SUPPLEMENTARY MATERIAL

Formal Radical Closure onto Aromatic Rings — a General Route to Carbocycles

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6-Butyl-6-hydroxy-1,2,3,6-tetrahydroindene-3a-carboxylic Acid tert-Butyl Ester (10k).

\[ \text{10e} \quad \text{10k} \]

n-BuMgCl (2 M in THF, 0.15 mL, 0.3 mmol) was added at a fast dropwise rate to a
stirred and cooled (-78 °C) solution of \textbf{10e} (57.9 mg, 0.25 mmol) in Et\textsubscript{2}O (5 mL). The cold bath was removed and stirring was continued overnight. The mixture was cooled to 0 °C, quenched by dropwise addition of water, and extracted with Et\textsubscript{2}O. The combined organic extracts were washed with brine, dried (MgSO\textsubscript{4}) and evaporated. The crude product (\textbf{10k}) was used directly in the next step.

\textbf{5-Butylindan (10l).}

\[
\begin{align*}
\text{t-BuO}_2\text{C} & \quad \text{OH} \\
\text{Bu} & \quad \text{Bu} \\
\text{10k} & \quad \text{10l}
\end{align*}
\]

General procedure B for rearomatization was followed, using Bi\textsubscript{3}Cl\textsubscript{3}.H\textsubscript{2}O (82.5 mg, 0.25 mmol), \textbf{10k} (total product from the previous step) in MeCN (5 mL) and water (0.1 mL), and a reaction time of 8 h. Flash chromatography of the crude product over silica gel, using hexane, gave \textbf{10l} (35.3 mg, 82% over two steps) as an oil: \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz) \(\delta\) 0.93 (t, \(J = 7.6\) Hz, 3 H), 1.32-1.42 (m, 2 H), 1.56-1.63 (m, 2 H), 2.07 (apparent quintet, \(J = 7.6\) Hz, 2 H), 2.58 (t, \(J = 8\) Hz, 2 H), 2.86-2.91 (m, 4 H), 6.95-7.15 (m, 3 H); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 100 MHz) \(\delta\) 14.2 (q), 22.7 (t), 25.5 (t), 32.7 (t), 33.1 (t), 34.3 (t), 35.8 (t), 124.3 (d), 124.7 (d), 126.5 (d), 141.1 (s), 141.6 (s), 144.5 (s); \(\nu_{\text{max}}\) (microscope, CDCl\textsubscript{3} cast; cm\textsuperscript{-1}) 3007, 2956, 2855, 1491, 1458, 1440;
exact mass $m/z$ calcd for C$_{13}$H$_{18}$ 174.14085, found 174.14076.

6-Hydroxy-6-isopropyl-1,2,3,6-tetrahydroindene-3a-carboxylic Acid tert-Butyl Ester (10m).

\[ \begin{align*}
\text{10e} & \quad \text{10m} \\
\end{align*} \]

$i$-PrMgBr (2 M in Et$_2$O, 0.12 mL, 0.24 mmol) was added at a fast dropwise rate to a stirred and cooled (-78 °C) solution of 10e (45.7 mg, 0.20 mmol) in Et$_2$O (5 mL). The cold bath was removed and stirring was continued overnight. The mixture was cooled to 0 °C, quenched by dropwise addition of water, and extracted with Et$_2$O. The combined organic extracts were washed with brine, dried (MgSO$_4$) and evaporated. The crude product (10m) was used directly in the next step.

5-Isopropylnidan (10n).\textsuperscript{21}

\[ \begin{align*}
\end{align*} \]
General procedure B for rearomatization was followed, using BiCl$_3$.H$_2$O (65 mg, 0.2 mmol), 10m (total product from the previous step) in MeCN (5 mL) and water (0.1 mL), and a reaction time of 2 h. Flash chromatography of the crude product over silica gel (1.5 x 12 cm), using hexane, gave 10n (23.4 mg, 75%) as an oil: $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 1.25 (d, $J = 7.0$ Hz, 6 H), 2.07 (apparent quintet, $J = 7.5$ Hz, 2 H), 2.85-2.92 (m, 5 H), 7.02-7.16 (m, 3 H); $^{13}$C NMR (CDCl$_3$, 125 MHz) $\delta$ 24.3 (q), 25.5 (t), 32.5 (t), 32.9 (t), 34.0 (d), 122.3 (d), 124.1 (d), 124.3 (d), 141.6 (s), 144.3 (s), 147.0 (s); $\nu_{\text{max}}$ (microscope, CDCl$_3$ cast; cm$^{-1}$) 3008, 2958, 2867, 1493, 1460; exact mass m/z calcld for C$_{12}$H$_{16}$ 160.12520, found 160.12504.

