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Unsymmetrical Chiral PCN Pincer Palladium(II) and Nickel(II) Complexes of (Imidazolinyl)aryl Phosphinite Ligands: Synthesis via Ligand C−H Activation, Crystal Structures, and Catalytic Studies

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Six unsymmetrical chiral PCN pincer Pd(II) complexes **3a**−**f** based on (imidazolinyl)aryl phosphinite ligands were easily synthesized from imidazolinyl-containing *m*-phenol derivatives **2a**−**e** by one-pot phosphorylation/palladation reaction via C−H bond activation of the related ligands. An unsymmetrical chiral PCN pincer Ni(II) complex, **4a**, was first obtained in a similar way. The palladium−chloride complex **3e** could be readily converted to the corresponding iodide derivative **5e** by the halide exchange reaction with KI. All eight complexes were characterized by X-ray crystal structure determination. Each complex adopts a typical distorted-square-planar geometry. The Pd complexes were shown to be active catalysts with rather moderate enantioselectivities (up to 32% ee) for asymmetric Suzuki−Miyaura reaction.

Introduction

Organometallic pincer complexes incorporating tridentate ligands represent an important and exciting class of structures, particularly from the point of view of their wide applications in catalysis.[1] Research into their chemistry has been dominated by various symmetrical and achiral pincer complexes consisting of a monoanionic bis-*ortho*-chelating YCY ligand (YCY = $[C_6H_3(Y)_2\text{-}2,6]^-$, Y = CH_2NR_2,[2] CH=NR,[3] CH_2PR_2,[4] OPR_2,[4b,5] $NHPR_2$,[6] CH_2SR,[7] etc.), while reports on the chiral[8] or unsymmetrical complexes[9] are relatively few, especially those on unsymmetrical and chiral pincer metal complexes. Among the chiral pincers, the symmetrical NCN bis(oxazolinyl)phenyl (abbreviated as Phebox) metal complexes including Rh, Pd, Pt, Ru, and Ni have been extensively investigated and widely used in asymmetric catalysis.[10,11] The chirality in these complexes can be easily introduced and tuned by the use of the readily available chiral

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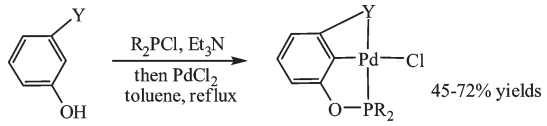
amino alcohols during the ligand synthesis. We recently described a series of chiral NCN pincer Pt and Pd pincer complexes with bis(imidazolinyl)phenyl (abbreviated as Phebim) where the chirality also originated from chiral amino alcohols.[12] It was found that metalation of the ligand's central C−H bond was more facile with Phebim-H versus Phebox-H. For instance, the Pd(Phebim) complexes could be prepared by the ligand C−H activation method, while this process did not seem to be applicable to the Phebox-H ligands.[11b,13] Additionally, the yields of Pt(Phebim) complexes were obviously higher (51−84%) than those of the related Pt(Phebox) complexes (9−49%)[13g,14] when this direct metalation methodology was used. On the other hand, we previously developed a facile, direct method based on one-pot phosphorylation/palladation reaction for the preparation of unsymmetrical PCN pincer palladium complexes containing a phosphinito group.[15] These compounds were conveniently synthesized by the reaction of N-donor (such as pyrazolyl, amino, or imino)-containing *m*-phenol derivatives with dialkylchorophosphine in the presence of triethylamine in refluxing toluene, followed by the addition of palladium chloride (Scheme 1). This one-pot phosphorylation/palladation strategy avoided the usually troublesome step of isolating the air- and moisture-sensitive phosphinite ligands and achieved the metalation of the related ligands' central C−H bond in the meanwhile. To our knowledge, only Motoyama et al. reported chiral versions of unsymmetrical PCN pincer palladium and platinum complexes,

Scheme 1. One-Pot Phosphorylation/Palladation Reaction for the Synthesis of Unsymmetrical PCN Pincer Palladium Complexes



R = Ph, Cy or *i*-Pr; Y = CH_2NEt_2, CH_2Pz and CH=NR'

which were based on (oxazolinyl)phenyl phosphinite ligands and prepared via oxidative addition of an appropriate bromo-substituted derivative (Scheme 2). Single-crystal structures and applications of the obtained chiral complexes were not studied.[16] Considering the different reactivties of Phebox-H and Phebim-H ligands toward metalation as mentioned above, we were interested to see whether the unsymmetrical chiral PCN pincer complexes with (imidazolinyl)aryl phosphinite could also be synthesized by the one-pot phosphorylation/metalation reaction via C−H activation of the related ligands (Scheme 3). Herein, we report in detail the preparation and crystal structures of a series of PCN pincer Pd(II) complexes bearing (imidazolinyl)aryl phosphinite ligands. A chiral Ni(II) complex with an unsymmetrical PCN ligand was first synthesized in a similar way.[17] Additionally, the catalytic activities of these complexes in the asymmetric Suzuki−Miyaura coupling reaction are presented.

Results and Discussion

Preparation of Chiral Ligand Precursors and the Pincer Pd(II) and Ni(II) Complexes. The required chiral imidazolinyl-containing *m*-phenol derivatives **2a**−**e** were prepared in a four-step sequence from commercially available *m*-hydroxybenzoic acid as shown in Scheme 4. Acetylation of 3-hydroxybenzoic acid with acetic anhydride in the presence of sodium hydroxide in water easily gave 3-acetoxybenzoic acid in a 94% yield. Then treatment with thionyl chloride and subsequently with chiral amino alcohols in the presence of triethylamine in THF at 0 °C afforded the corresponding 3-acetoxybenzamido alcohols **1a**−**c** as white solids. The obtained amido alcohol reacted with excess thionyl chloride, followed by the addition of arylamine to promote cyclization and deprotection of acetate during basic workup with 10% NaOH. After purification by preparative TLC on silica gel plates, five chiral compounds, **2a**−**e**, were isolated in 38−43% yields as white solids. With the expected ligand precursors in hand, the one-pot phosphorylation/metalation reaction was attempted. Thus, **2a**−**e** were treated with Ph_2PCl or *i*-Pr_2PCl in the presence of triethylamine as a base in refluxing toluene for 3 h, followed by the addition of $PdCl_2$ (or $PdCl_2(CH_3CN)_2$ for **3f**) and refluxing for another 12 h. We were pleased to find that the new chiral PCN pincer palladium complexes **3a**−**f** were obtained in 45−52% isolated yields as pale yellow solids after chromatography on silica gel. An unsymmetrical chiral PCN pincer Ni(II) complex, **4a**, could be prepared in a similar way in 41% yield when $NiCl_2(THF)_x$ was used instead of the Pd(II) salt (Scheme 5). To our

