

Supporting information

Rhodium-Catalyzed Asymmetric Ring Opening Reactions of Oxabicyclic Alkenes: The Application of Halide Effects in the Development of a General Process

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Experimental:

All flasks were flame-dried under a stream of nitrogen or argon and cooled before use. Solvents and solutions were transferred with syringes and cannulae using standard inert atmosphere techniques. ¹H NMR spectra were recorded at 200 MHz using a Varian Gemini NMR spectrometer or at 400 MHz using a Varian XL400 spectrometer with CDCl₃ as reference standard (δ 7.24 ppm) or some other suitable solvent. Spectral features are tabulated in the following order: chemical shift (δ, ppm); number of protons; multiplicity (s-singlet, d-doublet, t-triplet, q-quartet, m-complex multiplet, br-broad); coupling constants (*J*, Hz). ¹³C NMR spectra were recorded at 400 MHz with CDCl₃ as reference standard (δ = 77.0 ppm) or some other suitable solvent. IR spectra were obtained using a Nicolet DX FT-JR spectrometer as a KBr pellet or neat film between KBr plates. High resolution mass spectra were obtained from a VG 70-250S (double focusing) mass spectrometer at 70 eV. Combustion analyses were submitted to Canadian Microanalytical Service Ltd., BC. Optical rotations were measured on a Perkin Elmer Model 243 Polarimeter using the sodium D line with spectro-grade CHCl₃ in a 1 dm cell. Melting points were taken on a Fisher-Johns melting point apparatus and are uncorrected. Gas chromatography was performed on a Hewlett Packard 5890 gas chromatograph using an Advanced Separation Technologies G-TA or B-TA chiral columns. HPLC analysis was performed on a Waters 600E with Chiralcel OD, AD or OJ columns. Analytical TLC was performed using EM Separations precoated silica gel 0.2 mm layer UV 254 fluorescent sheets. Column chromatography was performed as “Flash Chromatography” as reported by Still¹ on Ultra Pure Silica Gel (Silicycle, 230-400 mesh, 60A) using the indicated eluent.

Diethyl ether, THF, benzene and toluene were distilled from sodium benzophenone ketyl immediately prior to use. CH₂Cl₂ was distilled from calcium hydride. DME was distilled from sodium benzophenone ketyl and stored. DMF was dried and stored over activated molecular sieves. Furan was distilled prior to use. Mosher's acid chloride

¹ Still, W.C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1989**, *54*, 5667.

was prepared by refluxing Mosher's acid (MTPA, obtained from Aldrich) in thionyl chloride in the presence of a catalytic amount of NaCl for 60 h and purified by bulb to bulb distillation. Oxabicyclic alkenes **1**² and **58a/b**³ were prepared according to literature procedure. Compounds **28** to **31** were prepared according to previously reported procedures.^{Error! Bookmark not defined.} All other reagents were obtained from Aldrich and used as received unless otherwise stated.

Representative procedure for the *in situ* exchange of chloride to iodide ligands:

To a flame-dried round bottomed flask under inert atmosphere was added [Rh(COD)Cl]₂ (5mg, 0.01mmol) and (*S,R*)-PPF-P^tBu₂ (12mg, 0.022mmol) which was dissolved in 2mL THF and stirred at room temperature for 5 min to produce a dark red solution. In a separate flame-dried round bottomed flask was added AgOTf (11mg, 0.04mmol). The rhodium-phosphine solution was transferred to the flask containing the AgOTf via cannula resulting in the formation of a white precipitate. This heterogeneous mixture was stirred at room temperature for 5 min prior to its transfer to a flame-dried flask containing TBAI (22mg, 0.06mmol). After stirring for 5 additional minutes, this red-brown solution was ready for use.

Preparation of Oxabicyclic Alkene Starting Materials:

1,4-Dihydro-6,7-dimethoxy-1,4-epoxynaphthalene (40):

A stirred solution of 1,2-dibromo-4,5-dimethoxybenzene (4.16 g, 14.06 mmol) in anhydrous THF 25 mL/ Furan 30 mL was cooled to -78°C. Under N₂ and was treated drop wise with 8.8 mL of BuLi (1.6 M in hexane). The solution was stirred at -78°C for 0.5hr. The resulting reaction mixture was kept at -78°C for 1hr. added 20 mL distilled water to reaction mixture, left to warm up to room temperature, the reaction mixture was extracted from diethyl ether and dried over Na₂SO₄. The ether was then removed in *vacuo* and the resulting mixture purified by flash chromatography (50% ethyl acetate in hexanes) to give **40** an white solid (2.5g, 87%). R_f = 0.14 on silica gel (50% ethyl acetate in hexanes). mp 147-149° (Et₂O). IR (KBr, cm⁻¹) 2926 (s), 2924 (s), 2839 (s), 1599 (s), 1485 (s), 1467 (s), 1325 (s), 1285 (s), 1063 (s). ¹H NMR (400MHz, CDCl₃) δ 7.04 (2H, t, *J* = 0.91 Hz), 6.97 (2H, s), 5.68 (2H, s), 3.85 (6H, s); ¹³C NMR (400MHz, CDCl₃) δ 146.1, 143.6, 141.9, 107.0, 82.8, 56.7.

1,4-Dihydro-5,8-dimethoxy-1,4-epoxynaphthalene (41):

A solution of LDA was freshly prepared by addition of 7.4 mL (1.1 eq) in anhydrous THF (15 mL) at -78°C, followed by a brief warm-up to room temperature. Furan (15 mL) was slowly added at -78°C and the resulting colorless solution was treated drop-wise with a solution of 1-bromo-2,5-dimethoxy benzene (2.16 g, 10 mmol) in anhydrous THF (5 mL). The yellow solution was kept at -78°C for 30min, then quenched with water and left to warm up. Standard extractive work-up with diethyl ether and brine yielded the crude product which was purified by flash chromatography (50% ethyl acetate in hexanes) to give **41** an white solid (2.10 g, 86%). R_f = 0.17 on silica gel (50% ethyl acetate in hexanes). mp 86-87° (Et₂O). IR (KBr, cm⁻¹) 3085 (s), 2989 (s), 2839 (s), 1619 (m), 1438 (s), 1253 (s), 1139 (s), 1075 (s), 997 (s). ¹H NMR (400MHz, CDCl₃) δ 7.06 (2H, s), 6.97 (2H, s), 6.54 (2H, s), 5.92 (2H, s), 3.78 (6H, s). ¹³C NMR (400MHz, CDCl₃) δ 148.1, 143.1, 111.9, 80.6, 56.6.

² Stiles, M.; Miller, R.G. *J. Am. Chem. Soc.* **1960**, 82, 3802.

³ Waymouth, R. M.; Millward, D. B.; Sammis, G. *J. Org. Chem.* **2000**, 65, 3902.

Rhodium-Catalyzed Asymmetric Ring Opening Reactions:

(1R*, 2R*)-2-Pyrrolidin-1-yl-1,2-dihydronaphthalen-1-ol (3):

To a flame dried round bottom flask were added [Rh(COD)Cl]₂ (4.3mg, 0.009 mmol), DPPF (9.6 mg, 0.017 mmol), pyrrolidine (146 mg, 3.47 mmol), triethylamine hydrochloride (478 mg, 3.47 mmol) and oxabenzonorbornadiene (125 mg, 0.865 mmol) followed by addition of THF (3 mL) and heating to reflux for 8 hours. The solvent was then removed *in vacuo* and the resulting mixture purified by flash chromatography (10% methanol in acetone) to give **3** an off white solid (119 mg, 80%). *R*_f = 0.14 on silica gel (10% methanol in acetone); mp 97-98° (Et₂O); IR (KBr, cm⁻¹) 3496 (br), 3035 (m), 2967 (s), 1454 (m), 1193 (s), 1117 (m), 1048 (s). ¹H NMR (400MHz, CDCl₃) δ 7.56 (1H, d, *J* = 7.1 Hz), 7.29-7.21 (2H, m), 7.08-7.06 (1H, m), 6.57 (1H, dd, *J* = 9.9, 2.4 Hz), 6.05 (1H, dd, *J* = 9.9, 2.4 Hz), 4.83 (1H, d, *J* = 11.3 Hz), 3.66 (1H, ddd, *J* = 11.3, 2.4, 2.4 Hz), 3.57 (1H, s), 2.81-2.79 (2H, m), 2.73-2.71 (2H, m), 1.84-1.80 (4H, m); ¹³C NMR (400MHz, CDCl₃) δ 136.9, 131.8, 129.6, 127.7, 127.3, 126.1, 125.4, 124.7, 69.8, 63.3, 48.7, 23.8. HRMS calcd for C₁₄H₁₇NO (M⁺): 215.1310. Found: 215.1314.

(1R*, 2R*)-2-Piperidin-1-yl-1,2-dihydronaphthalen-1-ol (4):

To a flame dried round bottom flask, [Rh(COD)Cl]₂ (4.3 mg, 0.0087 mmol), DPPF (9.6 mg, 0.0173 mmol), piperidine hydrochloride (422 mg, 3.47 mmol), triethylamine (350 μ L, 2.51 mmol) and oxabenzonorbornadiene (100 mg, 0.69 mmol) were added followed by THF (3 mL) and heating to 80°C for 12 hours. The reaction mixture was then concentrated *in vacuo* and purified by flash chromatography (50% ethyl acetate, 48% hexanes, 2% methanol) to give **4** a white solid (130 mg, 82%). *R*_f = 0.24 on silica gel (50% ethyl acetate, 48% hexanes, 2% methanol); mp 62-64° (Et₂O); IR (KBr, cm⁻¹) 3482 (br), 3036 (w), 2937 (s), 2853 (m), 1453 (s), 1193 (s), 1109 (s), 1046 (s). ¹H NMR (400MHz, CDCl₃) δ 7.57 (1H, d, *J* = 7.1 Hz), 7.27-7.18 (2H, m), 7.05 (1H, dd, *J* = 6.9, 0.9 Hz), 6.49 (1H, dd, *J* = 9.9, 2.6 Hz), 6.12 (1H, dd, *J* = 9.9, 2.4 Hz), 4.87 (1H, d, *J* = 12.2 Hz), 3.58 (1H, s), 3.37 (1H, ddd, *J* = 12.2, 2.4, 2.4 Hz), 2.79-2.73 (2H, m), 2.48 (2H, m), 1.67-1.57 (4H, m), 1.56-1.46 (2H, m); ¹³C NMR (400MHz, CDCl₃) δ 137.4, 131.8, 128.8, 127.1, 125.9, 125.2, 124.4, 68.2, 67.6, 50.4, 26.5, 24.6. HRMS calcd for C₁₅H₁₈NO (M⁺-H): 228.1388. Found: 228.1318.

(1R*, 2R*)-2-Diethylamino-1,2-dihydronaphthalen-1-ol (5):

To a flame dried round bottom flask were added [Rh(COD)Cl]₂ (4.3 mg, 0.009 mmol), DPPF (9.6 mg, 0.017 mmol), diethylamine hydrochloride (191 mg, 1.74 mmol), triethylamine (242 μ L, 1.74 mmol) and oxabenzonorbornadiene (50 mg, 0.347 mmol) followed by addition of THF (3 mL) and heating to reflux for 12 hours. The solvent was then removed *in vacuo* and the resulting mixture purified by flash chromatography (70% ethyl acetate in hexanes) to give **5** a white crystalline solid (62 mg, 82%). *R*_f = 0.15 on silica gel (70% ethyl acetate:hexanes); IR (KBr, cm⁻¹) 3482 (br), 3036 (w), 2937 (s), 2853 (m), 1453 (s), 1193 (s), 1109 (s), 1046 (s). ¹H NMR (400MHz, CDCl₃) δ 7.57 (1H, d, *J* = 7.3Hz), 7.27-7.18 (2H, m), 7.04-7.03 (1H, m), 6.47 (1H, dd, *J* = 9.9, 2.8Hz), 6.04 (1H, dd, *J* = 9.9, 2.2Hz), 5.80 (1H, d, *J* = 12.7Hz), 3.73 (1H, s), 3.58 (1H, ddd, *J* = 12.7, 2.4, 2.4Hz), 2.80 (2H, dq, *J* = 7.3, 5.9Hz), 2.57 (2H, dq, *J* = 7.3, 5.9Hz), 1.09 (6H, t, *J* = 7.2Hz); ¹³C NMR (400MHz, CDCl₃) δ 137.1, 131.8, 129.2, 127.7, 127.1, 125.8, 124.2, 68.9, 64.2, 44.7, 14.4. HRMS calcd for C₁₄H₁₉NO (M⁺): 217.1467; Found: 217.1460.

