Supporting Information to Accompany:

The First Intermolecular Transition Metal-Catalyzed [5+2] Cycloadditions with Simple, Unactivated, Vinylcyclopropanes

Paul A. Wender,* Claudia M. Barzilay, Alaric J. Dyckman
Department of Chemistry, Stanford University Stanford, California 94305.

General methods. Reactions were carried out in oven-dried glassware sealed with rubber septa under a positive pressure of dry nitrogen or argon from a manifold or balloon. Sensitive liquids and solutions were transferred via syringe or stainless steel cannula. Reactions were stirred using Teflon-coated magnetic stir bars. Elevated temperatures were maintained using Thermowatch-controlled silicone oil baths. Organic solutions were concentrated using a Buchi rotary evaporator with a recirculating aspirator pump. 1,2-Dichloroethane (DCE) and 2,2,2-triflluoroethanol were purchased from Aldrich, and used without further purification. $[Rh(CO)_2Cl]_2$ was purchased through Pressure Chemicals. Analytical TLC was performed with 0.25 mm silica gel 60F plates with 254 nm fluorescent indicator from Merck. Plates were visualized by ultraviolet light and treatment with acidic *p*-anisaldehyde stain followed by gentle heating. Purification of products was accomplished by flash chromatography. Silica gel 60, 230-400 mesh was purchased from EM.

NMR spectra were measured on a Varian INOVA 500 (^1H at 500 MHz, ^{13}C at 125 MHz), Varian XL-400 (^1H at 400 MHz, ^{13}C at 100 MHz), Varian Gem-300 (^1H at 300 MHz, ^{13}C at 75 MHz), or Varian Gem-200 (^1H at 200 MHz, ^{13}C at 50 MHz) magnetic resonance spectrometer. Data for ^1H NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, br s = broad singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, ddd = doublet of doublet of doublets, dddd = doublet of doublet of doublet of doublets, ddt = doublet of doublet of triplets, m = multiplet), coupling constant (Hz), and integration. Data for ^{13}C are reported in terms of chemical shift relative to residual solvent peak. Infrared spectra were recorded on a Perkin-Elmer 1600 Series Fourier transform spectrometer (FTIR) and are reported in wavenumbers (cm^{-1}). High-resolution mass spectra (HRMS) were recorded at the NIH regional mass spectrometry facility at the University of California, San Francisco and at the University of California, Riverside.

Representative Cycloaddition Procedure:

Conditions A:

To an Schlenk flask containing vinylcyclopropane **7** (27.2 mg, 107 μmol) and 1,2-DCE (2 ml) was added 5 mol% $[Rh(CO)_2Cl]_2$ (2.1 mg, 5.4 μmol). The solution was sparged with argon for 1 min and methyl propiolate (17 μl, 295 μmol) was added via syringe. The flask was sealed and placed in an oil bath at 80°C for 2 h leading to complete conversion of starting material. Upon cooling to room

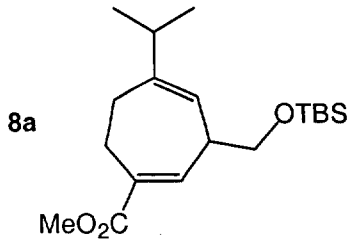
temperature the solution was filtered through a plug of silica gel and concentrated. Flash chromatography (silica gel, 6% EtOAc/hexane) afforded **8a** (33.7 mg, 99.5 μmol, 93%) as a colorless oil.

Conditions B:

The above procedure (**A**) was modified as follows: 0.1 ml 2,2,2-trifluoroethanol was added along with DCE (5 ml) as solvent. In 1 h at 80°C vinylcyclopropane **7** (25.6 mg, 100 μmol) was converted to **8a** (32.2 mg, 95 μmol, 95%)

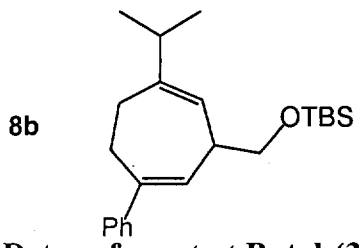
Conditions C:

The above procedure (**A**) was modified as follows: 2,2,2-trifluoroethanol (2 ml) was used as solvent in place of DCE. In 30 min at 80°C vinylcyclopropane **7** (23.8 mg, 94 μmol) was converted to **8a** (27 mg, 80 μmol, 85%)