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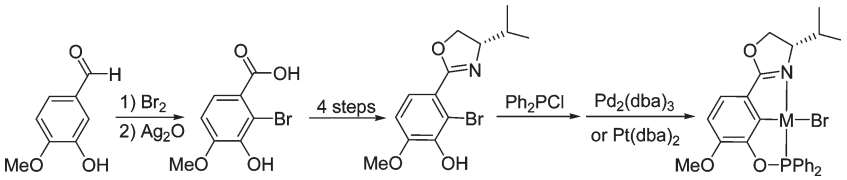
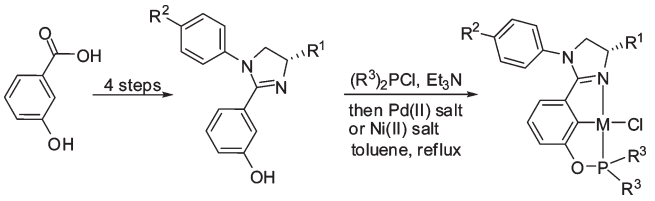
Scheme 2. Synthesis of Unsymmetrical Chiral PCN Pincer Pd and Pt Complexes Based on (Oxazolinyl)phenyl Phosphinite Ligands via Oxidative Addition



Scheme 3. Synthesis of Unsymmetrical Chiral PCN Pincer Metal Complexes with (Imidazolinyl)aryl Phosphinite by One-Pot Phosphorylation/Metalation Reaction



knowledge, this is the first example of unsymmetrical chiral PCN pincer Ni(II) complexes. The palladium−chloride complex **3e** was readily converted to the corresponding iodide derivative **5e** by a halogen exchange reaction with excess amounts of KI in MeOH−CH_2Cl_2 in 87% isolated yield as yellow solids (Scheme 6).

All of the chiral pincer Pd and Ni complexes are air- and moisture-stable both in the solid state and in solution. They were fully characterized by elemental analysis, ^{1}H NMR, ^{13}C NMR, ^{31}P{^{1}H} NMR, DEPT, HSQC, and IR spectra. The formation of the pincer complexes was confirmed by the single resonance at about 155 ppm (for Ph_2PO) or 200 ppm (for *i*-Pr_2PO) in the ^{31}P{^{1}H} NMR spectra and the absence of the singlet corresponding to the proton located ortho to both OH and the imidazoline ring in the ^{1}H NMR spectra. The ^{13}C NMR spectra of the complexes exhibited intensive ^{31}P−^{13}C couplings.

Molecular Structures of Pd and Ni Complexes. The structures of all the complexes **3a**−**f**, **4a**, and **5e** were unambiguously determined by single-crystal X-ray analysis. The molecules of three representative complexes, **3a**·H_2O, **3f**·CH_2Cl_2 and **4a**·0.5CH_2Cl_2, are illustrated in Figures 1−3, respectively. Selected bond lengths and bond angles are listed in Table 1. Crystal data are given in Table 2 (the molecules of the other five complexes and the related data are given in the Supporting Information). The structural features of the eight metal pincer complexes are almost identical. The ligand in each one is coordinated to the metal(II) center via imidazolinyl-N, phosphinite-P, and the central aryl-C in a tridentate manner, and a tetracyclic system is thus formed by the central aryl ring, the imidazoline ring, and the two five-membered metallacycles. It is found that the four rings are approximately coplanar. However, the N-aryl ring is not coplanar with the four rings, and the dihedral angles between the N-aryl ring and the attached imidazoline ring in complexes **3a**−**f**, **4a**, and **5e** are 76.0°, 71.7°, 66.6°, 69.5°, 87.5°, 85.9°, 74.0°, and 86.8°, respectively. The metal(II) center in each Pd or Ni complex adopts a typical distorted-square-planar configuration with bond angles of N−M−P being around 160° and C−M−X being 176−179°, which are in accordance with pincers consisting of two five-membered-ring metallacycles[5a,e,h,9d,9g,15b,18] and reflect a relative steric strain of the almost planar multicyclic system. The bond lengths of Pd−C (around 1.97 Å) and Pd−P (around 2.20 Å) in Pd complexes **3a**−**f** and **5e** are comparable to those in the related achiral PCN pincer Pd complexes,[9d,15b] but slightly shorter than those found in the symmetrical PCP-bis(phosphinite) pincer Pd complexes (1.97−2.02 and 2.26−2.29 Å, respectively).[5a,b,e] In comparison to the related (amino)phosphinite PCN pincer Ni complexes,[9g] complex **4a** also displays similar Ni−C (1.87 Å) and Ni−P (2.12 Å) bond lengths, which are somewhat shorter than those in the symmetrical PCP−bis(phosphinite) nickel complexes (1.88 and 2.16 Å).[5h,18] The Pd−N distances (around 2.10 Å) in Pd complexes **3a**−**f** and **5e** are slightly longer than NCN bis(imidazoline) pincer Pd complex (Pd−N(1), 2.031; Pd−N(2), 2.078 Å),[12b] but shorter than those in the (imino)phosphinite PCN Pd complexes (around 2.18 Å).[15b]

