Supporting Information
for
Synthesis of a New Class of Conformationally Rigid Phosphino-Oxazolines: Highly
Enantioselective Ligands for Ir-Catalyzed Asymmetric Hydrogenation

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Experimental Section:

2-(*tert*-Butyl-dimethyl-silanyloxy)-(1*R*)-(2-iodo-phenyl)-ethylamine 7. To a suspension of (*R*)- α -methylbenzylamine **5** (1.37 g, 10.0 mmol) in 40 mL THF at -78 °C was added *n*-BuLi (2.5 M solution in hexane, 8 mL) dropwise. The resulting purple solution was stirred at -78 °C for 30 min before a solution of TBSCl (*tert*-butyldimethylsilyl chloride) (3.17 g, 21.0 mmol) in 20 mL THF was added at the same temperature. The reaction mixture was allowed to warm to rt naturally and was stirred overnight. After removing the THF solvent under reduced pressure, the residue was redissolved in 50 mL ether. To this solution at -78 °C was added *n*-BuLi (2.5 M solution in hexane, 12 mL) dropwise. The reaction mixture was allowed to slowly warm to rt during 3 h and stirred at rt for 1 h. I₂ (5.08 g, 20.0 mmol) was added at -78 °C and the reaction mixture was allowed to warm to rt and stirred at rt for 1 h. 10% Na₂S₂O₃ solution (20 mL) was added and the resulting mixture was stirred vigorously for 10 min. After usual work up, the product **7** was isolated by flash column chromatography (hexane:EtOAc = 80:20) as a brown oil (2.27 g, 60%). $[\alpha]_D^{20} = -49.4$ ($c = 0.82$, CHCl₃); ¹H NMR (CDCl₃, 360 MHz) δ 7.79 (dd, $J = 1.1$ Hz, $J = 7.9$ Hz, 1H), 7.57 (dd, $J = 1.6$ Hz, $J = 7.8$ Hz, 1H), 7.32 (dt, $J = 1.0$ Hz, $J = 7.8$ Hz, 1H), 6.93 (dt, $J = 1.7$ Hz, $J = 7.7$ Hz, 1H), 4.33 (dd, $J = 3.6$ Hz, $J = 7.9$ Hz, 1H), 3.80 (dd, $J = 3.6$ Hz, $J = 9.9$ Hz, 1H), 3.42 (dd, $J = 7.9$ Hz, $J = 9.9$ Hz, 1H), 1.82 (s, 2H), 0.91 (s, 9H), 0.07 (s, 3H), 0.03 (s, 3H); ¹³C NMR (CDCl₃, 90 MHz) δ 144.5, 139.5, 129.1, 128.3, 99.9, 67.6, 60.9, 26.1, 18.4, -5.1, -5.2; HRMS ($M^+ + 1$) m/z calcd for C₁₄H₂₅NOSi 378.07447, found 378.07638.

2-(*tert*-Butyl-dimethyl-silanyloxy)-(1*R*)-[2-(diphenyl-phosphinothioyl)-phenyl]-ethylamine 9a. To a suspension of (*R*)- α -methylbenzylamine **5** (1.37 g, 10.0 mmol, 1 equiv) in 40 mL THF at -78 °C was added *n*-BuLi (2.5 M solution in hexane, 8 mL) dropwise. The resulting purple solution was stirred at -78 °C for 30 min before a solution of TBSCl (3.17 g, 21.0 mmol) in 20 mL THF was added at the same temperature. The reaction mixture was allowed to warm to rt naturally and stirred overnight. After removing the THF solvent under reduced pressure, the residue was redissolved in 50 mL ether. To this solution at -78 °C was added *n*-BuLi (2.5 M solution in hexane, 12 mL) dropwise. The reaction mixture was allowed to slowly warm to rt during 3 h and stirred at

