Supplementary Information

α -Hydroxy Cyclopentenones from α -Diketones

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Supplementary Information

General Procedures

^1H NMR and ^{13}C NMR spectra were recorded on a Varian Mercury spectrometer at 300MHz and 75MHz respectively. Chemical shifts (δ) are given in parts per million (ppm) and coupling constants (J) are given in Hertz. All spectra were obtained in CDCl_3 unless otherwise noted and in some spectra TMS (tetramethyl silane) was also used as an internal standard. Melting points were measured on a Mel-Temp Capillary melting point apparatus and are uncorrected. All reactions were performed in a flame dried flask under an inert atmosphere of nitrogen (N_2) unless otherwise noted.

Experimental Data

Pale yellow viscous liquid: ^1H NMR (300 MHz, CDCl_3): δ 7.84-7.81 (m, 2H), 7.54-7.48 (m, 3H), 4.60 (q, $J = 7.2$, 1H), 2.00 (s, 3H), 1.52 (d, $J = 7.2$, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 206.3, 179.2, 131.4, 130.4, 128.6, 127.7, 109.6, 80.1, 16.6, 7.2; IR (Neat) 3061, 2880, 2929, 1693, 1613, 1447, 1379, 1373, 1127, 1073, 1018, 694 cm^{-1} ; HRMS calcd for $\text{C}_{12}\text{H}_{12}\text{O}_2$ (M^+) 188.0837, Found 188.0822.

A colorless viscous liquid: ^1H NMR (300 MHz, CDCl_3): δ 7.60-7.57 (m, 2H), 7.39- 7.34 (m, 2H), 7.24-7.16 (m, 1H), 2.24 (s, 3H), 2.13 (s, 3H), 1.03 (s, 9H), 0.16 (s, 6H); ^{13}C NMR (75 MHz, CDCl_3): δ 144.4, 139.3, 135.8, 132.3, 128.4, 126.0, 124.4,

112.5, 25.7, 18.0, 11.2, 9.1, -4.3; IR (Neat) 2956, 2929, 2895, 2858, 1643, 1603, 1462, 1324, 1254, 1195, 902, 839, 780, 761, 693 cm^{-1} ; HRMS calcd for $\text{C}_{18}\text{H}_{26}\text{O}_2\text{Si}$ (M^+) 302.1702, Found 302.1683.

A yellow liquid: ^1H NMR (300 MHz, CDCl_3): δ 7.45–7.40 (m, 6H), 2.79 (t, $J = 7.3$, 2H), 2.13 (d, $J = 1.3$, 3H), 1.80–1.68 (m, 2H), 1.01 (t, $J = 7.3$, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 205.4, 197.3, 146.8, 135.1, 132.8, 130.4, 129.8, 128.8, 41.6, 16.6, 13.9, 12.5; IR (Neat) 3056, 3027, 2964, 2933, 2876, 1711, 1658, 1615, 1574, 1448, 1246, 1003, 760, 694 cm^{-1} ; HRMS calcd for $\text{C}_{14}\text{H}_{16}\text{O}_2$ (M^+) 216.1150, Found 216.1163.

A white solid: Melting point, 106–109 $^{\circ}\text{C}$; ^1H NMR (300 MHz, CDCl_3): δ 7.28–7.15 (m, 3H), 7.07–7.04 (m, 2H), 6.45 (s, 1H), 3.35 (s, 1H), 2.21–2.12 (m, 1H), 1.81–1.74 (m, 1H), 1.70 (s, 3H), 1.60–1.52 (m, 1H), 0.90 (t, $J = 7.4$, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 205.1, 149.26, 145.3, 124.0, 129.1, 127.8, 127.3, 54.9, 52.3, 24.4, 12.8, 11.5; IR (Neat) 3326, 3061, 3026, 2963, 2932, 2874, 1701, 1658, 1406, 1360, 1199, 1128, 702 cm^{-1} ; HRMS calcd for $\text{C}_{14}\text{H}_{16}\text{O}_2$ (M^+) 216.1150, Found 216.1167.

