Enantioselective Synthesis of Binaphthol Derivatives by Oxidative Coupling of Naphthol Derivatives Catalyzed by Chiral Diamine·Copper Complexes

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A highly efficient process of aerobic oxidative coupling of 2-naphthol derivatives catalyzed by 1 mol % of Cu(OH)Cl·TMEDA has been developed. Enantioselective oxidative coupling of naphthols was achieved by the use of 10 mol % of chiral catalysts prepared from proline-derived diamines and cuprous chloride, affording the corresponding binaphthols in good enantioselectivities of up to 78% ee. The ester moiety at the 3-position of the substrate was found to be essential for the good asymmetric induction observed in the present coupling reaction.

Introduction

Homochiral 1,1′-binaphthalene derivatives have been successfully utilized as chiral inducers for highly stereoselective reactions because of their axial dissymmetry and molecular flexibility.[1] From this point of view, there has recently been an intense interest in the preparation of optically active 1,1′-binaphthalene derivatives by methods other than optical resolution of racemic compounds.[2] Since oxidative coupling of 2-naphthols has been amply employed in the preparation of binaphthols, extensive efforts have been made to develop asymmetric coupling of naphthols for the past decade.[3,4] Although satisfactory selectivities were achieved employing stoichiometric amounts of chiral ligands,[3] so far only a few attempts at catalytic enantioselective oxidative coupling of naphthols have been reported.[4] We herein describe a highly efficient aerobic oxidative coupling of 2-naphthols catalyzed by a copper·TMEDA complex and its extension to the first successful enantioselective oxidative coupling of 2-naphthols catalyzed by chiral amine·copper complexes.[5]

Results and Discussion

Aerobic Oxidative Coupling of 2-Naphthols Catalyzed by Cu(OH)Cl·TMEDA. The oxidative coupling of naphthols are frequently performed with excess amount of oxidizing agent such as Fe(III),[6] Mn(III),[7] or Cu(II)[3,8] salts; however, these methods suffer from difficulty in isolation of the coupling product and waste disposal problem. Recently, several catalytic processes were developed by Toda,[6c] Smrčina,[4a] or Sakamoto.[8c] However, their systems still need to be improved in terms of catalytic activity and practicability. Aerobic oxidative coupling catalyzed by copper·amine complexes, known as the Glaser−Hay coupling, is a reliable method for the preparation of conjugate diynes from acetylenes or quinones from phenols. We were intrigued by the feasibility of this system toward the enantioselective oxidative coupling of naphthols catalyzed by chiral amine·copper complexes.

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(1) For recent reviews, see: (a) Bringmann, G.; Walter, R.; Weirich, R. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 977−991. (b) Rosini, C.; Franzini, L.; Raffaelli, A.; Salvadori, P. *Synthesis* **1992**, 503−517. (c) Noyori, R. *Asymmetric Catalysis in Organic Synthesis*; Wiley: New York, 1994. (d) Zimmer, R.; Suhrbier, J. *J. Prakt. Chem.* **1997**, *339*, 758−762.

(2) For recent methods for direct optical resolution of BINOL, see: (a) Kawashima, M.; Hirayama, A. *Chem. Lett.* **1990**, 2299−2300. (b) Cai, D.; Hughes, D. L.; Verhoeven, T. R.; Reider, P. J. *Tetrahedron Lett.* **1995**, 7991−7994. (c) Toda, F.; Tanaka, K. *Chem. Commun.* **1997**, 1087−1088. For enantioselective synthesis of binaphthyl skeletons by methods other than those of asymmetric oxidation, see: (d) Hayashi, T.; Hayashizaki, K.; Kiyoi, T.; Ito, Y. *J. Am. Chem. Soc.* **1988**, *110*, 8153−8156. (e) Shindo, M.; Koga, K.; Tomioka, K. *J. Am. Chem. Soc.* **1992**, *114*, 8732−8733.

(3) For asymmetric synthesis of binaphthols including second-order asymmetric transformation, see: (a) Feringa, B.; Wynberg, H. *Bioorg. Chem.* **1978**, *7*, 397−408. (b) Brussee, J.; Jansen, A. C. A. *Tetrahedron Lett.* **1983**, *24*, 3261−3262. (c) Yamamoto, K.; Fukushima, H.; Nakazaki, M. *J. Chem. Soc., Chem. Commun.* **1984**, 1490−1491. (d) Brussee, J.; Groenendijk, J. L. G.; te Koppele, J. M.; Jansen, A. C. A. *Tetrahedron* **1985**, *41*, 3313−3319. (e) Yamamoto, K.; Fukushima, H.; Yumioka, H.; Nakazaki, M. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 3633−3634. (f) Smrčina, M.; Lorenc, M.; Hanuš, V.; Sedmera, P.; Kočovský, P. *J. Org. Chem.* **1992**, *57*, 1917−1924. (g) Osa, T.; Kashiwagi, Y.; Yanagisawa, Y.; Bobbitt, J. M. *J. Chem. Soc., Chem. Commun.* **1994**, 2535−2537.

(4) For asymmetric synthesis of binaphthols by enantioselective oxidation with catalytic amount of chiral ligand, see: (a) Smrčina, M.; Poláková, J.; Vyskočil, Š.; Kočovský, P. *J. Org. Chem.* **1993**, *58*, 4534−4537. (b) Hamada, T.; Ishida, H.; Usui, S.; Watanabe, Y.; Tsumura, K.; Ohkubo, K. *J. Chem. Soc., Chem. Commun.* **1993**, 909−911.

(5) For our preliminary results, see: (a) Noji, M.; Nakajima, M.; Koga, K. *Tetrahedron Lett.* **1994**, *35*, 7983−7984. (b) Nakajima, M.; Kanayama, K.; Miyoshi, I.; Hashimoto, S. *Tetrahedron Lett.* **1995**, *36*, 9519−9520.

(6) (a) Pummerer, R.; Prell, E.; Rieche, A. *Ber.* **1926**, *59*, 2159−2161. (b) Feringa, B.; Wynberg, H. *J. Org. Chem.* **1981**, *46*, 2547−2557. (c) Toda, F.; Tanaka, K.; Iwata, S. *J. Org. Chem.* **1989**, *54*, 3007−3009. (d) Deussen, H.-J.; Frederiksen, P.; Bjørnholm, T.; Bechgaard, K. *Org. Prep. Proc. Int.* **1996**, *28*, 484−486. (e) Ding, K.; Wang, Y.; Zhang, L.; Wu, Y.; Matsuura, T. *Tetrahedron* **1996**, *52*, 1005−1010.

(7) (a) Dewar, M. J. S.; Nakaya, T. *J. Am. Chem. Soc.* **1968**, *90*, 7134−7135. (b) Yamamoto, K.; Fukushima, H.; Okamoto, Y.; Hatada, K.; Nakazaki, M. *J. Chem. Soc., Chem. Commun.* **1984**, 1111−1112.

(8) (a) Feringa, B.; Wynberg, H. *Tetrahedron Lett.* **1977**, 4447−4450. (b) Kantam, M. L.; Santhi, P. L. *Synth. Commun.* **1996**, *26*, 3075−3079. (c) Sakamoto, T.; Yonehara, H.; Pac, C. *J. Org. Chem.* **1997**, *62*, 3194−3199.

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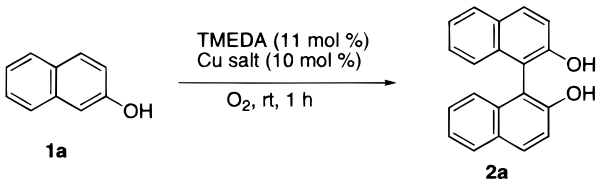
Table 1. Catalytic Oxidative Coupling of 2-Naphthol



entry	Cu salt	solvent	yield,[a] %
1	CuCl	MeOH	52
2	CuCl	acetone	47
3	CuCl	AcOEt	35
4	CuCl	benzene	56
5	CuCl	CH_2Cl_2	81
6	CuI	CH_2Cl_2	50
7	CuOTf	CH_2Cl_2	54
8	Cu_2O	CH_2Cl_2	0
9	$CuCl_2$	CH_2Cl_2	42
10	$Cu(OAc)_2$	CH_2Cl_2	36

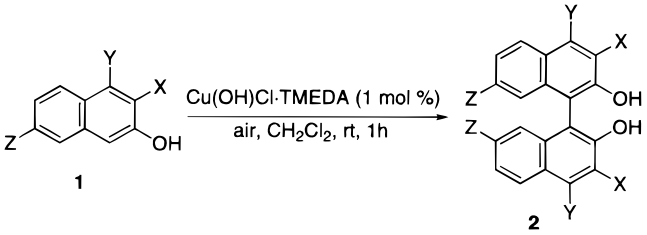
[a] Isolated yield.

