Chiral Pyranoside Phosphite-Oxazolines: A New Class of Ligand for Asymmetric Catalytic Hydrogenation of Alkenes.

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1. General Considerations. All reactions were carried out using standard Schlenk techniques under an atmosphere of argon. Solvents were purified and dried by standard procedures. Phosphorochloridites are easily prepared in one step from the corresponding biaryls.[1] Phosphite-oxazoline ligands **L1-L4a-e**[2] and phosphinite-oxazoline ligand **L1h**[3] were prepared as previously described. ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded using a 400 MHz spectrometer. Chemical shifts are relative to that of $SiMe_4$ (^{1}H and ^{13}C) as internal standard or H_3PO_4 (^{31}P) as external standard. ^{1}H and ^{13}C assignments were done based on ^{1}H-^{1}H gCOSY and ^{1}H-^{13}C gHSQC experiments.

2. Typical procedure for the preparation of ligands L1f-g. The corresponding phosphorochloridite (3.0 mmol) produced *in situ* was dissolved in toluene (12.5 mL) and pyridine (1.14 mL, 14 mmol) was added. The corresponding hydroxyl-oxazoline compound[3] (2.8 mmol) was azeotropically dried with toluene (3 x 2 mL) and then dissolved in toluene (12.5 mL) to which pyridine (1.14 mL, 14 mmol) was added. The oxazoline solution was transferred slowly at 0 ºC to the solution of phosphorochloridite. The reaction mixture was stirred overnight at 80 ºC, and the pyridine salts were removed by filtration. Evaporation of the solvent gave a white foam, which was purified by flash chromatography in alumina (toluene/NEt_3= 100/1) to produce the corresponding ligand as a white solid.

L1f: Yield: 0.40 g, 17 %. ^{31}P NMR (400 MHz, C_6D_6) δ: 151.7 (s, 1P). ^{1}H NMR (400 MHz, C_6D_6) δ: 0.57 (s, 9H, $Si(CH_3)_3$), 0.65 (s, 9H, $Si(CH_3)_3$), 3.37 (m, 1H, H-6’), 3.52 (m, 1H, H-5), 3.91 (m, 1H, H-4), 4.02 (m, 1H, H-6), 4.23 (m, 1H, H-2), 5.12 (m, H-3), 5.40 (d, 1H, H-1, $^{3}J_{1\text{-}2}$= 8.0 Hz), 5.47 (s, 1H, H-7), 6.86-8.19 (m, 22H, CH=). ^{13}C NMR (400 MHz, C_6D_6) δ: 0.6 ($Si(CH_3)_3$), 0.9 ($Si(CH_3)_3$), 63.1 (C-5), 69.1 (C-6), 70.1 (C-2), 77.0 (d, C-3, $^{2}J_{c\text{-}p}$= 13.6 Hz), 80.5 (d, C-4, $^{2}J_{c\text{-}p}$= 4.1 Hz), 101.8 (C-7), 102.2 (C-1), 110.4 (C), 124.4 (CH=), 124.7 (CH=), 125.5 (CH=), 126.0 (CH=), 127.1 (CH=), 127.3 (CH=), 127.4 (CH=), 127.6 (CH=), 127.8 (CH=), 127.9 (CH=), 128.1 (CH=), 128.4 (CH=), 128.6 (CH=), 128.8 (CH=), 129.1 (CH=), 129.1 (CH=), 129.3 (CH=), 129.3 (CH=), 129.7 (CH=), 130.2 (C), 131.7 (C), 132.0 (C), 132.8 (C), 135.0 (C), 135.1 (C), 135.4 (C), 137.4 (CH=), 138.0 (CH=), 138.2 (CH=), 138.6 (CH=), 152.5 (C), 152.9 (C), 163.6 (C). Anal. calcd (%) for $C_{46}H_{46}NO_7PSi_2$: C 68.04, H 5.71, N 1.72; found: C 68.12, H 5.78, N 1.69.

