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EFFICIENT CHIRAL Ru-BASED COMPLEXES FOR ASYMMETRIC OLEFIN METATHESIS. ENHANCEMENT OF CATALYST ACTIVITY THROUGH STERIC AND ELECTRONIC MODIFICATIONS

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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). ^1H NMR spectra were recorded on a Varian Gemini 2000 (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, $(CD_3)_2SO$: δ 2.50 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 Gemini 2000 (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 77.2 ppm, $(CD_3)_2SO$: δ 39.5 ppm). High-resolution mass spectra were recorded at the University of Illinois (Urbana-Champaign, IL) and 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, and Chiralcel OD (0.46 cm x 25 cm)) in comparison with authentic racemic materials, or by ^1H or ^{19}F NMR spectroscopy of the derived Mosher esters in comparison with Mosher esters derived from the authentic racemic materials.

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 Schlenk 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 in a drybox under an atmosphere of N_2. All reagent solvents were purchased from Doe and Ingalls, unless otherwise noted. Solvents were purified under positive pressure of dry Ar by

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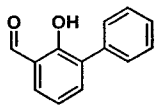
a modified Innovative Technologies purification system: toluene and benzene were purified through a copper oxide and an alumina column; CH_2Cl_2, Et_2O, and THF were purged with Ar and purified by passing them through two alumina columns. 1,2-Dichloroethane (Lancaster), $CDCl_3$ (Cambridge Isotope Labarotory, Inc.), triethylamine (Acros), 2-iodopropane (Aldrich), styrene (Aldrich), 1-heptene (Aldrich), 1-octene (Aldrich), and vinylcyclohexane (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. Boron tribromide (Aldrich) was fractionally distilled under vacuum. Ethyl chloroformate (Aldrich) was distilled from $CaCl_2$ under N_2. Triethylorthoformate (Aldrich) was distilled from Na under N_2. K_2CO_3 was stored in an oven (120 °C). $Cl_2Ru(=CH\text{-}o\text{-}OiPrC_6H_4)PPh_3$ was prepared as previously described.[1] $Cl_2Ru(=CHC_6H_5)(PCy_3)_2$ was purchased from Materia. *cis*-5-Norbornene-*endo*-2,3-dicarboxylic anhydride (Aldrich) was recrystallized from cyclohexane (Fisher). 2-Phenylphenol (Aldrich) was recrystallized from distilled hexane or pentane/Et_2O. Methyl 2-chloro-2,2-difluoroacetate (Acros) was distilled under N_2. CuI (Strem) was precipitated from a saturated aqueous solution of NaI with water. The following materials were purchased from commercial sources and used as received: EtOH (Fisher), acetonitrile (Aldrich), parafomaldehyde (Aldrich), ethylchloride (Aldrich), 2-hydroxy-4-methoxybenzaldehyde (Aldrich), 2-hydroxy-5-methoxybenzaldehyde (Aldrich), 2-hydroxy-5-nitrobenzaldehyde (Aldrich), methyltriphenylphosphonium bromide (Aldrich), Mg turnings (Strem), $AgCO_3$ (Strem), AgCl (Strem), 2-methoxy-naphthalene (Aldrich), acetic acid (Fisher), sulfuric acid (Fisher), KF (Aldrich), KOH (Fisher), sodium triacetoxyborohydride (Aldrich), HCl gas (AGA), I_2 (Aldrich), 57% aqueous solution of HI (Aldrich), iodic acid (Aldrich), *N*-bromosuccinimide (Aldrich), 0.05 M potassium phosphate monobasic/ sodium hydroxide pH 7 buffer (Fisher).

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). The use of other commercially available silica gels routinely gave lower yields for the purification of the Ru complex reported herein.



2-Hydroxy-biphenyl-3-carbaldehyde. A modified literature procedure[2] was followed. A three-neck round bottom flask was equipped with a reflux condenser, a Dewar condenser, and a stopper. Ethyl chloride was condensed into the flask

(1) Kingsbury, J. S.; Harrity, J. P A.; Bonitatebus, P. J., Jr.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1999**, *121*, 791-799.
(2) Wang, R. X.; You, X. Z.; Meng, Q. J.; Mintz, E. A.; Bu, X. R. *Synth. Commun.* **1994**, *24*, 1757-1760.

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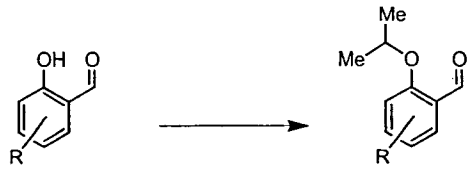
containing a stirring suspension of Mg turnings (1.00 g, 41.7 mmol) in 75 mL of Et_2O. The mixture was initiated by mild heating with a heat gun and once initiated, was allowed to reflux until all of the Mg was consumed (typically 6 h). A solution of 2-phenylphenol (7.09 g, 41.7 mmol) in 20 mL THF was added dropwise by syringe over 10 min, which caused the formation of a white precipitate. Benzene (100 mL) was added to this mixture to dissolve the precipitate, giving a clear burgundy solution. A short-path distillation apparatus was attached and the solution was heated to remove Et_2O and THF by distillation. Paraformaldehyde (3.13 g, 34.7 mmol) was added by cannula as a suspension in benzene (100 mL). Triethylamine (6.33 g, 62.3 mmol) was added by syringe and the mixture was heated to reflux for 12 h at which point TLC analysis (1:9 EtOAc:hexanes) indicated complete conversion of starting material to a new less-polar spot (R_f product = 0.3). The reaction was quenched by pouring the solution into a 1 L separatory funnel containing 10% aqueous solution of HCl (400 mL). The aqueous layer was washed three times with Et_2O (250 mL) and the combined organic layers were dried over $MgSO_4$, filtered and concentrated. The product was purified by silica gel chromatography (1:19 Et_2O/hexanes) to afford light yellow crystals (6.20 g, 31.3 mmol, 75%). IR (neat): 3057 (s), 2850 (s), 1656 (s), 1497 (m), 1440 (s), 1290 (s), 763 (s). ^1H NMR (400 MHz, $CDCl_3$): δ 11.57 (s, 1H), 9.96 (s, 1H), 7.65-7.60 (m, 3H), 7.57 (dd, J = 7.7, 1.7 Hz, 1H), 7.49-7.45 (m, 2H), 7.41-7.37 (m, 1H), 7.12 (dd, J = 7.7, 7.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.9, 159.0, 137.9, 136.4, 133.3, 130.6, 129.4, 128.4, 127.8, 121.0, 120.0. HRMS Calcd for $C_{13}H_{10}O_2$: 198.0681. Found: 198.0673. Anal. Calcd for $C_{13}H_{10}O_2$: C, 78.77; H, 5.09. Found: C, 78.69; H, 5.07.



General procedure for *O*-alkylation of *o*-phenoxyaldehyde. To a solution of 2-hydroxy-5-methoxy-benzaldehyde (1.00 mL, 8.01 mmol) in 10 mL of DMF in a 50 mL round-bottom flask was added K_2CO_3 (4.89 g, 34.8 mmol) and 2-iodopropane (1.00 mL, 10.0 mmol). The flask was equipped with a reflux condenser and submerged into a preheated oil bath at 45 °C. The resulting bright yellow mixture was allowed to stir for 12 h. The mixture was allowed to cool to 22 °C and diluted with water (100 mL). The resulting aqueous layer was washed three times with Et_2O (300 mL). The combined organic layers were washed three times with water (200 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo*.

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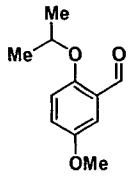
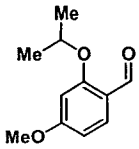
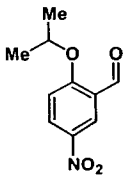


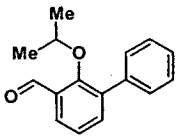
2-Isopropoxy-5-methoxybenzaldehyde. The O-alkylation procedure was followed to give a pale yellow oil (1.40 g, 7.22 mmol, 90%). IR (neat): 3352 (w), 3074 (w), 2980 (s), 2936 (m), 2867 (m), 1690 (s), 1621 (m), 1583 (m), 1488 (s), 1468 (m), 1432 (m), 1388 (m), 1325 (w), 1281 (s), 1224 (s), 1155 (s), 1098 (s), 1048 (s), 948 (s), 878 (w), 721 (w). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.43 (s, 1H), 7.29 (d, J = 3.2 Hz, 1H), 7.09 (dd, J = 9.2, 3.2 Hz, 1H), 6.94 (d, J = 9.2 Hz, 1H), 4.55 (septet, J = 6.4 Hz, 1H), 3.79 (s, 1H), 1.35 (d, J = 6.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.1, 155.5, 153.7, 126.5, 123.8, 116.9, 109.9, 72.4, 55.9, 22.2. HRMS Calcd for $C_{11}H_{14}O_3$: 194.0943. Found: 194.0943. Anal. Calcd for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27. Found: C, 67.76; H, 7.14.



2-Isopropoxy-4-methoxybenzaldehyde. The O-alkylation procedure was followed to give a pale yellow oil (1.17 g, 6.04 mmol, 90%). IR (neat): 2987 (m), 2949 (m), 2848 (m), 2779 (w), 1684 (s), 1608 (s), 1501 (m), 1451 (m), 1388 (m), 1306 (m), 1268 (s), 1205 (s), 1162 (s), 1224 (s), 1042 (m), 992 (m), 916 (m), 847 (m), 828 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.29 (s, 1H), 7.78 (d, J = 8.8 Hz, 1H), 6.49 (dd, J = 8.8, 2.0 Hz, 1H), 6.42 (d, J = 2.4 Hz, 1H), 4.61 (septet, J = 6.4 Hz, 1H), 3.83 (s, 1H), 1.37 (d, J = 6.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 188.8, 166.1, 162.4, 130.4, 120.1, 106.0, 100.0, 71.3, 55.7, 22.1. HRMS Calcd for $C_{11}H_{14}O_3$: 194.0943. Found: 194.0942.

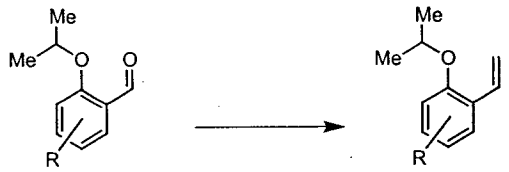


2-Isopropoxy-5-nitrobenzaldehyde. The O-alkylation procedure was followed to give a bright yellow solid (0.812 g, 3.83 mmol, 57%). IR (neat): 3332 (w), 3112 (w), 2999 (m), 2779 (w), 2942 (w), 2892 (w), 1677 (s), 1627 (s), 1590 (s), 1520 (s), 1483 (s), 1438 (m), 1388 (s), 1350 (s), 1281 (s), 1243 (m), 1180 (m), 1143 (s), 1124 (s), 854 (s), 916 (s) 840 (s), 752 (s) 714 (w). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.41 (s, 1H), 8.62 (d, J = 3.2 Hz, 1H), 8.35 (dd, J = 9.2, 3.2 Hz, 1H), 7.08 (d, J = 9.2 Hz, 1H), 4.82 (septet, J = 6.4 Hz, 1H), 1.45 (d, J = 6.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 188.0, 164.5, 141.2, 130.6, 125.1, 124.7, 113.8, 72.8, 21.9. HRMS Calcd for $C_{10}H_{11}NO_4$: 209.0688. Found: 209.0685. Anal. Calcd for $C_{10}H_{11}NO_4$: C, 57.41; H, 5.30. Found: C, 57.42; H, 5.14.

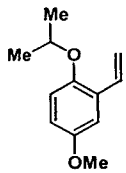


2-Isopropoxybiphenyl-3-carbaldehyde. The O-alkylation procedure was followed to give a light yellow oil (1.01 g, 4.21 mmol, 82%). IR (neat): 2968 (m), 2924 (m), 2855 (m), 1690 (s), 1252 (m), 1249 (m), 1105 (s), 810 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.53 (s, 1H), 7.84 (dd, J = 7.9, 1.8 Hz, 1H), 7.59-7.56 (m, 3H), 7.47-7.43 (m, 2H), 7.40-7.35 (m, 1H), 7.27-7.23 (m, 1H), 3.81 (septet, J = 6.1 Hz, 1H), 1.03 (d, J = 6.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.1, 158.6, 138.1, 137.5,

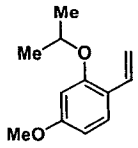
136.7, 131.2, 129.1, 128.6, 127.8, 127.2, 124.1, 77.5, 21.9. HRMS Calcd for $C_{16}H_{16}O_2$: 240.1150. Found: 240.1149.



General procedure for Wittig olefination of *o*-isopropoxyaldehyde. To a suspension of methyltriphenylphosphonium bromide (0.466 g, 1.31 mmol) in 10 mL of THF in a 50 mL round-bottom flask was added potassium *tert*-butoxide (1.70 g, 1.52 mmol). The resulting bright yellow mixture was allowed to stir for 2 h at 22 °C. The mixture was then cooled to –78 °C and a solution of 2-isopropoxy-5-methoxy-benzaldehyde (0.207 g, 1.07 mmol) in THF (5 mL) was slowly added by syringe. The reaction was allowed to warm to 22 °C and silica gel was added absorbing the full volume of solvent in the flask. Residual solvent was removed from the slurry under reduced pressure. The product-laden silica gel was loaded onto a short plug of silica gel and the product eluted with hexanes:Et_2O (see below). Product was stored under N_2 and in a freezer (–30 °C) to prevent polymerization.



1-Isopropoxy-5-methoxy-2-vinylbenzene. General procedure for the Wittig olefination was followed and purification through a silica gel plug in 95:5 hexanes:Et_2O (R_f = 0.35) afforded a colorless oil (0.206 g, 1.07 mmol, 100%). IR (neat): 3093 (w), 2974 (s), 2923 (m), 2835 (m), 1633 (w), 1608 (w), 1589 (m), 1488 (s), 1419 (s), 1388 (m), 1337 (m), 1318 (w), 1281 (s), 1218 (s) 1155 (m), 1117 (s), 1048 (s), 997 (s), 960 (s), 853 (m), 821 (m), 720 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.02 (dd, J = 17.6, 10.8 Hz, 1H), 7.01 (d, J = 2.6 Hz, 1H), 6.82 (d, J = 8.8 Hz, 1H), 6.75 (dd, J = 9.0, 2.8 Hz, 1H), 5.90 (d, J = 18.0 Hz, 1H), 5.35 (d, J = 11.2 Hz, 1H), 4.36 (septet, J = 6.0 Hz, 1H), 3.78 (s, 3H), 1.29 (d, J = 6.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.1, 148.6, 132.0, 129.5, 117.2, 114.3, 114.3, 111.3, 72.5, 55.8, 22.4.



2-Isopropoxy-4-methoxy-1-vinylbenzene. General procedure for the Wittig olefination was followed and purification through a silica gel plug in 95:5 hexanes:Et_2O (R_f = 0.35) afforded a colorless oil (0.211 g, 1.09 mmol, 100%). IR (neat): 3081 (w), 2974 (s), 2936 (m), 2841 (w), 2376 (w), 2338 (w), 1614 (s), 1583 (m), 1501 (s), 1469 (m), 1444 (m), 1425 (m), 1381 (m), 1325 (m), 1318 (s), 1262 (s), 1205 (s), 1167 (s), 1117 (s), 1060 (m), 991 (m), 916 (m), 827 (m), 802 (m), 720 (w). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (d, J = 8.4 Hz, 1H), 6.96 (dd, J = 17.6, 11.0 Hz, 1H), 6.45 (m, 2H), 5.62 (d, J =

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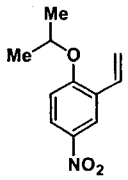
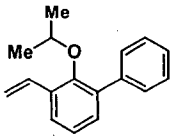
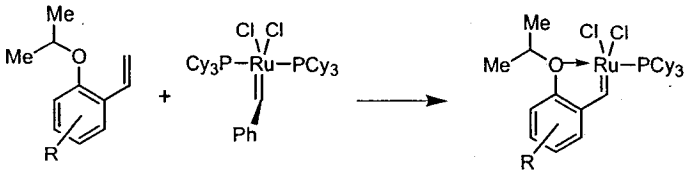
17.6 Hz, 1H), 5.10 (d, J = 10.8 Hz, 1H), 4.50 (septet, J = 6.0 Hz, 1H), 3.79 (s, 3H), 1.34 (d, J = 6.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.5, 156.4, 131.7, 127.4, 121.2, 111.9, 105.3, 101.3, 71.0, 55.5, 22.3.



