( J = 2.8, 13.6 \) Hz), 5.58 (1H, \( J = 2.8, 9.6 \) Hz), 7.16-7.31 (2H, m), 7.31-7.39 (3H, m), 7.53-7.64 (3H, m), 7.99 (1H, d, \( J = 8 \) Hz), 8.40 (1H, d, \( J = 8 \) Hz); \(^13\)C NMR (100 MHz, CDCl\(_3\)) 19.4, 44.3, 74.9, 119.3, 124.5, 124.9, 126.3, 126.7, 127.1, 127.8, 128.6 (2 x C), 129.5 (2 x C), 131.9, 133.3, 134.5, 138.2, 140.2; Elemental analysis: Found C, 67.02; H, 5.15. \( \text{C}_{19}\text{H}_{17}\text{BrO} \) requires C, 66.87; H, 5.02.

1-(1-Bromo-5-methoxy-naphthalene-2-yl)-2-o-tolyl-ethanol (3d)

Colorless semisolid; \( R_f \) (10:1 petroleum ether/ethylacetate) 0.21; IR (\( \nu_{\text{max}} \), in \( \text{CHCl}_3 \)): 3361, 1621, 1268.87, 821 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\), 400MHz) 2.46 (3H, s), 2.92-2.97 (1H, m), 2.22 (1H, dd, \( J = 3.6, 14 \) Hz), 5.61 (1H, dd, \( J = 3.6, 9.6 \) Hz), 6.87 (1H, d, \( J = 5.2 \) Hz), 7.19- 7.21 (3H, m), 7.31- 7.34 (3H, m), 7.47-7.53 (1H, m), 7.77 (1H, d, \( J = 8.8 \) Hz), 7.92-7.94 (1H, m), 8.33 (1H, dd, \( J = 8.4 \) Hz); \(^13\)C NMR (100 MHz, CDCl\(_3\)) 19.7, 41.3, 55.7, 73.8, 104.4, 119.5, 119.9, 122.2, 123.2, 123.5, 125.9, 126.9, 127.4, 128.2, 130.4, 130.5, 136.0, 137.2, 141.6, 155.3; Elemental analysis: Found C, 64.89; H, 5.09. \( \text{C}_{20}\text{H}_{19}\text{BrO}_2 \) requires C, 64.70; H, 5.16.

1-(1-Bromo-5-methoxy-naphthalene-2-yl)-2-p-tolyl-ethanol (3e)

Colorless semisolid; \( R_f \) (10:1 petroleum ether/ethylacetate) 0.21; IR (\( \nu_{\text{max}} \), in \( \text{CHCl}_3 \)): 3329, 1642, 1228, 815 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\), 200MHz) 2.36 (3H, s), 2.74-2.86 (1H, m), 3.22 (1H, dd, \( J = 3, 13.8 \) Hz), 4.02 (3H,
1-(1-Bromo-6-methoxy-naphthalen-2-y1)-2-phenyl-ethanol (3f)

Colorless semisolid; R<sub>f</sub> (10:1 petroleum ether/ethylacetate) 0.19; IR (v<sub>max</sub>, in CHCl<sub>3</sub>) 3332, 1613, 1238, 820 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400MHz) 2.83-2.87 (1H, m), 3.19-3.25 (1H, m), 3.94 (3H, s), 5.55 (1H, dd, J = 3.2, 9.2 Hz), 7.10-7.13 (1H, m), 7.24-7.27 (2H, m), 7.35-7.37 (4H, m), 7.67-7.73 (2H, m), 8.25 (1H, d, J = 9.2 Hz);<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 44.3, 55.4, 74.7, 106.0, 119.9, 121.4, 124.8, 126.7, 126.9, 128.0, 128.5 (2 × C), 128.9, 129.5 (2 × C), 135.2, 138.2, 138.4, 157.9; Elemental analysis: Found C, 63.99; H, 4.72. C<sub>19</sub>H<sub>17</sub>BrO<sub>2</sub> requires C, 63.88; H, 4.80.

