Supporting Information

Rh-Catalyzed Highly Regioselective Hydroformylation to Linear Aldehyde by Employing Porous Organic Polymer as

a Ligand

Zhaozhan Wang, and Yong Yang* *Corresponding author E-mail: <u>yangyong@qibebt.ac.cn</u>

Table Contents

1. General considerations	1
2. Synthesis of polymer supported phosphorus ligands	1
3. Characterization of the as-prepared ligand	10
4. Test of as-prepared ligands	11
 4.1 General procedure for the hydroformylation of 1-hexene 4.2 Recycling studies of the Rh/CPOL-BPa&1VB in hydroformylation of 1-h 	11 1exene 11
5. Characterization results	12
6. ¹ H and ¹³ C NMR spectra	13
7. GC Data for table 1	24
8. Reference	26

1. General considerations

Unless otherwise noted, all reagents were purchased commercially from Sigma-Aldrich, or Aladdin and used as received without further purification. All operations were carried out in an argon atmosphere using glove box and Schlenk techniques unless otherwise specified. Anhydrous tetrahydrofuran (THF), hexanes and toluene were obtained from an argon purged solvent purification system comprised of columns of activated alumina and molecular sieves. Gas chromatography analysis was performed on an Agilent HP-7890 instrument with a flame ionization detector (FID) and an HP-5MS capillary column (30 m, 0.25 mm i.d., 0.25 µm film thicknesses) using helium as the carrier gas. Gas chromatography-mass spectrometry analysis was carried out on an Agilent HP-7890 instrument with an Agilent HP-5975 with triple-axis detector and HP-5 capillary column using helium carrier gas. NMR spectra were received using DRX-400, or DRX-600, Chemical shifts are reported in ppm relative to the residual solvent signal (CDCl₃: 7.26 ppm (¹H), 77.16 ppm (¹³C), DMSO: 2.50 ppm (¹H), 39.52 ppm (^{13}C)). Multiplicities were reported using the following abbreviations: s = singlet, d =doublet, dd = doublet of doublets, t = triplet, q = quartet, m = multiplet, brs = broadsinglet. High-resolution mass data were recorded on Bruke Maxis UHR TOF mass spectrometers in ESI mode.

2. Synthesis of polymer supported phosphorus ligands

Synthesis of 1,1'-(chlorophosphanediyl)bis(1H-pyrrole).



The 1,1'-(chlorophosphanediyl)bis(1H-pyrrole) was synthesized according to the reported literature procedure^[1]. To a stirring solution of Et₃N (12.9 g, 3.5 eq) in THF

(100 mL) in a 250-mL three-necked round bottomed flask under argon was added PCl₃ (5.0 g, 1 eq) slowly at 0 °C. The solution was maintained at 0 °C and pyrrole (5.0 g, 2.05 eq) was added dropwise to it. The reaction mixture was stirred for 6 hours at room temperature. The mixture was then filtered, the filter cake was washed with THF and the filtrate was removed in vacuo. The residue was distilled in vacuo at 10⁻³ Torr to afford compound **2** (6.0 g, 81% yield) as a colorless liquid. ¹H NMR (400 MHz, C₆D₆) δ (ppm): 6.84-6.74 (m, 4H), 6.18 (t, *J* = 2.0 Hz, 4H); ¹³C NMR (101 MHz, C₆D₆) δ (ppm): 122.4 (d, *J* = 17.0 Hz), 113.7 (d, *J* = 5.0 Hz); ³¹P NMR (162 MHz, C₆D₆) δ (ppm): 104.4. Analytical data matches that reported in the literature^[1].

Synthesis of 2-hydroxy-5-methoxybenzaldehyde (2).



The compound **2** was synthesized according to the reported literature procedure^[2]. Et₃N (36.6 g, 3 eq) was added to a mixture of MgCl₂ (34.5 g, 3 eq) and paraformaldehyde (18.0 g, 5 eq) in THF (600 mL) in a 2-L three-necked round-bottomed flask under argon. The mixture was stirred for 10 min at room temperature. Compound **1** (15.0 g, 1 eq) was added to above reaction mixture. The resulting reaction mixture was stirred for 20 hours at 80°C. Cooled down to room temperature. The reaction mixture was acidified to pH=3 by 1M HCl and diluted with 1000 ml of water. The solution was extracted twice with 500 ml of ethyl acetate and the organic layer was washed with brine and dried over anhydrous Na₂SO₄. It was filtered and concentrated under vacuum. Purification by flash chromatography on silica gel provided compound **2** (17.0 g, 92% yield) as a yellow liquid. ¹H NMR (600 MHz, CDCl₃) δ (ppm): 10.62 (s, 1H), 9.83 (s, 1H), 7.12 (dd, *J* = 9.1, 3.1 Hz, 1H), 6.97 (d, *J* = 3.1 Hz, 1H), 6.90 (d, *J* = 9.0 Hz, 1H), 3.79 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ (ppm): 196.2, 156.0, 152.7, 125.2, 120.0, 118.6, 115.2, 55.8. Analytical data matches that reported in the

literature^[2].

