Supporting Information

Rh(I)-Catalyzed [2+2+1] Cycloadditions of 1,3-Dienes, Alkenes, and CO

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General methods. 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, as described by Still and co-workers.¹ Silica gel 60, 230-400 mesh was purchased from EM Science. $[\text{RhCl}(\text{CO})_2]_2$ and $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ were purchased from Strem Chemicals. AgSbF_6 was purchased from Aldrich Chemical Co. 1,2-dichloroethane (DCE) (99+%, ACS reagent grade) was purchased from Aldrich Chemical Co. and was stored over 4Å molecular sieves (activated in a vacuum oven). Carbon monoxide (2.5 grade) was purchased from Praxair.

NMR spectra were measured on a Varian INOVA 500 (^1H at 500 MHz, ^{13}C at 125 MHz) or Varian MERCURY 400 (^1H at 400 MHz, ^{13}C at 100 MHz) magnetic resonance spectrometer. Data for ^1H NMR spectra are reported as follows: chemical shift (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, septetd = septet of doublets, 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 ^{13}C 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. Low-resolution mass spectra (LRMS) were recorded at the Stanford University mass spectrometry facility.

Procedures and Characterization:

Alkenylcyclopentanone **2** and enone **3**:

In an oven-dried borosilicate glass test tube, equipped with a stir bar and capped with a rubber septum, diene-ene **1** (0.019 g, 0.075 mmol) was dissolved in DCE (0.75 mL, 0.10 M). $[\text{RhCl}(\text{CO})_2]_2$ (0.0015 g, 0.0038 mmol) was added and the solution was stirred under a balloon of

CO, vented to a bubbler, for 15 min. The reaction mixture was stirred vigorously under 1 atm of CO at 80°C for 3 h. The mixture was purified by flash column chromatography on silica gel (gradient elution: 0%→20% Et₂O in pentane). Product-containing fractions were concentrated to give **2** in 99% yield as a colorless oil.

Solvent-free conditions:

In an oven-dried borosilicate glass test tube, equipped with a stir bar and capped with a rubber septum, diene-ene **1** (0.023 g, 0.090 mmol) was added. [RhCl(CO)₂]₂ (0.0017 g, 0.0045 mmol) was added and the solution was stirred under a balloon of CO, vented to a bubbler, for 15 min. The reaction mixture was stirred vigorously under 1 atm of CO at 80°C for 1.75 h. The mixture was purified by flash column chromatography on silica gel (gradient elution: 0%→20% Et₂O in pentane). Product-containing fractions were concentrated to give **2** in 89% yield as a colorless oil.

Characterization for **2**:

¹H NMR (500MHz, CDCl₃, 25°C) δ = 4.94 (dq, *J* = 1.5 Hz, *J* = 1.5 Hz, 1H), 4.80 (s, 1H), 3.76 (s, 3H), 3.74 (s, 3H), 2.84-2.67 (m, 5H), 2.51 (dd, *J* = 19.2 Hz, *J* = 8.5 Hz, 1H), 2.25 (dd, *J* = 19.2 Hz, *J* = 3.0 Hz, 1H), 2.16 (dd, *J* = 13.5 Hz, *J* = 4.5 Hz, 1H), 1.98 (dd, *J* = 13.5 Hz, *J* = 9.5 Hz, 1H), 1.71 (s, 3H) ppm. **¹³C NMR** (125 MHz, CDCl₃, 25°C) δ = 217.2, 172.5, 172.4, 140.9, 114.5, 62.5, 61.5, 52.95, 52.92, 44.7, 42.9, 40.9, 39.6, 37.6, 20.4 ppm. **IR** (thin film) 3078 (w), 2954 (m), 1732 (s), 1681 (w), 1644 (w), 1435 (m), 1376 (w), 1253 (m), 1199 (m), 1175 (m), 1067 (w), 932 (w), 899 (w), 860 (w), 820 (w) cm⁻¹. **HRMS** Calculated for C₁₅H₂₀O₅: 280.1311. Found: 280.1300. **TLC** R_f = 0.11 (10% ethyl acetate/pentane) one spot.

