Supplementary Material (ESI) for Organic & Biomolecular Chemistry

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).

10e **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 **10e** (57.9 mg, 0.25 mmol) in Et_2O (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_2O. The combined organic extracts were washed with brine, dried ($MgSO_4$) and evaporated. The crude product (**10k**) was used directly in the next step.

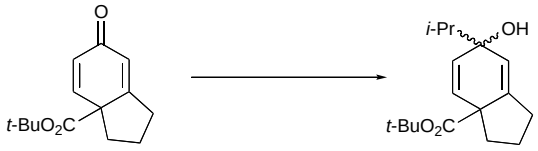
5-Butylindan (10l).

10k **10l**

General procedure B for rearomatization was followed, using $BiCl_3.H_2O$ (82.5 mg, 0.25 mmol), **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 **10l** (35.3 mg, 82% over two steps) as an oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 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); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 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); ν_{max} (microscope, $CDCl_3$ cast; cm^{-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).



10e **10m**

i-PrMgBr (2 M in Et_2O, 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_2O (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_2O. 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-Isopropylindan (10n).[21]

10m **10n**

General procedure B for rearomatization was followed, using $BiCl_3.H_2O$ (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) δ 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) δ 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); ν_{max} (microscope, $CDCl_3$ cast; cm^{-1}) 3008, 2958, 2867, 1493, 1460; exact mass *m*/*z* calcd for $C_{12}H_{16}$ 160.12520, found 160.12504.

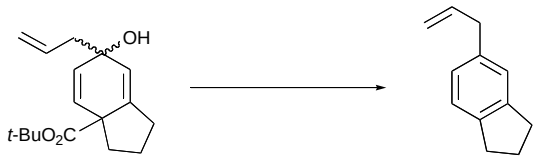
6-Allyl-6-hydroxy-1,2,3,6-tetrahydroindene-3a-carboxylic Acid *tert*-Butyl Ester (10q).

10e **10q**

Allylmagnesium bromide (1 M in Et_2O, 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_2O (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 Et_2O. The combined organic extracts were washed with brine, dried ($MgSO_4$) and evaporated. The crude product (**10q**) was used directly in the next step.

5-Allylindan (10r).[22]



10q **10r**

General procedure B for rearomatization was followed, using $BiCl_3.H_2O$ (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 ($CDCl_3$, 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); ^{13}C NMR ($CDCl_3$, 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, $CDCl_3$ cast; cm^{-1}) 3076, 3007, 2951, 2844, 1639, 1489, 1437; exact mass *m*/*z* calcd for $C_{12}H_{14}$ 158.10956, found 158.10989.

6-Hydroxy-6-prop-2-ynyl-1,2,3,6-tetrahydroindene-3a-carboxylic Acid *tert*-Butyl

Ester (10s).

10e **10s**

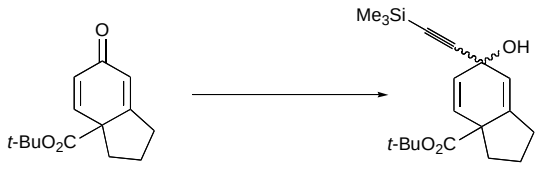
A mixture of propargyl bromide (80%$^{w}/_{w}$ in PhMe, 0.117 mL, 1.05 mmol), Mg (25 mg, 1.05 mmol) and $HgCl_2$ (1 mg, 0.004 mmol) was heated to reflux. The Mg dissolved, at which point the heat source was removed, and stirring was continued for 45 min. The resulting propargylmagnesium bromide was added at a fast dropwise rate to a stirred and cooled (-78 °C) solution of **10e** (84 mg, 0.358 mmol) in Et_2O (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 NH_4Cl, and extracted with Et_2O. The combined organic extracts were washed with brine, dried ($MgSO_4$) and evaporated. The crude product (**10s**) was used directly in the next step.

5-(Prop-2-ynyl)indane (10t).

10s **10t**

General procedure B for rearomatization was followed, using $BiCl_3.H_2O$ (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) δ 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) δ 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); ν_{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).



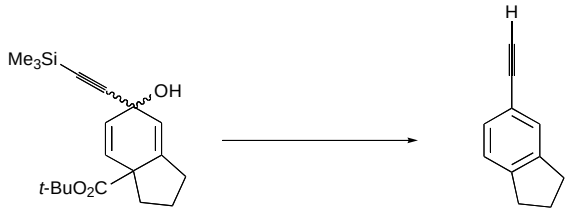
10e **10u**

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_2O, 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 Et_2O (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

NH_4Cl, and extracted with Et_2O. The combined organic extracts were washed with brine, dried ($MgSO_4$) and evaporated. The crude product (**10u**) was used directly in the next step.

5-Ethynylindan (10v).[23]



10u **10v**

General procedure B for rearomatization was followed, using $BiCl_3.H_2O$ (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: ^{1}H NMR ($CDCl_3$, 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); ^{13}C NMR ($CDCl_3$, 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, $CDCl_3$ cast; cm^{-1}) 3292, 2952, 2868, 2843, 2104, 1485; exact mass m/z calcd for $C_{11}H_{10}$ 142.07825, found 142.07818.

