Supporting Information

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Engineering Polymeric Chiral Catalyst Using Hydrogen Bonding and Coordination Interactions

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Methods

^1H -NMR and ^{13}C -NMR spectroscopies were taken in deuteriochloroform on a Varian Mercury 300 (^1H : 300 MHz; ^{13}C : 75 MHz) spectrometer. Chemical shifts are reported in ppm relative to an internal standard: tetramethylsilane (0 ppm) for ^1H -NMR and deuteriochloroform (77.0 ppm) for ^{13}C NMR. Coupling constants, J , are listed in hertz. ^{31}P -NMR spectra were referenced with an external 85% H_3PO_4 sample. ^{31}P NMR CP/MAS spectra were measured with a Bruker dsx300 NMR spectrometer (125 MHz) and the chemical shift of spectra were determined by taking the ^{31}P of 70% H_3PO_4 (0.0 ppm) as an external reference standard. EI (70 eV) and ESI mass spectra were obtained on HP5989A and Mariner LC-TOF spectrometers respectively. HRMS spectra were determined on a Q-ToF micro instrument or APEXIII 7.0 TESLA FTMS. Elemental analysis was performed with an Elemental VARIO EL apparatus. Optical rotations were measured on a Perkin-Elmer 341 automatic polarimeter. Infrared spectra were obtained on a BIO-RAD FTS-185 Fourier transform spectrometer in KBr pellets. Scanning electron micrographs were taken on a Hitachi S-570 Scanning electron microscope. Powder X-ray diffraction (XRD) spectra were carried out on a Bruker-AXS D8Advance. ICP analysis of Rh and P leaching was performed with Varian spectra AA. Liquid chromatographic analyses were conducted on a JASCO 1580 system. GC analyses were measured on Agilent 6890N network system. All the experiments sensitive to moisture or air were carried out under argon atmosphere using standard Schlenk techniques. Commercial reagents were used as received without further purification unless otherwise noted. Dichloromethane, chloroform were freshly distilled from calcium hydride and THF, diethyl ether and toluene from sodium benzophenone ketyl. Compound **1a** was prepared following a literature method.¹

Scheme S1. Preparation of ligands **1b** and **1c**. Conditions and reagents: 1) $\text{K}_2[\text{Fe}(\text{CN})_6]$ (0.25 eqv.) , $\text{Pd}(\text{OAc})_2$ (0.5 mol%), dppf (1.0 mol%), Na_2CO_3 (1.0 eq.) , NMP, 120°C , 5 h, 84%; 2) LiAlH_4 , dry THF, 60°C , 10 h, 99%; 3) CHCl_3 , 60°C , 5 h, 95%; 4) CHCl_3 , MeOH, HCl (12M), 40°C , 92%; 5) Toluene, HMPT, 80°C , 4 h, 65%

Synthesis of 6-cyano-2,2'-bismethoxymethoxy-1,1'-binaphthalene (S2): To a solution of **S1** (4.5 g, 10.0 mmol) and $\text{K}_2[\text{Fe}(\text{CN})_6]$ (920.0 mg, 2.5 mmol) in NMP (10 ml) were added $\text{Pd}(\text{OAc})_2$ (11.2 mg, 0.05 mmol), dppf (55.4 mg, 0.1 mmol) and Na_2CO_3 (1.06 g, 10.0 mmol) successively. The resulting mixture was heated at 120°C for 5 h under argon atmosphere until the starting material was almost consumed as monitored by TLC (hexane: ethyl acetate = 5:1). After being cooled

