Supporting Information for 
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Highly Enantioselective Hydrogenation of Acyclic Imines Catalyzed by Ir-f-Binaphane Complexes

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A. General Procedures: All reactions and manipulations were performed in a nitrogen-filled glovebox or using standard Schlenk techniques. THF and toluene were dried and distilled from sodium-benzophenone ketyl under nitrogen. Methylene chloride was distilled from CaH₂. Methanol was distilled from Mg under nitrogen. Column chromatography was performed using EM silica gel 60 (230~400 mesh). ¹H, ¹³C and ³¹P NMR were recorded on Bruker AM-300, and AMX-360 spectrometers. Chemical shifts were reported in ppm down field from tetramethylsilane with the solvent resonance as the internal standard. Optical rotation was obtained on a Perkin-Elmer 241 polarimeter. MS spectra were recorded on a KRATOS mass spectrometer MS 9/50 for LR-EI and HR-EI. GC analysis was carried on Helwett-Packard 6890 gas chromatography using chiral capillary columns.

Synthesis of (R,R)-1,1’-bis((R)-4,5-dihydro-3H-dinaphtho[1,2-c:2’,1’-e]phosphepino)ferrocene (1): To a solution of (R)-2,2’-dichloromethyl-1,1’-binaphthyl (3.71g, 10.6 mmol) and NaH (2 g, 83 mmol) in THF (125 mL) was added 1,1’-bis(phosphino)ferrocene (1.32g, 5.28mmol) at -78°C under nitrogen. The mixture was warmed to rt and kept stirring at the same temperature for 24 h and then heated to reflux for 48 h. After the reaction was completed (monitored by ³¹P NMR), the solvent was removed via vacuum and the residue was washed with CH₂Cl₂ (3 × 25 mL). The organic phase was filtered through a silica gel plug to give fairly pure product. Further purification by recrystallization from CH₂Cl₂/Hexanes afforded 1 as air stable yellow solid (2.15 g, 50%). [α]D²⁰ =160 (c =0.2, CHCl₃), ¹H NMR (CD₂Cl₂) 360MHz δ 8.07-7.99(6H, m, Ar-H), 7.87-7.85(2H, d, J = 8.34Hz), 7.80-7.78(2H, d, J = 8.31Hz), 7.53-7.50(4H, m, Ar-H), 7.31-7.28(8H, m, Ar-H), 7.07-7.04(2H, d, J=8.37Hz), 4.49(2H, s, Cp-H), 4.45(2H, s, Cp-H), 4.26(2H, s, Cp-H), 3.56(2H, s, Cp-H), 3.10-3.06(2H, m, ArCH₂), 2.82-2.72(4H, m, ArCH₂), 2.63-2.59(2H, m, ArCH₂); ¹³C NMR (CD₂Cl₂, 90 MHz) δ 135.79, 135.18, 134.28, 133.57, 133.21, 133.05, 132.96, 132.67, 129.28, 129.00, 128.94, 128.10, 128.04, 127.29, 127.19, 126.58, 126.45, 125.73, 125.46, 76.22(d, JCP=21.92Hz), 75.62(d, JCP=32.00Hz), 72.43, 71.63, 71.14, 34.60(d, JCP=20.90Hz), 31.36(d, JCP=11.74Hz); ³¹P NMR(CD₂Cl₂) δ -1.26 ppm. MS m/z: 807 (MH⁺).

General Procedure for the Synthesis of Imines 2(a-k): The ketone (1eq) and the appropriate amine (1 eq) were dissolved in dry
toluene (40 mL) in a flask under nitrogen. To this solution was added the catalytic amount of p-toluenesulfonic acid. The flask was equipped with a reflux condenser and a Dean-Stark trap and the mixture was heated to reflux for 5 h. The reaction was quenched by adding saturated NaHCO₃ solution and the product was extracted with ether (3 x 100 mL). The organic layer was combined, washed with brines, dried with Na₂SO₄ and then subject to distillation in vacuo or chromatography on basic Al₂O₃.