Data for 3-(*tert*-Butyl-dimethyl-silanyloxymethyl)-5-isopropyl-cyclohepta-1,4-dienecarboxylic acid methyl ester (8a):

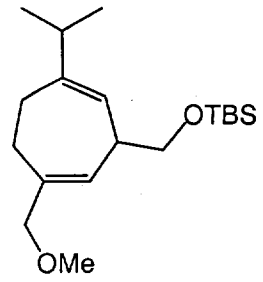
^{1}H-NMR (300 MHz, $CDCl_3$/TMS): δ = 6.93 (d, *J* = 2.4 Hz, 1H), 5.22 (d, *J* = 2.7 Hz, 1H), 3.72 (s, 3 H), 3.59-3.64 (m, 2H), 3.35-3.45 (m, 1H), 2.53-2.60 (m, 1H), 2.35-2.50 (m, 2H), 2.23 (septet, *J* = 6.8 Hz, 1H), 2.09-2.16 (m, 1H), 0.99 (d, *J* = 6.9 Hz, 6H), 0.91 (s, 9H), 0.09 (s, 3H), 0.08 (s, 3H) ppm. **^{13}C-NMR** (75 MHz, $CDCl_3$): δ= 168.56, 148.32, 142.23, 132.53, 120.91, 66.40, 51.66, 39.71, 36.46, 31.91, 29.69, 29.64, 29.35, 26.86, 25, 89, 25.74, 21.41, 21.23, 18.35, -5.30 ppm. **IR** (FT-IR, neat): ν= 2950.4 (s), 2922.0 (s), 2851.1 (s), 1713.6 (s), 1646.5 (w), 1462.6 (m), 1434.3 (m), 1384.8 (w), 1254.0 (s), 1109.1 (s), 1003.0 (w), 836.9 (s), 773.2 (s), 667.2 (w) cm^{-1}. **MS** (EI): m/z (%)= 323 (2), 281 (15), 185 (7), 162 (13), 115 (19), 89 (100), 75 (11), 73 (76). **HRMS:** Calculated for $C_{18}H_{31}O_3Si$ ($M-CH_3^+$): 323.2043 Found: 323.2042



Data for *tert*-Butyl-(3-isopropyl-6-phenyl-cyclohepta-2,6-dienylmethoxy)-dimethyl-silane (8b):

^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ= 7.20-7.36 (m, 5H), 5.87 (d, J=3.6 Hz, 1H), 5.32 (d, J=2.9 Hz, 1H), 3.67 (d, J=7.6 Hz, 2H), 3.41 (m, 1H), 2.77 (dd, J=22 Hz, J=12.9 Hz, 1H), 2.54 (dd, J=12.9 Hz, J=2 Hz, 2H), 2.17-2.29 (m, 2H), 1.03 (d, J=6.8 Hz, 6H), 0.92 (s, 9H), 0.09 (s, 6H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$): δ= 147.3, 144.2, 140.8, 128.9, 128.1, 126.5, 125.7, 122.1, 67.3, 65.9, 39.6, 36.6, 29.7, 27.6, 26.0, 21.6, 21.4, 18.4, 15.3, -5.2 ppm. **IR** (FT-IR, neat): ν= 3056.9 (w), 3027.9 (w), 2955.0 (s), 2891.9 (m), 2856.5 (m), 1598.0 (w), 1468.3 (m), 1384.8 (w), 1253.1 (m), 1110.1 (s), 1007.9 (w), 960.9 (w), 839.5 (s), 759.6 (s), 697.8 (s) cm^{-1}. **MS** (EI): m/z (%)= 299 (11), 224 (10), 211 (100), 181 (10), 167 (24), 155 (42), 91 (80), 73 (100) **HRMS**: Calculated for $C_{19}H_{27}OSi$ ($M-C_4H_9^+$): 299.1831 Found: 299.1804

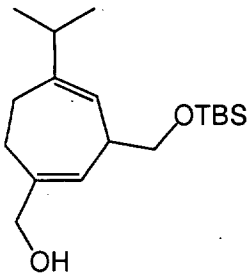
8c



Data for *tert*-Butyl-(3-isopropyl-6-methoxymethyl-cyclohepta-2,6-dienylmethoxy)-dimethyl-silane (8c):