Synthesis of 2,2'-dihydroxy-5,5'-dimethoxy-[1,1'-biphenyl]-3,3'dicarbaldehyde(3)



Compound **3** (1.0 g, 1 eq), MeOH (5 ml), Trimethoxymethane (1.05 g, 1.5 eq) and Tetrabutylammonium tribromide (0.16 g, 0.05 eq) were added to a 100-mL threenecked round bottomed flask under argon, and the reaction mixture was stirred at 80 °C for 2 hours. When the reaction was completed, it was allowed to cool down to room temperature and diluted with 25 ml of MeOH. A solution of $K_3Fe(CN)_6$ (2.16 g, 1eq) and KOH (1.29 g, 3.5 eq) in 30 ml of water was added dropwise to above reaction system under vigorous stirring over 1 hour at room temperature. The mixture was stirred for 2 hours at room temperature. It was acidified to pH=1 by 1M HCl and stirred unceasingly for 30 min at room temperature. The crude product was filtered out and further purified by flash chromatography on silica gel provided compound **3** (0.55 g, 56% yield) as a yellow solid. ¹H NMR (600 MHz, CDCl₃) δ (ppm): 11.04 (s, 2H), 9.95 (s, 2H), 7.30 (d, *J* = 3.1 Hz, 2H), 7.11 (d, *J* = 3.1 Hz, 2H), 3.88 (s, 6H); ¹³C NMR (151 MHz, CDCl₃) δ (ppm): 196.2, 153.5, 152.3, 126.7, 126.1, 120.5, 115.9, 56.0. Analytical data matches that reported in the literature^[3].

Synthesis of 5,5'-dimethoxy-3,3'-divinyl-[1,1'-biphenyl]-2,2'-diol(4).



t-BuOK (1.34 g, 4.5 eq) was added in portions to a mixture of Methyltriphenylphosphonium bromide (4.24 g, 4.5 eq) in THF (40 mL) in a 100-mL three-necked round-bottomed flask under argon. The mixture was stirred for 30 min at room temperature. Compound **3** (0.8 g, 1 eq) was added to above reaction system. The last reaction mixture was stirred for 15 hours at room temperature. The reaction mixture was quenched with 100 ml of water and extracted twice with 100 ml of ethyl acetate. The organic layer was washed with brine and dried over anhydrous Na₂SO₄. It was filtered and concentrated under vacuum. Purification by flash chromatography on silica gel provided compound **4** (0.72 g, 91% yield) as a white solid. ¹H NMR (400 MHz, DMSO) δ (ppm): 8.33 (s, 2H), 7.17-7.01 (m, 4H), 6.72 (d, *J* = 3.1 Hz, 2H), 5.82 (dd, *J* = 17.7, 1.4 Hz, 2H), 5.28 (dd, *J* = 11.1, 1.3 Hz, 2H), 3.75 (s, 6H); ¹³C NMR (101 MHz, DMSO) δ (ppm): 153.3, 145.4, 132.4, 129.4, 127.6, 117.1, 115.0, 110.4, 55.9.

Synthesis of 1,1',1'',1'''-(((5,5'-dimethoxy-3,3'-divinyl-[1,1'-biphenyl]-2,2'-diyl)bis (oxy))bis(phosphanetriyl))tetrakis(1H-pyrrole)(5).