rt for 1 h. Diphenylchlorophosphine (4.42 g, 20.0 mmol) was slowly added at -78 °C and the resulting solution was allowed to warm to rt and stirred overnight. Sulfur (0.480 g, 15.0 mmol) was added at rt and the mixture was stirred for 1 h before water was added. After usual work up, the product **9a** was isolated by flash column chromatography (hexane:EtOAc = 90:10) as a white solid (3.03 g, 65%). $[\alpha]_D^{20} = -66.6$ ($c = 1.6$, CHCl₃); ¹H NMR (360 MHz, CDCl₃) δ 7.85-7.74 (m, 5H), 7.56-7.46 (m, 7H), 7.14 (m, 1H), 6.87 (dd, $J = 7.8$ Hz, $J = 14.7$ Hz, 1H), 4.80 (dd, $J = 3.6$ Hz, $J = 8.0$ Hz, 1H), 3.60-3.47 (m, 2H), 1.73 (s, 2H), 0.83 (s, 9H), -0.04 (s, 3H), -0.07 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 147.2 (d, $J = 9.0$ Hz), 133.5-131.6 (m), 130.2 (d, $J = 10.2$ Hz), 128.6 (d, $J = 1.2$ Hz), 128.4 (d, $J = 1.6$ Hz), 126.8 (d, $J = 12.7$ Hz), 66.9, 53.6 (d, $J = 7.0$ Hz), 25.8, 18.2, -5.3, -5.5; ³¹P NMR (145 MHz, CDCl₃) δ 42.11; HRMS ($M^+ + 1$) m/z calcd for C₂₆H₃₅NOSiPS 468.19408, found 468.19092.

2-(tert-Butyl-dimethyl-silanyloxy)-(1R)-[2-(dicyclohexyl-phosphinothioyl)-phenyl]-ethylamine 9b. To a suspension of (*R*)-α-methylbenzylamine **5** (0.343 g, 2.50 mmol, 1 equiv) in 10 mL THF at -78 °C was added *n*-BuLi (2.5 M solution in hexane, 2 mL) dropwise. The resulting purple solution was stirred at -78 °C for 30 min before a solution of TBSCl (0.791 g, 5.25 mmol) in 5 mL THF was added at the same temperature. The reaction mixture was allowed to warm to rt naturally and was stirred overnight. After removing the THF solvent under reduced pressure, the residue was redissolved in 15 mL ether. To this solution at -78 °C was added *n*-BuLi (2.5 M solution in hexane, 3 mL) dropwise. The reaction mixture was allowed to slowly warm to rt during 3 h and was stirred at rt for 1 h. Dicyclohexylchlorophosphine (0.873 g, 3.75 mmol) was slowly added at -78 °C and the resulting solution was allowed to warm to rt and was stirred overnight. Sulfur (0.120 g, 3.75 mmol) was added at rt and the mixture was stirred for 1 h before water was added. After usual work up, the product **9b** was isolated by flash column chromatography (hexane:EtOAc = 90:10) as a yellow oil (0.660 g, 55%). $[\alpha]_D^{20} = -48.6$ ($c = 1.1$, CHCl₃); ¹H NMR (CDCl₃, 360 MHz) δ 8.00 (br s, 1H), 7.72-7.69 (m, 1H), 7.52-7.47 (m, 1H), 7.38-7.34 (m, 1H), 5.18 (br s, 1H), 3.82-3.70 (m, 2H), 2.41-2.35 (m, 2H), 2.11-2.08 (m, 2H), 1.87-1.19 (m, 20H), 0.95 (s, 9H), 0.11 (s, 6H); ¹³C NMR (CDCl₃, 90 MHz) δ 147.1, 133.5 (m), 130.9, 128.5 (m), 127.0, 126.6, 126.5, 126.3, 68.2, 53.1, 39.8 (d, $J = 44.6$ Hz), 39.3 (d, $J = 48.9$ Hz), 27.0, 26.8, 26.4-26.1 (m), 25.7, 25.5, 18.0, -5.4, -5.5; ³¹P NMR (CDCl₃, 145 MHz) δ 61.43 (br s); HRMS ($M^+ + 1$) m/z calcd for C₂₆H₄₆NOSiPS 480.28798, found 480.28543.