Characterization for **3**:

¹H NMR (500MHz, CDCl₃, 25°C) δ = 3.77 (s, 3H), 3.70 (s, 3H), 3.48-3.40 (m, 1H), 2.88 (ddd, *J* = 13.0 Hz, *J* = 8.0 Hz, *J* = 1.5 Hz, 1H), 2.74-2.62 (m, 1H), 2.64 (ddd, *J* = 12.5 Hz, *J* = 11.0 Hz, *J* = 1.5 Hz, 1H), 5.59 (dd, *J* = 18.5 Hz, *J* = 9.5 Hz, 1H), 2.212 (dd, *J* = 18.5 Hz, *J* = 4.5 Hz, 1H), 2.209 (d, *J* = 1.5 Hz, 3H), 1.97 (dd, *J* = 12.5 Hz, *J* = 7.0 Hz, 1H), 1.93 (dd, *J* = 13.5 Hz, *J* = 9.0 Hz, 1H), 1.87 (d, *J* = 1.0 Hz, 3H) ppm. **¹³C NMR** (125 MHz, CDCl₃, 25°C) δ = 206.5, 172.3, 171.8, 149.8, 135.1, 61.7, 52.9, 52.7, 45.5, 44.7, 41.2, 34.8, 29.7, 24.6, 10.7 ppm. **IR** (thin film) 2953 (m), 2924 (m), 2851 (w), 1732 (s), 1704 (s), 1622 (m), 1436 (m), 1368 (w), 1253 (s), 1197 (s), 1173 (s), 1090 (m), 1065 (w), 1034 (w), 968 (w), 936 (w), 902 (w), 821 (w) cm⁻¹. **HRMS** Calculated for C₁₅H₂₀O₅: 280.1311. Found: 280.1304. **TLC** R_f = 0.09 (10% ethyl acetate/pentane) one spot.

Cyclohexene **6**:

In an oven-dried borosilicate glass test tube, equipped with a stir bar and capped with a rubber septum, diene-ene **1** (0.020 g, 0.079 mmol) was dissolved in DCE (0.80 mL, 0.10 M). [(COD)Rh(naphth)]SbF₆ (0.0046g, 0.0080 mmol) was added and the solution was stirred under a balloon of CO, vented to a bubbler, for 15 min. The reaction mixture was stirred vigorously

under 1 atm of CO at 80°C for 3 h. The mixture was purified by flash column chromatography on silica gel (gradient elution: 0%→20% Et₂O in pentane). Product-containing fractions were concentrated to give **6** in 76% yield as a colorless oil.

6 is a known compound, see ref. 2.

Alkenylcyclopentanone **8**:

In an oven-dried borosilicate glass test tube, equipped with a stir bar and capped with a rubber septum, diene-ene **7** (0.026 g, 0.091 mmol) was dissolved in DCE (0.90 mL, 0.10 M). [RhCl(CO)₂]₂ (0.0018 g, 0.0046 mmol) was added and the solution was stirred under a balloon of CO, vented to a bubbler, for 15 min. The reaction mixture was stirred vigorously under 1 atm of CO at 80°C for 3.75 h. The mixture was purified by flash column chromatography on silica gel (gradient elution: 0%→20% Et₂O in pentane). Product-containing fractions were concentrated to give **8** in 84% yield as a colorless oil.

Solvent-free conditions:

In an oven-dried borosilicate glass test tube, equipped with a stir bar and capped with a rubber septum, diene-ene **7** (0.053 g, 0.191 mmol) was added. [RhCl(CO)₂]₂ (0.0037 g, 0.0095 mmol) was added and the solution was stirred under a balloon of CO, vented to a bubbler, for 15 min. The reaction mixture was stirred vigorously under 1 atm of CO at 80°C for 1.75 h. The mixture was purified by flash column chromatography on silica gel (gradient elution: 0%→20% Et₂O in pentane). Product-containing fractions were concentrated to give **8** in 83% yield as a colorless oil.

Scalable conditions:

In a 100 mL oven-dried round bottom flask, equipped with a stir bar and capped with a rubber septum, diene-ene **7** (1.022 g, 3.645 mmol) was dissolved in DCE (36.5 mL, 0.10 M). [RhCl(CO)₂]₂ (0.0354 g, 0.0911 mmol) was added and the solution was stirred under a balloon of CO, vented to a bubbler, for 15 min. The reaction mixture was stirred vigorously under 1 atm of CO at 80°C for 14 h. The mixture was purified by flash column chromatography on silica gel (gradient elution: 0%→20% Et₂O in pentane). Product-containing fractions were concentrated to give **8** in 89% yield as a colorless oil.

