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# Supporting Information

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# Chiral Porous Hybrid Solids for Highly Enantioselective Heterogeneous Asymmetric Hydrogenation of β-Keto Esters

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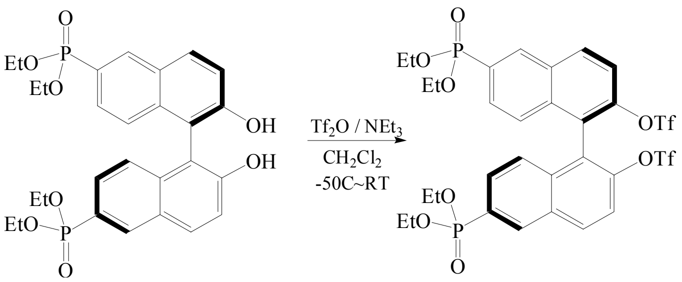
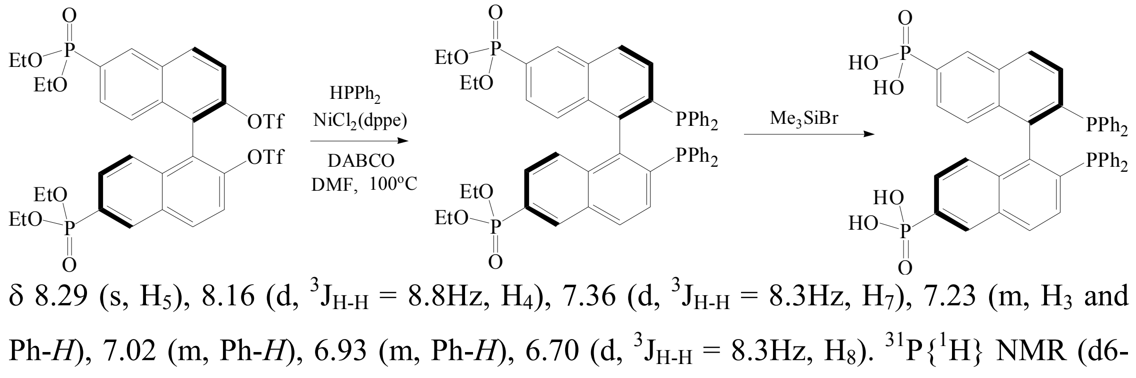
## Experimental Procedures.

1. **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 -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 $NaHCO_3$, water and then dried with anhydrous $MgSO_4$. 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 ($CDCl_3$): δ 8.59 (s, $H_5$), 8.27 (d, $^3J_{H\text{-}H}$ = 9.1Hz, $H_4$), 7.71 (d, $^3J_{H\text{-}H}$ = 9.1Hz, $H_3$), 7.69 (dd, $^3J_{H\text{-}H}$ = 8.8Hz, $^4J_{H\text{-}H}$ = 1.4Hz, $H_7$), 7.27 (d, $^3J_{H\text{-}H}$ = 8.8Hz, $H_8$), 4.16 (m, -$O\mathit{CH_2}CH_3$), 1.33 (m, -$OCH_2\mathit{CH_3}$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 17.6. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 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 $M^+$)



2. **Synthesis of 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl-6,6'-bis(phosphonic acid), $\mathbf{L_1}$-$H_4$.** Under Argon, $HPPh_2$ (0.5mL, 3 mmol) was added to a DMF (20 mL) solution of Ni(dppe)$Cl_2$ (0.28 g, 0.51 mmol) in a 50 mL Schlenk flask. The resulting red suspension was heated at 100°C for 0.5 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 $HPPh_2$ ($3 \times 0.5$ 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(triflato)-1,1’-binaphthyl-6,6’-bis(diethylphosphonate) after 48 hrs. The dark brown suspension was cooled to r.t., stirred for 1 h, 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. $^{1}H\{^{31}P\}$ NMR ($d_6$-DMSO): δ 8.33 (s, $H_5$), 7.99 (d, $^3J_{H\text{-}H} = 8.3$Hz, $H_4$), 7.43 (d, $^3J_{H\text{-}H} = 8.5$Hz, $H_7$), 7.21 (m, $H_3$ and Ph-*H*), 7.10 (m, Ph-*H*), 7.01 (m, Ph-*H*), 6.72 (d, $^3J_{H\text{-}H} = 8.5$Hz, $H_8$), 3.76 (m, -O$CH_2$$CH_3$), 1.18 (m, -O$CH_2CH_3$). $^{31}P\{^{1}H\}$ NMR ($d_6$-DMSO): δ 13.6 and 19.4, -15.1 and -14.4.

