Supporting Information

Application of *P,N*-Sulfinyl Imine Ligands to Iridium-Catalyzed Asymmetric Hydrogenation of Olefins

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General Methods. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. All reactions were performed under nitrogen atmosphere in flame-dried glassware. The following reaction solvents were distilled under nitrogen immediately before use: tetrahydrofuran and diethyl ether from Na/benzophenone ketyl, methylene chloride from CaH_2 , and toluene from Na. Chloroform, dichloroethane, and chlorobenzene were passed through a plug of basic alumina prior to use. ^1H NMR spectra were obtained in CDCl_3 and chemical shifts are expressed in ppm relative to tetramethylsilane. Coupling constants are reported in Hz. ^{31}P NMR shifts are referenced either to 85% H_3PO_4 or trimethylphosphate as external standards. Ligands **4** and **10**,¹ sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaBARF),² aldehyde **1**,¹ di-3,5-dimethylphenylchlorophosphine,³ and sulfinamides **19**,⁴ **20-21**,⁵ and **22**⁶ were prepared according to literature procedures. Sulfinamides **23-24** were prepared using modified literature procedures (*vide infra*).

2-(Di-3,5-dimethylphenylphosphino)-benzaldehyde (2). 2-(2-Bromophenyl)-[1,3]dioxolane (1.65 g, 7.23 mmol) was dissolved in diethyl ether and cooled to $-78\text{ }^\circ\text{C}$. *t*-BuLi (1.7 M in pentane, 8.50 mL, 14.6 mmol, 2.0 equiv) was added dropwise, and the bright yellow solution was stirred at $-78\text{ }^\circ\text{C}$ for 1 h. Di-3,5-dimethylphenylchlorophosphine (1.00g, 3.61 mmol, 0.5 equiv) was added, and the reaction mixture was allowed to warm to room temperature with stirring for 5 h. H_2O (10 mL) was added and the layers were separated. The aqueous portion was extracted with CH_2Cl_2 (25 mL), and the combined organics were dried (Na_2SO_4), concentrated and passed through a plug of silica gel (75/25 hexanes/ CH_2Cl_2). The crude material (300 mg,

~0.768 mmol) was dissolved in acetone (7 mL). H₂O (0.50 mL) and a catalytic amount of *p*-toluenesulfonic acid was added, and the reaction mixture was heated to reflux for 8 h. The reaction mixture was allowed to cool to room temperature, diluted with EtOAc (20 mL), and washed with H₂O (10 mL) and brine (10 mL). The organic portion was dried (Na₂SO₄), concentrated, and purified by flash chromatography (95/5 hexanes/EtOAc) to give **2** as a yellow oil that crystallized upon standing (280 mg, 11% over two steps). mp = 97-100 °C. IR: 1696 cm⁻¹. ¹H NMR (400 MHz): δ 2.24 (s, 12H), 6.84-6.89 (m, 4H), 6.96-7.00 (m, 3H), 7.44-7.49 (m, 2H), 7.94-7.98 (m, 1H), 10.54 (d, *J*_{HP} = 4.0). ³¹P NMR (160 MHz): δ -12.2. MS (ESI): *m/z* 347 (MH⁺). Exact mass calcd for C₂₃H₂₃OP requires *m/z* 346.1480, found *m/z* 346.1487 (M⁺, FAB).

General Procedure for the Synthesis of Sulfinamides. A three-necked round bottom flask equipped with a mechanical stirrer, an NH₃ condenser, and a nitrogen inlet was charged with liquid NH₃. A catalytic amount of Fe(NO₃)₃•9H₂O was added, followed by lithium bar pieces. A -78 °C bath was periodically raised to the bottom of the flask to slow the refluxing caused by the formation of LiNH₂. As pieces of Li bar were added, the mixture initially became blue, and then faded to a gray suspension. Once the addition of Li was complete, the flask was submerged in the -78 °C bath and allowed to cool for 30 min. The *cis*-1-amino-indan-2-ol-derived sulfinic acid ester⁵ in THF was slowly added via addition funnel. Once the addition was complete, the mixture was stirred for an additional 2 h before NH₄Cl (s) was carefully added. The cold bath was removed and stirring was continued until the mixture reached ambient temperature. The remaining NH₃ was allowed to evaporate from the mixture overnight. The residue was

then diluted with EtOAc and washed with H₂O, then brine. The desired sulfonamide was separated from the chiral auxiliary by flash chromatography. Analytically and enantiomerically (>99% ee) pure material was obtained by recrystallization.

