Preparation of an Amphiphilic Resin-Supported BINAP Ligand and Its Use for Rhodium-Catalyzed Asymmetric 1,4-Addition of Phenylboronic Acid in Water

Yusuke Otomaru, Taichi Senda, and Tamio Hayashi*

Department of Chemistry, Graduate School of Science, Kyoto University, Sakyo, Kyoto 606-8502, Japan

Supporting Data

General. All anaerobic and moisture-sensitive manipulations were carried out with standard Schlenk technique under predried nitrogen or glovebox techniques under prepurified argon. NMR spectra were recorded on a JEOL JNM LA-500 spectrometer (500 MHz for ^1H , 125 MHz for ^{13}C , and 202 MHz for ^{31}P). Chemical shifts are reported in δ ppm referenced to an internal SiMe_4 standard for ^1H NMR, chloroform-*d* (δ 77.05) for ^{13}C NMR, and external 85% H_3PO_4 standard for ^{31}P NMR. Optical rotations were measured on a JASCO DIP-370 polarimeter.

Materials. THF, Et_2O and dioxane were distilled from sodium benzophenone-ketyl under nitrogen. CH_2Cl_2 and DMF were distilled from CaH_2 under nitrogen. $\text{NiCl}_2(\text{dppe})^1$ and $\text{Rh}(\text{acac})(\text{C}_2\text{H}_4)_2^2$ were prepared according to the reported procedures. 2-Cyclohexenone, 2-cyclopentenone, 2-cycloheptenone, and trans-3-nonen-2-one were purchased and distilled before use. 5-Methyl-3-hexen-2-one, phenylboronic acid, (*S*)-2,2'-dihydroxy-1,1'-binaphthyl (BINOL), and 1-methyl-2-pyrrolidinone were purchased and used without further purification. (*S*)-6-Bromo-2,2'-dihydroxy-1,1'-binaphthyl (**2**) was prepared from (*S*)-BINOL according to the reported procedure.³

(*S*)-6-Bromo-2,2'-bis(trifluoromethanesulfonyloxy)-1,1'-binaphthyl (3**).** To a solution of (*S*)-6-bromo-2,2'-dihydroxy-1,1'-binaphthyl (**2**) (20.6 g, 56.3 mmol) and pyridine (13.7 mL, 170 mmol) in 100 mL of CH_2Cl_2 was added trifluoromethanesulfonic anhydride (22.7 mL, 135 mmol) at 0 °C, and the mixture was stirred at room temperature for 8 h. After removal of the solvent, the residue was diluted with 200 mL of ethyl acetate, and it was washed with 1N HCl, saturated NaHCO_3 , and brine. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by chromatography on silica gel column (benzene) to give 27.6 g (78% yield) of **3**. ^1H NMR (CDCl_3): δ 7.13 (d, J = 9.1 Hz, 1H), 7.20 (d, J = 8.6 Hz, 1H), 7.43 (t, J = 7.7 Hz, 1H), 7.47 (dd, J = 9.1, 2.0 Hz, 1H), 7.60 (t, J = 7.6 Hz, 1H), 7.61 (d, J = 9.3 Hz, 1H), 7.64 (d, J = 9.2 Hz, 1H), 8.02 (d, J = 8.2 Hz, 1H), 8.05 (d, J = 9.2 Hz, 1H), 8.16 (d, J = 9.2 Hz, 1H), 8.18 (d, J = 1.8 Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 118.15 (q, $J_{\text{C-F}}$ = 319 Hz), 118.20 (q, $J_{\text{C-F}}$ = 319 Hz), 119.38, 120.64, 121.83, 122.95, 123.97, 126.49, 127.46, 128.22, 128.49, 128.52, 130.44, 131.05, 131.49, 131.77, 132.34, 132.43, 133.03, 133.41, 145.39, 145.57. Anal. Calcd for $\text{C}_{22}\text{H}_{11}\text{O}_6\text{BrF}_6\text{S}_2$: C, 41.99; H, 1.76. Found: C, 42.24; H, 1.98. $[\alpha]^{20}_{\text{D}}$ +137 (*c* 0.49, CHCl_3).

(S)-6-Cyano-2,2'-bis(trifluoromethanesulfonyloxy)-1,1'-binaphthyl (4).