6-Allyl-6-hydroxy-1,2,3,6-tetrahydroindene-3a-carboxylic Acid tert-Butyl Ester (10q).

[Diagram of 10e and 10q]

Allylmagnesium bromide (1 M in Et$_2$O, 0.33 mL, 0.33 mmol) was added at a fast dropwise rate to a stirred and cooled (-78 °C) solution of 10e (51 mg, 0.22 mmol) in Et$_2$O (5 mL). The cold bath was removed and stirring was continued for 1 h. The mixture was cooled to
0 °C, quenched by dropwise addition of water, and extracted with Et₂O. The combined organic extracts were washed with brine, dried (MgSO₄) and evaporated. The crude product (10q) was used directly in the next step.

5-Allylindan (10r).²²

![Chemical structure of 5-Allylindan](image)

General procedure B for rearomatization was followed, using BiCl₃·H₂O (74 mg, 0.33 mmol), 10q (total product from the previous step) in MeCN (5 mL) and water (0.1 mL), and an overnight reaction period. Flash chromatography of the crude product over silica gel, using hexane, gave 10r (20 mg, 75%) as an oil: ^1^H NMR (CDCl₃, 400 MHz) δ 2.07 (apparent quintet, J = 7.4 Hz, 2 H), 2.88 (t, J = 7.4 Hz, 2 H), 2.89 (t, J = 7.4 Hz, 2 H), 3.36 (d, J = 6.8 Hz, 2 H), 5.05 (ddd, J = 10.0, 2.0, 1.2 Hz, 1 H), 5.10 (ddd J = 16.8, 1.6, 1.6 Hz, 1 H), 5.98 (ddd, J = 16.8, 10.0, 6.8 Hz, 1 H), 6.97 (d, J = 6.8 Hz, 1 H), 7.08 (s, 1 H), 7.16 (d, J = 7.6 Hz, 1 H); ^1^C NMR (CDCl₃, 100 MHz) δ 25.4 (t), 32.4 (t), 32.7 (t), 40.0 (t), 115.2 (t), 124.1 (d), 124.4 (d), 126.2 (d), 137.7 (s), 137.8 (d), 141.8 (s), 144.4 (s); ν_max (microscope, CDCl₃ cast; cm⁻¹) 3076, 3007, 2951, 2844, 1639, 1489, 1437; exact mass m/z calcld for C₁₂H₁₄ 158.10956, found 158.10989.

6-Hydroxy-6-prop-2-ynyl-1,2,3,6-tetrahydroindene-3a-carboxylic Acid tert-Butyl
Ester (10s).

A mixture of propargyl bromide (80% w/w in PhMe, 0.117 mL, 1.05 mmol), Mg (25 mg, 1.05 mmol) and HgCl₂ (1 mg, 0.004 mmol) was heated to reflux. The Mg dissolved, at which point the heat source was removed, and stirring was continued for 45 min. The resulting propargylmagnesium bromide was added at a fast dropwise rate to a stirred and cooled (-78 °C) solution of 10e (84 mg, 0.358 mmol) in Et₂O (5 mL). The cold bath was removed and stirring was continued overnight. The mixture was cooled to 0 °C, quenched by dropwise addition of saturated aqueous NH₄Cl, and extracted with Et₂O. The combined organic extracts were washed with brine, dried (MgSO₄) and evaporated. The crude product (10s) was used directly in the next step.

