Biaryl Phosphite-Oxazoline from Hydroxyl Aminoacid Derivatives: Highly Efficient Modular Ligands for Ir-Catalyzed Hydrogenation of Alkenes.

Montserrat Diéguez,[a,*] Javier Mazuela,[a] Oscar Pàmies,[a] J. Johan Verendel,[b] Pher G. Andersson.[b,*]

[a] Departament de Química Física i Inorgànica. Universitat Rovira i Virgili. Campus Sescelades, C/ Marcel·lí Domingo, s/n. 43007 Tarragona, Spain. [b] Department of Biochemistry and Organic Chemistry, Uppsala University, BOX 576, 751 23 Uppsala, Sweden.

montserrat.dieguez@urv.cat; pher.andersson@kemi.uu.se

Supporting Information

Table of Contents

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-L6a-e**[2] 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 [Ir(cod)(L)]BArF (L= L1-L6a-e)

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 123 mg (92 %). ^{31}P NMR ($CDCl_3$), δ: 97.8 (s). ^{1}H NMR ($CDCl_3$), δ: 1.06 (s, 3H, CH_3), 1.29 (s, 3H, CH_3), 1.35 (s, 9H, CH_3, *t*Bu), 1.38 (s, 9H, CH_3, *t*Bu), 1.55 (s, 9H, CH_3, *t*Bu), 1.61 (s, 9H, CH_3, *t*Bu), 1.69 (m, 4H, CH_2, cod), 2.32 (m, 3H, CH_2, cod), 2.52 (m, 1H, CH_2, cod), 3.62 (b, 1H, CH= cod), 4.39 (m, 2H, CH= cod and CH_2), 4.58 (b, 2H, CH= cod and CH_2), 4.67 (dd, 1H, CH, $^{3}J_{H\text{-}H}$= 10. 0 Hz, $^{3}J_{H\text{-}H}$= 3.2 Hz), 5.32 (b, 1H, CH=, cod), 7.1-8.5 (m, 21H, CH= aromatics). ^{13}C NMR ($CDCl_3$), δ: 21.3 (s,CH_3), 24.8 (b, CH_2, cod), 26.5 (m, CH_3), 28.09 (b, CH_2, cod), 31.2 (s, CH_3, *t*Bu), 31.4 (s, CH_3, *t*Bu), 31.6 (s, CH_3, *t*Bu), 33.2 (b, CH_2, cod), 34.8 (s, C, *t*Bu), 34.9 (s, C, *t*Bu), 35.2 (s, C, *t*Bu), 37.3 (b, CH_2, cod), 66.3 (s, CH=, cod), 69.8 (s, CH=, cod), 70.0 (s, CH_2), 71.2 (s, CH), 84.9 (d, CMe_2, $J_{C\text{-}P}$= 5.2 Hz), 93.5 (d, CH=, cod, $J_{C\text{-}P}$ = 21.1 Hz), 106.3 (d, CH=, cod, $J_{C\text{-}P}$ = 6.2 Hz), 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, $^1J_{C-B}$ = 48.6 Hz), 173.7 (s, C=N). Anal. calc (%) for $C_{80}H_{78}BF_{24}IrNO_4P$: C 53.16, H 4.35, N 0.77; found: C 53.63, H 4.41, N 0.74.