to room temperature, the reaction mixture was passed through a pad of Celite and the filtrate was then evaporated under reduced pressure. The residue was added water (40 ml) and dichloromethane (50 ml). The organic phase was separated and the water phase was extracted with dichloromethane (40 ml $\times$ 3). The combined organic phase was washed with saturated aqueous NaHCO₃ (60 ml), water (80 ml), and brine (50 ml), respectively. The organic phase was dried over Na₂SO₄ and then concentrated. The residue was purified by column chromatography on silica gel with hexane-ethyl acetate (10:1) as eluent to afford **S2** in 84% yield as a white solid. M.p. 76 – 77°C. $[\alpha]_D^{20} = +27.9$ ($c = 0.50$ in CHCl₃); ¹H NMR (300 MHz, CDCl₃): $\delta = 8.26$ (s, 1H), 8.02-7.96 (m, 2H), 7.89 (d, 1H, $J = 6$), 7.72 (d, $J = 9$, 1H), 7.65 (d, $J = 30$, 1H), 7.37-7.32 (m, 2H), 7.27-7.07 (m, 2H), 7.06 (d, 1H, $J = 6$), 5.16 – 4.98 (m, 4H), 3.18 (s, 3H), 3.14 (s, 3H); ¹³C NMR (75MHz, CDCl₃): $\delta = 154.9, 152.4, 135.4, 134.0, 133.4, 129.8, 129.8, 129.6, 128.2, 127.9, 126.5, 126.4, 124.7, 124.0, 121.0, 119.4, 119.3, 117.9, 116.6, 107.0, 94.7, 94.3, 55.8, 55.6$; FTIR (KBr pellet): $\nu = 3050, 2991, 2962, 2905, 2831, 2233, 1619, 1591, 1479, 1351, 1200, 1151, 1092, 1073, 1024, 918, 884, 808, 759, 692, 681$ cm⁻¹; ESI-MS (m/z): [M^+], 399.1; HRMS (MALDI - DHB) calcd. for C₂₅H₂₁NO₄Na⁺ [M^+ +Na]: 422.1376; Found: 422.1362.

Synthesis of 6-aminomethyl-2,2'-bismethoxymethoxy-1,1'-binaphthalene (S3): In a 25-ml round-bottomed flask, **S2** (400 mg, 1 mmol) was dissolved in THF (8 ml) under argon atmosphere. LiAlH₄ (114 mg, 3 mmol) was then added to the solution portion wise. The mixture was heated to 60°C and stirred for 10 h. After cooling to room temperature, methanol (1 ml) was added slowly and stirred for 10 min to quench the reaction. The reaction mixture was then passed through a pad of Celite and the filtrate was evaporated under reduced pressure to yield a compound **S3** in 99% yield. The compound is pure enough for the next reaction without further purification. $[\alpha]_D^{20} = -26.3$ ($c = 0.50$ in CHCl₃); ¹H NMR (300 MHz, CDCl₃): $\delta = 7.93-7.85$ (m, 3H), 7.78 (s, 1H), 7.58-7.54 (m, 2H), 7.36-7.31 (m, 2H), 7.24-7.10 (m, 4H), 5.06 (d, 2H, $J = 9$), 4.98-4.94 (m, 2H), 3.97 (s, 1H), 3.15-3.12 (m, 6H). FTIR (KBr pellet): $\nu = 3404, 2924, 1594, 1506, 1481, 1358, 1243, 1198,$

1150, 1070, 1032, 921, 812, 693 cm^{-1} .

Synthesis of 1c: The CDI-activated 6-(1-ethylpentyl)isocytosine **S4** (260 mg, 1.2 mmol) was mixed with **S3** (403 mg, 1 mmol) in chloroform (10 ml) and the mixture was heated at 60°C for 5 h. After cooling to room temperature, the solution was filtrated to remove the unreacted **S4**, and the filtrate was evaporated in vacuo. Finally, the residue was recrystallized from dichloromethane / hexane to yield **1c** in 95% yield as a white solid. M.p. 164 – 166°C. $[\alpha]_{\text{D}}^{20} = -34.4$ ($c = 0.60$ in CHCl_3); ^1H NMR (300 MHz, CDCl_3): $\delta = 12.99$ (s, 1H), 12.02 (s, 1H), 10.88 (s, 1H), 7.94-7.80 (m, 4H); 7.57-7.52 (m, 2H), 7.35-7.18 (m, 3H), 7.12-7.08 (m, 2H), 5.78 (s, 1H), 5.05 (q, 2H, $J = 3.5$), 4.95 (q, 2H, $J = 3.2$), 4.55 (d, 2H, $J = 5.4$), 3.15-3.12 (m, 6H), 2.18 (s, 3H); ^{13}C NMR (75MHz, CDCl_3): $\delta = 172.9$, 156.7, 154.5, 152.5, 152.4, 148.2, 134.3, 133.9, 133.1, 129.7, 129.2, 127.7, 126.1, 125.9, 125.5, 125.4, 123.9, 121.2, 121.1, 117.3, 117.2, 106.6, 95.1, 55.79, 55.72, 43.3, 18.8; FTIR (KBr pellet): $\nu = 3200$, 3050, 1699, 1663, 1586, 1506, 1245, 1198, 1149, 1070, 1015, 921, 811, 751 cm^{-1} ; ESI-MS (m/z): $[M^+]$, 555; HRMS (MALDI - DHB) calcd. for $\text{C}_{31}\text{H}_{31}\text{N}_4\text{O}_6^{+1}$ $[M^+]$: 555.2242; Found: 555.2238.

