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Synthesis and Optical Resolution of Aminophosphines with Axially Chiral C(aryl)−N(amine) Bonds for Use as Ligands in Asymmetric Catalysis

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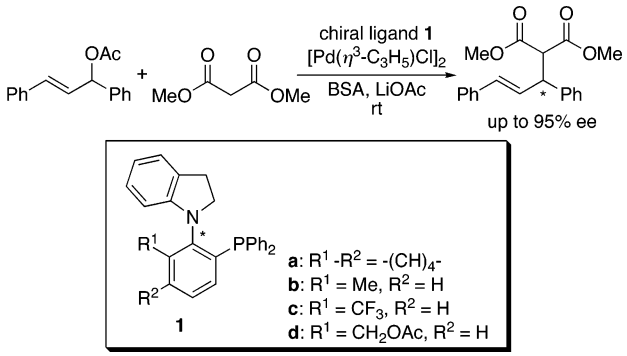

N-Aryl indoline-type aminophosphines **1a**−**c** were obtained in good yields by a nucleophilic aromatic substitution (S_NAr) reaction followed by silane reduction. Aminophosphine **1d** was also prepared from 2,3-difluorobenzaldehyde (**4**) via dimethylhydrazone. Optical resolution of C(aryl)−N(amine) bond atropisomers was achieved using (*S*)-(+)-di-μ-chlorobis[2-[(dimethylamino)ethyl]phenyl-C^2,*N*]dipalladium-(II) ((*S*)-**10**). The determination of absolute configuration and the investigation of the rotation barrier for C(aryl)−N(amine) bond axial stability of an aminophosphine **1** are described. Finally, the ability of the chiral phosphine ligand **1** is demonstrated in a catalytic asymmetric reaction, such as a palladium-catalyzed asymmetric allylic alkylation of 1,3-diphenyl-2-propenyl acetate with dimethyl malonate (up to 95% ee).

Introduction

Chiral phosphines are important molecules that effect asymmetric inductions as ligands for transition metal catalysts.[1,2] Atropisomeric biaryls[3] are also well established as one important class of ligands for asymmetric metal-catalyzed reactions by the discovery and application of BINAP.[4] It is suggested that this ligand's chiral environment and the chelating nature are imposed with two orthogonal naphthalene rings that induce high stereoselectivity in various asymmetric reactions.[5] Binaphthylmonophosphines (MOPs) and related ligands have also been found to be useful in catalytic asymmetric reactions,[6] and C(aryl)−C(aryl) bond atropisomeric aminophosphine ligands, such as QUINAP[7] and MAP,[8] were applied to transition-metal-catalyzed asymmetric reactions during the past decades. However, the synthesis of new axially chiral biaryls is still one of the challenges due to difficulties in forming central sterically hindered C(aryl)−C(aryl) bonds.[9] In the case of nonbiaryl C−C

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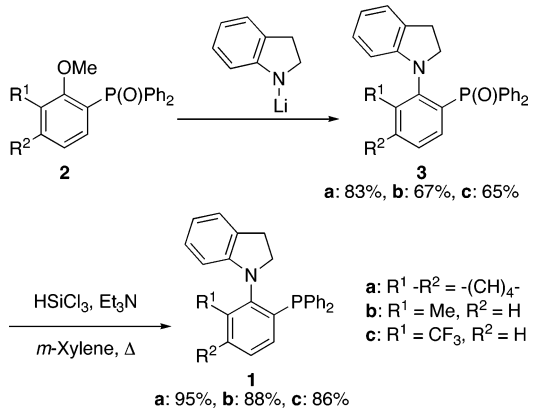
bond atropisomeric ligands, C(aryl)−C(amide carbonyl) bond atropisomeric phosphine ligands[10] and C(aryl)−N(non-amine) bond atropisomeric phosphine ligands, such as quinazolinone-containing *N*-anilide-type ligand[11] and *N*-arylimide-type ligand,[12] have been reported. Although the synthesis of C(aryl)−N(amine) bond atropisomeric *N*-aryl indoles by stereoselective S_NAr reaction of a planar chiral arene Cr complex was recently reported by Kamikawa,[13] even the discovery of C(aryl)−N(amine) bond atropisomeric compounds has been rarely described.[14] The use of the ligand for catalytic asymmetric reaction has hardly been discovered. Previously, we prepared those compounds using an approach similar to the synthesis of pyrrolidinyl-containing aminophosphines.[15] We herein report the synthesis of a C(aryl)−N(amine) bond atropisomeric *N*-aryl indoline-type aminophosphine **1**, the facile optical resolution by the separation of diastereomeric palladium complex mixtures, and applications to the palladium-catalyzed asymmetric allylic alkylation.[16]

Results and Discussion

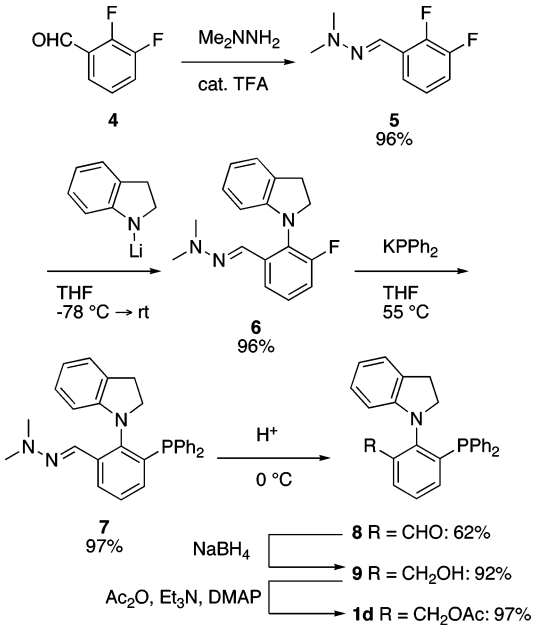
Preparation of *N*-Aryl Indoline-type Aminophosphine 1. Aminophosphine ligands **1a**−**c** were easily prepared in two steps. A nucleophilic aromatic substitution (S_NAr) reaction of the corresponding phosphine oxides, such as 1-methoxy-2-(diphenylphosphino)naphthalene oxide (**2a**), with lithium salt of indoline gave the corresponding aminophosphine oxide **3a**. This aminophosphine oxide was converted into the desired aminophosphine ligand **1a** using trichlorosilane triethylamine in good yield (Scheme 1). Aminophosphines **1b** and **1c** were easily prepared in the same manner.

N-Aryl indoline-type aminophosphine **1d** was prepared in six steps from 2,3-difluorobenzaldehyde (**4**).[17] Dimethylhydrazone **5** was easily prepared from the corresponding aldehyde **4** and *N*,*N*-dimethylhydrazine (DMH) as a protecting reagent with trifluoroacetic acid (TFA) as a catalyst in ether (Scheme 1). We examined the nucleophilic aromatic substitution (S_NAr) reaction of (*E*)-1-(2,3-difluorobenzaldehyde)-*N*,*N*-dimethylhydrazone (**5**) with lithiated indoline; as a result, dimethylhydrazone **5** was converted into the desired *N*-aryl indoline derivative **6** in a 96% yield, indicating that the hydrazone subunit of the 2-fluorine was activated as a leaving group. The next step is the introduction of a phosphine substituent, and we successfully prepared aminophosphine hydrazone **7** by nucleophilic phosphanilation with potassium diphenylphosphide in a 97% yield. The corresponding aldehyde **8** was obtained by hydrolysis of **7** using 6 M hydrochloric acid, and the reduction of aldehyde **8** with sodium borohydride gave the corresponding alcohol **9** in a 92% yield. Finally, this alcohol was converted into aminophosphine **1d** using acetic anhydride−triethylamine−DMAP in good yield.

SCHEME 1. Preparation of Aminophosphine Ligands 1a−c



SCHEME 2. Preparation of Aminophosphine Ligand 1d



Investigations of the Existence of the Axial Chirality of 1. We successfully conducted single-crystal X-ray diffraction analysis of *N*-aryl indoline-type aminophosphines **1a**−**d** and its precursor aminophosphine **9**, and their ORTEP diagrams are shown in Figures S1−S5 (see Supporting Information). The C(aryl)−N(amine) bonds are twisted between an aryl ring with a diphenylphosphino group and an indoline ring. To investigate whether C(aryl)−N(amine) bond axial chirality exists in aminophosphines **1a**−**d**, we analytically separated these isomers by using HPLC on a chiral phase. As a result, we obtained almost resolved UV plots for aminophosphines **1a**−**d** in addition

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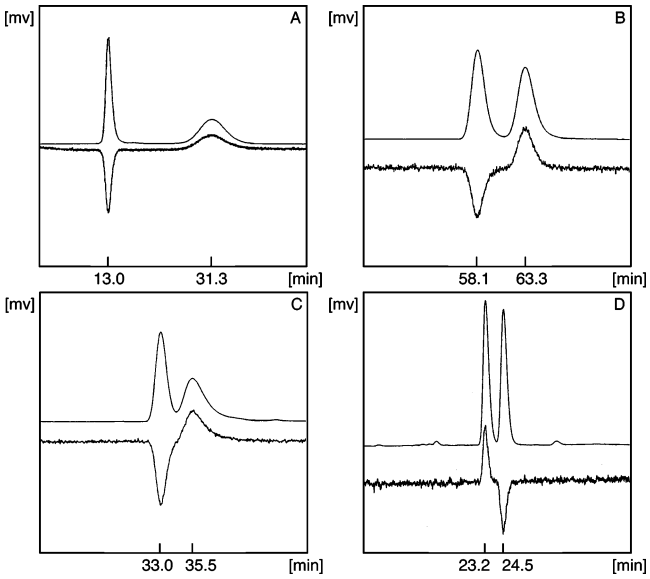


