Efficient Enantioselective Synthesis of Functionalized Tetrahydropyrans by Ru-Catalyzed Asymmetric Ring-Opening/Cross Metathesis (AROM/CM)

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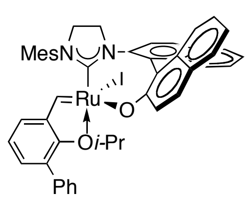
SUPPORTING INFORMATION

General. Infrared (IR) spectra were recorded on a Nicolet 210 spectrophotometer, ν_{max} in cm^{-1}. Bands are characterized as broad (br), strong (s), medium (m), and weak (w). ^{1}H NMR spectra were recorded on a Varian Unity INOVA 400 (400 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: δ 7.26 ppm, C_6D_6: δ 7.35 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz), integration, and assignment. ^{13}C NMR spectra were recorded on a Varian Unity INOVA 400 (100 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent as the internal reference ($CDCl_3$: δ 77.16 ppm). ^{19}F NMR spectra were recorded on a Varian Unity INOVA 400 (376 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from $CFCl_3$ with the solvent as the internal reference. High-resolution mass spectra were recorded at the University of Illinois (Urbana-Champaign, IL) or on a Micromass LCT ESI-MS (positive mode) at the Mass Spectrometry Facility, Boston College. Elemental microanalyses were performed by Robertson Microlit Laboratories (Madison, NJ). Enantiomer ratios were determined by chiral HPLC analysis (Chiral Technologies Chiralpak AS, Chiralpak AD, Chiralcel OJ, Chiralcel OB-H, and Chiralcel OD (0.46 cm x 25 cm)) in comparison with authentic racemic materials, or by ^{1}H or ^{19}F NMR spectroscopy of the derived Mosher esters in comparison with Mosher esters derived from the authentic racemic materials. Optical rotation values were measured on a Rudolph Research Analytical Autopol IV Polarimeter.

Materials. Unless otherwise noted, all reactions were carried out with distilled and degassed solvents under an atmosphere of dry N_2 in oven- (135 °C) and flame-dried glassware with standard drybox or vacuum-line techniques, and all work-up and purification procedures were carried out with reagent solvents in air. In most instances, solid organometallic compounds were stored under an atmosphere of N_2; although it has been determined that such precautions are unnecessary to maintain catalyst stability. All reagent solvents were purchased from Doe and Ingalls, unless otherwise noted. Solvents were purified under positive pressure of dry Ar by a modified Innovative Technologies purification system: toluene and benzene were purified through a copper oxide and an alumina column; CH_2Cl_2 and Et_2O were purged with Ar and purified by passing them through two alumina columns. THF was purified by distillation from a benzophenone ketyl immediately prior to use. 1,2-Dichloroethane (Lancaster), $CDCl_3$ (Cambridge Isotope Labarotory, Inc.), triethylamine (Acros), styrene (Aldrich), vinylcyclohexane (Aldrich), *p*-methoxystyrene (Aldrich), *p*-bromostyrene (Aldrich), and *p*-trifluoromethylstyrene (Aldrich) were distilled from CaH_2 under N_2. MeOH was distilled over Mg under N_2. Dimethylformamide (Fisher) was stored under N_2 over activated 4Å molecular sieves. K_2CO_3 was stored in an oven (120 °C). $Cl_2Ru(=CH$-*o*-O*i*PrC_6H_3Ph)PCy_3 was prepared as previously described.[1] $Cl_2Ru(=CHC_6H_5)(PCy_3)_2$ was purchased from Materia. The following materials were purchased from commercial sources and used as received: EtOH (Fisher), Calcium granules (Aldrich), Ag_2O (Strem), 0.05 M potassium phosphate monobasic/ sodium hydroxide pH 7 buffer (Fisher), NaI (Aldrich).

Silica gel column chromatography was driven with compressed air and performed with silica gel 60 (230–400 mesh; pH (10% suspension) 6.5–7.0; surface area 500 m^2/g; pore volume 0.75 ml/g) obtained from TSI Chemical Co. (Cambridge, MA).

Preparation of iodide catalyst (1b).



Chloride catalyst **1a** (50.3 mg, 0.0616 mmol) and NaI (97.1 mg, 0.648 mmol) were weighed into a 3 mL Teflon cap vial, THF (1 mL) was added by syringe and the vial was capped and sealed with Teflon tape and electrical tape. The mixture was submerged into a 70 ºC oil bath and stirred for 1 h. The THF was removed with a stream of N_2 and the mixture was loaded directly onto a column of silica gel and eluted (1:1 Hex:CH_2Cl_2) to deliver **1b** (47.0 mg, 85 %) as a brown solid. X-ray quality crystals were obtained by silica gel chromatography in hexane and diethyl ether (9:1); slow

(1) Van Veldhuizen, J. V.; Gillingham, D. G.; Garber, S. B.; Kataoka, O.; Hoveyda, A. H. *J. Am. Chem. Soc*. **2003**, *125*, 12502–12508.

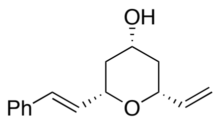
evaporatation of the coloured fractions deliver large crystals after 4–5 days. IR (neat): 3055 (w), 2974 (w), 2917 (w), 1680 (w), 1577 (m), 1470 (m), 1457 (s), 1420 (s), 1281 (s), 910 (m), 734 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 15.57 (s, 1H), 8.14 (dd, *J* = 8.7, 8.7 Hz, 2H), 7.93 (d, *J* = 8.2 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 9.0 Hz, 1H), 7.43 (m, 3H), 7.27–7.07 (m, 9H), 6.99 (s, 1H), 6.93 (ddd, *J* = 8.0, 0.9, 0.9 Hz, 1H), 6.85–6.83 (m, 2H), 6.79 (d, *J* = 9.0 Hz, 1H), 4.28–4.18 (m, 2H), 3.93–3.86 (m, 1H), 3.65–3.58 (m, 1H), 3.55–3.47 (m, 1H), 2.44 (s, 3H), 2.29 (s, 3H), 1.82 (s, 3H), 0.56 (d, *J* = 6.3 Hz, 3H), 0.33 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 279.09, 215.03, 169.08, 149.95, 148.20, 139.84, 138.82, 138.33, 138.10, 137.93, 137.58, 137.56, 134.88, 134.74, 133.69, 132.12, 131.61, 130.03, 129.56, 129.30, 128.86, 128.80, 128.64, 128.32, 128.23, 128.19, 127.93, 127.76, 126.74, 126.54, 126.09, 125.18, 124.79, 124.07, 121.65, 120.81, 119.24, 78.29, 53.32, 51.81, 21.49, 20.27, 20.24, 20.10, 18.64. X-ray data is included at the end of this document.

General procedure A: Ru-Catalyzed AROM/CM in THF at 0.1 M. **11a** (12.3 mg, 98.0 μmol) and styrene (46.4 mg, 0.446 mmol) were combined in a dried 3 mL vial containing a stir bar under nitrogen. Catalyst **1b** (3.6 mg, 4.4 μmol) was dissolved in THF (1 mL) and added by cannula to the vial containing substrate and styrene. The reaction was allowed to stir at 22 ºC for 3 h at which point the solvent was removed with a stream of N_2 and the mixture was loaded onto a silica gel column (0.5 cm W x 8 cm L) and eluted (3:2 Hex:Et_2O) to deliver recovered catalyst (1.7 mg, R_f = 0.5, 51%) and the desired product **12** (14.1 mg, R_f = 0.2, 64%) as a clear colourless oil.

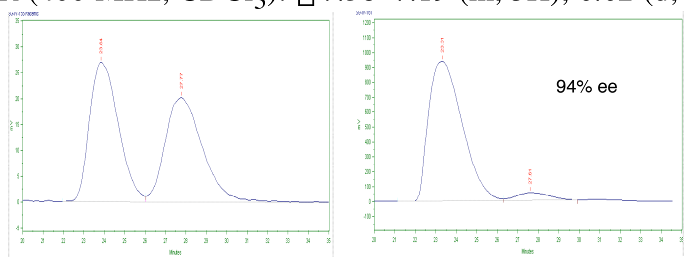
General procedure B: Ru-Catalyzed AROM/CM in the absence of solvent. Compound **5c** (10.0 mg, 46.0 μmol) and distilled vinylcyclohexane (67.2 mg, 0.610 mmol) were combined in a dried 3 mL vial in the glovebox and allowed to stir until all of **5c** dissolved. Catalyst **3** (2.2 mg, 2.4 μmol) was then weighed directly into the vial. The resulting solution was stirred for 2 h at 22 ºC at which point TLC analysis (4:1 Hex:Et_2O) indicated complete consumption of starting material. The crude mixture was loaded directly onto a silica gel column (0.5 cm W x 8 cm L) and eluted (9:1 Hex:Et_2O) to deliver bis-cross product (1.4 mg, R_f = 0.7, 10%), desired product **16** (9.1 mg, R_f = 0.5, 61%) and recovered catalyst (2.0 mg, R_f = 0.3, 90%).

General procedure C: Ru-Catalyzed AROM/CM by slow addition of olefin partner. Catalyst **1a** (3.7 mg, 5.0 μmol) and vinylcyclohexane (48.0 mg, 0.436 mmol) were weighed into a dried 3 mL vial containing a stir bar. Substrate **2a** (11.0 mg, 87.0 μmol) was added slowly by syringe or syringe pump as a solution in dichloroethane over 1 h at 22 ºC. The reaction was allowed to stir for an additional 12 h at 22 ºC at which time the solvent was removed under a stream of N_2 and the mixture was loaded directly onto a silica gel column (0.5 cm W x 8 cm L) and eluted (2:1 Hex:Et_2O) to deliver product **9** (14.8 mg, R_f = 0.3, 72%) as a clear colourless oil.

(2*S*,4*R*,6*R*)-Tetrahydro-2-(*E*)-styryl-6-vinyl-2*H*-pyran-4-ol (4a).



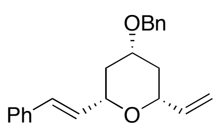
General procedure A was followed with substrate **2a** to afford a colourless oil after silica gel chromatography (3:1 Hex:Et_2O, R_f = 0.15). IR (neat): 3370 (br), 3074 (w), 3018 (w), 2955 (m), 2898 (m), 2848 (m), 1646 (m), 1488 (w), 1451 (w), 1362 (m), 1306 (m), 1054 (s), 960 (s), 758 (s), 695 (s). ^1H NMR (400 MHz, $CDCl_3$): δ 7.38–7.19 (m, 5H), 6.62 (d, *J* = 16.0 Hz, 1H), 6.24 (dd, *J* = 16.0, 6.0 Hz, 1H), 5.91 (ddd, *J* = 16.0, 10.8, 6.0 Hz, 1H), 5.30 (dd, *J* = 17.6, 1.2 Hz, 1H), 5.15 (dd, *J* = 10.8, 1.2 Hz, 1H), 4.09–4.05 (m, 1H), 3.97–3.90 (m, 2H), 2.12–2.04 (m, 2H), 1.55 (br s, 1H), 1.44–1.27 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.29, 136.94, 130.84, 129.59, 128.72, 127.86, 126.72, 115.77, 76.45, 76.19, 68.28, 41.31, 40.89. HRMS Calcd for $C_{15}H_{18}O_2Na$: 253.1204. Found: 253.1202. Absolute configuration is determined by conversion to **28** (See S18 & S19 for details).



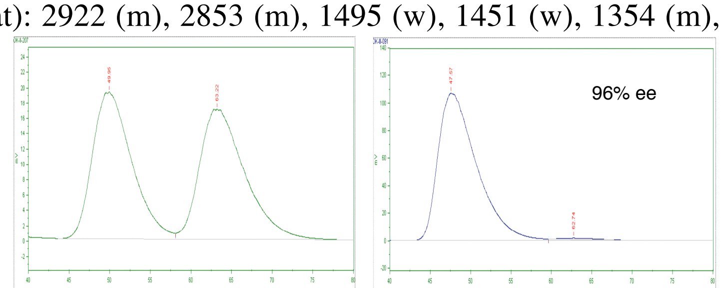
authentic racemic   asymmetric reaction with chloride catalyst

conditions: 98:2 Hex:iPA, Chiralpak AS,
1.0 mL/min, 254 nm
Retention Times: 23.8 min, 27.8 min

(2*S*,4*R*,6*R*)-4-Benzyloxytetrahydro-2-(*E*)-styryl-6-vinyl-2*H*-pyran (4b).



General procedure A was followed with substrate **2b** to afford a colourless oil after silica gel chromatography (40:1 Hex:Et_2O, R_f = 0.15). IR (neat): 2922 (m), 2853 (m), 1495 (w), 1451 (w), 1354 (m), 1157 (w), 1071 (s), 966 (m), 747 (s), 695 (s). ^1H NMR (400 MHz, $CDCl_3$): δ 7.42–7.20 (m, 10 H), 6.63 (d, *J* = 16.9 Hz, 1H), 6.26 (dd, *J* = 16.1, 6.0 Hz, 1H), 5.95 (ddd, *J* = 17.2, 10.6, 5.7 Hz, 1H), 5.32 (ddd, *J* = 17.2, 1.5, 1.5

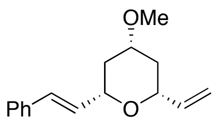


authentic racemic   asymmetric reaction with chloride catalyst

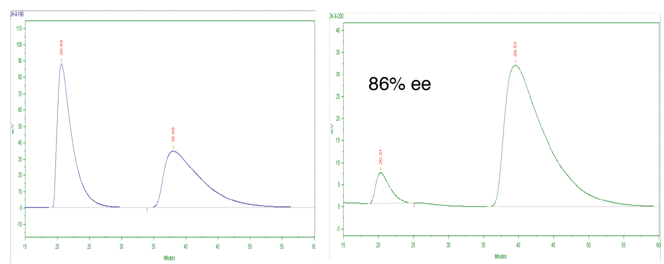
conditions: 99.8:0.2 Hex:iPA, Chiralcel OJ,
1.0 mL/min, 254 nm
Retention Times: 50.0 min, 53.2 min

Hz, 1H), 5.17 (ddd, *J* = 10.6, 1.5, 1.5 Hz, 1H), 4.62 (s, 2H), 4.10–4.03 (m, 1H), 3.98–3.91 (m, 1H), 3.71 (dddd, *J* = 11.0, 11.0, 4.6, 4.6 Hz, 1H), 2.21 (dddd, *J* = 12.5, 4.4, 2.2, 2.2 Hz, 1H), 2.15 (dddd, *J* = 12.5, 4.4, 2.2, 2.2 Hz, 1H), 1.48 (ddd, *J* = 11.4, 11.4, 11.4 Hz, 1H), 1.42 (ddd, *J* = 11.4, 11.4, 11.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.66, 138.39, 136.91, 130.74, 129.70, 128.65, 128.60, 127.77, 127.72, 126.66, 115.65, 76.53, 76.27, 74.54, 69.79, 38.21, 37.83. HRMS Calcd for $C_{22}H_{24}O_2$: 320.1776. Found: 320.1767. Absolute configuration is determined by conversion to **4a**.

Tetrahydro-4-methoxy-2-(*E*)-styryl-6-vinyl-2*H*-pyran (4c).



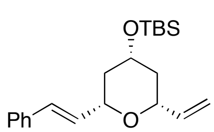
General procedure A was followed with substrate **2c** to afford a colourless oil after silica gel chromatography (20:1 Hex:Et_2O, R_f = 0.14). IR (neat): 2945 (m), 2923 (m), 2848 (m), 2824 (m), 1448 (m), 1379 (m), 1309 (m), 1081 (s), 966 (m), 748 (m), 694 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42–7.20 (m, 5H), 6.63 (d, *J* = 15.4 Hz, 1H), 6.26 (dd, *J* = 15.9, 6.0 Hz, 1H), 5.94 (ddd, *J* = 17.4, 10.6, 5.7 Hz, 1H), 5.32 (ddd, *J* = 17.4, 1.5, 1.5 Hz, 1H), 5.17 (ddd, *J* = 10.4, 1.5, 1.5 Hz, 1H), 4.08 (dddd, *J* = 11.2, 6.1, 1.5, 1.5 Hz, 1H), 4.00–3.81 (m, 1H), 3.50 (dddd, *J* = 11.0, 11.0, 4.4, 4.4 Hz, 1H), 3.40 (s, 3H), 2.17 (dddd, *J* = 12.5, 4.4, 2.2, 2.2 Hz, 1H), 2.12 (dddd, *J* = 12.5, 4.4, 2.2, 2.2 Hz, 1H), 1.36 (ddd, *J* = 11.4, 11.4, 11.4 Hz, 1H), 1.30 (ddd, *J* = 11.4, 11.4, 11.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.38, 136.88, 130.72, 129.69, 126.65, 127.77, 126.65, 115.66, 76.60, 76.51, 76.26, 55.57, 37.80, 37.41. HRMS Calcd for $C_{16}H_{20}O_2$: 244.1463. Found: 244.1470.



authentic racemic　　asymmetric reaction with chloride catalyst

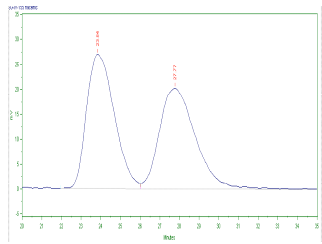
conditions: 99.7:0.3 Hex:iPA, Chiralpak AD,
0.1 mL/min, 254 nm
Retention Times: 20.6 min, 36.1 min

(2*S*,4*R*,6*R*)-4-[(*tert*-Butyldimethylsilyl)oxy]tetrahydro-2-styryl-6-vinyl-2*H*-pyran (4d).