L1g: Yield: 0.40 g, 17 %. ^{31}P NMR (400 MHz, C_6D_6) δ: 150.5 (s). ^{1}H NMR (400 MHz, C_6D_6) δ: 0.41 (s, 9H, $Si(CH_3)_3$), 0.55 (s, 9H, $Si(CH_3)_3$), 3.18 (m, 1H, H-6'), 3.49 (m, 1H, H-5), 3.66 (m, 1H, H-4), 3.90 (m, 1H, H-6), 4.41 (dd, 1H, H-2, $^{3}J_{2\text{-}1}$= 8.0 Hz, $^{3}J_{2\text{-}3}$= 2.4 Hz) 5.00 (s, 1H, H-7), 5.04 (m, 1H, H-3), 5.64 (d, 1H, H-1, $^{3}J_{1\text{-}2}$= 8.0 Hz), 6.80-8.01 (m, 22H, CH=). ^{13}C NMR (400 MHz, C_6D_6) δ= 0.5 ($Si(CH_3)_3$), 0.9 ($Si(CH_3)_3$), 63.4 (C-5), 69.0 (C-6), 70.9 (C-2), 77.1 (d, C-3, $^{2}J_{c\text{-}p}$= 9.1 Hz), 81.0 (C-4), 101.7 (C-1), 102.0 (C-7), 124.4 (C), 124.7 (C), 125.4 (CH=), 126.0 (CH=), 127.2 (CH=), 127.3 (CH=), 127.6 (CH=), 127.7 (CH=), 127.8 (CH=), 128.1 (CH=), 128.4 (CH=), 128.6 (CH=), 128.7 (CH=), 128.8 (CH=), 128.9 (CH=), 129.0 (CH=), 129.1 (CH=), 129.2 (CH=), 129.6 (C), 131.6 (CH=), 131.9 (CH=), 132.3 (CH=), 133.1 (CH=), 134.9 (C), 135.1 (C), 137.3 (CH=), 137.8 (CH=), 138.0 (C), 152.8 (C), 153.0 (C), 164.3 (C). Anal. calcd (%) for $C_{46}H_{46}NO_7PSi_2$: C 68.04, H 5.71, N 1.72; found: C 68.23, H 5.84, N 1.63.

3. Typical procedure for the preparation of [Ir(cod)(L)]BArF (L= L1-L4a-h)

The corresponding ligand (0.074 mmol) was dissolved in CH_2Cl_2 (2 mL) and $[Ir(COD)Cl]_2$ (25 mg, 0.037 mmol) was added. The reaction was refluxed at 50 °C for 1 hour. After 5 min at room temperature, NaBArF (77.1 mg, 0.082 mmol) and water (2 mL) were added and the reaction mixture was stirred vigorously for 30 min at room temperature. The phases were separated and the aqueous phase was extracted twice with CH_2Cl_2. The combined organic phases were filtered through a plug of celite, dried with $MgSO_4$ and the solvent was evaporated to give the product as orange solids.

[Ir(cod)(L1a)]BAr$_F$. Yield 131 mg (91 %). ^{31}P NMR ($CDCl_3$), δ: 102.9 (s). ^{1}H NMR ($CDCl_3$), δ: 1.21 (s, 9H, CH_3, *t*Bu), 1.38 (s, 9H, CH_3, *t*Bu), 1.59 (s, 9H, CH_3, *t*Bu), 1.63 (s, 9H, CH_3, *t*Bu), 1.67 (m, 4H, CH_2, cod), 2.22 (m, 2H, CH_2, cod), 2.41 (m, 2H, CH_2, cod), 3.69 (m, 1H, H-4), 3.79 (m, 1H, H-6'), 3.93 (b, 2H, CH= cod and H-5), 4.27 (m, 1H, H-3), 4.39 (b, 2H, CH= cod and H-6), 4.52 (b, 2H, CH= cod and H-2), 5.43 (b, 1H, CH=, cod), 5.44 (s, 1H, H-7), 6.32 (d, 1H, H-1, $^{3}J_{1\text{-}2}$ = 6.4 Hz), 7.1-8.5 (m, 26H, CH= aromatics). ^{13}C NMR ($CDCl_3$), δ: 25.1 (b, CH_2, cod), 29.3 (b, CH_2, cod), 31.2 (s, CH_3, *t*Bu), 31.5 (s, CH_3, *t*Bu), 31.6 (s, CH_3, *t*Bu), 33.2 (b, CH_2, cod), 34.9 (s, C, *t*Bu), 35.0 (s, C, *t*Bu), 35.4 (s, C, *t*Bu), 36.1 (s, C, *t*Bu), 36.9 (b, CH_2, cod), 66.4 (s, CH=, cod), 67.6 (s, C-