General procedure for preparation of 2-adamantan-1-yl-(4*R*)-[2-(diphenyl-phosphinothioyl)-phenyl]-4,5-dihydro-oxazole 10c (analogously **8, **10a-10d**).** A mixture of **9a** (437 mg, 0.934 mmol), EDC·HCl (1-[3-(dimethylamino)propyl]-3-ethylcarbodiimide hydrochloride) (357 mg, 1.87 mmol), HOBT·H₂O (1-hydroxybenzotriazole hydrate) (126 mg, 0.934 mmol), 1-adamantanecarboxylic acid (168 mg, 0.934 mmol), and TEA (triethylamine) (0.53 mL, 3.7 mmol) in 10 mL DMF was stirred at 70 °C overnight. To the cooled mixture was added 10 mL 2N HCl solution followed by 20 mL EtOAc. The resulting mixture was stirred at rt for 30 min and then the two layers were separated. The aqueous layer was extracted with EtOAc (10 mL × 2). The combined

organic layer was washed with water and brine, dried with Na₂SO₄. After removal of the solvent, the resulting residue was purified by column flash chromatography (hexane:EtOAc:CH₂Cl₂ = 70:20:10) to give condensation product as a white solid (336 mg). To a mixture of the above condensation product (316 mg, 0.613 mmol), DIPEA (diisopropylethylamine) (0.73 mL, 2.5 mmol) and TEA (triethylamine) (0.51 mL, 6.1 mmol) in 10 mL CH₂Cl₂, was added methanesulfonylchloride (95 µL, 1.2 mmol) at 0 °C. The resulting mixture was allowed to warm to rt and stirred overnight. After removal of the solvent and the excessive diisopropylethylamine and triethylamine under reduced pressure, **10c** was isolated by column flash chromatography (hexane:EtOAc = 85:15) as a white solid (235 mg, 54% two steps). [α]_D²⁰ = +9.35 (*c* = 0.77, CHCl₃); ¹H NMR (CDCl₃, 360 MHz) δ 7.83-7.66 (m, 4H), 7.52-7.40 (m, 7H), 7.32 (dd, *J* = 4.8 Hz, *J* = 6.8 Hz, 1H), 7.12 (m, 1H), 6.85 (ddd, *J* = 0.7 Hz, *J* = 7.8 Hz, *J* = 14.8 Hz, 1H), 5.74 (t, *J* = 9.0 Hz, 1H), 4.49 (dd, *J* = 9.0 Hz, *J* = 9.9 Hz, 1H), 3.78 (t, *J* = 8.4 Hz, 1H), 1.98 (s, 3H), 1.91 (s, 6H), 1.69 (s, 6H); ¹³C NMR (CDCl₃, 75 MHz) δ 175.5, 147.4 (d, *J* = 8.5 Hz), 133.0 (d, *J* = 5.5 Hz), 132.7-132.3 (m), 131.9-131.7 (m), 131.6 (d, *J* = 2.9 Hz), 130.5 (d, *J* = 83.4 Hz), 128.8-128.4 (m), 126.7 (d, *J* = 12.5 Hz), 75.3, 66.6 (d, *J* = 7.0 Hz), 39.6, 36.5, 35.3, 27.8; ³¹P NMR (CDCl₃, 145 MHz) δ 42.30; HRMS (*M*⁺ + 1) *m/z* calcd for C₃₁H₃₃NOPS 498.20150, found 498.19902.

2-tert-Butyl-(4R)-(2-iodo-phenyl)-4,5-dihydro-oxazole 8. This compound was produced from **7** and dimethyl acetic acid by the same method used for **10c** as a colorless oil (60%). [α]_D²⁰ = -87.5 (*c* = 1.3, CHCl₃); ¹H NMR (CDCl₃, 360 MHz) δ 7.79 (dd, *J* = 1.2 Hz, *J* = 7.9 Hz, 1H), 7.32 (dt, *J* = 1.2 Hz, *J* = 7.7 Hz, 1H), 7.20 (dd, *J* = 1.7 Hz, *J* = 7.8 Hz, 1H), 6.94 (dt, *J* = 1.8 Hz, *J* = 7.6 Hz, 1H), 5.37 (dd, *J* = 7.8, *J* = 10.3 Hz, 1H), 4.76 (dd, *J* = 8.5 Hz, *J* = 10.3 Hz, 1H), 3.85 (t, *J* = 8.1 Hz, 1H), 1.32 (s, 9H); ¹³C NMR (CDCl₃, 90 MHz) δ 176.3, 146.0, 139.2, 129.1 (d, *J* = 22.0 Hz), 128.6, 127.4, 98.3, 74.3, 72.8, 33.6, 28.1; HRMS (*M*⁺ + 1) *m/z* calcd for C₁₃H₁₇NOI 330.03494, found 330.03633.