5-(Prop-2-ynyl)indane (10t).
General procedure B for rearomatization was followed, using BiCl$_3$.H$_2$O (120 mg, 0.358 mmol), 10s (total product from the previous step) in MeCN (5 mL) and water (0.1 mL), and an overnight reaction period. Flash chromatography of the crude product over silica gel, using hexane, gave 10t (41 mg, 73%) as an oil: $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 2.10 (apparent quintet, $J = 7.6$ Hz, 2 H), 2.19 (t, $J = 2.8$ Hz, 1 H), 2.92 (apparent q, $J = 7.2$ Hz, 4 H), 3.60 (d, $J = 2.8$ Hz, 2 H), 7.12-7.27 (m, 3 H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 24.5 (t), 25.5 (t), 32.4 (t), 32.7 (t), 70.0 (d), 82.5 (s), 123.8 (d), 124.3 (d), 125.6 (d), 133.8 (s), 142.6 (s), 144.7 (s); $\nu$$_{\text{max}}$ (microscope, CDCl$_3$ cast; cm$^{-1}$) 3298, 3011, 2950, 2867, 2843, 2120, 1490; exact mass $m/z$ calcd for C$_{12}$H$_{12}$ 156.09390, found 156.09399.

6-Hydroxy-6-(trimethylsilanylethynyl)-1,2,3,6-tetrahydroindene-3a-carboxylic Acid tert-Butyl Ester (10u).

![Chemical structure](image)

Trimethylsilylacetylene (0.16 mL, 1.1 mmol) was added at a slow dropwise rate to a stirred and cooled (-78 °C) solution of $i$-PrMgBr (2 M in Et$_2$O, 0.55 mL, 1.1 mmol). The cooling bath was removed and stirring was continued for 2 h. The resulting Grignard reagent was taken up into a syringe and added at a fast dropwise rate to a stirred and cooled (-78 °C) solution of 10e
(52 mg, 0.222 mmol) in Et₂O (5 mL). The cold bath was removed and stirring was continued overnight. The mixture was cooled to 0 °C, quenched by dropwise addition of saturated aqueous NH₄Cl, and extracted with Et₂O. The combined organic extracts were washed with brine, dried (MgSO₄) and evaporated. The crude product (10u) was used directly in the next step.

5-Ethynylindan (10v).

General procedure B for rearomatization was followed, using BiCl₃·H₂O (74 mg, 0.222 mmol), 10u (total product from the previous step) in MeCN (5 mL) and water (0.1 mL), and an overnight reaction period. Flash chromatography of the crude product over silica gel, using hexane, gave 10v (18 mg, 57%) as an oil: ¹H NMR (CDCl₃, 300 MHz) δ 2.08 (apparent quintet, J = 7.6 Hz, 2 H), 2.90 (two overlapping apparent q, J = 7.2 Hz, 4 H), 3.01 (s, 1 H), 7.16-7.36 (m, 3 H); ¹³C NMR (CDCl₃, 100 MHz) δ 25.3 (t), 32.6 (t), 32.9 (t), 75.9 (d), 84.4 (s), 119.5 (s), 124.3 (d), 128.0 (d), 130.2 (d), 144.3 (s), 145.4 (s); ν max (microscope, CDCl₃ cast; cm⁻¹) 3292, 2952, 2868, 2843, 2104, 1485; exact mass m/z calcd for C₁₁H₁₀ 142.07825, found 142.07818.
6-Hydroxy-6-phenylethynyl-1,2,3,6-tetrahydroindene-3a-carboxylic Acid tert-Butyl Ester (10w).

\[
\begin{align*}
&\text{5-Phenylethynylindan (10x).}^{24}
\end{align*}
\]
General procedure B for rearomatization was followed, using BiCl$_3$·H$_2$O (73 mg, 0.218 mmol), 10w (total product from the previous step) in MeCN (5 mL) and water (0.1 mL), and an overnight reaction period. Flash chromatography of the crude product over silica gel, using hexane, gave 10x (29 mg, 62%) as an oil: $^1$H NMR (CDCl$_3$, 300 MHz) δ 2.16 (apparent quintet, $J = 7.5$ Hz, 2 H), 2.93 (two overlapping apparent t, $J = 7.5$ Hz, 4 H), 7.19-7.56 (m, 8 H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 25.3 (t), 32.7 (t), 32.9 (t), 88.2 (s), 90.1 (s), 120.7 (s), 123.6 (s), 124.3 (d), 127.5 (d), 127.9 (d), 128.3 (d), 129.6 (d), 131.5 (d), 144.4 (s), 144.8 (s); ν$_{\text{max}}$ (microscope, CDCl$_3$ cast; cm$^{-1}$) 3061, 3032, 2953, 2843, 2207, 1597, 1494; exact mass m/z calcd for C$_{17}$H$_{14}$BrO$_2$ 218.10956, found 218.10942.

