Supporting Information for

Chiral Porous Hybrid Solids for Practical Heterogeneous Asymmetric Hydrogenation of Aromatic Ketones

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Experimental procedures.

1. Synthesis of Zr-Ru-L₁·4H₂O. A mixture of [Ru(benzene)Cl₂]₂^[1] (23 mg, 0.046 mmol) and L₁-H₄^[2] (78 mg, 0.1 mmol) in anhydrous DMF (4 mL) was heated at 100 °C under argon for 30 min and then cooled to 25 °C. (R,R)-DPEN (1,2-diphenylethylenediamine, 21.5 mg, 0.1 mmol) was added under argon. With stirring, DPEN slowly dissolved (in ~15 min) and the color of solution slowly changed from orange-red to yellow. After stirring at 80 °C for 2 hr, all the volatile components were removed under vacuum to give a yellow solid. This solid was directly used for the formation of zirconium phosphonate precatalyst.

To the above yellow solid was added degassed methanol (15 mL), and after 10 mins of vigorous stirring, the solid slowly dissolved in methanol to give a yellowish solution. To this yellowish solution was slowly added zirconium tetra(*tert*-butoxide) (40 μL, 0.1 mmol), and yellow precipitate formed immediately. The resulting mixture was refluxed overnight. After centrifugation and rinsing with degassed methanol three times, the

residue was dried under vacuum to give a yellow solid (130 mg, quantitative yield). This solid is not soluble in common organic solvents. Anal. Calcd for $C_{58}H_{54}Cl_2N_2O_{10}P_4RuZr$ (Zr-Ru-L₁·4H₂O): C, 52.5; H, 4.10; N, 2.11. Found: C, 51.5; H, 3.89; N, 2.07.

2. Synthesis of 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl-6,6'-bis(phosphonic acid), L₂-H₄.

(a) Synthesis of 2,2'-bis(triflato)-1,1'-binaphthyl-6,6'-bis(diethylphosphonate). To a 250 mL round bottom flask was added 2,2'-dihydroxy-1,1'-binaphthyl-6,6'-bis(diethylphosphonate) (7.00g, 12.5 mmol), anhydrous dichloromethane (80 mL) and triethylamine (16.0 mL, 115 mmol) under Argon. This mixture was cooled down to -50°C. With vigorous stirring, trifluoromethanesulphonic anhydride (8.0 mL, 49 mmol) was added carefully (over a ~5 min period). The reaction mixture turned from pale yellow to dark red immediately, and the mixture was allowed to stir at -50°C for 1hr and then warmed to room temperature and stirred overnight. TLC indicated complete conversion after 16 hrs. The reaction mixture was washed with water, saturated NaHCO₃, water and then dried with anhydrous MgSO₄. Silica-gel column chromatography with dichloromethane/acetone (5:1 v/v) gave 7.7g (75%) of pure product as golden oil. $^1H\{^{31}P\}$ NMR (CDCl₃): δ 8.59 (s, H₅), 8.27 (d, $^3J_{H-H}$ = 9.1Hz, H₄), 7.71 (d, $^3J_{H-H}$ = 9.1Hz, H₃), 7.69 (dd, $^3J_{H-H}$ = 8.8Hz, $^4J_{H-H}$ = 1.4Hz, H₇), 7.27 (d, $^3J_{H-H}$ = 8.8Hz, H₈), 4.16 (m, -OCH₂CH₃), 1.33 (m, -OCH₂CH₃). $^{31}P\{^1H\}$ NMR (CDCl₃): δ 17.6. $^{13}C\{^1H\}$ NMR (CDCl₃): δ 146.8, 134.7, 134.2, 134.1, 133.3, 131.4, 131.2, 128.8, 128.7, 126.9, 126.8, 123.1, 120.4, 119.6, 62.6, 62.5, 16.3, 16.2. FAB MS: 823.0 (Calc. 822.6 for M⁺)