(S)-(+)-2,4,6-Trimethylbenzenesulfonamide (23). The general procedure was followed with liquid NH₃ (50.0 mL), Li (137 mg, 19.7 mmol, 3.0 equiv), and the trimethylbenzene sulfinate ester⁵ (3.27 g, 6.57 mmol) in 10 mL of THF. Flash chromatography (50/50 EtOAc/hexanes, then 75/25 EtOAc/hexanes) delivered **23** as a white solid that was 90% ee (862 mg, 72%). This material was recrystallized from hot toluene to provide 540 mg (45% yield overall) of enantiomerically pure (>99% ee) **23** (HPLC, Daicel Chiralpak OD column, 90/10 hexanes/*i*-PrOH, 1.0 mL/min, 254 nm; *t_R* = 24.0 min; *t_S* = 26.5 min). mp = 115-116 °C. ¹H NMR (400 MHz): δ 2.28 (s, 3H), 2.59 (s, 6H), 4.47 (br s, 2H), 6.86 (s, 2H). ¹H NMR shifts correspond with the literature data.⁵

(S)-(+)-2,4,6-Triisopropylbenzenesulfonamide (24). The general procedure was followed with liquid NH₃ (300 mL), Li (644 mg, 92.8 mmol, 3.0 equiv), and the triisopropylbenzene sulfinate ester⁷ (18.0 g, 30.9 mmol) in 53 mL of THF. Flash chromatography (100% CH₂Cl₂, then 50/50 CH₂Cl₂/EtOAc, then 100% EtOAc) delivered **24** as a white solid that was 91% ee (2.03 g, 25%). This material was recrystallized from a hot hexanes/toluene mixture to provide 333 mg (4% yield overall) enantiomerically pure (>99% ee) **24** (HPLC, Daicel Chiralpak OD column, 90/10 hexanes/*i*-PrOH, 1.0 mL/min, 254 nm, *t_R* = 5.17 min, *t_S* = 6.40 min). mp = 94-96 °C. ¹H NMR (300 MHz): δ 1.20-1.38 (m, 18H), 2.87

(septet, 1H, $J=6$), 4.03 (septet, 2H, $J=6$), 4.54 (br s, 2H), 7.07 (s, 2H). ^1H NMR shifts correspond with the literature data.⁷

General Procedure for the Synthesis of Ligands. To a flask containing a solution of the aldehyde in THF was added $\text{Ti}(\text{OEt})_4$ (containing 5-15% isopropanol, ~2 equiv), followed by the sulfinamide, and the reaction mixture was heated. Upon completion, the reaction mixture was allowed to cool to room temperature, diluted with EtOAc, and poured into brine with rapid stirring. The resulting suspension was filtered through a plug of Celite and the filter cake washed with EtOAc. The filtrate was transferred to a separatory funnel, and the organic layer was washed with an equal volume of brine. The organic phase was dried (Na_2SO_4), filtered, concentrated, and purified by flash chromatography.

(S)-(+)-N-(2-(Di-*o*-tolylphosphino)-benzylidene)-1-adamantanesulfinamide

(5). The general procedure was followed with sulfinamide **20** (100 mg, 0.502 mmol, 1.1 equiv), aldehyde **1** (152 mg, 0.478 mmol), and $\text{Ti}(\text{OEt})_4$ (0.230 mL, ~0.956 mmol, ~2.0 equiv) in 2.0 mL of THF at 40 °C. Flash chromatography (85/15 hexanes/EtOAc) afforded **5** as a light yellow solid (225 mg, 94%). mp = 85-89 °C. $[\alpha]_{\text{D}} = +57.5^\circ$ (c 1.0, CHCl_3). IR: 2894, 1085 cm^{-1} . ^1H NMR (400 MHz): δ 1.56-1.70 (m, 12H), 2.01-2.04 (m, 3H), 2.37 (s, 3H), 2.41 (s, 3H), 6.62-6.63 (m, 1H), 6.70-6.72 (m, 1H), 6.93-6.95 (m, 1H), 7.03-7.07 (m, 2H), 7.19-7.26 (m, 4H), 7.36-7.38 (m, 1H), 7.45-7.47 (m, 1H), 7.99-8.00 (m, 1H), 9.15-9.16 (d, 1H, $J_{\text{HP}} = 4$). ^{31}P NMR (160 MHz): δ -28.4. MS (ESI): m/z 500

(MH⁺). Anal. Calcd. for C₃₂H₃₆NOPS: C, 74.82; H, 7.06; N, 2.73. Found: C, 74.61; H, 7.06; N, 3.09.

