Supporting Information

A Convergent Approach to Polycyclic Aromatic Hydrocarbons

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General Experimental Methods

Purification procedures were in accordance with the instructions in D. D. Perrin and W. L. F. Armarego, “Purification of Laboratory Chemicals”, Fourth Edition, The Bath Press, Bath, 2002. All reactions were carried out under dry, oxygen free nitrogen. Flash chromatography was performed on silica gel (SDS, 60 Å C. C. 40-63 mm) as the stationary phase. Thin Layer Chromatography (TLC) was performed on alumina plates pre-coated with silica gel (Merck silica gel, 60 F254), which were visualized by the quenching of UV fluorescence when applicable (λmax = 254 nm and/or 366 nm) and/or by staining with vanillin or anisadehyde in acidic ethanol followed by heating. Infrared spectra were recorded as solutions in CH2Cl2 using NaCl cells, on a Perkin-Elmer FT 2000. Absorption maxima (nmax) are reported in wavenumbers (cm⁻¹) and only selected peaks are reported. Magnetic resonance spectra were recorded at room temperature on a Bruker Avance DPX 400 instrument. Proton magnetic resonance spectra (1H NMR) were recorded at 400 MHz and coupling constants (J) are reported to ± 0.5 Hz. The following abbreviations were utilized to describe peak patterns when appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, quint = quintuplet, hex = hexuplet, hept = heptuplet, oct = octuplet and m = multiplet. Carbon magnetic resonance spectra (13C NMR) were recorded in the same instrument at 100.6 MHz. Chemical shifts (δH, δC) are quoted in parts per million (ppm) and are referenced to TMS (0 ppm). Low-resolution mass spectra (m/z) were recorded by chemical ionization (CI/NH3) on a Hewlett-Packard HP 5989B and only report molecular species ([M+H]+, [M+NH4]+) and other major fragments. High-resolution mass spectra were recorded by positive electron impact ionization (EI+) at 70 e.V. on a JEOL JMS-GCmate II mass spectrometer. The quoted masses are accurate to ± 5 ppm. The names of the molecules that appear in the following pages were generated using either Beilstein AutoNom 2000 (CAS) or ChemBioDraw Ultra 10.0.
List of the Abbreviations Used

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Meaning</th>
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<tbody>
<tr>
<td>AcOEt</td>
<td>Ethyl acetate</td>
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<td>Dilauroyl peroxide</td>
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<td>p-Toluenesulfonic acid</td>
</tr>
<tr>
<td>RT</td>
<td>Room temperature</td>
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</table>
Experimental Procedures and Spectroscopic Data

General procedure A for the preparation of xanthates

To a solution of the corresponding bromo-acetophenone (1.0 eq) in acetone (1 mL.mmol$^{-1}$) under a nitrogen at 0 °C was added potassium O-ethylxanthate (1.2 eq) portionwise. The mixture was stirred for 15 min and then quenched by the addition of water (1 mL.mmol$^{-1}$). The solvent was removed under reduced pressure and the residue was diluted with ethyl acetate (5 mL.mmol$^{-1}$). The organic layer was separated and the aqueous layer extracted with ethyl acetate (5 mL.mmol$^{-1}$). The combined organic layers were washed with brine, dried over magnesium sulfate and concentrated under reduced pressure. The crude residue was purified by recrystallisation in a mixture of hexane and ethyl acetate.

General procedure B for radical addition/cyclisation reactions

A stirred solution of xanthate (1.0 eq) and olefin (2.0 eq) in ethyl acetate (3 mL.mmol$^{-1}$ with respect to the xanthate) was refluxed for 15 minutes under a nitrogen atmosphere. Dilauroyl peroxide (DLP) was then added in 20 %mol portions every 60 minutes until complete consumption of the starting material was observed. The reaction mixture was then cooled to room temperature and evaporated to dryness under reduced pressure. The crude residue was purified by flash chromatography on silica gel to yield the desired compound.

General procedure C for the addition of phenyl lithium to ketones

To a solution of iodobenzene (3.3 eq) in diethylether (1.0 ml.mmol$^{-1}$) at -78 °C under a nitrogen atmosphere was added nBuLi (3.0 eq) dropwise. The solution was stirred for 60 min at -78 °C. After this time a solution of the ketone (1.0 eq) in diethylether (0.15 mL.mmol$^{-1}$) was added dropwise to the mixture. After 15 min the solution was allowed to warm up to RT and the reaction was stirred for 1 h. Water (5 mL.mmol$^{-1}$) and NH$_4$Cl (sat. aq.) (5 mL.mmol$^{-1}$) were added to the reaction mixture. The layers were separated and the aqueous phase extracted further with DCM three times (5 mL.mmol$^{-1}$). The combined organic layers were dried over MgSO$_4$ and evaporated under reduced pressure. The crude residue was purified by flash chromatography on silica gel to give the desired product.
Compound 3a: O-ethyl S-2-(4-methoxyphenyl)-2-oxoethyl carbonodithioate

Following the general procedure A, the reaction was carried out with 2-bromo-1-(4-methoxyphenyl)ethanone (12.0 g, 52.4 mmol). Recrystallisation afforded the desired product as a yellow solid (12.2 g, 45.0 mmol, 86%).

$^1$H NMR (δ, ppm) (CDCl$_3$, 400 MHz): 8.01 (m, 2H, C$_2$H & C$_6$H); 6.96 (m, 2H, C$_3$H & C$_5$H); 4.63 (q, 2H, J = 7.1 Hz, OC$_{11}$H$_2$); 4.62 (s, 2H, SC$_8$H$_2$); 3.88 (s, 3H, OC$_9$H$_3$); 1.39 (t, 3H, J = 7.1 Hz, C$_{12}$H$_3$).

$^{13}$C NMR (δ, ppm) (CDCl$_3$, 100.6 MHz): 213.48 (C$_{10}$S); 190.78 (C$_7$O); 164.00 (C$_4$O); 130.82 (C$_2$H & C$_6$H); 128.78 (C$_1$); 113.96 (C$_3$H & C$_5$H); 70.61 (C$_{11}$H$_2$O); 55.54 (OC$_9$H$_3$); 43.36 (C$_8$H$_2$); 13.73 (C$_{12}$H$_3$). IR (cm$^{-1}$) (CCl$_4$): 2986, 2961, 2938, 2840, 1681, 1602, 1222.

HRMS (EI+) calcd for C$_{12}$H$_{14}$O$_3$S$_2$ 270.0384, found: 270.0392. Mp: 67 °C.

Compound 3b: O-ethyl S-2-(4-chlorophenyl)-2-oxoethyl carbonodithioate

Following the general procedure A, the reaction was carried out with 2-bromo-1-(4-chlorophenyl)ethanone (9.00 g, 38.5 mmol). Recrystallisation afforded the desired product as a white solid (8.79 g, 32.0 mmol, 83%).

$^1$H NMR (δ, ppm) (CDCl$_3$, 400 MHz): 8.02 (d, 2H, J = 8.7 Hz, C$_2$H & C$_6$H); 7.53 (d, 2H, J = 8.7 Hz, C$_3$H & C$_5$H); 4.69 (q, 2H, J = 7.1 Hz, OC$_{10}$H$_2$); 4.68 (s, 2H, SC$_8$H$_2$); 1.45 (t, 3H, J = 7.1 Hz, C$_{11}$H$_3$).