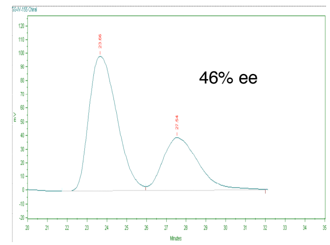


General procedure A was followed with substrate **2d** to afford a colourless oil after silica gel chromatography (50:1 Hex:Et_2O, R_f = 0.15). IR (neat): 2951 (s), 2928 (s), 2856 (s), 1471 (m), 1380 (m), 1255 (m), 1075 (s), 914 (m), 837 (m), 776 (m), 746 (m), 693 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44–7.16 (m, 5H), 6.61 (d, *J* = 15.9 Hz, 1H), 6.24 (dd, *J* = 15.9, 6.1 Hz, 1H), 5.92 (ddd, *J* = 17.2, 10.4, 6.0 Hz, 1H), 5.31 (ddd, *J* = 17.2, 1.5, 1.5 Hz, 1H), 5.15 (d, *J* =

10.4 Hz), 4.12–4.01 (m, 1H), 3.99–3.83 (m, 2H), 2.00–1.88 (m, 2H), 1.45 (ddd, J = 11.9, 11.9, 11.9 Hz, 1H), 1.39 (ddd, J = 11.9, 11.9, 11.9 Hz, 1H), 0.90 (s, 9H), 0.09 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.51, 136.96, 130.62, 129.85, 128.63, 127.71, 126.64, 115.57, 76.58, 76.30, 68.77, 41.73, 41.32, 25.97, 18.26, –4.35. HRMS Calcd for $C_{21}H_{32}O_2Si$: 344.2172. Found: 344.2167.

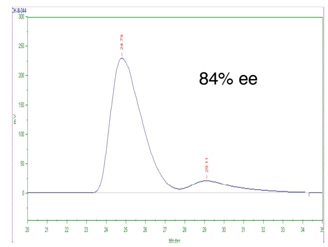


authentic racemic



asymmetric reaction with chloride catalyst

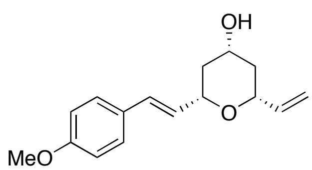
conditions: 98:2 Hex:iPA, Chiralpak AS, 1.0 mL/min, 254 nm
Retention Times: 23.8 min, 27.8 min



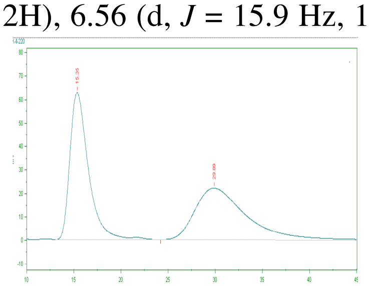
asymmetric reaction with iodide catalyst

Enantiopuritiy of **4d** was determined by analysis of HPLC of the corresponding alcohol after desilylation. Absolute configuration is determined by conversion to **4a**.

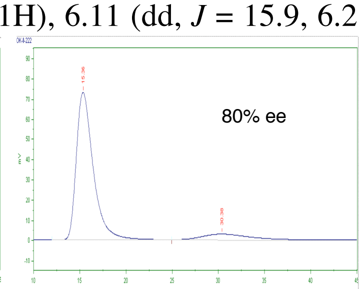
Tetrahydro-2-[(*E*)-2-(4-methoxyphenyl)vinyl]-6-vinyl-2*H*-pyran-4-ol (5).



General procedure A was followed with substrate **1a** to afford a colorless oil after silica gel chromatography (3:1 Hex:Et_2O, R_f = 0.15). IR (neat): 3388 (br), 2939 (m), 2920 (m), 1607 (s), 1512 (s), 1301 (m), 1248 (s), 1175 (m), 1063 (m), 1035 (m), 969 (m), 845 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (d, J = 8.8 Hz, 2H), 6.84 (d, J = 8.8 Hz, 2H), 6.56 (d, J = 15.9 Hz, 1H), 6.11 (dd, J = 15.9, 6.2 Hz, 1H), 5.92 (ddd, J = 17.4, 10.6, 6.0 Hz, 1H), 5.31 (ddd, J = 17.4, 1.1, 1.1 Hz, 1H), 5.16 (ddd, J = 10.6, 1.1, 1.1 Hz, 1H), 4.05 (dddd, J = 11.4, 6.2, 1.1, 1.1 Hz, 1H), 3.99–3.87 (m, 2H), 3.80 (s, 3H), 2.15–2.00 (m, 2H), 1.71 (br s, 1H), 1.41 (dd, J = 11.4, 11.4 Hz, 1H), 1.32 (dd, J = 11.4, 11.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) : δ 159.40, 138.27, 130.42, 129.60, 127.83, 115.68, 114.07, 76.34, 76.32, 68.18,

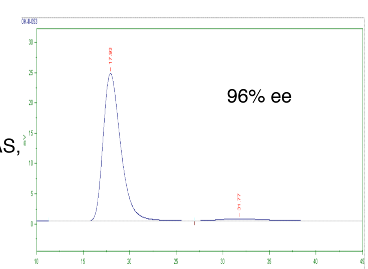


authentic racemic



asymmetric reaction with chloride catalyst

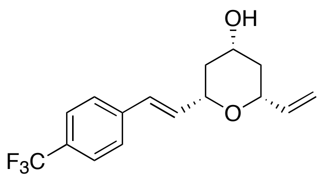
conditions: 85:15 Hex:iPA, Chiralpak AS, 1.0 mL/min, 254 nm
Retention Times: 15.4 min, 29.9 min



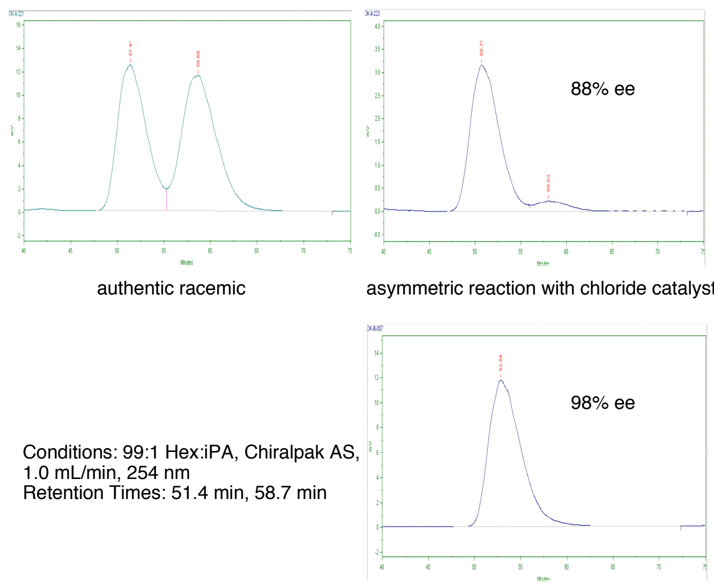
asymmetric reaction with iodide catalyst

55.40, 41.30, 40.79. HRMS Calcd for $C_{16}H_{20}O_3Na$: 283.1310. Found: 283.1304.

2-[(*E*)-4-(Trifluoromethyl)styryl]tetrahydro-6-vinyl-2*H*-pyran-4-ol (6).



General procedure A was followed with substrate **1a** to afford a colorless oil after silica gel chromatography (3:1 Hex:Et_2O, R_f = 0.18). IR (neat): 3387 (br), 2943 (m), 2921 (m), 1615 (m), 1415 (m), 1325 (s), 1165 (s), 1124 (s), 1067 (s), 970 (m), 858 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, *J* = 8.2 Hz, 2H), 7.47 (d, *J* = 8.2 Hz, 2H), 6.67 (d, *J* = 16.0 Hz, 1H), 6.33 (dd, *J* = 16.0, 5.6 Hz, 1H), 5.94 (ddd, *J* = 17.3, 10.6, 5.6 Hz, 1H), 5.33 (ddd, *J* = 17.3, 1.5, 1.5 Hz, 1H), 5.18 (ddd, *J* = 10.6, 1.5, 1.5 Hz, 1H), 4.15–4.07 (m, 1H), 4.01–3.90 (m, 2H), 2.13 (dddd, *J* = 12.4, 4.6, 2.2, 2.2 Hz, 1H), 2.08 (dddd, *J* = 12.4, 4.6, 2.2, 2.2 Hz, 1H), 1.58 (br s, 1H), 1.40 (ddd, *J* = 11.5, 11.5, 11.5 Hz, 1H), 1.36 (ddd, *J* = 11.5, 11.5, 11.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.38, 138.05, 132.18, 129.23 (q, *J* = 32.4 Hz), 129.17, 126.77, 125.63 (q, *J* = 3.8 Hz), 115.85, 76.45, 75.69, 41.05, 40.79. ^{19}F NMR (376 MHz, $CDCl_3$): δ –63.01. HRMS Calcd for $C_{16}H_{17}F_3O_2$: 298.1181. Found: 298.1174.



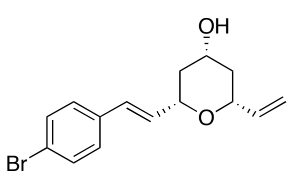
authentic racemic

asymmetric reaction with chloride catalyst

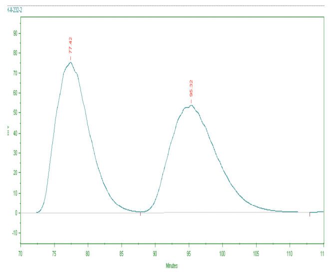
Conditions: 99:1 Hex:iPA, Chiralpak AS, 1.0 mL/min, 254 nm
Retention Times: 51.4 min, 58.7 min

asymmetric reaction with iodide catalyst

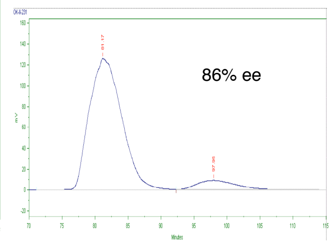
2-[(*E*)-2-(4-Bromophenyl)vinyl]tetrahydro-6-vinyl-2*H*-pyran-4-ol (7).



General procedure A was followed with **2a** to afford a colorless solid (mp 85.0–86.0 °C, pentane/Et_2O) after silica gel chromatography (3:1 Hex:Et_2O, R_f = 0.18). IR (neat): 3365 (br), 2935 (m), 2851 (m), 1487 (s), 1403 (m), 1307 (m), 1064 (s), 1008 (m), 963 (m), 808 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45–7.39 (m, 2H), 7.31–7.25 (m, 2H), 6.57 (dd, *J* = 15.9, 0.9 Hz, 1H), 6.23 (dd, *J* = 15.9, 5.9 Hz, 1H), 5.92 (ddd, *J* = 17.4, 10.6, 5.7 Hz, 1H), 5.31 (ddd, *J* = 17.4, 1.5, 1.5 Hz, 1H), 5.17 (ddd, *J* = 10.6, 1.3, 1.3 Hz, 1H), 4.06 (dddd, *J* = 11.2, 5.9, 1.7, 1.7 Hz, 1H), 4.00–3.87 (m, 2H), 2.15–2.01 (m, 2H), 1.67 (br s, 1H), 1.38 (ddd, *J* = 11.4, 11.4, 11.4 Hz, 1H), 1.34 (ddd, *J* = 11.4, 11.4, 11.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.11, 135.82, 131.77, 130.30, 129.51, 128.16, 121.55, 115.78, 76.41, 75.87, 68.12, 41.10, 40.79. HRMS Calcd for $C_{15}H_{17}BrO_2$: 308.0412. Found: 308.0417.

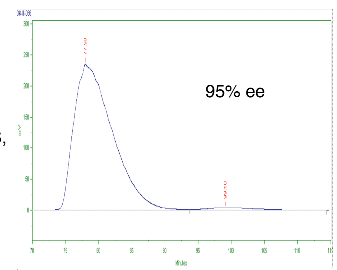


authentic racemic



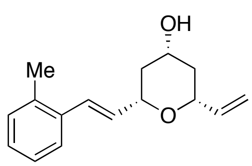
asymmetric reaction with chloride catalyst

conditions: 98:2 Hex:iPA, Chiralpak AS, 1.0 mL/min, 254 nm
Retention Times: 77.4 min, 95.3 min

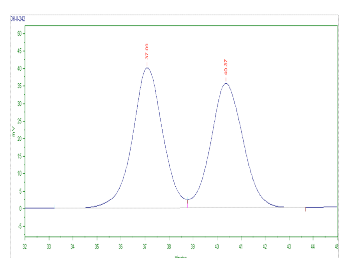


asymmetric reaction with iodide catalyst

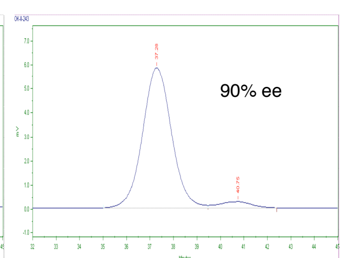
Tetrahydro-2-[(*E*)-2-(2-methylphenyl)vinyl]-6-vinyl-2*H*-pyran-4-ol (8).



General procedure A was followed with substrate **2a** to afford a colorless oil after silica gel chromatography (3:1 Hex:Et_2O, R_f = 0.18). IR (neat): 3388 (br), 2942 (m), 2920 (m), 2852 (m), 1514 (m), 1359 (m), 1309 (m), 1063 (m), 968 (m), 925 (m), 796 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48–7.42 (m, 1H), 7.18–7.10 (m, 3H), 6.84 (dd, *J* = 15.8, 1.1 Hz, 1H), 6.14 (dd, *J* = 15.8, 6.0 Hz, 1H), 5.94 (ddd, *J* = 17.2, 10.6, 5.5 Hz, 1H), 5.33 (ddd, *J* = 17.2, 1.5, 1.5 Hz, 1H), 5.17 (ddd, *J* = 10.6, 1.5, 1.5 Hz, 1H), 4.10 (dddd, *J* = 11.4, 6.0, 1.7, 1.7 Hz, 1H), 4.01–3.89 (m, 2H), 2.35 (s, 3H), 2.12 (dddd, *J* = 12.5, 4.8, 2.2, 2.2 Hz, 1H), 2.07 (dddd, *J* = 12.5, 4.8, 2.2, 2.2 Hz, 1H), 1.59 (br s, 1H), 1.42 (ddd, *J* = 11.4, 11.4, 11.4 Hz, 1H), 1.35 (ddd, *J* = 11.4, 11.4, 11.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.40, 136.03, 135.80, 130.99, 130.48, 128.64, 127.77, 126.31, 125.93, 115.67, 77.47, 76.43,

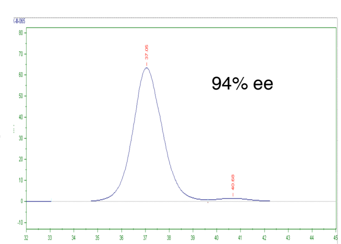


authentic racemic



asymmetric reaction with chloride catalyst

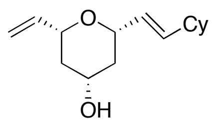
conditions: 99:1 Hex:iPA, Chiralpak AS, 1.0 mL/min, 254 nm
Retention Times: 37.1 min, 40.4 min



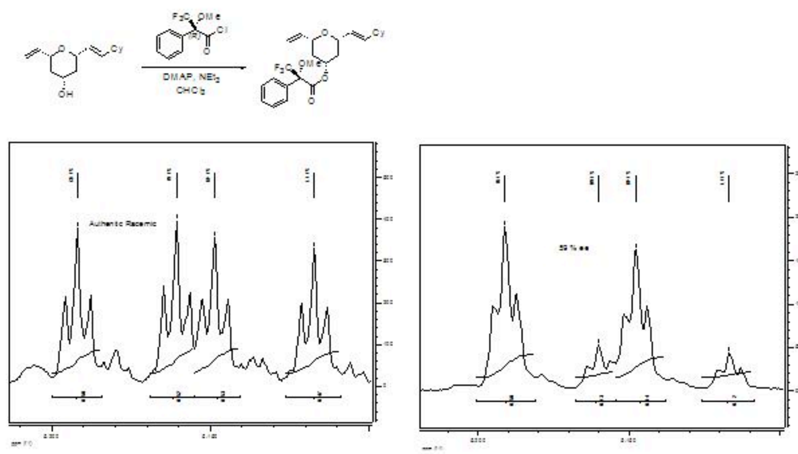
asymmetric reaction with iodide catalyst

68.35, 41.50, 40.97, 20.02. HRMS Calcd for $C_{16}H_{20}O_2$: 244.1463. Found: 244.1467.