5), 67.9 (s, C-2), 68.6 (s, C-6), 70.4 (s, CH=, cod), 74.2 (d, C-4, J_{C-P}= 8.4 Hz), 79.5 (s, C-3), 94.9 (d, CH=, cod, J_{C-P} = 22.3 Hz), 101.4 (s, C-7), 104.4 (s, C-1), 107.5 (m, CH=, cod), 117.7 (b, CH=, BAr_F), 119-132 (aromatic carbons), 135.0 (b, CH=, BAr_F), 135.5-150 (aromatic carbons), 161.9 (q, C-B, BAr_F, $^1J_{C-B}$ = 49 Hz) 171.4 (s, C=N). Anal. calc (%) for $C_{88}H_{82}BF_{24}IrNO_7P$: C 54.05, H 4.23, N 0.72; found: C 54.21, H 4.28, N 0.68.

[Ir(cod)(L1b)]BAr$_F$. Yield 125 mg (89 %). ^{31}P NMR ($CDCl_3$), δ: 104.4 (s). ^{1}H NMR ($CDCl_3$), δ: 1.57 (s, 9H, CH_3, *t*Bu), 1.58 (s, 9H, CH_3, *t*Bu), 1.80 (b, 4H, CH_2, cod), 2.31 (b, 3H, CH_2, cod), 2.52 (m, 1H, CH_2, cod), 3.67 (m, 1H, H-4), 3.76 (m, 3H, CH_3-O), 3.78 (m, 1H, H-6'), 3.82 (s, 3H, CH_3-O), 3.91 (m, 1H, H-5), 4.02 (m, 1H, CH=, cod), 4.24 (m, 1H, H-3), 4.38 (dd, 1H, H-6, $^2J_{6'-6}$ = 10.4 Hz, $^3J_{6-5}$ = 4.8 Hz), 4.44 (b, 1H, CH=, cod), 4.51 (dd, 1H, H-2, $^3J_{2-3}$ = 7.6 Hz, $^3J_{2-1}$ = 6.4 Hz), 5.38 (b, 1H, CH=, cod), 5.46 (s, 1H, H-7), 6.31 (d, 1H, H-1, $^3J_{1-2}$ = 6.4 Hz), 7.1-7.8 (m, 26H, CH=, aromatics). ^{13}C NMR ($CDCl_3$), δ: 25.2 (b, CH_2, cod), 29.4 (b, CH_2, cod), 31.1 (s, CH_3, *t*Bu), 31.4 (s, CH_3, *t*Bu), 32.9 (b, CH_2, cod), 35.5 (s, C, *t*Bu), 36.0 (s, C, *t*Bu), 36.5 (b, CH_2, cod), 55.7 (s, CH_3-O), 55.8 (s, CH_3-O), 66.8 (s, CH=, cod), 67.6 (s, CH, C-2), 67.9 (s, CH, C-5), 68.2 (s, CH, C-6), 70.0 (s, CH=, cod), 74.4 (d, C-4, J_{C-P} = 8.3 Hz), 79.0 (s, C-3), 96.3 (d, CH=, cod, J_{C-P}= 21.2 Hz), 101.2 (s, C-7), 104.4 (s, C-1), 107.3 (d, CH=, cod, J_{C-P} = 12.1 Hz), 112-116 (aromatic carbons), 117.7 (b, CH=, BAr_F), 120-132 (aromatic carbons), 135.0 (b, CH=, BAr_F), 135.5-160 (aromatic carbons), 161.9 (q, C-B BAr_F, $^1J_{C-B}$ = 49.2 Hz) 171.4 (s, C=N). Anal. calc (%) for $C_{82}H_{70}BF_{24}IrNO_9P$: C 51.74, H 3.71, N 0.74; found: C 51.69, H 3.80, N 0.79.

