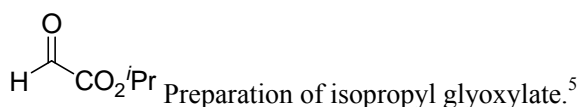
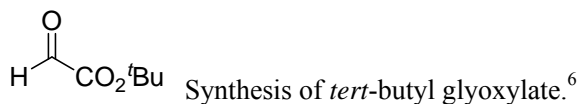


General

¹H-NMR spectra were recorded on a JEOL ECX-400 (400 MHz) in CDCl₃ with tetramethylsilane as an internal standard. Chemical shifts are reported in part per million (ppm), and signal are expressed as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), and broad (br). ¹³C-NMR spectra were recorded on a JEOL ECX-400 (100 MHz) in CDCl₃ (δ_C = 77.0) with tetramethylsilane as an internal standard. Chemical shifts are reported in part per million (ppm). HPLC analysis was directly performed with chiral stationary phase column, Chiralpak AD-H, IB or Chiralcel OD-H, OB-H purchased from DAICEL Co., Ltd. High resolution mass spectra (HRMS) were recorded on a JEOL JMS 700TZ mass spectrometer at the Center for Instrumental Analysis, Hokkaido University. Optical rotations were measured on a HORIBA SEPA-300 digital polarimeter. Kanto Chemical silica gel 60N (particle size 0.063–0.210 mm) was used for flash column chromatography. Glassware was oven dried at 130 °C and allowed to cool under a stream of dry nitrogen. RuCl₃·xH₂O were purchased from Strem Chemical, Inc. [RuCl₂(*p*-cymene)]₂,¹ RuCl₂(PPh₃)₃,² BIPAM ligands (Me-BIPAM,³ N-Me-BIPAM⁴) were prepared according to our previous procedure. Me-BIPAM was commercially available from Wako Pure Chemical Industries, Ltd. All chemicals were purchased from Aldrich, Wako, TCI, or Kanto chemicals and used as received.



Diisopropyl L-tartrate (40 mmol) in H₂O (20 mL) was added to a flask under nitrogen at 0 °C. A solution of NaIO₄ in H₂O (50 mL) was then added at 0 °C. After being stirred for 2 h at 0 °C, then reaction mixture was warmed to room temperature and extracted with ethyl acetate. The combined organic layers were dried (MgSO₄), filtered, and concentrated under reduced pressure. The residual oil was distilled under vacuum to afford corresponding product in 60% yield (25 mmHg, 64–65 °C).



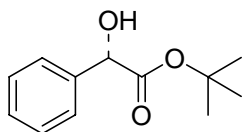
An autoclave tube was cooled to -78 °C and liquefied isobutene (30 ml, 321 mmol) was poured into the tube. Bromoacetic acid (14.32 g, 103 mmol) and Amberlyst-15 (0.07 g, 0.5 wt. percent) were added thereto, and the autoclave tube was tightly closed. The temperature was elevated to room temperature, and the reaction mixture was stirred for 24 hours. Amberlyst-15 was filtered out. The yield of obtained *tert*-butyl bromoacetate was 97% by dried under reduced pressure. ¹H NMR (CDCl₃, 400 MHz) δ = 3.75 (s, 2H), 1.48 (s, 9H)

A solution of *tert*-butyl bromoacetate (92.5 mmol) in anhydrous acetonitrile (80 mL) was treated with AgNO₃ (185 mmol) at room temperature in the dark for 48 h. The solvent was removed. AgBr was filtered out. The resulting residue was extracted with Et₂O. The organic layers were combined, washed with water and brine, dried (MgSO₄), and concentrated to yield *tert*-butoxycarbonylmethyl nitrate (87%). ¹H NMR (CDCl₃, 400 MHz) δ = 4.76 (s, 2H), 1.48 (s, 9H)

