

**A RECYCLABLE CHIRAL Ru CATALYST FOR ENANTIOSELECTIVE
OLEFIN METATHESIS. EFFICIENT ASYMMETRIC RING-
OPENING/CROSS METATHESIS IN AIR**

**Joshua J. Van Veldhuizen, Steven B. Garber, Jason S. Kingsbury, and
Amir H. Hoveyda***

*Department of Chemistry, Merkert Chemistry Center, Boston College
Chestnut Hill, Massachusetts 02467*

SUPPORTING INFORMATION

General. All crystalline intermediates involved in chiral ligand synthesis (*especially the heterocyclic and diamine hydrochloride salts*) were typically dried for >12 h in a vacuum dessicator or Abderhalden pistol containing P₂O₅. Unless otherwise stated, reactions were carried out using distilled and degassed solvents under an atmosphere of dry nitrogen in oven- (135 °C) and flame-dried glassware with standard Schlenk or vacuum-line techniques. Infrared (IR) spectra were recorded on a Perkin-Elmer 781 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 (CDCl₃: δ 7.26 ppm, (CD₃)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. ¹³C 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 (CDCl₃: δ 77.16 ppm, (CD₃)₂SO: δ 39.52 ppm). High-resolution mass spectra were recorded at the University of Illinois (Urbana-Champaign, IL). Elemental microanalyses and optical rotations were performed by Robertson Microlit Laboratories (Madison, NJ). Enantiomer ratios were determined by chiral HPLC analysis (Chiral Technologies Chiralpak AS, Chiralpak AD, and Chiralcel OD (0.46 cm x 25 cm)) in comparison with authentic racemic materials. See below for further details.

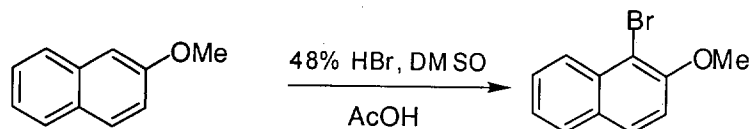
Materials. $\text{Cl}_2\text{Ru}(=\text{CH}-o\text{-OiPrC}_6\text{H}_4)\text{PPh}_3$ (**8**) was prepared as formerly described.¹ All other materials were obtained from commercial sources and rigorously purified before use. Tetrahydrofuran and toluene were distilled from sodium metal/benzophenone ketyl. CH_2Cl_2 , 1,2-dichloroethane, CDCl_3 , $(\text{CD}_3)_2\text{SO}$, pentane, hexanes, cyclohexane, triethylamine, ethanol, isopropanol, styrene, 1-heptene and vinylcyclohexane were distilled from calcium hydride. Methanol was distilled over Mg under nitrogen. Acetone was distilled from potassium carbonate. Dimethylformamide was stored under nitrogen over activated 4Å molecular sieves. 2,4,6-trimethylaniline (Aldrich) was vacuum distilled. 4-Bromo-2-methyl-2-butene (Aldrich) was vacuum distilled to a colorless oil prior to use. Potassium hydride (Aldrich) was washed with pentane, dried in vacuo, and stored in a glovebox. Boron tribromide (Aldrich) was vacuum distilled using a cold trap. Methyl iodide (Aldrich) and ethyl chloroformate (Aldrich) were distilled from calcium chloride. Triethylorthoformate (Aldrich) was distilled from sodium metal. *cis*-5-Norbornene-*endo*-2,3-dicarboxylic anhydride (Aldrich) was recrystallized from cyclohexane. The following materials were purchased from commercial sources and used as received: Mg turnings (Strem), di-*tert*-butyl dicarbonate (Advanced Chemtech), dimethyl sulfide (Aldrich), silver (I) carbonate (Strem), 2-methoxynaphthalene (Aldrich), 48% HBr (Fisher), $(\text{CH}_3)_2\text{SO}$ (Aldrich), acetic acid (Fisher), 1-hydroxy-2-naphthoic acid (Aldrich), (1*R*, 2*S*, 5*R*)-(-)-menthol (Aldrich), 60% sodium hydride in oil (Aldrich), potassium hydroxide (Fisher), sodium triacetoxyborohydride (Aldrich), and hydrogen chloride gas (AGA).

Silica gel column chromatography was driven with compressed air and performed using silica gel 60 (230-400 mesh; pH (10% suspension) 6.5-7.0; surface area 500 m²/g; pore volume 0.75 ml/g) obtained from TSI Chemical Co. (Cambridge, MA). Chiral catalyst **3** forms a dark brown solution in organic solvents. The progress of chromatography can thus be followed visually as a brown-colored band on a column, and the presence of catalyst in fractions of eluant is evident by simple visual inspection. Purification and recovery following olefin metathesis was routinely performed in air using reagent-grade solvents. Appropriate solvent mixtures for catalyst elution include the following: 4:1 hexanes:EtOAc, 3:1 hexanes:Et₂O, and 100% CH_2Cl_2 (*R_f* values ~ 0.15-0.30). Occasionally with polar reaction products, coelution is a problem. This problem is usually solved by passing the reaction mixture through a short plug of silica

(1) Kingsbury, J. S.; Harrity, J. P. A.; Bonitatebus, P. J., Jr.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1999**, *121*, 791-799.

gel in CH_2Cl_2 to separate the catalyst from reaction products, with recourse to a second column chromatographic separation of the organic materials.

Methods for the racemic synthesis of **4** and its corresponding resolution are available.² Unfortunately, these procedures proved to be impractical and inefficient for our purposes, particularly on larger scales. We currently favor a diastereoselective biaryl coupling reaction using (1*R*, 2*S*, 5*R*)-(-)-menthol as a chiral auxiliary.³



1-Bromo-2-methoxynaphthalene. Prepared according to a literature procedure.⁴ IR (NaCl): 3047 (w), 2972 (m), 2943 (m), 2843 (m), 1622 (s), 1596 (m), 1501 (s), 1467 (m), 1454 (m), 14.40 (w), 1353 (m), 1335 (m), 1271 (s), 1247 (w), 1219 (m), 1187 (m), 1173 (w), 1153 (w), 1064 (s), 1023 (m), 892 (m), 840 (m), 813 (m), 803 (s), 763 (m), 743 (s), 518 (m). ¹H NMR (400 MHz, CDCl_3): δ 8.19 (d, J = 8.6 Hz, 1H), 7.75 (t, J = 8.5 Hz, 2H), 7.53 (t, J = 8.2 Hz, 1H), 7.36 (t, J = 7.9 Hz, 1H), 7.22 (d, J = 9.0 Hz, 1H), 3.98 (s, 3H). ¹³C NMR (100 MHz, CDCl_3): δ 153.88, 133.25, 130.94, 129.09, 128.16, 127.86, 126.24, 124.43, 113.74, 108.78, 57.17. HRMS Calcd for $\text{C}_{11}\text{H}_9\text{BrO}$: 235.9837. Found: 235.9838. Anal. Calcd for $\text{C}_{11}\text{H}_9\text{BrO}$: C, 55.72; H, 3.83. Found: C, 55.66; H, 3.82.



Methyl 1-methoxynaphthoate. Prepared according to a literature procedure.⁵ IR (NaCl): 3058 (w), 2997 (w), 2948 (m), 2846 (w), 1725 (s), 1628 (m), 1597 (m), 1570

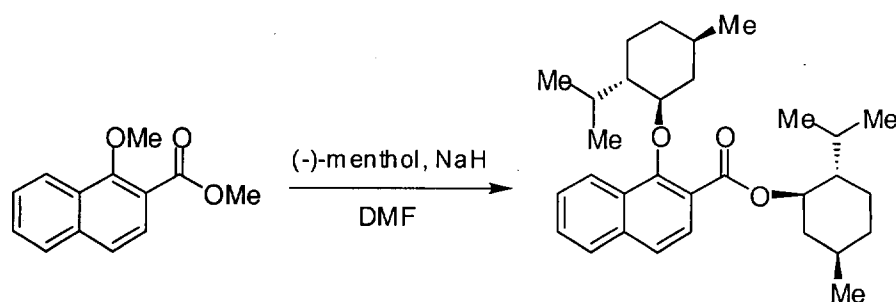
(2) (a) Smrcina, M.; Vyskocil, S.; Maca, M.; Polasek, M.; Claxton, T. A.; Abbott, A. P.; Kocovsky, P. *J. Org. Chem.* **1994**, 59, 2156-2163. (b) Ding, K.; Wang, Y.; Yun, H.; Liu, J.; Wu, Y.; Terada, M.; Okubo, Y.; Mikami, K. *Chem. Eur. J.* **1999**, 5, 1734-1737.

(3) Our procedures are adapted from: Ito, Y.; Miyake, T.; Hatano, S.; Shima, R.; Ohara, T.; Sugimoto, M. *J. Am. Chem. Soc.* **1998**, 120, 11880-11893. In several cases, we simply offer an alternative method of purification and a more complete characterization of these known biaryl intermediates.

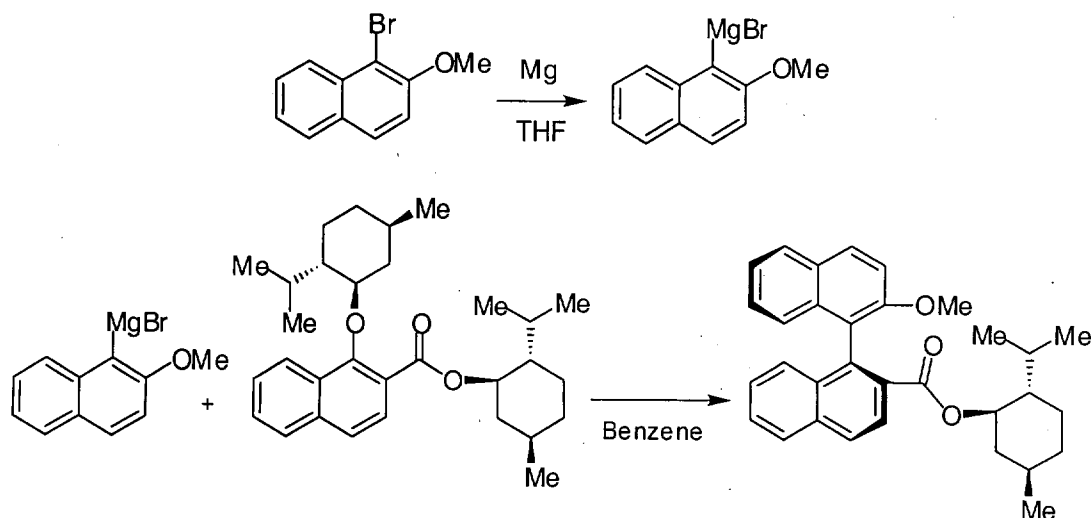
(4) Majetich, G.; Hicks, R.; Reister, S. *J. Org. Chem.* **1997**, 62, 4321-4326.

(5) Hattori, T.; Hotta, H.; Suzuki, T.; Miyano, S. *Bull. Chem. Soc. Jpn.* **1993**, 66, 613-622.

(m), 1504 (m), 1466 (m), 1445 (m), 1434 (m), 1373 (s), 1343 (s), 1279 (s), 1239 (s), 1214 (m), 1191 (m), 1153 (m), 1133 (s), 1084 (s), 1001 (m), 829 (m), 802 (m), 787 (m), 768 (s), 715 (w). ^1H NMR (400 MHz, CDCl_3): δ 8.30-8.26 (m, 1H), 7.87-7.84 (m, 2H), 7.62 (d, $J = 8.6$ Hz, 1H), 7.61-7.54 (m, 2H), 4.07 (s, 3H), 3.99 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 166.85, 158.44, 136.93, 128.47, 128.02, 126.83, 126.68, 123.78, 123.77, 119.34, 63.56, 52.41. HRMS Calcd for $\text{C}_{13}\text{H}_{12}\text{O}_3$: 216.0786. Found: 216.0787. Anal. Calcd for $\text{C}_{13}\text{H}_{12}\text{O}_3$: C, 72.21; H, 5.59. Found: C, 72.50; H, 5.52.

