

Supporting Information

Optically Active β -Ketoiminato Cationic Cobalt(III) Complexes: Efficient Catalysts for Enantioselective Carbonyl-Ene Reaction of Glyoxal Derivatives

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General Procedure for the Enantioselective Carbonyl-Ene Reaction of phenylglyoxal: To a solution of the cobalt complex **1f** (23.2 mg, 4.7 mol%) in dichloromethane (0.5 mL) was added α -methylstyrene (62.2 mg, 0.53 mmol) in dichloromethane (1.0 mL). A solution of the phenylglyoxal (145.9 mg, 1.09 mmol) in dichloromethane (1.0 mL) was then added at $-20\text{ }^{\circ}\text{C}$. The mixture was stirred for 24 h at $-20\text{ }^{\circ}\text{C}$. A standard workup and chromatography on silica gel afforded 1,4-diphenyl-2-hydroxy-4-penten-1-one (119.1 mg) in 90 %yield.

1,4-Diphenyl-2-hydroxy-4-penten-1-one (4a): ^1H NMR (400 MHz) δ = 2.59 (1H, dd, J = 8.3, 14.7 Hz), 3.02 (1H, dd, J = 2.9, 14.7 Hz), 3.59 (1H, brs), 5.00-5.10 (2H, m), 5.28 (1H, d, J = 7.8 Hz), 7.15-7.33 (5H, m), 7.39 (2H, t, J = 7.8 Hz), 7.54 (1H, t, J = 7.8 Hz), 7.71 (2H, d, J = 7.8 Hz); ^{13}C NMR (100 MHz) δ = 42.0, 71.6, 116.1, 126.5, 127.6, 128.3, 128.4, 128.7, 133.6, 133.8, 140.3, 143.8, 201.3; IR (neat) 3471, 3082, 3058, 3030, 2928, 1682, 1629, 1598, 1578, 1494, 1448, 1407, 1259, 1178, 1112, 1092, 1072, 975, 905, 779, 699 cm^{-1} . HRMS: Calcd for $\text{C}_{17}\text{H}_{16}\text{O}_2$: (M^+), 252.1150. Found: m/z 252.1166. HPLC: Chiralcel OB-H (3.0% 2-propanol in hexane, Flow 1.0 mL / min), 17.9 min (minor), 31.3 min (major).

4-(4-Fluorophenyl)-2-hydroxy-1-phenyl-4-penten-1-one (4b): ^1H NMR (400 MHz) δ = 2.61 (1H, dd, J = 8.3, 14.6 Hz), 3.00 (1H, dd, J = 3.4, 14.6 Hz), 3.63 (1H, brs), 5.00-5.12 (2H, m), 5.22 (1H, s), 6.90 (1H, d, J = 8.8 Hz), 6.92 (1H, d, J = 8.8 Hz), 7.21 (1H, d, J = 8.8 Hz), 7.22 (1H, d, J = 8.8 Hz), 7.39 (2H, t, J = 7.3 Hz), 7.54 (1H, t, J = 7.3 Hz), 7.70 (2H, d, J = 7.3 Hz); ^{13}C NMR (100 MHz) δ = 42.0, 71.6, 114.1 (d, J_{CF} = 21), 116.2, 128.1 (d, J_{CF} = 8), 128.5, 130.0, 133.5, 133.9, 136.5 (d, J_{CF} = 3), 142.7, 162.2 (d, J_{CF} = 246), 201.1; IR (neat) 3469, 3065, 2932, 1683, 1600, 1509, 1449, 1403, 1226, 1111, 1076, 975, 841, 711, 691, 524 cm^{-1} . HRMS: Calcd for $\text{C}_{17}\text{H}_{15}\text{FO}_2$: (M^+), 270.1056. Found: m/z 270.1033. HPLC: Chiralpak OB-H (5.0% 2-propanol in hexane, Flow 1.0 mL / min), 18.4 min (minor), 31.4 min (major).