$^{13}$C NMR (δ, ppm) (CDCl$_3$, 100.6 MHz): 213.18 (C$_9$S); 191.41 (C$_7$O); 140.39 (C$_1$); 130.17 (C$_{10}$Cl); 129.91 (C$_2$H & C$_6$H); 129.23 (C$_3$H & C$_5$H); 71.02 (C$_{11}$H$_2$O); 43.54 (C$_8$H$_2$); 13.73 (C$_{12}$H$_3$). IR (cm$^{-1}$) (CCl$_4$): 2987, 2902, 1690, 1590, 1221. HRMS (EI+) calcd for C$_{12}$H$_{14}$O$_3$S$_2$ 270.0384, found: 270.0373. Mp: 69 °C (decomp.).
Compound 3c: O-ethyl 5-2-(naphthalen-2-yl)-2-oxoethyl carbonodithioate

Following the general procedure A, the reaction was carried out with 2-bromo-1-(naphthalen-2-yl)ethanone (11.1 g, 44.58 mmol). Recrystallisation afforded the desired product as a yellow solid (11.4 g, 49.3 mmol, 88 %).

\[ ^1H \text{ NMR} (\delta, \text{ppm}) (\text{CDCl}_3, 400 \text{ MHz}): 8.57 (s, 1H, C_1\text{H}); 8.48 (dd, 1H, J_1 = 1.2 \text{ Hz}, J_2 = 8.5 \text{ Hz}, C_3\text{H}); 8.00 (d, 1H, J = 8.0 \text{ Hz}, C_5\text{H}); 7.93 (d, 1H, J = 8.7 \text{ Hz}, C_6\text{H}); 7.90 (d, 1H, J = 8.1 \text{ Hz}, C_8\text{H}); 7.63 (t, 1H, J = 7.4 \text{ Hz}, C_7\text{H}); 7.58 (t, 1H, J = 7.4 \text{ Hz}, C_6\text{H}); 4.80 (s, 2H, C_{10}\text{H}_2); 4.66 (q, 2H, J = 7.1 \text{ Hz}, O\text{C}_{12}\text{H}_2); 1.40 (t, 3H, J = 7.1 \text{ Hz}, C_{13}\text{H}_3). \]

\[ ^13C \text{ NMR} (\delta, \text{ppm}) (\text{CDCl}_3, 100.6 \text{ MHz}): 213.34 (C_1\text{S}); 192.27 (C_{10}\text{O}); 135.84 (C_2); 133.16 (C_{IV}); 132.43 (C_{IV}); 130.34 (C_1\text{H}); 129.68 (C_5\text{H}); 128.86 (C_7\text{H}); 128.72 (C_8\text{H}); 127.00 (C_4\text{H}); 123.90 (C_3\text{H}); 70.72 (OC_{12}\text{H}_2); 43.61 (C_{12}\text{H}_2); 13.74 (C_{13}\text{H}_3). \]

\[ \text{IR} (\text{cm}^{-1}) (\text{CCl}_4) : 3063, 2987, 2902, 1685, 1220. \]

\[ \text{HRMS} (\text{EI}+) \text{ calcd for } C_{15}H_{14}O_2S_2 290.0435, \text{ found: 290.0422.} \]

\[ \text{Mp: 98 }^\circ \text{C.} \]

Compound 4a: 7,12-epoxy-5,6,6A,7,12,12A-hexahydro-2-methoxybenz(a)anthrac-5-one

Following the general procedure B, the reaction was carried out with xanthate 3a (400 mg, 1.48 mmol). Total consumption of starting material took 160 %mol of DLP. Purification by column chromatography (EP/Ether from 90/10 to 60/40) yielded the desired product as a white solid (189 mg, 0.647 mmol, 43 %).

\[ ^1H \text{ NMR} (\delta, \text{ppm}) (\text{CDCl}_3, 400 \text{ MHz}): 7.86 (d, 1H, J = 8.5 \text{ Hz}, C_4\text{H}); 7.39 – 7.37 (m, 1H, C_{11}\text{H}); 7.34 – 7.32 (m, 1H, C_8\text{H}); 7.25 – 7.23 (m, 2H, C_9\text{H} & C_{10}\text{H}); 6.92 (d, 1H, J = 2.4 \text{ Hz}, C_3\text{H}); 6.89 (dd, 1H, J_{11} = 2.5 \text{ Hz}, J_2 = 8.5 \text{ Hz}, C_3\text{H}); 5.18 (s, 1H, C_{12}\text{H}); 5.05 (s, 1H, C_3\text{H}); 3.19 (d, 1H, J = 7.9 \text{ Hz}, C_{12}\text{H}); 2.89 (dd, 1H, J_1 = 3.4 \text{ Hz}, J_2 = 15.6 \text{ Hz}, C_6\text{H}); 2.82 (dd, 1H, J_1 = 8.2 \text{ Hz}, J_2 = 15.6 \text{ Hz}, C_6\text{H}); 2.52 (ddd, 1H, J_1 = 3.3 \text{ Hz}, J_2 = 7.9 \text{ Hz}, J_3 = 8.3 \text{ Hz}, C_6\text{H}). \]

\[ ^13C \text{ NMR} (\delta, \text{ppm}) (\text{CDCl}_3, 100.6 \text{ MHz}): 196.60 (C_5\text{O}); 163.74 (C_4); 145.17 (C_{IV}); 145.03 (C_{IV}); 144.49 (C_{IV}); 128.21 (C_4\text{H}); 128.05 (C_{IV}); 127.21 & 127.132 (C_4\text{H} & C_{11}\text{H}); 119.35 (C_6\text{H}); 119.24 (C_{11}\text{H}); 113.43 (C_3\text{H}); 112.67 (C_3\text{H}); 87.80 (OC_{12}\text{H}); 86.46 (OC_{12}\text{H}); 55.54 (OC_{13}\text{H}_3); 44.11 (C_{12}); 41.81 (C_{6}H_2); 37.66 (C_4\text{H}). \]

\[ \text{IR} (\text{cm}^{-1}) (\text{CCl}_4) : 3063, 2987, 2902, 1685, 1220. \]

\[ \text{HRMS} (\text{EI}+) \text{ calcd for } C_{19}H_{16}O_3 292.1099, \text{ found: 292.1102.} \]

\[ \text{Mp: 142 }^\circ \text{C.} \]
Compound 4b: 2-chloro-7,12-epoxy-5,6,6A,7,12,12A-hexahydrobenz(a)anthrac-5-one

Following the general procedure B, the reaction was carried out with xanthate 3b (1.88 g, 13.1 mmol). Total consumption of starting material took 160 %mol of DLP. Purification by column chromatography (EP/Ether: 85/15) yielded the desired product as a slightly yellow solid (713 mg, 2.40 mmol, 36%).

$^1$H NMR ($\delta$, ppm) (CDCl$_3$, 400 MHz): 7.80 (d, 1H, J = 8.3 Hz, C$_4$H); 7.48 (d, 1H, J = 1.7 Hz, C$_1$H); 7.40 – 7.38 (m, 1H, C$_{11}$H); 7.40 – 7.33 (m, 2H); 7.27 – 7.24 (m, 2H); 5.18 (s, 1H, OC$_{12}$H); 5.02 (s, 1H, OC$_7$H); 3.21 (d, 1H, J = 7.8 Hz; C$_{12}'$H); 2.93 (dd, 1H, J$_1$ = 2.8 Hz, J$_2$ = 15.4 Hz, C$_6$H$_2$); 2.81 (dd, 1H, J$_1$ = 8.3 Hz, J$_2$ = 15.4 Hz, C$_6$H$_2$); 2.55 (ddd, 1H, J$_1$ = 2.8 Hz, J$_2$ = 8.1 Hz, J$_3$ = 8.1 Hz, C$_6$H). $^{13}$C NMR ($\delta$, ppm) (CDCl$_3$, 100.6 MHz): 196.70 (C$_5$O); 144.88 (C$_{IV}$); 144.66 (C$_{IV}$); 144.07 (C$_{IV}$); 139.50 (C$_{V}$) 133.02 (C$_{V}$); 128.83 (C$_1$H); 127.44 (CH); 127.39 (CH); 127.32 (2CH); 119.37 (C$_8$H & C$_{11}$H); 87.61 (OC$_7$H); 86.32 (OC$_{12}$H); 43.81 (C$_{12}'$H); 41.94 (C$_6$H$_2$); 37.87 (C$_6$H). IR (cm$^{-1}$) (CCl$_4$): 2928, 2856, 1706, 1595, 1282. HRMS (EI+) calcd for C$_{19}$H$_{16}$O$_3$ 292.1099, found: 296.0604. Mp: 195 °C.

