Enantioselective synthesis of (-)-Pentalenene

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Supporting Information

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General Considerations: All reactions were carried out in glassware that was flame dried under vacuum, and cooled under nitrogen. Reactions were carried out in flasks with septum fitted inlet adapters (similar to CHEMGLASS CG1062-14) so that flasks could be evacuated and refilled with N₂ prior to the addition of liquids through the septum. THF was distilled under nitrogen from Na/benzophenone. CH₂Cl₂ was dried with a column packed with activated neutral alumina. Triethylamine and toluene were distilled under nitrogen from CaH₂. 1,3-Dimethyl-2-imidazolidinone was purchased from Fluka. Dicobalt octacarbonyl was purchased from Strem Chemicals Inc. Rh₂(OAc)₄ was purchased from Pressure Chemical Co or Aldrich. $Rh_2(R-MEPY)_4^1$ was purchased from Acros. (R,R)-Rh₂(OAc)(DPTI)₃² and 4,4-Dimethyl-1-dimethylphenylsilyl-1,6-heptadiyne³ were prepared based on literature protocols. Other reagents were purchased from Aldrich and used without further purification. Prolonged cooling at low temperature was accomplished by chilling a bath of ethanol with a Cryocool CC100 cryogenic cooler. Cryogenic temperatures could be maintained with an accuracy of +/- 2 °C. Chromatography was performed on silica gel (ICN SiliTech 32-62D, 60Å). For ¹³C NMR, multiplicities were distinguished using an APT pulse sequence: typical methylene and quaternary carbons appear 'up' (u); methine and methyl carbons 'down' (dn). Exceptions are methine carbons of cyclopropenes and alkynes which usually have the same phase as 'normal' methylenes and quaternary carbons. The purity of the compounds was determined by ¹H NMR, and verified by GC where possible. All compounds were measured to be >95% pure unless noted otherwise. Enantiomeric excesses were measured on materials directly after chromatography (i.e. the reported ee's have not been enhanced

through crystallization).

The structures of the chiral Rh-catalysts that were used are shown below:



(1*S*)-Ethyl 2-[5-(dimethylphenylsilyl)-2,2-dimethyl-pent-4-ynyl]-cycloprop-2-ene-1carboxylate (3):



Using (*R*,*R*)-Rh₂(OAc)(DPTI)₃ catalyst:

A dry 250 mL round bottomed flask was outfitted with a stir bar, gas inlet adapter and a rubber septum. The assembly was flame dried under vacuum and cooled under nitrogen. The flask was charged with (R,R)-Rh₂(OAc)(DPTI)₃² (173 mg, 0.12 mmol), evacuated and filled with nitrogen. 4,4-Dimethyl-1-dimethylphenylsilyl-1,6-heptadiyne³ (3.2 g, 13 mmol) and CH₂Cl₂ (145 mL) were sequentially added to the flask, and the mixture was allowed to stir. Ethyl diazoacetate (10 mL of a 2.5 M solution in CH₂Cl₂, 25 mmol) was then added dropwise via syringe pump at a rate of 0.50 mL/h. After the addition was complete, stirring was continued for 30 min. The mixture was concentrated and chromatographed over silica gel (gradient 2-3% ethyl acetate in hexanes) to give 3.5 g

(81%) of the title compound as colorless liquid. The material was measured to be of 91% ee by HPLC using a CHIRALCEL OJ column, eluting at 1 mL/min with 99.5/0.5 hexane/isopropanol. A similar experiment that started with 1.0 g gave 1.06 g (79%) of the title compound. [α] $^{23}_{D}$ +52.0° (*c* 1.00, CH₂Cl₂); ¹H NMR (CDCl₃, 400 MHz, δ): 7.62-7.61 (m, 2H), 7.38-7.36 (m, 3H), 6.46-6.45 (m, 1H), 4.15-4.09 (m, 2H), 2.56 (s, 2H), 2.29 (d, J=16.8 Hz, 1H), 2.25 (d, J=16.8 Hz, 1H), 2.14 (d, J=1.2 Hz, 1H), 1.24 (t, J=7.2 Hz, 3H), 1.10 (s, 6H), 0.39 (s, 6H); ¹³C NMR (CDCl₃, 100 MHz, δ): 176.9 (u), 138.1 (u), 134.2 (dn), 129.8 (dn), 128.4 (dn), 113.9 (u), 107.2 (u), 96.8 (u), 85.3 (u), 60.8 (u), 37.2 (u), 34.9 (u), 33.6 (u), 27.4 (dn), 27.3 (dn), 20.7 (dn), 15.0 (dn), 0.0 (dn); IR (neat, cm⁻¹): 2174, 1722, 1368, 1248, 1180, 1114, 1039, 836, 814, 779, 730, 699, 666; HRMS-EI m/z: [M+Na], calcd for C₂₁H₂₈NaO₂Si, 363.1756; found, 363.1764.

Using Rh₂(*R*-MEPY)₄:



A dry 25 mL round bottomed flask was outfitted with a stir bar, gas inlet adapter and a rubber septum. The assembly was flame dried under vacuum and cooled under nitrogen. The flask was charged with $Rh_2(R-MEPY)_4^1$ (1.52 mg, 0.002 mmol), evacuated and filled with nitrogen. 4,4-Dimethyl-1-dimethylphenylsilyl-1,6-heptadiyne³ (100 mg, 0.39 mmol) and CH_2Cl_2 (3 mL) were sequentially added to the flask, and the mixture was allowed to stir. Ethyl diazoacetate (1 mL of a 0.4 M solution in CH_2Cl_2 , 0.4 mmol) was then added dropwise via syringe pump at a rate of 0.10 mL/h. After the addition was complete, stirring was continued for 30 min. The mixture was concentrated and chromatographed

over silica gel (gradient 2-3% ethyl acetate in hexanes) to give 33 mg (25%) of the title compound as colorless liquid. An identical experiment gave 34 mg (26%) of the title compound. The product was measured to be of 52% ee by HPLC using a CHIRALCEL OJ column, eluting at 1 mL/min with 99.5/0.5 hexane/isopropanol.

A similar experiment was performed at 0 °C with 100 mg (0.39 mmol) of **4**, 90 mg (0.8 mmol) of ethyl diazoacetate and 3 mg (0.004 mmol) of $Rh_2(R-MEPY)_4$. The yield of **3a** was 78 mg (56%). The product was measured to be of 60% ee by HPLC using a CHIRALCEL OJ column, eluting at 1 mL/min with 99.5/0.5 hexane/isopropanol.

