

## Enantioselective catalysis with a chiral, phosphine-containing PMO material.

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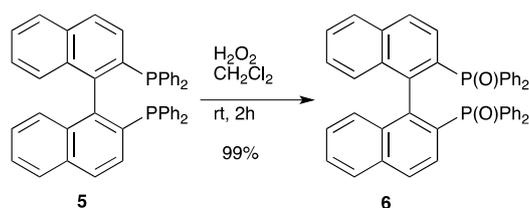
### 1. General information

2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (BINAP), dichloro(benzene)ruthenium(II) dimer, chloro(1,5-cyclooctadiene)rhodium(I) dimer and (1R,2R)-(+)-1,2-diphenylethylenediamine ((R,R)-DPEN) were purchased from Strem and used without further purification. Triethoxysilane and trifluoromethylsulfonic anhydride were purchased from TCI America. Toluene was obtained dry from a solvent purification system fitted with alumina columns. THF and hexane were freshly distilled from sodium/benzophenone ketyl. Triethylamine was purchased from Aldrich and distilled fresh from CaH<sub>2</sub> prior to use. Isopropanol was dried by storing with activated 4Å molecular sieves under argon then degassed by freeze-thaw technique prior to use. *N,N*-dimethylformamide (DMF), dichloromethane and acetonitrile were purchased dry from EMD and used without any further treatment. Methanol was purchased dry from EMD and degassed by freeze-thaw technique prior to use. Hydrochloric acid was purchased from Fisher scientific and used without further treatment. Hydrogen gas was purchased from Praxair and used through high-pressure tubings and autoclaves. The substrate for **Table 3 entry 6** (methyl 3-oxo-3-(4-methoxyphenyl)propanoate) was synthesized as reported by Vu *et al.*<sup>1</sup> The other chemicals were purchased from Sigma-Aldrich, Acros or Alfa Aesar and used without further treatment unless otherwise noted. Nitrogen adsorption experiments were performed using a Micromeritics ASAP 2010 physisorption analyzer with nitrogen gas as the adsorbate at 77 K. Samples were degassed at 80 °C for at least 8 hours and until 10-3 mm Hg pressure was maintained. Solid-state CP MAS <sup>13</sup>C, <sup>29</sup>Si and <sup>31</sup>P NMR measurements were recorded on a Bruker Avance 600 spectrometer operating at 150.9, 119.2 and 243.0 MHz for <sup>13</sup>C, <sup>29</sup>Si and <sup>31</sup>P respectively, and using a Bruker 5 mm CP MAS probe. A typical spinning

rate for CP MAS experiments is 11 kHz. A 2 ms cross polarization contact time was used to acquire  $^{13}\text{C}$ ,  $^{29}\text{Si}$  and  $^{31}\text{P}$  CP MAS spectra with a repetition delay of 2 s. The number of scans was in excess of 600, 2400 and 3000 for  $^{13}\text{C}$ ,  $^{29}\text{Si}$  and  $^{31}\text{P}$  respectively to obtain sufficient signal.  $^{13}\text{C}$ , and  $^{29}\text{Si}$  MAS spectra were referenced to tetramethylsilane, and  $^{31}\text{P}$  was referenced to phosphoric acid. TEM images were obtained using a 200keV JEOL 2010 STEM operated in both transmission and STEM modes. In STEM mode a Gatan High Angle Annular Dark Field Detector was used to image the sample. The sample was prepared by placing a small amount of powder in ethanol and sonicating for 5 minutes. 20 ul of the solution was pipetted onto a carbon coated, 200 mesh copper grid. Powder X-ray diffraction measurements were run on an automated Siemens/Bruker AXS D5000 diffractometer. The system is equipped with a high power line focus Cu- $\alpha$  source operating at 50 kV/35mA. A solid-state Si/Li Kevex detector was used for removal of k-beta lines. The diffraction patterns were collected on a theta/2-theta Bragg-Brentano reflection geometry with fixed slits. The slits were set up appropriately for both low- and wide-angle ranges in order to ensure the optimal quality of the diffraction patterns. A step scan mode was used for data acquisition with step size of 0.020 2-theta and counting time of 3.0 s per step for low-theta scans and 1.0 s per step for the wide range scans. ICPMS was measured by Robertson Microlit Laboratories (Ledgewood, NJ, U.S.A.). Centrifugation was performed with a Damon IEC HN-SII.