Characterization for **8**:

¹H NMR (500MHz, CDCl₃, 25°C) δ = 4.96 (d, *J* = 1.0 Hz, 1H), 4.74 (s, 1H), 3.76 (s, 3H), 3.73 (s, 3H), 2.88-2.81 (m, 1H), 2.82-2.68 (m, 2H), 2.73 (d, *J* = 7.0 Hz, 1H), 2.70 (dd, *J* = 14.5 Hz, *J* = 7.5 Hz, 1H), 2.58 (dd, *J* = 19.0 Hz, *J* = 9.0 Hz, 1H), 2.29 (septetd, *J* = 7.0 Hz, *J* = 1.0 Hz, 1H), 2.22 (ddd, *J* = 19.0 Hz, *J* = 4.5 Hz, *J* = 1.0 Hz, 1H), 2.13 (dd, *J* = 14.0 Hz, *J* = 5.5 Hz, 1H), 2.00 (dd, *J* = 13.5 Hz, *J* = 9.0 Hz, 1H), 1.05 (d, *J* = 7.0 Hz, 3H), 1.03 (d, *J* = 6.5 Hz, 3H) ppm. **¹³C NMR** (125 MHz, CDCl₃, 25°C) δ = 217.2, 172.23, 172.15, 152.9, 109.5, 61.2, 60.0, 52.74, 52.71, 46.3, 42.9, 40.7, 39.6, 37.2, 33.1, 22.0, 21.8 ppm. **IR** (thin film) 2958 (m), 2872 (w),

1732 (s), 1436 (m), 1271 (m), 1253 (m), 1198 (m), 1174 (m), 1131 (m), 1095 (m), 1064 (w), 1021 (w), 974 (w), 935 (w), 897 (w) cm^{-1} . **HRMS** Calculated for $\text{C}_{17}\text{H}_{24}\text{O}_5$: 308.1624. Found: 308.1613. **TLC** R_f = 0.12 (10% ethyl acetate/pentane), one spot.

Exo-enones **E-11** and **Z-11**:

In an oven-dried borosilicate glass test tube, equipped with a stir bar and capped with a rubber septum, diene-ene **9** (0.024 g, 0.101 mmol) was dissolved in DCE (1.0 mL, 0.10 M). $[\text{RhCl}(\text{CO})_2]_2$ (0.0020 g, 0.00504 mmol) was added and the solution was stirred under a balloon of CO, vented to a bubbler, for 15 min. The reaction mixture was stirred vigorously under 1 atm of CO at 80°C for 19 h. ^1H NMR of the crude reaction shows that the mixture contains approximately 58% **10** and 13% **Z-11**. The mixture was purified by flash column chromatography on silica gel (gradient elution: 5% $\rightarrow$ 20% Et_2O in pentane). **10** was not stable to silica gel and upon purification **Z-11** and **E-11** were obtained. Product-containing fractions were concentrated to give **E-11** in 39% yield and **Z-11** in 32% yield, both as colorless oils.

Characterization for **Z-11**:

^1H NMR (500MHz, CDCl_3 , 25°C) δ = 6.07 (qd, J = 7.5 Hz, J = 3.0 Hz, 1H), 3.75 (s, 3H), 3.69 (s, 3H), 3.32-3.25 (m, 1H), 2.82-2.70 (m, 1H), 2.80 (ddd, J = 14.0 Hz, J = 8.5 Hz, J = 1.0 Hz, 1H), 2.58 (dd, J = 9.0 Hz, J = 4.5 Hz, 1H), 2.55 (d, J = 9.0 Hz, 1H), 2.25 (dd, J = 18.5 Hz, J = 3.8 Hz, 1H), 2.17 (dd, J = 14.5 Hz, J = 6.0 Hz, 1H), 2.15 (dd, J = 7.5 Hz, J = 3.0 Hz, 3H), 1.96 (dd, J = 13.5 Hz, J = 8.5 Hz, 1H) ppm. ^{13}C NMR (125 MHz, CDCl_3 , 25°C) δ = 208.1, 172.4, 171.9, 139.6, 138.2, 61.7, 52.9, 52.8, 45.7, 44.8, 41.6, 41.0, 36.3, 14.5 ppm. **IR** (thin film) 2953 (m), 2850 (w), 1732 (s), 1713 (s), 1637 (m), 1435 (m), 1411 (w), 1374 (w), 1347 (w), 1267 (s), 1203 (s), 1174 (s), 1116 (m), 1097 (m), 1062 (w), 1003 (w), 966 (w), 892 (w), 821 (w), 702 (w) cm^{-1} . **LRMS** Mass hit for $\text{C}_{14}\text{H}_{18}\text{O}_5$ (266 m/z). **TLC** R_f = 0.45 (20% ethyl acetate/pentane). **nOe**: Ha $\rightarrow$ Hb (9.9%), Hc $\rightarrow$ Ha (1.9%), Hc $\rightarrow$ Hd (7.7%).

Characterization for **E-11**:

^1H NMR (500MHz, CDCl_3 , 25°C) δ = 6.67 (qd, J = 7.5 Hz, J = 2.5 Hz, 1H), 3.78 (s, 3H), 3.70 (s, 3H), 3.45 (ddd, J = 8.5 Hz, J = 8.5 Hz, J = 8.5 Hz, 1H), 2.92 (ddd, J = 13.0 Hz, J = 8.5, J = 1.3 Hz, 1H), 2.81 (dddd, J = 9.0 Hz, J = 9.0 Hz, J = 9.0 Hz, J = 9.0 Hz, J = 4.5 Hz, 1H), 2.66 (ddd, J = 13.5 Hz, J = 8.0 Hz, J = 1.0 Hz, 1H), 2.59 (dd, J = 19.5 Hz, J = 10 Hz, 1H), 2.24 (dd, J = 19.5 Hz, J = 9.0 Hz, 1H), 1.99 (dd, J = 13.5 Hz, J = 8.0 Hz, 1H), 1.95 (dd, J = 13.5 Hz, J = 8.5 Hz, 1H), 1.85 (dd, J = 7.0 Hz, J = 1.8 Hz, 3H) ppm. ^{13}C NMR (125 MHz, CDCl_3 , 25°C) δ = 206.1, 172.1, 171.6, 142.1, 133.9, 62.0, 52.9, 52.8, 43.8, 42.2, 41.3, 40.5, 35.7, 15.2 ppm. **IR** (thin film) 2954 (m), 2924 (m), 2852 (w), 1732 (s), 1645 (m), 1436 (m), 1251 (s), 1219 (s), 1173

(m), 1092 (w), 1065 (w), 964 (w), 828 (w) cm^{-1} . **HRMS** Calculated for $\text{C}_{14}\text{H}_{18}\text{O}_5$: 266.1154. Found: 266.1149. **TLC** R_f = 0.27 (20% ethyl acetate/pentane), one spot. **nOe**: Ha $\rightarrow$ Hb (7.3%), Hc $\rightarrow$ Hb (2.0%) Hc $\rightarrow$ Hd (5.5%).

Alkenylcyclopentanone **13**:

In an oven-dried borosilicate glass test tube, equipped with a stir bar and capped with a rubber septum, diene-ene **12** (0.031 g, 0.105 mmol) was dissolved in DCE (1.0 mL, 0.10 M). $[\text{RhCl}(\text{CO})_2]_2$ (0.0020 g, 0.0053 mmol) was added and the solution was stirred under a balloon of CO, vented to a bubbler, for 15 min. The reaction mixture was stirred vigorously under 1 atm of CO at 80°C for 22.5 h. The mixture was purified by flash column chromatography on silica gel (gradient elution: 0% $\rightarrow$ 20% Et_2O in pentane). Product-containing fractions were concentrated to give **13** in 92% yield as a colorless oil.