Yellow oil: ¹H NMR (300 MHz, CDCl₃): δ 7.46-7.37 (m, 6H), 3.02-2.92 (m, 1H), 2.14 (d, J = 1.2, 3H), 1.85-1.70 (m, 2H), 1.63-1.49 (m, 2H), 0.94 (t, J = 7.4, 6H); ¹³C NMR (75 MHz, CDCl₃): δ 207.2, 197.5, 146.3, 135.0,

133.1, 130.1, 129.5, 128.5, 50.7, 22.3, 12.3, 11.4; IR (Neat) 2966, 2943, 2877, 1706, 1655, 1616, 1448, 1217, 1163, 994, 820 cm⁻¹; HRMS calcd for C₁₆H₂₀O₂ (M⁺) 244.1463, found 244.1472.

A colorless solid: Melting Point, 64 - 66 °C, ¹H NMR (300 MHz, CDCl₃): δ 7.33-7.24 (m, 3H), 7.07 (d, J = 6.6, 2H), 6.33 (br, s, 1H), 3.6 (d, J = 0.9, 1H), 1.8 (d, J = 1.2, 3H),

1.73-1.66, m, 2H), 1.31-1.20 (m, 1H), 1.15-0.90 (m, 1H), 0.89 (t, J = 7.4, 3H), 0.59 (t, J = 7.4, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 207.6, 149.1, 143.7, 139.1, 129.9, 128.4, 127.1, 56.4, 52.5, 29.0, 25.9, 13.1, 8.9, 7.9; IR (Neat) 3336, 2966, 2937, 2880, 1697, 1655, 1453, 1404, 1360, 1204, 1090, 704 cm⁻¹; HRMS calcd for C₁₆H₂₀O₂ (M⁺) 244.1463, found 244.1449.

Yellow oil: ¹H NMR (300 MHz, CDCl₃): δ 7.48-7.33 (m, 6H), 3.29-3.15 (m, 1H), 2.14 (d, J = 1.2, 3H), 1.20 (d, J =

6.9, 6H); ^{13}C NMR (75 MHz, CDCl_3): δ 208.2, 198.0, 146.5, 134.9, 133.4, 130.1, 129.5, 128.5, 37.2, 17.0, 12.1; IR (Neat) 2971, 2933, 1708, 1654, 1617, 1448, 1255, 992, 909, 777, 695 cm^{-1} ; HRMS calcd for $\text{C}_{14}\text{H}_{16}\text{O}_2$ (M^+) 216.1150, found 216.1162.

Colorless solid: Melting Point, 108-110 $^{\circ}\text{C}$; ^1H NMR (300 MHz, CDCl_3): δ 7.34-7.25 (m, 3H), 7.03 (d, $J = 6.9$, 2H), 6.79 (br, s, 1H), 3.59 (d, $J = 1.2$, 1H), 1.90 (d, $J = 1.2$, 3H), 1.27 (s, 3H), 0.58 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 207.7, 148.0, 143.1, 138.9, 128.9, 128.3, 127.0, 58.8, 45.9, 26.9, 21.9, 13.0; IR (Neat) 3325, 2973, 1695, 1653, 1407, 1359, 1221, 1090, 765, 708 cm^{-1} ; HRMS calcd for $\text{C}_{14}\text{H}_{16}\text{O}_2$ (M^+) 216.1150, found 216.1141.

Yellow oil: ^1H NMR (300 MHz, CDCl_3): δ 7.47-7.34 (m, 6H), 2.69 (d, $J = 6.9$, 2H), 2.33-2.20 (m, 1H), 2.13 (d, $J = 1.2$, 3H), 1.01 (d, $J = 6.6$, 6H); ^{13}C NMR (75 MHz, CDCl_3): δ 204.7, 196.8, 146.5, 134.9, 132.5, 130.1, 129.5, 128.5, 48.3, 23.8, 22.5, 12.2; IR (Neat) 3027, 2959, 2929, 2872, 1707, 1655, 1616, 1449, 1366, 1246, 1216, 1144, 1006, 751, 694 cm^{-1} ; HRMS calcd for $\text{C}_{15}\text{H}_{18}\text{O}_2$ (M^+) 230.1306, found 230.1330.