^{1}H-NMR (300 MHz, $CDCl_3$/TMS): δ= 5.54 (d, J=2.1 Hz, 1H), 5.30 (d, J=3.2 Hz, 1H), 3.74 (s, 2H), 3.60 (d, J=7.8Hz, 2H), 3.28 (m, 1H), 3.27 (s, 3H), 2.40-2.49 (m, 1H), 2.19-2.33 (m, 2H), 2.04-2.14 (m, 2H), 1.01 (d, J=6.8 Hz, 6H), 0.90 (s, 9H), 0.07 (s, 6H) ppm. **^{13}C-NMR** (75 MHz, $CDCl_3$): δ= 147.9, 137.5, 128.0, 122.7, 79.0, 67.2, 65.9, 57.4, 39.2, 36.4, 29.7, 27.8, 27.2, 21.4, 21.3, 18.4, 15.3, -5.3 ppm. **IR** (FT-IR, neat): ν= 2950.4 (s), 2922.0 (s), 2886.5 (s), 2851.1 (s), 171.1 (w), 1462.6 (s), 1381.3 (m), 1360.1 (m), 1254.0 (s), 1186.9 (w), 1102.0 (s), 1006.6 (w), 939.4 (w), 833.3 (s), 776.8 (s), 667.2 (w) cm^{-1}. **MS** (EI): m/z (%)= 324 (2), 279 (2), 235 (2), 178 (2), 148 (100), 133 (20), 105 (35), 89 (90), 73 (93). **HRMS**: Calculated for $C_{19}H_{36}O_2Si$: 324.2485 Found: 324.2511.

8d

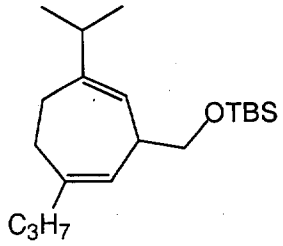


Data for [3-(*tert*-Butyl-dimethyl-silanyloxymethyl)-5-isopropyl-cyclohepta-1,4-dienyl]-methanol (8d):

^{1}H-NMR (300 MHz, $CDCl_3$/TMS): δ= δ= 5.55 (s, 1H), 5.29 (d, J=3.2 Hz, 1H), 3.95 (s, 2H), 3.60 (d, J=7.8Hz, 2H), 3.22-3.32 (m, 1H), 2.45 (m, 1H), 2.21-2.36 (m, 2H), 2.03-2.20 (m, 2H), 1.33 (br s, 1H), 1.01 (d, J=6.8 Hz, 6H), 0.91 (s, 9H), 0.07 (s, 6H) ppm. **^{13}C-NMR** (75 MHz, $CDCl_3$): δ= 147.9, 140.5, 125.9, 122.7, 69.2, 67.2, 39.1, 36.4, 27.2, 26.0, 21.4, 21.3, 18.4, -5.3 ppm.

Chemical correlation with compound 8c: treatment of 8d with NaH in THF and addition of MeI. Identical spectroscopic data (^{1}H-NMR) was obtained.

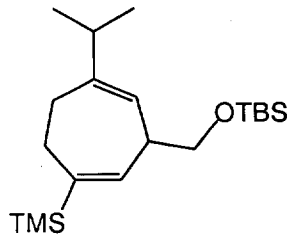
8e



Data for *tert*-Butyl-(3-isopropyl-6-propyl-cyclohepta-2,6-dienylmethoxy)-dimethyl-silane (8e):

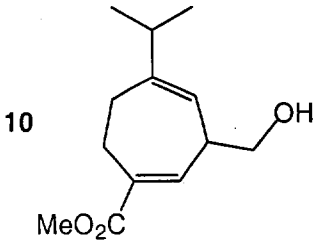
^{1}H-NMR (300 MHz, $CDCl_3$/TMS): δ= 5.31 (d, J=17.8 Hz, 2H), 3.57 (d, J=7.8 Hz, 2H), 3.23 (m, 1H), 2.25-2.40 (m, 1H), 2.18-2.24 (m, 2H), 1.98-2.10 (m, 2H), 1.85-1.93 (m, 2H), 1.35-1.44 (m, 2H), 1.00 (d, J=6.8 Hz, 6H), 0.92 (s, 3H), 0.91 (s, 9H), 0.07 (s, 6H) ppm. **^{13}C-NMR** (75 MHz, $CDCl_3$): δ= ppm. **IR** (FT-IR, neat): ν= 2957.4 (s), 2922.0 (s), 2886.5 (m), 2851.1 (s), 1692.4 (w), 1462.6 (m), 1384.8 (w), 1360.1 (w), 1254.0 (m), 1105.6 (s), 1006.6 (w), 939.4 (w), 836.9 (s), 776.8 (s), 667.2 (w) cm^{-1}. **MS** (DCI): m/z (%)= 263 (5), 221 (11), 189 (8), 147 (16), 75 (100). **HRMS**: Calculated for $C_{15}H_{25}OSi$ $(M-C_5H_{13})^+$: 249.1675 Found: 249.1677