A solution of *tert*-butoxycarbonylmethyl nitrate (42 mmol) in anhydrous DMSO (90 mL) was treated with anhydrous sodium acetate (37 mmol) at room temperature for 20 min. The reaction mixture of was poured into a mixture of brine and ice (200 mL). The mixture was extracted with Et₂O. The organic layers were combined, washed with saturated aqueous Na₂CO₃, and concentrated. The resulting oil was dissolved in CH₂Cl₂ and washed with brine. The organic layer was dried (MgSO₄), and concentrated. The residual oil was distilled under vacuum to afford corresponding product in 32% yield (2.4 kPa, 40-41 °C). ¹H NMR (CDCl₃, 400 MHz) δ = 9.28 (s, 1H), 1.55 (s, 9H)

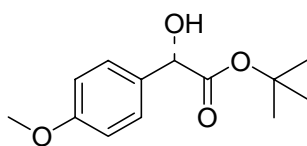
General Procedure for arylation of *tert*-butyl glyoxylate (Table 2)

A flask was charged with RuCl₂(PPh₃)₂ (0.01 mmol, 2 mol%) and (*R,R*)-Me-bipam (0.011 mmol, 2.2 mol%) under a nitrogen atmosphere. Toluene (3.0 mL) was added to the flask and the mixture was then stirred at room temperature for 30 min to prepare the catalyst. Freshly distilled *tert*-butyl glyoxylate (0.5 mmol), phenylboronic acid (1.0 mmol), KF (1.0 mmol), and H₂O (0.3 mL) were then added to this catalyst solution. The reaction mixture was stirred at 80 °C for 16 h, at which time the crude reaction mixture extracted using ethyl acetate, washed with saturated NH₄Cl and brine, and dried over MgSO₄, filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel to give (*S*)-*tert*-butyl mandelate in 90% yield.



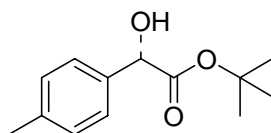
(*S*)-*tert*-Butyl mandelate

[α]_D¹⁸ = +108.0510 (c 3.8, CHCl₃) [lit. [α]_D²⁷ = -119.1 (C 1.05, CCl₄),^{7a} [α]_D²⁴ = +103.8 (C 1.10, CCl₄),^{7b} [α]_D²⁵ = +97.4 (C 1.0, MeOH),^{7c} [α]_D = +90.7 (C 1.0, MeOH),^{7d} [α]_D²³ = +35.8 (C 1.0, MeOH),^{7e} [α]_D³⁰ = -86.7 (C 1.0, CHCl₃),^{7f}], 96% ee [HPLC condition: Chiralcel OD-H column, hexane/2-propanol = 9/1, flow = 1.0 mL/min, wavelength = 254 nm, t_R = 7.4 min (major) and 12.9 min (minor)]; ¹H NMR (CDCl₃, 400 MHz) δ = 7.26-7.41 (m, 5H), 5.04 (d, 1H, J = 5.89 Hz), 3.52 (d, 1H, J = 5.89 Hz), 1.41 (s, 9H); ¹³C NMR (CDCl₃, 100 MHz) δ = 172.89, 138.95, 128.38, 128.08, 126.36, 83.07, 73.00, 27.81; HRMS m/z; calcd. for C₁₂H₁₆O₃Na 231.09917, found 231.09928.



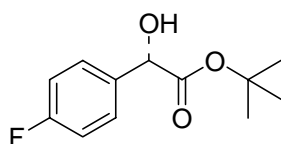
tert-butyl 2-hydroxy-2-(4-methoxyphenyl)acetate^{7d}

$[\alpha]_D^{18} = +72.9446$ (c 4.1, CHCl₃), 76% ee [HPLC condition: Chiralcel OD-H column, hexane/2-propanol = 9/1, flow = 1.0 mL/min, wavelength = 254 nm, t_R = 5.8 min (major) and 7.2 min (minor)]; ¹H NMR (CDCl₃, 400 MHz) δ = 7.31 (d, 2H, J = 8.61 Hz), 6.88 (d, 2H, J = 8.61 Hz), 4.98 (d, 1H, J = 5.89 Hz), 3.80 (s, 3H), 3.45 (d, 1H, J = 5.89 Hz), 1.41 (s, 9H); ¹³C NMR (CDCl₃, 100 MHz) δ = 173.10, 159.42, 131.20, 127.61, 113.79, 82.87, 72.56, 55.22, 27.83; HRMS m/z ; calcd. for C₁₃H₁₈O₄Na 261.10973, found 261.10981.