[Ir(cod)(L1c)]BAr$_F$. Yield 127 mg (92 %). ^{31}P NMR ($CDCl_3$), δ: 100.9 (s). ^{1}H NMR ($CDCl_3$), δ: 0.40 (s, 9H, CH_3-Si), 0.56 (s, 9H, CH_3-Si), 1.64 (m, 4H, CH_2, cod), 2.22 (m, 2H, CH_2, cod), 2.56 (m, 2H, CH_2, cod), 3.65 (m, 1H, H-4), 3.76 (m, 1H, H-6'), 3.85 (m, 1H, H-5), 3.98 (m, 1H, CH= cod), 4.27 (m, 1H, H-3), 4.37 (b, 2H, H-6 and CH= cod), 4.51 (dd, 1H, H-2, $^3J_{2-3}$ = 8.4 Hz, $^3J_{2-1}$ = 6.8 Hz), 4.66 (b, 1H, CH= cod), 5.42 (s, 1H, H-7), 5.54 (b, 1H, CH=, cod), 6.32 (d, 1H, H-1, $^3J_{1-2}$ = 6.8 Hz), 7.0-8.5 (m, 28H, CH=, aromatics). ^{13}C NMR ($CDCl_3$), δ: 0.26 (s, CH_3-Si), 0.61 (s, CH_3-Si), 24.8 (b, CH_2, cod), 29.1 (b, CH_2, cod), 33.8 (b, CH_2, cod), 37.2 (b, CH_2, cod), 66.9 (s, C-5), 67.6 (s, C-6), 67.8 (s, C-2), 68.9 (s, CH=, cod), 69.0 (s, CH=, cod), 74.3 (m, C-4), 79.1 (s, C-3), 95.0 (d, CH=, cod, $J_{C\text{-}P}$= 22.7 Hz), 101.9 (s, C-7), 104.4 (s, C-1), 107.2 (m, CH=, cod), 117.7 (b, CH BAr_F), 120-134 (aromatic carbons), 135.0 (b, CH BAr_F), 135.5-137 (aromatic carbons), 161.9 (q, C-B BAr_F, $^1J_{C\text{-}B}$ = 49 Hz), 171.5 (s, C=N). Anal. calc (%) for $C_{78}H_{66}BF_{24}IrNO_7PSi_2$: C 49.95, H 3.55, N 0.75; found: C 50.11, H 3.61, N 0.72.

[Ir(cod)(L1d)]BAr$_F$. Yield 126 mg (93 %). ^{31}P NMR ($CDCl_3$), δ: 108.3 (s). ^{1}H NMR ($CDCl_3$), δ: 1.74 (b, 4H, CH_2, cod), 2.00 (m, 1H, CH_2, cod), 2.13 (m, 2H, CH_2, cod), 2.21 (m, 1H, CH_2, cod), 3.90 (b, 2H, CH=, cod and H-4), 3.94 (m, 1H, H-6'), 4.06 (m, 1H, H-5), 4.11 (b, 1H, CH=, cod), 4.31 (m, 3H, CH=, cod, H-6 and H-3), 4.67 (m, 1H, H-2), 5.44 (b, 1H, CH=, cod), 5.51 (s, 1H, H-7), 6.41 (d, 1H, H-1, $^3J_{1\text{-}2}$ = 6.4 Hz), 6.9-8.7 (m, 34H, CH=, aromatics). ^{13}C NMR ($CDCl_3$), δ: 25.4 (b, CH_2, cod), 29.3 (b, CH_2, cod), 32.1 (b, CH_2, cod), 36.7 (b, CH_2, cod), 66.7 (s, CH=, cod), 67.1 (s, C-5), 67.4 (s, C-2), 67.9 (s, C-6), 68.4 (s, CH=, cod), 74.3 (m, C-4), 80.1 (s, C-3), 99.4 (m, CH=, cod), 100.8 (s, C-7), 104.7 (s, C-1), 110.4 (m, CH=, cod), 117.8 (b, CH=, BAr_F), 119-134 (aromatic carbons), 135.2 (b, CH=, BAr_F), 135.5-151 (aromatic carbons), 162.4 (q, C-B, BAr_F, $^1J_{C\text{-}B}$ = 50 Hz) 172.5 (s, C=N). Anal. calc (%) for $C_{80}H_{54}BF_{24}IrNO_7P$: C 52.47, H 2.97, N 0.76; found: C 52.53, H 3.02, N 0.79.