1-(1-Bromo-6-methoxy-naphthalen-2-y1)-2-o-tolyl-ethanol (3g)

Colorless semisolid; R<sub>f</sub> (10:1 petroleum ether/ethylacetate) 0.20; IR (v<sub>max</sub>, in CHCl<sub>3</sub>) 3326, 1620, 1255, 830 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400MHz) 2.45 (3H, s), 2.92-2.98 (1H, m), 3.19 (1H, dd, J = 3.6, 13.6 Hz), 3.94 (3H, s), 5.57-5.59 (1H, m), 7.03-7.34 (6H, m), 7.76 (2H, m), 8.38 (1H, d, J = 9.6 Hz);<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 19.7, 41.5, 55.4, 73.6, 106.4, 119.9, 121.4, 124.9, 125.9, 126.8, 126.9, 127.3, 129.0, 130.4, 130.6, 135.2, 136.1, 137.2, 138.7, 157.9; Elemental analysis: Found C, 64.61; H, 5.29. C<sub>20</sub>H<sub>19</sub>BrO<sub>2</sub> requires C, 64.70; H, 5.16.

1-(1-Bromo-6-methoxy-naphthalen-2-y1)-2-p-tolyl-ethanol (3h)
1-(1-Bromo-7-methoxy-naphthalen-2-yl)-2-phenyl-ethanol (3i)

Colorless semisolid; \( R_f \) (10:1 petroleum ether/ethylacetate) 0.21; IR (vmax, in CHCl\(_3\)): 3350, 1623, 1477, 1265, 848 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\), 200MHz) 2.38 (3H, s), 2.76-2.95 (1H, m), 3.20 (1H, dd, \( J = 3, 13.6 \) Hz), 3.94 (3H, s), 5.53 (1H, dd, \( J = 3.4, 9.6 \) Hz), 7.12-7.19 (3H, m), 7.24-7.28 (3H, m), 7.70 (2H, d, \( J = 1.4 \) Hz), 8.26 (1H, d, \( J = 9.2 \) Hz); \(^{13}\)C NMR (50 MHz, CDCl\(_3\)) 21.2, 44.0, 55.5, 74.9, 106.1, 119.9, 121.5, 124.9, 126.9, 127.5, 128.9, 129.3 (2 × C), 129.5 (2 × C), 135.2, 135.3, 136.3, 138.6, 158.1; Elemental analysis: Found C, 64.90; H, 5.05. \( C_{20}H_{19}BrO_2 \) requires C, 64.70; H, 5.16.

1-(1-Bromo-7-methoxy-naphthalen-2-yl)-2-p-tolyl-ethanol (3j)

1-(2-Bromo-napthalen-1-yl)-2-phenyl-ethanol (3k)
1-(2-Bromo-napthalen-1-yl)-2-o-tolyl-ethanol (3l)

Colorless semisolid; $R_f$ (10:1 petroleum ether/ethylacetate) 0.25; IR (vmax, in CHCl$_3$): 3369, 821 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 200MHz) 3.15-3.27 (1H, m), 3.42-3.56 (1H, m), 5.95-6.06 (1H, m), 7.25-7.39 (5H, m), 7.54-7.64 (4H, m), 7.84-7.88 (1H, m), 8.99 (1H, d, $J = 8$ Hz); $^{13}$C NMR (50 MHz, CDCl$_3$) 43.0, 121.4, 126.1, 126.4, 126.8, 128.6 (3 × C), 128.9, 129.7 (4 × C), 130.3, 132.4, 133.8, 136.9, 138.5; Elemental analysis: Found C, 65.90; H, 4.49. C$_{18}$H$_{15}$BrO requires C, 66.07; H, 4.62.