Synthesis of S5: To a solution of **1c** (403 g, 1.0 mmol) in mixed solvent of chloroform (30 ml) and methanol (10 ml) was added aqueous HCl (12 M, 0.5 ml, ~ 6 mmol). The resulting solution was stirred for 10 h at room temperature until the complete conversion of **1c** (monitored by TLC, dichloromethane: methanol = 15 : 1). The saturated aqueous NaHCO_3 solution was added to neutralize the reaction mixture and the precipitation was filtered off. The resulting precipitation was washed with water and dried under reduced pressure to give the product **S5** in 92 % yield as a white power. M.p. 216 – 218°C. $[\alpha]_{\text{D}}^{20} = -82.7$ ($c = 0.507$ in DMSO); ^1H NMR (300 MHz, $\text{DMSO}-d_6$): $\delta = 8.29$ (s, 1H), 7.84-7.79 (m, 3H), 7.71 (s, 1H), 7.30-7.26 (m, 2H) 7.21-7.09 (m, 3H), 6.90-6.86 (m, 2H), 5.67 (s, 1H), 4.41 (s, 2H), 2.06 (d, 3H, $J = 2.7$); ^{13}C NMR (75MHz, $\text{DMSO}-d_6$): $\delta = 155.2$, 153.0, 152.9, 151.9, 134.1, 133.3, 132.7, 128.6, 128.1, 127.9, 127.8, 125.85, 125.80, 124.8, 124.3, 122.2, 118.8, 118.5, 115.4, 104.5, 79.1, 42.8, 30.6; FTIR (KBr

pellet): $\nu = 3510, 3208, 3054, 1697, 1660, 1574, 1508, 1435, 1382, 1340, 1248, 1215, 1144, 817, 751, 607 \text{ cm}^{-1}$; ESI-MS (m/z): [M^+], 467; HRMS (MALDI - DHB) calcd. for $\text{C}_{27}\text{H}_{23}\text{N}_4\text{O}_4^{+1}$ [M^+]: 467.1716; Found: 467.1713.

Synthesis of 1b: A solution of **S5** (370 mg, 0.8 mmol) and hexamethylphosphorotriamide (0.2 ml, 1mmol) in dry toluene (2 ml) was heated at 80°C under Argon for 5h until the complete conversion of substrate **S5** (monitored by TLC, dichloromethane : methanol = 15 : 1). After cooling to room temperature, the mixture was concentrated under vacuum and the residue was purified by a flash column chromatography on silica gel with dichloromethane / acetone (20 / 1) as eluent to give the product **1b** in 65% yield as white power. M.p. 190 – 191°C. $[\alpha]_D^{20} = +348.6$ ($c = 0.50$ in CHCl_3); ^1H NMR (300 MHz, CDCl_3): $\delta = 12.98$ (s, 1H), 12.06 (s, 1H), 10.94 (s, 1H), 7.95-7.83 (m, 4H), 7.49-7.44 (m, 1H), 7.42-7.32 (m, 4H), 7.28-7.23 (m, 2H), 5.79, (s, 1H), 4.60-4.56 (m, 2H), 2.55-2.51 (m, 6H), 2.19 (s, 1H); ^{31}P NMR (121 MHz, CDCl_3) δ 149.69, 149.56 ppm; FTIR (KBr pellet): $\nu = 3051, 1700, 1662, 1588, 1507, 1468, 1333, 1251, 1068, 982, 945, 821, 751, 691 \text{ cm}^{-1}$; ESI-MS (m/z): [M^+], 540.45; HRMS (MALDI - DHB) calcd. for $\text{C}_{29}\text{H}_{27}\text{N}_5\text{O}_4\text{P}^{+1}$ [M^+]: 540.1819; Found: 540.1795.