1-(3-Bromopropyl)-2-methoxycyclohexa-2,5-dienecarboxylic Acid tert-Butyl Ester (15a).

The general procedure for reductive alkylation was followed, using 15 (427.1 mg, 2.05
mmol) in dry THF (15 mL), t-BuOH (0.22 mL, 2.26 mmol), liquid NH₃ (50 mL), Li (30.2 mg, 4.31 mmol), and 1,3-dibromopropane (0.52 mL, 5.13 mmol) in THF (15 mL). Flash chromatography of the crude product over silica gel (3 x 21 cm), using first hexane and then 1:9 EtOAc-hexane, gave 15a (583.9 mg, 86%) as an oil: ¹H NMR (CDCl₃, 400 MHz) δ 1.42 (s, 9 H), 1.70-1.78 (m, 3 H), 2.07-2.13 (m, 1 H), 2.80-2.86 (m, 2 H), 3.35-3.39 (m, 2 H), 3.55 (s, 3 H), 4.82-4.84 (m, 1 H), 5.37-5.41 (m, 1 H), 5.86-5.90 (m, 1 H); ¹³C NMR (CDCl₃, 100 MHz) δ 26.5 (t), 27.9 (q), 28.5 (t), 32.9 (t), 34.0 (t), 52.2 (s), 54.2 (q), 80.6 (s), 93.6 (d), 126.8 (d), 127.2 (d), 152.9 (s), 172.4 (s); ν_max (CDCl₃ cast; cm⁻¹) 2926, 2935, 1730, 1687, 1649, 1456, 1209; exact mass m/z calcd for C₁₅H₂₃⁷⁹BrNaO₃ (M + Na) 353.07228, found 353.07245.

1-(3-Bromopropyl)-2-methoxy-4-oxocyclohexa-2,5-diene-carboxylic Acid tert-Butyl Ester (15b).

General procedure A for oxidation was followed, using CrO₃ (1.51 g, 15.1 mmol), Ac₂O (2.6 mL), AcOH (5.2 mL), PhH (15 mL), 15a (1.00 g, 3.02 mmol) in PhH (20 mL), and a reaction time of 5 h. Flash chromatography of the crude product over silica gel (2 x 18 cm), using first hexane and then EtOAc-hexane mixtures up to 3:7 EtOAc-hexane, gave 15b (0.646 g, 62%) as an oil: ¹H NMR (CDCl₃, 400 MHz) δ 1.39 (s, 9 H), 1.42-1.59 (m, 1 H), 1.60-1.68 (m, 1
H, 2.05-2.12 (m, 1 H), 2.29-2.37 (m, 1 H), 3.33 (t, \( J = 6.6 \) Hz, 2 H), 3.76 (s, 3 H), 5.68 (d, \( J = 1.3 \) Hz, 1 H), 6.31 (dd, \( J = 9.9, 1.4 \) Hz, 1 H), 6.47 (d, \( J = 9.9 \) Hz, 1 H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \( \delta \) 27.0 (t), 27.6 (q), 32.6 (t), 32.7 (t), 55.7 (s), 55.8 (q), 82.8 (s), 104.2 (d), 130.3 (d), 143.0 (d), 167.5 (s), 173.2 (s), 187.6 (s); \( \nu_{\text{max}} \) (CDCl\(_3\) cast; cm\(^{-1}\)) 2977, 2940, 1737, 1660, 1599, 1249; exact mass \( m/z \) calcd for C\(_{15}\)H\(_{21}\)\(^{79}\)BrNaO\(_4\) (M + Na) 367.05154, found 367.05131.

The oxidation was also done using PDC-t-BuOOH:\(^{12}\) Celite (8 g) was added to a stirred solution of 15a (1.0 g, 3.02 mmol) in PhH (40 mL), followed by PDC (4.546 g, 12.08 mmol) and then t-BuOOH (70%, 1.55 mL, 12.08 mmol) was added dropwise. Stirring was continued for 4 h after the end of the addition, and the mixture was then filtered through a pad of Celite (4 x 6 cm). Evaporation of the filtrate and flash chromatography of the residue over silica gel (2 x 17 cm), using EtOAc-hexane mixtures from 1:9 to 3:7, gave 15b (771 mg, 74 %) as an oil identical with material made using CrO\(_3\).