Compound 4c: 9,14-epoxy-7,8,8A,9,14,14A-hexahydronaphth(1,2-a)anthrac-7-one

Following the general procedure B, the reaction was carried out with xanthate 3c (1.74 g, 6.00 mmol). Total consumption of starting material took 160 %mol of DLP. Purification by column chromatography (EP/Ether from 95/5 to 80/20) yielded the desired product as a slightly yellow solid (424 mg, 1.36 mmol, 23 %).

$^1$H NMR ($\delta$, ppm) (CDCl$_3$, 400 MHz): 8.16 (d, 1H, J = 8.2 Hz, C$_1$H); 7.97 (d, 1H, J = 8.5 Hz, C$_5$H); 7.96 - 7.94 (m, 1H, C$_4$H); 7.84 (d, 1H, J = 8.5 Hz, C$_5$H); 7.73 – 7.65 (m, 2H, C$_2$H & C$_3$H); 7.52 – 7.50 (m, 1H, C$_{13}$H); 7.41 – 7.39 (m, 1H, C$_{10}$H); 7.34 – 7.27 (m, 2H, C$_2$H & C$_{12}$H); 4.00 (s, 1H, C$_{1a}$H); 3.98 (s, 1H, C$_3$H); 7.85 (d, 1H, J = 7.8 Hz, C$_{14}$H); 3.07 (dd, 1H, J$_1$ = 1.9 Hz, J$_2$ = 15.6 Hz, C$_8$H$_2$); 2.93 (dd, 1H, J$_1$ = 8.9 Hz, J$_2$ = 15.6 Hz, C$_8$H$_2$); 2.71 – 2.66 (m, 1H, C$_8$H). $^{13}$C
**NMR** (δ, ppm) (CDCl₃, 100.6 MHz): 197.86 (C₂O); 145.25 (C₉); 144.38 (C₁₃); 140.14 (C₁₄); 136.23 (C₁₄); 132.07 (C₁₄); 131.13 (C₁₄); 129.47 (C₈); 127.88 (CH); 127.46 (CH); 127.39 (CH); 127.32 (2C, CH); 124.00 (C₁₁H); 122.24 (C₆H); 119.51 (C₁₀H); 119.10 (C₁₃H); 86.81 (C₁₄H); 86.56 (C₉H); 41.45 (C₈H₂); 40.00 (C₁₄′H); 37.40 (C₈′H).

**IR** (cm⁻¹) (CCl₄): 3067, 2953, 1696, 1282.

**HRMS** (EI+) calcd for C₂₂H₁₆O₂ 312.1150, found: 312.1149. **Mp**: 188 °C.

**Compound 5a**: 5-ethoxy-2-methoxybenz(a)anthracene

Ketone 4a (49.0 mg, 0.168 mmol, 1.0 eq) was dissolved in EtOH (2.0 ml) containing H₂SO₄ (1.0 M). The solution was refluxed. After 36 h, the reaction mixture was cooled down at room temperature and water (3 mL) was added. The layers were separated and the aqueous phase extracted further with DCM three times (3 mL). The combined organic layers were dried over MgSO₄ and evaporated under reduced pressure. The crude residue was purified by column chromatography (Pentane/Ether from 100/0 to 50/50). The desired compound was obtained as a brown solid and 3 mg of the starting material were recovered (35 mg, 0.168 mmol, 69 % (74 %)).

**¹H NMR** (δ, ppm) (CDCl₃, 400 MHz): 8.93 (s, 1H, C₁₂H); 8.29 (d, 1H, J = 8.9 Hz, C₄H); 8.16 (d, 1H, J = 2.4 Hz, C₁₁H); 8.14 (s, 1H, C₇H); 8.06 (d, 1H, J = 7.9 Hz, C₁₁H); 7.95 (d, 1H, J = 7.9 Hz, C₆H); 7.53 – 7.45 (m, 2H, C₉H & C₁₀H); 7.25 (dd, 1H, J₁ = 2.4 Hz, J₂ = 9.0 Hz, C₃H); 6.84 (s, 1H, C₆H); 4.28 (q, 2H, J = 6.9 Hz, OC₁₄H₂); 4.05 (s, 3H, OC₁₃H₃); 1.60 (t, 3H, J = 6.9 Hz, C₁₅H₃). **¹³C NMR** (δ, ppm) (CDCl₃, 100.6 MHz): 159.06 (C₂O); 152.73 (C₂O); 132.97 (C₂); 132.47 (C₁₂); 132.17 (C₁₁); 130.29 (C₇); 128.40 (C₁₁H); 127.00 (C₆H); 125.82 (C₆H); 125.73 (C₁₀H); 124.42 (C₉H); 124.34 (C₄H); 124.23 (C₉H); 121.63 (C₁₂); 124.38 (C₁₂H); 115.49 (C₃H); 105.30 (C₁₂H); 99.74 (C₆H); 63.39 (OC₁₄H₂); 55.49 (OC₁₃H₃); 14.78 (C₁₅H₃). **IR** (cm⁻¹) (CCl₄): 3055, 2929, 2855. **HRMS** (EI+) calcd for C₂₁H₁₈O₂ 302.1307, found: 302.1309. **Mp**: 102 °C.
Compound 5b: 2,5-dimethoxybenz(a)anthracene

Ketone 4a (51.2 mg, 0.178 mmol, 1.0 eq) was dissolved in MeOH (2.0 ml) containing H$_2$SO$_4$ (1.0 M). The solution was refluxed. After 18 h, the reaction mixture was cooled down at room temperature, water (3mL) was added and the precipitate was filtrated, dissolved in DCM and dried over MgSO$_4$. The solvent was then evaporated under reduced pressure and the crude residue dissolved in acetonitrile. This solution was washed with pentane and the solvent was evaporated under reduced pressure. We obtained a 2:1 mixture of the desired product and dimethylsulfate as a brown solid (45.5 mg, 0.158 mmol, 88%).

$^1$H NMR (δ, ppm) (CDCl$_3$, 400 MHz): 8.94 (s, 1H, C$_{12}$H); 8.24 (d, 1H, J = 8.9 Hz, C$_4$H); 8.17 (s, 2H, C$_7$H & C$_7$H); 8.06 (d, 1H, J = 7.9 Hz, C$_{11}$H); 7.95 (d, 1H, J = 8.0 Hz, C$_6$H); 7.52 – 7.45 (m, 2H, C$_9$H & C$_{10}$H); 7.24 (dd, 1H, J$_1$ = 2.4 Hz, J$_2$ = 8.9 Hz, C$_3$H); 6.88 (s, 1H, C$_6$H); 4.09 & 4.06 (s, 3H, OC$_{13}$H$_3$ & OC$_{14}$H$_3$).