## 2. Synthesis Procedures

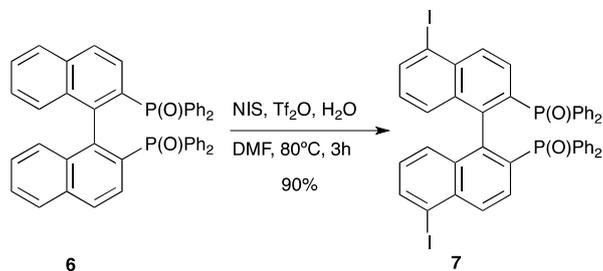
Diphenyl-[1,1'-binaphthalene]-2,2'-diylester (BINAPO) (**6**)



This procedure is derived from a literature that Lemaire et al reported<sup>2</sup> and the spectra obtained matched with those reported. In a 100mL round-bottom flask were placed BINAP (1.0 g, 1.6 mmol) and 8.0mL of CH<sub>2</sub>Cl<sub>2</sub>. The mixture was cooled in an ice water bath and 4.0mL of hydrogen peroxide (35%) was then added. The mixture was stirred for 2h. After 50mL of water was added, the organic layer was separated. The aqueous layer was extracted with 20mL of CH<sub>2</sub>Cl<sub>2</sub> twice. The combined organic layer was washed with brine, dried over sodium sulfate, and concentrated by rotary evaporator to give a white powder (1.0 g, mmol, quantitative yield). This product was used without further purification.  $^1\text{H}$  NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.88 (dd, 2H,  $J = 8, 3.5$  Hz), 7.84 (d, 2H,  $J = 7.5$  Hz), 7.73 (dd, 4H,  $J = 11, 6.5$  Hz), 7.35 – 7.94 (m, 12H), 7.22 – 7.32 (m, 8H), 6.79 – 6.86 (m, 4H).  $^{31}\text{P}$  NMR (135 MHz, CDCl<sub>3</sub>):  $\delta$  29.48. EI-HRMS (MH<sup>+</sup>) found 654.1889 m/z (calc.

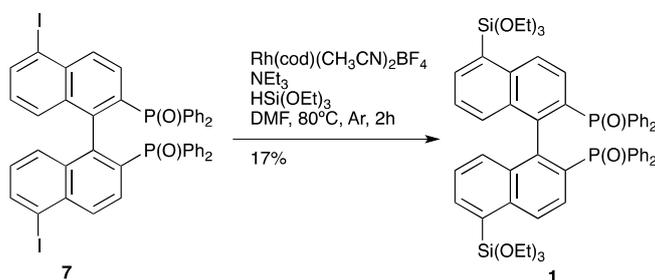
654.1878).

### 2,2'-Bis(diphenylphosphinyl)-5,5'-diiodo-1,1'-binaphthyl (**7**)



This procedure is modified from Olah *et al.*<sup>3</sup> and the spectra obtained matched with those reported in the literature.<sup>4</sup> To a solution of BINAPO (**6**) (3.15 g, 4.8 mmol) in MeCN (48 mL) was added Tf<sub>2</sub>O (4.05 mL, 6.77 g, 24 mmol, 5.0 equiv.) and H<sub>2</sub>O (0.44 mL, 24 mmol, 5.0 equiv.). Resulting orange solution was cooled in an ice-bath and then NIS (3.24 g, 14.4 mmol, 3.0 equiv.) was added portion by portion. After 15 min. of stirring in an ice-bath, the mixture was heated at 80°C for 3 hours. The reaction mixture was quenched with sodium thiosulfate and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic phase was washed with brine and water, dried over sodium sulfate, and concentrated by rotary evaporator. The crude brown oil was chromatographed through silica gel column (AcOEt/hexane = 3/1 - 2/1) to give pale yellow solid. (3.92 g, 90% yield). <sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>): δ 8.18 (d, 2H, *J* = 8.6 Hz), 7.97 (d, 2H, *J* = 7.2 Hz), 7.73 (dd, 4H, *J* = 11.7, 7.9 Hz), 7.54 (dd, 2H, *J* = 11.0, 9.3 Hz), 7.41 (m, 8H), 7.33 (m, 4H), 7.27 (m, 4H), 6.76 (d, 2H, *J* = 8.5 Hz), 6.51 (t, 2H, *J* = 7.7 Hz). <sup>13</sup>C NMR (125MHz, CDCl<sub>3</sub>): δ 141.39, 139.44, 135.68, 134.82, 132.71, 132.25, 131.90, 130.36, 130.21, 129.81, 128.77, 128.46, 128.34, 127.26, 99.17. <sup>31</sup>P NMR (135 MHz, CDCl<sub>3</sub>): δ 30.02. mp = 347-348 °C (decomp). EI-HRMS (MH<sup>+</sup>) found 906.9870 m/z (calc. 906.9888).

### 2,2'-Bis(diphenylphosphinyl)-5,5'-bis(triethoxysilyl)-1,1'-binaphthyl (**1**)



This procedure was adapted from Masuda *et al.*<sup>5,6</sup> Rh(cod)(CH<sub>3</sub>CN)<sub>2</sub>BF<sub>4</sub> was prepared as Collman *et al.* reported<sup>7</sup>, but used AgBF<sub>4</sub> instead of Ph<sub>3</sub>CBF<sub>4</sub>. This rhodium catalyst (8.0 mg, 0.021 mmol, 7.6 mol %) and **7** (252.0 mg, 0.278 mmol) were combined in a small schlenk tube under argon. DMF (1 mL) was added to the tube followed by triethylamine (230 μL, 1.65 mmol). This solution was stirred in an ice bath for 15 min before the addition of triethoxysilane (200 μL, 1.09 mmol). The

reaction was then stirred for 2 hours at 80 °C. The DMF was then removed under high vacuum and the residue was dissolved in ether. This solution was passed through a plug of celite/charcol to remove any residual rhodium and reduced byproduct.<sup>8</sup> The filtrate was then concentrated to some extent and purified by silica gel flash column chromatography (THF/Hexane = 3/2) very quickly, otherwise most of the product was captured by silica gel. This gave 45.5 mg (0.047 mmol, 17% yield) of **1** as pail yellow oil. Because this compound is sensitive for moisture, it was kept in a flask charged with argon, then stored in a fridge. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.37 (dd, 2H, *J* = 8.8, 2.0 Hz) 7.79 (dd, 2H, *J* = 6.6, 1.0 Hz), 7.74 (dd, 4H, *J* = 12.2, 7.0 Hz), 7.46 (dd, 2H, *J* = 11.6, 8.8 Hz), 7.38 - 7.41 (m, 12H), 7.18 (td, 4H, *J* = 7.6, 2.4 Hz), 6.72 (d, 2H, *J* = 8 Hz), 6.63 (dd, 2H, *J* = 8.4, 6.8 Hz), 3.96 (q, 12H, *J* = 7.0 Hz), 1.31 (t, 18H, *J* = 7.0 Hz). <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>): δ 138.11, 137.49, 132.82, 132.71, 132.34, 132.26, 131.41, 131.09, 130.32, 129.04, 128.45, 128.32, 128.10, 127.98, 124.99, 59.22, 18.58. <sup>31</sup>P NMR (135 MHz, CDCl<sub>3</sub>): δ 28.50. MALDI-HRMS (MH<sup>+</sup>) found 979.3370 m/z (calc. 979.3380).

### 3. Material Preparation

This procedure is modified from our previously reported procedure<sup>9</sup>. Molar ratio of the component is Si / Brij 76 / water / HCl / NaCl / EtOH = 1.00 / 0.533 / 600 / 8.40 / 19.0 / 18.4. For example, **5%BINAPO-PMO**: Brij 76 (1.93 g) was dissolved in deionized water (55 mL) and conc. HCl (3.5 mL), it was stirred at 60 °C in an oil bath for 1 hour before the addition of NaCl (5.68 g), then the solution was stirred further 3 hours at the same temperature. To this micelle solution was added ethanol solution of siloxane precursors (**1** (250 mg, 0.26 mmol) and **2** (2.32 g, 4.85 mmol) in 2.8 mL of ethanol) dropwise under vigorous stirring. The resulting mixture was stirred for 24 hours at 60 °C, and was aged for further 48 hours at 90 °C. The precipitated white powder was recovered carefully by vacuum filtration using a Kiriya-funnel, and washed with copious amount of ethanol, water and acetone in this order. The surfactant was removed by using a Soxhlet extractor (EtOH with 1% of HCl) for 24 hours. Again recovered powder was dried under high vacuum at 80 °C over night, gave 1.62 g of 5%BINAP-PMO.

### 4. Post-grafted Modification

Prior to every step of modification, the material was dried under high vacuum (0.2 mmHg) at 80 °C over night.

#### Trimethylsilyl (TMS)-capping of free silanols

In a 250 mL round bottom flask, **5%BINAPO-PMO** (1.5 g) was suspended in dry hexane (60 mL). To this suspension

was added hexamethyldisilazane (4 mL, excess) then stirred for 24 hours at 65 °C in an oil bath. The material was filtered, washed with copious amount of ethyl acetate, ethanol and acetone, then dried under high vacuum (0.2 mmHg) at 80 °C over night. 1.5 g of white powder was recovered.

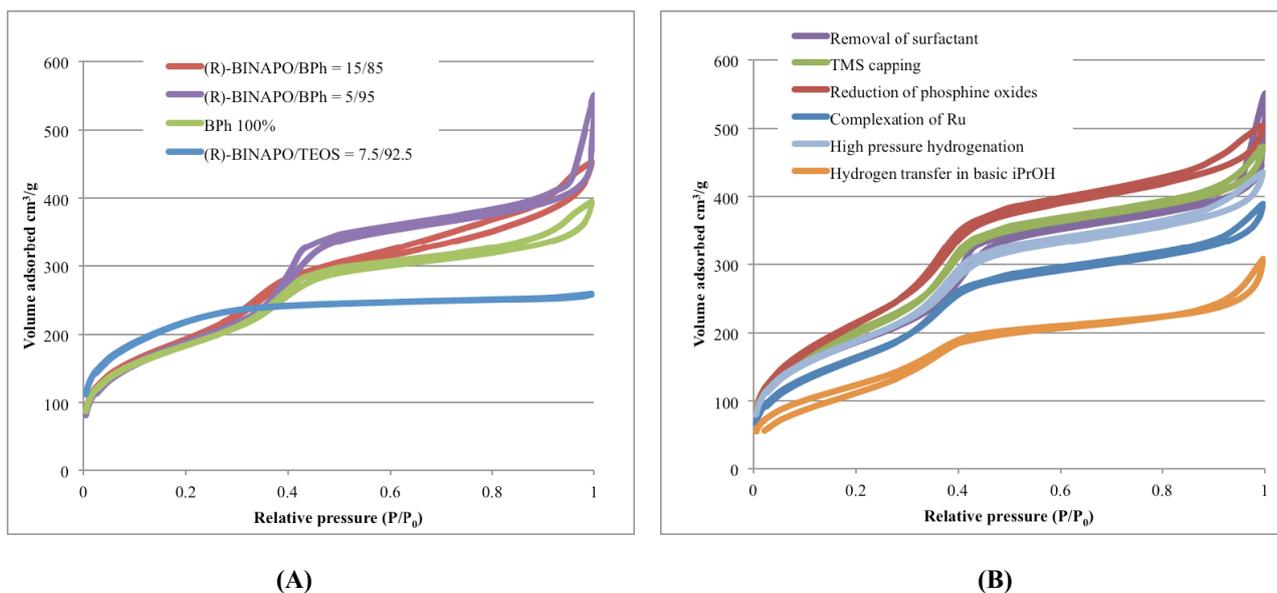
### **Reduction of phosphine oxides**

This procedure is based on Spencer *et al.*<sup>10</sup> but extreme purity of the trichlorosilane is important to prevent material from decomposing the ordered mesoporous structure by acid. An ampule packed trichlorosilane was purchased from Sigma-Aldrich, it was carefully transferred into a Schlenk tube with activated basic alumina under argon atmosphere, then was stored in a fridge. To a suspension of **TMS-capped 5%BINAPO-PMO** (100 mg) in toluene (4.0 mL) was added tributylamine (2.0 mL), triethylphosphite (0.05 mL) and extremely pure trichlorosilane (0.28 mL) under argon. The mixture was stirred for 24 hours at 80 °C in an oil bath. After cooling down the mixture at room temperature, the material was recovered by filtration and washed with copious amount of toluene, ethyl acetate and acetone. Drying this material under high vacuum (0.2 mmHg) at 80 °C over night gave **5%BINAP-PMO** quantitatively.

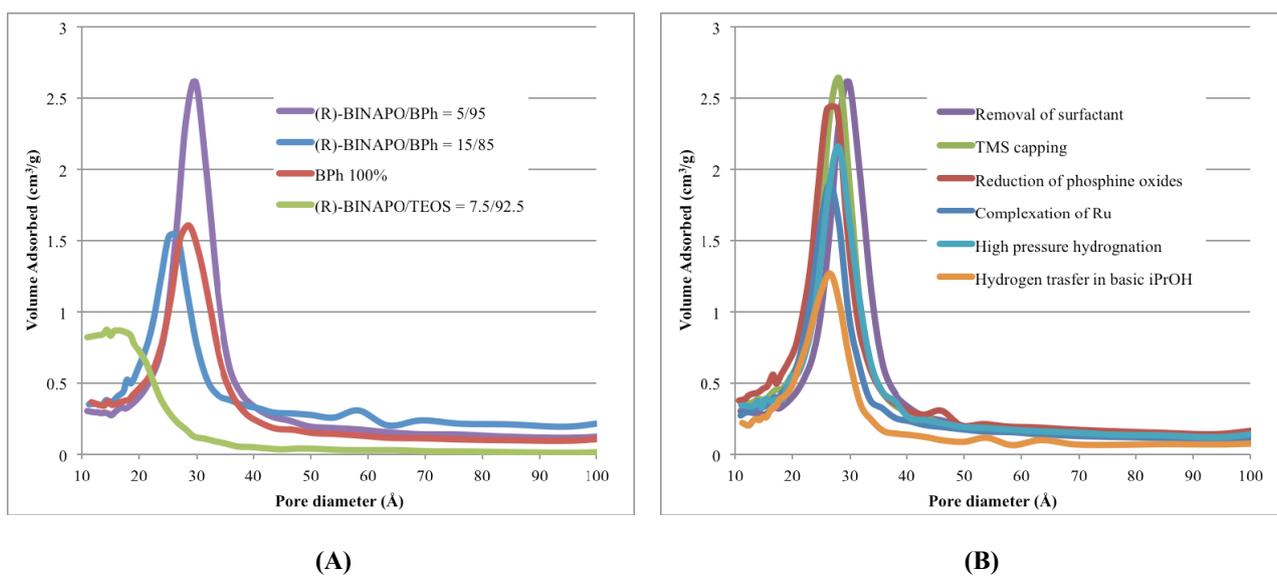
### **Ruthenium complexation**

This procedure is based on Mashima *et al.*<sup>11</sup> 5%BINAP-PMO (500 mg) and dichloro benzene ruthenium(II) dimer (30 mg, 0.12 mmol of ruthenium) were placed in a vial with a magnetic stirring bar in a glove box, then mixture of methanol/benzene (45 mL/5 mL) solution was added. The resulting suspension was stirred for 24 hours at 60 °C. The material is recovered by filtration, washed with copious amount of methanol and dichloromethane, and dried on a vacuum funnel in a glove box. The amount of the ruthenium doped on this material was determined as 0.084 mmol g<sup>-1</sup> by ICPMS elemental analysis.

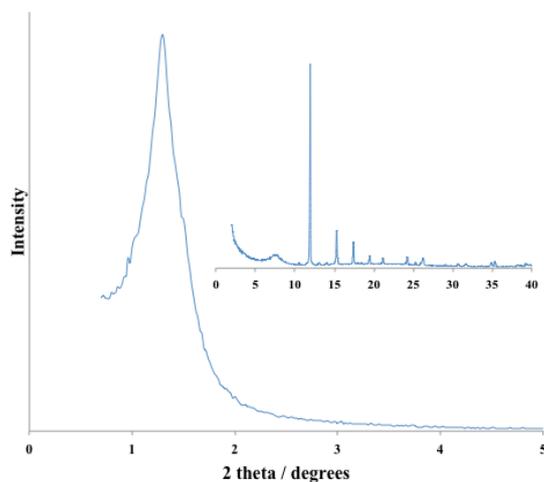
## **5. Material Characterization**



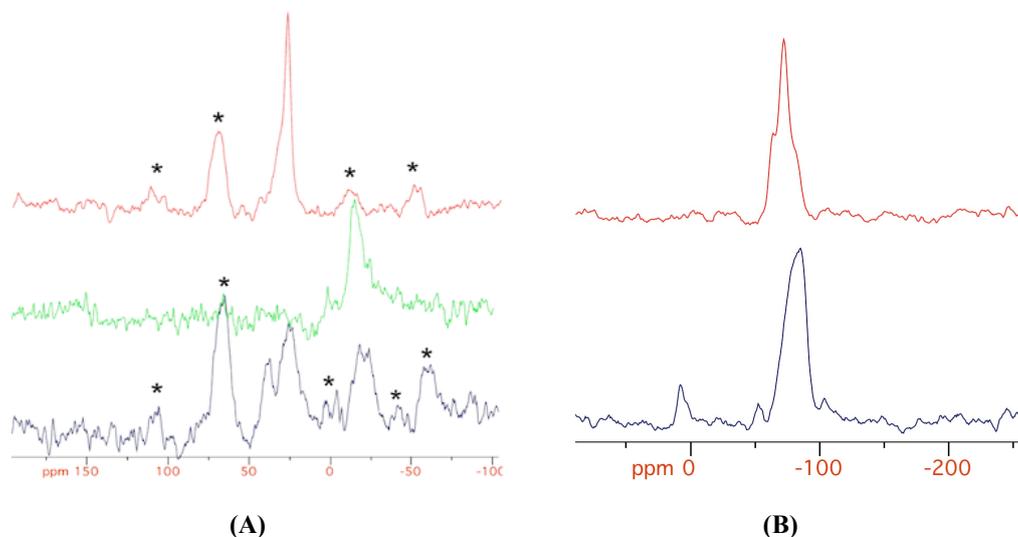
**Figure S-1.** Nitrogen adsorption isotherm plots of PMOs. All the materials in (B) are synthesized from the precursors with molar ratio; (R)-BINAPO/BPh = 5/95.



**Figure S-2.** Nitrogen adsorption, BJH adsorption pore diameter distribution of materials.



**Figure S-3.** Powder X-ray diffraction pattern of Ru/5%(R)-BINAP-BPh-PMO. The peak at 7.5 degree 2theta (inset) corresponds to  $d = 11.7 \text{ \AA}$ , which indicates the crystal-like structure of the BINAP and biphenylene bridged functionalities in the wall structure of the PMO.



**Figure S-4.** Solid state CP MAS NMR spectra (representative). Spinning side bands are shown with a star, and are confirmed by running two separate MAS NMR spectra of each sample at different spinning rates. **(A)**  $^{31}\text{P}$ : (Top) Before reduction of phosphane oxides, the peak at 30 ppm corresponds to phosphane oxides of BINAPO. (Middle) After reduction, the peak at -15 ppm is from the trivalent phosphane of BINAP, and no phosphane oxide remains. (Bottom) After complexation of ruthenium. The peaks at 28 and 40 ppm correspond to two phosphanes coordinating to ruthenium as forming  $[\text{Ru}(\text{binap})(\text{C}_6\text{H}_6)\text{Cl}]\text{Cl}$ . The signal at -15 ppm is due to residual phosphane since a sub-stoichiometric amount of Ru (relative to phosphane) was added. **(B)**  $^{29}\text{Si}$ : Before (top) and after (bottom) TMS capping of free silanols. Disappearance of T1 site and increased T3 site, also S site from TMS group are observed.

**Table S-1.** Physical characteristics of (R)-BINAP-PMOs after post-grafting modification and catalysis use.

Entry	Surface area /m <sup>2</sup> g <sup>-1</sup> <sup>a</sup>	Pore size /Å <sup>b</sup>	Pore Volume /cm <sup>3</sup> g <sup>-1</sup>	Modification/Catalysis use
1	750	28.2	0.669	TMS capping
2	812	26.0	0.717	Reduction of phosphane oxide
3	613	26.4	0.548	Complexation of ruthenium
4	694	28.2	0.607	High pressure hydrogenation
5	459	26.7	0.432	Hydrogen transfer in basic isopropanol

<sup>a</sup>Brij76 surfactant was used as a template. Molar ratio of 1/2 = 5/95.  
<sup>b</sup>Calculated from BET plot. <sup>b</sup>BJH adsorption average pore size.

## 6. Catalysis Procedures

### High-pressure hydrogenation

In an inert atmosphere glove box, a 15 mL vial was charged with a magnetic stirring bar and Ru/5%(R)BINAP-PMO (24mg, 2.0 μmol). After being sealed with a rubber septum, the vial was removed from the glove box, and degassed methylacetoacetate (0.21 mL, 2.0 mmol) in methanol (5.0 mL) was added by syringe. The vial was placed in an autoclave and the rubber septum was carefully removed under Ar flow, then it was purged with hydrogen. After purging, the hydrogen pressure was increased to 600 psi, and the reaction mixture stirred in an oil bath at 50 °C for 24 hours. After cooling the autoclave to room temperature, the hydrogen was carefully depressurized and the catalyst powder was separated by vacuum filtration. Concentrating the filtrate on a rotary evaporator gave 236 mg (99% yield) of a colorless oil. The spectra obtained were identical with those reported in the literature.<sup>12</sup>

### Recycling the catalyst

The procedure described above was followed, except that the rubber septum was not removed when the vial was placed in an autoclave, only a small needle was left through the septum while running the reaction. After the reaction, the needle was taken out then this vial and the rubber septum left on during centrifugation for 5 minutes at 2600 rpm. The supernatant was taken out by syringe, and another 5 mL of degassed methanol was added to rinse the catalyst. The suspension was again centrifuged then the supernatant was taken out. The same manipulation was repeated three times in total. The combined methanol solution was concentrated as above, and a fresh substrate solution in methanol was added to the catalyst to run the second cycle.

### Transfer hydrogenation

In a 25 mL round bottom flask was placed a magnetic stirring bar, Ru/5%(R)BINAP-PMO (79 mg, 6.7  $\mu\text{mol}$ ), potassium carbonate (93 mg, 0.67 mmol) and 4-methoxyacetophenone (1.0 g, 6.7 mmol). The flask was capped with a rubber septum before being purged with Ar. Degassed iPrOH (15 mL) was added by syringe, then the mixture was stirred at 100 °C in an oil bath for 24 hours. After cooling down the reaction mixture, it was filtrated on a Buchner funnel, and washed with copious amounts of ethylacetate. The combined filtrate was washed with brine, dried over magnesium sulfate, and concentrated on a rotary evaporator.  $^1\text{H}$  NMR of the obtained color less oil (1.0 g) was measured, estimated 87% yield. In asymmetric version, (R, R)-DPEN (2.8 mg, 13.4  $\mu\text{mol}$ ) was at first added with the PMO catalyst and potassium carbonate, purged with Ar, and iPrOH (5 mL) was added by syringe. This mixture was stirred at 50 °C in an oil bath for 1 hour. Then the substrate solution in iPrOH (10 mL) was added to the resulting bright orange mixture. The following procedure was the same as above, except that a filtration through a short Celite plug and a washing with 1M HCl aq. were done as well at work up.  $^1\text{H}$  NMR of the obtained orange oil (1.0 g) was measured, estimated 99% yield. The spectra obtained were identical with the one reported in the literature.<sup>13</sup>

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