Supporting Information For

Synthesis of New Monodentate Spiro Phosphoramidite Ligand and Its Application in Rh-catalyzed Asymmetric Hydrogenation Reactions

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Part1. Ligand Synthesis

Bis(2-methoxy-6-phenoxyphenyl)methanone (2). To a solution of **1** (10.0 g, 25.0 mmol) in dry THF (80 mL) was slowly added *n*-BuLi (20 mL, 50 mmol, 2.5 M in hexane) at -78 °C within 15 minutes. The solution was stirred at -78 °C for 30 minutes, then at room temperature for two hours. The solution was then cooled to -78°C again, and transferred through a cannular into the solution of methyl chloroformate (1.94 mL, 25 mmol) in dry THF (40 mL) at -78 °C, then stirred overnight. The reaction was quenched by slowly adding 20 mL of aqueous NH₄Cl (saturated) at 0 °C. The solvent THF was then removed under reduced pressure and the residue was extracted with EtOAc. The combined organic solution was washed with water and brine, dried over Na₂SO₄, and concentrated. The white precipitates were collected by filtration, and dried in vacuum to get **2** (6.6 g, 62% yield). ¹H-NMR (360 MHz, CD₂Cl₂) δ 3.69 (s, 6H, ArO-CH₃), 6.39, 6.40 (d, 2H, *J*=8.3Hz, Ar-H), 6.61, 6.63 (d, 2H, *J*=8.3Hz, Ar-H), 6.76-6.79 (m, 4H, Ar-H), 7.01-7.05 (m, 2H, Ar-H), 7.16-7.25 (m, 6H, Ar-H); ¹³C-NMR (91 MHz, CD₂Cl₂) δ 56.7, 107.1, 111.7, 119.1, 123.6, 124.7, 130.0, 131.7, 156.1, 157.7, 159.3, 191.9.

(±)-9,9'-spirobixanthene- 1,1'-diol (3). To a solution of **2** (1.0 g, 2.3 mmol) in dry toluene (20 mL) was added AlCl₃ (1.9 g, 14.3 mmol). The solution was warmed slowly and reflux for 30 minutes. Then it was cooled to 0°C and concentrated aqueous HCl (20 mL) was introduced with vigorous stirring. After refluxing for 1 hour, the reaction mixture was extracted with EtOAc, washed with concentrated HCl, water, aqueous NaHCO₃ and brine, dried over Na₂SO₄, and concentrated. Flash chromatography

(eluting with CH₂Cl₂) gave **3** as light-yellow powder (0.64 g, yield 72%). ¹H-NMR (360 MHz, CD₂Cl₂) δ 6.29, 6.31 (d, 2H, Ar-**H**), 6.59-6.61 (dd, 2H, *J*₁=8.2Hz, *J*₂=0.9Hz, Ar-**H**), 6.78-6.80 (m, 4H, Ar-**H**), 6.97-7.01 (m, 4H, Ar-**H**), 7.04-7.08 (m, 2H, Ar-**H**), 8.12 (s, 2H, Ar-OH); ¹³C-NMR (91 MHz, CD₂Cl₂) δ 38.5, 107.5, 111.0, 115.7, 116.6, 123.3, 127.8, 128.8, 131.7, 132.1, 150.2, 151.9, 156.7.

Resolution of (±)-9,9'-spirobixanthene- 1,1'-diol (3**).** A suspension of racemic **3** (3.14 g, 8.26 mmol) and *N*-benzylcinchonidinium chloride **6** (1.84 g, 4.37 mmol) in acetonitrile (30 mL) was refluxed for 6 hours, then cooled slowly to room temperature overnight. The white solid (1:1 inclusion complex, 99.1% ee) was collected by filtration, then refluxed in acetonitrile (20 mL) for 6 hours, and cooled slowly to room temperature overnight. This precipitate was collected by filtration, washed twice with small amount of CH₃CN and dried in vacuum. To a suspension of the purified 1:1 complex in ethyl acetate (30 mL) was added 2N HCl (20 mL). The mixture was stirred until the entire solid was dissolved. The organic layer was separated, washed with 2N HCl (20 mL) and brine, dried over Na₂SO₄. Concentration under reduced pressure produced enantiomerically pure (*R*)-(+)-**3** (1.24 g, 79% yield, >99.9% ee). [α]_D²⁰ = +40.2 (*c* = 1.0, CHCl₃). The mother solution containing enriched *S* enantiomer was concentrated, and refluxed with *N*-benzylquininium chloride (1.97 g, 4.37 mmol) in acetonitrile (30 mL) for 6 hours. The clear solution was allowed to cool overnight. The precipitate was collected by filtration, washed with small amount of acetonitrile. Then it was added into EtOAc, washed with 2N HCl and brine, dried over Na₂SO₄. Concentration under reduced pressure produced enantiomerically pure (*S*)-(-)-**3** (1.22 g, 78% yield, 99.8% ee). The ee value was determined by HPLC on a Chiralcel AD-H column with isopropanol/hexane (4:96) as eluent.