$^{13}$C NMR (δ, ppm) (CDCl$_3$, 100.6 MHz): 159.10 (C$_2$O); 153.59 (C$_5$O); 133.06 (C$_4'$); 132.50 (C$_{11}'$); 132.01 (C$_{12}'$); 130.36 (C$_7'$); 128.41 (C$_{11}$H); 127.03 (C$_8$H); 125.87 (C$_{12''}$); 125.84 & 124.56 (C$_9$ & C$_{10}$); 124.40 (C$_7$H); 124.30 (C$_4$H); 121.54 (C$_{6'}$), 124.47 (C$_{12}$H); 115.52 (C$_3$H); 105.49 (C$_1$H); 99.23 (C$_6$H); 55.60 & 55.35 (OC$_{13}$H$_3$ & OC$_{14}$H$_3$).

Compound 5c: 5-isopropoxy-2-methoxybenz(a)anthracene

Ketone 4a (100 mg, 0.342 mmol, 1.0 eq) was dissolved in iPrOH (3.4 ml) containing H$_2$SO$_4$ (1.0 M). The solution was refluxed. After 18 h, the reaction mixture was cooled down at room temperature and water (3mL) was added. The layers were separated and the aqueous phase extracted further with DCM three times (3mL). The combined organic layers were dried over MgSO$_4$ and evaporated under reduced pressure. The crude residue was purified by column chromatography (EP/AcOEt : 95/5). The desired compound was obtained as an orange solid (43 mg, 0.136 mmol, 40%).

$^1$H NMR (δ, ppm) (CDCl$_3$, 400 MHz): 8.97 (s, 1H, C$_{12}$H); 8.30 (d, 1H, J = 8.9 Hz, C$_4$H); 8.19 (d, 1H, J = 2.5 Hz, C$_1$H); 8.16 (s, 1H, C$_7$H); 8.08 (d, 1H, J = 8.0 Hz, C$_{11}$H); 7.96 (d, 1H, J = 8.0 Hz, C$_6$H); 7.53 – 7.45 (m, 2H, C$_9$H & C$_{10}$H); 7.25 (dd, 1H, J$_1$ = 2.5 Hz, J$_2$ = 8.9 Hz, C$_3$H); 6.90 (s, 1H, C$_6$H); 4.89 (sept, 1H, J = 6.0 Hz, OC$_{14}$H$_3$); 4.07 (s, 3H, OC$_{13}$H$_3$); 1.53 (t, 6H, J = 6.0 Hz, C$_{15}$H$_3$).

$^{13}$C NMR (δ, ppm) (CDCl$_3$, 100.6 MHz): 159.07 (C$_2$O); 151.42 (C$_5$O); 133.15
(C₄); 132.51 & 132.27 (C₁₁ & C₁₂); 130.29 (C₇); 128.41 (C₁₁H); 127.01 (C₆H); 125.75 (2C, C₉ & C₁₂'); 124.64 (C₄H); 125.42 (C₁₀H); 124.13 (C₆'); 122.30 (C₆'); 121.39 (C₁₂H); 115.50 (C₃H); 105.30 (C₁H); 100.94 (C₆H); 69.75 (OC₁₄H₂); 55.55 (OC₁₃H₃); 22.10 (2C, C₁₅H₃). IR (cm⁻¹) (CCl₄): 3055, 2979, 2929, 2855, 1622. HRMS (EI+) calcd for C₂₂H₂₀O₂ 316.1463, found: 316.1471.

Compound 5d: 2-methoxy-5-(2,2,2-trifluoroethoxy)benz(a)anthracene

Ketone 4a (55.6 mg, 0.190 mmol, 1.0 eq) was dissolved in 2,2,2-trifluoroethanol (2.0 ml) containing H₂SO₄ (1.0 M). The solution was refluxed. After 3 h, the reaction mixture was cooled down at room temperature and water (3mL) was added. The layers were separated and the aqueous phase extracted further with DCM three times (3 mL). The combined organic layers were dried over MgSO₄ and evaporated under reduced pressure. The crude residue was purified by column chromatography (Pentane/Ether from 100/0 to 80/20). The desired compound was obtained as a brown solid (31 mg, 8.7*10⁻² mmol, 46%).

¹H NMR (δ, ppm) (CDCl₃, 400 MHz): 8.94 (s, 1H, C₁₂H); 8.24 (d, 1H, J = 8.8 Hz, C₆H); 8.17 – 8.13 (m, 2H, C₁H & C₃H); 8.07 (d, 1H, J = 8.8 Hz, C₁₃H); 7.96 (d, 1H, J = 7.4 Hz, C₄H); 7.55 – 7.49 (m, 2H, C₁₁H & C₁₂H); 7.29 – 7.25 (m, 1H, C₈H); 6.80 (s, 1H, C₁₄H); 4.59 (q, 2H, J = 7.8 Hz, OC₁₄H₂); 4.06 (s, 3H, OC₁₃H₃). ¹³C NMR (δ, ppm) (CDCl₃, 100.6 MHz): 159.49 (C₂O); 151.29 (C₅O); 133.21 (C₄); 132.44 (C₁₂'); 130.98 (C₁₁); 130.78 (C₇); 128.44 (C₁₃H); 127.13 (C₈H); 126.06 (C₁₀H); 125.05 & 124.98 (C₇H & C₉H); 124.23 (C₄H); 123.47 (q, J = 277.7 Hz, C₁₅F₃); 121.63 (C₁₂H); 120.52 (C₁₁'); 115.79 (C₉H); 105.51 (C₁H); 100.73 (C₆H); 65.53 (q, J = 35.9 Hz, OC₁₄H₂); 55.55 (OC₁₃H₃). IR (cm⁻¹) (CCl₄): 3057, 2938, 2839, 1629, 1615, 1285. HRMS (EI+) calcd for C₂₁H₁₅F₃O₂ 356.1024, found: 356.1027. Mp: 120 °C.
Compound 5e: 2-chloro-5-(2,2,2-trifluoroethoxy)benz(a)anthracene

Ketone 4b (90 mg, 0.296 mmol, 1.0 eq) and P-TSA (15 mg) were dissolved in 2,2,2-trifluoroethanol (3.0 ml). The solution was refluxed. After 3 h, the reaction mixture was cooled down at room temperature and water (4 mL) was added. The layers were separated and the aqueous phase extracted further with DCM three times (4 mL). The combined organic layers were dried over MgSO$_4$ and evaporated under reduced pressure. The crude residue was purified by column chromatography (Pentane/Ether from 100/0 to 95/5). The desired compound was obtained as a yellow solid (69 mg, 0.192 mmol, 63%).

$^1$H NMR ($\delta$, ppm) (CDCl$_3$, 400 MHz): 8.80 (s, 1H, C$_{12}$H); 8.57 (s, 1H, C$_1$H); 8.16 (d, 1H, J = 8.7 Hz, C$_4$H); 8.08 (s, 1H, C$_7$H); 8.02 (d, 1H, J = 7.4 Hz, C$_{11}$H); 7.94 (d, 1H, J = 8.2 Hz, C$_6$H); 7.57 – 7.50 (m, 3H, C$_3$H, C$_9$H & C$_{10}$H); 6.80 (s, 1H, C$_6$H); 4.54 (q, 2H, J = 7.9 Hz, OC$_{13}$H$_2$).

$^{13}$C NMR ($\delta$, ppm) (CDCl$_3$, 100.6 MHz): 151.29 (C$_5$O); 134.15 (C$_{IV}$); 132.77 (C$_{IV}$); 132.58 (C$_{IV}$); 130.97 (C$_{IV}$); 130.40 (C$_{IV}$); 128.50 (C$_{11}$H); 127.41 (CH); 127.14 (C$_8$H); 126.40 (C$_H$); 125.43 (CH); 125.14 (C$_7$H & C$_{IV}$); 124.64 (C$_{IV}$); 124.10 (C$_4$H); 123.35 (q, J = 277.5 Hz, C$_{14}$F$_3$); 122.56 (C$_1$H); 121.82 (C$_{12}$H); 65.56 (q, J = 36.0 Hz, OC$_{13}$H$_2$).