2-Hydroxy-4-(4-methylphenyl)-1-phenyl-4-penten-1-one (4c): ^1H NMR (400 MHz) δ = 2.28 (3H, s), 2.57 (1H, dd, J = 8.3, 15.1 Hz), 2.99 (1H, dd, J = 3.4, 15.1 Hz), 3.56 (1H, brs), 5.02-5.09 (2H, m), 5.25 (1H, d, J = 1.0 Hz), 7.06 (2H, d, J = 7.8), 7.18 (2H, d, J = 7.8), 7.40 (2H, t, J = 7.3 Hz), 7.54 (1H, t, J = 7.3 Hz), 7.73 (2H, d, J = 7.3 Hz); ^{13}C NMR (100 MHz) δ = 21.2, 42.1, 71.6, 115.4, 126.1, 126.4, 128.4, 128.7, 129.0, 133.8, 137.37, 137.40, 143.6, 201.4; IR (neat) 3471, 3085, 3058, 3028, 2923, 2859, 1721, 1683, 1598, 1513, 1449, 1261, 1178, 1110, 1075, 1019, 974, 824, 710 cm^{-1} . HRMS: Calcd for $\text{C}_{18}\text{H}_{18}\text{O}_2$: (M^+), 266.1307. Found: m/z 266.1302. HPLC: Chiralpak OB-H (5.0% 2-propanol in hexane, Flow 1.0 mL / min), 9.5 min (minor), 13.7 min (major).

2-Hydroxy-4-(2-naphthyl)-1-phenyl-4-penten-1-one (4d): ^1H NMR (400 MHz) δ = 2.78 (1H, dd, J = 8.3, 14.5 Hz), 3.19 (1H, d, J = 14.5 Hz), 3.69 (1H, brs), 5.16 (1H, br), 5.27 (1H, s), 5.49 (1H, s), 7.38-7.62 (7H, m), 7.73-7.85 (5H, m); ^{13}C NMR (100 MHz) δ = 42.1, 71.6, 116.7, 124.8, 125.3, 125.9, 126.1, 127.4, 127.9, 128.0, 128.4, 128.7, 132.8, 133.1, 133.7, 133.8, 137.5, 143.5, 201.4; IR (KBr) 3421, 3383, 3059, 2937, 1683, 1596, 1447, 1408, 1258, 1212, 1197, 1173, 1132, 1109, 1005, 945, 901, 865, 832, 755, 692, 647, 633, 617, 476 cm^{-1} . HRMS: Calcd for $\text{C}_{21}\text{H}_{18}\text{O}_2$: (M^+),

302.1307. Found: m/z 302.1313. HPLC: Chiralpak OB-H (10.0% 2-propanol in hexane, Flow 1.0 mL / min), 16.4 min (minor), 25.9 min (major).

6-Dimethyl-2-hydroxy-4-methylene-1-phenylheptan-1-one (4e): ^1H NMR (400 MHz) δ = 0.80 (9H, s), 1.89 (1H, d, J = 13.0 Hz), 1.95 (1H, d, J = 13.0 Hz), 2.17 (1H, dd, J = 8.8, 14.7 Hz), 2.56 (1H, dd, J = 2.4, 14.7 Hz), 3.61 (1H, brs), 4.80 (1H, s), 4.94 (1H, s), 5.14 (1H, dd, J = 2.4, 8.8 Hz), 7.44 (2H, t, J = 7.3), 7.56 (1H, t, J = 7.3), 7.86 (2H, d, J = 7.3); ^{13}C NMR (100 MHz) δ = 29.9, 31.7, 44.1, 49.5, 72.6, 116.3, 128.5, 128.7, 133.6, 133.8, 142.8, 201.4; IR (neat) 3475, 3071, 2952, 1682, 1639, 1598, 1477, 1449, 1363, 1263, 900, 775, 692 cm^{-1} . HRMS: Calcd for $\text{C}_{16}\text{H}_{22}\text{O}_2$: (M^+), 246.1620. Found: m/z 246.1595. HPLC: Chiralpak OD-H (1.0% 2-propanol in hexane, Flow 1.0 mL / min), 9.9 min (major), 15.3 min (minor).