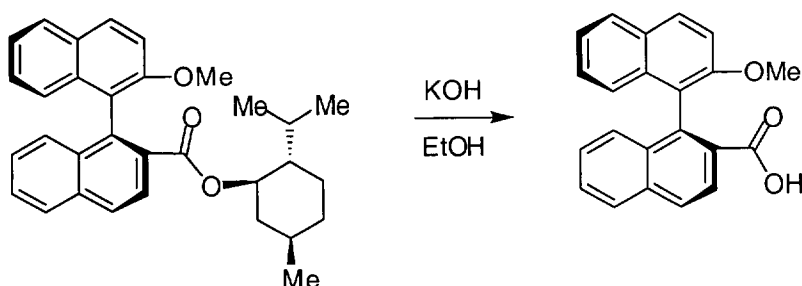


(-)-Menthyl 1-(-)-menthyloxy-2-naphthoate.⁵ IR (NaCl): 3058 (w), 2954 (s), 2956 (s), 2869 (m), 1719 (s), 1625 (w), 1598 (w), 1568 (w), 1502 (w), 1457 (m), 1387 (m), 1371 (m), 1342 (m), 1319 (m), 1277 (s), 1235 (s), 1215 (m), 1203 (m), 1181 (w), 1148 (s), 1137 (s), 1098 (m), 1081 (s), 1038 (w), 1007 (w), 983 (m), 962 (m), 920 (w), 823 (w), 801 (w), 766 (m), 741 (w). ^1H NMR (400 MHz, CDCl_3): δ 8.32 (d, $J = 8.5$ Hz, 1H), 7.81 (d, $J = 7.7$ Hz, 1H), 7.67 (d, $J = 8.6$ Hz, 1H), 7.56-7.48 (m, 3H), 5.04 (td, $J = 10.9$, 4.4 Hz, 1H), 4.34 (td, $J = 10.9$, 4.2 Hz, 1H), 2.67 (quintetd, $J = 6.8$, 2.2 Hz, 1H), 2.21-2.16 (m, 1H), 2.05 (quintetd, $J = 7.2$, 2.7 Hz, 1H), 1.79-1.52 (m, 7H), 1.28-0.83 (m, 23H), 0.74 (d, $J = 6.6$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 166.77, 154.10, 136.24, 130.12, 127.86, 127.74, 126.22, 126.00, 124.56, 122.40, 121.15, 82.11, 74.59, 49.64, 47.27, 41.17, 39.97, 34.59, 34.46, 31.67, 31.61, 26.38, 25.82, 23.50, 23.42, 22.24, 22.22, 21.60, 21.04, 16.77, 16.56. HRMS Calcd for $\text{C}_{31}\text{H}_{44}\text{O}_3$: 464.3290. Found: 464.3290. Anal. Calcd for $\text{C}_{31}\text{H}_{44}\text{O}_3$: C, 80.13; H, 9.54. Found: C, 80.22; H, 9.63.



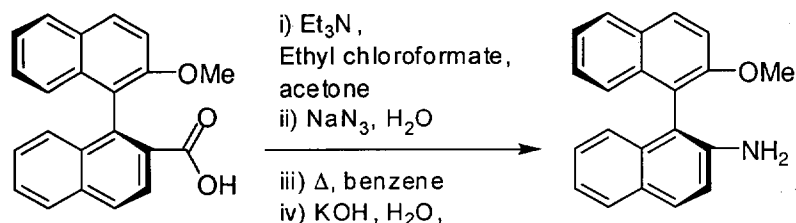
(-)-Menthyl (S)-2'-methoxy-1,1'-binaphthalene-2-carboxylate.⁵ Mg turnings (1.30 g, 58.2 mmol) were covered in 5 mL of THF in a 100 mL round bottom flask and treated with a solution of 1-bromo-2-methoxynaphthylene (4.60 g, 19.4 mmol in 20 mL of THF) using a cannula. This mixture was stirred at reflux for 1.5 h. Benzene (25 mL) was then added and the mixture was transferred through a cannula into a solution of (-)-menthyl 1-(1-(1-(1-methoxy-2-naphthyl)oxy)propan-2-yl)propanoate (7.64 g, 16.4 mmol in 15 mL of benzene) at 0 °C. The ice bath was removed and the resulting solution was stirred at 22 °C for 3 days. The mixture was then quenched by the addition of 50 mL of a saturated ammonium chloride solution. The mixture was diluted with 100 mL of water and 100 mL of benzene and transferred to a separatory funnel. The organic layer was washed with one volume each of water and a saturated sodium chloride solution. The solution was then dried over MgSO₄, filtered, and concentrated to a thick yellow oil. Purification by silica gel chromatography in 20:1 hexanes:Et₂O (*R_f* = 0.15) on a column 10 cm in diameter and 20 cm in length delivered a bright white solid (5.95 g, 12.8 mmol, 78%). Careful TLC analysis of the fractions of eluant is required, as the undesired minor diastereomer elutes just behind the major product. Owing to its convenience and simplicity, we routinely perform this procedure on large scale and combine mixed fractions for subsequent separation. IR (NaCl): 3059 (m), 3003 (w), 2954 (s), 2933 (s), 2868 (s), 1721 (s), 1697 (s), 1622 (m), 1294 (s), 1510 (s), 1461 (s), 1433 (m), 1367 (m), 1336 (s), 1321 (s), 1271 (s), 1250 (s), 1213 (w), 1180 (m), 1147 (s), 1136 (s), 1127 (s), 1084 (s), 1054 (m), 1038 (w), 1021 (m), 1008 (w), 982 (m), 963 (m), 907 (w), 869 (w), 832 (m), 808 (s), 788 (w), 768 (s), 738 (s), 704 (w). ¹H NMR (400 MHz, CDCl₃): δ 8.14 (d, *J* = 8.6 Hz, 1H), 7.99 (m, 2H), 7.94 (d, *J* = 8.1 Hz, 1H), 7.85 (d, *J* = 8.2 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.42 (d, *J* = 9.0 Hz, 1H), 7.36 (d, *J* = 8.4 Hz, 1H), 7.29 (t, *J* = 7.8 Hz, 2H), 7.17 (dd, *J* = 8.4, 7.2 Hz, 1H), 6.97 (d, *J* =

8.4Hz, 1H), 4.49 (td, $J = 10.8, 4.4$ Hz, 1H), 3.75 (s, 3H), 1.55-1.15 (m, 5H), 0.91-0.48 (m, 11H), -0.21 (q, $J = 12.3$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 167.60, 154.32, 136.60, 135.19, 134.31, 133.07, 129.94, 129.38, 129.14, 128.10, 127.98, 127.83, 127.63, 126.66, 126.62, 126.62, 126.52, 124.97, 123.58, 122.40, 113.29, 74.41, 56.51, 46.68, 39.67, 34.19, 31.11, 25.65, 22.90, 21.98, 21.06, 15.82. HRMS Calcd for $\text{C}_{32}\text{H}_{34}\text{O}_3$: 466.2508. Found: 466.2508. Anal. Calcd for $\text{C}_{32}\text{H}_{34}\text{O}_3$: C, 82.37; H, 7.34. Found: C, 82.13; H, 7.30.



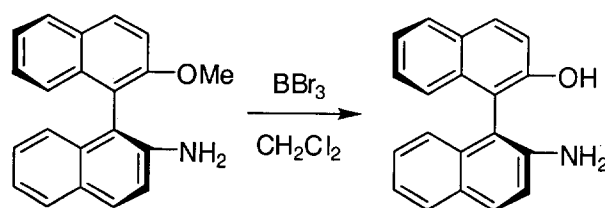
(S)-2'-Methoxy-1,1'-binaphthalene-2-carboxylic acid.³ A solution of KOH (18.7 g, 333 mmol, 20 equiv) in absolute ethanol (167 mL) was poured through a funnel into a 500 mL round bottom flask containing (-)-menthyl-(S)-2'-methoxy-1,1'-binaphthalene-2-carboxylate (7.80 g, 16.7 mmol). The flask was equipped with a reflux condenser and purged with nitrogen. As heat was applied from a heating mantle the sparingly soluble ester gradually dissolved, forming a light yellow solution. This solution was stirred at reflux for 24 h, at which point TLC analysis of the reaction mixture indicated an absence of starting material. The reaction mixture was cooled to 22 °C and concentrated to a volume <15 mL. This solution was diluted with 250 mL of water and washed three times with 200 mL portions of Et_2O (these organic layers were discarded). The aqueous layer was then acidified to $\text{pH} < 2$ using concentrated hydrochloric acid, resulting in a voluminous deposition of a cloudy white precipitate. This solid was extracted from the aqueous layer with three 200 mL volumes of Et_2O . These organic layers were combined, dried over MgSO_4 , and filtered. Concentration of the resulting solution routinely delivered acid of >98% purity as a light yellow crystalline solid (5.43 g, >98% yield). IR (NaCl): 3059 (br), 3013 (br), 2935 (w), 2898 (w), 2838 (m), 2635 (br), 2564 (br), 1691 (s), 1621 (m), 1593 (m), 1566 (w), 1508 (m), 1464 (m), 1432 (w), 1408 (w), 1360 (w), 1332 (w), 1288 (m), 1263 (s), 1249 (s), 1178 (w), 1145 (m), 1130 (w), 1084 (m), 1054 (w), 1020 (w), 956 (w), 908 (w), 835 (w), 806 (m), 772 (m), 752 (m), 735 (m). ^1H NMR (400 MHz, CDCl_3): δ 9.60 (br, 1H, COOH), 8.15 (d, $J = 8.8$ Hz, 1H, aromatic H), 8.01-7.97 (m, 2H, aromatic H), 7.94 (d, $J = 8.4$ Hz, 1H, aromatic H), 7.89 (d, $J = 8.2$ Hz, 1H,

aromatic H), 7.54 (m, 1H, aromatic H), 7.37 (d, $J = 9.2$ Hz, 1H, aromatic H), 7.33-7.21 (m, 3H, aromatic H), 7.17 (dd, $J = 7.5, 7.5$ Hz, 1H, aromatic H), 6.89 (d, $J = 8.6$ Hz, 1H, aromatic H), 3.68 (s, 3H, ArOCH₃). ¹³C NMR (100 MHz, CDCl₃): δ 154.30, 138.21, 135.65, 133.89, 133.07, 129.72, 129.07, 128.14, 128.09, 128.04, 127.88, 126.85, 126.61, 124.94, 123.61, 121.59, 113.74, 56.72. HRMS Calcd for C₂₂H₁₆O₃: 328.1099. Found: 328.1098. Anal. Calcd for C₂₂H₁₆O₃: C, 80.47; H, 4.91. Found: C, 80.24; H, 4.96.



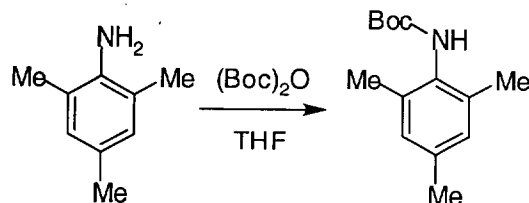
(S)-2-Amino-2'-methoxy-1,1'-binaphthalene.³ A 250 mL round bottom flask was charged with (S)-2'-methoxy-1,1'-binaphthalene-2-carboxylic acid (5.43 g, 16.5 mmol), 83 mL of acetone, and Et₃N (2.53 mL, 18.2 mmol, 1.10 equiv), and the resulting solution was cooled to -15 °C (CO₂/ethylene glycol bath). The subsequent dropwise addition of ethyl chloroformate (1.89 mL, 19.8 mmol, 1.20 equiv) caused a cloudy white precipitate to form. This suspension was stirred for 30 min at -15 °C, at which time a solution of NaN₃ (3.22 g, 49.5 mmol, 3.0 equiv) in 16 mL of water was added. After stirring for an additional 90 min at -15 °C, the reaction mixture was diluted with 150 mL of water and washed three times with 125 mL of cold benzene. The combined organic layers were washed with 400 mL of a cold saturated sodium chloride solution, dried over MgSO₄, and filtered directly into a 500 mL round bottom flask containing 1.0 g of activated 4 Å molecular sieves. This vessel was equipped with a reflux condenser and heating mantle and the bronze-colored solution was heated at reflux for 2 h. After cooling to 22 °C, the solution was filtered into another 500 mL round bottom flask containing a solution of KOH (46.3 g, 825 mmol, 50 equiv) in 85 mL of water. The resulting biphasic mixture was stirred vigorously for 16 h and transferred to a separatory funnel. The organic layer was isolated and the aqueous layer was washed two times with 100 mL of benzene. This solution was dried (MgSO₄), filtered, concentrated to afford a light yellow solid of >95% purity as judged by ¹H NMR analysis. This material was typically purified further before use. After dissolving the solid in 20-25 mL of CH₂Cl₂, 8-10 g of silica gel was added and the solvent was removed from the slurry under reduced pressure. The product-laden silica gel was loaded onto a wide plug of silica gel and

eluted with 1:1 hexanes:Et₂O (R_f = 0.30). This procedure delivered the product in excellent yield as a bright white solid (4.74 g, 96%). Alternatively, the unpurified product can be recrystallized as a white solid from absolute ethanol (3.95 g, 80%). IR (NaCl): 3483 (br), 3384 (m), 3056 (w), 3004 (w), 2964 (w), 2939 (w), 2838 (w), 1619 (s), 1591 (m), 1506 (s), 1474 (w), 1463 (m), 1431 (m), 1381 (m), 1352 (w), 1330 (w), 1261 (s), 1246 (s), 1213 (w), 1178 (w), 1146 (m), 1132 (w), 1111 (w), 1076 (m), 1048 (w), 1019 (w), 903 (w), 811 (s), 781 (w), 775 (w), 749 (m), 736 (m), 707 (w). ¹H NMR (400 MHz, CDCl₃): δ 8.00 (d, J = 9.0 Hz, 1H, aromatic H), 7.89 (d, J = 8.2 Hz, 1H, aromatic H), 7.81-7.77 (m, 2H, aromatic H), 7.48 (d, J = 9.0 Hz, 1H, aromatic H), 7.35 (m, 1H, aromatic H), 7.28-7.13 (m, 4H, aromatic H), 7.14 (d, J = 8.6 Hz, 1H, aromatic H), 6.99-6.96 (m, 1H, aromatic H), 3.79 (s, 3H, ArOCH₃), 3.57 (s, 2H, ArNH₂). ¹³C NMR (100 MHz, CDCl₃): δ 155.59, 142.03, 134.30, 133.76, 130.13, 129.72, 129.14, 128.38, 128.19, 128.14, 127.04, 126.42, 125.15, 124.43, 124.06, 122.29, 119.00, 118.35, 114.49, 114.05, 57.01. HRMS Calcd for C₂₁H₁₇NO: 299.1310. Found: 299.1310. Anal. Calcd for C₂₁H₁₇NO: C, 84.25; H, 5.72; N, 4.68. Found: C, 84.07; H, 5.77; N, 4.68. $[\alpha]_D^{25}$ -67.11° (c = 1.041, CHCl₃).