N-(1-Phenylethylidene)aniline (2a)

¹H NMR (CDCl₃, 300MHz), δ 8.05-8.02 (2H, m, Ar-H), 7.50-7.48 (3H, m, Ar-H), 7.40-7.37 (2H, m, Ar-H), 7.16-7.11 (1H, m, Ar-H), 6.87-6.84 (2H, d, J = 8.38Hz, Ar-H), 2.27 (3H, s, CH₃).

N-(1-Phenylethylidene)2,6-xylxlamine (2b)

¹H NMR (CDCl₃, 300 MHz), δ 8.10-8.07 (2H, m, Ar-H), 7.53 (m, Ar-H), 7.12-7.09 (2H, d, J = 7.47Hz, Ar-H), 6.99-6.94 (1H, m, Ar-H), 2.12 (3H, s, CH₃), 2.08 (6H, s, ArCH₃).

N-(1-p-Methoxyphenylidene)2,6-xylxlamine (2c)

¹H NMR (CDCl₃, 300MHz), δ 7.99-7.96 (2H, m, Ar-H), 7.09-7.07 (2H, d, J = 5.47Hz, Ar-H), 6.92-6.80 (1H, m, Ar-H), 3.87 (3H, s, OCH₃), 1.99 (9H, s, CH₃).

N-(1-p-Trifluromethylphenylidene)2,6-xylxlamine (2d): ¹H NMR (CDCl₃, 300MHz), δ 7.06-8.04 (2H, d, J = 6.73Hz, Ar-H), 7.64-7.62 (2H, d, J = 6.91Hz, Ar-H), 6.99-6.96 (2H, d, J = 6.30Hz, Ar-H), 6.87-6.83 (1H, t, Ar-H), 2.00 (3H, s, CH₃), 1.93 (6H, s, ArCH₃) ¹³C NMR (CDCl₃, 90 MHz) δ 164.75, 148.86, 142.49, 133.16, 132.80, 132.44, 132.08, 128.96, 128.38, 127.88, 125.93, 125.87, 125.83, 125.79, 125.75, 123.61, 122.94, 119.93, 18.30, 17.91ppm. MS m/z: 291 (M⁺).

N-(1-Tetrabutylethylidene)2,6-xylxlamine (2e):

¹H NMR (CDCl₃, 360MHz), δ 7.22-7.20 (2H, d, J = 7.56Hz, Ar-H), 2.19 (3H, s, CH₃), 1.84 (3H, s, CH₃), 1.50 (6H, s, CH₃). ¹³C NMR (CDCl₃, 90 MHz) δ 177.29, 149.33, 128.63, 127.97, 125.70, 122.93, 122.65, 122.31, 40.98, 28.46, 18.06, 15.69 ppm. MS m/z: 203 (M⁺).

N-(1-Isopropylethylidene)2,6-xylylamine (2f):

¹H NMR (CDCl₃, 360MHz) δ 7.00-6.98 (2H, d, J = 7.52Hz, Ar-H), 6.87-6.83 (1H, t, Ar-H), 2.73-2.65 (1H, m, CH), 1.99 (6H, s, ArCH₃), 1.59 (3H, s, CH₃), 1.25-1.21 (6H, d, J=13.60Hz, CH₃, major isomer (E)), 0.99-0.97(6H, d, J = 6.84Hz, CH₃, minor isomer (Z)) [(E)/(Z)=14:1], ¹³C NMR (CDCl₃, 90 MHz) δ 175.91, 149.10, 128.23, 126.04, 122.80, 39.22, 20.41, 18.08, 17.93ppm. MS m/z: 189 (M⁺).

N-(1-Cyclohexylethylidene)2,6-xylylamine (2g):

¹H NMR (CDCl₃, 360MHz) δ 6.89-6.87 (2H, d, J = 7.52Hz, Ar-H), 6.87-6.83 (1H, t, Ar-H), 2.27-2.25 (1H, m, CH), 1.88 (6H, s, ArCH₃), 1.92-1.50 (5H, m, CH₂), 1.49 (3H, s, CH₃), 1.49-1.22(5H, m, CH₂) ¹³C NMR (CDCl₃, 90 MHz) δ 175.37, 149.21, 127.88, 125.98, 122.73, 49.41, 30.93, 26.64, 18.60, 18.15ppm. MS m/z: 291 (M⁺).