IR (cm$^{-1}$) (CCl$_4$): 3058, 2942, 2856, 1629.

HRMS (EI+) calcd for C$_{21}$H$_{12}$F$_3$ClO$_3$ 360.0529, found: 360.0535. Mp: 87 °C.

Compound 5f: 7-(2,2,2-trifluoroethoxy)naphth(1,2-a)anthracene

Ketone 4c (80 mg, 0.256 mmol, 1.0 eq) and P-TSA (12 mg) were dissolved in 2,2,2-trifluoroethanol (2.5 ml). The solution was refluxed. After 130 h, the reaction mixture was cooled down at room temperature and water (3 mL) was added. The layers were separated and the aqueous phase extracted further with DCM three times (3 mL). The combined organic layers were dried over MgSO$_4$ and evaporated under reduced pressure. The crude residue was purified by column chromatography (Pentane/Ether from 100/0 to 90/10). The desired compound was obtained as a yellow solid (91 mg, 0.242 mmol, 94%).

$^1$H NMR ($\delta$, ppm) (CDCl$_3$, 400 MHz): 9.48 (s, 1H, C$_{14}$H); 9.21 (d, 1H, J = 8.4 Hz, C$_1$H); 8.34 (d, 1H, J = 8.8 Hz, C$_6$H); 8.31 (s, 1H, C$_9$H); 8.10 (d, 1H, J = 7.9 Hz, C$_{13}$H); 8.07 (dd, 1H, J = 0.9 Hz, J$_2$ = 7.9 Hz, C$_4$H); 8.03 – 8.01 (m, 1H, C$_{10}$H); 8.00 (d, 1H, J = 9.0 Hz, C$_8$H); 7.727 (ddd, 1H, J$_1$ = 1.4 Hz, J$_2$ = 6.9 Hz, J$_3$ = 8.5 Hz, C$_3$H); 7.69 – 7.65 (m, 1H,
To a solution of Ketone 4a (100 mg, 0.342 mmol, 1.0 eq) in diethylether (3.5 ml) at 0 °C under a nitrogen atmosphere was added MeLi (1.7 mmol, 5.0 eq) dropwise. The solution was stirred for 1 h at 0 °C and for another hour at RT. The reaction mixture was quenched by addition of NH₄Cl (sat. aq.) (5mL). The layers were separated and the aqueous phase extracted further with DCM three times (5 mL). The combined organic layers were dried over MgSO₄ and then evaporated. The crude residue was purified by two column chromatography (EP/AcOEt 70/30 and EP/AcOEt from 80/20 to 75/25). The desired compound was obtained as a brown solid and 8 mg of the starting material were recovered (50 mg, 0.16 mmol, 48 % (52 %)).

**1H NMR (δ, ppm) (CDCl₃, 400 MHz):** 7.58 (d, 1H, J = 8.6 Hz, C₄H); 7.40 – 7.38 (m, 1H, C₁₁H); 7.35 – 7.33 (m, 1H, C₈H); 7.24 – 7.22 (m, 2H, C₉H & C₁₀H); 6.89 (d, 1H, J = 2.6 Hz, C₁H); 6.85 (dd, 1H, J₁ = 2.7 Hz, J₂ = 8.6 Hz, C₃H); 5.35 (s, 1H, OC₁₂H); 5.23 (s, 1H, OC₁₃H); 4.03 (s, 1H, OH); 3.86 (s, 3H, OC₁₃H₃); 3.09 (d, 1H, J = 8.5 Hz, C₁₂H); 2.36 (ddd, 1H, J₁ = 4.0 Hz, J₂ = 7.4 Hz, J₃ = 8.3, C₆H); 2.23 (dd, 1H, J₁ = 3.9 Hz, J₂ = 13.9 Hz, C₈H₂); 2.10 (dd, 1H, J₁ = 7.3 Hz, J₂ = 13.9 Hz, C₈H₂); 1.59 (s, 3H, C₁₄H₃). **13C NMR (δ, ppm) (CDCl₃, 100.6 MHz):** 158.94 (C₂O); 145.10 (C₇); 144.37 (C₁₁); 137.78 (C₁₂); 136.05 (C₄); 127.12 & 126.97 (C₉H & C₁₀H); 126.26 (C₈H); 119.28 & 119.19 (C₉H & C₁₁H); 114.49 (C₁H); 112.32 (C₇H); 87.25 (OC₃H); 85.70 (OC₁₂H); 67.92 (C₅); 55.36 (OC₁₃H₃); 44.45 (C₁₂H); 41.39 (C₆H₂); 37.90 (C₆H); 28.33 (C₁₄H₃). **IR (cm⁻¹) (CCl₄):** 2927, 2855, 1789, 1464.
Compound 6b: 7,12-epoxy-5,6,6A,7,12,12A-hexahydro-2-methoxy-5-phenylbenz(a)anthrac-5-ol

Following the general procedure C, the reaction was carried out with ketone 4a (100 mg, 0.342 mmol). Purification by flash chromatography (EP/AcOEt: 90/10) gave the desired compound as an orange solid (60 mg, 0.162 mmol, 48 % (53 %)).

$^1$H NMR ($\delta$, ppm) (CDCl$_3$, 400 MHz): 7.41 – 7.36 (m, 3H, C$_{11}$H & C$_{16}$H); 7.33 – 7.30 (m, 3H, C$_{8}$H & C$_{15}$H); 7.27 – 7.25 (m, 1H, C$_{12}$H); 7.24 – 7.21 (m, 2H, C$_{9}$H & C$_{10}$H); 6.99 (d, 1H, J = 8.6 Hz, C$_4$H); 6.95 (d, 1H, J = 2.6 Hz, C$_1$H); 6.73 (dd, 1H, J$_1$ = 2.7 Hz, J$_2$ = 8.7 Hz, C$_3$H); 5.37 (s, 1H, OC$_{12}$H); 5.29 (s, 1H, OC$_7$H); 4.38 (s, 1H, OH); 3.86 (s, 3H, OC$_{13}$H$_3$); 3.14 (d, 1H, J = 8.4 Hz, C$_{12'}$H); 2.52 (dd, 1H, J$_1$ = 7.1 Hz, J$_2$ = 13.9 Hz, C$_6$H$_2$); 2.34 (dd, 1H, J$_1$ = 4.2 Hz, J$_2$ = 13.9 Hz, C$_6$H$_2$); 2.27 (dd, 1H, J$_1$ = 4.3 Hz, J$_2$ = 7.2 Hz, J$_3$ = 8.2 Hz, C$_6$H).

$^{13}$C NMR ($\delta$, ppm) (CDCl$_3$, 100.6 MHz): 159.06 (C$_2$O); 146.83 (C$_{14}$); 145.09 (C$_{11}$); 144.31 (C$_7$); 138.52 (C$_4$); 136.17 (C$_{12'}$); 129.63 (C$_4$H); 127.81 (2C, C$_{18}$H); 127.13 (C$_{17}$H); 126.99 & 126.65 (C$_9$H & C$_{16}$H); 126.49 (2C, C$_{15}$H); 119.31 & 119.24 (C$_8$H & C$_{11}$H); 114.00 (C$_1$H); 112.26 (C$_3$H); 87.38 (OC$_7$H); 85.56 (OC$_{12}$H); 73.20 (C$_3$); 55.35 (OC$_{13}$H$_3$); 44.35 (C$_{12'}$H); 43.07 (C$_6$H$_2$); 37.91 (C$_6$H). Mp: 99 °C.

