



Supporting Information

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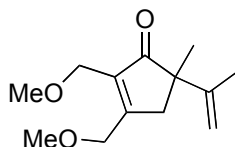
The Intermolecular Dienyl Pauson Khand Reaction

Paul A. Wender,* Nicole M. Deschamps, and Travis J. Williams

General methods: air and moisture sensitive reactions were carried out in oven-dried glassware sealed with rubber septa under a positive pressure of dry nitrogen from a manifold, unless otherwise indicated. Similarly, sensitive 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 thermoregulated oil baths. Organic solutions were concentrated using a Buchi or Heidolph rotary evaporator with a desktop vacuum pump. Thin layer chromatography plates were visualized by ultraviolet light and treatment with acidic *p*-anisaldehyde stain or potassium permanganate 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. 1,2-Dichloroethane was freshly distilled over calcium hydride or was used directly from commercial suppliers. 1,1,2,2-Tetrachloroethane was distilled over calcium hydride (batch-wise). Tetrahydrofuran, toluene, and dichloromethane were purified with a solv-tek solvent purification system using alumina columns. Other solvents were used directly from commercial suppliers.

NMR spectra were measured on a Varian INOVA 500 (^1H at 500 MHz, ^{13}C at 125 MHz), Varian Mercury 400 (^1H at 400 MHz, ^{13}C at 100 MHz), or Varian Gemini 300 (^1H at 300 MHz, ^{13}C 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, m = multiplet), coupling constant (Hz), and integration. Nuclear Overhauser effect (NOE) data 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 (FTIR) 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. LC/MS data was collected at the Stanford University Protein and Nucleic Acid facility. LRMS data was collected with an HP model 6890 gas chromatograph with model 5973 mass-selective detector. Elemental analyses (%C, %H, %Si) were determined by Desert Analytics, Tucson, Arizona. Reported atomic percentages are within error limits of $\pm 0.4\%$. Gas chromatography analyses were done with an HP series 6890 GC using undecane or dodecane as an external standard.

Alkenylcyclopentenone **3**:

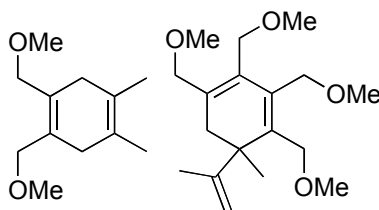


Chlorodicarbonylrhodium(I) dimer (4.6 mg, 0.012 mmol) was added to a solution of 1,4-dimethoxy-2-butyne (27.3 mg, 0.239 mmol) and 2,3-dimethylbutadiene (238 μL , 2.39 mmol) in

DCE (0.48 mL) in an oven-dried borosilicate test tube equipped with a magnetic stirrer and capped with a rubber septum. The solution was stirred under a balloon of CO, vented to a bubbler for 10 min. The solution was then stirred under a balloon of CO at 60°C (in a temperature-controlled oil bath) for 6 hrs. Purification by flash chromatography on silica gel (10% diethyl ether/pentane, followed by 50% diethyl ether/pentane) gave cyclopentenone **3** (52.3 mg, 98%) as a clear, colorless oil. Crude adduct **3** can be distilled under atmospheric pressure to give a colorless oil.

¹H NMR (500 MHz, [D]chloroform, 25 °C) δ = 4.88 (s, 1H), 4.86 (s, 1H), 4.44 (s, 2H), 4.11 (s, 2H), 3.38 (s, 3H), 3.31 (s, 3H), 2.83 (d, ²J(H,H) = 19.3 Hz, 1H), 2.48 (d, ²J(H,H) = 19.3 Hz, 1H), 1.61 (s, 3H), 1.25 (s, 3H) ppm; assigned with COSY. ¹³C NMR (100 MHz, [D]chloroform, 25 °C) δ = 210.2, 172.0, 145.4, 134.9, 111.7, 69.9, 63.6, 58.9, 58.4, 51.9, 42.6, 22.4, 19.6; assigned with HSQC and HMBC. FTIR (neat) ν = 3091 (w), 2981 (m), 2927 (s), 2821 (m), 1704 (s), 1650 (m), 1446 (m), 1377 (m), 1330 (w), 1278 (w), 1243 (w), 1174 (m), 1154 (m), 1106 (s), 1011 (m), 956 (m), 896 (m) cm⁻¹. HRMS for C₁₃H₂₀O₃: calc'd 224.141245 g/mol, found 224.141191 g/mol. Anal calc'd 69.61% C, 8.99% H; found 69.88% C, 9.31% H.

Cycloadducts **4** and **5**:



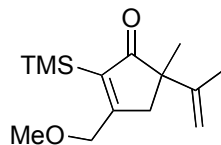
Chlorodicarbonylrhodium(I) dimer (18.5 mg, 0.048 mmol) was added to a solution of 1,4-dimethoxy-2-butyne **1** (109 mg, 0.95 mmol) and 2,3-dimethylbutadiene (1.07 mL, 9.5 mmol) in DCE (1.9 mL) in an oven-dried borosilicate test tube equipped with a magnetic stirrer and capped with a rubber septum. The solution was stirred under a balloon of CO, vented to a bubbler for 10 min. The solution was then stirred under a balloon of CO at 80°C (in a temperature-controlled oil bath) for 4.5 hrs. Purification by flash chromatography on silica gel (gradient elution 5% diethyl ether/pentane, to 25% diethyl ether/pentane) gave adduct **3** (21 mg, 11%), cyclohexadiene **4** (79 mg, 42%), and cyclohexadiene **5** (43 mg, 29%) as clear, colorless oils.

Cyclohexadiene **4**: ¹H NMR (400 MHz, [D]chloroform, 25 °C) δ = 3.98 (s, 4H), 3.29 (s, 6H), 2.71 (s, 4H), 1.64 (s, 6H) ppm. ¹³C NMR (100 MHz, [D]chloroform, 25 °C) δ = 130.3 (2C), 122.6 (2C), 71.0 (2C), 57.8 (2C), 36.1 (2C), 18.0 (2C) ppm. FTIR (neat) ν = 2980 (m), 2921 (s), 2872 (s), 2814 (s), 2723 (w), 2048 (w), 1716 (w), 1693 (w), 1610 (w), 1560 (w), 1448 (m), 1426 (m), 1401 (w), 1381 (m), 1288 (w), 1266 (w), 1228 (w), 1187 (s), 1150 (m), 1097 (s), 953 (m), 907 (m), 879 (w), 777 (w), 699 (w) cm⁻¹. LRMS for C₁₂H₂₀O₂: calc'd: 196 g/mol, found: 196 g/mol.

Vinylcyclohexadiene **5**: ¹H NMR (500 MHz, [D]chloroform, 25 °C) δ = 4.85 (s, 1H), 4.82 (s, 1H), 4.21 (d, ²J(H,H) = 11.2 Hz, 1H), 4.18 (d, ²J(H,H) = 19.5 Hz, 1H), 4.15 (d, ²J(H,H) = 11.2 Hz, 1H), 4.14 (d, ²J(H,H) = 19.8 Hz, 1H), 4.06 (s, 2H), 4.05 (d, ²J(H,H) = 10.7 Hz, 1H), 3.77 (d, ²J(H,H) = 10.7 Hz, 1H), 3.33 (s, 3H), 3.29 (s, 3H), 3.27 (s, 3H), 2.58 (d, ²J(H,H) = 16.8 Hz, 1H), 2.03 (d, ²J(H,H) = 16.8 Hz, 1H), 1.71 (d, ⁴J(H,H) = 1.0 Hz, 3H), 1.21 (s, 3H) ppm. ¹³C NMR (100 MHz, [D]chloroform, 25 °C) δ = 148.5, 140.0, 135.3, 134.0, 129.9, 111.9, 71.1, 68.9, 68.4, 66.9, 58.2, 57.9, 57.8, 57.6, 43.9, 37.8, 22.3, 20.2 ppm. FTIR (neat) ν = 3510 (w), 3087

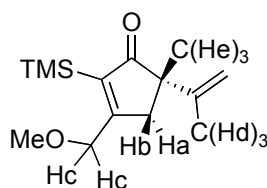
(w), 2977 (m), 2923 (s), 2890 (s), 2816 (m), 2362 (w), 2059 (w), 1708 (w), 1654 (w), 1636 (w), 1459 (m), 1449 (m), 1375 (m), 1282 (w), 1238 (w), 1217 (w), 1189 (m), 1154 (s), 1099 (s), 943 (m), 900 (m) cm^{-1} . LRMS for $\text{C}_{18}\text{H}_{30}\text{O}_4$: calc'd 310 g/mol, found 310 g/mol.

Alkenylcyclopentenone **7**:

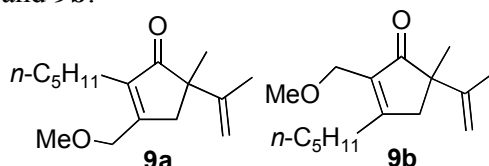


Chlorodicarbonylrhodium(I) dimer (6.3 mg, 0.016 mmol) was added to a solution of 1-trimethylsilyl-3-methoxy-1-propyne (45.5 mg, 0.32 mmol) and 2,3-dimethylbutadiene (362 μL , 3.2 mmol) in DCE (0.64 mL) in an oven-dried borosilicate test tube equipped with a magnetic stirrer and capped with a rubber septum. The solution was stirred under a balloon of CO, vented to a bubbler for 10 min. The solution was then stirred under a balloon of CO at 60°C (in a temperature-controlled oil bath) for 30 hrs. Purification by flash chromatography on silica gel (5% diethyl ether/pentane then 25% diethyl ether/pentane) gave cyclopentenone **7** (75 mg, 93%) as a clear, colorless oil.

