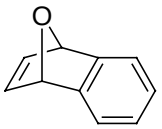
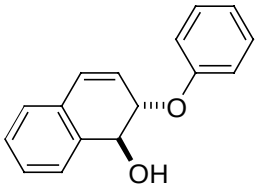
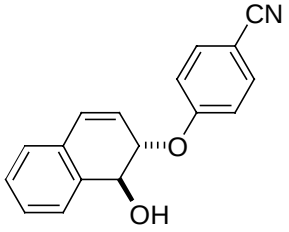


1



2

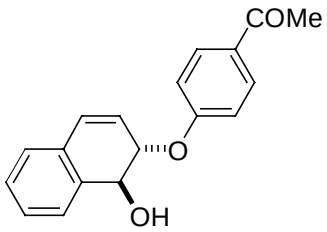
(1S,2S)-2-Phenoxy-1,2-dihydro-naphthalen-1-ol (2): To a flame dried round bottom flask, $[Rh(COD)Cl]_2$ (1.7 mg, 0.0035 mmol), (S)-(R)- PPF-P^{t}Bu$_2$ (3.8 mg, 0.0069 mmol, and **1** (100 mg, 0.694 mmol) were added. THF (2 mL) and phenol (327 mg, 3.47 mmol) were then added followed by heating to 80^{o}C for 1.5 hours. The reaction mixture was then poured in to ether and washed three times with 5% aqueous NaOH. The aqueous layers were combined and back extracted three times with ether. The organic layers were combined, washed with brine, dried over Na_2SO_4, and concentrated *in vacuo*. The resulting solid was purified by flash chromatography (20% ethyl acetate in hexanes) to give **2** as a white crystalline solid (130.7 mg, 83%). The ee was determined to be 99.2% using HPLC analysis on a CHIRALCEL OD column, λ= 486 nm. Retention times in 4% isopropanol in hexanes were 15.2 min (major) and 17.8 min. R_f = 0.26 on silica gel (10% ethyl acetate:hexanes); mp 109-110^{o}C (Et_2O); $[\alpha]^{25}_D$= +204.7^o (c= 10.1, $CHCl_3$); IR (KBr, cm^{-1}) 3337 (br), 3029 (w), 2866 (w), 1600 (m), 1496 (s), 1249 (s), 1062 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65-7.63 (1H, m), 7.33-7.25 (4H, m), 7.13-7.11 (1H, m), 7.01-6.95 (3H, m), 6.51 (1H, dd, *J*= 9.9, 1.6 Hz), 6.02 (1H, dd, *J*= 9.9, 2.2 Hz), 5.19 (1H, d, *J*= 10.4 Hz), 5.11 (1H, ddd, *J*= 10.4, 2.0, 2.0 Hz), 2.66 (1H, s); ^{13}C NMR (400 MHz, $CDCl_3$) δ 157.4, 135.5, 131.9, 129.7, 129.0, 128.2, 128.0, 126.4, 126.1, 125.2, 121.5, 115.9, 79.1, 72.4. HRMS calcd for $C_{16}H_{14}O_2$ (M^+): 238.0994. Found: 238.0984.



3

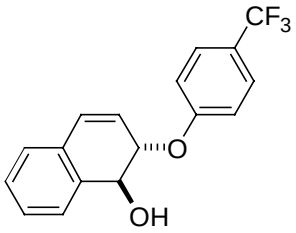
(1S,2S)-2-(4-cyanophenoxy)-1,2,-dihydro-naphthalen-1-ol (3): To a flame dried round-bottomed flask, $[Rh(COD)Cl]_2$ (1.7 mg, 0.0035 mmol), (S)-(R)- PPF-P^{t}Bu$_2$ (3.8 mg, 0.0069 mmol) and **1** (100 mg, 0.694 mmol) were added followed by addition of THF (2.5 mL) and 4-cyanophenol (413 mg, 3.47 mmol). The mixture was heated at 80^{o}C for

