Supporting Information

Reductive Desymmetrization of Symmetrical 2-Alkyl-1,3-diketones Catalyzed by Optically Active β-Ketoiminato Cobalt Complexes

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General:

^{1}H NMR spectra (400 MHz) were measured on a JOEL model GX-400 spectrometer using $CDCl_3$ as a solvent with tetramethylsilane (0.00 ppm) as an internal standard. ^{13}C NMR spectra (100 MHz) were measured on a JOEL model GX-400 spectrometer using $CDCl_3$ (77.0 ppm) or C_6D_6 (128.0 ppm) as a solvent. Infrared (IR) spectra were recorded on a JASCO model FT/IR-410 infrared spectrometer as KBr pellets. The melting points (Mp) were measured on an Electrothermal IA9100 apparatus and were uncorrected. Elemental analyses were determined with an Elemental Vario EL apparatus. High-resolution mass spectra (HRMS) were obtained with a HITACHI M-8013. High-performance liquid chromatography (HPLC) analyses were performed with a Shimadzu LC-6A chromatograph using an optically active column (Daicel Chiralcel OD-H, Chiralpak AD, or Chiralpak AD-H); the peak areas were obtained with a Shimadzu Chromatopack CR-4A or Varian Dynamax MacIntegrater. Optical rotations were measured with a JASCO DIP-370 digital polarimeter.

The typical preparation of 1,3-diaryl-2-alkyl-1,3-propanedions:

The 1,3-dialkyl-1,3-propanediones were prepared by conventional Claisen condensation of the corresponding ArCOMe and $ArCO_2Et$, and then their sodium enolates were treated with the corresponding RX to obtain the 1,3-diaryl-2-alkyl-1,3-propanedions.

1,3-Diphenyl-2-methyl-1,3-propanedione[1]: ^{1}H NMR ($CDCl_3$) δ = 1.61 (3H, d, J = 6.9 Hz), 5.27 (1H, q, J = 6.9 Hz), 7.41-7.50 (4H, m), 7.53-7.60 (2H, m), 7.90-8.01 (4H, m).

1,3-Di(*p*-methylphenyl)-2-methyl-1,3-propanedione: ^{1}H NMR ($CDCl_3$) δ = 1.58 (3H, d, *J* = 6.9 Hz), 2.39 (6H, s), 5.21 (1H, q, *J* = 6.9 Hz), 7.24 (4H, d, *J* = 8.3 Hz), 7.86 (4H, d, *J* = 8.3 Hz); ^{13}C NMR ($CDCl_3$) δ = 14.5, 21.7, 50.9, 128.5, 129.4, 133.0, 144.2, 196.6; IR (KBr) 2992, 2944, 1684, 1664, 1605, 1336, 1294, 1238, 1179, 966, 824, 565 cm^{-1}. Mp 132.8 - 133.7 °C. Anal. Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 81.25; H, 6.59.

1,3-Di(2-naphthyl)-2-methyl-1,3-propanedione: ^{1}H NMR ($CDCl_3$) δ = 1.75 (3H, d, *J* = 7.0 Hz), 5.57 (1H, q, *J* = 7.0 Hz), 7.51-7.57 (2H, m), 7.58-7.64 (2H, m), 7.84-7.93 (6H, m), 8.02-8.07 (2H, m), 8.54 (2H, s); ^{13}C NMR ($CDCl_3$) δ = 14.8, 51.4, 124.0, 126.8, 127.6, 128.6, 128.7, 129.6, 130.2, 132.4, 132.9, 135.6, 197.0; IR (KBr) 3058, 2985, 2937, 1687, 1675, 1623, 1361, 1315, 1280, 1171, 801, 760 cm^{-1}. Mp 132.3 - 132.9 °C. HRMS: calcd for $C_{24}H_{18}O_2$: (M^+) 338.1307. Found: 338.1329.

1,3-Di(*p*-methoxyphenyl)-2-methyl-1,3-propanedione: ^{1}H NMR ($CDCl_3$) δ = 1.58 (3H, d, *J* = 6.9 Hz), 3.85 (6H, s), 5.13 (1H, q, *J* = 6.9 Hz), 6.92 (4H, d, *J* = 9.3 Hz), 7.95 (4H, d, *J* = 9.3 Hz); ^{13}C NMR ($CDCl_3$) δ = 14.6, 51.1, 55.5, 113.9, 128.6, 130.7, 163.5, 195.6; IR (KBr) 2973, 2940, 2917, 1674, 1658, 1598, 1570, 1511, 1338, 1263, 1169, 1021, 973, 855, 565 cm^{-1}. Mp 78.4 - 79.4 °C. Anal. Calcd for $C_{18}H_{18}O_4$: C, 72.47; H, 6.08. Found: C, 72.41; H, 5.85.

