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Asymmetric Synthesis of Axially Chiral Biaryls by Nickel-Catalyzed Grignard Cross-Coupling of Dibenzothiophenes

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Catalytic asymmetric Grignard cross-coupling of 1,9-disubstituted dibenzothiophenes (**6a**−**c**) and dinaphthothiophene (**6d**) with aryl- and alkyl-Grignard reagents (**7**) proceeded with high enantioselectivity (up to 95% ee) in the presence of a nickel catalyst (3−6 mol %) coordinated with 2-diphenylphosphino-1,1′-binaphthyl (H-MOP) or oxazoline-phosphine ligand (*i*-Pr-phox) in THF to give 2-mercapto-2′-substituted-1,1′-biphenyls (**8a**−**c**) and 2-mercapto-2′-substituted-1,1′-binaphthyls (**8d**) in high yields. The mercapto group in the axially chiral cross-coupling products was converted into several functional groups by way of the methylsulfinyl group. The rate of flipping in dinaphthothiophene was measured by variable-temperature ^{31}P NMR analysis of methylphenylphosphinyldinaphthothiophene derivative (**21**).

Introduction

Axially chiral biaryls have found extensive use in chiral auxiliaries for a variety of asymmetric reactions. Although considerable attention has been paid to their preparation by asymmetric synthesis,[1] direct synthetic methods giving the enantiomerically enriched biaryls from achiral substrates are still rare. The asymmetric synthesis of axially chiral biaryls can be grouped into two categories according to the mode of generation of the axial chirality. One is cross- or homo-coupling of two aryl units where the axial chirality is generated at the formation of the biaryl skeleton. The best examples are nickel[2]- or palladium[3]-catalyzed asymmetric cross-coupling of aryl halides with aryl Grignard reagents or arylboronic acids. Oxidative coupling of 2-naphthol derivatives catalyzed by copper-chiral amine complexes[4,5] or chiral oxovanadium complexes[6] has been also reported. The other is enantioposition-selective cross-coupling of achiral biaryl ditriflates where the axially chiral biaryls can be prepared by the selective substitution of one of two enantiotopic triflate groups.[7]

Recently, we have reported the third type of catalytic asymmetric synthesis of axially chiral 1,1′-binaphthyls, which is realized by asymmetric Grignard cross-coupling of dinaphtho[2,1-*b*:1′,2′-*d*]thiophene with the Grignard reagents in the presence of a nickel catalyst coordinated with a chiral oxazoline-phosphine ligand.[8] In this type of reaction, the axial chirality is generated at the cleavage of the carbon−sulfur bond in the thiophene ring.[9]

Here we wish to report a full description of this type of catalytic asymmetric cross-coupling, including its reaction of 1,9-disubstituted dibenzothiophenes (**6a**−**c**) and dinaphthothiophene (**6d**). Also described are the conversion of the cross-coupling products into useful axially chiral compounds, the proposal of a stereochemical pathway in the catalytic cycle, and measurement of the flipping rate of the dinaphthothiophene.

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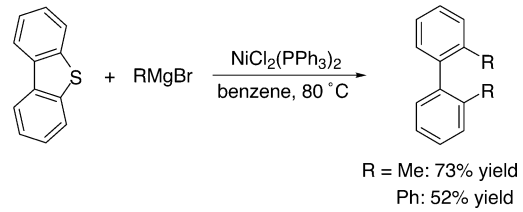
SCHEME 1



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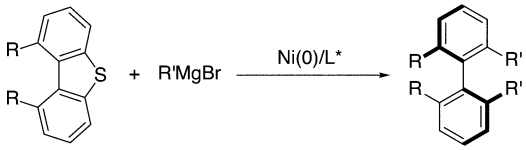

Results and Discussion

It has been well-documented that organosulfur compounds undergo the cross-coupling with organometallic reagents in the presence of transition metal catalysts.[10,11] In 1979, Wenkert reported that thiophenes participate in the nickel-catalyzed cross-coupling.[12]

The reaction of dibenzothiophene with methylmagnesium iodide and phenylmagnesium bromide in the presence of 10 mol % of $NiCl_2(PPh_3)_2$ in benzene at 80 °C gave 73% yield of 2,2′-dimethyl-1,1′-biphenyl and 52% yield of 2,2′-diphenyl-1,1′-biphenyl, respectively (Scheme 1).

These results suggest that axially chiral biaryls can be produced by the cross-coupling of a dibenzothiophene derivative containing substituents at 1- and 9-positions which will prevent the rotation around the biaryl axis from taking place. Use of a transition metal catalyst coordinated with a proper chiral ligand will give us a chance to obtain enantiomerically enriched biaryls (Scheme 2).

To realize the catalytic asymmetric synthesis of axially chiral biaryl compounds from dibenzothiophenes by cross-coupling, three 1,9-disubstituted dibenzothiophenes were prepared as substrates. Staiger has recently reported the synthesis of dinaphtho[2,1-*b*;1′,2′-*d*]thiophene by thermal rearrangement of 2,2′-bis(*N*,*N*-dimethylthiocarbamoyloxy)-1,1′-binaphthyl, readily accessible from 2,2′-dihydroxy-1,1′-binaphthyl.[13] These procedures were applied to the preparation of 1,9-disubstituted dibenzothiophenes.

Synthetic procedures to the 1,9-disubstituted dibenzothiophenes are depicted in Scheme 3. Triflation of 2,2′-dihydroxy-6,6′-dimethoxy-1,1′-biphenyl (**1**), whose preparation has been reported by Delogu,[14] gave bis(triflate) **2** in 90% yield. Nickel- or palladium-catalyzed cross-coupling of bis(triflate) **2** with organomagnesium or -zinc reagents gave the corresponding cross-coupling products **3a**−**c**.[15] In the presence of 20 mol % of $NiCl_2$(dppp), the dimethylation of **2** with methylmagnesium iodide was completed at room temperature in 12 h to give 80% yield of 2,2′-dimethoxy-6,6′-dimethyl-1,1′-biphenyl (**3a**).[16] Palladium-catalyzed cross-coupling of **2** with butyl- and phenylzinc chloride in the presence of $PdCl_2$(dppf) at 65 °C for 48 h gave the corresponding cross-coupling products **3b** and **3c** in 60% and 55% yield, respectively. Treatment of 2,2′-dihydroxybiphenyls **4**, which were obtained by treatment of dimethyl ethers **3** with BBr_3 in CH_2Cl_2, with *N*,*N*-dimethylthiocarbamoyl chloride[17] in the presence of 2.2 equiv of triethylamine and 10 equiv of pyridine at 65 °C for 12 h gave the corresponding thiocarbamoyl esters **5a** and **5b** in 90% and 93% yield, respectively. Under similar conditions with triethylamine and pyridine, the esterification of **4c** with *N*,*N*-dimethylthiocarbamoyl chloride did not proceed. It was found that the use of sodium hydride in DMF at higher temperature (85 °C) as the optimized reaction condition gave **5c** in 75% yield.[14a,17] We examined sodium hydride for the preparation of **5a** and **5b** to shorten the reaction time, but only poor yields (<30% yield) of the desired products were obtained.

The preparation of dibenzothiophenes **6** was carried out under optimized conditions for the Newman−Kwart rearrangement.[13,17] Thus, heating **5a**−**c** without solvents in an autoclave at 290 °C for 12 h gave the corresponding 1,9-disubstituted dibenzothiophenes **6a**−**c** in high yields (Scheme 4).

First, we examined the Grignard cross-coupling of 1,9-dimethyldibenzothiophene (**6a**) under the conditions reported by Wenkert.[12a] Thus, in the presence of 10 mol % of $NiCl_2(PPh_3)_2$, dibenzothiophene **6a** was allowed to react with 10 equiv of 4-methylphenylmagnesium bromide (**7m**) in benzene at 80 °C for 12 h. Hydrolysis gave 2-mercapto-2′-(4-methylphenyl)-6,6′-dimethyl-1,1′-biphenyl (**8am**) in 5% yield and 2,2′-bis(4-methylphenyl)-6,6′-dimethyl-1,1′-biphenyl (**9am**) in 85% yield (Scheme 5).

It was found that the reaction in THF at 40 °C proceeds with much higher selectivity in giving monoarylation product **8am**. Thus, the reaction of **6a** with 10 equiv of **7m** in the presence of a nickel catalyst generated from 6 mol % of $Ni(cod)_2$ and 18 mol % of triphenylphosphine in THF at 40 °C for 24 h gave the monoarylation product **8am** in 75% yield and starting material was recovered in 20% yield without formation of the diarylation product **9am** (entry 1 in Table 1). The use of 10 equiv of the Grignard reagent is required to ensure the high conversion of the thiophene.[8] A nickel−phosphine complex generated in situ from $Ni(cod)_2$ and phosphine ligand was an effective catalyst for this type of cross-coupling. To examine the ability of several ligands for the asymmetric cross-coupling, it is more convenient to use the in situ catalysts than isolated complexes containing chiral

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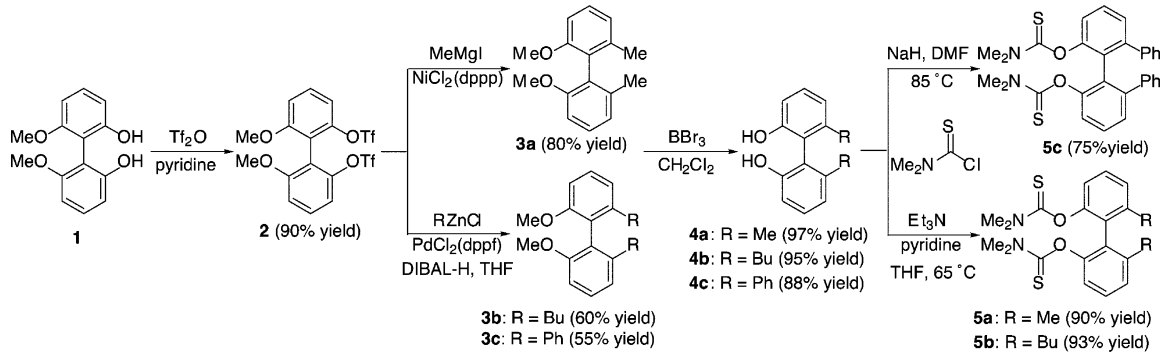
SCHEME 3



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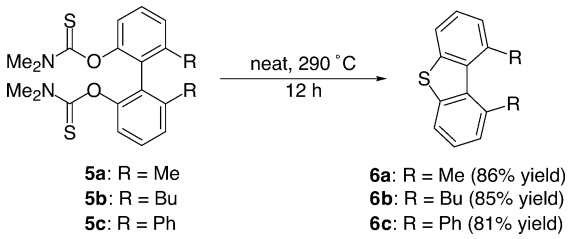

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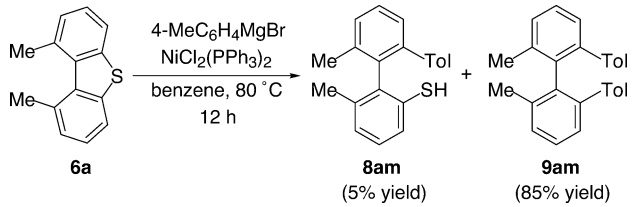

TABLE 1. Nickel-Catalyzed Asymmetric Cross-Coupling of 1,9-Dimethyldibenzothiophene (6a) with 4-Methylphenylmagnesium Bromide (7m)[a]

entry	ligand (equiv to Ni)	temp (°C)	time (h)	yield of **8am** (%)[b]	% ee of **8am** (config)[c]
1	PPh_3 (3.0)	40	24	75	
2	dppp (1.5)	40	24	69	
3	(*S*)-H-MOP (3.0)	55	10	87	82 (*S*)
4	(*S*)-H-MOP (3.0)	40	20	85	82 (*S*)
5	(*S*)-H-MOP (3.0)	20	24	32	83 (*S*)
6	(*S*)-H-MOP-xylyl (3.0)	40	24	85	74 (*S*)
7	(*S*)-H-MOP-tolyl (3.0)	40	24	84	72 (*S*)
8	(*S*)-H-MOP-anisyl (3.0)	40	24	63	67 (*S*)
9	(*R*)-MeO-MOP (3.0)	40	24	50	8 (*R*)
10	(*S*)-phephos (1.5)	40	24	78	35 (*S*)
11	(*S*)-(*R*)-PPF-OMe (3.0)	40	24	65	30 (*S*)
12	(*R*)-BINAP	40	24	58	23 (*R*)
13	(*S*)-*i*-Pr-phox (1.5)	40	24	0	
14	(*R*)-Ph-phox (1.5)	40	24	0	

[a] The reaction was carried out with thiophene **6a** (0.24 mmol) and **7m** (2.4 mmol) in 5.6 mL of THF in the presence of $Ni(cod)_2$ (0.014 mmol) and a ligand. [b] Isolated yield of **8am** by silica gel chromatography. [c] Determined by HPLC analysis of the phenylcarbamate ester of thiol **8am** with a chiral stationary phase column (Chiralcel OD-H (hexane/2-propanol = 90/10)).

ligands.[8] $NiBr_2$ and $Ni(acac)_2$ were also effective as catalyst precursors.

The reaction of **6a** with **7m** in the presence of 6 mol % of a nickel catalyst generated from $NiBr_2$ and $Ni(acac)_2$ with triphenylphosphine in THF at 40 °C for 24 h gave the corresponding cross-coupling product **8am** in 78% yield and 72% yield, respectively. Palladium catalysts such as $Pd(PPh_3)_4$ did not show any catalytic activity. The monoarylation product **8am** was also obtained in 69% yield in the presence of a nickel catalyst containing bisphosphine ligand, 1,3-bis(diphenylphosphino)propane (dppp), under the same conditions (entry 2).