A solution of 1,1'-(chlorophosphanediyl)bis(1H-pyrrole) (400 mg, 3 eq) in THF (5 mL) in a 50-mL three-necked round bottomed flask under argon was cooled down to 0°C. Another solution of compound **4** (200 mg, 1 eq) and Et₃N (203 mg, 3 eq) in THF (5 mL) was then added dropwise slowly to above solution. The mixture was stirred for 30 min at room temperature. Quenched with 50 ml of water and extracted twice with 20 ml of ethyl acetate. The organic layer was washed with brine and concentrated under vacuum. Purification by flash chromatography on silica gel provided compound **5** (380

mg, 91% yield) as a pink solid. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 6.83-6.76 (m, 6H), 6.67-6.60 (m, 4H), 6.51 (d, J = 3.1 Hz, 2H), 6.24-6.12 (m, 6H), 6.06 (t, J = 2.1 Hz, 4H), 5.45 (dd, J = 17.4, 1.2 Hz, 2H), 5.00 (dd, J = 10.9, 1.1 Hz, 2H), 3.62 (s, 6H); ¹³C NMR (101 MHz, CDCl₃) δ (ppm): 156.0, 142.4 (t, J = 5.1 Hz), 132.2 (t, J = 1.2 Hz), 131.4 (t, J = 2.3 Hz), 130.8, 121.7-121.1 (m), 116.4, 116.1, 112.1 (t, J = 2.3 Hz), 111.9 (t, J = 2.3), 111.6, 55.5; ³¹P NMR (162 MHz, CDCl₃) δ (ppm): 108.7; HRMS (ESI) m/z : calcd. for C₃₄H₃₂N₄O₄P₂ [M+H], 623.1932; found, 623.1980.

Synthesis of 4,4"-divinyl-5'-(4-vinylphenyl)-1,1':3',1"-terphenyl(7).



The compound **7** was synthesized according to the reported literature procedure^[4]. Pd(PPh₃)₄ (276.1 mg, 0.05 eq) was added to a mixture of compound **6** (1.5 g, 1 eq), 4-Vinylbenzeneboronic acid (4.2 g, 6 eq), K₂CO₃ (4.0 g, 6 eq) and water (4.5 mL) in toluene (30 mL) in a 50-mL three-necked round bottomed flask under argon. The mixture was stirred overnight at 110 °C. Quenched with 100 ml of water and extracted twice with 50 ml of ethyl acetate. The organic layer was washed with brine and concentrated under vacuum. Purification by flash chromatography on silica gel provided compound **7** (1.2 g, 65% yield) as a white solid. ¹**H NMR** (400 MHz, CDCl₃) δ (ppm): 7.76 (s, 3H), 7.65 (d, *J* = 8.2 Hz, 6H), 7.51 (d, *J* = 8.2 Hz, 6H), 6.77 (dd, *J* = 17.6, 10.9 Hz, 3H), 5.81 (d, *J* = 17.6 Hz, 3H), 5.29 (d, *J* = 11.0 Hz, 3H); ¹³C **NMR** (101 MHz, CDCl₃) δ (ppm): 142.0, 140.5, 137.0, 136.4, 127.5, 126.8, 124.9, 114.2. Analytical data matches that reported in the literature^[4]. Synthesis of tris(4-vinylphenyl)phosphane(9).



n-BuLi (6.0 mL, 1.1 eq) was added to THF (50 mL) at -78 °C in a 100-mL threenecked round bottomed flask under argon. A solution of compound **8** (2.5 g, 1 eq) in THF (5 mL) was added dropwise slowly to above solution over 1 hour at -78 °C. The solution was stirred for 1 hour at -78 °C. Another solution of PCl₃ (0.38 g, 0.2 eq) in THF (5 mL) was also added dropwise slowly to above solution over 1 hour at -78 °C. The resulting solution was stirred for 2 hours at room temperature. Quenched with 100 ml of water and extracted twice with 50 ml of ethyl acetate. The organic layer was washed with brine and concentrated under vacuum. Purification by flash chromatography on silica gel provided compound **9** (0.66 g, 70% yield) as a white solid. ¹**H NMR** (400 MHz, CDCl₃) δ (ppm): 7.39-7.35 (m, 6H), 7.27 (t, *J* = 7.9 Hz, 6H), 6.70 (dd, *J* = 17.6, 10.9 Hz, 3H), 5.77 (dd, *J* = 17.6, 0.4 Hz, 3H), 5.27 (d, *J* = 11.0 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ (ppm): 138.0, 136.7 (d, *J* = 10.8 Hz), 136.4, 133.9 (d, *J* = 19.6 Hz), 126.3 (d, *J* = 7.1 Hz), 114.7; ³¹**P NMR** (162 MHz, CDCl₃) δ (ppm): -6.7. Analytical data matches that reported in the literature^[5].