(1R, 2R)-2-Dibenzylamino-1,2-dihydronaphthalen-1-ol (6):

To a round bottom flask containing oxabenzonorbornadiene (50 mg, 0.347 mmol) was added a THF solution (1 mL) of the rhodium iodide (R, S)-PPF- P^tBu_2 complex (1 mol% to oxabenzonorbornadiene). This red-brown solution was then heated to reflux followed by addition of dibenzylamine (273 μ L, 1.39 mmol) and ammonium iodide (101 mg, 0.694 mmol). The reaction was allowed to stir at reflux for 5 hours then the solvent was then removed *in vacuo* and the resulting mixture purified by flash chromatography (40-70% ethyl acetate in hexanes) to give **6** a colourless oil which crystallized on sitting (92 mg, 84%). The ee was determined to be 99% using HPLC analysis on a CHIRALCEL OD column, $\lambda = 254$ nm. Retention times in 10% isopropanol in hexanes were 9.7 min (major) and 12.6 min. $[\alpha]_D^{25} = -113$ ($c = 15.9$, $CHCl_3$); $R_f = 0.30$ on silica gel (70% ethyl acetate:hexanes); IR (KBr, cm^{-1}) 3482 (br), 3036 (w), 2937 (s), 2853 (m), 1453 (s), 1193 (s), 1109 (s), 1046 (s) 1H NMR (400 MHz, $CDCl_3$) δ 7.50 (1H, d, $J = 7.1$ Hz), 7.28-7.34 (8H, m), 7.15-7.25 (4H, m), 7.00-7.04 (1H, m), 6.53 (1H, dd, $J = 2.3, 9.8$ Hz), 6.12 (1H, dd, $J = 2.3, 9.9$ Hz), 5.01 (1H, d, $J = 11.7$ Hz), 3.95 (2H, d, AB, $J = 13.6$ Hz), 3.65 (1H, d, $J = 11.7$ Hz), 3.57 (2H, d, AB, $J = 13.6$ Hz), 3.07 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.0, 136.7, 131.7, 129.6, 128.9, 128.5, 127.8, 127.3, 127.2, 126.0, 125.5, 124.8, 68.8, 62.3, 54.7. HRMS calcd for $C_{24}H_{23}NO$ (M^+): 341.1780; Found: 341.1786.

(1R, 2R)-2-(3,4-Dihydro-1H-isoquinolin-2-yl)-1,2-dihydronaphthalen-1-ol (7):

To a round bottom flask containing oxabenzonorbornadiene (50 mg, 0.347 mmol) was added a THF solution (1 mL) of the rhodium iodide (R,S)-PPF- P^tBu_2 complex (1 mol% to oxabenzonorbornadiene). This red-brown solution was then heated to reflux followed by addition of tetrahydroisoquinoline (185 mg, 1.39 mmol) and ammonium iodide (101 mg, 0.694 mmol). The reaction was allowed to stir at reflux for 10 hours then the solvent was then removed *in vacuo* and the resulting mixture purified by flash chromatography (40-70% ethyl acetate in hexanes) to give **7** a colourless oil (78 mg, 81%). $R_f = 0.25$ on silica gel (70% ethyl acetate:hexanes); The ee was determined to be 97% using HPLC analysis on a CHIRALCEL OD column, $\lambda = 254$ nm. Retention times in 3% isopropanol in hexanes were 19.545 min (major) and 18.395 min (minor). $[\alpha]_D^{25} = -154$ ($c = 10.0$, $CHCl_3$); IR (KBr, cm^{-1}) 3482 (br), 3036 (w), 2937 (s), 2853 (m), 1453 (s), 1193 (s), 1109 (s), 1046 (s) 1H NMR (400 MHz, $CDCl_3$) δ 7.61-7.60 (1H, m), 7.30-7.23 (2H, m), 7.18-7.13 (3H, m), 7.11-7.09 (1H, m), 7.06-7.04 (1H, m), 6.58 (1H, dd, $J = 9.9, 2.6$ Hz), 6.15 (1H, dd, $J = 9.9, 2.4$ Hz), 5.02 (1H, d, $J = 12.1$ Hz), 4.02 (1H, d, AB, $J = 14.8$ Hz), 3.80 (1H, d, AB, $J = 14.8$ Hz), 3.66 (1H, ddd, $J = 12.1, 2.5, 2.5$ Hz), 3.12-3.18 (1H, m), 2.90-3.00 (2H, m), 2.77-2.84 (1H, m); ^{13}C NMR (400 MHz, $CDCl_3$) δ 137.0, 134.7, 134.4, 131.7, 129.6, 128.8, 127.9, 127.4, 126.6, 126.2, 126.1, 125.7, 124.6, 124.5, 68.0, 67.6, 52.0, 46.9, 29.9; HRMS calcd for $C_{19}H_{19}NO$ (M^+): 277.1467; Found: 277.1462.

(1R*, 2R*)-2-Benzylamino-1,2-dihydro-naphthalen-1-ol (8):

To a flame dried round bottom flask, $[Rh(COD)Cl]_2$ (4.3 mg, 0.009 mmol), DPPF (9.6 mg, 0.017 mmol), benzylamine hydrochloride (279 mg, 1.74 mmol), triethylamine (242 μ L, 1.74 mmol) and oxabenzonorbornadiene (50 mg, 0.347 mmol) followed by addition of THF (3 mL) and heating to reflux for 3 days. The solvent was then removed *in vacuo* and the resulting mixture purified by flash chromatography (50% ethyl acetate in hexanes) to give **8** a white solid (26.9 mg, 31%). $R_f = 0.44$ on silica gel (50% ethyl acetate, 48% hexanes, 2% methanol); mp 115-117° (dec) (Et_2O); IR (KBr, cm^{-1}) 3528 (br), 3030 (w), 2849 (w), 1455 (s), 1190

(m), 1112 (m), 1048 (m). ^1H NMR (400MHz, CDCl_3) δ 7.47-7.45 (1H, m), 7.29-7.24 (4H, m), 7.24-7.17 (3H, m), 7.02-7.01 (1H, m), 6.41 (1H, dd, J = 9.7, 2.0 Hz), 6.00 (1H, dd, J = 9.7, 2.5 Hz), 4.64 (1H, d, J = 9.0 Hz), 3.94 (1H, AB, J = 13.0 Hz), 3.75 (1H, AB, J = 13.0 Hz), 3.42 (1H, ddd, J = 11.0, 2.4, 2.4 Hz), 2.44 (1H, s); ^{13}C NMR (400MHz, CDCl_3) δ 139.8, 136.6, 132.1, 128.8, 128.5, 128.2, 127.9, 127.8, 127.6, 127.2, 126.1, 124.9, 72.1, 59.7, 50.7. HRMS calcd for $\text{C}_{17}\text{H}_{17}\text{NO}$ (M^+): 251.1310. Found: 251.1316.

(1R, 2R)-2-(4-Methoxy-benzylamino)-1,2-dihydronaphthalen-1-ol (9):

To a round bottom flask containing oxabenzonorbornadiene (50 mg, 0.347 mmol) was added a THF solution (1mL) of the (R, S)-PPF- P^tBu_2 rhodium iodide complex (1 mol% to oxabenzonorbornadiene). This red-brown solution was then heated to reflux followed by addition of *p*-methoxybenzylamine (190 mg, 1.39 mmol) and ammonium iodide (101 mg, 0.694 mmol). The reaction was allowed to stir at reflux for 14 hours then the solvent was then removed *in vacuo* and the resulting mixture purified by flash chromatography (50% ethyl acetate in hexanes) to give **9** a white solid (43 mg, 44%). The ee was determined to be 81% using HPLC analysis on a CHIRALCEL OD column, λ =254nm. Retention times in 5% isopropanol in hexanes were 19.707 min (major) and 17.939 min (minor). $[\alpha]_D^{25}$ = -84 (c =9.2, CHCl_3); R_f = 0.27 on silica gel (50% ethyl acetate, 48% hexanes, 2% methanol); mp 96-98° (dec) (Et_2O); IR (KBr, cm^{-1}) 3528 (br), 3033 (w), 2835 (m), 1612 (m), 1512 (s), 1455 (m), 1248 (s), 1040 (m). ^1H NMR (400MHz, CDCl_3) δ 7.52-7.50 (1H, m), 7.26-7.22 (4H, m), 7.08-7.06 (1H, m), 6.85 (2H, d, J = 9.0 Hz), 6.47 (1H, dd, J = 9.7, 2.0 Hz), 6.05 (1H, dd, J = 9.9, 2.6 Hz), 4.68 (1H, d, J = 11.0 Hz), 3.95 (1H, d, J = 12.9 Hz), 3.79 (3H, s), 3.75 (1H, d, J = 2.9 Hz), 3.46 (1H, ddd, J = 11.0, 2.4, 2.4 Hz), 3.0-2.0 (2H, s (br)); ^{13}C NMR (400MHz, CDCl_3) δ 158.7, 136.7, 132.1, 131.9, 129.4, 128.9, 127.9, 127.7, 127.5, 126.0, 124.9, 113.9, 72.1, 59.6, 55.2, 50.1. HRMS calcd for $\text{C}_{18}\text{H}_{19}\text{NO}_2$ (M^+): 281.1416. Found: 281.1403.

(1S, 2S)-2-(4-Methyl-piperazin-1-yl)-1,2-dihydronaphthalen-1-ol (10):

To a round bottom flask containing the (S, R)-PPF- P^tBu_2 rhodium iodide complex (1 mol% to oxabenzonorbornadiene) was added oxabenzonorbornadiene (80 mg, 0.555 mmol). The red-brown solution was then heated to reflux followed by addition of 1-methylpiperazine (62 μL , 0.555 mmol). The reaction was allowed to stir at reflux for 3 hours. The solvent was then removed *in vacuo* and the resulting oil purified by flash chromatography (48% ethyl acetate, 2% methanol in hexanes) to give **10** yellow oil (130 mg, 96%). The ee was determined to be 99% using HPLC analysis on a CHIRALCEL OD column, λ = 254nm. Retention times in 10% isopropanol in hexanes were 15.8 min (major) and 7.70 min. R_f = 0.10 on silica gel (48% ethyl acetate, 2% methanol in hexanes); $[\alpha]_D^{25}$ = 98.2 (c = 11, CHCl_3); IR (KBr, cm^{-1}) 3356 (br), 2938 (s), 2806 (s), 1454 (s), 1373 (w), 1284 (s), 1142 (s), 1005 (s), 784 (s). ^1H NMR (400MHz, CDCl_3) δ 7.56 (1H, d, J = 7.14 Hz), 7.22-7.29 (2H, m), 7.08-7.09 (1H, d, J = 7.0 Hz), 6.54 (1H, dd, J = 9.8, 2.4 Hz), 6.09 (1H, dd, J = 9.8, 2.4 Hz), 4.87 (1H, d, J = 11.4 Hz), 3.55 (1H, s), 3.45 (1H, ddd, J = 11.4, 2.4, 2.4 Hz), 2.82 (2H, m), 2.59 (2H, m), 2.51 (4H, s(br)), 2.32 (3H, s); ^{13}C NMR (100MHz, CDCl_3) δ 137.3, 131.9, 129.4, 127.9, 127.6, 126.3, 124.9, 67.7, 67.4, 55.7, 46.1. HRMS calcd for $\text{C}_{15}\text{H}_{20}\text{N}_2\text{O}$ (M^+): 244.1576. Found: 244.1571.

(1R, 2R)-2-(Methyl-phenyl-amino)-1,2-dihydronaphthalen-1-ol (2):

To a round bottom flask containing the (R, S)-PPF- P^tBu_2 rhodium iodide complex (1

mol% to oxabenzonorbornadiene) was added oxabenzonorbornadiene (100 mg, 0.694 mmol). The red-brown solution was then heated to reflux followed by addition of N-methylaniline (371 μ L, 3.47 mmol). The reaction was allowed to stir at reflux for 2 hours. The solvent was then removed *in vacuo* and the resulting oil purified by flash chromatography (5% ethyl acetate in hexanes) to give **2** an off white solid (176.3 mg, 96%). The ee was determined to be 92% using HPLC analysis on a CHIRALCEL OD column, λ = 254nm. Retention times in 10% isopropanol in hexanes were 9.7 min (major) and 11.2 min. R_f = 0.41 on silica gel (20% ethyl acetate:hexanes); mp 55-56 $^{\circ}$ (Et₂O); $[\alpha]_D^{25}$ = 62 (c = 11.8, CHCl₃); IR (KBr, cm⁻¹) 3594 (br), 3037 (m), 2884 (m), 1596 (s), 1503 (s), 1463 (m), 1186 (m), 935 (m). ¹H NMR (400MHz, CDCl₃) δ 7.57-7.55 (1H, m), 7.31-7.26 (4H, m), 7.15-7.13 (1H, m), 6.99-6.97 (2H, m), 6.84-6.81 (1H, m), 6.61 (1H, dd, J = 9.8, 2.6 Hz), 5.94 (1H, dd, J = 9.7, 2.9 Hz), 5.11 (1H, d, J = 9.8 Hz), 4.76 (1H, ddd, J = 9.7, 2.6, 2.6 Hz), 2.85 (3H, s), 2.50 (1H, s); ¹³C NMR (100MHz, CDCl₃) δ 150.1, 136.4, 131.9, 129.6, 129.2, 128.0, 127.8, 127.7, 126.4, 125.5, 118.0, 114.5, 70.0, 63.3, 33.3. HRMS calcd for C₁₇H₁₇NO (M⁺): 251.1310. Found: 251.1307.