2-[(*E*)-2-Cyclohexylvinyl]tetrahydro-6-vinyl-2*H*-pyran-4-ol (9).

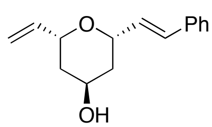


General procedure C was followed. IR (neat): 3358 (br), 2917 (s), 2848 (m), 1451 (m), 1067 (m), 960 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.90 (ddd, *J* = 16.7, 10.6, 5.5 Hz, 1H), 5.65 (dd, *J* = 15.7, 6.4 Hz, 1H), 5.46 (dd, *J* = 15.7, 6.2 Hz, 1H), 5.27 (d, *J* = 16.7 Hz, 1H), 5.13 (d, *J* = 10.6 Hz, 1H), 3.90–3.83 (m, 3H), 2.03–1.95 (m, 3H), 1.72–1.62 (m, 5H), 1.30–1.01 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.44, 138.27, 127.61, 115.53, 76.45, 76.28, 68.24, 41.45, 40.80, 40.41, 32.79, 26.31, 26.17. HRMS Calcd for $C_{15}H_{24}O_2Na$: 259.1674. Found: 259.1676. The ee for this compound was determined by analysis of the ^{1}H NMR of the derived Mosher ester (using (*S*)-Mosher's acid).

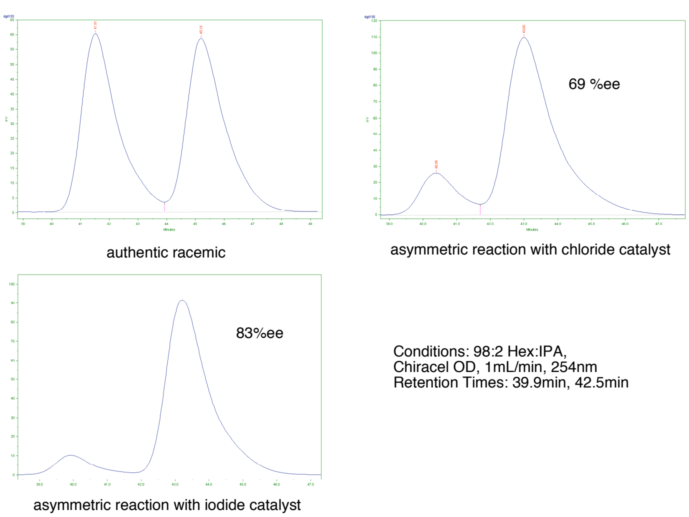


1H NMR in C_6D_6 analysis of Mosher Ester derived from endo-cyclohexyl ROCM

(2*S*,4*S*,6*R*)-Tetrahydro-2-(*E*)-styryl-6-vinyl-2*H*-pyran-4-ol (12).

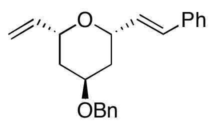


General procedure A was followed with substrate **11a** to afford **12** as a clear colourless oil after silica gel chromatography (1:2 Hex:Et_2O, R_f = 0.3). IR (neat): 3415 (br), 3024 (w), 2917 (m), 1430 (w), 1300 (m), 1055 (s), 960 (s), 746 (s), 696 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39–7.37 (m, 2H), 7.32–7.28 (m, 2H), 7.24–7.20 (m, 1H), 6.63 (d, *J* = 16.1, 1H), 6.22 (dd, *J* = 16.0, 6.1 Hz, 1H), 5.91 (ddd, *J* = 17.3, 10.6, 5.7 Hz, 1H), 5.32 (ddd, *J* = 17.3, 1.5, 1.5 Hz,

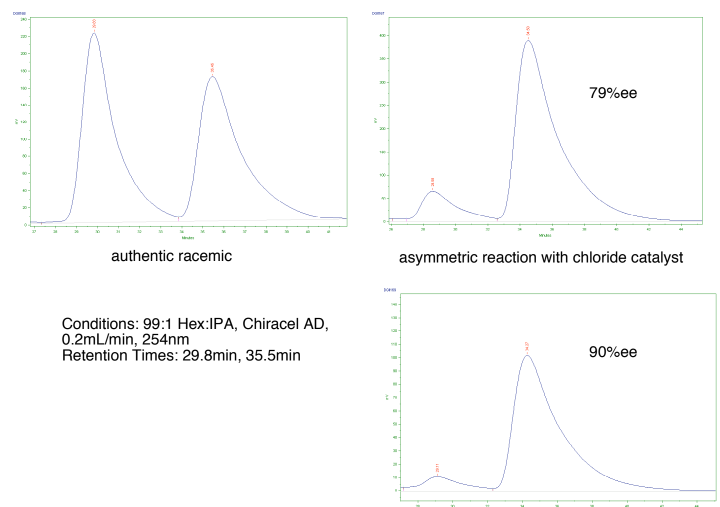


1H), 5.15 (ddd, *J* = 10.6, 1.3, 1.3 Hz, 1H), 4.59–4.54 (m, 1H), 4.46–4.42 (m, 1H), 4.36–4.35 (m, 1H), 1.83–1.61 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.99, 137.05, 130.49, 130.37, 128.61, 127.64, 126.60, 115.41, 72.44, 72.19, 64.57, 38.71, 38.27. HRMS Calcd for $C_{15}H_{18}O_2$: 230.1307. Found: 230.1307. Absolute configuration is determined by conversion to **4a**.

(2*S*,4*S*,6*R*)-4-Benzyloxytetrahydro-2-styryl-6-vinyl-2*H*-pyran (13).



General procedure A was followed with substrate **11a** to afford a colorless oil after silica gel chromatography (14:1 Hex:Et_2O, R_f = 0.4). IR (neat): 3081 (w), 3024 (w), 2917 (w), 2860 (w), 1501 (w), 1451 (w), 1338 (m), 1067 (s), 966 (m), 690 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41–7.36 (m, 6H), 7.33–7.28 (m, 3H), 7.24–7.20 (m, 1H), 6.62 (d, *J* = 16.0 Hz, 1H), 6.23 (dd, *J* = 16.0, 6.1 Hz, 1H), 5.92 (ddd, *J* = 17.3, 10.6, 5.7 Hz, 1H), 5.32 (ddd, *J* = 17.4, 1.5, 1.5 Hz, 1H), 5.15 (ddd, *J* = 10.6, 1.4, 1.4 Hz, 1H), 4.61 (s, 2H), 4.58–4.54 (m, 1H), 4.56–4.41 (m, 1H), 3.97–3.95 (m, 1H), 2.04–1.95 (m, 2H), 1.64–1.51 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.17, 138.95, 137.14, 130.59, 130.37, 128.60, 128.58, 127.71, 127.59, 127.53, 126.60, 115.28, 72.93, 72.70, 71.33, 70.40, 35.85, 35.41. HRMS Calcd for $C_{22}H_{24}O_2Na$: 343.1674. Found: 343.1674. Absolute configuration is determined by conversion to **4a**.

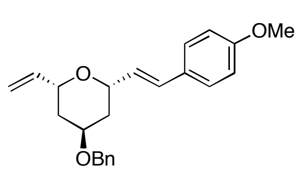


authentic racemic

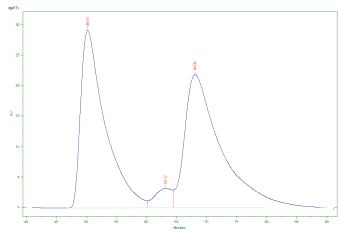
asymmetric reaction with chloride catalyst

asymmetric reaction with iodide catalyst

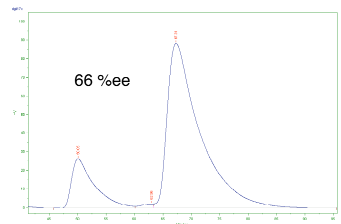
4-Benzyloxytetrahydro-2-[(*E*)-4-(methoxyphenyl)vinyl]-6-vinyl-2*H*-pyran (14).



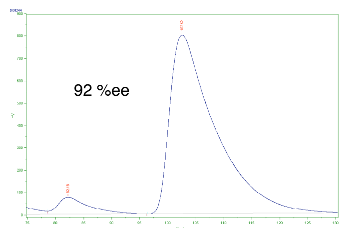
General procedure A was followed with substrate **11b** using the chloride catalyst and general procedure B was followed with **11b** using the iodide catalyst to afford a colorless oil after silica gel chromatography (19:1 Hex:Et_2O, R_f = 0.3). IR (neat): 3024 (w), 2924 (w), 2823 (w), 1608 (m), 1514 (s), 1243 (s), 1174 (m), 1061 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39–7.30 (m, 5H), 7.32 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.56 (d, *J* = 15.9 Hz, 1H), 6.10 (dd, *J* = 16.0, 6.3 Hz, 1H), 5.91 (ddd, *J* = 17.3, 10.6, 5.7 Hz, 1H), 5.31 (ddd, *J* = 17.3, 1.6, 1.6 Hz, 1H), 5.14 (ddd, *J* = 10.6, 1.5, 1.5 Hz, 1H), 4.60 (s, 2H), 4.55–4.51 (m ,1H), 4.45–4.40 (m, 1H), 3.96–3.94 (m, 1H), 3.80 (s, 3H), 2.03–1.94 (m, 2H), 1.63–1.50 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.26, 139.20, 138.95, 130.02, 129.88, 128.55, 128.34, 127.75, 127.67, 127.50, 115.25, 114.02, 72.91, 72.86, 71.34, 70.35, 55.37, 35.86, 35.40. HRMS Calcd for $C_{23}H_{26}O_3Na$: 373.1780. Found: 373.1776.



authentic racemic



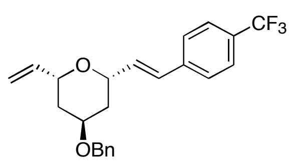
asymmetric reaction using chloride catalyst



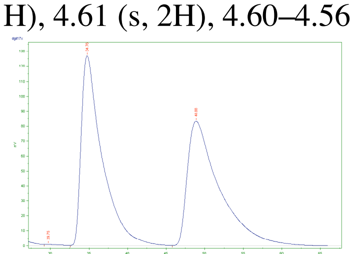
asymmetric reaction using iodide catalyst

Conditions: 99:1 Hex:IPA, Chiracel AD,
0.2 mL/min, 254 nm
Retention Times: 50.1min, 67.3min

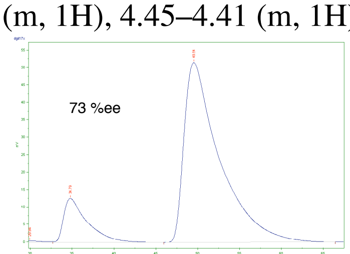
4-Benzyloxytetrahydro-2-[(*E*)-4-(trifluoromethylphenyl)vinyl]-6-vinyl-2*H*-pyran (15).



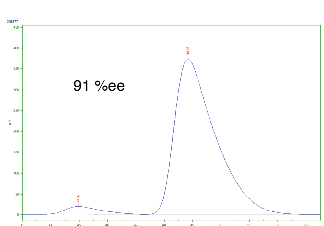
General procedure A was followed with substrate **11b** using the chloride catalyst and general procedure B was followed with substrate **11b** using the iodide catalyst to afford a colorless oil after siliga gel chromatography (19:1 Hex:Et_2O, R_f = 0.5). IR (neat): 3037 (w), 2924 (w), 2861 (w), 1621 (w), 1325 (s), 1168 (m), 1124 (s), 1067 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, *J* = 8.2 Hz, 2H), 7.46 (d, *J* = 8.3 Hz, 2H), 7.39–7.36 (m, 4H), 7.33–7.30 (m, 1H), 6.66 (d, *J* = 16.0 Hz, 1H), 6.32 (dd, *J* = 16.0, 5.7 Hz, 1H), 5.92 (ddd, *J* = 17.3, 10.6, 5.7 Hz, 1H), 5.32 (ddd, *J* = 17.3, 1.5, 1.5 Hz, 1H), 5.16 (ddd, *J* = 10.6, 1.3, 1.3 Hz, 1H), 4.61 (s, 2H), 4.60–4.56 (m, 1H), 4.45–4.41 (m, 1H), 3.98–3.96 (m, 1H), 2.04–1.96 (m, 2H), 1.62–1.50 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.87, 139.21, 139.07, 133.53, 129.73, 129.40, 128.97, 128.80, 127.96, 127.74, 126.90, 125.83 (q, *J* = 3.8 Hz), 115.60, 73.19, 72.53, 71.41, 70.65, 36.00, 35.55. HRMS Calcd for $C_{23}H_{23}O_2F_3Na$: 411.1548. Found: 411.1553.



authentic racemic



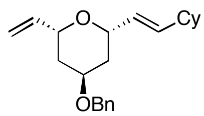
asymmetric reaction with chloride catalyst



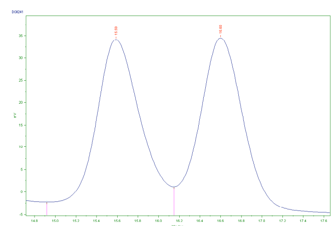
asymmetric reaction with iodide catalyst

Conditions: 99:1 Hex:IPA, Chiracel AD,
0.2 mL/min, 254 nm
Retention Times: 34.5min, 48.5min

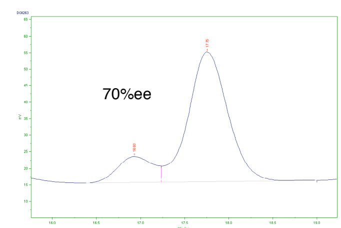
4-Benzyloxy-2-[(*E*)-2-Cyclohexylvinyl]tetrahydro-6-vinyl-2*H*-pyran (16).



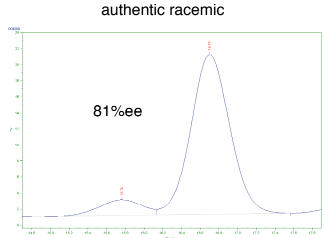
General procedure B was used with **11b** to afford **16** as a colorless oil after silica gel chromatography (19:1 Hex:Et_2O R_f = 0.5). IR (neat): 2917 (s), 2848 (m), 1451 (m), 1338 (w), 1061 (s), 966 (m), 702 (w). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38–7.35 (m, 4H), 7.31–7.27 (m, 1H), 5.88 (ddd, *J* = 17.3, 10.6, 5.8 Hz, 1H), 5.64 (dd, *J* = 15.7, 6.5 Hz, 1H), 5.43 (dd, *J* = 15.7, 6.4 Hz, 1H), 5.25 (d, *J* = 17.3, 1H), 5.10 (d, *J* = 10.6 Hz, 1H), 4.57 (s, 2H), 4.36–4.28 (m, 2H), 3.91–3.89 (m, 1H), 1.93–1.86 (m, 3H), 1.72–1.69 (m, 5H), 1.52–1.45 (m, 2H), 1.27–1.04 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.39, 139.04, 137.92, 128.54, 128.42, 127.64, 127.50, 115.14, 72.92, 72.86, 71.41, 70.28, 40.48, 35.91, 35.39, 32.85, 26.35, 26.21. HRMS Calcd for $C_{22}H_{30}O_2$: 326.2246. Found: 326.2250. The ee was determined by HPLC analysis of the debenzylated alcohol of **16**. Debenzylation was carried out under dissolving metal conditions using calcium.



authentic racemic



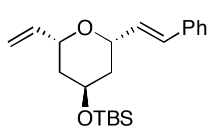
asymmetric reaction using chloride catalyst



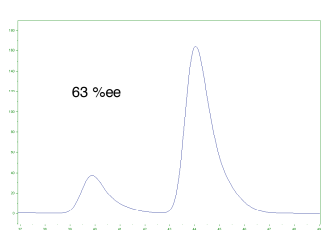
asymmetric reaction using iodide catalyst

Conditions: 98:2 Hex:IPA, Chiralpak AS, 0.5 mL/min, 210 nm
Retention Times: 15.8min, 16.7min

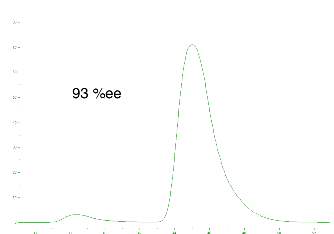
(2*S*,4*S*,6*R*)-4-[(*tert*-Butyldimethylsilyl)oxy]tetrahydro-2-styryl-6-vinyl-2*H*-pyran (17).