Characterization for **13**:

^1H NMR (500 MHz, CDCl_3 , 25 °C) δ = 4.99 (s, 1H), 4.74 (s, 1H), 3.76 (s, 3H), 3.72 (s, 3H), 2.87 (d, J = 9.5 Hz, 1H), 2.81 (dd, J = 14.5 Hz, J = 7.5 Hz, 1H), 2.52 (d, J = 19.0 Hz, 1H), 2.47 (d, J = 14.5 Hz, 1H), 2.39 (ddd, J = 9.5 Hz, J = 7.0 Hz, J = 2.5 Hz, 1H), 2.34 (d, J = 14.5 Hz, 1H), 2.32 (dd, J = 11.5 Hz, J = 3.0 Hz, 1H), 2.27 (dd, J = 7.0 Hz, J = 7.0 Hz, 1H), 2.22 (d, J = 17.5 Hz, 1H), 1.21 (s, 3H), 1.05 (d, J = 7.0 Hz, 3H), 1.03 (d, J = 6.5 Hz, 3H) ppm. **^{13}C NMR** (125 MHz, CDCl_3 , 25 °C) δ = 216.8, 173.2, 172.8, 152.9, 110.2, 60.7, 60.6, 54.2, 53.04, 52.97, 51.8, 46.5, 45.6, 38.0, 33.2, 26.9, 22.2, 22.1 ppm. **IR** (thin film) 2958 (m), 2873 (w), 1732 (s), 1458 (w), 1435 (m), 1382 (w), 1364 (w), 1324 (w), 1256 (s), 1199 (m), 1180 (m), 1149 (m), 1094 (w), 1024 (w), 943 (w), 896 (w), 867 (w), 818 (w) cm^{-1} . **HRMS** Calculated for $\text{C}_{18}\text{H}_{26}\text{O}_5$: 322.1780. Found: 322.1789. **TLC** R_f = 0.26 (10% ethyl acetate/pentane). **nOe**: Ha $\rightarrow$ Hb (4.2%), Hc $\rightarrow$ Hb (2.2%).

Alkenylcyclopentanone **15**:

In an oven-dried borosilicate glass test tube, equipped with a stir bar and capped with a rubber septum, diene-ene **14** (0.020 g, 0.0686 mmol) was dissolved in DCE (0.69 mL, 0.10 M). $[\text{RhCl}(\text{CO})_2]_2$ (0.0013 g, 0.0034 mmol) was added and the solution was stirred under a balloon of CO, vented to a bubbler, for 10 min. The reaction mixture was stirred vigorously under 1 atm of CO at 80°C for 3.5 h. The mixture was purified by flash column chromatography on silica gel (gradient elution: 20%→35% EtOAc in pentane). Product-containing fractions were concentrated to give **15** (0.0204 g, 0.0639 mmol) in 93% yield as a white solid.

Characterization for **15**:

^1H NMR (500 MHz, CDCl_3 , 25 °C) δ = 7.72-7.68 (m, 2H), 7.36-7.32 (m, 2H), 4.91 (dq, J = 1.5 Hz, J = 1.5 Hz, 1H), 4.60 (qd, J = 1.2 Hz, J = 0.8 Hz, 1H), 3.56 (dd, J = 10.1 Hz, J = 8.4 Hz, 1H), 3.40 (dd, J = 10.4 Hz, J = 6.5 Hz, 1H), 3.27 (dd, J = 10.4 Hz, J = 2.3 Hz, 1H), 2.99 (dd, J = 10.1 Hz, J = 7.1 Hz, 1H), 2.88 (dddd, J = 7.8 Hz, J = 7.8 Hz, J = 7.8 Hz, J = 7.8 Hz, J = 3.2 Hz, 1H), 2.77 (dddd, J = 9.2 Hz, J = 9.2 Hz, J = 7.0 Hz, J = 2.3 Hz, 1H), 2.44 (s, 3H), 2.43 (dd, J = 19.2 Hz, J = 8.7 Hz, 1H), 2.38 (d, J = 9.2 Hz, 1H), 2.21 (dd, J = 19.3 Hz, J = 2.2 Hz, 1H), 1.63 (dd, J = 1.5 Hz, J = 0.9 Hz, 3H) ppm. **^{13}C NMR** (125 MHz, CDCl_3 , 25 °C) δ = 215.1, 143.9, 139.8, 132.9, 129.8, 127.6, 115.4, 60.4, 53.1, 52.3, 44.0, 41.8, 36.6, 21.5, 20.0 ppm. **IR** (FTIR, thin film): ν = 3072 (w), 2952 (m), 2884 (w), 1740 (s), 1706 (w), 1646 (w), 1624 (w), 1597 (w), 1478 (w), 1452 (w), 1406 (w), 1377 (w), 1343 (s), 1305 (m), 1290 (m), 1184 (m), 1161 (s), 1116 (m), 1090 (m), 1042 (m), 1016 (m), 899 (m), 813 (m), 760 (w), 709 (w), 665 (s) cm^{-1} . **HRMS** Calculated for $\text{C}_{17}\text{H}_{21}\text{NO}_3\text{S}$: 319.1242. Found: 319.1239. **Melting Point** 77.5-79.0°C. **TLC** R_f = 0.50 (50% EtOAc/hexane), one spot. **nOe**: Ha→Hb (16%), Hb→Ha (26%), Hd→Hc (0.5%), Hd→Hb (1.5%).