Catalytic Studies. The Suzuki−Miyaura coupling reaction of organic halides and organoboron reagents is one of the most versatile and successful synthetic tools for the formation of carbon−carbon bonds.[19,20] Some of the achiral pincer Pd(II) complexes have been successfully applied as catalysts for this coupling by us[9i,15] and others.[5b,e,7,9d,f,21] In addition, the chiral Pd(Phebox) was found to exhibit moderate stereoselectivity in the asymmetric Suzuki−Miyaura coupling for the synthesis of axially chiral biaryl compounds (up to 49% ee).[13f] Accordingly, the potential of the obtained chiral PCN pincer complexes in the asymmetric Suzuki−Miyaura reaction was examined. It was found that except for Pd complex **3b**, with a *i*-Pr_2PO− group, the other Pd complexes were effective catalysts in the coupling reaction of 1-iodo-2-methoxynaphthalene with 1-naphthaleneboronic acid, of which complex **3a** was the most active, giving a 92% yield of the product (Scheme 7). Unfortunately, the enantioselectivities of the product was rather moderate (up to 32% ee) though a variety of reaction conditions were attempted. Additionally, the chiral Ni(II) complex **4a** was found to be inactive in this coupling under similar reaction conditions even with a catalyst loading as high as 20 mol %. The details of these results are summarized in the Supporting Information.

Several researchers have reported that pincer Pd complexes act as precatalysts or mere reservoirs of catalytically

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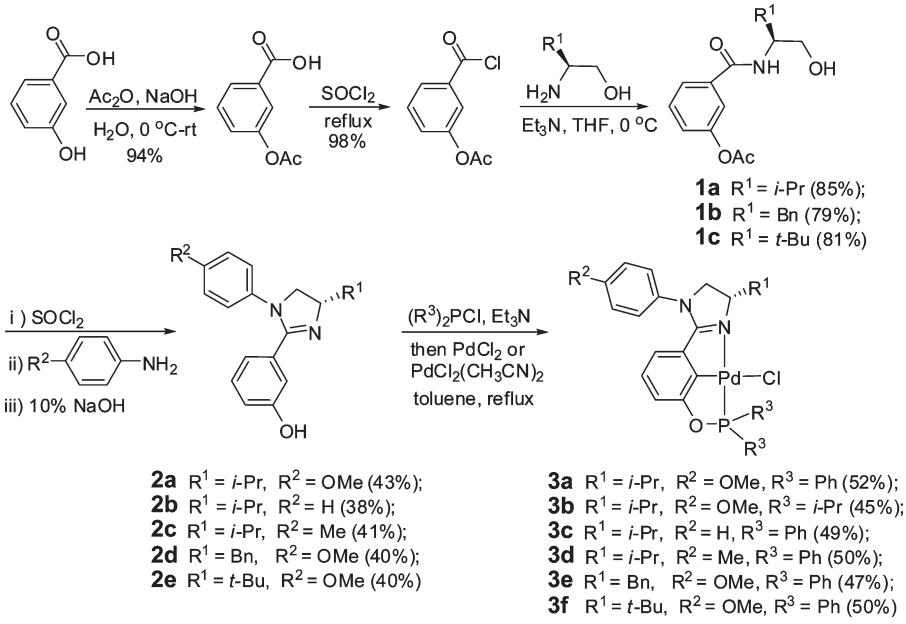
Scheme 4. Synthesis of Chiral PCN Pincer Pd(II) Complexes of (Imidazolinyl)aryl Phosphinite Ligands

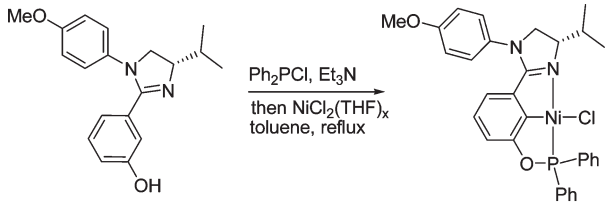


1a R^1 = *i*-Pr (85%);
1b R^1 = Bn (79%);
1c R^1 = *t*-Bu (81%)

2a R^1 = *i*-Pr, R^2 = OMe (43%);
2b R^1 = *i*-Pr, R^2 = H (38%);
2c R^1 = *i*-Pr, R^2 = Me (41%);
2d R^1 = Bn, R^2 = OMe (40%);
2e R^1 = *t*-Bu, R^2 = OMe (40%)

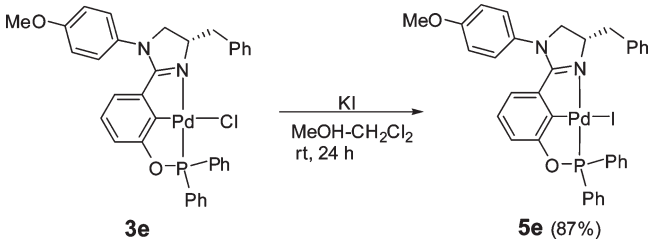
3a R^1 = *i*-Pr, R^2 = OMe, R^3 = Ph (52%);
3b R^1 = *i*-Pr, R^2 = OMe, R^3 = *i*-Pr (45%);
3c R^1 = *i*-Pr, R^2 = H, R^3 = Ph (49%);
3d R^1 = *i*-Pr, R^2 = Me, R^3 = Ph (50%);
3e R^1 = Bn, R^2 = OMe, R^3 = Ph (47%);
3f R^1 = *t*-Bu, R^2 = OMe, R^3 = Ph (50%)

Scheme 5. Synthesis of a Chiral PCN Pincer Ni(II) Complex of an (Imidazolinyl)aryl Phosphinite Ligand



2a **4a** (41%)

Scheme 6. Conversion of Pd−Cl Complex 3e to Pd−I Complex 5e by Halide Exchange Reaction with KI



