Supporting Information

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Rh(I)-Catalyzed C-C Bond Activation: Seven-Membered Ring Synthesis by a [6+1] Carbonylative Ring Expansion Reaction of Allenylcyclobutanes **

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Reactions were carried out in oven-dried glassware sealed with rubber septa under a positive pressure of carbon monoxide from a balloon, unless otherwise indicated. Liquids and solutions were transferred via syringe or stainless steel cannula. Reactions were run using Teflon-coated magnetic stir bars. Elevated temperatures were maintained in thermostat-controlled oil baths. Elevated carbon monoxide pressures were maintained using a pressure reaction vessel purchased from Andrew's Glass Co. Organic solutions were concentrated using a Büchi rotary evaporator with a desktop vacuum pump. Thin layer chromatography plates were visualized by ultraviolet light and treatment with acidic *p*-anisaldehyde stain followed by gentle heating. Chromatographic purification of products was accomplished by flash chromatography. Silica gel 60, 230-400 mesh was purchased from EM Science. {[RhCl(CO)₂]₂} was purchased from Strem Chemicals. DCE (99+%, ACS reagent grade), TCE, toluene, and *m*-xylene were purchased from Aldrich Chemical Co. and were used as received. Carbon monoxide (2.5 grade) was purchased from Praxair.

NMR spectra were measured on a Varian INOVA 500 (¹H at 500 MHz, ¹³C at 125 MHz), Varian Mercury 400 (¹H at 400 MHz, ¹³C at 100 MHz), or Varian Gem-300 (¹H at 300 MHz, ¹³C at 75 MHz) magnetic resonance spectrometer. Data for ¹H NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, ddd = doublet of doublet of doublets, dq = doublet of quartets, septd = septet of doublets, tsept = triplet of septets, m = multiplet), coupling constant (Hz), and integration. Nuclear Overhauser effect (nOe) data were measured at 500 MHz and are reported as follows: H (irradiated)→H (observed), % enhancement. Data for ¹³C are reported in terms of chemical shift and quantity of carbons. Infrared spectra were recorded on a Perkin-Elmer Spectrum BX Fourier transform spectrometer (IR) and are reported as follows: wavenumbers (cm⁻¹), description (w = weak, m = medium, s = strong, b = broad). High-resolution mass spectra (HRMS) were recorded at the NIH regional mass spectrometry facility at the University of California, San Francisco. Reported mass values are with error limits of ±1 millimass unit. Elemental analyses (EA), (%C, %H) were determined by Desert Analytics, Tucson, Arizona. Reported atomic percentages are within error limits of ±0.4%.

Experimental and Characterization

General Procedure for the 1,2 addition of 1-bromo-3-methyl-1,2-butadiene into cyclobutanones:

To a solution of 1-bromo-3-methyl-1,2-butadieneⁱ (2.52g, 17 mmol) in ether (16 mL) at -78 °C was added *n*-BuLi (1.6 M in hexane, 10.7 mL, 17 mmol) *via* syringe over five minutes. The

mixture was allowed to stir at -78 °C for 45 minutes. To this mixture was added a solution of cyclobutanone (400 mg, 5.7 mmol) in THF (8 mL) *via* syringe over two minutes. The mixture was allowed to stir for an additional 30 minutes before warming up to room temperature in 20 minutes. The reaction mixture was quenched with sat. NH₄Cl solution at room temperature. The crude was extracted with ether. The organic layer was washed with brine, and dried over Na₂SO₄. After concentration of solvent, the residue was purified *via* flash chromatography with silica gel (11% Et₂O/pentane) to afford alcohol **2i** (510 mg, 65%) as a colorless oil. The compound was chromatographically homogenous.

Data for **2i**:

R_f: 0.30 (4:1 hexane / EtOAc); one spot.

¹H-NMR (500 MHz, CDCl₃): δ = 5.27 (sept, *J* = 2.8 Hz, 1H, C4-H), 2.15-2.12 (dd, *J* = 8.9, 6.3 Hz, 4H, C1-CH₂, C3-CH₂), 1.99 (s, 1H, OH), 1.72 (d, *J* = 2.9 Hz, 6H, C5-Me, C6-Me), 1.69-1.62 (m, 1H, C2-H), 1.50-1.43 (m, 1H, C2-H) ppm.

¹³C-NMR (125 MHz, CDCl₃): δ = 198.3, 99.2, 95.9, 73.1, 36.4 (2C), 20.5 (2C), 11.8 ppm.

IR (FTIR, film): ν = 3338 (br), 2982 (s), 2935 (s), 2859 (m), 1970 (w), 1445 (m), 1394 (m), 1364 (m), 1256 (m), 1122 (s), 1038 (w), 958 (w) cm⁻¹.

EA calcd for C₉H₁₄O: C 78.21%, H 10.21%. Found: C 78.08%, H 10.22%.

To a solution of alcohol **2i** (1.32 g, 9.6 mmol) in DMF (8 mL) at room temperature was added imidazole (1.1 g, 16 mmol) and TBSCl (1.9 g, 13 mmol) in one portion. The mixture was allowed to stir for six hours at room temperature. The reaction mixture was quenched with sat. NH₄Cl solution at room temperature. The solution was extracted with ether. The organic layer was washed with brine and dried over Na₂SO₄. After concentration of solvent, the residue was purified *via* flash chromatography with silica gel (pentane) to afford TBS ether **2** (1.85 g, 76%, one spot by TLC) as a colorless oil. Compound was chromatographically homogeneous.

Data for **2**:

R_f: 0.90 (10:1 hexane / EtOAc); one spot.

¹H-NMR (500 MHz, CDCl₃): δ = 5.17-5.13 (m, 1H, C4-H), 2.11-2.20 (m, 4H, C1-CH₂, C3-CH₂), 1.77 (d, *J* = 2.9 Hz, 6H, C5-Me, C6-Me), 1.59-1.67 (m, 1H, C2-H), 1.49-1.38 (m, 1H, C2-H), 0.91 (s, 9H, TBS-*t*Bu), 0.08 (s, 6H, TBS-Me)

¹³C-NMR (125 MHz, CDCl₃): δ = 198.8, 97.6, 96.1, 74.7, 37.5 (2C), 25.8 (3C), 20.4 (2C), 17.8, 12.5, -2.9 (2C) ppm.

IR (FTIR, film): ν = 2983 (s), 2955 (s), 2933 (s), 2856 (s), 1969 (w), 1472 (m), 1462 (m), 1389 (m), 1362 (m), 1249 (s), 1134 (s), 1054 (w), 991 (s), 837 (s), 775 (s) cm⁻¹.

HRMS calcd for C₁₅H₂₈OSi: 252.1909 g/mol. Found: 252.1913 g/mol.

Allenyl cyclobutane **2** (20 mg, 0.079 mmol) was weighed into an oven-dried borosilicate test tube equipped with a magnetic stir bar. The substrate was dissolved in toluene (0.4 mL) and [RhCl(CO)₂]₂ (3.1 mg, 0.0079 mmol) was added in one portion. The test tube was capped with a rubber septum, the septum was then punctured with a disposable 16G1^{1/2} needle and the test tube was placed in the pressure vessel. The vessel was pressurized to two atmospheres of CO and was placed in a preheated thermostat-controlled oil bath at 80 °C. The solution was stirred for 24 h at which time TLC indicated that the starting material was consumed. The solution was cooled to room temperature and was purified *via* flash chromatography on silica gel (gradient elution 100% pentane → 10% Et₂O/pentane). Product-containing fractions were combined and concentrated by rotary evaporation to yield ketone **3** (21 mg, 93%) as a yellow oil. The compound was chromatographically homogeneous.

Data for **3**:

TLC: R_f = 0.56 (20% EtOAc/hexane), one blue spot with *p*-anisaldehyde stain.

¹H-NMR (500 MHz, CDCl₃): δ = 5.48 (s, 1H, C1-H), 2.53-2.47 (m, 2H, C4-CH₂), 2.32 (t, *J* = 6.3 Hz, 2H, C6-CH₂), 1.99-1.95 (m, 2H, C5-CH₂); 1.87 (s, 3H, C3-Me); 1.80 (s, 3H, C2-Me); 0.95 (s, 9H, *t*Bu); 0.19 (s, 6H, TBS-Me) ppm.

¹³C-NMR (125 MHz, CDCl₃): δ = 208.0, 153.3, 136.6, 132.3, 105.1, 42.6, 34.6, 25.6 (3C), 22.0, 21.6, 21.0, 18.0, -4.40 (2C) ppm.

IR (thin film): ν = 2931 (s), 2889 (s), 2859 (s), 1690 (vs), 1630 (m), 1446 (w), 1378 (m), 1260 (s), 1225 (s), 1173 (s), 1148 (s), 1057 (w), 914 (m), 867 (m), 840 (vs), 780 (s) cm⁻¹.