Alkenylcyclopentanone **17**:

In an oven-dried borosilicate glass test tube, equipped with a stir bar and capped with a rubber septum, diene-ene **16** (0.032 g, 0.192 mmol) was dissolved in DCE (1.90 mL, 0.10 M). $[\text{RhCl}(\text{CO})_2]_2$ (0.0037 g, 0.0096 mmol) was added and the solution was stirred under a balloon of CO, vented to a bubbler, for 15 min. The reaction mixture was stirred vigorously under 1 atm of CO at 80°C for 3 h. The mixture was purified by flash column chromatography on silica gel (gradient elution: 0%→20% Et_2O in pentane). Product-containing fractions were concentrated to give **17** in 84% yield as a colorless oil.

Characterization for **17**:

¹H NMR (500 MHz, CDCl₃, 25 °C) δ = 5.00 (s, 1H), 4.79 (s, 1H), 4.02 (dd, *J* = 9.0 Hz, *J* = 7.5 Hz, 1H), 3.94 (dd, *J* = 9.5 Hz, *J* = 6.5 Hz, 1H), 3.72 (dd, *J* = 9.5 Hz, *J* = 3.0 Hz, 1H), 3.62 (dd, *J* = 9.0 Hz, *J* = 5.0 Hz, 1H), 3.04-2.95 (m, 1H), 2.95-2.89 (m, 1H), 2.81 (d, *J* = 7.0 Hz, 1H), 2.67 (dd, *J* = 19.0 Hz, *J* = 9.5 Hz, 1H), 2.31 (septet, *J* = 7.0 Hz, 1H), 2.27 (dd, *J* = 19.0 Hz, *J* = 4.0 Hz, 1H), 1.06 (d, *J* = 7.0 Hz, 3H), 1.04 (d, *J* = 7.0 Hz, 3H) ppm. **¹³C NMR** (125 MHz, CDCl₃, 25 °C) δ = 216.9, 153.2, 109.9, 74.7, 73.7, 58.8, 47.2, 42.4, 37.5, 33.4, 22.1, 21.9 ppm. TLC *R_f* = 0.23 (10% ethyl acetate/pentane). **IR** (thin film) 2959 (s), 2922 (s), 2850 (s), 1742 (m), 1640 (w), 1464 (w), 1378 (w), 1260 (w), 1140 (w), 1097 (w), 1035 (w), 898 (w) cm⁻¹. **HRMS** Calculated for C₁₂H₁₈O₂: 194.1307. Found: 194.1318. **TLC** *R_f* = 0.14 (10% ethyl acetate/pentane). **nOe**: Ha→Hb (2.6%), Ha→Hc (0.5%), Ha→Hd (1.5%), Hd→Ha (1.4%).

Alkenylcyclopentanone **19**:

In an oven-dried borosilicate glass test tube, equipped with a stir bar and capped with a rubber septum, diene-ene **18** (0.069 g, 0.234 mmol) was dissolved in DCE (2.34 mL, 0.10 M). [RhCl(CO)₂]₂ (0.0046 g, 0.0117 mmol) was added and the solution was stirred under a balloon of CO, vented to a bubbler, for 10 min. The reaction mixture was stirred vigorously under 1 atm of CO at 80°C for 54 h. The mixture was purified by flash column chromatography on silica gel (gradient elution: 5%→20% EtOAc in pentane). Product-containing fractions were concentrated to give **19** (0.067 g, 0.0208 mmol) in 89% yield as a colorless oil.