Synthesis of 2. To a dichloromethane (1.0 mL) solution of **1b** (11.3 mg, 0.021 mmol) was added $[\text{Rh}(\text{COD})_2]\text{BF}_4$ (4.1 mg, 0.01 mmol) in dichloromethane (0.5 mL). The resulting mixture was stirred at room temperature for 1 h to afford the yellow precipitate. After removal of the solvent at 50 °C under reduced pressure, the resulting yellow powder was washed with toluene to remove the trace amount of soluble low molecular weight species. The isolated yellow solids (**2**) were dried *in vacuo* for 2 h at RT. IR (KBr): 3510, 3208, 3054, 2933, 1699, 1662, 1507, 1469, 1326, 1226, 1071, 988, 947, 828, 753 cm^{-1} ; Anal. calcd (%) for $[\text{C}_{58}\text{H}_{52}\text{N}_{10}\text{O}_8\text{P}_2 \cdot \text{Rh}(\text{COD})\text{BF}_4 \cdot \text{CH}_2\text{Cl}_2]_n$: C, 55.05; H, 4.55; N, 9.58; P, 4.24. Found: C, 55.36; H, 4.96; N, 8.99; P, 4.16. ^{31}P CPMAS (125 MHz): 135.7 ppm.

Hydrogenation. (a) Standard. For example, polymeric solid **2** (0.01 mmol, 10 mM), **3b** (1 mmol, 1.0 M) in anhydrous toluene (1.0 mL) were placed in a test

tube under argon atmosphere. The test tube was placed in a stainless steel autoclave, and then sealed. After purging with hydrogen for 3 times, final H₂ pressure was adjusted to 40 atm and stirring commenced. Following a period of 20 h, H₂ was released and the catalyst recovered by cannula filtration under an argon atmosphere. The product was analyzed following removal of toluene under the reduced pressure. Conversion and enantiomeric excess were determined by ¹H NMR and chiral GC (Supelco BETA-DEX225 column), respectively.

¹H NMR of products **4a-e**³.

product **4a**: ¹H NMR (300 MHz, CDCl₃): δ = 6.57 (s, 1H), 4.63-4.54 (m, 1H), 3.76 (s, 3H), 2.02 (s, 3H), 1.40 (d, 3H) ppm.

product **4b**: ¹H NMR (300 MHz, CDCl₃): δ = 6.35 (s, 1H), 4.62-4.56 (m, 1H), 3.72 (s, 3H), 2.01 (s, 3H), 2.03-1.67 (m, 2H), 0.88 (t, 3H) ppm.

product **4c**: ¹H NMR (300 MHz, CDCl₃): δ = 6.08 (s, 1H), 4.61-4.53 (m, 1H), 3.72 (s, 3H), 2.01 (s, 3H), 1.88-1.72 (m, 2H), 1.76-1.62 (m, 2H), 1.47-1.32 (m, 3H) ppm.

product **4d**: ¹H NMR (300 MHz, CDCl₃): δ = 5.88 (s, 1H), 4.76-4.61 (m, 1H), 3.73 (s, 3H), 2.01 (s, 3H), 1.78-1.62 (m, 2H), 1.65-1.54 (m, 1H), 0.94-0.93 (m, 6H) ppm.

product **4e**: ¹H NMR (300 MHz, CDCl₃): δ = 7.28-7.17 (m, 5H), 6.32 (s, 1H), 5.04-4.99 (q, 1H), 1.87 (s, 3H), 1.40-1.37 (d, 3H) ppm.

(b) Reaction Profile. Procedure as (a) above. An autoclave equipped with a sampling needle allowed for aliquots to be analyzed during hydrogenation under an atmosphere of H₂.² Conditions: [**2**] = 2 mM, [**3b**] = 0.2 M, *P* (H₂) = 15 atm. Conversion and ee% determined by GC (Supelco BETA-DEX225 column). Note, ¹H NMR and chiral GC analysis gave the same conversion results.

(c) Turn over frequency (TOF) determination. Procedure as (a) above. Reaction was stopped at ca. >50% conversion estimated from reaction profile above and the product mixture analyzed by ^1H NMR and chiral GC (Supelco BETA-DEX225 column). Following catalyst recovery by filtration under argon atmosphere the next hydrogenation was conducted. TOF = TON/reaction time (TON = mol of product/mol of catalyst).

run	1	2	3	4	5	6	7	8	9	10
time/min	35	45	70	80	90	120	150	210	240	480
Conv./%	99	83	97	91	66	65	62	69	44	65
TOF/h ⁻¹	>180	111	83	68	44	32	24	19	11	8

References

- [1] van den Berg, M. *et al.* Highly enantioselective rhodium-catalyzed hydrogenation with monodentate ligands. *J. Am. Chem. Soc.* **2000**, 122, 11539-11540.
- [2] Sandoval, C. A. *et al.* Mechanism of Asymmetric Hydrogenation of Ketones Catalyzed by BINAP/1,2-diamine-Ruthenium(II) Complexes. *J. Am. Chem. Soc.* **2003** 125, 13490-13503.