Cyclopropenation using Rh₂(OAc)₄:

A dry 100 mL round bottomed flask was outfitted with a stir bar, gas inlet adapter and a rubber septum. The assembly was flame dried under vacuum and cooled under nitrogen. The flask was charged with rhodium tetraacetate (21 mg, 0.05 mmol), evacuated and filled with nitrogen. 4,4-Dimethyl-1-dimethylphenylsilyl-1,6-heptadiyne ³ (600 mg, 2.36 mmol) and CH_2Cl_2 (20 mL) were sequentially added to the flask, and the mixture was allowed to stir with cooling by a bath of ice. Ethyl diazoacetate (3 mL of a 1.6 M solution in CH_2Cl_2 , 4.8 mmol) was then added dropwise via syringe pump at a rate of 0.2 mL/h. After the addition was complete, stirring was continued for 30 min and allowed to warm to rt. The mixture was concentrated and chromatographed over silica gel (gradient 2-3% ethyl acetate in hexanes) to give 402 mg (50%) of the title compound as colorless liquid. A similar experiment that started with 100 mg of **4** gave 69 mg (52%) of the title compound.

(1S)-Ethyl 2-[5-(dimethylphenylsilyl)-2,2-dimethyl-pent-4-ynyl]-3-trimethylsilyl-

cycloprop-2-ene-1-carboxylate (7):



A dry 250 mL round bottomed flask was outfitted with a stir bar, gas inlet adapter and a rubber septum. The assembly was flame dried under vacuum and cooled under nitrogen. THF (100 mL), 3 (3.5 g, 10 mmol), and trimethylsilyl chloride (2.2 g, 20 mmol) were sequentially added to the flask and the mixture was allowed to stir and cool in a bath of dry ice/acetone. A solution of LiHMDS (2.1 g, 13 mmol) in THF (15 mL) was added via syringe pump at a rate of 0.5 mL/min. The reaction was then allowed to warm to rt, and quenched with aqueous NH₄Cl solution. The mixture was concentrated on the rotary evaporator to remove the organic solvents and subsequently partitioned between water and CH₂Cl₂, and extracted three times with CH₂Cl₂. The organics were combined, dried over Na₂SO₄, concentrated, and the residue was chromatographed over silica gel (1% ethyl acetate in hexanes) to give 3.8 g (90%) of the title compound as a colorless oil. A similar experiment that started with 0.96 g of 3 gave 1.09 g (93%) of the title compound. $[\alpha]_{D}^{23} - 2.9^{\circ}$ (c 1.00, CH₂Cl₂); ¹H NMR (CDCl₃, 400 MHz, δ): 7.62-7.61 (m, 2H), 7.37-7.36 (m, 3H), 4.12-4.06 (m, 2H), 2.60 (s, 2H), 2.27 (d, J=16.8 Hz, 1H), 2.23 (d, J=16.8 Hz, 1H), 1.97 (s, 1H), 1.21 (t, J=7.2 Hz, 3H), 1.08 (s, 6H), 0.39 (s, 6H), 0.20 (s, 9H); ¹³C NMR (CDCl₃, 100 MHz, δ): 178.3 (u), 139.0 (u), 135.0 (dn), 130.7 (dn), 129.2 (dn), 125.2 (u), 108.2 (u), 107.0 (u), 86.1 (u), 61.2 (u), 39.4 (u), 35.8 (u), 34.4 (u), 28.3 (dn), 28.2 (dn), 22.6 (dn), 15.8 (dn), 0.8 (dn), 0.0 (dn); IR (neat, cm⁻¹): 2174, 1823, 1715,

1249, 1178, 840, 817; HRMS-EI m/z: [M+Na], calcd for C₂₄H₃₆NaO₂Si₂, 435.2152; found, 435.2151.

3-(Dimethyl phenyl-silyl)-5,5-dimethyl-2-oxo-1a-trimethylsilyl-1,1a,2,4,5,6hexahydro-cyclopropa[c]pentalene-1-carboxylic acid ethyl ester (8 & 9):



A dry 250 mL round bottomed flask was outfitted with a stir bar, gas inlet adapter and a rubber septum. The assembly was flame dried under vacuum and cooled under nitrogen. Compound 7 (3.8 g, 9.2 mmol), anhydrous toluene (190 ml) and dicobalt octacarbonyl (1.89 g, 5.51 mmol) were sequentially added to the flask and the mixture was allowed to stir in an oil bath at 36 °C for 20 min under nitrogen. Tetramethylthiourea (4.41 g, 33.2 mmol) was added and the reaction was allowed to stir with heating by an oil bath at 45° under an atmosphere of CO (balloon pressure, 1 atm) for 14 h. The reaction was then allowed to cool to rt. The solvent was removed under reduced pressure and the residue was chromatographed over silica gel (gradient of 10-15% methylene chloride in hexanes, followed by 2:18:80 ethyl acetate:methylene chloride:hexanes) to give **8** (2.6 g, 64%) and **9** (0.65 g, 16%). Both diastereomers are colorless oils. A similar experiment that started with 880 mg of **7** gave 615 mg (66%) of **8** and 125 mg (13%) of **9**.

Spectral data for 8:

 $[\alpha]_{D}^{23}$ -155.0° (*c* 1.00, CH₂Cl₂); ¹H NMR (CDCl₃, 400 MHz, δ): 7.52-7.49 (m, 2H), 7.35-7.34 (m, 3H), 4.13 (q, J=7.2 Hz, 2H), 2.33 (d, J= 19.2 Hz, 1H), 2.10 (d, J=19.2 Hz, 1H), 2

1H), 2.04 (s, 1H), 1.95 (s, 2H), 1.25 (t, J=7.2 Hz, 3H), 1.32 (s, 3H), 1.07 (s, 3H), 0.43 (s, 3H), 0.42 (m, 3H), 0.18 (s, 9H); ¹³C NMR (CDCl₃, 100 MHz, δ): 212.7 (u), 198.6 (u), 168.4 (u), 138.2 (u), 134.2 (dn), 129.5 (dn), 128.1 (dn), 125.7 (u), 61.1 (u), 52.0 (dn), 51.2 (u), 44.6 (u), 42.5 (u), 39.1 (u), 36.7 (u), 29.3 (dn), 29.1 (dn), 14.7 (dn), 0.0 (dn), - 2.2 (dn), -2.3 (dn); IR (neat, cm⁻¹): 1730, 1682, 1601, 1247, 1180, 844; HRMS-EI m/z: [M+Na], calcd for C₂₅H₃₆NaO₃Si₂, 463.2101; found, 463.2112.