Colorless solid: Melting Point, 110-112 °C; ^1H NMR (300 MHz, CDCl_3): δ 7.38-7.22 (m, 3H), 7.12 (d, $J = 6.9$, 2H), 5.57 (s, 1H), 3.49 (s, 1H), 2.35-2.32 (m, 1H), 2.30-2.20 (m, 1H), 1.76 (s, 3H), 0.97 (d, $J = 6.6$, 3H), 0.91 (d, $J = 6.6$, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ 204.5, 149.2, 145.4, 142.0, 128.8, 127.6, 126.9, 58.9, 48.6, 29.6, 20.1, 18.2, 12.5; IR (Neat) 3325, 2972, 1695, 1653, 1407, 1360, 1221, 1090, 766, 708 cm^{-1} ; HRMS calcd for $\text{C}_{15}\text{H}_{18}\text{O}_2$ (M^+) 230.1306, found 230.1291.

Yellow solid: Melting Point, 78-80 °C; ^1H NMR (300 MHz, CDCl_3): δ 7.64 (s, 1H), 7.42-7.38 (m, 3H), 7.26-7.16 (m, 5H), 7.10-7.07 (m, 2H), 2.46 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 201.9, 194.4, 146.0, 135.8, 134.1, 133.8, 131.1, 130.2, 129.5, 128.9, 128.4 (2 C), 27.1; IR (Neat) 3066, 2916, 1700, 1653, 1595, 1490, 1352, 1184, 1098, 1074, 933, 862 cm^{-1} ; HRMS calcd for $\text{C}_{17}\text{H}_{14}\text{O}_2$ (M^+) 250.0993, Found 250.1008.

Colorless solid: Melting Point, 158-160 °C; ^1H NMR (300 MHz, CDCl_3): δ 7.80 (d, $J = 6.9$, 2H), 7.33-7.17 (m, 8H), 6.71 (s, 1H), 4.50 (d, $J = 6.9$, 1H), 3.10 (dd, $J = 19.2$, 6.9, 1H), 2.39 (d, $J = 19.2$, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 202.5, 149.5, 143.6, 140.0, 133.0, 129.1 (2 C), 128.6 (2 C), 127.1 (2 C), 42.8, 41.8; IR (Neat) 3299, 3026, 1686, 1631, 1388, 1317, 1126, 763, 690 cm^{-1} ; HRMS calcd for $\text{C}_{17}\text{H}_{14}\text{O}_2$ (M^+) 250.0993, Found 250.0978.

Yellow solid: Melting Point, 63-65 °C; ^1H NMR (300 MHz, CDCl_3): δ 7.60 (s, 1H), 7.41-7.38 (m, 3H), 7.26-7.15 (m, 5H), 7.09-7.06 (m, 2H), 2.67 (d, $J = 6.9$, 2H), 2.30-2.18 (m, 1H), 0.97 (d, $J = 6.6$, 6H); ^{13}C NMR (75 MHz, CDCl_3): δ 204.4, 195.2, 145.6, 136.1, 134.1, 133.9, 131.1, 130.2, 129.6, 128.9, 128.3, 48.2, 23.8, 22.5 (2 C); IR (Neat) 3054, 2959, 2926, 2871, 1700, 1653, 1457, 1396, 1235, 1020, 932, 756 cm^{-1} ; HRMS calcd for $\text{C}_{20}\text{H}_{20}\text{O}_2$ (M^+) 292.1463, Found 292.1469.