5 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 (30% ethyl acetate in hexanes) giving a white crystalline solid **3** (160 mg, 88%). The ee was determined to be 97% by HPLC analysis on a CHIRALCEL OD column, λ= 256 nm. Retention times in 3% isopropanol in hexanes were 35.3 min and 37.7 min (major). R_f = 0.40 on silica (30% ethyl acetate in hexanes); mp 140-141^{o}C (Et_2O); $[\alpha]^{25}_D$ = +182.3^o (c = 11.2, $CHCl_3$) IR (KBr, cm^{-1}) 3303 (b) 3050 (w) 2210 (m) 1598 (s) 1503 (s) 1238 (s) 1025 (m) 859 (m) 778 (m); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62-7.57 (3H, m), 7.33-7.27 (3H, m), 7.14-7.12 (1H, m), 6.56 (1H, dd, *J*= 1.4, 9.7 Hz), 5.93 (1H, dd, *J*= 1.4, 9.7 Hz), 5.20-5.13 (2H, m), 2.25 (1H, s). ^{13}C NMR (400 MHz, $CDCl_3$): δ 160.8, 135.0, 134.2, 131.5, 130.0, 128.5, 128.3, 126.7, 125.4, 124.4, 119.0, 116.2, 104.6, 79.2, 72.0. HRMS calcd for $(M\text{-}H_2O)^+$ ($C_{17}H_{11}ON$): 245.0841. Found: 245.0845.



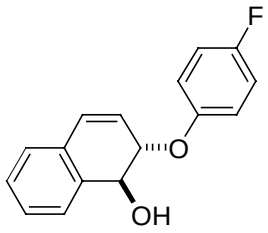
4

(1S,2S)-2-(4-acylphenoxy)-1,2,-dihydro-naphthalen-1-ol (4): To a flame dried round-bottomed flask, $[Rh(COD)Cl]_2$ (1.7 mg, 0.0035 mmol), (S)-(R)- PPF-P^{t}Bu$_2$ (3.8 mg, 0.0069 mmol) and **1** (100 mg, 0.694 mmol) were added followed by addition of THF (2.5 mL) and 4-hydroxyacetophenone (472 mg, 3.47 mmol). The mixture was heated at 80^o C for 2.5 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 (30% ethyl acetate in hexanes) giving a white crystalline solid **4** (177 mg, 91%). The ee was determined to be > 99% by formation of Mosher's ester; R_f = 0.28 on silica (30% ethyl acetate in hexanes); mp 124-126^{o}C (Et_2O); $[\alpha]^{25}_D$ = +153^o (c = 9.8, $CHCl_3$). IR (KBr, cm^{-1}) 3367 (b), 3069 (w), 2916 (w), 1668 (s), 1601 (s), 1265 (s), 1053 (m), 835 (m), 779 (m); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (2H, d, *J*=8.8 Hz), 7.66-7.64 (1H, m), 7.34-7.27 (2H, m), 7.16-7.14 (1H, m), 6.98 (2H, d, *J*= 8.8 Hz), 6.57 (1H, d, *J*= 9.9 Hz), 5.99 (1H, d, *J*= 9.9 Hz), 5.21 (2H, s), 2.85 (1H, s), 2.56 (3H, s); ^{13}C NMR (400 MHz, $CDCl_3$): δ 196.8, 161.4, 135.3, 131.7, 130.7, 130.6, 129.6, 128.3, 128.1, 126.6, 125.4, 125.0, 115.2, 79.0, 72.0, 26.3. HRMS calcd for $(M\text{-}H_2O)^+$ ($C_{18}H_{14}O_2$): 262.0994. Found: 262.0989.