[3] Evans, D. A. *et al.* Application of Chiral Mixed Phosphorus/Sulfur Ligands to Enantioselective Rhodium-Catalyzed Dehydroamino Acid Hydrogenation and Ketone Hydrosilylation Processes. *J. Am. Chem. Soc.* **2003**, 125, 3534 – 3543.

Figure S1. XRD pattern of solid-state catalyst **2**

Figure S2. DSC-TG Curve of catalyst **2**.

Figure S3. a) Polymeric supramolecular catalyst **2** (yellow solids at the bottom of the reactor) in toluene prior to hydrogenation. b) The colorless toluene filtrate obtained by simple filtration of solid catalyst **2** following the hydrogenation.

a)

b)

Figure S4. Chiral GC analysis of products **4a-4e**

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                          Area Percent Report
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Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000

Signal 1: FID1 A,

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Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	9.217	BB	0.0704	355.34988	67.47271	49.97347
2	10.485	BB	0.0998	355.72717	45.18896	50.02653
Totals :				711.07706	112.66167

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                          Area Percent Report
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Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000

Signal 1: FID1 A,

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Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	9.354	PB	0.0629	83.61109	18.09577	97.63435
2	10.762	BB	0.0488	2.02587	4.99696e-1	2.36565
Totals :				85.63696	18.59546

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 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	10.573	BB	0.0846	611.32092	102.45509	50.05760
2	12.031	PB	0.0885	609.91400	96.84952	49.94240

Totals : 1221.23492 199.30461

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 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	10.573	BB	0.0864	288.15656	51.38499	97.85301
2	12.180	BB	0.0980	6.32244	9.70930e-1	2.14699

Totals : 294.47900 52.35592

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                        Area Percent Report
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Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
  
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Signal 1: FID1 A,

Peak RetTime Type  Width    Area    Height    Area
#    [min]         [min]  [pA*s]   [pA]      %
-----|-----|-----|-----|-----|
  1   14.745   BB    0.1096  141.12712  18.17094  50.27838
  2   15.756   PP    0.1020  139.56436  17.22981  49.72162

Totals :                      280.69148  35.40076
  
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                        Area Percent Report
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Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
  
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Signal 1: FID1 A,

Peak RetTime Type  Width    Area    Height    Area
#    [min]         [min]  [pA*s]   [pA]      %
-----|-----|-----|-----|-----|
  1   14.795   BB    0.0926  268.28705  34.06500  97.35552
  2   15.779   BP    0.0822    7.28753    1.04039   2.64448

Totals :                      275.57457  35.10539
  
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product **4d**

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Area Percent Report
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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	17.808	BV	0.1751	897.39734	60.56636	49.92897
2	18.307	VP	0.1447	899.95074	72.94046	50.07103

Totals : 1797.34808 133.50682

=====
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	17.852	BV	0.1746	1274.87769	85.56016	96.50159
2	18.123	VB	0.0899	46.21727	6.04722	3.49841

Totals : 1321.09495 91.60738

File name : sl-4-17003.CH2

Info :

Vial # = 1 Rack # = 1
 Injection Date : 24-Sep-2005 12:39:02
 Curr. Date : 27-Sep-2005 11:29:30
 User : SL
 Group : DATA
 Control Method : BENJI-XIAN

#	Name	RT	Area[μV.Sec]	%Area
1		11.525	1870171.121	51.24
2		14.750	1779842.750	48.76

Total Area of Peak = 3650013.872 [μV.Sec]

File name : sl-3-90002.CH2

Info :

AD, i-PrOH:HEX=595, 250 nm,

Vial # = 1 Rack # = 1
 Injection Date : 13-Aug-2005 12:15:04
 Curr. Date : 27-Sep-2005 11:31:18
 User : SL
 Group : DATA
 Control Method : BENJI-XIAN

#	Name	RT	Area[μV.Sec]	%Area
1		11.867	3748201.000	95.31
2		14.875	184541.272	4.69

Total Area of Peak = 3932742.272 [μV.Sec]