^1H NMR (500 MHz, $[\text{D}]$ chloroform, 25 °C) δ = 4.85 (dq, $^2J(\text{H,H}) = ^4J(\text{H,H}) = 1.3$ Hz, 1H), 4.83 (s, 1H), 4.37 (ddd, $^2J(\text{H,H}) = 14.3$ Hz, $^4J(\text{H,H}) = ^4J(\text{H,H}) = 1.0$ Hz, 1H), 4.34 (ddd, $^2J(\text{H,H}) = 14.3$ Hz, $^4J(\text{H,H}) = ^2J(\text{H,H}) = 1.1$ Hz, 1H), 3.38 (s, 3H), 2.87 (ddd, $^2J(\text{H,H}) = 19.4$ Hz, $^4J(\text{H,H}) = ^4J(\text{H,H}) = 1.0$ Hz, 1H), 2.53 (ddd, $^2J(\text{H,H}) = 19.5$ Hz, $^4J(\text{H,H}) = ^4J(\text{H,H}) = 1.1$ Hz, 1H), 1.59 (dd, $^4J(\text{H,H}) = 1.3$ Hz, $^4J(\text{H,H}) = 0.6$ Hz, 3H), 1.21 (s, 3H), 0.216 (s, 9H) ppm. ^{13}C NMR (125 MHz, $[\text{D}]$ chloroform, 25 °C) δ = 215.3, 181.8, 146.1, 138.7, 111.3, 71.7, 58.8, 52.6, 45.6, 22.3, 19.6, 0.6 (3C). FTIR (neat) ν = 3373 (w), 3091 (w), 2962 (m), 2929, (m), 2899 (w), 1694 (strong), 1643 (m), 1597 (m), 1450 (m), 1376 (m), 1367 (m), 1307 (w), 1248 (s), 1197 (m), 1146 (m), 1111 (s), 1001 (w), 972 (w), 925 (w), 892 (m), 868 (m), 841 (s) cm^{-1} . HRMS for $\text{C}_{14}\text{H}_{24}\text{O}_2\text{Si}$: calc'd 252.1546 g/mol, found 252.1548 g/mol. NOE: Ha, Hb (21%), Ha, Hc (1.2%), Ha, Hd (3.8%), Hb, Ha (23%), Hb, Hc (1%), Hb, He (3.3%).



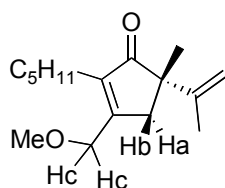
Alkenylcyclopentenones **9a** and **9b**:



Chlorodicarbonylrhodium(I) dimer (3.7 mg, 0.0095 mmol) was added to a solution of 1-methoxy-2-octyne **7** (26.7 mg, 0.19 mmol) and 2,3-dimethylbutadiene (189 μL , 1.9 mmol) in DCE (0.38 mL) in an oven-dried borosilicate test tube equipped with a magnetic stirrer and capped with a rubber septum. The solution was stirred under a balloon of CO, vented to a bubbler for 10 min. The solution was then stirred under a balloon of CO at 60°C (in a

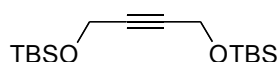
temperature-controlled oil bath) for 30 hrs. Purification by flash chromatography on silica gel (2.5% diethyl ether/pentane, 10% diethyl ether/pentane, then 50% diethyl ether/pentane) gave cyclopentenone **9a** (26.3 mg, 55%) and cyclopentenone **9b** (17 mg, 35%) as clear, colorless oils.

Cyclopentenone **9a**: ^1H NMR (500 MHz, [D]chloroform, 25 °C) δ = 4.86 (s, 1H), 4.84 (s, 1H), 4.29 (s, 2H), 3.38 (s, 3H), 2.73 (d, $^2J(\text{H,H})$ = 18.8 Hz, 1H), 2.39 (d, $^2J(\text{H,H})$ = 18.8 Hz, 1H), 2.21 (dt, $^2J(\text{H,H})$ = 13.3 Hz, $^3J(\text{H,H})$ = 8.1 Hz, 1H), 2.16 (dt, $^2J(\text{H,H})$ = 13.3 Hz, $^3J(\text{H,H})$ = 7.9 Hz, 1H), 1.58 (s, 3H), 1.33-1.38 (m, 2H), 1.21-1.31 (m, 4H), 1.22 (s, 3H), 0.85 (t, $^3J(\text{H,H})$ = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, [D]chloroform, 25 °C) δ = 211.6, 165.8, 145.9, 139.7, 111.4, 69.8, 58.9, 51.6, 42.5, 31.6, 28.1, 23.2, 22.4, 22.3, 19.5, 13.9 ppm. FTIR (neat): ν = 3090 (w), 2958 (s), 2928 (s), 2872 (m), 2859 (m), 2819 (m), 1704 (s), 1653 (m), 1648 (m), 1448 (m), 1376 (m), 1365 (w), 1350 (m), 1295 (w), 1174 (m), 1154 (m), 1100 (s), 1039 (w), 987 (w), 960 (w), 892 (m), 727 (w) cm^{-1} . HRMS for $\text{C}_{16}\text{H}_{26}\text{O}_2$: calc'd 250.1933 g/mol, found 250.1936 g/mol. NOE: Hc, Ha (1%), Hc, Hb (1%).



Cyclopentenone **9b**: ^1H NMR (400 MHz, [D]chloroform, 25 °C) δ = 4.90- 4.89 (m, 1H), 4.88 (s, 1H), 4.08 (s, 2H), 3.31 (s, 3H), 2.73 (d, $^2J(\text{H,H})$ = 18.8 Hz, 1H), 2.59 (dt, $^2J(\text{H,H})$ = 13.6 Hz, $^3J(\text{H,H})$ = 7.9 Hz, 1H), 2.51 (dt, $^2J(\text{H,H})$ = 13.9 Hz, $^2J(\text{H,H})$ = 7.6 Hz, 1H), 2.37 (d, $^2J(\text{H,H})$ = 18.9 Hz, 1H), 1.60 (dd, $^2J(\text{H,H})$ = 1.2 Hz, $^3J(\text{H,H})$ = 0.6 Hz, 3H), 1.52- 1.62 (m, 2H), 1.30- 1.37 (m, 4H), 1.25 (s, 3H), 0.93 (t, $^3J(\text{H,H})$ = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, [D]chloroform, 25 °C) δ = 210.7, 177.9, 145.7, 134.9, 111.7, 58.3, 63.0, 52.0, 44.8, 31.7, 31.1, 27.2, 22.5, 22.4, 19.6, 13.9 ppm. FTIR (neat) ν = 3090 (w), 2958 (s), 2928 (w), 2871 (m), 2811 (m), 1701 (s), 1646 (s), 1450 (m), 1396 (m), 1378 (m), 1334 (w), 1275 (w), 1242 (w), 1191 (m), 1096 (m), 1039 (w), 1011 (m), 954 (w), 891 (m), 797 (w), 727 (w), 631 (w) cm^{-1} . HRMS for $\text{C}_{16}\text{H}_{26}\text{O}_2$: calc'd 250.1933 g/mol, found 250.1944 g/mol.

Alkyne **10**:

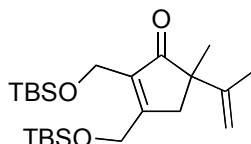


Freshly recrystallized 2-butyne-1,4-diol (1.00g, 11.6 mmol), imidazole (1.90 g, 27.9 mmol), and N,N-4-dimethylaminopyridine (142 mg, 1.16 mmol) were weighed out in an oven-dried 100 mL round-bottom flask with a stir bar. To this was added dichloromethane (solvetek, 80 mL) and recrystallized chloro-*tert*-butyldimethylsilane (4.20 g, 27.9 mmol), and the resulting solution was stirred for 1 hour. The solution was then poured over 40 mL 10% aqueous potassium carbonate and the organic layer was extracted. The resulting aqueous fraction was extracted three times with 40 mL diethyl ether. Combined organic fractions were dried with anhydrous sodium sulfate, concentrated by rotary evaporation, and the resulting residue was purified by flash column chromatography eluting with 5% diethyl ether in petroleum ether. Product-containing fractions were combined and concentrated by rotary evaporation to yield 3.25 g (89%) of silyl ether **10** as a colorless oil.

^1H NMR (400 MHz, [D]chloroform, 25 °C) δ = 4.34 (s, 4H), 0.903 (s, 18H), 0.11 (s, 12H). ^{13}C NMR (100 MHz, [D]chloroform, 25 °C) δ = 83.3 (2C), 51.8 (2C), 25.8 (6C), 18.3

(2C), -5.2 (4C). FTIR (neat) ν = 2956 (m), 2931 (m), 2896 (w), 2859 (m), 1473 (w), 1363 (w), 1256 (m), 1135 (m), 1099 (m), 1072 (m), 1006 (w), 837 (s), 778 (m) cm^{-1} . LRMS for $\text{C}_{16}\text{H}_{34}\text{O}_2\text{Si}_2$ calc'd: 314 g/mol, found: 314 (trace abundance), 299 (M^+ -Me, trace abundance), 257 (M^+ -tBu) g/mol. HRMS for $\text{C}_{16}\text{H}_{34}\text{O}_2\text{Si}_2$: calc'd 314.2097 g/mol, found 314.2057 (trace abundance).

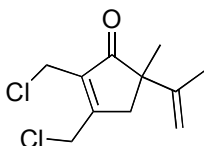
Alkenylcyclopentenone **11**:



Bis TBS ether **10** (40.0 mg, 127 μmol) was weighed out in an oven-dried 16x100 mm rest tube with a stir bar. To this was added 2,3-dimethylbutadiene (144 μL , 105 mg, 1.27 mmol), 1,2-dichloroethane (254 μL), and chlorodicarbonylrhodium(I) dimer (2.5 mg, 6.4 μmol). The test tube was capped with a septum and flushed 3 times with CO. The resulting solution was stirred at 60 $^\circ\text{C}$ for 6 hours under CO atmosphere. The resulting solution was purified by flash-column chromatography eluting with 5% diethyl ether/ pentane. Product-containing fraction were identified and concentrated by rotary evaporation to yield adduct **11** (47.2 mg, 87%) as a colorless oil.