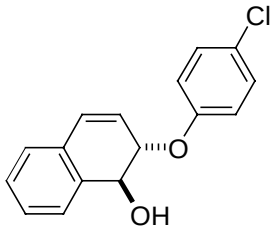
5

(1S,2S)- 2-(α,α,α)-trifluoro-4-methylphenoxy)-1,2,-dihydro-naphthalen-1-ol (5): To a flame dried round-bottomed flask, $[Rh(COD)Cl]_2$ (1.7 mg, 0.0035 mmol), (S)-(R)-PPF-P^{t}Bu$_2$ (3.8 mg, 0.0069 mmol) and **1** (100 mg, 0.694 mmol) were added followed by addition of THF (2.5 mL) and (α,α,α)-trifluoro-p-cresol (563 mg, 3.47 mmol). The mixture was heated at 80^o C for 8 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 (10% ethyl acetate in hexanes) to give a white crystalline solid **5** (184 mg, 87%). The ee was determined to be 95% by HPLC analysis on a CHIRALCEL OD column, λ= 486 nm. Retention times in 4% isopropanol in hexanes were 14.8 min and 17.3 min (major). R_f = 0.46 on silica (20% ethyl acetate in hexanes); mp 118-119^{o}C (Et_2O); $[\alpha]^{25}_D$ = +178^o (c = 9.6, $CHCl_3$). IR (KBr, cm^{-1}) 3360 (br), 3061 (w), 2874 (w), 1617 (m), 1518 (m), 1326 (s), 1103 (s), 1051 (m), 839 (m), 782 (m), 745 (w); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63-7.54 (1H, m), 7.55 (2H, d, *J*= 8.6 Hz), 7.33-7.24 (2H, m), 7.14-7.12 (1H, m), 7.01 (2H, d, *J*= 8.6 Hz), 6.55 (1H, dd, *J*= 1.6, 9.9 Hz), 5.97 (1H, dd, *J*= 2.0, 9.9 Hz), 5.21-5.13 (2H, m), 2.47 (1H, d, *J*= 3.6 Hz); ^{13}C NMR (400 MHz, $CDCl_3$): δ 159.9, 135.2, 131.7, 129.6, 128.4, 128.2, 127.1 (q, J^{C-F}= 3.6 Hz), 126.6, 125.4, 124.9, 123.4 (d, J^{C-F}= 33.0 Hz), 122.9 (d, J^{C-F}= 271.6 Hz), 115.6, 79.1, 72.1; HRMS calcd for (M^+) ($C_{17}H_{13}O_2F_3$): 306.0868. Found: 306.0852.



6

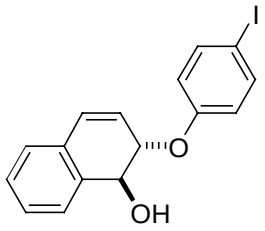
(1S,2S)-2-(4-fluorophenoxy)-1,2,-dihydro-naphthalen-1-ol (6): To a flame dried round-bottomed flask, $[Rh(COD)Cl]_2$ (1.7 mg, 0.0035 mmol), (S)-(R)- PPF-P^{t}Bu$_2$ (3.8 mg, 0.0069 mmol) and **1** (100 mg, 0.694 mmol) were added followed by addition of THF (2.5 mL) and 4-fluorophenol (389 mg, 3.47 mmol). The mixture was heated at 80^{o}C for 5 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 (10% ethyl acetate in hexanes) giving a white crystalline solid **6** (163 mg, 92%). 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 28.1 min (major) and 29.5 min. R_f = 0.39 on silica (20% ethyl acetate in hexanes); mp 127-129^{o}C (Et_2O); $[\alpha]^{25}_D$ = +216^o (c = 9.5, $CHCl_3$). IR (KBr, cm^{-1}) 3309 (b), 3071 (w), 2864 (w), 1504 (s), 1284 (m), 1052 (s), 781 (s), 692 (m); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63-7.61 (1H, m), 7.31-7.26 (2H, m), 7.12-7.10 (1H, m), 7.00-6.95 (2H, m), 6.92-6.88 (2H, m), 6.51 (1H, dd, *J*= 2.1, 9.9 Hz), 5.98 (1H, dd, *J*= 2.2, 9.9 Hz), 5.15 (1H, dd, *J*= 3.6, 10.0 Hz), 5.01 (1H, ddd, *J*= 2.1, 2.1, 10.1 Hz), 2.54 (1H, d, *J*= 3.8 Hz); ^{13}C NMR (400 MHz, $CDCl_3$): δ 157.6 (d, J^{C-F}= 239 Hz), 156.4, 153.4, 135.4, 131.8, 129.1, 128.2, 126.5, 125.7, 125.2, 117.5 (d, J^{C-F}= 8 Hz), 116.1 (d, J^{C-F}= 23.5 Hz);. HRMS calcd for (M^+) ($C_{16}H_{13}O_2F$): 256.0810. Found: 256.0911.