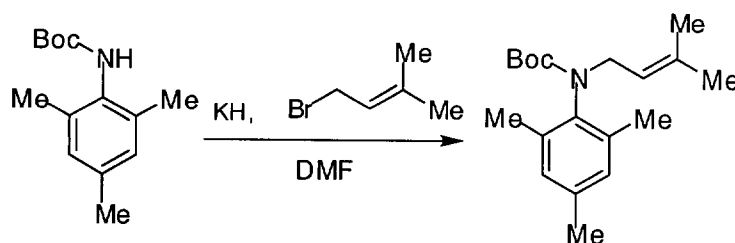
(S)-2-Amino-2'-hydroxy-1,1'-binaphthalene (NOBIN) (4). (S)-2-Amino-2'-methoxy-1,1'-binaphthalene (4.30 g, 14.4 mmol) was dissolved in 144 mL of CH₂Cl₂ in a 250 mL round bottom flask and the colorless solution was cooled to 0 °C. Boron tribromide (5.44 mL, 57.5 mmol, 4.0 equiv) was then added dropwise using a syringe, at which point the solution turned slightly yellow in color. The reaction mixture was warmed to 22 °C and stirred for 12 h, at which point a small aliquot worked up as described below confirmed the absence of starting material (¹H NMR analysis). The reaction mixture was cooled to 0 °C and carefully poured into a 1 L separatory funnel containing 100 mL of 5 M NaOH. Upon quench of the BBr₃, the mixture was diluted with 200 mL of water and 200 mL of EtOAc. The organic layer was removed, and the aqueous layer was washed two times with 100 mL of EtOAc. The combined organic layers were dried over MgSO₄, filtered, and concentrated to an off-white solid of >95% purity as judged by ¹H NMR analysis. This material was purified further prior to

reductive amination. After dissolving the solid in minimal 1:1 EtOAc:CH₂Cl₂ (approximately 50-60 mL), 25 g of silica gel was added and the solvent was removed from the slurry under reduced pressure. The product-laden silica gel was loaded onto a wide plug of silica gel and eluted with 3:1 hexanes:EtOAc (*R_f* = 0.29). This procedure delivered the product in good yield as a white solid (3.34 g, 96%). Alternatively, the unpurified product can be recrystallized as an off-white solid from absolute ethanol (3.07 g, 75%). IR (NaCl): 3396 (m), 3323 (m), 3300 (br), 3057 (w), 1616 (s), 1594 (s), 1508 (m), 1471 (w), 1461 (w), 1381 (s), 1344 (w), 1273 (w), 1214 (m), 1168 (m), 1142 (m), 1128 (m), 910 (w), 820 (s), 775 (w), 752 (w), 727 (s). ¹H NMR (400 MHz, CDCl₃): δ 7.93 (d, *J* = 9.0 Hz, 1H, aromatic H), 7.90-7.84 (m, 2H, aromatic H), 7.82-7.79 (m, 1H, aromatic H), 7.38 (d, *J* = 9.0 Hz, 1H, aromatic H), 7.35 (ddd, *J* = 8.0, 6.8, 1.5 Hz, 1H, aromatic H), 7.30-7.16 (m, 4H, aromatic H), 7.15 (d, *J* = 8.8 Hz, 1H, aromatic H), 7.07-7.03 (m, 1H, aromatic H), 5.13 (s, 1H, ArOH), 3.74 (s, 2H, ArNH₂). ¹³C NMR (100 MHz, CDCl₃): δ 151.97, 143.90, 134.27, 133.34, 130.78, 130.51, 129.67, 128.52, 128.46, 128.40, 127.47, 127.11, 124.69, 123.88, 123.80, 122.91, 118.31, 117.84, 114.42, 108.62. HRMS Calcd for C₂₀H₁₅NO: 285.1154. Found: 285.1154. Anal. Calcd for C₂₀H₁₅NO: C, 84.19; H, 5.30; N, 4.91. Found: C, 83.97; H, 5.18; N, 4.84. [α]_D²⁵ -56.38° (c = 1.002, CHCl₃).



***N*-(*tert*-Butyloxycarbonyl)-2,4,6-trimethylphenylamine.** A 100 mL round bottom flask was charged with 2,4,6-trimethylaniline (3.59 g, 26.6 mmol) and 20 mL of THF. Di-*tert*-butyl dicarbonate (5.81 g, 26.6 mmol, 1.0 equiv) was weighed into a 25 mL pear-shaped flask and dissolved in 30 mL of THF. The anhydride was then transferred to the arylamine solution through a cannula. A 3 mL portion of THF was used to complete the transfer (final concentration 0.5 M). The reaction flask was equipped with a reflux condenser and heating mantle, and the resulting colorless solution was heated at reflux for 7 days. At this time a ¹H NMR spectrum of the reaction mixture finally revealed an absence of the starting aniline. Solvent removal in vacuo typically delivered product of >98% purity in high yield as an off-white crystalline solid (6.25 g, >98%). If necessary, the product can be purified by silica gel chromatography in 8:1 hexanes:Et₂O (*R_f* = 0.20). Though UV active, the product is best observed with a ninhydrin TLC stain. IR (NaCl):

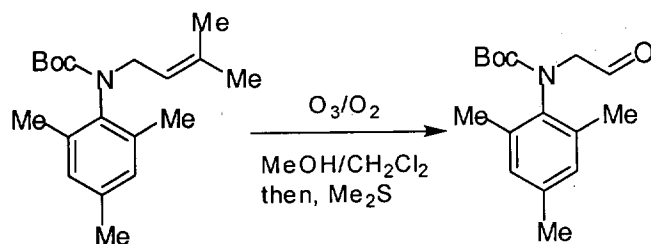
3303 (br), 3004 (w), 2978 (m), 2922 (m), 2862 (w), 1698 (s), 1611 (w), 1507 (s), 1458 (m), 1391 (m), 1366 (s), 1308 (w), 1248 (s), 1171 (s), 1055 (m), 1022 (m), 904 (w), 849 (m), 777 (w), 707 (w). ^1H NMR (400 MHz, CDCl_3): δ 6.88 (s, 2H, aromatic H), 5.89 (br, 1H, ArNH), 2.27 (s, 3H, *p*-CH₃), 2.23 (s, 6H, *o*-CH₃), 1.52 (br, 9H, OC(CH₃)₃). ^{13}C NMR (100 MHz, CDCl_3): δ 153.95, 136.45, 135.63, 131.48, 128.85, 79.69, 28.40, 20.95, 18.31. HRMS Calcd for $\text{C}_{14}\text{H}_{21}\text{NO}_2$: 235.1572. Found: 235.1567. Anal. Calcd for $\text{C}_{14}\text{H}_{21}\text{NO}_2$: C, 71.46; H, 8.99. Found: C, 71.56; H, 8.76.



***N*-(*tert*-Butyloxycarbonyl)-*N*-(3-methyl-but-2-enyl)-2,4,6-trimethylphenylamine.**

A suspension of KH (1.27 g, 31.7 mmol, 1.10 equiv) in 20 mL of DMF in a 100 mL round bottom flask was cooled to 0 °C. The aryl carbonate (6.67 g, 28.7 mmol, 1.0 equiv) was dissolved in DMF (40 mL) and added to the mixture dropwise through a cannula, causing vigorous gas evolution. The resulting mixture was warmed to 22 °C and stirred for 1 h. 4-Bromo-2-methyl-2-butene (3.98 mL, 34.5 mmol, 1.20 equiv) was next added dropwise from a syringe, inducing a rapid precipitation of white KBr salts. After 1 h of additional stirring at 22 °C, the mixture was transferred to a separatory funnel and diluted with 100 mL of a saturated sodium bicarbonate solution, 100 mL of H₂O, and 200 mL of Et₂O. The organic layer was removed and the aqueous layer was washed with two 150 mL portions of Et₂O. The combined organic layers were washed with one volume of a saturated sodium chloride solution. The resulting solution was dried over MgSO₄, filtered, and concentrated to a bronze oil of >95% purity as judged by ^1H NMR analysis. This material can be further purified before oxidative cleavage. This was achieved by silica gel chromatography in 10:1 hexanes:Et₂O (R_f = 0.32), affording the olefin as a colorless oil (7.85 g, 90% yield). In CDCl_3 at 22 °C, this material exists as a 2.4:1 mixture of amide rotamers. The ^1H NMR and ^{13}C NMR data given below report *each resonance in the mixture*. IR (NaCl): 2975 (m), 2925(m), 2861 (w), 1698 (s), 1483 (m), 1452 (m), 1390 (s), 1365 (m), 1329 (w), 1305 (m), 1290 (m), 1255 (m), 1239 (w), 1172 (s), 1136 (m), 1043 (w), 1000 (w), 870 (w), 851 (w), 770 (w). ^1H NMR (400 MHz, CDCl_3): δ 6.84 (s, 2H, aromatic H), 6.81 (s, 2H, aromatic H), 5.30 (m, 1H, olefinic H), 4.04 (d, J = 7.2 Hz, 2H, NCH₂), 3.97 (d, J = 7.2 Hz, 2H, NCH₂), 2.25 (s, 6H, *o*-CH₃),

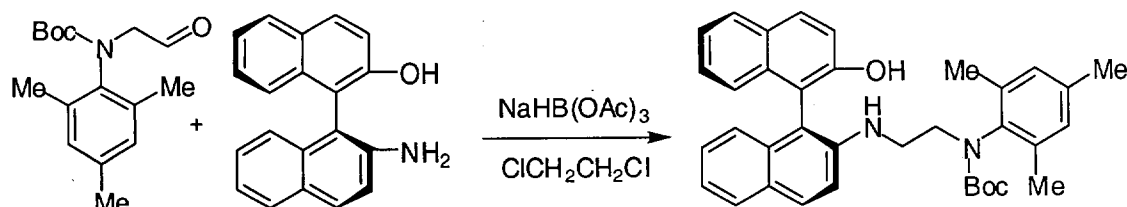
2.23 (s, 3H, *p*-CH₃), 2.16 (s, 3H, *p*-CH₃), 2.13 (s, 6H, *o*-CH₃), 1.66 (s, 3H, CHC(CH₃)₂), 1.63 (s, 3H, CHC(CH₃)₂), 1.51 (s, 9H, OC(CH₃)₃), 1.46 (s, 3H, CHC(CH₃)₂), 1.42 (s, 3H, CHC(CH₃)₂), 1.32 (s, 9H, OC(CH₃)₃). ¹³C NMR (100 MHz, CDCl₃): δ 155.07, 154.31, 137.91, 137.57, 136.64, 136.27, 136.01, 135.69, 135.22, 134.48, 129.21, 128.78, 120.96, 120.22, 79.68, 79.13, 47.67, 46.50, 28.61, 28.45, 25.81, 25.76, 21.06, 18.33, 18.25, 17.71, 17.59. HRMS Calcd for C₁₉H₂₉NO₂: 303.2198. Found: 303.2201. Anal. Calcd for C₁₉H₂₉NO₂: C, 75.21; H, 9.63; N, 4.62. Found: C, 75.50; H, 9.76; N, 4.55.