(1R, 2R)-2-(3,4-Dihydro-2H-quinolin-1-yl)-1,2-dihydronaphthalen-1-ol (11):

To a round bottom flask containing the (R, S)-PPF-P^tBu₂ rhodium iodide complex (1 mol% to oxabenzonorbornadiene) was added oxabenzonorbornadiene (100 mg, 0.694 mmol). The red-brown solution was then heated to reflux followed by addition of tetrahydroquinoline (461 μ L, 3.47 mmol). The reaction was allowed to stir at reflux for 45 minutes. The solvent was then removed *in vacuo* and the resulting oil purified by flash chromatography (5% ethyl acetate in hexanes) to give **11** as a colourless oil (183 mg, 95%). The ee was determined to be 91% using HPLC analysis on a CHIRALCEL OD column, λ = 254nm. Retention times in 10% isopropanol in hexanes were 15.4 min (major) and 16.4 min. R_f = 0.30 on silica gel (10% ethyl acetate:hexanes); $[\alpha]_D^{25}$ = -34 (c = 13.8, CHCl₃); IR (KBr, cm⁻¹) 3588 (br), 3037 (w), 2932 (w), 1601 (s), 1495 (m), 1190 (m). ¹H NMR (400MHz, CDCl₃) δ 7.54-7.52 (1H, m), 7.31-7.29 (2H, m), 7.17-7.14 (1H, m), 7.10-7.09 (1H, m), 7.06-7.04 (1H, m), 6.94-6.93 (1H, m), 6.68-6.67 (1H, m), 6.65 (1H, dd, J = 9.4, 2.2 Hz), 5.96 (1H, dd, J = 9.9, 3.3 Hz), 5.13 (1H, d, J = 8.8 Hz), 4.78 (1H, ddd, J = 8.8, 2.5, 2.5 Hz), 3.31-3.26 (1H, m), 3.14-3.08 (1H, m), 2.81-2.80 (2H, m), 2.30 (1H, s), 1.95-1.89 (2H, m); ¹³C NMR (100MHz, CDCl₃) δ 145.1, 136.5, 131.9, 129.7, 129.5, 128.0, 128.0, 128.0, 127.9, 127.0, 126.5, 125.9, 124.0, 116.8, 112.2, 69.5, 60.9, 44.1, 28.1, 22.5. HRMS calcd for C₁₉H₁₉NO (M⁺): 277.1467. Found: 277.1463.

(1R, 2R)-2-(1-hydroxy-1,2-dihydro-naphthalen-2-yl)-isoindole-1,3-dione (12):

To a round bottom flask containing the (R, S)-PPF-P^tBu₂ rhodium iodide complex (1 mol% to oxabenzonorbornadiene) was added oxabenzonorbornadiene (100 mg, 0.694 mmol). The red-brown solution was then heated to reflux followed by addition of phthalimide (510 mg, 3.47 mmol). The reaction was allowed to stir at reflux for 2 hours. The reaction mixture was then poured into water and extracted three times with ethyl acetate. The organic layers were combined, washed with brine dried over Na₂SO₄, and concentrated *in vacuo*. The resulting solid was purified by flash chromatography (30% ethyl acetate in hexanes) to give **12** as a white solid (181 mg, 90%). The ee was determined to be 98% using HPLC analysis on a CHIRALCEL OD column, λ = 254 nm. Retention times in 10% isopropanol in hexanes were 15.8 min (major) and 21.9 min. R_f = 0.36 on silica gel (30% ethyl acetate:hexanes); mp

175-176° (dec) (Et₂O); $[\alpha]_D^{25} = -9.9$ ($c = 12.9$, CHCl₃); IR (KBr, cm⁻¹) 3536 (br), 3067 (w), 2921 (w), 1772 (m), 1693 (s), 1388 (s), 1084 (m), 955 (m), 719 (s); ¹H NMR (400MHz, CDCl₃) δ 7.78-7.75 (2H, m), 7.68-7.64 (2H, m), 7.57-7.55 (1H, m), 7.26-7.22 (2H, m), 7.09-7.07 (1H, m), 6.51 (1H, dd, $J = 9.7, 2.7$ Hz), 5.84 (1H, ddd, $J = 9.7, 2.7, 2.2$ Hz), 5.48 (1H, d, $J = 12.8$ Hz), 5.12 (1H, ddd, $J = 12.8, 2.5, 2.4$ Hz), 2.82 (1H, s); ¹³C NMR (100MHz, CDCl₃) δ 168.6, 137.3, 134.2, 132.6, 132.1, 128.7, 128.2, 128.1, 126.9, 126.5, 124.4, 123.5, 70.9, 55.3. HRMS calcd for C₁₈H₁₁NO₂ (M⁺-H₂O): 273.2939. Found: 273.0793.

(1R, 2R)-[1-(*tert*-Butyl-dimethyl-silanoxy)-1,2-dihydronaphthalen-2-yl]-(4-nitrophenyl)-amine (13):

To a round bottom flask containing the (R, S)-PPF-P^tBu₂ rhodium iodide complex (1 mol% to oxabenzonorbornadiene) was added oxabenzonorbornadiene (100 mg, 0.694 mmol). The red-brown solution was then heated to reflux followed by addition of 4-nitroaniline (479 mg, 3.47 mmol). The reaction was allowed to stir at reflux for 4 hours. Upon completion, the solution was concentrated then dissolved in dichloromethane (2 ml). Imidazole (189 mg, 2.77 mmol), DMAP (10 mg, 0.08 mmol) and TBDMSCl (157mg, 1.04 mmol) were added and the reaction was allowed to stir at ambient temperature overnight (~15 h). The crude mixture was then poured into water and extracted with dichloromethane. The organic fractions were combined, dried over MgSO₄ and concentrated. Chromatography (5% EtOAc : Hexanes) gave a yellow oil **13** (236 mg, 86%). The ee was determined to be 92% using HPLC analysis on a CHIRALCEL OD column, $\lambda = 254$ nm. Retention times in 10% isopropanol in hexanes were 8.8 min and 13.6 min (major). $R_f = 0.20$ on silica gel (5% ethyl acetate:hexanes); $[\alpha]_D^{25} = -51$ ($c = 12.9$, CHCl₃); IR (KBr, cm⁻¹) 3536 (br), 3067 (w), 2921 (w), 1772 (m), 1693 (s), 1388 (s), 1084 (m), 955 (m), 719 (s); ¹H NMR (400MHz, CDCl₃) δ 8.13-8.07 (2H, m), 7.37-7.41 (1H, m), 7.25-7.35 (2H, m), 6.62 (2H, d, $J = 9.1$), 6.59-6.65 (1H, m), 5.96 (1H, dd, $J = 9.6, 3.7$ Hz), 4.88 (1H, d, $J = 7.5$ Hz), 4.48-4.55 (1H, m), 4.37-4.45 (1H, m), 0.90 (9H, s), 0.08 (3H, s), 0.00 (3H, s); ¹³C NMR (100MHz, CDCl₃) δ 152.5, 138.2, 136.0, 132.3, 129.5, 128.4, 127.9, 127.1, 127.0, 126.7, 126.4, 111.7, 72.4, 55.3, 25.8, 18.1, -4.1, -4.4. HRMS calcd for C₂₂H₂₈N₂O₃Si (M⁺): 396.1869. Found: 396.1874.

(1R, 2R)-[1-(*tert*-Butyl-dimethyl-silanoxy)-1,2-dihydronaphthalen-2-yl]-naphthalen-1-yl-amine (14):

To a round bottom flask containing the (R, S)-PPF-P^tBu₂ rhodium iodide complex (1 mol% to oxabenzonorbornadiene) was added oxabenzonorbornadiene (100 mg, 0.694 mmol). The red-brown solution was then heated to reflux followed by addition of 1-aminonaphthalene (496 mg, 3.47 mmol). The reaction was allowed to stir at reflux for 4 hours. Upon completion, the solution was concentrated then dissolved in dichloromethane (2 ml). Imidazole (189 mg, 2.77 mmol), DMAP (10 mg, 0.08 mmol) and TBDMSCl (157mg, 1.04 mmol) were added and the reaction was allowed to stir at ambient temperature overnight (~15 h). The crude mixture was then poured into water and extracted with dichloromethane. The organic fractions were combined, dried over MgSO₄ and concentrated. Chromatography (5% EtOAc : Hexanes) gave a colourless oil **14** (233 mg, 84%). The ee was determined to be 91% using HPLC analysis on a CHIRALCEL OD column, $\lambda = 254$ nm. Retention times in 10% isopropanol in hexanes were 5.0 min (major) and 10.6 min. $R_f = 0.20$ on silica gel (2.5% ethyl acetate:hexanes); $[\alpha]_D^{25} = -241$ ($c = 9.4$, CHCl₃); IR (KBr, cm⁻¹) 3536

(br), 3067 (w), 2921 (w), 1772 (m), 1693 (s), 1388 (s), 1084 (m), 955 (m), 719 (s); ^1H NMR (400MHz, CDCl_3) δ 7.78-7.66 (2H, m), 7.10-7.43 (7H, m), 6.77 (1H, d, J = 7.4), 6.56 (1H, d, J = 9.6), 6.07 (1H, dd, J = 9.6, 3.7 Hz), 5.04 (1H, d, J = 7.0), 4.42-4.50 (1H, m), 4.30-4.36 (1H, m), 0.90 (9H, s), 0.12 (3H, s), 0.00 (3H, s); ^{13}C NMR (100MHz, CDCl_3) δ 142.0, 136.6, 134.5, 132.6, 128.7, 128.5, 128.3, 128.1, 127.5, 127.5, 126.6, 126.4, 125.7, 124.7, 123.9, 120.0, 117.8, 105.7, 71.9, 55.4, 25.9, 18.2, -4.1, -4.2. HRMS calcd for $\text{C}_{26}\text{H}_{31}\text{NOSi}$ (M^+): 401.2175. Found: 401.2168.

(1S, 2S)-2-(hydroxy-1,2-dihydronaphthalen-2-yl)malonic acid dimethyl ester (19):

To a round bottom flask containing the (R,S)-PPF- P^tBu_2 rhodium iodide complex (1 mol% to oxabenzonorbornadiene) was added oxabenzonorbornadiene (100 mg, 0.694 mmol). The red-brown solution was then heated to reflux followed by addition of dimethylmalonate (458 mg, 3.47 mmol). The reaction was allowed to stir at reflux for 1 hour. The reaction mixture was then concentrated *in vacuo*. The resulting oil was purified by flash chromatography (30% ethyl acetate in hexanes) to give **19** as a colourless oil (186 mg, 97%). The ee was determined to be 97% using HPLC analysis on a CHIRALCEL AD column, retention times in 10% isopropanol in hexanes were 17.8 min (major) and 20.3 min. R_f = 0.27 on silica gel (50% ethyl acetate:hexanes); $[\alpha]_D^{25}$ = -229 (c = 9.3, CHCl_3); IR (neat, cm^{-1}) 3490 (br), 3024 (m), 2954 (s), 1744 (s), 1436 (s), 1159 (s), 1026 (s), 913 (m), 783 (s); ^1H NMR (400MHz, CDCl_3) δ 7.40-7.38 (1H, m), 7.30-7.24 (2H, m), 7.13-7.11 (1H, m), 6.57 (1H, dd, J = 9.7, 1.5 Hz), 5.97 (1H, dd, J = 9.7, 4.2 Hz), 4.70 (1H, dd, J = 6.2, 6.2 Hz), 3.73 (3H, s), 3.70 (3H, s), 3.52 (1H, d, J = 7.6 Hz), 3.37-3.35 (1H, m), 2.09 (1H, d, J = 6.2 Hz); ^{13}C NMR (400MHz, CDCl_3) δ 168.6, 168.3, 135.4, 131.9, 128.3, 128.1, 126.8, 126.7, 70.3, 52.6, 52.6, 52.5, 42.3. HRMS calcd for $\text{C}_{15}\text{H}_{16}\text{O}_5$ (M^+): 276.0998. Found: 276.0995.

(1-Hydroxy-1,2-dihydronaphthalen-2-yl)-nitro-acetic acid methyl ester (20):

To a round bottom flask containing the $[\text{Rh}(\text{COD})\text{Cl}]_2$ (1 mol%) and dppf (2 mol%) was added oxabenzonorbornadiene (100 mg, 0.694 mmol). The red-brown solution was then heated to reflux followed by addition of nitroacetic acid methyl ester (413 mg, 3.47 mmol). The reaction was allowed to stir at reflux for 1 hour after which time complete consumption of the starting material had occurred as determined by TLC analysis. The crude mixture was concentrated and chromatographed (10% increasing to 20% ethylacetate: hexanes) to give an oil **20** (171 mg, 94% yield) as an inseparable mixture of epimers. R_f = 0.15 on silica gel (20% ethyl acetate:hexanes); IR (KBr, cm^{-1}) 3490 (br), 3024 (m), 2954 (s), 1744 (s), 1580 (s), 1360 (s), 1026 (s), 913 (m), 783 (s). ^1H NMR (400MHz, CDCl_3) δ 7.40-7.33 (1H, m), 7.33-7.25 (2H, m), 7.15-7.09 (1H, m), 6.66-6.56 (1H, m), 5.94-5.86 (1H, m), 5.36 (1H, major diastereomer, d, J = 6.2 Hz), 5.11 (1H, minor diastereomer, d, J = 6.9 Hz), 4.80-4.70 (1H, m), 3.77 (3H, m), 3.72-3.47 (1H, m), 3.73 (1H, major diastereomer, d, J = 7.7 Hz), 2.56 (1H, minor diastereomer, d, J = 7.7 Hz); ^{13}C NMR (400MHz, CDCl_3) δ 164.2, 163.8, 135.1, 134.5, 131.6, 131.3, 130.1, 129.6, 128.9, 128.7, 128.6, 128.4, 126.9, 126.8, 126.7, 125.8, 12.9, 122.5, 87.2, 87.0, 68.7, 68.6, 53.6, 53.5, 43.8, 43.3. HRMS calcd for $\text{C}_{13}\text{H}_{13}\text{NO}_5$ (M^+): 263.0794, Found: 263.0793.