HRMS (EI, m/z): Calcd for $C_{16}H_{28}O_2Si$: 280.1859 g/mol (M^+). Found: 280.1861 g/mol.

nOe:

Cyclobutanone **5ii**ⁱⁱⁱ (330 mg, 1.73 mmol) was converted to allenyl alcohol **5i** (301 mg, 67%, colorless oil) according to the general procedure for the 1,2 addition of 1-bromo-3-methyl-1,2-butadiene into cyclobutanones (see: general procedure described for the synthesis of **2i**). The compound was chromatographically homogeneous.

Data for **5i**:

TLC: R_f = 0.69 (20% EtOAc/pentane), one blue spot with *p*-anisaldehyde stain.

1H NMR (500 MHz, $CDCl_3$): δ = 7.38-7.27 (m, 5H), 5.25 (sept, J = 2.8 Hz, 1H, C1-H), 4.57 (d, J = 12.0 Hz, 1H, C2-H), 4.53 (d, J = 12.0 Hz, 1H, C2-H), 3.76 (dd, J = 9.5, 7.0 Hz, 1H, C3-H), 3.71 (dd, J = 9.5, 5.1 Hz, 1H, C3-H), 3.04 (s, 1H, OH), 2.66-2.59 (m, 1H, C4-H), 2.22-2.14 (m, 2H), 1.78-1.69 (m, 1H), 1.74 (d, J = 2.8 Hz, 6H), 1.67-1.60 (m, 1H) ppm.

^{13}C NMR (125 MHz, $CDCl_3$): δ = 198.7, 138.1, 128.4 (2C), 127.7, 127.6 (2C), 99.1, 96.9, 74.4, 73.2, 70.6, 44.4, 34.8, 20.6 (2C), 16.3 ppm.

IR (thin film): ν = 3427 (broad), 3064 (w), 3030 (w), 2980 (s), 2937 (s), 2858 (s), 1968 (w), 1496 (w), 1454 (m), 1393 (m), 1363 (s), 1315 (w), 1234 (m), 1209 (m), 1190 (m), 1164 (m), 1122 (s), 1094 (s), 1075 (s), 1028 (m), 972 (w), 942 (w), 907 (w), 812 (w), 736 (m), 698 (m) cm^{-1} .

HRMS (EI, m/z): Calcd for $C_{17}H_{22}O_2$: 258.1620 g/mol (M^+). Found: 258.1629 g/mol.

nOe:

NaH (60% dispersion in mineral oil, 69 mg, 1.7 mmol) was added portion-wise over 2 min to a solution of allenyl alcohol **5i** (223 mg, 0.86 mmol) in DMF (1.7 mL). The mixture was stirred for 20 min at room temperature under a positive pressure of nitrogen. 2-bromoethyl methyl ether (0.808 mL, 8.6 mmol) was added drop-wise via syringe over 30 seconds. The reaction mixture was stirred at room temperature for 6 h at which point TLC indicated that the starting material had not been consumed. An additional batch of NaH (60% dispersion in mineral oil, 200 mg, 5 mmol) was added portion-wise over 2 min. This was followed by the drop-wise addition of 2-bromoethyl methyl ether (0.4 mL, 4.3 mmol) via syringe over 30 seconds. The reaction mixture was stirred for 1 h and was quenched by the portion-wise addition over 2 min of saturated aqueous NH_4Cl (30 mL). The product was extracted with diethyl ether (3x10 mL). The combined organic extracts were washed with brine (3x10 mL), dried over MgSO_4 , vacuum-filtered through a fritted funnel, and then concentrated using a rotary evaporator. The residue was purified by flash chromatography with silica gel (gradient elution 100% pentane $\rightarrow$ 8% Et_2O /pentane). Product-containing fractions were combined and concentrated using a rotary evaporator to yield allenyl ether **5** (246 mg, 90%) as a colorless liquid. The compound was chromatographically homogeneous.

Data for **5**:

TLC: R_f = 0.86 (16% EtOAc/pentane), one blue spot with *p*-anisaldehyde stain.

^1H NMR (500 MHz, CDCl_3): δ = 7.36-7.24 (m, 5H), 5.06 (sept, J = 2.9 Hz, 1H, C1-H), 4.55 (d, J = 12.1 Hz, 1H, C2-H), 4.51 (d, J = 12.1 Hz, 1H, C2-H), 3.81 (dd, J = 9.6, 6.3 Hz, 1H, C3-H), 3.61 (dd, J = 9.6, 8.5 Hz, 1H, C3-H), 3.49-3.47 (m, 2H), 3.45-3.42 (m, 2H), 3.36 (s, 3H, OMe), 2.67-2.61 (m, 1H, C4-H), 2.15 (ddd, J = 10.5, 9.2, 8.9 Hz, 1H), 2.05-2.00 (m, 1H), 1.76-1.67 (m, 1H), 1.734 (d, J = 2.1 Hz, 3H), 1.729 (d, J = 2.3 Hz, 3H), 1.62-1.55 (m, 2H) ppm.

^{13}C NMR (125 MHz, CDCl_3): δ = 201.0, 138.8, 128.3 (2C), 127.6, 127.4 (2C), 97.9, 93.5, 78.3, 73.1, 72.2, 70.2, 62.7, 59.1, 44.0, 30.4, 20.6, 20.4, 17.1 ppm.

IR (thin film): ν = 3063 (w), 3030 (w), 2979 (m), 2936 (s), 2864 (s), 2717 (w), 1968 (w), 1496 (w), 1453 (m), 1391 (w), 1364 (m), 1249 (m), 1199 (m), 1165 (m), 1124 (s), 1096 (s), 1029 (m), 971 (w), 908 (w), 850 (w), 814 (w), 735 (m), 698 (m) cm^{-1} .

HRMS (EI, m/z): Calcd for $\text{C}_{20}\text{H}_{28}\text{O}_3$: 316.2038 g/mol (M^+). Found: 316.2047 g/mol.

nOe:

Allenyl cyclobutane **5** (38 mg, 0.12 mmol) was weighed into an oven-dried borosilicate test tube equipped with a magnetic stir bar. The substrate was dissolved in *m*-xylene (0.24 mL, 0.5 M) and $[\text{RhCl}(\text{CO})_2]_2$ (0.9 mg, 0.0024 mmol) was added in one portion. The test tube was capped with a rubber septum. The resulting yellow solution was stirred under an atmosphere of CO (balloon, 1 atm) and was vented to a bubbler via an outlet needle for 10 min. The outlet needle was removed and the solution was then immersed into a thermostat-controlled oil bath preheated to 80 °C. The solution was stirred for 44 h at which time TLC indicated that the starting material was consumed. The solution was cooled to room temperature and was purified *via* flash chromatography on silica gel (gradient elution 15% Et_2O /pentane $\rightarrow$ 30% Et_2O /pentane). Fractions containing **6** were combined and concentrated by rotary evaporation to yield ketone **6** (24 mg, 58%) as a colorless oil. The compound was chromatographically homogeneous. Fractions containing **7** were combined and concentrated by rotary evaporation to yield ketone **7** (5 mg, 12%) as a colorless oil. The compound was chromatographically homogeneous.

Data for **6**:

TLC: R_f = 0.45 (25% EtOAc /pentane), one blue spot with *p*-anisaldehyde stain.

^1H NMR (500 MHz, CDCl_3): δ = 7.36-7.25 (m, 5H), 5.23 (s, 1H, C1-H), 4.52 (d, J = 12.0 Hz, 1H, C2-H), 4.47 (d, J = 12.1 Hz, 1H, C2-H), 3.89-3.85 (m, 1H), 3.82-3.78 (m, 1H), 3.73 (dd, J = 9.2, 4.5 Hz, 1H, C3-H), 3.67-3.59 (m, 2H), 3.48 (dd, J = 9.2, 8.2 Hz, 1H, C3-H), 3.39 (s, 3H, OMe), 2.79 (dddd, J = 9.4, 8.2, 4.5, 3.4 Hz, 1H, C4-H), 2.64 (ddd, J = 16.2, 9.3, 4.0 Hz, 1H, C6-

H), 2.45 (ddd, $J = 16.2, 8.1, 4.0$ Hz, 1H, C6-H), 2.13 (dddd, $J = 14.0, 9.4, 9.3, 4.6$ Hz, 1H, C5-H), 2.01-1.92 (m, 1H, C5-H), 1.89 (s, 3H, C7-Me), 1.77 (s, 3H, C8-Me) ppm.

^{13}C NMR (125 MHz, CDCl_3): δ 207.4, 156.6, 138.5, 138.1, 131.5, 128.3 (2C), 127.5, 127.4 (2C), 97.1, 73.0, 71.0, 70.8, 66.7, 59.2, 43.2, 40.1, 24.3, 22.1, 21.8 ppm.

IR (thin film): $\nu = 3362$ (w, br), 3062 (w), 3029 (w), 2924 (s), 2872 (m), 2358 (w), 2342 (w), 1686 (s), 1645 (m), 1627 (m), 1495 (w), 1453 (m), 1409 (w), 1365 (m), 1318 (w), 1288 (m), 1233 (m), 1209 (m), 1170 (m), 1151 (m), 1125 (s), 1100 (s), 1028 (m), 927 (w), 911 (w), 861 (w), 810 (m), 738 (m), 698 (m), 668 (w), 662 (w) cm^{-1} .