1-Isopropoxy-4-nitro-2-vinylbenzene. General procedure for the Wittig olefination was followed and purification through a silica gel plug in 9:1 hexanes:Et_2O (R_f = 0.32) afforded a bright yellow solid (0.412 g, 1.99 mmol, 77%). IR (neat): 3087 (w), 2993 (m), 2943 (w), 1627 (w), 1596 (m), 1526 (s), 1495 (s), 1432 (w), 1394 (w), 1350 (s), 1281 (s), 1193 (m), 1148 (s), 111(m), 1086 (w), 991 (m), 953 (m), 909 (w), 827 (w), 802 (w), 758 (m), 664 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (d, J = 3.2 Hz, 1H), 8.08 (dd, J = 9.2, 2.8 Hz, 1H), 6.97 (dd, J = 17.6, 11.2 Hz, 1H), 6.88 (d, J = 9.2 Hz, 1H), 5.84 (d, J = 17.2 Hz, 1H), 5.37 (d, J = 11.2 Hz, 1H), 4.69 (septet, J = 6.0 Hz, 1H), 1.39 (d, J = 6.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.2, 141.2, 130.4, 124.7, 122.6, 117.0, 112.4, 71.7, 22.1. HRMS Calcd for $C_{11}H_{13}NO_3$: 207.0895. Found: 207.0895. Anal. Calcd for $C_{11}H_{13}NO_3$: C, 63.76; H, 6.32. Found: C, 63.87; H, 6.50.

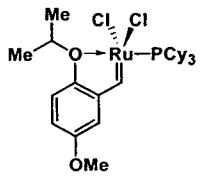


2-Isopropoxy-3-vinylbiphenyl. General procedure for the Wittig olefination was followed and purification through a silica gel plug in 95:5 hexanes:Et_2O (R_f = 0.35) afforded the product as a colorless oil (0.206 g, 1.07 mmol, 100%) that crystallized upon storage in freezer (-30 °C). IR (neat): 3056 (br), 2974 (s), 2924 (m), 1627 (m), 1408 (s), 1215 (s), 1108 (s), 935 (s), 791 (s), 761 (s), 700 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60-7.53 (m, 3H), 7.44-7.39 (m, 2H), 7.33 (dddd, J = 7.2, 7.2, 1.3, 1.3 Hz, 1H), 7.27 (dd, J = 1.7, 7.5 Hz, 1H) 7.22-7.12 (m, 2H), 5.77 (dd, J = 1.4, 17.9 Hz, 1H), 5.31 (dd, J = 1.4, 11.1 Hz, 1H) 3.76 (septet, J = 6.2 Hz, 1H), 0.98 (d, J = 6.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.1, 139.8, 136.3, 133.1, 133.0, 131.0, 129.6, 128.4, 127.3, 125.4, 124.0, 114.7, 76.1, 22.4. HRMS Calcd for $C_{17}H_{18}O$: 238.1358. Found: 238.1357. Anal. Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 85.65; H, 7.61.

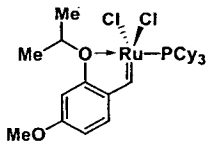


General procedure for carbene exchange. To a suspension of $Cl_2Ru(=CHC_6H_5)(PCy_3)_2$ (0.402 g, 0.489 mmol) and AgCl (0.137 g, 0.957 mmol) in 10 mL of CH_2Cl_2 in a 50 mL round-bottom flask was added a solution of 1-isopropoxy-4-methoxy-2-vinyl-benzene (0.206 g, 1.07 mmol) in CH_2Cl_2 (5 mL) by syringe. The flask was equipped with a condenser, and the solution

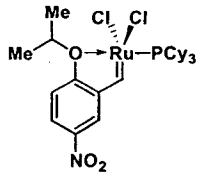
was allowed to stir at 40 °C for 1 h. Addition of silica gel to the mixture, absorbing the full volume of solvent in the flask. Residual solvent was removed from the slurry under reduced pressure. The product-laden silica gel was loaded onto a column of silica gel and the product eluted with 3:1 hexanes:CH_2Cl_2 to remove any starting Ru complex as a light pink band and then CH_2Cl_2 to remove the product as a greenish-brown band.



$Cl_2Ru(=CH\text{-}2\text{-}O\textit{i}Pr\text{-}5\text{-}OMeC_6H_3)PCy_3$. The general procedure for carbene exchange was followed to afford a light brown solid (0.238 g, 0.377 mmol, 77%). IR (neat): 2930 (s), 2848 (s), 2250 (w), 1589 (w), 1488 (s), 1444 (m), 1419 (w), 1388 (w), 1325 (w), 1293 (m), 1268 (m), 1211 (m), 1174 (w), 1142 (m), 1104 (m), 1048 (m), 1010 (w), 922 (s), 859 (m), 809 (w), 733 (s), 651 (w), 519 (m). ^1H NMR (400 MHz, $CDCl_3$): δ 17.34 (d, J = 4.8 Hz, 1H), 7.20 (d, J = 8.4 Hz, 1H), 7.18 (s, 1H), 6.96 (d, J = 8.4 Hz, 1H), 5.18 (qq, J = 6.0, 6.0 Hz, 1H), 3.84 (s, 3H), 2.35-2.26 (m, 3H), 2.09-2.06 (m, 6H), 1.82-1.70 (m, 12H), 1.76 (d, J = 6.0 Hz, 6H), 1.30-1.24 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.4, 147.2, 144.2, 115.6, 113.8, 107.1, 75.6, 56.3, 35.9, 35.7, 30.3, 28.0, 27.9, 26.4, 22.2. HRMS Calcd for $C_{29}H_{47}Cl_2O_2PRu$: 630.1734. Found: 630.1735. Anal. Calcd for $C_{29}H_{47}Cl_2O_2PRu$: C, 55.23; H, 7.51. Found: C, 55.25; H, 7.70.



$Cl_2Ru(=CH\text{-}2\text{-}O\textit{i}Pr\text{-}4\text{-}OMe\text{-}C_6H_3)PCy_3$. The general procedure for carbene exchange was followed to afford a light brown solid (0.242 g, 0.383 mmol, 81%). IR (neat): 2923 (s), 2860 (s), 2237 (w), 1589 (s), 1570 (m), 1488 (m), 1451 (s), 1388 (m), 1331 (m), 1262 (s), 1205 (s), 1161 (m), 1130 (m), 1117 (m), 1041 (w), 1004 (w), 985 (w), 916 (s), 834 (m), 739 (s), 651 (w), 582 (w), 525 (m). ^1H NMR (400 MHz, $CDCl_3$): δ 17.16 (d, J = 4.4 Hz, 1H), 7.55 (d, J = 8.4 Hz, 1H), 6.59 (s, 1H), 6.57 (s, 1H), 5.18 (qq, J = 6.0, 6.0 Hz, 1 H), 3.84 (s, 3H), 2.34-2.24 (m, 3H), 2.89-2.05 (m, 6H), 1.86-1.68 (m, 12H), 1.79 (d, J = 6.0 Hz, 6H), 1.28-1.20 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.8, 154.9, 139.7, 124.1, 106.4, 101.4, 75.9, 56.0, 36.0, 35.7, 30.3, 27.9, 27.8, 26.4, 22.3. HRMS Calcd for $C_{29}H_{47}Cl_2O_2PRu$: 630.1734. Found: 630.1732.



$Cl_2Ru(=CH\text{-}2\text{-}O\textit{i}Pr\text{-}5\text{-}NO_2\text{-}C_6H_3)PCy_3$. The general procedure for carbene exchange was followed to afford a burgundy solid (0.192 g, 0.297 mmol, 61%). IR (neat): 3093 (w), 2930 (s), 2848 (s), 2231 (w), 1608 (m), 1576 (m), 1520 (s), 1476 (m), 1451 (m), 1388 (m), 1344 (s), 1281 (s), 1243 (s), 1186 (m), 1136 (m), 1098 (s), 1010 (m), 960 (m), 922 (m), 859 (m), 846 (m), 796 (m), 733 (s), 664 (w). ^1H NMR (400 MHz, $CDCl_3$): δ 17.35 (d, J = 4.4 Hz, 1H), 8.58 (d, J = 2.4 Hz, 1H), 8.52 (dd, J = 9.2, 2.4 Hz, 1H), 7.16 (d, J = 9.2 Hz, 1H), 5.35 (septet, J = 6.0 Hz, 1H), 2.35-

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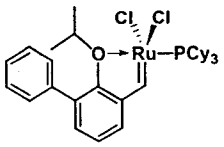
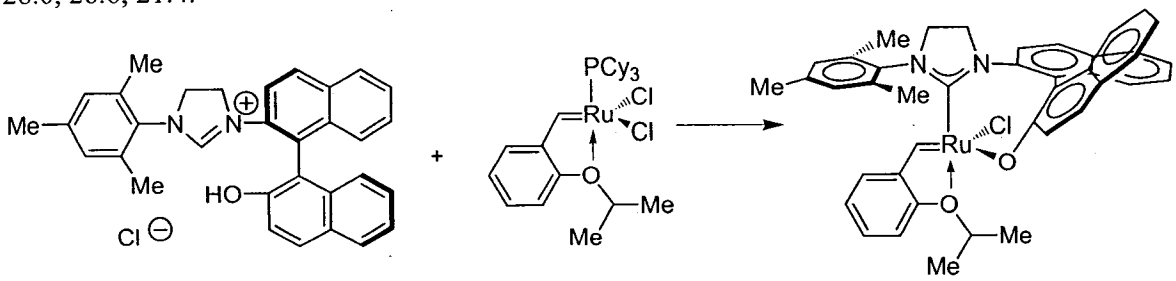
2.26 (m, 3H), 2.10-2.01 (m, 6H), 1.88-1.68 (m, 12 H), 1.82 (d, J = 6.0 Hz, 6H), 1.34-1.20 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.1, 143.4, 143.3, 124.4, 117.8, 113.4, 78.3, 36.1, 35.9, 30.3, 27.9, 27.8, 26.3, 22.3. HRMS Calcd for $C_{28}H_{44}Cl_2NO_2PRu$: 645.1479. Found: 645.1479. Anal. Calcd for $C_{28}H_{44}Cl_2NO_2PRu$: C, 52.09; H, 6.87. Found: C, 51.81; H, 6.59.



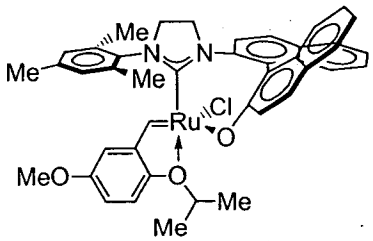
Cl_2Ru(=CH-2-O*i*Pr-3-biphenyl)PCy_3. A suspension of 2-isopropoxy-3-vinylbiphenyl (0.175 g, 0.734 mmol), silver chloride (0.110 g, 0.764 mmol), and $Cl_2Ru(=CHC_6H_5)(PCy_3)_2$ (0.231 g, 1.10 mmol) in CH_2Cl_2 (8 mL) in a 25 mL round-bottom flask was allowed to stir at 22 °C for 45 min. The mixture was concentrated by purging with a gentle stream of N_2. The product was purified by passing through a short plug of silica in 2:1 hexanes:CH_2Cl_2. Concentration gave a viscous oil containing residual methylene chloride. This residue was triturated by the addition of pentane to precipitate a light pink solid (0.245g, 0.362 mmol, 58%). IR (neat): 2930 (s), 2848 (m), 2232 (w), 1451 (m), 916 (m), 734 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 17.59 (d, J = 4.4, 1H), 7.63 (dd, J = 7.6, 1.8 Hz, 1H) 7.58-7.56 (m, 2H), 7.47-7.42 (m, 3H), 7.37 (dddd, J = 6.4, 6.4, 1.4, 1.4, 1H), 7.13 (dd, J = 7.6, 7.6 Hz, 1H), 4.75 (m, 1H), 2.39-2.30 (m, 3H), 2.12-2.09 (m, 6H), 1.86-1.77 (m, 15H), 1.74-1.69 (m, 2H) 1.37 (d, J = 6.2 Hz, 6H), 1.30-1.25 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 282.3, 139.7, 133.8, 129.3, 128.9, 128.2, 124.0, 122.2, 78.5, 36.0, 35.7, 30.3, 28.1, 28.0, 26.6, 21.4.



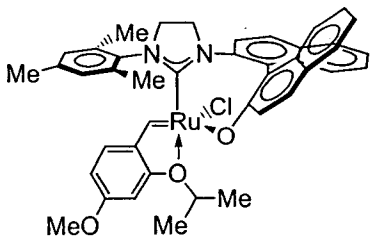
General procedure for phosphine-carbene exchange: To a mixture of Cl_2Ru(=CH-2-O*i*Pr-5-OMe-C_6H_4)PCy_3 (0.138 g, 0.219 mmol), silver (I) carbonate (0.114 g, 0.412 mmol), and the ligand salt (*cf.* **9**)[3] (0.165 g, 0.336 mmol) in a 25 mL round bottom flask was added THF (5 mL) and benzene (5 mL). The flask was equipped with a reflux condenser and submerged into an oil bath preheated to 80 °C. The reaction was allowed to stir for 1 h, during which time the mixture remained heterogeneous but turned color from light brown to dark brown. The mixture was allowed to cool to 22 °C and silica gel was added absorbing the full volume of solvent in the flask. Residual solvent was removed from the slurry under reduced pressure. The product-laden silica gel was loaded onto a column of silica gel and the products eluted with 1:1 hexanes:Et_2O

(3) Van Veldhuizen, J. J.; Garber, S. B.; Kingsbury, J. S.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2002**, *124*, 4954-4955.

to remove any starting Ru-phosphine complex, then 1:2 hexanes:Et_2O to remove the desired catalyst. The product was then dissolved in a minimum amount of CH_2Cl_2 and triturated with hexanes or pentane to precipitate the catalyst as a greenish-brown powder.



Ruthenium complex 3b: The general procedure for phosphine-carbene exchange was followed to afford a light greenish-brown solid residue (94.7 mg, 0.123 mmol, 56%). IR (neat): 3062 (w), 2980 (w), 2923 (w), 2848 (w), 1671 (w), 1614 (w), 1608 (w), 1558 (w), 1488 (s), 1451 (m), 1419 (m), 1394 (w), 1337 (m), 1281 (s), 1237 (m), 1211 (m), 1142 (w), 1098 (w), 1035 (w), 979 (w), 928 (w), 853 (w), 846 (w), 752 (m), 733 (w), 683 (w). ^{1}H NMR (400 MHz, $CDCl_3$): δ 15.83 (s, 1H), 8.19 (d, J = 8.8 Hz, 1H), 8.04 (d, J = 8.4 Hz, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.72 (d, J = 7.6 Hz, 1H), 7.57 (d, J = 8.8 Hz, 1H), 7.52-7.48 (m, 1H), 7.28-7.24 (m, 1H), 7.18-7.08 (m, 2H), 7.04 (br, 1H), 6.97 (br, 1H), 6.93 (d, J = 2.8 Hz, 1H), 6.91 (d, J = 3.2 Hz, 1H), 6.87 (d, J = 8.4 Hz, 1H), 6.66 (d, J = 8.8 Hz, 1H), 6.65 (d, J = 9.2 Hz, 1H), 6.43 (d, J = 3.2 Hz, 1H), 4.67 (qq, J = 6.0, 6.0 Hz, 1H), 4.26-4.20 (m, 1H), 3.90-3.84 (m, 1H), 3.73 (s, 3H), 3.59-3.48 (m, 2H), 2.40 (s, 3H), 2.21 (s, 3H), 1.72 (s, 3H), 1.00 (d, J = 6.4 Hz, 3H), 0.51 (d, J = 6.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 280.75, 214.36, 169.97,155.17, 146.56, 144.61, 138.59, 138.43, 137.90, 137.48, 137.36, 137.09, 134.47, 134.42, 133.63, 129.79, 129.30, 128.89, 128.54, 128.49, 128.13, 127.99, 127.90, 127.87, 127.81, 126.57, 125.89, 124.46, 121.65, 119.34, 113.10, 112.51, 106.75, 74.71, 55.98, 52.84, 51.49, 29.82, 21.22, 20.39, 20.36, 18.49, 18.00. HRMS Calcd for $C_{43}H_{41}ClN_2O_3Ru$: 770.1849. Found: 770.1851.



