

TETRAHEDRON

Enantioposition-Selective Arylation of Biaryl Ditriflates by Palladium-Catalyzed Asymmetric Grignard Cross-Coupling¹

Takashi Kamikawa and Tamio Hayashi*

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

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Abstract: Asymmetric cross-coupling of achiral biaryl ditriflates with aryl Grignard reagents in the presence of 1 equiv of lithium bromide and 5 mol % of palladium complex PdCl₂[(S)-alaphos], where alaphos stands for (2-dimethylamino)propyldiphenylphosphine, gave axially chiral monophenylation products with high enantioposition-selectivity. The remaining triflate group in the monophenylation products was substituted with carboxyl and diphenylphosphino groups through palladium-catalyzed carbonylation and diphenylphosphinylation, respectively. © 1999 Elsevier Science Ltd. All rights reserved.

1. Introduction

Axially chiral biaryls represented by 1,1'-binaphthyls have found extensive use as chiral auxiliaries for a variety of asymmetric reactions including catalytic ones,^{2,3} and considerable attention has been paid to their preparation by asymmetric reactions. In most of the asymmetric reactions so far reported, the axial chirality of biaryls has been generated at the coupling of two aryl units.⁴ Here we wish to report a new catalytic method for the preparation of axially chiral biaryls which is realized by an enantioposition-selective substitution reaction of one of the two enantiotopic triflate groups on achiral biaryl ditriflates (Scheme 1). The monoalkylated biaryls obtained here are very useful as axially chiral building blocks because the remaining triflate group can be readily substituted with some other functional groups by transition-metal-catalyzed coupling-type reactions.

Scheme 1



2. Results and discussion

2.1. Preparation of Biaryl Ditriflates

For the enantioposition-selective cross-coupling, three achiral biaryls containing two trifluoromethanesulfonyloxy (triflate) groups at 2 and 6 positions were prepared starting with 1,3-dimethoxybenzene according to Scheme 2. Lithiation of 1,3-dimethoxybenzene followed by bromination gave 2,6-dimethoxyphenyl bromide (1). Catalytic cross-coupling of 1 with 1-naphthyl-, 2-methylphenyl-, and 2-biphenylylboronic acids in the presence of barium hydroxide and 10 mol % of Pd(PPh_3)₄ in dioxane/H₂O⁵ gave high yields of biaryls 2, 3,

^{*} Corresponding author. Fax: +81-75-753-3988. E-mail: thayashi@kuchem.kyoto-u.ac.jp

and 4, respectively. Demethylation of methyl ethers in 2, 3, and 4 with boron tribromide followed by triflate formation of the resulting phenols with trifluoromethanesulfonic anhydride gave ditriflates 5, 6, and 7 in over 90% yields.



2.2. Chiral Phosphine Ligands for the Asymmetric Cross-Coupling of Ditriflate 5 with PhMgBr

For the cross-coupling of 1-[2,6-bis(trifluoromethanesulfonyloxy)phenyl]naphthalene (5) with phenylmagnesium bromide, several chiral phosphine-palladium complexes were examined for their catalytic activity and enantioselectivity (Scheme 3). The results are summarized in Table 1. The reaction was carried out with 2 equiv of phenylmagnesium bromide in the presence of 1 equiv of LiBr and 5 mol % of a phosphinepalladium complex in ether/toluene (1:1) at -20 °C for 48 h. The enantiomeric purity of a chiral monophenylated biaryl 8a was determined by HPLC analysis of a phenol obtained by alkaline hydrolysis of 8a using a chiral stationary phase column. It was found that the palladium complexes coordinated with β -(dimethylamino)alkyldiphenylphosphines are highly effective as catalysts.⁶ The reactivity was highest in the reaction with alaphos and phephos ligands, which gave 8a of 84% yield and 87% yield, respectively (entries 1 and 2). The highest enantioselectivity was observed in the reaction with alaphos ligand giving 8a of 90% ee (entry 1). The phosphine ligands with a smaller substituent at the chiral carbon atom was found to induce higher stereoselectivity, the order of enantioselectivity being alaphos > phephos > valphos > t-leuphos (entries 1-4).

The cross-coupling also took place with oxazoline-phosphine ligand *i*-Pr-PHOX⁷ which gave **8a** of 52% ee in 26% yield (entry 5). A palladium complex of ferrocenylmonophosphine, (S)-(R)-PPFA,^{4e} was as catalytically active as that of *i*-Pr-PHOX, but **8a** was racemic (entry 6). The reaction was very slow with palladium complexes coordinated with chelating bisphosphine ligands, DIOP⁸ and BINAP^{3a} (entries 7, 8). A palladium catalyst of axially chiral monophosphine ligand MeO-MOP^{3b} gave a low yield of **8a** in 40% ee (entry 9). For the present cross-coupling, palladium complexes of the ligands coordinating with phosphorus and nitrogen atoms are generally more catalytically active than others.

Scheme 3



entry	catalyst	recovered ditriflate (%) ^b	yield of 8a (%) ^b	yield of 9a (%) ^b	% ee of 8a ^c	
1	PdCl ₂ [(S)-alaphos]	0	84	10	90 (S)	
2	$PdCl_2[(S)-phephos]$	0	87	12	86 (S)	
3	$PdCl_2[(S)-valphos]$	28	56	9	78 (S)	
4	$PdCl_2[(S)-t-leuphos]$	64	24	0	49 (S)	
5	PdCl ₂ [(S)-i-Pr-PHOX]	47	26	11	52 (S)	
6	$PdCl_2[(S)-(R)-PPFA]$	69	27	3	0	
7	PdCl ₂ [(+)-DIOP]	82	6	0	46 (<i>R</i>)	
8	PdCl ₂ [(S)-BINAP]	92	2	0	0	
9	$PdCl_2[(R)-MeO-MOP]_2$	85	7	0	40 (<i>R</i>)	

Table 1. Effects of Phosphine Ligands on the Cross-Coupling of Ditriflate 5 with Phenylmagnesium $Bromide^{a}$

^a The cross-coupling was carried out with 2 equiv of Grignard reagent in the presence of 1 equiv of LiBr and 5 mol % of palladium catalyst in ether/toluene (1:1) at -20 °C for 48 h. ^b Isolated yield by silica gel chromatography. ^c Determined by HPLC analysis of phenol obtained by alkaline hydrolysis of triflate 8: Sumichiral OA-4700 (hexane/1,2-dichloroethane/ethanol = 250/20/1).