^1H NMR (400 MHz, $[\text{D}]$ chloroform, 25 $^\circ\text{C}$) δ = 4.89 (d, $^4J(\text{H,H})$ = 1.2 Hz, 1H), 4.88 (s, 1H), 4.85- 4.76 (m, 2H), 4.37 (s, 2H), 2.84 (d, $^2J(\text{H,H})$ = 19.2 Hz, 1H), 2.48 (d, $^2J(\text{H,H})$ = 19.4 Hz), 1.60 (s, 3H), 1.24 (s, 3H), 0.92 (s, 9H), 0.89 (s, 9H), 0.10 (s, 6H), 0.07 (s, 6H); assigned with COSY. ^{13}C NMR (100 MHz, $[\text{D}]$ chloroform, 25 $^\circ\text{C}$) δ = 210.1, 173.8, 145.8, 144.3, 135.4, 61.3, 56.5, 51.8, 42.5, 25.9 (3C), 25.8 (3C), 22.3, 19.6, 18.3, 18.2, -5.4 (2C), -5.5, -5.5; assigned with HSQC and HMBC. FTIR (neat) ν = 2934(s), 2860 (m), 1707 (m), 1651.1 (w), 1467 (w), 1394 (w), 1257 (m), 1100 (m), 1006 (w), 840 (s), 779 (m) cm^{-1} . HRMS for $\text{C}_{23}\text{H}_{44}\text{O}_3\text{Si}_2$: (M^+ -tBu $^+$) calc'd 367.2125 g/mol, found 367.2123 g/mol.

Alkenylcyclopentenone **13**:

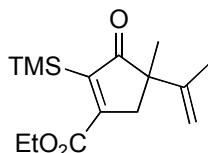


1,4-Dichloro-2-butyne (19.5 μL , 24.6 mg, 200 μmol), 2,3-dimethylbutadiene (226 μL , 164 mg, 2.00 mmol), 1,2-dichloroethane (distilled, 200 μL), and 1,1,2,2-tetrachloroethane (distilled, 200 μL) were mixed in an oven-dried 16x100 mm rest tube with a stir bar. To this was added and chlorodicarbonylrhodium(I) dimer (3.9 mg, 10 μmol). The test tube was capped with a septum and flushed three times with CO. A CO balloon was then affixed, and the resulting solution was stirred at 60 $^\circ\text{C}$ for 5.5 hours. The resulting solution was concentrated and the residue was purified by flash-column chromatography eluting with 10% diethyl ether/ pentane. Product-containing fraction were identified and concentrated by rotary evaporation to yield adduct **13** (17.5 mg, 38%) as a colorless oil.

^1H NMR (500 MHz, $[\text{D}]$ chloroform, 25 $^\circ\text{C}$) δ = 4.93 (s, 1H), 4.90 (s, 1H), 4.52- 4.45 (m, 2H), 4.25- 4.19 (m, 2H), 2.94 (d, $^2J(\text{H,H})$ = 19.0 Hz, 1H), 2.58 (d, $^2J(\text{H,H})$ = 19.0 Hz, 1H), 1.63 (s, 3H), 1.29 (s, 3H); assigned with COSY. ^{13}C NMR (75 MHz, $[\text{D}]$ chloroform, 25 $^\circ\text{C}$) δ =

208.4, 164.7, 144.8, 136.8, 112.3, 52.3, 43.3, 39.3, 32.2, 22.1, 19.5; assigned with HSQC and HMBC. FTIR (neat) $\nu = 3405$ (w), 2968 (m), 2924 (m), 2874 (w), 1713 (s), 1652 (m), 1446 (m), 1379 (w), 1351 (m), 1265 (w), 1215 (w), 1030 (w), 984 (w), 899 (w), 720 (w), 695 (w) cm^{-1} . HRMS for $\text{C}_{11}\text{H}_{14}\text{Cl}_2\text{O}$: calc'd 232.0414 g/mol, found 232.0422 g/mol.

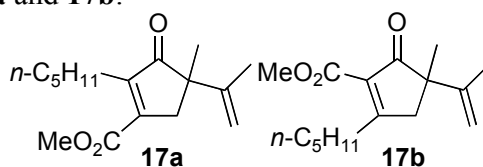
Alkenylcyclopentenone **15**:



Ethyl 3-trimethylsilylpropiolate (18.0 μL , 17.0 mg, 100 μmol), 2,3-dimethylbutadiene (113 μL , 82.2 mg, 1.00 mmol), 1,1,2,2-tetrachlorethane (distilled, 100 μL), and 1,2-dichlorethane (distilled, 100 μL), were mixed in an oven-dried 16x100 mm rest tube with a stir bar. To this was added and chlorodicarbonylrhodium(I) dimer (2.0 mg, 5.0 μmol). The test tube was capped with a septum and flushed 3 times with CO. The resulting solution was stirred at 60 $^{\circ}\text{C}$ for 24 hours under CO atmosphere. The resulting solution contained > 99% of adduct **15** by GC analysis. This was purified twice by flash-column chromatography eluting with 2% diethyl ether/ pentane. Product-containing fraction were identified and concentrated by rotary evaporation to yield adduct **15** (26.6 mg, 95%) as a colorless oil.

^1H NMR (500 MHz, [D]chloroform, 25 $^{\circ}\text{C}$) $\delta = 4.89$ (apparent quint., $^2J(\text{H,H}) = ^4J(\text{H,H}) = 1.3$ Hz, 1H), 4.85 (s, 1H), 4.33 (q, $^3J(\text{H,H}) = 7.2$ Hz, 2H), 3.02 (d, $^2J(\text{H,H}) = 19.3$ Hz, 1H), 2.67 (d, $^2J(\text{H,H}) = 19.3$ Hz, 1H), 1.65 (dd, $^4J_1(\text{H,H}) = 1.3$ Hz $^4J_2(\text{H,H}) = 0.5$ Hz, 3H), 1.39 (t, $^3J(\text{H,H}) = 7.2$ Hz, 3H), 1.29 (s, 3H), 0.294 (s, 9H); assigned with COSY. ^{13}C NMR (125 MHz, [D]chloroform, 25 $^{\circ}\text{C}$) $\delta = 214.5$, 168.8, 167.1, 147.0, 145.4, 111.9, 61.6, 53.3, 45.0, 22.2, 19.7, 14.1, -1.2 (3C); assigned with HMBC. FTIR (neat) $\nu = 3093$ (w), 2981 (m), 2903 (m), 1728 (s), 1707 (s), 1644 (w), 1588 (w), 1447 (m), 1368 (w), 1306 (w), 1249 (s), 1228.5 (w), 1193 (s), 1108 (m), 1072.9 (w), 1019 (w), 846 (s), 707 (w), 623 (w) cm^{-1} . HRMS for $\text{C}_{15}\text{H}_{24}\text{O}_3\text{Si}$: calc'd 280.1495 g/mol, found 280.1494 g/mol.

Alkenylcyclopentenones **17a** and **17b**:



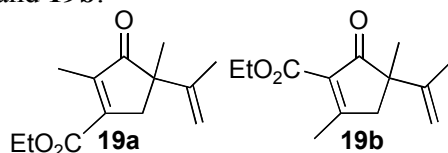
Chlorodicarbonylrhodium(I) dimer (6.0 mg, 0.0155 mmol) was added to a solution of methyloctynoate (48 mg, 0.31 mmol) and 2,3-dimethylbutadiene (351 μL , 3.1 mmol) in DCE (0.6 mL) in an oven-dried borosilicate test tube equipped with a magnetic stirrer and capped with a rubber septum. The solution was stirred under a balloon of CO, vented to a bubbler for 10 min. The solution was then stirred under a balloon of CO at 60 $^{\circ}\text{C}$ (in a temperature-controlled oil bath) for 28 hrs. Purification by flash chromatography on silica gel (2.5% diethyl ether/pentane, 10% diethyl ether/pentane, then 50% diethyl ether/pentane) gave cyclopentenone **17a** (21 mg, 31%) and cyclopentenone **17b** (18 mg, 22%) as clear, colorless oils.

Cyclopentenone **17a**: ^1H NMR (400 MHz, [D]chloroform, 25 $^{\circ}\text{C}$) $\delta = 4.90$ (apparent t, $J(\text{H,H}) = 1.3$ Hz, 1H), 4.86 (s, 1H), 3.86 (s, 3H), 2.91 (d, $^2J(\text{H,H}) = 18.9$ Hz, 1H), 2.57 (d,

$^2J(\text{H,H}) = 18.9$ Hz, 1H), 2.61-2.48 (m, 2H), 1.61 (dd, $^4J(\text{H,H}) = ^4J(\text{H,H}) = 0.61$ Hz, 3H), 1.45-1.39 (m, 2H), 1.32-1.27 (m, 4H), 1.26 (s, 3H), 0.87 (t, $^3J(\text{H,H}) = 7.2$ Hz, 3H) ppm. ^{13}C NMR (100 MHz, [D]chloroform, 25 °C) $\delta = 211.8, 165.8, 151.6, 150.1, 145.1, 112.0, 52.1, 52.0, 41.7, 31.8, 28.0, 24.2, 22.3, 22.4, 19.6, 13.9$ ppm. FTIR (neat) $\nu = 3408$ (w), 3091 (w), 2955 (s), 2930 (s), 2860 (m), 1718 (s), 1643 (m), 1438 (m), 1378 (m), 1272 (m), 1226 (s), 1188 (m), 1094 (m), 1030 (w), 985 (w), 948 (w), 895 (m), 767 (w), 730 (w) cm^{-1} . HRMS for $\text{C}_{16}\text{H}_{24}\text{O}_3$: calc'd 264.1725 g/mol, found 264.1729 g/mol.