(b) Synthesis of L₂-H₄. Under Argon, HPPPh₂ (0.5mL, 3 mmol) was added to a DMF (20 mL) solution of Ni(dppe)Cl₂ (0.28 g, 0.51 mmol) in a 50 mL Schlenk flask. The resulting red suspension was heated at 100°C for 1/2 hr, then followed by the addition of a DMF (15 mL) solution of 2,2'-bis(triflato)-1,1'-binaphthyl-6,6'-bis(diethylphosphonate) (4.1 g, 5.0 mmol) and DABCO (2.3 g, 20.5 mmol) via a cannula. The resulting greenish solution was kept at 100°C, and three additional portions of HPPPh₂ (3 × 0.5 mL) were added by syringe 1 hr, 3 hr and 7 hr later. After 36 hrs, a large amount of solid has

precipitated out. TLC indicated the disappearance of 2,2'-bis(triflate)-1,1'-binaphthyl-6,6'-bis(diethylphosphonate) after 48 hrs. The dark brown suspension was cooled to r.t., stirred for 1 hr, and then the product was filtered under Argon, washed with anhydrous DMF and acetone and dried in vacuo to give 2.6 g of partially deprotected 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl-6,6'-bis(diethylphosphonate) as white powder. NMR spectra indicated that the ethoxy groups have been partially deprotected. $^1\text{H}\{^{31}\text{P}\}$ NMR ($\text{d}_6\text{-DMSO}$): δ 8.33 (s, H_5), 7.99 (d, $^3J_{\text{H-H}} = 8.3\text{Hz}$, H_4), 7.43 (d, $^3J_{\text{H-H}} = 8.5\text{Hz}$, H_7), 7.21 (m, H_3 and Ph- H), 7.10 (m, Ph- H), 7.01 (m, Ph- H), 6.72 (d, $^3J_{\text{H-H}} = 8.5\text{Hz}$, H_8), 3.76 (m, $-\text{OCH}_2\text{CH}_3$), 1.18 (m, $-\text{OCH}_2\text{CH}_3$). $^{31}\text{P}\{^1\text{H}\}$ NMR ($\text{d}_6\text{-DMSO}$): δ 13.6 and 19.4, -15.1 and -14.4.

Under Argon, 2.6 g of partially deprotected 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl-6,6'-bis(diethylphosphonate) was stirred with bromotrimethylsilane (10 mL) at r.t. overnight. Then the volatile was removed in vacuo and anhydrous methanol (20 mL) added, and the mixture was stirred for 10 min. All the volatiles were removed under vacuum to give pale yellow powder of $\text{L}_2\text{-H}_4$ (2.44 g, 62%). $^1\text{H}\{^{31}\text{P}\}$ NMR (DMSO-d_6): δ 8.29 (s, H_5), 8.16 (d, $^3J_{\text{H-H}} = 8.8\text{Hz}$, H_4), 7.36 (d, $^3J_{\text{H-H}} = 8.3\text{Hz}$, H_7), 7.23 (m, H_3 and Ph- H), 7.02 (m, Ph- H), 6.93 (m, Ph- H), 6.70 (d, $^3J_{\text{H-H}} = 8.3\text{Hz}$, H_8). $^{31}\text{P}\{^1\text{H}\}$ NMR (DMSO-d_6): δ 13.1, -15.3. $^{13}\text{C}\{^1\text{H}\}$ NMR (DMSO-d_6): δ 144.0, 143.6, 136.7, 136.6, 136.5, 136.1, 136.0, 133.4, 133.3, 133.2, 133.1, 132.5, 132.4, 132.3, 132.0, 131.8, 131.4, 131.3, 131.2, 130.7, 129.1, 128.7, 128.4, 128.2, 126.9, 126.8, 126.2, 126.1, M.S.: 783.0 (Calc. M^+ 782.6), 822.9 (Calc. $(\text{M}+\text{K})^+$ 821.7).

3. Synthesis of Zr-Ru-L₂·4H₂O. A mixture of [Ru(benzene)Cl₂]₂^[1] (23 mg, 0.046 mmole) and L₂-H₄ (78 mg, 0.1 mmol) in anhydrous DMF (4 mL) was heated at 100 °C under argon for 30 min and then cooled to 25 °C. (R,R)-DPEN (1,2-diphenylethylenediamine, 21.5 mg, 0.1 mmol) was added under argon. With stirring, DPEN slowly dissolved and the color of solution changed from orange-red to yellow. After stirring at 80 °C for 2 hr, all the volatile components were removed under vacuum to give a yellow solid. This solid was directly used for the formation of zirconium phosphonate precatalyst.

To the yellow solid was added degassed methanol (15 mL), and after 10 mins of vigorous stirring, the solid slowly dissolved in methanol to give a yellowish solution. Zirconium tetra(*tert*-butoxide) (40 µL, 0.1 mmol) was then slowly added, and yellow precipitate formed immediately. The resulting mixture was refluxed overnight. After centrifugation and rinsing with degassed methanol for three times, the residue was dried under vacuum to give a yellow solid (130 mg, quantitative). This solid is not soluble in common organic solvents. Anal. Calcd for C₅₈H₅₄Cl₂N₂O₁₀P₄RuZr (Zr-Ru-L₂·4H₂O): C, 52.5; H, 4.10; N, 2.11. Found: C, 51.9; H, 3.88; N, 1.61.