1,3-Di(*p*-bromophenyl)-2-methyl-1,3-propanedione: ^{1}H NMR ($CDCl_3$) δ = 1.59 (3H, d, *J* = 7.1 Hz), 5.12 (1H, q, *J* = 7.1 Hz), 7.60 (4H, d, *J* = 8.5 Hz), 7.79 (4H, d, *J* = 8.5 Hz); ^{13}C NMR ($CDCl_3$) δ = 14.4, 51.4, 128.9, 129.9, 132.2, 134.1, 195.7; IR (KBr) 2986, 2935, 1697, 1671, 1583, 1281, 1195, 1068, 970, 797, 590 cm^{-1}. Mp 112.9 – 113.8 °C. Anal. Calcd for $C_{16}H_{12}Br_2O_2$: C, 48.52; H, 3.05. Found: C, 48.24; H, 2.77.

1,3-Diphenyl-2-ethyl-1,3-propanedione: ^{1}H NMR ($CDCl_3$) δ = 1.06 (3H, t, *J* = 7.3 Hz), 2.13-2.23 (2H, m), 5.12 (1H, t, *J* = 6.4 Hz), 7.41-7.49 (4H, m), 7.53-7.60 (2H, m), 7.93-8.01 (4H, m); ^{13}C NMR ($CDCl_3$) δ = 13.0, 23.0, 58.7, 128.4, 128.7, 133.3, 136.0, 195.9; IR (KBr) 2972, 2941, 1686, 1665, 1595, 1578, 1448, 1355, 1281, 1226, 1201, 991, 701, 692 cm^{-1}. Mp 88.1 - 88.6 °C. Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.93; H, 6.39. Found: C, 80.88; H, 6.17.

2-Allyl-1,3-diphenyl-1,3-propanedione: ^{1}H NMR ($CDCl_3$) δ = 2.88 (2H, t, *J* = 6.8 Hz), 5.04 (1H, dd, *J* = 1.5, 10.3 Hz), 5.11 (1H, dd, *J* = 1.5, 17.1 Hz), 5.30 (1H, t, *J* = 6.8 Hz), 5.81-5.94 (1H, m), 7.42-7.50 (4H, m), 7.55-7.60 (2H, m), 7.92-7.99 (4H, m); ^{13}C NMR ($CDCl_3$) δ = 33.6, 56.8, 117.2, 128.5, 128.8, 133.4, 135.0, 135.8, 195.3; IR (KBr) 3060, 2916, 1695, 1671, 1594, 1447, 1333, 1208, 908, 761, 685 cm^{-1}. Mp 65.9 – 66.6 °C. Anal. Calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 82.01; H, 6.01.

2-Benzyl-1,3-diphenyl-1,3-propanedione: ^{1}H NMR ($CDCl_3$) δ = 3.45 (2H, d, *J* = 6.5 Hz), 5.52 (1H, t, *J* = 6.5 Hz), 7.13-7.26 (5H, m), 7.36-7.45 (4H, m), 7.50-7.56 (2H, m), 7.85-7.92 (4H, m); ^{13}C NMR (C_6D_6) δ = 35.6, 59.6, 126.7, 128.7, 128.80, 128.82, 129.4, 133.1, 136.6, 139.7, 194.9; IR (KBr) 3037, 2905, 1695, 1664, 1594, 1446, 1350, 1214, 948, 760, 711, 696 cm^{-1}. Mp 106.4 – 107.4 °C. Anal. Calcd for $C_{22}H_{18}O_2$: C, 84.05; H, 5.77. Found: C, 84.24; H, 5.82.

1,3-diphenyl-2-isopropyl-1,3-propanedione: ^{1}H NMR ($CDCl_3$) δ = 1.02 (6H, d, *J* = 6.4 Hz), 2.85-2.98 (1H, m), 5.05 (1H, d, *J* = 9.3 Hz), 7.39-7.49 (4H, m), 7.51-7.59 (2H, m), 7.96-8.05 (4H, m); ^{13}C NMR ($CDCl_3$) _ = 21.4, 30.4, 64.9, 128.55, 128.64, 133.2, 136.9, 195.4; IR (KBr) 2965, 2935, 2876, 1696, 1657, 1448, 1292, 1224, 1204, 998, 705, 685 cm^{-1}. Mp 82.1 - 83.0 °C. Anal. Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 81.10; H, 6.63.

Typical procedure:

The preparation of pre-modified $NaBH_4$ solution: To the suspension of $NaBH_4$ (39.1 mg, 1.0 mmol) in $CHCl_3$ (6.9 mL), EtOH (60 μL, 1.0 mmol) and tetrahydrofurfuryl alcohol (1.4 mL, 14 mmol) were added at 0 °C under a dry nitrogen atmosphere. The mixture was stirred for 3 h at 0 °C, and then cooled at –20 °C.