Cyclopentenone **17b**: ^1H NMR (400 MHz, [D]chloroform, 25 °C) $\delta = 4.92$ (apparent t, $J(\text{H,H}) = 1.1$ Hz, 1H), 4.89 (s, 1H), 3.84 (s, 3H), 2.84 (d, $^2J(\text{H,H}) = 19.7$ Hz, 1H), 2.79 (dt, $^2J(\text{H,H}) = 15.8$ Hz, $^3J(\text{H,H}) = 7.5$ Hz, 1H), 2.60 (dt, $^2J(\text{H,H}) = 15.6$ Hz, $^3J(\text{H,H}) = 7.8$ Hz, 1H), 2.48 (d, $^2J(\text{H,H}) = 19.7$ Hz, 1H), 1.63 (dd, $^4J(\text{H,H}) = ^4J(\text{H,H}) = 0.61$ Hz, 3H), 1.61-1.56 (m, 2H), 1.38-1.32 (m, 4H), 1.28 (s, 3H), 0.91 (t, $^3J(\text{H,H}) = 7.0$ Hz, 3H) ppm. ^{13}C NMR (100 MHz, [D]chloroform, 25 °C) $\delta = 205.8, 186.7, 163.8, 145.0, 130.3, 112.2, 52.8, 51.8, 45.5, 32.4, 31.8, 27.3, 22.5, 22.3, 19.6, 13.9$ ppm. FTIR (neat) $\nu = 3418$ (w), 3091 (w), 2956 (m), 2931 (m), 2872 (m), 1745 (s), 1716 (s), 1626 (m), 1435 (m), 1378 (w), 1355 (m), 1290 (m), 1242 (m), 1198 (m), 1162 (w), 1121 (w), 1024 (w), 895 (w), 798 (w), 728 (w), 646 (w) cm^{-1} . HRMS for $\text{C}_{16}\text{H}_{24}\text{O}_3$: calc'd 264.1725 g/mol, found 264.1727 g/mol.

Alkenylcyclopentenones **19a** and **19b**:



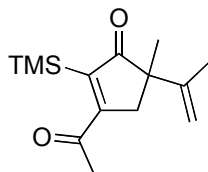
Chlorodicarbonylrhodium(I) dimer (7 mg, 0.018 mmol) was added to a solution of ethylbutyrate (40 mg, 0.36 mmol) and 2,3-dimethylbutadiene (407 μL , 3.6 mmol) in DCE (0.7 mL) in an oven-dried borosilicate test tube equipped with a magnetic stirrer and capped with a rubber septum. The solution was stirred under a balloon of CO, vented to a bubbler for 10 min. The solution was then stirred under a balloon of CO at 60 °C (in a temperature-controlled oil bath) for 28 hrs. Purification by flash chromatography on silica gel (5% diethyl ether/pentane, 10% diethyl ether/pentane, then 50% diethyl ether/pentane) gave cyclopentenone **19a** (18 mg, 18%) and cyclopentenone **19b** (31 mg, 39%) as clear, colorless oils.

Cyclopentenone **19a**: ^1H NMR (400 MHz, [D]chloroform, 25 °C) $\delta = 4.90$ (m, 1H), 4.86 (s, 1H), 4.32 (q, $^3J(\text{H,H}) = 7.1$ Hz, 2H), 2.91 (dq, $^2J(\text{H,H}) = 16.5$ Hz, $^4J(\text{H,H}) = 2.4$ Hz, 1H), 2.57 (dq, $^2J(\text{H,H}) = 16.5$ Hz, $^4J(\text{H,H}) = 2.3$ Hz, 1H), 1.27 (s, 3H), 2.07 (t, $^3J(\text{H,H}) = 2.3$ Hz, 3H), 1.62 (dd, $^4J(\text{H,H}) = ^4J(\text{H,H}) = 0.3$ Hz, 3H), 1.37 (t, $^3J(\text{H,H}) = 7.2$ Hz, 3H) ppm. ^{13}C NMR (100 MHz, [D]chloroform, 25 °C) $\delta = 212.2, 165.4, 152.3, 145.4, 145.1, 112.0, 61.2, 52.0, 41.7, 22.4, 19.7, 14.1, 10.1$ ppm. FTIR (neat) $\nu = 3416$ (w), 3092 (w), 2980 (m), 2932 (m), 2874 (w), 1784 (w), 1716 (s), 1640 (m), 1447 (m), 1378 (m), 1329 (m), 1296 (w), 1222 (s), 1146 (m), 1114 (w), 1095 (w), 1057 (m), 992 (m), 895 (m), 860 (w), 772 (m), 618 (w) cm^{-1} . HRMS for $\text{C}_{13}\text{H}_{13}\text{O}_3$: calc'd: 222.1256 g/mol, found: 222.1261 g/mol.

Cyclopentenone **19b**: ^1H NMR (400 MHz, [D]chloroform, 25 °C) $\delta = 4.90$ (s, 1H), 4.87 (s, 1H), 4.30 (q, $^3J(\text{H,H}) = 7.2$ Hz, 2H), 2.81 (d, $^2J(\text{H,H}) = 19.7$ Hz, 1H), 2.81 (d, $^2J(\text{H,H}) = 19.7$ Hz, 1H), 2.38 (s, 3H), 1.63 (dd, $^4J(\text{H,H}) = ^4J(\text{H,H}) = 0.6$ Hz, 3H), 1.34 (t, $^3J(\text{H,H}) = 7.2$ Hz, 3H), 1.27 (s, 3H) ppm. ^{13}C NMR (100 MHz, [D]chloroform, 25 °C) $\delta = 205.5, 182.1, 163.3, 144.9, 130.8, 112.2, 60.8, 52.9, 47.7, 22.4, 19.6, 19.1, 14.2$ ppm. FTIR (neat) $\nu = 3416$ (w), 3091 (w), 2980 (m), 2937 (m), 1742 (s), 1715 (s), 1634 (m), 1444 (m), 1378 (m), 1341 (m), 1293 (m),

1241 (s), 1171 (m), 1121 (m), 1097 (w), 1058 (m), 1022 (m), 949 (w), 896 (w), 641 (w) cm^{-1} .
HRMS for $\text{C}_{13}\text{H}_{13}\text{O}_3$: calc'd 222.1256 g/mol, found 222.1254 g/mol.

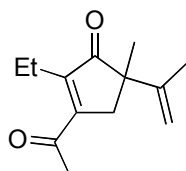
Alkenylcyclopentenone **21**:



4-Trimethylsilyl-3-butyn-2-one (24.5 mg, 175 μmol) was weighed out in an oven-dried 16x100 mm rest tube with a stir bar. To this was added 2,3-dimethylbutadiene (197 μL , 144 mg, 1.75 mmol), 1,1,2,2-tetrachlorethane (350 μL), and chlorodicarbonylrhodium(I) dimer (3.4 mg, 8.7 μmol). The test tube was capped with a septum and flushed 3 times with CO. The resulting solution was stirred at 60 $^{\circ}\text{C}$ for 32 hours under CO atmosphere. The resulting solution was purified by flash-column chromatography eluting with 5% diethyl ether/ pentane. Product-containing fraction were identified and concentrated by rotary evaporation to yield adduct **21** (17.1 mg, 39%) as a colorless oil.

^1H NMR (500 MHz, [D]chloroform, 25 $^{\circ}\text{C}$) δ = 4.91 (s, 1H), 4.86 (s, 1H), 2.96 (d, $^2J(\text{H,H})$ = 18.8 Hz, 1H), 2.62 (d, $^2J(\text{H,H})$ = 18.8 Hz, 1H), 2.40 (s, 3H), 1.63 (s, 3H), 1.28 (s, 3H), 0.185 (s, 9H); assigned with COSY. ^{13}C NMR (125 MHz, [D]chloroform, 25 $^{\circ}\text{C}$) δ = 214.1, 203.3, 177.2, 145.2, 143.1, 112.1, 53.3, 45.2, 29.3, 22.2, 19.6, -1.3 (3C); assigned with HMBC. FTIR (neat) ν = 2959 (w), 1699 (s), 1445 (w), 1358 (w), 1249 (m), 1178 (m), 1108 (w), 1061 (w), 897 (w), 841 (s), 624 (w) cm^{-1} . HRMS for $\text{C}_{14}\text{H}_{22}\text{O}_2\text{Si}$: calc'd 250.1389 g/mol, found 250.1394 g/mol.

Alkenylcyclopentenone **23**:



Chlorodicarbonylrhodium(I) dimer (5.3 mg, 0.0135 mmol) was added to a solution of 3-hexyn-2-one (30 μL , 0.27 mmol) and 2,3-dimethylbutadiene (310 μL , 2.7 mmol) in TCE (0.55 mL) in an oven-dried borosilicate test tube equipped with a magnetic stirrer and capped with a rubber septum. The solution was stirred under a balloon of CO, vented to a bubbler for 10 min. The solution was then stirred under a balloon of CO at 60 $^{\circ}\text{C}$ (in a temperature-controlled oil bath) for 19 hrs. Purification by flash chromatography on silica gel (pentane, then 12% diethyl ether/pentane) gave cyclopentenone **23** (35.5 mg, 63%) as a clear, colorless oil.