[Ir(cod)(L1b)]BAr_F. Yield 115 mg (89 %). ^{31}P NMR ($CDCl_3$), δ: 99.0 (s). ^{1}H NMR ($CDCl_3$), δ: 1.19 (s, 3H, CH_3), 1.34 (s, 3H, CH_3), 1.54 (s, 9H, CH_3, *t*Bu), 1.61 (s, 9H, CH_3, *t*Bu), 1.67 (m, 4H, CH_2, cod), 2.18 (m, 1H, CH_2, cod), 2.25 (m 1H, CH_2, cod), 2.37 (m, 1H, CH_2, cod), 2.55 (dd, 1H, cod, $^2J_{H-H}$ = 15.2 Hz, $^3J_{H-H}$ = 6.4 Hz), 3.65 (m, 1H, CH=, cod), 3.84 (s, 3H, CH_3-O), 3.86 (s, 3H, CH_3-O), 4.40 (b, 1H, CH=, cod), 4.45 (dd, 1H, CH_2, $^2J_{H-H}$ = 10 Hz, $^3J_{H-H}$ = 3.6 Hz), 4.57 (b, 1H, CH=, cod), 4.63 (m, 1H, CH_2), 4.72 (dd, 1H, CH, $^3J_{H-H}$ = 9.2 Hz, $^3J_{H-H}$ = 2.8 Hz), 5.37 (b, 1H, CH=, cod) 6.6-8.5 (m, 21H, CH= aromatic). ^{13}C NMR ($CDCl_3$), δ: 21.5 (s, CH_3), 24.7 (b, CH_2, cod), 26.6 (d, CH_3, J_{C-P} = 6.9 Hz), 28.8 (b, CH_2, cod), 31.2 (s, CH_3, *t*Bu), 31.3 (s, CH_3, *t*Bu), 33.6 (b, CH_2, cod), 35.4 (s, C, *t*Bu), 35.7 (s, C, *t*Bu), 37.2 (d, CH_2, cod, J_{C-P} = 6.9 Hz), 55.8 (s, CH_3-O), 68.3 (s, CH=, cod), 69.8 (s, CH_2), 70.6 (s, CH=, cod), 74.0 (s, CH), 84.9 (d, CMe_2, J_{C-P} = 5.3 Hz), 94.6 (d, CH=, cod, J_{C-P} = 22 Hz), 106.2 (d, CH=, cod, J_{C-P} = 12.1 Hz), 113-115 (aromatic carbons), 117.7 (b, CH=, BAr_F), 120-132 (aromatic carbons), 135.0 (b, CH=, BAr_F), 138-150 (aromatic carbons), 161.9 (q, C-B, BAr_F, $^1J_{C-B}$ = 49.3 Hz), 172.4 (s, C=N). Anal. calc (%) for $C_{74}H_{66}BF_{24}IrNO_6P$: C 50.64, H 3.79, N 0.80; found: C 50.82, H 4.09, N 0.75.

[Ir(cod)(L1c)]BAr_F. Yield 110 mg (86 %). ^{31}P NMR ($CDCl_3$), δ: 95.5 (s). ^{1}H NMR ($CDCl_3$), δ: 0.49 (s, 9H, $SiMe_3$), 0.54 (s, 9H, $SiMe_3$) 1.02 (s, 3H, CH_3), 1.29 (s, 3H, CH_3), 1.67 (m, 4H, CH_2, cod), 2.24 (b, 2H, CH_2, cod), 2.45 (m, 2H, cod), 3.81 (m, 1H, CH=, cod), 3.38 (b, 1H, CH=, cod), 4.43 (dd, 1H, CH_2, $^2J_{H-H}$ = 10.4 Hz, $^3J_{H-H}$ = 3.6 Hz), 4.66 (b, 2H, CH= cod and CH_2), 4.79 (dd, 1H, CH, $^3J_{H-H}$ = 9.6 Hz, $^3J_{H-H}$ = 2.8 Hz), 5.44 (b, 1H, CH=, cod) 7.1-8.6 (m, 23H, CH= aromatics). ^{13}C NMR ($CDCl_3$), δ: 0.2 (s, $SiMe_3$), 0.4 (s, $SiMe_3$), 21.2 (s, CH_3), 25.0 (b, CH_2, cod), 26.5 (d, CH_3, J_{C-P} = 7.6 Hz), 29.1 (b, CH_2, cod), 32.8 (b, CH_2, cod), 36.8 (d, CH_2, cod, J_{C-P} = 7.6 Hz), 67.5 (s, CH=, cod), 68.7 (s, CH=, cod), 69.9 (s, CH_2), 73.5 (s, CH), 84.7 (d, CMe_2, J_{C-P} = 5.3 Hz), 96.8 (d, CH=, cod, J_{C-P} = 21.2 Hz), 107.4 (d, CH=, cod, J_{C-P} = 13.7 Hz), 117.7 (b, CH=, BAr_F), 120-134 (aromatic carbons), 135.0 (b, CH=, BAr_F), 135.5-155 (aromatic carbons), 161.9 (q, C-B, BAr_F, $^1J_{C-B}$ = 49.3