Among the chiral ligands examined for the asymmetric cross-coupling of thiophene **6a** with 4-methylphenylmagnesium bromide (**7m**) (Scheme 6), (*S*)-2-diphenylphosphino-1,1′-binaphthyl[18] (H-MOP) was found to be most enantioselective (Table 1). Thus, the asymmetric cross-coupling of **6a** with 10 equiv of **7m** in THF in the presence of 6 mol % of $Ni(cod)_2$ and 18 mol % of (*S*)-H-MOP at 40 °C for 20 h gave 85% yield of the axially chiral 2-mercapto-2′-(4-methylphenyl)-6,6′-dimethyl-1,1′-biphenyl (**8am**). The mercapto group in **8am** was converted into thiocarbamoyl group by treatment with phenylisocyanate and its enantiomeric purity was determined to be 82% ee by HPLC analysis with a chiral stationary phase column (entry 4). The absolute configuration was determined to be *S* by correlation with the authentic sample, (*S*)-(+)-**9am** (vide infra). THF was the best solvent for the present cross-coupling, benzene and toluene giving a lower yield of **8am** and lower enantioselectivity. It was found that the enantiomeric purity of **8am** is not strongly dependent on the reaction temperature (entries 3−5).

A little lower enantioselectivity was observed in the reactions with use of other H-MOP derivatives, (*S*)-H-MOP-xylyl, (*S*)-H-MOP-tolyl, and (*S*)-H-MOP-anisyl, which gave **8am** of 74% ee, 72% ee, and 67% ee, respectively (entries 6−8). Other chiral phosphine ligands used successfully for other types of asymmetric cross-coupling[2,3,7] were much less enantioselective than (*S*)-H-MOP for the present reaction (entries 9−14). The use of oxazoline-phosphine ligands did not give any cross-coupling products under the same conditions (entries 13 and 14).

The best reaction conditions found for the asymmetric cross-coupling of **6a** with **7m** (Table 1), that is, $Ni(cod)_2$ (6 mol %) and (*S*)-H-MOP (18 mol %) in THF at 40 °C, were applied to the reaction of some other 1,9-disubstituted dibenzothiophenes **6a**−**c** and the Grignard reagents **7**.

The results summarized in Table 2 show that the monosubstitution products **8** are obtained in high yields irrespective of the alkyl or phenyl substituents at 1- and

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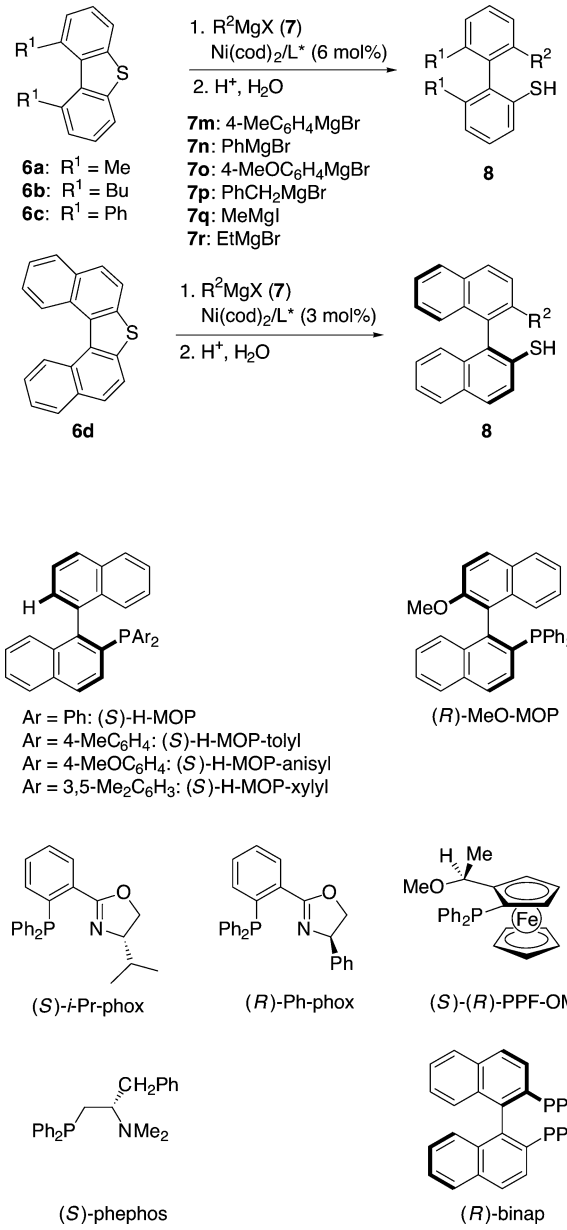
SCHEME 6



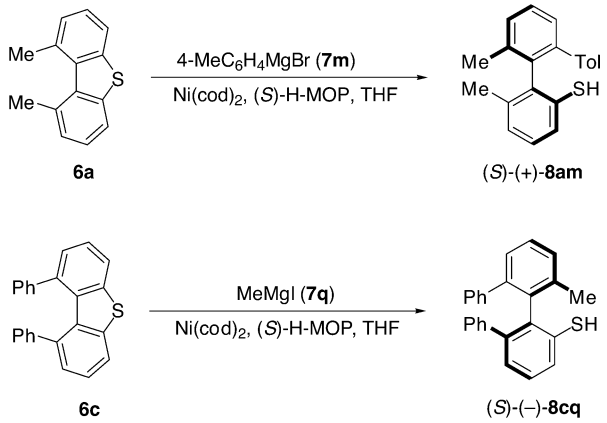
9-positions. The enantioselectivity was dependent on the 1,9-substituents on the dibenzothiophene **6** and the Grignard reagents **7**. Thus, the enantiomeric purity of **8am** and **8an** obtained for the reaction of **6a** with aryl Grignard reagents, 4-MeC_6H_4MgBr (**7m**) and PhMgBr (**7n**), was 81−82% ee (entries 1 and 2), while that of **8ap** formed by the reaction with the benzylmagnesium bromide (**7p**) was as low as 35% ee (entry 3). The dibenzothiophenes substituted with methyl (**6a**) and butyl (**6b**) gave the monosubstitution products **8** of around 80% ee on the reaction with **7m** (entries 1 and 4), while 1,9-diphenyldibenzothiophene (**6c**) gave **8cm** of 36% ee (entries 5 and 6). It was found that 1,9-diphenyldibenzothiophene (**6c**) is more reactive than the other thiophenes **6a** and **6b** toward the present nickel-catalyzed cross-coupling. The reaction of **6c** with the Grignard reagent **7m** proceeded faster than that of **6a** and **6b**, giving high yield of the monoarylation product **8cm** within 8 and 3 h in the reaction carried out at 40 and 55 °C, respectively

TABLE 2. Asymmetric Cross-Coupling of 1,9-Disubstituted Dibenzothiophenes 6 with the Grignard Reagents 7 Catalyzed by the Ni/(*S*)-H-MOP Catalyst[a]

entry	thiophene **1** (R^1)	R^2MgX **7** (R^2)	temp (°C)	time (h)	yield of **8** (%)[b]	% ee of **8** (config)[c]
1	**6a** (Me)	**7m** (4-MeC_6H_4)	40	20	85	82 (*S*)
2	**6a** (Me)	**7n** (Ph)	40	24	88	81 (*S*)
3	**6a** (Me)	**7p** ($PhCH_2$)	40	32	87	35 (*S*)
4	**6b** (Bu)	**7m** (4-MeC_6H_4)	40	24	89	78 (*S*)
5	**6c** (Ph)	**7m** (4-MeC_6H_4)	40	8	90	36 (*R*)
6	**6c** (Ph)	**7m** (4-MeC_6H_4)	55	3	85	36 (*R*)
7	**6c** (Ph)	**7q** (Me)	20	24	91	53 (*R*)

[a] The reaction was carried out with thiophene **6** (0.24 mmol) and the Grignard reagent **7** (2.4 mmol) in 5.6 mL of THF in the presence of $Ni(cod)_2$ (0.014 mmol) and (*S*)-H-MOP (0.042 mmol). [b] Isolated yield of **8** by silica gel chromatography. [c] Determined by HPLC analysis of the phenylcarbamate ester of thiol **8** with a chiral stationary phase column: (Chiralcel OD-H (hexane/2-propanol = 90/10)) for **8am**, **8an**, **8ap**, **8bm**, **8cm**, and **8cq**.

SCHEME 7



(entries 5 and 6). The reaction of methylmagnesium iodide (**7q**) was completed in 24 h at 20 °C (entry 7). The higher reactivity of 1,9-diphenyldibenzothiophene (**6c**) may be related to a larger torsion angle of thiophene ring in **6c**, which has bulky substituents at 1- and 9-positions. The more strained thiophene ring system caused by the larger torsion angle will result in the lower energy of the carbon−sulfur bond cleavage.[19]

It is noteworthy that the asymmetric cross-coupling of 1,9-dimethyldibenzothiophene (**6a**) and 1,9-diphenyldibenzothiophene (**6c**) proceeded in an opposite sense of stereorecognition (Scheme 7). Although the designation of the configuration is *S* for both of the two cross-coupling products **8am** and **8cq**, the stereochemistry at ring-opening of the thiophene is opposite. It follows that the substituents at the 1- and 9-positions play a key role in the enantioselection.

Higher enantioselectivity was observed in the asymmetric cross-coupling of dinaphthothiophene (**6d**) (Table 3). The reaction of **6d** proceeded in the presence of a smaller amount of the nickel catalyst at a lower reaction temperature than that of dibenzothiophenes. Bianchini reported that the energy barrier of carbon−sulfur bond cleavage of the thiophene ring in dinaphthothiophene by

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TABLE 3. Nickel-Catalyzed Asymmetric Cross-Coupling of Dinaphthothiophene 6d with the Grignard Reagents 7[a]

entry	R^2MgX**7** (R^2)	ligand (equiv to Ni)	temp (°C)	time (h)	yield of **8d** (%)[b]	% ee of **8d** (config)[c]
1	**7m** (4-MeC_6H_4)	(*S*)-H-MOP (3.0)	20	10	93	14 (*S*)
2	**7m** (4-MeC_6H_4)	(*S*)-*i*-Pr-phox (1.5)	20	24	97	95 (*S*)
3	**7m** (4-MeC_6H_4)	(*R*)-Ph-phox (1.5)	20	30	90	86 (*R*)
4	**7m** (4-MeC_6H_4)	(*S*)-(*R*)-PPF-OMe (3.0)	20	12	88	3 (*S*)
5	**7m** (4-MeC_6H_4)	(*S*)-phephos (1.5)	20	8	86	1 (*S*)
6	**7m** (4-MeC_6H_4)	(*R*)-BINAP (1.5)	20	10	72	2 (*S*)
7	**7n** (Ph)	(*S*)-*i*-Pr-phox (1.5)	20	24	92	95 (*S*)
8	**7o** (4-$MeOC_6H_4$)	(*S*)-*i*-Pr-phox (1.5)	20	30	96	93 (*S*)
9	**7q** (Me)	(*S*)-*i*-Pr-phox (1.5)	20	24	88	45 (*R*)
10	**7q** (Me)	(*S*)-H-MOP (3.0)	10	24	97	68 (*R*)
11	**7r** (Et)	(*S*)-*i*-Pr-phox (1.5)	20	48	93	50 (*R*)
12	**7r** (Et)	(*S*)-phephos (1.5)	20	48	41[d]	19 (*R*)

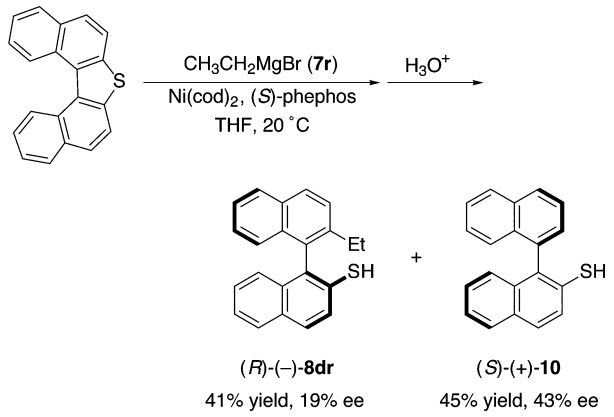
[a] The reaction was carried out with thiophene **6d** (0.24 mmol) and **7** (2.4 mmol) in 5.6 mL of THF in the presence of $Ni(cod)_2$ (0.007 mmol) and a ligand. [b] Isolated yield of **8d** by silica gel chromatography. [c] Determined by HPLC analysis of the phenylcarbamate ester of thiol **8d** with a chiral stationary phase column (Chiralcel OD-H (hexane/2-propanol = 90/10) for **8dn**, Chiralcel AD (hexane/2-propanol = 90/10) for **8dm**, **8do**, **8aq**, and **8dr**). [d] The formation of 45% yield of **10** (43% ee) was observed.

transition metal complexes is much lower than that of dibenzothiophene.[20] The X-ray analysis[21] of dinaphthothiophene (**6d**) showed its large torsion angle (25.9°), which presumably arises from strong repulsion between the two twisted naphthyl groups.

The reaction of **6d** with 4-methylphenylmagnesium bromide (**7m**) in THF in the presence of 3 mol % of $Ni(cod)_2$ and 9 mol % of (*S*)-H-MOP proceeded at 20 °C for 10 h to give 93% yield of (*S*)-2-mercapto-2-(4-methylphenyl)-1,1′-binaphthyl (*S*)-(−)-**8dm**, whose enantiomeric purity determined by HPLC analysis was 14% ee (entry 1). Considering that the (*S*)-H-MOP ligand gave the cross-coupling product **8am** of 82% ee in the reaction of dibenzothiophene **6a** with the Grignard reagent **7m**, this low enantioselectivity is rather surprising. It was found that oxazoline-phosphines[22] are much more enantioselective than H-MOP for the cross-coupling of dinaphthothiophene (**6d**). Thus, the reaction of **6d** with **7m** in the presence of 3 mol % of $Ni(cod)_2$ and 4.5 mol % of (*S*)-*i*-Pr-phox in THF at 20 °C for 24 h gave (*S*)-**8dm** of 95% ee in 97% yield (entry 2). The enantioselectivity was also high (86% ee) with (*R*)-Ph-phox as the ligand of the nickel catalyst (entry 3).

Other ligands[2,3,7] were much less enantioselective than the oxazoline-phosphine ligands (entries 4−6). The reactions of **6d** with phenylmagnesium bromide (**7n**) and 4-methoxyphenylmagnesium bromide (**7o**) also proceeded with high enantioselectivity in the presence of the nickel catalyst coordinated with (*S*)-*i*-Pr-phox to give high yields of the corresponding cross-coupling products (*S*)-(−)-**8dn** of 95% ee and (*S*)−(−)-**8do** of 93% ee, respectively (entries 7 and 8). For the reaction with methylmagnesium iodide (**7q**), (*S*)-H-MOP was more effective than (*S*)-*i*-Pr-phox (entries 9 and 10). In the presence of the nickel catalyst of (*S*)-H-MOP, the cross-coupling of **6d** with **7q** at 10 °C for 24 h gave 97% yield of (*R*)-2-mercapto-2′-methyl-1,1′-binaphthyl (**8dq**), which is 68% ee (entry 10).

SCHEME 8



In the reaction with ethylmagnesium bromide (**7r**), the (*S*)-*i*-Pr-phox ligand gave a unique result. With other ligands examined, a considerable amount of the reduced product **10** was formed in addition to the cross-coupling product **8dr**.

Thus, the reaction catalyzed by the nickel complex of (*S*)-*i*-Pr-phox gave a high yield of (*R*)-**8dr** (50% ee) without any detectable amount of **10** (entry 11), while the reaction with (*S*)-phephos[23]-nickel catalyst gave both **8dr** and **10** in 41% and 45% yield, respectively (entry 12). Interestingly, **8dr** has *R* configuration and **10** has *S* configuration (Scheme 8). The opposite configuration is important for us to understand the reaction mechanism (see Scheme 10).

According to the catalytic cycle generally accepted for the nickel-catalyzed cross-coupling, oxidative addition of thiophene **6** to a nickel(0) species forms nickelacycle **A**[19,20] (Scheme 9). Transmetalation of the aryl or alkyl group from the Grignard reagent **7** to **A** gives diorganonickel intermediate **B**. Reductive elimination from **B** leads to the magnesium thiolate **C**. Aqueous workup gives the cross-coupling product **8** (Scheme 9).

As has been shown in Tables 2 and 3, the stereochemical outcome is strongly dependent on the Grignard reagents in the reaction catalyzed by a nickel complex of H-MOP or *i*-Pr-phox. The strong dependency indicates

(20) (a) Bianchini, C.; Fabbri, D.; Gladiali, S.; Meli, A.; Pohl, W.; Vizza, F. *Organometallics* **1996**, *15*, 4604. (b) Bianchini, C.; Jiménez, M. V.; Meli, A.; Moneti, S.; Vizza, F.; Herrera, V.; Sanchez-Delgado, R. A. *Organometallics* **1995**, *14*, 2342.

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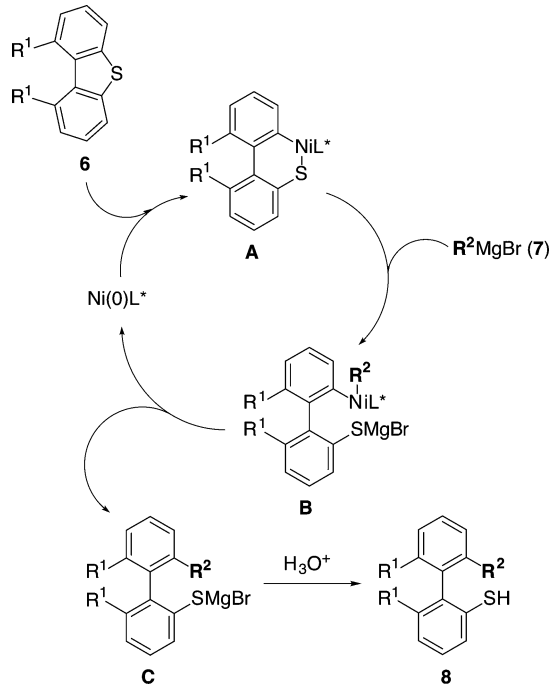
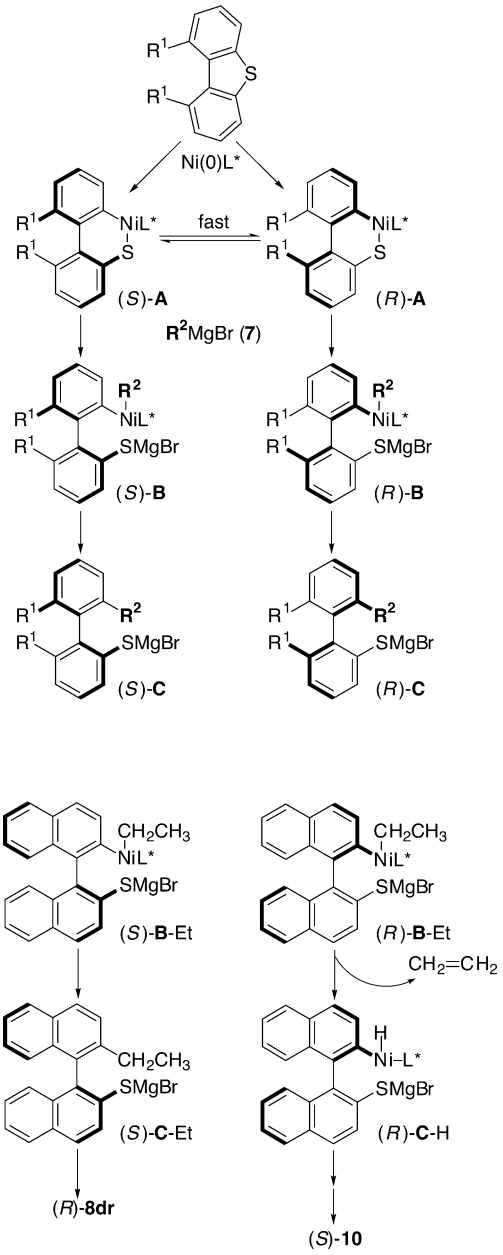
(22) (a) Sprinz, J.; Helmchen, G. *Tetrahedron Lett.* **1993**, *34*, 1769. (b) Von Matt, P.; Pfaltz, A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 566. (c) Dawson, G. J.; Frost, C. G.; Williams, J. M. J. *Tetrahedron Lett.* **1993**, *34*, 3149. (d) Helmchen, G.; Pfaltz, A. *Acc. Chem. Res.* **2000**, *33*, 336.

(23) Hayashi, T.; Konishi, M.; Fukushima, M.; Kanehira, K.; Hiroki, T.; Kumada, M. *J. Org. Chem.* **1983**, *48*, 2195.

SCHEME 9



SCHEME 10



that the stereochemistry of the corresponding products is determined at or after the transmetalation step. The determination before the transmetalation step, namely at the oxidative addition step, would result in the same enantioselectivity irrespective of the Grignard reagents used. The nickelacycle intermediates (*S*)-**A** and (*R*)-**A** are probably in a fast equilibration. It is unlikely that the diorganonickel intermediates **B** undergo the epimerization between (*S*)-**B** and (*R*)-**B**, because the substituted groups, Ni(R²)L* and SMgBr, at 2 and 2′ positions are sterically bulky enough to prevent the biaryl axis from rotating. The opposite absolute configuration observed in the reaction with ethylmagnesium bromide (Scheme 8, entry 12 in Table 3) may suggest that the (*S*)-isomer of the ethylnickel intermediate (*S*)-**B** (Et) undergoes the reductive elimination preferentially while the (*R*)-isomer (*R*)-**B** (Et) undergoes the *β*-hydrogen elimination followed by reductive elimination from the nickel-hydride (*R*)-**B** (H) leading to the reduction product (*S*)-**10** (Scheme 10).

The axially chiral cross-coupling products **8** obtained here are versatile intermediates for further transformation. The reactions starting from (*S*)-**8dn** and (*R*)-**8dr** are summarized in Scheme 11. The key compound is (*S*)-2-methylsulfinyl-2′-phenyl-1,1′-binaphthyl (**12**), which was obtained by methylation of the mercapto group in (*S*)-**8dn** (95% ee, entry 7 in Table 3) followed by oxidation of the sulfide with peracid. Treatment of (*S*)-**12** with 1.5 equiv of ethylmagnesium bromide according to the procedures reported by Hoffmann[24] at room temperature generated binaphthylmagnesium bromide (**12′**) in a high yield. Use of butyllithium[25] in place of ethylmagnesium bromide resulted a lower yield of a binaphthyllithium species. The binaphthylmagnesium bromide (**12′**) was allowed to react with electrophiles to give the corresponding substitution products in high yields without racemization. Thus, the reaction with iodine, trimethoxyborane, and chlorodiphenylphosphine gave iodide **13**, boronate **14**, and phosphine **15**, respectively. The phosphine **15** of (*R*)-configuration is known[26] to show (+)-specific rotation ([α]$^{20}_{D}$ +145 (*c* 1.0, chloroform)), and the (−)-specific rotation ([α]$^{20}_{D}$ −137 (*c* 1.0, chloroform)) of the phosphine **15** derived from (−)-**8dn** demonstrates that the absolute configuration of the cross-coupling product (−)-**8dn** is *S*. In a similar manner, the mercapto group in (−)-**8dr** was converted into the diphenylphosphino group by way of the sulfoxide. The configuration of (−)-**17** obtained was assigned to be *R* by comparison

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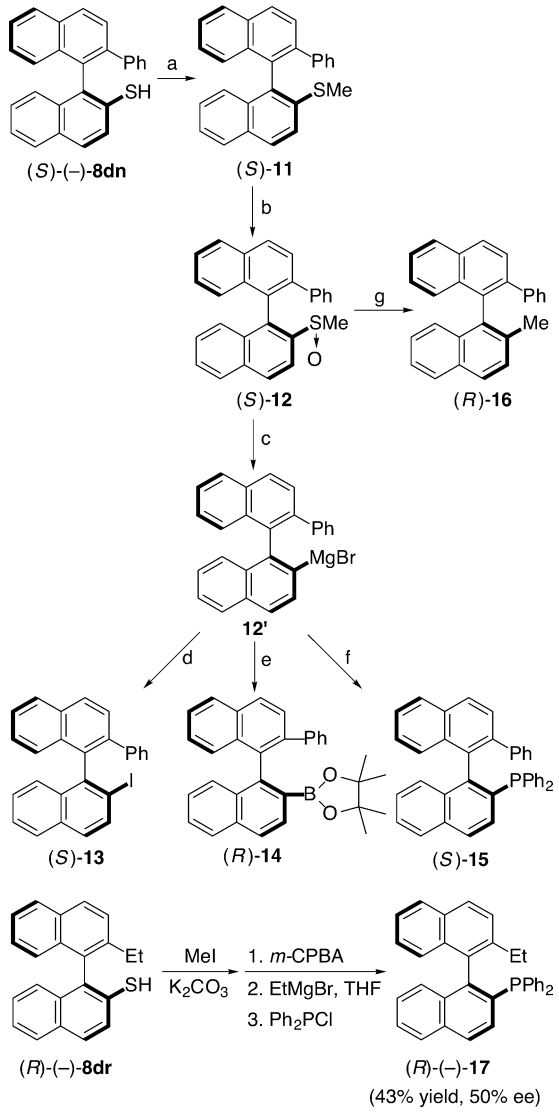
SCHEME 11[a]