3. Typical Procedure for Asymmetric Hydrogenation of Aromatic Ketones:

To (*R*)-solid precatalyst (6.5 mg, 5 µmol calculated based on Ru) and potassium *tert*-butoxide (5.6 mg, 50 µmol) in a test tube (reaction flask) was added 1-acetonaphthone (0.85 mL, 5 mmol) and anhydrous isopropanol (2 mL) under Argon. The test tube was quickly transferred inside a stainless steel autoclave and sealed. After purging with H₂ for 6 times, final H₂ pressure was adjusted to 700 psi. 20 hrs later, H₂ pressure was released and water (10 mL) and diethyl ether (2 mL) were added. The

organic layer was separated and passed through a mini silica-gel column. An aliquot was analyzed on GC to give the conversion and e.e.% value. The absolute configurations of enantio-enriched products from the present experiments were assigned on GC to be same as those obtained from R-BINAP-DPEN catalyzed reactions.

For the catalyst re-use experiment, the reaction mixture was centrifuged for 30 min and the liquid layer was siphoned out. The residual solid was washed with anhydrous degassed isopropanol twice. The ketone substrate and potassium *tert*-butoxide and isopropanol were then charged for subsequent round of hydrogenation reaction.

Determination of Ru Leaching Using Direct Current Plasma Spectroscopy (DCP). After the hydrogenation reaction (with a 3.3 mg of Zr-Ru-L1 solid loading), the reaction mixture was extracted with 5 mL of isopropanol and filtered to remove small particulates. Isopropanol was removed under reduced pressure, and the residue was then washed with 6.22 mL of concentrated nitric acid and diluted into 100 mL (to make a 1N HNO₃ solution). The Ru content in the 1N HNO₃ solution was determined to be less than 0.009 ppm by DCP. After adjusting for the amount of isopropanol used, we calculated the percent Ru leaching into the isopropanol solution in a typical hydrogenation reaction to be less than 0.2%.

4. Typical procedure for preparing racemic products:

In a 20 mL test tube, 1-acetonaphthone (0.85 mL, 5 mmol), sodium borohydride (0.2 g, 5.3 mmol) and ethanol (5 mL) were mixed and stirred overnight, and then carefully quenched with dilute HCl. Diethyl ether (5 mL) was added to this mixture, organic phase was separated and dried on MgSO₄, after removal of solvent, α -(1-naphthyl)ethanol was obtained as colorless oil (0.85 g, 100%).

α -phenylethanol: ¹H NMR (CDCl₃): δ 7.33 (m, 5H), 4.85 (q, ³J_{H-H} = 6.5Hz, 1H), 2.62 (br, 1H), 1.46 (d, ³J_{H-H} = 6.5Hz, 3H). GC (Supelco β -Dex 120 30m $\times$ 0.25mm $\times$

0.25 μ m, injector: 220°C, Column: from 100°C to 140°C programmed at 1°C/min, Detector: 250°C, carrier gas: He 1.0mL/min): t_1 = 20.4min; t_2 = 21.2min.

α -phenylpropanol: ^1H NMR (CDCl_3): δ 7.31 (m, 5H), 4.55 (t, $^3J_{\text{H-H}} = 6.6\text{Hz}$, 1H), 1.76 (m, 2H), 0.88 (t, $^3J_{\text{H-H}} = 7.4\text{Hz}$, 3H). GC (Supelco β -Dex 120 30m $\times$ 0.25mm $\times$ 0.25 μ m, injector: 220°C, Column: from 100°C to 140°C programmed at 1°C/min, Detector: 250°C, carrier gas: He 1.0mL/min): t_1 = 28.6min; t_2 = 29.3min.

α -(4-methylphenyl)ethanol: ^1H NMR (CDCl_3): δ 7.23 (d, $^3J_{\text{H-H}} = 8.0\text{Hz}$, 2H), 7.13 (d, $^3J_{\text{H-H}} = 8.0\text{Hz}$, 2H), 4.82 (q, $^3J_{\text{H-H}} = 6.3\text{Hz}$, 1H), 2.32 (s, 3H), 1.45 (d, $^3J_{\text{H-H}} = 6.3\text{Hz}$, 3H). GC (Supelco β -Dex 120 30m $\times$ 0.25mm $\times$ 0.25 μ m, injector: 220°C, Column: from 100°C to 140°C programmed at 1°C/min, Detector: 250°C, carrier gas: He 1.0mL/min): t_1 = 25.7min; t_2 = 26.5min.