1-(2-Bromo-napthalen-1-yl)-2-p-tolyl-ethanol (3m)

Colorless semisolid; $R_f$ (10:1 petroleum ether/ethylacetate) 0.26; IR (vmax, in CHCl$_3$): 3327, 2921, 1447, 750 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 200MHz) 2.491 (3H, s), 3.206 (1H, dd, $J = 4.6, 13.8$ Hz), 3.512-3.630 (1H, m), 5.947-6.018 (1H, m), 7.056-7.306 (4H, m), 7.505-7.656 (4H, m), 7.831-7.878 (1H, m), 9.013 (1H, d, $J = 8.2$ Hz); $^{13}$C NMR (50 MHz, CDCl$_3$) 19.95, 39.88, 76.18, 121.42, 126.04 (2 × C), 126.12, 126.38, 126.88, 128.89, 129.70, 130.28, 130.51, 130.74, 132.47, 133.85, 136.42, 136.97, 137.08; Elemental analysis: Found C, 66.82; H, 4.94. C$_{19}$H$_{17}$BrO requires C, 66.87; H, 5.02.

1-(2-Bromo-phenyl)-2-o-tolyl-ethanol (3n)

Colorless semisolid; $R_f$ (10:1 petroleum ether/ethylacetate) 0.28; IR (vmax, in CHCl$_3$): 3307, 1458, 1437, 753 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 200MHz) 2.38 (3H, s), 3.16 (1H, dd, $J = 3.6, 13.6$ Hz), 3.39-3.45 (1H, m), 5.92-5.97 (1H, m), 7.18-7.19 (2H, m), 7.29-7.31 (2H, m), 7.53-7.65 (4H, m), 7.85 (1H, d, $J = 8$ Hz), 8.99 (1H, d, $J = 6$ Hz); $^{13}$C NMR (100 MHz, CDCl$_3$) 20.8, 42.5, 76.76, 121.3, 125.9, 126.2, 126.3, 128.8, 129.3 (2 × C), 129.5 (2 × C), 129.6, 130.2, 132.3, 133.7, 135.3, 136.2, 136.8; Elemental analysis: Found C, 66.78; H, 4.90. C$_{19}$H$_{17}$BrO requires C, 66.87; H, 5.02.
dd, $J = 3.6, 9.6$ Hz), 7.12-7.20 (3H, m), 7.34-7.42 (2H, m), 7.53-7.58 (2H, m), 7.62-7.68 (1H, m); $^{13}$C NMR (50 MHz, CDCl$_3$) 19.9, 41.6, 72.9, 121.8, 126.1, 126.9, 127.6, 127.8, 128.9, 130.6 (2 × C), 132.6, 136.1, 137.2, 143.2; Elemental analysis: Found C, 62.01; H, 5.00. C$_{15}$H$_{15}$BrO requires C, 61.87; H, 5.19.

1-(2-Bromo-phenyl)-2- p-tolyl-ethanol (3o)

Colorless semisolid; $R_f$ (10:1 petroleum ether/ethylacetate) 0.29; IR (vmax, in CHCl$_3$): 3259, 1438, 1063, 801 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 200MHz) 2.37 (3H, s), 2.65-2.76 (1H, m), 3.19 (1H, dd, $J = 2.8, 13.8$ Hz), 5.24 (1H, dd, $J = 2.6, 9.4$ Hz), 7.15-7.25 (5H, m), 7.33-7.40 (1H, m), 7.55-7.59 (2H, m); $^{13}$C NMR (50 MHz, CDCl$_3$) 21.1, 43.9, 74.1, 121.8, 127.3, 127.8, 128.8, 129.3 (2 × C), 129.4 (2 × C), 132.6, 135.1, 136.4, 142.9; Elemental analysis: Found C, 61.96; H, 5.04. C$_{15}$H$_{15}$BrO requires C, 61.87; H, 5.19.