General procedure A was followed with **11d** using chloride catalyst and general procedure B was followed with **11d** using the iodide catalyst to afford a colourless oil after silica gel chromatography (24:1 Hex:Et_2O, R_f = 0.3). IR (neat): 3024 (w), 2949 (s), 2923 (s), 2855 (m), 1243 (m), 1092 (s), 1055 (s), 909 (m), 835 (s), 771 (m), 690 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39–7.37 (m, 2H), 7.31–7.28 (m, 2H), 7.23–7.20 (m, 1H), 6.61 (d, *J* = 16.0 Hz, 1H), 6.24 (dd, *J* = 16.0, 6.0 Hz, 1H), 5.91 (ddd, *J* = 16.7, 10.6, 5.6 Hz, 1H), 5.30 (dd, *J* = 16.7, 1.0 Hz, 1H), 5.13 (dd, *J*



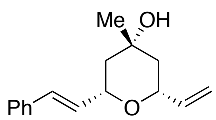
asymmtric reaction with chloride catalyst



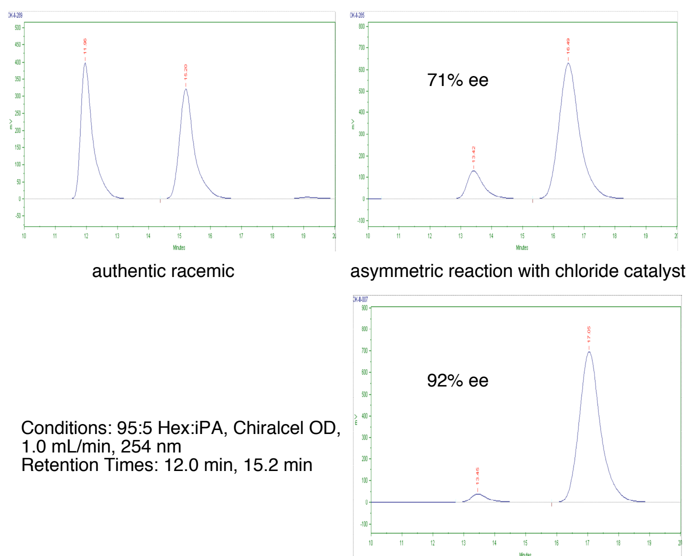
asymmetric reaction with iodide catalyst

= 10.6, 0.9 Hz, 1H), 4.59–4.54 (m, 1H), 4.46–4.42 (m, 1H), 4.28–4.27 (m, 1H), 1.73–1.55 (m, 4H), 0.94 (s, 9H), 0.09 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.44, 137.22, 130.90, 130.04, 128.60, 127.53, 126.59, 114.97, 72.57, 72.30, 64.96, 39.50, 39.08, 25.97, 18.23, 14.47. HRMS Calcd for $C_{21}H_{32}O_2Si$: 344.2172. Found: 344.2178. The enantiomeric excess was determined by deprotection in 10% $HCl_{(aq)}$/THF followed by HPLC using the conditions reported for alcohol **11a**. Absolute configuration is determined by conversion to **4a**.

Tetrahydro-4-methyl-2-(*E*)-styryl-6-vinyl-2*H*-pyran-4-ol (19).



General procedure A was followed with substrate **18** to afford a colourless oil after silica gel chromatography (3:1 Hex:Et_2O, R_f = 0.15). IR (neat): 3398 (br), 2971 (m), 2938 (m), 2918 (m), 1376 (m), 1103 (m), 1070 (m), 966 (m), 746 (m), 694 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41–7.20 (m, 5H), 6.63 (d, *J* = 15.9 Hz, 1H), 6.22 (d, *J* = 15.9, 6.0 Hz, 1H), 5.91 (ddd, *J* = 17.2, 10.6, 5.7 Hz, 1H), 5.32 (ddd, *J* = 17.2, 1.3, 1.3 Hz, 1H), 5.18 (ddd, *J* = 10.6, 1.3, 1.3 Hz, 1H), 4.17–4.06 (m, 1H), 4.03–3.94 (m, 1H), 1.82 (ddd, *J* = 12.1, 2.4, 2.4 Hz, 1H), 1.77 (ddd, *J* = 12.1, 2.4, 2.4 Hz, 1H), 1.58 (dd, *J* = 12.1, 12.1 Hz, 1H), 1.52 (dd, *J* = 12.1, 12.1 Hz, 1H), 1.51 (br s, 1H), 1.42 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.46, 136.88, 130.80, 129.75, 128.65, 127.78, 126.65, 115.71, 75.91, 75.67, 69.40, 46.24, 45.83, 26.01. HRMS Calcd for $C_{16}H_{20}O_2$: 244.1463. Found: 244.1460.

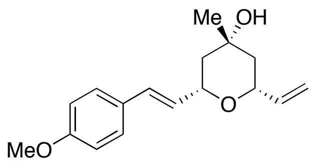


authentic racemic

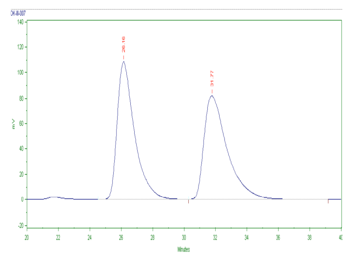
asymmetric reaction with chloride catalyst

asymmetric reaction with iodide catalyst

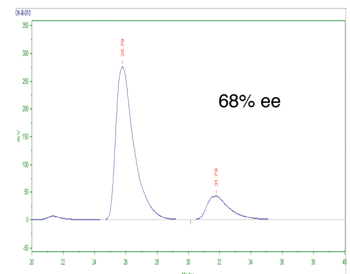
Tetrahydro-2-[(*E*)-2-(4-methoxyphenyl)vinyl]-4-methyl-6-vinyl-2*H*-pyran-4-ol (20).



General procedure A was followed with **18** to afford a colourless oil after silica gel chromatography (Hex:Et_2O = 3:1, R_f = 0.15). IR (neat): 3413 (br), 2936 (m), 2837 (m), 1607 (m), 1511 (m), 1250 (m), 1175 (m), 1106 (m), 1034 (m), 968 (m), 923 (m), 814 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (d, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 6.57 (d, *J* = 15.9 Hz, 1H), 6.08 (dd, *J* = 15.9, 6.2 Hz, 1H), 5.91 (ddd, *J* = 17.2, 10.6, 5.7 Hz, 1H), 5.31 (d, *J* = 17.2 Hz, 1H), 5.16 (d, *J* = 10.6 Hz, 1H), 4.08 (dd, *J* = 11.4, 6.2 Hz, 1H), 3.97 (dd, *J* = 11.4, 5.7 Hz, 1H), 3.80 (s, 3H), 1.84–1.72 (m, 2H), 1.63–1.43 (m, 2H), 1.51 (br s, 1H), 1.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.41, 138.52, 130.48, 129.63, 127.85, 127.55, 115.71, 114.08, 75.91, 75.88, 69.42, 55.41, 46.33, 45.82, 26.02. HRMS Calcd for $C_{17}H_{22}O_3$: 274.1569. Found: 274.1563.

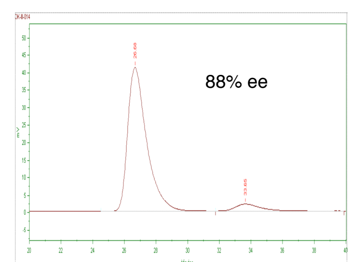


authentic racemic



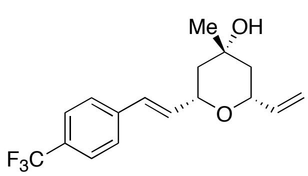
asymmetric reaction with chloride catalyst

conditions: 97:3 Hex:iPA, Chiralcel OD, 1.0 mL/min, 254 nm
Retention Times: 26.2 min, 31.8 min

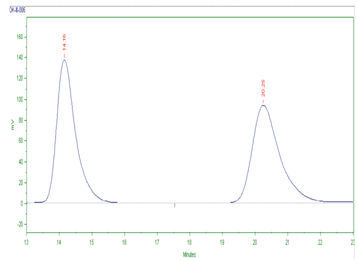


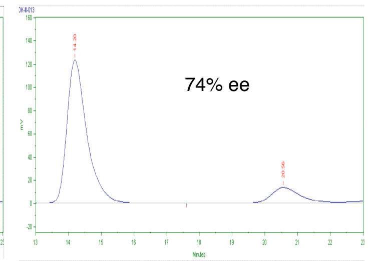
asymmetric reaction with iodide catalyst

2-[(*E*)-2-(4-trifluoromethylphenyl)vinyl]tetrahydro-4-methyl-6-vinyl-2*H*-pyran-4-ol (21).



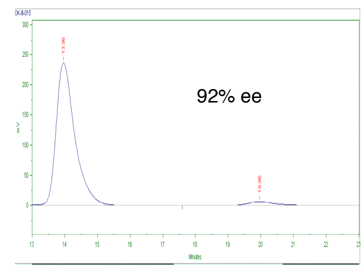
General procedure A was followed with substrate **18** to afford a colorless oil after silica gel chromatography (3:1 Hex:Et_2O, R_f = 0.18). IR (neat): 3398 (br), 2938 (m), 2933 (m), 1615 (m), 1378 (m), 1326 (s), 1123 (s), 1067 (s), 969 (m), 817 (m), 597 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, *J* = 8.3 Hz, 2H), 7.46 (d, *J* = 8.3 Hz, 2H), 6.67 (d, *J* = 16.1 Hz, 1H), 6.31 (dd, *J* = 16.1, 5.5 Hz, 1H), 5.91 (ddd, *J* = 17.2, 10.6, 5.7 Hz, 1H), 5.33 (ddd, *J* = 17.2, 1.5, 1.5 Hz, 1H), 5.18 (ddd, *J* = 10.6, 1.5, 1.5 Hz, 1H), 4.14 (dddd, *J* = 11.4, 5.5, 1.7, 1.7 Hz, 1H), 3.99 (ddddd, *J* = 11.7, 5.7, 2.0, 1.1, 1.1 Hz, 1H), 1.83 (ddd, *J* = 12.6, 2.4, 2.4 Hz, 1H), 1.78 (ddd, *J* = 12.6, 2.4, 2.4 Hz, 1H), 1.62–1.48 (m, 2H), 1.57 (br s, 1H), 1.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.43, 138.30, 132.43, 129.20, 126.77, 125.64 (q, *J* = 3.8 Hz), 115.85, 76.00, 75.25, 69.35, 46.05, 45.81, 25.99. ^{19}F NMR (376 MHz, $CDCl_3$): δ –63.01. HRMS Calcd for $C_{17}H_{19}F_3O_2$: 312.1337. Found: 312.1341.


authentic racemic



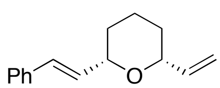
asymmetric reaction with chloride catalyst

conditions: 97:3 Hex:iPA, Chiralcel OD, 1.0 mL/min, 254 nm
Retention Times: 14.2 min, 20.3 min

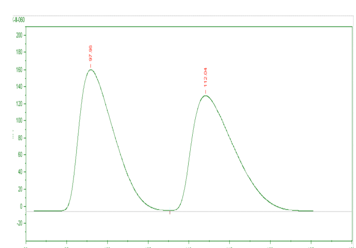


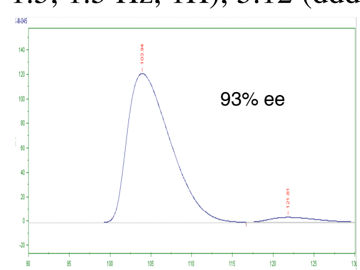
asymmetric reaction with iodide catalyst

Tetrahydro-2-(*E*)-styryl-6-vinyl-2*H*-pyran (23).



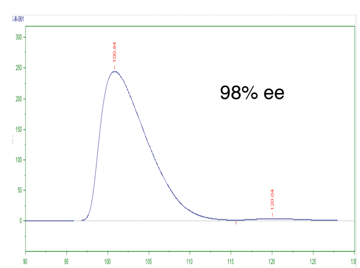
General procedure A was followed with substrate **22** to afford a colourless oil after silica gel chromatography (3:1 Hex:CH_2Cl_2, R_f = 0.10). IR (neat): 2935 (m), 2855 (w), 1495 (w), 1304 (w), 1198 (w), 1073 (m), 965 (m), 746 (m), 693 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40–7.35 (m, 2H), 7.31–7.18 (m, 3H), 6.61 (dd, J = 15.9. 1.1 Hz, 1H), 6.25 (dd, J = 15.9, 6.0 Hz, 1H), 5.93 (ddd, J = 17.4, 10.6, 5.5 Hz, 1H), 5.29 (ddd, J = 17.4, 1.5, 1.5 Hz, 1H), 5.12 (ddd, J = 10.6, 1.5, 1.5 Hz, 1H), 4.11–4.04 (m, 1H), 3.98–3.91 (m, 1H), 1.98–1.89 (m, 1H), 1.77–1.58 (m, 3H), 1.55–1.30 (m, 2H).^{13}C NMR (100 MHz, $CDCl_3$): δ 139.48, 137.22, 130.95, 130.03, 128.61, 127.55, 126.61, 114.96, 78.53, 78.24, 31.77, 31.32, 23.61. HRMS Calcd for $C_{15}H_{18}O$: 214.1358. Found: 214.1358.


authentic racemic



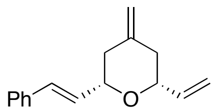
asymmetric reaction with chloride catalyst

conditions: 99.9:0.1 Hex:iPA, Chiralcel OJ, 0.2 mL/min, 254 nm
Retention Times: 98.0 min, 112.0 min

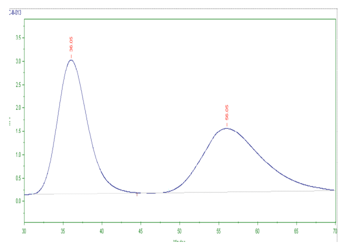


asymmetric reaction with iodide catalyst

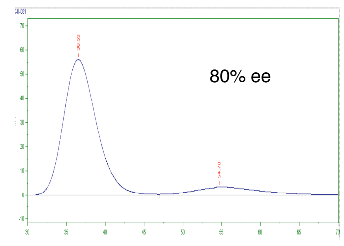
Tetrahydro-4-methylidene-2-(*E*)-styryl-6-vinyl-2*H*-pyran (25).



General procedure A was followed with **24** to afford a colorless oil after silica gel chromatography (3:1 Hex:CH_2Cl_2, R_f = 0.15). IR (neat): 3025 (m), 2941 (m), 1653 (m), 1449 (m), 1309 (m), 1061 (s), 893 (m), 747 (s), 693 (s). ^1H NMR (400 MHz, $CDCl_3$): δ 7.42–7.19 (m, 5H), 6.63 (d, *J* = 15.9 Hz, 1H), 6.27 (d, *J* = 15.9, 6.0 Hz, 1H), 5.95 (ddd, *J* = 17.4, 10.4, 6.0 Hz, 1H), 5.37–5.29 (m, 1H), 5.21–5.14 (m, 1H), 4.82 (d, *J* = 1.7 Hz, 1H), 4.82 (d, *J* = 1.7 Hz, 1H), 4.08–4.00 (m, 1H), 3.95–3.85 (m, 1H), 2.41–2.28 (m, 2H), 2.24–2.07 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.82, 138.67, 136.96, 130.78, 130.00, 128.65, 127.75, 126.67, 115.71, 109.48, 79.11, 78.90, 40.96, 40.51. HRMS Calcd for $C_{16}H_{18}O$: 226.1358. Found: 226.1352.

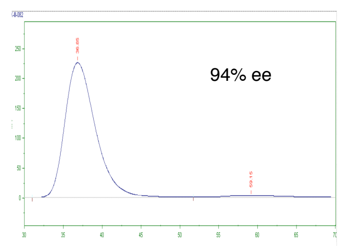


authentic racemic



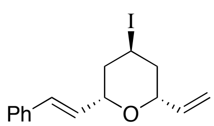
asymmetric reaction with chloride catalyst

conditions: 99.8:0.2 Hex:iPA, Chiralcel OB-H, 0.5 mL/min, 254 nm
Retention Times: 36.1 min, 56.1 min

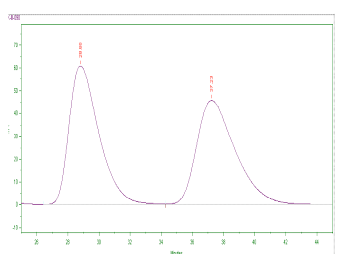


asymmetric reaction with iodide catalyst

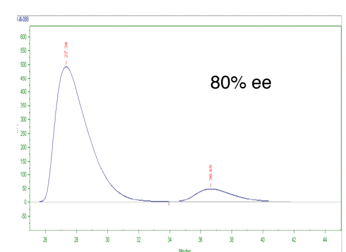
Tetrahydro-4-iodo-2-(*E*)-styryl-6-vinyl-2*H*-pyran (27).