The reductive desymmetrization of 1,3-diphenyl-2-methyl-1,3-propanedione: Under a dry nitrogen atmosphere in a pre-cooled vessel at -20 °C were placed the (*R*,*R*)-**3d** catalyst (7.2 mg, 0.0125 mmol), 1,3-diphenyl-2-methyl-1,3-propanedione (59.4 mg, 0.25 mmol), and $CHCl_3$ (12 mL). To this solution was added the solution of pre-modified $NaBH_4$ (2.0 mL), and stirred for 10 h at –20 °C. The reaction was quenched by pre-cooled aqueous THF solution at –20 °C and pH 7 buffer solution and the crude products were extracted with AcOEt. The combined

organic layers were washed with brine and dried over anhydrous sodium sulfate. After evaporation, the residue was purified by silica-gel column chromatography (hexane/AcOEt) to give 1,3-diphenyl-3-hydroxy-2-methyl-1-propanone in 93% yield (55.5 mg). The *anti*-selectivity was determined by ^{1}H NMR analysis to be 99%. The optical purity was determined by HPLC analysis to be 99% ee.

***anti*-1,3-Diphenyl-3-hydroxy-2-methyl-1-propanone**[2]: ^{1}H NMR ($CDCl_3$) δ = 1.05 (3H, d, *J* = 7.6 Hz), 3.05 (1H, br), 3.83 (1H, quintet, *J* = 7.6 Hz), 4.98 (1H, d, *J* = 7.6 Hz), 7.24-7.49 (7H, m), 7.52-7.59 (1H, m), 7.93-7.99 (2H, m); HPLC: Daicel Chiralpak AD (5% 2-propanol in hexane, Flow 1.0 mL/min), 23.6 min (major), 26.4 min (minor). $[\alpha]^{24}_D$ +111.4° (*c* 0.489, $CHCl_3$).

***anti*-1,3-Di(*p*-methylphenyl)-3-hydroxy-2-methyl-1-propanone**: ^{1}H NMR ($CDCl_3$) δ = 1.05 (3H, d, *J* = 7.4 Hz), 2.34 (3H, s), 2.41 (3H, s), 2.94 (1H, d, *J* = 4.6 Hz), 3.79 (1H, quintet, *J* = 7.4 Hz), 4.95 (1H, dd, *J* = 4.6, 7.4 Hz), 7.17 (2H, d, *J* = 7.9 Hz), 7.27 (2H, d, *J* = 7.9 Hz), 7.30 (2H, d, *J* = 7.9 Hz), 7.88 (2H, d, *J* = 7.9 Hz); ^{13}C NMR ($CDCl_3$) δ = 15.9, 21.2, 21.7, 47.8, 76.6, 126.5, 128.5, 129.0, 129.2, 134.1, 137.4, 139.1, 144.0, 204.3; IR (KBr) 3385, 2980, 2950, 1663, 1605, 1453, 1186, 999, 966, 818 cm^{-1}. Mp 95.0 – 95.6 °C. Anal. Calcd for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.57; H, 7.62. HPLC: Daicel Chiralpak AD-H (15% 2-propanol in hexane, Flow 1.0 mL/min), 13.7 min (minor), 15.5 min (major). $[\alpha]^{24}_D$ +126.1° (*c* 1.077, $CHCl_3$).

***anti*-1,3-Di(2-naphthyl)-3-hydroxy-2-methyl-1-propanone**: ^{1}H NMR ($CDCl_3$) δ = 1.17 (3H, d, *J* = 7.6 Hz), 3.12 (1H, d, *J* = 4.4 Hz), 4.11 (1H, quintet, *J* = 7.6 Hz), 5.24 (1H, dd, *J* = 4.4, 7.6 Hz), 7.45-7.66 (5H, m), 7.81-7.93 (6H, m), 7.95-7.99 (1H, m), 8.03-8.08 (1H, m), 8.52 (1H, s); ^{13}C NMR ($CDCl_3$) δ = 16.2, 48.0, 77.1, 124.0, 124.3, 125.88, 125.92, 126.1, 126.7, 127.59, 127.65, 127.9, 128.3, 128.49, 128.53, 129.6, 130.2, 132.4, 133.05, 133.08, 133.9, 135.6, 139.4, 204.5; IR (KBr) 3446, 3052, 2980, 1664, 1188, 823, 748, 477 cm^{-1}. Mp 120.7 – 121.6 °C. HRMS: calcd for $C_{24}H_{20}O_2$: (M^+) 340.1463. Found: 340.1456. HPLC: Daicel Chiralpak AD (25% 2-propanol in hexane, Flow 1.0 mL/min), 20.2 min (minor), 22.4 min (major). $[\alpha]^{24}_D$ +96.2° (*c* 1.083, $CHCl_3$).