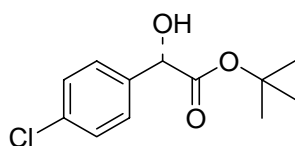
tert-butyl 2-hydroxy-2-p-tolylacetate^{7d}

$[\alpha]_D^{19} = +90.4379$ (c 3.9, CHCl₃), 90% ee [HPLC condition: Chiralcel OD-H column, hexane/2-propanol = 9/1, flow = 1.0 mL/min, wavelength = 254 nm, t_R = 4.6 min (major) and 5.6 min (minor)]; ¹H NMR (CDCl₃, 400 MHz) δ = 7.27 (d, 2H, J = 8.15 Hz), 7.15 (d, 2H, J = 7.70 Hz), 4.99 (d, 1H, J = 5.89 Hz), 3.45 (d, 1H, J = 5.89 Hz), 1.40 (s, 9H); ¹³C NMR (CDCl₃, 100 MHz) δ = 173.04, 137.78, 136.02, 129.08, 126.27, 82.89, 72.84, 27.82, 21.14; HRMS m/z ; calcd. for C₁₃H₁₈O₃Na 245.11482, found 245.11488.



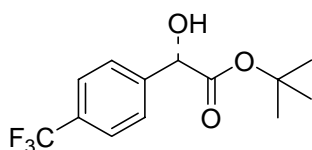
tert-butyl 2-(4-fluorophenyl)-2-hydroxyacetate

$[\alpha]_D^{18} = +92.3654$ (c 4.0, CHCl₃), 90% ee [HPLC condition: Chiralcel OD-H column, hexane/2-propanol = 98/2, flow = 1.0 mL/min, wavelength = 254 nm, t_R = 7.4 min (major) and 7.9 min (minor)]; ¹H NMR (CDCl₃, 400 MHz) δ = 7.36-7.40 (m, 2H), 7.00-7.05 (m, 2H), 5.02 (d, 1H, J = 5.44 Hz), 3.59 (d, 1H, J = 5.44 Hz), 1.40 (s, 9H); ¹³C NMR (CDCl₃, 100 MHz) δ = 172.67, 162.53 (d, J = 246 Hz), 134.75 (d, J = 2.86 Hz), 128.05 (d, J = 8.58 Hz), 115.24 (d, J = 20.98 Hz), 83.24, 27.30, 27.77; HRMS m/z ; calcd. for C₁₂H₁₆O₃FNa 249.08974, found 249.08993.



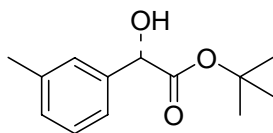
tert-butyl 2-(4-chlorophenyl)-2-hydroxyacetate^{7d}

$[\alpha]_D^{19} = +41.5952$ (c 3.5, CHCl_3), 99% ee [HPLC condition: Chiralcel OD-H column, hexane/2-propanol = 98/2, flow = 1.0 mL/min, wavelength = 254 nm, $t_R = 8.5$ min (major) and 10.1 min (minor)]; $^1\text{H NMR}$ (CDCl_3 , 400 MHz) $\delta = 7.36$ (d, 2H, $J = 8.61$ Hz), 7.32 (d, 2H, $J = 9.06$ Hz), 5.01 (d, 1H, $J = 5.44$ Hz), 3.55 (d, 1H, $J = 5.44$ Hz), 1.41 (s, 9H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) $\delta = 172.46$, 137.41, 133.90, 128.54, 127.71, 83.48, 72.27, 27.80; HRMS m/z ; calcd. for $\text{C}_{12}\text{H}_{15}\text{O}_3\text{ClNa}$ 265.06019, found 265.06047.