^1H NMR (400 MHz, [D]chloroform, 25 $^{\circ}\text{C}$) δ : 4.90 (d, $^2J(\text{H,H})$ = 0.6 Hz, 1H), 4.85 (d, $^2J(\text{H,H})$ = 0.6 Hz, 1H), 2.89 (d, $^2J(\text{H,H})$ = 18.5 Hz, 1H), 2.58 (d, $^2J(\text{H,H})$ = 19.1 Hz, 1H), 2.48 (q, $^3J(\text{H,H})$ = 7.2 Hz, 3H), 2.44 (s, 3H), 1.61 (s, 3H), 1.26 (s, 3H), 1.04 (t, $^3J(\text{H,H})$ = 7.5 Hz, 2H); assigned with COSY. ^{13}C NMR (100 MHz, [D]chloroform, 25 $^{\circ}\text{C}$) δ : 211.9, 199.3, 157.8, 147.5, 145.1, 112.0, 51.9, 42.0, 29.8, 19.6, 17.8, 12.9; assigned with HSQC and HMBC. FTIR (neat) ν = 3092 (w), 2972 (m), 2935 (m), 2877 (m), 1708 (s), 1645 (w), 1450 (m), 1361 (m), 1267 (w),

1199 (s), 1016 (m), 897 (m), 625 (w) cm^{-1} . HRMS for $\text{C}_{12}\text{H}_{18}\text{O}_2$: calc'd 206.1307 g/mol, found 206.1303 g/mol.

Product stability experiment: re-introducing cycloadduct **23** to the reaction conditions described above and quantifying the remaining material by GC resulted in < 3.4% deviation in each on 6 time points taken at 1, 2, 4.5, 6, 10, 20 hours.

Time course study: 7 identical experiments were run simultaneously as described above using DCE as solvent and quantified by GC analysis after 0, 1, 2, 4.5, 6, 8, and 10.5 hours. The quantity of starting alkyne, adduct **23** and 1-acetyl-2-ethyl-4,5-dimethylcyclohexa-1,4-diene (compared to an authentic sample prepared independently) were then quantified by GC.

Table 1. Mole Fraction of Materials Studied at Several Time Points^[a]

Time (h)	SM	P	4+2
0	100%	0	0
1	85%	16%	0
2	75%	22%	0
4.5	39%	37%	1%
6	23%	41%	1%
8	3%	42%	2%
10.5	0	44%	1%

[a] Error on each measurement < 2%.

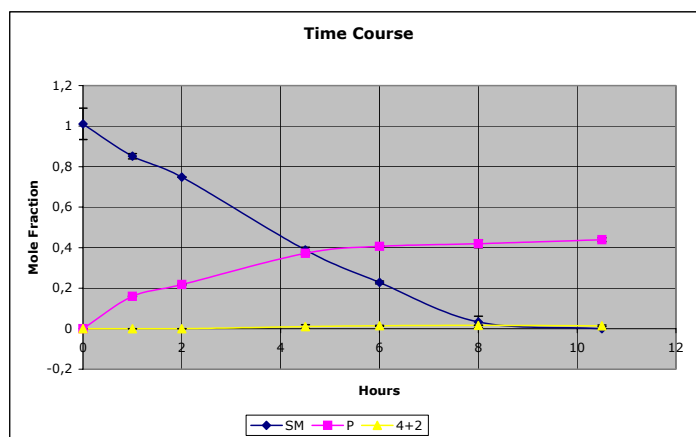


Chart 1. Mole Fraction of Materials over the Time Course of the Reaction.

Product inhibition experiment: The reaction was run as described above with 50% of the starting alkyne substituted for product. 67% product was recovered (50% added externally, 17% formed).

Although no reaction was noticed when the reaction was run in the absence of diene, treating 3-hexyn-2-one with **23** and catalyst (0.14 M in $[\text{D}_4]1,2$ -dichloroethane) in the presence of mesitylene (NMR standard) resulted in the decomposition of 3-hexyn-2-one. This data was quantified by $^1\text{H-NMR}$ (400 MHz, 12 sec pulse sequence) and is summarized in chart 2.

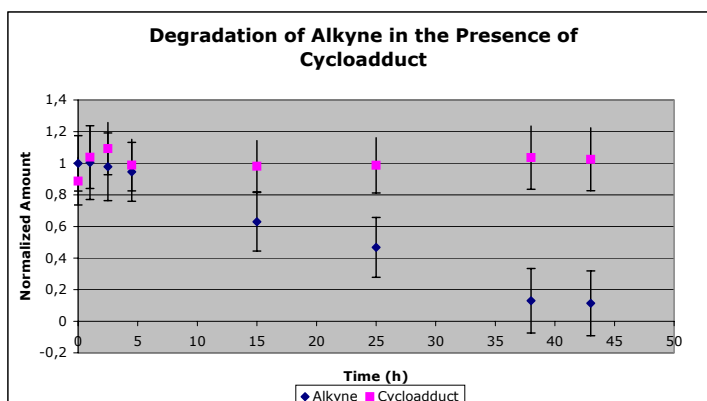
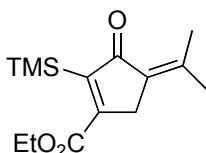


Chart 2. Alkyne Degradation.

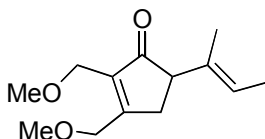
Cyclopentenone **25**:



Ethyl 3-trimethylsilylpropiolate (18.0 μL , 17.0 mg, 100 μmol), isoprene (100 μL , 68.1 mg, 1.00 mmol), 1,2-dichloroethane (distilled, 100 μL), and 1,1,2,2-tetrachloroethane (distilled, 100 μL) were mixed in an oven-dried 16x100 mm rest tube with a stir bar. To this was added and chlorodicarbonylrhodium(I) dimer (2.0 mg, 5.0 μmol). The test tube was capped with a septum and flushed three times with CO. A CO balloon was then affixed, and the resulting solution was stirred at 60 $^{\circ}\text{C}$ for 68 hours. The resulting solution was concentrated and the residue was purified by flash-column chromatography eluting with 5% diethyl ether/ pentane. Product-containing fraction were identified and concentrated by rotary evaporation to yield adduct **25** (8.3 mg, 31%) as a yellow oil.

^1H NMR (500 MHz, [D]chloroform, 25 $^{\circ}\text{C}$) δ = 4.31 (q, $^3J(\text{H,H})$ = 7.1 Hz, 2H), 3.35 (s, 2H), 2.29 (s, 3H), 1.91 (s, 3H), 1.36 (t, $^3J(\text{H,H})$ = 7.2 Hz, 3H), 0.25 (s, 9H); assigned with COSY. ^{13}C NMR (125 MHz HMBC, [D]chloroform, 25 $^{\circ}\text{C}$) δ = 200.1, 167.3, 162.3, 153.3, 148.3, 129.2, 61.6, 36.5, 24.9, 20.1, 14.1, -0.6 (3C). FTIR (neat) ν = 2981 (w), 2956 (w), 2904 (w), 1724 (s), 1685 (s), 1640 (m), 1580 (w), 1445 (w), 1369 (w), 1310 (w), 1248 (m), 1192 (s), 1099 (w), 847 (m) cm^{-1} . LRMS for $\text{C}_{14}\text{H}_{22}\text{O}_3\text{Si}$ calc'd: 266 g/mol, found: 266 g/mol.

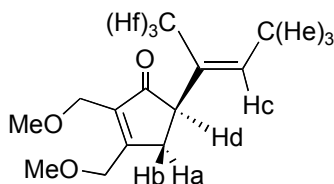
Alkenylcyclopentenone **27**:



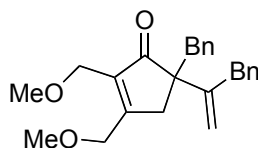
Chlorodicarbonylrhodium(I) dimer (25 mg, 0.0657 mmol) was added to a solution of 1,4-dimethoxy-2-butyne (75 mg, 0.66 mmol) and 3-methyl-1,3-pentadiene (~2.4:1 mixture of E and Z) (1.06 mL, 6.57 mmol) in DCE (1.3 mL) in an oven-dried borosilicate test tube equipped with a magnetic stirrer and capped with a rubber septum. The solution was stirred under a balloon of CO, vented to a bubbler for 10 min. The solution was then stirred under a balloon of CO at 60 $^{\circ}\text{C}$ (in a temperature-controlled oil bath) for 22 hrs. Purification by flash chromatography on silica

gel (10% diethyl ether/pentane, followed by 50% diethyl ether/pentane) gave alkenylcyclopentenone **27** (75 mg, 51%) as a pale yellow oil. Only E-3-methyl-1,3-pentadiene participated in reaction.

^1H NMR (400 MHz, [D]chloroform, 25 °C) δ = 5.38 (qd, $^3J(\text{H,H})$ = 6.7 Hz, $^4J(\text{H,H})$ = 0.6 Hz, 1H), 4.47 (d, $^2J(\text{H,H})$ = 15.0 Hz, 1H), 4.42 (d, $^2J(\text{H,H})$ = 15.3 Hz, 1H), 3.40 (s, 3H), 4.11 (s, 2H), 3.31 (s, 3H), 3.04 (dd, $^3J(\text{H,H})$ = 7.1 Hz, $^3J(\text{H,H})$ = 2.7 Hz, 1H), 2.86 (ddtdd, $^2J(\text{H,H})$ = 19.3 Hz, $^3J(\text{H,H})$ = 7.1 Hz, $^4J(\text{H,H})$ = $^4J(\text{H,H})$ = $^4J(\text{H,H})$ = 1.2 Hz, 1H), 2.51 (ddtdd, $^2J(\text{H,H})$ = 19.3 Hz, $^3J(\text{H,H})$ = 2.7 Hz, $^4J(\text{H,H})$ = $^4J(\text{H,H})$ = $^4J(\text{H,H})$ = 1.3 Hz, 1H), 1.68 (dd, $^3J(\text{H,H})$ = 6.7 Hz, $^4J(\text{H,H})$ = 0.5 Hz, 3H), 1.46 (apparent t, $^4J(\text{H,H})$ = 1.2 Hz, 3H) ppm. ^{13}C NMR (125 MHz, [D]chloroform, 25 °C) δ = 208.5, 173.4, 136.6, 132.3, 123.4, 70.0, 63.5, 59.1, 58.5, 54.4, 33.8, 13.5, 12.6 ppm. FTIR (neat) ν = 2981 (m), 2922 (m), 2820 (m), 1701 (s), 1654 (m), 1448 (m), 1380 (m), 1330 (w), 1193 (m), 1165 (m), 1106 (s), 1031 (m), 951 (m), 828 (w) cm^{-1} . HRMS for $\text{C}_{13}\text{H}_{20}\text{O}_3$: calc'd: 224.1412 g/mol, found 224.1417 g/mol. NOE: Hc, Hb (7%), Hc, He (5%), Hf, Hd (1%), Hf, He (1%), Hf, Hb (0.4%), He, Hc (2%), He, Hf (6%).