Hz), 172.7 (s, C=N). Anal. calc (%) for $C_{70}H_{62}BF_{24}IrNO_4PSi_2$: C 48.67, H 3.62, N 0.81; found: C 48.74, H 3.71, N 0.84.

[Ir(cod)(L1d)]BAr$_F$. Yield 113 mg (91 %). ^{31}P NMR ($CDCl_3$), δ: 100.9 (s). ^{1}H NMR ($CDCl_3$), δ: 1.39 (s, 3H, CH_3), 1.48 (s, 3H, CH_3), 1.57 (b, 2H, CH_2, cod), 1.75 (m, 2H, CH_2, cod), 2.20 (b, 3H, cod), 2.36 (b, 1H, CH_2, cod), 3.85 (m, 1H, CH=, cod), 4.06 (b, 1H, CH=, cod), 4.13 (b, 1H, CH=, cod), 4.56 (dd, 1H, CH_2, $^2J_{H-H}$ = 10.4 Hz, $^3J_{H-H}$ = 2.8 Hz), 4.69 (m, 1H, CH_2), 4.87 (dd, 1H, CH, $^3J_{H-H}$ = 8.8 Hz, $^3J_{H-H}$ = 2.8 Hz), 5.29 (b, 1H, CH=, cod) 7.1-8.4 (m, 29H, CH= aromatics). ^{13}C NMR ($CDCl_3$), δ: 22.8 (s, CH_3), 25.8 (b, CH_2, cod), 27.5 (d, CH_3, J_{C-P} = 6.2 Hz), 30.5 (s, CH_2, cod), 31.7 (b, CH_2, cod), 36.0 (s, CH_2, cod, J_{C-P} = 5.3 Hz), 64.8 (s, CH=, cod), 66.1 (s, CH=, cod), 70.8 (s, CH_2), 72.5 (d, CH, J_{C-P}= 4.6 Hz), 86.0 (d, CMe_2, J_{C-P}= 4.9 Hz), 99.0 (d, CH=, cod, J_{C-P} = 20.5 Hz), 107.3 (s, CH=, cod, J_{C-P} = 13.7 Hz), 117.7 (b, CH=, BAr_F), 120-132 (aromatic carbons), 135.0 (b, CH=, BAr_F), 136-152 (aromatic carbons), 161.9 (q, C-B BAr_F, $^1J_{C-B}$ = 49.3 Hz), 173.2 (s, C=N). Anal. calc (%) for $C_{72}H_{50}BF_{24}IrNO_4P$: C 51.38, H 2.99, N 0.83; found: C 51.54, H 3.03. N 0.89.