Ruthenium complex 3c: The general procedure for phosphine-carbene exchange was followed to afford a light greenish-brown solid residue (0.103 g, 0.134 mmol, 66%). IR (neat): 3068 (w), 2874 (m), 2930 (m), 1677 (m), 1602 (s), 1501 (s), 1488 (2), 1457 (s), 1432 (s), 1350 (m), 1281 (s), 1205 (m), 1161 (m), 1117 (s), 1104 (m), 1041 (w), 985 (m), 916 (m), 821 (m), 752 (s), 727 (m), 689 (m), 670 (w). ^{1}H NMR (400 MHz, $CDCl_3$): δ 15.75 (s, 1H), 8.20 (d, J = 8.8 Hz, 1H), 8.05 (d, J = 8.8 Hz, 1H), 7.99 (d, J = 8.4 Hz, 1H), 7.71 (d, J = 8.4 Hz, 1H), 7.56 (d, J = 8.8 Hz, 1H), 7.50 (ddd, J = 8.0, 6.0, 2.0 Hz, 1H), 7.29-7.23 (m, 2H), 7.17-7.07 (m, 2H), 7.03 (br, 1H), 6.96 (br, 1H), 6.85 (d, J = 8.0 Hz, 1H), 6.78 (d, J = 8.8 Hz, 1H), 6.66 (d, J = 8.8 Hz, 1H), 6.43 (dd, J = 8.4, 2.4 Hz, 1H), 6.32 (br, 1H), 4.68 (qq, J = 6.0, 6.0 Hz, 1H), 4.26-4.19 (m, 1H), 3.90-3.84 (m, 1H), 3.73 (s, 3H), 3.59-3.46 (m, 2H), 2.40 (s, 3H), 2.21 (s, 3H), 1.72 (s, 3H), 1.02 (d, J = 6.0 Hz, 3H), 0.52 (d, J = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 280.30,

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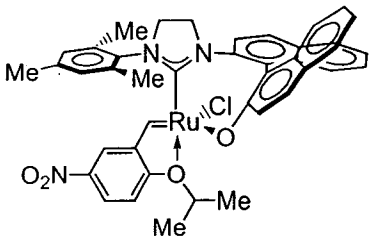
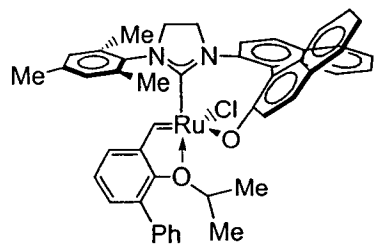
215.49, 170.07, 160.20, 153.99, 140.04, 138.51, 138.43, 138.06, 137.49, 137.46, 137.19, 134.58, 134.51, 133.66, 129.79, 129.25, 128.90, 128.62, 128.43, 128.10, 128.03, 127.91, 127.74, 126.78, 126.56, 125.83, 124.64, 124.43, 122.56, 121.48, 119.25, 106.27, 101.02, 75.08, 55.79, 52.90, 51.42, 29.83, 22.08, 21.26, 20.40, 20.32, 18.52, 18.03. HRMS Calcd for $C_{43}H_{41}ClN_2O_3Ru$: 770.1849. Found: 770.1851.

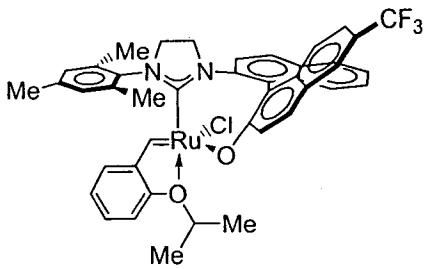


Ruthenium complex 3a: The general procedure for phosphine-carbene exchange was followed to afford a light greenish-brown solid residue (73.2 mg, 93.2 μmol, 59%). IR (neat): 3055 (w), 2980 (w), 2930 (m), 2835 (w), 1683 (w), 1614 (m), 1595 (m), 1513 (s), 1482 (s), 1451 (s), 1425 (s), 1337 (s), 1274 (s), 1230 (s), 1136 (w), 1092 (w), 991 (m), 953 (w), 922 (w), 859 (w), 827 (m), 739 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 15.72 (s, 1H), 8.28 (dd, J = 8.8, 2.8 Hz, 1H), 8.21 (d, J = 8.4 Hz, 1H), 8.01 (d, J = 8.8 Hz, 1H), 8.00 (d, J = 8.0 Hz, 1H), 7.76-7.73 (m, 2H), 7.61 (d, J = 9.2 Hz, 1H), 7.54-7.50 (m, 1H), 7.28 (s, 1H), 7.27 (s, 1H), 7.22-7.11 (m, 2H), 7.10 (br, 1H), 7.00 (br, 1H), 6.89 (d, J = 8.4 Hz, 1H), 6.84 (d, J = 8.8 Hz, 1H), 6.63 (d, J = 8.8 Hz, 1H), 4.82 (qq, J = 6.4, 6.4 Hz, 1H), 4.30-4.20 (m, 1H), 3.95-3.86 (m, 1H), 3.60-3.50 (m, 2H), 2.47 (s, 3H), 2.19 (s, 3H), 1.72 (s, 3H), 1.06 (d, J = 6.0 Hz, 3H), 0.59 (d, J = 6.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 279.31, 211.91, 169.39, 156.73, 143.87, 143.40, 139.26, 138.26, 137.74, 137.29, 136.93, 136.79, 134.34, 134.28, 133.65, 130.00, 129.57, 129.07, 128.84, 128.40, 128.24, 128.13, 127.98, 127.91, 127.01, 126.77, 126.16, 124.52, 123.83, 122.64, 122.07, 119.43, 116.55, 112.61, 52.87, 51.61, 29.83, 21.94, 21.26, 20.49, 20.42, 18.39, 17.91. HRMS Calcd for $C_{43}H_{41}ClN_2O_3Ru$: 785.1594. Found: 785.1604.

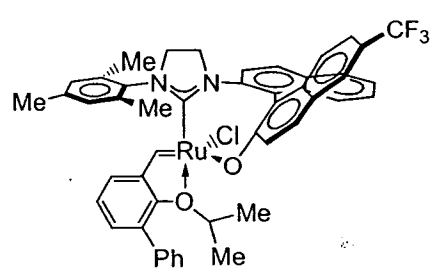


Ruthenium complex 3d: The general procedure for phosphine-carbene exchange was followed to afford a dark brown solid (0.203 g, 0.249 mmol, 74%). This material was further purified by a bilayer recrystallization with CH_2Cl_2 and pentane. The Ru-complex was dissolved in the minimum amount of CH_2Cl_2 in a 50 mL pear-shaped flask. Pentane was slowly added down the walls of the flask with a syringe (care must be taken to insure no mixing of the solvents). Slow diffusion (typically 12-24 h) of this bilayer gave large crystals of high purity. IR (neat): 3056 (m), 2968 (m), 2924 (m), 1590 (m), 1426 (s), 1275 (s), 752 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 16.05 (s, 1H), 8.16 (d, J = 8.6 Hz, 1H), 8.00 (d, J = 8.6 Hz, 1H), 7.93 (d, J = 8.0 Hz, 1H), 7.73 (d, J = 8.0 Hz, 1H), 7.61 (d, J = 8.9 Hz, 1H), 7.42 (m, 1H), 7.34 (m, 2H), 7.26-7.06 (m, 9H), 6.95 (m, 2H), 6.88 (d, J = 8.0 Hz, 1H), 6.77 (dd, J = 7.6, 1.6 Hz, 1H) 6.73 (d,

J = 8.9 Hz, 1H), 4.23-4.17 (m, 1H), 4.10 (qq, J = 6.2, 6.2 Hz, 1H), 3.89-3.83 (m, 1H), 3.61-3.48 (m, 2H), 2.44 (s, 3H), 2.16 (s, 3H), 1.82 (s, 3H), 0.45 (d, J = 6.2 Hz, 3H), 0.32 (d, J = 6.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 281.96-281.73 (multiplet), 213.90, 170.05, 149.48, 147.43, 139.62, 138.53, 138.36, 137.85, 137.41, 137.28, 137.03, 134.63, 134.50, 133.51, 131.60, 131.32, 129.60, 129.29, 128.88, 128.72, 128.48, 128.42, 128.06, 127.93, 127.87, 127.64, 127.41, 126.56, 126.33, 125.80, 124.57, 124.40, 123.75, 121.38, 120.55, 119.08, 52.75, 51.50, 30.95, 21.20, 19.41, 18.35, 17.99. HRMS Calcd for $C_{48}H_{43}ClN_2O_2Ru$: 816.2057. Found: 816.2057.



Ruthenium complex (3e): $Cl_2Ru(=CH\text{-}o\text{-}OiPrC_6H_4)PPh_3$ (44.6 mg, 76.6 μmol), silver (I) carbonate (21.1 mg, 76.6 μmol), and the ligand salt (**9**) (37.7 mg, 76.6 μmol) were added to a 5 mL round bottom flask equipped with a reflux condenser. The solids were suspended in THF (1 mL) and benzene (1 mL) and brought to reflux with a heating mantle. The reaction was allowed to stir for 30 min, during which time the mixture remained heterogeneous but turned color from light brown to dark greenish-brown. The mixture was then allowed to cool to 22 °C and concentrated by vacuum. The product was purified by silica gel column chromatogaphy with 1:1 hexanes:CH_2Cl_2 as the eluant to afford a light greenish-brown solid residue (29.7 mg, 36.7 μmol, 48%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 16.04 (s, 1H), 8.25 (d, J = 8.7 Hz, 1H), 8.08 (d, J = 8.7 Hz, 1H), 8.05-7.98 (m, 2H), 7.66 (d, J = 9.0 Hz, 1H), 7.54 (ddd, J = 1.3, 6.8, 8.1 Hz), 7.42-7.35 (m, 1H), 7.32-7.21 (m, 3H), 7.07 (s, 1H), 6.99 (s, 1H), 6.95 (d, J = 8.9 Hz, 1H), 6.91-6.89 (m, 2H), 6.78 (d, J = 8.5 Hz, 1H), 6.75 (d, J = 8.8 Hz, 1H), 4.77 (qq, J = 6.0, 6.0 Hz, 1H), 4.32-4.26 (m, 1H), 3.98-3.86 (m, 1H), 3.61-3.52 (m, 2H,), 2.43 (s, 3H), 2.22 (s, 3H), 1.03 (d, J = 6.1 Hz, 3H), 0.54 (d, J = 6.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 283.76, 214.34, 172.28, 152.36, 144.31, 138.79, 138.33, 137.25, 137.21, 136.93, 135.83, 134.34, 134.17, 134.07, 133.69, 129.89, 129.35, 128.62, 128.51, 128.47, 128.12, 128.09, 127.64, 127.02, 126.86, 126.24, 125.92, 125.04, 122.55, 121.86, 121.62 (q, J = 3.0 Hz) 119.65, 113.02, 74.93, 52.94, 51.50, 21.28, 20.40, 18.47, 17.96. HRMS Calcd for $C_{43}H_{38}F_3N_2O_2Ru$: 808.1617. Found: 808.1618.



Ruthenium complex (3f): $Cl_2Ru(=CH\text{-}2\text{-}OiPr\text{-}3\text{-}biphenyl)PPh_3$ (77.7 mg, 115 μmol), silver (I) carbonate (31.7 mg, 115 μmol), and the ligand salt (**9**) (56.6 mg, 115 μmol) were added to a 5 mL round bottom flask equipped with a reflux condenser. The solids were suspended in THF (1 mL) and benzene (1 mL) and the resulting mixture

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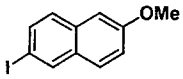
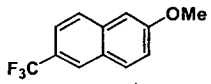
was brought to reflux with a heating mantle. The reaction was allowed to stir for 30 min, during which time the mixture remained heterogeneous but turned color from light brown to dark greenish-brown. The mixture was then allowed to cool to 22 °C and concentrated by vacuum. The desired product was purified by silica gel column chromatogaphy with 1:1 hexanes:CH_2Cl_2 as the eluant. Solvent removal under reduced pressure afforded a light greenish- brown solid residue (23.8 mg, 26.9 μmol, 23%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 16.12 (s, 1H), 8.21 (d, J = 9.3 Hz, 1H), 8.05-8.02 (m, 2H), 7.97 (d, J = 8.1 Hz, 1H), 7.70 (d, J = 9.1 Hz, 1H), 7.47 (ddd, J = 1.3, 6.6, 8.1 Hz, 2H), 7.37-7.34 (m, 3H), 7.30-7.19 (m, 5H), 7.09 (s, 1H), 7.00-6.94 (m, 3H), 6.84 (d, J = 8.7 Hz, 1H), 6.80 (dd, J = 1.6, 7.4 Hz, 1H), 4.25 (ddd, J = 4.5, 4.5, 10.7 Hz, 1H), 4.12 (qq, J = 6.0, 6.0 Hz, 1H), 3.90 (ddd, J = 5.0, 5.0, 10.9 Hz, 1H), 3.62-3.53 (m, 2H), 2.45 (s, 3H), 2.16 (s, 3H), 1.81 (s, 3H), 0.43 (d, J = 6.6 Hz, 3H), 0.31 (d, J = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 284.13, 213.70, 172.41, 149.59, 147.54, 139.59, 138.77, 138.39, 137.34, 137.23, 137.21, 136.93, 136.10, 134.40, 133.61, 131.71, 131.69, 129.77, 129.44, 129.39, 129.37, 128.77, 128.54, 128.38, 128.12, 126.83, 126.70, 126.14, 126.09, 125.93 (q, J = 4.6 Hz), 125.01, 123.91, 123.30, 122.98, 121.62 (q, J = 3.1 Hz), 120.65, 119.39, 77.72, 52.88, 51.55, 21.30, 19.50, 18.42, 18.04. HRMS Calcd for $C_{49}H_{42}F_3ClN_2O_2Ru$: 884.1930. Found: 884.1933.



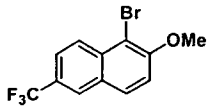
2-Methoxy-6-iodonaphthylene (4). A modified literature procedure was followed.[4] 2-Methoxynaphthylene (8.00 g, 50.6 mmol) was dissolved in HOAc (138 mL) at 65 °C. To this solution was added H_2O (7.5 mL), H_2SO_4 (3.75 mL), I_2 (10.2 g, 40.5 mmol) and HIO_3 (4.45 g, 40.5 mmol). The resulting solution was allowed to stir at 65 °C for 14 h, after which time a precipitate formed. The mixture was heated to 85 °C, which caused most of the precipitate to dissolve. To this mixture, 57% aqueous solution of HI (21.5 mL) was added and the mixture was allowed to stir for an additional 8 h at 85 °C. The mixture was then diluted with H_2O (500 mL), causing the further precipitation, which was collected by filtration. The solid was mixed with dilute $NaHS_2O_3$ (200 mL of 1:1 saturated aqueous solution of $NaHS_2O_3$: H_2O) and the resulting mixture was washed three times with CH_2Cl_2 (200 mL). Organic layers were combined, dried over Na_2SO_4, filtered, and absorbed onto silica gel. Solvent was removed from the slurry under reduced pressure. The product-laden silica gel was loaded onto a column of silica gel and the product eluted with 9:1 hexanes/Et_2O (R_f = 0.56) to yield an off-white solid (7.54 g, 26.5 mmol, 53%). See reference for spectroscopic data.



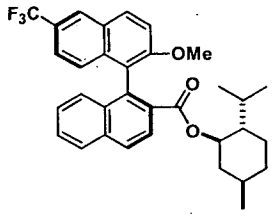
2-Methoxy-6-triflouromethylnaphthylene. To a mixture of 2-methoxy-6-iodonaphthylene (**4**) (5.82 g, 20.5 mmol), CuI (4.70 g, 24.6 mmol), and KF

(4) Smith, W. B. *J. Org. Chem.* **1985**, *50*, 3649-3651.

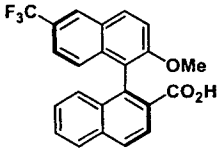
(1.43 g, 24.6 mmol) in a 100 mL round bottom flask with condenser was added ClF_2CCO_2Me (5.20 mL, 49.3 mmol) and DMF (41 mL). This mixture was allowed to stir at 120 °C for 20 h, diluted with H_2O (100 mL) and Et_2O (100 mL), and filtered through Celite. The isolated aqueous layer was washed twice with Et_2O (100 mL). The organic layers were combined, dried over $MgSO_4$, filtered and concentrated to give an off-white solid (6.16 g) as a 9:1 mixture of product:starting material by NMR spectroscopy. To remove the starting material the mixture was dissolved in THF (40 mL) and cooled to -78 °C (dry ice/acetone bath). To this solution was added *n*-BuLi (1.23 M solution in THF, 2.38 mL, 2.92 mmol) dropwise over 5 min. After 30 min, benzaldehyde (811 μL, 7.97 mmol) was added and the solution was allowed to warm to 22 °C by removing the cold bath. This solution allowed to stir for 45 min. Then, 2N aqueous solution of HCl (50 mL) was added and the mixture was washed three times with Et_2O (100 mL). The organic layers were combined, dried over $MgSO_4$, filtered, and absorbed onto silica. Solvent was removed from the slurry under reduced pressure. The product-laden silica gel was loaded on silica gel column and the product eluted with 50:1 hexanes:Et_2O (R_f = 0.35) to give a white solid (3.63 g, 16.0 mmol, 78%). IR (neat): 3069 (w), 2971 (m), 2946 (m), 2912 (w), 2850 (w), 1633 (s), 1613 (s), 1496 (s), 1420 (m), 1393 (m), 1346 (s), 1322 (s), 1275 (s), 1268 (s), 1211 (s), 1175 (s), 1123 (s), 1070 (s), 1029 (s), 908 (s), 858 (s), 824 (s), 684 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07-8.03 (m, 1H), 7.82 (dd, J = 2.0, 9.4 Hz, 2H), 7.60 (dd, J = 1.6, 8.9 Hz, 1H), 7.24 (dd, J = 2.5, 9.0 Hz, 1H), 7.18 (d, J = 2.5 Hz, 1H), 3.95 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.4, 136.3, 130.4, 127.8, 125.6 (q, J = 4.6 Hz), 122.2 (q, J = 3.4 Hz), 120.3, 105.9, 55.5.