3e **5e** (87%)

active Pd(0) species in the C−C couplings including Suzuki−Miyaura reactions, and the reactions proceed via a Pd(0)−Pd(II) catalytic cycle.[7a,22] However, there is still evidence that the Pd−C bond remains intact during catalysis and the pincer Pd complexes can be recovered and reused for Suzuki reactions, suggesting the mechanism of a Pd(II)−Pd(IV) catalytic cycle.[6b,13f] This was the case in the chiral pincer Pd(Phebox)-catalyzed asymmetric Suzuki−Miyaura reactions.[13f] As for the role of the present chiral PCN pincer Pd complex **3** or **5e** in the catalysis under the given reaction conditions, we

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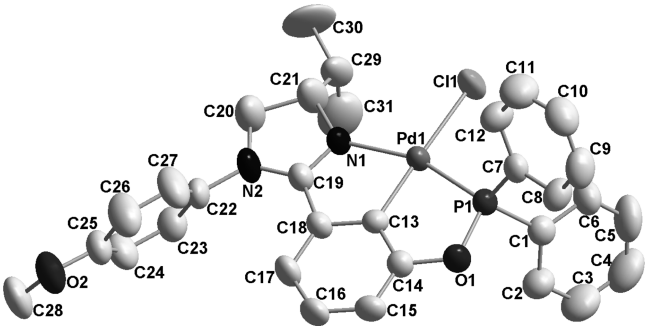


Figure 1. Molecular structure of **3a**·H_2O (ellipsoids drawn at the 50% probability level). Hydrogen atoms and solvent molecules are omitted for clarity.

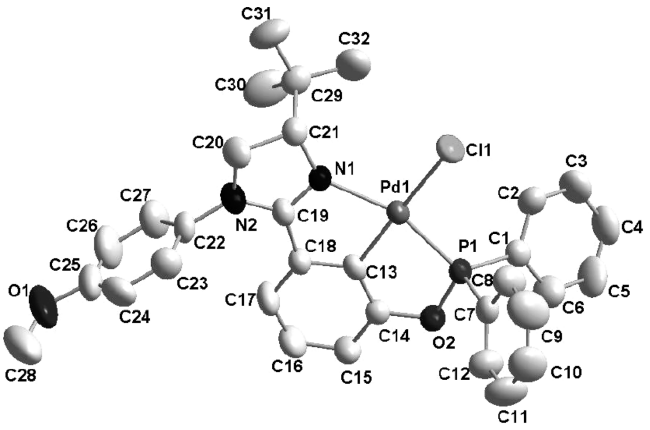


Figure 2. Molecular structure of **3f**·CH_2Cl_2 (ellipsoids drawn at the 50% probability level). Hydrogen atoms and solvent molecules are omitted for clarity.

propose the cleavage of the Pd−C bond in the complexes and the formation of the Pd(0) species based on the following experimental results: (a) the original Pd complexes or the corresponding Pd−I complexes were not detected at the end of the catalytic reaction, (b) complex **3b** gave no ee and the

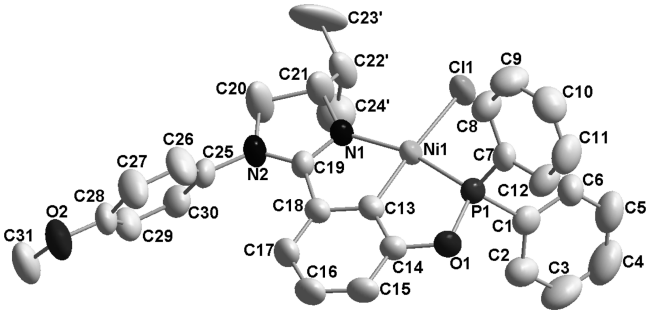


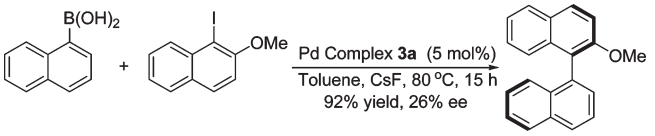
Figure 3. Molecular structure of **4a**·0.5CH_2Cl_2 (ellipsoids drawn at the 50% probability level). Hydrogen atoms and solvent molecules are omitted for clarity.

Table 1. Selected Bond Lengths [Å] and Angles [deg] for Complexes 3a·H_2O, 3f·CH_2Cl_2, and 4a·0.5CH_2Cl_2[a]

	3a·H_2O	**3f**·CH_2Cl_2	**4a**·0.5CH_2Cl_2
M−C	1.969(6)	1.970(5)	1.869(6)
M−N	2.107(5)	2.127(4)	1.949(5)
M−Cl	2.3766(18)	2.3875(14)	2.2106(19)
M−P	2.2037(16)	2.1948(14)	2.1156(17)
C−M−N	79.1(2)	79.14(18)	82.7(2)
N−M−Cl	101.93(15)	101.47(12)	101.11(15)
Cl−M−P	98.27(7)	99.41(5)	94.92(7)
P−M−C	80.70(17)	79.85(15)	81.27(19)
C−M−Cl	178.53(18)	176.69(15)	176.10(19)
N−M−P	159.78(15)	158.91(11)	163.96(15)

[a] For complexes **3a** and **3f**, M = Pd; for complex **4a**, M = Ni.

Scheme 7. Asymmetric Suzuki−Miyaura Reaction of 1-Iodo-2-methoxynaphthalene with 1-Naphthaleneboronic Acid Catalyzed by Chiral PCN Pincer Pd Complex 3a



other six Pd complexes with different chiral imidazoline groups exhibited similar stereoselectivity (~25% ee), and (c) lower reaction temperature led to a significant decrease in the catalytic activity of the Pd complex. For example, the yield of the product was only 45% at 70 °C in comparison with 88% yield at 80 °C (see Supporting Information). We thought that the markedly low activity might be caused by the slower release of the true catalytically active Pd(0) species at lower temperature since it was known that high temperature helped the cleavage of stable palladacycles [Pd(II)] to form Pd(0) species. If the above assumption of the formation of Pd(0) species was made, it was most likely that partial or complete dissociation of the chiral imidazoline nitrogen donor from Pd(0) occurred, which led to low and similar enantioselectivities or even loss of enantioselectivities in the asymmetric Suzuki−Miyaura reactions.