Amorphous solid: ^1H NMR (300 MHz, CDCl_3): δ 7.81-7.79 (m, 2H), 7.32-7.15 (m, 8H), 6.70 (s, 1H), 4.18 (d, $J = 0.9$

1H), 2.40-2.38 (m, 1H), 2.36-2.28 (m, 1H), 1.09 (d, $J = 6.0$, 3H), 0.98 (d, $J = 6.0$, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 204.8, 149.0, 143.5, 139.1, 132.8, 128.9 (2 C), 128.3, 127.1, 126.7 (2 C), 59.3, 45.5, 30.6, 20.0, 18.5; IR (Neat) 3302, 2959, 1682, 1632, 1392, 1279, 1127, 1076, 1030, 760, 691 cm^{-1} ; HRMS calcd for $\text{C}_{20}\text{H}_{20}\text{O}_2$ (M^+) 292.1463, Found 292.1473.

Yellow amorphous solid: ^1H NMR (300 MHz, CDCl_3): δ 7.52 (s, 1H), 7.42-7.36 (m, 3H), 7.27-7.16 (m, 5H), 7.09-7.07 (m, 2H), 3.25-3.12 (m, 1H), 1.20 (d, $J = 6.9$, 6H); ^{13}C NMR (75 MHz, CDCl_3): δ 207.9, 196.4, 145.9, 137.0, 134.0, 133.9, 131.1, 130.2, 129.6, 128.9, 128.4 (2 C), 37.2, 17.0; IR (Neat) 3056, 2971, 2933, 1704, 1654, 1613, 1447, 1386, 1319, 1245, 1010, 750 cm^{-1} ; HRMS calcd for $\text{C}_{19}\text{H}_{18}\text{O}_2$ (M^+) 278.1306, Found 278.1306.

Colorless solid: Melting Point, 150-152 $^{\circ}\text{C}$; ^1H NMR (300 MHz, CDCl_3): δ 7.82-7.79 (m, 2H), 7.31-7.17 (m, 8H), 6.89 (s, 1H), 4.22 (s, 1H), 1.38 (s, 3H), 0.66 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 208.0, 147.0, 140.4, 137.4, 133.0, 129.0, 128.8, 128.4 (2 C), 128.2, 126.8, 55.6, 45.9, 28.1, 21.7; IR (Neat) 3308, 2970, 1682, 1632,

1393, 1281, 1068, 1038, 757, 690 cm^{-1} ; HRMS calcd for $\text{C}_{19}\text{H}_{18}\text{O}_2$ (M^+) 278.1306, Found 278.1307.

Yellow oil: ^1H NMR (300 MHz, CDCl_3): δ 6.88 (m, 1H), 2.68 (t, $J = 7.3$, 2H), 2.27-2.21 (m, 4H), 1.68-1.63 (m, 6H), 0.94 (t, $J = 7.3$, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ

205.1, 195.6, 149.3, 135.4, 41.2, 26.8, 22.3, 21.6, 21.5, 16.5, 13.8; IR (Neat) 2970, 2935, 2873, 1708, 1656, 1630, 1275, 1060, 963, 793 cm^{-1} ; HRMS calcd for $\text{C}_{11}\text{H}_{16}\text{O}_2$ (M^+) 180.1150, Found 180.1162.

White solid: Melting Point, 104-106 $^{\circ}\text{C}$; ^1H NMR (300 MHz, CDCl_3): δ 5.72 (s, 1H), 3.01-2.96 (m, 1H), 2.19-2.13 (m, 2H), 2.09-2.01 (m, 1H), 1.89-1.76 (m, 4H), 1.49-1.28

(m, 3H), 1.08 (m, 1H), 0.98 (t, $J = 7.3$, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 204.5, 148.8, 145.2, 51.8, 43.1, 34.7, 25.8, 25.7, 23.8, 22.2, 11.9; IR (Neat) 3324, 2932, 2858, 1702, 1655, 1395, 1234, 1118 cm^{-1} ; HRMS calcd for $\text{C}_{11}\text{H}_{16}\text{O}_2$ (M^+) 180.1150, Found 180.1150.