Alkenylcyclopentenone **28**:



Chlorodicarbonylrhodium(I) dimer (8.3 mg, 0.021 mmol) was added to a solution of 1,4-dimethoxy-2-butyne **1** (48.7 mg, 0.43 mmol) and 2,3-benzylbutadiene (200 mg, 0.853 mmol) in DCE (0.86 mL) in an oven-dried borosilicate test tube equipped with a magnetic stirrer and capped with a rubber septum. The solution was stirred under a balloon of CO, vented to a bubbler for 10 min. The solution was then stirred under a balloon of CO at 60 °C (in a temperature-controlled oil bath) for 9 hrs. Purification by flash chromatography on silica gel (5% diethyl ether/pentane, 10% diethyl ether/pentane, then 25% diethyl ether/pentane) gave cyclopentenone **28** (129.5 mg, 81%) as a white solid.

Mp. 98.5- 99.0 °C. ^1H NMR (400 MHz, [D]chloroform, 25 °C) δ = 7.29-7.25 (m, 2H), 7.21-7.14 (m, 6H), 7.10-7.08 (m, 2H), 5.23 (1H, s), 4.76 (s, 1H), 4.20 (d, $^2J(\text{H,H})$ = 15.3Hz, 1H), 4.07 (d, $^2J(\text{H,H})$ = 15.3Hz, 1H), 4.01 (d, $^2J(\text{H,H})$ = 12.7Hz, 1H), 3.90 (d, $^2J(\text{H,H})$ = 12.5Hz, 1H), 3.33 (s, 2H), 3.25 (d, $^2J(\text{H,H})$ = 13.3 Hz, 1H), 3.11 (s, 3H), 3.10 (s, 3H), 2.99 (d, $^2J(\text{H,H})$ = 13.1Hz, 1H), 2.82 (d, $^2J(\text{H,H})$ = 9.5 Hz, 1H), 2.75 (d, $^2J(\text{H,H})$ = 9.5 Hz, 1H). ^{13}C NMR (100 MHz, [D]chloroform, 25 °C) δ = 209.2, 172.8, 149.2, 139.2, 136.8, 136.6, 130.3 (2C), 129.5 (2C), 128.2 (2C), 128.0 (2C), 126.5, 126.1, 114.3, 69.5, 63.6, 58.6, 58.1, 56.7, 41.4, 39.6, 38.5 ppm. FTIR (neat) ν = 3629 (w), 3384 (w), 3084 (m), 3061 (m), 3027 (m), 2984 (m), 2926 (s), 2820 (m), 1953 (w), 1886 (w), 1182 (w), 1702 (s), 1698 (s), 1652 (s), 1603 (m), 1583 (w), 1495 (m), 1453 (s), 1402 (m), 1372 (m), 1333 (m), 1275 (m), 1243 (w), 1192 (m), 1166 (s), 1106 (s), 1031 (m), 1002 (w), 956 (m), 906 (m), 828 (w), 743 (m), 702 (s), 642 (w) cm^{-1} . HRMS for $\text{C}_{25}\text{H}_{28}\text{O}_3$: calc'd 376.2038 g/mol, found 376.2039 g/mol.

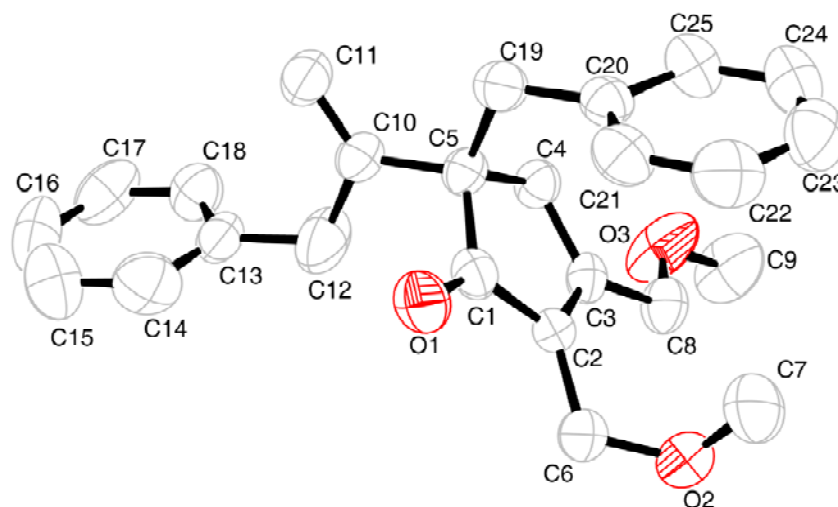
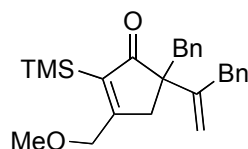


Figure 1. ORTEP Diagram of **28** (CCDC-232055); ellipsoids drawn at 50% probability level.

Alkenylcyclopentenone **29**:



3-Trimethylsilylpropargyl methyl ether (31.2 mg, 219 μmol), 2,3-dibenzyl-1,3-butadiene (103 mg, 439 μmol), and 1,2-dichloroethane (distilled, 440 μL) were mixed in an oven-dried 16x100 mm test tube with a stir bar. To this was added and chlorodicarbonylrhodium(I) dimer (4.3 mg, 11 μmol). The test tube was capped with a septum and flushed three times with CO. A CO balloon was then affixed, and the resulting solution was stirred at 60 $^{\circ}\text{C}$ for 6 hours. The resulting solution was concentrated and the residue was purified by flash-column chromatography eluting with 300 mL 2% diethyl ether/ pentane followed by 100 mL 10% diethyl ether/ pentane. Product-containing fractions were identified and concentrated by rotary evaporation to yield adduct **29** (87.1 mg, 98%) as a colorless solid.

Mp. 61- 61.5 $^{\circ}\text{C}$. ^1H NMR (500 MHz, $[\text{D}]\text{chloroform}$, 25 $^{\circ}\text{C}$) δ = 7.28- 7.08 (m, 10H), 5.21 (s, 1H), 4.75 (s, 1H), 4.06 (d, $^2J(\text{H,H})$ = 14.4 Hz, 1H), 3.95 (d, $^2J(\text{H,H})$ = 14.4 Hz, 1H), 3.27- 3.28 (m, 2H), 3.24 (d, $^2J(\text{H,H})$ = 12.9 Hz, 1H), 3.03 (s, 3H), 2.93 (d, $^2J(\text{H,H})$ = 12.9 Hz, 1H), 2.79- 2.80 (m, 2H), 0.129 (s, 9H); assigned with COSY, 1-D NOEs. ^{13}C NMR (75 MHz, $[\text{D}]\text{chloroform}$, 25 $^{\circ}\text{C}$) δ = 214.3, 183.1, 149.8, 140.7, 139.5, 137.2, 130.5 (2C), 129.5 (2C), 128.3 (2C), 127.9 (2C), 126.4, 126.1, 114.1, 71.2, 58.3, 57.3, 41.6, 41.4, 39.6, -0.7; assigned with HMBC. FTIR (neat) ν = 3058 (w), 3062 (w), 3028 (m), 2952 (m), 2925 (m), 2820 (s), 1690 (m), 1596 (m), 1495 (m), 1455 (m), 1304 (m), 1248 (s), 1195 (m), 1139 (m), 1105 (m), 1031 (w), 899 (w), 841 (s), 814, 733 (m), 701 (s), 630 (w) cm^{-1} . HRMS for $\text{C}_{22}\text{H}_{22}\text{O}_2\text{Si}$: calc'd 404.2172 g/mol, found 404.2191 g/mol.

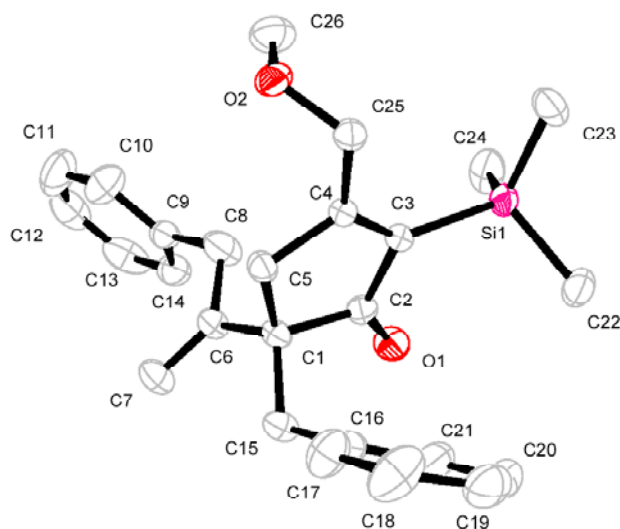
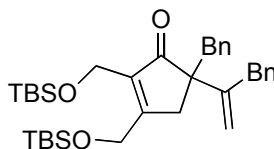


Figure 2. ORTEP Diagram of **29** (CCDC-232056); ellipsoids drawn at 25% probability level.

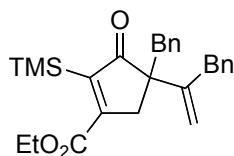
Alkenylcyclopentenone **30**:



1,4-Bis-*tert*-butyldimethylsilyloxy-2-butyne (31.6 mg, 101 μ mol), 2,3-dibenzyl-1,3-butadiene (47.2 mg, 201 μ mol), and 1,2-dichloroethane (distilled, 200 μ L) were mixed in an oven-dried 16x100 mm test tube with a stir bar. To this was added and chlorodicarbonylrhodium(I) dimer (2.0 mg, 5.0 μ mol). The test tube was capped with a septum and flushed three times with CO. A CO balloon was then affixed, and the resulting solution was stirred at 60 $^{\circ}$ C for 6 hours. The resulting solution was concentrated and the residue was purified by flash-column chromatography eluting with 2% diethyl ether/ pentane. Product-containing fractions were identified and concentrated by rotary evaporation to yield adduct **30** (43.5 mg, 75%) as a colorless oil.

