Supporting Text

General

Infrared (IR) spectra were recorded on a Perkin–Elmer 781 spectrophotometer (ν_{max} in cm^{-1}). Bands are characterized as broad (br), strong (s), medium (m), and weak (w). ^{1}H NMR spectra were recorded on a Varian Gemini 2000 (300 MHz), Varian GN-400 (400MHz), Varian Unity INOVA 400 (400 MHz), or Varian INOVA 500 (500 MHz). Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: δ 7.26 ppm, C_6H_6: 7.16 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz), and integration. ^{13}C NMR spectra were recorded on a Varian Gemini 2000 (75 MHz), Varian GN-400 (100 MHz), Varian Unity INOVA 400 (100 MHz), or Varian INOVA 500 (125 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent as the internal reference ($CDCl_3$: δ 77.7 ppm). Microanalyses were performed by RobertsonMicrolit Laboratories (Madison, NJ). High-resolution MS was performed by University of Illinois, Urbana-Champaign, Mass Spectrometry Laboratories. All reactions were conducted in oven (135°C)- and flame-dried glassware under an inert atmosphere of dry argon or nitrogen.

Preparation and Purification of Reagents

Solvents. Toluene, benzene, and pentane were purified by passage through activated copper and alumina columns using a positive pressure of inert gas (Ar). Methylene chloride, tetrahydrofuran, and diethyl ether were purified by passage through two activated alumina columns using a positive pressure of inert gas (Ar).

9-BBN. Synthesized according to the procedure published by Brown *et al.* (1)

***t*-BuLi.** Purchased as a 1.5-M solution in pentane from Strem Chemicals. The solution is titrated with *n*-BuOHusing 2,2'-bipyridyl as an indicator

***t*-butyldimethylsilyl triflouromethylsulfonate**. Purchased from Gelest Chemical and purified by distillation from CaH_2 under reduced pressure.

Tri-*n*-butylphosphine. Purchased from Aldrich Chemical and used without further purification.

***m*-chloroperbenzoic acid (*m*-CPBA).** Purchased from Aldrich Chemical. The reagent is dissolved in CH_2Cl_2, and the resulting solution is washed with pH 7 phosphate buffer. Recrystallization from anhydrous benzene yields colorless white needles (2).

1,3-diaminopropane. Purchased from Acros Chemical and distilled from CaH_2 under reduced pressure.

Hydrogen peroxide. Purchased from Acros Chemical as a 30% solution in water.

N-methylmorpholine-N-oxide (NMO). Purchased from Aldrich Chemical and used without further manipulation.

Four-Å molecular sieves. Flame-dried under reduced pressure, followed by cooling under dry nitrogen gas.

Norbornenone. Prepared as described (3-5).

Phenyl selenium cyanide. Purchased from Acros Chemical and recrystalized from benzene-pentane (2:1) and dried under reduced pressure. Purification is performed with minimal exposure to light.

Potassium hydride. Purchased as a 30% emulsion in mineral oil. The oil is removed by repeated washes with portions of pentane, followed by drying under reduced pressure.

Pyridine. Purchased from Aldrich Chemical and distilled from CaH_2 under reduced pressure.

$Rh(dppp)_2Cl$. Prepared in accordance with ref. 6. $Rh(dppp)_2Cl$ isolated as bright yellow crystals.

Sodium borohydride. Purchased from Aldrich Chemical and used without further manipulation.

Synthesis gas (Syn-gas). Purchased from AGA gas distributors and used without further manipulation.

Tetra-n-butylammonium fluoride (TBAF). Purchased from Aldrich Chemical Company as a 1M solution in THF and used without further manipulation.

Tetra-*n*-propylammonium peruthenate (TPAP). Purchased from Strem Chemicals and used without further manipulation.

Wilkinson's complex ($Rh(PPh_3)_3Cl$). Prepared according to ref. 7.

Experimental and Characterization

4a,5,6,6a,9,10-Hexahydro-2H-1-oxa-benzo[*c*]indene (13a). In a nitrogen-filled glovebox, 25.0 mg of **12a** (0.122 mmol) was weighed into a 4 ml vial containing a stir bar and subsequently diluted with 1.2 ml of anhydrous benzene. Catalyst **4** (5.0 mg, 0.0061 mmol, 0.05 equiv) was added and the vial was fitted with a teflon lined cap. The reaction was allowed to stir at 22°C for 3 h, at which time the mixture was removed from the glovebox, and the volatiles were evaporated *in vacuo* to give a black viscous oil. Analysis by ^1H NMR spectroscopy of the unpurified mixture indicated >98% conversion to a 4:1

mixture of desired product to a tricyclic compound arising from ring closure of the two terminal olefins of **12a**. The mixture was purified by silica gel chromatography (40:1 pentane:Et_2O) to give 17.7 mg of **13a** (80%). **IR** (Neat): 3024 (m), 2955 (m), 1465 (w), 1440 (w), 1095 (m); **^{1}H NMR** (400 MHz, C_6D_6): δ 5.85 (dq, *J* = 10.0, 2.4 Hz, 1H), 5.78-5.70 (m, 2H), 5.59 (dq, *J* = 9.2, 2.4 Hz, 1H), 4.36-4.22 (m, 2H), 2.64-2.54 (m, 1H), 2.24-2.06 (m, 3H), 2.02-1.86 (m, 2H), 1.84-1.74 (m, 1H), 1.40-1.30 (m, 2H), 1.22-1.12 (dt, *J* = 12.8, 5.6 Hz, 1H); **^{13}C NMR** (100 MHz, C_6D_6): δ 129.4, 126.5, 126.0, 77.3, 63.7, 45.5, 43.3, 29.2, 23.2, 21.9, 19.4; **Elem**. **Anal.** Calc'd for **13a** $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.84; H, 9.26; **GLC** CDGTA column, 105°C, 15 psi 1.0 ml min^{-1}. Retention times for racemic **13a** = 34.6 min and 42.3 min. Retention time for the major enantiomer = 42.3 min.