HRMS (EI, m/z): Calcd for $\text{C}_{21}\text{H}_{28}\text{O}_4$: 344.1988 g/mol (M^+). Found: 344.1998 g/mol.

HMBC:

Data for **7**:

TLC: $R_f = 0.54$ (25% EtOAc/pentane 3:1), one blue spot with *p*-anisaldehyde stain.

^1H NMR (500 MHz, CDCl_3): $\delta = 7.35$ -7.25 (m, 5H), 5.28 (s, 1H, C1-H), 4.52 (d, $J = 11.9$ Hz, 1H, C2-H), 4.46 (d, $J = 11.8$ Hz, 1H, C2-H), 3.89-3.83 (m, 3H), 3.68-3.66 (m, 2H), 3.49 (dd, $J = 9.2, 5.9$ Hz, 1H), 3.42 (s, 3H, OMe), 3.16-3.10 (m, 1H, C4-H), 2.47 (ddd, $J = 15.5, 11.6, 5.6$ Hz, 1H, C6-H), 2.20 (ddd, $J = 15.6, 5.1, 5.1$ Hz, 1H, C5-H), 2.16-2.09 (m, 1H, C6-H), 1.91 (s, 3H, C7-Me), 1.78 (s, 3H, C8-Me), 1.67-1.75 (m, 1H, C5-H) ppm.

^{13}C NMR (125 MHz, CDCl_3): $\delta = 207.6, 157.9, 138.3, 137.7, 133.3, 128.3$ (2C), 127.6, 127.5 (2C), 96.7, 73.2, 70.8, 70.2, 66.6, 59.2, 50.5, 29.8, 27.7, 22.5, 21.9 ppm.

IR (thin film): $\nu = 3835$ (w, br), 3741 (w, br), 3063 (w), 3030 (w), 2924 (s), 2862 (m), 1682 (m), 1629 (m, br), 1455 (m), 1367 (m), 1338 (w), 1284 (w), 1245 (m), 1199 (m), 1174 (m), 1152 (s), 1125 (s), 1099 (s), 1029 (m), 1001 (w), 861 (w), 809 (m), 737 (m), 698 (m) cm^{-1} .

HRMS (EI, m/z): Calcd for $\text{C}_{21}\text{H}_{28}\text{O}_4$: 344.1988 g/mol (M^+). Found: 344.1994 g/mol.

HMBC:

Cyclobutanone **8ii**ⁱⁱⁱ (600 mg, 3.4 mmol) was converted to allenyl cyclobutanol **8i** (328 mg, colorless oil, 39%) according to the general procedure for the 1,2 addition of 1-bromo-3-methyl-1,2-butadiene into cyclobutanones (see: general procedure described for the synthesis of **2i**). The compound was chromatographically homogeneous.

Data for **8i**:

TLC: R_f = 0.54 (10% EtOAc/pentane), one blue spot with *p*-anisaldehyde stain.

¹H NMR (500 MHz, CDCl₃): δ = 7.38-7.27 (m, 5H), 5.19 (sept, J = 2.9 Hz, 1H, C1-H), 4.57 (d, J = 11.7 Hz, 1H, C2-H), 4.53 (d, J = 11.7 Hz, 1H, C2-H), 3.95-3.91 (m, 1H, C3-H), 3.04 (s, 1H, OH), 2.19-1.92 (m, 3H), 1.88-1.10 (m, 1H), 1.73 (d, J = 2.9 Hz, 3H, Me), 1.72 (d, J = 2.9 Hz, 3H, Me) ppm.

¹³C NMR (125 MHz, CDCl₃): δ = 199.9, 137.8, 128.5 (2C), 127.84, 127.80 (2C), 98.7, 95.6, 78.2, 76.1, 71.4, 29.8, 23.9, 20.6, 20.5 ppm.

IR (thin film): ν = 3453 (broad), 3064 (w), 3030 (w), 2980 (s), 2940 (s), 2907 (s) 2866 (m), 1967 (w), 1495 (w), 1453 (m), 1397 (m), 1362 (m), 1348 (w), 1259 (w), 1216 (m), 1189 (m), 1131 (s), 1007 (s), 955 (w), 913 (w), 807 (w) cm⁻¹.

HRMS (EI, m/z): Calcd for C₁₆H₂₀O₂: 244.1463 g/mol (M^+), for C₁₄H₁₆O₂: 216.1150 g/mol (M^+ -C₂H₄). Found: 216.1166 g/mol.

NaH (60% dispersion in mineral oil, 166 mg, 4.14 mmol) was added portion-wise over 2 min to a solution of allenyl alcohol **8i** (253 mg, 1.04 mmol) in DMF (2 mL). The mixture was stirred for 20 min at room temperature under a positive pressure of nitrogen. 2-bromoethyl methyl ether (0.390 mL, 4.14 mmol) was added drop-wise via syringe over 30 seconds. The reaction mixture was stirred at room temperature for 6 h at which point TLC indicated that the starting material had been consumed. The reaction was quenched by the portion-wise addition over 2 min of saturated aqueous NH₄Cl (4 mL). The product was extracted with diethyl ether (3x4 mL). The combined organic extracts were washed with brine (3x4 mL), dried over MgSO₄, vacuum-filtered through a fritted funnel, and then concentrated using a rotary evaporator. The residue

was purified by flash chromatography with silica gel (gradient elution 100% pentane $\rightarrow$ 5% Et₂O/pentane). Product-containing fractions were combined and concentrated using a rotary evaporator to yield allenyl ether **8** (257 mg, 82%) as a colorless liquid. The compound was chromatographically homogeneous.

Data for **8**:

TLC: R_f = 0.53 (10% EtOAc/pentane), one blue spot with *p*-anisaldehyde stain.

¹H NMR (500 MHz, CDCl₃): δ = 7.37-7.24 (m, 5H), 5.10 (sept, J = 2.9 Hz, 1H, C1-H), 4.62 (d, J = 12.0 Hz, 1H, C2-H), 4.50 (d, J = 11.9 Hz, 1H, C2-H), 3.94-3.90 (m, 1H, C3-H), 3.74-3.66 (m, 1H), 3.64-3.54 (m, 3H), 3.40 (s, 3H, OMe), 2.11-1.94 (m, 3H), 1.75-1.68 (m, 1H), 1.71 (d, J = 2.9 Hz, 3H, Me), 1.70 (d, J = 2.9 Hz, 3H, Me) ppm.

¹³C NMR (125 MHz, CDCl₃): δ = 201.5, 138.5, 128.2 (2C), 127.8, 127.4 (2C), 97.8, 93.3, 82.2, 78.8, 72.3, 71.2, 63.2, 59.0, 26.0, 23.6, 20.4, 20.3 ppm.

IR (thin film): ν = 3029 (w), 2979 (m), 2873 (s), 1966 (w), 1496 (w), 1453 (m), 1395 (w), 1364 (m), 1192 (m), 1123 (s), 1077 (m), 1027 (m), 849 (w), 735 (m), 697 (m) cm⁻¹.

HRMS (EI, m/z): Calcd for C₁₉H₂₆O₃: 302.1882 g/mol (M⁺), for C₁₀H₁₆O₂: 168.1150 g/mol (M⁺-C₂H₄OBn). Found: 168.1131 g/mol.

nOe:

Allenyl cyclobutane **8** (20 mg, 0.066 mmol) was weighed into an oven-dried borosilicate test tube equipped with a magnetic stir bar. The substrate was dissolved in toluene (0.66 mL) and [RhCl(CO)₂]₂ (2.6 mg, 0.0066 mmol) was added in one portion. The test tube was capped with a rubber septum. The resulting yellow solution was stirred under an atmosphere of CO (balloon, 1 atm) and was vented to a bubbler via an outlet needle for 10 min. The outlet needle was

removed and the solution was then immersed into a thermostat-controlled oil bath preheated to 80 °C. The solution was stirred for 48 h at which time TLC indicated that the starting material was consumed. The solution was cooled to room temperature and was purified *via* flash chromatography on silica gel (gradient elution 10% Et₂O/pentane → 30% Et₂O/pentane). Product-containing fractions were combined and concentrated by rotary evaporation to yield ketone **9** (12 mg, 55%) as a colorless oil. The compound was chromatographically homogeneous.

Data for **9**:

TLC: R_f = 0.26 (30% EtOAc/pentane), one blue spot with *p*-anisaldehyde stain.

¹H NMR (500 MHz, CDCl₃): δ = 7.36-7.20 (m, 5H), 5.44 (s, 1H, C1-H), 4.57 (d, *J* = 11.7 Hz, 1H, C2-H), 4.42 (d, *J* = 11.7 Hz, 1H, C2-H), 4.09 (dd, *J* = 4.9, 4.4 Hz, 1H, C3-H), 3.99-3.88 (m, 2H), 3.75-3.64 (m, 2H), 3.43 (s, 3H, OMe), 2.59-2.54 (m, 2H, C5-H), 2.28-2.12 (m, 2H, C4-H), 1.99 (s, 3H, C6-H), 1.80 (s, 3H, C7-H) ppm.