1-(3-Iodopropyl)-2-methoxy-4-oxocyclohexa-2,5-diene-carboxylic Acid tert-Butyl Ester (15c).

![Diagram](image)

The general procedure for Finkelstein displacement was followed, using acetone (10 mL), 15b (180.7 mg, 0.52 mmol), anhydrous NaI (274.9 mg, 1.83 mmol), and a reaction time of
16 h. Flash chromatography of the crude product over silica gel (1.5 x 15 cm), using 10% EtOAc-hexane, gave 15c (184.8 mg, 90%) as an oil: \( ^1H \) NMR (CDCl\(_3\), 400 MHz) \( \delta \) 1.34 (s, 9 H), 1.40-1.60 (m, 2 H), 1.97-2.04 (m, 1 H), 2.22-2.29 (m, 1 H), 3.07 (t, \( J = 6.8 \) Hz, 2 H), 3.72 (s, 3 H), 5.64 (d, \( J = 1.3 \) Hz, 1 H), 6.23 (dd, \( J = 9.9, 1.5 \) Hz, 1 H), 6.44 (d, \( J = 9.9 \) Hz, 1 H); \( ^{13}C \) NMR (CDCl\(_3\), 100 MHz) \( \delta \) 5.3 (t), 27.6 (q), 27.7 (t), 34.8 (t), 55.6 (s), 55.9 (q), 82.8 (s), 104.1 (d), 130.2 (d), 143.0 (d), 167.4 (s), 173.3 (s), 187.6 (s); \( \nu_{\text{max}} \) (CH\(_2\)Cl\(_2\) cast; cm\(^{-1}\)) 2976, 2937, 1736, 1660, 1598, 1222; exact mass \( m/z \) calcd for C\(_{15}\)H\(_{21}\)INO\(_4\) (M + Na) 415.03768, found 415.03778.

**4-Methoxy-6-oxo-1,2,3,6,7,7a-hexahydroindene-3a-carboxylic Acid tert-Butyl Ester (15d).**

The general procedure for radical cyclization was followed, using Bu\(_3\)SnH (0.20 mL, 0.61 mmol) and AIBN (10.1 mg, 0.061 mmol) in PhH (5 mL), and 15c (241 mg, 0.61 mmol) in PhH (10 mL). Heating was continued for 18 h after the addition. Flash chromatography of the crude product over KF-flash chromatography silica gel (10%/w KF) (2 x 22 cm), using 1:9 to 3:7 EtOAc-hexane mixtures, gave 15d (153.8 mg, 94%) as an oil: \( ^1H \) NMR (CDCl\(_3\), 300 MHz) \( \delta \) 1.41 (s, 9 H), 1.60-1.75 (m, 3 H), 1.86-1.90 (m, 1 H), 2.06-2.19 (m, 1 H), 2.34-2.41 (m, 2 H),
2.59-2.67 (m, 2 H), 3.69 (s, 3 H), 5.41 (s, 1 H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 23.3 (t), 27.9 (q), 31.2 (t), 34.1 (t), 38.2 (t), 43.0 (d), 56.1 (q), 57.8 (s), 81.5 (s), 103.0 (d), 171.8 (s), 175.8 (s), 198.3 (s); $\nu_{\text{max}}$ (CH$_2$Cl$_2$ cast; cm$^{-1}$) 2974, 1732, 1662, 1218; exact mass m/z calcd for C$_{14}$H$_{22}$NaO$_4$ (M + Na) 289.14103, found 289.14112.

4-Methoxy-6-oxo-7-phenylselanyl-1,2,3,6,7,7a-hexahydro-indene-3a-carboxylic Acid tert-Butyl Ester (pre-15e).

