Cationic Palladium/Boxax Complexes for Catalytic Asymmetric Wacker-Type Cyclization

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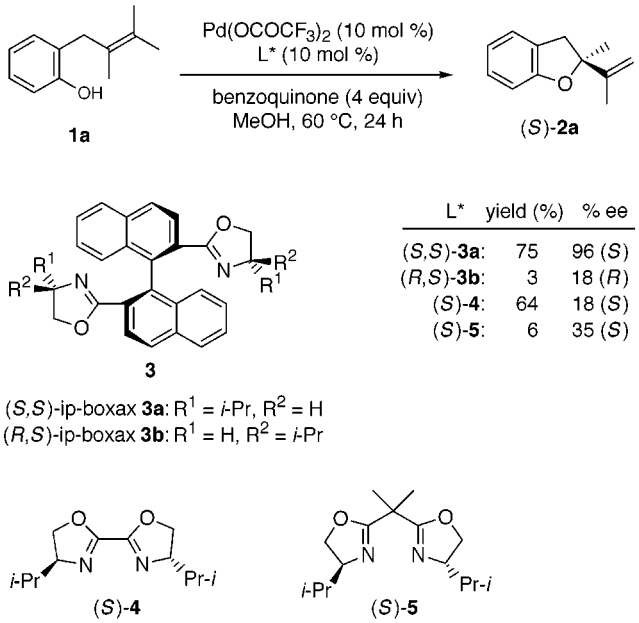
Received February 10, 1998

Catalyticasymmetric Wacker-type cyclization of 2-(2,3-dimethyl-2-butenyl)phenol (**1a**) was efficiently catalyzed by 1 or 2 mol % of a cationic palladium−boxax complex generated in situ by mixing $Pd(CH_3CN)_4(BF_4)_2$ with (*S*,*S*)-ip-boxax (**3a**) in the presence of *p*-benzoquinone to give (*S*)-(−)-2-isopropenyl-2-methyl-2,3-dihydrobenzofuran (**2a**) in 94−96% ee and 45−85% yield. An X-ray diffraction study of the crystal structure of $Pd(OCOCF_3)_2$\{(*S*,*S*)-ip-boxax\} (**6**) revealed that the orientation of alkyl substituents on the boxax ligand is perpendicular to the plane of the square planar complex.

Palladium(II) salts are known to be fairly active oxidizing agents for alkenes.[1] The oxidation of ethylene to acetaldehyde, often called the Wacker process,[2] is one of the best-known reactions catalyzed by palladium(II). Although this type of oxidation is of great value in the synthetic transformation of olefins, there has been little reported work on catalytic asymmetric Wacker-type reactions.[3] We have recently reported an enantioselective intramolecular Wacker-type cyclization of *o*-allylphenols (Scheme 1).[4] Typically, the oxidative cyclization of *o*-allylphenol **1a** is catalyzed by 10 mol % of the palladium−boxax complex generated in situ by mixing $Pd(OCOCF_3)_2$ with (*S*,*S*)-2,2′-bis(4-isopropyloxazolyl)-1,1′-binaphthyl ((*S*,*S*)-ip-boxax) (**3a**) in the presence of *p*-benzoquinone in methanol at 60 °C to give 75% yield of dihydrobenzofuran (*S*)-**2a** in 96% ee. There are two significant features to note in this asymmetric cyclization. First, the chiral bis(oxazoline) ligand must be an (*S*,*S*)-isomer of **3a** for high efficiency. The diastereomeric isomer, (*R*,*S*)-ip-boxax (**3b**), showed little enantioselectivity (18% ee (*R*) in 3% yield) under the same reaction conditions. Bis(oxazoline) ligands, 2,2′-bisoxazolyl (*S*)-**4**[5] and 2,2-bis(oxazolyl)propane (*S*)-**5**,[6] both of which have been frequently used for various catalytic asymmetric reactions,[7] gave **2a** with much lower selectivity (18% ee (*S*) in 64% yield and 35% ee (*S*) in 6% yield, respectively). Second, the catalytic activity is strongly dependent on

Scheme 1



L*	yield (%)	% ee
(*S*,*S*)-**3a**:	75	96 (*S*)
(*R*,*S*)-**3b**:	3	18 (*R*)
(*S*)-**4**:	64	18 (*S*)
(*S*)-**5**:	6	35 (*S*)

the anionic ligands of the palladium catalyst. The reaction is much faster with the palladium catalyst generated from palladium bis(trifluoroacetate) than that from palladium diacetate or dichlorobis(acetonitrile)-palladium, though the catalytic activity is still modest. Indeed, the reaction requires 10 mol % of the catalyst generated from $Pd(OCOCF_3)_2$ and (*S*,*S*)-ip-boxax (**3a**) for a reasonable reaction rate. We report here the studies on the stereochemical structure of the palladium/(*S*,*S*)-ip-boxax complex and the improvement of the catalytic activity of palladium(II)/boxax by modification of the anionic ligands of the complex.