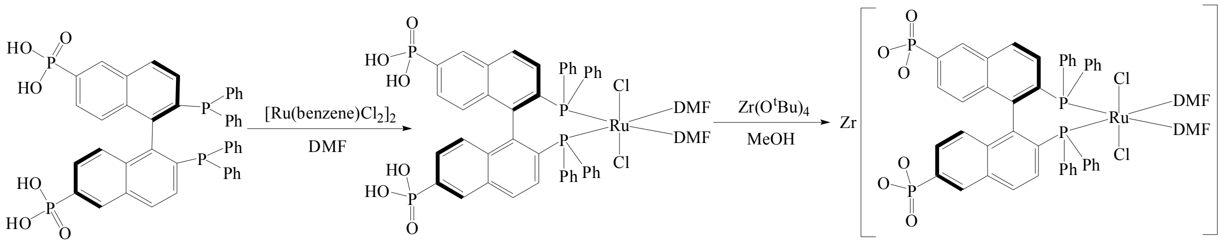
Under Argon, 2.6 g of partially deprotected 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl-6,6'-bis(diethylphosphonate) was stirred with bromotrimethylsilane (10 mL) at r.t. overnight. Then the volatile was removed in vacuo and anhydrous methanol (20 mL) added, and the mixture was stirred for 10min. All the volatiles were removed under vacuum to give pale yellow powder of $\mathbf{L_1}$-$H_4$ (2.44 g, 62%). $^{1}H\{^{31}P\}$ NMR (d6-DMSO): δ 8.29 (s, $H_5$), 8.16 (d, $^3J_{H\text{-}H} = 8.8$Hz, $H_4$), 7.36 (d, $^3J_{H\text{-}H} = 8.3$Hz, $H_7$), 7.23 (m, $H_3$ and Ph-*H*), 7.02 (m, Ph-*H*), 6.93 (m, Ph-*H*), 6.70 (d, $^3J_{H\text{-}H} = 8.3$Hz, $H_8$). $^{31}P\{^{1}H\}$ NMR (d6-



DMSO): δ 13.1, -15.3. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): 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. $(M+K)^+$ 821.7).

3. **Synthesis of Zr[Ru($L_1$)($DMF)_2Cl_2$]•2MeOH**. A mixture of $[Ru(benzene)Cl_2]_2$[1] (46 mg, 0.092 mmole) and **L**$_1$-$H_4$ (156 mg, 0.2 mmol) in DMF (4 mL) was heated at 100°C under argon for 40 min and then cooled to 40 °C. All the volatile components were removed under vacuum and the dark-red solid was directly used for the formation of zirconium phosphonate.

To the dark red solid intermediate was added anhydrous degassed methanol (40 mL) and after 2 hrs of vigorous stirring, the solid slowly dissolved in methanol to give dark red solution. Zirconium tetra(tert-butoxide) (80 μL, 0.2 mmol) was then slowly added, and brown precipitate formed immediately. The resulting mixture was refluxed overnight. After centrifugation and rinsing with anhydrous methanol for three times, the residue was dried under vacuum to gave a dark-brown solid (240 mg, 96%). This dark-brown solid is not soluble in common organic solvents including methanol. Anal. calc. for $C_{52}H_{52}Cl_2N_2O_{10}P_4RuZr$, Zr[Ru(**L**$_1$)$(DMF)_2Cl_2$]•2MeOH: C, 49.9; H, 4.19; N, 2.24; Cl, 5.66; P, 9.90; Ru, 8.07; Zr, 7.29%. Found: C, 50.6; H, 3.87; N, 2.54; Cl, 4.98; P, 9.32; Ru, 7.87; Zr, 7.70%.

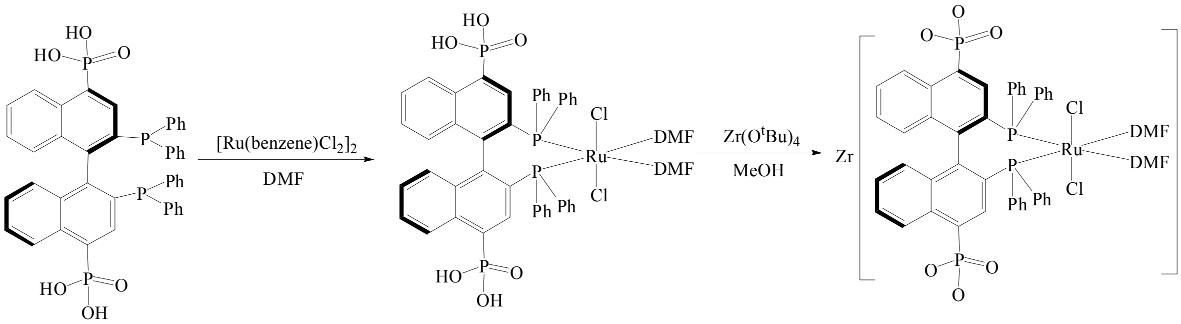


Zr-Ru-**L**$_1$

4. **Synthesis of Zr[Ru($L_2$)($DMF)_2Cl_2$]•2MeOH**. A mixture of $[Ru(benzene)Cl_2]_2$[1] (23 mg, 0.046 mmole) and **L**$_2$-$H_4$ (78 mg, 0.1 mmol) in DMF (2 mL) was heated at 100°C under argon for 40 min and then cooled to 40 °C. All the volatile components

were removed under vacuum and the dark-red solid was directly used for the formation of zirconium phosphonate.