***anti*-1,3-Di(*p*-methoxyphenyl)-3-hydroxy-2-methyl-1-propanone**: ^{1}H NMR ($CDCl_3$) δ = 1.06 (3H, d, *J* = 7.5 Hz), 2.98 (1H, d, *J* = 4.4 Hz), 3.75 (1H, quintet, *J* = 7.5 Hz), 3.81 (3H, s), 3.88 (3H, s), 4.94 (1H, dd, *J* = 4.4, 7.5 Hz), 6.89 (2H, d, *J* = 8.9 Hz), 6.94 (2H, d, *J* = 8.9 Hz), 7.34 (2H, d, *J* = 8.9 Hz), 7.97 (2H, d, *J* = 8.9 Hz); ^{13}C NMR ($CDCl_3$) δ = 16.0, 47.6, 55.3, 55.5, 76.4, 113.71, 113.73, 127.7, 129.6, 130.7, 134.4, 159.0, 163.5, 203.2; IR (KBr) 3366, 2977, 2934, 1664, 1599, 1516, 1252, 1174, 1032, 973, 825, 576 cm^{-1}. Anal. Calcd for $C_{18}H_{20}O_4$: C, 71.98; H, 6.71. Found: C, 71.86; H, 6.72. Mp 80.8 – 81.7 °C. HPLC: Daicel Chiralcel OD-H (10% 2-propanol in hexane, Flow 1.0 mL/min), 21.3 min (major), 26.4 min (minor). $[\alpha]^{24}_D$ +124.8° (*c* 1.079, $CHCl_3$).

***anti*-1,3-Di(*p*-bromophenyl)-3-hydroxy-2-methyl-1-propanone**: ^{1}H NMR ($CDCl_3$) δ = 1.05 (3H, d, *J* = 7.5 Hz), 2.92 (1H, d, *J* = 4.4 Hz), 3.70 (1H, quintet, *J* = 7.5 Hz), 4.95 (1H, dd, *J* = 4.4, 7.5 Hz), 7.29 (2H, d, *J* = 8.7 Hz), 7.50 (2H, d, *J* = 8.7 Hz), 7.62 (2H, d, *J* = 8.7 Hz), 7.83 (2H, d, *J* = 8.7 Hz); ^{13}C NMR ($CDCl_3$) δ = 15.6, 47.9, 76.1, 121.8, 128.3, 128.6, 129.8, 131.5, 131.9, 135.1, 140.9, 203.3; IR (KBr) 3494, 2978, 1661, 1581, 1396, 1244, 1069, 1009, 964, 822, 742 cm^{-1}. Mp 114.2 – 114.9 °C. HRMS: calcd for $C_{16}H_{14}Br_2O_2$: (M^+) 395.9362. Found: 395.9390. HPLC: Daicel Chiralpak AD-H (10% 2-propanol in hexane, Flow 1.0 mL/min), 22.5 min (minor), 24.9 min (major). $[\alpha]^{24}_D$ +97.8° (*c* 1.038, $CHCl_3$).

***anti*-1,3-Diphenyl-2-ethyl-3-hydrodxy-1-propanone**[2a]: ^{1}H NMR ($CDCl_3$) δ = 0.82 (3H, t, *J* = 7.3 Hz), 1.48-1.61 (1H, m), 1.66-1.80 (1H, m), 3.07 (1H, d, *J* = 6.4 Hz), 3.78 (1H, q, *J* = 6.4 Hz), 5.03 (1H, t, *J* = 6.4 Hz), 7.22-7.49 (7H, m), 7.51-7.58 (1H, m), 7.88-7.95 (2H, m); ^{13}C NMR ($CDCl_3$) δ = 11.8, 23.8, 54.3, 75.7, 126.3, 127.7, 128.2, 128.4, 128.5, 133.1, 138.1, 142.6, 205.4; IR (KBr) 3411, 3061, 2958, 2877, 1671, 1447, 1269, 1207, 1001, 768, 703 cm^{-1}. Mp 63.0 – 63.8 °C. Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.24; H, 7.28. HPLC: Daicel Chiralpak AD (1.5% 2-propanol in hexane, Flow 1.0 mL/min), 59.1 min (major), 67.5 min (minor). $[\alpha]^{24}_D$ +90.7° (*c* 1.046, $CHCl_3$).

***anti*-2-Allyl-1,3-diphenyl-3-hydrodxy-1-propanone**: ^{1}H NMR ($CDCl_3$) δ = 2.24-2.35 (1H, m), 2.37-2.50 (1H, m), 3.17 (1H, d, *J* = 5.4 Hz), 3.90 (1H, q, *J* = 6.8 Hz), 4.88-5.06 (3H, m),

5.55-5.69 (1H, m), 7.23-7.47 (7H, m), 7.51-7.58 (1H, m), 7.85-7.91 (2H, m); ^{13}C NMR ($CDCl_3$) δ = 34.8, 52.6, 75.5, 117.5, 126.3, 127.8, 128.2, 128.4, 128.5, 133.1, 134.2, 137.7, 142.2, 204.5; IR (KBr) 3374, 3073, 1671, 1448, 1241, 1209, 1012, 916, 767, 704, 607 cm^{-1}. Mp 79.3 – 80.2 °C. Anal. Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 81.07; H, 6.78. HPLC: Daicel Chiralcel OD-H (3% 2-propanol in hexane, Flow 1.0 mL/min), 17.7 min (minor), 19.1 min (major). $[\alpha]^{24}_D$ +74.7° (*c* 1.053, $CHCl_3$).