Results and Discussion

Studies on the Structure of the Palladium/Boxax Complexes. The coordination complex of (*S*,*S*)-boxax ligand **3a** with palladium, $Pd(OCOCF_3)_2$\{(*S*,*S*)-ip-boxax\} (**6**), was prepared by the reaction of $Pd(OCOCF_3)_2$ with

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(2) (a) Smidt, J.; Hafner, W.; Jira, R.; Sedlmeier, J.; Sieber, R.; Ruttinger, R.; Kojer, H. *Angew. Chem.* **1959**, *71*, 176. (b) Smidt, J.; Hafner, W.; Jira, R.; Sieber, R.; Sedlmeier, J.; Sabel, A. *Angew. Chem., Int. Ed. Engl.* **1962**, *1*, 80. (c) Smidt, J. *Chem. Ind.* **1962**, 54.

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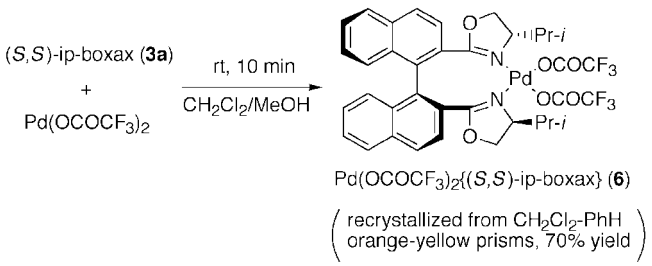
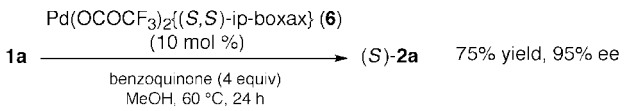
S0022-3263(98)00245-X CCC: $15.00
Published on Web 07/07/1998

Scheme 2





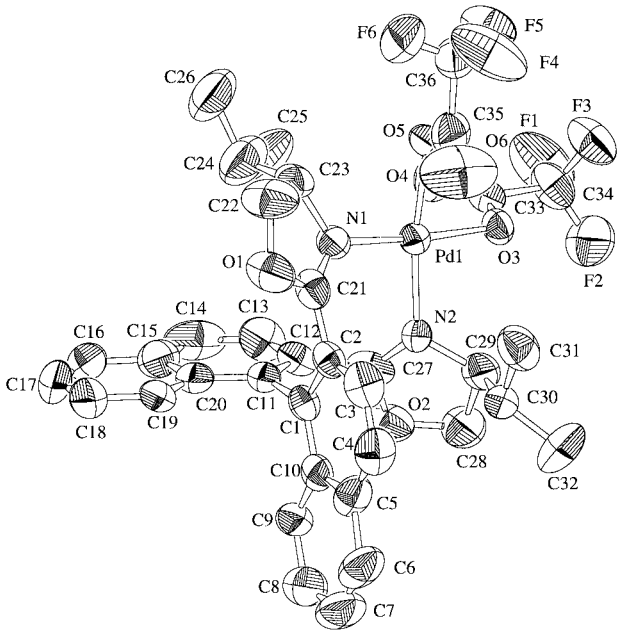


Figure 1. ORTEP drawing of Pd(OCOCF$_3$){(*S*,*S*)-ip-boxax} (**6**) (50% probability ellipsoids). All protons and the disorder are omitted for clarity.