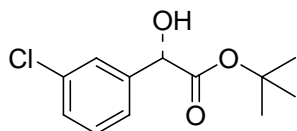
tert-butyl 2-hydroxy-2-(4-(trifluoromethyl)phenyl)acetate

$[\alpha]_D^{20} = +70.7900$ (c 3.5, CHCl_3), 88% ee [HPLC condition: Chiralcel OD-H column, hexane/2-propanol = 98/2, flow = 1.0 mL/min, wavelength = 254 nm, $t_R = 6.8$ min (minor) and 7.2 min (major)]; $^1\text{H NMR}$ (CDCl_3 , 400 MHz) $\delta = 7.61$ (d, 2H, $J = 8.15$ Hz), 7.56 (d, 2H, $J = 8.15$ Hz), 5.10 (d, 1H, $J = 5.44$ Hz), 3.67 (d, 1H, $J = 5.44$ Hz), 1.41 (s, 9H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) $\delta = 172.08$, 142.77, 130.27 (q, $J = 32.42$ Hz), 126.67, 125.28 (q, $J = 3.81$ Hz), 124.05 (q, $J = 273$ Hz), 83.76, 72.42, 27.77; HRMS m/z ; calcd. for $\text{C}_{13}\text{H}_{15}\text{O}_3\text{F}_3\text{Na}$ 299.08655, found 299.08664.



tert-butyl 2-hydroxy-2-m-tolylacetate

$[\alpha]_D^{19} = +89.1694$ (c 3.8, CHCl_3), 93% ee [HPLC condition: Chiralcel OD-H column, hexane/2-propanol = 9/1, flow = 1.0 mL/min, wavelength = 254 nm, $t_R = 6.8$ min (major) and 12.7 min (minor)]; $^1\text{H NMR}$ (CDCl_3 , 400MHz) $\delta = 7.10$ -7.26 (m, 4H), 5.00 (d, 1H, $J = 5.89$ Hz), 3.47 (d, 1H, $J = 5.89$ Hz), 2.35 (s, 3H), 1.41 (s, 9H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) $\delta = 172.96$, 138.85, 138.06, 128.83, 128.25, 126.99, 123.50, 82.97, 73.01, 27.83, 21.40; HRMS m/z ; calcd. for $\text{C}_{13}\text{H}_{18}\text{O}_3\text{Na}$ 245.11482, found 245.11504.



tert-butyl 2-(3-chlorophenyl)-2-hydroxyacetate

$[\alpha]_D^{19} = +80.2921$ c 4.6, CHCl_3 , 88% ee [HPLC condition: Chiralcel OJ-H column, hexane/2-propanol = 100/1, flow = 1.0 mL/min, wavelength = 254 nm, $t_R = 9.3$ (minor) min and 9.8 (major) min]; $^1\text{H NMR}$ (CDCl_3 , 400 MHz) $\delta = 7.43$ (s, 1H), 7.27-7.32 (m, 3H), 5.02 (d, 1H, $J = 5.44$ Hz), 3.63 (d, 1H, $J = 5.44$ Hz), 1.42 (s, 9H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) $\delta = 172.28$, 140.82, 134.25, 129.59, 128.20, 126.50, 124.49, 83.56, 72.27, 27.78; HRMS m/z ; calcd. for $\text{C}_{12}\text{H}_{15}\text{O}_3\text{ClNa}$

265.06019, found 265.06051.

Preparation of $\text{RuCl}_2((R,R)\text{-Me-bipam})(\text{PPh}_3)$

Following a literature procedure,⁸ $\text{RuCl}_2(\text{PPh}_3)_3$ (100 mg, 0.1043 mmol) and $(R,R)\text{-Me-BIPAM}$ (80 mg, 0.1053 mmol) were mixed together in a Schlenk tube under nitrogen in 10 mL of CH_2Cl_2 . The reaction mixture was stirred 0.5 h. Hexane was added to mixture. The precipitate was filtered, washed with hexane, and dried; yield 84 mg (67%). ³¹P NMR (toluene- d_8 , 160 MHz) $\delta = 29.3$ (dd, $J = 30.1, 494.3$ Hz), 153.1 (dd, $J = 73.1, 494.3$ Hz), 170.2 (dd, $J = 30.1, 73.1$ Hz). elemental analysis: $\text{C}_{64}\text{H}_{53}\text{Cl}_2\text{N}_2\text{O}_3\text{P}_3\text{Ru}$ requires C 64.3, H 4.47, N 2.34; found C 61.8, H 4.63, N 2.31.