General procedure A was followed with substrate **26** to afford a colorless solid (mp 69.0–70.0 °C, pentane) after silica gel chromatography (3:1 Hex:CH_2Cl_2, R_f = 0.10). IR (neat): 3024 (m), 2949 (m), 2888 (m), 1495 (m), 1412 (m), 1308 (m), 1236 (m), 1057 (s), 965 (m), 746 (s), 692 (s). ^1H NMR (400 MHz, $CDCl_3$): δ 7.42–7.20 (m, 5H), 6.66 (d, *J* = 16.1 Hz, 1H), 6.25 (dd, *J* = 16.1, 5.9 Hz, 1H), 5.94 (ddd, *J* = 17.4, 10.6, 5.5 Hz, 1H), 5.35 (ddd, *J* = 17.4, 1.5, 1.5 Hz, 1H), 5.19 (ddd, *J* = 10.6, 1.5, 1.5 Hz, 1H), 4.92 (dddd, *J* =

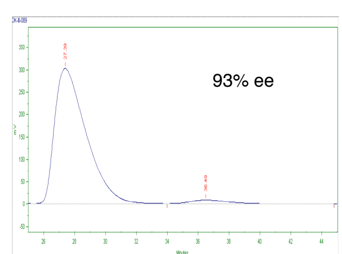


authentic racemic



asymmetric reaction with chloride catalyst

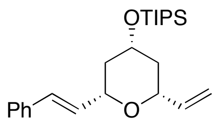
conditions: 99.8:0.2 Hex:iPA, Chiralcel OJ, 1.0 mL/min, 254 nm
Retention Times: 28.8 min, 37.2 min



asymmetric reaction with iodide catalyst

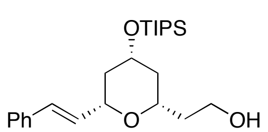
3.1, 3.1, 3.1, 3.1 Hz, 1H), 4.64–4.55 (m, 1H), 4.51–4.43 (m, 1H), 2.13 (dddd, *J* = 14.7, 2.2, 2.2, 2.2 Hz, 1H), 2.09 (dddd, *J* = 14.7, 2.2, 2.2, 2.2 Hz, 1H), 1.71 (ddd, *J* = 14.7, 10.6, 3.7 Hz, 1H), 1.65 (ddd, *J* = 14.7, 10.6, 3.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.84, 136.84, 131.10, 129.12, 128.67, 127.82, 126.65, 116.06, 74.31, 74.16, 40.68, 40.24, 29.59. HRMS Calcd for $C_{15}H_{17}IO$: 340.0324. Found: 340.0326.

(2*S*,4*R*,6*R*)-Tetrahydro-4-(triisopropylsilyloxy)-2-(*E*)-styryl-6-vinyl-2*H*-pyran.



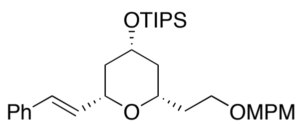
2,6-Lutidine (15 μL, 0.12 mmol, 2.5 equiv) was added to a solution of alcohol **4a** (12 mg, 51 μmol) in CH_2Cl_2 (0.5 mL) followed by triisopropylsilyl trifluoromethanesulfonate (21 μL, 78 μmol, 1.5 equiv) at –78 °C. After stirring for 2 h, the reaction mixture was treated with saturated aqueous $NaHCO_3$, warmed to 22 ºC, and the organic phase was separated. The aqueous layer was extracted with EtOAc, and the combined organic layers were washed with brine, dried ($MgSO_4$), filtered, and concentrated to dryness. Silica gel chromatography of the residue (50:1 Hex:Et_2O) afforded silyl ether (17 mg, 45 μmol, 88%) as a colourless oil. IR (neat): 2943 (m), 2866 (m), 1463 (m), 1381 (m), 1125 (m), 1068 (m), 964 (m), 883 (m), 691 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41–7.19 (m, 5H), 6.61 (d, *J* = 16.1 Hz, 1H), 6.25 (dd, *J* = 16.1, 6.0 Hz, 1H), 5.93 (ddd, *J* = 17.2, 10.4, 5.9 Hz, 1H), 5.31 (ddd, *J* = 17.2, 1.3, 1.3 Hz, 1H), 5.15 (ddd, *J* = 10.4, 1.3, 1.3 Hz, 1H), 4.10–3.88 (m, 3H), 2.03 (dddd, *J* = 12.6, 4.6, 2.0, 2.0 Hz, 1H), 1.99 (dddd, *J* = 12.6, 4.6, 2.0, 2.0 Hz, 1H), 1.47 (ddd, *J* = 11.7, 11.7, 11.7 Hz, 1H), 1.41 (ddd, *J* = 11.7, 11.7, 11.7 Hz, 1H), 1.18–1.10 (m, 21H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.57, 136.99, 130.60, 129.91, 128.63, 127.71, 126.65, 115.52, 76.56, 76.30, 68.74, 42.01, 41.59, 18.25, 12.51. HRMS Calcd for $C_{24}H_{38}O_2Si$: 386.2641. Found: 386.2639.

(2*R*,4*R*,6*S*)-Tetrahydro-2-(2-hydroxyethyl)-4-(triisopropylsilyloxy)-6-(*E*)-styryl-2*H*-pyran.



A solution of diene (37.5 mg, 97.0 μmol) in THF (1.0 mL) was added to a solution of 9-BBN (14.5 mg, 0.119 mmol, 1.2 equiv) in THF (1.0 mL) at 0 °C. After stirring at 22 °C for 3 h, the reaction mixture was cooled to 0 °C. EtOH/THF (1:1, 0.2 mL), pH 7.00 buffer (Fisher; 0.05 M potassium phosphate monobasic/sodium hydroxide, 0.2 mL), and then 30% H_2O_2 (0.2 mL) were added successively, and the mixture was stirred at 22 °C for 12 h. The reaction mixture was diluted with brine (1 mL) and extracted with EtOAc (5 mL x 3). The combined organic layers were dried, filtered, and concentrated. The residue was purified by silica gel chromatography (9:1 Hex:EtOAc, R_f = 0.18) to give the alcohol (33.3 mg, 82.3 □mol, 85%) as a colorless oil. IR (neat): 3414 (br), 2943 (m), 2866 (m), 1462 (m), 1384 (m), 1248 (m), 1085 (m), 883 (m), 690 (m). ^{1}H NMR (400 MHz, $CDCl_3$): □ 7.40–7.20 (m, 5H), 6.56 (d, *J* = 15.9 Hz, 1H), 6.20 (dd, *J* = 15.9, 6.0 Hz, 1H), 4.06–3.90 (m, 2H), 3.90–3.72 (m, 3H), 3.72–3.62 (m, 1H), 2.06–1.98 (m, 1H), 1.94–1.36 (m, 5H), 1.16–0.98 (m, 21H). ^{13}C NMR (100 MHz, $CDCl_3$): □ 136.66, 130.82, 129.42, 128.65, 127.86, 126.65, 76.78, 72.83, 68.39, 61.68, 41.95, 41.75, 37.64, 34.60, 18.21, 12.45.

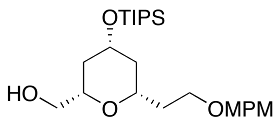
(2*S*,4*R*,6*R*)-Tetrahydro-4-(triisopropylsilyloxy)-2-[2-(4-methoxybenzyloxy)ethyl]-6-(*E*)-styryl-2*H*-pyran (27).



A solution of the alcohol (165 mg, 0.408 mmol) in THF (1.0 mL) was added to a suspension of KO*t*-Bu (95.0 mg, 0.846 mmol, 2.0 equiv) in THF (3.0 mL) at 0 °C. After stirred at 22 °C for 30 min, the reaction mixture was recooled to 0 °C, and MPMCl (85 □L, 0.63 mmol, 1.5 equiv) was added. The mixture was warmed to 22 °C and stirred for an additional 24 h. The mixture was diluted with saturated NH_4Cl solution (1 mL) and water (5 mL). The mixture was extracted with EtOAc (10 mL x 3) and the combined organic layers were washed with brine (10 mL), dried, filtered, and concentrated to dryness. The residue was purified by silica gel chromatography (15:1 Hex:Et_2O, R_f = 0.10) to afford MPM ether **27** (160 mg, 0.305 mmol, 75%) as a colorless oil. IR (neat): 2943 (m), 2865 (m), 1612 (m), 1513 (m), 1248 (m), 1091 (m), 821 (m), 685 (m). ^{1}H NMR (400 MHz, $CDCl_3$): □ 7.39 (d, *J* = 8.3 Hz, 2H), 7.33–7.19 (m, 5H), 6.89–6.83 (m, 2H), 6.57 (d, *J* = 15.9 Hz, 1H), 6.21 (dd, *J* = 15.9, 5.9 Hz, 1H), 4.47 and 4.43 (ABq, *J* = 11.7 Hz), 4.00–3.89 (m, 2H), 3.76 (s, 3H), 3.65 (ddd, *J* = 9.2, 8.2, 5.5 Hz, 1H), 3.62–3.53 (m, 1H), 3.56 (ddd, *J* = 9.2, 5.7, 5.7 Hz, 1H), 2.30–1.75 (m, 4H), 1.42 (ddd, *J* = 11.7, 11.7, 11.7 Hz), 1.30 (ddd, *J* = 11.7, 11.7, 11.7 Hz), 1.13–1.00 (m, 21H). ^{13}C NMR (100 MHz, $CDCl_3$): □ 138.46, 136.88, 130.80, 129.75, 128.65, 127.78, 126.65, 115.71, 75.91, 75.67, 69.40, 46.24, 45.83, 26.01. HRMS Calcd for $C_{32}H_{48}O_4Si$: 524.3322. Found: 524.3324.

•Proof of Stereochemistry: The absolute stereochemical identity of products obtained in this study have been determined by conversion of 4a to known compound 28.[2] The stereochemistry of other compounds has been determined by their conversion to 4a.

(2*S*,4*R*,6*R*)-Tetrahydro-2-hydroxymethyl-4-(triisopropylsilyloxy)-6-[2-(4-methoxybenzyloxy)ethyl]-2*H*-pyran (28).



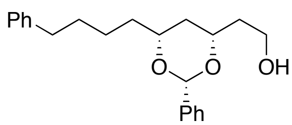
To a solution of olefin **27** (20.2 mg, 38.5 μmol) in THF (0.5 mL) were added water (0.5 mL), $NaIO_4$ (120 mg, 0.561 mmol, 15 equiv), and a solution of OsO_4 (2.5 wt% in *t*-BuOH, 20.0 mg 1.97 μmol) in *t*-BuOH (0.5 mL) at 0 °C. The reaction mixture was stirred at 22 °C for 12 h. The mixture was diluted with water (3 mL) and extracted with EtOAc (5 mL x 3). The combined organic layers were washed with brine (5 mL), dried, filtered, and concentrated to provide the crude aldehyde. A solution of $NaBH_4$ (3.5 mg, 93 μmol) in methanol (0.5 mL) was added to a solution of the aldehyde in methanol (0.5 mL) at 0 °C. After being stirred at 22 °C for 30 min, the methanol was evaporated and the residue was diluted with water (1 mL) and extracted with EtOAc (3 mL x 3). The combined extracts were washed with brine, dried over $MgSO_4$, filtered and concentrated to dryness. Silica gel chromatography of the residue (Hex:EtOAc 4:1, R_f = 0.10) afforded alcohol **28** (10.1 mg, 22.3 mmol, 58%) as a colorless oil. $[\alpha]^{25}_D$ –7.10° (*c* 1.36, $CHCl_3$) [lit.[2] $[\alpha]^{22}_D$ –7.7° (*c* 1.32, $CHCl_3$)]. IR (neat): 3458 (br), 2942 (s), 1514 (m), 1248 (m), 1093 (m), 883 (m), 820(m), 681 (m). ^1H NMR (400 MHz, $CDCl_3$): δ 7.25 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 1H), 4.45 and 4.41 (ABq, *J* = 11.7 Hz, 2H), 3.89 (dddd, *J* = 10.8, 10.8, 4.9, 4.9 Hz, 1H), 3.80 (s, 3H), 3.63–3.38 (m, 6H), 2.00–1.71 (m, 4H), 1.95 (br, 1H), 1.34–1.17 (m, 2H), 1.10–0.95 (m, 21H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.34, 130.71, 129.40, 113.96, 76.08, 72.87, 72.80, 68.61, 66.42, 66.28, 55.43, 42.20, 37.71, 36.37, 18.22, 12.47. HRMS Calcd for $C_{25}H_{44}O_5Si$: 452.2958. Found: 452.2958.

General procedure for reductive ring-opening of pyran. A 2-neck 25 mL round bottom flask equipped with a Dewar condenser was cooled to –78 ºC. UHP ammonia (3 mL) was condensed into the flask. Sodium (22.0 mg, 0.957 mmol) was added under a stream of nitrogen; the ammonia solution immediately turns deep blue, stirring was continued until all of the sodium dissolved. Substrate **33** (6.1 mg, 18 μmol) was added by cannula as a solution in Et_2O (0.3 mL) and *t*-BuOH (77.5 mg, 1.05 mmol). The reaction was quenched after one minute by adding solid NH_4Cl until the blue color disappears; 5 mL of CH_2Cl_2 was then added and the ammonia was allowed to evaporate. The reaction was diluted with 10 mL of H_2O and extracted with 10 mL portions of CH_2Cl_2 until no diol remained in the aqueous layer by TLC. The combined organic layers were dried over

(2) Paterson, I.; Tudge, M. *Tetrahedron* **2003**, *59*, 6833–6849.

$MgSO_4$, filtered, and the solvent removed *in vacuo* to deliver pure **34** (3.5 mg, 78%) as a clear colourless oil.

(2*R*,4*S*,6*R*)-2-Phenyl-6-(4-phenylbutyl)-1,3-dioxane-4-ethanol (29).

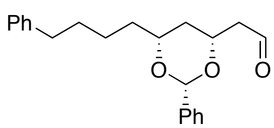


General procedure for reductive ring-opening of pyran was followed using **12** or **13** to yield a mixture of three products (*E*/*Z* isomers and over-reduction). It is imperative that a reaction time of one minute be employed to maximize the amount of desired product in the mixture: longer reaction times lead to a significant amount of reduction of the disubstituted olefin. This mixture was used without purification in the next step. A 25 mL flask was charged with the crude diol (214 mg, 0.921 mmol), benzaldehyde dimethylacetal (317 mg, 2.08 mmol), and a catalytic amount of *p*-toluenesulfonic acid (~ 10 mg). The flask was sparged with N_2 and benzene (8.0 mL) was added by syringe; the reaction was then allowed to stir for 1 h. The solvent was removed *in vacuo* and the reaction mixture was loaded directly onto a column of silica gel and eluted (24:1 Hex:Et_2O) to deliver a mixture of three inseparable products ostensibly assigned to be *E*/*Z* isomers and over-reduction at the disubstituted olefin site (7:2:1 *E*:*Z*:Saturated). The mixture was used without further purification in the next reaction (The mixture is inconsequential in the context of this formal synthesis as the three products coalesce to a single compound after the hydrogenation step).

9-BBN (275 mg, 1.13 mmol) was dissolved in THF (4.5 mL) and added by cannula to a 25 mL flask containing a solution of the mixture of benzylidene acetals (see above) (270 mg, 0.842 mmol) in THF (4.5 mL) at 22 °C, and the mixture was stirred for 1 h. The reaction was cooled to 0 ºC before adding pH 7 buffer (1.5 mL, 0.05 M) and 30% $H_2O_{2(aq)}$ (1.5 mL); the mixture was then allowed to warm to 22 ºC and stirred for an additional 12 h. The reaction mixture was diluted with H_2O (30 mL) and extracted with CH_2Cl_2 (4 x 30 mL). The combined organic extracts were washed with brine, dried over $MgSO_4$, filtered, and the solvent was removed *in vacuo*. The crude mixture was purified by silica gel chromatography using gradient elution (4:1 → 2:1 Hex:Et_2O) to deliver an inseparable mixture of three primary alcohols (192 mg, R_f = 0.2, 67%). The mixture of alcohols (87.0 mg, 0.257 mmol) was transferred to a 10 mL flask and dissolved in absolute EtOH. 10% Pt(C) (8 mg) was added and the flask was sparged with UHP H_2 and then equipped with a balloon of H_2. The mixture was stirred for 1 h at 22 ºC and then filtered through celite with Et_2O washings. The solvent was removed *in vacuo* to deliver pure **29** (86 mg, 0.25 mmol, 98%). IR (neat): 3415 (br), 3024 (w), 2924 (s), 2848 (m), 1451 (m), 1344 (m), 1130 (m), 1048 (m), 1023 (s), 752 (m), 702 (s). ^{1}H NMR (400 MHz,

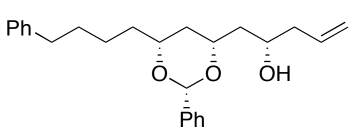
$CDCl_3$): □ 7.48–7.46 (m, 2H), 7.36–7.33 (m, 3H), 7.29–7.26 (m, 2H), 7.20–7.17 (m, 3H), 5.54 (s, 1H), 4.08 (dddd, *J* = 11.1, 8.4, 3.7, 3.7 Hz, 1H), 3.85–3.80 (m, 3H), 2.63 (t, *J* = 7.6 Hz, 2H), 2.14 (br, 1H), 1.91–1.82 (m, 2H), 1.74–1.43 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$): □ 142.71, 138.78, 128.81, 128.41, 128.38, 126.16, 125.80, 100.83, 76.96, 60.55, 38.21, 37.01, 35.97, 35.84, 31.54, 24.83. HRMS Calcd for $C_{22}H_{28}O_3Na$: 363.1936. Found: 363.1935.