2-Benzhydryl-(4R)-[2-(diphenyl-phosphinothioyl)-phenyl]-4,5-dihydro-oxazole 10a. This compound was produced from **9a** and diphenyl acetic acid by the same method used for **10c** as a white solid (52%). [α]_D²⁰ = +35.4 (*c* = 0.65, CHCl₃); ¹H NMR (CDCl₃, 360 MHz) δ 7.83-7.71 (m, 4H), 7.56-7.45 (m, 7H), 7.41-7.24 (m, 11H), 7.16 (m, 1H), 6.87 (dd, *J* = 7.7 Hz, *J* = 14.8 Hz, 1H), 5.91 (t, *J* = 9.1 Hz, 1H), 5.26 (s, 1H), 4.72 (t, *J* = 9.6 Hz, 1H), 3.96 (t, *J* = 8.5 Hz, 1H); ¹³C NMR (CDCl₃, 75 MHz) δ 169.4, 146.8 (d, *J* = 8.5 Hz), 139.2 (d, *J* = 8.7 Hz), 133.1-130.1 (m), 129.0-128.5 (m), 127.2 (d, *J* = 4.2 Hz), 127.0 (d, *J* = 12.5 Hz), 76.3, 66.8 (d, *J* = 7.2 Hz), 51.2; ³¹P NMR (CDCl₃, 145 MHz) δ 42.38; HRMS (*M*⁺ + 1) *m/z* calcd for C₃₄H₂₉NOPS 530.17020, found 530.17347.

2-(3,5-Di-tert-butyl-phenyl)-(4R)-[2-(diphenyl-phosphinothioyl)-phenyl]-4,5-dihydro-oxazole 10b. This compound was produced from **9a** and 3,5-di-tert-butylbenzoic acid by the same method used for **10c** as a white solid (50%). [α]_D²⁰ = +34.0 (*c* = 1.1, CHCl₃); ¹H NMR (CDCl₃, 360 MHz) δ 7.92-7.76 (m, 6H), 7.57-7.49 (m, 9H), 7.19 (t, *J* = 7.4 Hz, 1H), 6.95 (dd, *J* = 7.7 Hz, *J* = 14.8 Hz, 1H), 6.03 (t, *J* = 8.9 Hz, 1H), 4.72 (t, *J* = 9.7 Hz, 1H), 4.07 (t, *J* = 8.5 Hz, 1H), 1.35 (s, 18H); ¹³C NMR (CDCl₃, 90 MHz) δ 166.6, 151.1, 147.5 (d, *J* = 8.5 Hz), 133.4-131.6 (m), 130.7, 129.6-129.0 (m),

127.1, 125.9, 123.0, 75.9, 68.0, 35.2, 31.6; ^{31}P NMR (CDCl_3 , 145 MHz) δ 42.30; HRMS ($\text{M}^+ + 1$) m/z calcd for $\text{C}_{35}\text{H}_{39}\text{NOPS}$ 552.24845, found 552.24701.

2-tert-Butyl-(4R)-[2-(dicyclohexyl-phosphinothioyl)-phenyl]-4,5-dihydro-oxazole 10d.

This compound was produced from **9b** and dimethyl acetic acid by the same method used for **10c** as a colorless oil (52%). $[\alpha]_D^{20} = -78.0$ ($c = 0.50$, CHCl_3); ^1H NMR (CDCl_3 , 300 MHz) δ 7.54-7.49 (m, 2H), 7.37-7.31 (m, 2H), 6.53 (m, 1H), 4.94 (t, $J = 9.5$ Hz, 1H), 3.92 (t, $J = 8.0$ Hz, 1H), 2.54 (m, 1H), 2.31 (m, 1H), 2.09 (m, 1H), 1.91-1.13 (m, 19H), 1.34 (s, 9H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 175.7, 149.2, 131.7 (d, $J = 2.6$ Hz), 131.3, 128.6 (d, $J = 9.0$ Hz), 126.3 (d, $J = 10.5$ Hz), 125.0 (d, $J = 63.8$ Hz), 76.2, 66.5 (d, $J = 3.7$ Hz), 41.2 (d, $J = 48.2$ Hz), 36.5 (d, $J = 51.2$ Hz), 33.3, 27.9, 26.6-25.2 (m); ^{31}P NMR (CDCl_3 , 145 MHz) δ 57.27 (br); HRMS ($\text{M}^+ + 1$) m/z calcd for $\text{C}_{25}\text{H}_{39}\text{NOPS}$ 432.24845, found 432.24619.