1-(2-Bromo-5-fluoro-phenyl)-2-phenyl-ethanol (3p)

Colorless semisolid. $R_f$ (10:1 petroleum ether/ethylacetate) 0.31; $^1$H NMR (CDCl$_3$, 200MHz) 2.63-2.77 (1H, m), 3.21 (1H, dd, $J = 3, 13.8$ Hz), 5.18 (1H, dd, $J = 2.4, 9$ Hz), 6.84-6.97 (1H, m), 7.26-7.394 (6H, m), 7.47-7.56 (1H, m). $^{13}$C NMR (50 MHz, CDCl$_3$) 44.2, 73.9, 114.7 (d, $^1$C-$^1$F = 24.5 Hz), 116.0 (d, $^1$C-$^1$F = 22 Hz), 126.9, 128.4 (d, $^1$C-$^1$F = 6 Hz), 128.7 (2 × C), 129.5 (2 × C), 131.3 (d, $^1$C-$^1$F = 18.5 Hz), 133.8 (d, $^1$C-$^1$F = 8 Hz), 137.8, 145.3 (d, $^1$C-$^1$F = 7.5 Hz). Elemental analysis: Found C, 56.90; H, 4.04. C$_{14}$H$_{12}$BrFO requires C, 56.97; H, 4.10.

5,6-Dihydro-benzo[c]phenanthrene-6-ol (4)

Yellow semisolid; $R_f$ (5:1 petroleum ether/ethyl acetate) 0.20; IR (vmax, in CHCl$_3$): 3338.50, 1624.72, 861.22, 825.92 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 200MHz) 3.12 (2H, d, $J = 5.4$ Hz), 4.92 (1H, t), 7.28-7.54 (5H, m), 7.67 (1H, d, $J = 8.4$ Hz), 7.82-7.99 (3H, m), 8.56-8.61 (1H, m); $^{13}$C NMR (50 MHz, CDCl$_3$) 38.6, 69.5, 124.4, 125.9, 126.1, 126.5, 126.8, 127.6, 128.6, 128.9, 129.1, 129.8, 129.9, 130.8, 133.3, 134.8, 134.9, 137.3; Elemental analysis: Found C 87.71, H 5.80. C$_{18}$H$_{14}$O requires C 87.78, H 5.73.
Benzo[c]phenanthrene (5a)

Colorless solid; \( R_f \) (petroleum ether) 0.35; mp 65-67 °C (lit. mp 67-68 °C); \(^1\)H NMR (CDCl\(_3\), 200MHz) 7.50-7.78 (4H, m), 7.850-7.98 (4H, m), 8.05-8.15 (2H, m), 9.19 (2H, d, \( J = 8.2 \) Hz); \(^{13}\)C NMR (50 MHz, CDCl\(_3\)) 125.9 (2 × C), 126.1 (2 × C), 126.9 (2 × C), 127.5 (2 × C), 127.9 (2 × C), 128.6 (2 × C), 130.4 (2 × C), 131.0 (2 × C), 133.5 (2 × C); Elemental analysis: Found C, 94.96; H, 5.11. C\(_{18}\)H\(_{12}\) requires C, 94.70; H, 5.30.

2-Methyl-benzo[c]phenanthrene (5b)

Colorless solid; \( R_f \) (petroleum ether) 0.40; mp 80-83 °C (lit. mp 80-81 °C); \(^1\)H NMR (CDCl\(_3\), 200MHz) 2.68 (3H, s), 7.48 (1H, d, \( J = 8.2 \) Hz), 7.60-64 (1H, m), 7.67-7.76 (2H, m), 7.80-7.97 (4H, m), 8.02-8.06 (1H, m), 8.96 (1H, bs), 9.18 (1H, d, \( J = 8 \) Hz); \(^{13}\)C NMR (50 MHz, CDCl\(_3\)) 22.5, 125.9, 126.2, 126.2, 127.1, 127.2, 127.5, 127.5, 127.6, 127.9, 128.1, 128.6, 128.8, 130.7, 130.7, 131.4, 131.83, 133.7, 136.1; Elemental analysis: Found C, 93.99; H, 5.92. C\(_{19}\)H\(_{14}\) requires C, 94.18; H, 5.82.