Characterization for **19**:

¹H NMR (500 MHz, CDCl₃, 25 °C) δ = 5.03 (s, 1H), 4.77 (s, 1H), 3.75 (s, 3H), 3.71 (s, 3H), 2.59 (ddd, *J* = 12.8 Hz, *J* = 2.4 Hz, *J* = 2.4 Hz, 1H), 2.53 (dddd, *J* = 13.9 Hz, *J* = 3.2 Hz, *J* = 3.2 Hz, *J* = 2.6 Hz, 1H), 2.50 (d, *J* = 12.5 Hz, 1H), 2.43 (dd, *J* = 18.1 Hz, *J* = 6.6 Hz, 1H), 2.20 (septet, *J* = 6.8, 1H), 2.01 (dddd, *J* = 13.2 Hz, *J* = 3.7 Hz, *J* = 3.5 Hz, *J* = 3.5 Hz, 1H), 1.87 (dd, *J* = 17.9 Hz, *J* = 12.5 Hz, 1H), 1.82 (ddd, *J* = 13.6 Hz, *J* = 13.4 Hz, *J* = 4.2 Hz, 1H), 1.75 (dddd, *J* = 12.3 Hz, 12.3 Hz, *J* = 11.2 Hz, *J* = 3.1 Hz, 1H), 1.63-1.58 (m, 1H), 1.60 (dd, *J* = 2.6 Hz, *J* = 2.6 Hz, 1H), 1.38 (dddd, *J* = 13.2 Hz, *J* = 13.2 Hz, *J* = 11.7 Hz, *J* = 3.5 Hz, 1H), 1.06 (d, *J* = 6.8 Hz, 3H), 1.00 (d, *J* = 6.8 Hz, 3H) ppm. **¹³C NMR** (125 MHz, CDCl₃, 25 °C): δ = 215.5, 172.2, 171.3, 151.0, 111.0, 62.9, 55.3, 52.8, 52.5, 44.3, 44.0, 40.2, 34.9, 32.7, 31.5, 27.7, 22.6, 22.2 ppm. **IR** (FTIR, thin film): ν = 3463 (w, b), 3076 (w), 2957 (m), 2870 (m), 1742 (s), 1737 (s), 1732 (s), 1641 (w), 1451 (m), 1434 (m), 1411 (w), 1380 (w), 1364 (w), 1324 (w), 1288 (m), 1249 (s), 1219 (s), 1157 (s), 1128 (m), 1096 (w), 1077 (w), 1055 (w), 1018 (w), 1002 (w), 969 (w), 939 (w), 894 (w), 858

(w), 821 (w), 796 (w), 776 (w), 704 (w, b), 658 (w) cm^{-1} . **HRMS** Calculated for $\text{C}_{18}\text{H}_{26}\text{O}_5$: 322.1780. Found: 322.1764. **TLC** R_f = (% EtOAc/hexane), one spot. **nOe**: Hb→Ha (17%), Hb→Hc (4%), Hb→Hd (4%).

Alkenylcyclopentanone **21**:

Into an oven-dried borosilicate glass test tube, equipped with a stir bar and capped with a rubber septum, were added $[\text{RhCl}(\text{CO})\text{PPh}_3]_2$ (0.0075 g, 0.011 mmol), AgSbF_6 (0.0037 g, 0.001 mmol), and 1,2-dichloroethane (DCE) (1.1 mL, 0.01 M). The resulting suspension was stirred for 1.5 hours under a balloon of CO, vented through a bubbler. Diene-ene **20** (0.025 g, 0.099 mmol) was added to a separate oven-dried borosilicate glass test tube, equipped with a stir bar and capped with a rubber septum. The catalyst solution (0.99 mL) was added to diene-ene **20** and the reaction mixture was stirred vigorously under 1 atm of CO at 60°C for 48 h. The mixture was purified by flash column chromatography on silica gel (gradient elution: 5%→20% EtOAc in pentane). Product-containing fractions were concentrated to give **21** (0.0079 g, 0.028 mmol) in 28% yield as a colorless oil.