Benzenesulfonyl-(1-hydroxy-1,2-dihydronaphthalen-2-yl)-acetonitrile (21):

To a round bottom flask containing the $[\text{Rh}(\text{COD})\text{Cl}]_2$ (1 mol%) and dppf (2 mol%) was added oxabenzonorbornadiene (100 mg, 0.694 mmol). The red-brown solution

was then heated to reflux followed by addition of phenylsulfonylacetonitrile (628 mg, 3.47 mmol). The reaction was allowed to stir at reflux for 1 hour after which time complete consumption of the starting material had occurred as determined by TLC analysis. The crude mixture was concentrated and chromatographed (10% increasing to 20% ethylacetate: hexanes) to give an oil **21** (207 mg, 92% yield) as an inseparable mixture of epimers. After storage at 4°C for several months, crystallization of one of the diastereomers gradually occurred to give crystals suitable for X-ray analysis. The *trans* relative stereochemistry was proven by X-ray crystallographic analysis. R_f = 0.18 on silica gel (20% ethyl acetate:hexanes); IR (KBr, cm^{-1}) 3490 (br), 3024 (m), 2954 (s), 1744 (s), 1436 (s), 1159 (s), 1026 (s), 913 (m), 783 (s). ^1H NMR (400MHz, CDCl_3) δ 8.06-8.00 (2H, m), 7.82-7.74 (1H, m), 7.69-7.60 (2H, m), 7.48-7.40 (1H, m), 7.34-7.24 (2H, m), 7.18-7.08 (1H, m), 6.70 (1H, minor diastereomer, d, J = 9.7 Hz), 6.60 (1H, major diastereomer, dd, J = 2.4, 9.7 Hz), 6.08 (1H, major diastereomer, dd, J = 2.7, 9.8 Hz), 6.02 (1H, minor diastereomer, dd, J = 4.8, 9.8 Hz), 5.15 (1H, minor diastereomer, d, J = 5.5 Hz), 4.81 (1H, major diastereomer, d, J = 11.5 Hz), 4.54 (1H, s), 4.06 (1H, major diastereomer, s), 3.98 (1H, minor diastereomer, d, J = 6.7 Hz), 3.49 (1H, d, J = 11.3 Hz); ^{13}C NMR (400MHz, CDCl_3) δ 149.6, 136.4, 135.7, 135.4, 135.4, 131.9, 130.5, 129.8, 129.7, 129.5, 129.4, 128.9, 128.8, 128.6, 127.7, 127.2, 126.8, 124.4, 123.4, 123.1, 112.7, 69.9, 69.1, 58.7, 57.6, 45.7, 44.5, 42.1, 40.7. HRMS calcd for $\text{C}_{18}\text{H}_{15}\text{NO}_3\text{S}$ (M^+): 325.0773, Found: 325.0775.

3a, 9b-Dihydro-3H-naphtho[1,2-b]furan-2-one (24):

To a round bottom flask containing the (R, S)-PPF- P^tBu_2 rhodium iodide complex (1 mol% to oxabenzonorbornadiene) was added oxabenzonorbornadiene (100 mg, 0.694 mmol). The red-brown solution was then heated to reflux followed by addition of Meldrum's Acid (500 mg, 3.47 mmol). The reaction was allowed to stir at reflux for 1 hour after which time complete consumption of the starting material had occurred as determined by TLC analysis. Et_3N (1 mL) was then added and the reaction was stirred at reflux for an additional hour after which time the crude mixture was concentrated, diluted with Et_2O and extracted with H_2O . The organic layers were combined, dried over MgSO_4 and concentrated. Chromatography (5% increasing to 10% ethylacetate: hexanes) gave **24** as a viscous oil. The ee was determined to be 95% using HPLC analysis on a CHIRALCEL AD column, retention times in 1% isopropanol in hexanes were 18.9 min and 20.3 min (major). R_f = 0.2 on silica gel (10% ethyl acetate:hexanes); $[\alpha]_D^{25}$ = -102 (c = 7.7, CHCl_3); IR (KBr, cm^{-1}) 3040 (br), 2855 (s), 2100 (m), 1367 (m), 1183 (s), 1025 (s). ^1H NMR (400MHz, CDCl_3) δ 7.47-7.43 (1H, m), 7.34-7.29 (2H, m), 7.25-7.18 (1H, m), 6.60 (1H, dd, J = 3.1, 9.4 Hz), 6.22 (1H, dd, J = 2.2, 9.4 Hz), 5.01 (1H, d, J = 14.5 Hz), 3.04-2.94 (1H, m), 2.75 (1H, dd, J = 6.8, 16.0 Hz), 2.61 (1H, dd, J = 13.6, 16.0 Hz); ^{13}C NMR (400MHz, CDCl_3) δ 175.9, 134.3, 132.2, 129.9, 128.1, 127.9, 127.0, 125.8, 121.7, 82.5, 41.1, 34.2. HRMS calcd for $\text{C}_{12}\text{H}_{10}\text{O}_2$ (M^+): 186.0681. Found: 186.0680.

(1S, 2S)-2-(hydroxy-1,2-dihydronaphthalen-2-yl)malonic acid diethyl ester (26):

To a round bottom flask containing the (R, S)-PPF- P^tBu_2 rhodium iodide complex (1 mol% to oxabenzonorbornadiene) was added oxabenzonorbornadiene (100 mg, 0.694 mmol). The red-brown solution was then heated to reflux followed by addition of diethylmalonate (555 mg, 3.47 mmol). The reaction was allowed to stir at reflux for 1 hour. The reaction mixture was then concentrated *in vacuo*. The resulting oil was purified by flash chromatography (30% ethyl acetate in hexanes) to give **26** as a colourless oil (200 mg, 95%). The ee was determined to be 97% using HPLC

analysis on a CHIRALCEL AD column, retention times in 10% isopropanol in hexanes were 14.8 min (major) and 17.5 min. R_f = 0.26 on silica gel (30% ethyl acetate:hexanes); $[\alpha]_D^{25}$ = -208 (c = 10.1, CHCl_3); IR (neat, cm^{-1}) 3490 (br), 3024 (m), 2954 (s), 1744 (s), 1436 (s), 1159 (s), 1026 (s), 913 (m), 783 (s); ^1H NMR (400MHz, CDCl_3) δ 7.40-7.36 (1H, m), 7.30-7.21 (2H, m), 7.11-7.08 (1H, m), 6.55 (1H, dd, J = 1.5, 9.7 Hz), 5.98 (1H, dd, J = 4.0, 9.7 Hz), 4.72 (1H, dd, J = 7.0, 7.0 Hz), 4.22-4.08 (4H, m), 3.47 (1H, d, J = 7.8 Hz), 3.37-3.29 (1H, m), 2.24 (1H, d, J = 7.3 Hz), 1.25 (3H, t, J = 7.3 Hz), 1.23 (3H, t, J = 7.3 Hz); ^{13}C NMR (400MHz, CDCl_3) δ 168.3, 168.0, 135.4, 132.0, 128.5, 128.1, 128.0, 126.8, 126.6, 126.6, 70.2, 61.6, 61.5, 52.8, 42.1, 14.0. HRMS calcd for $\text{C}_{17}\text{H}_{20}\text{O}_5$ (M^+): 304.1311; Found: 304.1310.

(1S, 2S)-2-(1H-Indol-3-yl)-1,2-dihydronaphthalen-1-ol (27):

To a round bottom flask containing the (R, S)-PPF- P^tBu_2 rhodium iodide complex (1 mol% to oxabenzonorbornadiene) was added oxabenzonorbornadiene (100 mg, 0.694 mmol). The red-brown solution was then heated to reflux followed by addition of indole (406 mg, 3.47 mmol). The reaction was allowed to stir at reflux for 30 minutes. The reaction mixture was then concentrated *in vacuo*. The resulting oil was purified by flash chromatography (30% ethyl acetate in hexanes) to give **27** as a colourless oil (168 mg, 93%). The ee was determined to be 97% using HPLC analysis on a CHIRALCEL OD column, λ = 254nm. Retention times in 10% isopropanol in hexanes were 25.5 min (major) and 29.8 min. R_f = 0.26 on silica gel (30% ethyl acetate:hexanes); $[\alpha]_D^{25}$ = -56.2 (c = 11.3, CHCl_3); IR (KBr, cm^{-1}) 3485 (br), 3059 (m), 1592 (m), 1455 (s), 1414 (s), 1245 (m), 1091 (m), 908 (m); ^1H NMR (400MHz, CDCl_3) δ 8.13 (1H, s), 7.79 (1H, d, J = 7.8 Hz), 7.42 (1H, d, J = 7.3 Hz), 7.34-7.19 (6H, m), 6.85 (1H, d, J = 2.2 Hz), 6.69 (1H, dd, J = 9.5, 2.0 Hz), 6.20 (1H, dd, J = 9.5, 3.8 Hz), 5.06 (1H, d, J = 7.9 Hz), 4.12-4.08 (1H, m), 2.35 (1H, s); ^{13}C NMR (100MHz, CDCl_3) δ 136.5, 135.9, 132.5, 130.1, 128.0, 127.7, 126.9, 126.5, 126.4, 126.2, 122.6, 122.0, 119.3, 119.2, 113.9, 111.4, 72.7, 41.0. HRMS calcd for $\text{C}_{18}\text{H}_{15}\text{NO}$ (M^+): 261.1154. Found: 261.1141.

(1S, 2S)-2-(2-bromophenoxy)-1,2-dihydronaphthalen-1-ol (32):

To a flame dried round-bottomed flask, $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ (1.5 mg, 0.0035 mmol), (S)-(R)- PPF- P^tBu_2 (3.8 mg, 0.0069 mmol) and **1** (100 mg, 0.694 mmol) were added followed by addition of THF (2.5 mL) and 2-bromophenol (0.40 mL, 3.47 mmol). The mixture was heated at 80°C for 24 hours, then poured into diethyl ether and extracted 3 times with 10% aqueous sodium hydroxide solution. The aqueous extracts were combined and back-extracted three times with diethyl ether. The combined ether extracts were washed with brine and dried with anhydrous sodium sulfate. The solvents were removed *in vacuo*, yielding a solid which was purified by flash chromatography on silica gel (5% ethyl acetate in hexanes) as a white crystalline solid **32** (206 mg, 94%). The absolute **stereochemistry** was determined by X-ray crystallography. The ee was determined to be 97% by HPLC analysis on a CHIRALCEL OD column, λ = 486 nm. Retention times in 1.5% isopropanol in hexanes were 22.8 min and 32.1 min (major). R_f = 0.44 on silica (20% ethyl acetate in hexanes); m.p. 120-122°C (Et_2O); $[\alpha]_D^{25}$ = +254° (c = 9.2, CHCl_3). IR (KBr, cm^{-1}) 3341 (br), 3071 (w), 2884 (w), 1581 (m), 1472 (s), 1358 (m), 1237 (s), 1028 (s), 987 (s), 780 (s), 689 (m), 569 (m); ^1H NMR (400 MHz, CDCl_3): δ 7.67 (1H, d J = 6.8 Hz), 7.58 (1H, dd, J = 1.5, 7.9 Hz), 7.33-7.23 (3H, m), 7.14-7.12 (1H, m), 6.95 (1H, dd, J = 1.1, 8.2 Hz), 6.92-6.87 (1H, m), 6.52 (1H, dd, J = 2.0, 9.9 Hz), 6.06 (1H, dd, J = 1.8,

9.9 Hz), 5.32 (1H, d, J = 11.0 Hz), 5.10 (1H, ddd, J = 2.0, 2.0, 11.0 Hz), 2.85 (1H, d, J = 3.2 Hz). ^{13}C NMR (400 MHz, CDCl_3): δ 154.3, 135.4, 133.6, 131.8, 129.1, 128.6, 128.3, 128.0, 126.4, 126.0, 124.9, 122.9, 115.6, 113.5, 82.2, 72.5. HRMS calculated for $(\text{M}-\text{H}_2\text{O})^+$ ($\text{C}_{16}\text{H}_{11}\text{OBr}$): 297.9993. Found: 297.9976.

(1S, 2S)-2-(2-fluorophenoxy)-1,2-dihydro-naphthalen-1-ol (33):

To a flame-dried round bottomed flask under inert atmosphere was added $[\text{Rh}(\text{COD})\text{Cl}]_2$ (5 mg, 0.01 mmol) and (S, R)-PPF-PtBu₂ (12mg, 0.022mmol) which was dissolved in 2.0 ml THF and stirred at room temperature for 10 min to produce a dark red solution. Silver trifluoromethane sulfonate ($\text{AgOSO}_2\text{CF}_3$) (11 mg, 0.04 mmol) was added to the dark red solution to form a white precipitate. The heterogeneous mixture was stirred at room temperature for 10min and the tetrabutylammonium iodide (22 mg, 0.06 mmol) was then added to the mixture solution. After stirring for 10 additional minutes, **1** (100mg, 0.694 mmol) was added to the (S, R)-PPF-PtBu₂ rhodium iodide complex and then heated to reflux followed by addition of 2-fluorophenol (77.82 mg, 0.694 mmol). The reaction was allowed to stir at reflux for 3 hours. The reaction mixture was then poured in to ether and washed three times with 1.0N NaOH. The aqueous layers were combined and back extracted three times with ether. The organic layers were combined, washed with brine, dried over MgSO_4 , and concentrated *in vacuo*. The resulting solid was purified by flash chromatography (10% ethyl acetate in hexanes) to gave **33** as a white crystalline solid (153 mg, 86%). R_f = 0.24 on silica gel (10% ethyl acetate in hexanes); mp 143-145.5°C. The ee was determined to be 99% using HPLC analysis on a CHIRALCEL OD column (2% isopropanol in hexanes), λ = 254 nm. Retention times in 2% isopropanol in hexanes were 17.9 min (major) and 16.8 min (minor). $[\alpha]_D^{25}$ = 148.3 (c = 8.4, CHCl_3); IR (KBr, cm^{-1}), 3323 (br), 3225 (br), 3014 (w), 2929 (w), 1606 (s), 1584 (w), 1502 (s), 1454 (s), 1257 (s), 1103 (s), 985 (m), 763 (s). ^1H NMR (400MHz, CDCl_3) δ 7.66 (1H, d, J = 6.77 Hz), 7.26-7.33 (2H, m), 7.09-7.13 (2H, m), 7.02-7.05 (2H, m), 6.95-6.97 (1H, m), 6.50 (1H, dd, J = 9.9, 2.0 Hz), 6.03 (1H, dd, J = 9.9, 2.0 Hz), 5.24 (1H, dd, J = 10.1, 3.7 Hz), 5.08 (1H, ddd, J = 10.3, 2.2, 2.1 Hz), 2.69 (1H, d, J = 3.5 Hz). ^{13}C NMR (400MHz, CDCl_3) δ 155.1, 152.6, 135.6, 132.0, 129.3, 128.5, 128.2, 126.7, 126.1, 125.4, 124.7, 122.7, 117.9, 117.0, 81.9, 72.7. HRMS Calcd for $\text{C}_{16}\text{H}_{13}\text{FO}_2$ (M^+): 256.0900. Found: 256.0909.