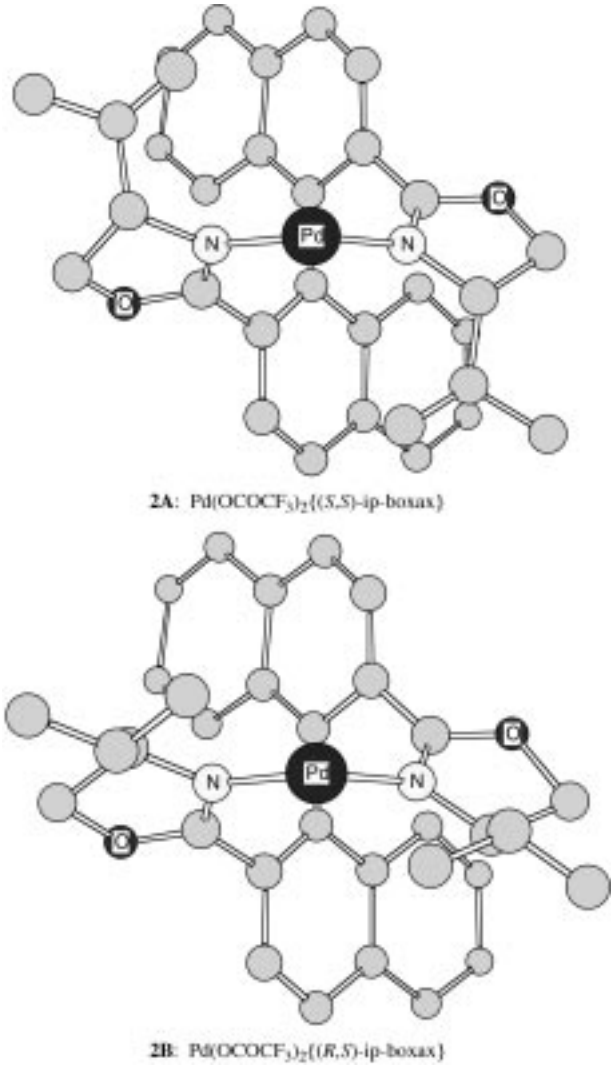


Figure 2. Chem 3D plots of Pd(OCOCF$_3$){(*S*,*S*)-ip-boxax} and Pd(OCOCF$_3$){(*R*,*S*)-ip-boxax}. All protons and trifluoroacatate groups are omitted for clarity.

3a in CH_2Cl_2/MeOH. The single crystals of **6** were obtained as orange-yellow prisms by recrystallization from CH_2Cl_2/benzene (Scheme 2). The isolated palladium/boxax complex **6** used for X-ray analysis showed essentially the same catalytic activity and enantioselectivity as the palladium catalyst generated in situ for the asymmetric cyclization of **1a** (Scheme 2), indicating that the complex **6** is a catalytically active species.

As can be seen from the ORTEP drawing shown in Figure 1, palladium/boxax **6** adopts a square-planar structure in which two nitrogen atoms of the oxazoline rings and two oxygen atoms of trifluoroacetate groups are attached to palladium. The boxax ligand (*S*,*S*)-**3a** coordinates to palladium forming a nine-membered ring, in which the $\angle\{N^1-Pd-N^2\}$ angle is 100.3° and the dihedral angle between two naphthyl rings ($\angle\{C^2-C^1\}-\{C^{11}-C^{12}\}$) is 90.2°. It is noteworthy that the isopropyl substituents on the oxazoline rings are oriented almost perpendicularly with respect to the square plane. The two oxazoline rings are twisted from each other by 69.5° ($\angle\{C^{21}-N^1\}-\{N^2-C^{27}\}$), and this twisted conformation with a large torsion angle allows the isopropyl groups on the (*S*)-oxazolines to be perpendicular to the coordination plane. The structure of **6** in solution is considered to be similar to that in the crystalline state. This contention is supported by a high field chemical shift (δ −0.01 ppm) in the ^{1}H NMR spectrum for one of the methyl protons of the isopropyl group (see Experimental Section). An isopropyl methyl group is in close proximity to the naphthyl ring, which would cause the high field shift. The conformation of the oxazolines observed here is very different from that in transition-metal complexes coordinated with bis(oxazoline) ligands lacking the binaphthyl backbone where the oxazolines are in almost the same plane as the chelate coordination plane.[8]

The structure of the palladium complex coordinated with diastereomeric ligand (*R*,*S*)-ip-boxax (**3b**) could not be determined by X-ray diffraction because of the difficulty in obtaining an adequate single crystal suitable for X-ray diffraction (Figure 2). Three-dimensional computer modeling of this complex was performed. The configuration of a stereogenic carbon on the oxazoline of the (*S*,*S*)-complex was changed from *S* to *R* keeping the