Spectral data for 9:

[α] 23 _D +152.0° (*c* 1.00, CH₂Cl₂); ¹H NMR (CDCl₃, 400 MHz, δ): 7.51-7.50 (m, 2H), 7.33-7.31 (m, 3H), 4.10-4.02 (m, 1H), 3.93-3.85 (m, 1H), 2.39 (s, 1H), 2.17 (d, J=18.4 Hz, 1H), 1.98-1.90 (m, 2H), 1.66 (d, J=12.8 Hz, 1H), 1.18 (s, 3H), 1.14 (t, J=7.2 Hz, 3H), 1.08 (s, 3H), 0.44 (s, 3H), 0.41 (s, 3H), 0.12 (s, 9H); ¹³C NMR (CDCl₃, 100 MHz, δ): 211.4 (u), 190.7 (u), 170.4 (u), 140.3 (u), 136.1 (dn), 131.0 (dn), 130.8 (u), 129.7 (dn), 62.9 (u), 53.8 (u), 52.6 (dn), 46.2 (u), 45.1 (u), 44.3 (u), 36.7 (u), 31.7 (dn), 31.1 (dn), 16.3 (dn), 0.26 (dn), 0.0 (dn), -0.4 (dn); IR (neat, cm⁻¹): 1734, 1689, 1607, 1247, 1174, 842; HRMS-EI m/z: [M+Na], calcd for C₂₅H₃₆NaO₃Si₂, 463.2101; found, 463.2116.

5,5-Dimethyl-2-oxo-1,1a,2,4,5,6-hexahydro-cyclopropa[c]pentalene-1-carboxylic acid ethyl ester (2):



A dry 250 mL round bottomed flask was outfitted with a stir bar, gas inlet adapter and a rubber septum. The assembly was flame dried under vacuum and cooled under nitrogen. To the flask was added a solution of **8** (2.6 g, 5.9 mmol) in dry THF (60 mL)

and was allowed to cool in a bath of salt/ice. TBAF (12 mL of 1.0 M solution in THF, 12 mmol) was added via syringe and the mixture allowed to stir under nitrogen atmosphere for 3 min. The reaction was then quenched with H₂O, allowed to warm to rt. The mixture was concentrated on the rotary evaporator to remove the organic solvents and subsequently partitioned between water and CH_2Cl_2 , and extracted three times with CH_2Cl_2 . The organics were combined, dried over Na_2SO_4 and concentrated. The residue could be quickly chromatographed to obtain a mixture of diastereomers suitable for use in the next step. The diastereomers could be separated by chromatography over silica gel (gradient of 2-4% ethyl acetate in hexanes). Obtained were 72 mg of (5%) of a faster eluting diastereomer (**2a**) and 1.04 g (69%) of the diastereomer that eluted more slowly (**2b**). A similar experiment that started with 770 mg of **8** gave 70 mg (15%) of **2a** and 260 mg (58%) of **2b**. Trace impurities were observed at 7.6, 7.4, 0.4 ppm in the ¹HNMR spectrum of the major diastereomer.

Properties of the diastereomer that eluted quickly by silica gel chromatography (2a):

A white solid, Mp 50-52 °C; $[\alpha]^{23}_{D}$ –25.2° (*c* 1.00, CH₂Cl₂); ¹H NMR (CDCl₃, 400 MHz, δ): 5.37 (br s, 1H), 4.22-4.16 (m, 2H), 2.71 (d, J=20.8 Hz, 1H), 2.61 (dd, J=2.4, 21.2 Hz, 1H), 2.56 (d, J=2.4 Hz, 1H), 2.23-2.18 (m, 2H), 1.90 (d, J=14.0 Hz, 1H), 1.27 (t, J=7.2 Hz, 3H), 1.21 (s, 3H), 1.16 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz, δ): 208.8 (u), 169.0 (u), 136.7 (u), 132.8 (dn), 61.1 (u), 52.6 (u), 46.6 (u), 41.2 (u), 39.8 (dn), 35.1 (u), 31.6 (dn), 29.0 (dn), 28.7 (dn), 14.3 (dn); IR (neat, cm⁻¹): 1737, 1714, 1668, 1182, 1163,

839, 667; HRMS-CI(NH3) m/z: [M+H], calcd for C₁₄H₁₉NaO₃, 235.1334; found, 235.1332.

Properties of the diastereomer that eluted slowly by silica gel chromatography (2b): A colorless liquid, $[α]^{23}_{D}$ +51.8° (*c* 1.00, CH₂Cl₂); ¹H NMR (CDCl₃, 400 MHz, δ): 5.35 (s, 1H), 4.18-4.13 (m, 2H), 2.74-2.73 (m, 1H), 2.62 (d, J=18.4 Hz, 1H), 2.38-2.33 (m, 2H), 2.05 (d, J=14.0 Hz, 1H), 1.83 (d, J=14.0 Hz, 1H), 1.25 (t, J=7.2 Hz, 3H), 1.19 (s, 3H), 1.17 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz, δ): 204.4 (u), 186.8 (u), 167.5 (u), 117.2 (dn), 60.9 (u), 47.7 (dn), 45.0 (u), 43.4 (u), 43.0 (u), 38.9 (u), 34.2 (dn), 29.1 (dn), 29.0 (dn), 14.2 (dn); IR (neat, cm⁻¹): 1725, 1713, 1623, 1325, 1188, 875, 838, 667; HRMS-CI(NH3) m/z: [M+H], calcd for C₁₄H₁₉NaO₃, 235.1334; found, 235.1337.

(3S)-ethoxycarbonylmethyl-1-oxo-5,5-dimethyl-octahydropentalene (10):



A dry 25 mL round bottomed flask was outfitted with a stir bar, gas inlet adapter and a rubber septum. The assembly was flame dried under vacuum and cooled under nitrogen. The flask was charged with 10% Pd-C (55 mg, 0.05 mmol), evacuated and filled with nitrogen. A solution of a mixture of isomers of **2** (220 mg, 0.94 mmol) in EtOH (5 mL) was added via syringe under nitrogen atmosphere. The mixture was then allowed to stir under an atmosphere of H₂ (balloon pressure) for 60 min. The reaction mixture filtered

through celite and the filtrate concentrated to provide 225 mg of 23 as a colorless oil. Crude 23 was dissolved in EtOH (5 mL) and transferred to a glass lined stainless steel pressure tube that had been charged with 10% Pd-C (110mg, 0.1 mmol) and allowed to stir under a pressure of H₂ (60 psi). The reaction mixture filtered through celite and the filtrate concentrated. The residue was purified over a column of silica gel (5% ethyl acetate in hexanes) to provide 199 mg (89%) of 10 as a colorless oil. A similar experiment that started with 400 mg of 2 gave 374 mg (92 %) of 10.