1-Bromo-2-methoxy-6-triflouromethylnaphthylene (5). To a solution of 2-methoxy-6-triflouromethylnaphthylene (4.12 g, 17.9 mmol) in acetonitrile (60 mL) was added N-bromosuccinimide (3.35 g, 18.8 mmol). The resulting solution was allowed to stir at 22 °C for 3 h and then concentrated by rotary evaporation. The solid was mixed with H_2O (40 mL) and washed three times with Et_2O (40 mL). The organic layers were combined, dried over $MgSO_4$, filtered, and absorbed onto silica gel. Residual solvent was removed from the slurry under reduced pressure. The product-laden silica gel was loaded onto a short plug of silica gel and the product eluted with 9:1 hexanes:Et_2O (R_f = 0.35). The resulting solid was dried in a vacuum dessicator over P_2O_5 for 18 h to give a white solid (4.48 g, 14.7 mmol, 82%). IR (neat): 2974 (w), 2943 (w), 2845 (w), 1633 (s), 1604 (m), 1499 (s), 1488 (s), 1454 (m), 1443 (w), 1341 (m), 1311 (s), 1275 (s), 1252 (s), 1185 (s), 1158 (s), 1125 (s), 1075 (s), 1062 (s), 973 (w), 905 (s), 858 (m), 822 (s), 805 (s), 740 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (d, J = 8.8 Hz, 1H), 8.09 (s, 1H), 7.92 (d, J = 8.8 Hz, 1H), 7.71 (dd, J = 9.0, 1.8 Hz, 1H), 7.37 (d, J = 9.0 Hz, 1H, aromatic H), 4.07 (s, 3H, OCH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.6, 130.1, 128.5, 127.6, 126.1 (q, J =4.6 Hz), 123.5 (q, J = 3.1 Hz), 114.7, 108.7, 57.2.

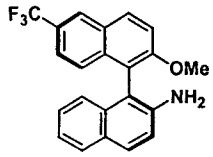


(–)-Menthyl-2'-methoxy-6'-triflouromethyl-1,1'-binaphthyl-ene-2-carboxylate (7). A solution of 1-bromo-2-methoxy-6-triflouromethylnaphthylene (**5**) (6.12 g, 20.0 mmol) in THF (20 mL) was cannulated slowly over 20 min to a mixture of Mg turnings (1.44 g, 60.2 mmol) in THF (5 mL) at reflux. The mixture turned brown and was allowed to stir at reflux with a heating mantle for 1 h. To this mixture was added benzene (20 mL) and the resulting solution was cannula filtered into a solution of (-)-menthyl-1-(-)-menthoxy-2-naphthoate (**6**)[3] (9.32 g, 20.0 mmol) in benzene (15 mL) and allowed to stir at reflux for 48 h. The reaction was quenched by the addition of 2N aqueous solution of HCl (100 mL) and the resulting aqueous layer was washed three times with Et_2O (100 mL). The organic layers were combined, dried over $MgSO_4$, filtered, and concentrated. The product was purified by silica gel column chromatography with 7:1 hexanes:Et_2O (R_f = 0.4) to give a white solid (9.00 g, 16.8 mmol, 84%) as a 95:5 mixture of diastereomers. Recrystallization in heptane gave one diastereomer. IR (neat): 3065 (w), 2956 (s), 2870 (m), 1699 (s), 1632 (m), 1600 (m), 1488 (s), 1463 (s), 1320 (s), 1309 (s), 1276 (s), 1257 (s), 1207 (s), 1195 (s), 1182 (s), 1156 (s), 1127 (s), 1086 (s), 1072 (s), 1049 (m), 982 (m), 957 (m), 916 (m), 900 (m), 829 (m), 805 (m), 769 (s), 739 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16-8.14 (m, 2H), 8.09 (d, J = 9.0 Hz, 1H), 8.02 (d, J = 9.0 Hz, 1H), 7.95 (d, J = 7.9 Hz, 1H), 7.55 (ddd, J = 8.0, 6.0, 2.0 Hz, 1H), 7.51 (d, J = 9.2 Hz, 1H), 7.34-7.26 (m, 3H), 7.08 (d, J = 8.8 Hz, 1H), 4.49 (ddd, J = 10.8, 10.8, 4.4 Hz), 3.77 (s, 3H), 1.54-1.16 (m, 6H), 0.90-0.45 (m, 11H), -0.19 (q, J = 11.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.7, 167.2, 156.0, 135.7, 135.6, 135.3, 132.9, 130.4, 129.9, 128.4, 128.3, 127.8, 127.6, 127.3, 126.9, 126.6, 126.0, 125.7 (q, J = 4.6 Hz), 122.7, 122.2 (q, J = 3.1 Hz), 114.3, 74.5, 56.4, 46.8, 40.0, 34.2, 31.1, 25.8, 22.9, 21.9, 21.0, 15.8.



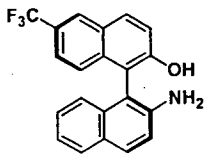
2'-Methoxy-6'trifluoromethyl-1,1'-binaphthalene-2-carboxylic acid. To a solution of (-)-menthyl-2'-methoxy-6'-triflouromethyl-1,1'-binaphthylene-2-carboxylate (**7**) (9.00 g, 16.8 mmol) in EtOH (170 mL) was added KOH (18.9 g, 336 mmol). This solution was allowed to stir at reflux for 20 h, and was then concentrated until most of the solvent had been evaporated (10-20 mL remaining). To the mixture was added H_2O (50 mL) followed by addition of 20% aqueous solution of HCl until the solution reached a pH < 2. The aqueous layer was washed three times with Et_2O (50 mL). The organic layers were combined, dried over $MgSO_4$, filtered and concentrated. The resulting solid was heated in a Kughelrohr at 130 °C in vacuum for 3 h to remove (-)-menthol by distillation. The remaining solid was used in the following step without

further purification. IR (neat): 3063 (br), 2958 (br), 2848 (w), 2637 (br), 2547 (br), 1696 (s), 1633 (w), 1603 (w), 1488 (m), 1467 (m), 1309 (s), 1277 (s), 1252 (s), 1208 (m), 1196 (m), 1182 (m), 1154 (m), 1121 (s), 1086 (m), 1071 (s), 770 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.2 (br, 1H), 8.16 (d, J = 8.8 Hz, 2H), 8.07 (d, J = 9.2 Hz, 1H), 8.01 (d, J = 8.8 Hz, 1H), 7.95 (d, J = 8.1 Hz, 1H), 7.56 (dd, J = 7.6, 7.6 Hz, 1H), 7.46 (d, J = 9.1 Hz, 1H), 7.33-7.26 (m, 2H), 7.17 (d, J = 8.8 Hz, 1H), 6.99 (d, J = 8.8 Hz, 1H), 3.71 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.2, 155.9, 137.6, 135.8, 135.1, 132.9, 130.6, 128.4, 128.3, 128.3, 127.5, 127.1, 126.6, 126.0, 122.1, 122.0, 114.5, 56.5.

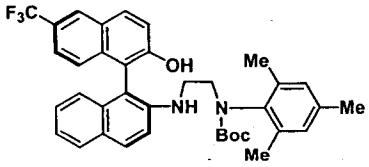


2-Amino-2'-methoxy-6'-trifluoromethyl-1,1'-binaphthalene. A 250 mL round-bottom flask was charged with 2'-methoxy-6'-trifluoromethyl-1,1'-binaphthalene-2-carboxylic acid (6.65 g, 16.8 mmol), acetone (87 mL), Et_3N (2.67 mL, 19.0 mmol), and the solution was cooled to -15 °C (CO_2/ethylene glycol bath). The subsequent dropwise addition of ethyl chloroformate (2.00 mL, 20.8 mmol) over 10 min caused a cloudy white precipitate to form. This suspension was allowed to stir for 30 min at -15 °C, at which time a solution of NaN_3 (3.37 g, 51.9 mmol) in water (17 mL) was added. After an additional 90 min at -15 °C, the mixture was diluted with water (150 mL) and the aqueous layer was washed three times with cold (4 °C) benzene (125 mL). The combined organic layers were washed with a cold saturated sodium chloride solution (400 mL), dried over $MgSO_4$, and filtered directly into a 500 mL round bottom flask containing activated 4 Å molecular sieves (1.0 g). This vessel was equipped with a reflux condenser and the bronze colored solution was heated at reflux for 2 h. The mixture was allowed to cool to 22 °C, and was filtered into another 500 mL round bottom flask containing a solution of KOH (48.5 g, 865 mmol) in water (85 mL). The resulting biphasic mixture was stirred vigorously for 16 h. Et_2O (100-200 mL) was then added to dissolve the precipitate in the organic layer. The isolated aqueous layer was washed two times with Et_2O (100 mL). The organic layers were combined and dried over $MgSO_4$, filtered, and absorbed onto silica gel (8-10 g). Residual solvent was removed from the slurry under reduced pressure. The product-laden silica gel was loaded onto a silica gel column and the product eluted with 3:1 hexanes:EtOAc (R_f = 0.24) to deliver the product as a white solid (5.20 g, 14.2 mmol, 84%). IR (neat): 3474 (w), 3384 (m), 3054 (w), 3012 (w), 2949 (w), 2844 (w), 1621 (s), 1598 (s), 1513 (s), 1487 (s), 1434 (m), 1380 (s), 1344 (s), 1305 (s), 1279 (s), 1263 (s), 1209 (s), 1195 (s), 1181 (s), 1120 (s), 1071 (s), 1044 (m), 915 (m), 901 (m), 831 (s), 815 (s), 748 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (s, 1H), 8.10 (d, J = 9.2 Hz, 1H), 7.80 (dd, J = 8.8, 8.8 Hz, 2H), 7.57 (d, J = 9.1 Hz, 1H), 7.40 (dd, J = 8.9, 1.8 Hz, 1H), 7.30, (d, J = 8.9 Hz, 1H), 7.25-7.16 (m, 3H), 6.90 (d, J = 8.4 Hz, 1H), 3.83 (s, 3H), 3.55 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.3, 142.3, 135.3, 134.2, 131.2, 129.6, 128.4, 128.4,

128.3, 126.7, 126.4, 126.2 (q, J = 4.5 Hz), 124.127, 122.7 (q, J = 3.0 Hz), 122.5, 119.3, 118.4, 115.4, 56.9.

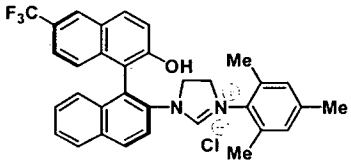


2-Amino-2'-hydroxy-6'-trifluoromethyl-1,1'-binaphthalene (8). To a solution of 2-amino-2'-methoxy-6'-trifluoromethyl-1,1'-binaphthalene (0.520 g, 1.42 mmol) in CH_2Cl_2 (14 mL) in a 25 mL round-bottom flask at 0 °C was added BBr_3 (535 μL, 5.66 mmol, 4.0 equiv) dropwise over 10 min, at which point the solution turned slightly yellow in color. The mixture was allowed to warm to 22 °C and to stir for 2 h. The mixture was cooled to 0 °C and equipped with a reflux condenser. To this solution was added 30% aqueous solution of NH_4OH (5 mL) carefully and quickly. The mixture was diluted with water (40 mL) and CH_2Cl_2 (40 mL). The aqueous layer was washed two times with CH_2Cl_2 (40 mL). (Note: speed in work-up led to increased yields.) If the biphasic mixture was left standing for prolonged period of time, the work-up is complicated by the formation of an insoluble solid. The combined organic layers were dried over $MgSO_4$, filtered, and absorbed onto silica gel. Residual solvent was removed from the slurry under reduced pressure. The product-laden silica gel was loaded onto a silica gel column and the product eluted with 3:1 hexanes:EtOAc (R_f = 0.21) to deliver the product as a white solid (450 mg, 1.27 mmol, 90%). IR (neat): 3479 (br), 3385 (br), 3060 (br), 1622 (s), 1602 (m), 1513 (w), 1481 (m), 1383 (m), 1350 (m), 1310 (s), 1289 (m), 1267 (w), 1251 (w), 1215 (s), 1177 (s), 1147 (s), 1124 (s), 1090 (w), 1071 (m), 1001 (w), 936 (w), 903 (w), 818 (m), 737 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19-8.15 (m, 1H), 8.02 (d, J = 8.8 Hz, 1H), 7.88 (d, J = 8.8 Hz, 1H), 7.82 (dd, J = 7.5, 1.7 Hz, 1H), 7.51-7.41 (m, 2H), 7.30-7.22 (m, 3H), 7.16 (d, J = 8.9 Hz, 1H), 7.00-6.96 (m, 1H), 5.31 (s, 1H), 3.73 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.8, 143.9, 134.9, 134.1, 131.4, 131.1, 128.5, 128.5, 128.4, 127.7, 126.2 (q, J = 4.2 Hz), 125.7, 123.5, 123.1, 122.7 (q, J = 3.2 Hz), 119.3, 199.3, 118.3, 114.8, 114.7, 107.7. HRMS Calcd for $C_{21}H_{14}F_3NO$: 353.1027. Found: 353.1028.



Chiral Boc-diamine. 2-Amino-2'-hydroxy-6'-trifluoromethyl-1,1'- binaphthalene (**8**) (684 mg, 1.93 mmol) and sodium triacetoxyborohydride (818 mg, 3.86 mmol) were added as solids to a 50 mL round-bottom flask and suspended in 19 mL of 1,2-dichloroethane. A solution of *N*-(*tert*-butyloxycarbonyl)-N-(formylmethyl)-2,4,6-trimethylphenylamine[3] (642 mg, 2.32 mmol) in 1,2-dichloroethane (8 mL) was then introduced dropwise over a period of 1 h by a gas-tight syringe. After 1 h of additional stirring, the mixture was diluted with saturated aqueous solution of $NaHCO_3$ (50 mL) and CH_2Cl_2 (50 mL). The isolated aqueous layer was washed twice with CH_2Cl_2 (50 mL). The

combined organic layers were dried over $MgSO_4$, filtered, and concentrated. Purification by silica gel chromatography in 2:1 hexanes: Et_2O (R_f = 0.26) delivered the protected diamine as a white foam (1.02 g, 1.66 mmol, 86%). In $CDCl_3$ at 25 °C, this material exists as a 4:1 mixture of amide rotamers. IR (neat): 3383 (br), 3056 (w), 2987 (m), 2930 (m), 2861 (w), 1688 (s), 1618 (s), 1599 (s), 1479 (s), 1394 (s), 1367 (s), 1313 (s), 1206 (s), 1178 (s), 1150 (s), 1123 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16-8.11 (m, 1H), 7.98 (d, J = 8.8 Hz, 1H), 7.92 (d, J = 9.0 Hz, 1H), 7.81-7.76 (m, 1H), 7.45 (d, J = 8.9 Hz, 1H), 7.42-7.32 (m, 1H), 7.27-7.14 (m, 3H), 6.88-6.75 (m, 2H), 5.34 (s, 1H), 5.27 (s, 1H), 4.25 (br, 1H), 3.71-3.58 (m, 1H), 3.42-3.30 (m, 3H), 2.23 (s, 3H), 2.20 (s, minor 3H), 2.08 (s, minor 3H), 2.06 (s, minor 3H), 2.03 (s, 3H), 1.98 (s, 3H), 1.49 (s, minor 9H), 1.15 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.6, 154.1, 145.2, 144.9, 137.5, 137.2, 136.7, 135.7, 135.4, 135.3, 135.2, 134.3, 131.4, 131.3, 129.6, 129.2, 129.1, 128.5, 127.7, 127.6, 127.5, 126.3 (q, J = 4.6 Hz), 125.7, 125.6, 125.4, 123.3, 122.7, 122.5, 122.3, 119.3, 119.3, 114.7, 113.6, 113.5, 106.7, 80.6, 79.8, 49.0, 42.8, 34.8, 31.7, 28.6, 28.2, 25.4, 22.8, 21.0, 18.1, 17.9, 14.2.



Chiral imidazolinium salt (9). The Boc-diamine (1.02 mg, 1.67 mmol) was dissolved in methanol (16 mL) in a 50 mL round-bottom flask and the resulting colorless solution was cooled to –78 °C. Anhydrous HCl was gently bubbled through the solution for 5 min. The reaction was then allowed to warm to 22 °C and the solvent was removed at reduced pressure. This delivered an off-white solid, which was rigorously dried (12 h) under vacuum in an Abderhalden pistol containing P_2O_5 over refluxing isopropanol. HRMS Calcd for $C_{32}H_{30}F_3N_2O$ (M-2Cl-H): 515.2310. Found: 515.2311.