¹³C NMR (125 MHz, CDCl₃): δ = 204.4, 156.5, 140.3, 138.4, 131.1, 128.2 (2C), 127.6 (2C), 127.3, 98.0, 77.0, 70.8, 70.7, 66.8, 59.2, 38.2, 29.3, 22.6, 22.5 ppm.

IR (thin film): ν = 2925 (m), 1717 (s), 1684 (m), 1634 (w), 1584 (w), 1451 (m), 1373 (w), 1314 (s), 1273 (s), 1176 (m), 1098 (m), 1070 (m), 1027 (m), 713 (m) cm⁻¹.

HRMS (EI, *m/z*): Calcd for C₂₀H₂₆O₄: 330.1831 g/mol (M⁺). Found: 330.1838 g/mol.

HMBC:

Cyclobutanone **11iii**^{iv} (420 mg, 3.4 mmol) was converted to allenyl cyclobutanol **11i** (520 mg, colorless oil, 80%) according to the general procedure for the 1,2 addition of 1-bromo-3-methyl-1,2-butadiene into cyclobutanones (see: general procedure described for the synthesis of **2i**). The compound was chromatographically homogeneous.

Data for **11i**:

TLC: R_f = 0.43 (7% EtOAc/pentane), one blue spot with *p*-anisaldehyde stain.

^1H NMR (500 MHz, CDCl_3): δ = 5.32 (sept, J = 2.9 Hz, 1H, C1-H), 2.31-2.22 (m, 1H, C2-H), 2.17-2.08 (m, 1H), 2.02-1.94 (m, 2H), 1.81 (s, 1H), 1.76-1.70 (m, 1H), 1.74 (d, J = 2.7 Hz, 6H, Me, Me), 1.69-1.62 (m, 2H), 1.54-1.29 (m, 4H), 1.11-0.98 (m, 1H) ppm.

^{13}C NMR (125 MHz, CDCl_3): δ = 198.3, 99.7, 96.8, 71.2, 43.4, 37.5, 25.8, 23.5, 22.8, 21.8, 21.7, 20.75, 20.72 ppm.

IR (thin film): ν = 3350 (broad), 2931 (s), 2852 (m), 1968 (w), 1464 (w), 1450 (m), 1392 (m), 1363 (m), 1292 (w), 1246 (m), 1204 (m), 1144 (m), 1118 (m), 1082 (m), 1016 (m), 979 (w), 900 (w), 816 (w), 762 (w), 726 (w) cm^{-1} .

HRMS (EI, m/z): Calcd for $\text{C}_{13}\text{H}_{20}\text{O}$: 192.1514 g/mol (M^+). Found: 192.1514 g/mol.

NaH (60% dispersion in mineral oil, 125 mg, 3.12 mmol) was added portion-wise over 2 min to a solution of allenyl alcohol **11i** (300 mg, 1.56 mmol) in DMF (1.5 mL). The mixture was stirred for 30 min at room temperature under a positive pressure of nitrogen. 2-bromoethyl methyl ether (0.37 mL, 3.9 mmol) was added drop-wise via syringe over 30 seconds. The reaction mixture was stirred at room temperature for 6 h at which point TLC indicated that the starting material had not been consumed. An additional 2 equivalents of NaH (60% dispersion in mineral oil, 125 mg, 3.12 mmol) was added portion-wise over 2 min. This was followed by the drop-wise addition of 2-bromoethyl methyl ether (0.37 mL, 3.9 mmol) via syringe over 30 seconds. The reaction mixture was stirred overnight at room temperature and was quenched by the portion-wise addition over 2 min of saturated aqueous NH_4Cl (30 mL). The product was extracted with diethyl ether (3x10 mL). The combined organic extracts were washed with brine (3x10 mL), dried over MgSO_4 , vacuum-filtered through a fritted funnel, and then concentrated using a rotary evaporator. The residue was purified by flash chromatography with silica gel (gradient elution 100% pentane $\rightarrow$ 8% Et_2O /pentane). Product-containing fractions were combined and concentrated using a rotary evaporator to yield allenyl ether **11** (296 mg, 76%) as a colorless liquid. The compound was chromatographically homogeneous.

Data for **11**:

TLC: R_f = 0.30 (2% EtOAc/pentane), one blue spot with *p*-anisaldehyde stain.

$^1\text{H-NMR}$ (500 MHz, CDCl_3): δ = 5.04 (sept, J = 2.9 Hz, 1H, C1-H), 3.52-3.44 (m, 3H, C5- CH_2 , C6-H), 3.36 (s, 3H, OMe), 3.29-3.25 (m, 1H, C6-H), 2.32-2.26 (m, 1H, C2-H), 2.10 (dd, J = 10.4, 10.3 Hz, 1H, C4 α -H), 1.96-1.90 (m, 1H, C3-H), 1.86 (ddd, J = 9.9, 7.7, 4.6 Hz, 1H, C4 β -H), 1.80-1.71 (m, 1H), 1.72 (d, J = 2.7 Hz, 3H), 1.71 (d, J = 2.8 Hz, 3H), 1.66-1.58 (m, 2H), 1.52-1.46 (m, 2H), 1.43-1.24 (m, 2H), 1.04-0.96 (m, 1H) ppm.

$^{13}\text{C-NMR}$ (125 MHz, CDCl_3): δ = 201.1, 97.2, 93.2, 76.0, 72.1, 62.5, 59.0, 40.7, 34.4, 25.9, 23.6, 22.9, 21.6, 21.4, 20.51, 20.47 ppm.

IR (thin film): ν = 2965 (m), 2930 (s), 2858 (s), 2815 (m), 2718 (w), 2664 (w), 1968 (w), 1454 (m), 1451 (m), 1391 (w), 1364 (m), 1334 (w), 1310 (w), 1283 (w), 1265 (w), 1253 (w), 1227 (w), 1204 (m), 1149 (m), 1131 (s), 1091 (s), 1050 (m), 1034 (m), 1002 (m), 977 (m), 962 (m), 940 (w), 928 (w), 915 (w), 894 (w), 882 (w), 850 (m), 817 (m), 762 (w) cm^{-1} .

HRMS (EI, m/z): Calcd for $\text{C}_{16}\text{H}_{26}\text{O}_2$: 250.1933 g/mol (M^+). Found: 250.1928 g/mol.

nOe:

Allenylcyclobutane **11** (41 mg, 0.163 mmol) was weighed into an oven-dried borosilicate test tube equipped with a magnetic stir bar. The substrate was dissolved in toluene (0.33 mL, 0.5 M) and $[\text{RhCl}(\text{CO})_2]_2$ (1.3 mg, 0.0033 mmol) was added in one portion. The test tube was capped with a rubber septum. The resulting yellow solution was stirred under an atmosphere of CO (balloon, 1 atm) and was vented to a bubbler via an outlet needle for 15 min. The outlet needle was removed and the solution was then immersed into a thermostat-controlled oil bath preheated to 80 °C. The solution was stirred for 11 h at which time TLC indicated that the starting material was consumed. The solution was cooled to room temperature and was purified *via* flash chromatography on silica gel (gradient elution 5% Et_2O /pentane $\rightarrow$ 10% Et_2O /pentane). Product-containing fractions were combined and concentrated by rotary evaporation to yield ketone **12** (40.3 mg, 89%) as a colorless oil. Compound purity was established by elemental analysis.

Data for **12**:

TLC: R_f = 0.51 (16% EtOAc/pentane), one blue spot with *p*-anisaldehyde stain.

^1H NMR (400 MHz, CDCl_3): δ = 5.27 (s, 1H, C6-H), 3.89 (dt, J = 10.4, 4.8 Hz, 1H), 3.84 (dt, J = 10.6, 4.4 Hz, 1H), 3.66 (dd, J = 4.7, 4.6 Hz, 2H), 3.42 (s, 3H, OMe), 2.80 (dd, J = 11.3 Hz, 5.6 Hz, 1H, C1-H), 2.49-2.42 (m, 1H, C2-H), 2.38 (dd, J = 14.9, 12.4 Hz, 1H, C3 β -H), 2.11 (dd, J = 15.0, 3.1 Hz, 1H, C3 α -H), 1.94-1.84 (m, 1H), 1.87 (s, 3H, C4-Me), 1.76 (s, 3H, C5-Me), 1.66 (dd, J = 11.7, 5.8 Hz, 2H), 1.61-1.54 (m, 1H), 1.52-1.44 (m, 1H), 1.42-1.26 (m, 3H) ppm.

^{13}C NMR (125 MHz, CDCl_3): δ = 209.5, 157.4, 135.1, 133.2, 96.0, 70.8, 66.5, 59.2, 49.3, 36.2, 35.8, 31.7, 24.0, 23.9, 23.2, 22.3, 21.5 ppm.