6-Hydroxy-6-phenylethynyl-1,2,3,6-tetrahydroindene-3a-carboxylic Acid *tert*-Butyl Ester (10w).

10e **10w**

i-PrMgBr (2 M in Et_2O, 0.164 mL, 0.328 mmol) was added at a slow dropwise rate to a stirred and cooled (-78 °C) solution of phenylacetylene (0.036 mL, 0.327 mmol) in dry THF (3 mL). The cooling bath was removed and stirring was continued for 1 h. The resulting acetylenic Grignard reagent was added a fast dropwise rate to a stirred and cooled (-78 °C) solution of **10e** (50 mg, 0.214 mmol) in Et_2O (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 NH_4Cl, and extracted with Et_2O. The combined organic extracts were washed with brine, dried ($MgSO_4$) and evaporated. The crude product (**10w**) was used directly in the next step.

5-Phenylethynylindan (10x).[24]

10w **10x**

General procedure B for rearomatization was followed, using $BiCl_3.H_2O$ (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_{max} (microscope, $CDCl_3$ cast; cm^{-1}) 3061, 3032, 2953, 2843, 2207, 1597, 1494; exact mass *m*/*z* calcd for $C_{17}H_{14}$ 218.10956, found 218.10942.

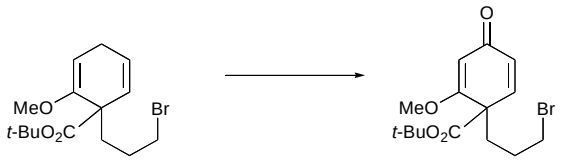
1-(3-Bromopropyl)-2-methoxycyclohexa-2,5-dienecarboxylic Acid *tert*-Butyl Ester (15a).

15 **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 NH_3 (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: ^{1}H NMR ($CDCl_3$, 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); ^{13}C NMR ($CDCl_3$, 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} ($CDCl_3$ cast; cm^{-1}) 2926, 2935, 1730, 1687, 1649, 1456, 1209; exact mass *m*/*z* calcd for $C_{15}H_{23}{}^{79}BrNaO_3$ (M + Na) 353.07228, found 353.07245.

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



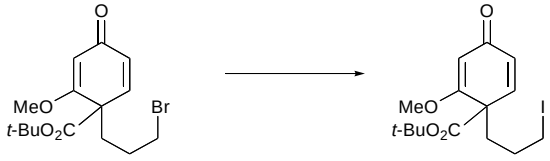
15a **15b**

General procedure A for oxidation was followed, using CrO_3 (1.51 g, 15.1 mmol), Ac_2O (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: ^{1}H NMR ($CDCl_3$, 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) δ 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); ν_{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).



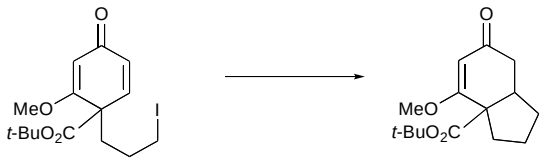
15b **15c**

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: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 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) δ 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); ν_{max} (CH_2Cl_2 cast; cm^{-1}) 2976, 2937, 1736, 1660, 1598, 1222; exact mass *m*/*z* calcd for $C_{15}H_{21}INaO_4$ (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).

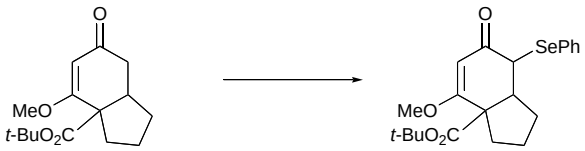


15c **15d**

The general procedure for radical cyclization was followed, using Bu_3SnH (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%$^{w}/_{w}$ KF) (2 x 22 cm), using 1:9 to 3:7 EtOAc-hexane mixtures, gave **15d** (153.8 mg, 94%) as an oil: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 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); ν_{max} (CH_2Cl_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).



15d **pre-15e**

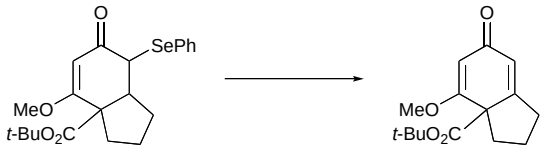
BuLi (2.5M in hexane, 0.26 mL, 0.64 mmol) was added dropwise to a stirred and cooled solution (-78 °C) of *i*-Pr_2NH (0.094 mL, 0.69 mmol) in THF (5 mL). Stirring was continued at (-78 °C) for 30 min and a solution of **15d** (148.9 mg) in THF (3 mL plus 1 mL as a rinse) was added dropwise. Stirring 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_4Cl and then with water, and extracted with Et_2O (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); ν_{max} (CH_2Cl_2 cast; cm^{-1}) 2926, 1731, 1654, 1265; exact mass *m*/*z* calcd for $C_{21}H_{27}NaO_4Se$ (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).