BuLi (2.5M in hexane, 0.26 mL, 0.64 mmol) was added dropwise to a stirred and cooled solution (-78 °C) of i-Pr$_2$NH (0.094 mL, 0.69 mmol) in THF (5 mL). Stirring was continued at (-78 °C) for 30 min and a solution of 15d (148.9 mg) in THF (3 mL plus 1 mL as a rinse) was added dropwise. Stirring was continued at (-78 °C) for 1 h. PhSeCl (128.6 mg, 0.67 mmol) in THF (3 mL) was added rapidly and stirring was continued at -78 °C for 1 h. The mixture was quenched with saturated aqueous NH$_4$Cl and then with water, and extracted with Et$_2$O (3 times). The combined organic extracts were washed with brine, dried (MgSO$_4$) and evaporated. Flash chromatography of the residue over silica gel (1.5 x 20 cm), using 30% EtOAc-hexane, gave pre-15e as a mixture of isomers [isomer with PhSe and adjacent ring fusion hydrogen cis, 164.9 mg (70%), isomer with PhSe and adjacent ring fusion hydrogen trans, 28.3 mg (12%)]. The
stereochemistry was assigned on the basis that only the cis isomer gave an olefin on oxidation and both isomers had very similar NMR spectra. The cis isomer had: $^1$H NMR (CDCl$_3$, 300 MHz) δ 1.28-1.42 (m, 2 H), 1.51 (s, 9 H), 1.55-1.81 (m, 2 H), 1.99-2.16 (m, 2 H), 2.26-2.42 (m, 1 H), 3.04-3.11 (m, 1 H), 3.71-3.78 (m, 4 H), 5.46 (s, 1 H), 7.24-7.31 (m, 3 H), 7.62-7.68 (m, 2 H); $^{13}$C NMR (CDCl$_3$, 100 MHz) (two signals are coincident; spectrum shows some impurity signals) δ 22.6 (t), 27.8 (q), 28.7 (t), 35.3 (t), 47.2 (d), 51.5 (d), 56.5 (d), 59.3 (s), 81.9 (s), 102.7 (d), 127.8 (d), 128.2 (s), 129.1 (d), 134.8 (d), 174.9 (s), 195.0 (s); $\nu_{\text{max}}$ (CH$_2$Cl$_2$ cast; cm$^{-1}$) 2926, 1731, 1654, 1265; exact mass $m/z$ calcd for C$_{21}$H$_{27}$NaO$_4$Se (M + Na) 423.10691, found 423.10720.

The trans isomer was not fully characterized; the integration of the $^1$H NMR spectrum was poor; the $^{13}$C NMR spectrum was very similar to that of the cis isomer: $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 22.5 (t), 27.7 (q), 28.6 (t), 35.2 (t), 47.1 (d), 51.4 (d), 56.4 (d), 62.0 (s), 81.8 (s), 102.7 (d), 127.7 (d), 128.1 (s), 129.1 (d), 134.7 (d), 170.7 (s), 174.8 (s), 194.6 (s).

4-Methoxy-6-oxo-1,2,3,6-tetrahydroindene-3a-carboxylic Acid tert-Butyl Ester (15e).

30% H$_2$O$_2$ (0.21 mL) was added dropwise over 5 min to a stirred and cooled (0 °C)
solution of **pre-15e** (presumed to have the PhSe group and adjacent H cis) (83.7 mg, 0.20 mmol) in THF (7 mL) and water (0.7 mL). After 10 min the ice bath was removed and stirring was continued for 2 h. The mixture was cooled to 0 °C and quenched with saturated aqueous Na₂S₂O₃ (2 mL). The ice bath was removed and stirring was continued for 10 min. The mixture was diluted with brine (10 mL) and extracted with EtOAc (3 x 10 mL). The combined organic extracts were dried (MgSO₄) and evaporated. Flash chromatography of the residue over silica gel (1.5 x 15 cm), using 35% EtOAc-hexane, gave **15e** as an oil (42.0 mg, 80%): ¹H NMR (CDCl₃, 400 MHz) δ 1.36 (s, 9 H), 1.57-1.65 (m, 1 H), 1.87-1.94 (m, 1 H), 2.03-2.09 (m, 1 H), 2.44-2.52 (m, 1 H), 2.56-2.62 (m, 1 H), 2.67-2.72 (m, 1 H), 3.71 (s, 3 H), 5.49 (d, J = 1.0 Hz, 1 H), 6.04 (s, 1 H); ¹³C NMR (CDCl₃, 100 MHz) (one signal not observed) δ 21.2 (t), 27.4 (q), 28.7 (t), 31.1 (t), 55.9 (q), 82.4 (s), 101.7 (d), 122.8 (d), 161.1 (s), 167.4 (s), 174.0 (s), 189.3 (s); νmax (CH₂Cl₂ cast; cm⁻¹) 2926, 2851, 1734, 1670, 1265; exact mass m/z calcd for C₁₅H₂₀NaO₄ (M + Na) 287.12538, found 287.12541.