3-Methyl-4a,5,6,6a,9,10-hexahydro-2H-1-oxa-benzo[*c*]**indene (13b).** In a nitrogen-filled glovebox, 10.0 mg **12b** (0.046 mmol) was weighed into a 4-ml vial containing a stir bar and then diluted with 0.5 ml benzene. Catalyst **1c** (1.90 mg, 0.002 mmol, 0.05 equiv) was added and the vial was fitted with a teflon lined cap. The reaction was allowed to stir at 22°C for 16 h. The mixture was removed from the glovebox, and the volatiles were evaporated *in vacuo* to give a black viscous oil. Analysis by ^{1}H NMR of the unpurified mixture indicated 100% conversion to a 4:1 mixture of desired product to a bicyclic compound arising from single ring closure. The product was purified by silica gel chromatography (97:3 pentane:Et_2O) to give 6.8 mg **13b** (80%). **IR** (Neat): 3018 (m), 2955 (s), 2879 (s), 1721 (m), 1451 (m); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.76-5.68 (m, 2H), 5.57-5.53 (m, 1H), 4.20-4.06 (m, 2H), 2.62-2.52 (m, 1H), 2.22-2.08 (m, 3H), 2.00-1.92 (m, 1H), 1.84-1.72 (m, 2H), 1.59 (s, 3H), 1.44-1.24 (m, 2H), 1.21-1.10 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 132.5, 129.1, 126.2, 121.0, 77.6, 67.4, 45.3, 42.8, 29.5, 23.6, 21.6, 19.1, 18.2; **Elem.** Calcd. for **13b** $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 82.00; H, 9.66; **GLC** CDGTA column, 105°C, 15 psi, 1.0 ml min^{-1}. Retention times for racemic **13b** 49.2 min and 53.3 min. Retention time for major enantiomer 53.3 min.

{2-[2-(2-Methyl-allyloxy)-3-vinyl-cyclopentyl]-vinyl}-benzene (14). For a representative procedure see ref. 8. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.37-7.13 (m, 5H), 6.40 (d, *J* = 7.00 Hz, 2H), 6.01 (ddd, *J* = 8.40 Hz, 10.2 Hz, 17.2 Hz, 1H), 5.07 (d, *J* = 17.2 Hz, 1H) 5.02 (d, *J* = 10.2 Hz, 1H), 4.96 (s, 1H), 4.84 (s, 1H), 4.81 (s, 3H), 3.73 (dd, *J* = 4.03 Hz, 4.03 Hz, 1H), 2.74 (br. s, 1H), 2.64-2.61 (m, 1H), 1.90-1.80 (m, 4H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 143.7, 140.4, 138.8, 132.5, 130.6, 129.5, 127.8, 127.0, 115.7, 112.8, 112.6, 88.4, 88.3, 76.9, 76.8, 76.7, 51.4, 50.7, 30.8, 30.6, 30.1, 21.0.

{2-[2-(3-Methyl-but-2-enyloxy)-3-vinyl-cyclopentyl]-vinyl}-benzene (16). ^{1}H NMR (400 MHz, $CDCl_3$): δ .739-7.20 (m, 5H), 6.40 (d, *J* = 23.9 Hz, 2H), 6.06-5.99 (m, 1H), 5.34 (t, *J* = 1.5 Hz, 1H), 5.10 (d, *J* = 19.5 Hz, 1H), 5.05 (d, *J* = 12.2 Hz, 1H), 4.01 (d, *J* = 6.8 Hz, 2H), 3.71-3.69 (dd, *J* = 3.9 Hz, 3.9 Hz, 1H), 2.74-2.73 (m, 1H), 2.64-2.61 (m, 1H), 1.90-1.80 (m, 4H), 1.71 (s, 3H), 1.61 (s, 3H).

5-Iodo-4,4-dimethyl-pent-1-ene (5). (ref. 9) **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 5.79-5.67 (m, 1H), 5.13-5.04 (m, 2H), 3.13 (s, 2H), 2.07 (d, *J* = 7.32 Hz, 2H), 1.02 (s, 6H); **^{13}C NMR** ($CDCl_3$, 100 MHz) d 134.6, 118.5, 45.5, 33.8, 27.1, 24.0.