(2*R*,4*R*,6*R*)-2-Phenyl-6-(4-phenylbutyl)-1,3-dioxane-4-acetaldehyde.



PCC (102 mg, 0.473 mmol), NaOAc (9.6 mg, 0.117 mmol), powdered flame-dried 4Å molecular sieves (120 mg) and celite (35 mg) were combined in a 25 mL flask and dissolved in CH_2Cl_2 (1.0 mL). Alcohol **29** is added quantitatively by cannula using 4.0 mL of CH_2Cl_2. The reaction was allowed to stir for 2 h at 22 ºC at which point Et_2O (5.0 mL) was added, to precipitate chromium salts, and the mixture was stirred for an additional 10 min. The resulting mixture was filtered through a column (1" W) containing one inch of celite (top layer) and one inch of silica gel (bottom layer). The aldehyde obtained was of sufficient purity (as judged by ^1H NMR analysis) for subsequent use. IR (neat): 3018 (w), 2924 (s), 2855 (m), 1728 (s), 1451 (m), 1344 (m), 1123 (m), 1029 (s), 759 (m), 696 (s). ^1H NMR (400 MHz, $CDCl_3$): □ 9.86 (t, *J* = 1.9 Hz, 1H), 7.48–7.46 (m, 2H), 7.36–7.34 (m, 3H), 7.28–7.26 (m, 2H), 7.18–7.16 (m, 3H), 5.60 (s, 1H), 4.41–4.38 (m, 1H), 3.87–3.84 (m, 1H), 2.84–2.78 (ddd, *J* = 16.9, 7.3, 2.0 Hz, 1H), 2.65–2.58 (m, 3H), 1.74–1.42 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): □ 200.64, 142.67, 138.49, 128.89, 128.54, 128.42, 128.35, 126.17, 125.82, 100.83, 76.77, 72.04, 49.59, 36.81, 35.96, 35.78, 31.53, 24.80.

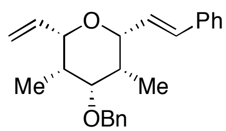
(□*S*,2*R*,4*S*,6*R*)-2-Phenyl-6-(4-phenylbutyl)-□-2-propenyl-1,3-dioxane-4-ethanol (30).



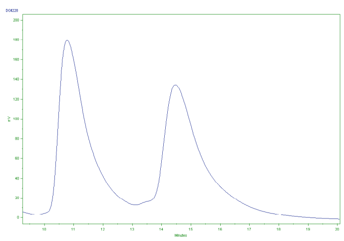
□-(–)-Methoxy isopinocampheylborane (8.0 mg, 25.3 □mol) was dissolved in 0.25 mL of Et_2O and cooled to 0 ºC. A solution of allyl magnesium bromide (21.3 □L, 0.95 M, 20.2 □mol) was added by syringe and the resulting solution was stirred for 1 h. The solution was then cooled to –78 ºC and the aldehyde (3.0 mg, 8.9 □mol) was added dropwise by syringe. The mixture was allowed to stir at –78 ºC for 2 h and then warmed to 0 ºC. One drop each of 30% $H_2O_{2(aq)}$ and 1N NaOH are added and the reaction was stirred at 22 ºC for 3 h. The reaction was diluted with H_2O (1 mL) and extracted with EtOAc (3 x 1 mL). The combined organic layers were dried over $MgSO_4$, filtered and the solvent removed *in vacuo*. The crude reaction mixture was further purified by silica gel chromatography (9:1 hex:Et_2O, R_f = 0.2) to deliver **31** as a clear colourless oil (2.8 mg, 82%) as a 3.5:1

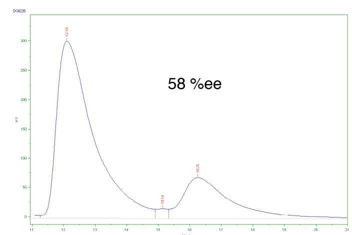
mixture of diastereomers. This compound was identical to that already reported[3] as judged by ^{1}H and ^{13}C NMR.

4-Benzyloxy-3,5-dimethyl-2-(*E*)-styryl-6-vinyltetrahydro-2*H*-pyran (33).

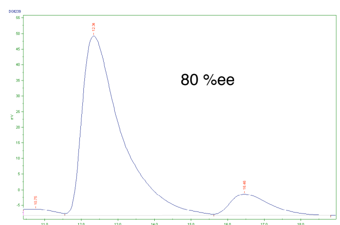


General procedure A was followed with substrate **32** using chloride catalyst **1a** and general procedure B was followed using iodide catalyst **1b** to afford a colorless oil after silica gel chromatography (19:1 → 4:1 Hex:Et_2O, R_f = 0.3). IR (neat): 3062 (w), 3024 (w), 2974 (w), 2886 (m), 2836 (w), 1495 (w), 1451 (m), 1357 (w), 1092 (s), 1080 (m), 960 (s), 752 (s), 683 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42–7.35 (m, 6H), 7.34–7.30 (m, 3H), 7.25–7.21 (m, 1H), 6.67 (d, *J* = 16.1 Hz, 1H), 6.23 (dd, *J* = 16.1, 5.4 Hz, 1H), 5.90 (ddd, *J* = 17.3, 10.7, 5.1 Hz, 1H), 5.38 (ddd, *J* = 17.3, 1.7, 1.7 Hz, 1H), 5.20 (ddd, *J* = 10.7, 1.6, 1.6 Hz, 1H), 4.59 (s, 2H), 4.17–4.15 (m, 1H), 4.05–4.03 (m, 1H), 3.75 (dd, *J* = 10.5, 10.5 Hz, 1H), 2.24–2.13 (m, 2H), 1.03 (d, *J* = 7.3 Hz, 3H), 1.01 (d, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.00, 137.29, 137.19, 130.11, 128.89, 128.63, 128.51, 127.56, 127.48, 127.39, 126.53, 115.22, 80.44, 80.07, 79.45, 69.26, 37.09, 36.57, 9.60, 9.37. HRMS Calcd for $C_{24}H_{28}O_2$: 348.2089. Found: No molecular ion detected.


authentic racemic



asymmetric reaction with chloride catalyst

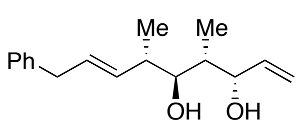


asymmetric reaction with iodide catalyst

Conditions: 95:5 Hex:IPA, Chiracel AD, 1.0 mL/min, 210 nm
Retention Times: 12.1min, 16.3min

The ee of **34** was determined by HPLC of diol **35**, which is generated from **34** as described below.

(2*S*,3*R*,4*S*,5*S*)-4,6-Dimethyl-9-phenylnona-1,7-dien-3,5-diol (34).

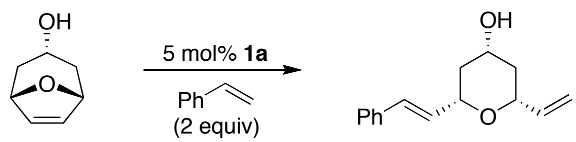


General procedure for reductive ring-opening of pyrans was followed with **33** to deliver pure **34** as a clear colourless oil. IR (neat): 3345 (br), 2968 (m), 2905 (s), 1451 (s), 1111 (w), 973 (s), 916 (m), 746 (m), 696 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36–7.26 (m, 2H), 7.24–7.15 (m, 3H), 5.91 (ddd, *J* = 17.1, 10.6, 5.3 Hz, 1H), 5.72 (ddd,

(3) Tosaki, S.; Nemoto, T.; Ohshima, T.; Shibasaki, M. *Org. Lett.* **2003**, *5*, 495–498.

J = 15.3, 6.8, 6.8 Hz, 1H), 5.51 (dd, *J* = 15.4, 8.5 Hz, 1H), 5.30 (ddd, *J* = 17.2, 1.1, 1.1 Hz, 1H), 5.19 (ddd, *J* = 10.6, 1.2, 1.2 Hz, 1H), 4.50 (br s, 1H), 3.45–3.42 (m, 1H), 3.39 (d, *J* = 6.8 Hz, 2H), 3.13 (d, *J* = 2.0 Hz, 1H), 2.47–2.38 (m, 2H), 1.91–1.84 (m, 1H), 1.06 (d, *J* = 6.9 Hz, 3H), 0.93 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): □ 140.62, 138.90, 132.45, 131.80, 128.64, 128.57, 126.23, 115.18, 78.77, 74.24, 40.39, 39.52, 39.31, 17.71, 11.98. HRMS Calcd for $C_{17}H_{21}O_2$[M-3H]: 257.1543. Found: [M-3H] 257.1542.

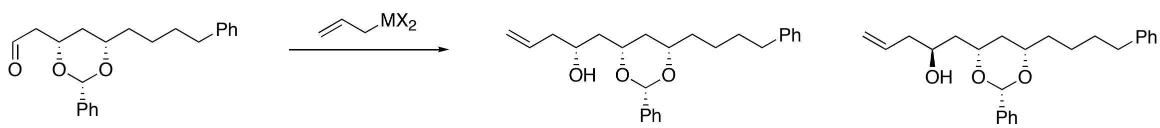
Table S1: Recycling studies using Chloride Catalyst 1a



2a THF, 22 °C **4a**

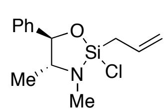
Cycle	time (h); conv (%)	yield (%)	*E*:*Z*	ee (%)	rec. cat. yield (%)
Cycle 1	1; >98	80	>98:2	94	90
Cycle 2	1; >98	75	>98:2	93	85
Cycle 3	1; >98	78	>98:2	94	88
Cycle 4	1.5; >98	78	>98:2	94	80
Cycle 5	1.5; >98	72	>98:2	94	67

Table S2: Optimization of Allylation Reaction of Aldehyde 30.5

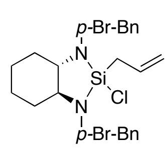


30.5 **30** **30b**

MX_2	Temp	Solvent	d.r (**30**:**30b**)
$MgBr_2$	0 °C -> rt	THF/Et_2O	1.1 : 1
$MgBr_2$	-78 °C	THF/Et_2O	1.3 : 1
(R,R)-**35**	-10 °C	PhMe	1 : 5
(S,S)-**35**	-10 °C	PhMe	1 : 1
(S,S)-**36**	-18 °C	CH_2Cl_2	1 : 9
(R,R)-**36**	-18 °C	CH_2Cl_2	1 : 1.2
(+)B(Ipc)$_2$	-78 °C	Et_2O	1 : 2.5
(-)B(Ipc)$_2$	-78 °C	Et_2O	3.5 : 1



35



36

Preparation of reagents **35**[4] and **36**[5] were completed as already reported with the exception that **36** was purified in a glovebox filled with N_2.

(4) Kinnaird, J. W.; Ng, P. Y.; Kubota, K.; Wang, X.; Leighton, J. L. *J. Am. Chem. Soc.* **2002**, *124*, 7920–7921.
(5) Kubota, K.; Leighton, J. L. *Angew. Chem. Int. Ed.* **2003**, *42*, 946–948.

General experimental for X-Ray analysis

Data was collected using a Bruker APEX CCD (charged coupled deviced) based diffractometer equipped with an LT-2 low temperature apparatus operating at 193 K. A suitable crystal was chosen and mounted on a glass fiber using grease. Data was measured using omega scans of 0.3° per frame for 30 seconds, such that a hemisphere was collected. A total of 1305 frames were collected with a maximum resolution of 0.90 Å. Cell parameters were retrieved using SMART[6] software and refined using SAINT on all observed reflections. Data reduction was performed using the SAINT software[7], which corrects for Lp and decay. Absorption corrections were applied using SADABS supplied by George Sheldrick. The structures ware solved by the direct method using the SHELXS-97[8] program and refined by least squares method on F^2, SHELXL-97[9], incorporated in SHELXTL-PC V 6.10[10].

All non-hydrogen atoms are refined anisotropically. Hydrogens were calculated by geometrical methods and refined as a riding model. The crystal used for the diffraction study showed no decomposition during data collection. All drawings are done at 30% ellipsoids.

X-Ray Data for Iodide Complex 1b

Table 1. Crystal data and structure refinement for DG01t

Identification code	dg01t	
Empirical formula	C48 H43 I N2 O2 Ru	
Formula weight	907.81	
Temperature	193(2) K	
Wavelength	0.71073 ≈	
Crystal system	Monoclinic	
Space group	P21	
Unit cell dimensions	a = 11.6174(7) ≈	a= 90∞.

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(6) SMART V5.626 (NT) Software for the CCD Detector Systems; Bruker Analytical X-ray Systems, Madison, WI (2001)
(7) SAINT V 5.01 (NT) Software for the CCD Detector Systems; Bruker Analytical X-ray Systems, Madison, WI (2001)
(8) Sheldrick, G. M. SHELXS-90, *Program for the Solution of Crystal Structure*, University of Göttingen, Germany, 1990
(9) Sheldrick, G. M. SHELXL-97, *Program for the Refinement of Crystal Structure*, University of Göttingen, Germany, 1997.
(10) SHELXTL 6.0 (PC-Version), Program Library for Structure Solution and Molecular Graphics; Bruker Analytical X-ray Systems, Madison, WI (1998)

	b = 9.8883(6) ≈	b= 92.5470(10)∞.
	c = 17.5221(11) ≈	g = 90∞.
Volume	2010.9(2) $≈^3$	
Z	2	
Density (calculated)	1.499 Mg/m^3	
Absorption coefficient	1.199 mm^{-1}	
F(000)	916	
Crystal size	0.5 x 0.5 x 0.5 mm^3	
Theta range for data collection	1.16 to 28.29∞.	
Index ranges	-11<=h<=15, -11<=k<=13, -20<=l<=23	
Reflections collected	15089	
Independent reflections	9365 [R(int) = 0.0142]	
Completeness to theta = 28.29∞	99.6 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9365 / 1 / 492	
Goodness-of-fit on F^2	1.014	
Final R indices [I>2sigma(I)]	R1 = 0.0219, wR2 = 0.0533	
R indices (all data)	R1 = 0.0227, wR2 = 0.0537	
Absolute structure parameter	-0.015(8)	
Largest diff. peak and hole	0.791 and -0.230 $e.≈^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($≈^2$x 10^3) for DG01t.