Alternatively crude 23 can be reduced to 10 by reacting with SmI₂, as follows:

A dry 100 mL round bottomed flask was outfitted with a stir bar, gas inlet adapter and a rubber septum. The assembly was flame dried under vacuum and cooled under nitrogen. The flask was charged with **23** (230 mg, 0.97 mmol) in THF:MeOH (6:1), (7 mL) and the mixture was allowed to stir. A freshly prepared solution of SmI_2^{11} was added over 15 min until the purple color persisted in the reaction solution. It was necessary to add 13 mL (6.5 mmol) of the SmI₂ solution. The reaction was then quenched with water and rendered acidic with 3M HCl. The mixture was concentrated on the rotary evaporator to remove most of the organic solvents, and subsequently partitioned between water and CH₂Cl₂, and extracted three times with CH₂Cl₂. The organics were combined, dried over Na₂SO₄ and concentrated. The residue was chromatographed over a column of silica gel (5% ethyl acetate in hexanes) to provide 220 mg (95%) of **10** as a colorless oil. A similar experiment that started with 102 mg of **23** gave 101 mg (98%) of **10**. [α] ²³_D +75.6° (*c* 1.00, CH₂Cl₂); ¹H NMR (CDCl₃, 400 MHz, δ): 4.12 (q, J=7.2 Hz, 2H), 2.66-2.58 (m, 2H), 2.52-2.45 (m, 3H), 2.27 (d, J=19.2 Hz, 1H), 2.15 (d, J= 19.2 Hz, 1H), 1.84-1.67 (m,

3H), 1.35 (dd, J=10.8, 12.8 Hz, 1H), 1.25 (t, J=7.2 Hz, 3H), 1.08 (s, 3H), 1.06 (3H); ¹³C NMR (CDCl₃, 100 MHz, δ): 219.6 (u), 171.7 (u), 60.4 (u), 54.0 (u), 51.4 (u), 48.7 (u), 48.5 (u), 45.8 (dn), 45.7 (u), 43.1 (u), 39.5 (u), 30.9 (dn), 30.3 (dn), 14.2 (dn); IR (neat, cm⁻¹): 1730, 1369, 1163, 1027, 668; HRMS-CI(NH3) m/z: [M+H], calcd for C₁₄H₂₃O₃, 239.1647; found, 239.1643.

(3S)-ethoxycarbonylmethyl-1,1-dioxolano-5,5-dimethyl-octahydropentalene (11):



A dry 100 mL round bottomed flask was outfitted with a stir bar, Dean-stark trap, and a gas inlet adapter. The assembly was oven dried, fitted with a rubber septum and cooled under nitrogen. Compound **10** (1.0 g, 4.2 mmol), dry toluene (40 mL), ethylene glycol (1.3 g, 21 mmol), pyridinium *p*-toluenesulfonate (10 mg) were sequentially added and the resulting mixture refluxed for 7 h. The reaction mixture was allowed to cool to rt and the solvent was removed under vacuum. The residue was partitioned between brine and hexanes and extracted three times with hexanes. The organics were combined, dried over Na₂SO₄, and concentrated. The residue was chromatographed over silica gel (10% ethyl acetate in hexanes) to provide **11** (1.01 g, 85%) as a colorless liquid. A similar experiment that started with 200 mg of **10** gave 210 mg (89%) of **11**. [α] ²³_D +5.2° (*c* 1.00, CH₂Cl₂); ¹H NMR (CDCl₃, 400 MHz, δ): 4.11 (q, J=7.2 Hz, 2H), 3.89-3.83 (m, 4H), 2.63 (d, J=14.8 Hz, 1H), 2.45 (d, J=14.8 Hz, 1H), 2.40-2.33 (m, 1H), 2.13-2.05 (m, 2H), 1.89 (d, J=18.0 Hz, 1H), 1.77-1.73 (m, 1H), 1.70-1.64 (m, 3H), 1.57-1.52 (m, 1H), 1.25 (t, J=7.2 Hz, 3H), 1.06 (s, 3H), 0.99 (3H); ¹³C NMR (CDCl₃, 100 MHz, δ): 172.6

(u), 118.7 (u), 64.1 (u), 63.8 (u), 60.0 (u), 53.3 (u), 50.5 (u), 48.5 (u), 48.0 (u), 47.8 (dn), 46.1 (u), 41.0 (u), 40.3 (u), 30.6 (dn), 29.7 (dn) 14.2 (dn); IR (neat, cm⁻¹): 1730, 1464, 1367, 1339, 1117, 1029, 947; HRMS-CI(NH3) m/z: [M+H], calcd for $C_{16}H_{27}O_4$, 283.1909; found, 283.1915.

Ethyl-(2S)-2-[1,1-dioxolano-5,5-dimethyl-octahydropentalen-(3aS)-3a-yl]-4-

pentenoate (12) and Ethyl-(2*R*)-2-[1,1-dioxolano-5,5-dimethyl-octahydropentalen-(*3aS*)-3a-yl]-4-pentenoate (13):



A dry 100 mL round bottomed flask was outfitted with a stir bar, gas inlet adapter and a rubber septum. The assembly was flame dried under vacuum and cooled under nitrogen. THF (25 mL) and diisopropylamine (682 mg, 6.74 mmol) were sequentially added to the flask and the mixture was allowed to stir and cool in an ice-bath. A solution of n-butyllithium (3.37 mL of a 2.0 M solution in hexanes, 6.74 mmol) was added to the reaction mixture and allowed to stir for 20 min. The reaction mixture was then cooled by a bath of dry ice/acetone. A solution of **11** (950 mg, 3.36 mmol) in THF (2 mL) was added dropwise and allowed to stir for 2 h. 1,3-dimethylimidazolidinone (3 mL) was added and the mixture was allowed to stir for 30 min. Allyl bromide (4.01 g, 33.7 mmol) was added and the mixture allowed to stir for 30 min. The reaction mixture was then allowed to warm to rt and quenched with water. The mixture was concentrated on the rotary evaporator to remove most of the organic solvents, and subsequently partitioned between brine and hexanes and extracted three times with hexanes. The organics were combined, dried over Na_2SO_4 , and concentrated. The residue was chromatographed over silica gel (gradient of 0.5-1% ethyl acetate in hexanes) to give 220 mg (20%) of **12** and 768 mg (71%) of **13** as colorless liquids. A similar experiment that started with 90 mg of **11** gave 21 mg (20%) of **12** and 69 mg (67%) of **13**.

Ethyl-(2*S*)-2-[1,1-dioxolano-5,5-dimethyl-octahydropentalen-(*3aS*)-3a-yl]-4pentenoate – 12:

[α] 23 _D +31.5° (*c* 1.00, CH₂Cl₂); ¹H NMR (CDCl₃, 400 MHz, δ): 5.78-5.68 (m, 1H), 5.07-5.03 (m, 1H), 4.98-4.95 (m, 1H), 4.11 (q, J=7.2 Hz, 2H), 3.91-3.82 (m, 4H), 2.65 (dd, J=11.2, 2.4 Hz, 1H), 2.44-2.34 (m, 2H), 2.23-2.19 (m, 2H), 2.04 (dd, J=13.6, 8.0 Hz, 1H), 1.93 (d, J=13.6 Hz, 1H), 1.79 (m, 2H), 1.68-1.59 (m, 2H), 1.50 (d, J=13.6 Hz, 1H), 1.24 (t, J=7.2 Hz, 3H), 1.07 (s, 3H), 0.98 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz, δ): 174.4 (u), 136.1 (dn), 118.4 (u), 116.2 (u), 64.1 (u), 63.8 (u), 59.9 (u), 54.9 (u), 52.9 (dn), 50.5 (u), 47.4 (u), 46.8 (u), 46.4 (dn), 41.2 (u), 39.2 (u), 33.1 (u), 31.1 (dn), 30.2 (dn), 14.4 (dn); IR (neat, cm⁻¹): 1728, 1642, 1344, 1157, 1117, 1042, 1019, 915; HRMS-CI(NH3) m/z: [M+H], calcd for C₁₉H₃₁O₄, 323.2222; found, 323.2228.

