Supporting Information for:

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**Conjugate Additions of Carbon Nucleophiles
to Cyclopentadienones**

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General Procedures. All reactions were performed under argon atmosphere, in freshly distilled (under nitrogen) solvents. All reagents used are commercially available. Analytical thin-layer chromatography was performed on aluminum plates precoated with Merck F₂₅₄ silica gel. Visualization was done either with UV light or with anisaldehyde. Flash chromatography was performed with hexanes-ethyl acetate mixtures on silica gel with mesh 170-400, under nitrogen pressure. NMR spectra were recorded on a Varian Gemini 200 (200 MHz) or a Varian Gemini 300 (300 MHz) spectrometer. Mass spectra were recorded in-house using a Kratos MS25A instrument. IR spectra were recorded on a Nicolet Impact 400 spectrometer. The melting points were measured on a Thomas Hoover apparatus and are uncorrected.

Addition Reaction of 2,5-Bis(trimethylsilyl)-3,4-bis(hydroxymethyl)cyclopentadienone (1a) with Grignard reagent

To a THF solution (10 mL) of **1a** (50.0 mg, 0.176 mmol) at -78 °C was added methylmagnesium bromide (0.88 mL of 1M in ether, 0.88 mmol). The reaction mixture was stirred for 20 min at -78 °C, quenched with saturated NH₄Cl solution, and extracted with ethyl acetate (3 × 15 mL). The combined organic phases were dried and concentrated to give a residue that was purified by flash chromatography on silica gel (elution with 40% ethyl acetate in hexanes). Enone **2a** was isolated as a colorless oil (50.2 mg, 0.167 mmol, 95%).

Methylation of 2,5-Bis(trimethylsilyl)-3,4-bis(hydroxymethyl)cyclopentadienone (1a)

To a stirred solution of methyl triflate (1.54 mL, 13.7 mmol) in di-tert-butylpyridine (6 mL) was added **1a** (1.20 g, 4.23 mmol) in chloroform (10 mL). After stirring for 8 h, the solution was poured into water and extracted with dichloromethane (3 × 10 mL). The combined organic layers were extracted with 10% HCl solution (3 × 50 mL), then dried and concentrated to give **1b** as a yellow oil (1.12 g, 3.59 mmol, 85%).

Addition Reaction of 2,5-Bis(trimethylsilyl)-3,4-bis(methoxymethyl)cyclopentadienone (**1b**) with Grignard reagent

To a THF solution (10 mL) of **1b** (40.0 mg, 0.128 mmol) at -78 °C was added methylmagnesium bromide (0.17 mL of 1M in ether, 0.17 mmol). The reaction mixture was stirred for 5 min at -78 °C, quenched with saturated NH₄Cl solution, and extracted with ethyl acetate (3 × 10 mL). The combined organic phases were dried and concentrated to leave a residue that was purified by flash chromatography on silica gel to give **5a** as a white solid (40.2 mg, 0.122 mmol, 95%).

Desilylation of **2** and **4**

To an ethanol solution (10 mL) of **2a** (25.0 mg, 0.083 mmol) at 23 °C, was added a catalytic amount of NaOH (ca. 0.5 mg). After stirring for 1 h at ca. 50 °C, the solution was cooled to 23 °C, poured into water (20 mL) and extracted with ethyl acetate (3 × 10 mL). The combined organic layers were partitioned with water (10 mL) and brine (10 mL), dried and concentrated to give **7a** as a colorless oil (18.1 mg, 0.078 mmol, 94%).

Characterization Data :

¹H NMR (C₆D₆) δ 4.37 and 4.08 (ABq, J = 10.8 Hz, 2H), 3.38 and 3.23 (ABq, J = 10.7 Hz, 2H), 2.06 (s, 1H), 1.10 (s, 3H), 0.37 (s, 9H), 0.13 (s, 9H). Attempts to obtain ¹³C NMR data were hampered by desilylation during acquisition.

¹H NMR (C₆D₆) δ 4.29 and 4.00 (ABq, J = 12.1 Hz, 2H), 3.29 and 3.09 (ABq, J = 10.8 Hz, 2H), 2.28 and 1.93 (ABq, J = 17.9 Hz, 2H), 0.79 (s, 3H), 0.38 (s, 9H).

¹³C NMR (C₆D₆) δ 210.8, 186.5, 144.2, 68.7, 57.6, 49.5, 48.3, 22.0, -0.05.

IR (neat, cm⁻¹) 3385 (br, OH), 1674.

TLC R_f 0.47 (50% ethyl acetate / hexane).

