Supporting Information

Development of 4,4'-Substituted-XylBINAP Ligands for Highly Enantioselective Hydrogenation of Ketones

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Representative chiral GC conditions

Figure S1 $^1\text{H}\{^{31}\text{P}\}$ NMR spectrum of (*R*)-4,4'-bis(trimethylsilyl)-2,2'-bis(bis(xylyl)phosphino)-binaphthyl ((*R*)-**L**₁) in CDCl_3 .

Figure S2. $^1\text{H}\{^{31}\text{P}\}$ NMR spectrum of (*R*)-4-trimethylsilyl-2,2'-bis(bis(xylyl)phosphino)-1,1'-binaphthyl ((*R*)-**L**₂) in CDCl_3 .

Figure S3 $^1\text{H}\{^{31}\text{P}\}$ NMR spectrum of (*R*)-4,4'-diphenyl-6,6'dichloro-2,2'-bis(bis(xyl)phosphino)-1,1'-binaphthyl ((*R*)-**L**₃) in CDCl_3 .

Figure S4 $^1\text{H}\{^{31}\text{P}\}$ NMR spectrum of (*R*)-4,4',6,6'-tetramethyl-2,2'-bis(bis(xyl)-phosphino)-1,1'-binaphthyl ((*R*)-**L**₄) in CDCl_3 .

Figure S5 $^1\text{H}\{^{31}\text{P}\}$ NMR spectrum of $\text{Ru}[(R)\text{-L}_3][(\text{R},\text{R})\text{-DPEN}]\text{Cl}_2$, **26** in CDCl_3 .

Figure S6 $^1\text{H}\{^{31}\text{P}\}$ NMR spectrum of $\text{Ru}[\text{((R)-L}_4\text{)}][\text{(R,R)-DPEN}]\text{Cl}_2$, **27** in CDCl_3 .

Figure S7 $^1\text{H}\{^{31}\text{P}\}$ NMR spectrum of $\text{Ru}[\text{((R)-L}_1\text{)}][\text{(R)-DAIPEN}]\text{Cl}_2$, **28** in acetone-d_6 .

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Figure S9 $^1\text{H}\{^{31}\text{P}\}$ NMR spectrum of $\text{Ru}[(R)\text{-L}_3][(R)\text{-DAIPEN}]\text{Cl}_2$, **30** in CDCl_3 .

Figure S10 $^1\text{H}\{^{31}\text{P}\}$ NMR spectrum of $\text{Ru}[(R)\text{-L}_4][(R)\text{-DAIPEN}]\text{Cl}_2$, **31** in CDCl_3 .

Figure S11 $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of $(R,RR)\text{-25}$ (top), $(R,RR)\text{-27}$ (middle), and $(R,R)\text{-28}$ (bottom).

Figure S12 Representative chiral GC traces for the secondary alcohol products using (*R,R*)-**28**.

Materials and Methods. All of the chemicals were obtained from commercial sources and used without further purification. All of the reactions and manipulations were carried out under N₂ with the use of standard inert atmosphere and Schlenk techniques. Solvents used in reactions were dried by standard procedures. ¹H and ¹³C NMR spectra were taken on a Spectrometer at 400 and 100 MHz, respectively. ³¹P NMR spectra were obtained a Spectrometer at 161 MHz. Mass spectrometry was carried out on a triple quadrupole mass spectrometer at Department of Chemistry at UNC-CH or a MALDI-MS mass spectrometer at Department of Chemistry at Duke University. Single crystal X-ray crystallographic studies were carried out on a 1000 CCD diffractometer with MoK α radiation.

Representative Chiral GC Conditions

α -phenylethanol: ¹H NMR (CDCl₃): δ 7.33 (m, 5H), 4.85 (q, ³J_{H-H} = 6.5 Hz, 1H), 2.62 (br, 1H), 1.46 (d, ³J_{H-H} = 6.5 Hz, 3H). GC (Supelco β -Dex 120 30m $\times$ 0.25mm $\times$ 0.25 μ m; Injector: 220°C; Column: Programmed from 100 °C to 140 °C at 1°C/min; Detector: 250 °C; Carrier gas: He 1.0 mL/min) t₁ = 20.4 min; t₂ = 21.2 min.

α -phenylpropanol: ¹H NMR (CDCl₃): δ 7.31 (m, 5H), 4.55 (t, ³J_{H-H} = 6.6 Hz, 1H), 1.76 (m, 2H), 0.88 (t, ³J_{H-H} = 7.4 Hz, 3H). GC (Supelco β -Dex 120 30m $\times$ 0.25mm $\times$ 0.25 μ m; Injector: 220°C; Column: Programmed from 100°C to 140°C at 1°C/min; Detector: 250°C; Carrier gas: He 1.0 mL/min) t₁ = 28.6 min; t₂ = 29.3 min.

α -(4-methylphenyl)ethanol: ¹H NMR (CDCl₃): δ 7.23 (d, ³J_{H-H} = 8.0 Hz, 2H), 7.13 (d, ³J_{H-H} = 8.0 Hz, 2H), 4.82 (q, ³J_{H-H} = 6.3 Hz, 1H), 2.32 (s, 3H), 1.45 (d, ³J_{H-H} = 6.3 Hz, 3H). GC (Supelco β -Dex 120 30m $\times$ 0.25mm $\times$ 0.25 μ m; Injector: 220 °C; Column: Programmed from 100 °C to 140 °C at 1 °C/min; Detector: 250 °C; Carrier gas: He 1.0 mL/min) t₁ = 25.7 min; t₂ =

26.5 min.