(S)-(+)-N-(2-(Di-*o*-tolylphosphino)-benzylidene)-3-ethylpentanesulfinamide

(6). The general procedure was followed with sulfinamide **21** (100 mg, 0.612 mmol, 1.1 equiv), aldehyde **1** (149 mg, 0.557 mmol), and Ti(OEt)₄ (0.270 mL, ~1.11 mmol, ~2.0 equiv) in 2.2 mL of THF at 40 °C. Flash chromatography (85/15 hexanes/EtOAc) delivered **6** as a light yellow solid (205 mg, 79%). mp = 72-74 °C. [α]_D = +52.8° (*c* 1.0, CHCl₃). IR: 1086 cm⁻¹. ¹H NMR (400 MHz): δ 0.84 (t, 9H, *J* = 6.0), 1.44-1.56 (m, 6H), 2.37-2.38 (m, 6H), 6.65-6.70 (m, 2H), 6.92-6.94 (m, 1H), 7.03-7.05 (m, 2H), 7.19-7.25 (m, 4H), 7.34-7.36 (m, 1H), 7.43-7.45 (m, 1H), 8.02-8.03 (m, 1H), 9.24 (d, 1H, *J*_{HP} = 4.0). ³¹P NMR (160 MHz): δ -29.1. MS (ESI): *m/z* 463 (MH⁺). Anal. Calcd. for C₂₉H₃₆NOPS: C, 72.54; H, 7.39; N, 3.02. Found: C, 72.65; H, 7.58; N, 3.04.

(S)-(+)-N-(2-(Di-*o*-tolylphosphino)-benzylidene)-4-methylbenzenesulfinamide

(7). The general procedure was followed with sulfinamide **22** (150 mg, 0.986 mmol, 1.1 equiv), aldehyde **1** (285 mg, 0.896 mmol), and Ti(OEt)₄ (0.410 mL, ~1.79 mmol, ~2.0 equiv) in 3.6 mmol of THF at 35 °C. Flash chromatography (90/10 hexanes/EtOAc) delivered **7** as a light yellow solid (308 mg, 75%). mp = 125-127 °C. [α]_D = +137° (*c* 1.0, CHCl₃). IR: 1094 cm⁻¹. ¹H NMR (400 MHz): δ 2.39 (s, 3H), 2.45-2.46 (m, 6H), 6.68-6.72 (m, 2H), 6.94-6.96 (m, 1H), 7.05-7.08 (m, 2H), 7.18-7.20 (m, 2H), 7.28-7.30 (m, 6H), 7.37-7.39 (m, 1H), 7.42-7.44 (m, 1H), 8.02-8.03 (m, 1H), 9.47 (d, 1H, *J*_{HP} = 6).

^{31}P NMR (160 MHz): δ -30.0. MS (ESI): m/z 456 (MH^+). Anal. Calcd. for $\text{C}_{28}\text{H}_{26}\text{NOPS}$: C, 73.82; H, 5.75; N, 3.07. Found: C, 73.66; H, 5.82; N, 2.96.