**7-Methoxyindan-5-ol (15f).**

General procedure A for rearomatization was followed, using BiCl₃.H₂O (20.2 mg, 0.06
mmol), 15e (40.0 mg, 0.15 mmol) in MeCN (5 mL) and water (0.1 mL), and a reaction time of 10 h after addition of the second portion of BiCl₃·H₂O. Flash chromatography of the crude product over silica gel (1 x 10 cm), using 30% EtOAc-hexane, gave 15f (22.8 mg, 92%) as a white solid: mp 95-97 °C; ¹H NMR (CDCl₃, 400 MHz) δ 2.02-2.10 (m, 2 H), 2.77-2.87 (m, 4 H), 3.79 (s, 3 H), 4.81 (s, 1 H), 6.23 (s, 1 H), 6.33 (s, 1 H); ¹³C NMR (CDCl₃, 100 MHz) δ 25.0 (t), 28.6 (t), 33.2 (t), 55.1 (q), 96.4 (d), 103.3 (d), 123.7 (s), 146.9 (s), 155.6 (s), 156.4 (s); νmax (CHCl₃ cast; cm⁻¹) 3303, 2949, 2849, 1613, 1596, 1468; exact mass m/z calcd for C₁₀H₁₂O₂ 164.08372, found 164.08362.

5-Hydroxy-5-methyl-1,2,3,5-tetrahydrocyclopenta[a]naphthalene-9b-carboxylic Acid tert-Butyl Ester (16g).

MeMgBr (3 M in THF, 0.17 mL, 0.502 mmol) was added at a fast dropwise rate to a stirred and cooled (-78 °C) solution of 16e (95 mg, 0.335 mmol) in Et₂O (10 mL). The cold bath was removed and stirring was continued for 40 min. The mixture was cooled to 0 °C, quenched slowly with water, and extracted with Et₂O. The combined organic extracts were washed with brine, dried (MgSO₄) and evaporated. The crude product (16g) was used directly in the next
5-Methyl-2,3-dihydro-1H-cyclopenta[a]naphthalene (16h).

General procedure B for rearomatization was followed, using BiCl$_3$.H$_2$O (88.4 mg, 0.265 mmol), 16g (79.6 mg, 0.265 mmol) in MeCN (5 mL) and water (0.1 mL), and a reaction time of 4 h. Flash chromatography of the crude product over silica gel (1 x 12 cm), using hexane, gave 16h (33.6 mg, 70%) as an oil: $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 2.21-2.28 (m, 2 H), 2.70 (s, 3 H), 3.09 (t, $J = 7.4$ Hz, 2 H), 3.25 (t, $J = 7.4$ Hz, 2 H), 7.28 (s, 1 H), 7.45-7.53 (m, 2 H), 7.81-7.83 (m, 1 H), 7.99-8.02 (m, 1 H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 19.5 (q), 24.4 (t), 31.0 (t), 33.8 (t), 124.0 (d), 124.4 (d), 124.6 (d), 124.8 (d), 125.4 (d), 130.5 (s), 131.4 (s), 132.6 (s), 137.4(s), 140.5 (s); $\nu_{\text{max}}$ (microscope, CDCl$_3$ cast; cm$^{-1}$) 3008, 2947, 2845, 1592, 1439; exact mass m/z calcd for C$_{14}$H$_{14}$ 182.10956, found 182.11250.