[Ir(cod)(L1e)]BAr$_F$. Yield 111 mg (89 %). ^{31}P NMR ($CDCl_3$), δ: 103.5 (s). ^{1}H NMR ($CDCl_3$), δ: 1.32 (s, 3H, CH_3), 1.40 (s, 3H, CH_3), 1.61 (b, 4H, CH_2, cod), 2.15 (m, 1H, CH_2, cod), 2.40 (m, 3H, cod), 3.12 (m, 1H, CH=, cod), 3.88 (b, 1H, CH=, cod), 3.99 (m, 1H, CH=, cod), 4.55 (dd, 1H, CH_2, $^2J_{H-H}$ = 10.4 Hz, $^3J_{H-H}$ = 2.8 Hz), 4.7 (m, 1H, CH_2), 4.89 (dd, 1H, CH, $^3J_{H-H}$ = 9.2 Hz, $^3J_{H-H}$ = 2.8 Hz), 5.40 (b, 1H, CH=, cod) 7.1-8.6 (m, 29H, CH= aromatics). ^{13}C NMR ($CDCl_3$), δ: 20.9 (s, CH_3), 25.9 (s, CH_2, cod), 26.9 (s, CH_3) 29.2 (s, CH_2, cod), 32.0 (b, CH_2, cod), 36.9 (s, CH_2, cod), 66.1 (s, CH=, cod), 68.2 (s, CH=, cod), 70.6 (s, CH_2), 73.6 (s, CH), 86.1 (d, CMe_2, J_{C-P}= 5.4 Hz), 100.5 (s, CH=, cod), 109.1 (s, CH=,cod), 117.7 (b, CH=, BAr_F), 120-132 (aromatic carbons), 135.0 (b, CH=, BAr_F), 138-150 (aromatic carbons), 161.9 (q, C-B BAr_F, $^1J_{C-B}$ = 49.3 Hz), 180.9 (s, C=N). Anal. calc (%) for $C_{72}H_{50}BF_{24}IrNO_4P$: C 51.38, H 2.99, N 0.83; found: C 51.29, H 2.93, N 0.78.

[Ir(cod)(L2a)]BAr$_F$. Yield 124 mg (92 %). ^{31}P NMR ($CDCl_3$), δ: 97.4 (s). ^{1}H NMR ($CDCl_3$), δ: 1.06 (s, 3H, CH_3), 1.27 (s, 3H, CH_3), 1.36 (s, 9H, CH_3, *t*Bu), 1.37 (s, 9H, CH_3, *t*Bu), 1.56 (s, 9H, CH_3, *t*Bu), 1.62 (s, 9H, CH_3, *t*Bu), 1.67 (b, 4H, CH_2, cod), 2.18 (b, 1H, CH_2, cod), 2.36 (m, 2H,

CH_2, cod), 2.53 (m, 4H, CH_2 cod and CH_3), 3.73 (m, 1H, CH=, cod), 4.37 (m, 2H, CH_2 and CH= cod), 4.55 (m, 2H, CH_2 and CH= cod), 4.66 (dd, 1H, CH, $^3J_{H-H}$ = 8.8 Hz, $^3J_{H-H}$ = 2.8 Hz), 5.34 (b, 1H, CH=, cod) 7.1-8.4 (m, 20H, CH= aromatics). ^{13}C NMR ($CDCl_3$), δ: 21.4 (s, CH_3), 24.8 (b, CH_2, cod), 26.4 (s, CH_3), 28.9 (b, CH_2, cod), 31.3 (s, CH_3, *t*Bu), 31.4 (s, CH_3, *t*Bu), 31.5 (s, CH_3, *t*Bu), 31.6 (s, CH_3, *t*Bu), 33.7 (b, CH_2, cod), 34.9 (s, C, *t*Bu), 35.0 (s, C, *t*Bu), 35.4 (s, C, *t*Bu), 35.8 (s, CH_3), 37.1 (b, CH_2, cod), 67.9 (s, CH=, cod), 69.6 (s, CH_2), 70.0 (s, CH=, cod), 73.7 (s, CH), 84.8 (d, CMe_2, J_{C-P} = 5.2 Hz), 92.6 (m, CH=, cod), 106.4 (m, CH=, cod), 117.7 (b, CH=, BAr_F), 119-132 (aromatic carbons), 135.0 (b, CH=, BAr_F), 138-150 (aromatic carbons), 161.9 (q, C-B, BAr_F, $^1J_{C-B}$ = 48.6 Hz), 174.8 (s, C=N). Anal. calc (%) for $C_{81}H_{80}BF_{24}IrNO_4P$: C 53.41, H 4.43, N 0.77; found: C 53.53, H 4.52, N 0.79.