***N*-(*tert*-Butyloxycarbonyl)-*N*-(formylmethyl)-2,4,6-trimethylphenylamine (5).**

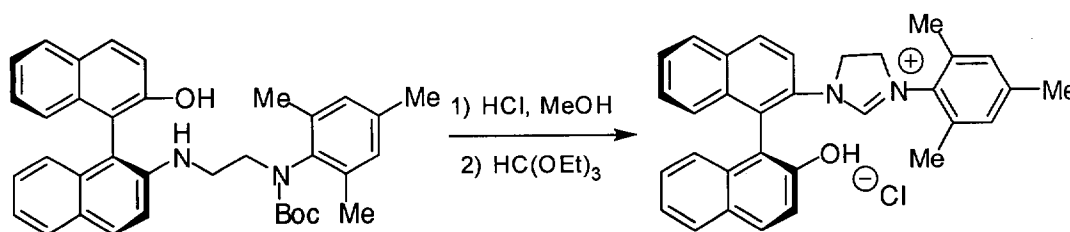
The olefin (6.07 g, 20.0 mmol, 1.0 equiv) was dissolved in 150 mL of CH₂Cl₂ and 50 mL of methanol (3:1 ratio, 0.1 M). Sodium bicarbonate was then added to the solution directly as a solid, forming a white suspension. The flask was fitted with a plastic cap punctured with both a (12 inch) 16 gage syringe needle and a smaller needle for gas release. The flask was cooled to -78 °C and ozone was bubbled into the reaction mixture through the syringe needle until TLC analysis indicated that no starting material remained (typically 10-15 minutes). The reaction mixture was then warmed to 22 °C and reduced with dimethyl sulfide (2.90 mL, 39.5 mmol, 2.0 equiv). Solvents and excess dimethyl sulfide were then removed under high vacuum. Silica gel chromatography of the resulting oily residue in 5:1 hexane:EtOAc (*R*_f = 0.35) on a short (product streaks), wide column (12 cm high; 10 cm diameter) delivered the desired aldehyde in good yield as a colorless, viscous oil (4.55 g, 82%). UV detection of this material on TLC plates is difficult, but it stains readily using ninhydrin. In CDCl₃ at 22 °C, this material exists as a 1.6:1 mixture of amide rotamers. The ¹H NMR and ¹³C NMR data given below report *each resonance in the mixture*. IR (NaCl): 3450 (br), 3369 (br), 2977 (s), 2923 (s), 2863 (m), 2820 (m), 2720 (w), 1737 (s), 1693 (s), 1610 (w), 1486 (s), 1455 (s), 1423 (s), 1368 (s), 1342 (m), 1319 (s), 1302 (s), 1277 (m), 1255 (s), 1224 (s), 1168 (s), 1151 (s), 1068 (m), 1038 (m), 988 (m), 951 (w), 913 (w), 874 (w), 854 (m), 816 (w), 773 (m), 733 (w), 675 (w), 625 (w), 601 (w), 585 (w). ¹H NMR (400 MHz, CDCl₃): δ 9.81 (m, 1H, CHO), 6.89 (d, *J* = 0.4 Hz, 2H, aromatic H), 6.87 (d, *J* = 0.6 Hz, 2H, aromatic H), 3.96 (d, *J* = 1.6 Hz, 2H, NCH₂), 3.95 (d, *J* = 1.4 Hz, 2H, NCH₂), 2.27 (s, 6H, *o*-CH₃), 2.25 (s, 3H, *p*-

CH₃), 2.23 (s, 3H, *p*-CH₃), 2.21 (s, 6H, *o*-CH₃), 1.49 (s, 9H, OC(CH₃)₃), 1.36 (s, 9H, OC(CH₃)₃). ¹³C NMR (100 MHz, CDCl₃): δ 198.87, 198.83, 155.54, 153.67, 137.83, 137.68, 137.64, 137.33, 135.66, 135.25, 129.58, 129.26, 81.59, 80.75, 59.79, 59.22, 28.28, 28.23, 20.99, 18.32, 18.25. HRMS Calcd for C₁₆H₂₃NO₃: 277.1678. Found: 277.1679. Anal. Calcd for C₁₆H₂₃NO₃: C, 69.29; H, 8.36; N, 5.05. Found: C, 69.44; H, 8.31; N, 5.01.



Diamine 6. (S)-2-Amino-2'-hydroxy-1,1'-binaphthalene (NOBIN) (**4**) (1.004 g, 3.519 mmol, 1.0 equiv) and sodium triacetoxyborohydride (1.492 g, 7.038 mmol, 2.0 equiv) were added as solids to a 100 mL round bottom flask and suspended in 30 mL of 1,2-dichloroethane. A solution of the aldehyde (976 mg, 3.25 mmol, 1.0 equiv) in 10 mL 1,2-dichloroethane was then introduced dropwise over a period of 1 h from a gas-tight syringe. As the reaction proceeds, the solids gradually dissolve. After 30 min of additional stirring, the reaction mixture was almost homogeneous and TLC analysis showed a minor amount of unreacted NOBIN (**4**). The reaction could be driven to completion by slowly adding additional aldehyde to the mixture (typically 0.2 more equiv). Upon complete consumption of NOBIN (**4**) by TLC, the reaction mixture was diluted with 100 mL of sodium bicarbonate and 50 mL of CH₂Cl₂. The organic layer was removed, and the aqueous layer was washed twice with 100 mL of CH₂Cl₂. The combined organic layers were dried over MgSO₄, filtered, and concentrated. Purification by silica gel chromatography in 7:3 hexanes: Et₂O (R_f = 0.25) delivered the protected diamine in high yield as a white foam (1.85 g, 96%). In CDCl₃ at 22 °C, this material exists as a 2.7:1 mixture of amide rotamers. The ¹H NMR and ¹³C NMR data given below report *each resonance in the mixture*. IR (NaCl): 3508 (m), 3470 (m), 3394 (br), 3055 (m), 2977 (s), 2927 (s), 2861 (m), 1737 (m), 1693 (s), 1619 (s), 1598 (s), 1573 (w), 1513 (s), 1494 (s), 1464 (m), 1455 (m), 1428 (m), 1393 (s), 1378 (s), 1367 (s), 1344 (m), 1311 (m), 1294 (m), 1268 (m), 1251 (m), 1217 (m), 1203 (m), 1174 (s), 1150 (s), 1080 (w), 1037 (w), 1026 (w), 1008 (w), 985 (w), 974 (w), 855 (m), 816 (m), 773 (m), 747 (m), 703 (w). ¹H NMR (400 MHz, CDCl₃): δ 7.94-7.89 (m, 2H, aromatic H), 7.87-7.84 (m, 1H, aromatic H), 7.82-7.77 (m, 1H, aromatic H), 7.35 (d, *J* = 9.2 Hz, 1H, aromatic H), 7.35-7.29 (m, 1H, aromatic H), 7.30 (d, *J* = 8.8 Hz, 1H, aromatic H), 7.25-7.15 (m,

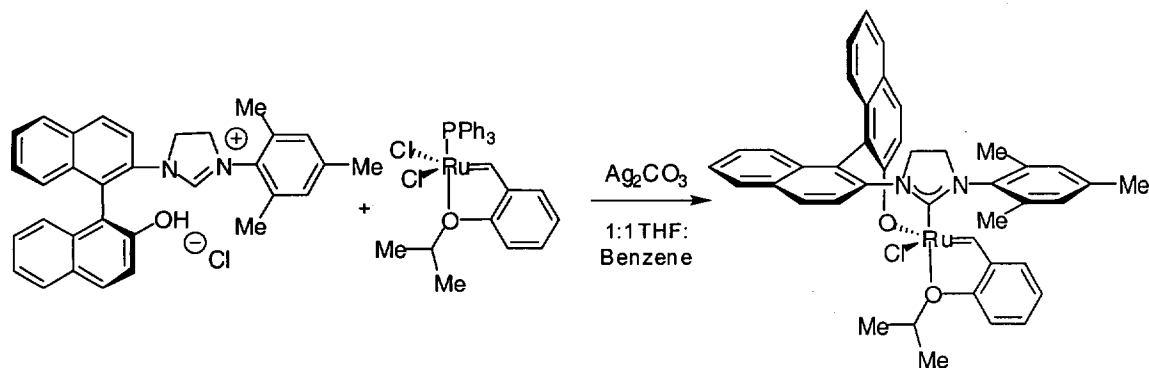
3H, aromatic H), 7.11-7.07 (m, 1H, aromatic H), 6.96-6.92 (m, 1H, aromatic H), 6.83-6.77 (m, 1H, aromatic H), 5.12 (s, 1H, ArOH), 5.06 (s, 1H, ArOH), 4.09 (br, 1H, ArNH), 3.78 (br, 1H, ArNH), 3.61-3.50 (m, 1H, ArNHCH₂), 3.45-3.33 (m, 3H, ArNHCH₂), 2.24 (s, 3H, *p*-CH₃), 2.22 (s, 3H, *p*-CH₃), 2.09 (s, 3H, *o*-CH₃), 2.07 (s, 3H, *o*-CH₃), 2.05 (s, 3H, *o*-CH₃), 2.03 (s, 3H, *o*-CH₃), 1.51 (s, 9H, OC(CH₃)₃), 1.23 (s, 9H, OC(CH₃)₃). ¹³C NMR (100 MHz, CDCl₃): δ 155.39, 154.15, 152.13, 144.99, 144.78, 137.48, 137.39, 137.06, 136.60, 135.70, 135.60, 135.34, 135.20, 134.33, 134.30, 133.54, 133.40, 131.01, 130.82, 130.59, 130.40, 129.69, 129.50, 129.10, 129.08, 128.46, 128.41, 128.29, 127.73, 127.59, 127.44, 127.21, 127.06, 126.88, 124.65, 124.51, 123.80, 123.64, 123.61, 122.50, 122.16, 117.83, 117.78, 114.16, 113.95, 113.62, 113.56, 108.32, 107.98, 80.55, 79.68, 49.75, 49.04, 42.40, 42.37, 28.58, 28.28, 20.99, 18.13, 18.09, 18.02, 17.99, 15.39. HRMS Calcd for C₃₆H₃₈N₂O₃: 546.2882. Found: 546.2882. Anal. Calcd for C₃₆H₃₈N₂O₃: C, 79.09; H, 7.01; N, 5.12. Found: C, 78.90; H, 7.26; N, 4.94.



Imidazolium chloride 7. The monoprotected diamine **6** (225 mg, 0.412 mmol) was dissolved in 4.5 mL of anhydrous methanol in a 10 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 >98% pure (¹H NMR analysis) product as an off-white crystalline solid (214 mg, >98%) which was rigorously dried (12 h) under vacuum in an Abderhalden pistol containing P₂O₅ over refluxing isopropanol. IR (KBr): 3396 (s), 3054 (s), 2956 (s), 2731 (s), 2363 (w), 1690. (w), 1619 (s), 1597 (s), 1511 (s), 1484 (m), 1431 (s), 1342 (m), 1272 (m), 1210 (m), 1148 (m), 1025 (w), 975 (w), 857 (w), 877 (s), 749 (s), 576 (w), 424 (w). ¹H NMR (400 MHz, (CD₃)₂SO): δ 9.41 (br, 1H, ArOH), 7.94-7.85 (m, 3H, aromatic H), 7.80 (d, *J* = 8.1 Hz, 1H, aromatic H), 7.39 (d, *J* = 9.0 Hz, 2H, aromatic H), 7.26 (dd, *J* = 7.6, 7.5 Hz, 1H, aromatic H), 7.19-7.07 (m, 3H, aromatic H), 6.93 (s, 2H, mesityl aromatic H), 6.88 (d, *J* = 8.4 Hz, 1H, aromatic H), 6.72 (d, *J* = 8.4 Hz, 1H, aromatic H), 4.07 (br, 4H, ArNH₂R), 3.78-3.70 (m, 1H, ArNH₂CH₂), 3.66-3.57 (m, 1H, ArNH₂CH₂), 3.25-3.37 (m, 2H, ArNH₂CH₂), 2.31 (s, 6H, *o*-CH₃), 2.20 (s, 3H, *p*-CH₃). ¹³C NMR (100 MHz, (CD₃)₂SO): δ 153.56,

143.12, 138.32, 133.90, 133.73, 131.71, 130.71, 130.31, 129.38, 128.78, 128.49, 128.06, 127.86, 127.21, 126.18, 125.98, 124.03, 123.73, 122.55, 121.42, 118.96, 114.14, 114.07, 113.69, 49.85, 20.21, 17.61. HRMS Calcd for $C_{31}H_{31}N_2O$: 447.2346. Found: 447.2346. $[\alpha]_D^{25}$ -27.92° (c = 1.018, MeOH).