Ethyl-(2*R*)-2-[1,1-dioxolano-5,5-dimethyl-octahydropentalen-(*3aS*)-3a-yl]-4-

pentenoate - 13:

[α] 23 _D -7.5° (*c* 1.00, CH₂Cl₂); ¹H NMR (CDCl₃, 400 MHz, δ): 5.76-5.69 (m, 1H), 5.05 (d, J=16.8 Hz, 1H), 4.97 (d, J=10.0 Hz, 1H), 4.13 (q, J=7.2 Hz, 2H), 3.92-3.81 (m, 4H), 2.63 (dd, J=11.6, 3.2 Hz, 1H), 2.56-2.50 (m, 1H), 2.44-2.34 (m, 2H), 2.25-2.19 (m, 1H), 1.85 (dd, J=13.6, 8.8 Hz, 1H), 1.76 (d, J=13.6 Hz, 1H), 1.70-1.55 (m, 5H), 1.25 (t, J=7.2 Hz, 3H), 1.06 (s, 3H), 1.02 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz, δ): 174.8 (u), 136.5

(dn), 118.6 (u), 116.7 (u), 64.5 (u), 64.1 (u), 60.4 (u), 54.7 (u), 54.2 (dn), 53.1 (u), 47.9 (u), 45.9 (u), 45.6 (dn), 40.9 (u), 39.9 (u), 33.8 (u), 30.9 (dn), 29.8 (dn), 14.8 (dn); IR (neat, cm⁻¹): 1729, 1642, 1345, 1161, 1138, 1079, 1019, 916;

HRMS-CI(NH3) m/z: [M+H], calcd for C₁₉H₃₁O₄, 323.2222; found, 323.2226.

Epimerisation of 13:



A dry 25 mL round bottomed flask was outfitted with a stir bar, condenser, gas inlet adapter and a rubber septum. The assembly was flame dried under vacuum and cooled under nitrogen. The flask was charged with 50% KH in paraffin⁵ (39 mg, 0.97 mmol), evacuated and filled with nitrogen. A solution of **13** (416 mg, 1.31 mmol) in toluene (12 mL) was added to the flask and the mixture was allowed to stir in an oil bath at 108 °C, for 3h, at which point both the epimers were detected by TLC. It was observed that heating for longer periods at reflux lead to decomposition. The reaction mixture was cooled to rt, and the solvent removed under reduced pressure. The crude product was diluted with hexanes, and washed with water. The organic layer was dried over anhydrous Na₂SO₄ and concentrated. The residue was purified over a column of silica gel (gradient of 0.5-1 % ethyl acetate in hexanes) to give 208 mg of **12** and 170 mg of **13** as colorless liquids. The mass recovery was 91%. A similar experiment that started with 258 mg of **13** gave 127 mg of **12** and 101 mg of **13**, a total mass recovery of 88%. (3S)-[1a-hydroxy-pent-4a-ene-(2aS)-yl]- 1,1-dioxolano-5,5-dimethyl-

octahydropentalene (24):



A dry 50 mL round bottomed flask was outfitted with a stir bar, gas inlet adapter and a rubber septum. The assembly was flame dried under vacuum and cooled under nitrogen. Compound 12 (170 mg, 0.52 mmol), THF (80 mL) and lithium aluminium hydride (129 mg, 3.31 mmol) were sequentially added to the flask and the mixture allowed to stir for 5 h at rt. The reaction mixture was cooled in an ice-bath and guenched with saturated Na₂SO₄ (aq). The reaction mixture allowed to warm to rt and then stirred for 60 min. A white precipitate formed. The reaction mixture was filtered through celite and the filtrate concentrated. The residue was purified by passing through a short plug of silica gel (20%) ethyl acetate in hexanes) to provide 134 mg (90 %) of 24 as a colorless liquid. $\left[\alpha\right]_{D}^{23}$ +20.5° (c 1.00, CH₂Cl₂); ¹H NMR (CDCl₃, 400 MHz, δ): 5.99-5.88 (m, 1H), 5.12 (d, J=16.0 Hz, 1H), 5.01 (d, J=10.0 Hz, 1H), 3.91-3.80 (m, 4H), 3.75-3.69 (m, 1H), 3.62-3.57 (m, 1H), 2.61-2.56 (m, 1H), 2.32-2.26 (m, 1H), 2.11-1.92 (m, 3H), 1.76-1.53 (m, 8H), 1.06 (s, 3H), 0.99 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz, δ): 139.1 (dn), 118.7 (u), 115.6 (u), 64.7 (u), 64.0 (u), 63.7 (u), 55.2 (u), 52.6 (u), 48.9 (dn), 47.5 (u), 46.4 (u), 45.5 (dn), 41.2 (u), 39.2 (u), 33.8 (u), 30.7 (dn), 29.9 (dn); IR (neat, cm⁻¹); 1640, 1464, 1433, 1335, 1137, 1117, 1017, 909; HRMS-CI(NH3) m/z: [M+H], calcd for C₁₇H₂₉O₃, 281.2117; found, 281.2126.



(3S)-[pent-1a-ene-(4aS)-yl]- 1,1-dioxolano-5,5-dimethyl-octahydropentalene (18):

A dry 50 mL round bottomed flask was outfitted with a stir bar, gas inlet adapter and a rubber septum. The assembly was flame dried under vacuum and cooled under nitrogen. Alcohol **24** (124 mg, 0.44 mmol) and CH₂Cl₂ (6 mL) were sequentially added to the flask and the mixture allowed to stir and cool in a bath of ice. To the cooled reaction mixture, triethylamine (112 mg, 1.11 mmol) and methanesulfonyl chloride (76.9 mg, 0.66 mmol) were sequentially added and allowed to stir for 30 min. The reaction mixture was diluted with hexanes and poured into ice cold water. The organic layer separated and the aqueous layer extracted three times with hexanes. The organics were combined, dried over Na₂SO₄ and concentrated. The residue was purified by passing through a short plug of silica gel (20% ethyl acetate in hexanes) to provide 150 mg (94 %) of **25** as a colorless liquid that was used directly for the next step without further purification.

¹H NMR (CDCl₃, 400 MHz, δ): 5.85-5.78 (m, 1H), 5.12 -5.06 (m, 2H), 4.27 (dd, J=4.0, 10.0 Hz, 1H), 4.19 (dd, J=4.8, 10.0 Hz, 1H), 3.92-3.80 (m, 4H), 2.98 (s, 3H), 2.58 (q, J=8.0 Hz, 1H), 2.33-2.26 (m, 1H), 2.13-2.05 (m, 1H), 2.00-1.93 (m, 3H), 1.76-1.56 (m, 6H), 1.08 (s, 3H), 0.99 (s, 3H).