[Ir(cod)(L1e)]BAr$_F$. Yield 122 mg (90 %). ^{31}P NMR ($CDCl_3$), δ: 109.8 (s). ^{1}H NMR ($CDCl_3$), δ: 1.66 (b, 2H, CH_2, cod), 1.83 (b, 2H, CH_2, cod), 2.18 (m, 1H, CH_2, cod), 2.25 (m, 1H, CH_2, cod), 2.34 (m, 1H, CH_2, cod), 2.42 (m, 1H, CH_2, cod), 3.36 (b, 1H, CH=, cod), 3.89 (m, 2H, H-6' and H-4), 3.91 (m, 1H, H-5), 4.01 (b, 1H, CH=, cod), 4.26 (m, 1H, CH=, cod), 4.40 (dd, 1H, H-6, $^2J_{6\text{-}6'}$ = 10.4 Hz, $^3J_{6\text{-}5}$ = 4 Hz), 4.46 (m, 1H, H-3), 4.71 (dd, 1H, H-2, $^3J_{2\text{-}3}$ = 8.4 Hz, $^3J_{2\text{-}1}$ = 6.0 Hz), 5.51 (b, 1H, CH=, cod), 5.54 (s, 1H, H-7), 6.41 (d, 1H, H-1, $^3J_{1\text{-}2}$ = 6.0 Hz), 6.9-8.7 (m, 34H, CH=, aromatics). ^{13}C NMR ($CDCl_3$), δ: 25.5 (b, CH_2, cod), 29.6 (b, CH_2, cod), 32.0 (b, CH_2, cod), 36.7 (b, CH_2, cod), 66.5 (s, CH=, cod), 67.5 (b, C-6 and C-5), 67.7 (s, C-2), 68.3 (s, CH=, cod), 74.1 (d, C-4, $J_{C\text{-}P}$ = 7.4 Hz), 79.7 (s, C-3), 100.5 (m, CH=, cod), 100.7 (s, C-7), 105.1 (s, C-1), 109.9 (d, CH=, cod, $J_{C\text{-}P}$ = 13.6 Hz), 117.7 (b, CH=, BAr_F), 120-133 (aromatic carbons), 135.0 (b, CH=, BAr$_F$), 135.5-150 (aromatic carbons), 161.9 (q, C-B, BAr$_F$, $^1J_{C-B}$ = 49 Hz) 172.0 (s, C=N). Anal. calc (%) for $C_{80}H_{54}BF_{24}IrNO_7P$: C 52.47, H 2.97, N 0.76; found: C 52.58, H 3.09, N 0.72.

[Ir(cod)(L1f)]BAr$_F$. Yield 126 mg (86 %). ^{31}P NMR (CDCl$_3$), δ: 108.3 (s). ^{1}H NMR (CDCl$_3$), δ: 0.56 (s, 9H, CH$_3$-Si), 0.65 (s, 9H, CH$_3$-Si), 1.63 (b, 2H, CH$_2$, cod), 1.79 (m, 2H, CH$_2$, cod), 2.20 (m, 2H, CH$_2$, cod), 2.39 (b, 1H, CH$_2$, cod), 2.49 (m, 1H, CH$_2$, cod), 3.72 (m, 1H, H-4), 3.76 (m, 1H, H-6'), 3.92 (b, 2H, CH= cod and H-5), 4.36 (b, 4H, H-3, H-6 and 2 CH= cod), 4.64 (m, 1H, H-2), 5.37 (s, 1H, H-7), 5.59 (b, 1H, CH=, cod), 6.35 (d, 1H, H-1, $^3J_{1-2}$ = 6.8 Hz), 6.7-8.5 (m, 32H, CH=, aromatics). ^{13}C NMR (CDCl$_3$), δ: 0.58 (s, CH$_3$-Si), 1.77 (s, CH$_3$-Si), 24.6 (b, CH$_2$, cod), 29.9 (b, CH$_2$, cod), 33.7 (b, CH$_2$, cod), 37.4 (b, CH$_2$, cod), 66.5 (s, CH=, cod), 67.5 (s, C-5), 68.0 (s, C-2), 69.4 (s, C-6), 70.8 (s, CH=, cod), 74.2 (d, C-4, J_{C-P}= 8.4 Hz), 79.1 (s, C-3), 93.6 (m, CH=, cod, J_{C-P}= 22.7 Hz), 100.9 (s, C-7), 104.1 (s, C-1), 107.6 (d, CH=, cod, J_{C-P} = 12.1 Hz), 117.6 (b, CH=, BAr$_F$), 120-134.5 (aromatic carbons), 135.0 (b, CH=, BAr$_F$), 135.5-152 (aromatic carbons), 161.9 (q, C-B, BAr$_F$, $^1J_{C-B}$ = 50 Hz) 171.3 (s, C=N). Anal. calc (%) for $C_{86}H_{70}BF_{24}IrNO_7PSi_2$: C 52.28, H 3.57, N 0.71; found: C 53.11, H 3.64, N 0.67.