***anti*-2-Benzyl-1,3-diphenyl-3-hydrodxy-1-propanone**[2a]: ^{1}H NMR ($CDCl_3$) δ = 2.91 (1H, dd, *J* = 7.0, 13.3 Hz), 3.05 (1H, dd, *J* = 7.0, 13.3 Hz), 3.45 (1H, d, *J* = 7.0 Hz), 4.09 (1H, q, *J* = 7.0 Hz), 4.97 (1H, t, *J* = 7.0 Hz), 7.07-7.37 (12 H, m), 7.42-7.48 (1H, m), 7.63-7.68 (2H, m); ^{13}C NMR ($CDCl_3$) δ = 36.7, 54.7, 75.4, 126.0, 126.3, 127.6, 128.0, 128.2, 128.3, 128.4, 128.9, 133.0, 137.8, 138.4, 142.5, 205.3; IR (KBr) 3434, 3062, 3035, 1674, 1456, 1206, 1047, 1010, 751, 703 cm^{-1}. Mp 115.6 – 116.5 °C. HRMS: calcd for $C_{22}H_{20}O_2$: (M^+) 316.1463. Found: 316.1481. HPLC: Daicel Chiralcel OD-H (5% 2-propanol in hexane, Flow 1.0 mL/min), 15.4 min (major), 17.3 min (minor). $[\alpha]^{24}_D$ –8.7° (*c* 1.024, $CHCl_3$).

***anti*-1,3-Diphenyl-3-hydrodxy-2-isopropyl-1-propanone**: ^{1}H NMR ($CDCl_3$) δ = 0.87 (3H, d, *J* = 6.8 Hz), 1.15 (3H, d, *J* = 6.8 Hz), 2.24-2.35 (1H, m), 3.59 (1H, dd, *J* = 4.4, 8.3 Hz), 4.04 (1H, d, *J* = 8.1 Hz), 5.17 (1H, dd, *J* = 4.4, 8.1 Hz), 7.08-7.14 (1H, m), 7.18-7.35 (6H, m), 7.42-7.48 (1H, m), 7.60-7.66 (2H, m); ^{13}C NMR ($CDCl_3$) δ = 21.1, 21.3, 29.6, 58.7, 73.5, 125.5, 127.1, 127.9, 128.2, 128.3, 133.0, 138.6, 143.0, 207.1; IR (KBr) 3435, 2952, 1666, 1447, 1271, 1207, 1010, 768, 700, 570 cm^{-1}. Mp 84.0 – 85.2 °C. HRMS: calcd for $C_{18}H_{20}O_2$: (M^+) 268.1463. Found: 268.1502. HPLC: Daicel Chiralpak AD-H (15% 2-propanol in hexane, Flow 1.0 mL/min), 8.3 min (minor), 11.2 min (major). $[\alpha]^{24}_D$ +40.1° (*c* 0.261, $CHCl_3$).

X-ray analysis:

The *anti*-1,3-di(*p*-bromophenyl)-3-hydroxy-2-methyl-1-propanone obtained by (*R*,*R*)-cobalt catalyst was converted into its (*R*)-α-methoxyphenylacetate by treatment with (*R*)-α-methoxyphenylacetic acid, DCC, and DMAP.

3-(2*S*,3*R*)-1,3-Di(*p*-bromophenyl)-3-hydroxy-2-methyl-1-propanonyl (2*R*)-2-phenyl-2-methoxyacetate: ^{1}H NMR ($CDCl_3$) δ = 0.91 (3H, d, *J* = 6.8 Hz), 3.27 (3H, s), 3.73-3.83 (1H, m), 4.52 (1H, s), 5.94 (1H, d, *J* = 9.8 Hz), 6.88-6.97 (2H, m), 7.09-7.15 (2H, m), 7.20-7.37 (5H,

m), 7.66 (2H, d, *J* = 8.3 Hz), 7.82 (2H, d, *J* = 8.3 Hz); ^{13}C NMR ($CDCl_3$) δ = 14.4, 45.4, 57.3, 77.8, 82.2, 122.4, 127.1, 128.4, 128.5, 128.6, 129.8, 131.4, 132.0, 135.1, 135.5, 136.3, 168.6, 199.6; IR (KBr) 2925, 1730, 1675, 1250, 969, 822, 733, 698, 554 cm^{-1}. Mp 105.9 – 108.2 °C. HRMS: calcd for $C_{25}H_{23}Br_2O_4$: ($M+H^+$) 544.9964. Found: 544.9987. $[\alpha]^{24}_D$ +43.3° (*c* 0.259, $CHCl_3$).