Yellow oil: ^1H NMR (300 MHz, CDCl_3): δ 6.82 (m, 1H), 3.20-3.06 (m, 1H), 2.23-2.22 (m, 4H), 1.66-1.62 (m, 4H), 1.13 (d, $J = 6.9$, 6H); ^{13}C NMR (75 MHz, CDCl_3): δ 208.2, 196.6, 149.1, 136.3, 36.9, 26.8, 22.2, 21.6, 21.5, 17.2 (2 C); IR (Neat) 2970, 2935, 2873, 1708, 1656, 1630, 1464, 1275, 1060, 963 cm^{-1} ; HRMS calcd for $\text{C}_{11}\text{H}_{16}\text{O}_2$ (M^+) 180.1150, Found 180.1154.

White solid: Melting Point, 106-108 $^{\circ}\text{C}$. ^1H NMR (300 MHz, CDCl_3): δ 5.74 (s, 1H), 3.01-2.98 (m, 1H), 2.10-1.87 (m, 4H), 1.52-1.25 (m, 3H), 1.11 (s, 3H), 1.08 (td, $J = 12.2$, 1.7, 1H), 0.99 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 207.9, 147.8, 143.3, 68.2, 49.0, 43.7, 29.8, 26.1, 25.8, 28.7, 20.3; IR (Neat) 3307, 2931, 2858, 1697, 1654, 1396, 1071 cm^{-1} ; HRMS calcd for $\text{C}_{11}\text{H}_{16}\text{O}_2$ (M^+) 180.1150, Found 180.1162.

Yellow oil: ^1H NMR (300 MHz, CDCl_3): δ 6.91-6.89 (m, 1H), 2.96-2.85 (m, 1H), 2.30-2.24 (m, 4H), 1.72-1.65 (m, 6H), 1.58-1.41 (m, 2H), 0.89 (t, $J = 7.3$, 6H); ^{13}C NMR (75 MHz, CDCl_3): δ 207.1, 195.9, 148.9, 135.9, 50.5, 26.8, 22.5, 22.4, 21.6, 21.5, 11.7; IR (Neat) 2970, 2935, 2873, 1708, 1656,

1630, 1275 cm^{-1} ; HRMS calcd for $\text{C}_{13}\text{H}_{20}\text{O}_2$ (M^+) 208.1463, Found 208.1450.

White solid: Melting Point, 88-90 $^{\circ}\text{C}$. ^1H NMR (300 MHz, CDCl_3): δ 5.42 (bs, 1H), 3.01-2.95 (m, 1H), 2.34-2.28 (m, 1H), 2.10-1.98 (m, 1H), 1.96-1.88 (m, 2H), 1.71-1.45 (m, 8H), 0.91 (t, $J = 7.4$, 3H), 0.81 (t, $J = 7.4$, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 207.8, 148.5, 144.8, 50.6, 46.5, 29.1, 28.6, 25.9 (2C), 25.7, 24.8, 9.2, 8.7; IR (Neat) 3333, 2964, 2937, 2860, 1698, 1654, 1396, 1076 cm^{-1} ; HRMS calcd for $\text{C}_{13}\text{H}_{20}\text{O}_2$ (M^+) 208.1463, Found 208.1475.

Yellow oil. ^1H NMR (300 MHz, CDCl_3): δ 7.50 (s, 1H), 7.45-7.34 (m, 5H), 5.33 (t, $J=2.9$, 1H), 5.10 (d, $J=2.1$, 1H), 5.04 (d, $J=2.1$, 1H), 3.92 (td, $J=11.0$, 2.8, 1H), 3.68-3.62 (m, 1H), 2.16 (s, 3H), 1.96-1.57 (m, 6H); ^{13}C NMR (75 MHz, CDCl_3): δ 194.6, 156.1, 141.4, 136.1, 136.0, 129.9, 128.7, 128.6, 98.4, 96.6, 62.2, 30.1, 25.3, 18.7, 14.3; IR (neat) 3200, 3165, 2945, 1655, 1614, 1022, 696 cm^{-1} , HRMS (EI) calcd for $\text{C}_{17}\text{H}_{20}\text{O}_3$ (M^+) 272.1412, found 272.1384.