2.3. Effects of Metal Salts on the Asymmetric Cross-Coupling

Effects of metal salts on the reactivity and the enantioselectivity in the asymmetric cross-coupling of ditriflate 5 with phenylmagnesium bromide are summarized in Table 2. The cross-coupling was carried out in the presence of 5 mol % of $PdCl_2[(S)-alaphos]$ at -20 °C for 48 h. In the absence of metal salts as additives, the reaction was very slow giving 21% yield of monophenylation product 8a together with 3% yield of diphenylation product 9a (entry 1). Addition of 1 equiv (to 5) of LiBr greatly accelerated the reactivity to give 84% yield of 8a and 10% yield of 9a under otherwise the same reaction conditions. The enantioselectivity was also improved by the addition of LiBr (entry 3).⁹ The enantiomeric purity of 8a was raised from 53% ee (S) to 90% ee (S). Highest enantioselectivity was observed in the presence of LiI, which gave 8a of 93% ee, though the reaction rate was not so fast as that in the presence of LiBr (entry 4). LiCl was not so effective as LiBr or LiI, giving a lower yield of 8a with lower enantioselectivity (entry 2). The same tendency of the salt effects was observed in the asymmetric cross-coupling with (S)-phephos ligand, where LiBr and LiI enhanced reactivity and enantioselectivity, respectively (entries 5, 6). The acceleration effects were dependent on the amount of the added lithium salts. Addition of 2 equiv of LiBr or LiI lowered the yields of 8a (entries 7, 10). With 0.1 equiv of LiBr or LiI, only a slight acceleration effect was observed (entries 9, 12). Interestingly, the enantioselectivity was not strongly affected by the amount of the lithium salts, the enantiomeric purity of 8a being kept high with the amount of the lithium salts from 0.1 to 2 equiv (entries 3-12). The addition of Bu₄NI or MgBr₂ raised slightly the enantiomeric purity of 8a, but did not improve the chemical yield (entries 13, 14). It was observed that only LiBr is completely soluble in the reaction mixture. Thus, acceleration of the reaction by the addition of LiBr may be due to the high solubility of the salt. The rate of cross-coupling is higher at higher temperature. At -10 °C and 0 °C, all of starting ditriflate 5 was consumed in 48 h and 20 h, respectively (entries 15, 16), while 22% of 5 was recovered after 48 h at -20 °C under otherwise the same reaction conditions (entry 4). At higher temperature, a considerable amount of diphenylation product 9a was formed (see section 2.5).

entry	ditriflate	Grignard reagent	additive (equiv)	reaction temp (°C)	reaction time (h)	recovered ditriflate (%) ^b	yield of 8 (%) ^b	yield of 9 (%) ^b	%ee of 8 ^c
1	5	PhMgBr	none	-20	48	69	21 (8a)	3 (9a)	53 (S)
2	5	PhMgBr	LiCl(1)	-20	48	58	33 (8a)	3 (9a)	71 (S)
3	5	PhMgBr	LiBr(1)	-20	48	0	84 (8a)	10 (9a)	90 (S)
4	5	PhMgBr	LiI (1)	-20	48	22	70 (8a)	2 (9a)	93 (S)
5d	5	PhMgBr	LiBr (1)	-20	. 48	0	87 (8a)	10 (9a)	86 (S)
6d	5	PhMgBr	LiI (1)	-20	48	53	35 (8a)	2 (9a)	88 (S)
7	5	PhMgBr	LiBr (2)	-20	48	52	39 (8a)	5 (9a)	87 (S)
8	5	PhMgBr	LiBr (0.5)	-20	48	26	66 (8a)	5 (9a)	87 (S)
9	5	PhMgBr	LiBr (0.1)	-20	48	37	45 (8a)	7 (9a)	77 (S)
10	5	PhMgBr	LiI (2)	-20	48	92	4 (8a)	0 (9a)	88 (S)
11	5	PhMgBr	LiI (0.5)	-20	48	21	71 (8a)	3 (9a)	94 (S)
12	5	PhMgBr	LiI (0.1)	-20	48	92	48 (8a)	3 (9a)	90 (S)
13	5	PhMgBr	Bu ₄ NI (1)	-20	48	72	23 (8a)	5 (9a)	76 (S)
14	5	PhMgBr	$MgBr_2(1)$) –20	48	69	20 (8a)	2 (9a)	63 (S)
15	5	PhMgBr	LiĨ (1)	-10	48	0	92 (8a)	6 (9a)	94 (S)
16	5	PhMgBr	LiI (1)	0	20	0	78 (8a)	18 (9a)	91 (S)
17	5	3-MeC ₆ H ₄ MgBr	LiI (1)	-10	72	22	90 (8b)	2 (9b)	95 (S)
18	5	3-MeC ₆ H ₄ MgBr	LiI (1)	0	48	12	73 (8b)	10 (9b)	92 (S)
19e	6	PhMgBr	LiI (1)	-10	72	0	85 (8c)	15 (9c)	95
20 ^e	7	PhMgBr	LiI (1)	-10	72	11	80 (8d)	8 (9d)	94

Table 2. Asymmetric Cross-Coupling of Ditriflates 5-7 with Grignard Reagents Catalyzed by $PdCl_2[(S)-alaphos]^a$

^a The cross-coupling was carried out with 2 equiv of Grignard reagent in the presence of 5 mol % of palladium catalyst in ether/toluene (1:1) for 48 h. ^b Isolated yield by silica gel chromatography. ^c Determined by HPLC analysis of phenol obtained by alkaline hydrolysis of triflate **8**: For entries 1-18, Sumichiral OA-4700 (hexane/1,2-dichloroethane/ethanol = 250/20/1); for entry 19, Chiralcel OD-H (hexane/2-propanol = 95/5); for entry 20, Chiralcel AD (hexane/2-propanol = 95/5). ^d The cross-coupling was carried out with 5 mol % of PdCl₂[(S)-phephos]. ^e The cross-coupling was carried out with 3 equiv of Grignard reagent in the presence of 1 equiv of LiI.

2.4. Asymmetric Cross-Coupling of Other Substrates

High enantioselectivity was also observed in the reaction of ditriflate 5 with 3-methylphenylmagnesium bromide under the same conditions, which gave 90% yield of the corresponding monoarylation product **8b** in 95% ee (Scheme 4, entry 17 in Table 2). The asymmetric phenylation was also successful for 1-[2,6-bis-(trifluoromethanesulfonyloxy)phenyl]-2-methylbenzene (6) and 2-phenylbenzene analog 7. The reaction of 6 and 7 with phenylmagnesium bromide in the presence of 1 equiv of LiI at -10 °C gave 8c of 95% ee and 8d of 94% ee, respectively (entries 19, 20). Unfortunately, 2-methylphenyl, 4-methylphenyl, or 4-chlorophenyl Grignard reagent was not reactive towards the present asymmetric cross-coupling reactions.



2.5. Kinetic Resolution at the Second Cross-Coupling

It was found in the asymmetric cross-coupling of ditriflate 5 with PhMgBr that the enantiomeric purity of 8a was dependent on the yield of diphenylation product 9a. Thus, in entry 2 (Table 3), where the reaction was accompanied by the formation of 13% yield of diphenylation product 9a in the presence of 1 equiv of LiBr and 5 mol % of PdCl₂[(S)-phephos] at -30 °C, the enantiomeric purity of 8a was 93% ee, higher than that of 8a obtained in entry 1 where the reaction was quenched before 9a was formed. That is, in this asymmetric cross-coupling of ditriflate 5, the enantiomeric purity of 8a was dependent on the yield of 9a.

A kinetic resolution at the second cross-coupling was demonstrated by a control experiment using racemic 8a (Scheme 5). At 20% conversion to diphenylation product 9a, the recovered 8a was an (S)-isomer of 17% ee, indicating that the (R)-isomer of 8a undergoes the phenylation about 5 times faster than its (S)-isomer (k(R)/k(S) = 5/1). It follows that the minor enantiomer of 8a formed at the first asymmetric cross-coupling is consumed preferentially at the second asymmetric cross-coupling, which causes an increase of

entr	y catalyst	Li salt	reaction temp (°C)	reaction time (h)	recovered ditriflate (%) ^b	yield of 8a (%) ^b	yield of 9a (%) ^b	%ее of 8a ^c
1 <i>d</i>	PdCl ₂ [(S)-phephos]	LiBr	-30	16	60	39	0	85 (S)
2	$PdCl_2[(S)-phephos]$	LiBr	-30	48	0	87	13	93 (S)
3	PdCl ₂ [(S)-alaphos]	LiBr	-20	12	57	40	1	87 (S)
4	PdCl ₂ [(S)-alaphos]	LiBr	-20	48	0	84	10	90 (S)
5	$PdCl_2[(S)-alaphos]$	LiBr	20	72	0	75	25	90 (S)
6	$PdCl_2[(S)-alaphos]$	LiI	-10	12	69	30	0	94 (S)
7	PdCl ₂ [(S)-alaphos]	LiI	-10	48	0	92	6	94 (S)

Table 3. Relationship between Conversion and Enantiomeric Exess in the Cross-Coupling of Ditriflate 5 withPhenylmagnesium Bromide^a

^a The cross-coupling was carried out with 2 equiv of Grignard reagent in the presence of 1 equiv of LiBr or LiI and 5 mol % of palladium catalyst in ether/toluene (1:1). ^b Isolated yield by silica gel chromatography. ^c Determined by HPLC analysis of phenol obtained by alkaline hydrolysis of triflate 8: Sumichiral OA-4700 (hexane/1,2-dichloroethane/ethanol = 250/20/1). ^d The cross-coupling was carried out with 1.1 equiv of Grignard reagent.

enantiomeric purity of 8a as the amount of diphenylation product 9a increases.¹⁰ The kinetic resolution was also observed in the reaction with alaphos/LiBr (entries 3-5), but not observed in a combination of alaphos with LiI (entries 6, 7).



2.6. Synthetic Application of the Cross-Coupling Product 8a

The monoalkylated biaryls 8 obtained here are very useful as axially chiral building blocks because the remaining triflate group can be readily substituted with some other functional groups by transition-metalcatalyzed coupling-type reactions.¹¹ Monophenylation product 8a was readily made enantiomerically pure with high recovery by simple recrystallization. For example, recrystallization of a crude reaction mixture consisting of 8a (93% ee) and 9a in a ratio of 87 to 13, obtained by the reaction shown in entry 2 in Table 3, from hexane gave 78% isolated yield of enantiomerically pure 8a ($[\alpha]^{20}D - 145$ (c 1.0, chloroform)). The absolute configuration of 8a was assigned to be (-)-(S) by the following transformations. The enantiomerically pure sample (-)-8a was converted into methyl ester (-)-10 and carboxylic acid (-)-11 in high yields by palladiumcatalyzed carbonylation.¹² The enantiomerically pure carboxylic acid 11 is a useful alternative for Fukushi's biarylcarboxylic acid 12 that has been successfully used for the determination of absolute configuration of secondary alkyl alcohols by NMR spectroscopy.¹³ A sample of enantiomerically enriched carboxylic acid (-)-11 (37% ee) was esterified with (*R*)-1-phenylethanol to give a pair of diastereomers 13. The NMR spectrum showed two doublets in a 2:1 ratio which are assigned to be methyl protons of phenylethyl moiety. These signals appeared at 0.71 ppm for the major isomer and at 0.57 ppm for the minor isomer. For the esters derived from 12 and (*R*)-1-phenylethanol, it has been reported that the methyl protons of the esters from (*aS*)-12 and (aR)-12 appear at 0.68 ppm and 0.50 ppm, respectively. By the similarity of the chemical shifts, (-) isomer of 8a was assigned to have axial chirality (S).



Another synthetic application is the preparation of a new chiral phosphine ligand. Thus, the triflate group in (S)-8a was substituted with diphenylphosphino group by the palladium-catalyzed diphenyl-phosphinylation¹⁴ followed by reduction of the diphenylphosphinyl group in (S)-14 with trichlorosilane and triethylamine, which gave axially chiral triarylmonophosphine (S)-15. This new monodentate chiral phosphine ligand (S)-15 was found to be effective for the palladium-catalyzed asymmetric hydrosilylation. The hydrosilylation of styrene with 1.2 equiv of trichlorosilane¹⁵ was carried out in the presence of 0.1 mol % of palladium catalyst generated from [PdCl(π -C₃H₅)]₂ and (S)-15 (Pd/15 = 1/2) at 0 °C for 24 h, which gave 85% yield of (R)-1-(trichlorosilyl)-1-phenylethane (16) (91% ee). The enantioselectivity attained here is comparable with that obtained with H-MOP ligand which we have recently reported¹⁶ and is much higher than that with other chiral phosphine ligands including MeO-MOP whose basic skeleton is analogous to the new ligand 15 obtained here.¹⁵





3. Experimental

General. All manipulations were carried out under a nitrogen atmosphere. Nitrogen gas was dried by passage through P_2O_5 (Merck, SICAPENT). Optical rotations were measured with a JASCO DIP-370 polarimeter. NMR spectra were recorded on a JEOL JNM-EX270 (270 MHz for ¹H and 109 MHz for ³¹P) or JEOL JNM LA500 spectrometer (500 MHz for ¹H and 125 MHz for ¹³C). Chemical shifts are reported in δ ppm referenced to an internal tetramethylsilane standard for ¹H NMR, and to an external 85% H₃PO₄ standard for ³¹P NMR. Residual chloroform (δ 77.0 for ¹³C) was used as internal reference for ¹³C NMR. HPLC analysis was performed on a Shimadzu LC-9A liquid chromatograph system with chiral stationary phase columns, Sumitomo Chemical Co. Ltd., Sumipax OA series and Daicel Chemical Co. Ltd., Chiralpak OD-H and AD.

Materials. PPh₃, dppb, (+)-DIOP, and (S)-BINAP from Aldrich Chemical Company, Inc. are commercially available. Palladium complexes $PdCl_2[(S)-alaphos],^6 PdCl_2[(S)-valphos],^6 PdCl_2[(S)-phephos],^6 PdCl_2[(S)-t-leuphos],^6 PdCl_2[(S)-(R)-PPFA],^{17} PdCl_2[(+)-DIOP], PdCl_2[(S)-BINAP],^{18} and PdCl_2[(R)-MeO-MOP]_2^{19}$ were prepared in a similar manner to the reported procedures. THF, benzene, ether, and toluene were distilled from sodium benzophenone ketyl under nitrogen. Dichloromethane and DMSO were distilled from calcium hydride under nitrogen.

Synthesis of Ditriflates. Ditriflates 5, 6, and 7 were prepared by palladium-catalyzed crosscoupling of 1 with arylboronic acid followed by demethylation and ditriflation. Naphthaleneboronic acid (Lancaster) and o-tolylboronic acid (Aldrich) were commercially available. Biphenyboronic acid were prepared in a similar manner to the reported procedures. Typical procedures for the preparation of ditriflates are shown below.

2-Bromo-1,3-dimethoxybenzene (1). To a solution of 1,3-dimethoxybenzene (5.52 g, 40.0 mmol) in 200 mL of ether was added dropwise at room temperature *n*-butyllithium (1.5 M hexane solution, 27 mL, 42 mmol). The reaction mixture was refluxed for 3 h, cooled to room temperature, then cooled to -50 °C, and Br₂ (2.0 mL, 39 mmol) was added at -50 °C. The mixture was slowly warmed up to room temperature and stirred at room temperature for 1 h and quenched with saturated sodium thiosulfate solution. The mixture was extracted with 500 mL of ether. Ether extracts were washed with brine (2 × 50 mL), dried over magnesium sulfate, and concentrated under reduced pressure. The residue was recrystallized from hexane to give 4.15g (49% yield) of 1: mp 91 °C; ¹H NMR (CDCl₃, 270 MHz) δ 3.90 (s, 6H), 6.58 (d, *J* = 8.3 Hz, 2H), 7.23 (t, *J* = 8.3 Hz, 1H).

1-(2,6-Dimethoxyphenyl)naphthalene (2). To a mixture of 1 (822 mg, 3.79 mmol), naphthaleneboronic acid (980 mg, 5.68 mmol), tetrakis(triphenylphosphine)palladium (440 mg, 0.381 mmol), and Ba(OH)₂·8H₂O (2.69 g, 8.52 mmol) was added 100 mL of 1,3-dioxane and 10 mL of water, and the mixture was refluxed for 2 h. After being cooled to room temperature, the reaction mixture was concentrated under reduced pressure. The residue was diluted with 200 mL of ethyl acetate, washed with water (2 × 50 mL), dried over magnesium sulfate, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/ethyl acetate = 10/1) to give 920 mg (92% yield) of 2: mp 147 °C; ¹H NMR (CDCl₃, 270 MHz) δ 3.64 (s, 6H), 6.72 (d, J = 8.3 Hz, 2H), 7.30–7.57 (m, 6H), 7.83–7.89 (m, 2H); IR (KBr) 3055, 3010, 2962, 1589, 1506, 1430, 1392 cm⁻¹; EI-MS m/z, 264 (M⁺, base), 249, 205. Anal. Calcd for C₁₈H₁₆O₂: C, 81.79; H, 6.10. Found: C, 81.66; H, 6.07. In a similar manner, 1-(2,6-dimethoxyphenyl)-2-methylbenzene (3) and 1-(2,6-dimethoxyphenyl)-2-phenylbenzene (4) were prepared by the cross-coupling with *o*-tolylboronic acid and biphenylboronic acid, respectively.

1-(2,6-Dimethoxyphenyl)-2-methylbenzene (3). ¹H NMR (CDCl₃, 270 MHz) δ 2.07 (s, 3H), 3.71 (s, 6H), 6.69 (d, J = 8.3 Hz, 2H), 7.11–7.35 (m, 5H); ¹³C NMR (CDCl₃, 125 MHz) δ 19.66, 55.77, 103.96, 118.93, 125.14, 127.14, 128.59, 129.46, 130.70, 134.18, 137.29, and 157.66; EI-MS m/z, 228 (M⁺, 100), 213 (23), 197 (44), 152 (23). Anal. Calcd for C₁₅H₁₆O₂: C, 78.92; H, 7.06. Found: C, 78.46; H, 6.90. **1-(2,6-Dimethoxyphenyl)-2-phenylbenzene (4).** ¹H NMR (CDCl₃, 500 MHz) δ 3.52 (s, 6H), 6.45 (d, J = 8.3 Hz, 2H), 7.10–7.17 (m, 6H), 7.30–7.46 (m, 4H); ¹³C NMR (CDCl₃, 125 MHz) δ 55.54, 103.68, 118.89, 126.12, 126.76, 127.11, 127.37, 128.64, 129.31, 131.62, 132.82, 142.24, 142.47, and 157.56; EI-MS m/z, 290 (M⁺, 100), 243 (16), 215 (31). Anal. Calcd for C₂₀H₁₈O₂: C, 82.73; H, 6.25. Found: C, 82.56; H, 6.20.

1-[2,6-Bis(trifluoromethanesulfonyloxy)phenyl[naphthalene (5). To a solution of 2 (4.67 g, 17.7 mmol) in 70 mL of dichloromethane was added dropwise BBr₃ (3.8 mL, 40 mmol) at -78 °C. The mixture was stirred at -78 °C for 1 h, slowly warmed up to room temperature, and stirred at room temperature for 3 h. The mixture was cooled to 0 °C, quenched with water, and extracted with 500 mL of dichloromethane. The organic layer was washed with water $(2 \times 70 \text{ mL})$, dried over magnesium sulfate, and concentrated under reduced pressure. To a solution of the residue, pyridine (5.7 mL, 70 mmol) in dichloromethane (40 mL) was added trifluoromethanesulfonic anhydride (8.9 mL, 53 mmol) at 0 °C. The mixture was stirred at room temperature for 2 h, then quenched with water, and extracted with 500 mL of dichloromethane. The organic layer was washed with water $(2 \times 70 \text{ mL})$, dried over magnesium sulfate, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/ethyl acetate = 10/1) to give 8.1 g (92% yield) of 5: mp 105 °C; ¹H NMR (CDCl₃ 270 MHz) δ 7.32 (d, J = 8.2 Hz, 1H), 7.43–7.70 (m, 7H), 7.93 (d, J = 7.9 Hz, 1H), 8.00 (d, J = 8.2 Hz, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ 118.05 (q, J = 1.0320.0 Hz), 121.86, 124.63, 124.83, 125.62, 126.26, 126.84, 127.75, 128.49, 129.33, 129.50, 130.25, 130.34, 131.42, 133.45, 134.42, and 148.35; IR (KBr) 1452, 1232, 1215, 1165, 972 cm⁻¹; EI-MS m/z 500 $(M^+, 35)$, 234 (100), 205 (19). Anal. Calcd for $C_{18}H_{10}O_6F_6S_2$: C, 43.21; H, 2.01. Found: C, 43.50; H, 1.83. In a similar manner, 1-[2,6-bis(trifluoromethanesulfonyloxy)phenyl]-2-methylbenzene (6) and 1-[2,6-bis(trifluoromethanesulfonyloxy)phenyl]-2-phenylbenzene (7) were prepared.

1-[2,6-Bis(trifluoromethanesulfonyloxy)phenyl]-2-methylbenzene (6). ¹H NMR (CDCl₃, 500 MHz) δ 2.13 (s, 3H), 7.19 (d, J = 7.9 Hz, 1H), 7.31 (t, J = 7.9 Hz, 1H), 7.33 (d, J = 7.9 Hz, 1H), 7.38 (t, J = 7.9 Hz, 1H), 7.47 (d, J = 8.3 Hz, 2H), 7.58 (t, J = 8.3 Hz, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ 19.38, 118.22 (q, J = 318.8 Hz), 121.83, 125.70, 127.67, 129.84, 130.32, 130.65, 130.98, 137.41, and 147.69; EI-MS m/z, 464 (M⁺, 16), 198 (100), 115 (23). Anal. Calcd for C₁₅H₁₀O₆F₆S₂: C, 38.80; H, 2.17. Found: C, 38.54; H, 2.27. **1-[2,6-Bis(trifluoromethanesulfonyloxy)phenyl]-2-phenylbenzene** (7). ¹H NMR (CDCl₃, 500 MHz) δ 7.11 (m, 2H), 7.20 (m, 3H), 7.28 (s, 1H), 7.29 (s, 1H), 7.39–7.58 (m, 6 H); ¹³C NMR (126 MHz, CDCl₃) δ 118.22 (q, J = 318.8 Hz), 121.48, 126.56, 127.17, 128.82, 129.68, 130.07, 130.22, 130.42, 131.72, 140.29, 142.55, and 147.54; EI-MS m/z, 526 (M⁺, 26), 260 (45), 244 (100), 215 (51). Anal. Calcd for C₂₀H₁₂O₆F₆S₂: C, 45.63; H, 2.30. Found: C, 45.59; H, 2.40.

Asymmetric Grignard Cross-Coupling of Ditriflates with Aryl Grignard Reagents Catalyzed by PdCl₂[(S)-alaphos]. Typical Procedure. To a mixture of ditriflate 5 (50 mg, 0.1 mmol), dichloro[(2-dimethylamino)propyldiphenylphosphine]palladium (PdCl₂[(S)-alaphos]) (2.2 mg, 0.005 mmol), and lithium iodide (13 mg, 0.1 mmol) in 200 μ L of toluene was added phenylmagnesium bromide (1 M, 200 μ L, 0.2 mmol) in ether at -20 °C, and the mixture was stirred at -10 °C for 48 h. The mixture was quenched with water and extracted with 70 mL of ether. The organic layer was washed with brine (2 × 20 mL), dried over magnesium sulfate, and concentrated under reduced pressure. The residue was purified by preparative TLC (silica gel, hexane/ethyl acetate = 10/1) to give 39 mg (92% yield) of **8a** and 2 mg (6% yield) of **9a**. The reaction conditions and results are summarized in Tables 2 and 3.

Determination of the Enantiomeric Excess of 8. Enantiomeric purities of 8 were determined by HPLC analysis of phenols obtained by alkaline hydrolysis of triflate 8 by the following procedure. To a solution of 8 (0.3 mg) in 300 μ L of methanol and 300 μ L of 1,3-dioxane was added 2N (300 μ L). The mixture was stirred at room temperature for 12 h, acidified with 10% HCl at 0°C, and extracted with 10 mL of ether. The organic layer was evaporated, and filtered. The filtrate was analyzed by HPLC with a chiral stationary phase column. for 8a, 8b, Sumichiral OA-4700 (hexane/1,2-dichloroethane/ethanol = 250/20/1); for 8c, Chiralcel OD-H (hexane/2-propanol = 95/5); for 8d, Chiralcel AD (hexane/2-propanol = 95/5). The data for HPLC analysis are reported below, together with the spectroscopic and optical rotation data.

(S)-1-[2-Phenyl-6-(trifluoromethanesulfonyloxy)phenyl]naphthalene (8a) (>99% ee). mp 142 °C; $[\alpha]^{20}_{D}$ -145 (c 1.0, chloroform); ¹H NMR (CDCl₃, 270 MHz) δ 6.97-7.06 (m, 5H), 7.19-7.21 (m, 1H), 7.31-7.64 (m, 7H), 7.78-7.84 (m, 2H); ¹³C NMR (CDCl₃, 125 MHz) δ 118.08 (q, J = 320.0 Hz), 120.23, 124.80, 125.33, 125.74, 126.30, 127.12, 127.68, 128.28, 128.65, 128.84, 129.30, 129.46, 130.17, 131.47, 132.25, 132.73, 133.20, 139.61, 145.33, and 148.02; IR (KBr) 3057, 1423, 1221, 1203, 910 cm⁻¹; EI-MS m/z, 428 (M⁺, 100), 295 (78), 277 (59). Anal. Calcd for C₂₃H₁₅O₃F₃S: C, 64.48; H, 3.53. Found: C, 64.35; H, 3.37. **1-(2,6-Diphenylphenyl)naphthalene (9a**). mp 146 °C; ¹H NMR (CDCl₃, 270 MHz) δ 7.04 (m, 10H), 7.05-7.29 (m, 4H), 7.47-7.63 (m, 6H); ¹³C NMR (CDCl₃, 125 MHz) δ 124.48, 125.09, 125.36, 126.15, 126.35, 126.99, 127.20, 127.70, 127.80, 129.07, 129.36, 129.73,

132.58, 132.87, 137.23, 137.42, 141.81, and 142.96; IR (KBr) 3052, 1498, 1448, 1387, 762 cm⁻¹; EI-MS m/z, 356 (M⁺, 100), 276 (14). Anal. Calcd for C₂₈H₂₀: C, 94.34; H, 5.66. Found: C, 94.51; H, 5.44. 1-[2-(3-Methylphenyl)-6-(trifluoromethanesulfonyloxy)phenyl]naphthalene (8b) (95% ee). $[\alpha]^{20}$ -149 (c 1.4, chloroform); ¹H NMR (CDCl₃, 270 MHz) δ 2.07 (s, 3H), 6.69-6.73 (m, 1H), 6.84-6.85 (m, 3H), 7.18–7.25 (m, 2H), 7.31–7.47 (m, 4H), 7.52-7.61 (m, 2H), 7.76-7.83 (m, 2H); ¹³C NMR (CDCl₃, 125 MHz) δ 21.08, 118.07 (g, J = 316.3 Hz), 120.05, 124.75, 125.33, 125.64, 125.84, 126.17, 127.42, 127.78, 128.16, 128.56, 129.17, 129.33, 129.68, 130.06, 131.56, 132.28, 132.68, 133.15, 137.19, 139.45, 145.43, and 147.99; EI-MS m/z, 442 (M⁺, 100), 309 (61), 265 (38). Anal. Calcd for C₂₄H₁₇O₃F₃S: C, 65.15; H, 3.87. Found: C, 64.84; H, 3.92. 1-[2,6-Di(3-methylphenyl)phenyl]naphthalene (9b). mp 97-98 °C; ¹H NMR (CDCl₃ 500 MHz) δ 0.71 (s, 18H), 7.25–7.51 (m, 8H), 7.82 (d, J = 8.4 Hz, 1H), 7.85 (d, J = 8.3 Hz, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ 21.11, 124.42, 125.01, 125.19, 126.15, 126.48, 126.84, 126.97, 127.57, 127.68, 129.17, 129.59, 130.01, 132.74, 132.87, 136.58, 137.27, 137.64, 141.72, and 142.99; EI-MS m/z, 384 (M⁺, 100), 369 (18). Anal. Calcd for C₃₀H₂₄: C, 93.70; H, 6.30. Found: C, 93.30; H, 6.40. 1-[2-Phenyl-6-(trifluoromethanesulfonyloxy)phenyl]-2methylbenzene (95% ee) (8c). mp 73-76 °C; [α]²⁰D -15.5 (c 1.5, chloroform); ¹H NMR (CDCl₃, 270 MHz) δ 1.94 (s, 3H), 7.06–7.21 (m, 9H), 7.35–7.39 (m, 1H), 7.46–7.52 (m, 2H); ¹³C NMR (CDCl₃, 125 MHz) δ 19.63, 118.27 (q, J = 317.5 Hz), 120.22, 125.24, 127.17, 127.80, 128.29, 128.93, 129.23, 129.87, 130.01, 131.36, 133.17, 133.96, 136.83, 139.60, 144.36, and 147.51; EI-MS m/z, 392 (M+, 100), 259 (86), 244 (79), 215 (56). Anal. Calcd C₂₀H₁₅O₃F₃S: C, 61.22; H,3.85. Found: C, 61.40; H, 3.86. 1-(2.6-**Diphenylphenyl)-2-methylbenzene (9c).** mp 104-105 °C; ¹H NMR (CDCl₃, 500 MHz) δ 1.80 (s, 3H), $6.86 \text{ (m, 4H)}, 6.95 \text{ (m, 1H)}, 7.05-7.17 \text{ (m, 10H)}, 7.90 \text{ (d, } J = 1.5 \text{ Hz}, 1\text{H}), 7.44 \text{ (s, 1H)}, 7.49 \text{ (dd, } J = 6.9, 100 \text{ (m, 1H)}, 7.49 \text{ (dd, } J = 6.9, 100 \text{ (m, 1H)}, 7.49 \text{ (m$ 8.3 Hz, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ 124.60, 126.23, 126.68, 127.39, 129.28, 129.35, 129.50, 132.03, 136.35, 139.02, 141.81, and 142.00; EI-MS m/z 320 (M+, 100), 305 (21), 145 (19). Anal. Calcd for C₂₅H₂₀: C, 93.71; H, 6.29. Found: C, 93.47; H, 6.44. 1-[2-Phenyl-6-(trifluoromethanesulfonyloxy)phenyl]-2-phenylbenzene (94% ee) (8d). mp 91-93 °C; $[\alpha]^{20}$ –26.7 (c 1.1, chloroform); ¹H NMR (CDCl₃ 500 MHz) δ 6.73 (d, J = 6.9 Hz, 2H), 6.78 (d, J = 6.9 Hz, 2H), 7.04–7.14 (m, 6H), 7.26–7.33 (m, 5H), 7.36–7.42 (m, 2H); ¹³C NMR (CDCl₃, 125 MHz) δ 118.23 (q, J = 320.0 Hz), 120.17, 126.50, 126.73, 126.87, 127.63, 128.70, 128.89, 129.31, 129.99, 130.24, 131.70, 132.45, 133.43, 139.30, 140.49, 141.81, 144.28, and 147.64; EI-MS m/z, 454 (M⁺, 85), 321 (25), 303 (100), 215 (41). Anal. Calcd for C₂₅H₁₇O₃F₃S: C, 66.07; H, 3.77. Found: C, 65.79; H, 3.86. 1-(2,6-**Diphenylphenyl)-2-phenylbenzene (9d).** ¹H NMR (CDCl₃ 500 MHz) δ 6.67 (d, J = 6.5 Hz, 2H), 6.82-6.84 (m, 4H), 6.97-7.17 (m, 13H), 7.30 (d, J = 7.5 Hz, 2H), 7.42 (t, J = 8.0 Hz, 2H); ¹³C NMR (CDCl₃, 125 MHz) δ 125.93, 126.02, 126.23, 127.20, 127.35, 127.43, 127.58, 128.87, 129.56, 129.69, 129.74, 133.35, 137.42, 137.92, 140.80, 141.10, 141.61, and 141.87; EI-MS m/z 382 (M+, 100), 303 (19), 289 (28). Anal. Calcd for C₃₀H₂₂: C, 94.20; H, 5.80. Found: C, 92.90; H, 5.84.

(S)-1-(2-Methoxycarbonyl-6-phenylphenyl)naphthalene (10) (>99% ee). To a solution of (S)-8a (0.21 g, 0.50 mmol), palladium diacetate (90 mg, 0.40 mmol), and 1,3-bis(diphenylphosphino)propane (0.16 g, 0.40 mmol) in mixture of DMSO (11 mL) and methanol (4 mL) was added 1.5 mL of triethylamine. The mixture was stirred under carbon monoxide (1 atm) at 80 °C for 15 h. After being cooled to room temperature, it was concentrated under reduced pressure. The residue was dissolved in 100 mL of ether and washed with water (2 × 20 mL). The organic layer was dried over magnesium sulfate, and concentrated under reduced pressure. The residue was dissolved in 100 mL of ether and washed with water (2 × 20 mL). The organic layer was dried over magnesium sulfate, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/ethyl acetate = 10/1) to give 0.14 g (82% yield) of (S)-10: mp 81 °C; $[\alpha]^{20}D^{-147}$ (c 1.0, chloroform); ¹H NMR (CDCl₃, 270MHz) δ 3.37 (s, 3H), 7.03–7.08 (m, 5H), 7.19–7.22 (m, 1H), 7.33–7.49 (m, 3H), 7.55–7.58 (m, 1H), 7.63–7.74 (m, 2H), 7.76–7.79 (m, 1H), 7.84–7.87 (m, 1H), 8.01–8.05 (m, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ 51.72, 124.67, 125.28, 125.56, 125.74, 126.50, 127.24, 127.32, 127.60, 127.67, 128.03, 128.54, 128.93, 132.64, 132.87, 133.15, 133.43, 137.26, 138.71, 140.75, 143.41, and 168.39; IR (KBr) 3057, 3006, 2949, 1705, 1308, 1279, 773 cm⁻¹. Anal. Calcd for C₂₄H₁₈O₂: C, 85.15; H, 5.36. Found: C, 85.25; H, 5.28.

(S)-2-(1-Naphthyl)-3-phenylbenzoic Acid (11) (>99% ee). To a solution of (S)-10 (139 mg, 0.411 mmol) in 5 mL of methanol was added 1 mL of 50% KOH solution and the mixture was refluxed for 8 h. The reaction mixture was acidified by addition of conc. HCl at 0 °C and extracted with 200 mL of ethyl acetate. The organic layer was dried over magnesium sulfate, and concentrated under reduced pressure. The

residue was purified by silica gel column chromatography (hexane/ethyl acetate = 1/1) to give 116 mg (87% yield) of (S)-11: mp 207-209 °C; $[\alpha]^{20}D^{-155}$ (c 0.5, chloroform); ¹H NMR (CDCl₃, 270MHz) δ 3.5 (broad, 1H), 6.88-6.98 (m, 5H), 7.09-7.12 (m, 1H), 7.24-7.43 (m, 5H), 7.53-7.69 (m, 3H), 7.74-7.77 (m, 1H), 7.98-8.01 (m, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ 124.67, 125.26, 125.51, 125.74, 126.51, 127.27, 127.39, 127.58, 127.67, 128.03, 128.90, 129.43, 131.59, 132.63, 132.89, 134.18, 136.86, 139.37, 140.64, 143.69, 171.92; IR (KBr) 3321, 3055, 1726, 1691, 1142, 779 cm⁻¹. Anal. Calcd for C₂₃H₁₆O₂: C, 85.19; H, 4.97. Found: C, 84.91; H, 5.07.