2-tert-Butyl-(4R)-(2-diphenylphosphanyl-phenyl)-4,5-dihydro-oxazole 2a. To a solution of **8** (94 mg, 0.286 mmol) in 4 mL ether was added *t*-BuLi (1.7 M solution, 0.34 mL) at -78°C . The reaction mixture was stirred at -78°C for 30 min before diphenylchlorophosphine (2.43 g, 11.0 mmol) was added slowly. The solution was allowed to warm to rt and was stirred overnight. Water was added. The aqueous layer was separated and extracted with CH_2Cl_2 . The combined organic layers were dried with Na_2SO_4 and concentrated. The residue was purified by flash column chromatography to give **2a** as a colorless oil (40%). $[\alpha]_D^{20} = -50.9$ ($c = 2.0$, CHCl_3); ^1H NMR (CD_2Cl_2 , 360 MHz) δ 7.40-7.26 (m, 12H), 7.19 (dt, $J = 1.5$ Hz, $J = 7.5$ Hz, 1H), 6.93-6.89 (m, 1H), 5.82-5.75 (m, 1H), 4.24 (dd, $J = 8.4$ Hz, $J = 10.2$ Hz, 1H), 3.64 (dt, $J = 0.5$ Hz, $J = 8.4$ Hz, 1H), 1.28 (s, 9H); ^{13}C NMR (CD_2Cl_2 , 90 MHz) δ 175.8, 148.4 (d, $J = 24.0$ Hz), 136.9 (d, $J = 10.2$ Hz), 135.4-134.2 (m), 130.0-129.3 (m), 127.9 (br s), 126.8 (br s), 75.4 (d, $J = 4.4$ Hz), 67.5 (m), 33.9, 28.3; ^{31}P NMR (CD_2Cl_2 , 145 MHz) δ -14.97; HRMS ($\text{M}^+ + 1$) m/z calcd for $\text{C}_{25}\text{H}_{27}\text{NOP}$ 388.18248, found 388.17930.

General procedure for preparation of 2-adamantan-1-yl-(4R)-(2-diphenylphosphanyl-phenyl)-4,5-dihydro-oxazole 2d (analogously 2b-2e). To a N_2 -flushed Schlenk flask was loaded about 1 g of Raney Ni 2800 slurry. The Raney Ni was washed sequentially with methanol (3 mL $\times$ 3), ether (3 mL $\times$ 3), and dried degassed CH_3CN (3 mL $\times$ 3). To this flask was then transferred a solution of **10c** (190 mg, 0.382 mmol) in 6 mL CH_3CN . The resulting mixture was stirred under N_2 at rt for 1 d. The mixture was filtered under N_2 . The Raney Ni solid was washed with CH_3CN (3 mL $\times$ 3). The combined filtrate was concentrated under reduced pressure and the residue was passed through a short silica gel plug under N_2 to give pure product **2d** as a white solid (91%). $[\alpha]_D^{20} = -66.1$ ($c = 0.75$, CHCl_3); ^1H NMR (CDCl_3 , 300 MHz) δ 7.31-7.05 (m, 12H), 6.79 (ddd, $J = 0.9$ Hz, $J = 4.4$ Hz, $J = 7.8$ Hz, 1H), 5.74 (ddd, $J = 5.1$ Hz, $J = 8.3$ Hz, $J = 13.4$ Hz, 1H), 4.15 (dd, $J = 8.5$ Hz, $J = 10.3$ Hz, 1H), 3.53 (t, $J = 8.3$ Hz, 1H), 1.96 (s, 3H), 1.90 (s, 6H), 1.66 (s, 6H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 175.2, 147.8 (d, $J = 24.3$ Hz), 136.4-136.1 (m), 134.7, 134.4, 134.0, 133.7, 133.5, 129.7, 129.2, 128.9, 128.8, 128.7, 127.6, 126.1 (d, $J = 5.7$ Hz), 74.6 (d, $J = 5.0$ Hz), 66.8 (d, $J = 24.2$ Hz), 39.9, 36.8,

35.6, 28.2; ^{31}P NMR (CDCl_3 , 145 MHz) δ -15.14; HRMS ($\text{M}^+ + 1$) m/z calcd for $\text{C}_{31}\text{H}_{33}\text{NOP}$ 466.22943, found 466.22620.