U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ru(1)	2793(1)	6397(1)	7634(1)	23(1)
I(2)	4673(1)	4898(1)	7879(1)	36(1)
O(4)	4003(1)	8151(2)	7877(1)	26(1)
C(5)	-142(2)	8112(2)	6787(1)	30(1)
C(6)	2394(2)	4870(3)	6100(1)	24(1)
C(7)	2421(2)	6433(3)	5042(1)	24(1)
C(8)	776(2)	6521(2)	5948(1)	24(1)
C(54)	2430(2)	6792(2)	8618(1)	29(1)
C(9)	-299(2)	6333(2)	5543(1)	24(1)

C(10)	1867(2)	5894(2)	5691(1)	24(1)
C(11)	-437(2)	5444(2)	4906(1)	28(1)
C(12)	4046(2)	4906(3)	5314(1)	32(1)
C(13)	5788(2)	9894(3)	8689(1)	29(1)
C(14)	3955(2)	8510(2)	8645(1)	25(1)
C(15)	-2461(2)	5945(3)	4783(2)	39(1)
C(16)	-272(2)	4929(3)	8708(1)	38(1)
C(17)	3587(2)	7533(3)	3813(1)	40(1)
C(18)	1917(2)	7456(2)	4573(1)	30(1)
C(19)	4092(2)	6546(3)	4244(1)	35(1)
C(20)	2914(2)	8149(3)	9788(1)	33(1)
C(21)	3490(2)	4356(2)	5911(1)	30(1)
C(22)	3076(2)	7838(2)	9018(1)	27(1)
C(23)	-1293(2)	7043(2)	5775(1)	29(1)
C(24)	-1173(2)	7964(3)	6397(1)	33(1)
C(25)	3535(2)	5944(2)	4863(1)	28(1)
N(2)	1109(2)	4033(2)	7836(1)	35(1)
C(27)	15(2)	4631(3)	10074(2)	45(1)
C(28)	756(2)	4236(3)	8607(1)	33(1)
C(29)	858(2)	7378(2)	6578(1)	25(1)
C(30)	4722(2)	9385(2)	9028(1)	28(1)
C(31)	2479(2)	7999(3)	3974(1)	37(1)
C(32)	6596(2)	8958(3)	8443(1)	36(1)
C(33)	-1492(2)	5259(2)	4541(1)	35(1)
C(34)	4291(2)	9173(2)	7300(1)	29(1)
C(35)	-2367(2)	6824(3)	5386(1)	36(1)
C(36)	1402(2)	3689(3)	9215(1)	38(1)
C(37)	3407(2)	10294(3)	7286(1)	40(1)
C(38)	5999(2)	11265(3)	8600(1)	41(1)
C(39)	6966(3)	11693(3)	8239(2)	52(1)
C(40)	7567(2)	9402(3)	8090(2)	46(1)
C(41)	1009(2)	3915(3)	9952(1)	44(1)
C(42)	3601(2)	9109(3)	10159(1)	37(1)
C(43)	4504(2)	9703(3)	9789(1)	34(1)
C(44)	7747(3)	10763(4)	7984(2)	53(1)
C(45)	-617(2)	5133(3)	9454(2)	43(1)

O(1)	1855(1)	7638(2)	6957(1)	27(1)
N(1)	1832(2)	4257(2)	6723(1)	26(1)
C(55)	1818(2)	4811(2)	7433(1)	26(1)
C(50)	4382(2)	8396(3)	6556(1)	36(1)
C(49)	-373(3)	4868(5)	10875(2)	66(1)
C(52)	991(3)	3183(3)	6592(1)	46(1)
C(51)	652(2)	2866(3)	7403(1)	41(1)
C(48)	2506(3)	2924(4)	9116(2)	52(1)
C(47)	-996(3)	5485(4)	8040(2)	57(1)

Table 3. Bond lengths [≈] and angles [∞] for DG01t.

Ru(1)-C(54)	1.835(2)
Ru(1)-C(55)	1.958(2)
Ru(1)-O(1)	1.9974(15)
Ru(1)-O(4)	2.2603(15)
Ru(1)-I(2)	2.6583(2)
O(4)-C(14)	1.395(2)
O(4)-C(34)	1.479(3)
C(5)-C(24)	1.360(3)
C(5)-C(29)	1.432(3)
C(5)-H(5)	0.9500
C(6)-C(10)	1.369(3)
C(6)-C(21)	1.424(3)
C(6)-N(1)	1.432(3)
C(7)-C(18)	1.414(3)
C(7)-C(25)	1.429(3)
C(7)-C(10)	1.434(3)
C(8)-C(29)	1.392(3)
C(8)-C(9)	1.421(3)
C(8)-C(10)	1.498(3)
C(54)-C(22)	1.441(3)
C(54)-H(54)	0.9500
C(9)-C(11)	1.423(3)
C(9)-C(23)	1.427(3)
C(11)-C(33)	1.370(3)

C(11)-H(11)	0.9500
C(12)-C(21)	1.366(3)
C(12)-C(25)	1.409(3)
C(12)-H(12)	0.9500
C(13)-C(38)	1.388(4)
C(13)-C(32)	1.400(3)
C(13)-C(30)	1.485(3)
C(14)-C(30)	1.392(3)
C(14)-C(22)	1.404(3)
C(15)-C(35)	1.369(4)
C(15)-C(33)	1.396(4)
C(15)-H(15)	0.9500
C(16)-C(28)	1.395(4)
C(16)-C(45)	1.399(3)
C(16)-C(47)	1.514(4)
C(17)-C(19)	1.352(4)
C(17)-C(31)	1.407(4)
C(17)-H(17)	0.9500
C(18)-C(31)	1.370(3)
C(18)-H(18)	0.9500
C(19)-C(25)	1.419(3)
C(19)-H(19)	0.9500
C(20)-C(42)	1.384(4)
C(20)-C(22)	1.406(3)
C(20)-H(20)	0.9500
C(21)-H(21)	0.9500
C(23)-C(35)	1.412(3)
C(23)-C(24)	1.422(3)
C(24)-H(24)	0.9500
N(2)-C(55)	1.349(3)
N(2)-C(28)	1.443(3)
N(2)-C(51)	1.468(3)
C(27)-C(41)	1.380(4)
C(27)-C(45)	1.377(4)
C(27)-C(49)	1.511(4)
C(28)-C(36)	1.385(4)

C(29)-O(1)	1.334(2)
C(30)-C(43)	1.404(3)
C(31)-H(31)	0.9500
C(32)-C(40)	1.381(4)
C(32)-H(32)	0.9500
C(33)-H(33)	0.9500
C(34)-C(37)	1.511(4)
C(34)-C(50)	1.521(3)
C(34)-H(34)	1.0000
C(35)-H(35)	0.9500
C(36)-C(41)	1.407(3)
C(36)-C(48)	1.505(4)
C(37)-H(37A)	0.9800
C(37)-H(37B)	0.9800
C(37)-H(37C)	0.9800
C(38)-C(39)	1.379(4)
C(38)-H(38)	0.9500
C(39)-C(44)	1.381(5)
C(39)-H(39)	0.9500
C(40)-C(44)	1.376(5)
C(40)-H(40)	0.9500
C(41)-H(41)	0.9500
C(42)-C(43)	1.388(3)
C(42)-H(42)	0.9500
C(43)-H(43)	0.9500
C(44)-H(44)	0.9500
C(45)-H(45)	0.9500
N(1)-C(55)	1.360(3)
N(1)-C(52)	1.454(3)
C(50)-H(50A)	0.9800
C(50)-H(50B)	0.9800
C(50)-H(50C)	0.9800
C(49)-H(49A)	0.9800
C(49)-H(49B)	0.9800
C(49)-H(49C)	0.9800
C(52)-C(51)	1.523(3)

C(52)-H(52A)	0.9900
C(52)-H(52B)	0.9900
C(51)-H(51A)	0.9900
C(51)-H(51B)	0.9900
C(48)-H(48A)	0.9800
C(48)-H(48B)	0.9800
C(48)-H(48C)	0.9800
C(47)-H(47A)	0.9800
C(47)-H(47B)	0.9800
C(47)-H(47C)	0.9800

C(54)-Ru(1)-C(55)	100.60(9)
C(54)-Ru(1)-O(1)	106.61(8)
C(55)-Ru(1)-O(1)	95.10(7)
C(54)-Ru(1)-O(4)	80.04(8)
C(55)-Ru(1)-O(4)	176.85(8)
O(1)-Ru(1)-O(4)	87.65(6)
C(54)-Ru(1)-I(2)	100.84(7)
C(55)-Ru(1)-I(2)	92.70(6)
O(1)-Ru(1)-I(2)	149.48(4)
O(4)-Ru(1)-I(2)	84.15(4)
C(14)-O(4)-C(34)	120.37(16)
C(14)-O(4)-Ru(1)	109.03(12)
C(34)-O(4)-Ru(1)	123.61(12)
C(24)-C(5)-C(29)	121.5(2)
C(24)-C(5)-H(5)	119.2
C(29)-C(5)-H(5)	119.2
C(10)-C(6)-C(21)	121.77(19)
C(10)-C(6)-N(1)	120.23(18)
C(21)-C(6)-N(1)	118.0(2)
C(18)-C(7)-C(25)	118.04(19)
C(18)-C(7)-C(10)	122.52(19)
C(25)-C(7)-C(10)	119.4(2)
C(29)-C(8)-C(9)	120.26(18)
C(29)-C(8)-C(10)	117.45(18)
C(9)-C(8)-C(10)	122.17(18)

C(22)-C(54)-Ru(1)	118.21(15)
C(22)-C(54)-H(54)	120.9
Ru(1)-C(54)-H(54)	120.9
C(11)-C(9)-C(8)	122.51(19)
C(11)-C(9)-C(23)	117.67(19)
C(8)-C(9)-C(23)	119.82(19)
C(6)-C(10)-C(7)	118.89(19)
C(6)-C(10)-C(8)	120.92(18)
C(7)-C(10)-C(8)	120.02(19)
C(33)-C(11)-C(9)	121.0(2)
C(33)-C(11)-H(11)	119.5
C(9)-C(11)-H(11)	119.5
C(21)-C(12)-C(25)	121.2(2)
C(21)-C(12)-H(12)	119.4
C(25)-C(12)-H(12)	119.4
C(38)-C(13)-C(32)	119.1(2)
C(38)-C(13)-C(30)	122.1(2)
C(32)-C(13)-C(30)	118.8(2)
O(4)-C(14)-C(30)	124.83(18)
O(4)-C(14)-C(22)	112.89(18)
C(30)-C(14)-C(22)	122.21(18)
C(35)-C(15)-C(33)	120.4(2)
C(35)-C(15)-H(15)	119.8
C(33)-C(15)-H(15)	119.8
C(28)-C(16)-C(45)	118.2(2)
C(28)-C(16)-C(47)	122.0(2)
C(45)-C(16)-C(47)	119.8(2)
C(19)-C(17)-C(31)	120.2(2)
C(19)-C(17)-H(17)	119.9
C(31)-C(17)-H(17)	119.9
C(31)-C(18)-C(7)	121.8(2)
C(31)-C(18)-H(18)	119.1
C(7)-C(18)-H(18)	119.1
C(17)-C(19)-C(25)	121.9(2)
C(17)-C(19)-H(19)	119.1
C(25)-C(19)-H(19)	119.1

C(42)-C(20)-C(22)	120.1(2)
C(42)-C(20)-H(20)	119.9
C(22)-C(20)-H(20)	119.9
C(12)-C(21)-C(6)	119.6(2)
C(12)-C(21)-H(21)	120.2
C(6)-C(21)-H(21)	120.2
C(14)-C(22)-C(20)	118.3(2)
C(14)-C(22)-C(54)	119.18(18)
C(20)-C(22)-C(54)	122.4(2)
C(35)-C(23)-C(24)	121.6(2)
C(35)-C(23)-C(9)	119.7(2)
C(24)-C(23)-C(9)	118.75(19)
C(5)-C(24)-C(23)	120.6(2)
C(5)-C(24)-H(24)	119.7
C(23)-C(24)-H(24)	119.7
C(12)-C(25)-C(19)	122.6(2)
C(12)-C(25)-C(7)	119.1(2)
C(19)-C(25)-C(7)	118.3(2)
C(55)-N(2)-C(28)	128.0(2)
C(55)-N(2)-C(51)	113.14(18)
C(28)-N(2)-C(51)	118.86(19)
C(41)-C(27)-C(45)	118.9(2)
C(41)-C(27)-C(49)	120.6(3)
C(45)-C(27)-C(49)	120.5(3)
C(36)-C(28)-C(16)	122.1(2)
C(36)-C(28)-N(2)	119.9(2)
C(16)-C(28)-N(2)	117.9(2)
O(1)-C(29)-C(8)	122.69(18)
O(1)-C(29)-C(5)	118.08(19)
C(8)-C(29)-C(5)	118.97(19)
C(14)-C(30)-C(43)	117.3(2)
C(14)-C(30)-C(13)	123.01(19)
C(43)-C(30)-C(13)	119.5(2)
C(18)-C(31)-C(17)	119.8(2)
C(18)-C(31)-H(31)	120.1
C(17)-C(31)-H(31)	120.1

C(40)-C(32)-C(13)	120.0(3)
C(40)-C(32)-H(32)	120.0
C(13)-C(32)-H(32)	120.0
C(11)-C(33)-C(15)	120.7(2)
C(11)-C(33)-H(33)	119.7
C(15)-C(33)-H(33)	119.7
O(4)-C(34)-C(37)	109.76(18)
O(4)-C(34)-C(50)	105.51(18)
C(37)-C(34)-C(50)	115.5(2)
O(4)-C(34)-H(34)	108.6
C(37)-C(34)-H(34)	108.6
C(50)-C(34)-H(34)	108.6
C(15)-C(35)-C(23)	120.6(2)
C(15)-C(35)-H(35)	119.7
C(23)-C(35)-H(35)	119.7
C(28)-C(36)-C(41)	117.2(2)
C(28)-C(36)-C(48)	122.9(2)
C(41)-C(36)-C(48)	119.9(2)
C(34)-C(37)-H(37A)	109.5
C(34)-C(37)-H(37B)	109.5
H(37A)-C(37)-H(37B)	109.5
C(34)-C(37)-H(37C)	109.5
H(37A)-C(37)-H(37C)	109.5
H(37B)-C(37)-H(37C)	109.5
C(39)-C(38)-C(13)	120.2(3)
C(39)-C(38)-H(38)	119.9
C(13)-C(38)-H(38)	119.9
C(38)-C(39)-C(44)	120.3(3)
C(38)-C(39)-H(39)	119.9
C(44)-C(39)-H(39)	119.9
C(44)-C(40)-C(32)	120.2(3)
C(44)-C(40)-H(40)	119.9
C(32)-C(40)-H(40)	119.9
C(27)-C(41)-C(36)	122.1(3)
C(27)-C(41)-H(41)	118.9
C(36)-C(41)-H(41)	118.9

C(20)-C(42)-C(43)	120.2(2)
C(20)-C(42)-H(42)	119.9
C(43)-C(42)-H(42)	119.9
C(42)-C(43)-C(30)	121.4(2)
C(42)-C(43)-H(43)	119.3
C(30)-C(43)-H(43)	119.3
C(40)-C(44)-C(39)	120.1(3)
C(40)-C(44)-H(44)	120.0
C(39)-C(44)-H(44)	120.0
C(27)-C(45)-C(16)	121.4(3)
C(27)-C(45)-H(45)	119.3
C(16)-C(45)-H(45)	119.3
C(29)-O(1)-Ru(1)	128.02(13)
C(55)-N(1)-C(6)	123.47(19)
C(55)-N(1)-C(52)	113.76(18)
C(6)-N(1)-C(52)	121.01(18)
N(2)-C(55)-N(1)	106.32(19)
N(2)-C(55)-Ru(1)	136.44(16)
N(1)-C(55)-Ru(1)	117.20(15)
C(34)-C(50)-H(50A)	109.5
C(34)-C(50)-H(50B)	109.5
H(50A)-C(50)-H(50B)	109.5
C(34)-C(50)-H(50C)	109.5
H(50A)-C(50)-H(50C)	109.5
H(50B)-C(50)-H(50C)	109.5
C(27)-C(49)-H(49A)	109.5
C(27)-C(49)-H(49B)	109.5
H(49A)-C(49)-H(49B)	109.5
C(27)-C(49)-H(49C)	109.5
H(49A)-C(49)-H(49C)	109.5
H(49B)-C(49)-H(49C)	109.5
N(1)-C(52)-C(51)	101.74(19)
N(1)-C(52)-H(52A)	111.4
C(51)-C(52)-H(52A)	111.4
N(1)-C(52)-H(52B)	111.4
C(51)-C(52)-H(52B)	111.4

H(52A)-C(52)-H(52B)	109.3
N(2)-C(51)-C(52)	102.58(19)
N(2)-C(51)-H(51A)	111.3
C(52)-C(51)-H(51A)	111.3
N(2)-C(51)-H(51B)	111.3
C(52)-C(51)-H(51B)	111.3
H(51A)-C(51)-H(51B)	109.2
C(36)-C(48)-H(48A)	109.5
C(36)-C(48)-H(48B)	109.5
H(48A)-C(48)-H(48B)	109.5
C(36)-C(48)-H(48C)	109.5
H(48A)-C(48)-H(48C)	109.5
H(48B)-C(48)-H(48C)	109.5
C(16)-C(47)-H(47A)	109.5
C(16)-C(47)-H(47B)	109.5
H(47A)-C(47)-H(47B)	109.5
C(16)-C(47)-H(47C)	109.5
H(47A)-C(47)-H(47C)	109.5
H(47B)-C(47)-H(47C)	109.5