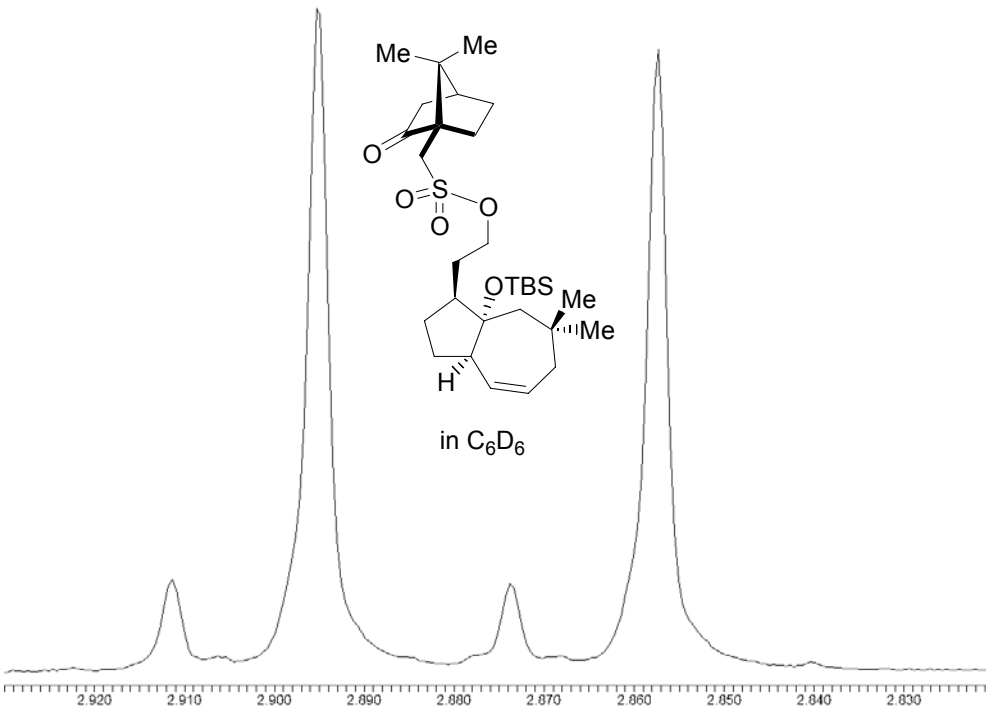
7-(2,2-Dimethyl-pent-4-enyl)-bicyclo[2.2.1]hept-2-en-7-ol. A solution of *t*-BuLi (5.70 ml, 1.57 M in *n*-pentane, 8.95 mmol) is added to 15 ml of *n*-pentane at –78°C under an Ar atmosphere. Iodide **18** (1.002 g, 4.475 mmol) in 10 ml of pentane was added to the *t*-BuLi solution via cannula and the mixture was allowed to stir at [minus]78°C for 3 h. At this point the mixture is warmed to –30°C and stirring was allowed to continue for an additional hour. The mixture is then cooled to –78°C and 90 ml of THF was added. The solution was allowed to stir for 30 min to equilibrate the temperature to –78°C. At this point norbornenone (417.9 mg, 3.867mmol) in 10 ml of THF was added dropwise by cannula. The mixture was allowed to stir for an additional 90 min at –78°C and then warmed to 23°C. A saturated aqueous solution of NH_4Cl (25 ml) was then added slowly and the mixture was washed with five 25-ml portions of Et_2O. Silica gel chromatography (100% pentane followed by 10% Et_2O in pentane) afforded 732 mg (91%) as a clear colorless oil. **IR** (thin film, cm^{-1}) 3622 (w), 3496 (br), 3144 (w), 3056 (s), 2930 (s), 1829 (w), 1640 (s); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 5.97 (s, 2H), 5.89-5.76-(m, 1H), 5.05-4.95 (m, 2H), 2.54 (s, 2H), 2.03 (d, *J* = 7.32 Hz, 2H), 1.94 (d, *J* = 7.32 Hz, 2H), 1.70 (s, 2H), 0.94 (s, 6H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 136, 135, 117, 93.1, 50.2, 48.5, 43.7, 34.2, 28.1, 23.2; **HRMS** calc'd. for $C_{14}H_{22}O$: 206.1671, Found: 206.1669.

***tert*-Butyl-[7-(2,2-dimethyl-pent-4-enyl)-bicyclo[2.2.1]hept-2-en-7-yloxy]-dimethyl-silane (19).** 7-(2,2-Dimethyl-pent-4-enyl)-bicyclo[2.2.1]hept-2-en-7-ol (1.00 g, 5.61 mmol) was dissolved in 25 ml of THF. Subsequently, 449 mg (11.2 mmol) of oil-free KH was added in one portion under an Ar atmosphere. The mixture was allowed to stir at 23°C for 4 h. At this time, 25 ml of Et_2O was added by syringe, followed by 1.93 ml (8.41 mmol) of TBSOTf and stirring was allowed to continue for an additional 6 h. The reaction was quenched by the addition of H_2O (50 ml) and the mixture was extracted five times with 25-ml portions of pentane. The organic layers are dried over $MgSO_4$ and volatiles were removed *in vacuo*. Purification by silica gel chromatography with 100% pentane afforded a clear colorless oil. Distillation at 0.3 mmHg gave 1.44 g (92%) of spectrospcopically pure silyl ether **19**. $\mathbf{R_f}$ = 0.95 (100% pentane). **IR** (thin film, cm^{-1}) 3081 (w), 3075 (w), 3056 (w), 2949 (s), 2886 (s), 2855 (s), 2703 (w), 1634 (w), 1476 (s); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 5.93 (dd, *J* = 4.4, 2.2 Hz, 2H), 5.81 (ddt, *J* = 9.9, 7.3, 4.8, 6.6 Hz, 1H), 5.03-4.92 (m, 2H), 2.60 (bs, 2H), 2.00-1.91 (m, 4H), 1.71 (s, 2H), 1.54 (s, 1H), 1.26 (s, 2H), 0.91 (d, *J* = 4.76 Hz, 6H), 0.87 (s, 9H), 0.14 (s, 6H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 136.7, 134.8, 116.9, 95.0, 50.7, 48.9, 43.5, 34.2, 27.2, 26.5, 26.0, 23.6, –0.9, –2.7; **HRMS** calc'd for $C_{20}H_{36}OSi$: 320.2535, Found: 320.2540.