The diamine hydrochloride salt (725 mg, 1.40 mmol) was suspended in 14 mL of triethylorthoformate (0.1 M) 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. As the reaction takes place, a sticky, gummy solid is deposited on the walls of the flask, and clumps may form in the reaction mixture. Using a spatula, these solids were scraped off the walls of the flask into the stirring suspension. The reaction 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). If this procedure is followed carefully, a white precipitate forms. Failure to maintain the consistency of the initial suspension may result in a low yield and incomplete consumption of the starting material. After cooling the flask to 22 °C, the mixture was diluted with 30 mL of Et₂O and filtered. The precipitate was washed with additional Et₂O (2 x 10 mL) and dried under vacuum (12 h) in an Abderhalden pistol charged with P₂O₅ over refluxing isopropanol (573 mg white solid, 83%). IR (KBr): 3422 (br), 2950 (m), 2839 (m), 2677 (w), 2590 (w), 1618 (s), 1590 (m), 1503 (m), 1478 (w), 1434 (w), 1344 (m), 1302 (w), 1276 (m), 1256 (s), 1225 (w), 1213 (w), 978 (w), 825 (w), 755 (w), 515 (w), 494 (w). ¹H NMR (400 MHz, (CD₃)₂SO): δ 10.56 (br, 1H, ArOH), 8.67 (s, 1H, NCHN), 8.28 (d, *J* = 8.6 Hz, 1H, aromatic H), 8.14 (d, *J* = 8.2 Hz, 1H, aromatic H), 8.04 (d, *J* = 9.0 Hz, 1H, aromatic H), 7.98 (d, *J* = 8.8 Hz, 1H, aromatic H), 7.95 (d, *J* = 8.2 Hz, 1H, aromatic H), 7.64-7.57 (m, 2H, aromatic H), 7.41 (ddd, *J* = 8.4, 7.1, 1.1 Hz, 1H, aromatic H), 7.32 (ddd, *J* = 8.0, 6.9, 1.1 Hz, 1H, aromatic H), 7.26 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 1H, aromatic H), 7.14 (d, *J* = 8.4 Hz, 1H, aromatic H), 6.93 (br, 2H, mesityl aromatic H), 6.87 (d, *J* = 8.2 Hz, 1H, aromatic H), 4.34 (dd, *J* = 21.6, 10.4 Hz, 1H, ArNH₂CH₂), 4.20 (dd, *J* = 21.6, 10.4 Hz, 1H, ArNH₂CH₂), 4.01 (dd, *J* = 11.2, 10.4 Hz, 2H, ArNH₂CH₂), 2.20 (s, 3H, *p*-CH₃), 1.98 (br, 3H, *o*-CH₃), 1.71 (br, 3H, *o*-CH₃). ¹³C NMR (100 MHz, (CD₃)₂SO): δ 158.24, 153.40, 139.54, 135.25, 133.34, 133.23, 132.93, 132.40, 130.84, 130.75, 130.48, 129.73, 129.16, 128.39, 128.36, 127.97, 127.47, 127.31, 127.26, 126.21, 123.62, 123.37, 123.12, 118.51, 113.01, 51.28, 50.62, 20.46, 16.67. HRMS Calcd for C₃₂H₂₉N₂O (M-Cl): 457.2280. Found (FAB on C₃₂H₂₉ClN₂O): 457.2281. Anal. Calcd for C₃₂H₂₉ClN₂O: C, 77.95; H, 5.93; N, 5.68. Found: C, 77.68; H, 5.82; N, 5.59. $[\alpha]_D^{25}$ -15.82° (c = 0.9818, DMSO).



Ruthenium complex 3. $\text{Cl}_2\text{Ru}(\text{=CH-}o\text{-O}i\text{PrC}_6\text{H}_4)\text{PPh}_3$ (**8**) (288 mg, 0.495 mmol), silver (I) carbonate (136 mg, 0.495 mmol), and the ligand salt (**7**) (244 mg, 0.495 mmol) were added to a 10 mL round bottom flask in a glovebox. The vessel was removed from the box and the solids were suspended in 2.5 mL of THF and 2.5 mL of benzene (0.10 M). The flask was equipped with a reflux condenser and submerged into an oil bath preheated to 75 °C. The reaction was stirred for 30 min, during which time the mixture remained heterogeneous but turned color from light pink to dark green/brown. The reaction mixture was then cooled to 22 °C and concentrated by a gentle N_2 purge. ^1H NMR analysis of the crude reaction mixture revealed 91% conversion to a new singlet at 15.98 ppm corresponding to the carbene proton of **3**. Also present was a doublet at 16.76 ppm (7%) derived from the starting material and another singlet at 16.64 ppm (2%). We attribute this minor resonance to the diastereomer of **3**, but have been unsuccessful in isolating this complex as a result of its instability and/or its conversion to **3** under the conditions of purification. The desired metal carbene is isolated by column chromatography (3 cm in diameter, 10 cm in length) on silica gel using CH_2Cl_2 as the eluant ($R_f = 0.10$). Solvent removal under reduced pressure affords a brown solid residue (191 mg, 52%). Crystals suitable for X-ray diffraction were obtained by slow diffusion of pentane into a concentrated CH_2Cl_2 solution of **3**. IR (NaCl): 3049 (w), 2974 (w), 2917 (w), 1615 (w), 1588 (m), 1575 (w), 1559 (w), 1506 (w), 1490 (w), 1475 (s), 1455 (m), 1424 (s), 1404 (w), 1384 (w), 1374 (w), 1355 (m), 1342 (m), 1312 (w), 1296 (m), 1275 (s), 1239 (m), 1211 (w), 1155 (w), 1112 (m), 1097 (w), 981 (w), 937 (w), 839 (w), 825 (w), 784 (w), 746 (s), 684 (w). ^1H NMR (400 MHz, CDCl_3): δ 15.96 (s, 1H, RuCH), 8.22 (d, $J = 8.7$ Hz, 1H, aromatic H), 8.07 (d, $J = 8.6$ Hz, 1H, aromatic H), 8.01 (d, $J = 8.4$ Hz, 1H, aromatic H), 7.74 (d, $J = 7.6$ Hz, 1H, aromatic H), 7.58 (d, $J = 9.0$ Hz, 1H, aromatic H), 7.52 (ddd, $J = 8.1, 6.0, 2.1$ Hz, 1H, aromatic H), 7.36 (ddd, $J = 8.2, 4.5, 4.1$ Hz, 1H, aromatic H), 7.31-7.10 (m, 4H, aromatic H), 7.06 (br, 1H, aromatic H), 6.98 (br, 1H, aromatic H), 6.90 (s, 2H, mesityl aromatic H), 6.89 (s, 1H, aromatic H), 6.67 (d, $J =$

8.6 Hz, 1H, aromatic H), 6.66 (d, $J = 8.9$ Hz, 1H, aromatic H), 4.77 (septet, $J = 6.1$ Hz, 1H, ArOCH(CH₃)₂), 4.28-4.22 (m, 1H, ArNH₂CH₂), 3.92-3.85 (m, 1H, ArNH₂CH₂), 3.61-3.48 (m, 2H, ArNH₂CH₂), 2.43 (s, 3H, *o*-CH₃), 2.22 (s, 3H, *o*-CH₃), 1.74 (s, 3H, *p*-CH₃), 1.05 (d, $J = 6.1$ Hz, 3H, ArOCH(CH₃)₂), 0.56 (d, $J = 6.1$ Hz, 3H, ArOCH(CH₃)₂). ¹³C NMR (100 MHz, CDCl₃): δ 281.62, 214.54, 169.96, 152.32, 144.30, 138.62, 138.36, 137.93, 137.40, 137.34, 137.12, 134.48, 134.41, 133.64, 129.79, 129.29, 128.89, 128.57, 128.49, 128.12, 127.98, 127.91, 127.84, 127.78, 126.81, 126.58, 125.88, 124.45, 122.44, 121.77, 121.63, 119.32, 112.98, 74.83, 52.88, 51.48, 21.27, 20.41, 20.39, 18.49, 18.00. HRMS Calcd for C₄₂H₃₉ClN₂O₂Ru: 740.1744. Found: 740.1746. Anal. Calcd for C₄₂H₃₉ClN₂O₂Ru: C, 68.14; H, 5.31; N, 3.78. Found: C, 67.89; H, 5.58; N, 3.55. $[\alpha]_D^{25}$ -980.2° ($c = 0.1752$, CHCl₃).

Representative Procedure for Ring-Closing Metathesis with Catalyst 3. A 5 mL round bottom flask was charged with N-allyl-N-tosyl methacrylamide (**9**) (26.7 mg, 0.0956 mmol) and 6.8 mg (0.0092 mmol, 9.6 mol%) of racemic **3** in a glovebox. The flask was removed from the box and the solids were dissolved in 0.96 mL of toluene (0.1 M). The vessel was equipped with a reflux condenser, submerged into an oil bath, and heated at 80 °C for 48 h. At this time, all starting material was consumed as indicated by TLC analysis. The dark brown solution was concentrated with a gentle N₂ purge, affording a dark brown crystalline solid. Column chromatography (3 cm in diameter and 10 cm high) in straight CH₂Cl₂ delivered the desired product (23.2 mg, 97%) and the recovered catalyst (6.2 mg, 91%) as white and brown solids, respectively. The catalyst residue was transferred directly into a clean 5 mL round bottom flask for subsequent reaction. A stream of N₂ was again used to concentrate this solution to a brown solid. The flask was loaded with fresh substrate (27.9 mg, 0.100 mmol) and the reaction was repeated as described above. ¹H NMR analysis of the reaction mixture after 48 h at 80 °C revealed 93% conversion to product (**11**). Purification as described above again provided the product (22.6 mg, 90%) and recovered catalyst (5.8 mg, 78%) in high yields.

Representative Procedure for AROM/CM of *cis*-5-Norbornene-endo-2,3-Dicarboxylic Anhydride. *cis*-5-Norbornene-endo-2,3-dicarboxylic anhydride (**13**) (12.2 mg, 0.0743 mmol), styrene (43 μ L, 0.375 mmol, 5.0 equiv), and **3** (5.5 mg, 0.0074 mmol, 10 mol%) were combined in a 5 mL flask in a glovebox. The flask was removed from the box and the solids were dissolved in 0.40 mL of THF (0.2 M). A reflux condenser was attached to the top of the vessel and the brown-colored solution was stirred for 1.5 h at 50 °C in an oil bath. At this time, no starting material was detectable by TLC analysis. Dry silica gel (750 mg) was then added to the reaction 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 directly onto a column 3 cm in diameter and 15 cm high, and elution with 5:1 hexanes:EtOAc provided the product (**14a**) as a colorless oil ($R_f = 0.16$, 14.2 mg, 71%) and the catalyst as a brown solid ($R_f = 0.20$, 5.3 mg, 96%).

4-Styrenyl-6-vinyl-tetrahydro-cyclopenta[c]furan-1,3-dione (14a). IR (NaCl): 3081 (w), 3024 (w), 2960 (w), 2923 (m), 2853 (w), 1854 (s), 1776 (s), 1640 (w), 1602 (w), 1494 (w), 1449 (w), 1324 (w), 1257 (m), 1205 (s), 1089 (m), 1004 (s), 968 (s), 921 (s), 794 (m), 752 (m), 695 (m). ^1H NMR (400 MHz, CDCl_3): δ 7.39 (d, $J = 7.0$ Hz, 2H), 7.32 (t, $J = 7.3$ Hz, 2H), 7.24 (t, $J = 7.3$ Hz, 1H), 6.53 (d, $J = 15.8$ Hz, 1H), 6.30 (dd, $J = 15.8, 7.9$ Hz, 1H), 6.03–5.93 (m, 1H), 5.24 (d, $J = 1.0$ Hz, 1H), 5.21 (dt, $J = 6.8, 1.0$ Hz, 1H), 3.59–5.51 (m, 2H), 3.22–3.12 (m, 1H), 3.11–3.01 (m, 1H), 2.14 (dt, $J = 12.8, 5.4$ Hz, 1H), 1.57 (quartet, $J = 12.8$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 170.71, 170.69, 136.78, 134.92, 132.44, 128.75, 127.90, 126.62, 126.50, 117.57, 49.98, 49.56, 46.94, 46.37, 36.72. Anal. Calcd for $\text{C}_{17}\text{H}_{16}\text{O}_3$: C, 76.10; H, 6.01. Found: C, 76.16; H, 6.28.