To the dark red solid intermediate was added anhydrous degassed methanol (20 mL) and after 2 hrs of vigorous stirring, the solid slowly dissolved in methanol to give dark red solution. Zirconium tetra(tert-butoxide) (40 μL, 0.1 mmol) was then slowly added, and brown precipitate formed immediately. The resulting mixture was refluxed overnight. After centrifugation and rinsing with anhydrous methanol for three times, the residue was dried under vacuum to gave a dark-brown solid (120 mg, 96%). This dark-brown solid is not soluble in common organic solvents including methanol. Anal. calc. for $C_{52}H_{52}Cl_2N_2O_{10}P_4RuZr$, Zr[Ru(**L**$_2$)(DMF)$_2$Cl$_2$]•2MeOH: C, 49.9; H, 4.19; N, 2.24; Cl, 5.66; P, 9.90; Ru, 8.07; Zr, 7.29%. Found: C, 49.3; H, 3.89; N, 2.01; Cl, 6.03; P, 9.50; Ru, 7.65; Zr, 6.85%.



Zr-Ru-**L**$_2$

## 5. Typical Procedures for Asymmetric Hydrogenation of β-Keto Ester.

Solid catalyst (6.0 mg, 5 μmole) was weighted into a test tube (reaction flask) in drybox, and to this tube was added methyl acetoacetate (55 μL, 0.5 mmol) and anhydrous methanol (1 mL) under Argon. The test tube was quickly transferred inside a stainless steel autoclave, and sealed. After purging with Hydrogen for 6 times, final $H_2$ pressure was adjusted to 1400 psi or 700 psi. 20 hrs later, $H_2$ pressure was released and methanol was removed in vacuo. The hydrogenated product was extracted with diethyl ether and passed through a mini silica-gel column to get rid of residual solid. The conversions were assessed based on the integration of $^1$H NMR peaks of the products and starting materials, while the e.e. values were determined using GC.

For the catalyst re-use experiments, the reaction mixture was centrifuged for 30 minutes and the liquid layer was siphoned out. The residual solid was washed with anhydrous degassed methanol twice. The β-keto ester substrates and methanol were then charged for another round of hydrogenation reaction.

Racemic samples were prepared using rac-BINAP as ligand, and were used to establish GC conditions. The absolute configurations of enantio- enriched products from the present experiments were assigned on GC to be same as those samples obtained from R-BINAP catalyzed reactions.

Methyl 3-hydroxybutyrate: $^{1}$H NMR ($CDCl_3$): δ 4.12 (m, $^{3}J_{H\text{-}H}$ = 6.2Hz, $^{3}J_{H\text{-}H}$ = 1.0Hz, 1H), 3.62 (s, 3H), 3.35(br, 1H), 2.39(m, $^{3}J_{H\text{-}H}$ = 2.8Hz, $^{3}J_{H\text{-}H}$ = 0.5Hz, 2H), 1.14 (d, $^{3}J_{H\text{-}H}$ = 6.2Hz, 3H). GC (Supelco γ-Dex 225 30m × 0.25mm × 0.25μm, injector: 220°C, Column: 70°C (iso), Detector: 250°C, carrier gas: He 1.0mL/min): $t_1$ = 24.7min; $t_2$ = 26.8min.

*Iso*-propyl 3-hydroxybutyrate: $^{1}$H NMR ($CDCl_3$): δ 4.97 (m, $^{3}J_{H\text{-}H}$ = 6.3Hz, 1H), 4.12(m, $^{3}J_{H\text{-}H}$ = 6.3Hz, 1H), 3.30(br, 1H), 2.34(m, 2H), 1.18 (d, $^{3}J_{H\text{-}H}$ = 6.3Hz, 6H), 1.15 (d, $^{3}J_{H\text{-}H}$ = 6.3Hz, 3H). GC (Supelco γ-Dex 225 30m × 0.25mm × 0.25μm, injector: 220°C, Column: 65°C (iso), Detector: 250°C, carrier gas: He 1.2mL/min): $t_1$ = 32.2min; $t_2$ = 33.4min.

*Tert*-butyl 3-hydroxybutyrate: $^{1}$H NMR ($CDCl_3$): δ 4.97 (m, $^{3}J_{H\text{-}H}$ = 6.3Hz, $^{3}J_{H\text{-}H}$ = 8.6Hz, $^{3}J_{H\text{-}H}$ = 3.9Hz, 1H), 3.20(br, 1H), 2.34 (m, $^{2}J_{H\text{-}H}$ = 16.4Hz, $^{3}J_{H\text{-}H}$ = 8.6Hz, $^{3}J_{H\text{-}H}$ = 3.9Hz, 2H), 1.44 (s, 9H), 1.17 (d, $^{3}J_{H\text{-}H}$ = 6.3Hz, 3H). GC (Supelco γ-Dex 225 30m × 0.25mm × 0.25μm, injector: 220°C, Column: 65°C (iso), Detector: 250°C, carrier gas: He 1.2mL/min): $t_1$ = 34.8min; $t_2$ = 35.8min.

Methyl 2,2-dimethyl-3-hydroxybutyrate: $^{1}$H NMR ($CDCl_3$): δ 3.82 (m, $^{3}J_{H\text{-}H}$ = 6.7Hz, 1H), 3.64 (s, 3H), 2.84(br, 1H), 1.11 (s, 6H), 1.07 (d, $^{3}J_{H\text{-}H}$ = 6.7Hz, 3H). GC (Supelco γ-Dex 225 30m × 0.25mm × 0.25μm, injector: 220°C, Column: from 60°C to 120°C programmed at 1.5°C/min, Detector: 250°C, carrier gas: He 1.2mL/min): $t_1$ = 32.2min; $t_2$ = 33.4min.