Yellow oil: ^1H NMR (300 MHz, CDCl_3): δ 7.56 (d, 1H), 7.04-6.98 (m, 5H), 3.75 (s, 2H), 1.90 (d, $J = 1.3$, 3H); ^{13}C NMR (75 MHz, C_6D_6): δ 193.8, 192.8, 147.6, 135.2, 133.2, 130.5, 129.7, 128.6, 31.2, 12.3; IR (Neat) 3054, 2963, 1713, 1651, 1613, 693 cm^{-1} ; HRMS calcd for $\text{C}_{12}\text{H}_{11}\text{O}_2\text{Br}$ (M^+) 265.9942, Found 265.9917.

White solid: Melting Point, 93-96°C. ^1H NMR (300 MHz, CDCl_3): δ 7.43-7.34 (m, 3H), 7.18-7.15 (br d, $J = 7.8$, 2H), 4.19 (s, 1H), 4.02 (s, 1H), 1.84 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 195.2, 148.1, 145.2, 138.8, 129.5, 128.4, 127.6, 57.3, 48.1, 13.1; IR (Neat) 3307, 1705, 1650, 1117, 700 cm^{-1} ; HRMS calcd for $\text{C}_{12}\text{H}_{11}\text{O}_2\text{Br}$ (M^+) 265.9942, Found 256.9919.

Assignment of Stereochemistry

The assignment of stereochemistry was made on the basis of nOe and ^1H NMR coupling constants. This is illustrated for compounds **8**, **23** and **35**.

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In order to make the stereochemical assignment, it is useful to consider the *cis* and *trans* isomers shown above. The *cis* isomer, shown on the left, was formed from a Pd(II) catalyzed cyclization that is described in the reference cited. The coupling constant of the two *cis* protons was 6.6 Hz. Upon standing, slow isomerization to the *trans* isomer, shown on the right, took place. In the *trans* isomer the vicinal coupling constant was zero. A series of nOe experiments confirmed the stereochemical assignments.

It is also useful to examine the data for **2**. The benzylic proton in **2** appears as a broad doublet ($J = 6.5$ Hz) whereas the *cis* proton is a dd ($J = 19.2, 6.5$ Hz) and the *trans* proton a dd ($J = 19.2, 0.9$ Hz). The *trans* protons have a very small coupling constant whereas the *cis* protons have a 6.5 Hz coupling constant. Therefore the coupling constant for *cis* protons is 6.5 or 6.6 Hz, whereas the *trans* protons either couple very weakly or not at all.

In the ^1H NMR spectrum of **8**, the signal for H_A is a singlet and for H_B a broad triplet. This indicates that H_A is not coupled to H_B , and that H_B couples only to the protons of the adjacent methylene group. This is consistent with *trans* stereochemistry, as shown. Irradiation of H_A resulted in enhancements of the signals for both methyl groups, and of the *ortho* aromatic protons. Irradiation of H_B resulted in enhancements of the signals for the methyl group of the ethyl, the *ortho* aromatic protons and also H_A . Since *both* H_A and H_B show a nOe to the *ortho* aromatic protons, and since H_A and H_B do not couple, the stereochemistry of **23** is *trans*.

Stereochemistry was more difficult to assign in **23**, since H_A and H_B overlapped with other signals in the ^1H NMR spectrum both in CDCl_3 and in C_6D_6 . A TOCSY experiment revealed that H_B was a broad triplet. Since H_A and H_B do not couple, the stereochemistry is *trans*.

In the ^1H NMR spectrum of **35** both H_A and H_B are singlets. Irradiation of H_A led to enhancement of the signals for the methyl group, of the *ortho* aromatic protons and also of H_B . Irradiation of H_B led to enhancement of H_A and of the *ortho* aromatic protons. Since both H_A and H_B show a nOe to the

ortho aromatic protons and since H_A and H_B do not couple, the stereochemistry of **35** is *trans*.

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