(*S*)-(+)-*N*-(2-(Di-*o*-tolylphosphino)-benzylidene)-2,4,6-trimethylbenzenesulfinamide (8). The general procedure was followed with sulfinamide **23** (100 mg, 0.546 mmol, 1.1 equiv), aldehyde **1** (166 mg, 0.520 mmol), and $\text{Ti}(\text{OEt})_4$ (0.260 mL, $\sim$ 1.09 mmol, $\sim$ 2.0 equiv) in 2.1 mL THF at 40 °C. Flash chromatography (90/10 hexanes/EtOAc) delivered **8** as a light yellow solid (200 mg, 80%). mp = 66-69 °C. $[\alpha]_{\text{D}} = +108^\circ$ (c 1.0, CHCl_3). IR: 1086 cm^{-1} . ^1H NMR (400 MHz): δ 2.26-2.27 (m, 9H), 2.38 (s, 6H), 6.63-6.64 (m, 1H), 6.70-6.71 (m, 1H), 6.77 (s, 2H), 6.95-6.97 (m, 1H), 7.05-7.06 (m, 2H), 7.17-7.28 (m, 4H), 7.37-7.39 (m, 1H), 7.43-7.45 (m, 1H), 8.06-8.08 (m, 1H), (9.54, d, 1H, $J_{\text{HP}} = 6$). ^{31}P NMR (160 MHz): δ -30.3. MS (ESI): m/z 484 (MH^+). Anal. Calcd. for $\text{C}_{30}\text{H}_{30}\text{NOPS}$: C, 74.51; H, 6.25; N, 2.90. Found: C, 74.27; H, 6.34; N, 3.09.

(*R*)-(-)-*N*-(2-(Di-3,5-dimethylbenzenephosphino)-benzylidene)-*tert*-butanesulfinamide (9). The general procedure was followed with sulfinamide **19** (19.2 mg, 0.158 mmol, 1.1 equiv), aldehyde **2** (50.0 mg, 0.144 mmol), and $\text{Ti}(\text{OEt})_4$ (0.070 mL, $\sim$ 0.288 mmol, $\sim$ 2.0 equiv) in 0.6 mL of THF at 40 °C. Flash chromatography (85/15 hexanes/EtOAc) delivered **9** as a light yellow solid (50.0 mg, 77%). mp = 57-60 °C. $[\alpha]_{\text{D}} = -40.7^\circ$ (c 1.7, CHCl_3). IR: 1086 cm^{-1} . ^1H NMR (400 MHz): δ 1.07 (s, 9H), 2.22-2.23 (m, 12H), 6.82-6.93 (m, 4H), 6.95-7.00 (m, 3H), 7.34-7.44 (m, 2H), 7.97-7.99 (m, 1H), 9.14 (d, 1H, $J_{\text{HP}} = 4$). ^{31}P NMR (160 MHz): δ -12.5. MS (ESI): m/z 450 (MH^+).

Exact mass calcd for C₂₇H₃₂NOPS requires m/z 450.2027, found m/z 450.2021 (MH⁺, FAB).

(S)-(+)-N-(2-(Di-*o*-tolylphosphino)-benzylidene)-2,4,6-triisopropylbenzenesulfinamide (11). The general procedure was followed with sulfinamide **24** (100 mg, 0.374 mmol, 1.1 equiv), aldehyde **1** (108 mg, 0.340 mmol), and Ti(OEt)₄ (0.160 mL, ~0.680 mmol, ~2.0 equiv) in 1.5 mL of THF at 50 °C. Flash chromatography (66/33 hexanes/CH₂Cl₂) delivered **11** as a light yellow solid (187 mg, 97%). Mp = 70-73 °C. $[\alpha]_D = +130^\circ$ (c 1.0, CHCl₃). IR: 1081 cm⁻¹. ¹H NMR (400 MHz): δ 1.00 (m, 6H), 1.18 (d, 6H, $J=6.4$), 1.24 (d, 6H, $J=6.8$), 2.36 (s, 3H), 2.38 (s, 3H), 2.85 (septet, 1H, $J=6.4$), 3.70 (septet, 2H, $J=6.8$), 6.66-6.74 (m, 2H), 6.94-6.97 (m, 1H), 7.02 (s, 2H), 7.05-7.07 (m, 2H), 7.22-7.26 (m, 4H), 7.33-7.39 (m, 2H), 8.09-8.10 (m, 1H), 9.66 (d, 1H, $J_{HP}=8$). ³¹P NMR (160 MHz): δ -32.3. MS (ESI): m/z 568 (MH⁺). Anal. Calcd. for C₃₆H₄₂NOPS: C, 76.16; H, 7.46; N, 2.47. Found: C, 76.09; H, 7.43; N, 2.51.