N-(1-Phenylidene)4'-methoxyaniline (2h)

¹H NMR (CDCl₃, 300MHz), δ 8.02-7.99 (2H, m, Ar-H), 7.49-7.46 (3H, m, Ar-H), 6.96-6.94 (2H, d, J = 6.59Hz, Ar-H), 6.80-6.78 (2H, d, J = 6.56Hz, Ar-H), 3.84 (3H, s, OCH₃), 2.29 (3H, s, CH₃).

N-(1-Phenylidene)2'-methoxyaniline (2i)

¹H NMR (CDCl₃, 360MHz), δ 7.99-7.96 (2H, m, Ar-H), 7.40-7.37 (3H, m, Ar-H), 6.94-
6.92 (1H, m, Ar-H), 6.88-6.84 (2H, m, Ar-H), 6.76-6.74 (1H, d, \( J = 7.59 \text{Hz} \), Ar-H), 3.71(3H, s, OCH\(_3\)), 2.13 (3H, s, CH\(_3\)).

**N-(1-Phenylidene)2'-methoxy-6'-methylaniline (2j):** \(^1\)H NMR (CDCl\(_3\), 360MHz) \( \delta \) 8.39-8.36 (2H, m, Ar-H), 7.76-7.74 (1H, d, \( J = 7.59 \text{Hz} \), Ar-H), 7.18-7.16 (1H, d, \( J = 8.09 \text{Hz} \)), 4.03 (3H, s, OCH\(_3\)), 2.42 (3H, s, CH\(_3\)), 2.41(3H, s, CH\(_3\)).

**N-(1-(1-Naphthyl)ethylidene)2'-methoxy-6'-methylaniline (2k):** \(^1\)H NMR (CDCl\(_3\), 360MHz) \( \delta \) 8.65-8.62(1H, d, \( J = 8.49 \text{Hz} \), Ar-H), 7.94-7.92(2H, d, \( J = 8.04 \text{Hz} \), Ar-H), 7.69-7.67(1H, d, \( J = 8.13 \text{Hz} \), Ar-H), 7.62-7.54(3H, m, Ar-H), 7.08-7.06 (1H, t, Ar-H), 6.96-6.70 (2H, m, Ar-H), 3.93(3H, s, OCH\(_3\)), 2.28(3H, s, CH\(_3\)), 2.24(3H, s, CH\(_3\)).

**General Procedure for Catalytic Asymmetric Hydrogenation of Imines (2a-k):** The Ir-f-Binaphane complex was made in situ by mixing [Ir(COD)Cl]\(_2\) (6.7 mg, 0.01 mmol) and 1 (17.7 mg, 0.022 mmol) in 20 mL of CHCl\(_3\). The mixture was stirred for 30 min and then 5 mL of this solution was transferred to a 10 mL vial with an imine substrate (0.5 mmol). The hydrogenation was performed at rt under 1000 psi of hydrogen. After the reaction was finished, hydrogen was released carefully and the reaction mixture was passed through a silica gel plug eluted with CHCl\(_3\). The enantiomeric excess was measured by using GC with a chiral column without further purification. The absolute configuration of products was determined by comparing the retention time with the standard chiral compounds.

**N-Phenyl-1-phenylethylamine (3a):** \(^1\)H NMR(CDCl\(_3\), 300 MHz), \( \delta \) 7.57-7.47 (4H, m, Ar-H), 7.43-7.40 (1H, m, Ar-H), 7.31-7.26 (2H, m, Ar-H), 6.87-6.82 (1H, m, Ar-H), 6.71-6.69 (2H, d, \( J = 7.91 \text{Hz} \), Ar-H), 4.70-4.63 (1H, m, CH), 4.19 (1H, s, NH), 1.69-1.67 (3H, d, \( J = 6.74 \text{Hz} \), CH\(_3\)).