5-Hydroxy-5-(trimethylsilanylethynyl)-1,2,3,5-tetrahydrocyclopenta[a]naphthalene-9b-carboxylic Acid tert-Butyl Ester (16m).
Trimethyldimethylacetylene (0.12 mL, 0.8 mmol) was added dropwise to a stirred and cooled (-78 °C) solution of i-PrMgBr (2 M in Et₂O, 0.4 mL, 0.8 mmol). The cooling bath was removed and the stirring was continued for 2 h. The resulting Grignard reagent was taken up into a syringe and added at fast dropwise rate to a stirred and cooled (-78 °C) solution of 16e (152 mg, 0.535 mmol) in Et₂O (5 mL). The cold bath was removed and stirring was continued overnight. The mixture was cooled to 0 °C, quenched by dropwise addition of saturated aqueous NH₄Cl, and extracted with Et₂O. The combined organic extracts were washed with brine, dried (MgSO₄) and evaporated. The crude product (16m) was used directly in the next step.

5-(1-Chlorovinyl)-2,3-dihydro-1H-cyclopenta[a]naphthalene (16n).
General procedure B for rearomatization was followed, using BiCl$_3$.H$_2$O (178 mg, 0.535 mmol), 16m (total product from the previous step) in MeCN (5 mL) and water (0.1 mL), and an overnight reaction period. Flash chromatography of the crude product over silica gel, using hexane, gave 16n (49 mg, 40%) as an oil: $^1$H NMR (CDCl$_3$, 400 MHz) δ 2.29 (apparent quintet, $J = 7.6$ Hz, 2 H), 3.14 (t, $J = 7.6$ Hz, 2 H), 3.30 (t, $J = 7.6$ Hz, 2 H), 5.57 (d, $J = 1.2$ Hz, 1 H), 5.85 (d, $J = 1.2$ Hz, 1 H), 7.49-8.23 (m, 5 H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 24.4 (t), 31.3 (t), 33.6 (t), 117.3 (t), 124.1 (d), 124.6 (d), 125.2 (d), 125.9 (d), 126.1 (d), 129.3 (s), 130.4 (s), 135.4 (s), 139.1 (s), 140.1 (s), 141.2 (s); $\nu$$_{\text{max}}$ (microscope, CDCl$_3$ cast; cm$^{-1}$) 3063, 2952, 2844, 1628, 1512; exact mass m/z calcd for C$_{15}$H$_{13}$Cl 228.07057, found 228.07063.

9-Hydroxy-1,3,4,9-tetrahydro-2H-phenanthrene-4a-carboxylic Acid tert-Butyl Ester (17f).

CeCl$_3$.7H$_2$O (119.5 mg, 0.32 mmol) and then NaBH$_4$ (6.67 mg, 0.12 mmol) were added to a stirred and cooled (-78 °C) solution of 17d (47.8 mg, 0.16 mmol) in dry MeOH (5 mL). After the addition, the cold bath was removed and stirring was continued for 40 min. The
mixture was quenched slowly with water and extracted with Et₂O. The combined organic extracts were washed with brine, dried (MgSO₄) and evaporated. The crude product (17f) was used directly in the next step.

1,2,3,4-Tetrahydrophenanthrene (17g).²⁵

General procedure B for rearomatization was followed, using BiCl₃·H₂O (56.7 mg, 0.17 mmol), 17f (51 mg, 0.17 mmol) in MeCN (5 mL) and water (0.1 mL), and a reaction time of 6 h. Flash chromatography of the crude product over silica gel (1 x 12 cm), using hexane, gave 17g (22.2 mg, 76%) as an oil: ¹H NMR (CDCl₃, 400 MHz) δ 1.88-1.93 (m, 2 H), 1.95-2.01 (m, 2 H), 2.93 (t, J = 6.2 Hz, 2 H), 3.14 (t, J = 6.3 Hz, 2 H), 7.21-7.23 (m, 1 H), 7.43-7.53 (m, 2 H), 7.62 (d, J = 8.4 Hz, 1 H), 7.80 (d, J = 8.6 Hz, 1 H), 7.98 (d, J = 8.4 Hz, 1 H); ¹³C NMR (CDCl₃, 100 MHz) δ 22.9 (t), 23.2 (t), 25.6 (t), 30.4 (t), 122.7 (d), 124.6 (d), 125.5 (d), 125.7 (d), 128.3 (d), 131.4 (s), 132.0 (s), 132.5(s), 134.2 (s); νmax (CDCl₃ cast; cm⁻¹) 3047, 2927, 2856, 1510, 1457; exact mass m/z calcd for C₁₄H₁₄ 182.10956, found 182.10936.

References
70. 4026-4031.