The off-white solid was suspended in triethylorthoformate (12 mL) in a 25 mL round bottom flask. The vessel was equipped with a short-path distillation head and submerged into an oil bath preheated to 125 °C. The mixture was stirred at 125 °C and the distillation head was heated periodically (approximately every 30 min) with a heat gun until ethanol no longer distilled over (typically 4 h). After cooling the flask to 22 °C, the mixture was diluted with 30 mL of Et_2O and filtered. The precipitate was washed with additional Et_2O (2 x 10 mL) and dried under vacuum (12 h) in an Abderhalden pistol charged with P_2O_5 over refluxing isopropanol to give an off white solid (750 mg, 1.34 mmol, 81%). IR (neat): 3371 (br), 2960 (br), 2603 (w), 1675 (w), 1630 (s), 1563 (m), 1486 (s), 1428 (w), 1354 (m), 1312 (s), 1260 (s), 1199 (s), 1168 (m), 1156 (m), 1120 (s), 1068 (m), 944 (m), 828 (m), 734 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.14 (br, 1H), 8.13-8.05 (m, 2H), 7.93 (d, J = 9.0 Hz, 1H), 7.81-7.71 (m, 3H), 7.50 (t, J = 7.3 Hz, 1H), 7.36 (s, 1H), 7.31-7.26 (m, 2H), 7.13 (d, J = 8.6 Hz, 1H), 6.92 (d, J = 8.6 Hz, 1H), 6.73 (br, 2H), 4.82-4.74 (m, 1H), 4.34-4.17 (m, 2H), 3.82-3.74 (m, 1H), 2.19 (s,

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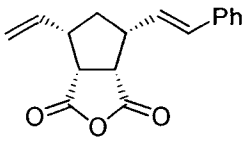
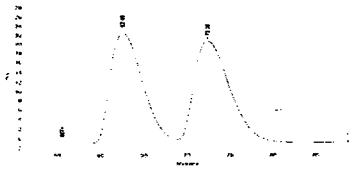
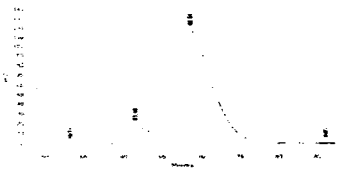
3H), 1.75 (br, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.1, 140.7, 135.5, 133.6, 132.9, 132.3, 131.6, 130.5, 130.0, 129.9, 129.9, 128.6, 127.8, 127.5, 127.3, 127.1, 126.6, 126.5, 126.5, 124.4, 122.9, 122.1, 122.0, 113.6, 52.3, 51.5, 21.1, 17.5. HRMS Calcd for $C_{33}H_{28}F_3N_2O$ (M-Cl): 525.2154. Found: 525.2156.



78% ee



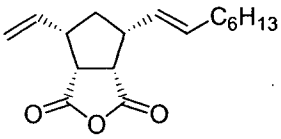
authentic racemic



from asymmetric reaction

95:5 hexanes:2-propanol, 0.65 mL/min, Chiralcel AS, 240 nm

Representative procedure for AROM/CM of *cis*-5-norbornene-*endo*-2,3-dicarboxylic anhydride. *cis*-5-Norbornene-*endo*-2,3-dicarboxylic anhydride (15.2 mg, 92.6 μmol) and styrene (43 μL, 0.46 mmol) were combined in a 3 mL vial in a glovebox. The vial was removed from the box and **3d** (3.70 mg, 4.50 μmol) was added as a solution in THF (0.93 mL). The vial was sealed under N_2 and allowed to stir for 25 min. The volume of solvent was reduced by a gentle stream of N_2. This concentrated THF solution was loaded directly onto a silica gel column, and the product eluted with 5:1 hexanes:EtOAc (R_f = 0.16, 20.3 mg, 76.0 μmol, 82%) to afford a white solid, and the catalyst as a brown solid (R_f = 0.20, 2.5 mg, 3.1 μmol, 68%).



4-Octyl -1- enyl - 6 -vinyltetrahydrocyclopenta[c]furan - 1,3 -dione (11b). The procedure for AROM/CM of *cis*-5-norbornene-*endo*-2,3-dicarboxylic anhydride was followed. IR (neat): 3092 (w), 2926 (br), 2855 (s), 1855 (s), 1778 (s), 1458 (m), 1204 (s), 1004 (s), 920 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.95 (ddd, J = 16.7, 10.8, 7.5 Hz, 1H), 5.59 (dt, J = 15.4, 6.6 Hz, 1H), 5.40 (dd, J = 15.3, 7.4 Hz, 1H), 5.19 (ddd, J = 10.8, 1.5, 1.5 Hz, 1H), 5.17 (ddd, J = 16.7, 1.5, 1.1 Hz, 1H), 3.48 (dd, J = 16.8, 8.2 Hz, 1H) 3.43 (dd, J = 16.8, 8.2 Hz, 1H), 3.01-2.94 (m, 2H), 2.07-1.98 (m, 3H), 1.48-1.27 (m, 9H), 0.88 (t, J = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.0, 170.7, 135.2, 134.0, 126.3, 117.3, 49.7, 49.7, 46.8, 46.1, 36.7, 32.6, 31.8, 29.3, 28.9, 22.8, 14.2. HRMS calcd for: [$C_{17}H_{24}O_3$ + Na]: 299.16. Found: 299.16.

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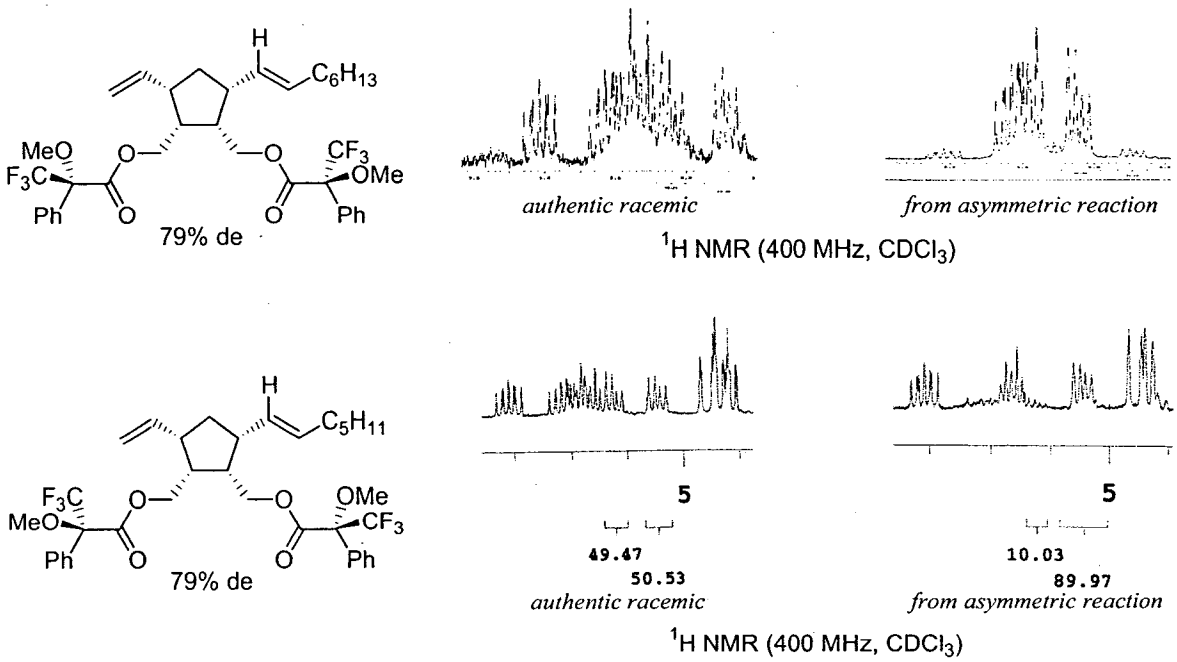
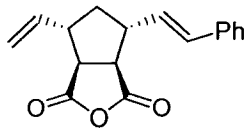
Enantiopurity of **11b** was determined by analysis of ^{1}H NMR spectrum of the corresponding (*R*)-MTPA or (*S*)-MTPA ester after reduction (LAH, Et_2O) and esterification [(*R*)-MTPA-Cl, DMAP, CH_2Cl_2].[5]



Representative Procedure for AROM/CM of *cis*-5-norbornene-*exo*-2,3-dicarbonyl anhydride: To a solution of *cis*-5-norbornene-*exo*-2,3-dicarboxyl anhydride (45.5 mg, 0.277 mmol) and styrene (65.0 μL, 0.567 mmol, 2.0 equiv) in THF (0.80 mL) in a 10 mL round bottom flask was added a solution of Ru catalyst **3** (9.8 mg,, 0.013 mmol, 5 mol%) in THF (0.30 mL) at 22 °C under an atmosphere of nitrogen. The solution was allowed to stir for 1 h, and the mixture was concentrated to dryness. The resulting residue was purified by silica gel column chromatography (CH_2Cl_2) to separate recovered catalyst (9.4 mg) from the organic mixture (52.6 mg). The product was further purified by silica gel chromatography in 10:1 hexane:EtOAc (R_f= 0.12) to give a colorless oil (47.1 mg, 0.175 mmol, 63%).



4-Styryl-6-vinyltetrahydrocyclopenta[*c*]furan-1,3-dione (13a). The general procedure for AROM/CM of *cis*-5-norbornene-*exo*-2,3-dicarbonyl anhydride to afford a colorless oil, after silica gel chromatography in 10:1 hexane:EtOAc (R_f = 0.12). IR (NaCl): 2981 (m), 1854 (m), 1775 (s),

(5) Ward. D. E.; Rhee, C. K. *Tetrahedron Lett.* **1991**, *32*, 7165-7166.

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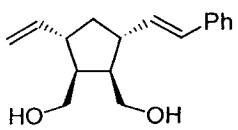
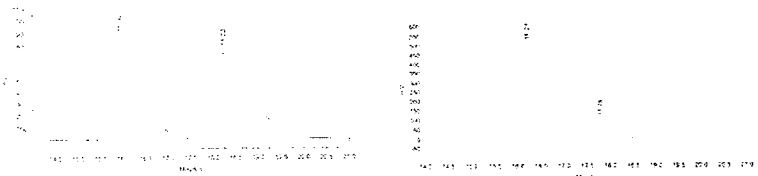
1640 (w), 1205 (m), 1003 (m), 920 (m), 751 (w). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40–7.22 (m, 5H), 6.57 (d, J = 15.7 Hz, 1H), 6.22 (dd, J = 15.7, 7.2 Hz, 1H), 5.91 (ddd, J = 17.0, 10.3, 6.8 Hz, 1H), 5.26 (ddd, J = 17.0, 1.1, 1.1 Hz, 1H), 5.19 (ddd, J = 10.3, 1.1, 1.1 Hz), 3.35 (dd, J = 9.9, 7.9 Hz, 1H), 3.31 (dd, J = 9.9, 7.9 Hz, 1H), 3.15–3.04 (m, 1H), 3.02–2.92 (m, 1H), 2.30 (ddd, J = 12.6, 6.2, 6.2 Hz, 1H), 1.76 (ddd, J = 12.6, 11.5, 11.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.15, 137.40, 136.52, 132.10, 128.79, 128.00, 126.51, 117.06, 51.77, 51.28, 47.89, 47.39, 42.17; HRMS Calcd for $C_{17}H_{16}O_3Na$ (M+Na+): 291.0997. Found: 291.0993.

Enantiopurity of **13a** was determined by analysis of HPLC spectrum of the corresponding alcohol after reduction (LAH, Et_2O).

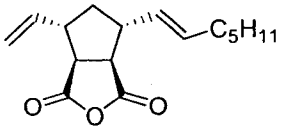


70% ee



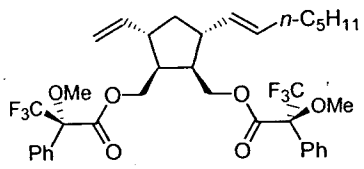
authentic racemic *from asymmetric reaction*

95:5 hexanes:2-propanol, 1.0 mL/min, Chiralcel OD, 254 nm



4 - (1 - Heptenyl) - 6 - vinyltetrahydrocyclopenta[*c*]furan -1,3-dione (13b). The general procedure for AROM/CM of *cis*-5-norbornene-*exo*-2,3-dicarbonyl anhydride to afford a colorless oil, after silica gel chromatography in 20:1 hexane:EtOAc (R_f = 0.10). IR (NaCl): 2927 (m), 2856 (m), 1854 (m), 1778 (s), 1642 (w), 1457 (w), 1205 (m), 1004 (m), 919 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.95 (ddd, J = 17.6, 9.8, 7.3 Hz, 1H), 5.58 (ddt, J = 15.4, 0.7, 6.6 Hz, 1H), 5.49 (ddt, J =15.4, 7.3, 1.2, 1H), 5.17 (ddd, J = 9.8, 1.2, 1.2 Hz, 1H), 5.17 (ddd, J = 17.6, 1.2, 1.2 Hz, 1H), 3.47 (dd, J = 8.3, 8.3 Hz, 1H), 3.43 (dd, J = 8.3, 8.3 Hz, 1H), 3.02–2.90 (m, 2H), 2.07–1.96 (m, 3H), 1.42 (ddd, J = 12.9 Hz, 1H), 1.42–1.21 (m, 7H), 0.88 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.97, 170.72, 135.17, 133.89, 126.34, 117.23, 49.70, 49.67, 16.77, 46.08, 36.70, 32.49, 31.43, 28.96, 22.60, 14.15. HRMS Calcd for $C_{16}H_{22}O_3Na$ ($M+Na^+$): 285.1467. Found: 285.1471.

Enantiopurity of **13b** was determined by analysis of HPLC spectrum of the corresponding (*R*)-MTPA ester after reduction (LAH, Et_2O) and esterification [(*R*)-MTPA-Cl, DMAP, CH_2Cl_2].



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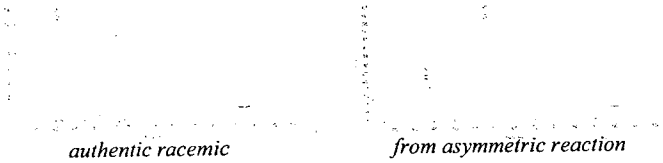
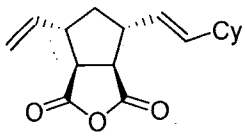
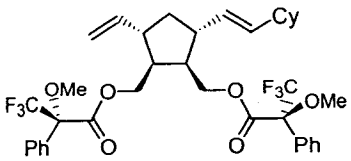


hexanes, 0.15 mL/min, Chiralcel AS, 210 nm



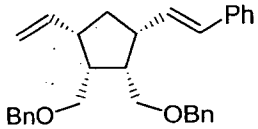
4-(2-Cyclohexylvinyl)-6-vinyltetrahydrocyclopenta[*c*]furan-1,3-dione (13c). The general procedure for AROM/CM of *cis*-5-norbornene-*exo*-2,3-dicarbonyl anhydride was followed to afford a clear colorless oil, after silica gel chromatography in 20:1 hexane:EtOAc (R_f = 0.10). IR (NaCl): 2924 (m), 2851 (m), 1855 (m), 1778 (s), 1641 (w), 1449 (m), 1203 (m), 1004 (m), 919 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.96 (ddd, J = 16.6, 10.8, 7.3 Hz, 1H), 5.53, (dd, J = 15.4, 6.1 Hz, 1H), 5.45 (dd, J = 15.4, 7.1 Hz, 1H), 5.18 (ddd, J = 10.8, 1.0, 1.0 Hz, 1H), 5.17 (ddd, J = 16.6, 1.0, 1.0 Hz, 1H), 3.47 (dd, J = 8.1, 8.1 Hz, 1H), 3.43 (dd, J = 8.1, 8.1 Hz, 1H), 3.02–2.89 (m, 2H), 2.05–1.92 (m, 1H), 2.01 (ddd, J = 12.9, 5.6, 5.6 Hz, 1H), 1.77–1.58 (m, 4H), 1.42 (ddd, 12.9, 12.9, 12.9 Hz, 1H), 1.34–0.99 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.99, 170.64, 139.53, 135.19, 124.03, 117.25, 49.79, 49.70, 46.85, 46.06, 40.65, 36.67, 32.99, 32.96, 26.26, 26.12. HRMS Calcd for $C_{17}H_{22}O_3Na$ ($M+Na^+$): 297.1467. Found: 297.1468.

Enantiopurity of **13c** was determined by analysis of HPLC spectrum of the corresponding (*R*)-MTPA ester after reduction (LAH, Et_2O) and esterification [(*R*)-MTPA-Cl, DMAP, CH_2Cl_2].