α -(1-naphthyl)ethanol: ^1H NMR (CDCl_3): δ 8.05 (m, 1H), 7.84 (m, 1H), 7.74 (d, $^3J_{\text{H-H}} = 8.0$ Hz, 1H), 7.65 (d, $^3J_{\text{H-H}} = 7.0$ Hz, 1H), 7.45 (m, 3H), 5.59 (q, $^3J_{\text{H-H}} = 6.5$ Hz, 1H), 1.60 (d, $^3J_{\text{H-H}} = 6.5$ Hz, 3H). GC (Supelco β -Dex 120 30m $\times$ 0.25mm $\times$ 0.25 μm ; Injector: 220 $^\circ\text{C}$; Column: Programmed from 140 $^\circ\text{C}$ to 180 $^\circ\text{C}$ at 1 $^\circ\text{C}/\text{min}$ and then kept at 180 $^\circ\text{C}$ for 20 min; Detector: 250 $^\circ\text{C}$; Carrier gas: He 1.0 mL/min) $t_1 = 38.8$ min; $t_2 = 39.3$ min.

α -(2-naphthyl)ethanol: ^1H NMR (CDCl_3): δ 7.82 (m, 4H), 7.48 (m, 3H), 5.00 (m, $^3J_{\text{H-H}} = 6.5$ Hz, $^3J_{\text{H-H}} = 3.6$ Hz, 1H), 2.49 (br, 1H), 1.55 (d, $^3J_{\text{H-H}} = 6.5$ Hz, 3H). GC (Supelco β -Dex 120 30m $\times$ 0.25mm $\times$ 0.25 μm ; Injector: 220 $^\circ\text{C}$; Column: Programmed from 140 $^\circ\text{C}$ to 180 $^\circ\text{C}$ at 1 $^\circ\text{C}/\text{min}$ and then kept at 180 $^\circ\text{C}$ for 20 min; Detector: 250 $^\circ\text{C}$; Carrier gas: He 1.0 mL/min) $t_1 = 38.1$ min; $t_2 = 38.4$ min.

α -(4-tertbutylphenyl)ethanol: ^1H NMR (CDCl_3): δ 7.35 (m, 4H), 4.88 (q, $^3J_{\text{H-H}} = 6.5$ Hz, 1H), 1.71 (br, 1H), 1.50 (d, $^3J_{\text{H-H}} = 6.5$ Hz, 3H), 1.32(s, 9H). GC (Supelco β -Dex 120 30m $\times$ 0.25mm $\times$ 0.25 μm ; Injector: 220 $^\circ\text{C}$; Column: Programmed from 110 $^\circ\text{C}$ to 150 $^\circ\text{C}$ at 1 $^\circ\text{C}/\text{min}$ and then kept at 180 $^\circ\text{C}$ for 20 min; Detector: 250 $^\circ\text{C}$; Carrier gas: He 1.0mL/min) $t_1 = 38.7$ min; $t_2 = 39.1$ min.

α -(4-methoxyphenyl)ethanol: ^1H NMR (CDCl_3): δ 7.24 (d, $^3J_{\text{H-H}} = 8.4$ Hz, 2H), 6.83 (d, $^3J_{\text{H-H}} = 8.4$ Hz, 2H), 4.77 (q, $^3J_{\text{H-H}} = 6.6$ Hz, 1H), 3.76 (s, 3H), 2.57 (br, 1H), 1.42 (d, $^3J_{\text{H-H}} = 6.6$ Hz, 3H). GC (Supelco β -Dex 120 30m $\times$ 0.25mm $\times$ 0.25 μm ; Injector: 220 $^\circ\text{C}$; Column: Programmed from 130 $^\circ\text{C}$ to 170 $^\circ\text{C}$ at 1 $^\circ\text{C}/\text{min}$; Detector: 250 $^\circ\text{C}$; Carrier gas: He 1.0 mL/min) $t_1 = 20.4$ min; $t_2 = 20.7$ min.

α -(4-chlorophenyl)ethanol: ^1H NMR (CDCl_3): δ 7.27 (m, 5H), 4.80 (q, $^3J_{\text{H-H}} = 6.5$ Hz,

1H), 2.68 (br, 1H), 1.42 (d, $^3J_{\text{H-H}} = 6.5$ Hz, 3H). GC (Supelco β -Dex 120 30m $\times$ 0.25mm $\times$ 0.25 μ m; Injector: 220 °C; Column: Programmed from 120 °C to 160 °C at 1°C/min; Detector: 250°C; Carrier gas: He 1.0 mL/min) $t_1 = 23.6$ min; $t_2 = 24.4$ min.

cyclopropylphenylmethanol: ^1H NMR (CDCl_3): δ 7.40 (m, 5H), 4.02 (d, $^3J_{\text{H-H}} = 8.4$ Hz, 1H), 2.33 (br, 1H), 1.25 (m, 1H), 0.67 (m, 1H), 0.59 (m, 1H), 0.51 (m, 1H), 0.41 (m, 1H). GC (Supelco β -Dex 120 30m $\times$ 0.25mm $\times$ 0.25 μ m; Injector: 220°C; Column: Programmed from 110°C to 150°C at 1°C/min; Detector: 250°C; Carrier gas: He 1.0 mL/min) $t_1 = 34.1$ min; $t_2 = 34.5$ min.