(1S, 2S)-2-(2-Chlorophenoxy)-1,2-dihydronaphthalen-1-ol (34):

To a flame-dried round bottomed flask under inert atmosphere was added $[\text{Rh}(\text{COD})\text{Cl}]_2$ (5 mg, 0.01 mmol) and (S, R)-PPF-PtBu₂ (12 mg, 0.022 mmol) which was dissolved in 2.0ml THF and stirred at room temperature for 10min to produce a dark red solution. Silver trifluoromethane sulfonate ($\text{AgOSO}_2\text{CF}_3$) (11 mg, 0.04 mmol) was added to the dark red solution to form a white precipitate. The heterogeneous mixture was stirred at room temperature for 10min and the tetrabutylammonium iodide (22 mg, 0.06 mmol) was then added to the mixture solution. After stirring for 10 additional minutes, **1** (100mg, 0.694 mmol) was added to the (S,R)-PPF-PtBu₂ rhodium iodide complex and then heated to reflux followed by addition of 2-chlorophenol (89 mg, 0.694 mmol). The reaction was allowed to stir at reflux for 4 hours. The reaction mixture was then poured in to ether and washed three times with 1.0N NaOH. The aqueous layers were combined and back extracted three times with ether. The organic layers were combined, washed with brine, dried over MgSO_4 , and concentrated *in vacuo*. The resulting solid was purified by flash chromatography (10% ethyl acetate in hexanes) to gave **34** as a white crystalline solid

(160mg, 85%). $R_f=0.29$ on silica gel (10% ethyl acetate in hexanes); mp 148-149°C. The ee was determined to be 97% using HPLC analysis on a CHIRALCEL OD column, $\lambda=254$ nm. Retention times in 2% isopropanol in hexanes were 22.5 min (major) and 16.8 min (minor). $[\alpha]_D^{25} = 203.4$ ($c = 9.0$, CHCl_3); IR (KBr, cm^{-1}), 3316 (br), 2929 (w), 2887 (w), 1634 (s), 1581 (w), 1479 (s), 1440 (s), 1268 (m), 1233 (m), 1159 (m), 1043 (s), 983 (s), 779 (s), 747 (s). ^1H NMR (400MHz, CDCl_3) δ 7.67 (1H, d, $J = 6.9$ Hz), 7.39 (1H, dd, $J = 7.9, 1.7$ Hz), 7.23-7.31 (2H, m), 7.19-7.24 (1H, m), 7.11-7.18 (1H, m), 6.93-6.99 (2H, m), 6.51 (1H, dd, $J = 9.9, 2.0$ Hz), 6.04 (1H, dd, $J = 9.9, 2.0$ Hz), 5.28 (1H, d, $J = 3.1$ Hz), 5.09 (1H, ddd, $J = 10.6, 2.2, 2.0$ Hz), 2.79 (1H, d, $J = 2.4$ Hz). ^{13}C NMR (400MHz, CDCl_3) δ 153.6, 143.2, 135.6, 132.4, 130.8, 129.3, 128.5, 128.2, 126.1, 125.4, 124.7, 122.7, 117.9, 117.1, 82.0, 72.7. HRMS Calcd for $\text{C}_{16}\text{H}_{13}\text{ClO}_2$ (M^+): 272.0604. Found: 276.0613.

(1S, 2S)-2-(2-iodophenoxy)-1,2-dihydronaphthalen-1-ol (35):

To a flame-dried round bottomed flask under inert atmosphere was added $[\text{Rh}(\text{COD})\text{Cl}]_2$ (5 mg, 0.01 mmol) and (S, R)-PPF- P^tBu_2 (12 mg, 0.022 mmol) which was dissolved in 2.0 ml THF and stirred at room temperature for 10min to produce a dark red solution. Silver trifluoromethane sulfonate ($\text{AgOSO}_2\text{CF}_3$) (11 mg, 0.04 mmol) was added to the dark red solution to form a white precipitate. The heterogeneous mixture was stirred at room temperature for 10min and the tetrabutylammonium iodide (22 mg, 0.06 mmol) was then added to the mixture solution. After stirring for 10 additional minutes, **1** (80 mg, 0.555 mmol) was added to the (S, R)-PPF- P^tBu_2 rhodium iodide complex and then heated to reflux followed by addition of 2-iodophenol (122 mg, 0.555 mmol). The reaction was allowed to stir at reflux for 3 hours. The reaction mixture was then poured in to ether and washed three times with 1.0N NaOH. The aqueous layers were combined and back extracted three times with ether. The organic layers were combined, washed with brine, dried over MgSO_4 , and concentrated *in vacuo*, the resulting solid was purified by flash chromatography (5% ethyl acetate in hexanes) to gave **35** as a white crystalline solid (60 mg, 60%). $R_f = 0.14$ on silica gel (5% ethyl acetate in hexanes); mp 66-67°C (ethyl acetate). The ee was determined to be 96% using HPLC analysis on a CHIRALCEL OD column, $\lambda=254$ nm. Retention times in 2% isopropanol in hexanes were 19.2 min (major) and 30.3 min (minor). $[\alpha]_D^{25} = 102.8$ ($c = 10$, CHCl_3); IR (KBr, cm^{-1}), 3387 (br), 3049 (w), 2922 (w), 1598 (s), 1577 (m), 1468 (m), 1384 (m), 1275 (s), 1240 (s), 1085 (m), 1043 (s), 770 (s). ^1H NMR (400MHz, CDCl_3) δ 8.16 (1H, dd, $J = 4.6, 3.5$ Hz), 7.79-7.83 (2H, m), 7.67 (1H, d, $J = 7.3$ Hz), 7.43-7.50 (1H, m), 7.26-7.33 (1H, m), 7.11 (1H, dd, $J = 8.6, 1.7$ Hz), 6.76-6.87 (1H, m), 6.51 (1H, dd, $J = 9.9, 2.0$ Hz), 6.04 (1H, dd, $J = 9.9, 2.0$ Hz), 5.24 (1H, s), 5.08 (1H, ddd, $J = 10.8, 2.0$ Hz), 2.84 (1H, d, $J = 3.3$ Hz). ^{13}C NMR (400MHz, CDCl_3) δ 151.6, 139.9, 129.8, 129.4, 128.2, 127.9, 126.6, 126.3, 125.5, 123.7, 121.7, 120.9, 124.4, 108.8, 82.5, 72.8. HRMS Calcd for $\text{C}_{16}\text{H}_{13}\text{IO}_2$ (M^+): 363.9960. Found: 363.9974.

(1S, 2S)-2-(2-nitrilphenoxy)-1,2-dihydronaphthalen-1-ol (36):

To a flame-dried round bottomed flask under inert atmosphere was added $[\text{Rh}(\text{COD})\text{Cl}]_2$ (5 mg, 0.01 mmol) and (S, R)-PPF- P^tBu_2 (12 mg, 0.022 mmol) which was dissolved in 2.0 mL THF and stirred at room temperature for 10min to produce a dark red solution. Silver trifluoromethane sulfonate ($\text{AgOSO}_2\text{CF}_3$) (11 mg, 0.04 mmol) was added to the dark red solution to form a white precipitate. The heterogeneous mixture was stirred at room temperature for 10min and the tetrabutylammonium iodide (22 mg, 0.06 mmol) was then added to the mixture

solution. After stirring for 10 additional minutes, **1** (100 mg, 0.694 mmol) was added to the rhodium iodide (S, R)-PPF-PtBu₂ complex and then heated to reflux followed by addition of 2-cyanophenol (82.66 mg, 0.694 mmol). The reaction was allowed to stir at reflux for 4 hours. The reaction mixture was then poured in to ether and washed three times with 1.0 N NaOH. The aqueous layers were combined and back extracted three times with ether. The organic layers were combined, washed with brine, dried over MgSO₄, and concentrated *in vacuo*. The resulting solid was purified by flash chromatography (33% ethyl acetate in hexanes) to give **36** as a white crystalline solid (118 mg, 65%). *R*_f = 0.41 on silica gel (33% ethyl acetate in hexanes); mp 182-183.5°C (ethyl acetate). The ee was determined to be 99% using HPLC analysis on a CHIRALCEL OD column, λ = 254 nm. Retention times in 2% isopropanol in hexanes were 37.1 min (major) and 29.7 min (minor). $[\alpha]_D^{25}$ = 334.6° (c = 8.2, CHCl₃); IR (KBr, cm⁻¹), 3330 (br), 3063 (w), 2929 (w), 2232 (s), 1595 (m), 1577 (w), 1482 (s), 1444 (s), 1275 (m), 1240 (s), 1103 (s), 1029 (s), 987 (s), 839 (w), 777 (s). ¹H NMR (400MHz, CDCl₃) δ 7.67 (1H, d, *J* = 6.9 Hz), 7.59 (1H, dd, *J* = 7.7, 1.3 Hz), 7.50 (1H, ddd, *J* = 9.2, 1.8, 1.7 Hz), 7.26-7.33 (2H, m), 7.13 (1H, d, *J* = 6.9 Hz), 7.04 (1H, t, *J* = 7.7 Hz), 6.99 (1H, d, *J* = 8.6 Hz), 6.53 (1H, dd, *J* = 9.9, 2.0 Hz), 5.97 (1H, dd, *J* = 9.9, 1.8 Hz), 5.31 (1H, dd, *J* = 10.4, 4.0 Hz), 5.20 (1H, d, *J* = 10.4 Hz), 2.80 (1H, d, *J* = 4.2 Hz). ¹³C NMR (400MHz, CDCl₃) δ 159.7, 135.5, 134.6, 134.3, 131.9, 129.9, 128.7, 128.4, 126.8, 125.4, 125.0, 121.8, 114.1, 103.4, 81.6, 72.5. HRMS Calcd for C₁₇H₁₃NO₂ (M⁺): 263.0946. Found: 263.0941.

(1S, 2S)-2-(2-methoxyphenoxy)-1,2-dihydronaphthalen-1-ol (37):

To a flame-dried round bottomed flask under inert atmosphere was added [Rh(COD)Cl]₂ (5 mg, 0.01 mmol) and (S,R)-PPF-PtBu₂ (12 mg, 0.022 mmol) which was dissolved in 2.0 ml THF and stirred at room temperature for 10min to produce a dark red solution. Silver trifluoromethane sulfonate (AgOSO₂CF₃) (11 mg, 0.04 mmol) was added to the dark red solution to form a white precipitate. The heterogeneous mixture was stirred at room temperature for 10min and the tetrabutylammonium iodide (22 mg, 0.06 mmol) was then added to the mixture solution. After stirring for 10 additional minutes, **1** (80 mg, 0.694 mmol) was added to the (S,R)-PPF-PtBu₂ rhodium iodide complex and then heated to reflux followed by addition of 2-methoxyphenol (68.89 mg, 0.555 mmol). The reaction was allowed to stir at reflux for 5 hours. The reaction mixture was then poured in to ether and washed three times with 1.0N NaOH. The aqueous layers were combined and back extracted three times with ether. The organic layers were combined, washed with brine, dried over MgSO₄, and concentrated *in vacuo*. The resulting solid was purified by flash chromatography (10% ethyl acetate in hexanes) to give **7** a colorless crystal (86mg, 58%). *R*_f = 0.20 on silica gel (10% ethyl acetate in hexanes); mp 42-43°C (ethyl acetate). The ee was determined to be 99% using HPLC analysis on a CHIRALCEL OD column, λ = 254 nm. Retention times in 2% isopropanol in hexanes were 23.7 min (major) and 28.4 min (minor). $[\alpha]_D^{25}$ = 126.4° (c = 12, CHCl₃); IR (KBr, cm⁻¹), 3474 (br), 3063 (w), 2941 (w), 2877 (s), 1590 (m), 1501 (s), 1456 (m), 1252 (s), 745 (s). ¹H NMR (400MHz, CDCl₃) δ 7.64 (1H, d, *J* = 7.3 Hz), 7.21-7.28 (2H, m), 7.06 (1H, d, *J* = 7.14 Hz), 6.99-7.04 (2H, m), 6.87-6.93 (2H, m), 6.43 (1H, dd, *J* = 9.9, 1.8 Hz), 6.08 (1H, dd, *J* = 9.9, 2.0 Hz), 5.24 (1H, d, *J* = 10.9 Hz), 4.91 (1H, ddd, *J* = 8.8, 2.2, 2.0 Hz), 3.87 (3H, s), 3.76 (1H, s). ¹³C NMR (400MHz, CDCl₃) δ 150.9, 147.5, 136.1, 132.1, 128.6, 128.2, 127.9, 127.7, 126.4, 125.0, 123.6, 121.4, 119.1, 112.4, 84.3, 72.9, 56.0. HRMS Calcd for C₁₇H₁₆O₃ (M⁺): 268.1099. Found: 268.1097.