IR (thin film): 3068 (w), 2922 (s), 2852 (m), 1678 (s), 1632 (s), 1584 (m), 1448 (m), 1372 (m), 1338 (w), 1279 (m), 1242 (m), 1199 (m), 1175 (s), 1125 (s), 1097 (s), 1055 (m), 1034 (m), 1016 (m), 996 (w), 975 (w), 961 (w), 934 (w), 892 (w), 879 (w), 855 (w), 819 (w), 805 (w), 777 (w), 694 (w), 664 (w) cm^{-1} .

HRMS (EI, m/z): Calcd for $\text{C}_{17}\text{H}_{26}\text{O}_3$: 278.1882 g/mol (M^+). Found: 278.1881 g/mol.

EA (atom%): Calcd for $\text{C}_{17}\text{H}_{26}\text{O}_3$: C 73.34, H 9.41. Found: C 73.55, H 9.41.

HMBC:

NaH (60% dispersion in mineral oil, 42 mg, 1.04 mmol) was added portion-wise over 2 min to a solution of allenyl alcohol **11i** (100 mg, 0.52 mmol) in DMF (2 mL). The mixture was stirred for 10 min at room temperature under a positive pressure of nitrogen. Benzyl bromide (0.052 mL, 0.44 mmol) was added drop-wise via syringe over 30 seconds. The reaction mixture was stirred at room temperature for 3 h. The reaction was quenched by the portion-wise addition over 2 min of water (3 mL). The product was extracted with pentane (3x5 mL). The combined organic extracts were washed with brine (3x5 mL), dried over MgSO_4 , vacuum-filtered through a fritted funnel, and then concentrated using a rotary evaporator. The residue was purified by flash

chromatography with silica gel (gradient elution 100% pentane $\rightarrow$ 2% Et₂O/pentane). Product-containing fractions were combined and concentrated using a rotary evaporator to yield allenyl ether **13** (111 mg, 89%) as a colorless liquid. The compound was chromatographically homogeneous.

Data for **13**:

TLC: R_f = 0.30 (49:1 pentane/EtOAc), one blue spot with *p*-anisaldehyde stain.

¹H NMR (500 MHz, CDCl₃): δ = 7.37-7.30 (m, 4H), 8.28-7.23 (m, 1H), 5.15 (sept, J = 2.7 Hz, 1H, C1-H), 4.38 (d, J = 11.5 Hz, 1H, C2-H), 4.22 (d, J = 11.5 Hz, 1H, C2-H), 2.44-2.36 (m, 1H, C3-H), 2.16 (dd, J = 9.9, 9.8 Hz, 1H, C4-H), 2.06-1.83 (m, 3H), 1.78 (d, J = 2.9 Hz, 3H, Me), 1.78-1.77 (m, 1H), 1.77 (d, J = 2.9 Hz, 3H, Me), 1.75-1.71 (m, 1H), 1.67-1.63 (m, 4H), 1.11-1.00 (m, 1H) ppm.

¹³C NMR (125 MHz, CDCl₃): δ = 201.2, 139.1, 128.2 (2C), 127.7 (2C), 127.2, 97.4, 93.5, 76.4, 65.7, 41.1, 34.5, 25.9, 23.8, 22.9, 21.7, 21.6, 20.6 (2C) ppm.

IR (thin film): ν = 3064 (w), 3030 (m), 2964 (s), 2930 (s), 2854 (s), 1967 (w), 1606 (w), 1497 (m), 1463 (m), 1453 (s), 1390 (m), 1390 (m), 1363 (m), 1252 (m), 1205 (s), 1144 (s), 1082 (s), 1039 (m), 1028 (m), 974 (m), 898 (w), 730 (s), 695 (s) cm⁻¹.

HRMS (EI, m/z): Calcd for C₂₀H₂₆O: 282.1984 g/mol (M⁺). Found: 282.1980 g/mol.

Allenyl cyclobutane **13** (36 mg, 0.127 mmol) was weighed into an oven-dried borosilicate test tube equipped with a magnetic stir bar. The substrate was dissolved in toluene (0.25 mL) and [RhCl(CO)₂]₂ (1 mg, 0.0026 mmol) was added in one portion. The test tube was capped with a rubber septum. The resulting yellow solution was stirred under an atmosphere of CO (balloon, 1 atm) and was vented to a bubbler via an outlet needle for 15 min. The outlet needle was removed and the solution was then immersed into a thermostat-controlled oil bath preheated to 80 °C. The solution was stirred for 22 h at which time TLC indicated that the starting material was consumed. The solution was cooled to room temperature and was purified *via* flash

chromatography on silica gel (gradient elution 100% pentane $\rightarrow$ 5% Et₂O/pentane). Product-containing fractions were combined and concentrated by rotary evaporation to yield ketone **14** (35.6 mg, 90%) as a colorless oil. The compound was chromatographically homogeneous.

Data for **14**:

TLC: R_f = 0.63 (pentane/ethyl acetate 47:3), one blue spot with *p*-anisaldehyde stain.

¹H NMR (400 MHz, CDCl₃): δ = 7.38–7.37 (m, 4H), 7.36–7.27 (m, 1H), 5.39 (s, 1H, C1-H), 4.80 (s, 2H, C2-CH₂), 2.85 (dd, J = 11.1, 5.6 Hz, 1H, C3-H), 2.50–2.36 (m, 2H, C4-H, C5-H), 2.15 (dd, J = 14.8, 2.1 Hz, 1H, C5-H), 1.96–1.88 (m, 1H), 1.89 (s, 3H, C6-Me), 1.76 (s, 3H, C7-Me), 1.72–1.26 (m, 7H) ppm.

¹³C NMR (125 MHz, CDCl₃): δ = 209.5, 157.3, 136.8, 135.7, 133.2, 128.5 (2C), 127.9, 127.5 (2C), 96.7, 70.8, 69.4, 49.2, 36.4, 31.7, 24.2, 23.9, 23.4, 22.4, 21.6 ppm.

IR (thin film): 3064 (w), 3032 (w), 2920 (s), 2851 (m), 1677 (s), 1632 (s), 1584 (m), 1497 (w), 1448 (m), 1371 (m), 1342 (w), 1279 (m), 1242 (s), 1196 (w), 1166 (s), 1138 (m), 1096 (m), 1015 (m), 974 (w), 946 (w), 934 (w), 862 (w), 821 (w), 805 (w), 736 (m), 696 (m) cm⁻¹.

HRMS (EI, m/z): Calcd for C₂₁H₂₆O₂: 310.1933 g/mol (M⁺). Found: 310.1931 g/mol.

Cyclobutanone **15ii**^{iv} (1.0 g, 7.2 mmol) was converted to allenyl cyclobutanol **15i** (1.11 g, colorless oil, 74%) according to the general procedure for the 1,2 addition of 1-bromo-3-methyl-1,2-butadiene into cyclobutanones (see: general procedure described for the synthesis of **2i**). The compound was chromatographically homogeneous.

Data for **15i**:

TLC: R_f = 0.29 (10% EtOAc/hexane), one blue spot with *p*-anisaldehyde stain.

^1H NMR (400 MHz, CDCl_3): δ = 5.17 (sept, J = 2.9 Hz, 1H, C1-H), 2.00-1.96 (m, 1H, C2-H), 1.93 (s, 2H), 1.82 (td, J = 12.5, 3.8 Hz, 1H), 1.72 (d, J = 2.9 Hz, 3H), 1.71 (d, J = 2.9 Hz, 3H), 1.67-1.38 (m, 6H), 1.29-1.18 (m, 2H), 1.07 (s, 3H, C3-H) ppm.

^{13}C NMR (100 MHz, CDCl_3): δ = 198.0, 99.9, 99.1, 73.3, 48.2, 48.1, 35.7, 31.2, 28.4, 22.3, 21.2, 20.8, 20.6, 20.4 ppm.

IR (thin film): ν = 3429 (broad), 2923 (s), 2860 (m), 1966 (w), 1449 (m), 1395 (w), 1373 (m), 1363 (m), 1306 (w), 1195 (m), 1163 (m), 1111 (w), 1009 (m), 974 (m), 900 (w), 856 (w) cm^{-1} .

HRMS (EI, m/z): Calcd for $\text{C}_{14}\text{H}_{22}\text{O}$: 206.1671 g/mol (M^+). Found: 206.1670 g/mol.

NaH (60% dispersion in mineral oil, 100 mg, 2.51 mmol) was added portion-wise over 2 min to a solution of allyl alcohol **15i** (259 mg, 1.25 mmol) in DMF (1.5 mL). The mixture was stirred for 45 min at room temperature under a positive pressure of nitrogen. 2-bromoethyl methyl ether (0.472 mL, 5.02 mmol) was added drop-wise via syringe over 5 seconds. The reaction mixture was stirred overnight at room temperature. The reaction was quenched by the portion-wise addition over 2 min of saturated aqueous NH_4Cl (20 mL). The product was extracted with diethyl ether (3x10 mL). The combined organic extracts were washed with brine (3x10 mL), dried over MgSO_4 , vacuum-filtered through a fritted funnel, and then concentrated using a rotary evaporator. The residue was purified by flash chromatography with silica gel (gradient elution 100% pentane $\rightarrow$ 5% Et_2O /pentane). Product-containing fractions were combined and concentrated using a rotary evaporator to yield allyl ether **15** (217 mg, 66%) as a colorless liquid. The compound was chromatographically homogeneous.