7

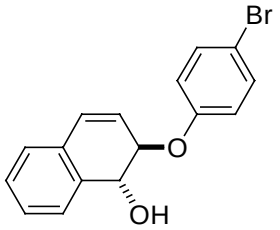
(1S,2S)-2-(4-chlorophenoxy)-1,2,-dihydro-naphthalen-1-ol (7): To a flame dried round-bottomed flask, $[Rh(COD)Cl]_2$ (1.7 mg, 0.0035 mmol), (S)-(R)- PPF-P^{t}Bu$_2$ (3.8 mg, 0.0069 mmol) and **1** (100 mg, 0.694 mmol) were added followed by addition of THF (2.5 mL) and 4-chlorophenol (446 mg, 3.47 mmol). The mixture was heated at 80^{o}C for 6 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) giving a white crystalline solid **7** (169 mg, 89%). The ee was determined to be 92% by formation of Mosher's ester. R_f = 0.47 on silica (20% ethyl acetate in hexanes); mp 125-125.5^{o}C (Et_2O); $[\alpha]^{25}_D$ = +150^o (c = 10.6, $CHCl_3$). IR (KBr, cm^{-1}) 3302 (br), 3064 (w), 2874 (w), 1590 (m), 1489 (s), 1362 (w), 1230 (s), 1052 (m), 890 (w), 846 (m), 778 (s), 663 (m); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65-7.64 (1H, m), 7.33-7.26 (4H, m), 7.16-7.13 (1H, m), 6.91(1H, ddd, *J*= 2.0, 2.0, 8.9 Hz), 6.55 (1H, dd, *J*= 1.8, 9.9 Hz), 5.99 (1H, dd, *J*= 2.2,

9.9 Hz), 5.19 (1H, dd, *J*= 3.8, 10.0 Hz), 5.07 (1H, ddd, *J*= 2.0, 2.0, 10.1 Hz), 2.56 (1H, d, *J*= 4.0 Hz); ^{13}C NMR (400 MHz, $CDCl_3$): δ 155.8, 135.2, 131.7, 129.5, 129.3, 128.2, 128.1, 126.5, 126.2, 125.3, 125.2, 116.9, 79.2, 72.1. HRMS calcd for $(M-H_2O)^+$ ($C_{16}H_{11}OCl$): 254.0498. Found: 254.0499.



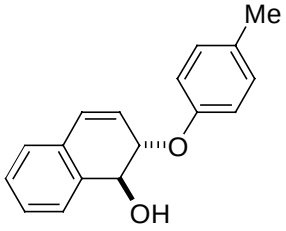
8

(1S,2S)-2-(4-iodophenoxy)-1,2,-dihydro-naphthalen-1-ol (8): To a flame dried round-bottomed flask, $[Rh(COD)Cl]_2$ (1.7 mg, 0.0035 mmol), (S)-(R)- PPF-P^{t}Bu$_2$ (3.8 mg, 0.0069 mmol) and **1** (100 mg, 0.694 mmol) were added followed by addition of THF (2.5 mL) and 4-iodophenol (763 mg, 3.47 mmol). The mixture was heated at 80^{o}C for 12 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 (10% ethyl acetate in hexanes) as a white crystalline solid **8** (193 mg, 73%). The ee was determined by deiodinating **8** (40 mg, 0.11 mmol) by reaction with t-BuLi (0.32 mL, 1.7M) in diethyl ether (2 mL) at -78^{o}C followed by quenching with isopropanol. Extraction with ether from water, washing with brine, drying over anhydrous sodium sulfate and removal of the solvents *in vacuo* gave a white crystalline solid (24 mg, 92%). The ee was determined to be 98% by HPLC analysis on a CHIRALCEL OD column, λ= 256 nm. Retention times in 4% isopropanol in hexanes were 15.2 min (major) and 17.9 min; R_f = 0.44 on silica (20% ethyl acetate in hexanes); mp 160-162^{o}C (Et_2O); $[\alpha]^{25}_D$ = +107^o (c = 9.7, $CHCl_3$). IR (KBr, cm^{-1}) 3264 (br), 3050 (w), 2926 (w), 2843 (w), 1581 (m), 1485 (s), 1388 (w), 1279 (m), 1246 (s), 1046 (m), 824 (m), 780 (m), 571 (w); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63-7.61 (1H, m), 7.58-7.55 (2H, m), 7.30-7.27 (2H, m), 7.13-7.11 (1H, m), 6.73 (2H, ddd, *J*= 2.2, 2.2, 9.0 Hz), 6.52 (1H, dd, *J*= 1.8, 9.8 Hz), 5.96 (1H,dd, *J*= 2.2, 9.8 Hz), 5.16 (1H, d, *J*= 10.0 Hz), 5.05 (1H, ddd, *J*= 2.0, 2.0, 10.0 Hz), 2.54 (1H, s); ^{13}C NMR (400 MHz, $CDCl_3$): δ 157.3, 138.5, 135.3, 131.7, 129.4, 128.3, 128.1, 126.6, 125.3, 125.3, 118.1, 83.6, 79.2, 72.2. HRMS calcd for $(M-H_2O)^+$ ($C_{16}H_{11}OI$): 345.9855. Found: 345.9849.