74% de

hexanes, 0.15 mL/min, Chiralcel AS, 210 nm



2,3-Bis(benzyloxymethyl)-1- styryl - 4 - vinylcyclopentane (15a). The general procedure for AROM/CM of *cis*-5-norborne ne-*endo*-2,3-dicarbonyl anhydride to afford a colorless oil, after silica gel chromatography in 50:1 hexanes:EtOAc (R_f = 0.12). IR (NaCl): 3027 (m), 2908(m), 2862 (m), 1637 (w), 1453 (w), 1364 (w), 1094 (m), 1072 (m), 1027 (w), 911 (w), 746 (m), 696 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37–7.12 (m, 15H), 6.31 (d, J = 15.7 Hz, 1H), 6.23 (dd, J = 15.7, 8.4 Hz, 1H), 5.91 (ddd, J = 17.2, 10.1, 8.4 Hz, 1H), 5.03 (ddd, J = 17.2, 1.0, 1.0 Hz, 1H), 4.97 (ddd, J = 10.1, 1.0, 1.0 Hz, 1H), 4.40 and 4.36 (ABq, J = 12.5 Hz, 2H),

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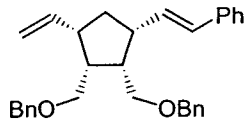
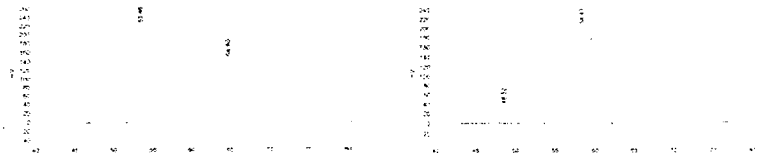
4.39 and 4.35 (Abq, J = 14.5 Hz, 2H), 3.58–3.42 (m, 4H) 2.91 (dddd, J.= 8.4, 8.4, 8.4, 8.4 Hz, 1H), 2.78 (dddd, J = 8.4, 8.4, 8.4, 8.4 Hz, 1H), 2.61–2.39 (m, 2H), 2.03 (ddd, J = 12.8, 8.4, 8.4 Hz, 1H), 1.74 (ddd, J = 12.8, 10.1, 10.1 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.67, 138.65, 137.98, 133.32, 129.50, 128.51, 128.48, 128.40, 128.07, 128.01, 127.64, 127.58, 126.80, 126.15, 114.57, 73.49, 73.39, 69.03, 68.89, 46.25, 45.91, 45.79, 44.74, 38.00. HRMS Calcd for $C_{31}H_{34}O_2Na$ (M+Na$^+$): 461.2457. Found: 461.2452.

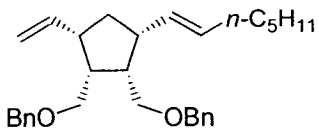


88% ee



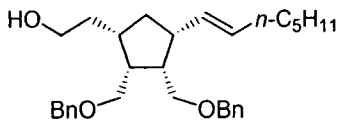
authentic racemic *from asymmetric reaction*

hexanes, 0.2 mL/min, Chiralcel AS, 254 nm



(1*R*,2*S*,3*R*,4*S*) - 2,3 - Bis(benzyloxymethyl) - 1 - (hept -1-enyl) -4-vinylcyclopentane (15b). The general procedure for AROM/CM of *cis*-5-norbornene-*endo*-2,3-dicarbonyl anhydride to afford a colorless oil, after silica gel chromatography in 50:1 hexane:EtOAc (R_f = 0.15). IR (neat): 2955 (m), 2934 (br), 2848 (br), 1451 (w), 1357 (w), 1099 (br), 1067 (w), 910 (w), 734 (m), 696 (m), 664 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.26 (m, 10H), 5.92–5.83 (ddd, J = 17.2, 10.0, 8.4 Hz, 1H), 5.40-5.34 (m, 2H), 5.02-4.96 (dt, J = 17.0, 1.8 Hz, 1H), 4.94-4.91 (dt, J = 10.2, 1.1 Hz, 1H), 4.43-4.34 (m, 4H), 3.51-3.43 (m, 4H), 2.80-2.61 (m, 2H), 2.47-2.37 (m, 2H), 1.99-1.92 (m, 3H), 1.61-1.52 (m, 1H), 1.35-1.20 (m, 6H), 0.91-0.87 (t, J = 7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.27, 139.01, 132.41, 130.85, 128.59, 128.19, 128.15, 127.76, 114.36, 73.52, 69.32, 69.32, 46.14, 45.93, 45.73, 44.49, 38.00, 32.87, 31.94, 31.75, 29.64, 23.00, 22.88, 14.46. HRMS Calcd for $C_{30}H_{40}O_2Na$: 455.2926. Found: 455.2926.

Enantiopurity of **15b** was determined by analysis of HPLC spectrum of the corresponding alcohol after hydroboration-oxidation (Sia_2BH or 9-BBN, THF then H_2O_2, aq. NaOH).



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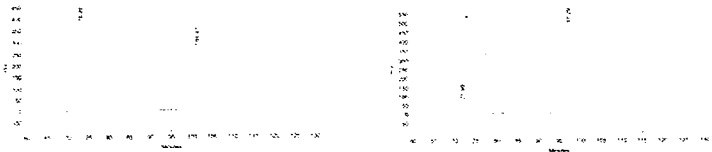

authentic racemic *from asymmetric reaction*

95:5 hexanes:2-propanol, 0.1 mL/min, Chiralcel AD, 210 nm

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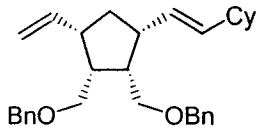
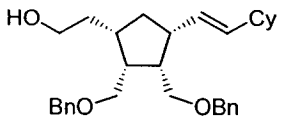
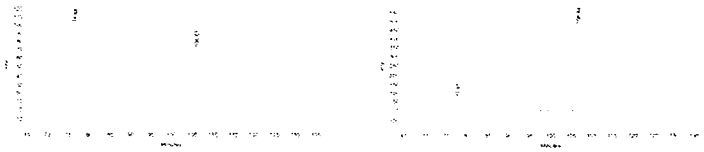


(1*R*,2*S*,3*R*,4*S*) - 2,3 - Bis(benzyloxymethyl) - 1 - (2-cyclohexylvinyl) -4-vinylcyclopentane (15c). The general procedure for AROM/CM of *cis*-5-norbornene-*endo*-2,3-dicarbonyl anhydride to afford a colorless oil, after silica gel chromatography in 50:1 hexane:EtOAc (R_f = 0.15). IR (neat): 3062 (w), 3031 (w), 2924 (s), 2848 (s), 1722 (w), 1455 (m), 1363 (m), 1092 (s), 734 (s), 696 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.24 (m, 10H), 5.91-5.82 (ddd, *J* = 17.1, 10.1, 8.3 Hz, 1H), 5.34-5.32 (m, 2H), 5.00-4.95 (dq, *J* = 17.2, 1.1 Hz, 1H), 4.95-4.90 (dd, *J* = 10.3, 0.9 Hz, 1H), 4.42-4.32 (m, 4H), 3.50-3.41 (m, 4H), 2.75-2.66 (m, 2H), 2.43-2.34 (m, 2H), 1.97-1.90 (m, 1H), 1.88-1.78 (m, 1H), 1.77-1.52 (m, 6H), 1.33-1.10 (m, 3H), 1.05-0.90 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.25, 138.99, 136.72, 129.90, 128.67, 128.57, 128.20, 128.19, 127.94, 127.74, 114.35, 73.52, 69.28, 69.23, 46.15, 45.99, 45.94, 45.78, 44.36, 40.92, 38.03, 33.60, 33.58, 26.57, 26.47.

Enantiopurity of **15c** was determined by analysis of HPLC spectrum of the corresponding alcohol after hydroboration-oxidation (Sia_2BH or 9-BBN, THF then H_2O_2, aq. NaOH).

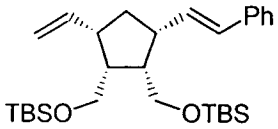


89% ee



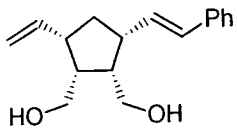
authentic racemic *from asymmetric reaction*

95:5 hexanes:2-propanol, 0.1 mL/min, Chiralcel AD, 210 nm



2,3 - Bis (tert - butyldimethylsilyloxymethyl) - 1 - styrenyl - 4 - vinylcyclopentane (17). The general procedure for AROM/CM of *cis*-5-norbornene-*endo*-2,3-dicarbonyl anhydride to afford a clear colorless oil, after silica gel chromatography in 100:1 hexane:EtOAc (R_f= 0.13). IR (neat): 2955 (s), 2930 (s), 2855 (s), 1470 (m), 1256 (s), 1073 (s), 841 (s), 771 (s), 690 (w). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.25 (m, 4H), 7.20-7.16 (m, 1H), 6.36-6.34 (m, 2H), 5.99-5.90 (ddd, *J* = 17.1, 10.0, 8.5 Hz, 1H), 5.03-4.98 (dq, *J* = 17.1, 1.0 Hz, 1H), 4.96-4.93 (dd, *J* = 10.0, 2.2 Hz, 1H), 3.73-3.69 (m, 4H), 2.93-2.84 (m, 1H), 2.79-2.71 (m, 1H), 2.39-2.30 (m, 2H), 2.04-1.97 (m, 1H), 1.81-1.72 (m, 1H), 0.91-0.87 (m, 18H), 0.07-0.00 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.20, 138.32, 133.51, 129.80, 128.73, 127.01, 126.36, 114.31, 61.64, 61.54, 48.76, 48.11, 45.76, 45.19, 38.36, 26.33, 26.29, 18.59, 18.53. HRMS Calcd for $C_{29}H_{50}O_2Si_2Na$: 509.3247. Found: 509.3247.

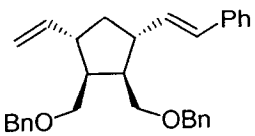
Enantiopurity of **17** was determined by analysis of HPLC spectrum of the corresponding alcohol after desilylation (aq. HCl, THF).



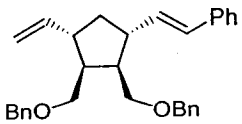
80% ee

authentic racemic *from asymmetric reaction*

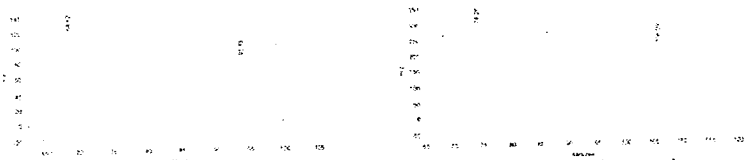
95:5 hexanes:2-propanol, 1.0 mL/min, Chiralcel OD, 254 nm



2,3-Bis(benzyloxymethyl)-1-styryl-4-vinylcyclopentane (21). The general procedure for AROM/CM of *cis*-5-norbornene-*exo*-2,3-dicarbonyl anhydride to afford a colorless oil, after silica gel chromatography in 50:1 hexane:EtOAc (R_f = 0.15). IR (NaCl): 3027 (m), 2860 (m), 1637 (w), 1454 (m), 1093 (m), 747 (m), 696 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39–7.17 (m, 15H), 6.36 (d, J = 15.8 Hz, 1H), 6.17 (dd, J = 15.8, 8.2 Hz, 1H), 5.81 (ddd, J = 17.0, 10.1, 8.1 Hz, 1H), 5.02 (ddd, J = 17.0, 1.8, 0.9 Hz, 1H), 4.96 (ddd, J = 10.1, 1.8, 0.7 Hz, 1H), 4.51–4.36 (m, 4H), 3.63–3.56 (m, 4H), 2.75–2.63 (m, 1H), 2.63–2.50 (m, 1H), 2.30–2.14 (m, 2H), 2.07 (ddd, J = 12.5, 6.6, 6.6 Hz), 1.43 (ddd, J = 12.5, 10.8, 10.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.59, 138.87, 138.83, 137.81, 134.59, 129.34, 128.60, 128.48, 128.43, 128.42, 127.82, 127.78, 127.74, 127.57, 127.02, 126.15, 113.84, 73.19, 73.16, 70.72, 70.24, 47.15, 46.48, 46.45, 45.87, 45.58, 40.03, 39.93, 33.63, 29.69. HRMS Calcd for $C_{31}H_{34}O_2Na$ ($M+Na^+$): 461.2457. Found: 461.2453.

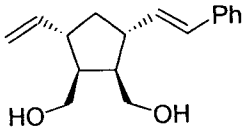


10% ee



authentic racemic *from asymmetric reaction*

99.5:0.5 hexanes:2-propanol, 0.2 mL/min, Chiralcel OD, 254 nm



(1*R*,2*R*,3*S*,4*S*) - 2,3 – Bis (hydroxymethyl) - 1 - styryl - 4 - vinylcyclopentane (23). The general procedure for AROM/CM of *cis*-5-norbornene-*exo*-2,3-dicarbonyl anhydride to afford a colorless oil, after silica gel chromatography in 4:1 hexanes:EtOAc (R_f = 0.10). IR (NaCl): 3292 (br), 2920 (m), 1638 (w), 1448 (w), 965 (w), 748 (m), 694 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37–7.17 (m, 5H), 6.38 (d, J = 15.6 Hz, 1H), 6.12 (dd, J = 15.6, 8.5 Hz, 1H), 5.75 (ddd, J = 17.1, 10.2 Hz, 1H), 5.03 (d, J = 17.1 Hz, 1H), 4.99 (d, J = 10.2 Hz, 1H), 3.82–3.66 (m, 4H), 3.40 (br, 1H), 3.39 (br,

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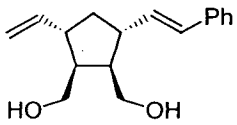
1H), 2.41–2.29 (m, 1H), 2.28–2.08 (m, 3H), 1.99 (ddd, J = 11.7, 6.1, 6.1 Hz, 1H), 1.40 (ddd, J = 11.7, 11.7, 11.7 hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.49, 137.47, 133.34, 130.13, 128.68, 127.28, 126.18, 62.07, 62.04, 49.18, 48.76, 46.29, 45.55, 39.79. HRMS Calcd for $C_{17}H_{22}O_2Na$ ($M+Na^+$): 281.1517. Found: 281.1510.

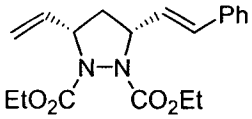


11% ee

authentic racemic *from asymmetric reaction*

97:3 hexanes:2-propanol, 1.0 mL/min, Chiralcel OD, 254 nm

Representative procedure for AROM/CM of 2,3-diazabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate. To a solution of diethyl-2,3-diazabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate (25.4 mg, 0.106 mmol) and styrene (25.0 μL, 0.218 mmol) in THF (0.70 mL) in a 10 mL two-necked round-bottom flask equipped with a reflux condenser at 50 °C was added a solution of Ru catalyst **3d** (4.10 mg, 5.10 μmol) in THF (0.30 mL). The reaction was allowed to stir for 3 h. A second portion of catalyst **3d** (4.30 mg, 5.30 μmol) in THF (0.30 mL) was added and the reaction was allowed to stir for an additional 3h. The mixture was then allowed to cool to 22 °C and concentrated in vacuo. The product was purified by silica gel chromatography.



3-Styryl-5-vinylpyrazolidine-1,2-dicarboxylic acid diethyl ester (26a). The general procedure for AROM/CM of 2,3-diazabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate was followed to afford a colorless oil, after silica gel chromatography in 7:1 hexanes:EtOAc (R_f = 0.10). IR (neat): 2981 (m), 1712 (s), 1410 (m), 1376 (m), 1304 (m), 1175 (m), 1127 (w), 1029 (w), 750 (m), 694 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.20 (m, 5H), 6.62 (d, J = 15.9 Hz, 1H), 6.17 (dd, J =15.9, 6.8 Hz, 1H), 5.88 (ddd, J = 16.9, 10.4, 6.6 Hz, 1H), 5.35 (d, J = 16.9 Hz, 1H), 5.16 (d, J = 10.4 Hz, 1H), 4.72 (br, 1H), 4.60 (br, 1H), 4.28-4.14 (m, 4H), 2.59 (ddd, J = 12.8, 8.4, 8.4 Hz, 1H), 1.97 (ddd, J = 12.8, 3.9, 3.9 Hz,1H), 1.28 (t, J = 7.1 Hz, 3H), 1.24 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.1, 136.9, 136.6, 128.7, 128.2, 127.8, 126.6, 116.1, 62.4, 60.9, 60.7, 40.3, 14.6, 14.6. HRMS Calcd for $C_{19}H_{24}N_2O_4Na$ [M+Na]: 367.1634. Found: 367.1634.