Data for **15**:

TLC: R_f = 0.84 (10% EtOAc /pentane), one blue spot with *p*-anisaldehyde stain.

^1H NMR (500 MHz, CDCl_3): δ = 5.05 (sept, J = 2.9 Hz, 1H, C1-H), 3.52-3.41 (m, 3H), 3.39-3.34 (m, 1H), 3.73 (s, 3H, OMe), 2.01 (dd, J = 14.5, 2.1 Hz, 1H, C2-H), 1.99 (d, J = 11.6 Hz, 1H, C4- α H), 1.84-1.76 (m, 1H), 1.75 (dd, J = 12.0, 2.4 Hz, 1H, C4 β -H), 1.71 (d, J = 2.7 Hz, 3H, Me), 1.70 (d, J = 2.6 Hz, 3H, Me), 1.68-1.59 (m, 2H), 1.50-1.41 (m, 2H), 1.36-1.28 (m, 3H), 1.08 (s, 3H, C3-Me) ppm.

^{13}C NMR (125 MHz, CDCl_3): δ = 201.4, 97.3, 95.2, 77.7, 76.7, 62.1, 59.0, 47.8, 41.6, 35.6, 29.4, 28.9, 21.8, 20.9, 20.6, 20.3, 20.2 ppm.

IR (thin film): ν = 2925 (s), 2862 (s), 1967 (w), 1454 (m), 1391 (w), 1364 (m), 1334 (w), 1308 (w), 1246 (m), 1199 (m), 1178 (m), 1132 (m), 1120 (m), 1084 (m), 1032 (w), 1004 (w), 977 (m), 930 (w), 888 (w) cm^{-1} .

HRMS (EI, m/z): Calcd for $\text{C}_{17}\text{H}_{28}\text{O}_2$: 264.2089 g/mol (M^+). Found: 264.2082 g/mol.

nOe:

Allenyl cyclobutane **15** (30 mg, 0.113 mmol) was weighed into an oven-dried borosilicate test tube equipped with a magnetic stir bar. The substrate was dissolved in *m*-xylene (0.23 mL) and $[\text{RhCl}(\text{CO})_2]_2$ (0.9 mg, 0.0023 mmol) was added in one portion. The test tube was capped with a rubber septum. The resulting yellow solution was stirred under an atmosphere of CO (balloon, 1 atm) and was vented to a bubbler via an outlet needle for 10 min. The outlet needle was removed and the solution was then immersed into a thermostat-controlled oil bath preheated to 80 °C. The solution was stirred for 20 h at which time TLC indicated that the starting material was consumed. The solution was cooled to room temperature and was purified *via* flash chromatography on silica gel (gradient elution 5% Et_2O /pentane $\rightarrow$ 10% Et_2O /pentane). Product-containing fractions were combined and concentrated by rotary evaporation to yield ketone **16** (17.5 mg, 53%) as a colorless oil. The compound was chromatographically homogeneous.

Data for **16**:

TLC: R_f = 0.58 (16% EtOAc /pentane), one blue spot with *p*-anisaldehyde stain.

^1H NMR (400 MHz, CDCl_3): δ = 5.24 (s, 1H, C1-H), 3.89-3.86 (m, 2H), 3.70-3.67 (m, 2H), 3.42 (s, 3H, OMe), 2.90 (d, J = 11.7 Hz, 1H, C4-H), 2.14 (dd, J = 8.2, 5.0 Hz, 1H, C2-H), 2.07 (d, J = 11.7 Hz, 1H, C4-H), 1.94 (s, 3H, C5-Me), 1.84-1.74 (m, 1H), 1.78 (s, 3H, C6-Me), 1.70-1.59 (m, 2H), 1.54-1.42 (m, 3H), 1.40-1.22 (m, 2H), 1.09 (s, 3H, C3-Me) ppm.

^{13}C NMR (125 MHz, CDCl_3): δ = 205.4, 160.4, 138.1, 132.7, 95.2, 70.9, 66.5, 59.1, 54.1, 48.6, 39.9, 38.3, 27.0, 25.4, 24.9, 22.6, 22.1, 21.2 ppm.

IR (thin film): 2925 (s), 2868 (m), 1675 (s), 1623 (s), 1582 (m), 1449 (m), 1379 (m), 1295 (w), 1265 (w), 1225 (m), 1194 (m), 1127 (s), 1102 (m), 1052 (w), 806 (w) cm^{-1} .

HRMS (EI, m/z): Calcd. for $\text{C}_{18}\text{H}_{28}\text{O}_3$: 292.2038 g/mol (M^+). Found: 292.2037 g/mol.

HMBC:

Cyclobutanone **17ii**^{iv} (2.5 g, 22.7 mmol) was converted to allenyl cyclobutanol **17i** (1.2 g, colorless oil, 30%) according to the general procedure for the 1,2 addition of 1-bromo-3-methyl-1,2-butadiene into cyclobutanones (see: general procedure described for the synthesis of **2i**). The compound was chromatographically homogeneous.

R_f: 0.21 (9:1 hexane / EtOAc); one spot.

^1H -NMR (500 MHz, CDCl_3): δ = 5.23 (sept, J = 2.9 Hz, 1H, C7-H), 2.68-2.64 (m, 1H, C1-H), 2.32-2.25 (m, 2H), 1.94 (dd, J = 13.3, 7.0 Hz, 1H, C6-H), 1.98 (br s, 1H, OH), 1.84-1.72 (m, 2H), 1.70 (d, J = 2.8 Hz, 6H, C8-Me, C9-Me), 1.53 (dd, J = 11.0, 5.1 Hz, 1H), 1.47 (dd, J = 12.4, 6.1 Hz, 1H), 1.48-1.36 (m, 2H) ppm.

^{13}C -NMR (125 MHz, CDCl_3): δ = 197.6, 99.7, 98.8, 69.3, 49.3, 39.4, 32.3, 30.3, 25.9, 25.5, 20.6 (2C) ppm.

IR (FTIR, film): ν = 3351 (br), 2946 (vs), 2853 (s), 1968 (w), 1466 (m), 1446 (s), 1393 (m), 1363 (m), 1252 (m), 1189 (s), 1115 (s), 1069 (m), 1007 (s), 908 (m) cm^{-1} .

HRMS calcd for $\text{C}_{12}\text{H}_{18}\text{O}$: 178.1358. Found: 178.1349.

To a solution alcohol **17i** (268 mg, 2.4 mmol) in DMF (8 mL) at room temperature was added NaH (60% in mineral oil, 151 mg, 3.8 mmol) portion wise over 5 minutes. The mixture was allowed to stir at room temperature for 45 minutes. This was followed by the addition of 2-bromoethyl methyl ether (2.2 mL, 23.6 mmol) *via* syringe over 20 seconds. The crude was allowed to stir at room temperature for 24 hours at which point TLC indicated the starting material was consumed. The reaction was quenched with sat. NaHCO_3 at room temperature. The mixture diluted with ether. The organic layer was washed with H_2O , brine, and dried over MgSO_4 . After removal of the solvent, the residue was purified *via* flash chromatography with silica gel (pentane / ether = 19 / 1) to afford glycol **17** (205 mg, 76%, one spot by TLC) as a colorless oil.

Data for **17**:

R_f: 0.36 (9:1 hexane / EtOAc); one spot.

^1H -NMR (500 MHz, CDCl_3): δ = 4.98 (sept, J = 2.9 Hz, 1H, C7-H), 3.45 (d, J = 6.0 Hz, 1H), 3.44 (d, J = 5.6 Hz, 1H), 3.32 (d, J = 5.6 Hz, 1H), 3.32 (s, 3H, -OMe), 3.30 (d, J = 6.0 Hz, 1H), 2.63-2.60 (m, 1H, C1-H), 2.27-2.25 (m, 1H, C5-H), 2.11 (ddd, J = 11.9, 8.4, 3.3 Hz, 1H, β -C6H), 1.93 (dt, J = 13.2, 7.4, 1.9 Hz, 1H, C2-H), 1.82-1.71 (m, 1H, C3-H), 1.68 (d, J = 3.0 Hz, 3H, C9-Me), 1.68 (d, J = 3.0 Hz, 3H, C8-Me), 1.49 (dd, J = 12.1, 7.0 Hz, 1H, α -C6H), 1.45-1.32 (m, 4H) ppm.

^{13}C -NMR (125 MHz, CDCl_3): δ = 200.7, 97.6, 95.2, 74.2, 72.0, 61.8, 58.9, 47.8, 35.3, 32.2, 30.8, 25.8, 25.7, 20.5, 20.4 ppm.