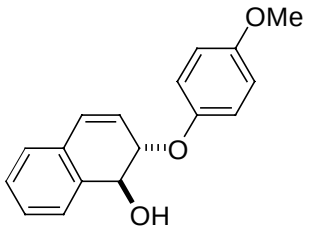
9

(1R,2R)-2-(4-Bromo-phenoxy)-1,2-dihydro-naphthalen-1-ol (9): To a flame dried round bottom flask, $[Rh(COD)Cl]_2$ (2.1 mg, 0.0043 mmol), (R)-(S)- PPF-P^{t}Bu$_2$ (4.6 mg, 0.0085 mmol, and **1** (122 mg, 0.85 mmol) were added.). THF (2 mL) and p-bromophenol (734 mg, 4.245 mmol) were then added followed by heating to 80^{o}C for 1.5 hours. The reaction mixture was then poured in to ether and washed three times with 5% aqueous NaOH. The aqueous layers were combined and back extracted three times with ether. The organic layers were combined, washed with brine, dried over Na_2SO_4, and concentrated *in vacuo*. The resulting solid was purified by flash chromatography (20% ethyl acetate in hexanes) to give **9** a white crystalline solid (239.7 mg, 90%). An X-Ray crystal structure proved the regiochemistry and the relative stereochemistry. The ee was determined by debrominating **9** (44 mg, 0.139 mmol) by reaction with t-BuLi (0.2 mL, 1.7M) in ether (2mL) at -78^{o}C followed by quenching with isopropanol. Extraction with ether from water, washing with brine, drying over Na_2SO_4 and concentration gave a white crystalline solid **2** (31.5 mg, 95%). The ee was determined to be 96.8% by HPLC analysis on a CHIRALCEL OD column, λ= 486nm. Retention times in 4% isopropanol in hexanes were 15.2 min and 17.5 min (major). R_f= 0.26 on silica gel (10% ethyl acetate:hexanes); mp 145-146^o (Et_2O); $[\alpha]^{25}_D$= -135.7^o (c= 10.2, $CHCl_3$); IR (KBr, cm^{-1}) 3290 (br), 3060 (m), 2870 (w), 1583 (m), 1484 (s), 1227 (s), 1052 (m), 980 (s), 776 (s); ^{1}H NMR (400MHz, $CDCl_3$) δ 7.70-7.65 (1H, m), 7.44-7.42 (2H, m), 7.35-7.32 (2H, m), 7.18-7.16 (1H, m), 6.88-6.86 (2H, m), 6.56 (1H, dd, *J*= 10.0, 2.0 Hz), 6.00 (1H, dd, *J*= 9.7, 2.2 Hz), 5.20 (1H, dd, *J*= 9.7, 3.6 Hz), 5.09 (1H, ddd, *J*= 10.0, 2.0, 2.0 Hz), 2.70 (1H, d, *J*= 3.9 Hz); ^{13}C NMR (400MHz, $CDCl_3$) δ 156.5, 135.3, 132.5, 131.7, 129.3, 128.3, 128.1, 126.5, 125.3, 117.6, 113.7, 79.4, 72.2. HRMS calcd for $C_{16}H_{11}OBr$ $(M-H_2O)^+$ 297.9994. Found: 297.9995.