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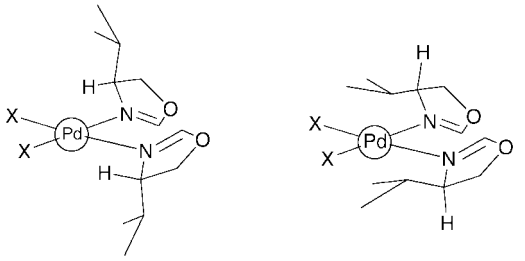
Table 1. Asymmetric Wacker-Type Cyclization of 1 with Cationic Palladium(II)/(*S,S*)-ip-boxax Complexes[a]

entry	palladium(II) catalyst Pd/(*S,S*)-ip-boxax (mol %/mol %)	*o*-allylphenol	temp (°C)	time (h)	yield[b] (%)	% ee[c] of **2**
1	$PdCl_2$\{(*S,S*)-ip-boxax\} (**7**) (10/10)	1a	60	24	<2	
2	$Pd(OCOCF_3)_2$\{(*S,S*)-ip-boxax\} (**6**) (10/10)	1a	60	24	75	96
3	$Pd(CH_3CN)_4(BF_4)_2$/(*S,S*)-ip-boxax (10/20)	1a	60	0.8	91	97
4	$Pd(CH_3CN)_4(BF_4)_2$/(*S,S*)-ip-boxax (10/10)	1a	60	0.5	88	85
5	$PdCl_2$\{(*S,S*)-ip-boxax\} (**7**)/2$AgBF_4$ (10/20)	1a	60	1	91	98
6	$PdCl_2$\{(*S,S*)-ip-boxax\} (**7**)/2$AgPF_6$ (10/20)	1a	60	1	87	95
7	$PdCl_2$\{(*S,S*)-ip-boxax\} (**7**)/2$AgSbF_6$ (10/20)	1a	60	1	86	97
8	$Pd(CH_3CN)_4(BF_4)_2$/(*S,S*)-ip-boxax (1/2)	1a	60	5	45	96
9[d]	$Pd(CH_3CN)_4(BF_4)_2$/(*S,S*)-ip-boxax (1/2)	1a	60	5	63	96
10[d]	$Pd(CH_3CN)_4(BF_4)_2$/(*S,S*)-ip-boxax (1/2)	1a	reflux	5	75	94
11[d]	$Pd(CH_3CN)_4(BF_4)_2$/(*S,S*)-ip-boxax (2/4)	1a	reflux	5	85	95
12[d]	$Pd(CH_3CN)_4(BF_4)_2$/(*S,S*)-ip-boxax (2/4)	1b	60	24	92	92
13[d]	$Pd(CH_3CN)_4(BF_4)_2$/(*S,S*)-ip-boxax (2/4)	1c	60	24	93	97

[a] All reactions were carried out in the presence of 4 equiv of benzoquinone in methanol. [b] Isolated yield by column chromatography. [c] Determined by GC analysis with a chiral stationary phase column (Cyclodex β236M19). [d] The reaction was carried out under oxygen atmosphere.



3A: PdX_2\{(*S,S*)-ip-boxax\} **3B:** PdX_2\{(*R,S*)-ip-boxax\}

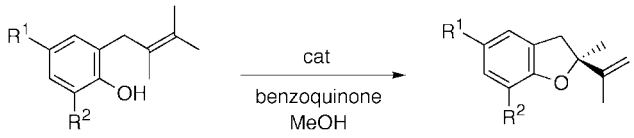
Figure 3. Schematic structures of PdX_2\{(*S,S*)-ip-boxax\} and PdX_2\{(*R,S*)-ip-boxax\}. The binaphthylene groups in the boxax ligands are omitted for clarity.

chelate coordination of binaphthylbisoxazoline moiety. Schematic structures of palladium/(*S,S*)-boxax and palladium/(*R,S*)-ip-boxax are shown in Figure 3. Isopropyl substituents in the palladium/(*R,S*)-boxax complex lie in close proximity to the coordination plane (2B and 3B), while those in the palladium/(*S,S*)-ip-boxax complex are located above and below the plane (2A and 3A). The two isopropyl groups in the (*R,S*)-ip-boxax complex probably disturb the coordination of olefin to palladium, and as a result, its catalytic activity for the cyclization is very low. It seems that the orientation of alkyl substituents on the oxazoline rings chelating to palladium plays an essential role in both the catalytic activity and the enantioselectivity.

Catalytic Asymmetric Cyclization Catalyzed by Cationic Palladium/Boxax Complexes. The catalytic activity of the palladium complexes for the present oxidative cyclization was strongly dependent on the anionic part of the catalyst (Scheme 3). Thus, the reaction of **1a** was not catalyzed by chloride complex $PdCl_2$\{(*S,S*)-ip-boxax\} (**7**) while the reaction proceeded well in the presence of trifluoroacetate complex $Pd(OCOCF_3)_2$\{(*S,S*)-ip-boxax\} (**6**) (entries 1 and 2 in Table 1). It was expected that a cationic palladium/boxax complex was generated as the active species by dissociation of the relatively stable trifluoroacetate anion from palladium in a polar solvent.

A dicationic palladium(II)/boxax species generated by addition of (*S,S*)-ip-boxax (**3a**) to $Pd(CH_3CN)_4(BF_4)_2$ was found to be catalytically much more active than $Pd(OCOCF_3)_2$\{(*S,S*)-ip-boxax\} (**6**) for the present reaction. Thus, treatment of $Pd(CH_3CN)_4(BF_4)_2$ with 2 equiv of (*S,S*)-ip-boxax (**3a**) in acetonitrile/dichloromethane at

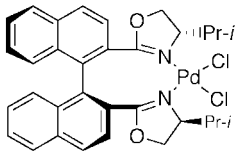
Scheme 3



1a: $R^1 = R^2 = H$
1b: R^1 = Me, $R^2 = H$
1c: $R^1 = H$, R^2 = Me

(*S*)-**2a-c**

(cat: **7**/Ag(I) or $Pd(CH_3CN)_4(BF_4)_2$/**3a**)



$PdCl_2$\{(*S,S*)-ip-boxax\} (**7**)

room temperature followed by removal of the solvent in vacuo gave an orange solid. The reaction of **1a** in the presence of 10 mol % of this solid and benzoquinone in methanol was complete in 50 min to give a 91% yield of (*S*)-**2a** which is 98% enantiomerically pure (entry 3). The enantioselectivity was a little lower with the catalyst generated by addition of 1 equiv of **3a** to $Pd(CH_3CN)_4(BF_4)_2$, though the reaction was a little faster (entry 4). Generation of the dicationic species by abstraction of chloride from $PdCl_2$\{(*S,S*)-ip-boxax\} (**7**) through treatment with 2 equiv of a silver(I) salt, silver(I) tetrafluroborate, hexafluorophosphate, or hexafluoroantimonate, was also successful. Essentially the same catalytic activity and enantioselectivity were observed for the reaction of **1a** (entries 5−7). The cationic palladium catalyst was so active that the amount of the catalyst could be reduced to 1 or 2 mol %. Thus, the reaction in the presence of 1 mol % of the dicationic palladium/boxax in methanol at 60 °C gave 45% yield of **2a** (96% ee) (entry 8). The yield of **2a** was increased by carrying out the reaction in refluxing methanol under an oxygen atmosphere, which gave a 75% yield of **2a** (94% ee) (entry 10). The cyclization of methyl-substituted *o*-allylphenols **1b** and **1c** proceeded smoothly in the presence of 2 mol % of the cationic palladium/boxax complex to give a 92% yield of (*S*)-**2b** and a 93% yield of (*S*)-**2c** with enantioselectivities of 92% and 97%, respectively (entries 12 and 13).

Experimental Section

Materials. $AgBF_4$, $AgSbF_6$, and $AgPF_6$ were purchased from Aldrich Chemical Co. Inc. $Pd(OCOCF_3)_2$ was purchased from Fluka Chemical Co. Inc. Bisoxazoline ligands (*S*,*S*)-ip-boxax and (*R*,*S*)-ip-boxax were prepared according to the reported procedures.[9] Dichloromethane and acetonitrile were distilled from calcium hydride under nitrogen.

Preparation of [(*S*,*S*)-2,2′-Bis{4-(isopropyl)oxazolyl}-1,1′-binaphthyl]palladium Bis(trifluoroacetate) (6). A solution of 479 mg (1.01 mmol) of (*S*,*S*)-2,2′-bis[4-(isopropyl)-oxazolyl]-1,1′-binaphthyl ((*S*,*S*)-ip-boxax) in 5 mL of dichloromethane was added to 330 mg (0.993 mmol) of $Pd(OCOCF_3)_2$ in 5 mL of methanol at room temperature. The reaction mixture was stirred at room temperature for 15 min and concentrated until about 5 mL. To the mixture was added 5 mL of benzene to give a brown precipitate. The brown precipitate was collected by filtration and washed with benzene to give 565 mg (70% yield) of [(*S*,*S*)-2,2′-bis{4-(isopropyl)-oxazolyl}-1,1′-binaphthyl]palladium bis(trifluoroacetate) ($Pd(OCOCF_3)_2$\{(*S*,*S*)-ip-boxax\}) (**6**). The brown powder was recrystallized from dichloromethane/benzene to give 362 mg (45% yield) of $Pd(OCOCF_3)_2$\{(*S*,*S*)-ip-boxax\} (**6**) as red-orange prisms: mp 227 °C (dec); $[\alpha]^{20}_D$ −24.4 (*c* 0.11, $CHCl_3$); ^{1}H NMR δ −0.01 (d, J = 6.9 Hz, 6H), 0.65 (br octet, 2H), 1.16 (d, J = 6.9 Hz, 6H), 3.49 (ddd, J = 9.8, 7.4, 5.9 Hz, 2H), 3.56 (dd, J = 9.3, 5.9 Hz, 2H), 4.16 (br t, J = 9.8 Hz, 2H), 6.98 (br d, J = 9.3 Hz, 2H), 7.33 (br t, J = 8.3 Hz, 2H), 7.58 (br t, J = 6.9 Hz, 2H), 7.96 (br d, J = 8.8 Hz, 2H), 8.04 (br d, J = 8.3 Hz, 2H), 8.25 (br d, J = 8.3 Hz, 2H); ^{13}C NMR δ 16.20, 20.62, 31.65, 70.88, 114.32 (q, J = 287.5 Hz), 124.33, 125.96, 126.63, 128.32, 128.71, 128.76, 130.29, 131.81, 134.28, 134.96, 162.09 (q, J = 36.3 Hz), 171.18. Anal. calcd for $C_{36}H_{32}N_2O_6F_6Pd$: C, 53.44; H, 3.99; N, 3.46; F, 14.09. Found: C, 53.45; H, 4.05, N, 3.36; F, 13.80.

The molecular structure of $Pd(OCOCF_3)_2$\{(*S*,*S*)-ip-boxax\} (**6**) determined by an X-ray diffraction study is shown in Figure 1. A single crystal (0.20 × 0.30 × 0.30 mm) of the palladium complex $Pd(OCOCF_3)_2$\{(*S*,*S*)-ip-boxax\} (**6**) obtained above was put on the top of a glass capillary tube. Intensity data were collected on a Rigaku AFC 7S diffractometer. Details of the X-ray diffraction study of **6**, including crystal data and structure refinement, fractional coordinates and equivalent isotropic thermal factors, anisotropic displacement parameters, bond lengths, and bond angles are reported in the Supporting Information.

Cyclization of 2-(2,3-Dimethyl-2-butenyl)phenol (2a) with $Pd(OCOCF_3)_2$\{(*S*,*S*)-ip-boxax\} (6). To a mixture of 12.3 mg (15 μmol) of $Pd(OCOCF_3)_2$\{(*S*,*S*)-ip-boxax\} (**6**) and 64.9 mg (0.60 mmol) of *p*-benzoquinone in 0.1 mL of methanol was added 28.9 mg (0.164 mmol) of 2-(2,3-dimethyl-2-butenyl)-phenol (**1a**) in 0.2 mL of methanol. The reaction mixture was stirred at 60 °C for 24 h and then chromatographed on silica gel (eluent: benzene) to give 21.7 mg (76% yield) of (*S*)-2-isopropenyl-2-methyl-2,3-dihydrobenzofuran (**2a**). The enantiomeric excess of **2a** was determined to be 95% ee by GC analysis using a chiral stationary phase column, Cyclodex β236M19 (0.32 mm × 25 m): $[\alpha]^{20}_D$ −83.1 (*c* 0.23, chloroform); ^{1}H NMR δ 1.55 (s, 3H), 1.82 (br s, 3H), 3.01 (d, J = 16.2 Hz, 1H), 3.26 (d, J = 16.2 Hz, 1H), 4.84 (br s, 1H), 5.09 (br s, 1H), 6.79 (br d, J = 7.8 Hz, 1H), 6.82 (t, J = 7.3 Hz, 1H), 7.11 (br t, J = 7.2 Hz, 1H), 7.13 (br d, J = 7.3 Hz, 1H); ^{13}C NMR δ 18.72, 26.01, 41.34, 89.70, 109.40, 109.90, 120.06, 124.93, 126.49, 127.98, 147.68, 158.88; mass 174 (M^+), 159 (bp), 141, 131. Anal. calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.79; H, 8.20.