According to the procedure of the Glaser−Hay coupling, we first examined oxidative coupling of 2-naphthol (**1a**) by the use of 11 mol % of TMEDA and 10 mol % of CuCl in methanol or acetone under oxygen atmosphere (1 atm) at room temperature (Table 1, entries 1 and 2). Unfortunately, binaphthol (**2a**) was obtained in low yield along with quinones and other byproducts. Five different solvents were tested, and the best result was obtained with dichloromethane (Table 1, entry 5). Unsatisfactory chemical yields were obtained with $Cu(OAc)_2$ or $CuCl_2$ (Table 1, entries 9 or 10), which had often been employed in stoichiometric oxidative coupling.[3,8a]

In view of these findings, we then undertook an aerobic oxidative coupling exploiting Cu(OH)Cl·TMEDA,[9,10] easily prepared from CuCl, TMEDA, water, and molecular oxygen. The reaction proceeded smoothly even in the open air using 1 mol % of Cu(OH)Cl·TMEDA, producing **2a** in high yield. The results obtained for the reaction of a variety of naphthol derivatives are summarized in Table 2. Naphthols with various substituent patterns were oxidatively coupled to produce the corresponding binaphthols in high yield. The present protocol could be extended to a reaction of naphthols with low reactivity such as **1e**, though the reaction was slow unless the amount of the catalyst was increased to 10 mol % (Table 2, entry 5). No binaphthyl derivative was obtained in the reaction of 2-methoxynaphthalene, which indicates the phenolic hydroxy group is crucial to this oxidative coupling. The present reaction has provided the first efficient process of catalytic oxidative coupling of 2-naphthols, which could be applied to a large-scale synthesis of binaphthols.[11]

Enantioselective Oxidative Coupling of 2-Naphthols Catalyzed by Chiral Amine·Copper Complexes. With an efficient process of catalytic oxidative coupling of naphthols established, we then turned our attention to the enantioselective oxidative coupling of naphthols. We first investigated asymmetric coupling

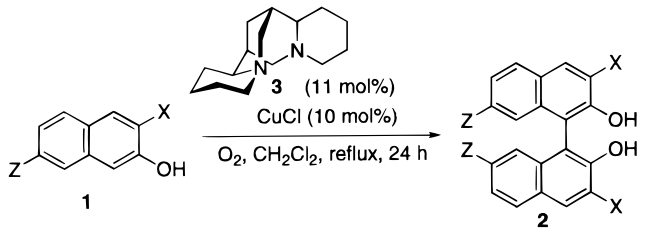
Table 2. Catalytic Aerobic Oxidation of 2-Naphthol Derivatives



	naphthol				binaphthol	
entry		X	Y	Z		yield,[a] %
1	**1a**	H	H	H	**2a**	92
2	**1b**	Me	H	H	**2b**	95
3	**1c**	OMe	H	H	**2c**	96
4	**1d**	H	H	OMe	**2d**	95
5	**1e**	COOMe	H	H	**2e**	90[b]
6	**1f**	−(CH=CH)$_2$−		H	**2f**	77

[a] Isolated yield. [b] Reaction was performed with 10 mol % of catalyst at room temperature for 48 h. Refluxing in CH_2Cl_2 for 24 h with 10 mol % of catalyst or refluxing in MeOH for 12 h with 10 mol % of catalyst afforded **2e** in 98% yield.

Table 3. Enantioselective Oxidative Coupling of Naphthols Catalyzed by Sparteine·Copper Complex



	naphthol			binaphthol			
entry		X	Z		yield,[a] %	ee,[b] %	confgn[c]
1	**1a**	H	H	**2a**	32	18	*S*
2	**1b**	Me	H	**2b**	54	10	*S*
3	**1d**	H	OMe	**2d**	31	16	*S*
4	**1e**	COOMe	H	**2e**	38	47	*S*

[a] Isolated yield. [b] Determined by HPLC analysis employing a Daicel Chiralcel OJ or Chiralpak AD. [c] Assignment by comparison to literature values of optical rotations.

with commercially available (−)-sparteine (**3**) as a chiral ligand having two tertiary nitrogens similar to TMEDA. According to the above procedure, 2-naphthol (**1a**) was added to the solution of the chiral catalyst prepared in situ from CuCl (10 mol %) and sparteine (**3**) (11 mol %) in dichloromethane, and the reaction mixture was heated at reflux under oxygen of atmospheric pressure. Chromatography afforded unreacted starting material (58%) and binaphthol (**2a**) (32%) in low enantiomeric excess (18% ee) (Table 3, entry 1). Among several substrates surveyed, we were gratified to find that the reaction of methyl 3-hydroxy-2-naphthoate (**1e**) afforded the corresponding binaphthol **2e** in 47% ee (Table 3, entry 4),[12] albeit with low chemical yield.

To improve both chemical yield and enantioselectivity, we then adopted diamines derived from L-proline as chiral ligand because of their availability and their

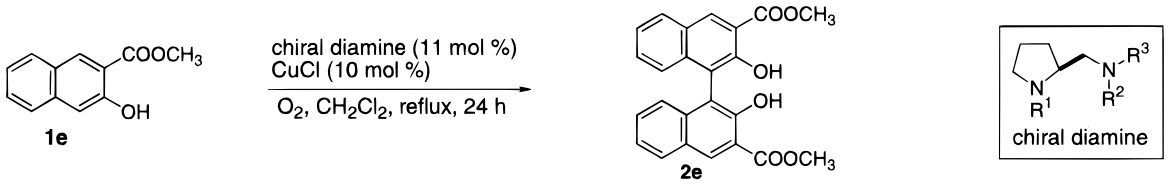
(9) (a) Hay, A. S. *J. Org. Chem.* **1962**, *27*, 3320−3321. (b) de Jong, C. R. H. I. In *Organic Syntheses by Oxidation with Metal Compounds*; Mijs, W. J., de Jong, C. R. H. I., Eds.; Plenum Press Inc.: New York, 1986; pp 423−443.

(10) Cu(OH)Cl·TMEDA dimer (di-μ-hydroxo-bis[(*N*,*N*,*N*′,*N*′-tetramethylethylenediamine)copper(II)] chloride) is now commercially available (TCI, D2542).

(11) Hu, Q.-S.; Vitharana, D.; Pu, L. *Tetrahedron: Asymmetry* **1995**, *6*, 2123-2126.

(12) Silica gel column chromatography (hexanes−EtOAc) of **2e** furnished fractions that differ in enantiomeric excess. We employed hexanes−EtOAc as eluent for removing unreacted **1e** and then dichloromethane for complete elution of **2e**. Fractionation of nonracemic chiral compound on achiral phase: Nicoud, R.-M.; Jaubert, J.-N.; Rupprecht, I.; Kinkel, J. *Chirality* **1996**, *8*, 234−243 and references therein.

Table 4. Enantioselective Oxidative Coupling of Methyl 3-Hydroxy-2-naphthoate



		chiral diamine			2e		
entry		R^1	R^2	R^3	yield,[a] %	ee,[b] %	confgn[c]
1	**4**	Me	$-(CH_2)_4-$		79	2	*S*
2	**5**	Me	Ph	H	77	4	*S*
3	**6**	H	H	H	11	0	
4	**7**	H	$-(CH_2)_4-$		82	31	*S*
5	**8**	H	Ph	H	74	30	*S*
6	**9**	H	Ph	Me	76	59	*S*
7	**10**	H	4-$MeOC_6H_4$	Me	25	58	*S*
8	**11**	H	4-$CF_3C_6H_4$	Me	49	61	*S*
9	**12**	H	1-naphthyl	Me	25	34	*S*
10	**13**	H	2-naphthyl	Me	69	53	*S*
11	**14**	H	^{c}Hex	Me	24	27	*S*
12	**15**	H	Ph	Et	78	70	*S*
13	**16**	H	Ph	CH_2Ph	87	65	*S*
14	**17**	H	Ph	Ph	66	12	*S*

[a] Isolated yield. [b] Determined by HPLC analysis employing a Daicel Chiralpak AD. [c] Assignment by comparison to literature values of optical rotations.

sterically rigid conformation in chelation with various metals.[13] Representative results are summarized in Table 4. By analogy with the process using TMEDA or sparteine (**3**), we initially examined asymmetric oxidation with the diamine **4** bearing two tertiary nitrogens. However, the binaphthol **2e** obtained in 79% yield appeared to be a racemic product (Table 4, entry 1). We then screened three types of ligands **5**−**9** containing a combination of one secondary and one primary nitrogens, two secondary nitrogens, or one secondary and one tertiary nitrogen. Clearly, the ligands **4**−**6** (Table 4, entries 1−3) were inferior to the ligands **7**−**9** (Table 4, entries 4−6), which suggested that a secondary nitrogen in the pyrrolidine ring and a secondary or tertiary nitrogen in the side-chain were crucial to the asymmetric induction. Encouraged by this finding, we fixed the pyrrolidine ring moiety and investigated the substituent effect of the side-chain nitrogen on enantioselectivities. Of various diamines surveyed, *N*-ethylaniline derivative **15** was found to induce good enantioselectivities, whereas substitution of cyclohexyl or 1-naphthyl rings for the phenyl ring of **9** resulted in only modest selectivities and poor yields (Table 4, entries 9 and 11). Little electronic effect of the aromatic ring on enantioselection was observed in the reaction with the catalysts derived from **9**−**11** (Table 4, entries 6−8).

With a promising diamine for enantioselective oxidation in hand, we then attempted the isolation of the copper·diamine complex. Addition of hexane into a solution of the complex prepared from CuCl and **15** in dichloromethane afforded a green powder. Although its structure remains ambiguous, it might be reasonable to suppose the complex to be Cu(OH)Cl·**15**, on the analogy of Cu(OH)Cl·TMEDA. The isolated complex possessed slightly better reactivity, which made it possible to conduct the reaction at room temperature. The results obtained for the enantioselective oxidation of a variety of naphthols catalyzed by the complex derived from **15** are summarized in Table 5. Little variation in enantioselectivities was observed with the ester moiety of the substrate (Table 5, entries 1−3), except for the *tert*-butyl ester (Table 5, entry 4). It should be noted that the enantiomeric excess up to 78% is so far the highest reported to date for catalytic, enantioselective oxidative coupling of naphthol derivatives.[14] Oxidation of naphthols with ketone, amide, alkyl, or alkoxy moieties at the 3-position (Table 5, entries 5−10) afforded the corresponding binaphthols with low enantioselectivities, which implies that the ester moiety is essential for the asymmetric induction.

Possible Mechanism of Enantioselective Coupling of 2e. Although extensive efforts have been made for the elucidation of the mechanism of the aerobic oxidation catalyzed by copper·amine complexes,[9b] the mechanism of the present oxidative coupling is unknown. We postulate that our coupling reaction consists of three successive processes: (1) exchange of the hydroxy group on the copper complex for a phenolic hydroxy group followed by the additional coordination of ester carbonyl to the copper atom, (2) oxidative coupling affording a diketone with central chirality, and (3) transfer of central chirality to axial chirality[15] through keto−enol isomerism along with dissociation of copper·amine complex (Scheme 1). Assuming the reversible formation of the copper·amine-diketone complex, the intermediacy of **18**, where the substituents of the chiral amines are in the least sterically demanding region, might be the best explanation for the present enantioselection.