The crystals were grown from a $CHCl_3$ solution by diffusion of a small amount of hexane over the course of several days. A crystal specimen of approximate dimension 0.6 x 0.3 x 0.2 mm^3 was chosen. The X-ray intensities were measured on a Rigaku AFC-7R diffractometer with Mo Kα radiation. The structure was solved by direct methods using SIR92 and refined by full-matrix least-squares calculations on F^2 using SHELXL-97. The refinement of the absolute configurations was performed and the structure presented yielding a value of 0.00(1) for the Flack parameter, indicating the structure had correct absolute configurations. This result was consistent with the fact that esterification was performed using (*R*)-α-methoxyphenylacetic acid. Crystal data for 3-(*2S,3R*)-1,3-di(*p*-bromophenyl)-2-methyl-1-propanonyl (*2R*)-2-methoxy-2-phenylacetate were summarized as follows.

Table 1. Crystal data and structure refinement for 3-(*2S,3R*)-1,3-di(*p*-bromophenyl)-2-methyl-1-propanonyl (*2R*)-2-methoxy-2-phenylacetate

Empirical formula	C25 H22 Br2 O4
Formula weight	546.25
Temperature	298(1) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	P2(1)2(1)2(1)
Unit cell dimensions	a=10.371(1) Å α=90° b=38.505(3) Å β=90° c=5.9020(9) Å γ=90°
Volume	2356.9(5) $Å^3$
Z	4
Density(calculated)	1.539 Mg/m^3
Absorption coefficient	3.467 mm^{-1}
F(000)	1096.0
Crystal Size	0.60 x 0.30 x 0.20 mm^3
The data range for data collection	2.50 to 27.50°
Index ranges	0<=h<=13, 0<=k<=49, -7<=l<=0
Reflection collected	3658
Independent reflections	3263
Completeness to theta = 7.50°	99.9%
Absorption correction	psi-scan
Max. and min. transmission	0.500 and 0.299
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3263 / 0 / 280
Goodness-of-fit on F^2	0.973
Final R indices [I>2sigma(I)]	R1 = 0.031
R indices (all data)	R1 = 0.123, wR2 = 0.086
Absolute structure parameter	0.00(1)
Largest diff. peak and hole	0.310 and –0.260 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3). U(eq) is defined as one third of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(20)	-3230.7(6)	2381.7(2)	827(2)	111.3(3)
Br(31)	6252.6(7)	15.0(2)	909(2)	123.4(4)
O(2)	4204(3)	1837(1)	4444(8)	73(1)
O(11)	2166(4)	1501(2)	8741(9)	116(2)
O(12)	1997(4)	1508(1)	4966(7)	67(1)
O(24)	1266(5)	698(1)	6853(9)	91(1)
C(1)	3591(7)	2161(2)	391(2)	119(3)
C(3)	3938(6)	1715(2)	663(1)	64(2)
C(4)	4935(5)	1436(1)	716(1)	54(1)
C(5)	5544(6)	1445(2)	923(1)	69(2)
C(6)	6495(6)	1200(2)	969(1)	82(2)
C(7)	6785(7)	944(2)	812(1)	79(2)
C(8)	6158(6)	937(1)	610(1)	74(2)
C(9)	5229(5)	1183(2)	560(1)	61(2)
C(10)	2587(6)	1566(2)	689(1)	65(2)
C(13)	687(5)	1361(1)	5011(9)	59(2)
C(14)	-240(5)	1628(1)	405(1)	60(1)
C(15)	-1415(5)	1685(1)	5103(10)	65(2)
C(16)	-2308(5)	1909(1)	411(1)	77(2)
C(17)	-2027(5)	2076(1)	216(1)	65(2)
C(18)	-855(6)	2024(1)	109(1)	76(2)
C(19)	31(5)	1800(2)	207(1)	70(2)
C(21)	786(5)	1033(1)	360(1)	68(2)
C(22)	-525(7)	876(2)	300(2)	114(3)
C(23)	1545(6)	758(2)	488(1)	65(2)
C(25)	2642(5)	568(1)	380(1)	58(2)
C(26)	3120(6)	657(1)	169(1)	68(2)
C(27)	4185(6)	490(2)	82(1)	72(2)
C(28)	4754(6)	228(2)	204(1)	73(2)
C(29)	4269(6)	128(1)	415(2)	81(2)
C(30)	3203(6)	299(1)	499(1)	71(2)

Table 3. Bond length[Å] and angles [°]

Br(20)-C(17)	1.887(6)
Br(31)-C(28)	1.882(6)
O(2)-C(1)	1.436(8)
O(2)-C(3)	1.400(8)
O(11)-C(10)	1.204(9)
O(12)-C(10)	1.309(9)
O(12)-C(13)	1.471(6)
O(24)-C(23)	1.222(8)
C(3)-C(4)	1.523(8)
C(3)-C(10)	1.523(9)
C(4)-C(5)	1.372(9)
C(4)-C(9)	1.377(8)
C(5)-C(6)	1.392(9)
C(6)-C(7)	1.38(1)