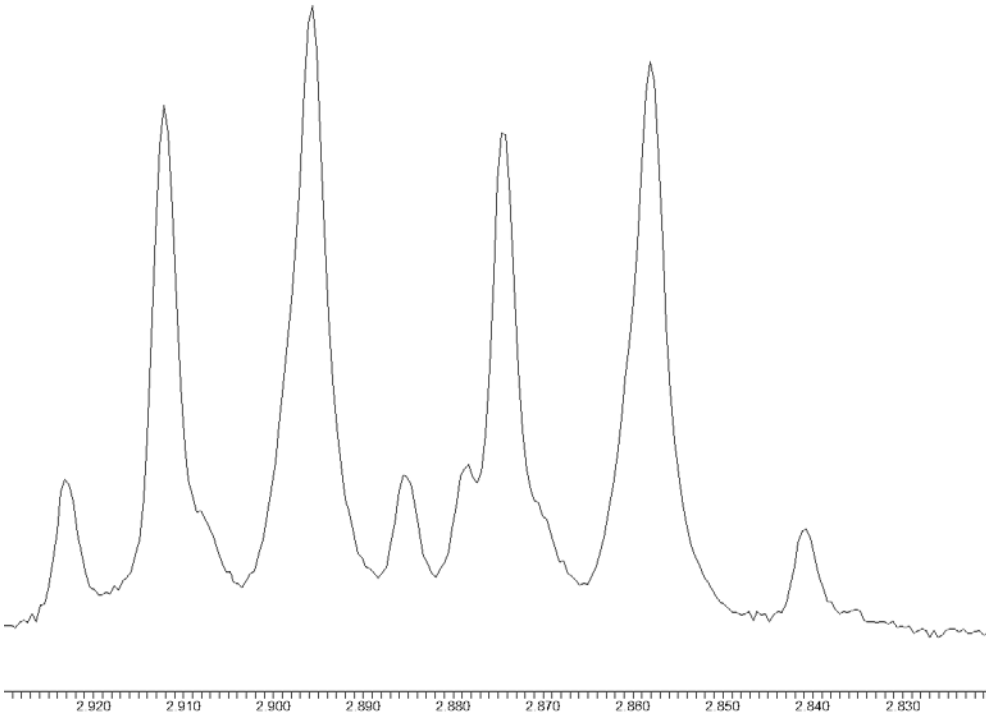
***tert*-Butyl-(5,5-dimethyl-3-vinyl-2,3,4,5,6,8a-hexahydro-1H-azulen-3a-yloxy)-dimethyl-silane (20).** To a solution of 445 mg (1.60 mmol) of diene **3.87** in 0.20 ml of C_6H_6, was added 56.0 mg (0.0479 mmol, 3 mol %) of Mo-complex **(*R*)-1.122**. The solution was allowed to stir at 23°C for 12 h. At this time, the reaction was quenched by the addition of 5 ml of hydrous Et_2O and volatiles were removed *in vacuo*. Purification by silica gel chromatography (100% pentane) afforded 431 mg (1.55 mmol, 97%) of diene **3.88** as a clear colorless oil. $\mathbf{R_f}$ = 0.95 (100% pentane). **IR** (thin film, cm^{-1}) 3080 (w), 2892 (s, br), 2722 (w), 2288 (w, br), 1816 (w), 1640 (s), 1558 (s, br), 1464 (s); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 5.90 (ddd, *J* = 17.1, 10.2, 5.9 Hz, 1H), 5.57-5.66 (m, 1H),

5.49 (dd, J = 11.2, 5.9 Hz, 1H), 5.05 (d, J = 10.7 Hz, 1H), 4.95 (d, J = 17.5 Hz, 1H), 2.80-2.70 (m, 1H), 2.64-2.53 (m, 1H), 2.28 (dd, J = 14.6, 7.3 Hz, 1H), 2.04-1.91 (m, 1H), 2.30 (dd, J = 14.6, 7.3 Hz, 1H), 1.81-1.70 (m, 1H), 1.63-1.22 (m, 6H), 1.06 (s, 3H), 0.90 (s, 9H), 0.88 (s, 3H), 0.16 (s, 3H), 0.13 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 138.3, 132.1, 127.9, 114.0, 85.1, 56.0, 50.7, 45.0, 39.9, 33.7, 32.6, 29.7, 28.1, 26.3, 25.3, 18.5, 9.88, -1.2, -2.3; **HRMS** calc'd for $C_{20}H_{36}OSi$: 320.2535 Found: 320.2532; $[\alpha]_D^{20.0°}$ = 10.93°.

2-[8a-(*tert*-Butyl-dimethyl-siloxy)-7,7-dimethyl-1,2,3,3a,6,7,8,8a-octahydro-azulen-1-yl]-ethanol. To a solution of 210 mg (0.655 mmol) of diene **22** in 2 ml of THF at 0°C was added 79.9 mg (0.655 mmol) of 9-BBN in 5 ml of THF by cannula. The mixture was warmed to 23°C and stirring was allowed to continue for 8 h. At this time, 3 ml of aqueous NaOH (1M) solution was added, followed by 3 ml of an aqueous H_2O_2 (30%) solution. The mixture was allowed to stir vigorously for an additional 6 h. To the solution was added 5 ml solution of saturated aqueous NH_4Cl and the organic layers were washed with three 10 ml portions of Et_2O followed by three 10-ml portions of CH_2Cl_2. The layers were dried over $MgSO_4$, and the volatiles were removed *in vacuo*. Chromatographic purification on silica gel chromatography (100% pentane→10% Et_2O in pentane→25% Et_2O in pentane) afforded 206 mg (0.609 mmol, 93%) of the desired alcohol as a clear colorless oil. **IR** (thin film, cm^{-1}) 3308 (br), 3006 (s), 2949 (s), 2855 (s), 1665 (w), 1470 (s); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 5.53-5.45 (m, 1H), 5.41 (dd, J = 5.86 Hz, 11.22 Hz, 1H), 3.60-3.51 (m, 2H), 3.42-3.51 (m, 2H), 2.60-2.51 (m, 2H), 2.13 (dd, J = 7.13 Hz, 7.13 Hz, 2H), 1.86-1.65 (m, 2H), 1.51-0.99 (m, 4H), 0.96 (s, 3H), 0.79 (s, 3H), 0.78 (s, 9H), 0.03 (s, 3H), 0.00 (s, 3H) ; **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 132, 128, 84.6, 62.8, 50.7, 49.4, 44.3, 40.3, 34.3, 33.2, 33.0, 29.6, 27.8, 27.1, 26.5, 18.7, –1.0, –2.3; **HRMS** calc'd for $C_{20}H_{38}O_2Si$: 338.2641, Found: 338.2637.