5-Methyl-benzo[c]phenanthrene (5c)

Colorless solid; \( R_f \) (petroleum ether) 0.41; mp 68-70 °C (lit. mp 69-70 °C); \(^1\)H NMR (CDCl\(_3\), 400MHz) 2.82 (3H, s), 7.58-7.62 (1H, m), 7.66-7.72 (4H, m), 7.77 (1H, d, \( J = 8.4 \) Hz), 7.89 (1H, d, \( J = 8.4 \) Hz), 8.01 (1H, d, \( J = 7.6 \) Hz), 8.18-8.20 (1H, m), 9.08 (1H, d, \( J = 8.4 \) Hz), 9.15 (1H, d, \( J = 8.8 \) Hz); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) 19.7, 124.4, 125.4, 125.6, 125.7, 126.0, 126.3, 126.4, 127.1, 127.4, 127.8, 128.3, 128.5, 130.16, 130.4, 130.7, 133.0 (2 × C), 133.2; Elemental analysis: Found C, 94.29; H, 5.86. C\(_{19}\)H\(_{14}\) requires C, 94.18; H, 5.82.

4-Methoxy-9-methyl benzo[c]phenanthrene (5d)
Colorless solid; $R_f$ (50:1 petroleum ether/ethyl acetate) 0.23; mp 79-80 °C; IR ($\nu_{\text{max}}$, in KBr): 1601, 1425, 1259, 838 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 400MHz) 2.83 (3H, s), 4.09 (3H, s), 7.03 (1H, d, $J = 7.6$ Hz), 7.46 (1H, d, $J = 6.8$ Hz), 7.53-7.59 (2H, m), 7.80-7.88 (2H, m), 8.11 (1H, d, $J = 8.8$ Hz), 8.41 (1H, d, $J = 8.8$ Hz), 8.68 (1H, d, $J = 8.4$ Hz), 8.98 (1H, d, $J = 8.4$ Hz); $^{13}$C NMR (100 MHz, CDCl$_3$) 20.2, 55.7, 104.7, 120.8 (2 × C), 123.2, 124.9, 125.3, 125.9, 125.9, 126.5, 126.6, 126.8, 127.5, 130.5, 130.7, 131.4, 132.2, 134.3, 155.6. Elemental analysis: Found C, 88.05; H, 5.61. C$_{20}$H$_{16}$O requires C, 88.20; H, 5.92.

9-Methoxy-2-methyl benzo[c]phenanthrene (5e)

![9-Methoxy-2-methyl benzo[c]phenanthrene (5e)](image)

Colorless solid; $R_f$ (50:1 petroleum ether/ethyl acetate) 0.28; mp 93-94 °C; IR ($\nu_{\text{max}}$, in KBr): 1601, 1255, 1066, 847 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 400MHz) 2.7 (3H, s), 4.1 (3H, s), 7.02 (1H, d, $J = 7.6$ Hz), 7.45 (1H, d, $J = 8$ Hz), 7.59-7.63 (1H, m), 7.76 (1H, d, $J = 8.8$ Hz), 7.81-7.86 (2H, m), 7.91 (1H, d, $J = 8$ Hz), 8.40 (1H, d, $J = 8.8$ Hz), 8.74 (1H, d, $J = 8.4$ Hz), 8.94 (1H, s); $^{13}$C NMR (50 MHz, CDCl$_3$) 22.2, 55.8, 104.8, 120.4, 120.8, 125.0, 125.9, 126.0, 126.2, 126.8, 127.4, 127.6, 127.8, 128.3, 130.8, 131.4, 131.6 (2 × C), 135.7, 155.8; Elemental analysis: Found C, 88.12; H, 6.05. C$_{20}$H$_{16}$O requires C, 88.20; H, 5.92.