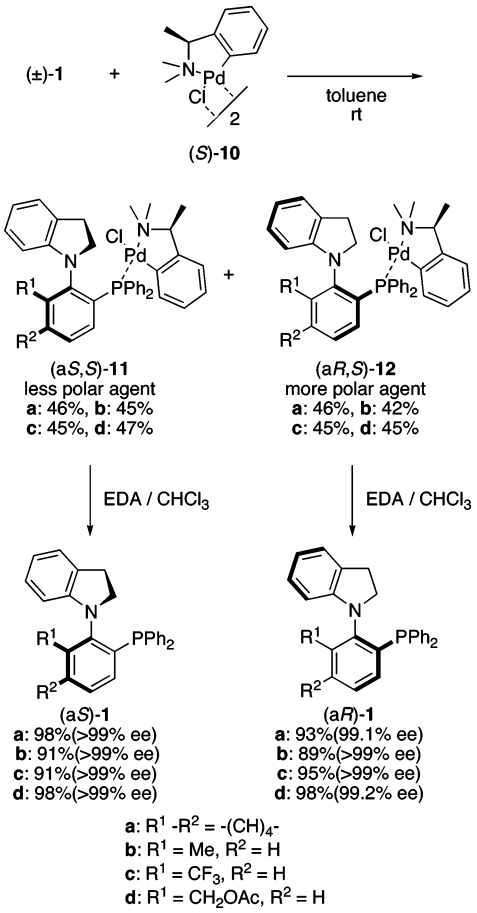
FIGURE 1. Chiral phase HPLC UV and CD charts of (±)-**1**. (A) (±)-**1a**: Daicel CHIRALCEL OJ (0.46 ϕ × 25 cm, hexane:ethanol = 90:10, 0.50 mL/min). (B) (±)-**1b**: Daicel CHIRALPAK AD-H × 2 (0.46 ϕ × 25 cm × 2, hexane:ethanol = 99.7:0.3, 0.25 mL/min). (C) (±)-**1c**: Daicel CHIRALPAK AD-H × 2 (0.46 ϕ × 25 cm × 2, hexane:ethanol = 99.7:0.3, 0.25 mL/min). (D) (±)-**1d**: Daicel CHIRALCEL OD + OD-H (0.46 ϕ × 25 cm × 2, hexane:ethanol = 99:1, 0.50 mL/min).

to a pair of clear positive (+) and negative (−) CD trace signals of HPLC run at 254 nm (Figure 1). This result indicated the existence of a pair of atropisomers in *N*-aryl indoline-type aminophosphines **1a**−**d**.

Optical Resolution and Determination of Absolute Configuration of 1. We next attempted the optical resolution of aminophosphines (±)-**1** into each C(aryl)−N(amine) bond atropisomer that used (*S*)-(+)-di-μ-chlorobis[2-[(dimethylamino)ethyl]phenyl-C^2,*N*]dipalladium(II) ((*S*)-**10**)[18] as a chiral resolving agent. We used a simple separation using a silica gel column chromatography procedure. Racemic *N*-aryl indoline-type aminophosphines (±)-**1** were resolved by coordination with a chiral palladium complex, such as (*S*)-**10**, in toluene at room temperature (Scheme 3). The resulting diastereomeric palladium complex mixture of (a*S*,*S*)-**11** and (a*R*,*S*)-**12** was kinetically stable, and a large difference in the polarity of the diastereomers was observed by using an ether eluent on TLC. In fact, diastereoisomers (a*S*,*S*)-**11** and (a*R*,*S*)-**12** were easily separable by silica gel column chromatography. The individual diastereomers of (a*S*,*S*)-**11** and (a*R*,*S*)-**12** were treated with ethylenediamine (EDA) to release the enantiomerically pure (a*S*)-**1** or (a*R*)-**1**. The optical purity of divided (a*S*)-**1** and (a*R*)-**1** was more than 99% ee from chiral HPLC analyses.

Determination of the absolute configurations of **1** was decided by single-crystal X-ray analysis of palladium complexes **11** or **12** (Figure S6−S9; see Supporting Information). On the basis of the known *S*-stereochemistry of the phenethylamine moiety, the absolute configuration of the C(aryl)−N(amine) bond chiral axis is assigned according to the Cahn−Ingold−Prelog rule.[19]

SCHEME 3. Optical Resolution Procedure of C(aryl)−N(amine) Bond Atropisomeric Aminophosphine (±)-1



Stability of the C−N Bond Axial Chirality of 1. We conducted a study on the thermal racemization of atropisomeric aminophosphines **1**. We assessed the rate of racemization by following first-order decay in enantiomeric excess in time at a suitable temperature. A small portion of the solution of optically active **1** in toluene was taken out at regular intervals and subsequently analyzed for enantiomeric excesses by chiral HPLC analysis. We repeated the experiment at three temperatures and determined the rate constant (k_{rac}) of **1** at each temperature (Figures S10−S13; see Supporting Information). For example, the rotational barrier ($\Delta G^{\ddagger}_{rac}$) of **1c** was found to be 27.9 kcal/mol in toluene at 25 °C according to the Arrhenius and the Eyring equation.[20] This result corresponds to a half-life of approximately 1.7×10^2 days.

X-ray Structure of Palladium Complex (±)-13. Ligand (±)-**1b** was treated with $PdCl_2(MeCN)_2$ to give the palladium complex (±)-**13**, and its suitable crystal was obtained from hexane−$CHCl_3$. X-ray analysis of (±)-**13** was carried out (Figure 2). The solid-state structure shows that ligand **1b** is coordinated to palladium with a five-membered chelate ring via a phosphorus and nitrogen group of **1b**, which is bonded to palladium. The *trans* influence of the P,N-ligand is reflected in the lengthening of the Pd−Cl bond in *trans* disposition to the

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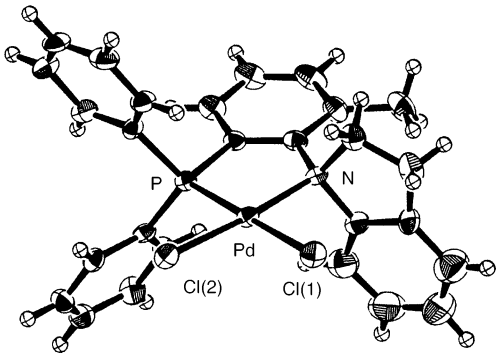
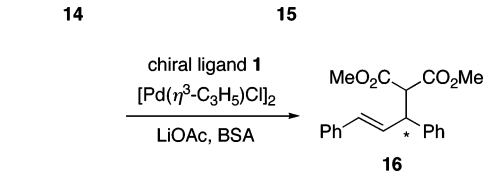


FIGURE 2. ORTEP drawing of palladium complex (±)-**13**. Two molecules of chloroform are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd−P, 2.193(2); Pd−N, 2.128(5); Pd−Cl(1), 2.392(2); Pd−Cl(2), 2.303(2); Cl(1)−Pd−Cl(2), 91.31(6); Cl(1)−Pd−P, 178.08(7); Cl(1)−Pd−N, 94.1(1); Cl(2)−Pd−P, 87.64(6); Cl(2)−Pd−N, 174.4(2); P−Pd−N, 86.9(1).

TABLE 1. Palladium-Catalyzed Asymmetric Allylic Alkylation Using 1[a]



entry	ligand	solvent	temp	time (h)	yield (%)[b]	ee (%) (config)[c]
1	(a*S*)-**1a**	PhMe	rt	24	88	89 (*R*)
2	(a*R*)-**1b**	PhMe	rt	24	89	90 (*S*)
3	(a*R*)-**1c**	PhMe	rt	24	93	93 (*S*)
4	(a*S*)-**1d**	PhMe	rt	24	91	95 (*R*)
5	(a*S*)-**1d**	Et_2O	rt	24	89	94 (*R*)
6	(a*S*)-**1d**	THF	rt	24	70	91 (*R*)
7	(a*S*)-**1d**	PhMe	0 °C	24	27	89 (*R*)

[a] The reactions were carried out on 0.2 mmol scale in various solvents (0.4 mL) at various temperatures with 3.0 equiv of **15** and BSA, in the presence of LiOAc (5 mol %) and ligand **1** (10 mol %) and $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (5 mol %). [b] Isolated yields. [c] Determined by HPLC analysis using a chiral column (Daicel CHIRALCEL OD-H).

phosphorus to the Pd−Cl distance *trans* to the nitrogen [2.392(2) vs 2.303(2) Å].

Palladium-Catalyzed Asymmetric Allylic Alkylation. Finally, we investigated the ability of chiral aminophosphines **1** as chiral ligands for the palladium-catalyzed asymmetric allylic alkylation[21] using 1,3-diphenyl-2-propenyl acetate (**14**) with dimethyl malonate (**15**). This reaction was carried out in the presence of 5 mol % of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$, 10 mol % of **1**, and a mixture of *N*,*O*-bis(trimethylsilyl)acetamide (BSA) and 5 mol % of LiOAc[22] (Table 1). The chiral ligands **1** are able to induce good enantioselectivities in toluene at room temperature (entries 1−4). When the reaction was carried out using (a*S*)-**1d** as a ligand, the enantioselectivity of product (*R*)-**16** was obtained higher than the case of chiral **1a**−**c** with good yield (entry 4 vs entries 1−3). We examined the effect of reaction solvents using the chiral ligand (a*S*)-**1d**. When the reaction was carried out in ether instead of PhMe, (*R*)-**16** was obtained with a similar level of enantioselectivity (entry 4 vs entry 5). By use of THF, the enantioselectivity and yield were slightly decreased (entry 6). We also investigated the effect of reaction temperature. The reaction under 0 °C proceeded slowly with 89% ee (entry 7).

Conclusion

N-Aryl indoline-type C(aryl)−N(amine) bond axially chiral aminophosphines **1** were prepared, and the resolution of these isomers was achieved by using chiral palladium dimer complex (*S*)-**10** as a resolving agent. Finally, the ability of the chiral phosphine ligand **1** is demonstrated in a catalytic asymmetric reaction, such as a palladium-catalyzed asymmetric allylic alkylation, of 1,3-diphenyl-2-propenyl acetate with high enantioselectivity.