[Ir(cod)(L1g)]BAr$_F$. All attempts to prepare this compound using different reaction conditions were unsuccessful. In all the cases decomposed product was obtained even at low temperature.

[Ir(cod)(L1h)]BAr$_F$. Yield 115 mg (91 %). ^{31}P NMR (CDCl$_3$), δ: 107.5 (s). ^{1}H NMR (CDCl$_3$), δ: 1.61 (b, 1H, CH$_2$, cod), 1.80 (b, 1H, CH$_2$, cod), 1.93 (b, 1H, CH$_2$, cod), 2.16 (b, 1H, CH$_2$, cod), 2.25 (b, 1H, CH$_2$, cod), 2.40 (m, 1H, CH$_2$ cod), 2.55 (m, 1H, CH$_2$, cod), 2.67 (m, 1H, CH$_2$, cod), 3.69 (b, 1H, CH, cod), 3.85 (m, 2H, H-5 and H-6'), 3.90 (m, 2H, H-3 and H-4), 3.98 (b, 2H, CH=, cod), 4.31 (m, 1H, H-6), 4.71 (m, 1H, H-2), 5.08 (b, 1H, CH=, cod), 5.58 (b, 2H, H-7 and CH= cod), 6.37 (d, 1H, H-1, $^3J_{1-2}$ = 6.4 Hz), 7.1-8.3 (m, 32H, CH=, aromatics). ^{13}C NMR (CDCl$_3$), δ: 26,1 (b, CH$_2$, cod), 29.8 (b, CH$_2$, cod), 31.7 (b, CH$_2$, cod), 36.2 (b, CH$_2$, cod), 63.6 (s, CH=, cod), 66.6 (s, C-5), 67.7 (s, C-6), 67.9 (s, CH, C-2), 69.3 (s, CH=, cod) 74.7 (d, C-4, J_{C-P}= 12.4 Hz), 79.8 (s, C-3), 95.5 (d, CH=, cod, J_{C-P}= 12.8 Hz), 101.9 (s, C-7), 103.7 (d, CH=, cod, J_{C-P} = 12.2 Hz), 104.1 (s, C-1), 117.7 (b, CH= BAr$_F$), 120-134 (aromatic carbons), 135.0 (b, CH= BAr$_F$), 135-137 (aromatic carbons), 161.9 (q, C-B BAr$_F$, $^1J_{C\text{-}B}$ = 49 Hz) 170.8 (s, C=N). Anal. calc (%) for $C_{72}H_{52}BF_{24}IrNO_5P$: C 50.83, H 3.08, N 0.82; found: C 51.10, H 3.14, N 0.81.