Diastereomers From Enriched Material



Diastereomers From Racemic Material

[8a-(*tert*-Butyl-dimethyl-siloxy)-7,7-dimethyl-1,2,3,3a,6,7,8,8a-octahydro-azulen-1-yl]-acetaldehyde (26) Under an N_2 atmosphere, 4.6 mg (0.013 mmol, 5 mol %) of tetra-*n*-propyl ammonium perruthenate was combined with 90 mg of 4 Å molecular sieves and

117 mg (0.524 mmol) of *N*-methyl morpholine *N*-oxide. 2-[8a-(*tert*-Butyl-dimethyl-siloxy)-7,7-dimethyl-1,2,3,3a,6,7,8,8a-octahydro-azulen-1-yl]-ethanol (88.7 mg, 0.26 mmol) in 3 ml of CH_2Cl_2 was added and the emulsion was allowed to stir for 1 h. The mixture was diluted with 10 ml of Et_2O and filtered through silica gel to give 176.1 mg (225 mmol, 86%) of spectroscopically pure product as a clear colorless oil. **IR** (thin film, cm^{-1}) 3012 (w), 2955 (s), 2924 (s), 2855 (s), 2710 (w), 1791 (w), 1728 (s), 1457 (s) 1250 (s); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 9.78 (dd, *J* = 2.6, 1.5 Hz, 1H), 5.62 (ddd, *J* = 5.9 Hz, 4.4 Hz, 11.7 Hz, 1H), 5.54 (dd, *J* = 11.3, 5.9 Hz, 1H), 2.76-2.61 (m, 2H), 2.43-2.32 (m, 1H), 2.28-2.19 (m, 2H), 2.01-1.86 (m, 3H), 1.50-1.63 (m, 1H), 1.44-1.10 (m, 5H), 1.08 (s, 3H), 0.91 (s, 3H), 0.88 (s, 9H), 0.13 (s, 3H), 0.12 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 202, 131, 128, 83.9, 49.9, 46.2, 44.7, 44.5, 40.0, 34.0, 32.8, 29.3, 27.5, 26.6, 26.2, 18.4, –1.3, –2.6; **HRMS** calc'd. for $C_{20}H_{36}O_2Si$: 336.2485 Found: 336.2491; $[\alpha]_D^{20.0°}$ = –13.84°.

***tert*-Butyl-dimethyl-(3,5,5-trimethyl-2,3,4,5,6,8a-hexahydro-1H-azulen-3a-yloxy)-silane (27)** $Rh(dppp)_2Cl$ (5.3 mg, 0.005 mmol, 10 mol %) was added to 18.6 mg (0.055 mmol) of aldehyde **26** in a flame-dried vial under an N_2 atmosphere. Anhydrous C_6H_6 (500 μl) was added and the tightly capped vial is heated to for 50°C 96 h. Volatiles were removed under a flow of Ar and the orange residue was suspended in *n*-pentane and filtered through basic Alumina (Brockman activity I) to give 14.0 mg (0.045 mmol, 82%) of bicycle **27** as a clear colorless oil. Alternatively, 85.5 mg (0.254 mmol) of aldehyde **26** was dissolved in 2 ml of anhydrous toluene and combined with 258 mg (0.279 mmol) of $Rh(PPh_3)_3Cl$. The dark-red mixture was heated under Ar to 110°C for 6 h. At this time, the volatiles were removed with an Ar stream and the residue purified by silica gel chromatography (100% hexanes) to yield 77.0 mg (0.249 mmol, 98%) of a clear colorless oil. $\mathbf{R_f}$ = 0.98 (100% pentane). **IR** (thin film, cm^{-1}) 3018 (w), 2955 (s), 2914 (s), 2854 (s), 1470 (s), 1357 (w), 1243 (s), 1099 (s); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 5.64-5.55 (m, 1H), 5.49 (dd, *J* = 11.0, 5.9 Hz, 1H), 2.64 (ddd, *J* = 9.52, 5.86, 3.66 Hz, 1H), 2.24 (dd, *J* = 14.6, 7.3 Hz, 1H), 2.02-1.68 (m, 5H), 1.60-1.08 (m, 10H), 1.06 (s, 3H), 0.90 (s, 3H), 0.88 (s, 9H), 0.87 (s, 3H), 0.10 (s, 3H), 0.09 (s, 3H) **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 132.5, 128.3, 84.4, 50.7, 46.8, 43.6, 40.0, 34.0, 32.4, 29.6, 29.1, 27.8, 26.2, 18.5, 13.8, –1.5, –2.3; **HRMS** calc'd for $C_{19}H_{36}OSi$: 308.2535 Found: 308.2538.