Experimental Section

1-Methoxy-2-diphenylphosphinonaphthalene oxide (**2a**)[23] and 2-methoxy-3-methylphenyldiphenylphosphine oxide (**2b**)[15g] were prepared according to the literature method.

Preparation of 2-Methoxy-3-trifluoromethylphenyldiphenylphosphine Oxide (2c): To a mixture of 2-trifluoromethylanisole (1.761 g, 10.0 mmol), TMEDA (1.51 mL, 10.0 mmol), and ether (25 mL) was added dropwise *n*-BuLi in hexane (9.2 mL, 14.7 mmol, 1.66 M) over 10 min. The mixture was stirred at room temperature for 2 h then treated with chlorodiphenylphosphine (1.8 mL, 10.0 mmol), and the resulting mixture was diluted with ether and quenched with 2 M aqueous HCl. The organic layer was washed with 2 M aqueous Na_2CO_3, brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was dissolved in AcOH (50 mL) and treated with 30% aqueous H_2O_2 (1.5 mL) then gradually heated to 80 °C for 2 h. The mixture was cooled to room temperature and diluted with ether (100 mL) then treated with 2 M aqueous NaOH at 0 °C. The water layer was extracted with ether, and the combined extracts were washed with water, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by silica gel chromatography (elution with *n*-hexane:EtOAc = 1:3): 87%; mp 105−106 °C; ^{1}H NMR ($CDCl_3$) δ 3.65 (s, 3H), 7.26 (dt, J = 1.1 and 7.8 Hz, 1H), 7.44−7.60 (m, 7H), 7.68−7.82 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 64.8 (d, J_{CP} = 2.4 Hz), 123.7 (dq, J_{CP} and J_{CF} = 2.4 and 273.3 Hz), 124.2 (d, J_{CP} = 12.2 Hz), 125.5 (dq, J_{CP} and J_{CF} = 7.3 and 31.2 Hz), 129.0 (d, J_{CP} = 12.4 Hz), 130.1 (d, J_{CP} = 101.2 Hz), 132.1 (d, J_{CP} = 10.0 Hz), 132.5 (dq, J_{CP} and J_{CF} = 2.0 and 5.1 Hz), 132.9 (d, J_{CP} = 10.8 Hz), 139.0 (d, J_{CP} = 8.9 Hz), 161.7 (q, J_{CF} = 1.7 Hz); ^{31}P NMR ($CDCl_3$) δ 27.0; EI-MS *m*/*z* (relative intensity) 376 (M^+, 47); HRMS (FAB-MS) *m*/*z* calcd for $C_{20}H_{16}O_2PF_3$ + H 377.0918, found 377.0922.

Typical Procedure for the Preparation of Aminophosphine Oxide 3. To the solution of indoline (0.104 g, 1.03 mmol) in THF (1 mL) was added slowly *n*-BuLi in hexane (0.71 mL, 1.1 mmol, 1.56 M) at −80 °C for 10 min, and then at room temperature for 2 h. After phosphine oxide (1.0 mmol) was added at 0 °C, stirring was continued for 20 h at room temperature. The mixture was diluted with ether and quenched with saturated aqueous NH_4Cl. The organic layer was washed with brine, dried over $MgSO_4$, and

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concentrated under reduced pressure. The residue was purified by silica gel chromatography.

1-[2′-(Diphenylphosphinyl)-1′-naphthalenyl]-2,3-dihydro-1*H*-indole (3a): 83%; mp 138 °C; ^{1}H NMR ($CDCl_3$) δ 2.95−3.01 (m, 2H), 3.80−3.87 (m, 1H), 4.34 (dt, J = 2.5 and 6.8 Hz, 1H), 5.42 (d, J = 5.5 Hz, 1H), 6.48−6.54 (m, 2H), 6.93 (d, J = 5.3 Hz, 1H), 7.14−7.33 (m, 4H), 7.43−7.67 (m, 8H), 7.83−7.93 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 28.7, 56.3, 108.3, 117.4, 123.9, 124.8, 126.2, 126.5, 127.5−128.0 (m), 128.3−129.1 (m), 130.4−130.7 (m), 131.3, 132.0−132.7 (m), 133.3 (d, J_{CP} = 24.9 Hz), 133.7, 137.4, 145.6, 150.8; ^{31}P NMR ($CDCl_3$) δ 25.8; FAB-MS *m*/*z* (relative intensity): 446 (M^+ + 1, 100), 445 (M^+, 90); HRMS (FAB-MS) *m*/*z* calcd for $C_{30}H_{24}NOP$ 445.1596, found 445.1565.

1-[2′-(Diphenylphosphinyl)-6′-methylphenyl]-2,3-dihydro-1*H*-indole (3b): 67%; mp 193 °C; ^{1}H NMR ($CDCl_3$) δ 1.97 (s, 3H), 2.86−2.92 (m, 2H), 3.48−3.61 (m, 1H), 4.31−4.38 (m, 1H), 5.50 (d, J = 7.7 Hz, 1H), 6.45 (t, J = 7.3 Hz, 1H), 6.61 (t, J = 7.6 Hz, 1H), 6.84 (d, J = 7.2 Hz, 1H), 7.11−7.26 (m, 5H), 7.41−7.48 (m, 4H), 7.56−7.63 (m, 2H), 7.80−7.87 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 18.6, 28.6, 54.6, 123.9 126.1, 126.8, 127.0, 127.9−128.5 (m), 130.3−130.4 (m), 130.5, 131.4 (d, J_{CP} = 11.7 Hz), 131.9, 132.2 (d, J_{CP} = 36.0 Hz), 132.5 (d, J_{CP} = 45.3 Hz), 133.5 (d, J_{CP} = 54.6 Hz), 135.8, 136.5 (d, J_{CP} = 8.4 Hz), 137.2, 139.8 (d, J_{CP} = 28.5 Hz), 145.0 (d, J_{CP} = 15.9 Hz), 149.4; ^{31}P NMR ($CDCl_3$) δ 26.3; FAB-MS *m*/*z* (relative intensity): 410 (M^+ + H, 100), 409 (M^+, 90); HRMS (FAB-MS) *m*/*z* calcd for $C_{27}H_{24}NOP$ 409.1596, found 409.1567.

1-[2′-(Diphenylphosphinyl)-6′-trifluoromethylphenyl]-2,3-dihydro-1*H*-indole (3c): 65%; mp 80−82 °C; ^{1}H NMR ($CDCl_3$) δ 2.88−3.03 (m, 2H), 3.73 (q, J = 9.3 Hz, 1H), 4.48 (dt, J = 5.7 and 8.4 Hz, 1H), 5.39 (d, J = 7.6 Hz, 1H), 6.39−6.51 (m, 2H), 6.81 (dd, J = 0.8 and 7.1 Hz, 1H), 7.02−7.25 (m, 3H), 7.43−7.62 (m, 7H), 7.76−7.83 (m, 2H), 7.92 (d, J = 7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 28.7, 55.9, 123.3 (dq, J_{CP} and J_{CF} = 2.4 and 274.7 Hz), 123.6, 125.8, 127.4 (d, J_{CP} = 12.9 Hz), 128.2 (d, J_{CP} = 12.6 Hz), 128.5−128.6 (m), 130.4−130.6 (m), 130.9 (d, J_{CP} = 2.9 Hz), 131.7−131.8 (m), 132.1 (d, J_{CP} = 9.2 Hz), 132.4−133.2 (m), 138.7, (d, J_{CP} = 11.2 Hz), 140.2 (d, J_{CP} = 102.5 Hz), 145.5−145.6 (m), 150.1; ^{31}P NMR ($CDCl_3$) δ 25.9; EI-MS *m*/*z* (relative intensity) 463 (M^+, 100); HRMS (FAB-MS) *m*/*z* calcd for $C_{27}H_{21}ONF_3P$ 463.1313, found 463.1282.

Typical Procedure for the Preparation of Aminophosphine 1a−c. To a mixture of phosphine oxide **3** (0.3 mmol) and triethylamine (0.34 mL, 1.2 mmol) in *m*-xylene (2 mL) was added trichlorosilane (0.24 mL, 1.2 mmol) at 0 °C under an Ar atmosphere. The reaction mixture was refluxed for 6 h. After being cooled to room temperature, the mixture was diluted with ether and quenched with 2 M aqueous NaOH solution. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by silica gel chromatography (elution with *n*-hexane:EtOAc = 6:1).

(±)-1-[2′-(Diphenylphosphino)-1′-naphthalenyl]-2,3-dihydro-1*H*-indole ((±)-1a): 95%; mp 162−163 °C; ^{1}H NMR ($CDCl_3$) δ 3.11 (t, J = 8.8 Hz, 2H), 3.63 (q, J = 7.6 Hz, 1H), 3.78 (q, J = 9.9 Hz, 1H), 5.90 (d, J = 7.6 Hz, 1H), 6.49 (dt, J = 0.7 and 7.4 Hz, 1H), 6.64 (t, J = 7.2 Hz, 1H), 7.03−7.08 (m, 2H), 7.14−7.29 (m, 11H), 7.36−7.40 (m, 1H), 7.58 (d, J = 8.4 Hz, 1H), 7.66 (d, J = 8.8 Hz, 1H), 7.80 (d, J = 8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 29.0, 54.1, 107.0, 124.0, 124.3, 126.4, 126.5, 127.2, 127.8 (d, J_{CP} = 10.0 Hz), 128.1, 128.2−128.8 (m), 129.9, 130.8, 133.8−134.0 (m), 135.7, 137.3, 137.4, 137.8, 137.9, 138.0, 138.1, 143.7, 144.0, 151.6; ^{31}P NMR ($CDCl_3$) δ −14.8; FAB-MS *m*/*z* (relative intensity): 429 (M^+, 10); HRMS (FAB-MS) *m*/*z* calcd for $C_{30}H_{24}NP$ 429.1601, found 429.1623; HPLC Daicel CHIRALCEL OJ (0.46 ϕ × 25 cm, UV 254 nm, hexane:ethanol = 90:10, 0.50 mL/min), t_R = 13.0 (CD, λ_{ext} ($\Delta\epsilon$) 254 (−)) and 31.3 min (CD, λ_{ext} ($\Delta\epsilon$) 254 (+)); X-ray diffraction analysis data of (±)-**1a** (Figure S1). Yellow plate crystals from ethanol, triclinic space group $P\bar{1}$, a = 9.129(4) Å, b = 11.674(4) Å, c = 11.962(4) Å, α = 68.03(3)°, β = 86.95(3)°, γ = 87.76(3)°, V = 1180.3(7) Å^3, Z = 2, ρ = 1.209 g/cm^3, μ (Cu Kα) = 11.5 cm^{-1}. The structure was solved by the direct method of full-matrix least-squares, where the final R and Rw were 0.057 and 0.128 for 2585 reflections, respectively.

(±)-1-[2′-(Diphenylphospino)-6′-methylphenyl]-2,3-dihydro-1*H*-indole ((±)-1b): 88%; mp 193 °C; ^{1}H NMR ($CDCl_3$) δ 1.95 (s, 3H), 2.92−2.98 (m, 2H), 3.50 (t, J = 8.7 Hz, 2H), 5.64 (d, J = 7.7 Hz, 1H), 6.44 (t, J = 7.2 Hz, 1H), 6.65−6.75 (m, 2H), 6.92−6.95 (m, 1H), 7.04−7.25 (m, 7H), 7.25−7.27 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 18.4 (d, J_{CP} = 10.0 Hz), 28.8, 52.6 (d, J_{CP} = 16.4 Hz), 106.4, 116.7, 124.1, 127.0, 127.5, 128.1 (t, J_{CP} = 24.6 Hz), 128.4 (t, J_{CP} = 28.0 Hz), 131.4, 132.5, 133.9 (d, J_{CP} = 36.4 Hz), 134.1 (d, J_{CP} = 36.4 Hz), 137.1 (d, J_{CP} = 10.0 Hz), 137.2, 137.8 (d, J_{CP} = 13.2 Hz), 138.0 (d, J_{CP} = 6.8 Hz), 141.5 (dd, J_{CP} = 11.4 and 21.4 Hz), 150.3; ^{31}P NMR ($CDCl_3$) δ −14.1; FAB-MS *m*/*z* (relative intensity): 393 (M^+, 9); HRMS (FAB-MS) *m*/*z* calcd for $C_{27}H_{24}NP$ 393.1646, found 393.1624; HPLC Daicel CHIRALPAK AD-H × 2 (0.46 ϕ × 25 cm × 2, UV 254 nm, hexane:ethanol = 99.7:0.3, 0.15 mL/min), t_R = 58.1 (CD, λ_{ext} ($\Delta\epsilon$) 254 (−)) and 63.3 min (CD, λ_{ext} ($\Delta\epsilon$) 254 (+)); X-ray diffraction analysis data of (±)-**1b** (Figure S2). Colorless prismatic crystals from hexanes−ethanol, monoclinic space group $P2_1/c$, a = 11.445(3) Å, b = 11.105(4) Å, c = 14.798(8) Å, β = 113.59(8)°, V = 2189.3(15) Å^3, Z = 4, ρ = 1.194 g/cm^3, μ (Cu Kα) = 11.9 cm^{-1}. The structure was solved by the direct method of full-matrix least-squares, where the final R and Rw were 0.043 and 0.072 for 1783 reflections, respectively.

(±)-1-[2′-(Diphenylphosphino)-6′-trifluoromethylphenyl]indoline ((±)-1c): 86%; mp 95−96 °C; ^{1}H NMR ($CDCl_3$) δ 3.07−3.25 (m, 2H), 3.75−3.92 (m, 2H), 5.64 (d, J = 7.7 Hz, 1H), 6.53 (dt, J = 0.74 and 7.3 Hz, 1H), 6.66 (t, J = 7.3 Hz, 1H), 7.04−7.12 (m, 3H), 7.16−7.38 (m, 10H), 7.72−7.76 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 29.0, 54.8 (dd, J_{CP} = 1.3 and 7.7 Hz), 107.1, 117.1, 123.7 (dq, J_{CP} and J_{CF} = 2.2 and 273.8 Hz), 124.1, 126.8, 127.8, 128.2−128.9 (m), 132.5 (dq, J_{CP} and J_{CF} = 4.7 and 30.1 Hz), 133.4 (d, J_{CP} = 19.6 Hz), 134.0 (d, J_{CP} = 21.2 Hz), 135.8 (d, J_{CP} = 12.7 Hz), 137.3 (d, J_{CP} = 12.7 Hz), 139.9, 144.1 (d, J_{CP} = 17.5 Hz), 146.1 (dd, J_{CP} = 1.4 and 24.5 Hz), 151.7 (d, J_{CP} = 1.9 Hz); ^{31}P NMR ($CDCl_3$) δ −17.9; EI-MS *m*/*z* (relative intensity) 447 (M^+, 100); HRMS (FAB-MS) *m*/*z* calcd for $C_{26}H_{20}NF_3P$ 447.1364, found 447.1352; HPLC Daicel CHIRALPAK AD-H × 2 (0.46 ϕ × 25 cm × 2, UV 254 nm, hexane:ethanol = 99.7:0.3, 0.15 mL/min), t_R = 33.0 (CD, λ_{ext} ($\Delta\epsilon$) 254 (−)) and 35.5 min (CD, λ_{ext} ($\Delta\epsilon$) 254 (+)); X-ray diffraction analysis data of (±)-**1c** (Figure S3). Colorless prismatic crystals from hexane, triclinic space group $P\bar{1}$, a = 9.550-(2) Å, b = 10.913(6) Å, c = 11.511(5) Å, α = 108.01(4)°, β = 92.35(3)°, γ = 96.46(3)°, V = 1130.1(8) Å^3, Z = 2, ρ = 1.203 g/cm^3, μ (Cu Kα) = 12.4 cm^{-1}. The structure was solved by the direct method of full-matrix least-squares, where the final R and Rw were 0.053 and 0.158 for 3658 reflections, respectively.

Preparation of (*E*)-1-(2,3-Difluorobenzaldehyde)-*N*,*N*-dimethylhydrazone (5). A mixture of 2,3-difluorobenzaldehyde (**4**) (2.84 g, 20.0 mmol) and *N*,*N*-dimethylhydrazine (1,202 g, 20.0 mmol) in diethyl ether (20 mL) was stirred at room temperature for 1 h in the presence of a catalytic amount of trifluoroacetic acid (ca. 1 drop). The mixture was concentrated under reduced pressure, and the residue was purified by silica gel column chromatography (elution with *n*-hexane:EtOAc = 15:1): 3.53 g, 19.1 mmol, 96%; ^{1}H NMR ($CDCl_3$) δ 3.03 (s, 6H), 6.94−7.01 (m, 2H), 7.30 (s, 1H), 7.57−7.62 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 42.1, 114.2 (d, J_{CF} = 17.1 Hz), 119.3 (t, J_{CF} = 3.0 Hz), 122.2 (t, J_{CF} = 4.4 Hz), 123.2 (dd, J_{CF} = 4.6 and 7.1 Hz), 126.5 (d, J_{CF} = 6.8 Hz), 149.1 (d, J_{CF} = 12.5 Hz), 152.4 (d, J_{CF} = 12.5 Hz); EI-MS *m*/*z* (relative intensity) 184 (M^+, 100); HRMS (FAB-MS) *m*/*z* calcd for $C_9H_{10}F_2N_2$ 184.0812, found 184.0816.

Preparation of (*E*)-1-[3-Fluoro-2-(indolin-1-yl)benzaldehyde]-*N*,*N*-dimethylhydrazone (6). To a solution of indoline (4.29 g, 36.0 mmol) in THF (36 mL) was added slowly *n*-BuLi in hexane (23.9 mL, 37.8 mmol, 1.58 M) at −78 °C, and then stirred at the same temperature for 10 min. After the THF solution of **5** (3.32 g,

18.0 mmol in 18 mL) was added at −78 °C, stirring was continued for 24 h at room temperature. The mixture was quenched with saturated aqueous NH_4Cl and diluted with ether. The organic layer was washed with water and brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (elution with *n*-hexane:EtOAc = 40:1): 4.87 g, 17.2 mmol, 96%; ^{1}H NMR ($CDCl_3$) δ 2.89 (s, 6H), 3.17−3.22 (m, 2H), 3.77−3.91 (m, 2H), 6.17 (d, J = 7.8 Hz, 1H), 6.67 (dt, J = 0.7 and 7.4 Hz, 1H), 6.94−7.01 (m, 2H), 7.15 (d, J = 1.0 Hz, 1H), 7.19 (dd, J = 2.8 and 8.3 Hz, 1H), 7.35 (s, 1H), 7.75 (d, J = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 29.5, 43.1, 54.3, 107.9, 115.4 (d, J_{CF} = 20.0 Hz), 118.3, 120.9, 125.0, 127.7, 128.0 (d, J_{CF} = 8.8 Hz), 128.6−129.1 (m), 129.4, 134.1 (dd, J_{CF} = 17.0 and 55.0 Hz), 138.5 (d, J_{CF} = 3.0 Hz), 151.6, 161.0 (d, J_{CF} = 250.4 Hz); EI-MS *m*/*z* (relative intensity) 283 (M^+, 12); HRMS (FAB-MS) *m*/*z* calcd for $C_{17}H_{18}FN_3$ 283.1485, found 283.1484.