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

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

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

α -(4-methoxyphenyl)ethanol: ^1H NMR (CDCl_3): δ 7.24 (d, $^3J_{\text{H-H}} = 8.4\text{Hz}$, 2H), 6.83 (d, $^3J_{\text{H-H}} = 8.4\text{Hz}$, 2H), 4.77 (q, $^3J_{\text{H-H}} = 6.6\text{Hz}$, 1H), 3.76 (s, 3H), 2.57 (br, 1H), 1.42 (d,

$^3J_{\text{H-H}} = 6.6\text{Hz}$, 3H). GC (Supelco β -Dex 120 $30\text{m} \times 0.25\text{mm} \times 0.25\mu\text{m}$, injector: 220°C , Column: from 130°C to 170°C programmed at $1^\circ\text{C}/\text{min}$, Detector: 250°C , carrier gas: He $1.0\text{mL}/\text{min}$): $t_1 = 20.4\text{min}$; $t_2 = 20.7\text{min}$.

α -(4-chlorophenyl)ethanol: ^1H NMR (CDCl_3): δ 7.27 (m, 5H), 4.80 (q, $^3J_{\text{H-H}} = 6.5\text{Hz}$, 1H), 2.68 (br, 1H), 1.42 (d, $^3J_{\text{H-H}} = 6.5\text{Hz}$, 3H). GC (Supelco β -Dex 120 $30\text{m} \times 0.25\text{mm} \times 0.25\mu\text{m}$, injector: 220°C , Column: from 120°C to 160°C programmed at $1^\circ\text{C}/\text{min}$, Detector: 250°C , carrier gas: He $1.0\text{mL}/\text{min}$): $t_1 = 23.6\text{min}$; $t_2 = 24.4\text{min}$.

cyclopropylphenylmethanol: ^1H NMR (CDCl_3): δ 7.40 (m, 5H), 4.02 (d, $^3J_{\text{H-H}} = 8.4\text{Hz}$, 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 $30\text{m} \times 0.25\text{mm} \times 0.25\mu\text{m}$, injector: 220°C , Column: from 110°C to 150°C programmed at $1^\circ\text{C}/\text{min}$, Detector: 250°C , carrier gas: He $1.0\text{mL}/\text{min}$): $t_1 = 34.1\text{min}$; $t_2 = 34.5\text{min}$.

5 Other General Experimental procedures.

Thermogravimetric analysis was performed in air at a scan speed of $4^\circ\text{C}/\text{min}$ on a Shimadzu TGA-50 analyzer. Infrared spectra were measured from KBr pellets on a Nicolet Magna-560 FT-IR spectrometer. Microanalysis was performed by the School of Chemical Sciences Microanalytical Laboratory at the University of Illinois at Urbana-Champaign. Scanning electron micrographs were taken on a Cambridge/Leica Stereoscan 440 Scanning electron microscope.

Nitrogen adsorption experiments were performed on a Quantachrome-1C surface area analyzer at liquid nitrogen temperature. All the surface areas were calculated based on multi-point BET plots, while the pore volumes were estimated based on BJH method.

References

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2. Kant, M.; Bischoff, S.; Siefken, R.; Gruendemann, E.; Koeckritz, A. *Eur. J. Org. Chem.*, **2001**, 477.

Figure S1. SEM micrograph of Zr-Ru-L₁ catalyst

Figure S2. SEM micrograph of Zr-Ru-L₂ catalyst

Figure S3. TGA Curves of Zr-Ru-L₁ and Zr-Ru-L₂

Figure S4. Microporous BET plot for Zr-Ru-L₁

Figure S5. BET plot for Zr-Ru-L₂

Figure S6. Microporous BET plot for Zr-Ru-L₂

Figure S7. FT-IR spectrum of Ru(L₁-H₄)(DPEN)Cl₂

Figure S8. FT-IR spectrum of Zr-Ru-L₁

Figure S9. FT-IR spectrum of Ru(L₂-H₄)(DPEN)Cl₂

Figure S10. FT-IR spectrum of Zr-Ru-L₂