C(7)-C(8)	1.36(1)
C(8)-C(9)	1.384(8)
C(13)-C(14)	1.515(8)
C(13)-C(21)	1.517(8)
C(14)-C(15)	1.385(8)
C(14)-C(19)	1.372(9)
C(15)-C(16)	1.395(8)
C(16)-C(17)	1.353(10)
C(17)-C(18)	1.386(8)
C(18)-C(19)	1.388(8)
C(21)-C(22)	1.529(9)
C(21)-C(23)	1.520(8)
C(23)-C(25)	1.494(8)
C(25)-C(26)	1.382(9)
C(25)-C(30)	1.379(8)
C(26)-C(27)	1.378(9)
C(27)-C(28)	1.373(9)
C(28)-C(29)	1.39(1)
C(29)-C(30)	1.381(9)

C(1)-O(2)-C(3)	114.0(5)
C(10)-O(12)-C(13)	118.8(5)
O(2)-C(3)-C(4)	107.0(5)
O(2)-C(3)-C(10)	113.6(5)
C(4)-C(3)-C(10)	109.8(5)
C(3)-C(4)-C(5)	118.7(5)
C(3)-C(4)-C(9)	120.7(5)
C(5)-C(4)-C(9)	120.6(5)
C(4)-C(5)-C(6)	119.0(6)
C(5)-C(6)-C(7)	120.4(6)
C(6)-C(7)-C(8)	119.7(6)
C(7)-C(8)-C(9)	120.5(6)
C(4)-C(9)-C(8)	119.8(6)
O(11)-C(10)-O(12)	125.6(6)
O(11)-C(10)-C(3)	120.2(6)
O(12)-C(10)-C(3)	114.1(6)
O(12)-C(13)-C(14)	108.7(4)
O(12)-C(13)-C(21)	104.3(4)
C(14)-C(13)-C(21)	113.7(5)
C(13)-C(14)-C(15)	119.9(5)
C(13)-C(14)-C(19)	121.0(5)
C(15)-C(14)-C(19)	119.0(5)
C(14)-C(15)-C(16)	119.7(6)
C(15)-C(16)-C(17)	120.6(5)
Br(20)-C(17)-C(16)	120.6(4)
Br(20)-C(17)-C(18)	118.8(5)
C(16)-C(17)-C(18)	120.6(5)
C(17)-C(18)-C(19)	118.6(6)
C(14)-C(19)-C(18)	121.5(5)
C(13)-C(21)-C(22)	113.3(5)
C(13)-C(21)-C(23)	110.2(5)
C(22)-C(21)-C(23)	107.4(5)
O(24)-C(23)-C(21)	118.7(5)
O(24)-C(23)-C(25)	119.7(6)
C(21)-C(23)-C(25)	121.6(6)
C(23)-C(25)-C(26)	122.4(5)
C(23)-C(25)-C(30)	118.1(6)
C(26)-C(25)-C(30)	119.5(5)
C(25)-C(26)-C(27)	120.6(6)

C(26)-C(27)-C(28)	119.3(6)
Br(31)-C(28)-C(27)	119.2(5)
Br(31)-C(28)-C(29)	119.5(5)
C(27)-C(28)-C(29)	121.2(6)
C(28)-C(29)-C(30)	118.4(6)
C(25)-C(30)-C(29)	121.0(6)

Table 4. Anisotropic displacement parameters ($Å^2$ x 10^3). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11}+...+2hka^*b^*U^{12}]$