(28 and 29). Under an N_2 atmosphere, 2.3 mg (0.009 mmol, 10 mol %) of $Rh(acac)(CO)_2$ and 8.6 mg (0.018 mmol, 20 mol %) of tris-(2-*tert*-butyl-phenyl) phosphite were dissolved in 1 ml of toluene and allowed to stir for 30 min to give a clear yellow solution. This solution was subsequently transferred to a vessel containing 30.3 mg (0.089 mmol) of bicycle **27** under an atmosphere of syn-gas. The vessel was transferred to a pressure reactor containing 15 ml of toluene (to prevent volume changes of the solvent in the mixture). The reactor was purged three times with 800 p.s.i. of syn-gas and is subsequently placed in a 70°C oil bath and allowed to stir for 12 h. The reactor was allowed to cool to 23°C, the vessel was removed. Evaporation of volatiles was effected under a stream of Ar. Chromatographic purification on silica gel afforded 29.0 mg (0.086 mmol, 96%) of a clear colorless oil as a equimolar mixture of regioisomeric aldehydes **28** and **29**. **IR** (thin film, cm^{-1}) 3434 (w), 3062 (w), 2924 (br s), 2697 (m), 2068 (w), 2011 (m), 1785 (w), 1728 (s); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 9.62 (desired isomer) (d, *J* =

0.76 Hz, 1H), 9.59 (s, 0.06 H), 9.44 (d, *J* = 3.60 Hz, 1H), 2.43-2.32 (m, 2H), 2.25-1.95 (m, 5H), 1.94-1.59 (m, 12H), 1.56 (s, 1H), 1.49 (s, 1H), 1.45 (s, 1H), 1.41-1.15 (m, 7H), 1.14 (s, 5H), 1.10 (s, 3H), 0.98-0.90 (m, 12H), 0.90-0.87 (m, 18H), 0.135 (s, 3H), 0.142 (s, 3H), 0.11 (s, 6H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 205, 203, 88.8, 87.1, 56.3, 51.2, 50.7, 49.5, 48.6, 48.2, 47.4, 47.1, 46.5, 45.2, 44.3, 43.3, 40.6, 40.2, 38.8, 33.6, 33.4, 33.3, 33.0, 32.8, 32.5, 32.3, 32.1, 31.1, 30.9, 30.3, 30.1, 29.5, 28.4, 28.0, 26.6, 26.5, 26.4, 23.8, 18.8, 18.7, 16.8, 15.9, 14.8, –1.2, –1.2, –1.3, –1.5, –1.5.

[8a-(*tert*-Butyl-dimethyl-silanyloxy)-1,7,7-trimethyl-decahydro-azulen-4-yl]-methanol. Aldehydes **28** and **29** (57.0 mg, 0.169 mmol) were dissolved in 1.6 ml of THF and 19.2 mg (0.508 mmol) of $NaBH_4$ was added in air. Water (10 μl) was added and the mixture was allowed to stir for 1 h. At this time, an additional 1 ml of H_2O was added and the organic layers were washed with two 1-ml portions of Et_2O, followed by two 1-ml portions of EtOAc. The layers were dried over $MgSO_4$ and volatiles removed *in vacuo*. Purification by silica gel chromatography (12% Et_2O in pentane) delivered 56.0 mg (0.168 mmol, 99%) of a mixture of regioisomeric alcohols. Subsequent purification by radial chromatography (4-mm silica plate at 8 ml/min) through the use of solvent gradients (100% pentane, 5% CH_2Cl_2 in pentane, 12% CH_2Cl_2 in pentane, 5% Et_2O in pentane, 100% C_6H_6) afforded 14.0 mg (0.041 mmol, 24%) of the desired alcohol as a clear colorless oil. **IR** (thin film, cm^{-1}) 3314 (br), 2949 (s), 2861 (m), 2357 (s), 2332 (m), 1464 (m), 1388 (w), 1363 (w), 1256 (m), 1105 (m); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 3.59 (dd, *J* = 4.2 Hz, 10.5 Hz, 2H), 3.46 (d, *J* = 7.1 Hz, 1H), 3.43 (d, *J* = 7.1 Hz, 1H), 3.41 (d, *J* = 7.2 Hz, 2H), 2.22-2.12 (m, 2H), 2.09-2.00 (m, 3H), 1.98-1.87 (m, 5H), 1.84-1.71 (m, 6H), 1.69-1.12 (m, 7H), 1.10 (d, *J* = 4.7, 5H), 0.94-0.84 (m, 5H), 0.14-0.11 (m, 12H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 89.0, 86.5, 68.0, 67.4, 52.0, 50.4, 47.8, 47.2, 45.3, 43.7, 43.1, 42.0, 40.7, 39.6, 34.9, 34.1, 33.5, 33.1, 32.0, 31.1, 30.6, 30.2, 29.9, 28.0, 26.7, 26.6, 26.5, 26.2, 21.4, 20.0, 18.9, 18.8, 15.9, 14.7, –1.0, –1.1, –1.1, –1.4; **HRMS** calc'd for $C_{20}H_{40}O_2Si$: 340.2798, Found: 340.2801