Preparation of (*E*)-1-[3-Diphenylphosphino-2-(indolin-1-yl)-benzaldehyde]-*N*,*N*-dimethylhydrazone (7). To a solution of **6** (3.54 g, 12.5 mmol) in THF (5.0 mL) was added slowly potassium diphenylphosphide in THF (50.0 mL, 25.0 mmol, 0.50 M) at room temperature, and then stirred at 55 °C for 24 h. After cooled to room temperature, the mixture was quenched with saturated aqueous NH_4Cl and diluted with EtOAc. The organic layer was washed with water and brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (elution with *n*-hexane:EtOAc = 40:1): 5.10 g, 11.3 mmol, 97%; mp 133−134 °C; ^{1}H NMR ($CDCl_3$) δ 2.69 (s, 6H), 2.98−3.03 (m, 2H), 3.54−3.63 (m, 2H), 5.83 (d, J = 7.8 Hz, 1H), 6.52 (dt, J = 0.7 and 6.9 Hz, 1H), 6.75 (t, J = 7.4 Hz, 1H), 6.85 (ddd, J = 1.5, 3.1, and 7.5 Hz, 1H), 6.92 (s, 1H), 7.01 (d, J = 7.1 Hz, 1H), 7.18−7.24 (m, 5H), 7.32−7.35 (m, 5H), 6.52 (dd, J = 1.3 and 7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 29.2, 42.9, 54.6 (d, J_{CP} = 4.4 Hz), 107.9, 117.6, 124.5, 127.4−129.8 (m), 133.2, 134.5 (d, J_{CP} = 20.5 Hz), 136.1 (d, J_{CP} = 3.0 Hz), 137.6 (d, J_{CP} = 11.7 Hz), 138.3 (d, J_{CP} = 12.7 Hz), 141.8 (d, J_{CP} = 8.7 Hz), 144.5 (d, J_{CP} = 22.5 Hz), 151.9; ^{31}P NMR ($CDCl_3$) δ −14.8; EI-MS *m*/*z* (relative intensity) 449 (M^+, 20); HRMS (FAB-MS) *m*/*z* calcd for $C_{29}H_{28}N_3P$ + H 450.2099, found 450.2074.

Preparation of 3-Diphenylphosphino-2-(indolin-1-yl)benzaldehyde (8). A mixture of **7** (0.45 g, 1.00 mmol) and aqueous HCl (10.0 mL, 6 M) in THF (10 mL) was stirred at 0 °C for 5 h. The mixture was diluted with ether, then the organic layer was washed with 6 M aqueous HCl and brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (elution with *n*-hexane:EtOAc = 8:1): 0.25 g, 0.62 mmol, 62%; mp 134−136 °C; ^{1}H NMR ($CDCl_3$) δ 3.10 (dd, J = 7.7 and 9.5 Hz, 2H), 3.66 (q, J = 9.6 Hz, 1H), 3.86−3.94 (m, 1H), 5.80 (d, J = 7.8 Hz, 1H), 6.58 (t, J = 7.2 Hz, 1H), 6.74 (t, J = 7.4 Hz, 1H), 7.05 (d, J = 7.2 Hz, 1H), 7.20−7.40 (m, 12H), 7.97 (dd, J = 1.7 and 7.5 Hz, 1H), 10.0 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 28.9, 56.3 (d, J_{CP} = 5.9 Hz), 106.6, 118.0, 124.5, 127.3, 127.9−128.9 (m), 130.3, (d, J_{CP} = 5.2 Hz), 135.4 (d, J_{CP} = 3.4 Hz), 136.0 (d, J_{CP} = 11.5 Hz), 136.7 (d, J_{CP} = 12.3 Hz), 140.2, 142.9 (d, J_{CP} = 13.8 Hz), 150.5 (d, J_{CP} = 22.7 Hz), 152.1, 190.4; ^{31}P NMR ($CDCl_3$) δ −16.2; EI-MS *m*/*z* (relative intensity) 407 (M^+, 100); HRMS (FAB-MS) *m*/*z* calcd for $C_{27}H_{22}$-NOP 407.1439, found 407.1429.

Preparation of 3-Diphenylphosphino-2-(indolin-1-yl)benzyl Alcohol (9). A mixture of **8** (1.02 g, 2.50 mmol) and sodium borohydride (0.47 g, 12.5 mmol) in MeOH (25 mL) was stirred at 0 °C for 1 h. After the mixture was diluted with ether, the organic layer was washed with water and brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (elution with *n*-hexane:EtOAc = 6:1): 0.94 g, 2.30 mmol, 92%; mp 134−135 °C; ^{1}H NMR ($CDCl_3$) δ 1.93 (t, J = 5.2 Hz, 2H), 3.01−3.07 (m, 2H), 3.51−3.74 (m, 2H), 4.35−4.47 (m, 2H), 5.67 (d, J = 7.7 Hz, 1H), 6.52 (dt, J = 0.8 and 7.3 Hz, 1H), 6.70 (t, J = 7.3 Hz, 1H), 6.95−7.02 (m, 2H), 7.16−7.34 (m, 11H), 7.54 (dd, J = 0.9 and 7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 28.9, 54.1 (d, J_{CP} = 5.5 Hz), 61.4 (d, J_{CP} = 2.2 Hz), 106.2, 117.3, 124.5, 127.2, 128.1−128.7 (m), 130.4, 133.8−134.3 (m), 136.9 (d, J_{CP} = 11.7 Hz), 137.7 (d, J_{CP} = 12.4 Hz), 141.0 (d, J_{CP} = 2.7 Hz), 141.6 (d, J_{CP} = 10.4 Hz), 144.2 (d, J_{CP} = 22.9 Hz), 151.0; ^{31}P NMR ($CDCl_3$) δ −15.3; EI-MS *m*/*z* (relative intensity) 409 (M^+, 100); HRMS (FAB-MS) *m*/*z* calcd for $C_{27}H_{24}NOP$ 409.1596, found 409.1602; X-ray diffraction analysis data of **9** (Figure S5). Colorless prismatic crystals from methanol, $C_{27}H_{24}NOP$, monoclinic space group *C*2/*c*, a = 32.489-(13) Å, b = 8.345(5) Å, c = 21.857(8) Å, β = 132.24(3)°, V = 4387(4) Å^3, Z = 8, ρ = 1.240 g/cm^3, μ (Cu Kα) = 12.4 cm^{-1}. The structure was solved by the direct method of full-matrix least-squares, where the final R and Rw were 0.0585 and 0.1612 for 4170 reflections, respectively.

Preparation of (±)-3-Diphenylphosphino-2-(indolin-1-yl)benzyl Acetate ((±)-1d). A mixture of **9** (0.45 g, 1.10 mmol) and acetic anhydride (0.24 mL, 2.20 mmol) in triethylamine (22 mL) was stirred at room temperature for 2 h in the presence of a catalytic amount of DMAP (0.01 g, 0.11 mmol). After the mixture was diluted with ether, the organic layer was washed with water and brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (elution with *n*-hexane:EtOAc = 8:1): 0.48 g, 1.07 mmol, 97%; mp 106−107 °C; ^{1}H NMR ($CDCl_3$) δ 1.97 (s, 3H), 3.04−3.10 (m, 2H), 3.63−3.80 (m, 2H), 4.91 (t, J = 13.2 Hz, 2H), 5.67 (d, J = 7.7 Hz, 1H), 6.52 (t, J = 7.3 Hz, 1H), 6.71 (t, J = 7.6 Hz, 1H), 7.00−7.35 (m, 10H), 7.45 (dd, J = 0.8 and 7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 21.3, 29.3, 54.2 (d, J_{CP} = 5.9 Hz), 63.0 (d, J_{CP} = 2.2 Hz), 106.8, 117.6, 124.7, 127.4, 128.2, 128.6−129.0 (m), 131.3, 134.1−135.0 (m), 137.1−137.2 (m), 137.9 (d, J_{CP} = 12.7 Hz), 142.5 (d, J_{CP} = 11.4 Hz), 145.5 (d, J_{CP} = 22.9 Hz), 124.1, 151.0, 171.0; ^{31}P NMR ($CDCl_3$) δ −15.2; EI-MS *m*/*z* (relative intensity) 451 (M^+, 100); HRMS (FAB-MS) *m*/*z* calcd for $C_{28}H_{25}O_2NP$ 451.1701, found 451.1679; HPLC Daicel CHIRALCEL OD + OD-H (0.46 ϕ × 25 cm × 2, UV 254 nm, hexane:ethanol = 99:1, 0.50 mL/min), t_R = 23.2 (CD, λ_{ext} ($\Delta\epsilon$) 254 (+)) and 24.5 min (CD, λ_{ext} ($\Delta\epsilon$) 254 (−)); X-ray diffraction analysis data of (±)-**1d** (Figure S4). Colorless needle crystals from *n*-hexane, $C_{28}H_{25}O_2NP$, orthorhombic space group *Pbca*, a = 18.401(6) Å, b = 35.757(11) Å, c = 7.264(3) Å, V = 4779.(3) Å^3, Z = 8, ρ = 1.255 g/cm^3, μ (Cu Kα) = 12.2 cm^{-1}. The structure was solved by the direct method of full-matrix least-squares, where the final R and Rw were 0.047 and 0.099 for 1620 reflections, respectively.

Typical Procedure for Preparation and Separation of Diastereomeric Complex Mixtures (a*S*,*S*)-11 and (a*R*,*S*)-12. A mixture of (±)-**1** (0.50 mmol) and (*S*)-(+)-di-μ-chlorobis[2-[(dimethylamino)ethyl]phenyl-*C*^{2},*N*]dipalladium(II) ((*S*)−(+)-**10**) (0.15 g, 0.25 mmol) in toluene (1.0 mL) was stirred at room temperature for 1 h. The mixture was concentrated under reduced pressure, and the residue was purified by silica gel column chromatography (elution with *n*-hexane:Et_2O = 2:1) to separate the diastereomeric mixture of (a*S*,*S*)-**11** and (a*R*,*S*)-**12**.

(a*S*,*S*)-(+)-[Dimethyl(1-(1-phenyl)ethyl)aminato-*C*^{2},*N*]-[1-(indolin-1-yl)(2-naphthyl)diphenylphosphine]palladium(II) chloride ((a*S*,*S*)-(+)-11a): 46%; R_f = 0.68 (Et_2O) (less polar agent on silica gel column chromatography); $[\alpha]^{25}_D$ +92.8° (*c* 1.01, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.44 (d, J = 6.5 Hz, 3H), 2.50 (d, J = 2.4 Hz, 3H), 2.71 (d, J = 2.1 Hz, 3H), 2.99−3.29 (m, 2H), 3.70−3.93 (m, 2H), 4.36 (s, 1H), 5.47 (d, J = 6.8 Hz, 2H), 6.36−6.55 (m, 4H), 6.80−6.88 (m, 2H), 7.00−7.10 (m, 3H), 7.19−7.25 (m, 2H), 7.37−7.48 (m, 6H), 7.60−7.69 (m, 2H), 7.78 (d, J = 8.6 Hz, 1H), 7.87−7.99 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 16.7, 29.4, 44.2, 49.1, 55.5, 74.2, 109.9, 117.7, 122.5, 123.7 (d, J_{CP} = 8.0 Hz), 124.7−124.9 (m), 125.7, 126.6, (d, J_{CP} = 5.4 Hz), 127.2−130.1 (m), 130.5 (d, J_{CP} = 7.1 Hz), 131.1 (d, J_{CP} = 46.7 Hz), 135.8−137.5 (m), 143.5 (d, J_{CP} = 8.3 Hz), 149.7, 151.8, 153.6; ^{31}P NMR ($CDCl_3$) δ 33.3; FAB-MS *m*/*z* (relative intensity) 718 (M^+, 7), 683 ([M − Cl]$^+$, 65); HRMS (FAB-MS) *m*/*z* calcd for $C_{40}H_{38}ClN_2PPd$ + H 719.1586, found 719.1638.

(a*R*,*S*)-(−)-[Dimethyl(1-(1-phenyl)ethyl)aminato-*C*^{2},*N*]-[1-(indolin-1-yl)(2-naphthyl)diphenylphosphine]palladium(II) chloride ((a*R*,*S*)-(−)-12a): 46%; R_f = 0.61 (Et_2O) (more polar agent on silica gel column chromatography); $[\alpha]^{25}_D$ −192.5° (*c* 1.00, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.86 (d, J = 6.4 Hz, 3H), 2.69 (d, J = 1.3 Hz, 3H), 2.76 (d, J = 3.3 Hz, 3H), 3.12−3.34 (m, 2H), 3.62 (quint, J = 6.0 Hz, 1H), 3.86−3.96 (m), 4.99 (d, J = 7.7 Hz, 1H), 5.45 (t, J = 9.1 Hz, 1H), 6.29−6.48 (m, 4H), 6.79−7.06 (m, 6H), 7.15−7.20 (m, 1H), 7.33−7.41 (m, 5H), 7.47−7.56 (m), 7.74 (d, J = 8.6 Hz, 1H), 7.86 (d, J = 8.0 Hz, 1H), 8.26−8.30 (m); ^{13}C NMR ($CDCl_3$) δ 23.1, 29.2, 47.0, 50.5, 55.0, 75.6 (d, J_{CP} = 3.2 Hz), 109.0, 117.6, 122.1, 123.5, 123.9, 124.6−125.7 (m), 126.5 (d, J_{CP} = 16.8 Hz), 127.0 (d, J_{CP} = 9.2 Hz), 127.4 (d, J_{CP} = 10.8 Hz), 128.0−128.7 (m), 129.2, 129.5−130.8 (m), 131.3, 135.5, 135.6, 136.4−136.9 (m), 137.1 (d, J_{CP} = 11.2 Hz), 143.0 (d, J_{CP} = 7.3 Hz), 148.3, 151.5, 155.1; ^{31}P NMR ($CDCl_3$) δ 34.4; FAB-MS *m*/*z* (relative intensity) 718 (M^+, 10), 683 ($[M - Cl]^+$, 75); HRMS (FAB-MS) *m*/*z* calcd for $C_{40}H_{38}ClN_2PPd$ + H 719.1586, found 719.1631; X-ray diffraction analysis data of (a*R*,*S*)-(−)-**12a** (Figure S6). Yellow prismatic crystals from ethanol:*n*-hexane, $C_{40}H_{38}ClN_2PPd$, orthorhombic space group $P2_12_12_1$, a = 10.4700(13) Å, b = 15.561(2) Å, c = 22.835(3) Å, V = 3720.3(9) Å^3, Z = 4, ρ = 1.285 g/cm^3, μ (Mo Kα) = 6.42 cm^{-1}. The structure was solved by the direct method of full-matrix least-squares, where the final R and Rw were 0.056 and 0.074 for 4346 reflections, respectively.

(a*S*,*S*)-(+)-[Dimethyl(1-(1-phenyl)ethyl)aminato-*C*^{2},*N*]-[1-(indolin-1-yl)-6-methyl(2-phenyl)diphenylphosphine]palladium(II) chloride ((a*S*,*S*)-(+)-11b): 45%; R_f = 0.53 (Et_2O) (less polar agent on silica gel column chromatography); $[\alpha]^{25}_D$ +94.8° (*c* 0.51, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.42 (d, J = 6.5 Hz, 3H), 1.90 (s, 3H), 2.49 (d, J = 2.3 Hz, 3H), 2.74 (d, J = 1.8 Hz, 3H), 2.86−3.48 (m, 3H), 3.96 (d, J = 2.4 Hz, 1H), 4.39 (s, 1H), 5.51 (s, 1H), 6.36−6.51 (m, 4H), 6.80−7.43 (m, 7H), 7.57 (t, J = 8.9 Hz, 2H), 7.95 (t, J = 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 16.4, 19.2, 29.4, 44.1, 49.3, 54.3, 74.2, 109.0, 117.6, 122.7, 123.8 (d, J_{CP} = 11.2 Hz), 125.0 (d, J_{CP} = 6.2 Hz), 126.7−126.8 (m), 127.6 (d, J_{CP} = 10.6 Hz), 128.0 (d, J_{CP} = 10.2 Hz), 128.6−131.8 (m), 134.9, 135.8−137.7 (m), 138.4, 139.0 (d, J_{CP} = 6.0 Hz), 144.0 (d, J_{CP} = 8.8 Hz), 149.9, 150.7, 153.6; ^{31}P NMR ($CDCl_3$) δ 33.1; FAB-MS *m*/*z* (relative intensity) 682 (M^+, 5) 647 ($[M - Cl]^+$, 25); HRMS (FAB-MS) *m*/*z* calcd for $C_{37}H_{38}ClN_2PPd$ 682.1496, found 682.1492; X-ray diffraction analysis data of (a*S*,*S*)-(+)-**11b** (Figure S7). Yellow prismatic crystals from ethanol:*n*-hexane, $C_{37}H_{38}ClN_2PPd$, monoclinic space group C_2, a = 38.3957(12) Å, b = 9.6498(3) Å, c = 9.6342(3) Å, V = 3499.74(19) Å^3, Z = 4, ρ = 1.297 g/cm^3, μ (Mo Kα) = 6.78 cm^{-1}. The structure was solved by the direct method of full-matrix least-squares, where the final R and Rw were 0.0600 and 0.1932 for 6992 reflections, respectively.

(a*R*,*S*)-(−)-[Dimethyl(1-(1-phenyl)ethyl)aminato-*C*^{2},*N*]-[1-(indolin-1-yl)-6-methyl(2-phenyl)diphenylphosphine]palladium(II) chloride ((a*R*,*S*)-(−)-12b): 42%; R_f = 0.36 (Et_2O) (more polar agent on silica gel column chromatography); $[\alpha]^{25}_D$ −139.4° (*c* 0.52, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.84 (s, 3H), 1.86 (s, 3H), 2.68 (d, J = 1.6 Hz, 3H), 2.79 (d, J = 3.3 Hz, 3H), 2.98−3.19 (m, 2H), 3.54−3.69 (m, 2H), 5.04 (d, J = 6.9 Hz, 1H), 5.46 (s, 1H), 6.35−6.44 (m, 4H), 6.78−7.08 (m, 7H), 7.14 (dt, J = 2.0 and 7.6 Hz, 1H), 7.23−7.25 (m, 2H), 7.42−7.49 (m, 5H), 8.24 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 19.7 (d, J_{CP} = 1.4 Hz), 23.8, 29.5, 30.1, 47.6, 51.0 (d, J_{CP} = 2.9 Hz), 108.4, 117.8, 122.4, 123.8, 124.3, 125.1 (d, J_{CP} = 6.1 Hz), 126.7−128.8 (m), 129.9 (d, J_{CP} = 2.3 Hz), 130.6 (d, J_{CP} = 2.2 Hz), 131.2−131.3 (m), 131.9, 135.1 (d, J_{CP} = 2.1 Hz), 135.7 (d, J_{CP} = 11.5 Hz), 137.2 (d, J_{CP} = 12.2 Hz), 138.2 (d, J_{CP} = 11.1 Hz), 139.1 (d, J_{CP} = 6.4 Hz), 139.1 (d, J_{CP} = 57.6 Hz), 144.0 (d, J_{CP} = 8.1 Hz), 148.5, 150.6, 155.5 (d, J_{CP} = 2.0 Hz); ^{31}P NMR ($CDCl_3$) δ 34.1; FAB-MS *m*/*z* (relative intensity) 682 (M^+, 5), 647 ($[M - Cl]^+$, 15); HRMS (FAB-MS) *m*/*z* calcd for $C_{37}H_{38}ClN_2PPd$ 682.1496, found 682.1558.

(a*S*,*S*)-(+)-[Dimethyl(1-(1-phenyl)ethyl)aminato-*C*^{2},*N*]-[1-(indolin-1-yl)-6-trifluoromethyl(2-phenyl)diphenylphosphine]palladium(II) chloride ((a*S*,*S*)-(+)-11c): 45%; R_f = 0.50 (Et_2O) (less polar agent on silica gel column chromatography); $[\alpha]^{25}_D$ +109.9° (*c* 1.01, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.41 (d, J = 6.6 Hz, 3H), 2.45 (d, J = 2.4 Hz, 3H), 2.94 (d, J = 2.9 Hz, 3H), 2.97−3.24 (m, 2H), 3.61−3.71 (m, 1H), 5.04 (s, 1H), 5.24 (s, 1H), 6.34−6.47 (m, 4H), 6.82−6.96 (m, 5H), 7.13 (t, J = 7.0 Hz, 1H), 7.37−7.55 (m, 7H), 7.77 (d, J = 7.7 Hz, 1H), 8.09−8.15 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 13.8, 29.6 (d, J_{CP} = 18.0 Hz), 42.9, 49.2 (d, J_{CP} = 2.7 Hz), 55.6 (d, J_{CP} = 2.0 Hz), 73.7 (d, J_{CP} = 2.6 Hz), 108.3, 117.6, 123.1 (d, J_{CP} = 10.1 Hz), 124.0−132.0 (m), 135.6 (d, J_{CP} = 11.4 Hz), 136.7−137.3 (m), 142.8 (d, J_{CP} = 7.0 Hz), 143.6 (d, J_{CP} = 9.2 Hz), 150.2, 150.9, 152.9; ^{31}P NMR ($CDCl_3$) δ 33.9; FAB-MS *m*/*z* (relative intensity) 736 (M^+, 10), 701 ($[M - Cl]^+$, 35); HRMS (FAB-MS) *m*/*z* calcd for $C_{37}H_{35}ClF_3N_2PPd$ 736.1213, found 736.1158.

(a*R*,*S*)-(−)-[Dimethyl(1-(1-phenyl)ethyl)aminato-*C*^{2},*N*]-[1-(indolin-1-yl)-6-trifluoromethyl(2-phenyl)diphenylphosphine]palladium(II) chloride ((a*R*,*S*)-(−)-12c): 45%; R_f = 0.39 (Et_2O) (more polar agent on silica gel column chromatography); $[\alpha]^{25}_D$ −147.6° (*c* 1.00, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.89 (d, J = 6.4 Hz, 3H), 2.68 (d, J = 1.5 Hz, 3H), 2.84 (d, J = 3.5 Hz, 3H), 3.06−3.24 (m, 2H), 3.55 (quint, J = 6.2 Hz, 1H), 3.81 (q, J = 10.1 Hz, 1H), 4.95 (d, J = 7.6 Hz, 1H), 5.86 (s, 1H), 6.29−6.42 (m, 4H), 6.77−6.89 (m, 5H), 6.96−7.05 (m, 2H), 7.33−7.54 (m, 7H), 7.75 (d, J = 7.7 Hz, 1H), 8.28−8.33 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 13.8, 24.6, 29.5, 48.3, 51.3 (d, J_{CP} = 3.0 Hz), 55.6, 76.5 (d, J_{CP} = 3.2 Hz), 108.3, 118.0, 122.2−124.6 (m), 125.1 (d, J_{CP} = 6.2 Hz), 125.5−126.4 (m), 127.2 (d, J_{CP} = 9.3 Hz), 128.1−128.4 (m), 129.1 (d, J_{CP} = 10.0 Hz), 130.3−131.9 (m), 135.8 (d, J_{CP} = 11.7 Hz), 137.0 (d, J_{CP} = 12.2 Hz), 137.3 (d, J_{CP} = 5.2 Hz), 138.2 (d, J_{CP} = 11.2 Hz), 142.7−143.4 (m), 144.1 (d, J_{CP} = 8.0 Hz), 147.9, 150.2 (d, J_{CP} = 1.4 Hz), 155.8 (d, J_{CP} = 2.0 Hz); ^{31}P NMR ($CDCl_3$) δ 34.9; FAB-MS *m*/*z* (relative intensity) 736 (M^+, 10), 701 ($[M - Cl]^+$, 50); HRMS (FAB-MS) *m*/*z* calcd $C_{37}H_{35}ClF_3N_2PPd$ 736.1213, found 736.1221. X-ray diffraction analysis data of (a*R*,*S*)-(−)-**12c** (Figure S8). Yellow prismatic crystals from ethanol:*n*-hexane, $C_{37}H_{35}ClF_3N_2PPd$, orthorhombic space group $P2_12_12_1$, a = 9.2400(10) Å, b = 14.715(2) Å, c = 27.222(4) Å, V = 3701.4(8) Å^3, Z = 8, ρ = 1.223 g/cm^3, μ (Mo Kα) = 6.58 cm^{-1}. The structure was solved by the direct method of full-matrix least-squares, where the final R and Rw were 0.065 and 0.086 for 4483 reflections, respectively.

(a*S*,*S*)-(+)-[Dimethyl-(1-phenylethyl)aminato-*C*^{2},*N*]-[3-diphenylphosphino-2-(indolin-1-yl)benzyl acetate]palladium(II) chloride ((a*S*,*S*)-(+)-11d): 47%; R_f = 0.42 (Et_2O) (less polar agent on silica gel column chromatography); $[\alpha]^{25}_D$ +70.5° (*c* 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.40 (d, J = 6.5 Hz, 3H), 1.98 (s, 3H), 2.48 (d, J = 2.5 Hz, 3H), 2.73 (s, 3H), 2.88−3.38 (m, 2H), 3.39−3.49 (m, 1H), 3.92 (s, 1H), 4.27 (s, 1H), 4.71 (dd, J = 13.3 and 20.1 Hz, 2H), 5.60 (s, 1H), 6.39−6.44 (m, 4H), 6.81−6.94 (m, 3H), 7.05−7.10 (m, 2H), 7.19−7.72 (m, 9H), 7.91−7.97 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 16.5, 21.0, 29.4, 44.2, 49.4 (d, J_{CP} = 2.6 Hz), 55.8, 62.0 (d, J_{CP} = 1.9 Hz), 74.3 (d, J_{CP} = 2.7 Hz), 109.0, 118.2, 122.7, 123.9, 125.0 (d, J_{CP} = 6.2 Hz), 126.7, 127.7 (d, J_{CP} = 9.1 Hz), 127.7 (d, J_{CP} = 10.5 Hz), 128.1 (d, J_{CP} = 10.1 Hz), 128.2, 128.6, 128.9, 130.2 (dd, J_{CP} = 2.2 and 21.7 Hz), 130.6, 131.2, 132.8 (d, J_{CP} = 11.8 Hz), 133.2, (d, J_{CP} = 4.3 Hz), 136.0 (d, J_{CP} = 11.3 Hz), 136.8 (d, J_{CP} = 12.2 Hz), 137.2−137.4 (m), 138.4, 139.1, 144.3 (d, J_{CP} = 9.2 Hz), 149.7, 150.8, 153.7, 170.5; ^{31}P NMR ($CDCl_3$) δ 33.1; FAB-MS *m*/*z* (relative intensity) 740 (M^+, 5); HRMS (FAB-MS) *m*/*z* calcd for $C_{39}H_{40}ClN_2O_2PPd$ 740.1562, found 740.1513; X-ray diffraction analysis data of (a*S*,*S*)-(+)-**11d** (Figure S8). Yellow prismatic crystals from acetone:*n*-hexane mixed solvent, $C_{39}H_{40}ClN_2O_2PPd$, monoclinic space group $C2$, a = 39.149(8) Å, b = 9.736(2) Å, c = 9.566(2) Å, β = 96.414(5)°, V = 3623.3(13) Å^3, Z = 4, ρ = 1.359 g/cm^3, μ (Mo Kα) = 6.65 cm^{-1}. The structure was solved by the direct method of full-matrix

least-squares, where the final *R* and *Rw* were 0.050 and 0.055 for 36582 reflections, respectively.

(a*R*,*S*)-(−)-[Dimethyl-(1-phenylethyl)aminato-*C*^{2},*N*]-[3-diphenylphosphino-2-(indolin-1-yl)benzyl acetate]palladium(II) chloride ((a*R*,*S*)-(−)-12d): 45%; R_f = 0.32 (Et_2O) (more polar agent on silica gel column chromatography); $[\alpha]^{25}_D$ −100.6° (*c* 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.85 (d, J = 6.4 Hz, 3H), 1.95 (s, 3H), 2.67 (s, 3H), 2.79 (d, J = 3.2 Hz, 3H), 3.01−3.23 (m, 2H), 3.57−3.67 (m, 2H), 4.68 (dd, J = 13.4 and 15.4 Hz, 2H), 5.07 (d, J = 7.1 Hz, 1H), 5.49 (s, 1H), 6.35−6.45 (m, 4H), 6.78−6.96 (m, 6H), 7.19−7.30 (m, 2H), 7.30−7.51 (m, 6H), 8.24 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 21.3, 23.8, 29.5, 47.7, 51.0 (d, J_{CP} = 2.9 Hz), 55.8, 62.9 (d, J_{CP} = 1.8 Hz), 76.1 (d, J_{CP} = 3.1 Hz), 108.4, 118.5, 122.5, 124.2 (d, J_{CP} = 23.6 Hz), 125.1 (d, J_{CP} = 6.1 Hz), 126.8, 127.2 (d, J_{CP} = 9.3 Hz), 127.9 (d, J_{CP} = 10.9 Hz), 128.5, 128.8 (d, J_{CP} = 10.0 Hz), 130.1 (d, J_{CP} = 2.3 Hz), 130.8 (d, J_{CP} = 2.1 Hz), 130.9, 131.5, 133.1 (d, J_{CP} = 1.8 Hz), 133.6 (d, J_{CP} = 4.8 Hz), 135.8 (d, J_{CP} = 11.5 Hz), 137.1−137.4 (m), 138.1 (d, J_{CP} = 11.2 Hz), 139.4, 140.1, 144.4 (d, J_{CP} = 8.5 Hz), 148.5, 150.8, 155.5 (d, J_{CP} = 2.0 Hz), 170.9; ^{31}P NMR ($CDCl_3$) δ 34.2; FAB-MS *m*/*z* (relative intensity) 740 (M^+, 3); HRMS (FAB-MS) *m*/*z* calcd for $C_{39}H_{40}ClN_2O_2PPd$ 740.1562, found 740.1584.

Typical Procedure for the Preparation of Optically Active Atropisomers 1. To an individual diastereomer (a*S*,*S*)-**11** or (a*R*,*S*)-**12** (0.02 mmol) was added 0.1 M solution of ethylenediamine in chloroform (0.4 mL, 0.04 mmol) at room temperature, and stirred for 10 min. The mixture was concentrated under reduced pressure, and the residue was purified by silica gel column chromatography (elution with *n*-hexane/EtOAc = 8/1) to afford the optically active (a*S*)-**1** or (a*R*)-**1**.

(a*S*)-(+)-1-[2′-(Diphenylphosphino)-1′-naphthalenyl]-2,3-dihydro-1*H*-indole ((a*S*)-(+)-1a): 98% from (a*S*,*S*)-**11a**; >99% ee; $[\alpha]^{25}_D$ +18.2° (*c* 0.11, $CHCl_3$); HPLC (Daicel CHIRALCEL OJ, 0.46 ϕ × 25 cm, UV 254 nm), t_R = 12.9 min (hexane:ethanol = 90:10, 0.50 mL/min) (CD, λ_{ext} ($\Delta\epsilon$) 254 (−)).

(a*R*)-(−)-1-[2′-(Diphenylphosphino)-1′-naphthalenyl]-2,3-dihydro-1*H*-indole ((a*R*)-(−)-1a): 93% from (a*R*,*S*)-**12a**; 99.1% ee; $[\alpha]^{25}_D$ −18.1° (*c* 0.11, $CHCl_3$); HPLC (Daicel CHIRALCEL OJ, 0.46 ϕ × 25 cm, UV 254 nm), t_R = 34.0 min (hexane:ethanol = 90:10, 0.50 mL/min) (CD, λ_{ext} ($\Delta\epsilon$) 254 (+)).

(a*S*)-(+)-1-[2′-(Diphenylphospino)-6′-methylphenyl]-2,3-dihydro-1*H*-indole ((a*S*)-(+)-1b): 91% from (a*S*,*S*)-**11b**; >99% ee; $[\alpha]^{25}_D$ +19.1° (*c* 0.26, $CHCl_3$); HPLC (Daicel CHIRALPAK AD-H × 2, 0.46 ϕ × 25 cm × 2, UV 254 nm), t_R =36.0 min (hexane:ethanol = 99.7:0.3, 0.30 mL/min) (CD, λ_{ext} ($\Delta\epsilon$) 254 (−)).

(a*R*)-(−)-1-[2′-(Diphenylphospino)-6′-methylphenyl]-2,3-dihydro-1*H*-indole ((a*R*)-(−)-1b): 89% from (a*R*,*S*)-**12b**; >99% ee; $[\alpha]^{25}_D$ −19.2° (*c* 0.27, $CHCl_3$); HPLC (Daicel CHIRALPAK AD-H × 2, 0.46 ϕ × 25 cm × 2, UV 254 nm), t_R =61.0 min (hexane:ethanol = 99.7:0.3, 0.15 mL/min) (CD, λ_{ext} ($\Delta\epsilon$) 254 (+)).

(a*S*)-(−)-1-[2′-(Diphenylphosphino)-6′-trifluoromethylphenyl]-indoline ((a*S*)-(−)-1c): 91% from (a*S*,*S*)-**11c**; >99% ee; $[\alpha]^{25}_D$ −32.4° (*c* 0.86, $CHCl_3$); HPLC (Daicel CHIRALPAK AD-H × 2, 0.46 ϕ × 25 cm × 2, UV 254 nm), t_R = 32.1 min (hexane:ethanol = 99.7:0.3, 0.25 mL/min) (CD, λ_{ext} ($\Delta\epsilon$) 254 (−)).

(a*R*)-(+)-1-[2′-(Diphenylphosphino)-6′-trifluoromethylphenyl]-indoline ((a*R*)-(+)-1c): 95% yield from (a*R*,*S*)-**12c**; >99% ee; $[\alpha]^{25}_D$ +32.4° (*c* 0.81, $CHCl_3$); HPLC (Daicel CHIRALPAK AD-H × 2, 0.46 ϕ × 25 cm × 2, UV 254 nm), t_R = 57.8 min (hexane:ethanol = 99.7:0.3, 0.15 mL/min) (CD, λ_{ext} ($\Delta\epsilon$) 254 (+)).

(a*S*)-(−)-3-Diphenylphosphino-2-(indolin-1-yl)benzyl acetate ((a*S*)-(−)-1d): 98% yield from (a*S*,*S*)-**11d**; >99% ee; $[\alpha]^{25}_D$ −35.2° (*c* 0.83, $CHCl_3$); HPLC (Daicel CHIRALCEL OD, 0.46 ϕ × 25 cm, UV 254 nm), t_R = 15.3 min (hexane:ethanol = 99:1, 0.40 mL/min) (CD, λ_{ext} ($\Delta\epsilon$) 254 (−)).

(a*R*)-(+)-3-Diphenylphosphino-2-(indolin-1-yl)benzyl acetate ((a*R*)-(+)-1d): 98% yield from (a*R*,*S*)-**12d**; 99.2% ee; $[\alpha]^{25}_D$ +35.1° (*c* 0.96, $CHCl_3$); HPLC (Daicel CHIRALCEL OD + OD-H, 0.46 ϕ × 25 cm × 2, UV 254 nm), t_R = 45.5 min (hexane:ethanol = 99:1, flow = 0.25 mL/min) (CD, λ_{ext} ($\Delta\epsilon$) 254 (+)).

Elucidation of the Thermal Racemization of Optically Active 1. A small amount of optically active (a*S*)-**1** or (a*R*)-**1** was dissolved in toluene at room temperature. The solution was kept at a constant temperature in the thermostat oil bath; small portion was taken out every passage of times, and the transitions of enantiomeric excess were measured by chiral HPLC analysis.

Preparation of Palladium Complex (±)-13. To a solution of $PdCl_2(MeCN)_2$ (0.026 g, 0.10 mmol) in a $CHCl_3$ (1.0 mL) was added (±)-**1b** (0.039 g, 0.10 mmol) at room temperature and stirred for 30 min. The reaction mixture was filtered and evaporated under reduced pressure: 82%; mp 145−147 °C (dec); ^{1}H NMR ($CDCl_3$) δ 1.78 (s, 3H), 3.36 (ddd, J = 3.7, 10.3, and 15.7 Hz, 1H), 3.96−4.33 (m, 1H), 5.47 (dt, J = 3.7 and 11.3 Hz, 1H), 6.64−6.69 (m, 1H), 7.12−7.19 (m, 2H), 7.28−7.37 (m, 4H) 7.47−7.54 (m, 4H), 7.57−7.63 (m, 2H), 7.74−7.94 (m, 4H); ^{31}P NMR ($CDCl_3$) δ 41.9; FAB-MS *m*/*z* (relative intensity) 534 ($[M - Cl]^+$, 10); HRMS (FAB-MS) *m*/*z* calcd for $C_{27}H_{24}Cl_2NPPdCl$ 534.0370, found 534.0331. Anal. Calcd for $C_{29}H_{26}Cl_8NPPd$: C, 43.03; H, 3.24; N, 1.73. Found: C, 43.20; H, 3.22; N, 1.68. X-ray diffraction analysis data of **13** (Figure 2) (containing two $CHCl_3$ molecules): yellow plate crystals from hexane:$CHCl_3$, $C_{29}H_{26}Cl_8NPPd$, triclinic space group $P\bar{1}$, a = 8.652(3) Å, b = 10.517(3) Å, c = 18.683(6) Å, α = 92.460(4)°, β = 97.8730(4)°, γ = 106.201(4)°, V = 1611.3(8) Å^3, Z = 2, ρ = 1.668 g/cm^3, μ (Mo Kα) = 13.11 cm^{-1}. The structure was solved by the direct method of full-matrix least-squares, where the final *R* and *Rw* were 0.095 and 0.084 for 9766 reflections, respectively.

General Procedure for the Palladium-Catalyzed Allylic Alkylation. To a mixture of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (0.01 mmol, 3.9 mg), chiral aminophosphine ligand **1** (0.02 mmol), and LiOAc (0.01 mmol, 1 mg) in a solvent (0.4 mL) were added BSA (0.6 mmol, 0.15 mL) and racemic allylic ester **14** (0.2 mmol, 50.7 mg) at room temperature under an Ar atmosphere. After 30 min, dimethyl malonate (0.6 mmol, 0.07 mL) was added at the desired temperature. After 24 h, the reaction mixture was diluted with ether and water. The organic layer was washed with brine and dried over $MgSO_4$. The filtrate was concentrated with a rotary evaporator, and the residue was purified by column chromatography. **(*R*)-Methyl-2-carbomethoxy-3,5-diphenylpent-4-enonate ((*R*)-16):**[15b] (Table 1, entry 4) 91%; 95% ee; ^{1}H NMR ($CDCl_3$) δ 3.52 (s, 3H), 3.71 (s, 3H), 3.95 (d, J = 11.0 Hz, 1H), 4.28 (dd, J = 8.6 and 11.0 Hz, 1H), 6.33 (dd, J = 8.6 and 15.9 Hz, 1H), 6.49 (d, J = 15.9 Hz, 1H), 7.22−7.34 (m, 10H).

Supporting Information Available: ORTEP drawing of (±)-**1a**−**d**, **9**, **12a**, **11b**, **12c**, and **11d** (Figures S1−S9); data of thermal racemization (Figures S10−S13) of (±)-**1a**−**d**; NMR spectra of all compounds; copy of HPLC charts of (a*S*)- and (a*R*)-**1a**−**d**, **9**, and (*R*)-**16**; and X-ray crystallographic file (CIF) for (±)-**1a**−**d**, **9**, **11b**, **11d**, **12a**, **12c**, and **13**. This material is available free of charge via the Internet at http://pubs.acs.org.

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