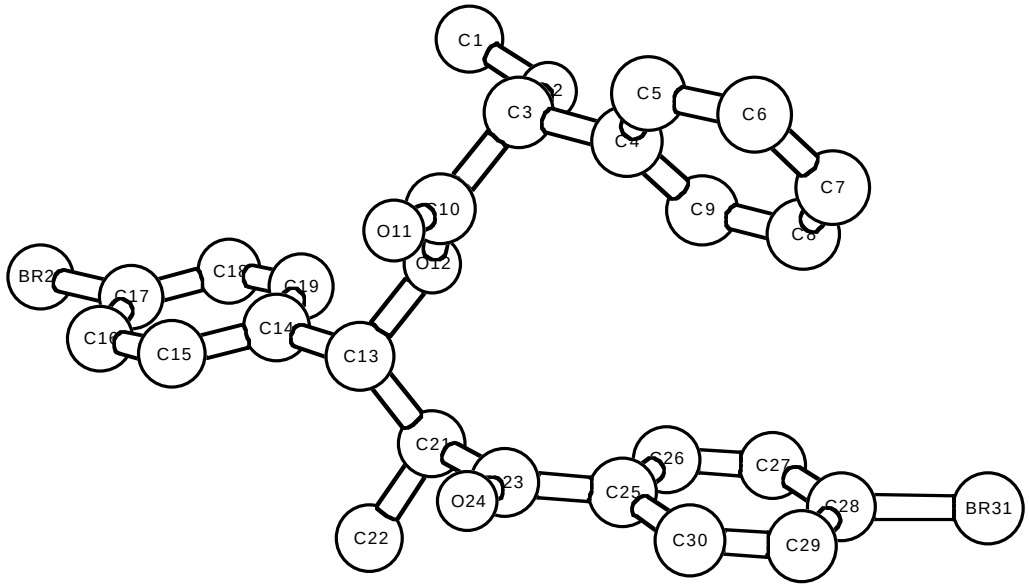
	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(20)	68.0(4)	90.5(5)	175.5(9)	51.5(6)	2.4(6)	15.1(4)
Br(31)	83.7(5)	103.0(5)	183.6(10)	-8.6(7)	19.1(7)	25.8(4)
O(2)	51(2)	-83(3)	85(3)	23(3)	17(3)	12(2)
O(11)	74(3)	207(5)	66(3)	-5(4)	16(3)	-18(3)
O(12)	48(2)	96(3)	57(3)	12(2)	4(2)	-8(2)
O(24)	100(4)	96(3)	75(3)	18(3)	17(3)	24(3)
C(1)	91(5)	88(5)	178(8)	54(6)	19(6)	27(4)
C(3)	44(3)	81(4)	68(5)	6(4)	5(4)	-2(3)
C(4)	44(3)	63(4)	54(4)	6(3)	-1(3)	-4(3)
C(5)	60(4)	88(4)	60(5)	0(4)	4(4)	-5(3)
C(6)	66(4)	112(5)	68(5)	15(5)	-12(4)	-1(4)
C(7)	68(4)	71(4)	98(6)	20(4)	0(5)	5(4)
C(8)	64(4)	66(4)	91(5)	3(4)	4(5)	1(3)
C(9)	52(3)	74(4)	56(4)	-5(4)	-2(4)	-5(3)
C(10)	54(4)	86(4)	54(5)	1(4)	13(4)	2(3)
C(13)	42(3)	72(4)	63(5)	11(3)	3(3)	-1(3)
C(14)	47(3)	72(4)	60(4)	8(4)	9(4)	-4(3)
C(15)	55(4)	66(4)	73(5)	12(3)	13(3)	-3(3)
C(16)	49(3)	63(4)	119(6)	15(5)	17(5)	10(3)
C(17)	51(4)	51(3)	92(5)	17(3)	-2(4)	-1(3)
C(18)	60(4)	79(4)	89(5)	28(4)	16(4)	-1(3)
C(19)	48(3)	90(4)	71(5)	20(4)	12(4)	11(3)
C(21)	55(3)	74(4)	76(5)	6(4)	-3(4)	15(3)
C(22)	87(5)	88(5)	166(8)	-21(5)	-47(6)	11(4)
C(23)	64(4)	68(4)	62(5)	10(4)	3(4)	3(3)
C(25)	55(3)	53(3)	64(4)	8(3)	-14(4)	-5(3)
C(26)	60(4)	70(4)	73(5)	8(3)	-11(4)	5(3)
C(27)	66(4)	78(4)	73(5)	2(4)	4(4)	-1(3)
C(28)	52(4)	67(4)	101(6)	-8(4)	1(4)	-2(3)
C(29)	65(4)	65(4)	111(6)	13(5)	-12(5)	9(3)
C(30)	70(4)	61(3)	82(5)	17(3)	-13(4)	-6(3)

Table 5. Calculated hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3)

	x	y	z	U(eq)
H(1A)	2691	2139	4110	136.5
H(1B)	3802	2232	2456	136.5
H(1C)	3897	2336	4990	136.5
H(3)	4047	1908	7722	81.7

H(5)	5298	1605	10404	88.7
H(6)	6949	1207	11090	98.7
H(7)	7470	782	8480	94.8
H(8)	6343	755	5013	96.6
H(9)	4776	1180	4162	78.5
H(13)	446	1298	6564	75.0
H(15)	-1613	1568	6527	86.4
H(16)	-3139	1955	4853	91.0
H(18)	-669	2149	-277	93.1
H(19)	869	1763	1305	81.9
H(21)	1243	1090	2191	85.2
H(22A)	-451	679	2119	130.4
H(22B)	-984	823	4388	130.4
H(22C)	-1050	1047	2209	130.4
H(26)	2679	834	818	82.3
H(27)	4522	555	-648	91.9
H(29)	4678	-58	5023	97.3
H(30)	2805	224	6390	88.5

Crystal Structure of 3-(*2S*,*3R*)-1,3-Di(*p*-bromophenyl)-2-methyl-1-propanonyl (*2R*)-2-methoxy-2-phenylacetate



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