HRMS(EI) M⁺ calcd. for C₁₁H₂₀O₃Si 228.1182 found 213.0942, M⁺-(CH₃, H₂O) calcd. for C₁₀H₁₅O₂Si 195.0841 found 195.0858.

^1H NMR (C_6D_6) δ 5.82 (dd, J = 17.8, 10.8 Hz, 1H), 5.27 (d, J = 10.8 Hz, 1H), 5.04 (d, J = 17.8 Hz, 1H), 4.51 and 4.32 (ABq, J = 11.5 Hz, 2H), 4.07 and 3.64 (ABq, J = 11.2 Hz, 2H), 2.28 (s, 1H), 0.29 (s, 9H), 0.12 (s, 9H). Attempts to obtain ^{13}C NMR data were hampered by desilylation during acquisition.

^1H NMR (C_6D_6) δ 5.92 (dd, J = 17.6, 10.8 Hz, 1H), 5.19 (d, J = 10.8 Hz, 1H), 5.06 (d, J = 17.8 Hz, 1H), 4.77 (HOD, 2H), 4.57 and 4.38 (ABq, J = 11.9 Hz, 2H), 4.03 and 3.69 (ABq, J = 11.1 Hz, 2H), 2.56 and 2.38 (ABq, J = 18.1 Hz, 2H), 0.28 (s, 9H)

^{13}C NMR (CDCl_3) δ 211.4, 182.6, 145.9, 139.7, 115.7, 66.4, 58.2, 56.1, 46.9, -0.38

IR (neat, cm^{-1}) 3400 (br, OH), 1681.

TLC R_f 0.52 (50% ethyl acetate / hexane).

HRMS(EI) M^+ -2H calcd. for $\text{C}_{12}\text{H}_{18}\text{O}_3\text{Si}$ 238.1025 found 238.1031, M^+ -(CH_3) calcd. for $\text{C}_{11}\text{H}_{17}\text{O}_3\text{Si}$ 225.0947 found 225.0942.

^1H NMR (C_6D_6) δ 5.34 (tdd, J = 6.8, 17.3, 10.2 Hz, 1H), 4.96 (dd, J = 17.3, 2.1 Hz, 1H), 4.89 (dd, J = 10.2, 2.1 Hz, 1H), 4.32 and 4.14 (2 $\times$ ABq, J = 11.9 Hz, 4H), 3.11 (br, OH, 2H), 2.84 (d, J = 6.8 Hz, 2H), 1.49 (s, OH, 1H), 0.33 (s, 18H)

^{13}C NMR (C_6D_6) δ 155.0, 153.4, 133.5, 117.3, 96.5, 58.6, 40.3, 1.17

IR (KBr, cm^{-1}) 3400 (br, OH), 1686, 1603.

TLC R_f 0.13 (20% ethyl acetate / hexane).

M_p = 101 $^\circ\text{C}$.

HRMS(EI) M^+ calcd. for $\text{C}_{16}\text{H}_{30}\text{O}_3\text{Si}_2$ 326.1733 found 308.1613, M^+ -(CH_3) calcd. for $\text{C}_{15}\text{H}_{28}\text{O}_3\text{Si}_2$ 308.1628 found 308.1613, M^+ -(CH_3 , H_2O) calcd. for $\text{C}_{15}\text{H}_{25}\text{O}_3\text{Si}_2$ 293.1393 found 293.1374.

^1H NMR (CDCl_3) δ 4.32(s, 4H), 3.38(s, 6H), 0.21(s, 18H).

^{13}C NMR (CDCl_3) δ 210.0, 165.9, 132.9, 67.9, 58.4, 0.157.

IR (neat, cm^{-1}) 2955, 1690.

TLC R_f 0.58 (10% ethyl acetate / hexane).

HRMS(EI) M^+ calcd. for $\text{C}_{15}\text{H}_{28}\text{O}_3\text{Si}_2$ 312.1577 found 312.1574.

^1H NMR (C_6D_6) δ 4.21 and 4.16 (2 $\times$ ABq, J = 10.7 Hz, 4H), 3.36 (s, 6H), 1.47 (s, 3H), 0.23 (s, 18H).

^{13}C NMR (CDCl_3) δ 157.8, 149.2, 94.5, 68.2, 58.4, 23.1, 1.03.

IR (KBr, cm^{-1}) 3400 (br, OH), 1686, 1603.

TLC R_f 0.61 (30% ethyl acetate / hexane).

M_p = 97 $^\circ\text{C}$.

HRMS(EI) M^+ calcd. for $\text{C}_{16}\text{H}_{32}\text{O}_3\text{Si}_2$ 328.1890 found 328.1888.