IR (FTIR, film): ν = 2946 (vs), 2932 (vs), 2874 (s), 1968 (w), 1447 (m), 1390 (w), 1364 (w), 1252 (w), 1240 (w), 1196 (s), 1119 (vs), 1086 (s), 969 (w), 935 (w) cm^{-1} .

HRMS calcd for $\text{C}_{15}\text{H}_{24}\text{O}_2$: 236.1776. Found: 236.1776.

nOe:

Allenyl cyclobutane **17** (60 mg, 0.25 mmol) was weighed into an oven-dried borosilicate test tube equipped with a magnetic stir bar. The substrate was dissolved in *m*-xylene (2.5 mL) and $[\text{RhCl(CO)}_2]_2$ (9.7 mg, 0.025 mmol) was added in one portion. The test tube was capped with a rubber septum. The resulting yellow solution was stirred under an atmosphere of CO (balloon, 1 atm) and was vented to a bubbler via an outlet needle for 10 min. The outlet needle was removed and the solution was then immersed into a thermostat-controlled oil bath preheated to 85 °C. The solution was stirred for 40 h at which time TLC indicated that the starting material was consumed. The solution was cooled to room temperature and concentrated by rotary evaporation. The residue was purified *via* flash chromatography on silica gel (10% Et₂O/pentane). Fractions containing **18** were combined and concentrated by rotary evaporation to yield ketone **18** (15.9 mg, 24%) as a yellow oil. The compound was chromatographically homogeneous. Fractions containing **19** were combined and concentrated by rotary evaporation to yield ketone **19** (23.1 mg, 32%) as a yellow oil. The compound was chromatographically homogeneous.

Data for **18**:

TLC: R_f = 0.21 (10% EtOAc/hexane), one blue spot with *p*-anisaldehyde stain.

¹H NMR (500 MHz, CDCl₃): δ = 5.32 (s, 1H, C1-H), 3.90-3.82 (m, 2H), 3.66 (dd, J = 5.2, 5.0 Hz, 2H), 3.40 (s, 3H, -OMe), 3.19 (ddd, J = 13.9, 10.3, 5.5 Hz, 1H, C4-H), 2.72-2.63 (m 1H, C3-H), 2.21 (d, J = 8.7 Hz, 2H, C2-H, C2-H), 2.19-2.12 (m, 1H), 1.87-1.80 (m, 1H), 1.84 (s, 3H, C5-H), 1.76 (s, 3H, C6-H), 1.73-1.63 (m, 1H), 1.59-1.51 (m, 1H), 1.50-1.44 (m, 1H), 1.25-1.17 (m, 1H) ppm.

¹³C NMR (125 MHz, CDCl₃): δ = 208.7, 158.9, 135.1, 134.3, 95.5, 70.8, 66.6, 59.2, 53.8, 46.5, 35.5, 32.5, 26.1, 25.4, 22.7, 21.6 ppm.

IR (thin film): ν = 2929 (s), 2870 (s), 2819 (w), 1679 (s), 1632 (s), 1590 (m), 1448 (s), 1374 (m), 1359 (m), 1289 (w), 1268 (m), 1235 (s), 1210 (s), 1160 (s), 1123 (s), 1074 (m), 1055 (m), 1035 (m), 967 (w), 857 (m), 808 (m) cm^{-1} .

HRMS (EI, m/z): Calcd for $\text{C}_{16}\text{H}_{24}\text{O}_3$: 265.1804 g/mol (M^+). Found: 265.1798 g/mol.

nOe:

Data for **19**:

TLC: R_f = 0.14 (10% EtOAc/hexane), one blue spot with *p*-anisaldehyde stain.

^1H NMR (500 MHz, CDCl_3): δ = 5.21 (s, 1H, C1-H), 3.89-3.82 (m, 2H), 3.70-3.63 (m, 2H), 3.41 (s, 3H, OMe), 2.78 (dd, J = 15.3, 7.2 Hz, 1H, C4-H), 2.59 (ddd, J = 11.6, 4.5, 0.8 Hz, 1H, C2 β -H), 2.54-2.47 (m, 1H, C3-H), 2.44 (ddd, J = 11.6, 8.0, 0.7 Hz, 1H, C2 α -H), 2.05 (s, 3H, C5-Me), 1.89-1.78 (m, 2H), 1.80 (s, 3H, C6-Me), 1.76-1.64 (m, 2H), 1.47-1.36 (m, 2H) ppm.

^{13}C NMR (125 MHz, CDCl_3): δ = 204.4, 159.5, 143.8, 131.2, 95.9, 70.9, 66.6, 59.2, 46.1, 45.4, 40.8, 31.8, 29.9, 24.1, 23.5, 23.1 ppm.

IR (thin film): ν = 2928 (s), 2872 (s), 1676 (s), 1627 (s), 1582 (m), 1449 (m), 1368 (m), 1297 (m), 1246 (m), 1198 (s), 1182 (s), 1124 (s), 1098 (m), 1035 (m) cm^{-1} .

MS (ESI, m/z): Calcd for $\text{C}_{16}\text{H}_{24}\text{O}_3$: 265.2 g/mol (M^+). Found: 287.1 g/mol ($\text{M}+\text{Na}^+$).

nOe:

Cyclobutanone **20ii**^{iv} (1.63 g, 12 mmol) was converted to allenyl cyclobutanol **20i** (1.618 g, white solid, 66%) according to the general procedure for the 1,2 addition of 1-bromo-3-methyl-1,2-butadiene into cyclobutanones (see: general procedure described for the synthesis of **2i**). The compound was chromatographically homogeneous.

Data for **20i**:

TLC: R_f = 0.37 (10% EtOAc/pentane), one blue spot with *p*-anisaldehyde stain.

¹H NMR (500 MHz, CDCl₃): δ = 5.24 (sept, J = 2.9 Hz, 1H, C1-H), 2.67-2.23 (m, 2H), 2.21-2.18 (m, 1H), 2.14-2.09 (m, 1H, C2-H), 2.04 (d, J = 1.4 Hz, 1H), 1.91-1.84 (m, 1H), 1.74 (d, J = 2.9 Hz, 3H, Me), 1.73 (d, J = 2.9 Hz, 3H, Me), 1.74-1.69 (m, 2H), 1.50-1.45 (m, 2H), 1.24-1.21 (m, 1H), 1.04-1.02 (m, 2H) ppm.

¹³C NMR (125 MHz, CDCl₃): δ = 197.3, 100.2, 99.4, 71.7, 53.6, 38.9, 38.0, 35.4, 33.7, 33.1, 28.2, 28.1, 20.8 (2C) ppm.

IR (thin film): ν = 3369 (broad), 2946 (s), 2868 (s), 1968 (w), 1480 (w), 1459 (m), 1389 (m), 1363 (m), 1290 (w), 1254 (w), 1236 (m), 1159 (m), 1096 (m), 1071 (m), 998 (m) cm⁻¹.

HRMS (EI, m/z): Calcd for C₁₄H₂₀O: 204.1514 g/mol (M⁺). Found: 204.1516 g/mol.

Melting point: 50.5-51.0 °C.

NaH (60% dispersion in mineral oil, 117 mg, 2.94 mmol) was added portion-wise over 2 min to a solution of allenyl alcohol **20i** (300 mg, 1.47 mmol) in DMF (3.5 mL). The mixture was stirred for 45 min at room temperature under a positive pressure of nitrogen. 2-Bromoethyl methyl ether (0.37 mL, 3.9 mmol) was added drop-wise via syringe over 30 seconds. The reaction mixture was stirred at room temperature for 24 h. The reaction was quenched by the portion-wise addition over 2 min of saturated aqueous sodium hydrogen carbonate (30 mL). The product was extracted with diethyl ether (3x10 mL). The combined organic extracts were washed with brine (3x10 mL), dried over MgSO₄, vacuum-filtered through a fritted funnel, and then concentrated using a rotary evaporator. The residue was purified by flash chromatography with

silica gel (gradient elution 100% pentane $\rightarrow$ 5% Et₂O/pentane). Product-containing fractions were combined and concentrated using a rotary evaporator to yield allenyl ether **20** (200 mg, 52%) as a colorless liquid. The compound was chromatographically homogeneous.

Data for **20**:

TLC: R_f = 0.64 (10% EtOAc/pentane), one blue spot with *p*-anisaldehyde stain.

¹H NMR (500 MHz, CDCl₃): δ = 4.99 (sept, J = 2.8 Hz, 1H, C1-H), 3.52-3.50 (m, 2H), 3.41-3.22 (m, 2H), 3.38 (s, 3H, OMe), 2.28-2.25 (m, 1H), 2.16 (d, J = 6.5 Hz, 1H, C2-H), 2.13-2.09 (m, 1H), 2.08 (ddd, J = 12.9, 4.6, 2.1 Hz, 1H), 2.03-2.00 (m, 1H), 1.89-1.84 (m, 1H, C3-H), 1.74 (d, J = 2.8 Hz, 3H, Me), 1.72 (d, J = 2.8 Hz, 3H, Me), 1.66 (dd, J = 13.1, 5.4 Hz, 1H), 1.48-1.42 (m, 2H), 1.16 (dt, J = 10.1, 1.3 Hz, 1H), 1.04-0.98 (m, 2H) ppm.