Ethyl 3-hydroxyvalerate: $^{1}$H NMR ($CDCl_3$): δ 4.16 (m, $^{3}J_{H\text{-}H}$ = 7.1Hz, 2H), 3.92 (m, $^{3}J_{H\text{-}H}$ = 6.6Hz, $^{3}J_{H\text{-}H}$ = 9.0Hz, $^{3}J_{H\text{-}H}$ = 3.1Hz, 1H), 2.44 (m, $^{2}J_{H\text{-}H}$ = 16.4Hz, $^{3}J_{H\text{-}H}$ =

9.0Hz, ${}^{3}J_{H\text{-}H}$ = 3.1Hz, 2H), 1.51 (m, ${}^{3}J_{H\text{-}H}$ = 6.6Hz, ${}^{3}J_{H\text{-}H}$ = 7.4Hz, 2H), 1.26 (t, ${}^{3}J_{H\text{-}H}$ = 7.1Hz, 3H), 0.94 (t, ${}^{3}J_{H\text{-}H}$ = 7.4Hz, 3H). GC: (Supelco γ-Dex 225 30m × 0.25mm × 0.25μm, injector: 220°C, Column: 75°C (iso), Detector: 250°C, carrier gas: He 1.0mL/min): $t_1$ = 29.1min; $t_2$ = 29.6min.

Ethyl 3-hydroxy-3-phenyl-propionate: ${}^{1}$H NMR ($CDCl_3$): δ 7.29 (m, 5H), 5.08 (m, ${}^{3}J_{H\text{-}H}$ = 8.6Hz, ${}^{3}J_{H\text{-}H}$ = 3.1Hz, 1H), 4.12 (m, ${}^{3}J_{H\text{-}H}$ = 7.1Hz, 2H), 3.61(br, 1H), 2.68 (m, ${}^{2}J_{H\text{-}H}$ = 16.2Hz, ${}^{3}J_{H\text{-}H}$ = 9.0Hz, ${}^{3}J_{H\text{-}H}$ = 3.9Hz, 2H), 1.21 (t, ${}^{3}J_{H\text{-}H}$ = 7.1Hz, 3H). GC (Supelco γ-Dex 225 30m × 0.25mm × 0.25μm, injector: 220°C, Column: from 70°C to 180°C programmed at 1.5°C/min, Detector: 250°C, carrier gas: He 1.0mL/min): $t_1$ = 60.5min; $t_2$ = 60.8min.

6. Other General Experimental procedures.

Thermogravimetric analysis was performed in air at a scan speed of 4 °C/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.

## 7. General Procedure for Determination of Ru Leaching Using Direct Current Plasma Spectroscopy (DCP).

After the hydrogenation reaction, the reaction mixture was extracted with (2×50 mL) of diethyl ether. In both extractions, the solvent mixture was allowed to stir for ½ hr and filtered to remove particulates. The methanol/diethyl ether 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 $HNO_3$ solution). The Ru content in the 1N $HNO_3$ solution was determined to be less than 0.003 ppm. The percent Ru leaching was calculated based on a total of 10 mL of ether used for typical extraction of organic products.

Reference:

1. Zelonka, R.A.; Baird. M.C. *Can. J. Chem.*, **1972**, *50*, 3063.

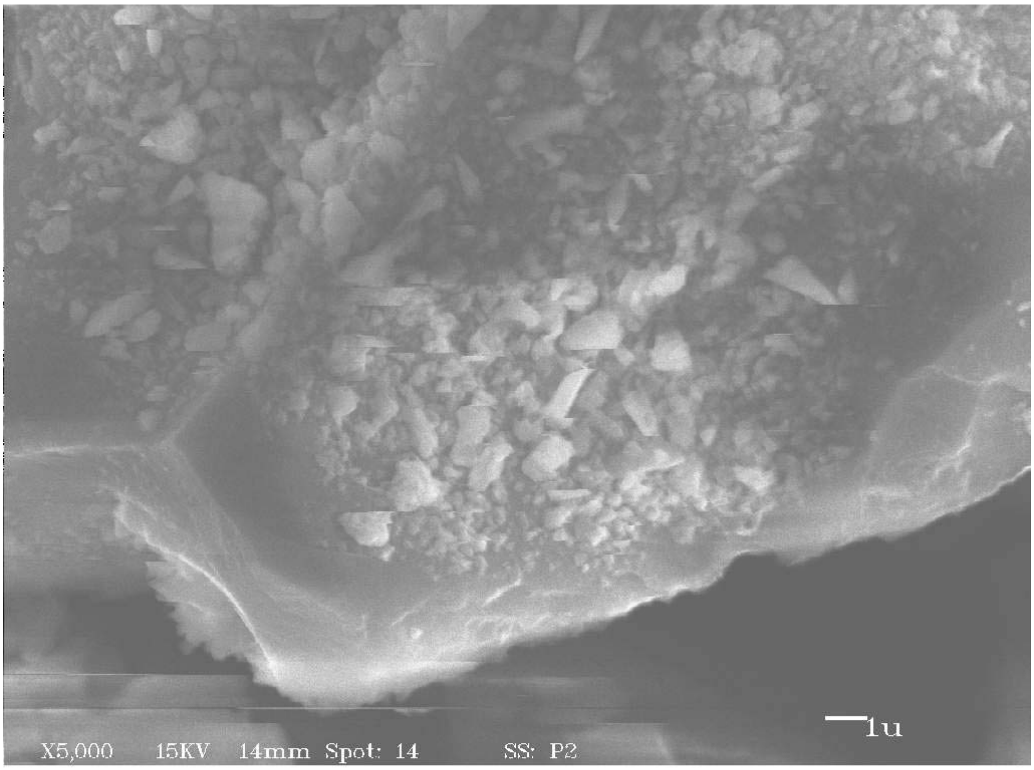


Figure S1. SEM micrograph of Zr-Ru-$\mathbf{L}_2$ solid precatalyst

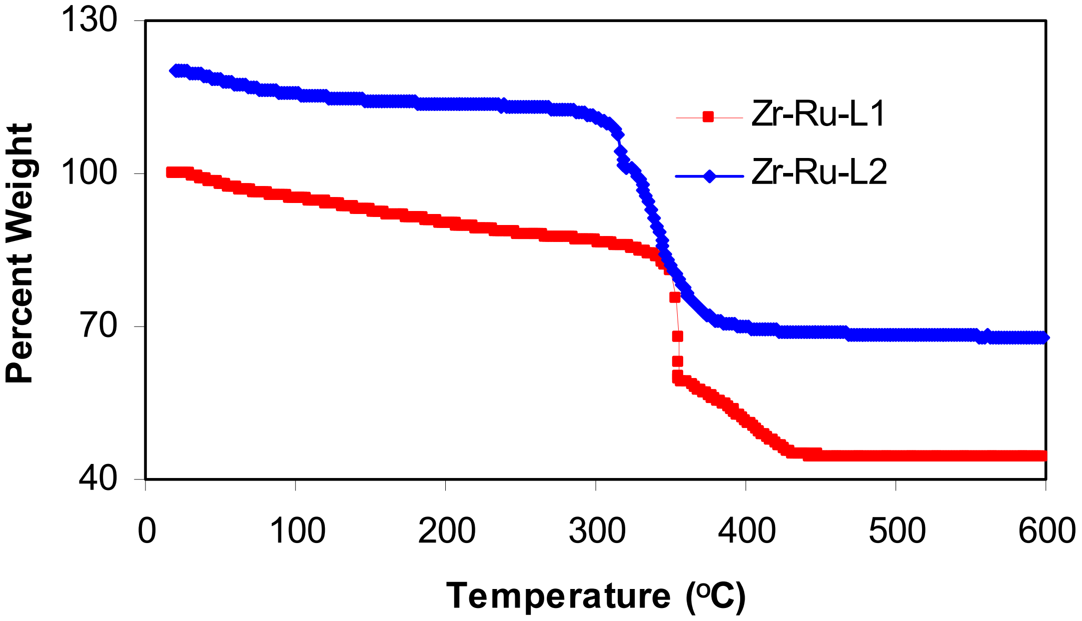


Figure S2. TGA Curves of Zr-Ru-$\mathbf{L}_1$ and Zr-Ru-$\mathbf{L}_2$.