2-Benzhydryl-(4*R*)-(2-diphenylphosphanyl-phenyl)-4,5-dihydro-oxazole 2b. This compound was produced from **10a** by the same method used for **2d** as a white solid (94%). $[\alpha]_D^{20} = -67.9$ ($c = 0.66$, CHCl_3); ^1H NMR (CD_2Cl_2 , 360 MHz) δ 7.44-7.21 (m, 23H), 6.98-6.95 (m, 1H), 5.97 (dt, $J = 5.6$ Hz, $J = 9.4$ Hz, 1H), 5.24 (s, 1H), 4.38 (dd, $J = 8.6$ Hz, $J = 10.3$ Hz), 3.74 (t, $J = 8.6$ Hz); ^{13}C NMR (CD_2Cl_2 , 90 MHz) δ 169.3, 147.9 (d, $J = 24.4$ Hz), 140.4 (d, $J = 3.6$ Hz), 136.7 (d, $J = 10.3$ Hz), 135.5-134.0 (m), 130.1-126.9 (m), 75.6 (d, $J = 5.3$ Hz), 68.0, 51.7; ^{31}P NMR (CD_2Cl_2 , 145 MHz) δ -15.10; HRMS ($\text{M}^+ + 1$) m/z calcd for $\text{C}_{34}\text{H}_{29}\text{NOP}$ 498.19813, found 498.19772.

2-(3,5-Di-*tert*-butyl-phenyl)-(4*R*)-(2-diphenylphosphanyl-phenyl)-4,5-dihydro-oxazole 2c. This compound was produced from **10b** by the same method used for **2d** as a white solid (95%). $[\alpha]_D^{20} = -48.3$ ($c = 0.87$, CHCl_3); ^1H NMR (CD_2Cl_2 , 360 MHz) δ 7.95 (d, $J = 1.8$ Hz, 2H), 7.67 (t, $J = 1.8$ Hz, 1H), 7.50-7.47 (m, 1H), 7.43-7.34 (m, 1H), 7.24 (dt, $J = 1.3$ Hz, $J = 7.5$ Hz, 1H), 7.01 (ddd, $J = 1.1$ Hz, $J = 4.4$ Hz, $J = 7.6$ Hz, 1H), 6.11 (ddd, $J = 5.9$ Hz, $J = 8.7$ Hz, $J = 14.5$ Hz, 1H), 4.48 (dd, $J = 8.4$ Hz, $J = 10.2$ Hz, 1H), 3.90 (t, $J = 8.5$ Hz, 1H), 1.42 (s, 18H); ^{13}C NMR (CD_2Cl_2 , 90 MHz) δ 166.1, 151.7, 148.2 (d, $J = 23.9$ Hz), 137.0 (m), 135.6-133.9 (m), 130.2-126.3 (m), 123.3, 75.4 (d, $J = 4.2$ Hz), 68.6, 35.5, 31.9; ^{31}P NMR (CD_2Cl_2 , 145 MHz) δ -14.83. HRMS ($\text{M}^+ + 1$) m/z calcd for $\text{C}_{35}\text{H}_{39}\text{NOP}$ 520.27638, found 520.27501.

2-*tert*-Butyl-(4*R*)-(2-dicyclohexylphosphanyl-phenyl)-4,5-dihydro-oxazole 2e. This compound was produced from **10d** by the same method used for **2d** as a colorless oil (90%). $[\alpha]_D^{20} = -70.9$ ($c = 0.53$, CHCl_3); ^1H NMR (CD_2Cl_2 , 360 MHz) δ 7.49-7.47 (m, 1H), 7.37-7.24 (m, 3H), 6.02 (ddd, $J = 5.7$ Hz, $J = 8.4$ Hz, $J = 14.1$ Hz, 1H), 4.76 (dd, $J = 8.3$ Hz, $J = 10.3$ Hz, 1H), 3.79 (t, $J = 8.3$ Hz, 1H), 2.00-0.85 (m, 31H); ^{13}C NMR (CD_2Cl_2 , 75 MHz) δ 175.2, 151.0 (d, $J = 25.3$ Hz), 133.2 (d, $J = 20.8$ Hz), 133.1 (d, $J = 3.4$ Hz), 129.5, 126.7, 126.2 (d, $J = 6.3$ Hz), 75.9 (d, $J = 7.2$ Hz), 67.9 (d, $J = 25.9$ Hz), 35.2 (d, $J = 12.9$ Hz), 34.0 (d, $J = 11.7$ Hz), 33.7, 31.3-30.9 (m), 30.0 (d, $J = 10.2$ Hz), 29.2 (d, $J = 6.2$ Hz), 28.1, 27.7-27.3 (m), 26.8 (d, $J = 3.9$ Hz); ^{31}P NMR (CD_2Cl_2 , 145 MHz) δ -14.46; HRMS ($\text{M}^+ + 1$) m/z calcd for $\text{C}_{25}\text{H}_{39}\text{NOP}$ 400.27638, found 400.27262.