8f

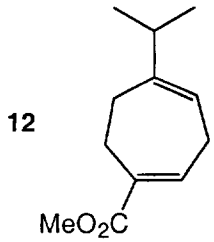


Data for 3-(*tert*-Butyl-dimethyl-silanyloxymethyl)-1-isopropyl-5-(trimethyl-silanyl)-cyclohepta-1,4-diene (8f):

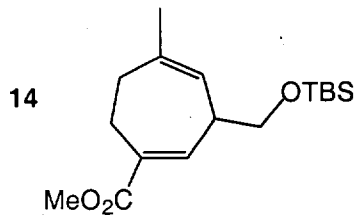
^{1}H-NMR (300 MHz, $CDCl_3$/TMS): δ= 5.89 (d, J=3.5 Hz, 1H), 5.20 (d, J=3.3 Hz, 1H), 3.61 (d, J=7.6 Hz, 2H), 3.37 (m, 1H), 2.39-2.48 (m, 1H), 2.30-2.35 (m, 1H), 2.14 (m, 2H), 1.57-2.00 (m, 1H), 0.98 (d, J=1.5 Hz, 3H), 0.96 (d, J=1.5 Hz), 3H), 0.91 (s, 9H), 0.07 (s, 6H), 0.04 (s, 9H) ppm. **^{13}C-NMR** (75 MHz, $CDCl_3$): δ=147.4, 143.0, 139.9, 121.2, 67.2, 40.8, 36.9, 28.2, 27.7, 25.9, 61.7, 21.4, -2.0, -5.3 ppm. **IR** (FT-IR, neat): ν= 2956.3 (s), 2928.7 (s), 2895.6 (s), 2856.9 (s), 1615.7 (w), 1463.1 (m), 1381.3 (w), 1360.8 (w), 1247.3 (s), 1110.4 (s), 1005.7 (w), 919.3 (w), 835.9 (s), 774.4 (s), 749.4 (m), 688.2 (w), 667.4 (w) cm^{-1}. **MS** (EI): m/z (%)= 295 (3), 279 (10), 237 (4), 221 (2), 197 (5), 148 (5), 133 (9), 75 (58). **HRMS**: Calculated for $C_{16}H_{31}OSi_2$ $(M-C_3H_{10}Si^+)$: 278.2066 Found: 278.2050



Data for 3-Hydroxymethyl-5-isopropyl-cyclohepta-1,4-dienecarboxylic acid methyl ester (10):
^{1}H-NMR (500 MHz, $CDCl_3$/TMS): δ = 6.94 (d, *J* = 2.9 Hz, 1H), 5.29 (d, *J* = 3.4 Hz, 1H), 3.73-3.76 (m, 2H), 3.72 (s, 3 H), 3.45-3.55 (m, 1H), 2.54-2.61 (m, 1H), 2.47 (d, *J* = 10.0 Hz, 1H), 2.40 (d, *J* = 10.0 Hz, 1H), 2.26 (septet, *J* = 6.8 Hz, 1H), 2.12-2.19 (m, 1H), 1.77 (br s, 1H), 1.00 (d, *J* = 6.8 Hz, 6H) ppm. Chemical correlation with compound 8a: treatment of 8a with TBAF in THF. Identical spectroscopic data (^{1}H-NMR) was obtained.

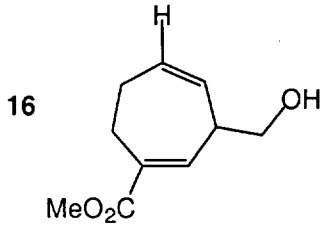


Data for 5-Isopropyl-cyclohepta-1,4-dienecarboxylic acid methyl ester
^{1}H-NMR (500 MHz, $CDCl_3$/TMS): δ = 7.00 (t, *J* = 6.0 Hz, 1H), 5.56 (t, *J*= 6.1 Hz, 1H), 3.71 (s, 3 H), 2.94 (t, *J* = 5.6 Hz, 2H), 2.48-2.52 (m, 2H), 2.27-2.31 (m, 2H), 2.17 (s, 1H), 0.99 (d, *J* = 6.8 Hz, 6H) ppm. **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = 140.10, 112.25, 34.87, 29.69, 22.33, 19.66, 14.06, 12.87 ppm.