A dry 50 mL round bottomed flask was outfitted with a stir bar, gas inlet adapter and a rubber septum. The assembly was flame dried under vacuum and cooled under nitrogen. Compound **25** (143 mg, 0.41 mmol), THF (4 mL) and lithium triethylborohydride (4.0

mL of 1.0 M solution in THF, 4.0 mmol) were sequentially added to the flask and the mixture allowed to stir for 3 h. The reaction mixture was quenched with water, partitioned between brine and hexanes, and extracted three times with hexanes. The organics were combined, dried over Na₂SO₄ and concentrated. The residue was purified by passing through a short plug of silica gel (20% ethyl acetate in hexanes) to provide 95 mg (90 %) of **18** as a colorless liquid. [α]²³_D +19.6° (*c* 1.00, CH₂Cl₂); ¹H NMR (CDCl₃, 400 MHz, δ): 5.83-5.72 (m, 1H), 5.03-4.98 (m, 2H), 3.93-3.81 (m, 4H), 2.53-2.46 (m, 1H), 2.28-2.24 (m, 1H), 2.00-1.89 (m, 2H), 1.77-1.57 (m, 7H), 1.48-1.43 (m, 1H), 1.07 (s, 3H), 0.97 (s, 3H) 0.83 (d, J=6.4 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz, δ): 138.7 (dn), 118.7 (u), 115.2 (u), 64.0 (u), 63.7 (u), 56.5 (u), 51.7 (u), 47.7 (u), 45.9 (u), 45.2 (dn), 41.1 (u), 40.6 (dn), 39.2 (u), 36.9 (u), 30.8 (dn), 29.8 (dn), 15.0 (dn); IR (neat, cm⁻¹): 1640, 1463, 1334, 1114, 1087, 1024, 994, 908; HRMS-CI(NH3) m/z: [M+H], calcd for C₁₇H₂₉O₂, 281.2168; found, 281.2179.

Benzenesulfonic acid 3-(2,2-dimethyl-5-oxo-hexahydro-pentalen-3a*S*-yl)-butyl ester (20):



A dry 25 mL pear shaped flask was outfitted with a stir bar. The assembly was oven dried and cooled under nitrogen. Compound **18** (90 mg, 0.34 mmol), Sudan red (1 mg) and EtOH (8 mL) were sequentially added to the flask and the mixture allowed to stir and cool in dry ice/acetone bath. Ozone was bubbled through the reaction mixture until the deep orange color of the indicator disappeared. Sodium borohydride (52 mg, 1.4 mmol)

was added and the mixture was allowed to stir while warming to rt over 1h. The reaction mixture was quenched with 3M HCl and allowed to stir for 3 min. The mixture was concentrated on a rotary evaporator to remove all of the volatile organics and subsequently partitioned between brine and CH_2Cl_2 , and extracted three times with CH_2Cl_2 . The organics were combined, dried over Na_2SO_4 and concentrated to provide 80 mg of **19** as a colorless oil that was used in the next step without further purification. ¹H NMR (CDCl₃, 400 MHz, δ): 3.79-3.72 (m, 1H), 3.64-3.59 (m, 1H), 2.70-2.60 (m, 1H), 2.48-2.40 (m, 2H), 2.19-2.09 (m, 2H), 1.80 (dd, J=7.2, 12.8 Hz, 1H), 1.72 (d, J=13.6 Hz, 1H), 1.69-1.56 (m, 3H), 1.51 (d, J=13.6 Hz, 1H), 1.38-1.32 (m, 1H), 1.21-1.15 (m, 1H), 1.07 (s, 3H), 1.03 (s, 3H), 0.93 (d, J=6.4 Hz, 3H).

A dry 25 mL round bottomed flask was outfitted with a stir bar, gas inlet adapter and a rubber septum. The assembly was flame dried under vacuum and cooled under nitrogen. Crude alcohol **19** (80 mg, 0.35 mmol), CH₂Cl₂ (4 mL), triethylamine (144 mg, 1.41 mmol), 4-dimethylaminopyridine (3 mg) and benzenesulfonyl chloride (126 mg, 0.71 mmol) were sequentially added to the flask and the mixture was allowed to stir at rt for 4 h. The reaction mixture was diluted with CH₂Cl₂ and washed with brine. The organic layer was separated and the aqueous layer extracted three times with CH₂Cl₂. The organics were combined, dried over Na₂SO₄ and concentrated. The residue was purified over a column of silica gel (5% ethyl acetate in hexanes) to provide **20** (90 mg, 72 % from **18**) as a colorless oil. [α]²³_D +43.6° (*c* 1.00, CH₂Cl₂); ¹H NMR (CDCl₃, 400 MHz, δ): 7.92-7.89 (m, 2H), 7.69-7.65 (m, 1H), 7.59-7.55 (m, 2H), 4.17-4.12 (m, 1H), 4.08-4.02 (m, 1H), 2.64-2.57 (m, 1H), 2.36-2.29 (m, 2H), 2.13-2.05 (m, 2H), 1.82-1.74 (m,

2H), 1.65 (d, J=14.0 Hz, 1H), 1.55-1.50 (m, 1H), 1.47 (d, J=14.0 Hz, 1H), 1.34-1.29 (m, 1H), 1.22-1.16 (m, 1H), 1.05 (s, 3H), 1.01 (s, 3H), 0.83 (d, J=6.4 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz, δ): 219.9 (u), 136.1 (u), 133.7 (dn), 129.2 (dn), 127.7 (dn), 69.1 (u), 54.6 (u), 51.9 (u), 49.2 (u), 48.9 (u), 43.8 (u), 43.1 (dn), 38.9 (u), 37.4 (dn), 31.8 (u), 30.8 (dn), 30.2 (dn), 14.5 (dn); IR (neat, cm⁻¹): 1735, 1448, 1359, 1185, 1096, 1096, 939, 890, 753, 730, 688, 586; HRMS-CI(NH3) m/z: [M+H], calcd for C₂₀H₂₉O₄S, 365.1787; found, 365.1803.