**N-(2',6'-Dimethylphenyl)-1-phenylethylamine (3b):** [\( \alpha \rceil_{D}^{25} \) = -136.6 (c=1, CHCl\(_3\)), \(^1\)H NMR (CDCl\(_3\), 360 MHz) \( \delta \) 7.19-7.10 (5H, m, Ar-H), 6.85-6.83 (2H, d, \( J = 7.41 \text{Hz} \), Ar-H), 6.70-6.66 (1H, t, Ar-H), 4.24-4.19 (1H, q, CH), 3.09 (1H, b, NH), 2.07 (6H, s, ArCH\(_3\)), 1.42-1.39 (3H, d, \( J = 6.76 \text{Hz} \), CH\(_3\)). \(^{13}\)C NMR(CDCl\(_3\), 90 MHz) \( \delta \) 145.76, 145.31, 137.77, 129.23, 127.63, 122.08, 114.06, 56.50, 55.83, 22.98, 19.35ppm. MS m/z: 227 (M\(^+\)).

**N-(2',6'-Dimethylphenyl)-1-p-Methoxyphenylethylamine (3c):** [\( \alpha \rceil_{D}^{25} \) = -161.2 (c=1, CHCl\(_3\)), \(^1\)H NMR (CDCl\(_3\), 360 MHz) \( \delta \) 7.35-7.33 (2H, d, \( J = 6.93 \text{Hz} \), Ar-H), 7.09-7.07 (2H, d, \( J = 7.51 \text{Hz} \), Ar-H), 6.98-6.90 (3H, m, Ar-H), 4.44-4.39 (1H, q, CH), 3.91 (3H, s, OCH\(_3\)), 3.30 (1H, b, NH), 2.31 (6H, s, ArCH\(_3\)), 1.63-1.61(3H, d, CH\(_3\)). \(^{13}\)C NMR(CDCl\(_3\), 90 MHz) \( \delta \) 159.00, 145.31, 137.87, 129.91, 129.23, 127.63, 122.02, 114.06, 56.50, 55.83, 22.98, 19.35ppm. MS m/z: 255 (M\(^+\)).
N-(2',6'-Dimethylphenyl)-1-p-Trifluromethylphenylethylamine (3d): $[\alpha]_D^{25} = -128.1$ (c=1, CHCl$_3$), $^1$H NMR (CDCl$_3$, 300MHz), $\delta$ 7.49-7.46 (2H, d, $J=8.24$Hz, Ar-H), 7.35-7.32 (2H, d, $J=8.21$Hz, Ar-H), 6.89-6.87(2H, d, $J=7.47$Hz, Ar-H), 6.75-6.70 (1H, t, Ar-H). 4.32-4.25 (1H, q, CH), 3.11(1H, b, NH), 2.08(6H, s, ArCH$_3$), 1.47-1.44 (3H, d, $J=6.74$Hz, CH$_3$). $^{13}$C NMR (CDCl$_3$, 90 MHz), $\delta$ 144.90, 129.74, 129.37, 126.87, 126.40, 125.82, 122.80, 122.35, 56.98, 23.26, 19.30ppm. MS m/z: 293 (M$^+$).

N-(2',6'-Dimethylphenyl)-1-Tetrabutylethylamine (3e): $[\alpha]_D^{25} = +7.2$ (c=1, CHCl$_3$), $^1$H NMR (CDCl$_3$, 360MHz) $\delta$ 6.88-6.85(2H, d, $J=7.44$Hz, Ar-H), 6.69-6.65(1H, t, Ar-H), 3.08-3.02 (1H, q, CH), 2.82 (1H, b, NH), 2.16 (6H, s, ArCH$_3$), 0.96 (9H, s, CH$_3$), 0.79-0.77 (3H, d, $J=6.49$Hz, CH$_3$). $^{13}$C NMR (CDCl$_3$, 90 MHz) $\delta$ 145.78, 129.46, 129.29, 121.31, 60.29, 35.33, 27.00, 19.73, 17.99, 17.22ppm. MS m/z: 205 (M$^+$).