[Ir(cod)(L3a)]BAr$_F$. Yield 120 mg (87 %). ^{31}P NMR ($CDCl_3$), δ: 97.9 (s). ^{1}H NMR ($CDCl_3$), δ: 1.05 (s, 3H, CH_3), 1.25 (s, 3H, CH_3), 1.32 (s, 9H, CH_3, *t*Bu), 1.34 (s, 9H, CH_3, *t*Bu), 1.52 (s, 9H, CH_3, *t*Bu), 1.59 (s, 9H, CH_3, *t*Bu), 1.64 (m, 3H, CH_2, cod), 1.92 (m, 1H, CH_2, cod), 2.27 (b, 3H, CH_2, cod), 2.57 (m, 1H, cod, $^2J_{H-H}$ = 15.6 Hz, $^3J_{H-H}$ = 9.6 Hz), 3.54 (m, 1H, CH=, cod), 4.38 (dd, 1H, CH_2, $^2J_{H-H}$ = 10 Hz, $^3J_{H-H}$ = 3.2 Hz), 4.43 (b, 1H, CH=, cod), 4.57 (m, 1H, CH_2), 4.61 (b, 1H, CH=, cod), 4.71 (dd, 1H, CH, $^3J_{H-H}$ = 9.2 Hz, $^3J_{H-H}$ = 3.2 Hz), 5.31 (b, 1H, CH=, cod) 7.1-8.6 (m, 20H, CH= aromatics). ^{13}C NMR ($CDCl_3$), δ: 21.3 (s, CH_3), 24.8 (b, CH_2, cod), 26.4 (d, CH_3, J_{C-P} = 6.8 Hz), 28.7 (b, CH_2, cod), 31.3 (s, CH_3, *t*Bu), 31.4 (s, CH_3, *t*Bu), 31.5 (s, CH_3, *t*Bu), 33.4 (b, CH_2, cod), 34.9 (s, C, *t*Bu), 35.0 (s, C, *t*Bu), 35.4 (s, C, *t*Bu), 35.7 (s, C, *t*Bu), 37.3 (d, CH_2, cod, J_{C-P} = 6.9 Hz), 69.1 (s, CH=, cod), 70.2 (s, CH_2), 71.0 (s, CH=, cod), 74.5 (s, CH), 84.5 (d, CMe_2, J_{C-P} = 5.3 Hz), 94.7 (d, CH=, cod, J_{C-P} = 21.9 Hz), 106.5 (d, CH=, cod, J_{C-P} = 12.2 Hz), 117.7 (b, CH=, BAr_F), 120-132 (aromatic carbons), 135.0 (b, CH=, BAr_F), 136.6 (q, CF_3, $^1J_{C-F}$ = 33.3 Hz), 138-150 (aromatic carbons), 161.9 (q, C-B, BAr_F, $^1J_{C-B}$ = 49.3 Hz), 171.0 (s, C=N). Anal. calc (%) for $C_{81}H_{77}BF_{27}IrNO_4P$: C 51.87, H 4.14, N 0.75; found: C 51.93, H 4.17, N 0.79.

[Ir(cod)(L4a)]BAr$_F$. Yield 117 mg (87 %). ^{31}P NMR ($CDCl_3$), δ: 95.0 (s). ^{1}H NMR ($CDCl_3$), δ: 1.09 (s, 3H, CH_3), 1.34 (s, 9H, CH_3, *t*Bu), 1.35 (s, 9H, CH_3, *t*Bu), 1.49 (s, 9H, CH_3, *t*Bu), 1.52 (s,