2-Hydroxy-4-isopropyl-1-phenyl-4-hepten-1-one (4f): ^1H NMR (400 MHz) δ = 0.94 (3H, d, J = 6.8 Hz), 0.96 (3H, d, J = 6.8 Hz), 2.13 (1H, dd, J = 9.3, 15.1 Hz), 2.23 (1H, q, J = 6.8 Hz), 2.54 (1H, dd, J = 2.5, 15.1 Hz), 3.64 (1H, brs), 4.82 (1H, s), 4.86 (1H, s), 5.16 (1H, dd, J = 2.5, 9.3 Hz), 7.43 (2H, t, J = 7.3 Hz), 7.55 (1H, t, J = 7.3 Hz), 7.85 (2H, d, J = 7.3 Hz); ^{13}C NMR (100 MHz) δ = 21.6, 21.8, 33.6, 41.0, 72.2, 109.6, 128.4, 128.7, 133.5, 133.8, 151.0, 201.4; IR (neat) 3468, 3065, 2962, 1683, 1643, 1598, 1579, 1450, 1263, 1091, 974, 899, 713, 695 cm^{-1} . HRMS: Calcd for $\text{C}_{14}\text{H}_{18}\text{O}_2$: (M^+), 218.1307. Found: m/z 218.1305. HPLC: Chiralpak OD-H (0.8% 2-propanol in hexane, Flow 0.5 mL / min), 28.4 min (major), 59.7 min (minor).

3-(1'-Cyclohexenyl)-2-hydroxy-1-phenyl-4-propen-1-one (4g): ^1H NMR (400 MHz) δ = 1.25-1.65 (4H, m), 1.80-2.00 (4H, m), 2.07 (1H, dd, J = 8.3, 14.2 Hz), 2.40 (1H, dd, J = 3.4, 14.2 Hz), 3.67 (1H, brs), 5.12 (1H, dd, J = 3.4, 8.3 Hz), 5.38 (1H, s), 7.41 (2H, t, J = 7.3 Hz), 7.53 (1H, t, J = 7.3 Hz), 7.83 (2H, d, J = 7.3 Hz); ^{13}C NMR (100 MHz) δ = 22.1, 22.8, 25.3, 28.7, 44.5, 72.0, 124.8, 128.4, 128.6, 133.0, 133.6,

133.7, 201.7; IR (neat) 3453, 3061, 2931, 2858, 1684, 1598, 1449, 1262, 1174, 1096, 976, 703 cm^{-1} . HRMS: Calcd for $\text{C}_{15}\text{H}_{18}\text{O}_2$: (M^+), 230.1307. Found: m/z 230.1291. HPLC: Chiralpak OD-H (1.0% 2-propanol in hexane, Flow 1.0 mL / min), 12.4 min (major), 20.9 min (minor).

Benzyl 2-hydroxy-4-phenyl-4-pentenoic acid (6a): ^1H NMR (400 MHz) δ = 2.72-2.88 (1H, br), 2.85 (1H, dd, J = 7.3, 14.7 Hz), 3.07 (1H, dd, J = 4.4, 14.7 Hz), 4.95 (1H, d, J = 12.2 Hz), 5.09 (1H, d, J = 12.2 Hz), 5.17 (1H, d, J = 12.2 Hz), 5.36 (1H, s), 7.21-7.42 (10H, m); ^{13}C NMR (100 MHz) δ = 40.5, 67.2, 69.2, 116.2, 126.3, 126.8, 127.6, 127.2, 1128.3, 128.4, 128.4, 128.5, 134.9, 140.0, 143.2, 174.0; IR (neat) 3462, 3084, 3061, 3033, 2952, 1738, 1629, 1600, 1574, 1496, 1455, 1266, 1199, 1113, 1093, 1028, 906, 780, 751, 698 cm^{-1} . HRMS: Calcd for $\text{C}_{18}\text{H}_{18}\text{O}_3$: (M^+), 282.1256. Found: m/z 282.1300. HPLC: Chiralpak OB-H (2.0% 2-propanol in hexane, Flow 1.0 mL / min), 23.0 min (major), 26.1 min (minor).