Conclusions

In summary, a series of unsymmetrical chiral PCN pincer Pd(II) and Ni(II) complexes of (imidazolinyl)aryl phosphinite ligands have been prepared via C−H bond activation of the related ligands and characterized by X-ray crystal structure determination. The complexes can be easily accessed by a simple assembly from commercially available *m*-hydroxybenzoic acid, chiral amino alcohols, amines, and chlorophosphines. A combination of these materials provides a high diversification of the unsymmetrical chiral PCN pincer Pd and Ni complexes. The new Pd complexes show rather moderate stereoselectivities in the asymmetric Suzuki−Miyaura reaction.

Experimental Section

General Procedures. Solvents were dried with standard methods and freshly distilled prior to use if needed. 1-Iodo-2-methoxynaphthalene,[23] 1-naphthaleneboronic acid,[24] chiral amino alcohols,[25] $NiCl_2(THF)_x$,[26] and $PdCl_2(CH_3CN)_2$[27] were prepared according to the literature methods. All other chemicals were used as purchased. Melting points were measured on a XT4A melting point apparatus and are uncorrected. Infrared spectra were obtained with a Bruker VECTOR 22 spectrophotometer. ^1H, ^{13}C, and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker DPX-400 or Bruker DPX-300 spectrometer in $CDCl_3$ with TMS as an internal standard for ^1H and ^{13}C NMR and 85% H_3PO_4 as external standard for $^{31}P\{^1H\}$ NMR. HRMS were determined on a Waters Q-Tof Micro MS/MS System ESI spectrometer. Elemental analyses were measured on a Thermo Flash EA 1112 elemental analyzer. Optical rotations were recorded on a Perkin-Elmer 341 polarimeter.

General Procedure for the Synthesis of 3-Acetoxybenzamido Alcohol 1. To a well-stirred solution of sodium hydroxide (3.0 g, 75.0 mmol) in water (40 mL) was added commercially available 3-hydroxybenzoic acid (5.0 g, 36.2 mmol). After cooling to 0 °C, acetic anhydride (8.64 g, 84.7 mmol) was added once. The resultant mixture was stirred at room temperature for 6 h, filtered, and washed with cold water to afford 3-acetoxybenzoic acid (6.2 g, 94% yield). The obtained 3-acetoxybenzoic acid (6.2 g, 34.4 mmol) was then dissolved in $SOCl_2$ (3.8 mL, 52.0 mmol) and one drop of DMF. After it was refluxed for 5 h, the reaction mixture was concentrated under reduced pressure to give 3-acetoxybenzoyl chloride as a pale yellow oil (6.68 g, 98% yield), which was used in the next step without further purification. To a stirred solution of amino alcohol (12.0 mmol) and Et_3N (1.65 mL, 12.0 mmol) in THF (60 mL) was added dropwise a solution of 3-acetoxybenzoyl chloride (2.0 g, 10.1 mmol) in 40 mL of THF at 0 °C. After stirring at 0 °C for 12 h, the reaction mixture was filtered and evaporated. The residue was purified by passing through a silica gel column with acetone−dichloromethane (1:2) as eluent, giving the corresponding amido alcohol **1**.

3-Acetoxybenzoic acid: white solids; mp 134−135 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 8.01 (td, J = 1.2, 8.0 Hz, 1H, Ar-H), 7.85 (t, J = 2.0 Hz, 1H, Ar-H), 7.51 (t, J = 8.0 Hz, 1H, Ar-H), 7.37 (ddd, J = 1.2, 2.4, 8.0 Hz, 1H, Ar-H), 2.35 (s, 3H, Ac); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.3, 169.2, 150.7, 130.8, 129.6, 127.6, 127.3, 123.4, 21.1.

3-Acetoxybenzoyl chloride: ^1H NMR (400 MHz, $CDCl_3$) δ 8.01−7.99 (m, 1H, Ar-H), 7.84 (t, J = 2.0 Hz, 1H, Ar-H), 7.53 (t, J = 8.0 Hz, 1H, Ar-H), 7.43 (ddd, J = 0.9, 2.3, 8.0 Hz, 1H, Ar-H), 2.34 (s, 3H, Ac); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 167.2, 150.6, 134.3, 129.7, 128.5, 128.4, 124.2, 20.7.

3-Acetoxy-*N*-((*S*)-1-hydroxy-3-methylbutan-2-yl)benzamide (1a): 2.28 g, 85% yield; white solids; mp 66−68 °C; $[\alpha]_D^{20}$ −33 (*c* 0.126,

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Table 2. Summary of Crystal Structure Determination for Complexes 3a·H_2O, 3f·CH_2Cl_2, and 4a·0.5CH_2Cl_2