3H, CH_3),1.56 (s, 3H, $\underline{CH_3}$-CH), 1.57 (s, 9H, CH_3, *t*Bu), 1.64 (m, 4H, CH_2, cod), 2.27 (b, 3H, CH_2, cod), 2.55 (dd, 1H, cod, $^2J_{H\text{-}H}$ = 16.4 Hz, $^3J_{H\text{-}H}$ = 7.6 Hz), 3.63 (m, 1H, CH=, cod), 4.37 (b, 1H, CH=, cod), 4.39 (d, 1H, CH-N, $^3J_{H\text{-}H}$ = 8.4 Hz), 4.60 (b, 1H, CH=, cod), 5.06 (m, 1H, CH), 5.26 (b, 1H, CH=, cod) 7.1-8.6 (m, 21H, CH= aromatics). ^{13}C NMR ($CDCl_3$), δ: 23.6 (s, CH_3), 25.0 (b, CH_2, cod), 27.7 (d, CH_3, $J_{C\text{-}P}$ = 6.8 Hz), 29.1 (b, CH_2, cod), 31.1 (s, CH_3, *t*Bu), 31.3 (s, CH_3 *t*Bu), 31.5 (s, CH_3, *t*Bu), 31.6 (s, CH_3, *t*Bu), 33.1 (b, CH_2, cod), 34.9 (s, C, *t*Bu), 35.0 (s, C, *t*Bu), 35.3 (s, C, *t*Bu), 35.8 (s, $\underline{CH_3}$-CH), 36.9 (d, CH_2, cod, $J_{C\text{-}P}$ = 6.1 Hz), 67.7 (s, CH=, cod), 69.7 (s, CH=, cod), 76.0 (s, CH-N), 81.1 (s, CH-O), 84.5 (d, CMe_2, $J_{C\text{-}P}$ = 6.9Hz), 95.7 (d, CH=, cod, $J_{C\text{-}P}$ = 22 Hz), 106.6 (d, CH=, cod, $J_{C\text{-}P}$ = 12.9 Hz), 117.7 (b, CH=, BAr_F), 120-132 (aromatic carbons), 135.0 (b, CH=, BAr_F),138-150 (aromatic carbons), 161.9 (q, C-B, BAr_F, $^1J_{C\text{-}B}$ = 49.3 Hz), 172.5 (s, C=N). Anal. calc (%) for $C_{81}H_{80}BF_{24}IrNO_4P$: C 53.41, H 4.43, N 0.77; found: C 53.74, H 4.56, N 0.81.

[Ir(cod)(L5a)]BAr$_F$. Yield 120 mg (91 %). ^{31}P NMR ($CDCl_3$), δ: 103.3 (s). ^{1}H NMR ($CDCl_3$), δ: 1.36 (s, 9H, CH_3, *t*Bu), 1.37 (s, 9H, CH_3, *t*Bu), 1.55 (s, 9H, CH_3, *t*Bu), 1.56 (s, 9H, CH_3, *t*Bu), 1.75 (b, 4H, CH_2, cod), 2.30 (m, 3H, CH_2, cod), 2.40 (m, 1H, cod), 2.52 (s, 3H, CH_3), 3.79 (m, 1H, CH=, cod), 4.10 (m, 1H, CH_2-OP), 4.20 (m, 2H, CH_2-OP and CH_2) 4.40 (b, 1H, CH=, cod), 4.63 (m, 1H, CH_2), 4.68 (b, 1H, CH=, cod), 4.81 (m, 1H, CH), 5.45 (b, 1H, CH=, cod) 7.1-8.6 (m, 20H, CH= aromatics). ^{13}C NMR ($CDCl_3$), δ: 24.8 (b, CH_2, cod), 28.8 (b, CH_2, cod), 31.2 (s, CH_3, *t*Bu), 31.4 (s, CH_3, *t*Bu), 31.5 (s, CH_3, *t*Bu), 31.6 (s, CH_3, *t*Bu), 33.7 (b, CH_2, cod), 34.9 (s, C, *t*Bu), 35.0 (s, C, *t*Bu), 35.4 (s, C, *t*Bu), 36.0 (s, CH_3), 37.2 (d, CH_2, cod, $J_{C\text{-}P}$ = 6.9 Hz), 66.9 (s, CH), 68.5 (s, CH=, cod), 69.5 (s, CH_2), 69.6 (s, CH=, cod), 70.2 (s, CH_2-OP), 94.2 (d, CH=, cod, $J_{C\text{-}P}$ = 22 Hz), 106.5 (d, CH=, cod, $J_{C\text{-}P}$ = 12.1 Hz), 117.7 (b, CH=, BAr_F), 119-132 (aromatic carbons), 135.0 (b, CH=, BAr_F), 138-150 (aromatic carbons), 161.9 (q, C-B, BAr_F, $^1J_{C\text{-}B}$ = 49.3 Hz), 171.3 (s, C=N). Anal. calc (%) for $C_{79}H_{76}BF_{24}IrNO_4P$: C 52.91, H 4.27, N 0.78; found: C 53.07, H 4.32, N 0.82.