Table 4. Anisotropic displacement parameters (≈^{2}x 10^3) for DG01t. The anisotropic displacement factor exponent takes the form: -2p^2[h^2 a*^{2}U^{11} + ... + 2 h k a* b* U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ru(1)	24(1)	25(1)	19(1)	0(1)	0(1)	-2(1)
I(2)	33(1)	39(1)	35(1)	2(1)	-4(1)	7(1)
O(4)	32(1)	29(1)	17(1)	0(1)	0(1)	-4(1)
C(5)	33(1)	33(1)	25(1)	-6(1)	4(1)	4(1)
C(6)	25(1)	26(1)	22(1)	-3(1)	1(1)	-3(1)
C(7)	22(1)	26(1)	23(1)	-6(1)	1(1)	-2(1)
C(8)	23(1)	27(1)	21(1)	1(1)	2(1)	1(1)
C(54)	28(1)	34(1)	24(1)	1(1)	3(1)	-5(1)
C(9)	23(1)	25(1)	23(1)	2(1)	-1(1)	1(1)

C(10)	23(1)	26(1)	22(1)	-6(1)	-1(1)	0(1)
C(11)	30(1)	28(1)	25(1)	0(1)	-2(1)	2(1)
C(12)	25(1)	39(1)	33(1)	-4(1)	3(1)	7(1)
C(13)	29(1)	37(1)	22(1)	-4(1)	-5(1)	-6(1)
C(14)	26(1)	30(1)	18(1)	-3(1)	-1(1)	1(1)
C(15)	28(1)	49(2)	39(1)	4(1)	-13(1)	-2(1)
C(16)	35(1)	41(1)	38(1)	6(1)	4(1)	-7(1)
C(17)	40(1)	50(2)	30(1)	3(1)	11(1)	-8(1)
C(18)	28(1)	33(1)	28(1)	1(1)	4(1)	2(1)
C(19)	31(1)	43(1)	32(1)	-3(1)	9(1)	-2(1)
C(20)	32(1)	46(2)	20(1)	-2(1)	4(1)	-2(1)
C(21)	30(1)	29(1)	31(1)	-3(1)	-2(1)	6(1)
C(22)	28(1)	32(1)	21(1)	-2(1)	-1(1)	0(1)
C(23)	24(1)	36(1)	27(1)	1(1)	1(1)	2(1)
C(24)	28(1)	40(1)	30(1)	-5(1)	3(1)	9(1)
C(25)	23(1)	34(1)	28(1)	-6(1)	1(1)	-1(1)
N(2)	42(1)	34(1)	29(1)	-1(1)	5(1)	-13(1)
C(27)	41(1)	61(2)	33(1)	-6(1)	6(1)	-13(1)
C(28)	36(1)	34(1)	29(1)	2(1)	5(1)	-10(1)
C(29)	25(1)	26(1)	24(1)	1(1)	1(1)	0(1)
C(30)	27(1)	30(1)	26(1)	-1(1)	-3(1)	-1(1)
C(31)	39(1)	41(1)	31(1)	7(1)	0(1)	1(1)
C(32)	33(1)	42(1)	31(1)	0(1)	-2(1)	0(1)
C(33)	38(1)	34(1)	32(1)	-1(1)	-7(1)	-6(1)
C(34)	34(1)	32(1)	22(1)	2(1)	0(1)	-9(1)
C(35)	22(1)	49(2)	37(1)	3(1)	-2(1)	5(1)
C(36)	39(1)	38(1)	36(1)	3(1)	7(1)	-4(1)
C(37)	58(2)	32(1)	29(1)	2(1)	-6(1)	1(1)
C(38)	43(1)	38(1)	41(1)	-7(1)	-2(1)	-8(1)
C(39)	56(2)	47(2)	53(2)	2(1)	2(1)	-19(1)
C(40)	32(1)	65(2)	40(1)	-3(1)	4(1)	1(1)
C(41)	41(1)	61(2)	29(1)	3(1)	1(1)	-8(1)
C(42)	40(1)	49(2)	23(1)	-6(1)	1(1)	2(1)
C(43)	32(1)	43(2)	26(1)	-9(1)	-5(1)	-1(1)
C(44)	38(1)	79(2)	44(2)	7(1)	7(1)	-17(1)
C(45)	36(1)	47(2)	46(1)	-3(1)	9(1)	-6(1)

O(1)	28(1)	27(1)	24(1)	0(1)	-4(1)	-3(1)
N(1)	29(1)	25(1)	24(1)	0(1)	-1(1)	-4(1)
C(55)	25(1)	28(1)	24(1)	2(1)	0(1)	2(1)
C(50)	44(1)	42(1)	23(1)	1(1)	6(1)	-7(1)
C(49)	53(2)	108(3)	36(1)	-18(2)	8(1)	-13(2)
C(52)	58(2)	44(2)	36(1)	-11(1)	8(1)	-25(1)
C(51)	50(2)	37(1)	38(1)	-4(1)	4(1)	-18(1)
C(48)	47(2)	62(2)	47(2)	10(1)	7(1)	7(1)
C(47)	52(2)	71(2)	48(2)	19(2)	6(1)	9(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (≈^{2}x 10 ^{3}) for DG01t.

	x	y	z	U(eq)
H(5)	-84	8716	7209	36
H(54)	1833	6319	8857	35
H(11)	214	4971	4732	33
H(12)	4789	4584	5201	39
H(15)	-3189	5800	4527	47
H(17)	3980	7913	3401	48
H(18)	1169	7776	4676	36
H(19)	4843	6248	4129	42
H(20)	2331	7700	10055	39
H(21)	3833	3634	6197	36
H(24)	-1818	8481	6541	39
H(31)	2122	8687	3668	45
H(32)	6477	8018	8519	43
H(33)	-1566	4657	4119	42
H(34)	5063	9567	7445	35
H(35)	-3031	7292	5543	44
H(37A)	2643	9918	7157	60
H(37B)	3601	10968	6901	60
H(37C)	3404	10725	7789	60
H(38)	5477	11911	8788	49

H(39)	7094	12632	8165	62
H(40)	8112	8765	7921	55
H(41)	1443	3563	10379	52
H(42)	3454	9363	10669	45
H(43)	4986	10337	10057	40
H(44)	8410	11063	7734	64
H(45)	-1302	5629	9534	51
H(50A)	4837	7573	6650	54
H(50B)	4760	8963	6183	54
H(50C)	3609	8151	6356	54
H(49A)	49	5637	11102	98
H(49B)	-218	4058	11185	98
H(49C)	-1201	5062	10857	98
H(52A)	1338	2387	6349	55
H(52B)	321	3498	6272	55
H(51A)	-195	2798	7433	49
H(51B)	1010	2012	7590	49
H(48A)	2494	2519	8605	78
H(48B)	2581	2210	9503	78
H(48C)	3160	3546	9176	78
H(47A)	-498	5961	7691	86
H(47B)	-1570	6114	8228	86
H(47C)	-1388	4738	7767	86

Table 6. Torsion angles [∞] for DG01t.

C(54)-Ru(1)-O(4)-C(14)	6.83(14)
C(55)-Ru(1)-O(4)-C(14)	-95.2(12)
O(1)-Ru(1)-O(4)-C(14)	114.15(13)
I(2)-Ru(1)-O(4)-C(14)	-95.29(12)
C(54)-Ru(1)-O(4)-C(34)	-143.79(17)
C(55)-Ru(1)-O(4)-C(34)	114.1(12)
O(1)-Ru(1)-O(4)-C(34)	-36.47(15)
I(2)-Ru(1)-O(4)-C(34)	114.10(15)
C(55)-Ru(1)-C(54)-C(22)	173.30(18)

O(1)-Ru(1)-C(54)-C(22)	-88.06(19)
O(4)-Ru(1)-C(54)-C(22)	-3.56(17)
I(2)-Ru(1)-C(54)-C(22)	78.45(18)
C(29)-C(8)-C(9)-C(11)	-178.5(2)
C(10)-C(8)-C(9)-C(11)	5.7(3)
C(29)-C(8)-C(9)-C(23)	1.1(3)
C(10)-C(8)-C(9)-C(23)	-174.8(2)
C(21)-C(6)-C(10)-C(7)	1.8(3)
N(1)-C(6)-C(10)-C(7)	-176.36(19)
C(21)-C(6)-C(10)-C(8)	-173.42(19)
N(1)-C(6)-C(10)-C(8)	8.4(3)
C(18)-C(7)-C(10)-C(6)	177.7(2)
C(25)-C(7)-C(10)-C(6)	-3.4(3)
C(18)-C(7)-C(10)-C(8)	-7.0(3)
C(25)-C(7)-C(10)-C(8)	171.9(2)
C(29)-C(8)-C(10)-C(6)	73.6(3)
C(9)-C(8)-C(10)-C(6)	-110.4(2)
C(29)-C(8)-C(10)-C(7)	-101.6(2)
C(9)-C(8)-C(10)-C(7)	74.3(3)
C(8)-C(9)-C(11)-C(33)	178.2(2)
C(23)-C(9)-C(11)-C(33)	-1.3(3)
C(34)-O(4)-C(14)-C(30)	-39.9(3)
Ru(1)-O(4)-C(14)-C(30)	168.36(19)
C(34)-O(4)-C(14)-C(22)	143.28(19)
Ru(1)-O(4)-C(14)-C(22)	-8.5(2)
C(25)-C(7)-C(18)-C(31)	-1.6(4)
C(10)-C(7)-C(18)-C(31)	177.3(2)
C(31)-C(17)-C(19)-C(25)	0.4(4)
C(25)-C(12)-C(21)-C(6)	-2.3(4)
C(10)-C(6)-C(21)-C(12)	1.0(3)
N(1)-C(6)-C(21)-C(12)	179.3(2)
O(4)-C(14)-C(22)-C(20)	-177.8(2)
C(30)-C(14)-C(22)-C(20)	5.3(3)
O(4)-C(14)-C(22)-C(54)	6.5(3)
C(30)-C(14)-C(22)-C(54)	-170.4(2)
C(42)-C(20)-C(22)-C(14)	0.8(4)

C(42)-C(20)-C(22)-C(54)	176.3(2)
Ru(1)-C(54)-C(22)-C(14)	-0.2(3)
Ru(1)-C(54)-C(22)-C(20)	-175.66(18)
C(11)-C(9)-C(23)-C(35)	1.4(3)
C(8)-C(9)-C(23)-C(35)	-178.2(2)
C(11)-C(9)-C(23)-C(24)	-178.4(2)
C(8)-C(9)-C(23)-C(24)	2.1(3)
C(29)-C(5)-C(24)-C(23)	1.5(4)
C(35)-C(23)-C(24)-C(5)	176.9(2)
C(9)-C(23)-C(24)-C(5)	-3.4(4)
C(21)-C(12)-C(25)-C(19)	179.4(2)
C(21)-C(12)-C(25)-C(7)	0.7(4)
C(17)-C(19)-C(25)-C(12)	179.4(2)
C(17)-C(19)-C(25)-C(7)	-1.9(4)
C(18)-C(7)-C(25)-C(12)	-178.8(2)
C(10)-C(7)-C(25)-C(12)	2.2(3)
C(18)-C(7)-C(25)-C(19)	2.4(3)
C(10)-C(7)-C(25)-C(19)	-176.5(2)
C(45)-C(16)-C(28)-C(36)	3.6(4)
C(47)-C(16)-C(28)-C(36)	-177.9(3)
C(45)-C(16)-C(28)-N(2)	-179.8(2)
C(47)-C(16)-C(28)-N(2)	-1.3(4)
C(55)-N(2)-C(28)-C(36)	-89.6(3)
C(51)-N(2)-C(28)-C(36)	91.5(3)
C(55)-N(2)-C(28)-C(16)	93.7(3)
C(51)-N(2)-C(28)-C(16)	-85.1(3)
C(9)-C(8)-C(29)-O(1)	-176.84(19)
C(10)-C(8)-C(29)-O(1)	-0.8(3)
C(9)-C(8)-C(29)-C(5)	-2.9(3)
C(10)-C(8)-C(29)-C(5)	173.1(2)
C(24)-C(5)-C(29)-O(1)	175.8(2)
C(24)-C(5)-C(29)-C(8)	1.6(3)
O(4)-C(14)-C(30)-C(43)	176.1(2)
C(22)-C(14)-C(30)-C(43)	-7.4(3)
O(4)-C(14)-C(30)-C(13)	-8.9(4)
C(22)-C(14)-C(30)-C(13)	167.6(2)

C(38)-C(13)-C(30)-C(14)	121.9(3)
C(32)-C(13)-C(30)-C(14)	-57.2(3)
C(38)-C(13)-C(30)-C(43)	-63.1(3)
C(32)-C(13)-C(30)-C(43)	117.7(2)
C(7)-C(18)-C(31)-C(17)	0.1(4)
C(19)-C(17)-C(31)-C(18)	0.5(4)
C(38)-C(13)-C(32)-C(40)	-2.5(3)
C(30)-C(13)-C(32)-C(40)	176.7(2)
C(9)-C(11)-C(33)-C(15)	0.3(4)
C(35)-C(15)-C(33)-C(11)	0.6(4)
C(14)-O(4)-C(34)-C(37)	-60.7(2)
Ru(1)-O(4)-C(34)-C(37)	86.80(19)
C(14)-O(4)-C(34)-C(50)	174.32(18)
Ru(1)-O(4)-C(34)-C(50)	-38.2(2)
C(33)-C(15)-C(35)-C(23)	-0.5(4)
C(24)-C(23)-C(35)-C(15)	179.2(2)
C(9)-C(23)-C(35)-C(15)	-0.5(4)
C(16)-C(28)-C(36)-C(41)	-3.1(4)
N(2)-C(28)-C(36)-C(41)	-179.6(2)
C(16)-C(28)-C(36)-C(48)	179.3(3)
N(2)-C(28)-C(36)-C(48)	2.7(4)
C(32)-C(13)-C(38)-C(39)	3.2(3)
C(30)-C(13)-C(38)-C(39)	-175.9(2)
C(13)-C(38)-C(39)-C(44)	-2.0(4)
C(13)-C(32)-C(40)-C(44)	0.4(4)
C(45)-C(27)-C(41)-C(36)	0.4(4)
C(49)-C(27)-C(41)-C(36)	-179.3(3)
C(28)-C(36)-C(41)-C(27)	1.0(4)
C(48)-C(36)-C(41)-C(27)	178.8(3)
C(22)-C(20)-C(42)-C(43)	-4.4(4)
C(20)-C(42)-C(43)-C(30)	2.2(4)
C(14)-C(30)-C(43)-C(42)	3.6(4)
C(13)-C(30)-C(43)-C(42)	-171.6(2)
C(32)-C(40)-C(44)-C(39)	0.9(5)
C(38)-C(39)-C(44)-C(40)	-0.2(5)
C(41)-C(27)-C(45)-C(16)	0.1(4)

C(49)-C(27)-C(45)-C(16)	179.8(3)
C(28)-C(16)-C(45)-C(27)	-2.1(4)
C(47)-C(16)-C(45)-C(27)	179.4(3)
C(8)-C(29)-O(1)-Ru(1)	-70.7(3)
C(5)-C(29)-O(1)-Ru(1)	115.3(2)
C(54)-Ru(1)-O(1)-C(29)	-97.75(17)
C(55)-Ru(1)-O(1)-C(29)	4.92(17)
O(4)-Ru(1)-O(1)-C(29)	-176.63(16)
I(2)-Ru(1)-O(1)-C(29)	109.06(16)
C(10)-C(6)-N(1)-C(55)	-80.4(3)
C(21)-C(6)-N(1)-C(55)	101.4(3)
C(10)-C(6)-N(1)-C(52)	83.5(3)
C(21)-C(6)-N(1)-C(52)	-94.7(3)
C(28)-N(2)-C(55)-N(1)	-176.4(2)
C(51)-N(2)-C(55)-N(1)	2.5(3)
C(28)-N(2)-C(55)-Ru(1)	6.0(4)
C(51)-N(2)-C(55)-Ru(1)	-175.1(2)
C(6)-N(1)-C(55)-N(2)	173.4(2)
C(52)-N(1)-C(55)-N(2)	8.4(3)
C(6)-N(1)-C(55)-Ru(1)	-8.4(3)
C(52)-N(1)-C(55)-Ru(1)	-173.41(18)
C(54)-Ru(1)-C(55)-N(2)	-4.9(3)
O(1)-Ru(1)-C(55)-N(2)	-112.9(2)
O(4)-Ru(1)-C(55)-N(2)	96.6(12)
I(2)-Ru(1)-C(55)-N(2)	96.6(2)
C(54)-Ru(1)-C(55)-N(1)	177.61(17)
O(1)-Ru(1)-C(55)-N(1)	69.63(17)
O(4)-Ru(1)-C(55)-N(1)	-80.9(13)
I(2)-Ru(1)-C(55)-N(1)	-80.84(16)
C(55)-N(1)-C(52)-C(51)	-14.9(3)
C(6)-N(1)-C(52)-C(51)	179.7(2)
C(55)-N(2)-C(51)-C(52)	-11.4(3)
C(28)-N(2)-C(51)-C(52)	167.6(2)
N(1)-C(52)-C(51)-N(2)	14.6(3)