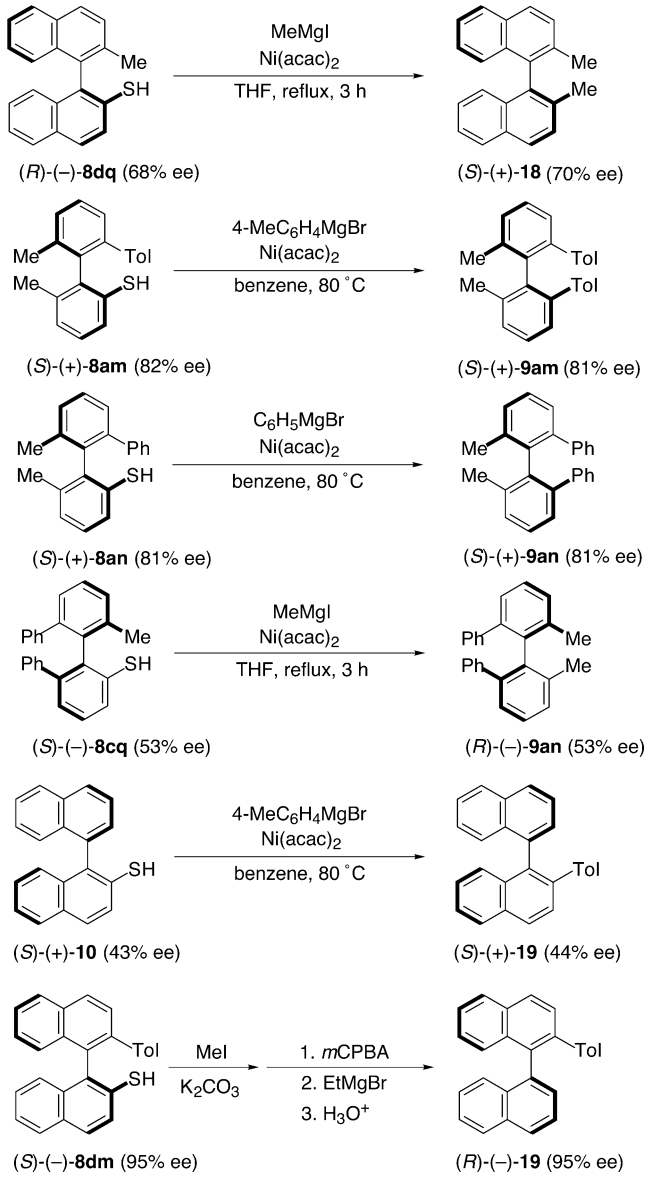
[a] Reaction conditions: (a) MeI, K_2CO_3, acetone, rt, 99%; (b) *m*CPBA, CH_2Cl_2, 0 °C, 92%; (c) EtMgBr, THF, rt; (d) I_2, rt, 67%; (e) (i) $B(OMe)_3$, (ii) 10% HCl, (iii) pinacol, benzene, reflux 48%; (f) Ph_2PCl, rt 62%; (g) $Ni(acac)_2$, MeMgI, THF 50 °C, 76%.

of its specific rotation ($[\alpha]^{20}_D$ −28 (*c* 0.3, chloroform)) with the reported value ($[\alpha]^{20}_D$ −85 (*c* 0.2, chloroform)) for (*R*)-**17**.[27]

The substitution of the methylsulfinyl group with a nucleophile is also possible by nickel-catalyzed cross-coupling.[11b,12a] For example, the cross-coupling of (*S*)-(−)-**12** with the methyl Grignard reagent proceeded in THF at 65 °C to give 76% yield of the methylation product (*R*)-(−)-**16** in the presence of 10 mol % of $Ni(acac)_2$ (Scheme 11).

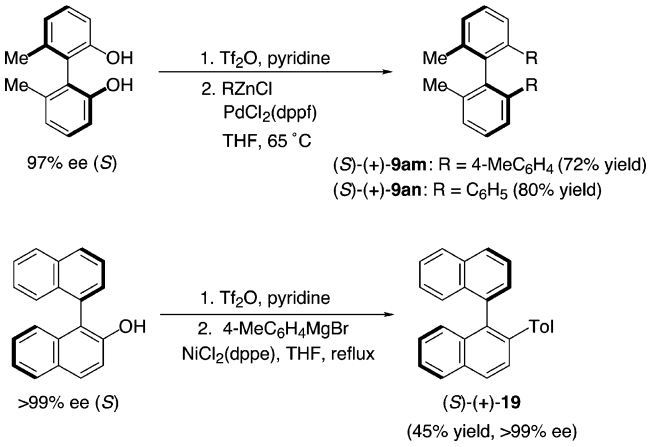
Although the mercapto group is less reactive than the methylsulfinyl group toward the cross-coupling, the reaction of biarylthiols with the Grignard reagents in the presence of $Ni(acac)_2$ as a catalyst in refluxing THF or in benzene at 80 °C gave the cross-coupling products in moderate to high yields. Taking advantage of this cross-coupling protocol, the biarylthiols obtained by the present asymmetric cross-coupling were converted into the compounds whose absolute configurations are known (Scheme 12). For example, the cross-coupling of (−)-**8dq** (68% ee, entry 10 in Table 3) with methylmagnesium iodide catalyzed by $Ni(acac)_2$ gave (*S*)-(+)-2,2′-dimethyl-1,1′-binaphthyl (**18**) ($[\alpha]^{20}_D$ +36 (*c* 0.5, chloroform)), the specific rotation of (*R*)-(−)-**18** being reported to be ($[\alpha]^{20}_D$ −37 (*c* 1.0, chloroform)).[2a] The biarylthiol (+)-**8am** (82% ee, entry 4 in Table 1) was converted into 2,2′-bis(4-methylphenyl)-6,6′-dimethyl-1,1′-biphenyl (**9am**) by the cross-coupling with 4-methylphenylmagnesium bromide, and its specific rotation ($[\alpha]^{20}_D$ +43 (*c* 1.0, chloroform)) was compared with that ($[\alpha]^{20}_D$ +75 (*c* 1.0, chloroform)) of the authentic sample prepared from (*S*)-2,2′-dihydroxy-6,6′-dimethyl-1,1′-biphenyl[15] (Scheme 13) to determine that (+)-**8am** has *S* configuration. The absolute configurations of the thiols (+)-**8an** (81% ee, entry 2 in Table 2) and (−)-**8cq** (53% ee, entry 7 in Table 2) were determined to be (*S*)-(+) and (*S*)-(−), respectively, by correlation with the authentic sample (*S*)-(+)-**9an** whose preparation is

SCHEME 12



(27) Uozumi, Y.; Tanahashi, A.; Lee, S.-Y.; Hayashi, T. *J. Org. Chem.* **1993**, *58*, 1945.

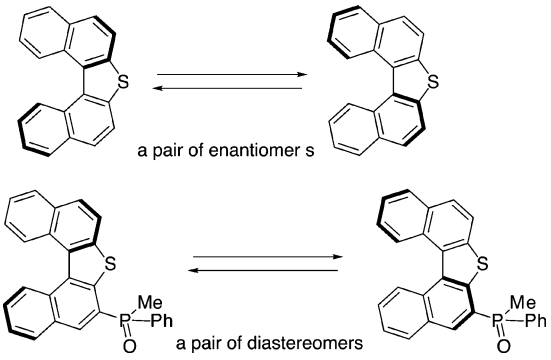
SCHEME 13



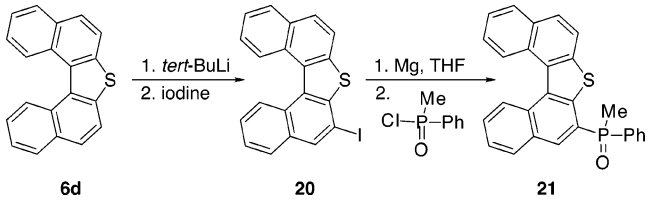
shown in Scheme 13. Similarly, the absolute configuration of (+)-**10** (43% ee, entry 12 in Table 3) was determined to be (*S*)-(+) by comparison of the specific rotation ($[\alpha]^{20}_D$ +65 (*c* 0.5, chloroform)) of 2-(4-methylphenyl)-1,1′-binaphthyl (**19**) obtained from (+)-**10** with that ($[\alpha]^{20}_D$ +96 (*c* 1.0, chloroform)) of (*S*)-(+)-**19** derived from known (*S*)-2-hydroxy-1,1′-binaphthyl.[18a] By way of the sulfoxide, (−)-2-mercapto-2′-(4-methylphenyl)-1,1′-binaphthyl (**8dm**) was converted into (−)-**19**. Treatment of (−)-2-methylsulfinyl-2′-(4-methylphenyl)-1,1′-binaphthyl, prepared from (−)-**8dm** according to the procedure described for the preparation of **12**, with ethylmagnesium bromide and 10% HCl gave (−)-**19** of 95% ee and the absolute configuration of (−)-**8dm** was assigned to be *S* by correlation with the authentic sample (Scheme 13).

It has been reported[21] that the structure of dinaphthothiophene (**6d**) is not flat but distorted due to the steric repulsion between the two naphthyl rings. It is interesting to study the rate of flipping of the dinaphthothiophene (**6d**), because the flipping rate is related to the mechanism of stereocontrol in the present asymmetric cross-coupling reaction where the carbon−sulfur bond in the thiophene ring is cleaved. If the flipping is slow compared to the cross-coupling, the present asymmetric reaction is expected to involve a kinetic resolution of the starting substrate. If it is fast, the starting substrate is recognized to be always racemic. The interconversion of various dinaphthoheteroles such as *S*-methylthiophenium salt[21] and phosphole[28] have been studied by NMR analysis. The dinaphthoheteroles containing substituents on the central heteroatom exist in solution as a mixture of two diastereomeric enantiomers, which facilitates the studies of the interconversion by the NMR analysis. On the other hand, dinaphthothiophene (**6d**) has no substituents on the central atom, and hence exists as a mixture of two enantiomers. Thus, our strategy for solving the problem is the introduction of a chiral substituent on **6d**, which makes the dinaphthothiophene become a mixture of two diastereoisomers. PhMeP(O)− was selected as the substituent because of its utility in the NMR analysis by using ^{31}P NMR spectra (Scheme 14).

SCHEME 14



SCHEME 15



Dinaphthothiophene derivative **21** containing the phosphinyl group was prepared from **6d** according to the procedures shown in Scheme 15. Lithiation of the 6-position of **6d** with *tert*-butyllithium followed by treatment with iodine gave the 6-iododinaphthothiophene (**20**). The reaction of the Grignard reagent prepared from **20** with phosphinyl chloride in THF gave the desired dinaphthothiophene derivative **21**.

The rate of the interconversion of **21** was estimated in the temperature range between −60 and −15 °C by line-shape analysis of the ^{31}P NMR spectra. At and below ca. −35 °C, the ^{31}P NMR spectra of **21** gave clearly separated two signals from two atropisomers, and at higher temperature the single coalesced signal was detected. The relative molar ratios between the two isomers were directly obtained at −60, −55, and −50 °C to be ca. 55:45 constantly. The interconversion rate constants *k* were determined between −55 and −15 °C by the line-shape analysis (shown in the Supporting Information). An Eyring plot (ln *k*/T vs 1/*T*) is linear ($R^2 > 0.999$), and the activation parameters for the interconversion of **21** are $\Delta H^{\ddagger}$ = 46.1 kJ/mol, $\Delta S^{\ddagger}$ = −196 J/(mol·K), and $\Delta G^{\ddagger}$ (at −35 °C) = 46.5 kJ/mol. The $\Delta G^{\ddagger}$ value is similar to the activation barrier of *S*-methyldinaphthothiophenium tetrafluoroborate and dinaphthothiophene *S*-oxide.[21] The $\Delta G^{\ddagger}$(at 40 °C) = 50 kJ/mol and *k*(at 40 °C) = 3.0×10^4 Hz at the catalytic reaction temperature were estimated by the extrapolation of the Eyring plot. In other words, the flipping of dinaphthothiophene (**6d**) is 30 000 times per second at the reaction temperature and the half-life for racemization of **6d** is calculated to be shorter than 0.0001 s ($t_{1/2} = 2.31 \times 10^{-5}$). It is concluded that the racemization of **6d** is much faster than the catalytic cross-coupling reaction. As shown in Scheme 10, it is most likely that the stereochemical outcome in the present asymmetric cross-coupling is determined at the transmetalation step after the epimerization of the diastereomeric nickelacycle intermediates. A kinetic resolution at the oxidative addition step would not affect the stereochemical outcome, because the nickelacycle intermediates are in fast equilibration.

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Conclusion

We have developed a new efficient route to axially chiral biaryls, which have been realized by nickel-catalyzed asymmetric cross-coupling of thiophene **6** with the Grignard reagents. Monosubstitution products **8** were obtained in high yield with high enantiomeric purity. By replacement of the mercapto group in **8** by some functional groups, the thiols **8** can be converted into useful chiral building blocks.

Experimental Section

Materials. The compounds 2,2′-dihydroxy-6,6′-dimethoxy-1,1-biphenyl (**1**),[14] (*S*)-2,2′-dihydroxy-6,6′-dimethyl-1,1′-biphenyl,[15] and methylphenylphosphinyl chloride[29] were prepared according to the reported procedures. THF, Et_2O, toluene, and benzene were distilled from sodium benzophenone-ketyl under nitrogen. DMF, triethylamine, and pyridine were dried over CaH_2, and distilled under nitrogen. $PdCl_2$(dppf),[30] $NiCl_2$(dppp),[31] and $NiCl_2$(dppe)[32] were prepared according to the reported procedures.

Preparation of 2,2′-Bis(trifluoromethanesulfonyloxy)-6,6′-dimethoxy-1,1-biphenyl (2).[15] To a solution of 2,2′-dihydroxy-6,6′-dimethoxy-1,1′-biphenyl (**1**)[14] (6.7 g, 27 mmol) in 1,2-dichloroethane (150 mL) was added pyridine (5.5 mL, 68 mmol) and triflic anhydride (10 mL, 60 mmol) at 0 °C. The mixture was allowed to stir at room temperature for 10 h and quenched with 10% HCl. It was then diluted with ethyl acetate and the organic layer was washed with saturated $NaHCO_3$ solution and brine, dried over anhydrous $MgSO_4$, and evaporated under reduced pressure. Silica gel column chromatography (hexane/ethyl acetate = 80/20) gave 13 g (90% yield) of bis(triflate) **2**: ^{1}H NMR ($CDCl_3$) δ 3.80 (s, 6H), 7.01 (d, J = 8.6 Hz, 2H), 7.02 (d, J = 8.3 Hz, 2H), 7.48 (t, J = 8.6 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 56.1, 110.4, 112.9, 114.5, 118.2 (q, J = 3.6 Hz), 130.7, 148.4, 158.5.

Preparation of 2,2′-Dimethoxy-6,6′-dimethyl-1,1′-biphenyl (3a). To a solution of bis(triflate) **2** (9.0 g, 18 mmol) and $NiCl_2$(dppp)[16] (1.9 g, 3.5 mmol) in dry diethyl ether (120 mL) was slowly added methylmagnesium iodide in diethyl ether (66 mL, 0.11 mol) at 0 °C under nitrogen atmosphere. The mixture was allowed to stir at room temperature for 12 h and quenched with water carefully at 0 °C. It was diluted with ether and the organic layer was washed with 10% HCl and brine. The separated organic layer was dried over anhydrous $MgSO_4$ and evaporated under reduced pressure. Silica gel column chromatography (hexane/ethyl acetate = 90/10) gave 3.4 g (80% yield) of 2,2′-dimethoxy-6,6′-dimethyl-1,1′-biphenyl (**3a**):[33] ^{1}H NMR ($CDCl_3$) δ 1.94 (s, 6H), 3.69 (s, 6H), 6.82 (d, J = 8.2 Hz, 2H), 6.90 (d, J = 8.2 Hz, 2H), 7.23 (t, J = 7.8 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 19.5, 55.7, 108.3, 122.2, 126.2, 127.8, 138.1, 156.9.

Preparation of 2,2′-Dimethoxy-6,6′-dibutyl-1,1′-biphenyl (3b). To a solution of bis(triflate) **2** (10 g, 20 mmol) and $PdCl_2$(dppf) (1.4 g, 2.0 mmol) in dry THF (30 mL) was slowly added diisobutylaluminum hydride solution in hexane (4.0 mL, 3.9 mmol) at 0 °C and the mixture was stirred at 0 °C for 15 min. *n*-Butylzinc chloride, which is a white slurry prepared from *n*-butyllithium and $ZnCl_2$ in THF (80 mL, 80 mmol), was slowly added at 0 °C. The mixture was refluxed for 24 h, *n*-butylzinc chloride solution in THF (40 mL, 40 mmol) was slowly added, and the mixture was refluxed for another 24 h. When the reaction was confirmed to be completed by a TLC analysis, the mixture was quenched with water at 0 °C. It was then diluted with diethyl ether and the organic layer was washed with 10% HCl and brine. The organic layer was dried over anhydrous $MgSO_4$ and evaporated under reduced pressure. Silica gel column chromatography (hexane/ethyl acetate = 90/10) gave 3.8 g (60% yield) of 2,2′-dimethoxy-6,6′-dibutyl-1,1′-biphenyl (**3b**): ^{1}H NMR ($CDCl_3$) δ 0.75 (t, J = 7.3 Hz, 6H), 1.16 (m, 4H), 1.38 (m, 4H), 2.20 (m, 4H), 3.67 (s, 6H), 6.80 (d, J = 8.2 Hz, 2H), 6.92 (d, J = 7.7 Hz, 2H), 7.27 (t, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 13.9, 22.5, 32.2, 32.7, 55.5, 107.9, 120.9, 125.5, 127.8, 142.8, 157.1. Anal. Calcd for $C_{22}H_{30}O_2$: C, 80.94; H, 9.26. Found: C, 80.86; H, 9.23.

Preparation of 2,2′-Dimethoxy-6,6′-diphenyl-1,1′-biphenyl (3c).[15] **3c** was prepared in a manner similar to **3b** with phenylzinc chloride. ^{1}H NMR ($CDCl_3$) δ 3.67 (s, 6H), 6.73 (d, J = 7.2 Hz, 4H), 6.81 (d, J = 7.7 Hz, 2H), 6.84 (d, J = 8.3 Hz, 2H), 7.02 (t, J = 7.2 Hz, 4H), 7.08 (t, J = 7.2 Hz, 2H), 7.26 (t, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 55.7, 109.5, 122.2, 124.9, 126.1, 127.0, 128.3, 128.9, 141.3, 143.0, 157.9.

Preparation of 2,2′-Dihydroxy-6,6′-dimethyl-1,1′-biphenyl (4a). To a solution of **3a** (3.3 g, 14 mmol) in dry CH_2Cl_2 (120 mL) was slowly added a solution of BBr_3 (3.2 mL, 34 mmol) in dry CH_2Cl_2 (50 mL) at −78 °C under nitrogen atmosphere. The mixture was allowed to stir at room temperature for 5 h, and quenched carefully with 10% HCl at 0 °C. It was then extracted with diethyl ether and the organic layer was dried over anhydrous $MgSO_4$. After evaporation under reduced pressure, silica gel column chromatography (hexane/ethyl acetate = 50/50) gave 2.8 g (97% yield) of 2,2′-dihydroxy-6,6′-dimethyl-1,1′-biphenyl (**4a**):[15] ^{1}H NMR ($CDCl_3$) δ 2.00 (s, 6H), 4.69 (br, 2H), 6.90 (d, J = 8.2 Hz, 2H), 6.93 (d, J = 7.6 Hz, 2H), 7.25 (t, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 19.4, 113.1, 119.5, 122.6, 130.1, 138.9, 153.8. The diols **4b** and **4c** were prepared in a similar manner.

2,2′-Dihydroxy-6,6′-dibutyl-1,1′-biphenyl (4b):[15a] ^{1}H NMR ($CDCl_3$) δ 0.78 (t, J = 7.4 Hz, 6H), 1.20 (sextet, J = 7.5 Hz, 4H), 1.91 (m, 4H), 2.25 (m, 4H), 4.67 (br, 2H), 6.90 (dd, J = 8.2, 1.0 Hz, 2H), 6.95 (dd, J = 7.6, 1.0 Hz, 2H), 7.29 (t, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 13.7, 22.5, 32.4, 32.8, 113.0, 118.8, 121.5, 130.1, 143.8, 153.8.

2,2′-Dihydroxy-6,6′-diphenyl-1,1′-biphenyl (4c):[15] ^{1}H NMR ($CDCl_3$) δ 5.18 (br, 2H), 6.63 (dd, J = 8.2, 1.1 Hz, 4H), 6.83 (dd, J = 7.7, 1.1 Hz, 2H), 7.03 (dt, J = 8.2, 1.1 Hz, 4H), 7.05 (d, J = 7.7 Hz, 2H), 7.12 (t, J = 7.4 Hz, 2H), 7.31 (t, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 114.4, 122.9, 126.7, 127.4, 128.6, 130.3, 144.0, 154.2.

Preparation of 2,2′-Bis(*N*,*N*-dimethylthiocarbamoyloxy)-6,6′-dimethyl-1,1′-biphenyl (5a). To a solution of **4a** (1.8 g, 8.4 mmol), triethylamine (2.6 mL, 19 mmol), and pyridine (6.8 mL, 84 mmol) in dry THF (50 mL) was added *N*,*N*-dimethylthiocarbamoyl chloride (2.3 g, 19 mmol) at 0 °C under nitrogen atmosphere. The mixture was allowed to stir at 65 °C for 24 h. *N*,*N*-Dimethylthiocarbamoyl chloride (1.2 g, 9.2 mmol) was added and the mixture was stirred at 65 °C for another 12 h. The resulting mixture was quenched with saturated $NaHCO_3$ solution and was extracted with $CHCl_3$. The separated organic phase was dried over anhydrous $MgSO_4$ and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 70/30) to give 2.9 g (90% yield) of 2,2′-bis(*N*,*N*-dimethylthiocarbamoyloxy)-6,6′-dimethyl-1,1′-biphenyl (**5a**): ^{1}H NMR ($CDCl_3$) δ 2.13 (s, 6H), 2.89 (s, 6H), 3.22 (s, 6H), 7.12 (d, J = 8.1 Hz, 2H), 7.16 (d, J = 7.5 Hz, 2H), 7.29 (t, J = 7.9 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 19.9, 38.0, 42.9, 121.3, 127.3, 127.5, 129.1, 139.2, 151.5, 186.6. Anal. Calcd for $C_{20}H_{24}N_2O_2S_2$: C, 61.82; H, 6.23. Found: C, 61.78; H, 6.15.

Preparation of 2,2′-Bis(*N*,*N*-dimethylthiocarbamoyloxy)-6,6′-dibutyl-1,1′-biphenyl (5b). 5b was prepared from **4b** in a manner similar to that for **5a**. ^{1}H NMR ($CDCl_3$) δ 0.81 (t, J = 7.3 Hz, 6H), 1.25 (m, 4H), 1.46 (m, 4H), 2.34 (m, 4H), 2.79 (s, 6H), 3.23 (s, 6H), 7.19 (d, J = 7.6 Hz, 2H), 7.25 (dd, J

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= 8.1, 1.0 Hz, 2H), 7.34 (t, J = 8.1 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 13.9, 22.6, 32.0, 32.6, 38.3, 40.0, 100.5, 121.7, 125.3, 127.2, 143.4, 151.1, 186.1. Anal. Calcd for $C_{26}H_{36}N_2O_2S_2$: C, 66.06; H, 7.68. Found: C, 65.76; H, 7.65.

Preparation of 2,2′-Bis(*N*,*N*-dimethylthiocarbamoyloxy)-6,6′-diphenyl-1,1′-biphenyl (5c). To a solution of **4c** (1.4 g, 4.1 mmol) in dry DMF (50 mL) was added sodium hydride (60% oil dispersion; 0.30 g, 10 mmol) in portions at 0 °C, before *N*,*N*-dimethylthiocarbamoyl chloride (1.5 g, 12 mmol) was added in one portion. The mixture was allowed to stir at 85 °C for 2 h and quenched with 1 N KOH (150 mL) at 0 °C. The precipitate was collected on a filter and then thoroughly washed with H_2O. The collected solid was dissolved in $CHCl_3$ and the solution was dried over anhydrous $MgSO_4$. After evaporation of the solvent, the crude solid was recrystallized from hexane/chloroform to give 1.6 g (75% yield) of 2,2′-bis(*N*,*N*-dimethylthiocarbamoyloxy)-6,6′-diphenyl-1,1′-biphenyl (**5c**): ^{1}H NMR ($CDCl_3$) δ 3.00 (s, 6H), 3.32 (s, 6H), 6.77 (dd, J = 8.0, 1.3 Hz, 4H), 7.01 (t, J = 7.7 Hz, 4H), 7.02 (dd, J = 7.7, 1.3 Hz, 2H), 7.09 (t, J = 7.3 Hz, 2H), 7.35 (t, J = 8.0 Hz, 2H), 7.51 (dd, J = 8.2, 1.3 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 38.6, 43.3, 122.9, 126.4, 127.0, 127.2, 127.3, 129.2, 139.8, 143.3, 151.7, 185.6. Anal. Calcd for $C_{30}H_{28}N_2O_2S_2$: C, 69.07; H, 5.60. Found: C, 69.10; H, 5.27.

Preparation of 1,9-Dimethyldibenzo[2,1-*b*:1′,2′-*d*]thiophene (6a). 2,2′-Bis(*N*,*N*-dimethylthiocarbamoyloxy)-6,6′-dimethyl-1,1′-biphenyl (**5a**) (2.8 g, 7.2 mmol) was heated in an autoclave at 290 °C for 12 h. The reaction mixture was cooled to room temperature and then purified by column chromatography on silica gel (hexane/ethyl acetate = 95/5) to give 1.3 g (86% yield) of 1,9-dimethyldibenzothiophene (**6a**):[34] ^{1}H NMR ($CDCl_3$) δ 2.77 (s, 6H), 7.26 (m, 2H), 7.35 (t, J = 7.6 Hz, 2H), 7.67 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 25.6, 119.9, 126.0, 127.9, 134.3, 135.4, 140.1. Similarly, the thiophenes **6b** and **6c** were prepared from **5b** and **5c**, respectively.

1,9-Dibutyldibenzo[2,1-*b*:1′,2′-*d*]thiophene (6b): ^{1}H NMR ($CDCl_3$) δ 0.86 (t, J = 7.4 Hz, 6H), 1.27 (sextet, J = 7.5 Hz, 4H), 1.57−1.62 (m, 4H), 3.08 (m, 4H), 7.35 (d, J = 6.7 Hz, 2H), 7.39 (t, J = 7.5 Hz, 2H), 7.65 (dd, J = 7.6, 1.1 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 13.9, 22.8, 33.5, 36.2, 119.7, 125.6, 126.1, 134.7, 139.7, 139.9. Anal. Calcd for $C_{20}H_{24}S$: C, 81.02; H, 8.16. Found: C, 81.15; H, 8.24.

1,9-Diphenyldibenzo[2,1-*b*:1′,2′-*d*]thiophene (6c): ^{1}H NMR ($CDCl_3$) δ 6.76 (d, J = 7.1 Hz, 4H), 6.94 (t, J = 7.6 Hz, 4H), 7.01 (t, J = 7.3 Hz, 2H), 7.03 (d, J = 7.3 Hz, 2H), 7,42 (t, J = 7.6 Hz, 2H), 7.78 (d, J = 7.8 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 121.0, 125.9, 126.2, 127.6, 127.8, 128.2, 132.5, 140.6, 140.7, 142.9. Anal. Calcd for $C_{24}H_{16}S$: C, 85.68; H, 4.79. Found: C, 85.41; H, 4.92.

Preparation of Dinaphtho[2,1-*b*:1′,2′-*d*]thiophene (6d). 1,1′-Binaphthyl-2,2′-diyl *O*,*O*-bis(*N*,*N*-dimethylthiocarbamate) (18.4 g, 39.9 mmol) prepared from 1,1′-binaphthol according to De Lucchi's procedures[17a] was heated in an autoclave at 285 °C for 30 min. The reaction mixture was cooled to room temperature and the crude solid was recrystallized from chloroform/methanol to give 9.5 g (68% yield) of dinaphthothiophene (**6d**): ^{1}H NMR ($CDCl_3$) δ 7.57 (m, 4H), 7.93 (d, J = 8.6 Hz, 2H), 7.96 (d, J = 8.6 Hz, 2H), 8.03 (m, 2H), 8.87 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 120.8, 124.8, 125.2, 126.0, 127.4, 128.6, 129.8, 131.4, 132.1, 138.4.

Asymmetric Grignard Cross-Coupling of Thiophenes 6a−d with Grignard Reagents. The reaction conditions and results are summarized in Tables 1−3. A typical procedure is given for the reaction of 1,9-dimethyldibenzothiophene (**6a**) with 4-methylphenylmagnesium bromide (**7m**) in the presence of Ni(cod)$_2$ and (*S*)-H-MOP (entry 4 in Table 1).

To a solution of 1,9-dimethyldibenzothiophene (**6a**) (50 mg, 0.24 mmol), Ni(cod)$_2$ (3.9 mg, 14 μmol), and (*S*)-H-MOP (18.6 mg, 42 μmol) in dry THF (4 mL) was added slowly 4-methylphenylmagnesium bromide in THF (1.60 mL, 2.35 mmol) at 0 °C under nitrogen atmosphere. The mixture was allowed to stir at 40 °C for 24 h and quenched with water. It was then diluted with $CHCl_3$ and the organic layer was washed with 10% HCl, saturated $NaHCO_3$, and brine. The organic layer was dried over anhydrous $MgSO_4$ and evaporated under reduced pressure. Silica gel preparative thin-layer chromatography (hexane/ethyl acetate = 98/2) gave 61 mg (85% yield, 82% ee) of **(*S*)-2-mercapto-2′-(4-methylphenyl)-6,6′-dimethyl-1,1′-biphenyl (8am):** $[\alpha]^{20}_D$ +98 (*c* 0.5, chloroform) for **8am** of 82% ee; ^{1}H NMR ($CDCl_3$) δ 1.78 (s, 3H), 2.04 (s, 3H), 2.25 (s, 3H), 3.21 (s, 1H), 6.85 (d, J = 7.6 Hz, 1H), 6.96 (d, J = 8.0 Hz, 2H), 7.00 (t, J = 7.6 Hz, 1H), 7.11 (d, J = 8.1, 3H), 7.27−7.31 (m, 2H), 7.36 (t, J = 7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 19.8, 20.5, 21.1, 125.6, 126.7, 127.3, 128.0, 128.2, 128.3, 128.5, 129.3, 132.6, 136.1, 136.6, 137.0, 138.0, 138.4, 141.3. Anal. Calcd for $C_{21}H_{20}S$: C, 82.85; H, 6.62. Found: C, 82.70; H, 6.84. **(*S*)-2-Mercapto-2′-phenyl-6,6′-dimethyl-1,1′-biphenyl (8an):** $[\alpha]^{20}_D$ +92 (*c* 1.0, chloroform) for **8an** of 81% ee; ^{1}H NMR ($CDCl_3$) δ 1.77 (s, 3H), 2.05 (s, 3H), 3.20 (s, 1H), 6.82 (d, J = 7.6 Hz, 1H), 6.97 (t, J = 7.7 Hz, 1H), 7.09 (d, J = 7.8 Hz, 1H), 7.13−7.14 (m, 3H), 7.22−7.24 (m, 2H), 7.29 (d, J = 11.9 Hz, 1H), 7.31 (d, J = 11.3 Hz, 1H), 7.37 (t, J = 7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 19.8, 20.5, 125.6, 126.6, 126.8, 127.4, 128.1, 128.2, 128.7, 129.5, 132.6, 136.7, 137.0, 137.3, 137.8, 141.3, 141.4. Anal. Calcd for $C_{20}H_{18}S$: C, 82.71; H, 6.25. Found: C, 82.61; H, 6.61. **(*S*)-2-Mercapto-2′-benzyl-6,6′-dimethyl-1,1′-biphenyl (8ap):** $[\alpha]^{20}_D$ +4.7 (*c* 1.0, chloroform) for **8ap** of 35% ee; ^{1}H NMR ($CDCl_3$) δ 1.68 (s, 3H), 1.96 (s, 3H), 3.03 (s, 1H), 3.55 (d, J = 15.3 Hz, 1H), 3.66 (d, J = 15.3 Hz, 1H), 6.95 (d, J = 6.6 Hz, 2H), 6.99 (d, J = 7.6 Hz, 1H), 7.07 (d, J = 7.6 Hz, 1H), 7.13 (m, 2H), 7.18 (m, 3H), 7.23 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 19.6, 19.9, 39.4, 125.8, 126.1, 127.0, 127.6, 127.7, 127.9, 128.1, 128.3, 129.4, 131.9, 136.4, 137.5, 137.6, 138.6, 139.3, 140.1. Anal. Calcd for $C_{21}H_{20}S$: C, 82.85; H, 6.62. Found: C, 82.68; H, 6.85. **(*S*)-2-Mercapto-2′-(4-methylphenyl)-6,6′-dibutyl-1,1′-biphenyl (8bm):** $[\alpha]^{20}_D$ +37 (*c* 1.0, chloroform) for **8bm** of 78% ee; ^{1}H NMR ($CDCl_3$) δ 0.75 (t, J = 7.3 Hz, 3H), 0.80 (t, J = 7.4 Hz, 3H), 1.09 (m, 3H), 1.24 (m, 3H), 1.41 (m, 1H), 1.53 (m, 1H), 1.93 (ddd, J = 14.6, 10.4, 5.5 Hz, 1H), 2.06 (ddd, J = 14.6, 10.4, 5.5 Hz, 1H), 2.23 (s, 3H), 2.27 (ddd, J = 14.6, 10.4, 5.5 Hz, 1H), 2.39 (ddd, J = 14.6, 10.4, 5.5 Hz, 1H), 3.21 (s, 1H), 6.88 (d, J = 7.6 Hz, 1H), 6.94 (d, J = 8.0 Hz, 2H), 7.05 (t, J = 7.7 Hz, 1H), 7.08 (d, J = 8.0 Hz, 2H), 7.11 (d, J = 7.7 Hz, 1H), 7.28 (d, J = 7.6 Hz, 1H), 7.34 (d, J = 6.7 Hz, 1H), 7.41 (t, J = 7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.9, 21.1, 22.7, 22.8, 31.4, 32.1, 32.6, 32.9, 124.9, 125.3, 127.3, 127.8, 128.0, 128.1, 128.2, 128.8, 133.2, 136.0, 136.6, 137.1, 138.6, 141.4, 141.5, 141.7. Anal. Calcd for $C_{27}H_{32}S$: C, 83.45; H, 8.30. Found: C, 83.25; H, 8.24. **(*R*)-2-Mercapto-2′-(4-methylphenyl)-6,6′-diphenyl-1,1′-biphenyl (8cm):** $[\alpha]^{20}_D$ −18 (*c* 1.0, chloroform) for **8cm** of 36% ee; ^{1}H NMR ($CDCl_3$) δ 2.28 (s, 3H), 3.23 (s, 1H), 6.66 (dd, J = 8.3, 1.1 Hz, 2H), 6.89 (m, 6H), 6.95 (dd, J = 6.9, 2.2 Hz, 1H), 7.02 (t, J = 7.7 Hz, 2H), 7.06 (m, 4H), 7.12 (m, 2H), 7.29 (dd, J = 7.7, 1.4 Hz, 1H), 7.35 (dd, J = 7.7, 1.4 Hz, 1H), 7.46 (t, J = 7.7 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 21.1, 126.29, 126.34, 127.18, 127.24, 127.3, 127.8, 127.9, 128.1, 128.6, 129.08, 129.12, 129.2, 129.7, 129.9, 133.4, 135.2, 136.1, 136.5, 138.0, 140.6, 140.9, 142.1, 142.4; HRMS (FAB) calcd for $C_{31}H_{24}S$ $(M)^+$ 428.1598, found 428.1592. **(*S*)-2-Mercapto-2′,6-diphenyl-6′-methyl-1,1′-biphenyl (8cq):** $[\alpha]^{20}_D$ −43 (*c* 1.0, chloroform) for **8cq** of 53% ee; ^{1}H NMR ($CDCl_3$) δ 2.31 (s, 3H), 3.43 (s, 1H), 6.50 (dd, J = 8.2, 1.4 Hz, 2H), 6.69 (dd, J = 8.2, 1.4 Hz, 2H), 6.92 (dd, J = 7.7, 1.2 Hz, 1H), 7.00 (m, 5H), 7.08 (m, 2H), 7.15 (t, J = 7.8 Hz, 1H), 7.25 (m, 2H), 7.31 (dd, J = 7.7, 1.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 20.3, 126.2, 126.3, 126.96, 127.04, 127.2, 127.7, 128.12, 128.14, 128.9, 129.0, 134.2, 136.5, 136.9, 137.8, 140.7, 141.0, 141.6, 142.1. Anal. Calcd for $C_{25}H_{20}S$: C, 85.18; H, 5.72. Found: C, 85.07; H, 5.55. **(*S*)-2-Mercapto-2′-(4-methylphenyl)-1,1′-binaphthyl (8dm):** $[\alpha]^{20}_D$ −98 (*c* 1.0, chloroform) for **8dm** of 95% ee; ^{1}H NMR ($CDCl_3$) δ 2.11 (s, 3H), 3.15 (s, 1H), 6.82 (d, J = 8.0 Hz, 2H),

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7.08 (d, J = 8.0 Hz, 2H), 7.14 (m, 3H), 7.27 (m, 3H), 7.43 (t, J = 7.5 Hz, 1H), 7.64 (dd, J = 8.5, 3.1 Hz, 2H), 7.71 (d, J = 8.2 Hz, 1H), 7.92 (d, J = 8.2 Hz, 1H), 8.01 (d, J = 8.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 21.1, 124.9, 125.9, 126.1, 126.2, 126.8, 126.85, 126.93, 128.1, 128.2, 128.3, 128.4, 128.65, 128.67. 128.9, 131.2, 131.3, 132.1, 133.0, 133.1, 133.3, 134.2, 136.3, 138.3, 140.0. Anal. Calcd for $C_{27}H_{20}S$: C, 86.13; H, 5.35. Found: C, 86.02; H, 5.42. **(*S*)-2-Mercapto-2′-phenyl-1,1′-binaphthyl (8dn):** $[\alpha]^{20}_D$ −79 (*c* 1.0, chloroform) for **8dn** of 95% ee; ^{1}H NMR ($CDCl_3$) δ 3.19 (s, 1H), 7.06 (m, 3H), 7.13 (d, J = 8.5 Hz, 1H), 7.21 (m, 4H), 7.32 (m, 2H), 7.35 (d, J = 8.5 Hz, 1H), 7.51 (ddd, J = 8.1, 7.0, 1.1 Hz, 1H), 7.69 (dd, J = 8.5, 4.4 Hz, 2H), 7.77 (d, J = 8.2 Hz, 1H), 7.99 (d, J = 8.2 Hz, 1H), 8.08 (d, J = 8.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 124.8, 125.8, 126.10, 126.13, 126.68, 126.72, 126.74, 126.9, 127.4, 128.0, 128.14, 128.19, 128.6, 128.7, 128.8, 131.1, 131.2, 132.0, 133.0, 133.0, 133.2, 134.0, 139.0, 141.1. Anal. Calcd for $C_{26}H_{18}S$: C, 86.15; H, 5.01. Found: C, 85.96; H, 5.29. **(*S*)-2-Mercapto-2′-(4-methoxyphenyl)-1,1′-binaphthyl (8do):** $[\alpha]^{20}_D$ −91 (*c* 1.0, chloroform) for **8do** of 93% ee; ^{1}H NMR ($CDCl_3$) δ 3.18 (s, 1H), 3.65 (s, 3H), 6.58 (d, J = 8.8 Hz, 2H), 7.11 (m, 3H), 7.14 (d, J = 9.0 Hz, 1H), 7.21 (ddd, J = 8.2, 7.0, 1.2 Hz, 1H), 7.29 (ddd, J = 8.2, 7.0, 1.2 Hz, 1H), 7.33 (ddd, J = 8.2, 7.0, 1.2 Hz, 1H), 7.36 (d, J = 8.7 Hz, 1H), 7.47 (ddd, J = 8.2, 7.0, 1.2 Hz, 1H), 7.66 (d, J = 8.5 Hz, 1H), 7.70 (d, J = 8.5 Hz, 1H), 7.77 (d, J = 8.2 Hz, 1H), 7.96 (d, J = 8.2 Hz, 1H), 8.04 (d, J = 8.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 55.0, 112.9, 124.8, 125.8, 125.9, 126.0, 126.74, 126.77, 126.8, 128.0, 128.10, 128.14, 128.3, 128.7, 128.8, 129.9, 131.2, 132.1, 132.9, 133.0, 133.2, 133.5, 134.0, 139.5, 158.3. HRMS (FAB) calcd for $C_{27}H_{20}OS$ $(M + H)^+$ 393.1313, found 393.1324. **(*R*)-2-Mercapto-2′-methyl-1,1′-binaphthyl (8dq):** $[\alpha]^{20}_D$ −19 (*c* 1.0, chloroform) for **8dq** of 68% ee; ^{1}H NMR ($CDCl_3$) δ 2.08 (s, 3H), 3.15 (s, 1H), 6.97 (d, J = 8.6 Hz, 1H), 7.08 (d, J = 8.6 Hz, 1H), 7.20 (ddd, J = 8.2, 7.0, 1.3 Hz, 1H), 7.23 (ddd, J = 8.1, 7.0, 1.1 Hz, 1H), 7.36 (ddd, J = 8.1, 7.0, 1.1 Hz, 1H), 7.40 (ddd, J = 8.1, 7.0, 1.1 Hz, 1H), 7.51 (d, J = 8.7 Hz, 2H), 7.81 (d, J = 8.7 Hz, 1H), 7.85 (d, J = 8.1 Hz, 1H), 7.89 (t, J = 8.1 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 19.9, 124.2, 125.1, 125.2, 125.3, 126.6, 126.8, 126.9, 127.4, 128.07, 128.09, 128.2, 128.4, 128.9, 130.6, 131.6, 132.1, 132.4, 133.0, 133.1, 135.2. Anal. Calcd for $C_{21}H_{16}S$: C, 83.96; H, 5.37. Found: C, 83.84; H, 5.64. **(*R*)-2-Mercapto-2′-ethyl-1,1′-binaphthyl (8dr):** $[\alpha]^{20}_D$ −5 (*c* 0.8, chloroform) for **8dr** of 50% ee; ^{1}H NMR ($CDCl_3$) δ 1.07 (t, J = 7.6 Hz, 3H), 2.36 (dq, J = 15.1, 7.6 Hz, 1H), 2.43 (dq, J = 15.1, 7.6 Hz, 1H), 3.17 (s, 1H), 7.00 (dd, J = 8.5, 1.0 Hz, 1H), 7.05 (dd, J = 8.5, 1.1 Hz, 1H), 7.20 (ddd, J = 8.2, 6.7, 1.1 Hz, 1H), 7.24 (ddd, J = 8.2, 6.7, 1.1 Hz, 1H), 7.37 (ddd, J = 8.2, 6.7, 1.1 Hz, 1H), 7.41 (ddd, J = 8.2, 6.7, 1.1 Hz, 1H), 7.52 (d, J = 8.6 Hz, 1H), 7.59 (d, J = 8.6 Hz, 1H), 7.82 (d, J = 8.6 Hz, 1H), 7.85 (d, J = 8.2 Hz, 1H), 7.90 (d, J = 8.2 Hz, 1H), 7.96 (d, J = 8.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.6, 26.6, 125.1, 125.3, 125.5, 125.6, 126.6, 126.8, 127.2, 128.0, 128.1, 128.2, 128.3, 128.7, 131.0, 131.5, 132.1, 132.4, 132.9, 133.1, 133.6, 140.9. Anal. Calcd for $C_{22}H_{18}S$: C, 84.03; H, 5.77. Found: C, 84.07; H, 6.06.

Asymmetric Grignard Cross-Coupling of Dinaphthothiophene (6d) with Ethylmagnesium Bromide (7r) in the Presence of (*S*)-phephos. To a solution of dinaphthothiophene (**6d**) (57 mg, 0.20 mmol), $Ni(cod)_2$ (1.7 mg, 6.0 μmol), and (*S*)-phephos (11 mg, 9.0 μmol) in dry THF (4 mL) was added slowly ethylmagnesium bromide in Et_2O (1.1 mL, 2.0 mmol) at 0 °C under nitrogen atmosphere. The mixture was allowed to stir at 20 °C for 48 h, and quenched with water. It was diluted with $CHCl_3$ and the organic layer was washed with 10% HCl, saturated $NaHCO_3$, and brine. The organic layer was dried over anhydrous $MgSO_4$ and evaporated under reduced pressure. Silica gel preparative thin-layer chromatography (hexane/ethyl acetate = 90/10) gave 26 mg (41% yield, 19% ee) of (*R*)-2-mercapto-2′-ethyl-1,1′-binaphthyl (**8dr**) ($[\alpha]^{20}_D$ −1.8 (*c* 1.1, chloroform) for **8dr** of 19% ee) and 27 mg (45% yield, 43% ee) of **(*S*)-2-mercapto-1,1′-binaphthyl (10):**[20a] $[\alpha]^{20}_D$ −16 (*c* 0.8, chloroform) for **10** of 43% ee; ^{1}H NMR ($CDCl_3$) δ 3.23 (s, 1H), 7.06 (d, J = 8.6 Hz, 1H), 7.23 (ddd, J = 8.1, 7.0, 1.1 Hz, 1H), 7.25 (d, J = 8.2 Hz, 1H), 7.31 (ddd, J = 8.1, 7.0, 1.1 Hz, 1H), 7.38 (ddd, J = 8.1, 7.0, 1.1 Hz, 1H), 7.43 (dd, J = 8.2, 1.1 Hz, 1H), 7.49 (ddd, J = 8.1, 7.0, 1.1 Hz, 1H), 7.51 (d, J = 8.7 Hz, 1H), 7.64 (dd, J = 8.2, 1.3 Hz, 1H), 7.82 (d, J = 8.7 Hz, 1H), 7.85 (d, J = 8.2 Hz, 1H), 7.96 (d, J = 8.3 Hz, 1H), 7.99 (d, J = 8.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 120.8, 125.0, 125.2, 125.6, 125.76, 125.83, 126.0, 126.2, 126.5, 126.7, 127.0, 127.9, 128.28, 128.30, 128.4, 128.5, 131.5, 131.9, 133.8, 134.1.

Preparation of (*S*)-2-Methylthio-2′-phenyl-1,1′-binaphthyl (11). To a stirred solution of (*S*)-**8dn** (1.1 g, 3.1 mmol, 95% ee) in acetone (25 mL) were added iodomethane (0.20 mL, 3.4 mmol) and potassium carbonate (1.3 g, 9.2 mmol) and the mixture was allowed to stir for 12 h at room temperature under nitrogen atmosphere. When the reaction was completed, the reaction mixture was quenched with water and extracted with $CHCl_3$. After drying over anhydrous $MgSO_4$ and evaporation, the purification of the crude solid by column chromatography (hexane/ethyl acetate = 95/5) on silica gel gave 1.2 g (99% yield) of (*S*)-2-methylthio-2′-phenyl-1,1′-binaphthyl (**11**): $[\alpha]^{20}_D$ −50 (*c* 1.0, chloroform) for **11** of 95% ee; ^{1}H NMR ($CDCl_3$) δ 2.29 (s, 3H), 7.01 (m, 3H), 7.15 (m, 4H), 7.22 (t, J = 8.0 Hz, 1H), 7.27 (t, J = 8.0 Hz, 1H), 7.34 (t, J = 7.5 Hz, 1H), 7.39 (d, J = 8.8 Hz, 1H), 7.46 (t, J = 7.5 Hz, 1H), 7.66 (d, J = 8.5 Hz, 1H), 7.79 (d, J = 8.2 Hz, 1H), 7.81 (d, J = 8.8 Hz, 1H), 7.96 (d, J = 8.2 Hz, 1H), 8.05 (d, J = 8.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 16.0, 123.1, 124.8, 125.8, 126.3, 126.4, 126.5, 126.6, 127.2, 127.9, 128.1, 128.3, 128.4, 128.5, 128.8, 130.8, 132.5, 132.8, 133.2, 133.7, 133.7, 136.5, 139.8, 141.3. Anal. Calcd for $C_{27}H_{20}S$: C, 86.13; H, 5.35. Found: C, 86.10; H, 5.62.

Preparation of (*S*)-2-Methylsulfinyl-2′-phenyl-1,1′-binaphthyl (12). To a solution of **15** (1.2 g, 3.1 mmol) in dry CH_2Cl_2 (25 mL) was added *m*-chloroperbenzoic acid (0.58 g, 3.4 mmol) at 0 °C. The reaction mixture was stirred for 15 min at 0 °C, before it was quenched with saturated $NaHCO_3$ solution and extracted with CH_2Cl_2. The separated organic layer was dried over anhydrous $MgSO_4$ and evaporated. The purification by column chromatography (hexane/ethyl acetate = 1/1) on silica gel gave 1.1 g (92% yield) of (*S*)-2-methylsulfinyl-2′-phenyl-1,1′-binaphthyl (**12**) as a 1:1 mixture of diastereomers. Anal. Calcd for $C_{27}H_{20}OS$: C, 82.62; H, 5.14. Found: C, 82.55; H, 5.39. Separation of the diastereomers was carried out by silica gel preparative thin-layer chromatography with hexane/ethyl acetate (1/1 to 0/1). One of the diastereomers: $[\alpha]^{20}_D$ +19 (*c* 0.7, chloroform) for **12** of 95% ee; ^{1}H NMR ($CDCl_3$) δ 2.09 (s, 3H), 6.96 (d, J = 8.6 Hz, 1H), 7.06 (m, 5H), 7.28 (t, J = 7.5 Hz, 1H), 7.44 (m, 2H), 7.49 (t, J = 7.5 Hz, 1H), 7.59 (ddd, J = 8.2, 6.2, 2.0 Hz, 1H), 7.69 (d, J = 8.6 Hz, 1H), 8.00 (m, 3H), 8.08 (d, J = 8.6 Hz, 1H), 8.10 (t, J = 8.6 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 42.1, 118.9, 125.9, 126.0, 126.9, 127.1, 127.2, 127.4, 127.5. 127.8, 128.56, 128.58, 128.66, 128.68, 129.4, 129.6, 130.0, 132.6, 132.6, 133.5, 134.0, 134.2, 140.3, 140.5, 142.0. The other diastereomer: $[\alpha]^{20}_D$ −482 (*c* 1.1, chloroform) for **12** of 95% ee; ^{1}H NMR ($CDCl_3$) δ 1.86 (s, 3H), 6.98 (d, J = 8.6 Hz, 1H), 7.08 (m, 5H), 7.23 (ddd, J = 8.2, 7.1, 1.1 Hz, 1H), 7.42 (m, 2H), 7.46 (ddd, J = 8.2, 7.1, 1.1 Hz, 1H), 7.61 (ddd, J = 8.2, 7.1, 1.1 Hz, 1H), 7.71 (d, J = 8.6 Hz, 1H), 7.95 (d, J = 8.2 Hz, 1H), 8.01 (d, J = 8.7 Hz, 2H), 8.10 (d, J = 8.6 Hz, 1H), 8.14 (d, J = 8.7 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 41.5, 100.5, 119.8, 126.3, 126.8, 127.2, 127.3, 127.7, 127.8, 127.8, 127.9, 128.2, 128.6, 129.4, 129.6, 130.6, 130.7, 132.5, 132.9, 134.0, 134.1, 136.3, 139.4, 140.9, 141.2.

Preparation of (*S*)-2-Iodo-2′-phenyl-1,1′-binaphthyl (13). To a solution of **12** (0.34 g, 0.87 mmol) as a diastereomeric mixture (1:1) in dry THF (30 mL) was slowly added ethylmagnesium bromide in diethyl ether (0.70 mL, 1.3 mmol) at 0 °C. The resulting mixture was stirred at room temperature for 35 min and iodine (0.44 g, 1.7 mmol) was added. The reaction mixture was allowed to stir at room temperature for 12 h under nitrogen atmosphere and quenched with water. It was then diluted with ethyl acetate, and the organic layer was washed with saturated $Na_2S_2O_3$ solution and water, dried over

anhydrous $MgSO_4$, and evaporated under reduced pressure. The residue was chromatographed on silica gel (hexane/ethyl acetate = 98/2) to give 0.27 g (67% yield) of (*S*)-2-iodo-2′-phenyl-1,1′-binaphthyl (**13**) and 52 mg (18% yield) of 2-phenyl-1,1′-binaphthyl[35] as a byproduct. $[\alpha]^{20}_D$ −105 (*c* 1.0, chloroform) for **13** of 95% ee; ^{1}H NMR ($CDCl_3$) δ 7.03 (m, 3H), 7.12 (d, J = 8.6 Hz, 1H), 7.16 (m, 2H), 7.25 (m, 2H), 7.30 (ddd, J = 8.1, 7.0, 1.1 Hz, 1H), 7.42 (ddd, J = 8.1, 7.0, 1.1 Hz, 1H), 7.49 (ddd, J = 8.1, 7.0, 1.1 Hz, 1H), 7.52 (d, J = 8.8 Hz, 1H), 7.64 (d, J = 8.6 Hz, 1H), 7.80 (d, J = 8.2 Hz, 1H), 7.85 (d, J = 8.6 Hz, 1H), 7.98 (d, J = 8.2 Hz, 1H), 8.07 (d, J = 8.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 101.1, 125.9, 126.1, 126.3, 126.6, 126.7, 126.9, 127.27, 127.32, 128.0, 128.5, 128.6, 129.0, 131.9, 132.7, 134.5, 135.4, 137.6, 139.0, 141.1, 141.5. HRMS (FAB) calcd for $C_{26}H_{17}I$ $(M)^+$ 456.0375, found 456.0381.