***tert*-Butyl-dimethyl-[3,5,5-trimethyl-8-(2-nitro-phenylselanylmethyl)-octahydro-azulen-3a-yloxy]-silane.** [8a-(*tert*-Butyl-dimethyl-silanyloxy)-1,7,7-trimethyl-decahydro-azulen-4-yl]-methanol (9.3 mg, 0.027 mmol) and 12.4 mg (0.0546 mmol) of *o*-$NO_2C_6H_5SeCN$ were combined under an atmosphere of N_2. THF (300 μl) was added followed by 30 μl of pyridine. Tributylphosphine (11.1 mg, 13.6 μl, 0.0546 mmol) was added dropwise via syringe to give a clear red-brown solution. The mixture was stirred for 4 h at 23°C at which time the solvents were removed under a stream of Ar and the resulting residue was suspended in *n*-pentane and immediately purified by silica gel chromatography (100% pentane→5% Et_2O in pentane) to provide 13.9 mg (0.026 mmol, 97%) of a bright yellow wax. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.33-8.23 (m, 2H), 7.55-7.43 (m, 4H), 7.35-7.27 (m, 2H), 3.08 (dd, *J* = 10.8, 4.03 Hz, 1H), 2.93 (dd, *J* = 7.39, 7.39 Hz, 1H), 2.86-2.78 (m, 2H), 2.22-1.89 (m, 2H), 1.89-1.73 (m, 6H), 1.59-1.52 (m, 8H), 1.5-0.81 (m, 9H), 0.17 (s, 3H), 0.15 (s, 3H), 0.08 (s, 3H), 0.02 (s, 3H).

***tert*-Butyl-dimethyl-[3,5,5-trimethyl-7/8-(2-nitro-phenylselanylmethyl)-octahydro-azulen-3a-yloxy]-silane (Regioisomeric mixture). IR** (thin film, cm^{-1}) 2961 (s), 2861 (s), 2364 (w), 2326 (w, br), 1589 (m), 1564 (m), 1514 (s), 1470 (M), 1331 (s), 1294 (m),

1250 (m); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.26 (br d, *J* = 7.8 Hz, 2H), 7.56-7.46 (m, 4H), 7.34-7.27 (m, 2H), 3.08 (dd, *J* = 10.8, 4.1 Hz, 1H), 2.87-2.79 (m, 3H), 2.20-1.96 (m, 5H), 1.92-1.61 (m, 11H), 1.53 (d, *J* = 14.9 Hz, 2H), 1.46-1.38 (m, 3H), 1.34-1.24 (m, 5H), 1.22-1.05 (m, 9H), 1.01-0.82 (m, 33H), 0.176 (s, 3H), 0.157 (s, 2H), 0.149 (s, 3H), 0.128 (s, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 134, 133, 129, 127, 125, 89.0, 87.0, 55.9, 47.9, 47.3, 47.2, 47.0, 43.5, 43.3, 41.4, 40.0, 38.1, 35.6, 35.2, 34.6, 33.6, 33.3, 32.7, 32.6, 31.8, 30.9, 30.7, 30.5, 30.4, 29.8, 29.4, 28.4, 26.7, 26.6, 26.5, 26.4, 22.8, 19.0, 18.8, 16.0, 14.8, 14.3, –0.9, –1.1, –1.1, –1.5.

3,5,5-Trimethyl-8-(2-nitro-phenylselanylmethyl)-octahydro-azulen-3a-ol. Tetra-*n*-butyl ammonium fluoride (393 μl, 1M in THF, 0.393 mmol) was added dropwise by syringe to 20.6 mg (0.039 mmol) of silyl ether **3.134**. The resulting solution was heated to reflux and heating was continued for an additional 20 h under Ar. At this time, water (5 ml) was added to the mixture and the organic layers were washed four times with 2-ml portions of Et_2O. Purification by silica gel chromatography (100% pentane gradient to 100% Et_2O) afforded 14.2 mg (0.346 mmol, 88%) of a yellow wax. **IR** (thin film, cm^{-1}) 3559 (w, br), 3446 (w, br), 2949 (s), 2867 (s), 1564 (m), 1514 (s), 1451 (w), 1331 (s), 1325 (m); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.26 (d, *J* = 9.52, 1H), 7.53-7.45 (m, 3H), 7.28 (dd, *J* = 12.8, 6.2 Hz, 1H), 3.11 (dd, *J* = 10.6, 3.7 Hz, 1H), 2.78 (dd, *J* = 10.6, 8.1 Hz, 1H), 2.09-1.17 (m, 22H), 1.11 (s, 5H), 0.92 (s, 3H) 0.83 (d, *J* = 7.32, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 134, 129, 127, 125, 85.7, 54.9, 50.0, 44.1, 41.9, 40.2, 34.7, 33.7, 33.4, 30.7, 30.4, 30.3, 30.2, 30.0, 15.5; **HRMS** calc'd for $C_{20}H_{29}NO_3Se$: 411.1313, Found: 411.1315.

3,5,5-Trimethyl-7-(2-nitro-phenylselanylmethyl)-octahydro-azulen-3a-ol. IR (thin film, cm^{-1}) 3452 (br w), 2955 (s), 2364 (w), 1589 (m), 1564 (m), 1514 (s), 1457 (m), 1331 (s), 1325 (s). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.28 (d, *J* = 8.06 Hz, 1H), 7.54-7.46 (m, 3H), 7.27-7.35 (m, 1H), 2.92-2.78 (m, 2H), 2.12-1.97 (br m, 2H), 1.95-1.20 (m, 20H), 1.121 (s, 3H), 0.941 (s, 3H), 0.853 (d, *J* = 6.96 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 134, 133, 129, 125, 85.0, 50.2, 45.8, 45.8, 42.2, 37.3, 35.1, 33.9, 33.0, 31.9, 31.5, 30.9, 30.5, 29.9, 15.4.