Compound 6c: 2-chloro-7,12-epoxy-5,6,6A,7,12,12A-hexahydro-5-phenylbenz(a)anthrac-5-ol

Following the general procedure C, the reaction was carried out with ketone 4b (55 mg, 0.185 mmol). Purification by flash chromatography (EP/AcOEt: from 90/10 to 75/25) gave the desired compound as a white solid (39.9 mg, 0.106 mmol, 57 %).
$^1$H NMR (δ, ppm) (CDCl$_3$, 400 MHz): 7.46 (d, 1H, $J = 1.9$ Hz, C$_1$H); 7.41 (dd, 1H, $J_1 = 1.5$ Hz, $J_2 = 6.1$ Hz, C$_{11}$H), 7.33 – 7.20 (m, 8H, C$_8$H, C$_9$H, C$_{10}$H, C$_{12}$H, C$_{13}$H & C$_{16}$H); 7.16 (dd, 1H, $J_1 = 2.1$ Hz, $J_2 = 8.4$ Hz, C$_3$H); 7.07 (d, 1H, $J = 8.4$ Hz, C$_4$H); 5.34 (s, 1H, C$_{12}$H); 5.31 (s, 1H, C$_7$H); 4.35 (s, 1H, OH); 3.10 (d, 1H, $J = 8.4$ Hz, C$_{12'}$H); 2.53 (dd, 1H, $J_1 = 7.0$ Hz, $J_2 = 13.9$ Hz, C$_6$H), 2.32 (dd, 1H, $J_1 = 5.0$ Hz, $J_2 = 13.9$ Hz, C$_6$H); 2.27 – 2.21 (m, 1H, C$_{6'}$H).

$^{13}$C NMR (δ, ppm) (CDCl$_3$, 100.6 MHz): 145.94 (C$_{IV}$); 144.78 (C$_{IV}$); 144.11 (C$_{IV}$); 142.10 (C$_{IV}$); 139.02 (C$_{IV}$); 133.52 (C$_{IV}$); 129.67 (C$_4$H); 128.67 (C$_1$H); 128.33 (2C, C$_{14}$H); 127.97 (2C, C$_{14}$H); 127.23 (CH); 127.10 (CH); 126.97 (CH); 126.90 (CH); 126.38 (2C, C$_{15}$H); 87.00 (OC$_7$H); 85.30 (OC$_{12}$H); 73.26 (C$_5$); 43.93 (C$_{12'}$H); 42.69 (C$_6$H$_2$); 37.83 (C$_{6'}$H).

Compound 6d: 9,14-epoxy-7,8,8A,9,14,14A-hexahydro-7-phenylnapth(1,2-a)anthrac-7-ol

Following the general procedure C, the reaction was carried out with ketone 4c (70 mg, 0.224 mmol). Purification by flash chromatography (EP/AcOEt: from 95/5 to 85/15) gave the desired compound as a white solid (64.2 mg, 0.164 mmol, 73 %).

$^1$H NMR (δ, ppm) (CDCl$_3$, 400 MHz): 8.14 (d, 1H, $J = 8.5$ Hz, C$_1$H); 7.89 (d, 1H, $J = 8.0$ Hz, C$_4$H); 7.70 (t, 1H, $J = 7.6$ Hz, C$_2$H); 7.64 (d, 1H, $J = 8.7$ Hz, C$_3$H); 7.60 – 7.57 (m, 2H, C$_3$H & C$_{13}$H); 7.53 – 7.51 (m, 2H); 7.435 – 7.29 (m, 6H); 7.08 (d, 1H, $J = 8.7$ Hz, C$_6$H); 5.56 (s, 1H, OC$_{14}$H); 5.16 (s, 1H, OC$_3$H); 5.1 (s, 1H, OH); 4.04 (d, 1H, $J = 8.1$ Hz, C$_{14}$H); 2.61 – 2.54 (m, 3H, C$_8$H$_2$ & C$_{8'}$H). $^{13}$C NMR (δ, ppm) (CDCl$_3$, 100.6 MHz): 147.40 (C$_{IV}$); 145.29 (C$_{IV}$); 143.84 (C$_{IV}$); 140.68 (C$_{IV}$); 133.41 (C$_{IV}$); 132.07 (C$_{IV}$); 131.56 (C$_{IV}$); 129.52 (C$_{IV}$); 129.19 (C$_4$H); 127.81 (2C, C$_{16}$H); 127.35 (CH); 127.18 (CH); 127.06 (CH); 126.97 (CH); 126.78 (CH); 126.53 (CH); 126.46 (2C, C$_{17}$H); 125.81 (CH); 123.11 (C$_1$H); 119.36 (CH); 119.23 (CH); 115.27 (C$_{IV}$); 86.24 & 86.16 (OC$_3$H & OC$_{14}$H); 73.47 (C$_7$); 42.41 (C$_{8}$H$_2$); 40.17 (C$_{15}$H); 37.76 (C$_8$H). HRMS (El+) calcd for C$_{28}$H$_{22}$O$_2$ 390.1620, found: 390.1620. Mp: 64 °C.
Compound 7a: 2-methoxy-5-(methyl)benz(a)anthracene

Alcohol 6a (36.0 mg, 0.117 mmol, 1.0 eq) was dissolved in EtOH (3.0 ml) containing H$_2$SO$_4$ (1.0 M). The solution was refluxed. After 12 h, the reaction mixture was cooled down at room temperature and water (3 mL) was added. The precipitate was filtrated, dissolved in DCM and dried over MgSO$_4$. The solvent was evaporated under reduced pressure and the crude residue was dissolved in acetonitrile. This solution was washed with pentane and the solvent was evaporated under reduced pressure. The desired product was obtained as a brown solid (24 mg, 8.8*10$^{-2}$ mmol, 75 %).

$^1$H NMR (δ, ppm) (CDCl$_3$, 400 MHz): 9.03 (s, 1H, C$_{12}$H); 8.26 (d, 1H, J = 2.5 Hz, C$_1$H); 8.23 (s, 1H, C$_7$H); 8.10 (dd, 1H, J$_1$ = 4.1 Hz, J$_2$ = 5.4 Hz, C$_{11}$H); 8.01 (dd, 1H, J$_1$ = 4.1 Hz, J$_2$ = 5.4 Hz, C$_8$H); 7.94 (d, 1H, J = 8.8 Hz, C$_3$H); 7.54 – 7.51 (m, 2H, C$_9$H & C$_{10}$H); 7.49 (s, 1H, C$_6$H); 7.28 (dd, 1H, J$_1$ = 2.6 Hz, J$_2$ = 8.9 Hz, C$_2$H); 4.07 (s, 3H, OC$_{13}$H$_3$); 2.68 (s, 3H, C$_{14}$H$_3$).

$^{13}$C NMR (δ, ppm) (CDCl$_3$, 100.6 MHz): 158.33 (C$_2$O); 132.27 & 132.15 & 132.06 & 131.27 & 131.10 (C$_{4'}$ & C$_5$ & C$_7$ & C$_{11'}$ & C$_{12'}$); 128.40 (C$_{11}$H); 128.27 (C$_{12'}$H); 127.52 (C$_8$H); 126.63 (C$_6'$); 126.16 & 125.67 & 125.52 & 125.14 (C$_4$H & C$_7$H & C$_9$H & C$_{10}$H); 124.46 (C$_{12}$H); 121.34 (C$_3$H); 115.54 (C$_1$H); 105.83 (C$_6$H); 55.54 (OC$_{13}$H$_3$); 20.24 (C$_{14}$H$_3$). IR (cm$^{-1}$) (CCl$_4$): 3057, 2929, 1613, 1514. HRMS (El+) calcd for C$_{20}$H$_{16}$O 272.1201, found: 272.1200. Mp: 107 °C.