General procedure for preparation of complex 11d (analogously 11a-11e). To a Schlenk tube was added **2d** (76 mg, 0.163 mmol), $[\text{Ir}(\text{COD})\text{Cl}]_2$ (54.8 mg, 0.0816 mmol) and dried CH_2Cl_2 (3 mL). The resulting red solution was heated under N_2 at 50 °C for 1 h. TLC indicated that **2d** was consumed completely. After the solution was cooled to rt, $\text{Na}[\text{BARF}]$ (217 mg, 0.245 mmol) was added followed by H_2O (3 mL). The resulting mixture was stirred vigorously for 30 min. The two layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3 mL $\times$ 2). The combined organic layer was dried with Na_2SO_4 and evaporated. The residue was purified by flash column chromatography (hexanes: $\text{CH}_2\text{Cl}_2 = 1:1$) to give **11d** as an orange solid (57%). ^1H NMR (CD_2Cl_2 , 360 MHz) δ 7.75 (s, 8H), 7.66-7.58 (m, 8H), 7.43-7.38 (m, 5H), 7.35-7.26 (m,

4H), 7.05 (m, 1H), 5.84 (dd, $J = 3.5$ Hz, $J = 9.8$ Hz, 1H), 5.05 (m, 1H), 5.01 (dd, $J = 4.0$ Hz, $J = 9.4$ Hz, 1H), 4.84 (t, $J = 9.6$ Hz, 1H), 4.35 (m, 1H), 4.28 (m, 1H), 3.23 (m, 1H), 2.52-2.36 (m, 3H), 2.25 (m, 1H), 2.16-2.01 (m, 2H), 1.84-1.74 (m, 7H), 1.64-1.52 (m, 4H), 1.41-1.36 (m, 6H); ^{31}P NMR (CD_2Cl_2 , 145 MHz) δ 15.89; HRMS (cation) m/z calcd for $\text{C}_{39}\text{H}_{44}\text{NOPIr}$ 766.27845, found 766.27163; HRMS (anion) m/z calcd for $\text{C}_{32}\text{H}_{12}\text{BF}_{24}$ 863.06434, found 863.07188.

11a. This compound was produced from **2a** by the same method used for **11d** as a yellow solid (52%). ^1H NMR (CDCl_3 , 360 MHz) δ 7.74 (s, 8H), 7.60-6.54 (m, 8H), 7.46-7.31 (m, 6H), 7.25-7.17 (m, 3H), 7.05 (ddd, $J = 1.2$ Hz, $J = 7.9$ Hz, $J = 10.9$ Hz, 1H), 5.81 (dd, $J = 3.7$ Hz, $J = 9.7$ Hz, 1H), 4.96 (m, 1H), 4.94 (dd, $J = 4.2$ Hz, $J = 9.4$ Hz, 1H), 4.81 (t, $J = 9.7$ Hz, 1H), 4.26 (m, 1H), 4.16 (m, 1H), 3.22 (m, 1H), 2.50-2.33 (m, 2H), 2.24 (m, 1H), 2.13-2.00 (m, 2H), 1.71 (m, 1H), 1.55 (m, 1H), 0.93 (s, 9H); ^{31}P NMR (CDCl_3 , 145 MHz) δ 15.55; HRMS (cation) m/z calcd for $\text{C}_{33}\text{H}_{38}\text{NOPIr}$ 688.23150, found 688.22827; HRMS (anion) m/z calcd for $\text{C}_{32}\text{H}_{12}\text{BF}_{24}$ 863.06434, found 863.06754.