1 H NMR (500 MHz, [D]chloroform, 25 $^{\circ}$ C) δ : 7.28- 7.05 (m, 10 H), 5.22 (s, 1H), 4.75 (t, $^4J(\text{H,H}) = 1.3$ Hz, 1H), 4.58 (dt, $^2J_1(\text{H,H}) = 16.6$ Hz, $^5J_2(\text{H,H}) = 1.0$ Hz, 1H), 4.32 (dt, $^2J_1(\text{H,H}) = 16.6$ Hz, $^4J_2(\text{H,H}) = 1.2$ Hz, 1H), 4.24 (d, $^2J(\text{H,H}) = 13.8$, 1H), 4.11 (dd, $^2J_1(\text{H,H}) = 13.7$ Hz, $^5J_2(\text{H,H}) = 1.0$ Hz, 1H), 3.29 (s, 2H), 3.23 (d, $^2J(\text{H,H}) = 13.1$ Hz, 1H), 2.96 (d, $^2J(\text{H,H}) = 12.9$ Hz, 1H), 2.82- 2.71 (m, 2H), 0.88 (s, 9H), 0.84 (s, 9H), 0.02 (s, 3H), 0.01 (s, 3H), -0.03 (s, 3H), -0.31 (s, 3H); assigned with COSY. 13 C NMR (125 MHz, [D]chloroform, 25 $^{\circ}$ C) δ : 209.0, 174.5, 149.6, 139.4, 136.9, 136.8, 130.1 (2C), 129.5 (2C), 128.2 (2C), 127.9 (2C), 126.4, 126.1, 114.1, 61.0, 56.6, 41.4, 39.5, 38.4, 25.8 (3C), 25.8 (3C), 18.2, 18.2, -5.6 (4C); assigned with HMBC. FTIR (neat) $\nu = 3086$ (w), 3063 (w), 3028 (w), 2954 (s), 2929 (s), 2885 (m), 2857 (s), 1699 (s), 1651 (m), 1495 (w), 1471 (m), 1464 (m), 1404 (w), 1361 (w), 1312 (w), 1257 (s), 1165 (m), 1106 (s), 1060 (m), 1030 (m), 1006 (w), (m) 898 (w), 837 (s), 815, (m) 777 (s), 743 (w), 701 (s) cm^{-1} . LC/MS for $\text{C}_{35}\text{H}_{52}\text{O}_3\text{Si}_2$: calc'd 576.3 g/mol, found 599.6 (M + Na $^+$) g/mol.

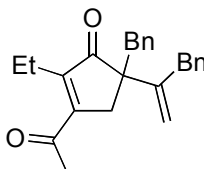
Alkenylcyclopentenone **31**:



Ethyl 3-trimethylsilylpropiolate (18.0 μL , 17.0 mg, 100 μmol), 2,3-dibenzyl-1,3-butadiene (46.9 mg, 200 μmol), 1,2-dichloroethane (distilled, 100 μL), and 1,1,2,2-tetrachlorethane (distilled, 100 μL) were mixed in an oven-dried 16x100 mm test tube with a stir bar. To this was added and chlorodicarbonylrhodium(I) dimer (2.0 mg, 5.0 μmol). The test tube was capped with a septum and flushed three times with CO. A CO balloon was then affixed, and the resulting solution was stirred at 60 $^{\circ}\text{C}$ for 24 hours. The resulting solution was concentrated and the residue was purified by flash-column chromatography eluting with 10% diethyl ether/pentane. Product-containing fraction were identified and concentrated by rotary evaporation to yield adduct **31** (43.1 mg, 99%) as a colorless oil.

^1H NMR (400 MHz, [D]chloroform, 25 $^{\circ}\text{C}$) δ : 7.29- 7.06 (m, 10H), 5.23 (s, 1H), 4.81 (t, $^4J(\text{H,H}) = 1.4$ Hz, 1H), 4.17 (q, $^3J(\text{H,H}) = 7.1$ Hz, 2H), 3.22 (s, 2H), 3.01 (d, $^2J(\text{H,H}) = 13.1$ Hz, 1H), 2.99- 2.87 (m, 2H), 2.98 (d, $^2J(\text{H,H}) = 13.1$ Hz, 1H), 1.27 (t, $^3J(\text{H,H}) = 7.2$ Hz, 3H), 0.102 (s, 9H); assigned with COSY. ^{13}C NMR (100 MHz, [D]chloroform, 25 $^{\circ}\text{C}$) δ : 213.6, 169.2, 166.4, 148.8, 148.7, 139.1, 136.7, 130.2 (2C), 129.4 (2C), 128.3 (2C), 128.0 (2C), 126.6, 126.2, 114.8, 61.3, 58.2, 41.9, 41.1, 39.7, 14.0, -1.2; assigned with HMBC. FTIR (neat) $\nu = 3086$ (m), 3063 (m), 3029 (s), 2981 (s), 2955 (s), 2926 (s), 2903 (s), 2854 (m), 1713 (s), 1634 (w), 1602 (m), 1495 (m), 1455 (m), 1368 (m), 1303 (s), 1248 (s), 1179 (s), 1093 (m), 1076 (m), 1030 (m), 1013 (m), 901 (m), 844 (s), 820 (m), 782 (m), 732 (m), 702 (s), 634 (w) cm^{-1} . HRMS for $\text{C}_{27}\text{H}_{32}\text{O}_3\text{Si}$: calc'd 432.2121 g/mol, found 432.2127 g/mol.

Alkenylcyclopentenone **32**:

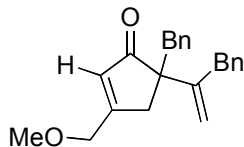


3-Hexy-2-one (30.2 mg, 34 μmol), 2,3-dibenzyl-1,3-butadiene (147 mg, 628 μmol), and 1,1,2,2-tetrachlorethane (distilled, 630 μL) were mixed in an oven-dried 16x100 mm test tube with a stir bar. To this was added and chlorodicarbonylrhodium(I) dimer (6.1 mg, 15.7 μmol). The test tube was capped with a septum and flushed three times with CO. A CO balloon was then affixed, and the resulting solution was stirred at 60 $^{\circ}\text{C}$ for 27 hours. The resulting solution was concentrated and the residue was purified by flash-column chromatography eluting with 2% diethyl ether/pentane. Product-containing fractions were identified and concentrated by rotary evaporation to yield adduct **32** (68.2 mg, 61%) as a colorless oil.

^1H NMR (400 MHz, [D]chloroform, 25 $^{\circ}\text{C}$) δ : 7.28- 7.05 (m, 10H), 5.24 (s, 1H), 4.85 (s, 1H), 3.31- 3.32 (m, 2H), 3.27 (d, $^2J(\text{H,H}) = 13.0$ Hz, 1H), 3.00 (d, $^2J(\text{H,H}) = 13.1$ Hz, 1H), 2.82 (s, 2H), 2.27- 2.24 (m, 2H), 2.10 (s, 3H), 0.846 (t, $^3J(\text{H,H}) = 7.5$ Hz, 3H); assigned with COSY. ^{13}C NMR (100 MHz, [D]chloroform, 25 $^{\circ}\text{C}$) δ : 211.2, 199.1, 158.9, 148.7, 148.2, 138.9, 136.3, 130.2 (2C), 129.3 (2C), 128.3, (2C) 128.1 (2C), 126.8, 126.3, 114.9, 56.6, 42.1, 39.9, 38.0, 29.6, 17.5, 15.5; assigned with HMBC. FTIR (neat): 3085 (s), 3062 (s), 3027 (s), 2972 (s), 2932 (s),

2875 (s), 1695 (s), 1634 (s), 1603 (s), 1583 (s), 1495 (s), 1455 (s), 1360 (s), 1265 (m), 1198 (s), 1075 (m), 1030 (s), 992 (m), 911 (s), 825 (m), 743 (s), 704 (s) cm^{-1} . HRMS for $\text{C}_{25}\text{H}_{26}\text{O}_2$: calc'd 358.1933 g/mol, found 358.1938 g/mol.

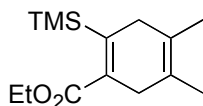
Desilylated Alkenylcyclopentenone **33**:



Cycloadduct **29** (42.1 mg, 104 μmol) was weighed out in an oven-dried 16 x 100 mm test tube with stir bar. To this was added tetrahydrofuran (solvtex, 1 mL), freshly-prepared tetrabutylammonium fluoride (1.0 M in tetrahydrofuran, 156 μL , 156 μmol), and acetic acid (8.9 μL , 9.4 mg, 160 μmol), and the resulting solution was stirred for 19 hours, then the portions of TBAF and acetic acid were doubled. The solution was stirred for four additional days, then the solution was poured over 10 mL each of saturated aqueous sodium bicarbonate and diethyl ether, and the organic layer was extracted. The resulting aqueous fraction was extracted three times with 25 mL diethyl ether. Combined organic fractions were dried with anhydrous sodium sulfate, concentrated by rotary evaporation, and the resulting residue was purified by flash column chromatography eluting with 15% diethyl ether in petroleum ether. Product-containing fractions were combined and concentrated by rotary evaporation to yield 25.2 mg (75%) of adduct **33** as a colorless oil.