Synthesis of 4-vinylphenol(11).



t-BuOK (4.1 g, 2.25 eq) was added in portions to a mixture of Methyltriphenylphosphonium bromide (13.2 g, 2.25 eq) in THF (120 mL) in a 250-mL three-necked round-bottomed flask under argon. The mixture was stirred for 30 min at room temperature. Compound **10** (2.0 g, 1 eq) was added to above reaction system. The resulting reaction mixture was stirred for 8 hours at room temperature. The reaction mixture was quenched with 300 ml of water and extracted twice with 300 ml of ethyl acetate. The organic layer was washed with brine and dried over anhydrous Na₂SO₄. It was filtered and concentrated under vacuum. Purification by flash chromatography on silica gel provided compound **11** (1.9 g, 96% yield) as a white solid. ¹**H NMR** (600 MHz, DMSO) δ (ppm): 9.54 (s, 1H), 7.29 (d, *J* = 10.9, 2H), 6.77 (d, *J* = 5.5, 2H), 6.62 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.59 (d, *J* = 17.6 Hz, 1H), 5.05 (d, *J* = 10.9 Hz, 1H); ¹³**C NMR** (151 MHz, DMSO) δ (ppm): 157.9, 136.9, 128.8, 127.9, 115.8, 111.1. Analytical data matches that reported in the literature^[6].

Synthesis of tris(4-vinylphenyl) phosphite (12).



The compound **12** was synthesized according to the reported literature procedure^[6]. PCl₃ (0.68 g, 1 eq) in THF (2 mL) was added to a solution of Et₃N (2.3 g, 4.5 eq) and compound **11** (1.8 g, 3 eq) in THF (40 mL) in a 100-mL three-necked, round bottomed flask under argon at 0°C. The mixture was stirred for 1 hour at 0°C. Quenched with 100 ml of water and extracted twice with 50 ml of ethyl acetate. The organic layer was washed with brine and concentrated under vacuum. Purification by flash chromatography on silica gel provided compound **12** (1.45 g, 75% yield) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.28 (d, *J* = 8.6 Hz, 6H), 7.05-6.94 (m, 6H), 6.59 (dd, *J* = 17.6, 10.9 Hz, 3H), 5.58 (dd, *J* = 17.6, 0.6 Hz, 3H), 5.12 (dd, *J* = 10.9, 0.4

Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ (ppm): 150.1 (d, J = 3.1 Hz), 134.9, 132.9 (d, J = 1.1 Hz), 126.5, 119.7 (d, J = 7.0 Hz), 112.3; ³¹P NMR (162 MHz, CDCl₃) δ (ppm): 127.6. Analytical data matches that reported in the literature^[6].

Synthesis of CPOL-BPa&1VB.



Compound **5** (100 mg, 1 eq), styrene (167.2 mg, 10 eq), AIBN (6.6 mg, 0.25 eq) and THF (2 mL) were added to a 25-mL sealed tube under argon. The solution was stirred for 48 h at 100°C. The product was precipitated by adding methanol (10 mL), it was filtered out and washed with methanol, the solid was dried in vacuum to afford CPOL-BPa&1VB (245 mg, 92% yield) as a pink solid.

Synthesis of CPOL-BPa&2VB.



Compound **5** (200 mg, 1 eq), divinylbenzene (418.0 mg, 10 eq), AIBN (13.2 mg, 0.25 eq) and THF (5 mL) were added to a 25-mL sealed tube under argon. The solution was stirred for 24 h at 100°C. The product was precipitated by adding methanol (15 mL), it was filtered out and washed with methanol, the solid was dried in vacuum to afford CPOL-BPa&2VB (550 mg, 89% yield) as a pink solid.

Synthesis of CPOL-BPa&3VTPB.



Compound 5 (100 mg, 1 eq), compound 7 (617.0 mg, 10 eq), AIBN (6.6 mg, 0.25 eq) and THF (10 mL) were added to a 25-mL sealed tube under argon. The solution was stirred for 24 h at 100°C. The product was precipitated by adding methanol (30 mL), it was filtered out and washed with methanol, the solid was dried in vacuum to afford CPOL-BPa&3VTPB (650 mg, 91% yield) as a white solid.

Synthesis of CPOL-BPa&3VPPh₃.



Compound **5** (100 mg, 1 eq), compound **9** (546 mg, 10 eq), AIBN (6.6 mg, 0.25 eq) and THF (10 mL) were added to a 25-mL sealed tube under argon. The solution was stirred for 24 h at 100°C. The product was precipitated by adding methanol (30 mL), it was filtered out and washed with methanol, the solid was dried in vacuum to afford CPOL-BPa&3VPPh₃ (600 mg, 93% yield) as a white solid.

Synthesis of CPOL-BPa&3VTPPi.