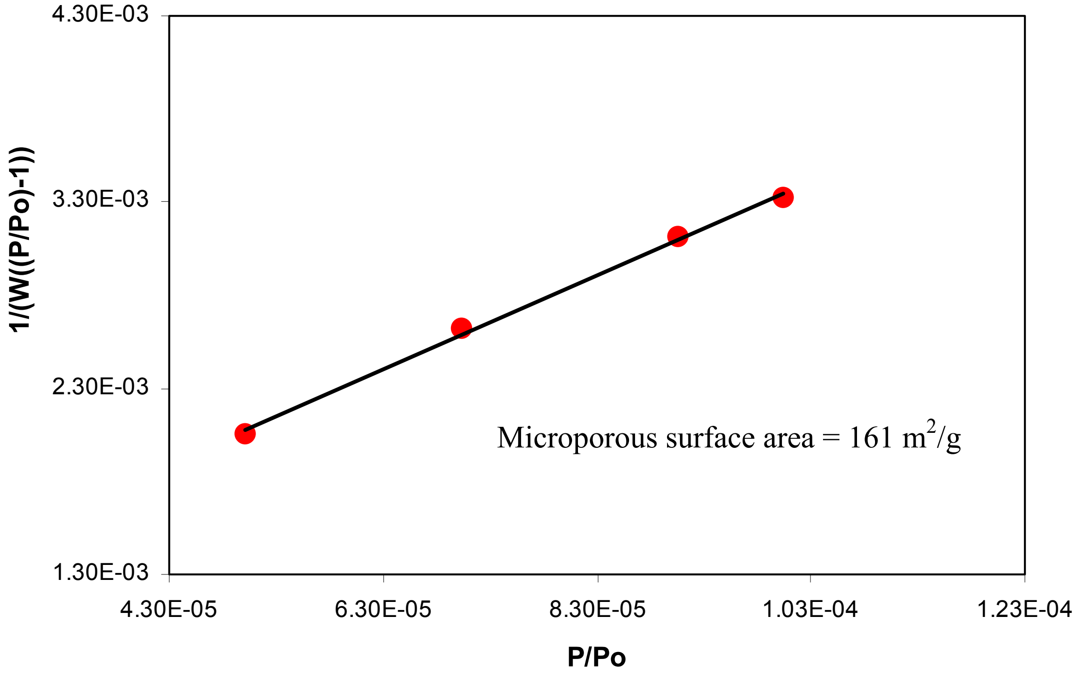


Figure S3. Microporous BET plot for Zr-Ru-$\mathbf{L}_1$

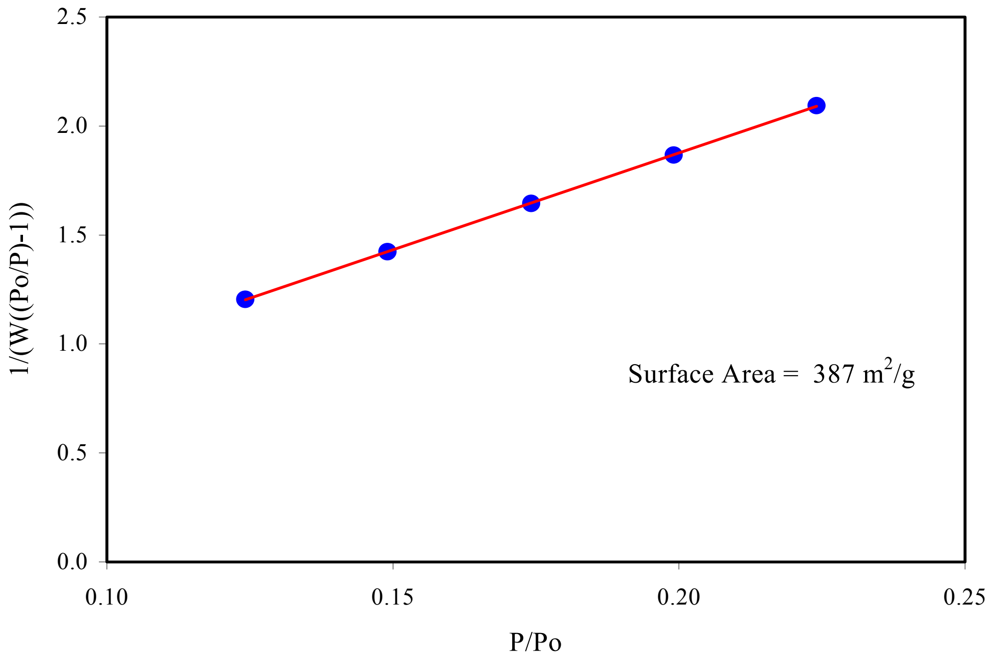


Figure S4. BET plot for Zr-Ru-$\mathbf{L}_2$

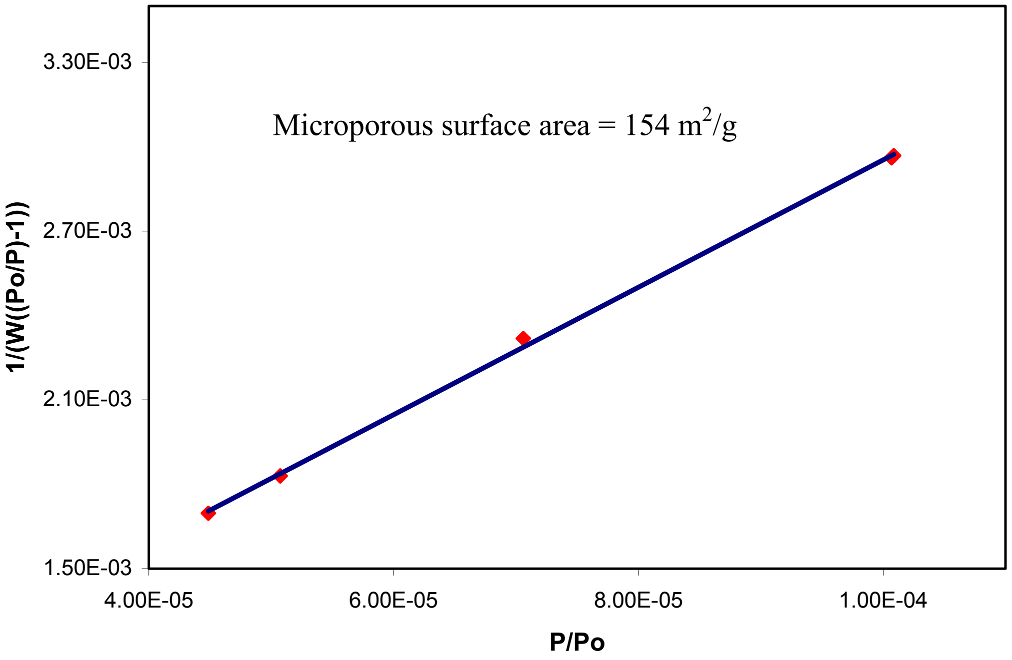