10

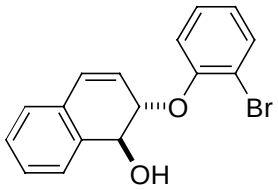
(1S,2S)-2-(4-methylphenoxy)-1,2,-dihydro-naphthalen-1-ol (10): To a flame dried round-bottomed flask, $[Rh(COD)Cl]_2$ (1.7 mg, 0.0035 mmol), (S)-(R)- PPF-P^{t}Bu$_2$ (3.8 mg, 0.0069 mmol) and **1** (50 mg, 0.347 mmol) were added followed by addition of THF (2.5 mL) and p-cresol (188 mg, 1.74 mmol). The mixture was heated at 80^{o}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) giving a white crystalline solid **10** (57 mg, 65%). The ee was determined to be 91% by HPLC analysis on a CHIRALCEL OD column, λ=256 nm. Retention times in 1% isopropanol in hexanes were 33.8 min (major) and 37.1 min. R_f = 0.49 on silica (20% ethyl acetate in hexanes); mp 80-81^{o}C (Et_2O); $[\alpha]^{25}_D$ = +145^o (c = 12.1, $CHCl_3$). IR (KBr, cm^{-1}) 3303 (br), 3050 (w), 2210 (m), 1598 (s), 1503 (s), 1238 (s), 1025 (m), 859 (m), 778 (m); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67-7.65 (1H, m), 7.33-7.28 (2H, m), 7.14-7.11 (3H, m), 6.88 (2H, d, *J*= 8.4 Hz), 6.51 (1H, dd, *J*= 1.8, 9.9 Hz), 6.04 (1H, dd, *J*= 2.0, 9.9 Hz), 5.20 (1H, dd, *J*= 1.6, 10.2 Hz), 5.09 (1H, ddd, *J*= 1.8, 1.8, 10.2 Hz), 2.87 (1H, d, *J*= 2.7 Hz), 2.33 (3H, s). ^{13}C NMR (400 MHz, $CDCl_3$): δ 155.0, 135.4, 131.8, 130.7, 130.1, 128.8, 128.1, 127.9, 126.4, 126.2, 125.1, 115.6, 79.0, 72.3, 20.5. HRMS calcd for (M^+) ($C_{17}H_{16}O_2$): 252.1150. Found: 252.1140.



11

(1S,2S)-2-(4-methoxyphenoxy)-1,2,-dihydro-naphthalen-1-ol (11): To a flame dried round-bottomed flask, $[Rh(COD)Cl]_2$ (1.7 mg, 0.0035 mmol), (S)-(R)- PPF-P^{t}Bu$_2$ (3.8 mg, 0.0069 mmol) and **1** (100 mg, 0.694 mmol) were added followed by addition of THF (2.5 mL) and 4-methoxyphenol (431 mg, 3.47 mmol). The mixture was heated at 80^{o}C

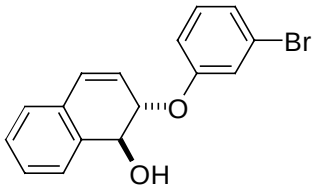
for 6 hours, then poured into diethyl ether and extracted 3 times with 10% aqueous sodium hydroxide solution. The aqueous extracts were combined and back-extracted three times with diethyl ether. The combined ether extracts were washed with brine and dried with anhydrous sodium sulfate. The solvents were removed *in vacuo*, yielding a solid which was purified by flash chromatography on silica gel (10% ethyl acetate in hexanes) as a white crystalline solid **11** (159 mg, 85%). The ee was determined to be 95% by HPLC analysis on a CHIRALCEL OD column, λ= 256 nm. Retention times in 4% isopropanol in hexanes were 22.1 min (major) and 25.9 min. R_f = 0.33 on silica (20% ethyl acetate in hexanes); mp 91-92°C (Et_2O); $[\alpha]^{25}_D$ = +129° (c = 9.9, $CHCl_3$); IR (KBr, cm^{-1}) 3349 (br), 3050 (w), 2822 (w), 1508 (s), 1233 (s), 1046 (m), 825 (m), 751 (m), 695 (w); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66-7.64 (1H, m), 7.30-7.27 (2H, m), 7.12-7.10 (1H, m), 6.91 (2H, ddd, *J*= 2.3, 2.3, 9.1 Hz), 6.84 (2H, ddd, *J*= 2.4, 2.4, 9.2 Hz), 6.49 (1H, dd, *J*= 2.0, 9.9 Hz), 6.02 (1H, dd, *J*= 2.4, 9.9 Hz), 5.17 (1H, dd, *J*= 3.3, 10.1 Hz), 5.02 (1H, ddd, *J*= 2.0, 2.0, 10.3 Hz), 3.77 (3H, s), 3.12 (1H, d, *J*= 3.4 Hz). ^{13}C NMR (400 MHz, $CDCl_3$): δ 154.3, 151.2,135.5, 131.9, 128.7, 128.1, 127.9, 126.4, 126.3, 125.2, 117.2, 114.8, 80.0, 72.4, 55.7. HRMS calcd for (M^+) ($C_{17}H_{14}O_2$): 250.0994. Found: 250.1006.