Dichloro[(*S*,*S*)-(−)-2,2′-bis{4-(isopropyl)oxazolyl}-1,1′-binaphthyl]palladium(II) ($PdCl_2$\{(*S*,*S*)-ip-boxax\}) (7). A solution of 349 mg (0.731 mmol) of (*S*,*S*)-2,2′-bis[4-(isopropyl)-oxazolyl]-1,1′-binaphthyl ((*S*,*S*)-ip-boxax) in 5 mL of dichloromethane was added to 182 mg (0.700 mmol) of $PdCl_2(CH_3CN)_2$ in 5 mL of dichloromethane. The reaction mixture was stirred for 5 min and concentrated until about 3 mL. To the mixture was added 3 mL of hexane to give yellow precipitates. The yellow precipitates were collected by filtration and washed with hexane to give 394 mg (86% yield) of dichloro[(*S*,*S*)-2,2′-bis{4-(isopropyl)oxazolyl}-1,1′-binaphthyl]palladium ($PdCl_2$\{(*S*,*S*)-ip-boxax\}) (**7**) as yellow powder: mp 243 °C (dec); $[\alpha]^{20}_D$ −54.1 (*c* 0.10, $CHCl_3$); ^{1}H NMR δ −0.01 (d, J = 6.9 Hz, 6H), 0.62 (br octet, 2H), 1.20 (d, J = 6.6 Hz, 6H), 3.47 (dd, J = 8.8, 6.1 Hz, 2H), 4.15 (dd, J = 10.1, 8.8 Hz, 2H), 4.68 (ddd, J = 10.1, 8.1, 6.1 Hz, 2H), 6.98 (br d, J = 8.6 Hz, 2H), 7.31 (br t, J = 6.9 Hz, 2H), 7.56 (br t, J = 6.9 Hz, 2H), 7.78 (br d, J = 8.6 Hz, 2H), 7.99 (br d, J = 8.3 Hz, 2H), 8.16 (br d, J = 8.1 Hz, 2H); ^{13}C NMR δ 16.48, 21.48, 31.75, 70.73, 72.11, 124.06, 126.53, 126.72, 128.05, 128.46, 128.56, 130.10, 131.89, 134.41, 134.71, 169.27. Anal. calcd for $C_{32}H_{32}N_2O_2Cl_2Pd$: C, 58.77; H, 4.93; N, 4.28; Cl, 10.84. Found: C, 58.49; H, 5.11; N, 4.39; Cl, 11.17.

Cyclization of 2-(2,3-Dimethyl-2-butenyl)phenol with $PdCl_2$\{(*S*,*S*)-ip-boxax\} (7) and Silver Salts. A typical procedure is given for the cyclization of 2-(2,3-dimethyl-2-butenyl)phenol by use of $AgBF_4$ as a silver salt. To a solution of 5.84mg (30 μmol) of $AgBF_4$ in 0.1 mL of dichloromethane was added 9.80 mg (15 μmol) of $PdCl_2$\{(*S*,*S*)-ip-boxax\} (**7**) in 0.1 mL of dichloromethane at room temperature. The mixture was stirred at room temperature for 5 min. Precipitated silver(I) chloride was removed by filtration. The filtrate was concentrated in vacuo to give an orange solid. To a residual solid was added 7.15 mg (15 μmol) of (*S*,*S*)-ip-boxax, 26.6 mg (0.15 mmol) of 2-(2,3-dimethyl-2-butenyl)phenol, and 64.9 mg (0.60 mmol) of *p*-benzoquinone in 0.3 mL of methanol. The reaction mixture was stirred at 60 °C under air atmosphere for 1 h and then chromatographed on silica gel (eluent benzene) to give 23.7 mg (91% yield) of (*S*)-2-isopropenyl-2-methyl-2,3-dihydrobenzofuran (**2a**). The enantiomeric excess of **2a** was determined to be 98% ee by GC analysis using chiral stationary phase column, Cyclodex β236M19 (0.32 mm × 25 m).

Cyclization of *o*-Allylphenols with $Pd(CH_3CN)_4(BF_4)_2$ and (*S*,*S*)-ip-boxax (3a). A typical procedure is given for cyclization of 6-methyl-2-(2,3-dimethyl-2-butenyl)phenol (**1c**). To a solution of 6.66 mg (15 μmol) of $Pd(CH_3CN)_4(BF_4)_2$ in 0.1 mL of acetonitrile was added 14.3 mg (30 μmol) of (*S*,*S*)-ip-boxax (**3a**) in 0.1 mL of dichloromethane at room temperature. The mixture was stirred at room temperature for 3 min and concentrated in vacuo to give an orange solid. To the orange solid was added 324 mg (3.00 mmol) of *p*-benzoquinone, 0.1 mL of methanol, and 135 mg (0.71 mmol) of 6-methyl-2-(2,3-dimethyl-2-butenyl)phenol (**1c**) in 0.2 mL of methanol. The reaction mixture was stirred at 60 °C under oxygen atmosphere for 24 h and then chromatographed on silica gel (eluent benzene) to give 125 mg (93% yield) of (*S*)-2-isopropenyl-2,7-dimethyl-2,3-dihydrobenzofuran (**2c**). The enantiomeric excess of **2c** was determined to be 97% ee by GC analysis using chiral stationary phase column, Cyclodex β236M19 (0.32 mm × 25 m). $[\alpha]^{20}_D$ −83.4 (*c* 0.48, chloroform); ^{1}H NMR δ 1.55 (s, 3H), 1.78 (br s, 3H), 2.22 (s, 3H), 3.01 (d, J = 14.4 Hz, 1H), 3.24 (d, J = 14.4 Hz, 1H), 4.82 (br s, 1H), 5.08 (br s, 1H), 6.73 (t, J = 7.3 Hz, 1H), 6.9−7.0 (m, 2H); ^{13}C NMR δ 15.28, 18.70, 26.19, 41.66, 89.20, 109.68, 119.52, 119.87, 122.21, 125.69, 129.10, 147.89, 157.40; mass 188 (M^+), 173 (bp), 158, 145. Anal. calcd for $C_{13}H_{16}O$: C, 82.94; H, 8.57. Found: C, 82.63; H, 8.69.

(*S*)-2-Isopropenyl-2,5-dimethyl-2,3-dihydrobenzofuran (2b). (92% yield, 92% ee): $[\alpha]^{20}_D$ −51.3 (*c* 0.44, chloroform); ^{1}H NMR δ 1.56 (s, 3H), 1.81 (br s, 3H), 2.27 (s, 3H), 2.97 (d, J = 15.5 Hz, 1H), 3.22 (d, J = 15.5 Hz, 1H), 4.82 (br s, 1H), 5.08 (br s, 1H), 6.68 (d, J = 8.4 Hz, 1H), 6.92 (d, J = 8.4 Hz, 1H), 6.94 (s, 1H); ^{13}C NMR δ 18.72, 20.72, 25.97, 41.41, 89.66, 108.92, 109.82, 125.53, 126.50, 128.31, 129.28, 147.78, 156.81; mass 188 (M^+), 173 (bp), 158, 145. Anal. calcd for $C_{13}H_{16}O$: C, 82.94; H, 8.57. Found: C, 82.92; H, 8.70.

Acknowledgment. This work was supported by "Research for the Future" Program, the Japan Society for the Promotion of Science, and a Grant-in-Aid for Scientific Research, the Ministry of Education, Japan.

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Y. U. thanks Uehara Memorial Foundation for partial financial support of this work.

Supporting Information Available: Tables of X-ray analysis of $Pd(OCOCF_3)_2$\{(*S*,*S*)-ip-boxax\} (**6**), crystal data and structure refinement, fractional coordinates and equivalent isotropic thermal factors, anisotropic displacement parameters, bond lengths, and bond angles (9 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO980245I