3-Methoxy-benzo[c]phenanthrene (5f)

![3-Methoxy-benzo[c]phenanthrene (5f)](image)

Colorless solid; $R_f$ (50:1 petroleum ether/ethyl acetate) 0.17; mp 89-90 °C (lit. mp 90-91 °C); $^1$H NMR (CDCl$_3$, 400MHz) 4.01 (3H, m), 7.32-7.37 (2H, m), 7.59-7.69 (2H, m), 7.79-7.86 (4H, m), 8.01 (1H, d, $J = 7.6$ Hz), 9.04-9.08 (2H, m); $^{13}$C NMR (50 MHz, CDCl$_3$) 55.6, 108.1, 117.3, 125.3, 126.0, 126.1, 126.7, 126.9, 127.1, 127.7, 127.8, 128.1, 128.7, 129.7, 129.9, 130.3, 133.8, 135.3, 157.7.

3-Methoxy-9-methyl-benzo[c]phenanthrene (5g)

![3-Methoxy-9-methyl-benzo[c]phenanthrene (5g)](image)

Colorless solid; $R_f$ (50:1 petroleum ether/ethyl acetate) 0.16; mp 65-66 °C; IR ($\nu_{\text{max}}$, in KBr): 1624, 1429, 1261, 867 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 200MHz) 2.83 (3H, s), 4.01 (3H, s), 7.29-7.38 (2H, m), 7.45-7.59 (2H, m), 7.90-7.95 (3H, m), 8.08-8.15 (3H, m), 8.39-8.45 (2H, m), 8.75-8.78 (2H, m), 8.95-8.98 (1H, s); $^{13}$C NMR (200 MHz, CDCl$_3$) 20.2, 55.7, 104.7, 120.8 (2 × C), 123.2, 124.9, 125.3, 125.9, 126.5, 126.6, 126.8, 127.5, 130.5, 130.7, 131.4, 132.2, 134.3, 155.6. Elemental analysis: Found C, 89.05; H, 5.97. C$_{20}$H$_{18}$O requires C, 89.20; H, 5.92.
7.77-7.87 (3H, m), 8.06 (1H, d, J = 8.8 Hz), 8.92 (1H, d, J = 8.4 Hz), 9.01 (1H, d, J = 9.2 Hz); $^{13}$C NMR (100 MHz, CDCl$_3$) 20.2, 55.4, 107.9, 116.8, 122.2, 125.1, 125.3, 126.3, 126.6, 126.7, 126.9, 127.2, 128.1, 129.2, 129.8, 130.0, 132.4, 134.4, 135.1, 157.4. Elemental analysis: Found C, 88.12; H, 5.79. C$_{20}$H$_{16}$O requires C, 88.20; H, 5.92.

10-Methoxy-2-methyl-benzo[c]phenanthrene (5h)

![Image of 5h]

Colorless solid; $R_f$ (50:1 petroleum ether/ethyl acetate) 0.16; mp 95-96 °C; IR (vmax, in KBr): 1616, 1269, 855, 835 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 200MHz) 2.66 (3H, s), 4.01 (3H, m), 7.31-7.37 (2H, m), 7.43-7.48 (1H, dd, J = 8.2, 1.4 Hz), 7.71-7.75 (1H, m), 7.79-7.83 (3H, m), 7.91 (1H, d, J = 8 Hz), 8.87 (1H, s), 9.06 (1H, d, J = 8.8 Hz); $^{13}$C NMR (50 MHz, CDCl$_3$) 22.3, 55.4, 108.0, 116.9, 125.2, 125.9, 126.3, 126.6, 127.3, 127.4, 127.5, 127.7, 128.4, 129.4, 129.9, 130.3, 131.7, 135.1, 135.7, 157.4. Elemental analysis: Found C, 87.98; H, 5.92. C$_{20}$H$_{16}$O requires C, 88.20; H, 5.92.