(1S, 2S)-2-(2-trifluoromethylphenoxy)-1,2-dihydronaphthalen-1-ol (38):

To a flame-dried round bottomed flask under inert atmosphere was added [Rh(COD)Cl]₂ (5 mg, 0.01 mmol) and (S, R)-PPF-P^tBu₂ (12 mg, 0.022 mmol) which was dissolved in 2.0 mL THF and stirred at room temperature for 10min to produce a dark red solution. Silver trifluoromethane sulfonate (AgOSO₂CF₃) (11 mg, 0.04 mmol) was added to the dark red solution to form a white precipitate. The heterogeneous mixture was stirred at room temperature for 10min and the tetrabutylammonium iodide (22 mg, 0.06 mmol) was then added to the mixture solution. After stirring for 10 additional minutes, **1** (80 mg, 0.555 mmol) was added to the rhodium iodide (S,R)-PPF-PtBu₂ complex and then heated to reflux followed by addition of 2-trifluoromethylphenol (90 mg, 0.55 mmol). The reaction was allowed to stir at reflux for 4 hours. The reaction mixture was then poured in to ether and washed three times with 1.0 N NaOH. The aqueous layers were combined and back extracted three times with ether. The organic layers were combined, washed with brine, dried over MgSO₄, and concentrated *in vacuo*. The resulting solid was purified by flash chromatography (10% ethyl acetate in hexanes) to give **38** a colorless oil (136 mg, 80%). R_f = 0.25 on silica gel (10% ethyl acetate in hexanes). The ee was determined to be 97% using HPLC analysis on a CHIRALCEL OD column, λ = 254 nm. Retention times in 2% isopropanol in hexanes were 13.8 min (major) and 11.8 min (minor). [α]_D²⁵ = 170.1° (c = 7.0, CHCl₃); IR (KBr, cm⁻¹), 3377 (br), 3075 (w), 2995 (w), 2900 (w), 1606 (s), 1590 (m), 1494 (s), 1453 (s), 1322 (m), 1243 (s), 1102 (s), 987 (s), 765 (s). ¹H NMR (400MHz, CDCl₃) δ 7.64 (1H, d, *J* = 6.0 Hz), 7.58 (1H, d, *J* = 7.7 Hz), 7.41-7.47 (1H, m), 7.22-7.30 (2H, m), 7.08-7.12 (1H, m), 6.94-7.05 (2H, m), 6.48 (1H, dd, *J* = 9.9, 2.2 Hz), 5.99 (1H, dd, *J* = 9.9, 1.9 Hz), 5.25 (1H, d, *J* = 10.9 Hz), 5.13 (1H, ddd, *J* = 10.9, 2.2, 1.9 Hz), 2.84 (1H, s). ¹³C NMR (400MHz, CDCl₃) δ 156.1, 149.2, 143.2, 135.6, 133.6, 132.0, 129.6, 128.5, 128.2, 127.7, 126.6, 125.8, 125.1, 120.9, 120.6, 120.9, 120.4, 114.3, 82.5, 81.6, 72.8. HRMS Calcd for C₁₇H₁₃F₃O₂ (M⁺): 306.0868. Found: 306.0864.

(1S, 2S)-[2-(1-hydroxy-1,2-dihydronaphthalen-2-yloxy)-phenyl]ethanone (39):

To a flame-dried round bottomed flask under inert atmosphere was added [Rh(COD)Cl]₂ (5 mg, 0.01 mmol) and (S,R)-PPF-P^tBu₂ (12 mg, 0.022 mmol) which was dissolved in 2.0 mL THF and stirred at room temperature for 10min to produce a dark red solution. Silver trifluoromethane sulfonate (AgOSO₂CF₃) (11 mg, 0.04 mmol) was added to the dark red solution to form a white precipitate. The heterogeneous mixture was stirred at room temperature for 10min and the tetrabutylammonium iodide (22 mg, 0.06 mmol) was then added to the mixture solution. After stirring for 10 additional minutes, **1** (80 mg, 0.555 mmol) was added to the (S, R)-PPF-PtBu₂ rhodium iodide complex and then heated to reflux followed by addition of 2'-hydroxyacetophenol (76 mg, 0.56 mmol). The reaction was allowed to stir at reflux for 6 hours. The reaction mixture was then poured in to ether and washed three times with 1.0N NaOH. The aqueous layers were combined and back extracted three times with ether. The organic layers were combined, washed with brine, dried over MgSO₄, and concentrated *in vacuo*. The resulting solid was purified by flash chromatography (20% ethyl acetate in hexanes) to give **39** a colorless oil (64 mg, 41%). R_f = 0.30 on silica gel (20% ethyl acetate in hexanes); The ee was determined to be 97% using HPLC analysis on a CHIRALCEL OD column, λ = 254 nm. Retention times in 2% isopropanol in hexanes were 19.2 min (major) and 22.8 min (minor). [α]_D²⁵ = 294.2° (c = 7.9, CHCl₃); IR (KBr, cm⁻¹), 3420 (br), 3068 (w), 2924 (w), 2868 (w), 1671 (s), 1596 (s), 1480 (s), 1451 (s), 1358 (s), 1293 (s), 1239 (s), 1124 (s), 1048

(s), 986 (s). ^1H NMR (400MHz, CDCl_3) δ 7.66(1H, dd, J = 7.9, 1.8 Hz), 7.63(1H, d, J = 6.2 Hz), 7.41 (1H, ddd, J = 7.3, 1.8, 1.1 Hz), 7.26-7.33 (2H, m), 7.11-7.14 (1H, m), 6.99-7.06 (2H, m), 6.53(1H, dd, J = 9.8, 2.0 Hz), 6.08(1H, dd, J = 9.9, 2.2 Hz), 5.21 (1H, dd J = 10.3 Hz), 5.12 (1H, ddd, J = 12.3, 2.2, 2.0 Hz), 3.83 (1H, s), 2.50 (3H, s). ^{13}C NMR (400MHz, CDCl_3) δ 200.8, 157.5, 135.9, 133.8, 131.9, 130.5, 129.8, 128.6, 128.3, 127.3, 126.7, 125.6, 121.6, 115.6, 82.4, 72.5, 54.4, 31.2. HRMS Calcd for $\text{C}_{18}\text{H}_{16}\text{O}_3$ (M^+): 280.1099. Found: 280.1076.

General procedure for 1,4-dihydro-6,7-dimethoxy-1,4-epoxynaphthalene **40** and 1,4-dihydro-5,8-dimethoxy-1,4-epoxynaphthalene **41** react with heteroatomnucleophiles. A round bottom flask was equipped with a reflux condenser, flame dried under a stream of nitrogen and charged with an 1,4-dihydro-6,7-dimethoxy-1,4-epoxynaphthalene **40** or 1,4-dihydro-5,8-dimethoxy-1,4-epoxynaphthalene **41** substrate (100 mg, 0.489 mmol) which was dissolved in anhydrous THF (2.5 mL). $[\text{Rh}(\text{COD})\text{Cl}]_2$ (2.5 mol%) and 1,1'-Bis(diphenylphosphino)ferrocene (dppf) (5 mol%) were added simultaneously before immediately heating the resulting dark orange solution to reflux. As soon as boiling was observed heteroatomnucleophiles (0.5 mmol) was added and the reaction mixture was stirred at reflux temperature until the starting material was consumed, as determined by TLC (typically 1-5h). Volatile nucleophiles were used in smaller excess (5 eq). The additive ammonium iodide was used (2.5 eq) when the nucleophile reagent is an amine. It was added together with catalyst. After completion, concentrated in *vacuo* and purification by flash chromatography gave the product.

(1R*, 2R*)-2,6,7-trimethoxy-1,2-dihydronaphthalen-1-ol (42):

Following the general procedure starting from 1,4-dihydro-6,7-dimethoxy-1,4-epoxynaphthalene **40** and using the nucleophile methanol, **42** was obtained as a yellow oil (73.4 mg, 64%) by flash chromatography. R_f = 0.28 on silica gel (50% ethyl acetate in hexanes). IR (KBr, cm^{-1}) 3450 (br), 3007 (w), 2936 (w), 2832 (w), 1598 (s), 1503 (s), 1462 (m), 1268 (m), 1156 (m), 1120 (m), 990 (w), 864 (w), 750 (s). ^1H NMR (300MHz, CDCl_3) δ 7.13 (1H, s), 6.62 (1H, s), 6.34 (1H, dd, J = 6.8, 1.8 Hz), 5.92 (1H, dd, J = 7.3, 2.6 Hz), 4.82 (1H, d, J = 10 Hz), 4.04-4.08 (1H, m), 3.89 (3H, s), 3.84 (3H, s), 3.46 (3H, s), 2.82 (1H, s(br)). ^{13}C NMR (400MHz, CDCl_3) δ 148.8, 148.4, 128.9, 128.2, 124.9, 110.2, 109.2, 82.4, 72.5, 56.9, 56.2. HRMS Calcd for $\text{C}_{13}\text{H}_{16}\text{O}_4$ (M^+): 236.1049. Found: 236.1055.

(1R*, 2R*)-2,5,8-trimethoxy-1,2-dihydronaphthalen-1-ol (43):

Following the general procedure starting from 1,4-dihydro-5,8-dimethoxy-1,4-epoxynaphthalene **41** and using the nucleophile methanol, **43** was obtained as a yellow oil (90 mg, 78%) by flash chromatography, R_f = 0.43 on silica gel (50% ethyl acetate in hexanes). IR (KBr, cm^{-1}) 3425 (br), 3056 (w), 2937 (s), 2835 (m), 1642 (w), 1596 (m), 1484 (s), 1461 (s), 1261 (s), 1087 (s), 956 (s), 804 (s), 746 (s), 715 (s). ^1H NMR (300MHz, CDCl_3) δ 7.04 (1H, d J = 9.9 Hz), 6.79 (2H, s), 6.09 (1H, dd, J = 5.2, 4.6 Hz), 5.17 (1H, d, J = 3.0 Hz), 4.04-4.07 (1H, m), 3.84 (3H, s), 3.81 (3H, s), 3.45 (3H, s), 2.64 (1H, s(br)). ^{13}C NMR (400MHz, CDCl_3) δ 151.8, 150.2, 124.4, 124.2, 123.8, 121.6, 111.8, 111.3, 77.1, 65.1, 56.7, 56.4, 56.1. HRMS Calcd for $\text{C}_{13}\text{H}_{16}\text{O}_4$ (M^+): 236.1049. Found: 236.1048.

(1R*, 2R*)-2-phenoxy-6,7-dimethoxy-1,2-dihydronaphthalen-1-ol (44):

Following the general procedure starting from 1,4-dihydro-6,7-dimethoxy-1,4-epoxynaphthalene **40** and using the nucleophile phenol, **44** was obtained as a yellow oil (90 mg, 78%) by flash chromatography. R_f = 0.43 on silica gel (50% ethyl acetate in hexanes). IR (KBr, cm^{-1}) 3456 (br), 3042 (w), 3003 (w), 2929 (s), 2830 (m), 1598 (w), 1581 (m), 1514 (s), 1494 (s), 1463 (m), 1271 (s), 1230 (s), 1125 (s), 988 (s), 755 (s). ^1H NMR (300 MHz, CDCl_3) δ 7.29 (2H, t, J = 8.5 Hz), 7.22 (1H, s), 6.96-7.03 (2H, m), 6.95 (1H, s), 6.44 (1H, d, J = 10 Hz), 5.94 (1H, d, J = 7.9 Hz), 5.10-5.14 (2H, m), 3.90-4.02 (1H, m), 3.94 (3H, s), 3.90 (3H, s), 2.77 (1H, s). ^{13}C NMR (400 MHz, CDCl_3) δ 157.6, 148.9, 148.6, 129.8, 128.9, 128.6, 124.9, 124.5, 124.4, 121.7, 116.1, 110.4, 109.4, 79.3, 72.5, 60.7, 56.3. HRMS Calcd for $\text{C}_{18}\text{H}_{18}\text{O}_4$ (M^+): 298.1205. Found: 298.1210.

(1R*, 2R*)-2-phenoxy-5,8-dimethoxy-1,2-dihydronaphthalen-1-ol (45):

Following the general procedure starting from 1,4-dihydro-5,8-dimethoxy-1,4-epoxynaphthalene **41** and using the nucleophile phenol, **45** was obtained as a yellow oil (124 mg, 86%) by flash chromatography. R_f = 0.63 on silica gel (50% ethyl acetate in hexanes). IR (KBr, cm^{-1}) 3429 (br), 3056 (w), 3007 (w), 2936 (w), 2838 (w), 1595 (m), 1485 (s), 1458 (m), 1261 (s), 1222 (m), 1088 (w), 1003 (m), 804 (m), 754 (m). ^1H NMR (300MHz, CDCl_3) δ 7.23-7.29 (2H, m), 6.94-7.11 (4H, m), 6.78-6.82 (2H, m), 6.10 (1H, q, J = 4.7 Hz), 5.29 (1H,s), 5.05 (1H, s), 3.85 (3H, s), 3.80 (3H, s), 2.64 (1H, s). ^{13}C NMR (400MHz, CDCl_3) δ 150.3, 129.7, 124.3, 123.2, 121.3, 116.2, 111.8, 111.4, 74.2, 65.4, 56.4, 56.2. HRMS Calcd for $\text{C}_{18}\text{H}_{18}\text{O}_4$ (M^+): 298.1205. Found: 298.1215.