A dry 25 mL round bottomed flask was outfitted with a stir bar, gas inlet adapter and a rubber septum. The assembly was flame dried under vacuum and cooled under nitrogen. Compound **20** (72 mg, 0.19 mmol) and THF (3 mL) were added to the flask and the mixture was allowed to stir and cool in a bath of ice. A solution of NaHMDS (44 mg, 0.24 mmol) in THF (0.5 mL) was added and the resulting mixture allowed to stir for 1 h. The reaction mixture was quenched with water, diluted with hexanes and partitioned with brine. The organic layer separated and the aqueous layer was extracted three times with hexanes. The organics were combined, dried over Na₂SO₄ and concentrated. The residue was purified through a short plug of silica gel (10% ethyl acetate in hexanes) to provide 38 mg (97 %) of **21** as a colorless liquid. [α] ²³_D +145.1° (*c* 1.00, CH₂Cl₂); ¹H NMR (CDCl₃, 400 MHz, δ): 2.55-2.38 (m, 3H), 2.20 (d, J=18.8 Hz, 1H), 2.01-1.98 (m, 1H), 1.82-1.65 (m, 4H), 1.57-1.53 (m, 1H), 1.37-1.23 (m, 3H), 1.09 (s, 3H), 1.02 (s, 3H), 0.98

(d, J=6.8 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz, δ): 223.9 (u), 62.3 (u), 61.5 (dn), 49.5 (u), 45.9 (u), 42.9 (u), 42.1 (dn), 41.4 (dn), 39.6 (u), 34.6 (u), 30.9 (dn), 29.5 (dn), 26.0 (u), 14.4 (dn); IR (neat, cm⁻¹): 1732, 1463, 1054, 1032; HRMS-CI(NH3) m/z: [M+H], calcd for C₁₄H₂₃O, 207.1749; found, 207.1740. The ¹H NMR spectrum corresponded to that reported for racemic **20** by Rowley and Schore⁶.

1,7,7-Trimethyl-4-methylene-decahydro-cyclopenta[c]pentalene (22):



A dry 25 mL round bottomed flask was outfitted with a stir bar, gas inlet adapter and a rubber septum. The assembly was flame dried under vacuum and cooled under nitrogen. The flask was charged with PPh₃CH₃Br (68 mg, 0.19 mmol), evacuated and filled with nitrogen. Toluene (1 mL), and *t*-BuOK (14 mg, 0.13 mmol) were sequentially added and the resulting mixture allowed to stir at rt for 30 min. To the resulting deep yellow reaction mixture, a solution of **21** (13 mg, 0.06 mmol) in toluene (0.5 mL) was added and the mixture was allowed to stir for 2 h. The reaction mixture was directly loaded on to a long column (25 x 3 cm) of silica gel and eluted with pentanes to provide 12 mg (95%) of hydrocarbon **22** as a colorless liquid. A similar experiment that started with 18 mg of **21** gave 17 mg of **22** (94%). [α]²³_D +90.4°; ¹H NMR (CDCl₃, 400 MHz, δ): 4.75 (m, 2H), 2.57-2.47 (m, 2H), 2.19-2.13 (m, 1H), 2.04-1.98 (m, 2H), 1.81-1.72 (m, 3H), 1.58-1.52 (m, 1H), 1.35-1.21 (m, 3H), 1.16-1.11 (m, 1H), 1.02 (s, 3H), 0.96 (s, 3H), 0.93 (d, J=6.4 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz, δ): 158.5 (u), 105.3 (u), 65.4 (u), 58.2 (dn), 48.5 (dn), 48.2 (u), 47.5 (u), 43.4 (dn), 39.6 (u), 38.4 (u), 35.4 (u), 31.2 (u), 30.2 (dn), 28.7

(dn), 16.4 (dn); IR (neat, cm⁻¹): 1657, 1459, 1370, 876; HRMS-CI(NH3) m/z: [M+H], calcd for $C_{15}H_{25}$, 205.1956; found, 205.1958. The NMR data corresponded to the partial spectral data reported by Hudlicky⁷.

(-)-pentalenene (1):



A dry 25 mL round bottomed flask was outfitted with a stir bar, gas inlet adapter and a rubber septum. The assembly was flame dried under vacuum and cooled under nitrogen. A solution of the hydrocarbon 22 (12 mg, 0.04 mmol) in CH₂Cl₂ (2 mL) and p-toluene sulfonic acid (21 mg, 0.11 mmol) were sequentially added to the flask and the mixture was stirred at rt for 24 h. The reaction mixture was directly loaded on to a long column (25 x 3 cm) of silica gel and eluted with pentanes to provide 12 mg (100%) of (-)-1 as a colorless liquid. A similar experiment starting with 15 mg of 22 gave 15 mg (100%) of (-)-1. $[\alpha]_{D}^{23} - 27^{\circ}$ (*c* 0.45, CHCl₃) [Lit: natural isomer, 82% ee, synthesised⁸ $[\alpha]_{D}^{25} + 32^{\circ}$ $(c \ 0.06, \text{CH}_2\text{Cl}_2)$; isolated⁹ $[\alpha]^{25}_{\text{D}} + 11.8^{\circ} (c \ 6.8, \text{CHCl}_3)$]; ¹H NMR (CDCl₃, 400 MHz, δ): 5.16 (s, 1H), 2.69-2.65 (m, 1H), 2.56-2.54 (m, 1H), 1.86-1.77 (m, 2H), 1.74 (d, J=12.8 Hz, 1H), 1.64-1.54 (m, 5H), 1.36 (d, J=12.8 Hz, 1H), 1.33-1.25 (m, 2H), 1.18 (dd, J=5.2, 12.4 Hz, 1H), 0.99-0.98 (m, 6H), 0.91 (d, J=7.2 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz, δ): 140.6 (u), 129.5 (dn), 64.7 (u), 62.0 (dn), 59.3 (dn), 48.9 (u), 46.8 (u), 44.5 (dn), 40.5 (u), 33.5 (u), 29.9 (dn), 29.1 (dn), 27.5 (u), 17.0 (dn), 15.4 (dn); IR (neat, cm^{-1}): 1643, 1467, 1373, 830; HRMS-CI(NH3) m/z: [M+], calcd for C₁₅H₂₄, 204.1878; found, 204.1870. The spectral corresponded to those previously reported $^{6-10}$.

4-Benzenesulfonyloxy-2-(2,2-dimethyl-5-oxo-hexahydro-pentalen-3a-yl)-butyric acid ethyl ester (14):



A dry 25 mL pear shaped flask was outfitted with a stir bar and a gas dispersion tube. The assembly was oven dried and cooled under nitrogen. **12** (180 mg, 0.56 mmol), and EtOH (10 mL) were sequentially added to the flask and the mixture was allowed to stir and was cooled by a dry ice/acetone bath (-78 °C). Ozone was introduced via the gas dispersion tube for 5 min. Sodium borohydride (106 mg, 2.79 mmol) was added, and the dry ice bath removed and the mixture was allowed to stir while warming to rt over 90 min. The reaction mixture was quenched with 3M HCl and allowed to stir for 3 min. The reaction mixture was concentrated on a rotary evaporator to remove all of the organic solvents and subsequently partitioned between brine and CH_2Cl_2 and extracted three times with CH_2Cl_2 . The organics were combined, dried over Na_2SO_4 and concentrated to provide 155 mg of **26** as a colorless residue that was used immediately in the next step with out further purification.