N-(2',6'-Dimethylphenyl)-1-Isopropylethylamine (3f): $[\alpha]_D^{25} = +15.3$ (c=1, CHCl$_3$), $^1$H NMR (CDCl$_3$, 360MHz) $\delta$ 6.90-6.88 (2H, d, $J=7.46$Hz, Ar-H), 6.71-6.67 (1H, t, Ar-H), 3.14-3.07 (1H, m, CH), 2.90 (1H, b, NH), 2.18 (6H, s, ArCH$_3$), 2.14-1.66 (1H, m, CH), 0.94-0.86 (9H, m, CH$_3$). $^{13}$C NMR (CDCl$_3$, 90 MHz) $\delta$ 145.57, 129.34, 129.07, 121.30, 57.49, 33.87, 19.91, 19.58, 17.99, 17.22ppm. MS m/z: 191 (M$^+$).

N-(2',6'-Dimethylphenyl)-1-Cyclohexylethylamine (3g): $[\alpha]_D^{25} = +32.4$ (c=1, CHCl$_3$), $^1$H NMR (CDCl$_3$, 360MHz) $\delta$ 6.90-6.88 (2H, d, $J=7.42$Hz, Ar-H), 6.72-6.68 (1H, t, Ar-H), 3.08-3.03 (1H, m, CH), 2.91 (1H, b, NH), 2.18 (6H, s, ArCH$_3$), 1.91-1.55 (5H, m, CH/CH$_2$), 1.17-1.08 (6H, m, CH$_2$), 1.54-0.87(3H, d, $J=6.51$Hz, CH$_3$). $^{13}$C NMR (CDCl$_3$, 90 MHz) $\delta$ 129.24, 128.22, 121.36, 57.29, 44.52, 30.43, 28.80, 27.12, 27.01, 26.90, 19.57ppm. MS m/z: 293 (M$^+$).

N-(p-Methoxyphenyl)-1-phenylethylamine (3h): $[\alpha]_D^{25} = +3.6$ (c=1, CHCl$_3$), $^1$H NMR (CDCl$_3$, 360MHz) $\delta$ 7.27-7.20 (4H, m, Ar-H), 7.13-7.10 (1H, t, Ar-H), 6.60-6.58 (2H, d, $J=6.69$Hz, Ar-H), 6.37-6.35(2H, d, $J=6.70$Hz, Ar-H), 4.33-4.28 (1H, m, CH), 3.58(1H, b, NH), 3.57 (6H, s, ArCH$_3$), 1.39-1.37 (3H, d, $J=6.70$Hz, CH$_3$). $^{13}$C NMR (CDCl$_3$, 90 MHz) $\delta$ 152.39, 145.95, 142.00, 129.09, 127.30, 126.38, 115.23, 115.07, 56.17, 54.74, 25.57ppm. MS m/z: 227 (M$^+$).

N-(o-Methoxyphenyl)-1-phenylethylamine (3j): $[\alpha]_D^{25} = +30.6$ (c=1, CHCl$_3$), $^1$H NMR (CDCl$_3$, 360MHz) $\delta$ 7.27-7.20 (4H, m, Ar-H), 7.13-7.10 (1H, t, Ar-H), 6.60-6.58 (2H, d, $J=6.69$Hz, Ar-H), 6.37-6.35(2H, d, $J=6.70$Hz, Ar-H), 4.33-4.28 (1H, m, CH), 3.58(1H, b, NH), 3.57 (6H, s, ArCH$_3$), 1.39-1.37 (3H, d, $J=6.70$Hz, CH$_3$). $^{13}$C NMR (CDCl$_3$, 90 MHz) $\delta$ 152.39, 145.95, 142.00, 129.09, 127.30, 126.38, 115.23, 115.07, 56.17, 54.74, 25.57ppm. MS m/z: 227 (M$^+$).