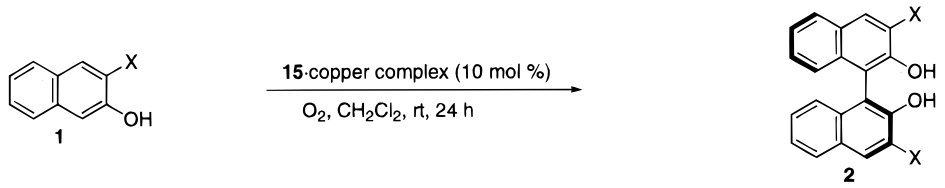
Preparation of Homochiral Binaphthol. Since homochiral binaphthol (**2a**) is a reliable source of a

(13) (a) Asami, M.; Ohno, H.; Kobayashi, S.; Mukaiyama, T. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 1869−1873. (b) Mukaiyama, T.; Iwasawa, N.; Stevens, R. W.; Haga, T. *Tetrahedron* **1984**, *40*, 1381−1390. (c) Kobayashi, S.; Uchiro, H.; Fujishita, Y.; Shiina, I.; Mukaiyama, T. *J. Am. Chem. Soc.* **1991**, *113*, 4247−4252.

(14) Catalytic oxidative cross-coupling of 2-naphthol and methyl 3-hydroxy-2-naphthoate employing copper·sparteine complex as catalyst and AgCl as oxidant afforded the corresponding binaphthol of 32% ee in 41% yield.[4a] Photocatalytic oxidation of 2-naphthol with chiral Ru-complex afforded 2,2′-binaphthol in 16% ee.[4b]

(15) (a) Meyers, A. I.; Lutomski, K. A. *J. Am. Chem. Soc.* **1982**, *104*, 879−881. (b) Meyers, A. I.; Wettlaufer, D. G. *J. Am. Chem. Soc.* **1984**, *106*, 1135−1136.

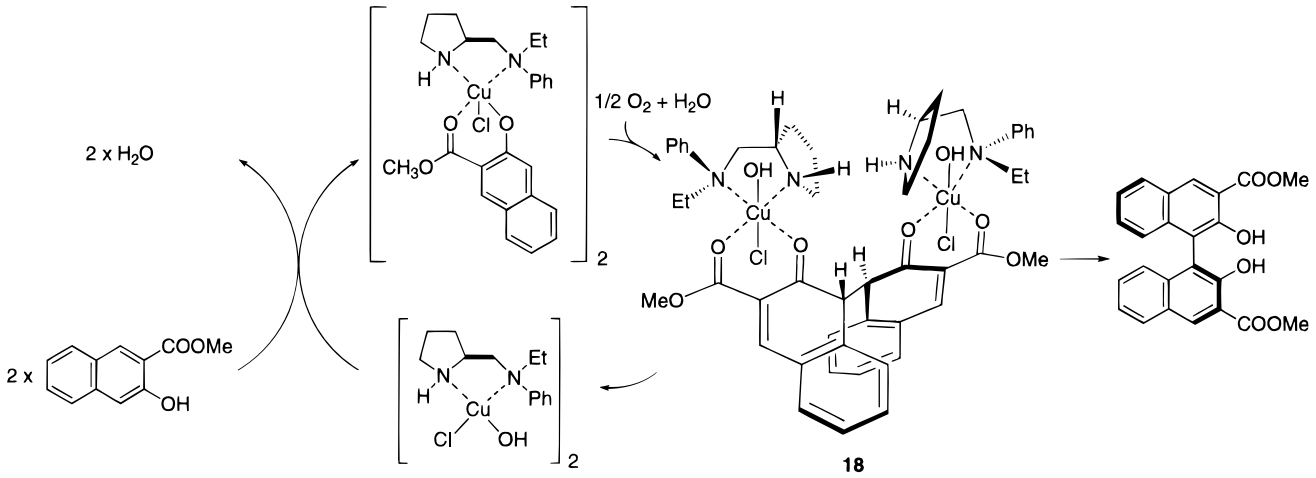
Table 5. Enantioselective Oxidative Coupling of 2-Naphthol Derivatives



	naphthol			binaphthol			
entry		X		yield,[a] %	ee,[b] %	config[c]	$[\alpha]_D$ (*c*, THF)
1	**1e**	COOMe	**2e**	85	78	*S*	−125.0 (1.0)
2	**1g**	COOEt	**2g**	77	73	*S*[d]	−112.2 (1.1)
3	**1h**	$COOCH_2Ph$	**2h**	77	76	*S*[d]	−81.3 (1.1)
4	**1i**	COO^tBu	**2i**	69	58	*S*[d]	−79.6 (1.0)
5	**1j**	COMe	**2j**	71	37	*S*	−78.8 (1.0)
6	**1k**	$CONHCH_2Ph$	**2k**	65	24	*S*[e]	−3.3 (0.9)
7	**1a**	H	**2a**	89	17	*S*	−20.1 (1.0)
8	**1b**	Me	**2b**	93	12	*S*	−3.1 (1.0)[f]
9	**1l**	^iPr	**2l**	58	5[g]		−1.6 (1.4)
10	**1m**	OCH_2Ph	**2m**	95	24[h]	*S*[h]	−8.2 (0.8)

[a] Isolated yield. [b] Determined by HPLC analysis employing a Daicel Chiralcel OD, OJ, or Chiralpak AD. [c] Assignment by comparison to literature values of optical rotations. [d] Assignment after conversion to **2e**. [e] Assignment by comparison to the values of optical rotation of **2k** prepared from (*R*)-diacid. [f] Optical rotation was measured in $CHCl_3$ at 578 nm. [g] Determined by ^1H NMR analysis with $Eu(hfc)_3$. [h] Determined after conversion to (*S*)-1,1′-binaphthalene-2,2′,3,3′-tetrol.

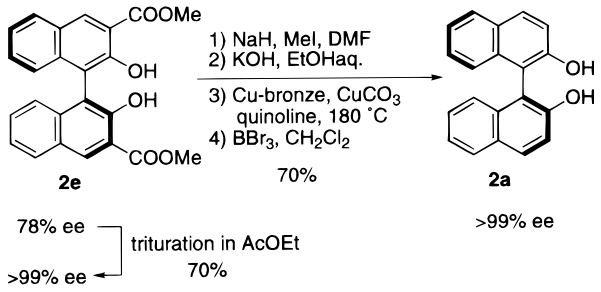
Scheme 1



variety of binaphthyl compounds, the development of efficient preparation of homochiral **2a** has attracted much attention. Toward this end, we then addressed the enrichment of enantiomeric excess of **2e** and its transformation into homochiral **2a**.[16]

Enantioselective oxidation of **1e** was performed by the aid of a catalyst prepared from **15**. Without aqueous workup, the solvent was evaporated and the residue was triturated in MeOH to afford **2e** as needles (85%, 78% ee). The homochiral **2e** was easily obtained by a consequence of the large solubility difference between racemic **2e** and homochiral **2e**. Thus, trituration of the above scalemic mixture (78% ee) in ethyl acetate gave racemic crystals (30%, mp 278−280 °C), which were filtered off, and the mother liquor containing **2e** (70%, mp 242−244 °C) of >99% ee. Protection of the hydroxy group in **2e** (MeI, NaH, DMF), hydrolysis of ester (KOH, aqueous EtOH), and decarboxylation (Cu-bronze, $CuCO_3$, quinoline) gave *O*-methyl protected **2a**. Finally, deprotection of hydroxy group with BBr_3 afforded homochiral **2a** in 70% overall yield shown in Scheme 2.

Scheme 2



Conclusion

We have demonstrated the effectiveness of Cu(OH)Cl·TMEDA as a catalyst for aerobic oxidative coupling of 2-naphthol derivatives affording binaphthol derivatives in excellent yields. Enantioselective oxidative coupling was achieved by the use of chiral amine·copper complexes as catalysts, which afforded binaphthol derivatives in

(16) Conversion of **2e** into **2a** via Curtius rearrangement has been reported, though the chemical yield of the decarboxylation step is low. See: Akimoto, H.; Yamada, S. *Tetrahedron* **1971**, *27*, 5999−6009.

good enantioselectivities up to 78% ee. Oxidation of naphthols without an ester moiety at the 3-position afforded the corresponding binaphthols with low enantioselectivities, which implies that the ester moiety is essential for the asymmetric induction. The present catalytic system has proven to be a potent addition to the existing method for the preparation of homochiral binaphthyl compounds.

Experimental Section

General Experimental Procedures. Reactions were monitored by thin-layer chromatography (TLC). All yields reported refer to isolated material. Solvents were dried according to established procedures by distillation under argon atmosphere from the appropriate drying agent. Column chromatography purifications were carried out using silica gel (70−230 mesh). ^{1}H NMR (270 MHz) and ^{13}C NMR (68 MHz) were recorded in $CDCl_3$ unless otherwise specified. Chemical shift values are expressed in ppm relative to tetramethylsilane (0.0 ppm) for ^{1}H and $CDCl_3$ (77.0 ppm) for ^{13}C NMR. Coupling constants (J) are reported in hertz (Hz). Abbreviations are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. Mass spectra were obtained by electron impact (EI) with ionization voltage of 70 eV.

Chiral amines **4**−**9** were prepared by the literature methods.[13] Naphthols **1b,c,g**−**m** were prepared by the literature methods.[17]

Preparation of Cu(OH)Cl·TMEDA.[5a,9b] A mixture of CuCl (8.2 g, 0.083 mol) and TMEDA (19 g, 0.16 mol) in 95% methanol was stirred under oxygen atmosphere at room temperature for 1 h. The resulting precipitates were collected by filtration and washed with acetone. Drying in vacuo gave a purple powder (19 g, 98%) of mp 137−138 °C dec.

General Procedure for the Oxidative Coupling of Naphthol Derivatives Catalyzed by Cu(OH)Cl·TMEDA. A mixture of CuCl(OH)·TMEDA (8.0 mg, 0.035 mmol) and naphthol derivative (3.5 mmol) in dichloromethane (35 mL) was stirred at room temperature for 1 h in the open air. Concentration followed by silica gel column chromatography afforded the corresponding binaphthol derivative. The spectroscopic properties of the products were coincident with those previously reported.[8c,18]

Preparation of Chiral Amines 10−17. (*S*)-*N*-(4-Methoxyphenyl)-*N*-methyl-2-pyrrolidinemethanamine (10). To a solution of *N*-benzyloxycarbonyl-L-proline (1.5 g, 6.0 mmol) and *N*-methyl-*p*-anisidine (0.91 g, 6.6 mmol) in THF (10 mL) was added 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide (EDC) (1.3 g, 6.6 mmol), and the reaction mixture was stirred at room temperature for 12 h. After addition of water, the mixture was extracted with EtOAc and washed with 10% HCl, saturated $NaHCO_3$, and brine. Drying over Na_2SO_4 and concentration followed by silica gel column chromatography (hexanes−EtOAc 1:2) afforded (*S*)-1-benzyloxycarbonyl-*N*-(4-methoxyphenyl)-*N*-methyl-2-pyrrolidinecarboxamide (2.1 g, 94%) as a mixture of rotamers. $[\alpha]^{21}_D$: +122.4 (*c* 1.0, $CHCl_3$). IR (Nujol): 1712, 1680 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.66−2.11 (m, 4H), 3.11 and 3.26 (2 × s, 3H), 3.41−3.71 (m, 2H), 4.11−4.32 (m, 1H), 5.01−17 (m, 2H), 6.59−6.84 (m, 2H), 6.93 (d, J = 8.8 Hz, 1H), 7.27−7.45 (m, 6H). ^{13}C NMR ($CDCl_3$): δ 23.6, 24.3, 30.2, 31.2, 37.6, 37.8, 46.9, 47.4, 55.3, 55.4, 56.6, 57.1, 66.7, 67.3, 114.6, 114.8, 127.5, 127.7, 128.2, 128.3, 128.4, 128.8, 135.7, 136.1, 136.6, 136.7, 154.0, 154.7, 158.8, 158.9, 172.7. MS *m*/*z*: 368 (M^+), 204, 91 (bp), 70. HRMS: calcd for $C_{21}H_{24}N_2O_4$ 368.1732, found 368.1702. Anal. Calcd for $C_{21}H_{24}N_2O_4$: C, 68.46; H, 6.57; N, 7.60. Found: C, 68.44; H, 6.63; N, 7.53.

To a solution of above amide (1.7 g, 4.6 mmol) in THF (10 mL) was added BH_3·THF (1 M in THF, 15 mL, 15 mmol), and the reaction mixture was heated at reflux for 1 h. After addition of 10% HCl, the mixture was neutralized with NaOH and extracted with Et_2O. Drying over Na_2SO_4 and concentration afforded crude amide, which was dissolved in MeOH (10 mL) with Pd−C (ca. 100 mg), and the reaction mixture was stirred at room temperature for 12 h under a hydrogen atmosphere. Filtration followed by silica gel column chromatography (CH_2Cl_2−MeOH−aqueous NH_3, 100:10:1) afforded **10** (1.0 g, 80%) as a pale yellow oil. $[\alpha]^{23}_D$: +2.6 (*c* 1.0, EtOH). IR (neat): 3331 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.32−1.45 (m, 1H), 1.67−1.93 (m, 3H), 2.08 (s, 3H), 2.82−2.89 (m, 1H), 2.91(s, 3H), 2.98−3.06 (m, 1H), 3.21 (d, J = 6.7 Hz, 2H), 3.37 (d, J = 6.7 Hz, 1H), 3.76 (s, 3H), 6.74 (d, J = 9.2 Hz, 2H), 6.83 (d, J = 9.2 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 24.7, 29.3, 39.8, 45.9, 55.6, 57.1, 59.1, 114.5, 114.6, 144.8, 151.6. MS *m*/*z*: 204 (M^+), 107, 97 (bp). HRMS: calcd for $C_{13}H_{20}N_2$ 204.1628, found 204.1601.

(*S*)-*N*-Methyl-*N*-(4-trifluoromethyl)phenyl-2-pyrrolidinemethanamine (11). To a solution of *N*-*tert*-butoxy-L-proline (1.0 g, 4.56 mmol) and *N*-methylmorpholine (0.61 mL, 5.6 mmol) in EtOAc (10 mL) were added ethyl chloroformate (0.50 mL, 5.0 mmol) and 4-aminobenzotrifluoride (0.91 g, 5.6 mmol) successively at −15 °C, and the mixture was stirred for 1 h at the same temperature. After addition of water, the mixture was extracted with EtOAc and washed with 10% HCl, saturated $NaHCO_3$, and brine. Drying over Na_2SO_4 and concentration followed by silica gel column chromatography (hexanes−EtOAc 4:1) afforded (*S*)-1-(*tert*-butoxycarbonyl)-*N*-(4-trifluoromethylphenyl)-2-pyrrolidinecarboxamide (1.3 g, 76%). $[\alpha]^{26}_D$: −109.0 (*c* 1.04, $CHCl_3$). IR (Nujol): 1711, 1678, 844 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.51 (s, 9H), 2.01 (bs, 3H), 2.43 (bs, 1H), 4.11−4.14 (m, 2H), 4.51 (bs, 1H), 7.48−7.60 (m, 4H), 9.92 (bs, 1H). ^{13}C NMR ($CDCl_3$): δ 24.8, 28.7, 29.0, 47.6, 60.8, 81.2, 119.1, 126.0, 141.8, 156.2, 171.4. MS *m*/*z*: 358 (M^+), 339, 285, 170, 145, 70 (bp). HRMS: calcd for $C_{17}H_{21}F_3N_2O_3$ 358.1504, found 358.1475. Anal. Calcd for $C_{17}H_{21}F_3N_2O_3$: C, 56.98; H, 5.91; N, 7.82. Found: C, 56.85; H, 5.91; N, 7.71.

To a solution of above amide (1.1 g, 3.1 mmol) in THF (17 mL) was added sodium hydride (60% in oil, 0.14 g, 3.5 mmol) at 0 °C, and the mixture was stirred at the same temperature for 1 h. Iodomethane (0.30 mL, 5.0 mmol) was added, and the reaction mixture was stirred for 12 h at room temperature. After addition of 10% HCl, the mixture was extracted with EtOAc and washed with saturated $NaHCO_3$ and brine. Drying over Na_2SO_4 and concentration followed by silica gel chromatography (hexanes−EtOAc 2:1) afforded (*S*)-1-(*tert*-butoxycarbonyl)-*N*-methyl-*N*-(4-trifluoromethylphenyl)-2-pyrrolidinecarboxamide (0.96 g, 92%) as a mixture of rotamers. $[\alpha]^{27}_D$: +83.0 (*c* 1.1, $CHCl_3$). IR (neat): 1693, 1682 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.44 and 1.47 (2 × s, 9H), 1.67−2.06 (m, 4H), 3.29 (s, 3H), 3.29−3.60 (m, 2H), 4.07−4.25 (m, 1H), 7.37 (d, J = 8.3 Hz, 1H), 7.52 (d, J = 8.2 Hz, 1H), 7.67−7.72 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 23.4, 24.2, 28.5, 28.6, 30.2, 47.0, 47.1, 56.8, 57.1, 79.4, 79.8, 126.9, 127.9, 128.3, 128.3, 172.5. MS *m*/*z*: 372 (M^+), 299, 271, 202, 170, 70 (bp). HRMS: calcd for $C_{18}H_{23}F_3N_2O_3$ 372.1661, found 372.1632. Anal. Calcd for $C_{18}H_{23}F_3N_2O_3$: C, 58.06; H, 6.22; N, 7.52. Found: C, 58.01; H, 6.35; N, 7.39.

To a solution of above amide (1.0 g, 2.7 mmol) in THF (10 mL) was added BH_3·THF complex (1 M in THF, 5.0 mL, 5.0 mmol), and the reaction mixture was heated at reflux for 1 h. After addition of 10% HCl, the mixture was neutralized with NaOH and extracted with Et_2O. Drying over Na_2SO_4 and concentration gave crude amide, which was treated with trifluoroacetic acid (2 mL) in CH_2Cl_2 (2 mL) at 0 °C for 1 h. After addition of water, the mixture was neutralized with NaOH and extracted with Et_2O. Drying over Na_2SO_4 and concentration followed by silica gel column chromatography (CH_2Cl_2−MeOH−aqueous NH_3 100:10:1) afforded **11** (0.53 g,

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73%) as a pale yellow oil. $[\alpha]^{28}_D$: +9.7 (*c* 1.1, EtOH). IR (neat): 3335, 1481 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.35−1.48 (m, 1H), 1.66−1.96 (m, 3H), 2.80−3.07 (m, 2H), 3.05 (s, 3H), 3.38−3.41 (m, 3H), 6.72 (d, J = 8.9 Hz, 1H), 7.43 (d, J = 8.9 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 24.9, 29.4, 39.2, 46.3, 57.1, 57.6, 110.9, 117.1 (q, J_{CF} = 33 Hz), 125.1 (q, J_{CF} = 270 Hz), 126.4, 151.4. MS *m*/*z*: 258 (M^+), 239, 189, 145, 70 (bp). HRMS: calcd for $C_{13}H_{17}F_3N_2$ 258.1344, found 258.1333.

(*S*)-*N*-Methyl-*N*-(1-naphthyl)-2-pyrrolidinemethanamine (12). To a solution of (*S*)-1-benzyloxycarbonyl-*N*-(1-naphthyl)-2-pyrrolidinecarboxamide[13] (1.5 g, 4.0 mmol) in DMF (10 mL) was added sodium hydride (60% in oil, 0.24 g, 5.0 mmol) at 0 °C, and the mixture was stirred at the same temperature for 15 min. Iodomethane (0.37 mL, 6.0 mmol) was added, and the reaction mixture was stirred for 2 h at room temperature. After addition of 10% HCl, the mixture was extracted with EtOAc and washed with saturated $NaHCO_3$ and brine. Drying over Na_2SO_4 and concentration followed by silica gel chromatography (hexanes−EtOAc 1:2) afforded (*S*)-1-benzyloxycarbonyl-*N*-methyl-*N*-(1-naphthyl)-2-pyrrolidinecarboxamide (1.3 g, 82%) as a mixture of rotamers. $[\alpha]^{28}_D$: +108.0 (*c* 0.56, $CHCl_3$). IR (neat): 1680, 1595, 1460, 1377 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.90−2.07 (m, 4H), 3.25, 3.29, 3.38, and 3.40 (4 × s, 3H), 3.37−3.67 (m, 2H), 3.85−4.27 (m, 1H), 4.95−6.56 (m, 2H), 7.08−8.30 (m, 12H). ^{13}C NMR ($CDCl_3$): δ 23.5, 23.7, 24.4, 24.5, 29.2, 30.6, 31.1, 31.6, 32.3, 30.9, 37.3, 37.5, 37.5, 39.8, 46.8, 47.1, 47.3, 47.7, 48.1, 52.0, 53.4, 56.6, 57.1, 57.8, 58.3, 60.4, 66.7, 66.7, 66.8, 67.5, 122.3, 123.0, 123.9, 124.7, 125.3, 125.4, 125.8, 125.9, 126.0, 126.3, 126.3, 126.5, 126.6, 126.7, 126.8, 127.1, 127.2, 127.2, 127.6, 127.7, 127.8, 127.9, 128.1, 128.3, 128.3, 128.4, 128.6, 128.6, 128.7, 128.7, 129.0, 129.0, 130.0, 130.0, 130.1, 134.6, 134.7, 134.8, 136.7, 136.8, 137.3, 139.0, 139.1, 139.3, 139.4, 141.9, 154.1, 154.6, 154.8, 160.2, 172.6, 172.8, 173.4, 173.7, 206.9. MS *m*/*z*: 388 (M^+), 312, 253, 204, 184, 91 (bp). HRMS: calcd for $C_{24}H_{24}N_2O_3$ 388.1787, found 388.1816. Anal. Calcd for $C_{24}H_{24}N_2O_3$: C, 74.21; H, 6.23; N, 7.21. Found: C, 74.12; H, 5.98; N, 7.18.

To a solution of above amide (198 mg, 0.51 mmol) in THF (2 mL) was added BH_3·THF complex (1 M in THF, 5.0 mL, 5.0 mmol), and the reaction mixture was heated at reflux for 1 h. After addition of 10% HCl, the mixture was neutralized with NaOH and extracted with Et_2O. Drying over Na_2SO_4 and concentration gave crude amide, which was treated with 30% HBr in acetic acid (1 mL) at 0 °C for 3 h. After addition of water, the mixture was neutralized with NaOH and extracted with Et_2O. Drying over Na_2SO_4 and concentration followed by silica gel column chromatography (CH_2Cl_2−MeOH−aqueous NH_3 100:10:1) afforded **12** (94 mg, 77%) as a pale yellow oil. $[\alpha]^{24}_D$: +11.0 (*c* 1.1, $CHCl_3$). IR (neat): 3335, 802, 775 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.32−1.51 (m, 1H), 1.63−1.95 (m, 3H), 2.89 (s, 3H), 2.80−2.89 (m, 1H), 2.97 (td, J = 6.8, 13.3 Hz, 1H), 3.13 (t, J = 13.0 Hz, 1H), 3.15 (dd, J = 13.9, 13.0 Hz, 1H), 3.42 (t, J = 6.6 Hz, 1H), 3.53 (s, 1H), 7.16 (d, J = 7.1 Hz, 1H), 7.37−7.57 (m, 4H), 7.81 (dd, J = 6.7, 2.7 Hz, 1H), 8.36 (dd, J = 7.5, 2.0 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 24.9, 29.7, 44.1, 46.0, 56.0, 61.6, 116.1, 123.4, 123.8, 125.2, 125.6, 125.7, 128.1, 129.7, 134.7, 150.3. MS *m*/*z*: 240 (M^+), 171 (bp), 70. HRMS: calcd for $C_{16}H_{20}N_2$ 240.1626, found 240.1638. Anal. Calcd for $C_{16}H_{20}N_2$·HCl: C, 69.43; H, 7.65; N, 10.12. Found: C, 69.28; H, 7.70; N, 10.09.

(*S*)-*N*-Methyl-*N*-(2-naphthyl)-2-pyrrolidinemethanamine (13). Prepared by the same method as for **12** starting from (*S*)-1-benzyloxycarbonyl-*N*-(2-naphthyl)-2-pyrrolidinecarboxamide.[13] (*S*)-1-benzyloxycarbonyl-*N*-methyl-*N*-(1-naphthyl)-2-pyrrolidinecarboxamide. $[\alpha]^{27}_D$: +184.6 (*c* 1.0, $CHCl_3$). IR (Nujol): 1712, 1680, 864, 821, 754 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.66−2.11 (m, 4H), 3.23 and 3.38 (2 × s, 3H), 3.43−3.72 (m, 2H), 4.15−4.37 (m, 1H), 5.01−5.19 (m, 2H), 6.75−6.82 (m, 1H), 7.19−7.94 (m, 12H). ^{13}C NMR ($CDCl_3$): δ 14.1, 23.6, 24.4, 30.3, 31.4, 37.6, 37.8, 46.9, 47.4, 56.8, 57.4, 66.8, 67.4, 125.2, 125.7, 125.9, 126.1, 126.2, 126.7, 126.8, 127.6, 127.8, 128.0, 128.4, 128.6, 129.0, 129.8, 129.9, 132.3, 132.5, 133.4, 133.6, 136.7, 140.4, 140.8, 154.0, 172.6. MS *m*/*z*: 388 (M^+), 204, 91 (bp). HRMS: calcd for $C_{24}H_{24}N_2O_3$ 388.1787, found 388.1801. Anal. Calcd for $C_{24}H_{24}N_2O_3$: C, 74.21; H, 6.23; N, 7.21. Found: C, 74.01; H, 6.00; N, 7.28. **13**. $[\alpha]^{24}_D$: −1.3 (*c* 0.55, EtOH). IR (neat): 3337, 862, 823, 744 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.39−1.96 (m, 4H), 2.92 (ddd, J = 6.5, 7.9, 10.2 Hz, 1H), 3.00 (ddd, J = 5.5, 7.5, 10.2 Hz, 1H), 3.09 (s, 3H), 3.43 (d, J = 2.3 Hz, 1H), 7.03 (d, J = 2.6 Hz, 1H), 7.18 (m, 2H), 7.35 (td, J = 6.9, 1.4 Hz, 1H), 7.65 (t, J = 9.1 Hz, 2H), 7.68 (d, J = 9.1 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 24.8, 29.4, 39.3, 46.1, 57.3, 58.1, 105.8, 116.1, 121.8, 126.0, 126.0, 126.6, 127.3, 128.6, 135.0, 147.5. MS *m*/*z*: 240 (M^+), 171 (bp), 70. HRMS: calcd for $C_{16}H_{20}N_2$ 240.1626, found 240.1608. Anal. Calcd for $C_{16}H_{20}N_2$·HCl: C, 69.43; H, 7.65; N, 10.12. Found: C, 69.70; H, 7.51; N, 10.02.

(*S*)-*N*-Cyclohexyl-*N*-methyl-2-pyrrolidinemethanamine (14). To a solution of *N*-*tert*-butoxycarbonyl-L-proline (0.50 g, 2.3 mmol) and *N*-methylcyclohexylamine (0.35 g, 3.1 mmol) in CH_2Cl_2 (3 mL) was added EDC (0.59 g, 3.1 mmol), and the reaction mixture was stirred at room temperature for 12 h. After addition of water, the mixture was extracted with EtOAc and washed with 10% HCl, saturated $NaHCO_3$, and brine. Drying over Na_2SO_4 and concentration followed by silica gel column chromatography (hexanes−EtOAc 1:1) afforded (*S*)-1-*tert*-butoxycarbonyl-*N*-cyclohexyl-*N*-methyl-2-pyrrolidinecarboxamide (0.39 g, 54%) as a mixture of rotamers. $[\alpha]^{29}_D$: −25.0 (*c* 1.0, $CHCl_3$). IR (Nujol): 1699, 1685 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.00−1.89 (m, 16H), 1.39, 1.40, 1.45, and 1.45 (s × 4, 9H), 1.93−2.23 (m, 2H), 2.81−2.91 (m, 5H), 3.37−3.66 (m, 4H), 4.36−4.43 (m, 1H), 4.45−4.53 (m, 1H), 4.65 (td, 8.4, 2.9 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 23.1, 23.7, 24.9, 25.0, 25.2, 25.3, 25.4, 25.6, 27.0, 27.0, 28.1, 28.2, 28.8, 29.3, 29.4, 29.5, 29.8, 30.1, 30.3, 30.4, 30.6, 30.7, 30.7, 46.3, 46.5, 52.4, 52.5, 55.7, 55.8, 56.6, 56.9, 153.5, 153.7, 154.1, 171.6, 171.6, 172.0. MS *m*/*z*: 310 (M^+), 237, 170, 70 (bp). HRMS: calcd for $C_{17}H_{30}N_2O_3$ 310.2256, found 310.2256. Anal. Calcd for $C_{17}H_{30}N_2O_3$: C, 65.81; H, 9.75; N, 9.03. Found: C, 65.90; H, 9.62; N, 8.88.

To a solution of above amide (0.39 g, 0.87 mmol) in CH_2Cl_2 (1 mL) was added trifluoroacetic acid (1 mL) at 0 °C, and the reaction mixture was stirred at the same temperature for 1 h. The mixture was neutralized with saturated $NaHCO_3$ and extracted with CH_2Cl_2. Drying over Na_2SO_4 and concentration gave crude amide, which was added to a solution of lithium aluminum hydride (0.13 g, 3.3 mmol) in THF (20 mL) and the mixture was heated at reflux for 1 h. After the addition of water (0.13 mL), 15% NaOH (0.13 mL), and water (0.39 mL) successively, the mixture was filtered through a Celite pad. Concentration followed by silica gel column chromatography (CH_2Cl_2−MeOH−aqueous NH_3 100:10:1) afforded **14** (0.10 g, 36%) as a colorless oil. $[\alpha]^{26}_D$: −3.5 (*c* 1.0, EtOH). IR (neat): 3319 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.97−1.37 (m, 6H), 1.56−1.91 (m, 8H), 2.26 (s, 3H), 2.20−2.50 (m, 2H), 2.32 (d, J = 6.8 Hz, 2H), 2.83 (dt, J = 7.0, 9.9 Hz, 1H), 2.94 (dt, J = 6.6, 10.0 Hz, 1H), 3.18 (dd, J = 6.7, 6.7 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 25.1, 26.4, 26.7, 28.7, 29.1, 29.8, 38.7, 46.0, 56.7, 58.9, 63.7. MS *m*/*z*: 196 (M^+), 126, 84 (bp), 70. HRMS: calcd for $C_{12}H_{24}N_2$ 196.1940, found 196.1941.

(*S*)-*N*-Ethyl-*N*-phenyl-2-pyrrolidinemethanamine (15). Prepared by the same method as for **10** starting from *N*-benzyloxycarbonyl-L-proline and *N*-ethylaniline. (*S*)-1-Benzyloxycarbonyl-*N*-ethyl-*N*-phenyl-2-pyrrolidinecarboxamide. $[\alpha]^{22}_D$: +119.3 (*c* 1.2, $CHCl_3$). IR (Nujol): 1730, 1668, 702 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.02−1.17 (m, 3H), 1.67−2.14 (m, 5H), 3.45−3.87 (m, 4H), 4.06−4.26 (m, 1H), 5.09−5.19 (m, 2H), 6.72 (bs, 1H), 7.23−7.50 (m, 9H). ^{13}C NMR ($CDCl_3$): δ 12.8, 12.9, 23.6, 24.4, 30.3, 31.4, 44.3, 44.4, 47.0, 47.5, 57.0, 57.6, 66.8, 67.4, 127.6, 127.8, 127.9, 128.0, 128.3, 128.4, 128.5, 128.6, 128.9, 129.0, 129.5, 129.7, 136.6, 136.8, 141.4, 141.7, 154.1, 154.7, 171.8, 171.9. MS *m*/*z*: 352 (M^+), 204, 148, 120, 91 (bp). HRMS: calcd for $C_{21}H_{24}N_2O_3$ 352.1787, found 352.1779. Anal. Calcd for $C_{21}H_{24}N_2O_3$: C, 71.57; H, 6.86; N, 7.95. Found: C, 71.79; H, 6.97; N, 7.86. **15**. $[\alpha]^{22}_D$: +10.1 (*c* 1.0, EtOH). IR (neat): 3329, 1599, 1248, 1196, 694 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.14 (t, J = 7.0 Hz, 3H), 1.38−1.51 (m, 1H), 1.68−1.98 (m, 3H), 2.83 (bs, 1H), 2.90 (ddd, J = 6.6, 8.2, 10.3 Hz, 1H), 3.06 (ddd, J = 5.7, 7.7, 10.3 Hz, 1H), 3.23−3.50 (m, 3H), 3.46 (q, J = 7.0 Hz, 2H), 6.68−6.82 (m, 3H), 7.18−7.27 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 11.5, 24.6, 29.0, 45.5, 46.0, 55.4, 57.2, 112.2, 115.7, 129.0, 148.1. MS *m*/*z*: 204 (M^+), 135, 120, 106, 70 (bp).

HRMS: calcd for $C_{13}H_{20}N_2$ 204.1627, found 204.1616. Anal. Calcd for $C_{13}H_{20}N_2 \cdot 2HCl$: C, 56.32; H, 8.00; N, 10.10, Found: C, 56.10; H, 7.93; N, 10.00.

(*S*)-*N*-Benzyl-*N*-phenyl-2-pyrrolidinemethanamine (16). To a solution of *N*-benzyloxycarbonyl-L-proline (10 g, 40 mmol) and *N*-benzylaniline (8.8 g, 48 mmol) in THF was added EDC (8.3 g, 43 mmol), and the reaction mixture was stirred at room temperature for 12 h. After addition of water, the mixture was extracted with EtOAc and washed with 10% HCl, saturated $NaHCO_3$, and brine. Drying over Na_2SO_4 and concentration followed by recrystallization from EtOAc−hexane afforded (*S*)-1-benzyloxycarbonyl-*N*-phenyl-*N*-phenylmethyl-2-pyrrolidinecarboxamide (6.9 g, 41%) as a mixture of rotamers. $[\alpha]^{25}_D$: +76.9 (*c* 1.0, $CHCl_3$). IR (Nujol): 1696, 1662, 1593 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.68−2.14 (m, 4H), 3.44−3.74 (m, 2H), 4.09−4.29 (m, 1H), 4.64−5.18 (m, 4H), 6.56 (d, J = 6.8 Hz, 1H), 7.06−7.39 (m, 14H). ^{13}C NMR ($CDCl_3$): δ 23.5, 24.4, 30.3, 31.3, 46.9, 47.4, 53.2, 53.3, 56.9, 57.5, 66.7, 67.2, 127.2, 127.3, 127.5, 127.7, 127.9, 128.0, 128.1, 128.3, 128.4, 128.5, 128.6, 128.7, 128.9, 129.0, 129.3, 129.5, 129.6, 129.7, 129.8, 136.5, 136.7, 137.2, 137.3, 141.2, 141.6, 154.0, 154.7, 172.4, 172.5. MS *m*/*z*: 414 (M^+), 204, 182, 91 (bp). HRMS: calcd for $C_{26}H_{26}N_2O_3$ 414.1945, found 414.1906. Anal. Calcd for $C_{26}H_{26}N_2O_3$: C, 75.34; H, 6.32; N, 6.76. Found: C, 75.44; H, 6.50; N,6.61.

To a solution of above amide (6.5 g, 15.7 mmol) in THF (16 mL) was added BH_3·THF complex (1 M in THF, 17 mL, 17 mmol), and the reaction mixture was heated at reflux for 1 h. After addition of 10% HCl, the mixture was neutralized with NaOH and extracted with Et_2O. Drying over Na_2SO_4 and concentration gave crude amide, which was treated with 30% HBr in acetic acid (18 mL) at 0 °C for 3 h. After addition of water, the mixture was neutralized and extracted with Et_2O. Drying over Na_2SO_4 and concentration followed by silica gel column chromatography (CH_2Cl_2−MeOH−aqueous NH_3 100:10:1) afforded **16** (3.6 g, 85%) as a pale yellow oil. $[\alpha]^{28}_D$: +9.6 (*c* 1.1, EtOH). IR (neat): 3339, 1599, 1504, 1392, 1358 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.33−1.46 (m, 1H), 1.63−1.99 (m, 3H), 2.07 (s, 1H), 2.86 (ddd, J = 6.7, 7.9, 10.2 Hz, 1H), 2,98 (ddd, J = 5.7, 7.6, 10.2 Hz, 1H), 3.35−3.54 (m, 3H), 4.64 (d, J = 22.2 Hz, 1H), 4.70 (d, J = 22.2 Hz, 1H), 6.65−6.75 (m, 3H), 7.14−7.36 (m, 7H). ^{13}C NMR ($CDCl_3$): δ 24.9, 29.5, 46.3, 55.2, 56.7, 57.4, 112.6, 116.5, 126.5, 126.7, 128.5, 129.2, 138.8, 148.8. MS *m*/*z*: 266 (M^+), 197, 190, 84 (bp). HRMS: calcd for $C_{18}H_{22}N_2$ 266.1783, found 266.1796. Anal. Calcd for $C_{18}H_{22}N_2$: C, 81.16; H, 8.32; N, 10.52. Found: C, 79.7; H, 8.33; N, 10.27.

(*S*)-*N*,*N*-Diphenyl-2-pyrrolidinemethanamine (17). To a solution of *N*-trifluoro-L-proline (3.0 g, 14 mmol) in dichloromethane (10 mL) was added thionyl chloride (10 mL) at 0 °C, and the mixture was stirred at room temperature for 1 h. After evaporation in vacuo, diphenylamine (5.0 g, 29 mmol) was added to the solution of the residue in dichloromethane (20 mL) at 0 °C, and the reaction mixture was stirred at room temperature for 12 h. After addition of water, the mixture was extracted with EtOAc and washed with 10% HCl, saturated $NaHCO_3$, and brine. Drying over Na_2SO_4 and concentration followed by recrystallization from benzene−hexane afforded (*S*)-1-trifluoro-*N*,*N*-diphenyl-2-pyrrolidinecarboxamide (1.0 g, 21%) as pale brown needles. Mp: 102−104 °C. $[\alpha]^{26}_D$: −32.5 (*c* 1.0, benzene). IR (Nujol): 1749, 1682, 906, 869 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.86−2.33 (m, 4H), 3.76 (s, 2H), 3.63−3.91 (m, 2H), 4.36−4.66 (m, 1H), 7.29−7.58 (m, 8H). ^{13}C NMR ($CDCl_3$): δ 25.2, 28.5, 29.0, 47.9, 59.5, 60.1, 117.8, 126.3, 129.0, 129.3, 170.8. MS *m*/*z*: 362 (M^+), 166 (bp). HRMS: calcd for calcd for $C_{19}H_{17}F_3N_2O_2$ 362.1242, found 362.1263. Anal. Calcd for $C_{19}H_{17}F_3N_2O_2$: C, 62.98; H, 4.73; N, 7.73. Found: C, 63.22; H, 4.64; N, 7.65.