2-Methoxy-benzo[c]phenanthrene (5i)

![Image of 5i]

Colorless solid; $R_f$ (50:1 petroleum ether/ethyl acetate) 0.22; mp 80-82 °C (lit.mp 78-79 °C); $^1$H NMR (CDCl$_3$, 400MHz) 4.03 (3H, s), 7.26-7.31 (1H, m), 7.60-7.72 (3H, m), 7.81-7.96 (4H, m), 8.02 (1H, d, J = 7.6 Hz), 8.59 (1H, s), 9.21 (1H, d, J = 8.4 Hz); $^{13}$C NMR (50 MHz, CDCl$_3$) 55.5, 109.0, 116.4, 124.6, 125.6, 125.9, 126.9, 127.0, 127.1, 127.4, 128.5, 128.6, 129.9, 130.5, 130.8, 131.5 (2 × C), 133.3, 158.2; Elemental analysis: Found C, 88.50; H, 5.61. C$_{19}$H$_{14}$O requires C, 88.34; H, 5.46.

2-Methoxy-11-methyl-benzo[c]phenanthrene (5j)

![Image of 5j]

Colorless solid; $R_f$ (50:1 petroleum ether/ethyl acetate) 0.20; mp 118-120 °C; IR (vmax, in KBr): 1606, 1217, 840 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 200MHz) 2.65 (3H, s), 4.04 (3H, s), 7.26-7.31 (1H, m), 7.44-7.48 (1H, m),
7.66-7.95 (6H, m), 8.62 (1H, d, \(J = 2.2\) Hz), 9.03 (1H, s); \(^{13}\)C NMR (50 MHz, CDCl\(_3\)) 22.2, 55.4, 108.7, 116.4, 124.6, 126.0, 126.2, 126.7, 126.9, 127.2, 127.4, 128.4, 128.4, 129.8, 130.6, 131.4, 131.5, 131.6, 135.6, 158.0. Elemental analysis: Found C 88.28, H 5.80. \(C_{20}H_{16}O\) requires C 88.20, H 5.92.

**Chrysene (5k)**

![Chrysene](image)

Colorless solid; \(R_f\) (petroleum ether) 0.30; mp 250-152 °C (lit. mp 254 °C), IR (\(v_{\max}\), in KBr): 816.54, 756.05; \(^1\)H NMR (CDCl\(_3\), 200MHz) 7.59-7.76 (4H, m), 7.98-8.04 (4H, m), 8.71-8.87 (4H, m); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) 121.2 (2 × C), 123.1 (2 × C), 126.3 (2 × C), 126.6 (2 × C), 127.3 (2 × C), 128.2 (2 × C), 128.5 (2 × C), 130.5 (2 × C), 132.1 (2 × C); Elemental analysis: Found C, 94.50; H, 5.13. \(C_{18}H_{12}\) requires C, 94.70; H, 5.30.

**1-Methyl-Chrysene (5l)**

![1-Methyl-Chrysene](image)

Colorless solid; \(R_f\) (petroleum ether) 0.36; mp 250-253 °C (lit. mp 253-254 °C); \(^1\)H NMR (CDCl\(_3\), 200MHz) 2.83 (3H, s), 7.51-7.73 (4H, m), 7.99-8.03 (2H, m), 8.22 (1H, d, \(J = 9.4\) Hz), 8.67-8.83 (4H, m); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) 19.8, 120.9, 121.3, 121.5, 123.0, 123.3, 126.2, 126.3, 126.6, 127.4, 128.4, 129.7, 130.5, 130.6, 131.0, 131.2, 132.0, 134.8; Elemental analysis: Found C, 94.29; H, 5.99. \(C_{19}H_{14}\) requires C, 94.18; H, 5.82.