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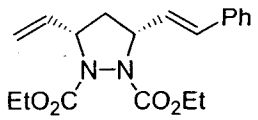
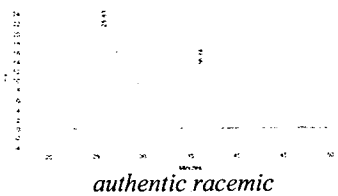


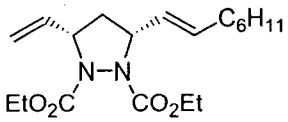
92% ee



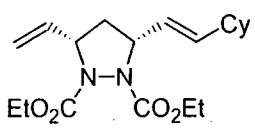
authentic racemic

from asymmetric reaction

95:5 hexanes:2-propanol, 1.0 mL/min, Chiralcel OJ, 254 nm



Diethyl - (3*S*,5*R*) – 3 – ethenyl – 5 - (oct-1-enyl)pyrazolidine – 1 , 2 - dicarboxyl-ate (26b). The general procedure for AROM/CM of 2,3-diazabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate was followed to afford a colorless oil, after silica gel chromatography in 10:1 hexanes:EtOAc (R_f = 0.13). IR (neat): 2980 (m), 1710 (s), 1410 (m), 1376 (m), 1304 (m), 1174 (m), 1127 (m), 1030 (m), 752 (m), 696 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.83 (ddd, *J* = 17.0, 10.3, 6.6 Hz, 1H), 5.68 (dt, *J* = 15.4, 7.3 Hz, 1H), 5.40 (dd, *J* = 15.4, 6.8 Hz, 1H), 5.29 (d, *J* = 17.0 Hz, 1H), 5.10 (d, *J* = 10.3 Hz, 1H), 4.49 (br, 2H), 4.22-4.09 (m, 4H), 2.47 (ddd, *J* = 12.8, 8.4, 8.4 Hz, 1H), 2.06-1.98 (m, 2H), 1.84 (ddd, *J* = 12.8, 4.0, 4.0 Hz, 1H), 1.40-1.20 (m, 8H), 1.27 (t, *J* = 7.0 Hz, 3H), 1.26 (t, *J* = 7.0 Hz, 3H), 0.88 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.9, 137.0, 132.7, 128.2, 115.7, 62.1, 60.7, 40.3, 32.1, 31.7, 29.0, 28.8, 22.6, 14.5, 14.5, 14.1. HRMS Calcd for $C_{19}H_{32}N_2O_4Na$ ($M+Na^+$): 375.2260. Found: 375.2249.



Diethyl-(3*R*,5*S*)-3-(2-cyclohexylethenyl)-5-ethenylpyrazolidine-1,2-di-carboxylate (26c). The general procedure for AROM/CM of 2,3-diazabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate was followed to afford a colorless oil, after silica gel chromatography in 10:1 hexanes:EtOAc (R_f = 0.10). IR (neat): 2980 (m), 2925 (s), 2851 (m), 1711 (s), 1411 (m), 1375 (m), 1304 (m), 1175 (m), 1127 (m), 1037 (w), 968 (w), 754 (w). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.85 (ddd, *J* = 17.4, 10.3, 6.8 Hz, 1H), 5.64 (dd, *J* = 15.6, 6.4 Hz, 1H), 5.39 (dd, *J* = 15.6, 6.6 Hz, 1H), 5.31 (d, *J* = 17.4 Hz, 1H), 5.12 (dd, *J* = 10.3, 1.1 Hz, 1H), 4.52 (br, 2H), 4.25-4.10 (m, 4H), 2.47 (ddd, *J* = 12.6, 8.4, 8.4 Hz, 1H), 2.01-1.90 (m, 1H), 1.83 (ddd, *J* = 12.6, 3.9, 3.9 Hz, 1H), 1.75-1.58 (m, 5H), 1.35-0.98 (m, 11H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.9, 138.3, 137.3, 126.0, 115.8, 62.2, 60.8, 40.5, 40.3, 32.8, 32.8, 26.2, 26.1, 14.7, 14.6. Calcd for $C_{19}H_{30}N_2O_4Na$ (M+Na): 373.2103. Found: 373.2110.

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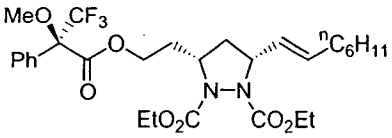
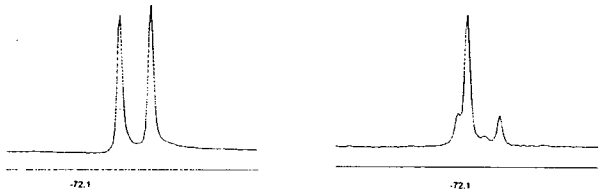
Enantiopurity of **26b-c** was determined by analysis of ^{19}F NMR spectrum of the corresponding product form AROM/CM was subjected to standard catalytic hydroboration with neutral oxidative workup[6] followed by esterification to afford (R)-MTPA esters.[5]

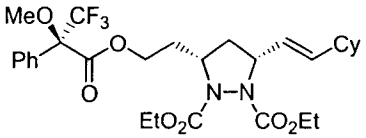


68% ee

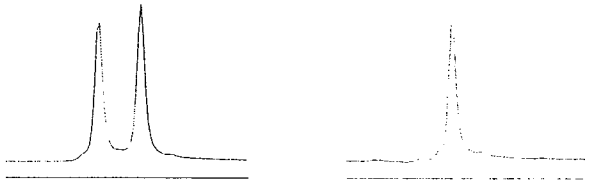


authentic racemic *from asymmetric reaction*

^{19}F NMR (376 MHz, $CDCl_3$)

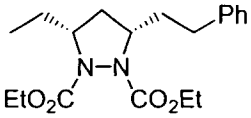


87% ee



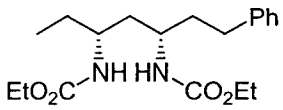
authentic racemic *from asymmetric reaction*

^{19}F NMR (376 MHz, $CDCl_3$)



Diethyl - (3*R*,5*S*)-3-ethyl-5-(2-phenylethyl)pyrazolidine-1,2-dicarboxylate. A 10 mL round-bottom flask was charged with the diene **26a** (72.5 mg, 0.211 mmol) and EtOH (1.0 mL). To the solution was added 10% Pd/C (6.8 mg) and the flask was equipped with a H_2 balloon. The flask was purged with H_2 and the mixture was allowed to stir vigorously at 22 °C for 30 min. The catalyst was removed by vacuum filtration and the filtrate was concentrated. Purification by silica gel chromatography in 10:1 hexanes:EtOAc (R*f* = 0.11) provided a colorless oil (68.6 mg, 0.197 mmol, 94%). IR (neat): 2978 (m), 2935 (m), 1706 (s), 1454 (m), 1418 (m), 1379 (m), 1342 (m), 1305 (m), 1273 (m), 1174 (m), 1133 (m), 1030 (w), 753 (w), 701 (w). ^1H NMR (400 MHz, $CDCl_3$): δ 7.31-7.14 (m, 5H), 4.21-4.11 (m, 4H), 3.75 (br, 2H), 2.81-2.64 (m, 2H), 2.38 (ddd, *J* = 12.6, 8.1, 8.1 Hz, 1H), 2.16 (br, 3H), 1.85-1.71 (m, 1H), 1.52 (ddd, *J* = 12.6, 6.0, 6.0 Hz, 1H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.26 (t, *J* = 7.1 Hz, 3H), 0.95 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.8, 141.7, 128.6, 128.5, 126.1, 62.1, 62.0, 61.0, 59.3, 38.5, 35.7, 33.3, 26.8, 14.7, 14.6, 11.1. HRMS Calcd for $C_{19}H_{28}N_2O_4Na$ (M+Na): 371.1947. Found: 371.1956.

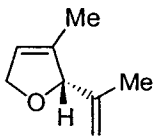
(6) Evans, D. A.; Fu, G. C.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1992**, *114*, 6671-6679.



(3*R*,5*S*)-3,5-Bis(ethoxycarbonylamino)-1-phenylheptane (27). To a 25 mL pear-shaped flask equipped with a stirring bar and a Dewar condenser was added a solution of pyrazolidine (60.3 mg, 0.173 mmol) in THF (1 mL). The solution was cooled to –78 °C and liq. NH_3 (ca. 5 mL) was condensed into the mixture. Lithium (12.0 mg, 1.72 mmol, 10 equiv) was added to the solution causing the mixture to turn blue and this was allowed to stir vigorously for 10 min. Solid NH_4Cl was added to the mixture until the blue color disappeared and the mixture was allowed to warm to 22 °C. A steam of N_2 was used to concentrate this solution. The residue was diluted with 0.05M potassium phosphate monobasic/sodium hydroxide pH 7 buffer (10 mL) and the resulting aqueous layer was washed three times with EtOAc (3x10 mL). The combined organic layers were washed with brine (10 mL), dried, and concentrated. The product was purified by silica gel chromatography in 5:1 hexanes:EtOAc (R_f = 0.12) to provide the product (45.0 mg, 0.128 mmol, 74%) as a colorless oil. IR (neat): 3323 (s), 2964 (s), 2931 (s), 1698 (s), 1602 (w), 1538 (s), 1456 (m), 1378 (m), 1335 (m), 1245 (s), 1172 (m), 1096 (m), 702 (w). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.10 (m, 5H), 4.84 (d, J = 8.5 Hz, 1H), 4.69 (d, J = 8.3 Hz, 1H), 4.09 (q, J = 7.1 Hz, 2H), 4.07 (q, J = 7.1 Hz, 2H), 3.78-3.43 (m, 2H), 2.74-2.51 (m, 2H), 1.81-1.28 (m, 6H), 1.22 (t, J = 7.1 Hz, 3H), 1.22 (t, J = 7.1 Hz, 3H), 0.87 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.5, 141.8, 128.5, 128.4, 126.0, 60.8, 60.7, 50.0, 48.7, 40.6, 37.3, 32.4, 28.1, 14.7, 10.2. HRMS Calcd for $C_{19}H_{30}N_2O_4Na$: 373.2103. Found: 373.2092.

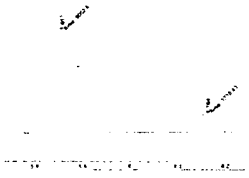
Representative Procedure for RCM. To a solution of 3-allyloxy-2,4-dimethylpenta-1,4-diene (31.0 mg, 0.204 mmol) in toluene (1.8 mL) was added Ru catalyst **3d** (5.0 mg, 0.0061 mmol, 3 mol%). The solution was heated to 60 °C and allowed to stir for 24 h. The solution was cooled to 22 °C, and silica gel chromatography of the solution in 49:1 pentane:Et_2O (R_f = 0.2) gave the product **29** (17.4 mg, 0.140 mmol, 56%) as a colorless oil.

(*S*)-2,5-Dihydro-2-isopropenyl-3-methylfuran (29). All spectral data coincided with those of the authentic sample.



68% ee

authentic racemic



from asymmetric reaction

CDGTA, 15 psi, 75 °C

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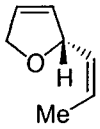
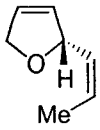


(*S*)-2-[(*Z*)-Propenyl]-2,5-dihydrofuran (32). The general procedure for RCM was followed to afford a colorless oil, after silica gel chromatography in 50:1 pentane:Et_2O (R_f = 0.15). IR (NaCl): 2925(m), 1653 (m), 1457 (m), 1384 (m), 1072(m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.91 (dq, *J* = 6.2, 1.7 Hz, 1H), 5.77–5.67 (m, 2H), 5.36 (ddq, *J* = 7.7, 7.7, 1.7 Hz, 1H), 5.20–5.13 (br s, 1H), 4.69 (ddd, *J* = 12.6, 5.9, 1.7 Hz, 1H), 4.60 (ddd, *J* = 12.6, 4.0, 1.7 Hz, 1H), 1.71 (dd, *J* = 6.6, 1.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 131.35, 129.43, 128.20, 126.87, 87.02, 75.13, 17.78. HRMS Calcd for $C_7H_{10}ONa$ ($M+Na^+$):133.0629. Found: 133.0627.

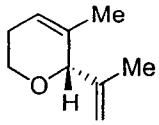


72% ee

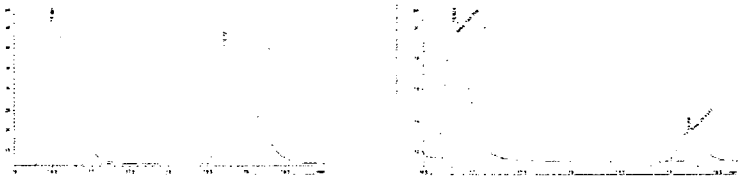
authentic racemic *from asymmetric reaction*

CDGTA, 15 psi, 50 °C

3,6-Dihydro-6-isopropenyl-5-methyl-2*H*-pyran (36). The general procedure for RCM was followed to afford a colorless oil, after silica gel chromatography in 50:1 pentane:Et_2O (R_f = 0.16). All spectral data coincided with those of the authentic sample.

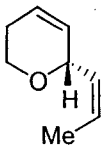


66% ee



authentic racemic *from asymmetric reaction*

CDGTA, 15 psi, 60 °C



6-[(*Z*)-Propenyl]-3,6-dihydro-2*H*-pyran (38). The general procedure for RCM was followed to afford a colorless oil, after silica gel chromatography in 50:1 pentane:Et_2O (R_f = 0.15). IR (NaCl): 2919 (m), 1648 (w), 1182 (w), 1081 (m), 1056 (w), 965 (w). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.92–5.82 (m, 1H), 5.78–5.60 (m, 2H), 5.42 (ddq, *J* = 11.0, 8.4, 1.7 Hz, 1H), 4.58 (br s, 1H), 3.98 (ddd, *J* = 11.2, 5.2, 4.3 Hz, 1H), 3.72 (ddd, *J* = 11.2, 7.9, 4.4 Hz, 1H), 2.32–2.21 (m, 1H), 2.08–2.00 (m, 1H), 1.76 (dd, *J* = 7.0, 1.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 130.16, 129.58, 128.63, 125.31, 74.68, 62.48, 25.14, 18.04. HRMS Calcd for $C_9H_{12}ONa$ ($M+Na^+$): 147.0786. Found: 147.0786.

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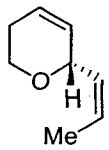
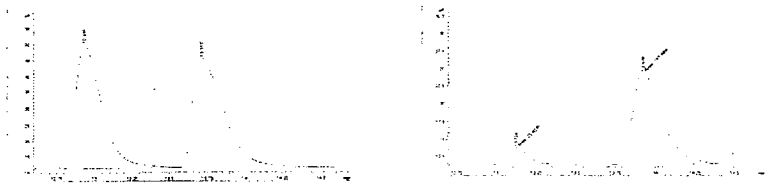
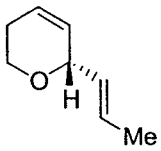


76% ee

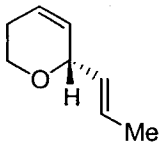


authentic racemic *from asymmetric reaction*

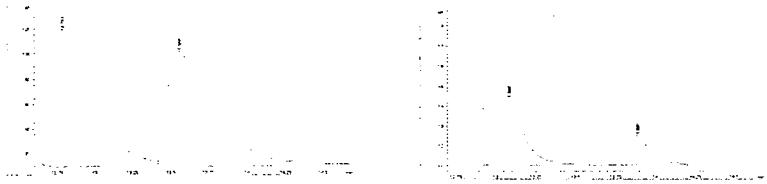
CDGTA, 15 psi, 60 °C



6-[(*E*)-Propenyl]-3,6-dihydro-2*H*-pyran (40). The general procedure for RCM was followed to afford a clear colorless oil, after silica gel chromatography in 50:1 pentane:Et2O (R_f = 0.15). IR (NaCl): 2919 (m), 1649 (w), 1182 (w), 1081 (m), 1056 (w), 968 (w). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.90–5.83 (m, 1H), 5.72 (ddq, *J* = 15.4, 1.1, 6.4 Hz, 1H), 5.66–5.60 (m, 1H), 5.49 (ddq, *J* = 15.4, 6.4, 1.7 Hz, 1H), 4.51 (br s, 1H), 3.94 (ddd, *J* = 11.2, 5.1, 4.2 Hz, 1H), 3.69 (ddd, *J* = 11.2, 8.3, 4.4 Hz, 1H), 2.26–2.15 (m, 1H), 2.04–1.95 (m, 1H), 1.71 (dd, *J* = 6.4, 1.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 130.76, 129.35, 128.88, 124.97, 74.50, 62.60, 25.27, 17.93. HRMS Calcd for $C_9H_{12}ONa$ ($M+Na^+$): 147.0786. Found: 147.0787.



42% ee



authentic racemic *from asymmetric reaction*

CDGTA, 15 psi, 60 °C

Determination of Relative Rates. AROM/CM reactions were carried out as outlined above. Aliquots were taken at appropriate time intervals and quenched by adding a drop of ethyl vinyl ether. Volatiles were removed under reduced pressure and conversion was determined by 400 MHz ^{1}H NMR. To calculate a relative rate value the time for the reaction to reach full conversion was determined. The inverse of this time is the absolute rate. This value is normalized for complex **3** (i.e., relative rate = 1) and relative rates for all other catalysts were determined by comparing to the absolute rate for complex **3**.