General Procedure for the Synthesis of Iridium(I)-BARF Complexes. The ligand and [Ir(COD)Cl]₂ were added to a flask in an inert atmosphere glovebox. The flask was covered with a rubber septum, removed from the glovebox, and charged with CH₂Cl₂ under an N₂ atmosphere. The reaction mixture was stirred at room temperature until thin layer chromatography indicated that the free ligand had been consumed (~15 min). At this time sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaBARF) was added, followed by an equal volume of H₂O. The deep purple reaction mixture was

stirred rapidly until thin layer chromatography indicated that the chloride complex had been consumed (~15 min, R_f chloride complex = 0.0; R_f BARF complex = 0.8, 100% CH_2Cl_2). The reaction mixture was transferred to a separatory funnel, the layers separated, and the aqueous layer extracted with an additional portion of CH_2Cl_2 . The combined organic layers were dried (Na_2SO_4), filtered, and concentrated. The aliphatic sulfinamide-based complexes could be chromatographed on silica gel (CH_2Cl_2 /hexanes), but crude complexes were of sufficient purity to be utilized in subsequent hydrogenation reactions.

(12). The general procedure was followed with **4** (100 mg, 0.237 mmol) and $[\text{Ir}(\text{COD})\text{Cl}]_2$ (80.0 mg, 0.119 mmol, 0.5 equiv) in 2.4 mL of CH_2Cl_2 , followed by NaBARF (210 mg, 0.237 mmol, 1.0 equiv) and 2.4 mL of H_2O . Workup provided **12** as a purple solid (337 mg, 90%). ^1H NMR (400 MHz): δ 0.90 (br s, 9H), 1.51-1.57 (m, 1H), 1.62-1.64 (m, 1H), 2.09-2.17 (m, 2H), 2.25-2.30 (m, 1H), 2.36 (s, 6H), 2.40-2.47 (m, 1H), 2.99 (br s, 2H), 3.35 (m, 1H), 3.85 (m, 1H), 5.01 (m, 1H), 5.28 (m, 1H), 6.23 (m, 1H), 6.85 (m, 1H), 7.05 (m, 1H), 7.23-7.27 (m, 2H), 7.37-7.40 (m, 3H), 7.44-7.46 (m, 1H), 7.52 (s, 4H), 7.71-7.72 (m, 1H), 7.73 (s, 8H), 7.77-7.79 (m, 1H), 7.96 (m, 1H), 8.61 (s, 1H). ^{31}P NMR (160 MHz): δ 12.61.

(13). The general procedure was followed with **5** (50.0 mg, 0.100 mmol) and $[\text{Ir}(\text{COD})\text{Cl}]_2$ (34.0 mg, 0.050 mmol, 0.5 equiv) in 1.0 mL of CH_2Cl_2 followed by NaBARF (88.6 mg, 0.100 mmol, 1.0 equiv) and 1.0 mL of H_2O . Workup provided **13** as a purple solid (157 mg, 94%). ^1H NMR (400 MHz): δ 1.13 (m, 3H), 1.24 (m, 3H), 1.38-

1.70 (m, 6H), 1.91-2.00 (m, 5H), 2.16 (s, 3H), 2.31-2.38 (m, 6H), 3.06-3.25 (m, 3H), 3.69 (m, 1H), 5.03 (m, 1H), 5.39 (m, 1H), 6.33 (m, 1H), 6.65-6.70 (m, 1H), 7.07 (m, 1H), 7.18-7.21 (m, 2H), 7.32-7.41 (m, 5H), 7.50 (s, 4H), 7.70 (s, 8H), 7.76-7.79 (m, 2H), 7.96 (m, 1H), 8.62 (s, 1H). ^{31}P NMR (160 MHz): δ 10.65.

(14). The general procedure was followed with **6** (50.0 mg, 0.108 mmol) and $[\text{Ir}(\text{COD})\text{Cl}]_2$ (36.0 mg, 0.054 mmol, 0.5 equiv) in 1.1 mL of CH_2Cl_2 followed by NaBARF (96.0 mg, 0.108 mmol, 1.0 equiv) and 1.1 mL of H_2O . Workup provided **14** as a purple solid (158 mg, 90%). ^1H NMR (400 MHz): δ 0.75 (t, 9H, $J = 8.0$), 1.22-1.27 (m, 3H), 1.32-1.38 (m, 3H), 1.40-1.43 (m, 2H), 1.57-1.62 (m, 1H), 1.95-2.11 (m, 2H), 2.24-2.26 (m, 1H), 2.37-2.44 (m, 5H), 2.98 (s, 3H), 3.28 (m, 1H), 3.92 (m, 1H), 5.01 (m, 1H), 5.16 (m, 1H), 6.24-6.29 (m, 1H), 6.79-6.84 (m, 1H), 7.05-7.10 (m, 1H), 7.21-7.27 (m, 2H), 7.36-7.50 (m, 5H), 7.50 (s, 4H), 7.70 (s, 8H), 7.76-7.79 (m, 1H), 7.94-7.96 (m, 1H), 8.61 (s, 1H). ^{31}P NMR (160 MHz): δ 12.43.