[Ir(cod)(L2a)]BAr$_F$. Yield 126 mg (89 %). ^{31}P NMR (CDCl$_3$), δ: 103.2 (s). ^{1}H NMR (CDCl$_3$), δ: 1.22 (d, 3H, CH$_3$, *i*Pr, $^3J_{H\text{-}H}$= 7.2 Hz), 1.31 (s, 9H, CH$_3$, *t*Bu), 1.35 (m, 3H, CH$_3$, *i*Pr), 1.37 (s, 9H, CH$_3$, *t*Bu), 1.49 (s, 9H, CH$_3$, *t*Bu), 1.61 (s, 9H, CH$_3$, *t*Bu), 1.98 (m, 1H, CH$_2$, cod), 2.11 (m, 3H, CH$_2$, cod), 2.34 (m, 4H, CH$_2$, cod), 2.76 (m, 1H, CH, *i*Pr), 3.41 (b, 1H, CH=, cod), 3.74 (m, 1H, H-4), 3.79 (m, 1H, H-6'), 3.88 (m, 1H, H-5), 4.16 (m, 2H, H-3 and CH= cod), 4.39 (dd, 1H, H-6, $^2J_{6\text{-}6'}$ = 10.8 Hz, $^3J_{6\text{-}5}$ = 4.8 Hz), 4.40 (dd, 1H, H-2, $^3J_{2\text{-}3}$ = 8.4 Hz, $^3J_{2\text{-}1}$ = 6.8 Hz), 4.71 (m, 1H, CH=, cod), 5.28 (b, 1H, CH=, cod), 5.49 (s, 1H, H-7), 6.10 (d, 1H, H-1, $^3J_{1\text{-}2}$ = 6.8 Hz), 7.1-7.8 (m, 21H, CH=, aromatics). ^{13}C NMR (CDCl$_3$), δ: 18.7 (s, CH$_3$, *i*Pr), 20.5 (s, CH$_3$, *i*Pr), 25.9 (b, CH$_2$, cod), 29.2 (b, CH$_2$, cod), 30.9 (s, CH, *i*Pr), 31.5 (s, CH$_3$, *t*Bu), 31.6 (s, CH$_3$, *t*Bu), 31.7 (s, CH$_3$, *t*Bu), 32.6 (b, CH$_2$, cod), 32.7 (s, CH$_3$, *t*Bu), 34.9 (s, C, *t*Bu), 35.0 (s, C, *t*Bu), 35.6 (s, C, *t*Bu), 36.1 (s, C, *t*Bu), 36.2 (b, CH$_2$, cod), 64.4 (s, CH=, cod), 66.4 (s, C-2), 67.1 (s, C-5), 67.6 (s, C-6), 70.4 (s, CH=, cod), 74.3 (s, C-4), 79.6 (s, C-3), 96.1 (m, CH=, cod), 101.7 (s, C-7), 104.4 (s, C-1), 105.9 (d, CH=, cod, $J_{C\text{-}P}$ = 13.4 Hz), 117.7 (b, CH=, BAr$_F$), 120-132 (aromatic carbons), 135.0 (b, CH=, BAr$_F$), 135.5-150 (aromatic carbons), 161.9 (q, C-B, BAr$_F$, $^1J_{C\text{-}B}$ = 49 Hz) 181.4 (s, C=N). Anal. calc (%) for $C_{85}H_{84}BF_{24}IrNO_7P$: C 53.13, H 4.41, N 0.73; found: C 53.21, H 4.47, N 0.72.

[Ir(cod)(L3a)]BAr$_F$. Yield 136 mg (95 %). ^{31}P NMR (CDCl$_3$), δ: 106.9 (s). ^{1}H NMR (CDCl$_3$), δ: 1.16 (s, 9H, CH$_3$, *t*Bu), 1.36 (s, 9H, CH$_3$, *t*Bu), 1.54 (s, 9H, CH$_3$, *t*Bu), 1.55 (s, 9H, CH$_3$, *t*Bu), 1.57 (s, 9H, CH$_3$, *t*Bu), 1.65 (m, 2H, CH$_2$ cod), 2.05 (m, 1H, CH$_2$, cod), 2.20 (m, 2H, CH$_2$, cod), 2.34 (m, 2H, CH$_2$, cod), 2.53 (m, 1H, CH$_2$, cod), 3.59 (m, 1H, H-4), 3.75 (m, 2H, H-6' and H-5), 3.97 (m, 1H, H-3), 4.21 (m, 1H, CH=, cod), 4.32 (m, 1H, H-6), 4.36 (m, 1H, H2), 4.49 (b, 1H, CH=, cod), 4.72 (b, 1H, CH=, cod), 5.40 (s, 1H, H-7), 5.42 (b, 1H, CH=, cod), 5.99 (d, 1H, CH, H1, $^3J_{1\text{-}2}$ = 6 Hz), 7.1-7.8 (m, 21H, CH=, aromatics). ^{13}C NMR (CDCl$_3$), δ: 24.2 (b, CH$_2$, cod), 28.3 (b, CH$_2$, cod), 28.6 (s, CH$_3$, *t*Bu-N), 31.4 (s, CH$_3$, *t*Bu), 31.6 (s, CH$_3$, *t*Bu), 31.8 (s, C, *t*Bu), 34.8 (s, C, *t*Bu), 35.0 (s, C, *t*Bu), 35.1 (b, CH$_2$, cod), 35.4 (s, C, *t*Bu), 36.1 (s, C, *t*Bu), 37.4 (b, CH$_2$, cod), 66.2 (s, C-

5), 67.5 (s, C-6), 68.4 (s, C-2), 69.8 (s, CH=, cod), 70.1 (s, CH=, cod), 74.1 (m, C-4), 79.8 (s, C-3), 90.8 (m, CH=, cod), 101.2 (s, C-7), 103.5 (s, C-1), 104.3 (m, CH=, cod), 117.7 (b, CH= BAr_F), 120-132 (aromatic carbons), 135.0 (b, CH= BAr_F), 135.5-150 (aromatic carbons), 161.9 (q, C-B, BAr_F, $^1J_{C\text{-}B}$ = 50 Hz) 183.6 (s, C=N). Anal. calc (%) for $C_{86}H_{86}BF_{24}IrNO_7P$: C 53.37, H 4.48, N 0.72; found: C 53.42, H 4.53, N 0.69.