Compound **5** (100 mg, 1 eq), compound **12** (624 mg, 10 eq), AIBN (6.6 mg, 0.25 eq) and THF (10 mL) were added to a 25-mL sealed tube under argon. The solution was stirred for 24 h at 100°C. The product was precipitated by adding methanol (30 mL), it was filtered out and washed with methanol, the solid was dried in vacuum to afford CPOL-BPa&3VTPPi (650 mg, 90% yield) as a white solid.

3. Characterization of the as-prepared ligand

¹³ C (101 MHz) cross-polarization magic-angle spinning (CP-MAS) and ³¹ P (162 MHz) HPDEC-MAS solid-state NMR experiments were recorded on a Bruker 400 MHz. The morphology of the ligand was examined using a Hitachi S-4800 scanning electron microscope (SEM) and a Hitachi H-7650 transmission electron microscope (TEM). Nitrogen adsorption-desorption data were obtained using a Micromeritics ASAP 2020 static volumetric sorption analyzer. The samples were outgassed for 15 h at 150 °C before the measurements. The specific surface area of the samples was calculated using the Brunauer-Emmett-Teller (BET) method. The pore size distribution was determined using non-local density functional theory (DFT). Thermogravimeric analysis (TGA) was determined on a STA449F5 jupiter, the sample was heated at the rate of 10 K•min⁻¹ from 298 K up to 973 K under a nitrogen atmosphere.

4. Test of as-prepared ligands

4.1. General procedure for the hydroformylation of 1-hexene.

In a glove box, a 25-mL sealed tube was charged with CPOL-BPa&1VB (8 mg), Rh(acac)(CO)₂ (0.49 mg, 1.9 x 10⁻³ mmol) and 1-hexene (3 mL, 24.2 mmol). The mixture was stirred for 24 hours at room temperature and then it was transferred to a stainless steel autoclave (25 mL). After sealing and purging with syngas (CO/H₂ = 1:1) for 3 times, the pressure of syngas was adjusted to 2 MPa. The reaction was stirred for 8 hours at 80°C. The autoclave was cooled to room temperature, and the gas was released slowly in a well-ventilated hood. Add decane (2.3 mL, 12.1 mmol) as the internal standard. The mixture subsequently was analyzed by GC.

4.2. Recycling studies of the Rh/CPOL-BPa&1VB in hydroformylation of 1hexene

In a glove box, a 25-mL sealed tube was charged with CPOL-BPa&1VB (32 mg), Rh(acac)(CO)₂ (1.96 mg, 7.6 x 10^{-3} mmol) and 1-hexene (3 mL, 24.2 mmol). The mixture was stirred for 24 hours at room temperature and then it was transferred to a stainless steel autoclave (25 mL). After sealing and purging with syngas (CO/H₂ = 1:1) for 3 times, the pressure of syngas was adjusted to 2 MPa. The reaction was stirred for 1 hours at 80°C. The autoclave was cooled to room temperature, and the gas was released slowly in a well-ventilated hood. Add decane (2.3 mL, 12.1 mmol) as the internal standard. The mixture subsequently was analyzed by GC. The catalyst was separated from reaction mixture by centrifugation and used to test next recycling reaction with the same condition and procedure. The mixture subsequently was analyzed by GC.

5. Characterization results



Figure S1. TGA curve of the CPOL-BPa&1VB.

6. ¹H and ¹³C NMR spectra















250 230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -20 -40 fl (ppm)



















Figure S2. ³¹P MAS NMR spectrum for the as-prepared catalyst upon reaction of Rh(acac)(CO)₂ with CPOL-BPa&1VB.



7. Partial GC Data

Hydroformylation of 1-Hexene at 60℃



Hydroformylation of 1-Hexene at 80°C



Hydroformylation of 1-Octene at 80°C



Hydroformylation of 2-Octene at 100°C



Hydroformylation of styrene at 80°C

8. Reference

- [1] Jackstell R, Klein H, Beller M, et al. *European Journal of Organic Chemistry*, 2001, 20, 3871-3877.
- [2] Fugard A J, Thompson B K, Slawin A M Z, et al. Organic letters, 2015, 17, 5824-5827.
- [3] Neelamegam R, Palatnik M T, Fraser-Rini J, et al. Tetrahedron Letters, 2010, 51,

2497-2499.

- [4] Gopalakrishnan D, Dichtel W R. Journal of the American Chemical Society, 2013, 135, 8357-8362.
- [5] Li C, Xiong K, Yan L, et al. Catalysis Science & Technology, 2016, 6, 2143-2149.
- [6] Sun Q, Aguila B, Verma G, et al. Chem, 2016, 1, 628-639.