^1H NMR (500 MHz, $[\text{D}]\text{chloroform}$, 25 $^\circ\text{C}$) δ = 7.27- 7.07 (m, 10H), 5.91 (t, $^4J(\text{H,H})$ = 1.6 Hz, 1H), 5.23 (s, 1H), 4.78 (t, $^4J(\text{H,H})$ = 1.5 Hz, 1H), 3.91 (dd, $^2J_1(\text{H,H})$ = 16.3 Hz $^4J_2(\text{H,H})$ = 1.3 Hz, 1H), 3.84 (dd $^2J_1(\text{H,H})$ = 16.4 Hz, $^4J_2(\text{H,H})$ = 1.3 Hz, 1H), 3.31-3.32 (m, 2H), 3.31 (d $^2J(\text{H,H})$ = 13.2 Hz, 1H), 3.10 (s, 3H), 2.95 (d 2J = 13.2 Hz, 1H), 2.63- 2.64 (m, 2H); assigned with COSY, 1-D NOEs. ^{13}C NMR (75 MHz, $[\text{D}]\text{chloroform}$, 25 $^\circ\text{C}$) δ : 210.3, 176.6, 149.1, 139.3, 136.8, 130.3 (2C), 129.4 (2C), 128.3 (2C), 128.0 (2C), 126.6, 126.2, 129.1, 129.0, 114.5, 71.4, 58.6, 57.5, 41.3, 39.6, 38.9; assigned with HMBC. FTIR (neat) ν = 3085 (m), 3061 (m), 3027 (m), 2988 (m), 2926 (s), 2825 (m), 1700 (s), 1627 (s), 1603 (m), 1583 (w), 1495 (s), 1455 (s), 1265 (m), 1196 (s), 1135 (s), 1103 (s), 1030 (m), 969 (m), 918 (m), 864 (m), 847 (m), 772 (m), 737 (m), 702 (s) cm^{-1} . HRMS for $\text{C}_{23}\text{H}_{24}\text{O}_2$: calc'd 332.177630 g/mol, found 332.176927 g/mol.

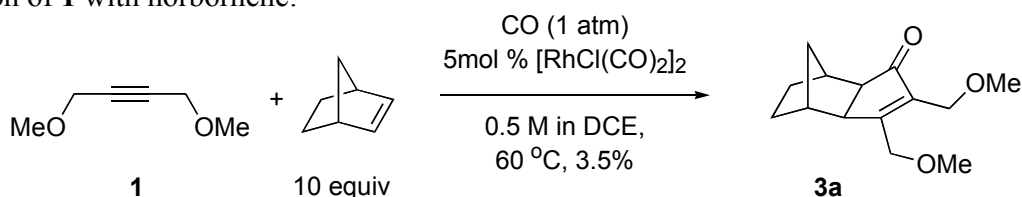
Cyclohexadiene **34**:



Ethyl 3-trimethylsilylpropionate (18.0 μL , 17.0 mg, 144 μmol), 2,3-dimethyl-1,3-butadiene (113 μL , 82.2 mg, 1.00 mmol), and 1,1,2,2-tetrachlorethane (distilled, 200 μL), were mixed in an oven-dried 16x100 mm rest tube with a stir bar. To this was added and chlorodicarbonylrhodium(I) dimer (2.0 mg, 5.0 μmol). The test tube was capped with a septum and the resulting solution was stirred at 60 $^\circ\text{C}$ for 8.5 hours. No CO was introduced to the system. This was purified by flash-column chromatography eluting with 2% diethyl ether/pentane. Product-containing fraction were identified and concentrated by rotary evaporation to yield adduct **34** (11.9 mg, 47%) as a colorless oil.

^1H NMR (400 MHz, $[\text{D}]\text{chloroform}$, 25 °C) δ = 4.19 (q, $^3J(\text{H,H}) = 7.1$ Hz, 2H), 2.86-2.82 (m, 4H), 1.65 (s, 3H), 1.64 (s, 3H), 1.30 (t, $^3J(\text{H,H}) = 7.1$ Hz, 3H), 0.15 (s, 9 H); assigned with COSY. ^{13}C NMR (100 MHz, $[\text{D}]\text{chloroform}$, 25 °C) δ = 168.6, 148.5, 136.1, 122.6, 122.1, 60.4, 38.9, 34.5, 18.2, 17.9, 14.3, -0.4 (3C); assigned with HMBC. FTIR (neat) ν = 2982 (m), 2953 (m), 2906 (m), 2860 (m), 1717 (s), 1606 (w), 1447 (w), 1386 (w), 1368 (w), 1259 (s), 1227 (s), 1143 (m), 1105 (w), 1048 (m), 1016 (w), 954 (w), 920 (w), 844 (s), 757 (m), 678 (w), 642 (w) cm^{-1} . LRMS for $\text{C}_{14}\text{H}_{24}\text{O}_2\text{Si}$: calc'd 252 g/mol, found 251 (M-H^+) g/mol. HRMS for $\text{C}_{14}\text{H}_{24}\text{O}_2\text{Si}$: (M-H^+) calc'd 251.1467 g/mol, found 251.1477 g/mol.

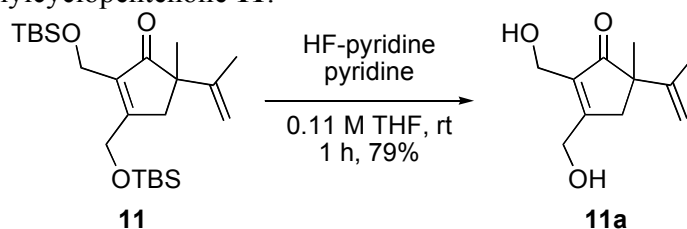
Reaction of **1** with norbornene:



1,4-Dimethoxy-2-butyne (26.3 μL , 24.8 mg, 217 μmol), freshly distilled norbornene (204 mg, 2.17 mmol), and 1,2-dichloroethane (distilled, 434 μL) were mixed in an oven-dried 16x100 mm test tube with a stir bar. To this was added and chlorodicarbonylrhodium(I) dimer (4.2 mg, 0.011 μmol). The test tube was capped with a septum and flushed three times with CO. A CO balloon was then affixed, and the resulting solution was stirred at 60 °C for 20 hours. The resulting solution was concentrated and the residue was purified by flash-column chromatography eluting with 300 mL 25% diethyl ether/ petroleum ether followed by 200 mL 50% diethyl ether/ petroleum ether. Product-containing fractions were identified and concentrated by rotary evaporation to yield adduct **3a** (1.8 mg, 3.5%) as a colorless oil.

^1H NMR (500 MHz, $[\text{D}]\text{chloroform}$, 25 °C) δ = 4.50 (d, $^2J(\text{H,H}) = 14.9$ Hz, 1H), 4.34 (d, $^2J(\text{H,H}) = 15.0$ Hz, 1H), 4.12 (d, $^2J(\text{H,H}) = 11.7$ Hz, 1H), 4.08 (d, $^2J(\text{H,H}) = 11.7$ Hz, 1H), 3.41 (s, 3H), 3.31 (s, 3H), 2.76 (d, $^3J(\text{H,H}) = 4.6$ Hz, 1H), 2.42 (d, $^3J(\text{H,H}) = 4.3$ Hz, 1H), 2.37 (d, $^3J(\text{H,H}) = 4.0$ Hz, 1H), 2.22 (d, $^3J(\text{H,H}) = 5.4$ Hz, 1H), 1.71- 1.65 (m, 1H), 1.60- 1.56 (m, 1H), 1.43- 1.24 (m, 4H); assigned by COSY and 1D-NOEs (ring junction). ^{13}C NMR (100 MHz, $[\text{D}]\text{chloroform}$, 25 °C) δ = 209.5, 174.7, 136.9, 69.2, 63.3, 59.1, 58.6, 53.6, 49.2, 39.1, 39.7, 31.3, 29.2, 28.5. FTIR (neat) ν = 3955 (s), 2926 (s), 2873 (s), 2820 (m), 1699 (s), 1653 (m), 1456 (w), 1399 (w), 1375 (w), 1296 (w), 1271 (w), 1197 (m), 1174 (m), 1106 (s), 955 (w) cm^{-1} . LRMS for $\text{C}_{14}\text{H}_{20}\text{O}_3$ calc'd: 236 g/mol, found: 236 g/mol.

Desilylation of alkenylcyclopentenone **11**:



Bis-TBS-ether cycloadduct **11** (28.6 mg, 67.3 μmol) was weighed out in an oven-dried 16x100 mm test tube. To this was added tetrahydrofuran (solvtex, 600 μL), pyridine (150 μL), and HF-pyridine (75 μL). The resulting white suspension was stirred for 1 hour at room

temperature before aqueous citric acid (1 mL, 1M) was added. The resulting slurry was extracted three times with 2 mL diethyl ether and nine times with 2 mL ethyl acetate. Organic fractions were concentrated and purified by flash column chromatography eluting with ethyl acetate to yield diol **11a** (10.4 mg, 79%) as a colorless oil.

¹H NMR (500 MHz, [D]chloroform, 25 °C) δ: 4.91 (s, 1H), 4.87 (s, 1H), 4.60 (s, 2H), 4.45 (s, 2H), ~3.8-3.2 (s, 1H), 2.74 (d, ²J(H,H) = 18.8 Hz, 1H), 2.40 (d, ²J(H,H) = 18.8 Hz, 1H), 1.61 (s, 3H), 1.26 (s, 3H), 1.25 (s, 3H); assigned with COSY. HMBC ¹³C (125 MHz, [D]chloroform, 25 °C) δ: 212, 173, 146, 137, 113, 63, 56, 53, 43, 23, 20. FTIR (neat) ν = 3401 (s, b), 2924 (s), 2854 (w), 1687 (s), 1645 (s), 1446 (m), 1379 (w), 1346 (w), 1301 (w), 1237 (w), 1170 (w), 1125 (w), 1075 (w), 989 (m), 898 (w), 898 (w) cm⁻¹. HRMS for C₁₁H₁₆O₃: calc'd 196.1099 g/mol, found 196.1108 g/mol.