N-(2'-Methoxy-6'-methylphenyl)-1-phenylethylamine (3j): $[\alpha]_D^{25} = -85.0$ (c = 1, CHCl$_3$), $^1$H NMR (CDCl$_3$, 360MHz) $\delta$ 7.22-7.14(4H, m, Ar-H), 7.09-7.07 (1H, t, Ar-H), 6.69-6.64 (1H, t, Ar-H), 6.59-6.53 (2H, m, Ar-H), 4.44-4.39 (m, 1H, CH), 3.83 (1H, b, NH), 3.63 (3H, s, OCH$_3$), 2.16 (3H, s, ArCH$_3$), 1.39-1.37(3H, d, $J=6.73$Hz, CH$_3$). $^{13}$C NMR (CDCl$_3$, 90 MHz) $\delta$ 151.77, 146.14,
N-(2'-Methoxy-6'-methylphenyl)-1-naphthylethylamine (3k): \([\alpha]^25_d = +81.8\) (c=1, CHCl₃), \(^1\)H NMR (CDCl₃, 300 MHz) \(\delta\) 8.08-8.05 (1H, d, J = 8.06Hz, Ar-H), 7.74-7.71 (1H, d, J=7.49Hz, Ar-H), 7.61-7.59 (1H, D, J = 8.16Hz, Ar-H), 7.54-7.51(1H, d, J = 6.84Hz, Ar-H), 7.38-7.30 (3H, m, Ar-H), 6.64-6.54 (3H, m, Ar-H), 5.39-5.33(1H, m, CH), 4.08(1H, b, NH), 3.64(3H, s, OCH₃), 2.13(3H, s, ArCH₃), 1.48-1.46 (3H, d, J = 6.66Hz, CH₃). \(^{13}\)C NMR (CDCl₃, 75 MHz) \(\delta\) 151.25, 142.46, 136.52, 134.32, 131.42, 129.29, 128.92, 127.62, 126.30, 126.04, 125.76, 124.23, 123.62, 122.86, 120.87, 109.09, 56.17, 52.37, 24.32, 19.61ppm. MS m/z: 291 (M⁺).

General Procedure for deprotection of amines 3(j-k): The \(N\)-protected amine 3j/3k was dissolved in a mixture of MeOH/H₂O (4:1). CAN (4 eq) was added at 0°C, and the mixture was stirred for 6 h at the same temperature. Water was added and the solution was washed with CH₂Cl₂. The aqueous solution was made alkaline by adding 1N NaOH, and then extracted with ethyl acetate. The combined organic layer was washed with brine and dried over Na₂SO₄. The solvent was removed and the residue was subject to chromatography to afford the pure product 4j/4k.

(S)-(−)-α-Methylbenzylamine (4j): \([\alpha]^25_d = -30.4\) (c=1, CHCl₃), \(^1\)H NMR (CDCl₃, 360MHz) \(\delta\) 7.45-7.39(4H, m, Ar-H), 7.34-7.29(1H, m, Ar-H), 1.57(2H, s, NH₂), 1.48-1.46 (3H, d, J = 6.56Hz, CH₃); \(^{13}\)C NMR (CDCl₃, 90 MHz) \(\delta\)148.3, 129.2, 127.1, 125.8, 51.7, 26.2ppm.

(S)-(−)-Naphthylethylamine (4K): \([\alpha]^25_d = -32.1\) (c=1, CHCl₃), \(^1\)H NMR (CDCl₃, 360 MHz) \(\delta\) 8.16-8.14(1H, d, J = 8.25Hz, Ar-H), 7.92-7.90(1H, d, J=7.64Hz, Ar-H), 7.80-7.77(1H, d, J = 8.16Hz, Ar-H), 7.68-7.66(1H, d, J = 7.08Hz, Ar-H), 4.93-4.88 (1H, m, CH), 1.86 (2H, s, NH₂), 1.57-1.55(3H, d, J = 6.68Hz); \(^{13}\)C NMR (CDCl₃, 90 MHz) \(\delta\)143.8, 134.4, 131.2, 129.5, 127.7, 126.5, 126.2, 125.9, 123.4, 121.9, 46.9, 25.3 ppm.

References: