averaged. The concentration of the free amide remaining after complexation could then be calculated from the extinction coefficient and used to determine the apparent equilibrium constant. The equilibrium between free amide and the *sec*-butyllithium–amide complex was established within less than ca. 3 ms, which is the time required for the flowing solutions to move from the mixer to the observation chamber.

Kinetic data were obtained by digitizing 100 transmittance measurements at a specified wavelength and time interval under rapid stopped-flow conditions. Plots of percent transmittance vs time were generated via computer using measured zero and infinity light readings. The data were stored and then processed according to whether the absorbance increased or decreased and to the appropriate rate law. Unweighted linear regression analysis of the treated data versus time yielded the pseudo-first-order rate constants which were typically reproducible within 5%.

Freezing Point Depression Measurements and Data Analysis. The thermistor tube was hermetically sealed with a septum and connected to a vacuum line via a 2-ft stainless steel needle. Inside the tube was a glass stirring rod to which was attached a magnet and a 100-kΩ thermistor. Two wire leads connected to the thermistor were threaded through the septum and connected to the Wheatstone bridge. As the temperature of the environment about the thermistor changes, its resistance changes in a nearly linear fashion within a certain temperature range. A Wheatstone bridge transforms this change in resistance into a voltage change which is amplified, digitized, and recorded on a PLATO V computer using the same system as described in the previous section.

The thermistor was calibrated by immersing it in an ethanol–water/dry ice bath along with a precision calibrated thermometer from the National Bureau of Standards graduated in tenths of a degree Celsius. The digitized signal was measured as a function of temperature over the range of −5 to +7 °C, and all subsequent signal readings were transformed into temperatures with this calibration curve.

Cyclohexane was introduced into the thermistor tube with the aid of a gas-tight calibrated syringe. It was then chilled and agitated by moving an external magnet up and down adjacent to the internal magnete. The temperature was measured as a function of time, giving an initial endotherm and supercooling, followed by an exotherm resulting from the heat of crystallization, followed by a plateau. Extrapolating the plateau back to the endotherm gives the temperature of the freezing point. Changes in freezing point depression and observable precipitation did occur after ~30 min, so these experiments were carried out for no longer than 20 min.

Computer Modeling. The fitting of a model to the data was done by deriving equations from the rate and equilibrium expressions defined by the scheme being tested. The initial concentrations of the reagent, substrate, and catalyst employed in the experiment being modeled were used in these equations and the results compared to the experimental observations.

Acknowledgment. We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation for support.

Registry No. 4, 57199-01-6; **5**, 64712-52-3; *sec*-butyllithium, 598-30-1.

Supplementary Material Available: Tables, figures, and discussion of kinetic data for reactions of **4** and **5**, freezing point depressions, and general analyses of Schemes VI and VIII (28 pages). Ordering information is given on any current masthead page.

Asymmetric Synthesis Catalyzed by Chiral Ferrocenylphosphine–Transition-Metal Complexes. 6.[1] Practical Asymmetric Synthesis of 1,1′-Binaphthyls via Asymmetric Cross-Coupling with a Chiral [(Alkoxyalkyl)ferrocenyl]monophosphine/Nickel Catalyst

Tamio Hayashi,* Keiichi Hayashizaki, Takao Kiyoi, and Yoshihiko Ito*

Contribution from the Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606, Japan. *Received March 28, 1988*

Abstract: Cross-coupling of (2-methyl-1-naphthyl)magnesium bromide (**1a**) with 2-methyl-1-naphthyl bromide (**2a**) at −15 or 0 °C in the presence of nickel catalyst prepared in situ from nickel bromide and (*S*)-1-[(*R*)-2-(diphenylphosphino)ferrocenyl]ethyl methyl ether (**3a**) gave high yield of (*R*)-(−)-2,2′-dimethyl-1,1′-binaphthyl (**4a**) in up to 95% ee. Ferrocenylphosphine **3a** was also effective for the reaction of **1a** with 1-naphthyl bromide (**2b**) and that of (2-ethyl-1-naphthyl)magnesium bromide (**1c**) with **2b** to give corresponding cross-coupling products in 83 and 77% ee, respectively.

Optically active 1,1′-binaphthyl derivatives constitute an important class of compounds which have found extensive use in chiral auxiliaries for asymmetric synthesis,[2-6] and there has recently been an intense interest in obtaining the optically active binaphthyls by methods[7-10] other than those of optical resolution

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(3) For 2,2′-bisphosphine derivatives: (a) Takaya, H.; Mashima, K.; Koyano, K.; Yagi, M.; Kumobayashi, H.; Taketomi, T.; Akutagawa, S.; Noyori, R. *J. Org. Chem.* **1986**, *51*, 629. (b) Kitamura, M.; Ohkuma, T.; Inoue, S.; Sayo, N.; Kumobayashi, H.; Akutagawa, S.; Ohta, T.; Takaya, H.; Noyori, R. *J. Am. Chem. Soc.* **1988**, *110*, 629, and their previous papers cited therein.

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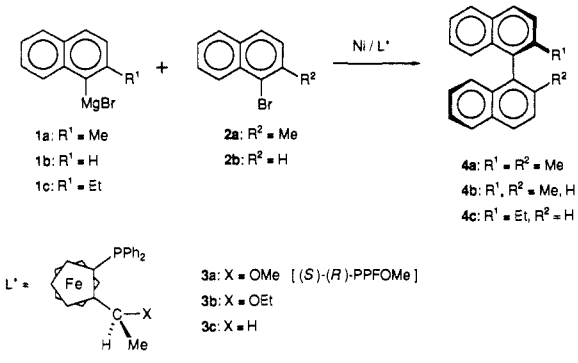
Table I. Asymmetric Cross-Coupling of the Grignard Reagents **1** with Bromides **2** in the Presence of Chiral Ferrocenylphosphine/Nickel Catalysts[a]

entry	Grignard reagent **1**	bromide **2**	catalyst (mol %)	reaction conditions: temp, °C	reaction conditions: time, h	product (yield %)[b]	$[\alpha]^{20}_D$, deg (c 1, $CHCl_3$)	% ee[c] (confign)
1	**1a** (R^1 = Me)	**2a** (R^2 = Me)	Ni/**3a** (5)	−15	92	**4a** (69)	−37.1[d]	95 (*R*)
2	**1a**	**2a**	Ni/**3a** (4)	−5	96	**4a** (68)	−35.6	94 (*R*)
3	**1a**	**2a**	Ni/**3a** (5)	0	37	**4a** (74)		93 (*R*)
4	**1a**	**2b** (R^2 = H)	Ni/**3a** (2)	−30	96	**4b** (92)	−33.2	83 (*R*)
5	**1a**	**2b**	Ni/**3a** (2)	−10	16	**4b** (84)	−33.9	80 (*R*)
6	**1a**	**2b**	Ni/**3a**[e] (2)	−10	21	**4b** (87)	+33.3	80 (*S*)
7	**1a**	**2b**[f]	Ni/**3a** (2)	−10	48	**4b** (40)		83 (*R*)
8	**1a**	**2b**	Ni/**3b** (2)	−10	24	**4b** (82)	−26.4	68 (*R*)
9	**1a**	**2b**	Ni/**3c** (2)	−10	88	**4b** (81)	−0.5	1 (*R*)
10	**1b** (R^1 = H)	**2a** (R^2 = Me)	Ni/**3a** (2)	−10	98	**4b** (25)		16 (*R*)
11	**1c** (R^1 = Et)	**2b** (R^2 = H)	Ni/**3a** (5)	−20	95	**4c** (85)	−26.9	77 (*R*)
12	**1c**	**2b**	Ni/**3a** (5)	0	45	**4c** (81)	−25.6	71 (*R*)

[a] The reaction was carried out in ether/toluene (1/1). [b] Isolated yield by silica gel chromatography (hexane) and based on the Grignard reagent **1**. [c] The enantiomeric purities of **4a**, **4b**, and **4c** were determined by HPLC analysis of **6**, **8**, and **10**, respectively, with a chiral column (Sumitomo Chemical Co., Sumipax OA, hexane/dichloroethane/ethanol = 250/20/1: OA-1100 for **6** and OA-2000 for **8** and **10**). [d] $[\alpha]^{22}_D$ − 17° (c 1.0, ethanol). Literature rotation for optically pure (*S*)-**4a** is $[\alpha]^{22}_D$ +19° (c 1.3, ethanol) (ref 18). [e] The enantiomeric phosphine ligand (*R*)-(*S*)-PPFOMe was used instead of (*S*)-(*R*)-PPFOMe. [f] Reaction with 1-chloronaphthalene.

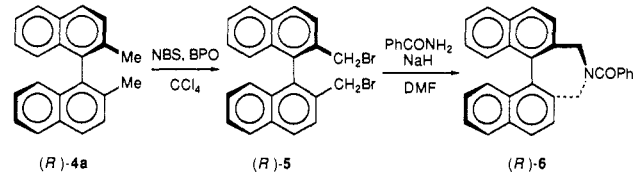
Scheme I



of racemic compounds.[11] Although high stereoselectivity has been achieved in some asymmetric reactions using a stoichiometric amount of chiral auxiliaries which are represented by nucleophilic aromatic substitution of oxazoline derivatives by Meyers[7] and Cram,[8] use of a chiral catalyst for the asymmetric synthesis still remains to be developed. Here we report the first efficient catalytic asymmetric synthesis of optically active 1,1′-binaphthyls via nickel-catalyzed asymmetric cross-coupling.[12]

The asymmetric cross-coupling reported so far to form binaphthyls suffers from both low conversion (<32% yield) and low stereoselectivity (<18% ee),[2a,12] which is due to the low activity of the catalyst for the reaction of sterically hindered substrates. We screened a variety of nickel catalysts for the reaction of (2-methyl-1-naphthyl)magnesium bromide (**1a**) with 2-methyl-1-naphtyl bromide (**2a**) and it turned out that nickel complexes of monodentate phosphine ligands are generally much more catalytically active than those of bidentate ligands containing two phosphorus atoms or phosphorus and nitrogen atoms.[13] These

Scheme II



results suggested to us the use of (*S*)-1-[(*R*)-2-(diphenylphosphino)ferrocenyl]ethyl methyl ether ((*S*)-(*R*)-**PPFOMe 3a**),[14,15] which is a chiral monodentate ligand[16] bearing a methoxy group on the side chain. The methoxy functionality is expected to participate in the catalytic cycle of the cross-coupling by coordinating to the magnesium atom of the Grignard reagent to bring about high stereoselectivity.[15] Actually, ferrocenylphosphine **3a** affected the asymmetric cross-coupling of the 1-naphthyl Grignard reagents **1** with bromides **2**, giving rise to optically active 1,1′-binaphthyls **4** with high stereoselectivity in high yields (Scheme I).

A typical procedure is given for the reaction of (2-methyl-1-naphthyl)magnesium bromide (**1a**) with 2-methyl-1-naphthyl bromide (**2a**) in the presence of 4 mol % of nickel/**3a** catalyst at −5 °C (entry 2 in Table I). To a mixture of 0.80 mmol of ferrocenylphosphine **3a**, 0.40 mmol of anhydrous nickel bromide, and 13 mmol of isomerically pure **2a**[17] was added 1.0 mmol of 0.2 M methylmagnesium bromide in ether, and the mixture was refluxed for 10 min to activate the nickel catalyst. The Grignard reagent **1a** (10 mmol), which is an orange slurry prepared in ether and diluted with toluene, was added at −5 °C. The mixture was stirred at −5 °C for 96 h (monitoring by GLC) and hydrolyzed with diluted hydrochloric acid. Extraction with ether followed by silica gel column chromatography with hexane as an eluent gave 68% yield of (*R*)-(−)-2,2′-dimethyl-1,1′-binaphthyl (**4a**):

(7) (a) Meyers, A. I.; Lutomski, K. A. *J. Am. Chem. Soc.* **1982**, *104*, 879. (b) Meyers, A. I.; Flisak, J. R.; Aitken, R. A. *J. Am. Chem. Soc.* **1987**, *109*, 5446.

(8) (a) Wilson, J. M.; Cram, D. J. *J. Am. Chem. Soc.* **1982**, *104*, 881. (b) Wilson, J. M.; Cram, D. J. *J. Org. Chem.* **1984**, *49*, 4930.

(9) (a) Miyano, S.; Tobita, M.; Hashimoto, H. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 3522. (b) Miyano, S.; Shimizu, K.; Sato, S.; Hashimoto, H. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 1345.

(10) Brussee, J.; Groenedijk, J. L. G.; te Koppele, J. M.; Jansen, A. C. A. *Tetrahedron* **1985**, *41*, 3313. (b) Yamamoto, K.; Fukushima, H.; Nakazaki, M. *J. Chem. Soc., Chem. Commun.* **1984**, 1490. (c) Yamamoto, K.; Fukushima, H.; Yumioka, H.; Nakazaki, M. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 3633.

(11) For examples: (a) Hall, D. M.; Terner, E. E. *J. Chem. Soc.* **1955**, 1242. (b) Maigrot, N.; Mazaleyrat, J. P. *Synthesis* **1985**, 317. (c) Kyba, E. P.; Gokel, G. W.; de Jong, F.; Koga, K.; Sousa, L. R.; Siegel, M. G.; Kaplan, L.; Sogah, G. D. Y.; Cram, D. J. *J. Org. Chem.* **1977**, *42*, 4173. (d) Brown, K. J.; Berry, M. S.; Murdoch, J. R. *J. Org. Chem.* **1985**, *50*, 4345.

(12) (a) Tamao, K.; Minato, A.; Miyake, N.; Matsuda, T.; Kiso, Y.; Kumada, M. *Chem. Lett.* **1975**, 133. (b) Tamao, K.; Yamamoto, H.; Matsumoto, H.; Miyake, N.; Hayashi, T.; Kumada, M. *Tetrahedron Lett.* **1977**, 1389.

(13) Nickel complexes containing 1,3-bis(diphenylphosphino)propane (dppp), (*S*,*S*)-2,3-bis(diphenylphosphino)butane (chiraphos), 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP), and (*S*)-*N*,*N*-dimethyl-1-[(*R*)-2-(diphenylphosphino)ferrocenyl]ethylamine (PPFA) were almost inactive as catalyst for the cross-coupling at room temperature. Palladium–phosphine complexes so far tried were catalytically less active than the corresponding nickel–phosphine complexes. It has been reported that $NiCl_2(PPh_3)_2$ is more effective than nickel–bisphosphine complexes for the reaction of the mesityl Grignard reagent (ref 12a).

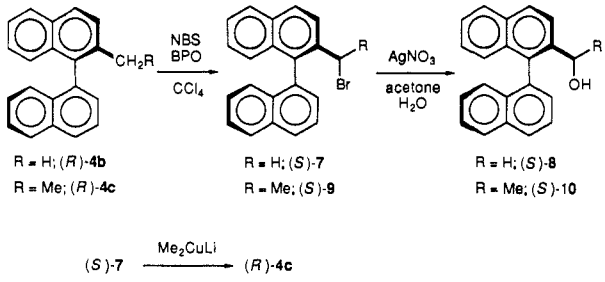
(14) (a) Hayashi, T.; Mise, T.; Fukushima, M.; Kagotani, M.; Nagashima, N.; Hamada, Y.; Matsumoto, A.; Kawakami, S.; Konishi, M.; Yamamoto, K.; Kumada, M. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1138. (b) Hayashi, T.; Kumada, M. *Acc. Chem. Res.* **1982**, *15*, 395.

(15) Hayashi, T.; Konishi, M.; Fukushima, M.; Mise, T.; Kagotani, M.; Tajika, M.; Kumada, M. *J. Am. Chem. Soc.* **1982**, *104*, 180.

(16) Most of the chiral phosphine ligands used for the transition-metal catalysis are those chelating to the metal, and there appeared only a few chiral monophosphine ligands: Kagan, H. B. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic: New York, 1985; Vol. 5, p 1.

(17) The purification is shown in the Experimental Section.

Scheme III



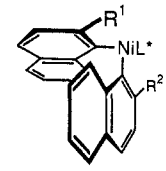
$[\alpha]^{20}_D$ −35.6° (*c* 1.0, chloroform).[11b,18] The phosphine ligand was recovered optically pure in over 80% yield by elution of the column with hexane/ethyl acetate (5/1) and was reused for the next run. The activation of nickel/**3a** catalyst by treatment with methylmagnesium bromide in refluxing ether is essential for the present asymmetric cross-coupling to proceed at the low temperature. The pretreatment initiates the catalytic cycle of the cross-coupling[19] by reduction of the nickel(II), which is accompanied by the formation of the methyl-substituted naphthalene.

Optically active dimethylbinaphthyl **4a**, whose synthetic utility has been well-established,[20] was converted into cyclic amide **6** ($[\alpha]^{20}_D$ +145° (*c* 1.0, chloroform)) by benzylic bromination with NBS followed by treatment of the resulting dibromide **5** with benzamide and sodium hydride in DMF (Scheme II). The enantiomeric purity was determined to be 94% by HPLC analysis of **6** with a chiral stationary phase column (Sumitomo Chemical Co., Sumipax OA-1100, hexane/dichloroethane/ethanol = 250/20/1). It should be noted that binaphthyls **4a** and **6** can be readily made enantiomerically pure with high recovery by simple recrystallization due to their high crystallinity, and hence particular attention was paid, during the conversion, to the manipulation in order to prevent any fractionation causing enantiomeric enrichment (see the Experimental Section).

Table I summarizes the results obtained for the cross-coupling forming optically active binaphthyls **4a–c**. The enantiomeric purity of **4a** was slightly dependent on the reaction temperature (entries 1–3), the highest (95% ee) being obtained at −15 °C (entry 1). The reaction at 0 °C, which gave a higher yield of **4a** in a reasonable reaction time with only a slight loss of enantiomeric purity (93% ee) (entry 3), may be practically most useful.

Reaction of the Grignard reagent **1a** with 1-bromonaphthalene (**2b**) proceeded more rapidly with a smaller amount (2 mol %) of the nickel catalyst to give cross-coupling product **4b** selectively in high yields (entries 4–6). The enantiomeric purity (83% ee) and configuration (*R*) for (−)-**4b** were assessed by its conversion ((1) NBS, BPO, CCl_4; (2) $AgNO_3$, acetone/H_2O (1/1); 63% yield) to known alcohol (*S*)-(−)-**8** ($[\alpha]^{20}_D$ −47.4° (*c* 0.8, chloroform))[7a] via bromide **7** (Scheme III), and the % ee was confirmed by HPLC analysis with the chiral column Sumipax OA-2000. It should be noted again that **4b** can also be made enantiomerically pure by recrystallization. Cross-coupling of **1a** with 1-chloronaphthalene gave a little higher stereoselectivity than that with 1-bromonaphthalene though the reaction was slower (entry 7). The 2-ethyl-1-naphthyl Grignard reagent **1c** was also successfully used for the reaction with **2b**, which gave cross-coupling product (−)-**4c** of over 70% ee (entries 11 and 12). The % ee was determined by the HPLC analysis with the chiral column of alcohol **10**, which is a mixture of diastereoisomers consisting of the same ratio of enantiomers. Methylation of the bromide (*S*)-**7** with dimethyl cuprate gave (−)-**4c**, indicating that (−)-**4c** has *R* configuration.

Binaphthyl (*R*)-**4b** with a much lower % ee was produced in the reaction of the other combination, that is, cross-coupling of 1-naphthylmagnesium bromide (**1b**) with **2a** (entry 10). The large difference between the enantiomeric purities of **4b** obtained in entries 5 and 10 may allow us to propose that the stereochemistry of binaphthyl is determined kinetically at the formation of diastereomeric diorganonickel(II)[21] species **11**, which has a chiral



11

propeller structure and hardly undergoes epimerization due to a steric hindrance preventing rotation on nickel–carbon bonds.[22] Use of ferrocenylphosphine ligand **3c**,[14a] which lacks methoxy group on the side chain, resulted in the formation of racemic **4b** (entry 9), indicating that the presence of the alkoxy group on the ligand **3a** is essential for the high selectivity. Ethoxy-substituted ferrocenylphosphine ligand **3b** was also effective, giving **4b** of high % ee (entry 8). It is likely that coordination of the functional group with the magnesium atom in the Grignard reagent at the transmetalation step forming the diorganonickel **11** greatly enhances the stereoselectivity, as has been shown in the asymmetric cross-coupling of secondary alkyl Grignard reagents.[15,23]

Experimental Section

General Procedures. Optical rotations were measured with a Perkin-Elmer 241 polarimeter. ^{1}H NMR spectra were measured with a JEOL JNM-MH-100 (100 MHz) or Varian VXR-200 (200 MHz) spectrometer. Analytical HPLC was carried out with a Shimadzu HPLC system equipped with a chiral stationary phase column, Sumitomo Chemical Co., Sumipax OA series, and with hexane/dichloroethane/ethanol as eluting solvent. Preparative medium-pressure liquid chromatography (MPLC) was performed with a silica gel prepacked C.I.G. (Kusano) column.

Materials. 1-Bromonaphthalene (**2b**) and 1-chloronaphthalene are commercially available and were distilled before use. The preparation of optically active ferrocenylphosphine (*R*)-**3c** has been reported.[14]

Preparation of (*S*)-1-[(*R*)-2-(Diphenylphosphino)ferrocenyl]ethyl Methyl Ether [(*S*)-(*R*)-PPFOMe (3a)]. The reported procedure[14] for the preparation of (*S*)-(*R*)-PPFOMe (**3a**) was improved as follows. A solution of 919 mg (2.02 mmol) of (*S*)-1-(*R*)-2-(diphenylphosphino)-ferrocenyl]ethyl acetate[14] in 20 mL of dry methanol was heated to reflux for 40 min under nitrogen. The solvent was evaporated and the residue was chromatographed on silica gel (hexane/ethyl acetate = 10/1) to give 752 mg (87% yield) of **3a**.

Preparation of (*S*)-1-[(*R*)-2-(Diphenylphosphino)ferrocenyl]ethyl Ethyl Ether (3b). In a similar manner as above, refluxing a solution of 61 mg (0.13 mmol) of (*S*)-1-[(*R*)-2-(diphenylphosphino)ferrocenyl]ethyl acetate[14] in 1.3 mL of dry ethanol for 2 h gave 58 mg (98% yield) of (*S*)-(*R*)-**3b**: ($[\alpha]^{20}_D$ +323° (*c* 0.4, chloroform)); ^{1}H NMR ($CDCl_3$) δ 0.54 (t, *J* = 7 Hz, 3 H), 1.59 (d, *J* = 6 Hz, 3 H), 3.13 (dq, *J* = 8 and 7 Hz, 1 H), 3.35 (dq, *J* = 8 and 7 Hz, 1 H), 3.78–3.83 (m, 1 H), 3.97 (s, 5 H), 4.29 (t, *J* = 2 Hz, 1 H), 4.51–4.56 (m, 1 H), 4.72 (dq, *J* = 3 and 6 Hz, 1 H), 7.16–7.27 (m, 5 H), 7.34–7.44 (m, 3 H), 7.52–7.66 (m, 2 H). Anal. Calcd for $C_{26}H_{27}OP$: C, 70.60; H, 6.15. Found: C, 70.55; H, 6.12.

Preparation and Purification of 1-Bromo-2-methylnaphthalene (2a). The crude bromide **2a**, which was found to be contaminated with about 5% of a regioisomer, was obtained by bromination of 2-methyl-

(18) Fitts, D. D.; Siegel, M.; Mislow, K. *J. Am. Chem. Soc.* **1958**, *80*, 480.
(19) Tamao, K.; Sumitani, K.; Kiso, Y.; Zembayashi, M.; Fujioka, A.; Kodama, S.; Nakajima, I.; Minato, A.; Kumada, M. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1958.
(20) Miyano, S.; Okada, S.; Suzuki, T.; Handa, S.; Hashimoto, H. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 2044 and references cited therein. See also ref 11.
(21) Diorganonickel(II) species has been proposed as a key intermediate in the cross-coupling. For reviews: (a) Tamao, K.; Kumada, M. In *The Chemistry of the Metal-Carbon Bond*; Hartley, F. R., Patai, S., Eds.; Wiley: Chichester, 1987; Vol. 4, p 819. (b) Jolly, P. W. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Vol. 8, p 713. See also ref 19. (c) Yamamoto, A.; Yamamoto, T.; Komiya, S.; Ozawa, F. *Pure Appl. Chem.* **1984**, *56*, 1621.
(22) One referee suggested the role of unreacted aryl halides which should influence the rate of reductive elimination from the diastereomeric diorganonickel(II) intermediate. Concerning the mechanism of reductive elimination induced by aryl halides, see: Morrell, D. G.; Kochi, J. K. *J. Am. Chem. Soc.* **1975**, *97*, 7262.
(23) Ferrocenylphosphines containing a dialkylamino group on the side chain were more effective for the reaction of secondary alkyl Grignard reagents, but their nickel complexes were catalytically inactive for the present cross-coupling (see ref 13).

naphthalene according to the reported, procedure.[24] The regioisomer was removed by selective methylation, forming a dimethylnaphthalene by the nickel-catalyzed cross-coupling with methylmagnesium bromide. The procedure is given below. To a mixture of 220 g (0.993 mol) of the crude bromide **2a** and 1.29 g (1.97 mmol) of $NiCl_2(PPh_3)_2$ was added at 0 °C under nitrogen 75 mL (0.15 mol) of 2.0 M methylmagnesium bromide in ether. The mixture was refluxed for 5 h and then hydrolyzed with 10% hydrochloric acid at 0 °C. The organic layer and ether extracts from the aqueous layer were combined, washed with saturated sodium hydrogen carbonate solution and then water, and dried over anhydrous calcium chloride. Evaporation of the solvent followed by distillation (109–117 °C/1.3–1.7 mmHg) gave 160 g (0.727 mol) of isomerically pure bromide **2a**: ^{1}H NMR ($CDCl_3$) δ 2.59 (s, 3 H), 7.29 (d, J = 8 Hz, 1 H), 7.42 (ddd, J = 8, 7, and 1 Hz, 1 H), 7.53 (ddd, J = 8, 7, and 1 Hz, 1 H), 7.65 (d, J = 8 Hz, 1 H), 7.75 (d, J = 8 Hz, 1 H), 8.27 (d, J = 8 Hz, 1 H).

Preparation and Purification of 1-Bromo-2-ethylnaphthalene. The crude bromide (12.2 g, 52 mmol), which was prepared in 89% yield by bromination of 2-ethylnaphthalene in a similar manner to that of 2-methylnaphthalene[24] and was contaminated with about 5% of a regioisomer, was purified by treatment with 4.8 mmol of methylmagnesium bromide in the presence of 0.9 mmol of $NiCl_2(PPh_3)_2$ in refluxing ether for 5 h. Workup in a similar manner as above gave 9.4 g (40 mmol) of the bromide (bp 112–116 °C/2 mmHg): ^{1}H NMR ($CDCl_3$) δ 1.26 (t, J = 7.6 Hz, 3 H), 2.96 (q, J = 7.6 Hz, 2 H), 7.28 (d, J = 8 Hz, 1 H), 7.41 (ddd, J = 8, 7, and 1 Hz, 1 H), 7.51 (ddd, J = 8, 7, and 1 Hz, 1 H), 7.66 (d, J = 8 Hz, 1 H), 7.72 (d, J = 8 Hz, 1 H), 8.29 (d, J = 8 Hz, 1 H).

Preparation of the Grignard Reagents 1a–c. The Grignard reagents were prepared by adding a solution of a bromide in ether to magnesium ribbons under ultrasonic irradiation according to a literature procedure[20] and were diluted with toluene (toluene/ether = 1/1). The Grignard reagent **1a** was obtained as a yellow slurry whose concentration was 0.3–0.4 M. The Grignard reagents **1b** and **1c** were obtained as 0.45 M yellow, clear solutions.

Asymmetric Cross-Coupling of the Grignard Reagents 1 with Bromides 2. All the reactions were carried out under a dry nitrogen atmosphere. A typical procedure is given for the reaction of (2-methyl-1-naphthyl)-magnesium bromide (**1a**) with 2-methyl-1-naphthyl bromide (**2a**). To a mixture of 0.34 g (0.80 mmol) of ferrocenylphosphine **3a**, 87 mg (0.40 mmol) of anhydrous nickel bromide, and 2.92 g (13 mmol) of **2a** was added 5 mL (1.0 mmol) of 0.2 M methylmagnesium bromide in ether, and the mixture was refluxed for 10 min. The orange solution turned dark brown. The Grignard reagent **1a** (10 mmol), which is an orange slurry prepared in ether (15 mL) and diluted with toluene (15 mL), was added at −5 °C. The mixture was stirred at −5 °C for 96 h (monitoring by GLC) and hydrolyzed with diluted hydrochloric acid. The organic layer and ether extracts from the aqueous layer were combined, washed with saturated sodium hydrogen carbonate and then water, dried over anhydrous magnesium sulfate, and stripped of solvent in vacuo. The residue was chromatographed on a silica gel column with hexane as an eluent to give 1.91 g (68%) of (*R*)-(−)-2,2′-dimethyl-1,1′-binaphthyl (**4a**): ^{1}H NMR ($CDCl_3$) δ 2.03 (s, 6 H), 7.04 (d, J = 8 Hz, 2 H), 7.20 (ddd, J = 8, 7, and 1 Hz, 2 H), 7.39 (ddd, J = 8, 7, and 1 Hz, 2 H), 7.51 (d, J = 8 Hz, 2 H), 7.87 (d, J = 8 Hz, 2 H), 7.89 (d, J = 8 Hz, 2 H); $[\alpha]^{20}_D$ −35.6° (c 1.0, chloroform); $[\alpha]^{22}_D$ −17° (c 1.0, ethanol) (lit.[18] $[\alpha]^{22}_D$ +19° (c 1.3, ethanol) for (*S*)-**4a**). The optical rotation in ethanol seems inaccurate since binaphthyl **4a** is only slightly soluble in the solvent. Elution of the silica gel column with hexane/ethyl acetate (5/1) gave 0.28 g (82% recovery) of ferrocenylphosphine ligand **3a**. Enantiomerically pure (>99% ee) binaphthyl **4a** was obtained by recrystallization of **4a** (94% ee) from 90% ethanol by slow evaporation of the solvent under nitrogen stream in 70% recovery of theory.

Cross-coupling reactions forming **4b** and **4c** were carried out in a similar manner. Experimental results are summarized in Table I. **4b**: ^{1}H NMR ($CDCl_3$) δ 2.11 (s, 3 H), 7.11–7.66 (m, 9 H), 7.84–7.99 (m, 4 H). Recrystallization of **4b** (83% ee) from hexane gave enantiomerically pure (99% ee) sample ($[\alpha]^{20}_D$ −43.9° (c 1.0, chloroform), mp 132–137 °C) with 75% of the theoretical recovery. (lit.[20] mp 86–88 °C for *dl*-**4b**). **4c**: ^{1}H NMR ($CDCl_3$) δ 1.04 (t, J = 7.6 Hz, 3 H), 2.25–2.56 (m centered at 2.40, 2 H), 7.05–7.64 (m, 9 H), 7.83–7.98 (m, 4 H). Anal. Calcd for $C_{22}H_{18}$: C, 93.58; H, 6.42. Found: C, 93.39; H, 6.36.

Conversion of 4a into Amide 6. According to the reported procedure,[11b] a mixture of 152 mg (0.54 mmol) of (*R*)-**4a** ($[\alpha]^{20}_D$ −35.6° (c 1.0, chloroform), 192 mg (1.08 mmol) of *N*-bromosuccinimide, and 2 mg of benzoyl peroxide in 3 mL of carbon tetrachloride was heated to reflux for 18 h. Removal of the precipitates by filtration over a silica gel pad followed by preparative MPLC on silica gel (hexane/benzene = 1/1) gave 152 mg (64% yield) of dibromide **5**: ^{1}H NMR ($CDCl_3$) δ 4.26 (s, 4 H), 7.08 (d, J = 8 Hz, 2 H), 7.27 (ddd, J = 8, 7, and 1 Hz, 2 H), 7.49 (ddd, J = 8, 7, and 2 Hz), 7.75 (d, J = 9 Hz, 2 H), 7.92 (d, J = 8 Hz, 2 H), 8.02 (d, J = 9 Hz, 2 H); $[\alpha]^{23}_D$ +149° (c 1.0, benzene) (lit.[11b] $[\alpha]^{23}_D$ −159.2° (c 1, benzene) for (*S*)-**5**).

A mixture of 29 mg (0.24 mmol) of benzamide and 35 mg (0.88 mmol) of 60% sodium hydride in mineral oil in 1.5 mL of DMF was stirred at 70 °C for 20 min. A solution of 97 mg (0.22 mmol) of the dibromide **5** obtained above in 2 mL of DMF was added. The mixture was stirred at 70 °C for 1 h, treated with aqueous sodium bicarbonate, and extracted with ether. The ether extracts were washed twice with water, dried over anhydrous magnesium sulfate, and concentrated in vacuo. Preparative TLC on silica gel (hexane/ethyl acetate = 3/2) gave 74 mg (84% yield) of amide **6**: $[\alpha]^{20}_D$ +145° (c 1.0, chloroform); ^{1}H NMR ($CDCl_3$) δ 3.75 3.97, 4.56, 5.43 (4 br d, J = 13 Hz, 4 H), 7.23–8.06 (m, 17 H). The enantiomeric purity was determined to be 94% by HPLC analysis with a chiral stationary phase column (Sumipax OA-1100, hexane/dichloroethane/ethanol = 250/20/1). Enantiomerically pure (>99% ee) amide **6** ($[\alpha]^{20}_D$ +151° (c 1.0, chloroform), mp 259–260 °C) was obtained by recrystallization of **6** (94% ee) from ethanol with 85% of the theoretical recovery. Anal. Calcd for $C_{29}H_{21}NO$: C, 87.19; H, 5.30; N, 3.51. Found: C, 87.05; H, 5.07; N, 3.38.

Conversion of 4b into Alcohol 8. A mixture of 136 mg (0.51 mmol) of methylbinaphthyl **4b** ($[\alpha]^{20}_D$ −33.2° (c 1.0, chloroform), 109 mg (0.61 mmol) of *N*-bromosuccinimide, and 3 mg of benzoyl peroxide in 2.5 mL of carbon tetrachloride was heated to reflux for 2 h. Removal of the solvent followed by preparative TLC on silica gel (hexane) gave 145 mg (82% yield) of **7**: $[\alpha]^{20}_D$ +87.2° (c 1.0, chloroform); ^{1}H NMR ($CDCl_3$) δ 4.19 (d, J = 10 Hz, 1 H), 4.41 (d, J = 10 Hz, 1 H), 7.10–7.33 (m, 4 H), 7.42–7.56 (m, 3 H), 7.60–7.74 (m, 2 H), 7.87–8.04 (m, 4 H). Bromide **7** thus obtained was dissolved in 20 mL of 70% aqueous acetone and added dropwise to a solution of 250 mg (1.47 mmol) of silver nitrate in 15 mL of 50% aqueous acetone at 50 °C. The mixture was stirred at 50 °C for 1 h, diluted with 50 mL of water, and extracted with ether. The ether extracts were washed twice with water, dried over anhydrous magnesium sulfate, and stripped of solvent. Preparative TLC on silica gel (hexane/ether = 2/3) gave 100 mg (84% yield) of alcohol **8**: $[\alpha]^{20}_D$ −47.4° (c 0.8, chloroform) (lit.[7a] $[\alpha]^{20}_D$ +67.3° (c 0.04, chloroform) for (*R*)-**8** (90% ee)); ^{1}H NMR ($CDCl_3$) δ 4.41 (s, 2 H), 7.13–7.32 (m, 4 H), 7.37–7.52 (m, 3 H), 7.60 (dd, J = 7 and 8 Hz, 1 H), 7.79 (d, J = 8 Hz, 1 H), 7.89–8.03 (m, 4 H). The enantiomeric purity was determined to be 83% by HPLC analysis using OA-2000 (hexane/dichloroethane/ethanol = 250/20/1).

Conversion of 4c into Alcohol 10. In similar manner to the conversion of **4b**, 95 mg (0.34 mmol) of **4c** ($[\alpha]^{20}_D$ −26.9° (c 1.0, chloroform)) was brominated with 66 mg (0.37 mmol) of *N*-bromosuccinimide in refluxing carbon tetrachloride for 2 h. Removal of the solvent gave crude bromide **9**: ^{1}H NMR ($CDCl_3$) δ 1.23, 1.37 (a pair of d, J = 7 Hz, 3 H), 4.55, 4.68 (a pair of q, J = 7 Hz, 1 H), 7.0–7.7, 7.8–8.1 (m, 13 H). Crude **9** was treated with silver nitrate in aqueous acetone to give 84 mg (84% yield from **4c**) of alcohol **10** as a mixture of diastereoisomers in a ratio of 52:48. The enantiomeric purities of the diastereoisomers determined by the HPLC analysis with OA-2000 (hexane/dichloroethane/ethanol = 250/20/1) were 77.3% ee and 77.4% ee, respectively. **10**: ^{1}H NMR ($CDCl_3$) δ 1.25, 1.40 (a pair of d, J = 6.4 Hz, 3 H), 4.57, 4.72 (a pair of q, J = 6.4 Hz, 1 H), 7.06–7.67, 7.85–8.07 (m, 13 H). Anal. Calcd for $C_{22}H_{18}O$: C, 88.56; H, 6.08. Found: C, 88.35; H, 6.05.

Methylation of Bromide 7 Forming 4c. The methylation was carried out according to the reported procedure.[25] A solution of 64 mg (0.18 mmol) of the bromide (*S*)-**7** (83% ee) in 3 mL of dry ether was added at 0 °C to a solution of lithium dimethylcuprate which had been prepared from 381 mg (2 mmol) of cuprous iodide and 4 mmol of methyllithium in ether. The mixture was stirred at 0 °C for 1 h and quenched with 1 mL of methanol. Workup in a usual manner[25] followed by preparative TLC on silica gel (hexane) gave 21 mg (40% yield) of (*R*)-2-ethyl-1,1′-binaphthyl (**4c**): $[\alpha]^{20}_D$ −29.1° (c 1.0, chloroform).

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