***tert*-Butyl-dimethyl-(3,5,5-trimethyl-8-methylene-octahydro-azulen-3a-yloxy)-silane (30).** *tert*-Butyl-dimethyl-[3,5,5-trimethyl-8-(2-nitro-phenylselanylmethyl)-octahydro-azulen-3a-yloxy]-silane (13.9 mg, 0.026 mmol) was dissolved in 500 μl of anhydrous toluene. Freshly recrystalized *m*-CPBA (4.6 mg, 0.026 mmol) was added as a solid and the mixture was allowed to stir for 2 h at 23°C; the mixture was heated to 50°C for an additional 4 h. The bright yellow solution was cooled to 23°C and the volatiles removed undr a stream of A. Purification by silica gel chromatography (100% pentane) afforded 7.5 mg (0.023 mmol, 88%) of a clear colorless oil. **R_f** = 0.98 (100% pentane). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 4.68-4.67 (m, 1H), 4.63 (d, *J* = 2.44 Hz, 1H), 2.75 (dd, *J* = 9.9, 9.9 Hz, 1H), 2.24-2.12 (m, 2H), 2.04-1.88 (m, 1H), 1.88-1.72 (m, 1H), 1.71-1.57 (m, 3H), 1.43-1.32 (m, 2H), 1.24 (br s, 3H), 1.10-1.02 (m, 4H), 0.96-0.80 (m, 17H), 0.126 (s, 6H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 152, 111, 87.2, 57.6, 46.6, 40.4, 39.3, 33.2, 31.7, 30.3, 29.9, 29.2, 27.8, 26.6, 26.5, 18.8, 14.9, –0.9, –1.3.

3,5,5-Trimethyl-8-methylene-octahydro-azulen-3a-ol. IR (thin film, cm^{-1}) 3471 (m br), 3081 (w), 2955 (s), 2867 (s), 2364 (m), 2338 (m), 1640 (m), 1470 (s); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 4.79 (br. s, 1H), 4.78 (br. s, 1H), 2.63 (dd, *J* = 9.52, 1H), 2.41-2.25 (m, 2H), 2.02-1.90 (m, 1H), 1.89-1.70 (m, 4H), 1.57-1.18 (m, 7H), 1.10 (s, 3H), 0.915 (s, 3H), 0.86 (d, *J* = 6.96, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 151.2, 110.8, 84.3, 57.1, 49.0, 43.1, 39.0, 33.6, 33.4, 32.1, 30.5, 29.9, 26.7, 14.8.

***tert*-Butyl-dimethyl-(3,5,5,8-tetramethyl-2,3,4,5,6,8α-hexahydro-1H-azulen-3α-yloxy)-silane.** 1,3-diaminopropane (250 µl) was added to 1.5 mg (0.0046 mmol) of **30** in a drybox. Freshly washed KH (1.50 mg, 0.0372 mmol, 8 equiv) was added in one portion to the solution and the mixture was sealed under N_2 in a tightly capped vial. The mixture was removed from the drybox, and stirring was allowed to continue until the Teflon stir bar discolors (25 min) from white to dark brown. At this time, 1 ml of hydrated Et_2O was added and the organics were filtered through silica gel with Et_2O. Volatiles were removed *in vacuo*, and the residue was filtered through silica gel with *n*-pentane. The solvents were again removed *in vacuo* to provide 1.2 mg (0.0035 mmol, 77%) of the desired compound as a clear colorless oil. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 5.37 (ddt, *J* = 5.59 Hz, 1.41 Hz, 1.63 Hz, 1H), 2.43 (dd, *J* = 7.7 Hz, 9.8 Hz, 1H), 2.11 (dd, *J* = 7.7 Hz, 15.2 Hz, 1H), 2.01-1.75 (m, 7H), 1.72 (s, 3H), 1.59-1.33 (m, 21H), 1.05 (s, 3H), 0.94-0.81 (m), 0.11 (s, 3H), 0.08 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 138, 123, 84.2, 56.4, 46.2, 44.3, 40.4, 34.8, 32.6, 29.9, 29.3, 28.6, 27.0, 26.4, 25.3, 18.7, 14.1, –1.3, –2.0.

3,5,5,8-Tetramethyl-2,3,4,5,6,8a-hexahydro-1H-azulen-3a-ol (31). To *tert*-Butyl-dimethyl-(3,5,5,8-tetramethyl-2,3,4,5,6,8α-hexahydro-1H-azulen-3α-yloxy)-silane (1.2 mg, 0.0037 mmol) under Ar, was added tetra-*n*-butyl ammonium fluoride (200 µl, 1M in THF, 0.2 mmol) dropwise by syringe. The mixture was sealed under Ar in a tightly capped vial and heated to 70°C for 48 h. At this time, the mixture was allowed to cool to 23°C and 1 ml of hydrated Et_2O was added. The mixture was allowed to stir for 30 min and the ether layer was washed with water. The water layer was washed three times with Et2O times. Organic layers were then combined and volatiles were removed volatiles under a stream of Ar. The resulting residue was purified by silica gel chromatography (100% pentane gradient to 25% Et_2O in pentane) to provide **3.34** as a clear colorless wax (0.48 mg, 0.0023 mmol, 62%). **^{1}H NMR** ($CDCl_3$, 400 MHz) 5.45-5.50 (m, 1 H), 2.49 (dd, *J* = 12.2, 8.2 Hz, 1 H), 1.99-1.20 (m, 10 H), 1.49 (s, 3 H), 1.19 (s, 3 H), 0.93 (s, 3 H), 0.84 (d, *J* = 6.7 Hz, 3 H).

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