(15). The general procedure was followed with **7** (35.0 mg, 0.077 mmol) and $[\text{Ir}(\text{COD})\text{Cl}]_2$ (26.0 mg, 0.038 mmol, 0.5 equiv) in 0.8 mL of CH_2Cl_2 , followed by NaBARF (68.0 mg, 0.077 mmol, 1.0 equiv) and 0.8 mmol of H_2O . Workup provided **15** as a purple solid (118 mg, 95%). ^1H NMR (400 MHz): δ 2.00 (br s, 2H), 2.01-2.03 (m, 3H), 2.11 (s, 3H), 2.11-2.28 (m, 3H), 2.41 (m, 6H), 3.28-3.39 (m, 2H), 4.55-4.57 (m, 2H), 7.26-7.29 (m, 2H), 7.33-7.34 (m, 3H), 7.35-7.44 (m, 3H), 7.50 (s, 4H), 7.50-7.53 (m, 3H), 7.60-7.66 (m, 4H), 7.71 (s, 8H), 8.16-8.20 (m, 1H), 9.42-9.44 (m, 1H). ^{31}P NMR (160 MHz): δ 10.77.

(16). The general procedure was followed with **8** (50.0 mg, 0.103 mmol) and $[\text{Ir}(\text{COD})\text{Cl}]_2$ (35.0 mg, 0.052 mmol, 0.5 equiv) in 1.0 mL of CH_2Cl_2 , followed by NaBARF (91.0 mg, 0.103 mmol, 1.0 equiv) and 1.0 mL of H_2O . Workup provided **16** as a purple solid (158 mg, 93%). ^1H NMR (400 MHz): δ 1.42-1.46 (m, 1H), 1.59-1.57 (m, 1H), 2.03-2.54 (m, 21H), 3.05 (m, 1H), 3.96 (m, 1H), 4.85 (m, 1H), 5.25 (m, 1H), 6.26-6.30 (m, 1H), 6.46-6.50 (m, 1H), 6.86-6.89 (m, 2H), 7.03-7.08 (m, 2H), 7.35-7.37 (m, 6H), 7.45-7.50 (m, 5H), 7.70-7.82 (s, 8H), 7.90 (m, 1H), 8.90 (s, 1H). ^{31}P NMR (160 MHz): δ 10.93.

(17). The general procedure was followed with **9** (25.0 mg, 0.056 mmol) and $[\text{Ir}(\text{COD})\text{Cl}]_2$ (18.7 mg, 0.029 mmol, 0.5 equiv) in 0.6 mL of CH_2Cl_2 , followed by NaBARF (49.0 mg, 0.056 mmol, 1.0 equiv) and 0.6 mL of H_2O . Workup provided **17** as a purple solid (86.0 mg, 95%). ^1H NMR (400 MHz): δ 0.97 (s, 9H), 1.40-1.50 (m, 1H), 1.57-1.62 (m, 1H), 1.95-2.15 (m, 2H), 2.23-2.27 (m, 12H), 2.43-2.50 (m, 4H), 3.38 (m, 1H), 3.80 (m, 1H), 5.10 (m, 1H), 5.38 (m, 1H), 6.69-6.72 (m, 2H), 6.84-6.87 (m, 2H), 7.12-7.15 (m, 2H), 7.43-7.45 (m, 1H), 7.50 (s, 4H), 7.69 (s, 8H), 7.72-7.74 (m, 2H), 7.91-7.95 (m, 1H), 8.57 (s, 1H). ^{31}P NMR (160 MHz): δ 18.70.