To a solution of above amide (1.2 g, 3.3 mmol) in EtOH (18 mL) was added sodium borohydride (0.23 g, 5.8 mmol), and the reaction mixture was refluxed for 3 h. After addition of water, the mixture was extracted with EtOAc and washed with 10% HCl, saturated $NaHCO_3$, and brine. Drying over Na_2SO_4 and concentration followed by recrystallization from benzene−hexane afforded (*S*)-*N*,*N*-diphenyl-2-pyrrolidinecarboxamide (0.67 g, 76%) as pale brown needles. Mp: 113 °C. $[\alpha]^{25}_D$: +23.4 (*c* 1.0, benzene). ^1H NMR ($CDCl_3$): δ 1.62−1.95 (m, 4H), 2.02−2.42 (bs, 1H), 2.64−2.75 (m, 1H), 3.15−3.23 (m, 1H), 3.69−3.76 (m, 1H), 7.12−7.67 (m, 10H). ^{13}C NMR ($CDCl_3$): δ 26.7, 31.8, 48.0, 59.5, 128.8, 129.2, 129.3, 174.9. MS *m*/*z*: 266 (M^+), 196, 169, 70 (bp). HRMS: calcd for $C_{17}H_{18}N_2O$ 266.1420, found 266.1432. Anal. Calcd for $C_{17}H_{18}N_2O$: C, 76.67; H, 6.81; N, 10.52. Found: C, 76.43; H, 6.89; N, 10.30.

To a solution of above amide (0.67 g, 2.5 mmol) in THF (1 mL) was added $BF_3 \cdot OEt_2$ (0.30 mL, 2.4 mmol), and the reaction mixture was heated at reflux for 1 h. After cooling, $BH_3 \cdot SMe_2$ complex (1 M in THF, 1.8 mL, 1.8 mmol) was added, and the mixture was heated at reflux for 3 h. After evaporation of the solvent, 10% HCl (0.5 mL) was added to the residue, and the mixture was refluxed for 1 h. The mixture was neutralized with 10% aqueous NaOH and extracted with Et_2O. Drying over Na_2SO_4 and concentration followed by silica gel column chromatography (CH_2Cl_2−MeOH−aqueous NH_3 200:10:1) afforded **17** (536 mg, 65%) as a colorless oil. $[\alpha]^{22}_D$: −21.5 (*c* 1.1, EtOH). IR (neat): 3339, 1589, 866 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.32−1.46 (m, 1H), 1.57−1.88 (m, 3H), 2.79−3.02 (m, 2H), 3.36−3.47 (m, 1H), 3.74 (d, J = 7.0 Hz, 2H), 3.95 (bs, 1H), 6.84−7.21 (m, 10H). ^{13}C NMR ($CDCl_3$): δ 24.5, 29.3, 45.9, 56.6, 57.3, 121.2, 121.6, 129.3, 148.3. MS *m*/*z*: 252 (M^+), 183 (bp), 70. HRMS: calcd for calcd for $C_{17}H_{20}N_2$ 52.1627, found 252.1638. Treatment of **17** with picric acid afforded the corresponding picrate as orange prisms of mp 153 °C. Anal. Calcd for $C_{17}H_{20}N_2 \cdot C_6H_3N_3O_7$: C, 57.37; H, 4.81; N, 14.54. Found: C, 57.07; H, 4.95; N, 14.39.

Enantioselective Oxidative Coupling of 1e Catalyzed by Chiral Amine·Copper Complex Prepared in Situ. To a solution of amine (0.15 mmol) in dichloromethane (10 mL) was added CuCl (14 mg, 0.14 mmol), and the mixture was sonicated to afford a green solution. A solution of **1e** (400 mg, 1.4 mmol) in dichloromethane (10 mL) was added, and the mixture was heated at reflux in oxygen of atmospheric pressure for 24 h. Purification by silica gel column chromatography[12] afforded **2e**, the enantiomeric excess of which was determined by HPLC analysis (Daicel Chiralpak AD).

Preparation of Chiral Amine·Copper Complex. To a solution of **15** (220 mg) in dichloromethane (20 mL) was added CuCl (99 mg), and the mixture was sonicated in an oxygen atmosphere to afford a green solution to which hexane (100 mL) was added at room temperature. The resultant precipitate was collected by filtration to afford a green powder (180 mg). Mp: 98−102 °C dec.

General Procedure for the Enantioselective Oxidation of 2-Naphthol Derivatives. To a solution of 2-naphthol derivative (2.5 mmol) in dichloromethane (20 mL) was added catalyst (10 mol %), and the reaction mixture was stirred at room temperature in an oxygen atmosphere for 24 h. The reaction was quenched by 10% aqueous NH_3 (10 mL), and the mixture was extracted with EtOAc. The organic phase was dried with Na_2SO_4 and evaporated in vacuo. The residue was purified by silica gel column chromatography to afford the corresponding binaphthol derivative. For purification by silica gel column chromatography of **2e**, see ref 12.

Dimethyl 2,2′-Dihydroxy-1,1′-binaphthalene-3,3′-dicarboxylate (2e). $[\alpha]^{25}_D$: −125.0 (*c* 1.0, THF), for 78% ee (lit.18a $[\alpha]^{25}_D$ +172 (*c* 0.82, THF) for (*R*)-**2e**). HPLC: Daicel Chiralpak AD, hexane−isopropyl alcohol 9:1, 1 mL/min, 11.0 (*S*) and 20.0 (*R*) min.

Diethyl 2,2′-Dihydroxy-1,1′-binaphthalene-3,3′-dicarboxylate (2g). $[\alpha]^{21}_D$: −112.2 (*c* 1.1, THF) for 73% ee. HPLC: Daicel Chiralpak AD, hexane−isopropyl alcohol 9:1, 1 mL/min, 7.5 (*S*) and 11.6 (*R*) min. IR ($CHCl_3$): 3223, 1680 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.52 (t, J = 7.1 Hz, 6H), 4.52 (q, J = 6.6 Hz, 8H), 7.15 (dd, J = 6.3, 3.6 Hz, 2H), 7.30−7.37 (m, 4H), 7.94 (dd, J = 6.4, 3.1 Hz, 2H), 8.69 (s, 2H), 10.80 (s, 2H). ^{13}C NMR ($CDCl_3$): δ 14.7, 62.3, 114.8, 117.4, 124.3, 125.1, 127.6, 129.6 129.8, 130.2, 133.2, 137.6, 154.6, 170.6. MS *m*/*z*: 430 (M^+, bp), 412, 384, 356, 310. HRMS: calcd for $C_{26}H_{22}O_6$ 430.1417, found 430.1429. Anal. Calcd for $C_{26}H_{22}O_6$: C, 72.55; H, 5.15. Found: C, 72.50; H, 5.26. Absolute configuration of **2g** was determined after conversion of **2g** ($[\alpha]^{21}_D$ −112.2 (*c* 1.1, THF)) into **2e** ($[\alpha]^{21}_D$ −157.5 (*c* 1.0, THF)) by transesterification catalyzed by dibutyltin oxide.[19b]

Dibenzyl 2,2′-dihydroxy-1,1′-binaphthalene-3,3′-dicarboxylate (2h). $[\alpha]^{20}_D$: −81.3 (*c* 1.0, THF) for 76% ee. HPLC: Daicel Chiralpak AD, hexane−isopropyl alcohol 9:1, 1 mL/min, 15.4 (*S*) and 23.9 (*R*) min. IR (Nujol): 3194, 1672, 794 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.48 (s, 4H), 7.12−7.17 (m, 2H), 7.29−7.54 (m, 14H), 7.87−7.92 (m, 2H), 8.71 (s, 2H), 10.69 (s, 2H). ^{13}C NMR ($CDCl_3$): δ 67.4, 114.2, 117.0, 124.0, 124.7, 127.2, 128.4, 128.5, 128.7, 128.8, 129.2, 129.5, 129.8, 132.9, 135.2, 137.2, 154.1, 169.9. MS *m*/*z*: 554 (M^+), 445, 356, 91 (bp). Anal. Calcd for $C_{36}H_{26}O_6$: C, 77.96; H, 4.73. Found: C, 78.10; H, 4.90. Absolute configuration of **2h** was determined after conversion of **2h** ($[\alpha]^{21}_D$ −76.7 (*c* 1.0, THF)) into **2e** ($[\alpha]^{21}_D$ −123.5 (*c* 1.1, THF)) by hydrogenolysis (H_2/Pd−C) followed by esterification with diazomethane.

Di-*tert*-butyl 2,2′-Dihydroxy-1,1′-binaphthalene-3,3′-dicarboxylate (2i). $[\alpha]^{25}_D$: −79.6 (*c* 1.0, THF) for 58% ee. HPLC: Daicel Chiralpak AD, hexane−isopropyl alcohol 9:1, 1 mL/min, 9.9 (*R*) and 12.0 (*S*) min. IR ($CHCl_3$): 3221, 1682 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.69 (s, 18H), 7.14 (dd, J = 6.3, 3.4 Hz, 2H), 7.29−7.35 (m, 4H), 7.91 (dd, J = 6.2, 3.2 Hz, 2H), 8.59 (s, 2H), 11.0 (s, 2H). ^{13}C NMR ($CDCl_3$): δ 52.7, 114.2, 117.0, 124.0, 124.7, 127.2, 129.5, 129.8, 132.9, 137.2, 154.0, 170.6. MS *m*/*z*: 486 (M^+), 430, 374 (bp). Anal. Calcd for $C_{30}H_{30}O_6$: C, 74.06; H, 6.21. Found: C, 73.81; H, 6.55. Absolute configuration of **2i** was determined after conversion of **2i** ($[\alpha]^{26}_D$ −79.6 (*c* 1.0, THF)) into **2e** ($[\alpha]^{26}_D$ −100 (*c* 1.0, THF)) by successive treatment with trifluoroacetic acid and diazomethane.

3,3′-Diacetyl-1,1′-binaphthalene-2,2′-diol (2j). $[\alpha]^{21}_D$: −78.8 (*c* 1.0, THF) for 37% ee. HPLC: Daicel Chiralpak AD, hexane−isopropyl alcohol 9:1, 1 mL/min, 13.8 (*S*) and 30.5 (*R*) min. IR ($CHCl_3$): 3532, 1647 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.87 (s, 6H), 7.13−7.17(m, 2H), 7.32−7.39 (m, 4H), 7.92−7.96 (m, 2H), 8.55 (s, 2H), 11.87 (s, 2H). ^{13}C NMR ($CDCl_3$): δ 27.0, 117.3, 121.1, 124.1, 124.6, 127.0, 129.9, 130.0, 134.0, 137.5, 154.8, 204.9. MS *m*/*z*: 370 (M^+, bp), 352, 337. HRMS: calcd for $C_{24}H_{18}O_4$ 370.1206, found 370.1190. Anal. Calcd for $C_{24}H_{18}O_4$: C, 77.83; H, 4.90. Found: C, 77.71; H, 5.10. The absolute configuration of **2j** was determined after conversion of (*R*)-2,2′-dihydroxy-1,1′-binaphthalene-3,3′-dicarboxylic acid[18a] into **2j** ($[\alpha]^{21}_D$ +212.8 (*c* 1.01, THF)) by methyllithium with trimethylsilyl chloride in THF.[19a]

***N,N′*-Dibenzyl-2,2′-dihydroxy-1,1′-binaphthalene-3,3′-dicarboxamide (2k).** $[\alpha]^{26}_D$: −27.1 (*c* 0.61, THF) for 24% ee. ^1H NMR (CD_3COCD_3): δ 4.72 (d, J = 5.8 Hz, 4H), 7.07−7.12 (m, 2H), 7.24−7.47 (m, 12H), 7.84−7.89 (m, 2H), 8.67 (s, 2H), 9.07 (bs, 2H), 12.40 (s, 2H). ^{13}C NMR (CD_3COCD_3): δ 43.9, 117.7, 124.2, 125.3, 127.8, 128.0, 128.6, 129.1, 129.3, 130.1, 139.6. MS *m*/*z*: 552 (M^+), 461, 446, 91 (bp). Anal. Calcd for $C_{36}H_{28}N_2O_4$: C, 78.24; H, 5.11; N, 5.07. Found: C, 78.41; H, 5.03; N, 4.90. The enantiomeric excess was determined after conversion of **2k** into the corresponding diacetate. ^1H NMR ($CDCl_3$): δ 1.56 (s, 6H), 4.62 (ddd, J = 20.6, 14.6, 5.8 Hz, 4H), 6.57 (t, J = 5.6 Hz, 2H), 7.12 (d, J = 8.5 Hz, 2H), 7.24−7.36 (m, 12H), 7.50 (t, J = 7.6 Hz, 2H), 7.96 (d, J = 8.1 Hz, 2H), 8.38 (s, 2H). HPLC: Daicel Chiralpak OD, EtOH, 1 mL/min, 3.8 (*S*) min. and 4.6 (*R*) min. The absolute configuration of **2k** was determined after conversion of optically pure (*R*)-2,2′-dihydroxy-1,1′-binaphthalene-3,3′-dicarboxylic acid[18a] into **2k** ($[\alpha]^{25}_D$ +111.6 (*c* 0.78, THF)) by amide formation with benzylamine and thionyl chloride.

1,1′-Binaphthalene-2,2′-diol (2a). $[\alpha]^{29}_D$: −20.1 (*c* 1.0, THF) for 17% ee. (lit.[18b] $[\alpha]^{20}_D$ −35.5 (*c* 1.0, THF) for (*S*)-**2a**.) HPLC: Daicel Chiralpak OJ, hexane−isopropyl alcohol 9:1, 1 mL/min, 34 (*S*) and 49 (*R*) min.

3,3′-Dimethyl-1,1′-binaphthalene-2,2′-diol (2b). $[\alpha]^{25}_{578}$: −3.1 (*c* 1.0, $CHCl_3$) for 12% ee. (lit.[18a] $[\alpha]^{25}_{578}$ +37.3 (*c* 1.0, $CHCl_3$) for (*R*)-**2b**.) HPLC: Daicel Chiralpak AD, hexane−isopropyl alcohol 9:1, 1 mL/min, 6.7 (*S*) and 8.8 (*R*) min.

7,7′-Dimethoxy-1,1′-binaphthalene-2,2′-diol (2d). $[\alpha]^{25}_D$: +12.1 (*c* 1.0, MeOH) for 16% ee. (lit.[18c] $[\alpha]^{21}_D$ −126.4 (*c* 1.0, MeOH) for (*R*)-**2d**.) HPLC: Daicel Chiralpak AD, hexane−isopropyl alcohol 9:1, 1.5 mL/min, 29 (*S*) and 36 (*R*) min.

3,3′-Diisopropyl-1,1′-binaphthalene-2,2′-diol (2l). $[\alpha]^{24}_D$: −1.6 (*c* 1.4, THF), 5% ee determined by ^1H NMR analysis with Eu(hfc)$_3$. IR ($CHCl_3$): 2543 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.19 (d, J = 6.9 Hz, 12H), 3.07 (septet, J = 6.9 Hz, 2H), 7.15 (s, 2H), 7.31 (d, J = 7.5 Hz, 2H), 7.42 (ddd, J = 7.5, 7.5, 1.2 Hz, 2H), 7.61 (ddd, J = 7.5, 7.5, 1.2 Hz, 2H), 8.04 (d, J = 7.5 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 21.5, 27.0, 129.3, 129.6, 129.7, 130.4, 135.4, 135.8, 138.3, 146.3, 179.5, 180.7. MS *m*/*z*: 370 (M^+, bp). HRMS: calcd for $C_{26}H_{26}O_2$ 370.1934, found 370.1940. Anal. Calcd for $C_{26}H_{26}O_2$: C, 84.29; H, 7.07. Found: C, 84.01; H, 6.95.

3,3′-Dibenzyloxy-1,1′-binaphthalene-2,2′-diol (2m). $[\alpha]^{24}_D$: −8.2 (*c* 0.8, THF) for 24% ee. IR ($CHCl_3$): 3528, 1458 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.32 (s, 4H), 5.98 (s, 2H), 7.16 (d, J = 3.7 Hz, 4H), 7.26−7.52 (m, 14H), 7.75 (d, J = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 71.1, 107.6, 114.8, 124.0, 124.6, 124.8, 126.9, 127.9, 128.4, 128.8, 129.0, 129.2, 136.0, 143.8, 146.4. MS *m*/*z*: 498 (M^+), 407, 91 (bp). HRMS: calcd for $C_{34}H_{26}O_4$ 498.1831, found 498.1856. Anal. Calcd for $C_{34}H_{26}O_4$: C, 81.91; H, 5.26. Found: C, 81.81; H, 5.33. Enantiomeric excess and absolute configuration were determined after conversion (H_2, Pd−C) into 1,1′-binaphthalene-2,2′,3,3′-tetrol: $[\alpha]^{23}_D$ −8.2 (*c* 0.29, THF) for 24% ee. HPLC: Daicel Chiralpak AD, EtOH, 1 mL/min, 3.8 (*S*) and 4.4 (*R*) min.

Preparation of Homochiral Binaphthol (2a) from Methyl 3-Hydroxy-2-naphthoate (1e) as a Starting Material. To a solution of **1e** (0.75 g, 3.7 mmol) in dichloromethane (30 mL) was added chiral catalyst (0.16 g, 0.37 mmol) prepared from **15**, and the reaction mixture was stirred at room temperature under oxygen atmosphere for 24 h. The mixture was concentrated and then triturated in MeOH (10 mL). The resulting precipitate was collected by filtration to afford **2e** ($[\alpha]^{23}_D$ −125.0 (*c* 1.0, THF), 78% ee) as pale yellow needles. Trituration of **2e** in EtOAc (10 mL) followed by filtration afforded the filtrate containing 0.50 g of **2e** ($[\alpha]^{28}_D$ −162.0 (*c* 1.1, THF) of >99% ee.

To a solution of optically pure **2e** (0.50 g, 1.2 mmol) in DMF (7 mL) was added sodium hydride (60% in oil, 0.11 g, 2.8 mmol) followed by iodomethane (0.2 mL, 3.2 mmol) at 0 °C, and the mixture was stirred at room temperature for 2 h. The reaction was quenched with saturated NH_4Cl, and the mixture was extracted with EtOAc. Drying over Na_2SO_4 and evaporation of solvent afforded dimethyl 2,2′-dimethoxy-1,1′-binaphthalene-3,3′-dicarboxylate as a viscous oil, which was hydrolyzed with KOH (0.40 g) in 10% EtOH (5 mL) at 80 °C for 1 h. Acidification with HCl followed by extraction with EtOAc gave the diacid, which was decarboxylated with Cu-bronze (0.20 g) and $CuCO_3$ (0.15 g) in quinoline (8 mL) at 180 °C for 30 min. After cooling, the mixture was diluted with benzene and filtered through a Celite pad. The filtrate was washed with brine, and the organic phase was evaporated to afford the diether, which was purified with silica gel column chromatography (hexanes−EtOAc 10:1) to afford 2,2′-dimethoxy-1,1′-binaphthalene (0.33 g, 85% from **2e**) as colorless needles of mp 227−229 °C. BBr_3 (0.2 mL, 2.1 mmol) was added to a solution of above diether in CH_2Cl_2 (3 mL) at −78 °C, and the mixture was stirred at room temperature for 30 min. The reaction was quenched with ice water and the mixture was extracted with EtOAc. Evaporation of solvent followed by recrystallization from benzene afforded **2a** (0.25 g, 82%) as colorless needles. Mp: 205−206 °C. $[\alpha]^{24}_D$: −36.0 (*c* 1.0 THF) (lit.[18b] $[\alpha]^{24}_D$ −35.5 (*c* 1.0 THF)), >99% by HPLC.

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Supporting Information Available: ^1H and ^{13}C NMR spectra of chiral amines **10**−**17**. This material is available free of charge via the Internet at http://pubs.acs.org.

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