1-Phenylethyl 2-(1-Naphthyl)-3-phenylbenzoate (13). To a mixture of 11 (37% ee, 43.5 mg, 0.134 mmol) and thionyl chloride (1 mL) was added DMF (10 μ L), and the mixture was heated with stirring at 90 °C for 8 h. After being cooled to room temperature, the reaction mixture was concentrated under reduced pressure. To the residue benzene (10 mL) was added, the reaction mixture was concentrated under reduced pressure. To a solution of the residue, (R)-1-phenylethanol (17.8 mg, 0.146 mmol) in pyridine (1 mL) was added 4-(N,N-dimethylamino)pyridine (18.1 mg, 0.148 mmol), the mixture was stirred at ambient temperature for 24 h, then quenched with 10% hydrochloric acid, and extracted with 100 mL of ether. The organic layer was washed with (2 × 20 mL), dried over magnesium sulfate, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/ethyl acetate = 1/1) to give 39.1 mg (68% yield) of 13 as a mixture of diastereomers. The diastereomers ratio was determined from NMR spectrum ((*R*, *aS*)-13/(*R*, *aR*)-13 = 2/1). ¹H NMR (CDCl₃, 270 MHz) δ 0.57 (d, *J* = 6.6 Hz, 1/3H), 0.71 (d, *J* = 6.6 Hz, 2/3H, 5.50-5.59 (m, 1H), 6.55-8.00 (m, 20H).

(S)-1-[2-(Diphenylphosphinyl)-6-phenylphenyl]naphthalene (14) (>99% ee). To a mixture of (S)-8a (108 mg, 0.252 mmol), diphenylphosphine oxide (106 mg, 0.522 mmol), palladium diacetate (2.9 mg, 0.013 mmol), and 1,4-bis(diphenylphosphino)butane (dppb, 5.6 mg, 0.013 mmol) was added 1 mL of DMSO and diisopropylethylamine (108 μ L, 0.620 mmol), and the mixture was heated with stirring at 100 °C for 12 h. After being cooled to room temperature, the reaction mixture was concentrated under reduced pressure. The residue was diluted with 100 mL of ethyl acetate, washed with water (2 × 20 mL), dried over magnesium sulfate, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/ethyl acetate = 1/1) to give 120 mg (99% yield) of (S)-14: mp 179 °C; [α]²⁰_D +49.2 (c 1.0, chloroform); ¹H NMR (CDCl₃, 270MHz) δ 6.73–6.80 (m, 2H), 6.84–6.87 (m, 4H), 6.95–6.99 (m, 4H), 7.04–7.10 (m, 1H), 7.18–7.39 (m, 8H), 7.49–7.55 (m, 1H), 7.60–7.69 (m, 5H); ³¹P{¹H} NMR (CDCl₃) δ 28.0 (s); IR (KBr) 3055, 1631, 1439, 1113, 723, 698 cm⁻¹. Anal. Calcd for C₃₄H₂₅OP: C, 84.98; H, 5.24. Found: C, 85.01; H, 5.05.

(S)-1-[2-(Diphenylphosphino)-6-phenylphenyl]naphthalene (15) (>99% ee). To a mixture of (S)-13 (120 mg, 0.250 mmol) and triethylamine (1 mL) in toluene (6 mL) was added trichlorosilane (300 μ L, 0.297 mmol) at 0 °C. The reaction mixture was refluxed for 12 h. After being cooled to room temperature, the mixture was diluted with 100 mL of ether and quenched with a small amount of saturated NaHCO₃. The resulting suspension was filtered through celite and the filter cake was washed with ether. The combined organic layer was dried over magnesium sulfate, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/ethyl acetate = 5/1) to give 85 mg (73% yield) of (S)-15: mp 194-197 °C; $[\alpha]^{20}_{D}$ +15.3 (c 0.5, chloroform); ¹H NMR (CDCl₃, 270MHz) δ 6.84–7.03 (m, 6H), 7.06–7.39 (m, 15H), 7.44–7.54 (m, 2H), 7.58–7.69 (m, 2H); ³¹P{¹H} NMR (CDCl₃) d –12.5 (s); IR (KBr) 3053, 1633, 1437, 746, 698 cm⁻¹. *m/e* calcd for C₃₄H₂₅P: 464.1694, found 464.1708.

Palladium-Catalyzed Asymmetric Hydrosilylation of Styrene with (S)-15. To a mixture of $[PdCl(\pi-C_3H_5)]_2$ (0.54 mg, 1.5 µmol), (S)-15 (2.5 mg, 5.4 mmol), and styrene (264 mg, 2.54 mmol) was added trichlorosilane (300 µL, 3 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 24 h. The crude mixture was purified by bulb-to-bulb distillation under reduced pressure to give 518 mg (85%) of 16. ¹H NMR (CDCl₃, 270MHz) δ 1.62 (d, J = 7.6 Hz, 3H), 2.90 (q, J = 7.6 Hz, 1H), 7.21-7.37 (m, 5H).

Determination of the Enantiomeric Excess of 16. Enantiomeric purities of **16** was determined by HPLC analysis of (3,5-dinitrophenyl)carbamate ester obtained by Tamao's oxidation and esterification by the following procedure. To a suspension of KF (764 mg, 29.4 mmol) and KHCO₃ (2.61 g, 26.0 mmol) in 100 mL of THF/MeOH (1:1) was added **16**. To the suspension was added 2.2 mL of 30% H₂O₂ at ambient temperature. Then the reaction mixture was vigorously stirred for 12 h. To this reaction mixture was added 4 g of Na₂S₂O₃·5H₂O and then entire mixture was stirred for 1 h. The mixture was filtered through a Celite plug, and the filter cake was rinsed with Et₂O. The filtrate was concentrated in vacuo and the resulting residue was dissolved in CH₂Cl₂. After drying over MgSO₄, organic solvent was removed in vacuo. The residue was purified by silica gel column chromatography (hexane/ethyl acetate = 5/1) to give 196 mg (74% yield) of 1-phenylethanol. A mixture of alcohol (2 mg), 3,5-dinitrophenyl isocyanate (5 mg), and pyridine (5 μ L) in toluene (0.5 mL) was stirred at ambient temperature for 30 min. The mixture was evaporated, diluted with chloroform, and filtered. The filtrate was analyzed by HPLC with a chiral stationary phase column, Sumichiral OA-4700 (hexane/1,2-dichloroethane/ethanol = 50/15/1). The enantiomeric excess of the (3,5-dinitrophenyl)carbamate ester was determined to be 91% ee.

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