	3a·H_2O	**3f**·CH_2Cl_2	**4a**·0.5CH_2Cl_2
formula	$C_{31}H_{32}ClN_2O_3PPd$	$C_{33}H_{34}Cl_3N_2O_2PPd$	$C_{31.5}H_{31}Cl_2N_2NiO_2P$
M_r	653.44	734.34	630.17
temperature [K]	291(2)	293(2)	291(2)
wavelength [Å]	0.71073	0.71073	0.71073
cryst syst	monoclinic	orthorhombic	monoclinic
space group	*P*2(1)/*n*	*P*2(1)2(1)2(1)	*P*2(1)/*n*
cryst size [mm]	0.20 × 0.20 × 0.18	0.24 × 0.20 × 0.18	0.20 × 0.18 × 0.16
a [Å]	15.395(3)	9.918(2)	15.198(3)
b [Å]	13.024(3)	14.418(3)	13.158(3)
c [Å]	15.650(3)	23.256(5)	15.455(3)
α [deg]	90	90	90
β [deg]	99.36(3)	90	99.24(3)
γ [deg]	90	90	90
V [Å^3]	3095.9(11)	3325.6(12)	3050.6(10)
Z	4	4	2
D_{calcd} [g cm^{-3}]	1.400	1.467	1.372
μ [mm^{-1}]	0.770	0.879	0.894
θ range [deg]	2.33 − 25.00	1.66 − 27.93	1.74 −25.00
index ranges	$0 \le h \le 18$	$-13 \le h \le 12$	$0 \le h \le 17$
	$-15 \le k \le 15$	$-18 \le k \le 18$	$-15 \le k \le 15$
	$-18 \le l \le 18$	$-30 \le l \le 30$	$-18 \le l \le 18$
no. of data collected	9622	40 906	9502
no. of unique data	5281	7947	5047
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
goodness-of-fit on F^2	1.103	1.074	1.046
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0635	R1 = 0.0501	R1 = 0.0775
	wR2 = 0.1526	wR2 = 0.1285	wR2 = 0.1818
R indices (all data)	R1 = 0.0698	R1 = 0.0544	R1 = 0.0947
	wR2 = 0.1563	wR2 = 0.1370	wR2 = 0.1918
F(000)	1332	1496	1308
peak/hole [e Å^{-3}]	0.992/−0.540	0.481/ −0.554	0.626/−0.401

CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.58 (d, *J* = 7.7 Hz, 1H, Ar-H), 7.50 (s, 1H, Ar-H), 7.36 (t, *J* = 7.9 Hz, 1H, Ar-H), 7.17(dd, *J* = 1.0, 7.9 Hz, 1H, Ar-H), 6.75 (d, *J* = 8.6 Hz, 1H, NH), 3.89−3.86 (m, 1H, C*H*NH), 3.71−3.69 (m, 2H, CH_2OH), 3.43−3.42 (m, 1H, OH), 2.28 (s, 3H, Ac), 1.97−1.94 (m, 1H, C*H*(CH_3)$_2$), 0.98 (d, *J* = 7.6 Hz, 3H, CH_3CHCH_3), 0.96 (d, *J* = 7.3 Hz, 3H, CH_3CHCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 169.5, 167.2, 150.6, 136.2, 129.5, 124.6, 124.3, 120.6, 63.0, 57.4, 29.0, 21.0, 19.5, 19.0; IR (KBr) *ν* 3363, 3073, 2963, 2876, 1768, 1642, 1583, 1542, 1481, 1370, 1201, 1078, 1017, 809, 752, 699 cm^{-1}; HRMS (positive ESI): [M + Na]$^+$ calcd for $C_{14}H_{19}NNaO_4$ 288.1212, found 288.1206.

3-Acetoxy-*N*-((*S*)-1-hydroxy-3-phenylpropan-2-yl)benzamide (1b): 2.50 g, 79% yield; white solids; mp 97−98 °C; $[\alpha]_D^{20}$ −60 (*c* 0.132, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.46 (d, *J* = 7.8 Hz, 1H, Ar-H), 7.43 (s, 1H, Ar-H), 7.33−7.16 (m, 7H, Ar-H), 6.67 (d, *J* = 7.7 Hz, 1H, NH), 4.35−4.31 (m, 1H, C*H*NH), 3.73−3.70 (m, 1H, CH_2OH), 3.64−3.60 (m, 1H, CH_2OH), 3.26 (br s, 1H, OH), 2.96 (d, *J* = 7.2 Hz, 2H, CH_2Ph), 2.29 (s, 3H, Ac); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 169.5, 167.0, 150.7, 137.7, 135.9, 129.7, 129.3, 128.7, 126.7, 124.8, 124.3, 120.7, 63.6, 53.3, 36.9, 21.0; IR (KBr) *ν* 3309, 2954, 2924, 2860, 1766, 1640, 1582, 1544, 1370, 1207, 1044, 904, 871, 811, 751, 700 cm^{-1}; HRMS (positive ESI) [M + Na]$^+$ calcd for $C_{18}H_{19}NNaO_4$ 336.1212, found 336.1208.

3-Acetoxy-*N*-((*S*)-1-hydroxy-3,3-dimethylbutan-2-yl)benzamide (1c): 2.28 g, 81% yield; white solids; mp 92−93 °C; $[\alpha]_D^{20}$ −14 (*c* 0.259, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.60 (d, *J* = 7.2 Hz, 1H, Ar-H), 7.49 (t, *J* = 1.9 Hz, 1H, Ar-H), 7.40 (t, *J* = 7.9 Hz, 1H, Ar-H), 7.22−7.19 (m, 1H, Ar-H), 6.46 (d, *J* = 9.2 Hz, 1H, NH), 4.04−3.99 (m, 1H, C*H*NH), 3.89−3.84 (m, 1H, CH_2OH), 3.68−3.62 (m, 1H, CH_2OH), 2.86−2.84 (m, 1H, OH), 2.30 (s, 3H, Ac), 1.01 (s, 9H, C(CH_3)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 169.5, 167.6, 150.7, 136.3, 129.6, 124.8, 124.3, 120.6, 62.7, 59.8, 34.0, 27.0, 21.1; IR (KBr) *ν* 3383, 3073, 2963, 2901, 2876, 1768, 1643, 1584, 1540, 1479, 1369, 1201, 1126, 1049, 1019, 815, 751, 698 cm^{-1}; HRMS (positive ESI) [M + Na]$^+$ calcd for $C_{15}H_{21}NNaO_4$ 302.1368, found 302.1371.

General Procedure for the Synthesis of 3-(Imidazolinyl)phenol 2. The obtained amido alcohol (7.5 mmol) was reacted with thionyl chloride (2.2 mL, 30.0 mmol) at reflux for 6 h. Excess thionyl chloride was evaporated. The residue was dissolved in dry diethyl ether (25 mL) and filtered to remove insoluble impurities. To this solution was added dry triethylamine (3.2 mL, 22.5 mmol), followed by the corresponding amine (8.25 mmol). After stirring for 12 h at room temperature, 10% NaOH (20 mL) was added and stirred for another 6 h. The aqueous solution was extracted with dichloromethane, and the organic layer was washed with brine, dried over $MgSO_4$, and evaporated. The residue was purified by preparative TLC on silica gel plates to afford the corresponding 3-(imidazolinyl)phenol **2**.

3-((*S*)-4-Isopropyl-1-(4-methoxyphenyl)-4,5-dihydro-1*H*-imidazole-2-yl)phenol (2a): 0.98 g, 43% yield; white solids; mp 153−154 °C; $[\alpha]_D^{20}$ +561 (*c* 0.196, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.56 (s, 1H, Ar-H), 6.89 (t, *J* = 7.9 Hz, 1H, Ar-H), 6.79 (d, *J* = 8.9 Hz, 2H, NAr), 6.72 (d, *J* = 8.9 Hz, 2H, NAr), 6.68 (dd, *J* = 1.7,8.0 Hz 6.48 (d, *J* = 7.5 Hz, 1H, Ar-H), 4.24 (app t, *J* = 10.0 Hz, 1H, NC*H*H), 4.17−4.11 (m, 1H, NCH), 3.74 (s, 3H, OCH_3), 3.57 (dd, *J* = 6.6, 9.2 Hz, 1H, NCH*H*), 2.00−1.96 (m, 1H, C*H*(CH_3)$_2$), 1.03 (d, *J* = 6.6 Hz, 3H, CH_3CHCH_3), 1.02 (d, *J* = 6.5 Hz, 3H, CH_3CHCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 163.8, 158.1, 156.4, 135.1, 130.4, 129.0, 124.7, 119.0, 118.2, 116.6, 114.0, 67.7, 56.1, 55.3, 33.0, 18.0, 17.6; IR (KBr) *ν* 3448, 2954, 2862, 1584, 1569, 1509, 1455, 1395, 1242, 1175, 1040, 878, 833, 797, 711, 685 cm^{-1}; HRMS (positive ESI) [M + H]$^+$ calcd for $C_{19}H_{23}N_2O_2$ 311.1760, found 311.1753.

3-((*S*)-4-Isopropyl-1-phenyl-4,5-dihydro-1*H*-imidazole-2-yl)-phenol (2b): 0.79 g, 38% yield; white solids; mp 197−198 °C; $[\alpha]_D^{20}$ +546 (*c* 0.174, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.49 (s, 1H, Ar-H), 7.17 (t, *J* = 7.8 Hz, 2H, NPh), 7.00 (t, *J* = 7.1 Hz, 1H, NPh), 6.92 (t, *J* = 7.9 Hz, 1H, Ar-H), 6.81 (d, *J* = 8.1 Hz, 2H, NPh), 6.72−6.69 (m, 1H, Ar-H), 6.54 (d, *J* = 7.5 Hz, 1H, Ar-H), 4.30 (app t, *J* = 10.1 Hz, 1H, NC*H*H), 4.17−4.11 (m, 1H, NCH), 3.66 (dd, *J* = 6.2, 9.4 Hz, 1H, NCH*H*), 2.00−1.95 (m, 1H, C*H*(CH_3)$_2$), 1.02 (d, *J* = 6.8 Hz, 3H, CH_3CHCH_3), 1.01 (d, *J* = 6.8 Hz, 3H, CH_3CHCH_3); ^{13}C

NMR (100 MHz, $CDCl_3$) δ 163.2, 158.2, 141.6, 130.4, 129.2, 128.7, 123.8, 122.4, 119.1, 118.5, 116.4, 67.5, 55.4, 33.0, 18.0, 17.6; IR (KBr) ν 3061, 2960, 2929, 2884, 2807, 1586, 1497, 1453, 1416, 1377, 1306, 1263, 1135, 967, 853, 789, 758, 697 cm^{-1}; HRMS (positive ESI) $[M + H]^+$ calcd for $C_{18}H_{21}N_2O$ 281.1654, found 281.1652.

3-((*S*)-4-Isopropyl-1-*p*-tolyl-4,5-dihydro-1*H*-imidazole-2-yl)-phenol (2c): 0.90 g, 41% yield; white solids; mp 164−165 °C; $[\alpha]_D^{20}$ +398 (*c* 0.125, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.33 (s, 1H, Ar-H), 6.99 (d, J = 8.3 Hz, 2H, NAr), 6.92 (t, J = 8.0 Hz, 1H, Ar-H), 6.77 (dd, J = 2.1, 8.4 Hz, 1H, Ar-H), 6.74 (d, J = 8.3 Hz, 2H, NAr), 6.59 (d, J = 7.7 Hz, 1H, Ar-H), 4.28 (app t, J = 10.6 Hz, 1H, NC*H*H), 4.14−4.08 (m, 1H, NCH), 3.65 (dd, J = 6.6, 9.8 Hz, 1H, NCH*H*), 2.26 (s, 3H, CH_3), 1.98−1.91 (m, 1H, C*H*(CH_3)$_2$), 0.99 (d, J = 6.4 Hz, C*H*$_3$CHCH$_3$), 0.98 (d, J = 6.6 Hz, CH_3CHC*H*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 158.2, 138.3, 134.7, 129.6, 129.3, 128.9, 123.1, 119.3, 119.1, 116.6, 66.2, 55.8, 32.7, 20.9, 18.0, 17.3; IR (KBr) ν 3445, 3031, 2958, 2917, 2872, 1569, 1513,1479, 1451, 1391, 1307, 1245, 1133, 863, 817, 789, 716 cm^{-1}; HRMS (positive ESI) $[M + H]^+$ calcd for $C_{19}H_{23}N_2O$ 295.1810, found 295.1805.