(1R*, 2R*)-2-(4-acetophenoxy)-6,7-dimethoxy-1,2-dihydronaphthalen-1-ol (46):

Following the general procedure starting from 1,4-dihydro-6,7-dimethoxy-1,4-epoxynaphthalene **40** and using the nucleophile p-acetophenol, **46** was obtained as a colorless oil (120 mg, 72%) by flash chromatography. R_f = 0.11 on silica gel (33% ethyl acetate in hexanes). IR (KBr, cm^{-1}) 3443 (br), 3070 (w), 3000 (w), 2964 (w), 2936 (w), 1672 (s), 1597 (s), 1574 (m), 1507 (s), 1249 (s), 1173 (m). ^1H NMR (300MHz, CDCl_3) δ 7.95 (1H, s), 7.92 (1H, s), 7.19 (1H, s), 6.93 (2H, d, J = 4.8 Hz), 6.69 (1H, s), 6.46 (1H, dd, J = 8.2, 1.6 Hz), 5.88(1H, dd, J = 7.7, 2.0 Hz), 5.14-5.15 (2H, m), 3.94 (3H, s), 3.89 (3H, s), 2.56 (3H, s), 1.59 (1H, s). ^{13}C NMR (400MHz, CDCl_3) δ 196.9, 161.7, 149.2, 148.8, 131.0, 129.6, 128.3, 124.7, 123.2, 115.5, 110.5, 109.5, 79.4, 72.3, 56.3, 26.6. HRMS Calcd for $\text{C}_{20}\text{H}_{20}\text{O}_5$ (M^+): 340.1311. Found: 340.1318.

(1R*, 2R*)-2-(4-acetophenoxy)-5,8-dimethoxy-1,2-dihydronaphthalen-1-ol (47):

Following the general procedure starting from 1,4-dihydro-5,8-dimethoxy-1,4-epoxynaphthalene **41** and using the nucleophile p-acetophenol; **47** was obtained as colorless crystals by flash chromatography (148 mg, 89%), mp. 166-167°C (ethyl acetate). R_f = 0.17 on silica gel (33% ethyl acetate in hexanes). IR (KBr, cm^{-1}) 3415 (br), 3007 (w), 2936 (w), 2838 (w), 1671 (s), 1596 (s), 1570 (m), 1507 (m), 1484 (m), 1261 (s), 1243 (s), 1173 (m), 986 (m), 835 (w). ^1H NMR (300MHz, CDCl_3) δ 7.92 (2H, d, J = 8.8Hz), 7.16 (1H, d, J = 9.8 Hz), 7.04 (2H, d, J = 8.8 Hz), 6.8 (2H, s), 6.09 (1H, q, J = 4.6 Hz), 5.27(1H, t, J = 3.3 Hz), 5.14(1H, t, J = 3.3 Hz), 3.83 (3H, s), 3.81 (3H, s), 2.75 (1H, d, J = 4.1 Hz), 2.56 (3H, s). ^{13}C NMR (400MHz, CDCl_3) δ 197.1, 161.8, 151.7, 150.3, 149.8, 130.9, 130.6, 124.9, 123.4, 122.1, 121.1, 115.5, 111.8, 111.5, 74.3, 65.4, 56.4, 56.1, 26.6. HRMS Calcd for $\text{C}_{20}\text{H}_{20}\text{O}_5$ (M^+) , 340.1311. Found:340.1314.

(1R*, 2R*)-6,7-dimethoxy-2-benzoic acid-1-hydroxy-1,2-dihydronaphthalen-2-yl)ester (48):

Following the general procedure starting from 6,7-dimethoxy-1,4-dihydro-1,4-epoxynaphthalene **40** and using the nucleophile benzoic acid; **48** was obtained as a brown oil by flash chromatography (139 mg, 87%). R_f = 0.70 on silica gel (ethyl acetate : hexanes : methanol 2:3:0.1 v/v). IR (KBr, cm^{-1}) 3443 (br), 3007 (w), 2936 (w), 2838 (w), 1715 (s), 1604 (m), 1514 (s), 1491 (m), 1452 (m), 1272 (s), 1118 (m), 988 (m), 713 (m). ^1H NMR (300MHz, CDCl_3) δ 8.10 (1H, s), 8.00 (1H, s), 7.43-7.48 (2H, m), 7.38-7.40 (2H, m), 5.06 (1H, d, J = 8.2 Hz), 3.97 (3H, s), 3.86 (3H, s), 3.30 (1H, s(br)). ^{13}C NMR (400MHz, CDCl_3) δ 167.1, 149.2, 148.9, 143.6, 133.5, 130.6, 129.7, 128.6, 128.3, 124.7, 123.5, 119.2, 110.6, 110.2, 107.6, 106.5, 100.9, 82.9, 76.4, 72.2, 56.3, 56.1. HRMS Calcd for $\text{C}_{19}\text{H}_{18}\text{O}_5$ (M^+): 326.1154. Found: 326.1159.

(1R*, 2R*)-5,8-dimethoxy-2-benzoic acid-1-hydroxy-1,2-dihydronaphthalen-2-yl)-ester (49):

Following the general procedure starting from the 5,8-dimethoxy-1,4-dihydro-1,4-epoxynaphthalene **41** and using the nucleophile benzoic acid; **49** was obtained as a yellow oil by flash chromatography (158 mg, 98%). R_f = 0.60 on silica gel (50% ethyl acetate in hexanes). IR (KBr, cm^{-1}), 3472 (br), 3063 (w), 3007 (w), 2939 (w), 2836 (w), 1713 (s), 1599 (w), 1584 (w), 1485 (s), 1451 (m), 1263 (s), 1112 (m), 1068 (m), 946 (m), 803 (m), 713 (s). ^1H NMR (300MHz, CDCl_3) δ 7.96 (1H, t, J = 1.6 Hz), 7.94 (1H, t, J = 1.6 Hz), 7.48 (1H, t, J = 1.3 Hz), 7.26 (2H, t, J = 1.8 Hz), 7.13 (1H, d, J = 9.8 Hz), 6.83 (2H, s), 6.14 (1H, q, J = 5.0 Hz), 5.73 (1H, q, J = 2.9 Hz), 5.27 (1H, d, J = 2.6 Hz), 3.84 (3H, s), 3.82 (3H, s), 2.62 (1H, s). ^{13}C NMR (400MHz, CDCl_3) δ 166.1, 151.7, 150.2, 133.1, 130.3, 129.9, 128.4, 125.1, 123.5, 122.4, 121.4, 111.8, 111.6, 70.9, 64.9, 56.3, 56.2. HRMS Calcd for $\text{C}_{19}\text{H}_{18}\text{O}_5$ (M^+): 326.1154. Found: 326.1143.

(1R*, 2R*)-6,7-dimethoxy-2-(N-methylphenylamino)-1,2-dihydronaphthalen-1-ol (50):

Following the general procedure starting from 6,7-dimethoxy-1,4-dihydro-1,4-epoxynaphthalene **40** and using the nucleophile N-methylphenylamine; **50** was obtained as a yellow oil by flash chromatography (126 mg, 83%). R_f = 0.60 on silica gel (50% ethyl acetate in hexanes). IR (KBr, cm^{-1}), 3442 (br), 3030 (w), 2935 (m), 2833 (s), 1604 (m), 1574 (m), 1513 (s), 1463 (s), 1275 (s), 1226 (s), 1009 (w), 882 (w), 765 (w). ^1H NMR (300MHz, CDCl_3) δ 7.25 (2H, t, J = 2.0 Hz), 6.95 (1H, s), 6.80 (2H, t, J = 2.0 Hz), 6.6 (1H, s), 6.48 (1H, dd, J = 7.3, 2.3 Hz), 5.81 (1H, dd, J = 6.6, 3.2 Hz), 5.04 (1H, d, J = 9.3 Hz), 4.69 (1H, dd, J = 3.8, 2.8 Hz), 3.96-4.00 (1H, m), 3.90 (3H, s), 3.88 (3H, s), 2.82 (3H, s), 2.36 (1H, s). ^{13}C NMR (400MHz, CDCl_3) δ 150.1, 149.2, 149.0, 143.0, 143.6, 129.5, 125.8, 118.3, 114.8, 110.4, 109.7, 107.1, 82.8, 70.3, 63.7, 56.3, 33.6. HRMS Calcd for $\text{C}_{19}\text{H}_{21}\text{NO}_3$ (M^+): 311.1521. Found: 311.1520.

(1R*, 2R*)-5,8-dimethoxy-2-(N-methylphenylamino)-1,2-dihydronaphthalen-1-ol (51):

Following the general procedure starting from 5,8-dimethoxy-1,4-dihydro-1,4-epoxynaphthalene **41** and using the nucleophile N-methylphenylamine; **51** was obtained as a yellow oil by flash chromatography (117 mg, 77%). R_f = 0.40 on silica gel (33% ethyl acetate in hexanes). IR (KBr, cm^{-1}), 3459 (br), 3421 (br), 3056 (w), 2992 (w), 2937 (m), 2835 (m), 1597 (s), 1503 (s), 1483 (s), 1360 (m), 1314 (m), 1260 (s), 1195 (m), 1105 (s), 1195 (m), 1004 (m), 803 (m), 751 (m), 732 (m). ^1H NMR

(300MHz, CDCl₃) δ 7.27-7.32 (2H, m), 7.18 (1H, dd, J = 8.2, 1.6 Hz), 6.99 (1H, s), 7.01 (1H, s), 6.77-6.82 (2H, m), 5.95 (1H, ddd, J = 1.6, 0.9 Hz), 5.19 (1H, m), 4.69 (1H, dd, J = 1.3, 0.9 Hz), 4.69-4.72 (1H, m), 3.84 (3H, s), 3.80 (3H, s), 2.85 (1H, s), 2.57 (3H, s). ¹³C NMR (400MHz, CDCl₃) δ 151.2, 149.9, 149.4, 129.4, 125.1, 124.7, 123.3, 121.8, 117.4, 114.0, 111.4, 110.8, 64.8, 58.9, 56.3, 55.9, 32.8. HRMS Calcd for C₁₉H₂₁NO₃ (M⁺): 311.1521. Found: 311.1531.

(1R*, 2R*)-6,7-dimethoxy-2-pyrrolidin-1,2-dihydronaphthalen-1-ol (52):

Following the general procedure starting from 6,7-dimethoxy-1,4-dihydro-1,4-epoxynaphthalene **40** and using the nucleophile pyrrolidine; **52** was obtained as a brown oil (106 mg, 80%) by flash chromatography. R_f= 0.20 on silica gel (ethyl acetate : hexanes : methanol 3:2:1 v/v). IR (KBr, cm⁻¹), 3247 (br), 3030 (w), 2992 (w), 2961 (w), 2832 (w), 1604 (m), 1509 (w), 1513 (s), 1463 (s), 1276 (s), 1116 (s), 991 (w), 862 (m), 730 (m). ¹H NMR (300MHz, CDCl₃) δ 7.17 (1H, s), 6.62 (1H, s), 6.52 (1H, s), 6.46 (1H, d, J = 9.8 Hz), 5.97 (1H, d, J = 9.8 Hz), 3.91 (3H, s), 3.85 (3H, s), 3.56 (1H, d, J = 12 Hz), 3.36 (1H, s(br)), 2.69-2.77 (4H, m), 1.97 (4H, s). ¹³C NMR (400MHz, CDCl₃) δ 148.8, 148.2, 129.9, 129.7, 124.8, 123.0, 110.2, 108.9, 69.9, 64.1, 56.2, 49.2, 24.1. HRMS Calcd for C₁₆H₂₁NO₃ (M⁺): 275.1521. Found: 275.1525.

(1R*, 2R*)-5,8-dimethoxy-2-pyrrolidin-1,2-dihydronaphthalen-1-ol (53):

Following the general procedure starting from 5,8-dimethoxy-1,4-dihydro-1,4-epoxynaphthalene **41** and using the nucleophile pyrrolidine; **53** was obtained as a yellow oil (120 mg, 89%) by flash chromatography. R_f= 0.10 on silica gel (ethyl acetate : hexanes : methanol 3:2:0.3 v/v). IR (KBr, cm⁻¹), 3394 (br), 3046 (w), 2959 (w), 2833 (s), 1596 (m), 1483 (s), 1463 (m), 1437 (m), 1396 (m), 1357 (m), 1259 (s), 1193 (m), 1087 (s), 1061 (m), 1015 (s), 954 (m), 798 (s). ¹H NMR (400MHz, CDCl₃) δ 7.02 (1H, dd, J = 5.86, 4.03 Hz), 6.74 (2H, s), 5.97 (1H, dd, J = 4.6, 1.8 Hz), 5.10 (1H, s), 3.81 (3H, s), 3.76 (3H, s), 3.46-3.48 (1H, m), 2.62-2.63 (2H, m), 2.64 (1H, s), 2.47-2.49 (2H, m), 1.65-1.66 (4H, m). ¹³C NMR (400MHz, CDCl₃) δ 151.2, 149.8, 124.9, 124.6, 122.6, 121.9, 111.3, 110.8, 63.1, 61.3, 56.3, 56.1, 49.9, 23.4. HRMS Calcd for C₁₆H₂₁NO₃ (M⁺): 275.1521. Found: 275.1520.