A solution of (S)-6-bromo-2,2'-bis(trifluoromethanesulfonyloxy)-1,1'-binaphthyl (**3**) (5.88 g, 9.34 mmol) and cuprous cyanide (1.50 g, 16.8 mmol) in 20 mL of 1-methyl-2-pyrrolidinone was stirred at 180 °C for 4 h. After cooled to about 100 °C, the reaction mixture was poured into 100 mL of 14% aqueous NH₃, and it was extracted with benzene. The organic layer was washed with 5% aqueous NH₃ (50 mL x 4) and brine (50 mL x 2), before it was dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by chromatography on silica gel column (benzene) to give 3.73 g (73% yield) of **4**. ¹H NMR (CDCl₃): δ 7.16 (d, *J* = 8.6 Hz, 1H), 7.37 (d, *J* = 8.9 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 1H), 7.55 (dd, *J* = 8.9, 1.5 Hz, 1H), 7.62 (t, *J* = 7.2 Hz, 1H), 7.62 (d, *J* = 9.2 Hz, 1H), 7.77 (d, *J* = 9.2 Hz, 1H), 8.04 (d, *J* = 8.4 Hz, 1H), 8.19 (d, *J* = 9.0 Hz, 1H), 8.23 (d, *J* = 9.2 Hz, 1H), 8.42 (s, 1H). ¹³C{¹H} NMR (CDCl₃): δ 111.36, 118.10 (q, *J*_{C-F} = 319 Hz), 118.15 (q, *J*_{C-F} = 319 Hz), 118.25, 119.42, 121.50, 122.33, 124.36, 126.17, 127.63, 128.29, 128.46, 128.65, 131.31, 132.45, 132.51, 132.68, 132.84, 134.30, 134.78, 145.36, 147.39. Anal. Calcd for C₂₃H₁₁NO₆F₆S₂: C, 48.01; H, 1.93; N, 2.43. Found: C, 48.21; H, 2.20; N, 2.24. [α]_D²⁰ +165 (*c* 0.98, CHCl₃).

(S)-6-Cyano-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (5).

To a solution of NiCl₂(dppe) (317 mg, 0.60 mmol) in DMF (12 mL) was added diphenylphosphine (610 μL, 3.5 mmol) at room temperature, and then the resulting solution was heated at 100 °C. After stirring at 100 °C for 30 min, to the mixture was added a solution of (S)-6-cyano-2,2'-bis(trifluoromethanesulfonyloxy)-1,1'-binaphthyl (**4**) (3.45 g, 6.0 mmol) and DABCO (2.69 g, 24 mmol) in DMF (18 mL). The reaction mixture was kept at 100 °C, and three additional portions of diphenylphosphine (610 μL x 3) were added at 1, 3, and 7 h later. The reaction mixture was stirred at 100 °C for 3 days, and then added to degassed methanol under nitrogen. The precipitate was filtered and washed with methanol. The desired product was purified by recrystallization (DMF) to give 2.82 g (73% yield) of **5**. ¹H NMR (CDCl₃): δ 6.65 (d, *J* = 8.6 Hz, 1H), 6.74 (d, *J* = 8.8 Hz, 1H), 6.85-6.90 (m, 2H), 6.96-7.03 (m, 4H), 7.06-7.12 (m, 6H), 7.15-7.25 (m, 10H), 7.33 (t, *J* = 8.1 Hz, 1H), 7.42 (dd, *J* = 8.6, 2.6 Hz, 1H), 7.57 (dd, *J* = 8.5, 2.3 Hz, 1H), 7.82 (d, *J* = 8.2 Hz, 1H), 7.90 (d, *J* = 8.6 Hz, 2H), 8.17 (s, 1H). ³¹P NMR (CDCl₃): δ -13.8 (d, *J*_{P-P} = 17.4 Hz, 1P), -13.9 (d, *J*_{P-P} = 17.4 Hz, 1P). Anal. Calcd for C₄₅H₃₁NP₂: C, 83.45; H, 4.82; N, 2.16; P, 9.56. Found: C, 83.19; H, 4.82; N, 2.09; P, 9.31. [α]_D²⁰ -130 (*c* 0.925, CHCl₃).

(S)-6-Hydroxycarbonyl-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (6).