Preparation of $\text{RuCl}_2(p\text{-cymene})(\text{PPh}_3)$:⁹ A suspension of $[\text{RuCl}_2(p\text{-cymene})]_2$ (200 mg, 0.327 mmol) and triphenylphosphine (200 g, 0.763 mmol) in hexane (15 mL) was heated under reflux for 5h. After solvent removal under reduced pressure, $\text{RuCl}_2(p\text{-cymene})(\text{PPh}_3)$ was obtained by crystallizing the residue at -30 °C from dichloromethane and pentane, yield 0.263 g (0.463 mmol), 70%, ¹H NMR (CDCl_3 , 400 MHz) $\delta = 7.85\text{-}7.80$ (m, 6H), 7.41-7.33 (m, 9H), 5.20 (d, 2H, $J = 6.34$ Hz), 4.99 (d, 2H, $J = 4.98$ Hz), 2.85 (sept, 1H, $J = 6.8$ Hz), 1.87 (s, 3H), 1.10 (d, 1H, $J = 7.25$ Hz); ¹³C NMR (CDCl_3 , 100 MHz) $\delta = 134.4$ (d, $J = 8.58$), 130.3, 128.0 (d, $J = 10.49$ Hz), 114.1, 96.0, 89.1, 87.3, 30.3, 21.9, 17.8; ³¹P NMR (CDCl_3 , 160MHz) $\delta = 24.8$; elemental analysis: $\text{C}_{28}\text{H}_{29}\text{Cl}_2\text{PRu}$ requires C 59.2, H 5.14; found C 54.2, H 4.85.

Preparation of $\text{RuCl}(\text{Ph})(p\text{-cymene})(\text{PPh}_3)$:¹⁰ $\text{RuCl}_2(p\text{-cymene})(\text{PPh}_3)$ (50 mg, 0.088 mmol) was dissolved in dry THF (5 mL). Phenylboronic acid (54 mg, 0.44 mmol) and KF (30 mg, 0.517 mmol) were added and the mixture stirred at 50 °C for 2 h. The solvent was removed under vacuum and then the residue was purified by filtration through a short plug of silica gel (CH_2Cl_2). The solvent was removed under vacuum, yield 33 mg (0.054 mmol), 61%, ¹H NMR (CDCl_3 , 400 MHz) $\delta = 7.78\text{-}6.99$ (m, 17H), 7.67 (m, 3H), 5.22 (d, 1H, $J = 5.89$ Hz), 4.97 (d, 1H, $J = 5.89$ Hz), 4.88 (d, 1H, $J = 6.80$ Hz), 4.87 (d, 1H, $J = 6.34$ Hz), 2.06 (sept, 1H, $J = 6.8$ Hz), 1.50 (s, 3H), 0.98 (d, 3H, $J = 7.25$ Hz), 0.87 (d, 3H, $J = 7.25$ Hz); ¹³C NMR (CDCl_3 , 100 MHz) $\delta = 159.5$ (d, $J = 21.9$ Hz), 142.3 (d, $J = 4.77$ Hz), 134.3 (m), 129.6, 127.7, 126.2, 121.5, 116.0 (d, $J = 3.81$ Hz), 107.2, 88.4, 88.2 (d, $J = 4.77$ Hz), 87.7 (m), 29.9, 22.9, 22.1, 18.0; ³¹P NMR (CDCl_3 , 160MHz) $\delta = 39.6$; elemental analysis: $\text{C}_{34}\text{H}_{34}\text{ClPRu}$ requires C 66.9, H 5.62; found C 67.4, H 6.02.

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