4-Hept-1-enyl-6-vinyl-tetrahydro-cyclopenta[c]furan-1,3-dione (14b). IR (NaCl): 3055 (w), 2959 (s), 2927 (s), 2855 (s), 1855 (s), 1778 (s), 1642 (w), 1456 (m), 1378 (w), 1325 (m), 1264 (s), 1205 (s), 1092 (s), 1004 (s), 972 (s), 920 (s), 797 (s), 739 (s), 704 (s), 574 (m). ^1H NMR (400 MHz, CDCl_3): δ 5.96 (ddd, $J = 16.7, 10.6, 7.3$ Hz, 1H), 5.60 (dt, $J = 15.4, 6.4$ Hz, 1H), 5.50 (dd, $J = 15.2, 7.5$ Hz, 1H), 5.18 (s, 1H), 5.15 (dt, $J = 8.1, 1.1$ Hz, 1H), 3.4 (quartet, $J = 8.4$ Hz, 2H), 3.00–2.90 (m, 2H), 2.06–1.97 (m, 3H), 1.47–1.23 (m, 7H), 0.87 (t, $J = 6.9$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 170.96, 170.71, 135.17, 133.92, 126.34, 117.26, 49.71, 49.67, 46.80, 46.11, 36.72, 32.50, 31.45, 28.98, 22.62, 14.17. HRMS Calcd for $\text{C}_{16}\text{H}_{22}\text{O}_3$: 262.1569. Found: 262.1569.

4-(2-Cyclohexyl-vinyl)-6-vinyl-tetrahydro-cyclopenta[c]furan-1,3-dione (14c). IR (NaCl): 2933 (s), 2848 (m), 1848 (m), 1785 (s), 1643 (w), 1445 (w), 1259 (w), 1199 (m), 1093 (s), 1004 (w), 969 (w), 960 (w), 929 (m), 792 (w). ^1H NMR (400 MHz, CDCl_3): δ 5.96 (ddd, $J = 17.4, 10.8, 6.6$ Hz, 1H), 5.55–5.41 (m, 2H), 5.18 (d, $J = 1.2$ Hz, 1H), 5.15 (dt, $J = 7.9, 1.3$ Hz, 1H), 3.44 (q, $J = 8.2$ Hz, 2H), 3.00–2.89 (m, 2H), 2.04–1.91 (m, 2H), 1.76–1.58 (m, 4H), 1.42 (q, $J = 13.0$ Hz, 1H), 1.32–0.98 (m, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 170.97, 170.63, 139.58, 135.19, 124.02, 117.30, 49.80, 46.89, 46.10, 40.67, 36.69, 33.01, 32.98, 26.28, 26.13. HRMS Calcd for $\text{C}_{17}\text{H}_{22}\text{O}_3$: 274.1569. Found: 274.1571. Anal. Calcd for $\text{C}_{17}\text{H}_{22}\text{O}_3$: C, 74.42; H, 8.08. Found: C, 74.29; H, 7.95.

The 7-anti-norbornenyl aryl ethers reported herein were prepared under standard Mitsunobu etherification conditions⁶ from the appropriate phenol and 7-anti-norbornenol.⁷ These substitution reactions proceed with retention of configuration.

7-Anti-norbornenyl *p*-trifluorophenyl ether (15a). IR (NaCl): 3064 (w), 2979(m), 2945 (m), 2871 (w), 1617 (m), 1590 (w), 1518 (m), 1458 (w), 1423 (w), 1329 (s), 1311 (m), 1277 (w), 1256 (s), 1244 (m), 1161 (m), 1120 (s), 1109 (s), 1072 (m), 1048 (s), 1010 (w), 858 (w), 835 (m), 713 (m), 631 (m). ¹H NMR (400 MHz, CDCl₃): δ 7.52 (d, *J* = 9.1 Hz, 2H, aromatic H), 6.97 (d, *J* = 9.1 Hz, 2H, aromatic H), 6.07 (t, *J* = 2.2 Hz, 2H, olefinic H), 4.01 (s, 1H, ArOCH), 2.88-2.84 (m, 2H, ArOCH(CHR¹R²)₂), 1.90-1.8 (m, 2H, aliphatic H), 1.07 (ddd, *J* = 11.4, 3.8, 0.8 Hz, 2H, aliphatic H). ¹³C NMR (100 MHz, CDCl₃): δ 160.12, 133.97, 126.88 (q, *J*_{CF} = 3.8 Hz), 115.27, 85.95, 43.69, 21.88. HRMS Calcd for C₁₄H₁₃F₃O: 254.0918. Found: 254.0918. Anal. Calcd for C₁₄H₁₃F₃O: C, 66.14; H, 5.15. Found: C, 66.36; H, 5.06.

7-Anti-norbornenyl *p*-methoxyphenyl ether (15b). IR (NaCl): 3060 (w), 2975(m), 2944 (m), 2868 (w), 2833 (w), 1506 (s), 1464 (w), 1456 (w), 1442 (w), 1350 (w), 1335 (w), 1305 (w), 1258 (w), 1228 (s), 1181 (w), 1127 (w), 1106 (w), 1092 (w), 1065 (m), 1039 (m), 825 (m), 749 (m), 712 (m). ¹H NMR (400 MHz, CDCl₃): δ 6.83 (ddt, *J* = 18.3, 9.1, 2.8 Hz, 4H, aromatic H), 6.04 (t, *J* = 2.2 Hz, 2H, olefinic H), 3.89 (br, 1H, ArOCH), 3.77 (s, 3H, ArOCH₃), 2.82-2.79 (m, 2H, ArOCH(CHR¹R²)₂), 1.92-1.87 (m, 2H, aliphatic H), 1.04 (dd, *J* = 10.5, 3.8 Hz, 2H, aliphatic H). ¹³C NMR (100 MHz, CDCl₃): δ 154.08, 151.77, 134.17, 116.77, 114.70, 86.97, 55.85, 43.82, 21.88. HRMS Calcd for C₁₄H₁₆O₂: 216.1150. Found: 216.1150. Anal. Calcd for C₁₄H₁₆O₂: C, 77.75; H, 7.46. Found: C, 77.48; H, 7.21.

Representative Procedure for Room-Temperature AROM/CM of 7-Anti-Norbornenyl Aryl Ethers. 7-Anti-norbornenyl *p*-trifluorophenyl ether (15a) (67.2 mg, 0.264 mmol) and styrene (55.8 mg, 0.536 mmol, 2.0 equiv) were weighed in air as neat oils into a 5 mL round bottom flask and dissolved in 2.6 mL of THF (0.1 M). Complex 3 (9.9 mg, 0.0134 mmol, 5 mol%) was then added directly to the colorless solution as a solid in one portion. The flask was stirred uncapped for 1 h at 22 °C, at which point TLC analysis indicated that the reaction was complete. Dry silica gel (1.25 g) was added to the mixture in one portion. Residual solvent was removed from the resulting slurry at reduced pressure. The dry silica gel containing the product was then loaded directly onto

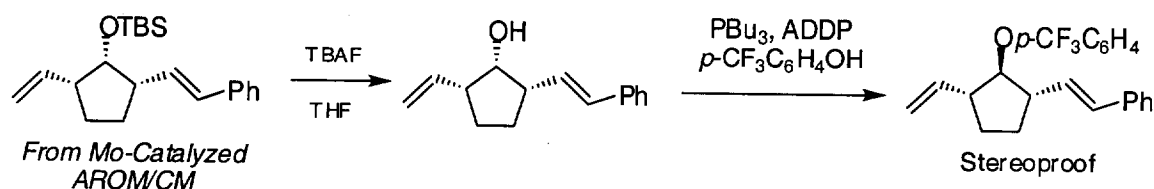
(6) (a) Mitsunobu, O. *Synthesis* **1981**, 1-28. (b) Tsunoda, T.; Yamamiya, Y.; Ito, S. *Tetrahedron Lett.* **1993**, 34, 1639-1642.

(7) Franzus, B.; Snyder, E. I. *J. Am. Chem. Soc.* **1965**, 87, 3423-3429.

a column (2.5 cm in diameter, 10 cm high) packed in CH_2Cl_2 ; elution with 100% CH_2Cl_2 provided the catalyst as a brown solid ($R_f \sim 0.10$, 8.5 mg, 86%) and a crude mixture of non-polar organic products. This fraction was then rechromatographed over silica gel in 100:1 hexanes: Et_2O to afford the desired product as a colorless oil ($R_f = 0.25$, 62.4 mg, 66%).

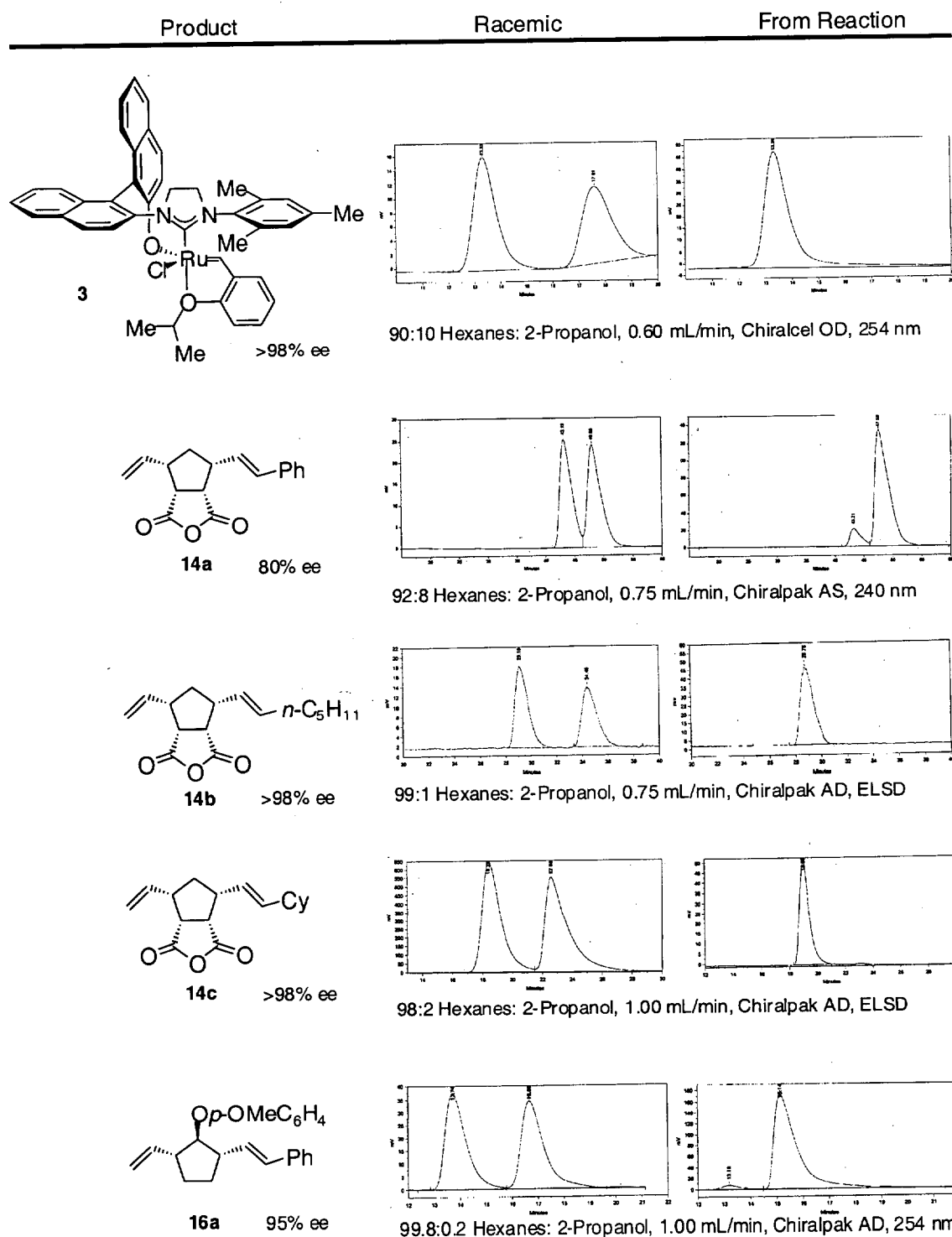
2-Styrenyl-5-vinyl-cyclopentyl-*p*-trifluoromethylphenyl ether (16a). IR (NaCl): 2956 (w), 2929 (w), 2872 (w), 1615 (m), 1589 (w), 1517 (m), 1493 (w), 1449 (w), 1422 (w), 1327 (s), 1311 (m), 1253 (s), 1178 (m), 1161 (m), 1112 (s), 1068 (m), 1009 (m), 965 (w), 917 (w), 836 (m), 747 (m), 693 (m). ^1H NMR (400 MHz, CDCl_3): δ 7.48 (d, $J = 8.4$ Hz, 2H, aromatic H), 7.34-7.27 (m, 4H, aromatic H), 7.24-7.19 (m, 1H, aromatic H), 6.97 (d, $J = 8.4$ Hz, 2H, aromatic H), 6.44 (dd, $J = 15.8, 1.0$ Hz, 1H, PhCHCHR), 6.21 (dd, $J = 15.8, 8.0$ Hz, 1H, PhCHCHR), 5.90 (ddd, $J = 18.2, 10.4, 7.8$ Hz, 1H, RCHCH_2), 5.12 (ddd, $J = 17.2, 1.6, 1.4$ Hz, 1H, RCHCH_2), 5.07 (ddd, $J = 10.2, 1.4, 1.0$ Hz, 1H, RCHCH_2), 4.38 (t, $J = 5.1$ Hz, 1H, ArOCH), 2.99-2.90 (m, 1H, $\text{ArOCH}(\text{CHR}^1\text{R}^2)_2$), 2.87-2.79 (m, 1H, $\text{ArOCH}(\text{CHR}^1\text{R}^2)_2$), 2.16-2.04 (m, 2H, aliphatic H), 1.79-1.67 (m, 2H, aliphatic H). ^{13}C NMR (100 MHz, CDCl_3): δ 161.29, 139.69, 137.34, 131.41, 130.79, 128.72, 127.48, 126.90 (q, $J_{\text{CF}} = 3.9$ Hz), 126.25, 116.29, 115.53, 89.23, 50.06, 49.71, 29.83, 29.41. HRMS Calcd for $\text{C}_{22}\text{H}_{21}\text{F}_3\text{O}$: 358.1544. Found: 358.1544. Anal. Calcd for $\text{C}_{22}\text{H}_{21}\text{F}_3\text{O}$: C, 73.73; H, 5.91. Found: C, 74.00; H, 6.20.