Characterization for **21**:

^1H NMR (500 MHz, CDCl_3 , 25 °C) δ = 5.71 (dd, J = 17.5 Hz, J = 10.6 Hz, 1H), 5.10 (d, J = 10.6 Hz, 1H), 5.06 (d, J = 17.5 Hz, 1H), 3.76 (s, 3H), 3.72 (s, 3H), 2.86-2.79 (m, 1H), 2.77-2.64 (m, 2H), 2.75 (ddd, J = 14.3 Hz, J = 8.2 Hz, J = 1.2 Hz, 1H), 2.44 (dd, J = 13.3 Hz, J = 6.8 Hz, 1H), 2.12 (dd, J = 14.3 Hz, J = 2.8 Hz, 1H), 1.96 (dd, J = 19.4 Hz, J = 7.2 Hz, 1H), 1.76 (dd, J = 13.1 Hz, J = 13.1 Hz, 1H), 1.13 (s, 3H) ppm. **^{13}C NMR** (125 MHz, CDCl_3 , 25 °C): δ = 218.2, 172.5, 172.2, 140.6, 114.7, 60.6, 56.8, 53.0, 52.9, 50.7, 42.7, 40.2, 36.4, 34.8, 18.4 ppm. **IR** (FTIR, thin film): ν = 2954 (m,b), 1733 (s), 1630 (w), 1435 (m,b), 1409 (s), 1373 (w), 1272 (s), 1254 (s), 1212 (m), 1197 (m), 1176 (m), 1128 (m), 1111 (m), 1051 (w), 999 (w), 966 (w), 925 (m), 852 (w), 821 (w), 669 (w,b) cm^{-1} . **HRMS** Calculated for $\text{C}_{15}\text{H}_{20}\text{O}_5$: 280.1311. Found: 280.1318. **TLC** R_f = 0.51 (18% EtOAc/hexane), one spot.

Cyclopentanone **23**:

In an oven-dried borosilicate glass test tube, equipped with a stir bar and capped with a rubber septum, norbornene (0.086 g, 0.913 mmol) and 2,3-dimethyl-1,3-butadiene (0.150 mg, 1.826 mmol) were dissolved in DCE (1.8 mL, 0.10 M). $[\text{RhCl}(\text{CO})_2]_2$ (0.018 g, 0.046 mmol) was added and the solution was stirred under a balloon of CO, vented to a bubbler, for 15 min. The reaction mixture was stirred vigorously under 1 atm of CO at 80°C for 52 h. The mixture was purified by flash column chromatography on silica gel (gradient elution: 0%→2% Et_2O in pentane). Product-containing fractions were concentrated to give **23** in 73% yield as a colorless

oil.

Characterization for **23**:

¹H NMR (500 MHz, CDCl₃, 25 °C) δ = 4.87 (s, 1H), 4.84 (s, 1H), 2.55 (s, 1H), 2.50 (dd, *J* = 14.5 Hz, *J* = 9.0 Hz, 1H), 2.23 (d, *J* = 9.0 Hz, 1H), 2.15 (ddd, *J* = 9.0 Hz, *J* = 9.0 Hz, *J* = 8.5 Hz, 1H), 2.09 (s, 1H), 1.69 (s, 3H), 1.58-1.47 (m, 2H), 1.21-0.97 (m, 5H), 1.08 (s, 3H). **¹³C NMR** (125 MHz, CDCl₃, 25 °C) δ = 220.0, 145.3, 111.7, 56.3, 54.2, 42.0, 40.1, 38.68, 38.66, 34.1, 28.2, 28.0, 20.9, 19.2. **IR** (thin film) 3087 (w), 2952 (s), 2871 (s), 1735 (s), 1632 (w), 1453 (m), 1370 (w), 1315 (w), 1297 (w), 1251 (w), 1226 (w), 1160 (m), 1089 (w), 1066 (w), 894 (m), 858 (w), 828 (w) cm⁻¹. **HRMS** Calculated for C₁₄H₂₀O: 204.1514. Found: 204.1509. **TLC** R_f = 0.19 (1% ethyl acetate/pentane). **nOe**: Ha→Hb (2.8%), Ha→Hd (2.0%), Ha→He (0.9%), Hb→Hc (5.5%), Hb→Hd (8.5%), Hc→Hf (2.8%).

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