^1H NMR (C_6D_6) δ 5.59 (tdd, J = 8.0, 16.2, 10.9 Hz, 1H), 5.05 (d, 10.9 Hz, 1H), 5.04 (d, J = 16.2 Hz, 1H), 4.26 and 4.16 (ABq, J = 12.4 Hz, 2H), 3.50 and 3.43 (ABq, J = 9.3 Hz, 2H), 3.35 (s, 3H), 3.25 (s, 3H), 2.38 (dd, J = 13.6, 8.0 Hz, 1H), 2.19 (dd, J = 13.6, 8.0 Hz, 1H), 2.16 (s, 1H), 0.21 (s, 9H), 0.09 (s, 9H).

^{13}C NMR (CDCl_3) δ 213.0, 181.6, 144.5, 133.7, 118.9, 75.3, 68.6, 58.7, 58.2, 56.2, 51.1, 42.1 -0.162, -0.304.

TLC R_f 0.48 (20% ethyl acetate / hexane).

^1H NMR (C_6D_6) δ 5.63 (tdd, $J = 7.8, 17.0, 10.0$ Hz, 1H), 4.17 and 4.10 (ABq, $J = 12.3$ Hz, 2H), 3.39 and 3.34 (ABq, $J = 9.0$ Hz, 2H), 3.32 (s, 3H), 3.30 (s, 3H), 2.54 (dd, $J = 7.8, 7.4$ Hz, 1H), 2.45 (dd, $J = 7.8$ Hz, 1H), 2.42 (s, 1H), 0.21 (s, 9H) 0.17 (s, 9H).
 ^{13}C NMR (CDCl_3) δ 212.7, 181.4, 145.0, 134.7, 117.3, 78.3, 68.8, 59.1, 58.5, 56.5, 50.8, 38.0, 0.144, -0.163.
 TLC R_f 0.45 (20% ethyl acetate / hexane).
 IR (neat, cm^{-1}) 1697, 1677, 1590.
 HRMS(EI) M^+ calcd. for $\text{C}_{18}\text{H}_{32}\text{O}_3\text{Si}_2$ 354.2046 found 354.2040, $M^+ - \text{CH}_3$ calcd. for $\text{C}_{17}\text{H}_{31}\text{O}_3\text{Si}_2$ 339.1812 found 339.1810.

^1H NMR (CDCl_3) δ 5.57 (dddd, $J = 7.8, 7.2, 16.1, 11.3$ Hz, 1H), 5.06 (d, $J = 16.1$ Hz, 1H), 5.05 (dd, $J = 11.3$ Hz, 1H), 4.24 and 4.20 (ABq, $J = 12.7$ Hz, 2H), 3.46 and 3.36 (ABq, $J = 9.0$ Hz, 2H), 3.37 (s, 3H), 3.31 (s, 3H), 2.38 (dd, $J = 13.8, 7.8$ Hz, 1H), 2.33 (dd, $J = 13.8, 7.2$ Hz, 1H), 2.36 and 2.27 (ABq, $J = 18.1$ Hz, 2H), 0.22 (s, 9H).
 ^{13}C NMR (CDCl_3) δ 211.3, 183.3, 144.8, 133.2, 118.8, 77.6, 68.9, 59.3, 58.7, 52.0, 44.9, 39.0, -0.27.
 IR (neat, cm^{-1}) 1694, 1588.
 TLC R_f 0.38 (20% ethyl acetate / hexane).
 HRMS(EI) M^+ calcd. for $\text{C}_{15}\text{H}_{26}\text{O}_3\text{Si}$ 282.1651 found 282.1654, $M^+ - \text{CH}_3$ calcd. for $\text{C}_{14}\text{H}_{23}\text{O}_3\text{Si}$ 267.1416 found 267.1428.

^1H NMR (C_6D_6) δ 5.83 (dd, $J = 17.8, 10.8$ Hz, 1H), 5.21 (dd, $J = 10.8, 0.9$ Hz, 1H), 5.04 (dd, $J = 17.8, 0.9$ Hz, 1H), 4.11 and 4.04 (ABq, $J = 10.3$ Hz, 2H), 3.51 and 3.47 (ABq, $J = 6.2$ Hz, 2H), 3.31 (s, 3H), 3.30 (s, 3H), 2.36 (s, 1H), 0.22 (s, 9H), 0.10 (s, 9H).
 ^{13}C NMR (CDCl_3) δ 213.0, 180.5, 145.7, 139.4, 115.9, 76.8, 68.2, 59.3, 58.7, 58.4, 50.8, -0.43.
 IR (neat, cm^{-1}) 1698, 1590.
 TLC R_f 0.37 (20% ethyl acetate / hexane).
 HRMS(EI) M^+ calcd. for $\text{C}_{17}\text{H}_{32}\text{O}_3\text{Si}_2$ 340.1890 found 340.1893.

^1H NMR (CDCl_3) δ 5.91 (dd, $J = 17.6, 10.8$ Hz, 1H), 5.16 (d, $J = 10.8$ Hz, 1H), 5.08 (d, $J = 17.6$ Hz, 1H), 4.20 and 4.15 (ABq, $J = 12.8$ Hz, 2H), 3.53 and 3.50 (ABq, $J = 9.0$ Hz, 2H), 3.34 (s, 3H), 3.33 (s, 3H), 2.59 and 2.37 (ABq, $J = 18.0$ Hz, 2H), 0.23 (s, 9H).

^{13}C NMR (CDCl_3) δ 211.3, 182.4, 144.1, 139.8, 115.0, 76.2, 68.7, 59.3, 58.6, 54.7, 47.0, -0.39.

IR (neat, cm^{-1}) 1698, 1588.

TLC R_f 0.35 (20% ethyl acetate / hexane).

HRMS(EI) M^+ calcd. for $\text{C}_{14}\text{H}_{24}\text{O}_3\text{Si}$ 268.1495 found 268.1508.

^1H NMR (C_6D_6) for major diastereomer : δ 4.17 and 4.15 (ABq, $J = 12.0$ Hz, 2H), 3.48 and 3.27 (ABq, $J = 9.0$ Hz, 2H), 3.35 (s, 3H), 3.30 (s, 3H), 2.35 (s, 1H), 1.71 (dq, $J = 7.2, 7.2$ Hz, 1H), 1.64 (dq, $J = 7.2, 7.2$ Hz, 1H), 0.67 (t, $J = 7.2$ Hz, 3H), 0.22 (s, 9H), 0.17 (s, 9H).

for minor diastereomer : δ 4.22 and 4.13 (ABq, $J = 12.6$ Hz, 2H), 3.48 and 3.45 (ABq, $J = 9.6$ Hz, 2H), 3.35 (s, 3H), 3.26 (s, 3H), 1.67 (dq, $J = 7.8, 7.2$ Hz, 1H), 1.48 (dq, $J = 7.8, 7.2$ Hz, 1H), 0.75 (t, $J = 7.8$ Hz, 3H), 0.22 (s, 9H), 0.10 (s, 9H).

^{13}C NMR (CDCl_3) δ for major: 213.0, 181.5, 144.6, 78.0, 68.7, 59.1, 58.7, 57.1, 48.8, 25.7, 10.1, 0.058. for minor: 213.4, 181.9, 144.2, 75.5, 68.5, 58.6, 58.1, 56.7, 51.4, 30.1, 8.69, -0.15, -0.30.

IR (neat, cm^{-1}) 1682, 1582.

TLC R_f 0.52 (20% ethyl acetate / hexane).

HRMS(EI) M^+ calcd. for $\text{C}_{17}\text{H}_{34}\text{O}_3\text{Si}_2$ 342.2046 found 342.2052.

^1H NMR (CDCl_3) δ 4.23 and 4.12 (ABq, $J = 22.1$ Hz, 2H), 3.46 and 3.32 (ABq, $J = 9.0$ Hz, 2H), 3.35 (s, 3H), 3.30 (s, 3H), 2.39 and 2.18 (ABq, $J = 18.1$ Hz, 2H), 1.64 (dq, $J = 7.2, 7.2$ Hz, 1H), 1.60 (dq, $J = 7.2, 7.2$ Hz, 1H), 0.74 (t, $J = 7.2$ Hz, 3H), 0.21 (s, 9H).

^{13}C NMR (CDCl_3) δ 211.8, 184.0, 144.5, 77.7, 68.8, 59.3, 58.7, 52.5, 44.8, 27.0, 8.4, -0.24.

IR (neat, cm^{-1}) 1698, 1587.

TLC R_f 0.41 (20% ethyl acetate / hexane).

HRMS(EI) $M^+ - CH_3$ calcd. for $C_{13}H_{23}O_3Si$ 255.1416 found 255.1406.

1H NMR ($CDCl_3$) δ 4.24 and 4.18 (2 $\times$ ABq, J = 10.0Hz, 4H), 3.37 (s, 6H), 2.00 (q, J = 7.5Hz, 2H), 1.53 (s, OH, 1H), 0.60 (t, J = 7.5Hz, 3H), 0.23 (s, 18H).

^{13}C NMR ($CDCl_3$) δ 155.4, 151.2, 98.3, 68.2, 58.3, 28.3, 7.83, 0.79.

IR (KBr, cm^{-1}) 3401 (br, OH), 1687, 1604.

TLC R_f 0.42 (30% ethyl acetate / hexane).

Mp = 75 °C.

HRMS(EI) M^+ calcd. for $C_{17}H_{34}O_3Si_2$ 342.2046 found 342.2059, $M^+ - CH_4O$ calcd. for $C_{16}H_{30}O_3Si_2$ 310.1784 found 310.1767.

1H NMR ($CDCl_3$) δ 4.23 and 4.16 (2 $\times$ ABq, 11.2 Hz, 4H), 3.36 (s, 6H), 2.24 (septet, J = 6.8 Hz, 1H), 0.92 (d, J = 6.8 Hz, 6H), 0.24 (s, 18H)

^{13}C NMR ($CDCl_3$) δ 155.9, 151.9, 101.3, 68.4, 58.3, 33.9, 18.9, 1.29

IR (KBr, cm^{-1}) 3400 (br, OH), 1686, 1603.

TLC R_f 0.44 (40% ethyl acetate / hexane).

Mp = 105 °C

HRMS(EI) M^+ calcd. for $C_{18}H_{36}O_3Si_2$ 356.2203 found 356.2189, $M^+ - CH_4O$ calcd. for $C_{17}H_{32}O_2Si_2$ 324.1941 found 324.1935, $M^+ - C_2H_7O$ calcd. for $C_{16}H_{29}O_2Si_2$ 309.1706 found 305.1709.

1H NMR ($CDCl_3$) for major diastereomer: δ 4.24 and 4.18 (ABq, J = 12.4 Hz, 2H), 3.60 and 3.46 (ABq, J = 9.3 Hz, 2H), 3.34 (s, 3H) 3.24 (s, 3H), 2.09 (s, 1H), 2.06 (septet, J = 6.8 Hz, 1H), 0.89 (d, J = 6.8 Hz, 3H), 0.61 (d, J = 6.8 Hz, 3H), 0.20 (s, 9H), 0.10 (s, 9H); for minor diastereomer: δ 4.08 (s, 2H), 3.81 and 3.72 (ABq, J = 9.3 Hz, 2H), 3.33 (s, 3H) 3.32 (s, 3H), 2.57 (s, 1H), 2.06 (septet, J = 6.8 Hz, 1H), 0.96 (d, J = 6.8 Hz, 3H), 0.61 (d, J = 6.8 Hz, 3H), 0.21 (s, 9H), 0.17 (s, 9H).

^{13}C NMR (CDCl_3) for major diastereomer: δ 214.0, 182.5, 143.9, 75.0, 68.7, 59.8, 58.8, 58.1, 46.4, 31.9, 19.2, 17.3, -0.16, -0.23; for minor diastereomer: δ 213.2, 180.7, 146.2, 74.9, 68.6, 60.2, 59.1, 58.4, 48.9, 32.9, 20.5, 18.3, -0.04, -0.23.

IR (neat, cm^{-1}) 1674, 1597.

TLC R_f 0.56 (20% ethyl acetate / hexane).

HRMS(EI) M^+ calcd. for $\text{C}_{18}\text{H}_{36}\text{O}_3\text{Si}_2$ 356.2203 found 356.2205, $M^+ - \text{CH}_3$ calcd. for $\text{C}_{17}\text{H}_{33}\text{O}_3\text{Si}_2$ 341.1968 found 341.1978.

^1H NMR (CDCl_3) δ 4.21 and 4.15 (ABq, $J = 8.7$ Hz, 2H), 3.54 and 3.33 (ABq, $J = 6.0$ Hz, 2H), 3.36 (s, 3H), 3.29 (s, 3H), 2.26 and 2.04 (ABq, $J = 12.1$ Hz, 2H), 2.14 (septet, $J = 4.5$ Hz, 1H), 0.91 (d, $J = 4.5$ Hz, 3H), 0.68 (d, $J = 4.5$ Hz, 3H), 0.21 (s, 9H).

^{13}C NMR (CDCl_3) δ 212.0, 185.8, 143.6, 77.3, 69.1, 59.2, 58.7, 55.4, 40.9, 29.4, 18.5, 17.5, -0.27.

IR (neat, cm^{-1}) 1694, 1586.

TLC R_f 0.42 (20% ethyl acetate / hexane).

HRMS(EI) M^+ calcd. for $\text{C}_{15}\text{H}_{28}\text{O}_3\text{Si}$ 284.1808 found 284.1816, $M^+ - \text{CH}_3$ calcd. for $\text{C}_{14}\text{H}_{25}\text{O}_3\text{Si}$ 269.1573 found 269.1564.