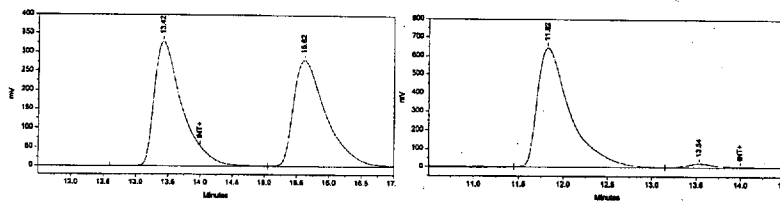
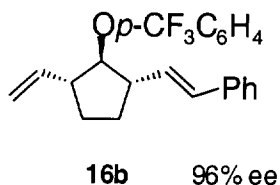
2-Styrenyl-5-vinyl-cyclopentyl-*p*-methoxyphenyl ether (16b). IR (NaCl): 2951 (m), 2931 (m), 2871 (w), 1506 (s), 1464 (w), 1448 (w), 1228 (s), 1180 (w), 1039 (m), 965 (w), 914 (w), 825 (m), 749 (m), 693 (m). ^1H NMR (400 MHz, CDCl_3): δ 7.34-7.26 (m, 4H, aromatic H), 7.23-7.18 (m, 1H, aromatic H), 6.86 (d, $J = 9.2$ Hz, 1H, aromatic H), 6.86 (dd, $J = 10.4, 6.1$ Hz, 1H, aromatic H), 6.77 (d, $J = 9.2$ Hz, 1H, aromatic H), 6.77 (dd, $J = 10.4, 6.1$ Hz, 1H, aromatic H), 6.43 (dd, $J = 15.8, 0.8$ Hz, 1H, PhCHCHR), 6.21 (dd, $J = 15.8, 8.2$ Hz, 1H, PhCHCHR), 5.89 (ddd, $J = 18.0, 10.4, 7.6$ Hz, 1H, RCHCH_2), 5.11 (dt, $J = 17.2, 1.6$ Hz, 1H, RCHCH_2), 5.04 (ddd, $J = 10.4, 1.8, 1.2$ Hz, 1H, RCHCH_2), 4.20 (t, $J = 5.7$ Hz, 1H, ArOCH), 3.74 (s, 3H, ArOCH_3), 2.97-2.88 (m, 1H, $\text{ArOCH}(\text{CHR}^1\text{R}^2)_2$), 2.85-2.77 (m, 1H, $\text{ArOCH}(\text{CHR}^1\text{R}^2)_2$), 2.12-2.00 (m, 2H, aliphatic H), 1.74-1.62 (m, 2H, aliphatic H). ^{13}C NMR (100 MHz, CDCl_3): δ 154.19, 152.96, 140.30, 137.65, 132.22, 130.31, 128.64, 127.25, 126.24, 118.19, 115.03, 114.61, 90.52, 55.82, 50.05, 49.67, 29.54, 29.09. HRMS Calcd for $\text{C}_{22}\text{H}_{24}\text{O}_2$: 320.1776. Found: 320.1776. Anal. Calcd for $\text{C}_{22}\text{H}_{24}\text{O}_2$: C, 82.46; H, 7.55. Found: C, 82.34; H, 7.80.



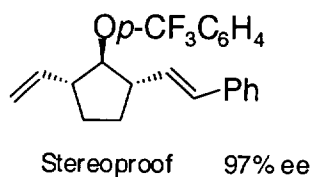
Proof of Absolute Stereochemistry for 2-Styrenyl-5-vinyl-cyclopentyl-*p*-trifluoromethylphenyl ether (16a). The *tert*-butyldimethylsilyl ether of 7-*syn*-norbornenol was subjected to Mo-catalyzed AROM/CM in the presence of 2.0 equiv of styrene as previously reported.⁸ The purified silyl ether was then deprotected in 97% yield under standard conditions (TBAF, THF). The resulting all *syn* alcohol (12.7 mg, 0.59 mmol, 1.0 equiv) was subjected to standard Mitsunobu etherification conditions using *p*-trifluoromethylphenol (17.0 mg, 0.105 mmol, 1.78 equiv), ADDP (26.2 mg, 0.104 mmol, 1.77 equiv), and PBu₃ (26 μ L, 0.104 mmol, 1.77 equiv) in benzene (0.1 M). After 1 h of stirring at 22 °C, TLC and ¹H NMR analysis of the reaction mixture suggested that a complex mixture of *elimination* products had formed. Nonetheless, a minor amount (<5%) of the desired *substitution* product was present. This material was carefully purified by silica gel chromatography (see conditions reported above) to afford ~0.5 mg of 2-styrenyl-5-vinyl-cyclopentyl-*p*-trifluoromethylphenyl ether (**16a**). Chiral HPLC analysis (see below) gave 97% ee for the *same major enantiomer* obtained using the Ru-catalyzed AROM/CM reaction reported herein.

(8) La, D.; Sattely, E. S.; Ford, J. G.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2001**, *123*, 7767-7778.





99.9:0.1 Hexanes: 2-Propanol, 0.75 mL/min, Chiralcel OD, 254 nm



See Above

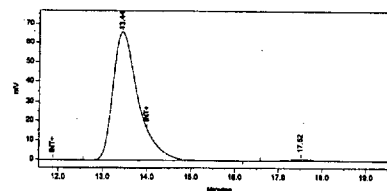


Table 1. Crystal data and structure refinement for complex (3).

Identification code	Ru Complex (3)	
Empirical formula	C43 H40.50 Cl N2.50 O2 Ru	
Formula weight	760.80	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 13.703(8) Å	a = 90°.
	b = 14.104(8) Å	b = 90°.
	c = 39.10(2) Å	g = 90°.
Volume	7557(7) Å ³	
Z	8	
Density (calculated)	1.337 Mg/m ³	
Absorption coefficient	0.524 mm ⁻¹	
F(000)	3144	
Crystal size	0.40 x 0.32 x 0.28 mm ³	
Theta range for data collection	1.81 to 25.00°.	
Index ranges	-16<=h<=16, -16<=k<=16, -38<=l<=46	
Reflections collected	41093	
Independent reflections	6663 [R(int) = 0.0981]	

Completeness to theta = 25.00°	100.0 %
Absorption correction	Semi-Empirical, SADABS
Max. and min. transmission	0.8671 and 0.8177
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	6663 / 1 / 442
Goodness-of-fit on F ²	1.018
Final R indices [I>2sigma(I)]	R1 = 0.0563, wR2 = 0.1172
R indices (all data)	R1 = 0.1027, wR2 = 0.1300
Largest diff. peak and hole	0.962 and -0.598 e.Å ⁻³

Table 2. Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters (Å²x 10³) for complex (3). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Ru(1)	576(1)	4671(1)	1306(1)	28(1)
Cl(1)	1595(1)	5368(1)	901(1)	38(1)
O(1)	-366(3)	5980(3)	1313(1)	36(1)
O(2)	-682(3)	4040(3)	1402(1)	34(1)
N(1)	2178(3)	3228(3)	1476(1)	32(1)
N(2)	1225(3)	2884(3)	1053(1)	31(1)
C(1)	2612(4)	3678(4)	1770(1)	32(1)
C(2)	3359(4)	4321(4)	1725(2)	35(2)
C(3)	3723(4)	4780(4)	2012(2)	45(2)
C(4)	3355(5)	4596(5)	2334(2)	47(2)
C(5)	2630(5)	3936(5)	2371(2)	43(2)
C(6)	2247(4)	3453(4)	2091(2)	37(2)
C(7)	3783(5)	4526(5)	1377(2)	55(2)
C(8)	3760(6)	5110(5)	2648(2)	75(3)
C(9)	1443(5)	2747(5)	2131(2)	58(2)
C(10)	2547(4)	2314(4)	1353(2)	43(2)
C(11)	1985(4)	2170(4)	1029(2)	45(2)
C(12)	557(4)	3062(4)	777(1)	30(1)
C(13)	943(4)	3406(4)	469(1)	34(2)
C(14)	350(4)	3596(4)	201(2)	37(2)

C(15)	-665(5)	3452(4)	225(1)	35(2)
C(16)	-1295(5)	3661(5)	-47(2)	44(2)
C(17)	-2260(5)	3492(5)	-22(2)	52(2)
C(18)	-2660(5)	3107(5)	274(2)	49(2)
C(19)	-2078(4)	2911(4)	550(2)	38(2)
C(20)	-1057(4)	3080(4)	535(1)	30(1)
C(21)	-419(4)	2881(4)	816(1)	28(1)
C(22)	-802(4)	2500(4)	1149(1)	29(1)
C(23)	-868(4)	3105(4)	1424(2)	33(2)
C(24)	-1243(4)	2762(5)	1744(2)	43(2)
C(25)	-1527(5)	1843(5)	1776(2)	53(2)
C(26)	-1468(4)	1214(5)	1501(2)	42(2)
C(27)	-1786(5)	266(5)	1530(2)	56(2)
C(28)	-1733(5)	-339(5)	1261(2)	63(2)
C(29)	-1349(5)	-26(5)	952(2)	55(2)
C(30)	-1035(4)	885(4)	913(2)	42(2)
C(31)	-1085(4)	1543(4)	1184(2)	32(1)
C(32)	972(4)	5212(4)	1705(1)	34(1)
C(33)	541(4)	6112(4)	1807(1)	32(1)
C(34)	807(4)	6588(4)	2106(2)	41(2)
C(35)	371(5)	7434(5)	2193(2)	51(2)
C(36)	-342(6)	7798(5)	1986(2)	56(2)
C(37)	-634(5)	7341(4)	1689(2)	51(2)
C(38)	-176(4)	6508(4)	1601(2)	35(2)
C(39)	-927(4)	6398(4)	1034(2)	42(2)
C(40)	-345(5)	7197(5)	873(2)	56(2)
C(41)	-1128(5)	5610(5)	786(2)	49(2)
C(42)	1397(4)	3536(4)	1299(1)	28(1)
C(43)	10000	0	10000	164(8)
C(44)	9265(18)	673(18)	9826(6)	145(10)
N(5)	8785(11)	981(11)	9659(4)	89(5)

Table 3. Bond lengths [Å] and angles [°] for complex (3).