X-ray diffraction of molecular complex crystal of (*R*)-**3** and **6**

Single crystals containing (*R*)-**3/6** complex was grown from acetonitrile for X-ray diffraction. The results are listed in Table 1.

Table 1. X-ray diffraction data.

Diffractometer	CCD area detector
Radiation source	fine-focus sealed tube, MoK
Generator power	1600 watts (50 kV, 32mA)
Detector distance	5.8 cm
Data collection method	omega scans
Theta range for data collection	1.20 to 28.30°
Index ranges	-19 ≤ <i>h</i> ≤ 18, -11 ≤ <i>k</i> ≤ 11, -22 ≤ <i>l</i> ≤ 15
Empirical formula	C ₅₃ H ₄₈ ClN ₃ O ₅
Formula weight	842.39

Temperature	95(2)K	
Wavelength	0.71073Å	
Crystal size	0.40 x 0.18 x 0.05mm	
Crystal habit	clear flat-needle	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 14.322(4) Å	$\alpha = 90^\circ$
	b = 8.975(2) Å	$\beta = 97.742(5)^\circ$
	c = 17.157(4) Å	$\gamma = 90^\circ$
Volume	2185.2(10) Å ³	
Z	2	
Density (calculated)	1.280g/cm ³	
Absorption coefficient	0.141mm ⁻¹	
F(000)	888	

(*R*)-*O,O'*-(9,9'-spirobixanthene-1,1'-diyl)-*N,N*-dimethylphosphoradmidte [(*R*)-4].

To the solution of (*R*)-**3** (0.5 g, 1.32 mmol) in 10mL dry toluene was added hexamethylphosphorous triamide (287 μ L, 1.58 mmol). The solution was stirred at reflux for 72 hours. Then the toluene was removed under reduced pressure. Flash chromatography on silica gel with CH₂Cl₂ afforded (*R*)-**4** as white powders. (0.21 g, 35%). ¹H-NMR (360 MHz, CD₂Cl₂) δ 2.29 (s, 6H, -N(CH₃)₂), 6.33-6.35 (m, 1H, Ar-**H**), 6.43-6.45 (m, 1H, Ar-**H**), 6.72-6.75 (m, 1H, Ar-**H**), 6.84-6.89 (m, 2H, Ar-**H**), 7.03-7.07 (m, 2H, Ar-**H**), 7.11-7.15 (m, 2H, Ar-**H**), 7.21-7.25 (m, 2H, Ar-**H**), 7.39-7.48 (m, 2H, Ar-**H**); ¹³C-NMR (91 MHz, CD₂Cl₂) δ 35.7 (d, *J*=15.5Hz, -N(CH₃)₂), 43.5 (s, C), 113.4 (s, C-H), 114.1 (d, *J*=2.6Hz, C-H), 117.2 (d, *J*=4.2Hz, 2(C-H)), 119.9 (s, C), 121.1-121.2(m, C-H), 121.6 (d, *J*=1.4Hz, C-H), 124.2 (d, *J*=1.7Hz, 2(C-H)), 126.5 (d, *J*=1.5Hz, 2(C-H)), 128.3 (s, C), 128.7 (s, C-H), 128.9 (d, *J*=2.7Hz, C-H), 129.7 (s, C-H), 129.9 (d, *J*=2.1Hz, C-H), 148.2 (d, *J*=4.1Hz, 2C), 150.3 (s, C), 150.4 (s, C), 151.6 (d, *J*=3.5Hz, 2C), 155.3 (s, C), 155.4 (s, C); ³¹P-NMR (146 MHz, CD₂Cl₂) δ 123.2 (s).

Part 2. General Procedure of Hydrogenation

A solution of [Rh(nbd)₂]BF₄ (0.374 mg, 0.001 mmol) and ligand (*R*)-**3** (1.0 mg, 0.0022 mmol) in CH₂Cl₂ (0.5 mL) was stirred in a glove-box for 10 min to allow the catalyst precursor to form. Then it was added into the solution of substrate (0.1 mmol) in 2.5 mL of CH₂Cl₂. Hydrogenation was performed in an autoclave with 25 psi of H₂ at room temperature for 12 hours. After releasing H₂, the reaction mixture was passed through a short silica gel plug to remove the catalyst. The concentrated solution was used for chiral GC to measure the enantiomeric excess. For hydrogenation of itaconic acid, the ee was determined by its corresponding dimethyl ester.