12

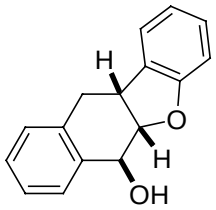
(1S,2S)-2-(2-bromophenoxy)-1,2,-dihydro-naphthalen-1-ol (12): To a flame dried round-bottomed flask, $[Rh(CO)_2Cl]_2$ (1.5 mg, 0.0035 mmol), (S)-(R)- PPF-P^{t}Bu$_2$ (3.8 mg, 0.0069 mmol) and **1** (100 mg, 0.694 mmol) were added followed by addition of THF (2.5 mL) and 2-bromophenol (0.40 mL, 3.47 mmol). 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 **12** (206 mg, 94%). 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); mp 120-122°C (Et_2O); $[\alpha]^{25}_D$ = +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); ^{1}H 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 $(M\text{-}H_2O)^+$ ($C_{16}H_{11}OBr$): 297.9993. Found: 297.9976.



13

(1S,2S)-2-(3-bromophenoxy)-1,2,-dihydro-naphthalen-1-ol (13): To a flame dried round-bottomed flask, $[Rh(COD)Cl]_2$ (1.7 mg, 0.0035 mmol), (S)-(R)- PPF-P^{t}Bu$_2$ (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^{o}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 **13** (200 mg, 92%). The ee was determined to be 96% 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); mp 120-122^{o}C (Et_2O); $[\alpha]^{25}_D$ = +254^o (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); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57-7.62 (1H, m), 7.22-7.30 (2H, m), 7.14-7.08 (4H, m), 6.82-6.88 (1H, m), 6.49 (1H, dd, *J*= 1.4, 9.9 Hz), 5.94 (1H, dd, *J*= 2.1, 9.9 Hz), 5.13 (1H, dd, *J*= 2.9, 9.9 Hz), 5.03 (1H, ddd, *J*= 1.9, 1.9, 9.9 Hz), 2.76 (1H, d, *J*= 3.6 Hz). ^{13}C NMR (400 MHz, $CDCl_3$): δ 158.1, 135.3, 131.7, 130.7, 129.6, 128.3, 128.1, 126.5, 125.3, 125.3, 124.5, 122.9, 119.2, 114.5, 79.3, 72.1. HRMS calculated for $(M\text{-}H_2O)^+$ ($C_{16}H_{11}OBr$): 297.9993. Found: 297.9976.



14

5a,6,11,11a-Tetrahydro-benzo[b]naphtho[2,3-d]furan-6-ol (14): To a flame dried round bottm flask fitted with a condenser was added 50mg **12**, 65mg tributyltin hydride and 26mL benzene. The solution was heated to 55^{o}C then 10mg AIBN was added. After 5 hours, the reation mixture was cooled, and 50 ml of a 5% NaOH solution was added.

Extraction with ether, concentration and chromatography (20%EtOAc in Hexanes) gave a white crystaline solid **14** (31mg, 86%). R_f = 0.33 on silica (20% ethyl acetate in hexanes); mp 174-178^oC ($CDCl_3$); $[\alpha]^{25}_D = +81^o$ (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 7.60 (1H, d, *J*= 7.3 Hz), 7.12-7.35 (5H, m), 6.90 (1H, m), 6.81 (1H, d, *J*= 8.0 Hz), 4.87 (1H, d, *J*= 7.3 Hz), 4.80 (1H, t, *J*= 10.0 Hz), 3.83 (1H, dt, *J*= 7.0, 9.7 Hz), 3.30 (1H, dd, AB, *J*= 6.8, 14.5 Hz), 2.74 (1H, dd, AB, *J*= 9.9, 14.3 Hz), 2.70 (1H, s). ^{13}C NMR (400 MHz, $CDCl_3$): δ 159.2, 136.9, 135.8, 129.8, 128.6, 127.4, 127.0, 126.9, 124.3, 124.2, 120.9, 109.7, 88.1, 71.2, 40.4, 33.4. HRMS calculated for $(M)^+$ ($C_{16}H_{14}O_2$): 238.0994. Found: 238.0991.