A mixture of (S)-6-cyano-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (**5**) (259 mg, 0.40 mmol) and KOH (280 mg, 5.0 mmol) in dioxane (4 mL), MeOH (4 mL), and H₂O (1.5 mL) was refluxed for 24 h. The reaction mixture was acidified with 2N HCl, and then extracted with ethyl acetate. The organic layer was dried over MgSO₄ and concentrated under reduced pressure. The residue was purified by recrystallization (2-PrOH) to give 226 mg (85% yield) of **6**. ¹H NMR (CDCl₃): δ 6.71 (d, *J* = 8.5 Hz, 1H), 6.81 (d, *J* = 9.0 Hz, 1H), 6.87 (t,

$J = 7.6$ Hz, 1H), 6.98-7.22 (m, 20H), 7.33 (t, $J = 7.5$ Hz, 1H), 7.45 (t, $J = 8.9$ Hz, 2H), 7.52 (d, $J = 8.5$ Hz, 1H), 7.83 (d, $J = 8.1$ Hz, 1H), 7.90 (d, $J = 8.6$ Hz, 1H), 8.00 (d, $J = 8.7$ Hz, 1H), 8.65 (s, 1H), 11.47 (br s, 1H). ^{31}P NMR (CDCl_3): δ -14.1 (d, $J_{\text{P-P}} = 15.6$ Hz, 1P), -14.2 (d, $J_{\text{P-P}} = 15.6$ Hz, 1P). Anal. Calcd for $\text{C}_{45}\text{H}_{32}\text{O}_2\text{P}_2$: C, 81.07; H, 4.84; P, 9.29. Found: C, 80.84; H, 5.01; P, 9.37. $[\alpha]^{20}_{\text{D}} -149$ (c 0.92, CHCl_3).

PS-PEG resin-supported (S)-binap (1). TentaGel[®] S-NH₂ beads (2.0 g, 0.26 mmol N/g) were washed with acetonitrile (20 mL x 6) and chloroform (20 mL x 5) prior to use. A suspension of the washed TentaGel[®] S-NH₂ beads, (S)-6-Hydroxycarbonyl-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (**6**) (507 mg, 0.76 mmol), EDCI HCl (230 mg, 1.2 mmol), and HOBt (211 mg, 1.56 mmol) in DMF (40 mL) was stirred at room temperature for 4 h. The reaction mixture was filtered and the resin was washed with DMF (20 mL x 5) and dichloromethane (20 mL x 8). The resin was dried under reduced pressure to give 1.9 g of **1** (0.168 mmol BINAP/g). ^{31}P NMR (THF): δ -14.5 (br s). Found: C, 66.77; H, 8.06; N, 0.33; P, 1.04.

Reaction of Rh(acac)(C₂H₄)₂ with PS-PEG resin-supported (S)-binap (1). In an NMR sample tube, Rh(acac)(C₂H₄)₂ (2.6 mg, 10 μmol Rh) and PS-PEG resin-supported binap (**1**) (59.5 mg, 10 μmol binap) were charged and THF (0.5 mL) was added at room temperature. Within 3 min, Rh(acac)(C₂H₄)₂ was converted into Rh(acac)(PS-PEG-(S)-binap-**1**). ^{31}P NMR (THF): δ 55.0 (dd, $J_{\text{Rh-P}} = 194$ Hz, $J_{\text{P-P}} = 64$ Hz, 1P), 55.3 (dd, $J_{\text{Rh-P}} = 193$ Hz, $J_{\text{P-P}} = 64$ Hz, 1P).

Rhodium-catalyzed asymmetric 1,4-addition of phenylboronic acid to α,β -unsaturated ketones. The reaction conditions and results are summarized in Table 1. A typical procedure is shown below: A mixture of Rh(acac)(C₂H₄)₂ (1.5 mg, 6 μmol), phenylboronic acid (122 mg, 1.0 mmol), and **1** (53.6 mg, 9 μmol BINAP) in 0.5 mL of THF was stirred at room temperature for 3 min. After evaporation of the solvent, 2-cyclopentenone (16.4 mg, 0.20 mmol) and H₂O (1.0 mL) were added and the mixture was stirred at 100 °C for 3 h. The reaction mixture was filtered and the resin was washed with Et₂O. The filtrate was washed with saturated NaHCO₃ and brine. The organic layer was dried over MgSO₄ and concentrated under reduced pressure. The residue was purified by preparative TLC (silica gel, hexane/ethyl acetate = 3/1) to give 30.4 mg (95% yield) of 3-phenylcyclopentanone.

For the recycling of the catalyst, see footnote d of Table 1.

References

- (1) Booth, G.; Chatt, J. J. *Chem. Soc.* **1965**, 3239.
- (2) Cramer, R. *Inorg. Synth.* **1974**, 15, 16.
- (3) (a) Cai, D.; Larsen, R. D.; Reider, P. J. *Tetrahedron Lett.* **2002**, 43, 4055. (b) Hocke, H.; Uozumi, Y. *Tetrahedron*, **2003**, 59, 619.