11b. This compound was produced from **2b** by the same method used for **11d** as a red solid (50%). ^1H NMR (CD_2Cl_2 , 360 MHz) δ 7.77-6.78 (m, 34H), 5.93 (d, $J = 7.2$ Hz, 2H), 5.76 (dd, $J = 5.6$ Hz, $J = 9.7$ Hz, 1H), 5.20-5.11 (m, 2H), 4.90-4.80 (m, 2H), 3.95 (m, 1H), 3.80 (m, 1H), 3.00 (m, 1H), 2.53-2.45 (m, 2H), 2.35-2.19 (m, 2H), 1.90 (m, 1H), 1.75 (m, 1H), 1.52-1.34 (m, 2H); ^{31}P NMR (CD_2Cl_2 , 145 MHz) δ 16.33; HRMS (cation) m/z calcd for $\text{C}_{42}\text{H}_{40}\text{NOPIr}$ 798.24715, found 798.24948; HRMS (anion) m/z calcd for $\text{C}_{32}\text{H}_{12}\text{BF}_{24}$ 863.06434, found 863.07128.

11c. This compound was produced from **2c** by the same method used for **11d** as an orange solid (63%). ^1H NMR (CD_2Cl_2 , 360 MHz) δ 7.79 (m, 2H), 7.73 (s, 9H), 7.62 (m, 1H), 7.56 (br s, 4H), 7.50-7.36 (m, 12H), 7.22 (m, 1H), 6.04 (dd, $J = 4.2$ Hz, $J = 9.1$ Hz, 1H), 5.21 (dd, $J = 4.4$ Hz, $J = 9.5$ Hz, 1H), 5.07 (t, $J = 9.4$ Hz, 1H), 5.04 (m, 1H), 4.08 (m, 1H), 3.87 (m, 1H), 3.52 (m, 1H), 2.54-2.39 (m, 2H), 2.30 (m, 1H), 2.22-2.14 (m, 2H), 1.90 (m, 1H), 1.70-1.64 (m, 2H), 1.31 (s, 18H); ^{31}P NMR (CD_2Cl_2 , 145 MHz) δ 12.47; HRMS (cation) m/z calcd for $\text{C}_{43}\text{H}_{50}\text{NOPIr}$ 820.32540, found 820.32552; HRMS (anion) m/z calcd for $\text{C}_{32}\text{H}_{12}\text{BF}_{24}$ 863.06434, found 863.06159.

11e. This compound was produced from **2e** by the same method used for **11d** as an orange solid (58%). ^1H NMR (CD_2Cl_2 , 360 MHz) δ 7.74 (m, 8H), 7.65-7.51 (m, 7H), 7.39 (m, 1H), 5.67 (d, $J = 7.2$ Hz, 1H), 5.28 (dd, $J = 1.2$ Hz, $J = 10.2$ Hz, 1H), 5.06 (m, 1H), 4.92 (m, 1H), 4.43 (dd, $J = 7.5$ Hz, $J = 10.2$ Hz, 1H), 3.76 (m, 1H), 3.56 (m, 1H), 2.97 (m, 1H), 2.60-2.51 (m, 2H), 2.39-2.10 (m, 5H), 1.94-1.63 (m, 12H), 1.52-1.32 (m, 19H); ^{31}P NMR (CD_2Cl_2 , 145 MHz) δ 9.00; HRMS (cation) m/z calcd for $\text{C}_{33}\text{H}_{50}\text{NOPIr}$ 700.32540, found 700.32349; HRMS (anion) m/z calcd for $\text{C}_{32}\text{H}_{12}\text{BF}_{24}$ 863.06434, found 863.07146.

General Hydrogenation Procedure:

α -Methylstilbene (25.9 mg, 0.133 mmol) and Ir-complex **11d** (1 mg, 0.614 μ mol) was dissolved in CH₂CH₂ (2 mL). This solution was then transferred into an autoclave. The hydrogenation was performed at room temperature under 50 bar of H₂ (or under reaction conditions described in Table 1 and Table 2) for 12 h. After carefully releasing the hydrogen, the reaction mixture was directly passed through a short silica gel plug and flashed with ether. After evaporation, the residue was directly used for chiral HPLC analysis to measure the enantiomeric excess and for GC to measure the conversion.