(1R*, 2R*)-6,7-dimethoxy-2-dibenzylamino-1,2-dihydronaphthalen-1-ol (54):

Following the general procedure starting from 6,7-dimethoxy-1,4-dihydro-1,4-epoxynaphthalene **40** and using the nucleophile N,N-dibenzylamine; **54** was obtained as colourless crystals (190 mg, 97%) by flash chromatography, m.p. 112-114°C (ethyl acetate). R_f= 0.82 on silica gel (ethyl acetate : hexanes : methanol 3:2:0.1 v/v). IR (KBr, cm⁻¹), 3503 (br), 3061 (w), 3027 (w), 2938 (s), 2832 (w), 1602 (m), 1573 (w), 1511 (s), 1493 (s), 1452 (s), 1259 (s), 1116 (s), 747 (s), 698 (s). ¹H NMR (300MHz, CDCl₃) δ 7.71 (1H, dd, J = 3.3, 2.8 Hz), 7.30-7.38 (5H, m), 7.25-7.29 (4H, m), 7.11 (1H, s), 6.63 (1H, s), 6.49-6.52 (1H, dd, J = 7.3, 2.6 Hz), 6.06-6.09 (1H, dd, J = 7.4, 2.4 Hz), 4.9 (1H, d, J = 11.5 Hz), 3.97-4.02 (1H, m), 3.97 (2H, s), 3.87 (2H, s), 3.83 (6H, s), 3.60-3.69 (1H, m). ¹³C NMR (400MHz, CDCl₃) δ 166.2, 151.7, 150.2, 133.9, 133.1, 130.4, 129.9, 128.7, 128.4, 125.1, 123.5, 122.4, 121.5, 111.9, 111.6, 70.9, 65.1, 56.4, 56.2. HRMS Calcd for C₂₆H₂₇NO₃ (M⁺): 401.1991. Found: 401.1998.

(1R*, 2R*)-5,8-dimethoxy-2-dibenzylamino-1,2-dihydronaphthalen-1-ol (55):

Following the general procedure starting from 5,8-dimethoxy-1,4-dihydro-1,4-epoxynaphthalene **41** and using the nucleophile N,N-dibenzylamine; **55** was obtained as a brown oil (150 mg, 76%) by flash chromatography, R_f = 0.40 on silica gel (33% ethyl acetate in hexanes). IR (KBr, cm^{-1}), 3563 (br), 3450 (br), 3063 (w), 3035 (w), 2929 (w), 2830 (w), 1598 (w), 1481 (s), 1454 (m), 1437 (w), 1259 (s), 1120 (w), 1086 (m), 733 (m), 698 (m). ^1H NMR (400MHz, CDCl_3) δ 7.40-7.42 (2H, m), 7.23-7.29 (4H, m), 7.15-7.21 (4H, m), 7.12-7.14 (2H, m), 6.78 (2H, s), 6.03 (1H, q, J = 5.1 Hz), 5.41 (1H, s), 3.88 (3H, s), 3.80 (3H, s), 3.66-3.67 (1H, m), 3.59 (2H, d, J = 13.7 Hz), 3.46 (2H, d, J = 13.7 Hz). ^{13}C NMR (400MHz, CDCl_3) δ 151.1, 149.8, 140.4, 128.9, 128.3, 126.9, 126.1, 124.9, 122.4, 122.2, 111.2, 110.5, 62.8, 58.3, 56.3, 56.1, 53.8. HRMS Calcd for $\text{C}_{26}\text{H}_{27}\text{NO}_3$, (M^+): 401.1991. Found: 401.1987.

(1R*, 2R*)-6,7-dimethoxy-2-morpholin-4-yl-1,2-dihydronaphthalen-1-ol (56):

Following the general procedure starting from 6,7-dimethoxy-1,4-dihydro-1,4-epoxynaphthalene **40** and using the nucleophile morpholine; **56** was obtained as a brown oil (124 mg, 87%) by flash chromatography, R_f = 0.17 on silica gel (ethyl acetate : hexanes : methanol 2 : 3 : 0.2 v/v). IR (KBr, cm^{-1}), 3455 (br), 3035 (br), 3000 (w), 2956 (s), 2835 (s), 1604 (s), 1573 (m), 1513 (s), 1453 (s), 1278 (s), 1115 (s), 985 (m), 870 (s), 731 (m). ^1H NMR (400MHz, CDCl_3) δ 7.11 (1H, s), 6.63 (1H, s), 6.45-6.63 (1H, dd, J = 7.4, 2.4 Hz), 5.97-6.01 (1H, dd, J = 7.1, 2.8 Hz), 4.79 (1H, d, J = 12 Hz), 3.92 (3H, s), 3.86 (3H, s), 3.67-3.69 (4H, m), 3.72-3.74 (1H, m), 3.15 (1H, s(br)), 2.27-2.80 (2H, m), 2.52-2.58 (2H, m). ^{13}C NMR (400MHz, CDCl_3) δ 148.8, 148.2, 129.9, 129.3, 124.7, 122.5, 110.1, 108.8, 68.2, 67.8, 67.6, 56.3, 49.6. HRMS Calcd for $\text{C}_{16}\text{H}_{21}\text{NO}_4$ (M^+): 291.1471. Found: 291.1464.

(1R*, 2R*)-5,8-dimethoxy-2-morpholin-4-yl-1,2-dihydro-naphthalen-1-ol (57):

Following the general procedure starting from 5,8-dimethoxy-1,4-dihydro-1,4-epoxynaphthalene **41** and using the nucleophile morpholine; **57** was obtained as a brown oil (80 mg, 53%) by flash chromatography, R_f = 0.30 on silica gel (ethyl acetate : hexanes : methanol 1 : 1 : 0.2 v/v). IR (KBr, cm^{-1}), 3411 (br), 3030 (w), 2953 (w), 2834 (m), 1595 (w), 1483 (s), 1462 (m), 1451 (m), 1260 (s), 1114 (s), 1086 (m), 1003 (m), 802 (m). ^1H NMR (400MHz, CDCl_3) δ 7.08 (1H, d, J = 8.9 Hz), 6.77 (2H, s), 5.92 (1H, q, J = 5.3 Hz), 5.25 (1H, s), 3.84 (3H, s), 3.79 (3H, s), 3.95 (4H, t, J = 4.7 Hz), 3.45 (1H, dd, J = 2.2, 1.6 Hz), 2.62-2.67 (2H, m), 2.34-2.39 (2H, m), 2.30 (1H, s(br)). ^{13}C NMR (400MHz, CDCl_3) δ 150.8, 149.8, 125.0, 124.2, 123.0, 122.0, 111.3, 110.6, 67.5, 64.1, 61.5, 56.3, 56.1, 48.9. HRMS Calcd for $\text{C}_{16}\text{H}_{21}\text{NO}_4$ (M^+): 291.1471. Found: 291.1472.

Representative procedure for the ARO of [2.2.1] oxabicyclic alkenes (58):

To a flame-dried round bottomed flask under inert atmosphere was added $[\text{Rh}(\text{COD})\text{Cl}]_2$ (10mg, 0.02mmol) and (*R,S*)-PPF- P^tBu_2 (24mg, 0.044mmol) which was dissolved in a minimal amount of THF (~0.5mL) and stirred at room temperature for 5 min to produce a dark red solution. In a separate flame-dried round bottomed flask was added AgOTf (22mg, 0.08mmol). The rhodium-phosphine solution was transferred to the flask containing the AgOTf via cannula resulting in the formation of a white precipitate. This heterogeneous mixture was stirred at room temperature for 5 min prior to its transfer to a flame-dried flask containing TBAI (44mg, 0.12mmol). After stirring for 5 additional minutes, **58** (R = PMB) (200mg, 0.8mmol) was added and the solution heated to reflux in an oil bath heated at 110°C. Once reflux temperature was reached, the nucleophile was added (5eq) and the reaction

mixture was reduced in volume by steady flow of nitrogen until refluxing ceased (all the THF had evaporated off). This solution was then heated at 110°C until the reaction was complete as determined by TLC analysis (7-9 hours).

(1R,2R,5R,6S)-2-(4-Bromo-phenoxy)-5,6-bis-methoxymethyl-cyclohex-3-enol (59):

Following the general procedure, **58** (R = Me) (147mg, 0.8mmol) was reacted with 4-bromophenol (692mg, 4.0mmol) and the (R,S)-PPF-P^tBu₂ rhodium iodide complex (5 mol% to **58**). When the reaction was complete as determined by TLC analysis, the crude mixture was dissolved in ether and extracted twice with an aqueous 10%NaOH solution which was then back extracted twice with ether. The organic extracts were combined, dried over MgSO₄ and concentrated. The crude residue was purified by chromatography to give **59** (236mg, 83% yield) as a colorless oil. The ee was determined to be 94% using HPLC analysis on a CHIRALCEL AD column, retention times in 10% isopropanol in hexanes were 7.6 min and 8.7 min (major). R_f = 0.18 on silica gel (40% ethyl acetate:hexanes); [α]_D²⁵ = -185 (c = 14.6, CHCl₃); IR (KBr, cm⁻¹) 3381(s), 2908(s), 1584(m), 1481(s), 1394(m), 1230(s), 1093(s); ¹H NMR (400MHz, CDCl₃) δ 7.36 (2H, d, J = 9.0 Hz), 6.84 (2H, d, J = 9.0 Hz), 6.01-5.86 (2H, m), 4.58-4.54 (2H, m), 3.88 (1H, dm, J = 9.9 Hz), 3.62-3.31 (4H, m), 3.40 (3H, s), 3.36 (3H, s), 2.70-2.62 (2H, m); ¹³C NMR (400MHz, CDCl₃) δ 156.7, 133.9, 132.3, 124.3, 117.4, 113.0, 74.2, 72.1, 70.4, 66.7, 59.0, 58.9, 36.8, 36.2. HRMS calcd for C₁₆H₂₁BrO₄ (M⁺): 356.0623; Found: 356.0624.

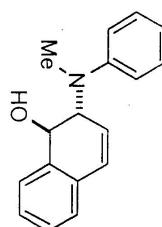
(1R, 2R, 5R ,6S)-5,6-Bis-(4-methoxy-benzyloxymethyl)-2-phenoxy-cyclohex-3-enol (60):

Following the general procedure, **58** (R = PMB) (200mg, 0.8mmol) was reacted with phenol (376mg, 4.0mmol) and the (R,S)-PPF-P^tBu₂ rhodium iodide complex (5 mol% to **58**). When the reaction was complete as determined by TLC analysis, the crude mixture was dissolved in ether and extracted twice with an aqueous 10%NaOH solution that was then back extracted twice with ether. The organic extracts were combined, dried over MgSO₄ and concentrated. The crude residue was purified by chromatography to give **60** (330mg, 84% yield) as a colorless oil. The ee was determined to be 93% using HPLC analysis on a CHIRALCEL AD column, retention times in 10% isopropanol in hexanes were 17.1 min and 18.0 min (major). R_f = 0.21 on silica gel (20% ethyl acetate:hexanes); [α]_D²⁵ = -112 (c = 8.5, CHCl₃); IR (KBr, cm⁻¹) 3381(s), 2908(s), 1584(m), 1481(s), 1394(m), 1230(s), 1093(s); ¹H NMR (400MHz, CDCl₃) δ 7.29-7.16 (6H, m), 6.96-6.84 (7H, m), 6.00-5.90 (2H, m), 4.64-4.58 (2H, m), 4.50 (1H, AB, d, J = 11.5 Hz), 4.35 (1H, AB, d, J = 11.5 Hz), 4.34 (1H, AB, d, J = 11.5 Hz), 4.26 (1H, AB, d, J = 11.5 Hz), 3.90 (1H, dm, J = 10.1 Hz), 3.78 (3H, s), 3.77 (3H, s), 3.56-3.41 (4H, m), 2.76-2.64 (2H, m); ¹³C NMR (100MHz, CDCl₃) δ 159.5, 159.2, 157.5, 133.8, 130.1, 129.8, 129.5, 129.5, 128.7, 124.5, 120.8, 115.5, 113.8, 113.7, 73.6, 73.0, 72.7, 69.3, 67.3, 67.0, 55.2, 55.2, 36.9, 36.1. HRMS calcd for C₃₀H₃₄O₆ (M⁺): 490.2355; Found: 490.2352.

(1R,2R,5R,6S)-5,6-Bis-(4-methoxy-benzyloxymethyl)-2-(methyl-phenyl-amino)-cyclohex-3-enol (61):

Following the general procedure, **58** (R = PMB) (200mg, 0.8mmol) was reacted with N-methylaniline (428mg, 4.0mmol) and the (R,S)-PPF-P^tBu₂ rhodium iodide complex (5 mol% to **58**). When the reaction was complete as determined by TLC analysis, the crude mixture was concentrated and chromatographed to give **61** (374mg, 93% yield)

as a colorless oil) The ee was determined to be 95% using HPLC analysis on a CHIRALCEL AD column, retention times in 10% isopropanol in hexanes were 22.9 min and 25.2 min (major). $R_f = 0.28$ on silica gel (20% ethyl acetate:hexanes); $[\alpha]_D^{25} = -82$ ($c = 12.6$, CHCl_3); IR (KBr, cm^{-1}) 3366(s), 3007(s), 2885(s), 1603(m), 1504, (m), 1249(m), 1059(m), 826(m); ^1H NMR (400MHz, CDCl_3) δ 7.26-7.14 (6H, m), 6.92-6.79 (6H, m), 6.74-6.68 (1H, m), 5.87 (1H, dm, $J = 10.2$ Hz), 5.68 (1H, dm, $J = 10.2$ Hz), 4.45 (1H, AB, d, $J = 11.5$ Hz), 4.36 (1H, AB, d, $J = 11.5$ Hz), 4.34 (4H, m), 3.78 (3H, s), 3.77 (3H, s), 3.61-3.42 (5H, m), 2.81 (3H, s), 2.75-2.67 (1H, m), 2.52-2.42 (1H, m); ^{13}C NMR (400MHz, CDCl_3) δ 159.4, 159.2, 149.4, 131.6, 129.9, 129.7, 129.5, 129.1, 127.0, 116.4, 113.8, 112.6, 73.0, 72.9, 69.1, 68.9, 68.2, 60.2, 55.2, 39.2, 37.0, 32.8. HRMS calcd for $\text{C}_{31}\text{H}_{37}\text{NO}_5$ (M^+): 503.2672; Found: 503.2671.



2