(18). The general procedure was followed with **10** (50.0 mg, 0.127 mmol) and $[\text{Ir}(\text{COD})\text{Cl}]_2$ (43.0 mg, 0.064 mg, 0.5 equiv) in 1.3 mL of CH_2Cl_2 , followed by NaBARF (113 mg, 0.127 mmol, 1.0 equiv) and 1.3 mL of H_2O . Workup provided **18** as a purple solid (177 mg, 90%). ^1H NMR (300 MHz): δ 0.96 (s, 9H), 1.43-1.48 (m, 1H), 1.61-1.70

(m, 1H), 1.98-2.05 (m, 2H), 2.43-2.51 (m, 4H), 3.36 (m, 1H), 3.82 (m, 1H), 5.17 (m, 1H), 5.44 (m, 1H), 7.13-7.19 (m, 2H), 7.26-7.33 (m, 2H), 7.39-7.51 (m, 11H), 7.71 (s, 8H), 7.75-7.80 (m, 2H), 7.94-7.97 (m, 1H), 8.60 (s, 1H). ^{31}P NMR (160 MHz): δ 19.05.

(4-[Ir⁺Cl⁻]). Ligand **4** (50.0 mg, 0.119 mmol) and [Ir(COD)Cl]₂ (40.0 mg, 0.059 mmol, 0.5 equiv) were added to a flask in an inert atmosphere glovebox. The flask was covered with a septum, removed from the glovebox and charged with CH₂Cl₂ (1.2 mL) under a N₂ atmosphere. The reaction mixture was stirred at room temperature until thin layer chromatography indicated that the free ligand had been consumed (~15 min). At this point the reaction mixture was concentrated, and flash chromatography (CH₂Cl₂, then 50/50 CH₂Cl₂/EtOAc) provided **4-[Ir⁺Cl⁻]** as an orange solid (83.0 mg, 92%). ^1H NMR (300 MHz): δ 1.03 (s, 9H), 1.50-1.53 (m, 1H), 1.78-1.82 (m, 1H), 1.87 (s, 3H), 2.17-2.28 (m, 4H), 2.39 (s, 3H), 2.42-2.46 (m, 1H), 2.83-2.92 (m, 2H), 3.17 (m, 1H), 5.65 (m, 1H), 5.82 (m, 1H), 6.36 (m, 1H), 7.01 (m, 1H), 7.14-7.37 (m, 8H), 7.59-7.62 (m, 1H), 7.70-7.73 (m, 1H), 9.10-9.16 (m, 1H). ^{31}P NMR (160 MHz): δ 10.98.

General Procedure for Hydrogenation Reactions. To a vial equipped with a stir bar was added substrate, catalyst, and solvent. The reaction mixture was placed in a Parr bomb and pressurized with H₂. To work up the reaction, the bomb was vented and the reaction mixture was concentrated. The crude material was passed through a short silica plug using hexanes/EtOAc as eluent and concentrated. The conversion was determined by ^1H -NMR and the % ee was determined by chiral HPLC. For the hydrogenation product of α -methylstilbene: Daicel Chiralcel OJ, 99/1 hexanes/*i*-PrOH,

1.0 mL/min, 254 nm; t_s = 6.1 min, t_R = 8.1 min. Absolute stereochemistry was determined by comparison of the HPLC trace with that of product obtained from hydrogenation of α -methylstilbene with a known catalyst.⁸ For the hydrogenation product of ester **25**: Daicel Chiralcel OD, 97/3 hexanes/*i*-PrOH, 1.0 mL/min, 254 nm; t_R = 4.9 min, 7.8 min. Absolute stereochemistry was not determined. For the hydrogenation product of alcohol **26**: Daicel Chiralcel OD, 95/5 hexanes/*i*-PrOH, 1.0 mL/min, 254 nm; t_R = 10.0 min, 12.8 min. Absolute stereochemistry was not determined.

Hydrogenation of α -methylstilbene. To a vial equipped with a stir bar was added α -methylstilbene (12.3 mg, 0.063 mmol), followed by **12** (5.00 mg, 0.003 mmol, 0.05 equiv) and CH₂Cl₂ (0.320 mL). The reaction mixture was placed in a Parr bomb and pressurized to 50 bar H₂. After 1h the reaction vessel was vented, and the reaction mixture was concentrated. The crude material was dissolved in 95/5 hexanes/EtOAc, filtered through a short plug of silica gel, and concentrated to provide 12.3 mg (99%) of hydrogenated product that was pure by ¹H NMR and HPLC. ¹H NMR correspond with the literature data.⁹

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