Figure S5. Microporous BET plot for Zr-Ru-$\mathbf{L}_2$

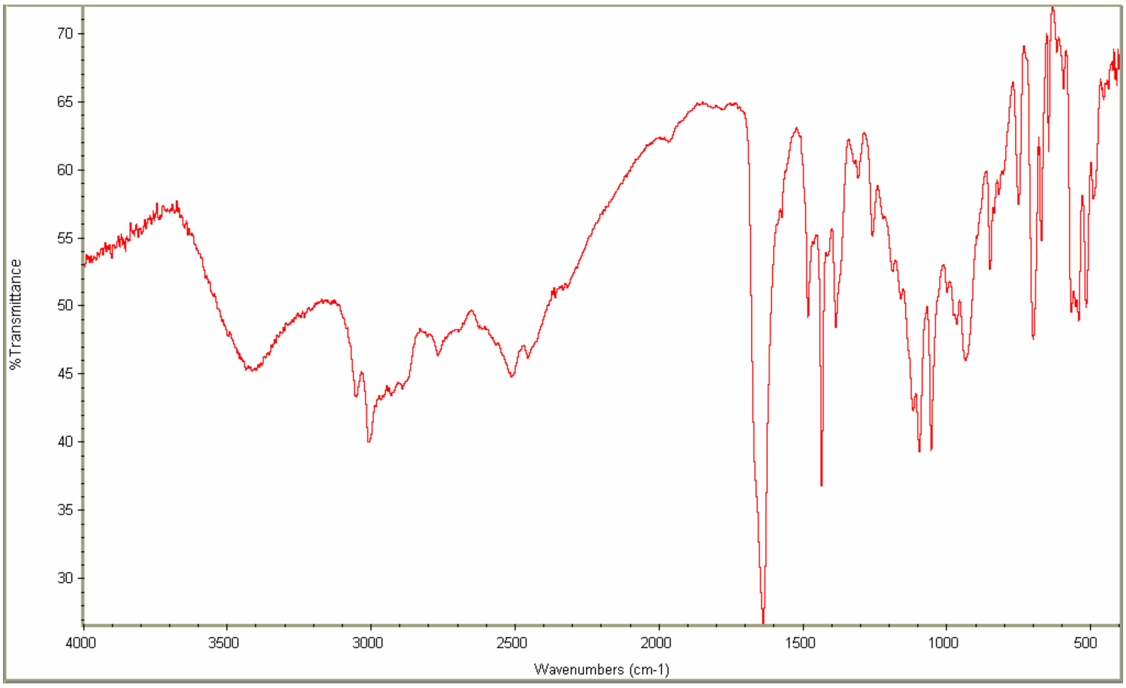


Figure S6. FT-IR spectrum of Ru($\mathbf{L_1}$-$H_4$)(DMF)$_2$Cl$_2$.

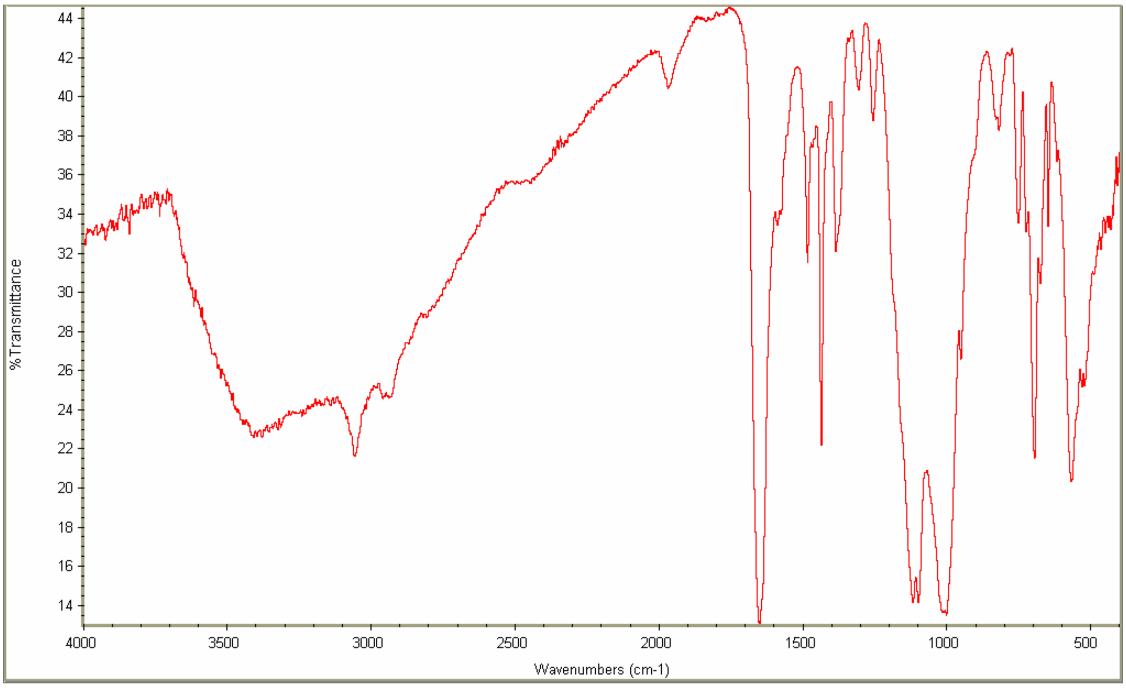


Figure S7. FT-IR spectrum of Zr-Ru-$\mathbf{L}_1$.