Ru(1)-C(32)	1.820(6)
-------------	----------

Ru(1)-C(42)	1.957(5)
Ru(1)-O(2)	1.976(4)
Ru(1)-O(1)	2.252(4)
Ru(1)-Cl(1)	2.3304(17)
O(1)-C(38)	1.376(7)
O(1)-C(39)	1.459(6)
O(2)-C(23)	1.347(7)
N(1)-C(42)	1.345(7)
N(1)-C(1)	1.442(7)
N(1)-C(10)	1.466(7)
N(2)-C(42)	1.353(7)
N(2)-C(12)	1.438(7)
N(2)-C(11)	1.451(7)
C(1)-C(2)	1.378(8)
C(1)-C(6)	1.390(8)
C(2)-C(3)	1.388(8)
C(2)-C(7)	1.509(8)
C(3)-C(4)	1.381(8)
C(4)-C(5)	1.367(8)
C(4)-C(8)	1.531(8)
C(5)-C(6)	1.394(8)
C(6)-C(9)	1.492(8)
C(10)-C(11)	1.497(8)
C(12)-C(21)	1.371(7)
C(12)-C(13)	1.402(7)
C(13)-C(14)	1.350(7)
C(14)-C(15)	1.409(8)
C(15)-C(16)	1.402(8)
C(15)-C(20)	1.426(7)
C(16)-C(17)	1.347(8)
C(17)-C(18)	1.391(8)
C(18)-C(19)	1.373(8)
C(19)-C(20)	1.420(7)
C(20)-C(21)	1.432(7)
C(21)-C(22)	1.501(7)
C(22)-C(23)	1.377(7)

C(22)-C(31)	1.411(7)
C(23)-C(24)	1.437(7)
C(24)-C(25)	1.358(8)
C(25)-C(26)	1.396(9)
C(26)-C(27)	1.410(9)
C(26)-C(31)	1.425(8)
C(27)-C(28)	1.356(10)
C(28)-C(29)	1.389(9)
C(29)-C(30)	1.364(8)
C(30)-C(31)	1.409(8)
C(32)-C(33)	1.455(7)
C(33)-C(38)	1.389(8)
C(33)-C(34)	1.398(8)
C(34)-C(35)	1.376(8)
C(35)-C(36)	1.371(9)
C(36)-C(37)	1.386(9)
C(37)-C(38)	1.376(8)
C(39)-C(41)	1.500(8)
C(39)-C(40)	1.516(8)
C(43)-C(44)#1	1.54(2)
C(43)-C(44)	1.54(2)
C(44)-N(5)	1.023(16)

C(32)-Ru(1)-C(42)	100.5(2)
C(32)-Ru(1)-O(2)	106.6(2)
C(42)-Ru(1)-O(2)	97.81(19)
C(32)-Ru(1)-O(1)	79.5(2)
C(42)-Ru(1)-O(1)	179.8(2)
O(2)-Ru(1)-O(1)	82.33(15)
C(32)-Ru(1)-Cl(1)	103.17(18)
C(42)-Ru(1)-Cl(1)	89.48(16)
O(2)-Ru(1)-Cl(1)	147.39(11)
O(1)-Ru(1)-Cl(1)	90.36(11)
C(38)-O(1)-C(39)	119.6(4)
C(38)-O(1)-Ru(1)	110.2(3)
C(39)-O(1)-Ru(1)	128.6(3)

C(23)-O(2)-Ru(1)	128.2(3)
C(42)-N(1)-C(1)	126.5(5)
C(42)-N(1)-C(10)	113.0(5)
C(1)-N(1)-C(10)	120.4(4)
C(42)-N(2)-C(12)	121.8(5)
C(42)-N(2)-C(11)	113.2(5)
C(12)-N(2)-C(11)	121.9(4)
C(2)-C(1)-C(6)	122.1(6)
C(2)-C(1)-N(1)	119.8(5)
C(6)-C(1)-N(1)	118.1(5)
C(1)-C(2)-C(3)	118.2(6)
C(1)-C(2)-C(7)	121.6(6)
C(3)-C(2)-C(7)	120.2(6)
C(4)-C(3)-C(2)	121.2(6)
C(5)-C(4)-C(3)	119.3(6)
C(5)-C(4)-C(8)	120.0(6)
C(3)-C(4)-C(8)	120.6(6)
C(4)-C(5)-C(6)	121.5(6)
C(1)-C(6)-C(5)	117.6(6)
C(1)-C(6)-C(9)	120.9(6)
C(5)-C(6)-C(9)	121.4(6)
N(1)-C(10)-C(11)	102.6(5)
N(2)-C(11)-C(10)	102.7(5)
C(21)-C(12)-C(13)	121.9(5)
C(21)-C(12)-N(2)	120.3(5)
C(13)-C(12)-N(2)	117.8(5)
C(14)-C(13)-C(12)	120.4(5)
C(13)-C(14)-C(15)	121.0(5)
C(16)-C(15)-C(14)	121.8(6)
C(16)-C(15)-C(20)	119.4(6)
C(14)-C(15)-C(20)	118.7(5)
C(17)-C(16)-C(15)	120.8(6)
C(16)-C(17)-C(18)	121.1(6)
C(19)-C(18)-C(17)	120.3(6)
C(18)-C(19)-C(20)	120.4(6)
C(19)-C(20)-C(15)	118.0(5)

C(19)-C(20)-C(21)	122.4(5)
C(15)-C(20)-C(21)	119.6(5)
C(12)-C(21)-C(20)	118.2(5)
C(12)-C(21)-C(22)	120.3(5)
C(20)-C(21)-C(22)	121.5(5)
C(23)-C(22)-C(31)	119.8(5)
C(23)-C(22)-C(21)	118.6(5)
C(31)-C(22)-C(21)	121.6(5)
O(2)-C(23)-C(22)	123.1(5)
O(2)-C(23)-C(24)	116.9(5)
C(22)-C(23)-C(24)	119.8(6)
C(25)-C(24)-C(23)	120.3(6)
C(24)-C(25)-C(26)	121.3(6)
C(25)-C(26)-C(27)	121.6(6)
C(25)-C(26)-C(31)	118.9(6)
C(27)-C(26)-C(31)	119.5(6)
C(28)-C(27)-C(26)	121.2(7)
C(27)-C(28)-C(29)	119.6(7)
C(30)-C(29)-C(28)	121.0(7)
C(29)-C(30)-C(31)	121.4(6)
C(30)-C(31)-C(22)	122.9(6)
C(30)-C(31)-C(26)	117.2(6)
C(22)-C(31)-C(26)	119.9(5)
C(33)-C(32)-Ru(1)	118.6(4)
C(38)-C(33)-C(34)	118.5(6)
C(38)-C(33)-C(32)	118.6(5)
C(34)-C(33)-C(32)	122.8(6)
C(35)-C(34)-C(33)	120.6(6)
C(36)-C(35)-C(34)	119.2(6)
C(35)-C(36)-C(37)	121.9(7)
C(38)-C(37)-C(36)	118.3(7)
O(1)-C(38)-C(37)	125.5(6)
O(1)-C(38)-C(33)	113.1(5)
C(37)-C(38)-C(33)	121.4(6)
O(1)-C(39)-C(41)	106.3(5)
O(1)-C(39)-C(40)	109.5(5)

C(41)-C(39)-C(40)	112.3(6)
N(1)-C(42)-N(2)	106.5(5)
N(1)-C(42)-Ru(1)	135.7(4)
N(2)-C(42)-Ru(1)	117.8(4)
C(44)#1-C(43)-C(44)	180.0(16)
N(5)-C(44)-C(43)	164(3)

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y,-z+2

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for ahh1. The anisotropic displacement factor exponent takes the form: $-2p^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Ru(1)	28(1)	31(1)	26(1)	3(1)	0(1)	1(1)
Cl(1)	37(1)	40(1)	35(1)	7(1)	3(1)	-6(1)
O(1)	36(2)	35(2)	36(2)	4(2)	-3(2)	8(2)
O(2)	25(2)	37(2)	39(2)	-6(2)	6(2)	-3(2)
N(1)	34(3)	31(3)	33(3)	-4(2)	-8(2)	7(2)
N(2)	28(3)	34(3)	31(3)	-4(2)	-1(2)	5(2)
C(1)	31(3)	34(4)	30(3)	4(3)	-9(3)	1(3)
C(2)	30(3)	36(4)	39(4)	9(3)	-5(3)	3(3)
C(3)	39(4)	43(4)	52(4)	11(3)	-12(3)	-6(3)
C(4)	53(4)	37(4)	49(4)	-2(3)	-23(4)	0(4)
C(5)	51(4)	50(4)	29(4)	6(3)	-4(3)	5(4)
C(6)	37(4)	38(4)	37(4)	3(3)	-9(3)	0(3)
C(7)	41(4)	66(5)	57(5)	14(4)	8(4)	0(4)
C(8)	99(7)	61(5)	64(5)	-8(4)	-30(5)	-22(5)
C(9)	54(5)	71(5)	50(5)	8(4)	9(4)	-19(4)
C(10)	40(4)	46(4)	43(4)	-5(3)	-11(3)	8(3)
C(11)	49(4)	41(4)	44(4)	-12(3)	-12(3)	16(3)
C(12)	33(3)	31(3)	25(3)	-4(2)	-2(3)	4(3)
C(13)	30(3)	44(4)	29(4)	0(3)	6(3)	-5(3)
C(14)	41(4)	43(4)	26(3)	2(3)	8(3)	-8(3)
C(15)	42(4)	35(4)	28(3)	3(3)	-6(3)	3(3)

C(16)	53(5)	60(5)	18(3)	7(3)	-1(3)	4(4)
C(17)	49(5)	73(5)	33(4)	8(4)	-15(4)	8(4)
C(18)	32(4)	75(5)	42(4)	6(4)	-6(3)	-1(4)
C(19)	30(3)	56(4)	27(3)	9(3)	2(3)	-2(3)
C(20)	35(3)	33(4)	20(3)	0(3)	-3(3)	0(3)
C(21)	30(3)	27(3)	25(3)	-1(2)	-3(3)	6(3)
C(22)	26(3)	36(3)	24(3)	0(3)	-1(3)	1(3)
C(23)	23(3)	41(4)	35(4)	10(3)	0(3)	-4(3)
C(24)	46(4)	53(5)	28(4)	5(3)	5(3)	0(3)
C(25)	60(5)	61(5)	37(4)	20(4)	7(4)	-14(4)
C(26)	39(4)	43(4)	45(4)	13(3)	-3(3)	-8(3)
C(27)	54(4)	57(5)	57(5)	21(4)	1(4)	-15(4)
C(28)	55(4)	42(4)	92(6)	26(5)	-12(5)	-10(4)
C(29)	56(5)	38(4)	72(6)	-4(4)	-13(4)	-1(4)
C(30)	37(4)	39(4)	49(4)	5(3)	-11(3)	-4(3)
C(31)	25(3)	35(4)	36(4)	4(3)	-10(3)	-2(3)
C(32)	30(3)	33(4)	37(4)	2(3)	1(3)	-2(3)
C(33)	32(3)	32(3)	33(3)	-3(3)	12(3)	-6(3)
C(34)	39(4)	49(4)	36(4)	-4(3)	14(3)	-12(3)
C(35)	54(5)	46(5)	53(5)	-15(4)	18(4)	-14(4)
C(36)	72(6)	37(4)	60(5)	-10(4)	33(4)	-2(4)
C(37)	61(5)	42(4)	48(4)	8(3)	15(4)	13(4)
C(38)	38(4)	33(4)	33(4)	7(3)	11(3)	-1(3)
C(39)	36(4)	45(4)	47(4)	12(3)	-3(3)	9(3)
C(40)	58(5)	57(5)	54(5)	21(4)	1(4)	3(4)
C(41)	38(4)	61(5)	50(4)	14(4)	-12(3)	-5(3)
C(42)	28(3)	29(3)	27(3)	3(3)	5(3)	-4(3)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for complex (3).

	x	y	z	U(eq)
H(3A)	4235	5228	1987	53

H(5A)	2383	3805	2593	52
H(7A)	4306	4996	1398	82
H(7B)	3271	4774	1227	82
H(7C)	4048	3940	1279	82
H(8A)	3417	4890	2854	112
H(8B)	3664	5794	2622	112
H(8C)	4459	4974	2671	112
H(9A)	1273	2484	1907	87
H(9B)	870	3059	2230	87
H(9C)	1659	2235	2283	87
H(10A)	2413	1801	1519	52
H(10B)	3258	2342	1308	52
H(11A)	2402	2275	825	54
H(11B)	1703	1524	1018	54
H(13A)	1626	3505	448	41
H(14A)	621	3830	-6	44
H(16A)	-1038	3925	-252	52
H(17A)	-2674	3639	-210	62
H(18A)	-3340	2978	284	59
H(19A)	-2359	2662	753	45
H(24A)	-1293	3179	1934	51
H(25A)	-1771	1625	1989	63
H(27A)	-2043	48	1741	67
H(28A)	-1958	-973	1284	75
H(29A)	-1305	-453	765	66
H(30A)	-777	1081	699	50
H(32A)	1451	4913	1844	40
H(34A)	1293	6325	2252	50
H(35A)	563	7762	2394	61
H(36A)	-646	8379	2047	67
H(37A)	-1138	7597	1550	61
H(39A)	-1557	6651	1124	51
H(40A)	-233	7695	1044	85
H(40B)	-710	7461	680	85
H(40C)	283	6953	793	85
H(41A)	-1507	5113	900	74

H(41B)	-509	5345	704	74
H(41C)	-1499	5858	591	74
H(43A)	10549	365	10078	196
H(43B)	10231	-495	9852	196
H(43C)	9696	-295	10194	196