¹³C NMR (125 MHz, CDCl₃): δ = 200.1, 98.0, 95.9, 77.1, 72.2, 62.4, 59.1, 51.7, 39.0, 35.7, 33.7, 33.32, 33.29, 28.3, 28.0, 20.7, 20.5 ppm.

IR (thin film): ν = 2936 (s), 2869 (m), 1728 (w), 1459 (m), 1364 (w), 1291 (w), 1291 (w), 1237 (w), 1199 (w), 1160 (m), 1129 (s), 1098 (m), 1073 (m), 1002 (m), 945 (w), 847 (w) cm⁻¹.

HRMS (EI, m/z): Calcd for C₁₇H₂₆O₂: 262.1933 g/mol (M⁺). Found: 262.1927 g/mol.

nOe:

Allenyl cyclobutane **20** (32 mg, 0.122 mmol) was weighed into an oven-dried borosilicate test tube equipped with a magnetic stir bar. The substrate was dissolved in *m*-xylene (1.22 mL, 0.5 M) and [RhCl(CO)₂]₂ (4.7 mg, 0.0122 mmol) was added in one portion. The test tube was capped with a rubber septum. The resulting yellow solution was stirred under an atmosphere of CO (balloon, 1 atm) and was vented to a bubbler via an outlet needle for 105 min. The outlet needle was removed and the solution was then immersed into a thermostat-controlled oil bath preheated to 80 °C. The solution was stirred for 44 h at which time TLC indicated that the

starting material was consumed. The solution was cooled to room temperature and was purified *via* flash chromatography on silica gel (gradient elution 5% Et₂O/pentane → 10% Et₂O/pentane). Product-containing fractions were combined and concentrated by rotary evaporation to yield ketone **21** (30 mg, 85%) as a colorless oil. The compound was chromatographically homogeneous.

TLC: R_f = 0.58 (15% EtOAc/pentane), one blue spot with *p*-anisaldehyde stain.

¹H NMR (500 MHz, CDCl₃): δ = 5.21 (s, 1H, C1-H), 3.92-3.80 (m, 2H), 3.76-3.65 (m, 2H), 3.44 (s, 3H, OMe), 2.77 (d, J = 12.1, 12.1 Hz, 1H, C4 β -H), 2.76 (s, 1H), 2.60 (d, J = 9.3 Hz, 1H, C2-H), 2.37 (dd, J = 11.9, 3.1 Hz, 1H, C4 α -H), 2.13 (s, 3H), 2.20-1.95 (m, 1H), 1.92-1.12 (m, 1H, C3-H), 1.82 (s, 3H), 1.58-1.43 (m, 2H), 1.34-1.29 (m, 1H), 1.28-1.21 (m, 1H), 1.19-1.12 (m, 1H), 1.07 (dt, J = 9.8, 1.5 Hz, 1H) ppm.

¹³C NMR (125 MHz, CDCl₃): δ = 202.9, 157.9, 146.0, 130.0, 97.3, 71.0, 66.8, 59.3, 49.3, 46.6, 44.9, 43.0, 39.3, 35.1, 30.3, 28.0, 24.0, 23.4 ppm.

IR (thin film): 2950 (s), 2872 (s), 1678 (s), 1631 (s), 1572 (m), 1453 (m), 1368 (w), 1298 (w), 1234 (m), 1214 (m), 1184 (m), 1199 (m), 1127 (s), 1079 (m), 1004 (w), 918 (w), 857 (w), 802 (w) cm⁻¹.

LRMS (EI, m/z): Calcd for C₁₈H₂₆O₃: 290 g/mol (M⁺). Found: 290 g/mol.

Enol ether hydrolysis - support for the regiochemical assignment of cycloadducts **12** and **21**

Cycloheptenone **12** (10.5 mg, 0.038 mmol) was weighed into a round bottom flask equipped with a stir bar and then was dissolved in CHCl₃ (1 mL). HCl (1% in MeOH, 10 μ L) was added in one portion and the reaction mixture was stirred at room temperature for 2 h and then at 80°C in a thermostat-controlled oil bath for 3 min. The solution was cooled to room temperature and was purified *via* flash chromatography on silica gel (gradient elution 4% Et₂O/pentane → 14%

Et₂O/pentane). Product-containing fractions were combined and concentrated by rotary evaporation to yield cycloheptadienone **12-hydrolyzed** (7.3 mg, 87%) as a colorless oil. The compound was chromatographically homogeneous.

Data for **12-hydrolyzed**:

TLC: R_f = 0.41 (16% EtOAc/pentane), one blue spot with *p*-anisaldehyde stain.

¹H NMR (500 MHz, CDCl₃): δ = 3.36 (d, J = 18.1 Hz, 1H, C4-H), 3.17 (d, J = 18.3 Hz, 1H, C4-H), 2.85 (dd, J = 9.9, 5.0 Hz, 1H, C1-H), 2.74 (dd, J = 12.8, 10.1 Hz, 1H, C3 α -H), 2.51 (dd, J = 12.9, 5.4 Hz, 1H, C3 β -H), 2.29-2.22 (m, 1H, C2-H), 2.13-2.06 (m, 1H), 1.99 (s, 3H, C5-Me), 1.84 (s, 3H, C6-Me), 1.82-1.73 (m, 1H), 1.69-1.61 (m, 2H), 1.57-1.46 (m, 2H), 1.40-1.32 (m, 1H), 1.26-1.16 (m, 1H) ppm.

¹³C NMR (125 MHz, CDCl₃): δ = 209.5, 206.7, 141.81, 129.4, 50.1, 46.8, 44.1, 34.6, 31.5, 25.7, 24.4, 22.9, 22.8, 21.8 ppm.

IR (thin film): 2931 (s), 2854 (m), 1710 (s), 1682 (s), 1615 (w), 1446 (m), 1373 (w), 1339 (w), 1319 (w), 1278 (w), 1232 (m), 1168 (m), 1123 (w), 1066 (w), 1037 (w), 1004 (w), 911 (w), 852 (w), 799, (w), 767 (w) cm⁻¹.

HRMS (EI, m/z): Calcd for C₁₄H₂₀O₂: 220.1463 g/mol (M⁺). Found: 220.1468 g/mol.

HMBC:

nOe:

Cycloheptenone **21** (16 mg, 0.057 mmol) was dissolved in CHCl_3 (1 mL). HCl (1% in MeOH, 10 μL) was added in one portion and the reaction mixture was stirred at room temperature for 3 min at which point TLC indicated that the starting material had been consumed. The solution was cooled to room temperature and was purified *via* flash chromatography on silica gel (gradient elution 100% pentane $\rightarrow$ 5% Et_2O /pentane $\rightarrow$ 10% Et_2O /pentane). Product-containing fractions were combined and concentrated by rotary evaporation to yield cycloheptadienone **21-hydrolyzed** (11.5 mg, 87%) as a colorless oil. The compound was chromatographically homogeneous.

Data for **21-hydrolyzed**:

TLC: R_f = 0.70 (12% EtOAc /pentane), one blue spot with *p*-anisaldehyde stain.

^1H NMR (500 MHz, CDCl_3): δ = 3.50 (d, J = 18.4 Hz, 1H, C1-H), 2.93 (d, J = 18.4 Hz, 1H, C1-H), 2.71 (d, J = 1.7 Hz, 1H), 2.62 (dd, J = 9.5, 1.5 Hz, 1H, C2-H), 2.42 (dd, J = 15.9, 2.6 Hz, 1H, C4-H), 2.34 (dd, J = 15.9, 14.0 Hz, 1H, C4-H), 2.15-1.99 (m, 2H, C3-H), 1.98 (d, J = 2.0 Hz, 3H, C5-HMe), 1.83 (d, J = 1.2 Hz, 3H, C6-Me), 1.56-1.54 (m, 2H), 1.41-1.36 (m, 1H), 1.26-1.21 (m, 1H), 1.17-1.13 (m, 2H) ppm.

^{13}C NMR (125 MHz, CDCl_3): δ = 210.0, 204.8, 142.9, 128.6, 58.4, 46.7, 44.5, 43.3, 41.7, 37.5, 34.5, 30.0, 26.9, 22.5, 21.7 ppm.

IR (thin film): 2950 (m), 2871 (m), 1699 (s), 1636 (m), 1449 (w), 1372 (w), 1288 (w), 1250 (w), 1226 (w), 1200 (w), 1180 (w), 1070 (w), 1041 (w), 998 (w), 933 (w), 876 (w), 784 (w) cm^{-1} .

HRMS (EI, m/z): Calcd for $\text{C}_{15}\text{H}_{20}\text{O}_2$: 232.1463 g/mol (M^+). Found: 232.1462 g/mol.

Melting point: 79-80 $^\circ\text{C}$.

Figure 1. ORTEP Diagram of **21-hydrolyzed** (CCDC 299569).

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