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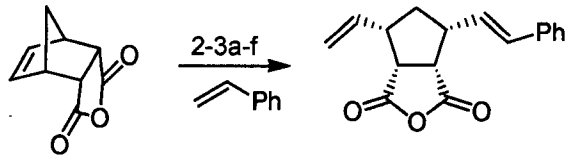
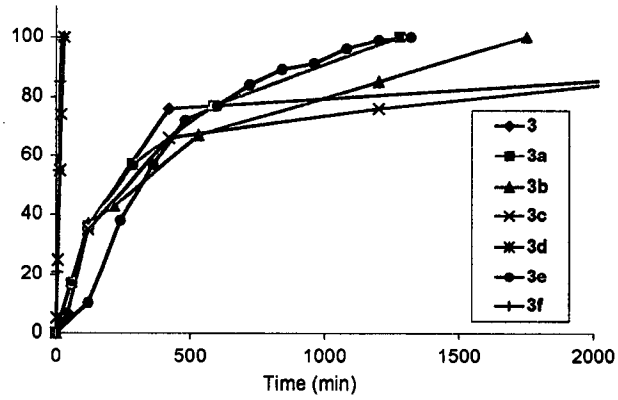
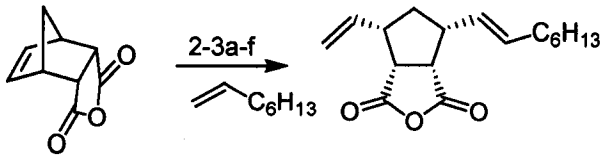


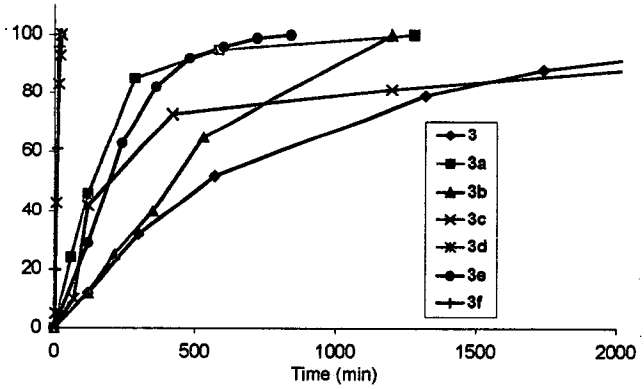
AROM/CM with Styrene



Catalyst	2	3a	3b	3c	3d	3e	3f
Relative Activity	1	3	2	1	133	3	160



AROM/CM with Octene



Catalyst	2	3a	3b	3c	3d	3e	3f
Relative Activity	1	2	2	1	110	3	110

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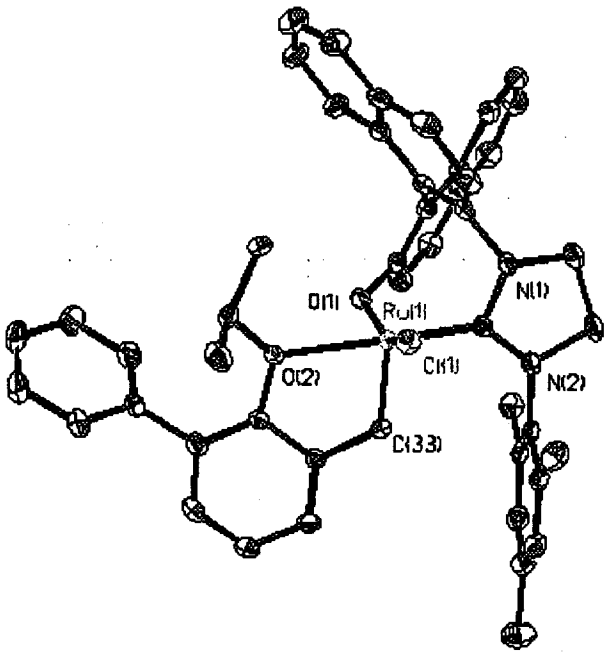

Table 1. Crystal data and structure refinement for DGK01t.

Identification code	dgk01t	
Empirical formula	C48 H43 Cl N2 O2 Ru	
Formula weight	858.83	
Temperature	273(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P1	
Unit cell dimensions	a = 8.8427(6) Å	a= 100.107(2)°.
	b = 14.0094(10) Å	b= 96.2100(10)°.
	c = 17.1887(12) Å	g = 95.706(2)°.
Volume	2068.7(2) $Å^3$	
Z	2	
Density (calculated)	1.379 Mg/m^3	
Absorption coefficient	0.550 mm^{-1}	
F(000)	886	

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Crystal size	0.4 x 0.2 x 0.2 mm^3
Theta range for data collection	1.21 to 28.28°
Index ranges	-11<=h<=11, -15<=k<=18, -22<=l<=22
Reflections collected	15364
Independent reflections	12221 [R(int) = 0.0313]
Completeness to theta = 28.28°	98.5 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	12221 / 3 / 1000
Goodness-of-fit on F^2	1.046
Final R indices [I>2sigma(I)]	R1 = 0.0340, wR2 = 0.0868
R indices (all data)	R1 = 0.0359, wR2 = 0.0920
Absolute structure parameter	-0.023(18)
Largest diff. peak and hole	0.944 and -0.389 e.$Å^{-3}$

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Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for DGK01t. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Ru(2)	6507(1)	1362(1)	4075(1)	23(1)
Ru(1)	7498(1)	7126(1)	7338(1)	22(1)
Cl(2)	4726(1)	652(1)	4795(1)	33(1)
Cl(1)	9039(1)	6095(1)	6637(1)	30(1)
C(44)	5694(7)	5410(5)	10550(3)	56(1)
O(1)	7080(3)	8097(2)	8262(2)	29(1)
N(1)	9404(4)	8590(2)	6837(2)	28(1)
C(80)	6322(4)	2604(3)	4760(2)	25(1)
C(33)	5596(4)	6581(3)	6845(2)	26(1)
C(81)	8273(4)	1020(3)	4559(2)	27(1)
C(35)	5361(4)	5625(3)	7915(2)	25(1)
C(10)	8947(4)	9490(3)	8414(2)	26(1)
C(39)	3197(4)	5537(3)	6904(2)	31(1)
N(3)	5064(4)	3045(3)	4563(2)	30(1)
C(12)	11237(4)	8731(3)	8922(2)	29(1)
C(86)	8953(4)	-868(3)	2836(2)	28(1)
C(13)	10442(4)	8483(3)	7508(2)	27(1)
C(83)	10414(4)	-4(3)	4379(2)	29(1)
C(60)	4050(4)	2668(3)	3854(2)	27(1)
C(74)	8407(5)	2409(3)	6439(2)	31(1)
C(11)	10195(4)	8879(3)	8267(2)	25(1)
C(23)	5745(4)	8030(3)	5650(2)	27(1)
C(82)	8957(4)	227(3)	4114(2)	25(1)
C(40)	4987(4)	4842(3)	9131(2)	33(1)
C(73)	8487(4)	2951(3)	5838(2)	30(1)
C(84)	11082(4)	-699(3)	3898(2)	33(1)
N(2)	7199(4)	8447(3)	6094(2)	29(1)
C(59)	4478(5)	2791(3)	3120(2)	33(1)
C(9)	7445(4)	9067(3)	8384(2)	26(1)
C(16)	12525(4)	8224(3)	8771(3)	33(1)
C(88)	8397(4)	-1190(3)	1973(2)	29(1)
C(58)	5986(5)	3324(3)	3058(2)	30(1)

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N(4)	7102(4)	3174(2)	5428(2)	31(1)
C(22)	8149(5)	9191(3)	5802(3)	39(1)
C(78)	11191(5)	2950(4)	5952(3)	40(1)
C(28)	5674(5)	7197(3)	5056(2)	32(1)
C(76)	9750(5)	2139(3)	6785(3)	35(1)
C(8)	6294(4)	9686(3)	8555(2)	33(1)
C(37)	2990(5)	4705(3)	7992(3)	34(1)
C(70)	6313(5)	4012(3)	5730(3)	40(1)
C(34)	4718(4)	5884(3)	7208(2)	25(1)
C(61)	2615(5)	2160(3)	3908(2)	33(1)
C(77)	11159(5)	2383(3)	6530(3)	39(1)
C(38)	2337(4)	4929(3)	7291(3)	33(1)
C(71)	9989(6)	3903(4)	4986(3)	47(1)
C(63)	1994(5)	1889(4)	2485(3)	39(1)
C(31)	4536(5)	9357(4)	6459(3)	41(1)
C(85)	10366(4)	-1105(3)	3136(2)	32(1)
C(29)	7093(6)	6753(4)	4846(3)	43(1)
C(5)	8149(5)	11128(3)	8788(2)	35(1)
C(87)	8215(4)	-259(3)	3370(2)	26(1)
C(26)	2923(5)	7181(4)	4836(3)	40(1)
C(14)	11713(4)	7986(3)	7356(3)	34(1)
C(79)	12596(7)	2037(5)	6876(4)	57(1)
C(32)	7978(4)	8098(3)	6679(2)	24(1)
C(62)	1619(5)	1775(3)	3242(3)	36(1)
C(21)	9552(5)	9426(3)	6430(3)	38(1)
C(41)	5048(6)	3883(4)	9241(3)	44(1)
C(69)	5118(5)	4032(3)	5033(3)	35(1)
C(27)	4247(5)	6778(4)	4664(3)	37(1)
C(90)	8196(5)	-2374(4)	757(3)	48(1)
C(75)	6888(5)	2082(4)	6692(3)	39(1)
C(89)	8601(5)	-2115(3)	1566(3)	38(1)
C(19)	12033(6)	8934(5)	10340(3)	51(1)
C(45)	5291(6)	5586(4)	9790(3)	45(1)
C(15)	12746(5)	7877(3)	7986(3)	38(1)
C(17)	13549(5)	8105(4)	9429(3)	48(1)
C(7)	6641(5)	10676(4)	8746(3)	41(1)

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C(91)	7586(5)	-1730(4)	324(3)	50(1)
C(18)	13317(6)	8434(5)	10183(3)	59(2)
C(92)	7360(5)	-815(4)	708(3)	45(1)
C(43)	5781(7)	4435(5)	10642(3)	61(2)
C(6)	9324(4)	10528(3)	8615(2)	29(1)
C(65)	3833(7)	2427(6)	1648(3)	71(2)
C(72)	9887(5)	3261(3)	5605(2)	35(1)
C(24)	4437(5)	8458(3)	5823(2)	32(1)
C(42)	5460(7)	3689(5)	10003(3)	55(1)
C(64)	3452(6)	2371(4)	2414(3)	43(1)
C(25)	3043(5)	8019(4)	5395(3)	37(1)
C(68)	957(6)	1485(5)	1786(3)	57(1)
C(36)	4492(5)	5055(3)	8332(2)	30(1)
C(93)	7779(5)	-540(3)	1528(2)	36(1)
C(66)	2809(9)	2044(7)	983(4)	88(3)
C(67)	1351(8)	1565(6)	1043(3)	85(3)
O(2)	6868(3)	6062(2)	8159(2)	25(1)
O(4)	6754(3)	-3(2)	3192(2)	25(1)
C(95)	5517(4)	-800(3)	2860(2)	28(1)
C(94)	5203(5)	-1432(3)	3461(3)	38(1)
C(1)	10843(5)	10997(3)	8669(2)	35(1)
C(52)	7549(5)	4784(3)	2819(2)	36(1)
C(55)	8828(5)	4255(4)	2835(3)	40(1)
C(56)	8699(5)	3318(4)	2957(3)	39(1)
C(48)	9483(4)	6208(4)	8743(3)	37(1)
C(53)	6097(5)	4301(3)	2922(2)	32(1)
C(46)	8118(5)	4556(3)	8028(3)	43(1)
C(47)	8010(5)	5528(3)	8555(3)	31(1)
C(20)	11023(5)	9076(4)	9725(3)	40(1)
C(51)	7660(6)	5743(3)	2682(3)	45(1)
C(96)	4168(4)	-287(4)	2600(3)	37(1)
C(54)	4807(6)	4827(4)	2863(3)	41(1)
C(3)	10023(7)	12570(4)	9050(3)	53(1)
C(50)	6408(8)	6226(4)	2629(3)	53(1)
C(4)	8538(7)	12159(4)	8995(3)	48(1)
O(3)	7210(4)	1908(2)	3166(2)	38(1)

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C(57)	7267(5)	2834(3)	3079(2)	32(1)
C(2)	11176(6)	11981(4)	8882(3)	45(1)
C(49)	4966(7)	5765(4)	2723(3)	51(1)
C(30)	1374(6)	6695(5)	4399(4)	61(2)
Cl(4)	2100(5)	6574(5)	1296(5)	280(4)
C(97)	1782(15)	5227(14)	872(11)	187(7)
Cl(3)	-98(5)	4927(5)	738(3)	219(2)

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Table 3. Bond lengths [Å] and angles [°] for DGK01t.

Ru(2)-C(81)	1.835(4)
Ru(2)-C(80)	1.956(4)
Ru(2)-O(3)	1.987(3)
Ru(2)-O(4)	2.267(3)
Ru(2)-Cl(2)	2.3549(9)
Ru(1)-C(33)	1.828(4)
Ru(1)-C(32)	1.961(3)
Ru(1)-O(1)	1.995(3)
Ru(1)-O(2)	2.294(2)
Ru(1)-Cl(1)	2.3522(9)
C(44)-C(45)	1.387(7)
C(44)-C(43)	1.411(9)
O(1)-C(9)	1.338(5)
N(1)-C(32)	1.351(5)
N(1)-C(13)	1.433(5)
N(1)-C(21)	1.468(5)
C(80)-N(4)	1.352(5)
C(80)-N(3)	1.365(5)
C(33)-C(34)	1.453(5)
C(81)-C(82)	1.457(5)
C(35)-C(36)	1.392(5)
C(35)-O(2)	1.397(4)
C(35)-C(34)	1.407(5)
C(10)-C(9)	1.392(5)
C(10)-C(6)	1.430(6)
C(10)-C(11)	1.479(5)
C(39)-C(38)	1.388(5)
C(39)-C(34)	1.395(5)
N(3)-C(60)	1.418(5)
N(3)-C(69)	1.467(5)
C(12)-C(20)	1.419(6)
C(12)-C(16)	1.425(5)
C(12)-C(11)	1.433(5)
C(86)-C(85)	1.393(5)

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C(86)-C(87)	1.399(5)
C(86)-C(88)	1.488(5)
C(13)-C(11)	1.375(5)
C(13)-C(14)	1.404(5)
C(83)-C(84)	1.385(6)
C(83)-C(82)	1.407(5)
C(60)-C(59)	1.389(5)
C(60)-C(61)	1.412(5)
C(74)-C(76)	1.387(6)
C(74)-C(73)	1.389(6)
C(74)-C(75)	1.509(6)
C(23)-C(24)	1.391(5)
C(23)-C(28)	1.400(6)
C(23)-N(2)	1.435(5)
C(82)-C(87)	1.398(5)
C(40)-C(45)	1.380(7)
C(40)-C(41)	1.395(6)
C(40)-C(36)	1.486(6)
C(73)-C(72)	1.394(6)
C(73)-N(4)	1.435(5)
C(84)-C(85)	1.389(6)
N(2)-C(32)	1.347(5)
N(2)-C(22)	1.465(5)
C(59)-C(64)	1.431(6)
C(59)-C(58)	1.486(6)
C(9)-C(8)	1.423(5)
C(16)-C(15)	1.393(6)
C(16)-C(17)	1.414(6)
C(88)-C(89)	1.399(6)
C(88)-C(93)	1.402(6)
C(58)-C(57)	1.381(6)
C(58)-C(53)	1.425(6)
N(4)-C(70)	1.471(5)
C(22)-C(21)	1.522(6)
C(78)-C(77)	1.378(7)
C(78)-C(72)	1.384(6)

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C(28)-C(27)	1.386(6)
C(28)-C(29)	1.506(6)
C(76)-C(77)	1.396(6)
C(8)-C(7)	1.363(7)
C(37)-C(38)	1.379(6)
C(37)-C(36)	1.396(6)
C(70)-C(69)	1.515(6)
C(61)-C(62)	1.359(6)
C(77)-C(79)	1.504(7)
C(71)-C(72)	1.512(6)
C(63)-C(62)	1.408(6)
C(63)-C(64)	1.422(6)
C(63)-C(68)	1.423(6)
C(31)-C(24)	1.505(6)
C(5)-C(7)	1.407(7)
C(5)-C(4)	1.423(6)
C(5)-C(6)	1.424(6)
C(87)-O(4)	1.391(4)
C(26)-C(25)	1.367(7)
C(26)-C(27)	1.388(6)
C(26)-C(30)	1.522(7)
C(14)-C(15)	1.380(6)
C(41)-C(42)	1.401(7)
C(90)-C(89)	1.372(6)
C(90)-C(91)	1.381(8)
C(19)-C(20)	1.365(6)
C(19)-C(18)	1.418(8)
C(17)-C(18)	1.342(8)
C(91)-C(92)	1.380(8)
C(92)-C(93)	1.393(6)
C(43)-C(42)	1.360(9)
C(6)-C(1)	1.421(6)
C(65)-C(66)	1.370(9)
C(65)-C(64)	1.407(7)
C(24)-C(25)	1.391(6)
C(68)-C(67)	1.380(8)