Compound 7b: 2-methoxy-5-phenylbenz(a)anthracene

Alcohol 6b (56.0 mg, 0.151 mmol, 1.0 eq) was dissolved in EtOH (1.5 ml) containing H$_2$SO$_4$ (1.0 M). The solution was refluxed. After 6 h, the reaction mixture was cooled down at room temperature and water (2mL) was added. The precipitate was filtrated, dissolved in DCM and dried over MgSO$_4$. The solvent was evaporated under reduced pressure and the crude residue was dissolved in acetonitrile. This solution was washed with pentane and the solvent was evaporated under reduced pressure. The crude residue was purified by column
chromatography (EP/AcOEt: 90/10). The desired product was obtained as a brown solid (29 mg, 8.7*10^{-2} mmol, 57%).

^1^H NMR (δ, ppm) (CDCl₃, 400 MHz): 9.11 (s, 1H, C₁₂H); 8.35 (s, 1H, C₇H); 8.33 (d, 1H, J = 2.5 Hz, C₁H); 8.15 – 8.13 (m, 1H, C₁₁H); 8.05 – 8.02 (m, 1H, C₈H); 7.81 (d, 1H, J = 8.9 Hz, C₄H); 7.61 (s, 1H, C₆H); 7.59 – 7.51 (m, 6H, C₉H, C₁₀H, C₁₅H & C₁₆H); 7.49 – 7.45 (m, 1H, C₁₇H), 7.18 (dd, 1H, J₁ = 2.6 Hz, J₂ = 8.9 Hz, C₃H); 4.08 (s, 3H, OC₁₃H₃).

^1^C NMR (δ, ppm) (CDCl₃, 100.6 MHz): 158.50 (C₂O); 140.88 (C₁V); 138.54 (C₄'); 132.38 (C₁IV); 132.27 (C₁IV); 131.70 (C₁IV); 130.62 (C₁IV); 129.89 (2C, C₁₅H); 128.57 (CH); 128.46 (CH); 128.30 (2C, C₁₆H); 128.26 (C₁IV); 127.63 (CH); 127.35 (C₁₇H); 126.74 (C₇H); 125.89 (C₉/₁₀H); 125.52 (CH); 125.39 (C₈H); 124.45 (C₁₂H); 115.53 (C₃H); 105.81 (C₁H); 55.60 (OC₁₃H₃).

Compound 8a: 1-phenylphenanthrene

Alcohol 6d (44 mg, 0.11 mmol, 1.0 eq) and P-TSA (5 mg) were refluxed in EtOH (1.2 ml). After 11h, the reaction mixture was cooled down at RT and water (2 mL) was added. The layers were separated and the aqueous phase extracted further with DCM three times (3 mL). The combined organic layers were dried over MgSO₄ and then evaporated. The crude residue was purified by column chromatography (EP/AcOEt: from 100/0 to 95/5). The product was obtained as a white solid (23 mg, 9.1*10^{-2} mmol, 81%).

^1^H NMR (δ, ppm) (CDCl₃, 400 MHz): 8.81 (d, 1H, J = 8.2 Hz, C₅H); 8.80 (d, 1H, J = 8.3 Hz, C₄H); 7.90 (d, 1H, J = 7.6 Hz, C₆H); 7.84 (d, 1H, J = 9.2 Hz, C₉/₁₀H); 7.74 – 7.68 (m, 3H, C₃H, C₆H & C₉/₁₀H); 7.69 – 7.65 (m, 1H, C₇H); 7.58 (d, 1H, J = 7.1 Hz, C₇H); 7.54 – 7.53 (m, 4H, C₁₁H & C₁₂H); 7.50 – 7.45 (m, 1H, C₁₄H). ^1^C NMR (δ, ppm) (CDCl₃, 100.6 MHz): 141.07 (C₁IV); 140.97 (C₁V); 131.69 (C₁V); 130.64 (C₁V); 130.37 (C₁V); 130.19 (2C, C₁₃H); 129.88 (C₁V); 128.43 (C₈H); 128.24 (2C, C₁₂H); 127.86 (C₁₄H); 127.21 (C₇H); 126.83 (CH); 126.66 (CH); 126.62 (CH); 125.92 (CH); 124.57 (C₉/₁₀H); 122.93 (C₅H); 122.10 (C₄H). IR (cm⁻¹) (CCl₄): 3061, 2927, 2855, 1455. HRMS (El+) calcd for C₂₀H₁₄ 254.1096, found: 254.1095. Mp: 75 °C.
Compound 8b: 6-chloro-1-phenynaphthalene

Alcohol 6c (38 mg, 0.10 mmol, 1.0 eq) and P-TSA (5 mg) were refluxed in EtOH (1.2 ml). After 30 h, the reaction mixture was cooled down at RT and water (2mL) was added. The layers were separated and the aqueous phase extracted further with DCM three times (3 mL). The combined organic layers were dried over MgSO$_4$ and then evaporated. The crude residue was purified by column chromatography (EP/AcOEt: from 100/0 to 90/10). The product was obtained as a transparent oil (22 mg, 9.1*10$^{-2}$ mmol, 90%).

$^1$H NMR (δ, ppm) (CDCl$_3$, 400 MHz): 7.89 (d, 1H, J = 2.1 Hz, C$_5$H); 7.84 (d, 1H, J = 9.1 Hz, C$_8$H); 7.77 (d, 1H, J = 8.2 Hz, C$_4$H); 7.55 (dd, 1H, J$_1$ = 7.2 Hz, J$_2$ = 8.1 Hz, C$_3$H); 7.53 – 7.45 (m, 5H, C$_{10}$H, C$_{11}$H & C$_{12}$H); 7.42 (dd, 1H, J$_1$ = 1.1 Hz, J$_2$ = 7.0 Hz, C$_2$H); 7.36 (dd, 1H, J$_1$ = 2.2 Hz, J$_2$ = 9.1 Hz, C$_7$H). $^{13}$C NMR (δ, ppm) (CDCl$_3$, 100.6 MHz): 140.41 (C$_{IV}$); 140.21 (C$_{IV}$); 134.48 (C$_{IV}$); 131.62 (C$_{IV}$); 129.94 (2C, C$_{10}$H); 129.91 (C$_6$); 128.35 (2C, C$_{11}$H); 127.85 (CH); 127.47 (CH); 127.11 (CH); 126.81 (2CH); 126.73 (CH); 126.54 (CH). IR (cm$^{-1}$) (CCl$_4$): 3060, 2927, 2855, 1590.

HRMS (EI+) calcd for C$_{16}$H$_{11}$Cl 238.0549, found: 238.0548.

Compound 8c: 1-bromo-6-methoxynaphthalene

To a solution of ketone 4a (50 mg, 0.17 mmol, 1.0 eq) in toluene (1.7 ml) at 0 °C under a nitrogen atmosphere was added PBr$_3$ (80 µL, 0.86 mmol, 5.0 eq) dropwise. The solution was refluxed for 16 h. The reaction mixture was cooled down at RT and water (3 mL) was added. The solution was washed with NaHCO$_3$ (sat. aq.) (3 mL). The layers were separated and the aqueous phase extracted further with DCM three times (3 mL). The combined organic layers were dried over MgSO$_4$ and then evaporated. The crude residue was purified by
column chromatography (EP/AcOEt 90/10). The product was obtained as a yellowish oil (17 mg, 7.2*10^{-2} mmol, 44%).

$^1$H NMR (δ, ppm) (CDCl$_3$, 400 MHz): 8.14 (d, 1H, J = 9.2 Hz, C$_8$H); 7.69 (d, 1H, J = 8.2 Hz, C$_3$H ou C$_4$H); 7.62 (dd, 1H, J$_1$ = 1.0 Hz, J$_2$ = 7.4 Hz, C$_2$H ou C$_4$H); 7.27 (dd, J$_1$ = 7.7 Hz, J$_2$ = 8.0 Hz, C$_3$H); 7.24 (dd, 1H, J$_1$ = 2.4 Hz, J$_2$ = 9.3 Hz, C$_1$H); 7.12 (d, 1H, J = 2.5 Hz, C$_5$H); 3.93 (s, 3H, OC$_9$H$_3$).