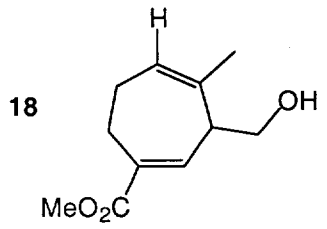
Data for 3-(*tert*-Butyl-dimethyl-silanyloxymethyl)-5-methyl-cyclohepta-1,4-dienecarboxylic acid methyl ester (14):
^{1}H-NMR (500 MHz, $CDCl_3$/TMS): δ = 6.98 (d, *J* = 4.0 Hz, 1H), 5.19 (s, 1H), 3.74 (s, 3 H), 3.69 (dd, *J* = 9.5 Hz, *J* = 7.3 Hz, 1H), 3.64 (dd, *J* = 9.5 Hz, *J* = 7.5 Hz, 1H), 3.40-3.45 (m, 1H), 2.60-2.63 (m, 1H), 2.31 (dm, *J* = 15.4 Hz, 1H), 2.00-2.10 (m, 1H), 1.70 (s, 3H), 0.93(s, 9H), 0.10 (s, 3H), 0.09 (s, 3H) ppm. **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = 168.11, 143.83, 138.28, 132.96, 121.90, 66.37, 51.68, 39.88, 30.54, 25.91, 25.77, 24.43, 18.37, -5.31, -5.34 ppm. **IR** (FT-IR, neat): ν = 2952.7 (m), 2927.0 (m), 2894.0 (m), 2857.1 (m), 1715.4 (s), 1647.8 (m), 1471.9 (m), 1435.8 (m), 1388.1 (w), 1361.4 (w),

1277.5 (m), 1235.4 (s), 1191.9 (m), 1110.2 (s), 1034.8 (w), 1006.3 (w), 968.2 (w), 939.2 (w), 837.8 (s), 776.7 (m), 668.1 (w) cm^{-1}. **MS** (DCI): m/z (%) = 328(11) $(MNH_4)^+$, 311(39) (MH^+), 310(3), 295(20), 254(19), 253(100), 179(55), 134(27), 132(13), 119(34), 106(12), 105(13), 90(15), 89(51), 75(27), 73(35), 57(11). **HRMS:** Calculated for $C_{17}H_{31}O_3Si$ $(MH)^+$; 311.2042 Found: 311.2032.



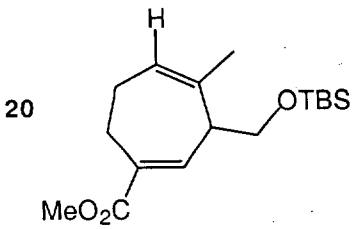
Data for 3-Hydroxymethyl-cyclohepta-1,4-dienecarboxylic acid methyl ester (16):

^{1}H-NMR (500 MHz, $CDCl_3$/TMS): δ = 7.01 (d, *J* = 4.4 Hz, 1H), 5.79 (ddd, *J* = 11.4 Hz, *J* = 5.3 Hz, *J* = 2.0 Hz, 5.43 (dm, *J* = 11.4 Hz, 1H), 3.77-3.81 (m, 2H), 3.74 (s, 3 H), 3.50-3.55 (m, 1H), 2.64-2.69 (m, 2H), 2.26-2.33 (m, 1H), 2.14-2.21 (m, 1H), 1.60 (br s, 1H) ppm. **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = 168.00, 143.04, 134.58, 132.14, 126.97, 66.15, 51.83, 40.83, 25.82, 25.86 ppm. **IR** (FT-IR, neat): ν = 3456.7 (br), 2944.6 (s), 2923.7 (s), 2881.9 (m), 1704.0 (s), 1427.0 (m), 1380.0 (w), 1275.5 (m), 1228.4 (s), 1191.9 (w), 1061.2 (m), 747.6 (w) cm^{-1}. **HRMS:** Calculated for $C_{10}H_{15}O_3$ $(M+H)^+$; 183.1021 Found: 183.1038.