A dry 25 mL round bottomed flask was outfitted with a stir bar, gas inlet adapter and a rubber septum. The assembly was flame dried under vacuum and cooled under nitrogen. Alcohol **26** (155 mg, 0.55 mmol), CH_2Cl_2 (5 mL), triethylamine (226 mg, 2.24 mmol), 4-dimethylaminopyridine (3 mg) and benzenesulfonyl chloride (217 mg, 1.23 mmol) were sequentially added to the flask and the mixture allowed to stir at rt for 12 h. The reaction

mixture was diluted with CH₂Cl₂ and partitioned with brine. The organic layer separated and the aqueous layer was extracted three times with CH₂Cl₂. The organics were combined, dried over Na₂SO₄ and concentrated. The residue was purified on a column of silica gel (gradient of 5-15% ethyl acetate in hexanes) to provide 138 mg (58%) of **14** as a colorless oil. A similar experiment that started with 125 mg of **12** gave 100 mg (61%) of **14**. $[\alpha]^{23}_{D}$ +40.8° (*c* 1.00, CH₂Cl₂); ¹H NMR (CDCl₃, 400 MHz, δ): 7.89-7.87 (m, 2H), 7.67-7.64 (m, 1H), 7.57-7.53 (m, 2H), 4.15-4.01 (m, 3H), 3.94-3.88 (m, 1H), 2.56-2.40 (m, 4H), 2.15-2.11 (m, 2H), 2.03-1.95 (m, 2H), 1.79-1.74 (m, 2H), 1.48 (d, J=14.0 Hz, 1H), 1.37-1.30 (m, 1H), 1.22 (t, J=7.2 Hz, 3H), 1.05 (s, 3H), 0.98 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz, δ): 218.9 (u), 173.1 (u), 135.8 (u), 133.9 (dn), 129.3 (dn), 127.8 (dn), 68.7 (u), 60.7 (u), 52.9 (u), 50.4 (u), 49.8 (u), 49.7 (dn), 48.7 (u), 44.1 (dn), 43.4 (u), 38.9 (u), 31.0 (dn), 30.4 (dn), 28.2 (u), 14.2 (dn); IR (neat, cm⁻¹): 1723, 1686, 1654, 1363, 1175, 1096, 914, 754, 688, 586.





A dry 25 mL round bottomed flask was outfitted with a stir bar, gas inlet adapter and a rubber septum. The assembly was flame dried under vacuum and cooled under nitrogen. Compound **14** (135 mg, 0.32 mmol) and THF (3 mL) were added to the flask and the mixture was allowed to stir. The mixture was cooled in a bath of ice, and LiHMDS (107

mg, 0.64 mmol) in THF (1 mL) was added. The ice bath was then removed, and the mixture was allowed to stir while warming to rt over 2 h. The reaction mixture was quenched with water, diluted with hexanes and partitioned with brine. The organic layer separated and the aqueous layer was extracted three times with hexanes. The organics were combined, dried over Na_2SO_4 and concentrated. The residue was purified on a column of silica gel (10% ethyl acetate in hexanes) to provide 71 mg (84 %) of a colorless liquid that was a 7:1 mixture of 15:16. A similar experiment that started with 78 mg gave 43 mg (88%) of this mixture. A pure sample of 15 was obtained by chromatography (5% ethyl acetate in hexanes). However we were unable to completely resolve 15 & 16 with single column. $[\alpha]_{D}^{23} + 160.2^{\circ}$ (c 0.45, CH₂Cl₂); ¹H NMR (CDCl₃, 400 MHz, δ): 4.24-4.08 (m, 2H), 2.88-2.81 (m, 1H), 2.62-2.47 (m, 3H), 2.27-2.16 (m, 2H), 1.92-1.80 (m, 3H), 1.73-1.57 (m, 3H), 1.29 (t, J=7.2 Hz, 3H), 1.28-1.25 (m, 1H) 1.07 (s, 3H), 0.98 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz, δ): 222.4 (u), 173.5 (u), 62.4 (u), 61.4 (dn), 60.4 (u), 53.3 (dn), 49.3 (u), 48.9 (u), 42.6 (u), 42.4 (dn), 39.5 (u), 30.7 (dn), 29.6 (u), 29.4 (dn), 26.3 (u), 14.3 (dn); IR (neat, cm⁻¹): 1718, 1175, 1041; HRMS-CI(NH3) m/z: [M+H], calcd for C₁₆H₂₅O₃, 265.1804; found, 265.1806.

7,7-Dimethyl-4-methylene-decahydro-cyclopenta[c]pentalene-1-carboxylic acid ethyl ester (17):



A dry 25 mL round bottomed flask was outfitted with a stir bar, gas inlet adapter and a rubber septum. The assembly was flame dried under vacuum and cooled under nitrogen.

The flask was charged with PPh₃CH₃Br (68 mg, 0.19 mmol), evacuated and filled with nitrogen. Toluene (1 mL) and t-BuOK (21 mg, 0.19 mmol) were sequentially added and allowed to stir at rt for 30 min. To the resulting deep yellow reaction mixture, a solution of 15 (25 mg, 0.09 mmol) in toluene (0.5 mL) was added and the mixture was allowed to stir at rt for 2 h. The reaction was guenched with water, diluted with hexanes and partitioned with brine. The organic layer separated and the aqueous layer was extracted three times with hexanes. The organics were combined, dried over Na₂SO₄ and concentrated. The residue was purified on a column of silica gel (5 % ethyl acetate in hexanes) to provide 21 mg (84 %) of 17 as a colorless liquid. A similar experiment that started with 13 mg of 15 gave 11 mg (85%) of 17. $[\alpha]_{D}^{23}$ +116.8° (c 0.45, CH₂Cl₂); ¹H NMR (CDCl₃, 400 MHz, δ): 4.79 (br s, 2H), 4.19-4.05 (m, 2H), 2.67-2.54 (m, 3H), 2.49-2.42 (m, 1H), 2.27-2.18 (m, 1H), 2.04 (d, J=15.6 Hz, 1H), 1.87-1.81 (m, 2H), 1.61-1.61 (m, 2H), 1.47-1.34 (m, 2H), 1.27 (t, J=7.2 Hz, 3H), 1.16-1.11 (m, 1H), 1.00 (s, 3H), 0.93 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz, δ): 175.0 (u), 156.9 (u), 106.2 (u), 65.3 (u), 60.0 (u), 58.9 (dn), 55.2 (dn), 50.2 (u), 48.8 (dn), 48.0 (u), 39.6 (u), 37.8 (u), 31.7 (u), 30.6 (u), 30.1 (dn), 28.7 (dn), 15.1 (dn); IR (neat, cm⁻¹): 1729, 1661, 1462, 1368, 1177, 1158, 1039, 879; HRMS-CI(NH3) m/z: [M+H], calcd for C₁₇H₂₇O₂, 263.2011; found, 263.2007. The ¹H NMR spectra agrees with that reported by Hudlicky⁷.

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