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Synthesis of (*R*)- and (*S*)-7,7'-Bis(diphenylphosphino)-2,2'-dimethoxy-1,1'-binaphthyl, a New Axially Dissymmetric Bis(triarylphosphine)

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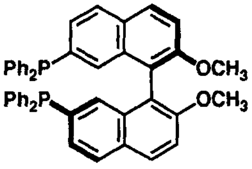
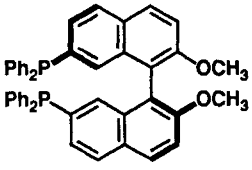
Abstract: A new axially dissymmetric bis(triarylphosphine) ligand 7,7'-bis(diphenylphosphino)-2,2'-dimethoxy-1,1'-binaphthyl has been synthesized in enantiomerically pure form.

Axially dissymmetric 2,2'-disubstituted 1,1'-binaphthyl compounds have been successfully used as chiral elements for a variety of asymmetric transformations.[1] These kinds of molecules serve as stoichiometric chiral auxilliaries[1b,c] as well as ligands in transition metal-catalyzed asymmetric processes.[1a,d—f] There are, however, very few examples of the use of the corresponding 7,7'-disubstituted derivatives.[2] Since small modifications of structures and electronic properties of chiral ligands are often reflected in the efficiencies of the asymmetric reactions,[3] we designed and synthesized a new type of diphosphine ligand **1**. This ligand is notable in that it has phosphine substituents at 7- and 7'-positions of binaphthyl moiety instead of at the conventional 2- and 2'-positions as in the case of BINAP (BINAP = 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl). Compound **1** is expected to form transition metal complexes with larger bite angle P-M-P than BINAP,[4] so metal complexes of **1** might have different properties as catalysts for asymmetric reactions from those of BINAP.

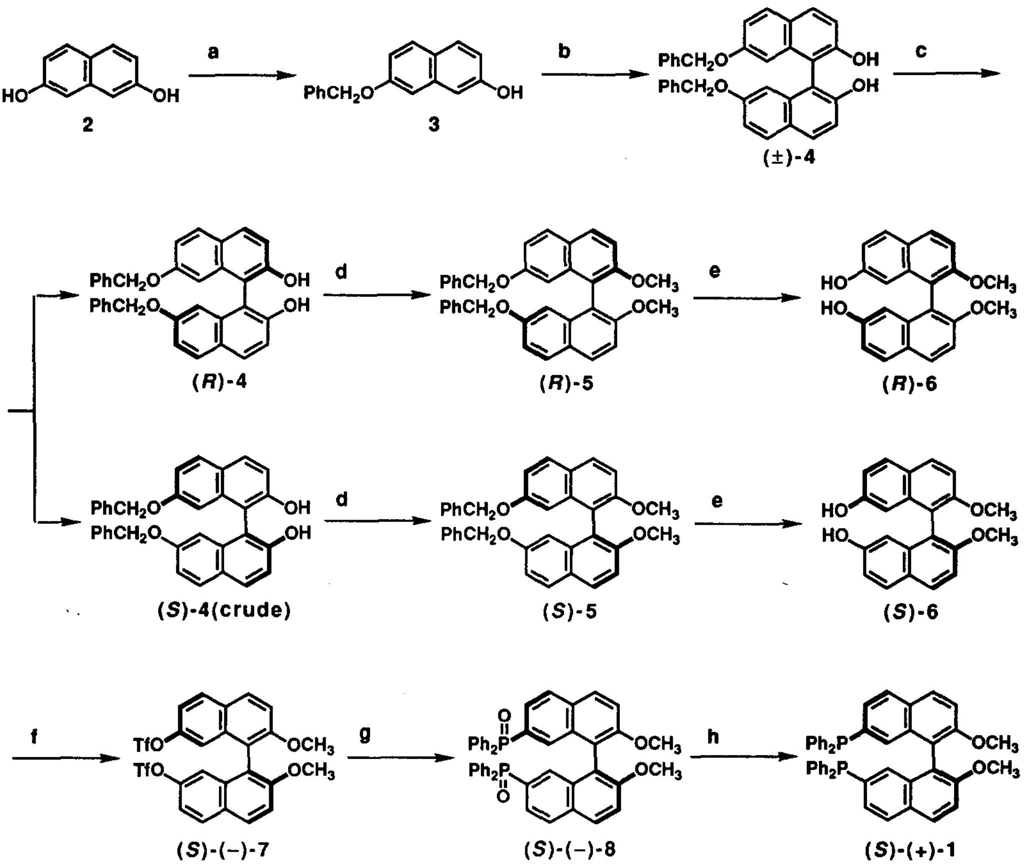


(*R*)-1



(*S*)-1

Enantiomerically pure (*R*)- and (*S*)-**1** were prepared starting from 2,7-naphthalenediol (**2**) as outlined in Scheme 1. Oxidative coupling of the monobenzylated compound **3**[2b] was conducted with $FeCl_3$ in a mixture of acetonitrile and water (1 : 2) to give (±)-**4** in 47% yield. When $Mn(acac)_3$ (acac = acetylacetonate) was used as oxidizing agent,[2b] the subsequent work up procedure was somewhat troublesome for us and the product (±)-**4** was obtained in poor yield (*ca.* 10%).



Scheme 1

Reagents and conditions: (a) $PhCH_2Br$, K_2CO_3, DMF, 35 °C. (b) $FeCl_3$, H_2O/CH_3CN (2:1), 90 °C, 1 h, 47%. (c) i) quinine, EtOH. ii) 1 *N* HClaq. (d) CH_3I, K_2CO_3, DMF, rt, overnight. (e) 10% Pd/C, $HCOONH_4$ (10 eq), MeOH, reflux, 0.5 h, quant. (f) $(CF_3SO_2)_2O$, 2,6-lutidine, 4-dimethylaminopyridine (0.4 eq), CH_2Cl_2, -40 °C—rt, quant. (g) $Ph_2P(O)H$, $Pd(OAc)_2$ (10 mol%), DPPP (10 mol%), HCOONa (0.22 eq), EtN^iPr_2, DMSO, 90 °C, 24 h, 93%. (h) $HSiCl_3$ (10 eq), Et_3N (11 eq), xylene, 100—140 °C, 55%.

Optical resolution of (±)-**4** was carried out as described by Diederich *et al*[2c] with some modifications. Enantiomerically pure (*R*)-(-)-**4**[7,8] was obtained in 37% yield based on (±)-**4** through clathrate formation with quinine followed by acidic aqueous workup. Resolved (*R*)-**4** was treated with methyl iodide, and recrystallization of the product from 2-propanol led to enantiomerically pure (*R*)-(-)-**5**[9] in 94% yield. On the other hand, preparation of enantiomerically pure (*S*)-**4** was rather difficult by simple recrystallization of the (*S*)-**4**—quinine complex recovered from the mother liquor. Thus, the crude (*S*)-**4** (*ca.* 91% *ee*) obtained by the treatment of the mother liquor with HCl was methylated with CH_3I and K_2CO_3. Recrystallization of *S* rich **5** from diethyl ether afforded enantiomerically pure (*S*)-(+)-**5**[9] in 27% yield from (±)-**4**.

Catalytic transfer hydrogenation[2b,c,10] of (*S*)-**5** afforded (*S*)-(+)-**6**[11] in quantitative yield, which was then converted quantitatively to ditriflate (*S*)-(-)-**7**.[6,12e,13]

Transition metal-mediated functionalization of aryl triflates[12] seems to be very attractive method for the conversion of **7** to **8**, though the reaction of ditriflate of 1,1'-binaphthalene-2,2'-diol with diphenylphosphine oxide catalyzed by $Pd(OAc)_2$ /DPPP (DPPP = 1,3-bis(diphenylphosphino)propane)/HCOONa resulted in the replacement of only one of the two trifluoromethanesulfonyloxy groups.[12k] Fortunately, however, less sterically hindered (*S*)-**7** was successfully converted to diphosphine dioxide (*S*)-(-)-**8**[6,14,15] in very high yield. Attempted coupling of (*S*)-**7** with $Ph_2(H)PBH_3$ catalyzed by $Pd(PPh_3)_4$[16] in acetonitrile was unsuccessful, probably due to the formation of only the monosubstituted product followed by decomposition. Reduction of (*S*)-**8** to the desired enantiomerically pure (*S*)-(+)-**1**[6,17] was performed by heating (*S*)-**8** with a large excess of trichlorosilane and triethylamine in xylene,[18] initially at 100 °C for 1 h, at 120 °C for 1 h, and finally at 140 °C for 6 h.

For the optical resolution of chiral diphosphine dioxides with C_2 chirality, (+)- or (-)-2,3-*O*-dibenzoyltartaric acid has often been used as a resolving agent.[18,19] Compound (±)-**8**, however, could not be resolved in this way.

The absolute configurations of (+)-**4** and (-)-**4** have been assigned as *S* and *R*, respectively.[2c] Since the subsequent transformations can be considered to proceed stereospecifically with retention of their configurations, the absolute configurations of (+)-**1** and (-)-**1** were assigned as *S* and *R*, respectively.

Further studies on the applications of this new diphosphine ligand **1** for asymmetric catalysis are in progress.

Acknowledgment

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1. See, for example, (a) Miyashita, A.; Yasuda, A.; Takaya, H.; Toriumi, K.; Ito, T.; Souchi, T.; Noyori, R. *J. Am. Chem. Soc.* **1980**, *102*, 7932. (b) Noyori, R.; Tomino, I.; Tanimoto, Y.; Nishizawa, M. *J. Am. Chem. Soc.* **1984**, *106*, 6709. (c) Sakamoto, A.; Yamamoto, Y.; Oda, J. *J. Am. Chem. Soc.* **1987**, *109*, 7188. (d) Maruoka, K.; Itoh, T.; Shirasaka, T.; Yamamoto, H.; *J. Am. Chem. Soc.* **1988**, *110*, 310. (e) Mikami, K.; Terada, M.; Nakai, T. *J. Am. Chem. Soc.* **1989**, *111*, 1940. (f) Uozumi, Y.; Hayashi, T. *J. Am. Chem. Soc.* **1991**, *113*, 9887.
2. (a) Diederich, F.; Hester, M. R.; Uyeki, M. A. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1705. (b) Hester, M. R.; Uyeki, M. A.; Diederich, F. *Isr. J. Chem.* **1989**, *29*, 201. (c) Castro, P. P.; Georgiadis, T. M.; Diederich, F. *J. Org. Chem.* **1989**, *54*, 5835.
3. See, for example, Takaya, H.; Ohta, T.; Noyori, R. "Catalytic Asymmetric Synthesis", Ojima, I., Ed. VCH Publishers, Inc. New York, NY, 1993, Chapter 1.

4. According to the molecular mechanics calculations using the CACHE system and the bond distance of 2.315 Å for Rh—P bond,[5] the optimum bite angles of Rh(I) complexes of **1** without any other coordinated ligands are 110° (square planar) and 125° (trigonal bipyramidal), while those of BINAP are 96° (square planar) and 100° (trigonal bipyramidal).
5. For the calculations of natural bite angles, see Casey, C. P.; Whiteker, G. T. *Isr. J. Chem.* **1990**, *30*, 299.
6. Satisfactory elemental analyses and consistent spectral data were obtained for all new compounds.
7. (*R*)-(-)-**4**—quinine: mp 186—187 °C; $[\alpha]_D^{20}$ -163 (*c* 0.52, $CHCl_3$).
8. (*R*)-(-)-**4**: mp 61—62 °C; $[\alpha]_D^{25}$ -248 (*c* 1.25, $CHCl_3$) (lit.[2c] -232.0).
9. (*R*)-(-)-**5**: mp 126.5—127 °C; $[\alpha]_D^{23}$ -132 (*c* 1.28, $CHCl_3$).
   (*S*)-(+)-**5**: mp 127—128 °C; $[\alpha]_D^{22}$ +136 (*c* 1.31, $CHCl_3$).
10. Ram, S.; Spicer, L. D. *Synth. Commun.* **1987**, *17*, 415.
11. (*R*)-(-)-**6**·Et_2O: mp 207—209 °C; $[\alpha]_D^{22}$ -119 (*c* 1.07, EtOH).
   (*S*)-(+)-**6**·Et_2O: mp 207—208 °C; $[\alpha]_D^{22}$ +113 (*c* 1.25, EtOH).
12. See, for example, (a) Stang, P. J.; Hanack, M.; Subramanian, L. R. *Synthesis* **1982**, 85. (b) McMurry, J. E.; Mohanraj, S. *Tetrahedron Lett.* **1983**, *24*, 2723. (c) Chen, Q.-Y.; Yang, Z.-Y. *Tetrahedron Lett.* **1986**, *27*, 1171. (d) Cacchi, S.; Ciattini, P. G.; Morera, E.; Ortar, G. *Tetrahedron Lett.* **1986**, *27*, 5541. (e) Dolle, R. E.; Schmidt, S. J.; Kruse, L. I. *J. Chem. Soc., Chem. Commun.* **1987**, 904. (f) Peterson, G. A.; Kunng, F.-A.; McCallum, J. S.; Wulff, W. D. *Tetrahedron Lett.* **1987**, *28*, 1381. (g) Chen, Q.-Y.; He, Y. B. *Synthesis* **1988**, 896. (h) Hirota, K.; Isobe, Y.; Maki, Y. *J. Chem. Soc., Perkin Trans. 1* **1989**, 2513. (i) Huth, A.; Beetz, I.; Schumann, I. *Tetrahedron* **1989**, *45*, 6679. (j) Echavarren, A. M.; Stille, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 5478. (k) Kurz, L.; Lee, G.; Morgans, D., Jr.; Waldyke, M. J.; Ward, T. *Tetrahedron Lett.* **1990**, *31*, 6321. (l) Ohta, T.; Ito, M.; Inagaki, K.; Takaya, H. *Tetrahedron Lett.* **1993**, *34*, 1615.
13. (*R*)-(+)-**7**: mp 139—141 °C; $[\alpha]_D^{22}$ +61 (*c* 1.17, $CHCl_3$).
   (*S*)-(-)-**7**: mp 140—141 °C; $[\alpha]_D^{21}$ -58 (*c* 1.11, $CHCl_3$).
14. (*R*)-(+)-**8**: $^{31}P\{^1H\}$ NMR ($CDCl_3$, 85% H_3PO_4 as external standard for all of the ^{31}P NMR determination in this work) δ 30.4; $[\alpha]_D^{24}$ +26 (*c* 0.76, $CHCl_3$).
   (*S*)-(-)-**8**: $[\alpha]_D^{23}$ -27 (*c* 1.01, $CHCl_3$).
15. Optically active **8** did not show clear melting point.
16. Imamoto, T.; Oshiki, T.; Onozawa, T.; Kusumoto, T.; Sato, K. *J. Am. Chem. Soc.* **1990**, *112*, 5244.
17. (*R*)-(-)-**1**: mp 79—80 °C; $[\alpha]_D^{22}$ -104 (*c* 0.55, $CHCl_3$); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 4.8; HRMS *m/z* (M^+, $C_{46}H_{36}O_2P_2$) calcd 682.2193, obsd 682.2191.
   (*S*)-(+)-**1**: mp 80—82 °C; $[\alpha]_D^{23}$ +109 (*c* 0.58, $CHCl_3$).
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