Preparation of (*S*)-2-Phenyl-1,1′-binaphthyl-2′-boronic Acid Pinacol Ester (14).[35] To a solution of **12** (0.11 g, 0.30 mmol) in dry THF (5.0 mL) was slowly added ethylmagnesium bromide in diethyl ether (0.20 mL, 0.42 mmol) at 0 °C. The resulting mixture was stirred at room temperature for 35 min and trimethyl borate (73 mg, 0.70 mmol) was added. The reaction mixture was allowed to stir at room temperature for 12 h under nitrogen atmosphere and all volatiles were evaporated under reduced pressure. To the residue was added 10% HCl (10 mL) and it was then extracted with diethyl ether. The extracts were washed with water, dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. The residue was dissolved in dry toluene (50 mL) and 2,3-dimethyl-2,3-butanediol (77 mg, 0.70 mmol) was added. The solution was heated at 120 °C for 15 h, using a Dean−Stark trap under nitrogen atmosphere. The solvent was removed under reduced pressure and the concentrated residue was chromatographed on silica gel (hexane/ethyl acetate = 90/10) to give 61 mg (48% yield) of (*S*)-2-phenyl-1,1′-binaphthyl-2′-boronic acid pinacol ester (**14**) and 42 mg (45% yield) of 2-phenyl-1,1′-binaphthyl as a byproduct. $[\alpha]^{20}_D$ −128 (*c* 1.0, chloroform) for **14** of 95% ee; ^{1}H NMR ($CDCl_3$) δ 0.75 (s, 6H), 0.95 (s, 6H), 6.97 (m, 3H), 7.19 (m, 5H), 7.40 (m, 3H), 7.59 (d, J = 8.4 Hz, 1H), 7.79 (m, 3H), 7.91 (d, J = 8.1 Hz, 1H), 7.99 (t, J = 8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 24.0, 24.5, 83.0, 125.1, 125.6, 125.8, 126.0, 126.3, 126.5, 126.9, 127.0, 127.2, 127.3, 127.4, 127.8, 128.0, 129.3, 130.1, 132.6, 132.8, 134.1, 134.4, 136.3, 139.2, 142.3, 144.1.

Preparation of (*S*)-2-Diphenylphosphino-2′-phenyl-1,1′-binaphthyl (15). To a solution of **12** (0.22 g, 0.55 mmol) in dry THF (15 mL) was slowly added ethylmagnesium bromide in diethyl ether (0.40 mL, 0.82 mmol) at 0 °C. The resulting mixture was stirred at room temperature for 35 min and chlorodiphenylphosphine (0.24 g, 1.1 mmol) was added. The reaction mixture was allowed to stir at room temperature for 12 h under nitrogen atmosphere and quenched with saturated NH_4Cl solution. It was then diluted with benzene and the organic layer was washed with saturated $NaHCO_3$ solution and brine. It was then dried over anhydrous $MgSO_4$, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 95/5) to give 0.18 g (62% yield) of (*S*)-2-diphenylphosphino-2′-phenyl-1,1′-binaphthyl (**15**) and 63 mg (35% yield) of 2-phenyl-1,1′-binaphthyl as a byproduct. $[\alpha]^{20}_D$ −137 (*c* 1.0, chloroform) for **15** of 95% ee (lit.[26] $[\alpha]^{20}_D$ +145 (*c* 1.0, chloroform) for (*R*)-**15** of >99% ee); ^{1}H NMR ($CDCl_3$) δ 6.60 (t, J = 6.9 Hz, 2H), 6.77 (d, J = 8.6 Hz, 1H), 6.91 (m, 4H), 6.97 (t, J = 8.2 Hz, 1H), 7.03 (m, 5H), 7.11 (m, 3H), 7.17 (t, J = 7.5 Hz, 1H), 7.22 (dd, J = 8.6, 2.7 Hz, 1H), 7.33 (t, J = 7.3 Hz, 1H), 7.35 (t, J = 7.7 Hz, 1H), 7.43 (d, J = 8.6 Hz, 1H), 7.49 (t, J = 7.7 Hz, 1H), 7.67 (d, J = 8.6 Hz, 1H), 7.75 (d, J = 8.6 Hz, 1H), 7.86 (d, J = 8.1 Hz, 1H), 7.92 (d, J = 8.1 Hz, 1H), 8.06 (d, J = 8.6 Hz, 1H); ^{31}P{^{1}H} NMR ($CDCl_3$) δ −13.8.

Preparation of (*S*)-2′-Methyl-2-phenyl-1,1′-binaphthyl (16).[36] To a solution of **12** (90 mg, 0.23 mmol) and 10 mol % of $N(acac)_2$ (5.0 mg, 0.02 mmol) in dry THF (5.0 mL) was added methylmagnesium iodide in diethyl ether (0.60 mL, 1.2 mmol). The mixture was allowed to stir at 50 °C for 8 h under nitrogen atmosphere. After being cooled to 0 °C, the reaction mixture was quenched with saturated NH_4Cl solution. It was then diluted with $CHCl_3$ and the organic layer was washed with saturated $NaHCO_3$ solution and brine, dried over anhydrous $MgSO_4$, and evaporated under reduced pressure. The purification by silica gel preparative thin-layer chromatography (hexane/ethyl acetate = 95/5) gave 60 mg (76% yield) of (*S*)-2′-methyl-2-phenyl-1,1′-binaphthyl (**16**): $[\alpha]^{20}_D$ −113 (*c* 1.0, chloroform) for **16** of 95% ee; ^{1}H NMR ($CDCl_3$) δ 1.91 (s, 3H), 7.03 (m, 5H), 7.12 (d, J = 8.6 Hz, 1H), 7.22 (m, 2H), 7.27 (t, J = 8.6 Hz, 2H), 7.35 (ddd, J = 8.7, 4.1, 3.6 Hz, 1H), 7.46 (ddd, J = 8.2, 7.1, 1.0 Hz, 1H), 7.66 (d, J = 8.5 Hz, 1H), 7.74 (d, J = 8.5 Hz, 1H), 7.81 (d, J = 8.2 Hz, 1H), 7.96 (d, J = 8.2 Hz, 1H), 8.03 (d, J = 8.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 20.4, 124.6, 125.7, 126.0, 126.4, 126.4, 126.6, 127.36, 127.44, 127.86, 127.90, 127.93, 128.4, 128.5, 128.7, 131.6, 132.7, 132.8, 134.0, 134.5, 134.6, 139.3, 141.7.

Preparation of (*R*)-2-Diphenylphosphino-2′-ethyl-1,1′-binaphthyl (17). To a solution of (*R*)-2-methylsufinyl-2′-ethyl-1,1′-binaphthyl (30 mg, 0.10 mmol), obtained by methylation of the mercapto group in (*R*)-2-mercapto-2′-ethyl-1,1′-binaphthyl (**8dr**) followed by oxidation of the sulfide with *m*CPBA according to the procedures described for the preparation of **12**, in dry THF (3.0 mL) was slowly added ethylmagnesium bromide in diethyl ether (0.10 mL, 0.10 mmol) at 0 °C. The resulting mixture was stirred at room temperature for 35 min and chlorodiphenylphosphine (40 mg, 0.20 mmol) was added. The reaction mixture was allowed to stir at room temperature for 12 h under nitrogen atmosphere and quenched with saturated NH_4Cl. It was then diluted with benzene and the organic layer was washed with saturated $NaHCO_3$ solution and brine, dried over anhydrous $MgSO_4$, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 95/5) to give 18 mg (45% yield) of (*R*)-2-diphenylphosphino-2′-ethyl-1,1′-binaphthyl (**17**): $[\alpha]^{20}_D$ −28 (*c* 0.3, chloroform) for **17** of 50% ee (lit.[27] $[\alpha]^{20}_D$ −85 (*c* 0.2, chloroform) for (*R*)-**17** of >99% ee); ^{1}H NMR ($CDCl_3$) δ 0.90 (t, J = 7.6 Hz, 3H), 2.17 (m, 2H), 6.80 (d, J = 8.5 Hz, 1H), 6.98 (dt, J = 7.2, 1.5 Hz, 1H), 7.02 (dt, J = 7.2, 1.5 Hz, 2H), 7.13 (dt, J = 7.2, 1.5 Hz, 2H), 7.23 (m, 8H), 7.30 (t, J = 7.2 Hz, 1H), 7.47 (m, 2H), 7.51 (d, J = 8.5 Hz, 1H), 7.84 (d, J = 8.2 Hz, 1H), 7.87 (d, J = 8.5 Hz, 1H), 7.88 (d, J = 8.2 Hz, 1H), 7.94 (d, J = 8.5 Hz, 1H); ^{31}P{^{1}H} NMR ($CDCl_3$) δ −14.3.

Preparation of (*S*)-2,2′-Dimethyl-1,1′-binaphthyl (18). To a solution of (*R*)-**8dq** (68% ee, 50 mg, 0.17 mmol) and $Ni(acac)_2$ (13 mg, 0.05 mmol) in dry benzene (4 mL) was added methylmagnesium iodide in Et_2O (0.40 mL, 0.83 mmol) at 0 °C. The reaction mixture was allowed to stir at 80 °C for 5 h and quenched with H_2O. It was diluted with $CHCl_3$ and the organic layer was washed with 10% HCl, saturated $NaHCO_3$, and brine. The organic layer was dried over anhydrous $MgSO_4$ and evaporated under reduce pressure. Silica gel preparative thin-layer chromatography (hexane/ethyl acetate = 95/5) gave 35 mg (75% yield, 70% ee) of (*S*)-2,2′-dimethyl-1,1′-binaphthyl (**18**): $[\alpha]^{20}_D$ +36 (*c* 0.5, chloroform) for **18** of 70% ee (lit.[2a] $[\alpha]^{20}_D$ −37 (*c* 1.0, chloroform) for (*R*)-**18** of 95% ee); ^{1}H NMR ($CDCl_3$) δ 2.03 (s, 6H), 7.04 (d, J = 8.5 Hz, 2H), 7.20 (t, J = 8.2 Hz, 2H), 7.39 (t, J = 8.2 Hz, 2H), 7.50 (d, J = 8.5 Hz, 2H), 7.88 (d, J = 8.2 Hz, 2H), 7.90 (d, J = 8.2 Hz, 2H).

Preparation of 6-Methylphenylphosphinyldinaphtho-[2,1-*b*:1′,2′-*d*]thiophene (21). To a solution of dinaphthothiophene (**6d**) (400 mg, 1.4 mmol) in dry THF (40 mL) was added a solution of *tert*-butyllithium in pentane (3.8 mL, 5.6

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mmol) at −78 °C under nitrogen atmosphere. The reaction mixture was allowed to stir at −78 °C for 5 h and iodine (2.1 g, 8.5 mmol) was added. The mixture was stirred at room temperature for an additional 17 h and quenched with saturated Na_2SO_3. After removal of THF under reduced pressure, the mixture was diluted with water and extracted with ethyl acetate. The organic layer was washed with brine, dried over anhydrous $MgSO_4$, and evaporated under reduced pressure to give a mixture of 6-iododinaphthothiophene (**20**) (66% yield determined by ^{1}H NMR) and **6d**. This mixture was used for the subsequent reaction without further purification.

To a solution of the Grignard reagent prepared from the above iodide compound and magnesium (32 mg, 1.3 mmol) in dry THF (1.3 mL) was added phenylmethylphosphinyl chloride[29] (0.25 g, 1.5 mmol). The reaction mixture was allowed to stir at 65 °C for 10 h and quenched with aqueous NH_4Cl. The resulting mixture was extracted with ethyl acetate and the organic layer was washed with brine. The separated organic layer was dried over anhydrous $MgSO_4$ and evaporated under reduced pressure. The residue was chromatographed on silica gel (ethyl acetate only) to give 36 mg (6% yield) of 6-methylphenylphosphinyldinaphthothiophene (**21**): ^{1}H NMR ($CDCl_3$ at 27 °C) δ 2.32 (d, J = 13.3 Hz, 3H), 7.48 (m, 2H), 7.55 (m, 3H), 7.63 (m, 2H), 7.87 (m, 4H), 8.00 (d, J = 9.4 Hz, 1H), 8.11 (d, J = 9.4 Hz, 1H), 8.40 (d, J = 14.2 Hz, 1H), 8.75 (d, J = 9.4 Hz, 1H), 8.85 (d, J = 9.4 Hz, 1H); ^{13}C NMR ($CDCl_3$ at 27 °C) δ 15.9 (d, J = 74.4 Hz), 120.6, 125.1, 125.4, 125.6 (d, J = 100.2 Hz), 125.9, 126.0, 126.1, 127.0, 128.0, 128.8, 128.8 (d, J = 9.4 Hz), 129.6, 129.7, 130.0, 130.8 (d, J = 10.3 Hz), 131.1 (d, J = 10.3 Hz), 131.1 (d, J = 4.1 Hz), 132.1, 132.2 (d, J = 3.0 Hz), 132.4 (d, J = 8.3 Hz), 132.9 (d, J = 8.3 Hz), 133.1 (d, J = 102.2 Hz), 137.5 (d, J = 7.3 Hz), 139.8; ^{31}P NMR ($CDCl_3$ at 27 °C) δ 37.8; HRMS (FAB) calcd for $C_{27}H_{19}OPS$ $(M + H)^+$ 423.0973, found 423.0974.

Supporting Information Available: Experimental procedures for the determination of absolute configurations of the compounds **9am**, **9an**, and **19**, and variable-temperature ^{31}P NMR spectra of **21**. This material is available free of charge via the Internet at http://pubs.acs.org.

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