Data for 3-Hydroxymethyl-4-methyl-cyclohepta-1,4-dienecarboxylic acid methyl ester (18):

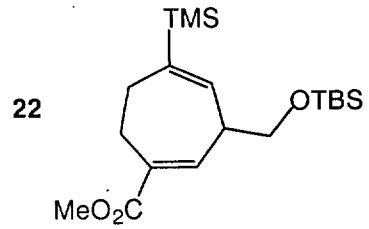
^{1}H-NMR (500 MHz, $CDCl_3$/TMS): δ = 6.98 (dt, *J* = 6 Hz, *J* = 1.3 Hz, 1H), 5.73 (ddd, *J* = 7 Hz, *J* = 6 Hz, *J* = 1.5 Hz, 1H), 3.87 (dd, *J* = 6 Hz, *J* = 6 Hz, 2H), 3.73 (s, 3 H), 3.17 (dt, *J* = 6 Hz, *J* = 6 Hz, 1H), 2.59 (dddd, *J* = 16.5 Hz, *J* = 8.2 Hz, *J* = 1.5 Hz, *J* = 1.3 Hz, 1H), 2.40 (ddm, *J* = 13.5 Hz, *J* = 11.4 Hz, 1H), 2.31 (ddm, *J* = 15 Hz, *J* = 13.5 Hz, 1H), 2.18 (dddd, *J* = 15 Hz, *J* = 7.3 Hz, *J* = 7.3 Hz, *J* = 2.7 Hz, 1H), 1.78 (s, 3H), 1.72 (br s, 1H) ppm. **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = 168.68, 139.99, 135.42, 134.59, 127.57, 64.59, 51.90, 47.52, 25.72, 25.23, 24.83 ppm. **IR** (FT-IR, neat): ν = 3447.7 (br), 2950.7 (m), 1711.1 (s), 1647.9 (w), 1436.0 (m), 1388.8 (w), 1274.7 (m), 1236.2 (s), 1067.9 (m), 1015.2 (m), 916.6 (w), 819.2 (w), 748.8 (w) cm^{-1}. **HRMS:** Calculated for $C_{11}H_{15}O_3$ $(M-H)^+$; 195.1043 Found: 195.1021.



20

Data for 3-(*tert*-Butyl-dimethyl-silanyloxymethyl)-4-methyl-cyclohepta-1,4-dienecarboxylic acid methyl ester (20):

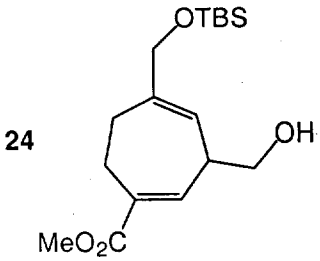
^{1}H-NMR (300 MHz, $CDCl_3$/TMS): δ= 6.99 (d, J=6.6 Hz, 1H), 5.61 (t, J=5.9 Hz, 1H), 3.69-3.82 (m, 2H), 3.67 (s, 3H), 3.11 (tt, J=6.8 Hz, J=6.6 Hz, 1H), 2.47-2.54 (m, 1H), 2.32-2.37 (m, 1H), 2,10-2.32 (m, 2H), 1.76 (s, 3H), 0.90 (s, 9H), 0.06 (s, 6H) ppm. **^{13}C-NMR** (75 MHz, $CDCl_3$): δ= 168.7, 140.9, 136.7, 126.5, 122.9, 65.1, 60.2, 51.8, 47.2, 26.0, 25.9, 25.1, 4.4, -5.4 ppm. **IR** (FT-IR, neat): ν= 2950.4 (s), 2922.0 (s), 2851.1 (s), 1713.6 (s), 1646.5 (w), 1462.6 (m), 1430.8 (m), 1388.4 (w), 1360.1 (w), 1271.7 (s), 1250.5 (s), 1226.0 (s), 1186.9 (w), 1091.4 (s), 1003.0 (w), 918.2 (w), 836.9 (s), 773.2 (s), 748.5 (w), 663.6 (w) cm^{-1}. **MS** (EI): m/z (%)= 310 (2), 253 (12), 178 (3), 119 (11), 115 (16), 95 (16), 91 (11), 73 (97). **HRMS**: Calculated for $C_{17}H_{30}O_3Si$: 310.1964 Found: 310.1968.



22

Data for 3-(*tert*-Butyl-dimethyl-silanyloxymethyl)-5-(trimethyl-silanyl)-cyclohepta-1,4-dienecarboxylic acid methyl ester (22):

^{1}H-NMR (500 MHz, $CDCl_3$/TMS): δ = 6.87 (d, *J* = 5.3 Hz, 1H), 5.85 (s, 1H), 3.74 (s, 3H), 3.69-3.73 (m, 2H), 3.59 (td, *J* = 7.0 Hz, *J* = 3.5 Hz, 1H), 2.64 (dm, *J* = 17.0, 1H), 2.56 (dd, J = 13.1 Hz, J = 11.5 Hz, 1H), 2.31 (tm, J = 17.0 Hz, 1H), 2.25-2.30 (m, 1H), 0.94 (s, 9H), 0.11 (s, 6H), 0.08 (s, 6H) ppm. **13C-NMR** (125 MHz, CDCl3): δ = 168.64, 144.53, 140.92, 138.45, 132.71, 66.06, 51.71, 40.86, 36.67, 26.08, 23.87, 18.35, -2.13, -5.30, -5.36 ppm. **IR** (FT-IR, neat): ν = 2953.2 (m), 2929.4 (m), 2897.1 (m), 2857.1 (m), 1715.7 (s), 1653.4 (w), 1617.2 (w), 1474.9 (w), 1463.2 (w), 1435.2 (w), 1388.7 (w), 1248.3 (s), 1232.1 (s), 1121.7 (m), 1094.6 (m), 836.2 (s), 776.5 (m), 750.0 (w), 690.0 (w), 668.0 (w), 628.3 (w) cm^{-1} **MS** (CI): m/z (%) = 397(16) $(MNH_4)^+$, 369(46) (MH^+), 353(100), 337(12), 312(12), 311(45), 238(11), 237(52), 192(7), 133(52), 105(18), 89(36), 73(24). **HRMS:** Calculated for $C_{19}H_{37}O_3Si_2$ $(MH)^+$; 369.2281 Found: 369.2282.



24

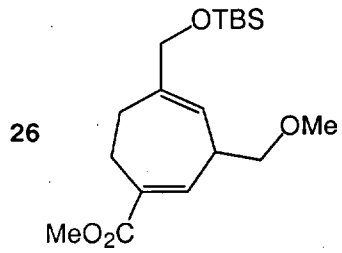
Data for 5-(*tert*-Butyl-dimethyl-silanyloxymethyl)-3-hydroxymethyl-cyclohepta-1,4-dienecarboxylic acid methyl ester (24):

^{1}H-NMR (300 MHz, $CDCl_3$/TMS):δ = 6.98 (d, *J* = 4.0 Hz, 1H), 5.30 (s, 1H), 3.74 (s, 3H), 3.70-3.76 (m, 4H), 3.47-3.50 (m, 1H), 2.58-2.65 (m, 2H), 2.28-2.40 (m, 1H), 2.05-2.13 (m, 1H), 1.60 (br s, 1H), 0.90 (s, 9H), 0.06 (s, 6H) ppm.

13C-NMR (125 MHz, CDCl3): δ =

IR (FT-IR, neat): ν =

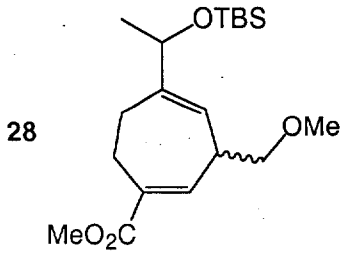
MS (+CI): m/z (%) = 358(4), 328 (38), 311(27), 309(28), 253(15), 180(11), 179(100), 177(16), 134(14), 132(18), 119(20), 106(38), 105(14), 91(20), 89(15), 76(13), 74(23), 73(27), 59(12) **HRMS:** Calculated for $C_{18}H_{36}NO_4Si$ $(MNH_4)^+$; 358.2414 Found: 358.2400



26

Data for 5-(*tert*-Butyl-dimethyl-silanyloxymethyl)-3-methoxymethyl-cyclohepta-1,4-dienecarboxylic acid methyl ester (26):

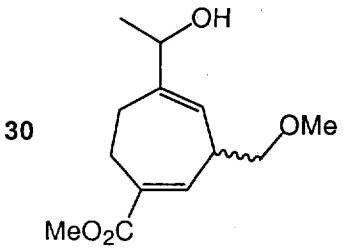
^{1}H-NMR (300 MHz, $CDCl_3$/TMS): δ = 6.94 (d, *J* = 3.9 Hz, 1H), 5.46 (s, 1H), 3.97 (s, 2 H), 3.72 (s, 3H), 350-3.63 (m, 1H), 3.47 (s, 2H), 3.39 (s, 3H), 2.59-2.63 (m, 2H), 2.28-2.40 (m, 1H), 1.95-2.10 (m, 1H), 0.90 (s, 9H), 0.05 (s, 6H) ppm. **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = 168.07, 142.95, 141.42, 133.45, 121.89, 75.93, 67.67, 58.99, 51.77, 37.23, 25.90, 25.75, 24.49, 18.38, -5.32, -5.35 ppm. **IR** (FT-IR, neat): ν = 2952.3 (m), 2926.0 (m), 2855.9 (m), 1715.1 (s), 1435.9 (w), 1388.1 (w), 1234.2 (m), 1191.7 (w), 1119.8 (m), 1070.3 (m), 836.6 (m), 776.2 (w) cm^{-1}. **MS** (+CI):m/z (%) = 358(4) $(MNH_4)^+$, 328 (38), 311(27), 309(28), 253(15), 180(11), 179(100), 177(16), 134(14), 132(18), 119(20), 106(38), 105(14), 91(20), 89(15), 76(13), 74(23), 73(27), 59(12) **HRMS:** Calculated for $C_{18}H_{36}NO_4Si$ $(MNH_4)^+$; 358.2414 Found: 358.2400.



28

Data for 5-[1-(*tert*-Butyl-dimethyl-silanyloxy)-ethyl]-3-methoxymethyl-cyclohepta-1,4-dienecarboxylic acid methyl ester(28): (2 diastereomers)

^{1}H-NMR (300 MHz, $CDCl_3$/TMS): δ = 6.896 (m, 1H), 5.45 (m, 1H, minor diastereomer), 5.42 (m, 1H, minor diastereomer), 4.13 (q, *J* = 6.6 Hz, 1H), 3.72 (s, 3H), 3.50 (m, 1H), 3.46 (m, 2H), 3.39 (s, 3H), 2.50-2.54 (m, 2H), 2.31-2.38 (m, 2H), 1.18 (d, *J*= 6.5 Hz), 0.87 (s, 9H), 0.03 (s, 3H). 0.02 (s, 3H) ppm. **IR** (FT-IR, neat): ν = 2926.1 (m), 2850.5 (m), 1717.4 (s), 1654.1 (w), 1458.2 (w), 1234.6 (m), 1186.0 (w), 1103.0 (m), 1068.6 (m), 836.9 (m), 768.5 (w) cm^{-1}. Chemical correlation with compound 28: treatment of 28 with TBSCl and imidaole in DMF. Identical spectroscopic data (^{1}H-NMR) was obtained.



30

Data for 5-(1-Hydroxy-ethyl)-3-methoxymethyl-cyclohepta-1,4-dienecarboxylic acid methyl ester (30): (2 diastereomers)

^{1}H-NMR (300 MHz, $CDCl_3$/TMS): δ = 6.87-6.89 (m, 1H), 5.30-5.55 (m, 1H), 4.20 (q, *J* = 6.3 Hz, 1H), 3.72 (s, 3H, one diastereomer), 3.72 (s, 3H, one diastereomer), 3.46-3.48 (m, 2H), 3.46-3.48 (m, 2H), 3.40 (s, 3H), 2.51-2.58 (m, 1H), 2.39-2.52 (m, 2H), 2.17-2.25 (m, 1H), 1.64 (br. s, 1H), 1.26 (d, *J* = 3.2 Hz, 3H, one diastereomer), 1.25 (d, *J* = 3.2 Hz, 3H, one diastereomer) ppm. **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = 168.19, 168.13, 145.95, 145.87, 141.67, 141.64, 133.32, 133.26, 123.72, 123.02, 75.89, 75.87, 72.75, 72.62, 59.07, 52.11, 51.81, 37.18, 37.10, 29.68, 25.39, 25.18, 24.65, 24.16, 21.75, 21.54 ppm. **IR** (FT-IR, neat): ν = 3456.7 (br), 2961.7 (m), 2913.2 (w), 2850.5 (w), 1717.9 (s), 1437.5 (w), 1259.7 (s), 1097.2 (m), 1029.3 (m), 798.3 (m) cm^{-1} **HRMS:** Calculated for $C_{13}H_{18}O_3$ $(M-H_2O)^+$; 222.1256 Found: 222.1270.