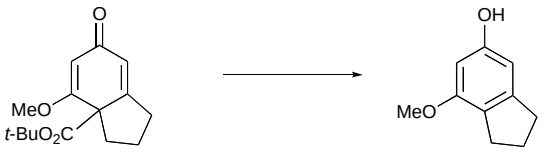


pre-15e **15e**

30% H_2O_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 $Na_2S_2O_3$ (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 ($MgSO_4$) 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%): ^{1}H NMR ($CDCl_3$, 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); ^{13}C NMR ($CDCl_3$, 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); ν_{max} (CH_2Cl_2 cast; cm^{-1}) 2926, 2851, 1734, 1670, 1265; exact mass *m*/*z* calcd for $C_{15}H_{20}NaO_4$ (M + Na) 287.12538, found 287.12541.

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



15e **15f**

General procedure A for rearomatization was followed, using $BiCl_3.H_2O$ (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 $BiCl_3.H_2O$. 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; ^{1}H NMR ($CDCl_3$, 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); ^{13}C NMR ($CDCl_3$, 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); ν_{max} ($CHCl_3$ cast; cm^{-1}) 3303, 2949, 2849, 1613, 1596, 1468; exact mass *m*/*z* calcd for $C_{10}H_{12}O_2$ 164.08372, found 164.08362.

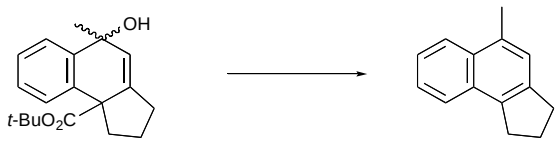
5-Hydroxy-5-methyl-1,2,3,5-tetrahydrocyclopenta[*a*]naphthalene-9b-carboxylic Acid *tert*-Butyl Ester (16g).

16e **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 Et_2O (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 Et_2O. The combined organic extracts were washed with brine, dried ($MgSO_4$) and evaporated. The crude product (**16g**) was used directly in the next

step.

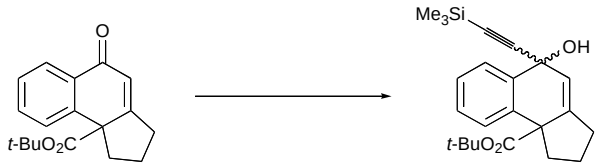
5-Methyl-2,3-dihydro-1*H*-cyclopenta[*a*]naphthalene (16h).



16g **16h**

General procedure B for rearomatization was followed, using $BiCl_3.H_2O$ (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) δ 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) δ 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); ν_{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).



16e **16m**

Trimethylsilylacetylene (0.12 mL, 0.8 mmol) was added dropwise to a stirred and cooled (-78 °C) solution of *i*-PrMgBr (2 M in Et_2O, 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 Et_2O (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 NH_4Cl, and extracted with Et_2O. The combined organic extracts were washed with brine, dried ($MgSO_4$) and evaporated. The crude product (**16m**) was used directly in the next step.

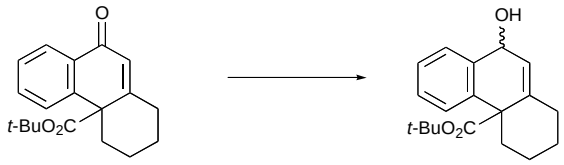
5-(1-Chlorovinyl)-2,3-dihydro-1*H*-cyclopenta[*a*]naphthalene (16n).

16m **16n**

General procedure B for rearomatization was followed, using $BiCl_3.H_2O$ (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); ν_{max} (microscope, $CDCl_3$ cast; cm^{-1}) 3063, 2952, 2844, 1628, 1512; exact mass *m*/*z* calcd for $C_{15}H_{13}{}^{35}Cl$ 228.07057, found 228.07063.

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

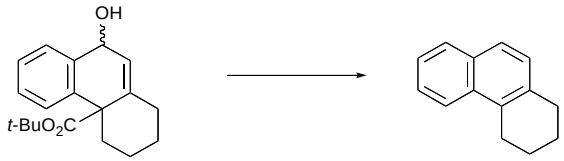


17d **17f**

$CeCl_3.7H_2O$ (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 Et_2O. The combined organic extracts were washed with brine, dried ($MgSO_4$) and evaporated. The crude product (**17f**) was used directly in the next step.

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



17f **17g**

General procedure B for rearomatization was followed, using $BiCl_3.H_2O$ (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: ^{1}H NMR ($CDCl_3$, 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); ^{13}C NMR ($CDCl_3$, 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), 128.2 (d), 128.3 (d), 131.4 (s), 132.0 (s), 132.5(s), 134.2 (s); ν_{max} ($CDCl_3$ cast; cm^{-1}) 3047, 2927, 2856, 1510, 1457; exact mass *m*/*z* calcd for $C_{14}H_{14}$ 182.10956, found 182.10936.

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