[Ir(cod)(L6a)]BAr$_F$. Yield 136 mg (92 %). ^{31}P NMR ($CDCl_3$), δ: 92.8 (s). ^{1}H NMR ($CDCl_3$), δ: 1.08 (s, 9H, CH_3, *t*Bu), 1.35 (s, 9H, CH_3, *t*Bu), 1.39 (s, 9H, CH_3, *t*Bu), 1.81 (m, 4H, CH_2, cod), 1.87 (s, 9H, CH_3, *t*Bu), 2.33 (m, 3H, CH_2, cod), 2.55 (m, 1H, CH_2, cod), 3.93 (m, 1H, CH=, cod), 4.51 (b,

1H, CH=, cod), 4.63 (b, 1H, CH=, cod), 4.68 (dd, 1H, CH_2, $^2J_{H-H}$ = 10 Hz, $^3J_{H-H}$ = 3.2 Hz), 4.87 (m, 1H, CH_2), 5.27 (b, 1H, CH=, cod), 5.78 (dd, 1H, CH, $^3J_{H-H}$ = 8.4 Hz, $^3J_{H-H}$ = 2.8 Hz), 6.5-8.6 (m, 30H, CH= aromatics). ^{13}C NMR ($CDCl_3$), δ: 25.9 (b, CH_2, cod), 29.9 (b, CH_2, cod), 30.5 (s, CH_3, *t*Bu), 31.2 (b, CH_2, cod), 31.5 (s, CH_3, *t*Bu), 31.6 (s, CH_3, *t*Bu), 31.7, (s, CH_3, *t*Bu), 34.9 (s, C, *t*Bu), 35.0 (s, C, *t*Bu), 35.4 (s, C, *t*Bu), 35.7 (s, C, *t*Bu), 36.0 (b, CH_2, cod), 67.7 (s, CH=, cod), 71.2 (s, CH_2), 71.3 (s, CH=, cod), 71.4 (s, CH), 92.7 (s, CPh_2), 99.0 (d, CH=, cod, J_{C-P} = 19.7 Hz), 108.1 (d, CH=, cod, J_{C-P} = 13.6 Hz), 117.7 (b, CH=, BAr_F), 120-132 (aromatic carbons), 135.0 (b, CH=, BAr_F), 136.1 (m, CF_3), 138-150 (aromatic carbons), 161.9 (q, C-B, BAr_F, $^1J_{C-B}$ = 49.3 Hz), 172.3 (s, C=N). Anal. calc (%) for $C_{91}H_{81}BF_{27}IrNO_4P$: C 54.66, H 4.08, N 0.70; found: C 54.78, H 4.11, N 0.73.

3. 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 enantiomeric excess was determined by chiral GC or chiral HPLC and conversions were determined by ^{1}H NMR.[3]

---

[1] Buisman, G. J. H.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Tetrahedron: Asymmetry* **1993**, *4*, 1625

[2] Diéguez, M.; Claver, C. *Chem. Eur. J.* **2008**, *14*, 3653.

[3] a) Hedberg, C.; Källström, K.; Brandt, P.; Hansen, L. K.; Andersson, P. G. *J. Am. Chem. Soc.* **2006**, *128*, 2995. b) McIntyre, S.; Hörmann, E.; Menges, F.; Smidt, S. P. Pfaltz, A. *Adv. Synth. Catal.* **2005**, *347*, 282. c) Diéguez, M.; Mazuela, J.; Pàmies, O.; Verendel, J. J.; Andersson, P. G. *J. Am. Chem. Soc.* in press.