**3-Methyl-Chrysene (5m)**

![3-Methyl-Chrysene](image)

Colorless solid; \(R_f\) (petroleum ether) 0.34; mp 173-175 °C (lit. mp 171-172 °C); \(^1\)H NMR (CDCl\(_3\), 200MHz) 2.67 (3H, s), 7.45-7.49 (1H, m), 7.59-7.75 (2H, m), 7.88-8.10 (4H, m), 8.57-8.75 (4H, m); Elemental analysis: Found C, 94.37; H, 5.90. \(C_{19}H_{14}\) requires C, 94.18; H, 5.82.

**1-Methyl-Phenanthrene (5n)**

![1-Methyl-Phenanthrene](image)

Colorless solid; \(R_f\) (petroleum ether) 0.34; mp 173-175 °C (lit. mp 171-172 °C); \(^1\)H NMR (CDCl\(_3\), 200MHz) 2.67 (3H, s), 7.45-7.49 (1H, m), 7.59-7.75 (2H, m), 7.88-8.10 (4H, m), 8.57-8.75 (4H, m); Elemental analysis: Found C, 94.37; H, 5.90. \(C_{19}H_{14}\) requires C, 94.18; H, 5.82.
Colorless solid; $R_f$ (petroleum ether) 0.37; mp 120-122 °C (lit. mp 122-122.5 °C); $^1$H NMR (CDCl$_3$, 400MHz) 2.77 (3H, s), 7.45 (1H, d, $J = 7.2$ Hz), 7.53-7.65 (3H, m), 7.79 (1H, d, $J = 9.2$ Hz), 7.90 (1H, d, $J = 8$ Hz), 7.97 (1H, d, $J = 9.2$ Hz), 8.59 (1H, d, $J = 8.4$ Hz), 8.71 (1H, d, $J = 8.4$ Hz); $^{13}$C NMR (50 MHz, CDCl$_3$) 19.9, 120.9, 122.9, 122.9, 126.2, 126.4, 126.6, 126.7, 127.8, 128.5, 130.4, 130.7, 130.8, 131.7, 134.9; Elemental analysis: Found C, 93.90; H, 6.17. C$_{15}$H$_{12}$ requires C, 93.71; H, 6.29.

3- Methyl-Phenanthrene (5o)$^8$

![3-Methyl-Phenanthrene (5o)]

Colorless solid; $R_f$ (petroleum ether) 0.38; mp 64-66 °C (lit. mp 63 °C); $^1$H NMR (CDCl$_3$, 400MHz) 2.63 (3H, s), 7.43 (1H, d, $J = 8$ Hz), 7.56-7.72 (4H, m), 7.79 (1H, d, $J = 8$ Hz), 7.87 (1H, d, $J = 8$ Hz), 8.48 (1H, s), 8.68 (1H, d, $J = 8$ Hz); $^{13}$C NMR (100 MHz, CDCl$_3$) 22.1, 122.3, 122.5, 125.9, 126.3, 126.4, 126.7, 128.2, 128.3, 128.5, 129.7, 129.9, 130.3, 132.1, 136.2; Elemental analysis: Found C, 93.55; H, 6.45. C$_{15}$H$_{12}$ requires C, 93.71; H, 6.29.

2-Fluoro-phenanthrene (5p)$^9$

![2-Fluoro-phenanthrene (5p)]

Colorless solid; $R_f$ (petroleum ether) 0.35; mp 100-103 °C (lit. mp 102-104 °C); $^1$H NMR (CDCl$_3$, 200MHz) 7.32-7.38 (1H, m), 7.41-7.48 (1H, m), 7.51-7.56 (1H, m), 7.59-7.67 (2H, m), 7.73-7.78 (1H, m), 7.84-7.89 (1H, m), 8.570-8.678 (2H, m). Elemental analysis: Found C, 85.69; H, 4.62. C$_{14}$H$_9$F requires C, 85.70; H, 4.55.

References:
