Supporting Information for

Self-Supported Heterogeneous Catalysts for Enantioselective Hydrogenation

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General Methods. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AM300 NMR spectrometer (300 MHz) in CDCl₃. Chemical shifts were expressed in ppm with TMS as an internal standard ($\delta = 0$ ppm) for ¹H NMR. Coupling constants, *J*, are listed in hertz. ³¹P NMR spectra were referenced with an external H₃PO₄ sample. The IR spectra were measured on Rio-Rad FTS-185 spectrometer in KBr pellets. ESI mass spectra were obtained on Mariner LC-TOF spectrometer. HRMS were determined on a IonSpect 4.7 TESLA FTMS. Elemental analyses were performed with an Elemental VARIO EL apparatus. Optical rotations were measured on a Perkin-Elmer 341 automatic polarimeter. HPLC analyses were carried out on a JASCO 1580 liquid chromatograph with a JASCO CD-1595 detector and AS-1555 autosampler. GC analyses were measured on Agilent 6890N network system. Scanning electron micrographs were taken on a Hitachi S-2150 Scanning electron microscope. Powder X-ray diffraction (PXD) spectra were carried out on a D8 Discover GADDS. ICP analysis of Rh and P leaching was performed with IRIS Advantage 1000 instrument. Toluene and diethyl ether were distilled from sodium benzophenone ketyl under argon. Dichloromethane were purified by distillation under argon after drying over calcium hydride. All manipulations involving air- and moisture-sensitive organometallic compounds were carried out using standard Schlenk technique under argon atmosphere. Bis-BINOL derivatives were prepared according to the literature method.¹

General procedure for the preparation of bisMonoPhos derivatives 1a-c.

A mixture of bis-BINOL derivative (1.0 mmol) and hexamethylphosphorous triamide (0.46 mL, 2.5 mmol,) in anhydrous toluene (3.0 mL) was heated under reflux for 9 h under an argon atmosphere. After cooling down to room temperature, the solvent was removed under the reduced pressure. The crude pale yellow residue was purified by flash chromatography on silica gel with petroleum ether / ethyl acetate (10 / 1) as eluent. Recrystallization of the product from diethyl ether affords the pure product as white solids in good yields.

1a: 83.5% yield. $[\alpha]_D^{20} = 650.1^\circ$ (c 1.0, CHCl_3). IR (KBr): 3055, 2800, 1621, 1588, 1504, 1462, 1330, 1293, 1232, 1207, 1189, 1076, 983, 944, 821, 780, 749, 692, 678 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): δ 8.24-8.26 (m, 2H), 7.94-8.08 (m, 6H), 7.64-7.71 (m, 2H), 7.39-7.58 (m, 10 H), 7.29-7.37 (m, 2H), 2.58-2.62 (m, 12H). ^{31}P NMR (121 MHz, CDCl_3) δ 149.87 ppm. MS (ESI): (M+H), 717.35; HRMS (MALDI): calcd. for $\text{C}_{44}\text{H}_{35}\text{N}_2\text{O}_4\text{P}_2$: 717.2072; Found: 717.2053.

1b: 78.5% yield. $[\alpha]_D^{20} = 500.6^\circ$ (c 1.0, CHCl_3). IR (KBr): 3054, 2799, 1590, 1494, 1464, 1333, 1292, 1232, 1208, 1047, 984, 945, 819, 790, 749, 693 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): δ 8.18 (s, 2H), 7.91-8.06 (m, 6H), 7.82 (s, 4H), 7.26-7.62 (m, 14H), 2.55-2.59 (m, 12H). ^{31}P NMR (121 MHz, CDCl_3) δ 149.87 ppm. MS (ESI): (M+H), 793.55; HRMS (MALDI): calcd. for $\text{C}_{50}\text{H}_{39}\text{N}_2\text{O}_4\text{P}_2$: 793.2385; Found: 793.2379.

1c: 85.0% yield. $[\alpha]_D^{20} = 485.0^\circ$ (c 1.0, CHCl_3). IR (KBr): 3054, 2799, 1621, 1588, 1505, 1463, 1332, 1292, 1232, 1207, 1188, 1155, 1075, 984, 945, 884, 820, 796, 749, 693 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): 8.18-8.19(m, 2H), 7.91-8.05(m, 7H), 7.69-7.71(m, 2H), 7.41-7.65 (m, 13H), 7.29-7.34 (m, 2H), 2.55-2.59 (m, 12H). ^{31}P NMR (121 MHz, CDCl_3) δ 149.48 ppm. MS (ESI): (M+H), 793.35; HRMS (MALDI): calcd. for $\text{C}_{50}\text{H}_{39}\text{N}_2\text{O}_4\text{P}_2$: 793.2385; Found: 793.2379.

General procedure for preparation and uses of self-supported heterogeneous Rh catalysts in enantioselective hydrogenation.

To a solution of **1a** (11.1 mg, 0.0155 mmol) in toluene (1.0 mL) was added $\text{Rh}(\text{COD})_2\text{BF}_4$ (6.0 mg, 0.0148 mmol) in dichloromethane (0.5 mL). The solution was stirred at room temperature for 30 min to afford the orange precipitate. After removal of the solvents at 50 $^\circ\text{C}$ under reduced pressure, the residue was dried in vacuo for 2 h. The resulting orange powders **2a** were washed with toluene to remove the trace amount of soluble low molecular weight species. IR (KBr): 3060, 3018, 2975, 2888, 1621, 1588, 1505, 1463, 1326, 1226, 1075, 986, 946, 826, 695, 597 cm^{-1} . Anal. Calcd for $[(\mathbf{1a})_{1.05} \cdot \text{Rh}(\text{COD})\text{BF}_4 \cdot \text{CH}_2\text{Cl}_2]_n$: C, 58.41; H, 4.38; N, 2.59. Found: C, 59.39; H, 5.05; N, 3.08. SEM images and PXD spectra of the self-supported catalysts were enclosed in the coming text.

The polymeric solids of the Rh complex prepared above in a test tube was then charged with α -dehydroamino acid or enamide derivatives (1.477 mmol) and anhydrous toluene (7.38 mL) under Argon. The test tube was placed in a stainless steel autoclave, and then sealed. After purging with hydrogen for 6 times, final H₂ pressure was adjusted to 40 atm. After stirring at room temperature for 10 h, H₂ was released and the catalyst was recovered by filtration under Ar. Removal of toluene under the reduced pressure, the residue of the product was submitted to ¹H NMR analysis to assess the conversion of the starting materials. The enantiomeric excess of the product was determined by chiral HPLC or GC.

For the catalyst re-use experiments, the reaction mixture was filtered through cannula under Ar and the residual solids were washed with anhydrous degassed toluene. To the test tube containing solid catalyst, the substrate and toluene were added again followed by recharge of the H₂ for the next run of the hydrogenation.

References

(1) Guo, H.; Wang, W.; Ding, K. *Tetrahedron Lett.* **2004**, 45, 2009.

2b

2c

Figure S1. SEM image of the self-supported Rh catalyst **2b** and **2c**. The scale bar indicates 5 μ m.

2a

2b

2c

Figure S2. PXD pattern of self-supported Rh catalyst **2a-2c**.

Figure S3. Chiral HPLC or GC analysis of products 4a-4d

Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	19.302	PB	0.3475	1254.76233	45.24617	50.33900
2	20.909	BB	0.4359	1237.86218	35.75163	49.66100

Totals : 2492.62451 80.99779

Results obtained with enhanced integrator!

*** End of Report ***

Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	19.176	PB	0.4695	2173.57739	57.96687	97.86506
2	21.671	PP	0.3376	47.41687	2.21618	2.13494

Totals : 2220.99426 60.18305

Results obtained with enhanced integrator!

*** End of Report ***

File name : wxw-6-123rac019.CH2

Info :
AD, 230nm

Vial # = 1 Rack # = 1
Injection Date : 4-May-2004 11:52:54
Curr. Date : 4-May-2004 15:43:52
User : DEFAULT
Group : DATA
Control Method : ZBG-A-AMINE

#	Name	RT	Area[v.Sec]	Quantity
1		8.950	2560267.038	0.000
2		11.500	2916646.838	0.000

Total Area of Peak = 5476913.876 [v.Sec]

File name : wxw-5-102335.CH2

Info :
90/10.1.0.ad,230, LY-h

Vial # = 1 Rack # = 1
Injection Date : 16-Feb-2004 22:47:42
Curr. Date : 4-May-2004 15:30:04
User : LY
Group : DATA
Control Method : LY-A-AMIN

#	Name	RT	Area[v.Sec]	Quantity
1		9.333	2539444.723	0.000
2		12.217	40202.870	0.000

Total Area of Peak = 2579647.593 [v.Sec]

File name : wxw-6-21-rac006.CH2

Info :
benyl-enomide

Vial # = 1 Rack # = 1
Injection Date : 2-May-2004 16:17:52
Curr. Date : 4-May-2004 16:09:00
User : DEFAULT
Group : DATA
Control Method : ZBG-ENOMIDE

#	Name	RT	Area[v.Sec]	Quantity
1		11.258	2699824.222	0.000
2		13.992	2707788.987	0.000

Total Area of Peak = 5407613.209 [v.Sec]

File name : wxw-6-15-014.CH2

Info :
AD, 230nm

Vial # = 1 Rack # = 1
Injection Date : 3-May-2004 23:43:50
Curr. Date : 4-May-2004 16:20:26
User : DEFAULT
Group : DATA
Control Method : WXW-ENOMIDE

#	Name	RT	Area[v.Sec]	Quantity
1		11.008	11891236.216	0.000
2		14.333	161908.332	0.000

Total Area of Peak = 12053144.548 [v.Sec]