[Ir(cod)(L4a)]BAr$_F$. Yield 130 mg (93 %). ^{31}P NMR ($CDCl_3$), δ: 102.2 (s). ^{1}H NMR ($CDCl_3$), δ: 1.28 (s, 9H, CH_3, *t*Bu), 1.36 (s, 9H, CH_3, *t*Bu), 1.49 (s, 9H, CH_3, *t*Bu), 1.61 (s, 9H, CH_3, *t*Bu), 1.71 (b, 3H, CH_2, cod), 1.93 (m, 1H, CH_2, cod), 2.08 (m, 2H, CH_2, cod), 2.21 (s, 3H, CH_3-N), 2.28 (b, 2H, CH_2 cod), 3.30 (b, 1H, CH=, cod), 3.70 (m, 1H, H-4), 3.78 (m, 1H, H-6'), 3.90 (m, 1H, H-5), 4.10 (b, 1H, CH= cod), 4.21 (m, 1H, H-3), 4.36 (dd, 1H, H-6, $^2J_{6\text{-}6'}$ = 10.4 Hz, $^3J_{6\text{-}5}$ = 5.6 Hz), 4.40 (m, 1H, H-2), 4.67 (m, 1H, CH=, cod), 5.29 (b, 1H, CH=, cod), 5.48 (s, 1H, H-7), 6.05 (d, 1H, H-1, $^3J_{1\text{-}2}$ = 6.4 Hz), 7.0-7.8 (m, 21H, CH=, aromatics). ^{13}C NMR ($CDCl_3$), δ: 16.3 (s, CH_3-N), 25.8 (b, CH_2, cod), 29.4 (b, CH_2, cod), 31.5 (s, CH_3, *t*Bu), 32.4 (b, CH_2, cod), 32.7 (s, CH_3, *t*Bu), 34.9 (s, C, *t*Bu), 35.0 (s, C, *t*Bu), 35.6 (s, C, *t*Bu), 36.1 (b, CH_2 cod and C, *t*Bu), 65.2 (b, CH=, cod), 66.6 (s, C-5), 67.4 (s, C-2), 67.6 (s, C-6), 70.4 (b, CH=, cod), 74.4 (d, C-4, $J_{C\text{-}P}$= 8.3 Hz), 79.2 (s, C-3), 95.9 (d, CH=, cod, $J_{C\text{-}P}$= 20.5 Hz), 101.9 (s, C-7), 104.6 (s, C-1), 105.7 (d, CH, cod, $J_{C\text{-}P}$ = 12.1 Hz), 117.7 (b, CH= BAr_F), 120-132 (aromatic carbons), 135.0 (b, CH= BAr_F), 135.5-150 (aromatic carbons), 161.9 (q, C-B BAr_F, $^1J_{C\text{-}B}$ = 50 Hz), 174.8 (s, C=N). Anal. calc (%) for $C_{83}H_{80}BF_{24}IrNO_7P$: C 52.65, H 4.26, N 0.74; found: C 53.91, H 4.33, N .071.

4. Typical procedure of hydrogenation of olefins. The alkene (1 mmol) and Ir complex (0.2 mol%) were dissolved in CH_2Cl_2 (2 mL) in a high-pressure autoclave. The autoclave was purged 4 times with hydrogen. Then, it was pressurized at the desired pressure. After the desired reaction time, the autoclave was depressurised and the solvent evaporated off. The residue was dissolved in Et_2O (1.5 ml) and filtered through a short plug of celite. The conversions were determined by ^{1}H NMR and enantiomeric excess was determined by chiral GC or chiral HPLC as previously described[4] except for substrate **S10** which was analyzed by GC-MS: Chiraldex β-DM 75 ºC isotherm 30 min, 20 ºC/min to 175 ºC, t_{r1}= 20.3 min (S, major), t_{r2} = 21.5 min (R, minor) and the absolute configuration determined by optical rotation.[5]

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