$^{13}$C NMR (δ, ppm) (CDCl$_3$, 100.6 MHz): 158.12 (C$_6$O); 135.84 (C$_4'$); 128.73 (C$_8$H); 127.57 (C$_2$H ou C$_4$H); 127.43 (C$_8'$); 126.75 (C$_3$H); 126.70 (C$_2$H ou C$_4$H); 122.64 (C$_1$Br); 119.96 (C$_7$H); 106.06 (C$_5$H); 55.40 (OC$_9$H$_3$).

IR (cm$^{-1}$) (CCl$_4$): 3059, 3006, 2958, 2937, 2838, 1625. HRMS (EI+) calcd for C$_{11}$H$_9$BrO 235.9837, found: 235.9835.

Compound 9b: N-benzyl-2-chlorotetraphen-5-amine

To a solution of ketone 4b (70 mg, 0.24 mmol, 1.0 eq) and benzylamine (29 µL, 0.26 mmol, 1.1 eq) in chlorobenzene (1.2 mL) at 0 °C under a nitrogen atmosphere was added TiCl$_4$ (16 µL, 0.14 mmol, 0.6 eq) dropwise. After 16 h at RT, H$_2$SO$_4$ (60 µL) and TiCl$_4$ (32 µL, 0.28 mmol, 1.2 eq) were added to the crude mixture at 0 °C. The solution was warmed at 80 °C for 3 h. The reaction mixture was cooled down at RT and water (2 mL) was added. The solution was filtrated and the crude residue was purified by column chromatography (EP/AcOEt: from 95/5 to 90/10). The product was obtained as a yellowish solid (11 mg, 3.0*10^{-2} mmol, 12%).

$^1$H NMR (δ, ppm) (CDCl$_3$, 400 MHz): 8.92 (s, 1H, C$_{12}$H); 8.79 (d, 1H, J = 2.0 Hz, C$_4$H); 8.08 (s, 1H, C$_7$H); 8.03 (d, 1H, J = 8.1 Hz, C$_{11}$H); 7.91 (d, 1H, J = 7.9 Hz, C$_8$H); 7.81 (d, 1H, J = 8.7 Hz, C$_3$H); 7.57 (dd, 1H, J$_1$ = 1.8 Hz, J$_2$ = 8.6 Hz, C$_3$H); 7.53 – 7.40 (m, 6H, C$_9$H, C$_{10}$H, C$_{15}$H & C$_{16}$H); 7.37 – 7.33 (m, 1H, C$_{17}$); 6.85 (s, 1H, C$_6$H); 4.58 (s, 3H, NC$_{13}$H$_2$ & NH). $^{13}$C NMR (δ, ppm) (CDCl$_3$, 100.6 MHz): 140.04 (C$_{IV}$); 138.65 (C$_{IV}$); 133.11 (C$_{IV}$); 132.99 (C$_{IV}$); 132.84 (C$_{IV}$); 130.07 (C$_{IV}$); 128.83 (2C, C$_{15}$H); 128.52 (C$_{11}$H); 127.96 (2C, C$_{16}$H); 127.63 (C$_3$H); 127.04 (C$_3$H); 126.92 (C$_8$H); 126.07 (C$_3$H); 124.90 (C$_{IV}$); 124.63 (C$_{IV}$); 124.35 (C$_{10}$H); 123.49 (C$_4$H); 123.42 (C$_3$H); 122.03 (C$_3$H); 121.64 (C$_{12}$H); 102.13 (C$_{6}$H); 48.70 (NC$_{13}$H$_2$). IR (cm$^{-1}$) (CCl$_4$): 3059, 2928, 2856, 1623. HRMS (EI+) calcd for C$_{25}$H$_{18}$NCl 367.1128, found: 367.1132.
Compound 10: N-benzyl-N-(2-methoxytetraphen-5-yl)acetamide

To a solution of ketone 4a (70 mg, 0.24 mmol, 1.0 eq) and benzylamine (29 µL, 0.26 mmol, 1.1 eq) in chlorobenzene (1.2 mL) at 0 °C under a nitrogen atmosphere was added TiCl$_4$ (16 µL, 0.14 mmol, 0.6 eq) dropwise. After 12 h at RT, H$_2$SO$_4$ (60 µL) and TiCl$_4$ (32 µL, 0.28 mmol, 1.2 eq) were added to the crude mixture at 0 °C. The solution was warmed at 80 °C for 3 h. The reaction mixture was cooled down at RT and water (2 mL) was added. The layers were separated and the aqueous phase extracted further with DCM three times (3 mL). The combined organic layers were dried over MgSO$_4$ and concentrated under reduced pressure. The crude residue was directly treated with acetic anhydride (190 µL). The reaction was stirred for 2.5 h at RT then water (3 mL) was added. The layers were separated and the aqueous phase extracted further with DCM three times (3 mL). The combined organic layers were dried over MgSO$_4$ and concentrated under reduced pressure. The crude residue was purified by column chromatography (EP/AcOEt: from 95/5 to 80/20). The product was obtained as a strong yellow solid (19.6 mg, 4.8*10$^{-2}$ mmol, 20 %).

$^1$H NMR (δ, ppm) (CDCl$_3$, 400 MHz): 9.07 (s, 1H, C$_{12}$H); 8.29 (d, 1H, J = 2.4 Hz, C$_7$H); 8.16 (s, 1H, C$_7$H); 8.14 – 8.12 (m, 1H, C$_{11}$H); 7.99 – 7.96 (m, 1H, C$_6$H); 7.73 (d, 1H, J = 8.9 Hz, C$_4$H); 7.59 – 7.53 (m, 2H, C$_9$H & C$_{10}$H); 7.29 – 7.25 (m, 6H, C$_3$H, C$_{18}$H, C$_{19}$H & C$_{20}$H); 7.13 (s, 1H, C$_6$H); 5.74 (d, 1H, J = 14.0 Hz, NC$_{16}$H$_2$); 4.21 (d, 1H, J = 14.0 Hz, NC$_{16}$H$_2$); 4.09 (s, 3H, OC$_{13}$H$_3$); 1.93 (s, 3H, C$_{15}$H$_3$).

$^{13}$C NMR (δ, ppm) (CDCl$_3$, 100.6 MHz): 171.34 (C$_{14}$O); 159.34 (C$_2$); 137.73 (C$_{16}$); 136.79 (C$_{17}$); 133.64 (C$_{18}$); 132.15 (C$_{19}$); 132.08 (C$_{20}$); 129.90 (C$_{12}$); 129.35 (2C, C$_{16}$H); 128.41 (C$_{11}$H); 128.33 (2C, C$_{15}$H); 127.89 (C$_{13}$); 127.61 (C$_8$H); 127.48 (C$_7$H); 127.37 (C$_6$H); 126.32 & 126.19 (C$_9$H & C$_{10}$H); 125.55 (C$_4$H); 124.87 (C$_3$H); 123.07 (C$_{17}$); 121.70 (C$_{12}$H); 116.36 (C$_{18}$H); 106.51 (C$_1$H); 55.67 (OC$_{13}$H$_3$); 51.91 (NC$_{16}$H$_2$); 22.24 (C$_{15}$H$_3$).

IR (cm$^{-1}$) (CCl$_4$): 2927, 2855, 1686, 1622. HRMS (EI+) calcd for C$_{28}$H$_{23}$NO$_2$: 405.1729, found: 405.1719. Mp: 130°C.
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