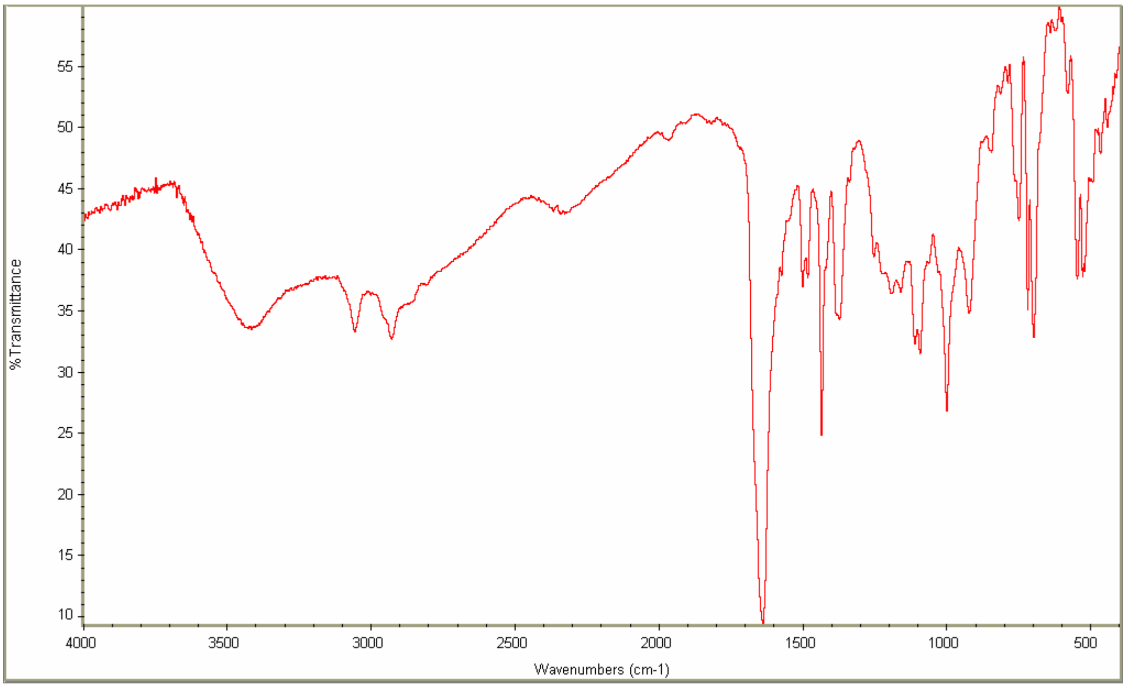


Figure S8. FT-IR spectrum of Ru($\mathbf{L_2}$-$H_4$)(DMF)$_2$Cl$_2$.

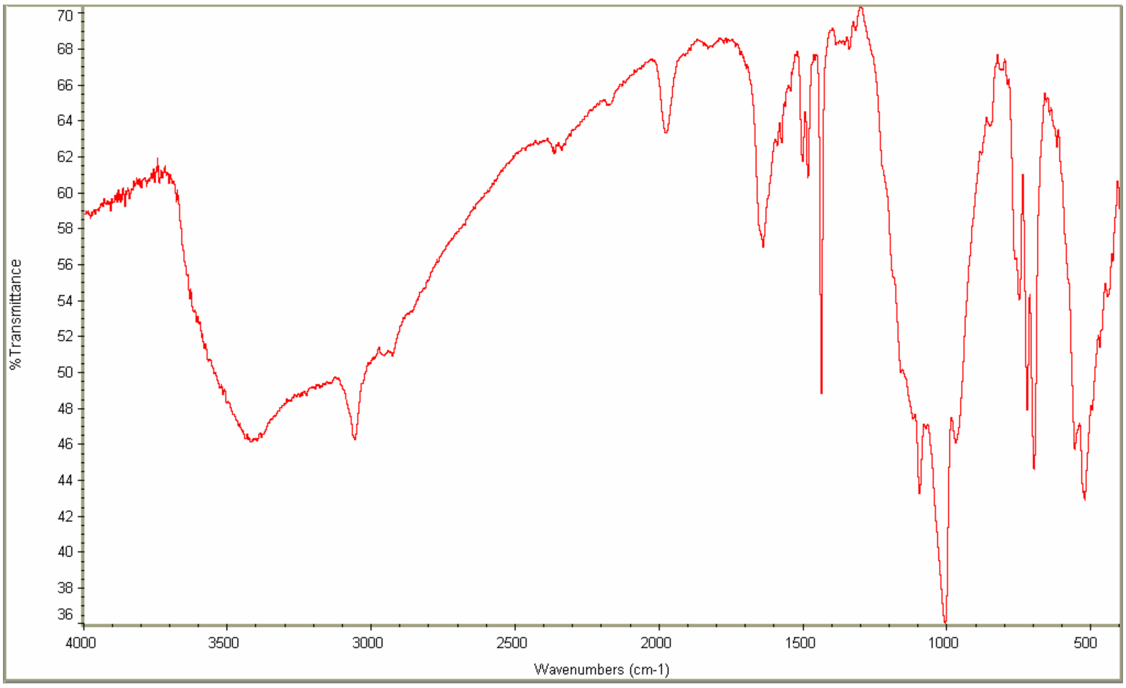


Figure S9. FT-IR spectrum of Zr-Ru-$\mathbf{L}_2$.