3-((*S*)-4-Benzyl-1-(4-methoxyphenyl)-4,5-dihydro-1*H*-imidazole-2-yl)phenol (2d): 1.07 g, 40% yield; white solids; mp 97−98 °C; $[\alpha]_D^{20}$ +291 (*c* 0.216, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.37 (s, 1H, Ar-H), 7.31−7.26 (m, 4H, Ph-H), 7.22−7.18 (m, 1H, Ph-H), 6.92 (t, J = 7.9 Hz, 1H, Ar-H), 6.75 (ddd, J = 0.7, 2.3, 8.2 Hz, 1H, Ar-H), 6.68−6.64 (m, 2H, NAr), 6.61−6.57 (m, 2H, NAr), 6.49 (d, J = 7.6 Hz, 1H, Ar-H), 4.61−4.54 (m, 1H, NCH), 4.09 (app t, J = 10.1 Hz, 1H, NC*H*H), 3.71 (s, 3H, OCH_3), 3.67 (dd, J = 6.5, 9.7 Hz, 1H, NCH*H*), 3.17 (dd, J = 4.5, 13.6 Hz, 1H, C*H*HPh), 2.93 (dd, J = 8.0, 13.6 Hz, 1H, CH*H*Ph); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8, 158.1, 156.8, 137.4, 134.5, 129.7, 129.5, 129.1, 128.4, 126.5, 125.1, 119.3, 118.7, 116.6, 114.0, 62.5, 58.1 (NCH_2), 55.3, 41.7 (CH_2Ph); IR (KBr) ν 3403, 3056, 3023, 2928, 2840, 1570, 1511, 1451, 1399, 1289, 1246, 1178, 1036, 832, 791, 706 cm^{-1}; HRMS (positive ESI) $[M + H]^+$ calcd for $C_{23}H_{23}N_2O_2$ 359.1760, found 359.1750.

3-((*S*)-4-*tert*-Butyl-1-(4-methoxyphenyl)-4,5-dihydro-1*H*-imidazole-2-yl)phenol (2e): 0.97 g, 40% yield; white solids; mp 164−165 °C; $[\alpha]_D^{20}$ +696 (*c* 0.81, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.77 (s, 1H, Ar-H), 6.88 (t, J = 7.9 Hz, 1H, Ar-H), 6.79 (d, J = 7.9 Hz, 2H, NAr), 6.73 (d, J = 7.9 Hz, 2H, NAr), 6.65 (dd, J = 1.8, 8.1 Hz, 1H, Ar-H), 6.45 (d, J = 7.6 Hz, 1H, Ar-H), 4.31 (app t, J = 10.5 Hz, 1H, NC*H*H), 4.01 (dd, J = 6.3, 11.1 Hz 1H, NCH), 3.74 (s, 3H, OCH_3), 3.61 (dd, J = 6.3, 9.8 Hz, 1H, NCH*H*), 1.04 (s, 9H, C(CH_3)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 158.3, 156.4, 135.1,130.3, 128.9, 124.8, 118.9, 118.1, 116.8, 114.1, 71.5, 55.38, 55.36, 34.6, 25.6; IR (KBr) ν 3411, 3050, 2955, 2900, 2868, 2835, 1573, 1511, 1451, 1396, 1365, 1309, 1280, 1245, 1178, 1035, 1003, 862, 830, 786 cm^{-1}; HRMS (positive ESI) $[M + H]^+$ calcd for $C_{20}H_{25}N_2O_2$ 325.1916, found 325.1920.

General Procedure for the Synthesis of PCN Pincer Chloropalladium Complexes 3. To a stirred solution of **2a**−**e** (0.55 mmol) and triethylamine (93 μL, 0.66 mmol) in toluene (20 mL) was added diphenylchlorophosphine or diisopropylphosphine (0.66 mmol) under N_2 atmosphere at rt. The resultant mixture was refluxed for 3 h. $PdCl_2$ (97 mg, 0.55 mmol for **3a**−**3e**) or $PdCl_2(CH_3CN)_2$ (144 mg, 0.55 mmol for **3f**) was then added, and the reaction mixture was refluxed for another 12 h. After cooling, filtration, and evaporation, the residue was purified by preparative TLC on silica gel plates eluting with CH_2Cl_2 to afford the corresponding PCN pincer Pd(II) complexes **3a**−**f**.

2-((*S*)-4-Isopropyl-1-(4-methoxyphenyl)-4,5-dihydro-1*H*-imidazole-2-yl)-6-(diphenylphosphinoxy)phenylchloropalladium(II) (3a): 181.7 mg, 52% yield; pale yellow solids; mp 239−240 °C; $[\alpha]_D^{20}$ +89 (*c* 0.174, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 8.03−8.00 (m, 4H, Ph-H), 7.50−7.45 (m, 6H, Ph-H), 7.18 (d, J = 8.8 Hz, 2H, NAr), 6.94 (d, J = 8.8 Hz, 2H, NAr), 6.88 (d, J = 8.0 Hz, 1H, Ar-H), 6.74 (t, J = 8.0 Hz, 1H, Ar-H), 6.09 (d, J = 7.7 Hz, 1H, Ar-H), 4.44−4.39 (m, 1H, NCH), 3.98 (app t, J = 10.7 Hz, 1H, NC*H*H), 3.85 (s, 3H, OCH_3), 3.78 (dd, J = 5.8, 10.0 Hz, 1H, NCH*H*), 2.85−2.80 (m, 1H, C*H*(CH_3)$_2$), 0.95 (d, J = 6.7 Hz, 3H, C*H*$_3$-CHCH$_3$), 0.94 (d, J = 6.9 Hz, 3H, CH_3CHC*H*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 162.5 (d, $^2J_{P-C}$ = 11.7 Hz), 159.2, 151.2, 135.7, 133.8 (d, $^1J_{P-C}$ = 52.1 Hz), 133.4 (d, $^1J_{P-C}$ = 53.3 Hz), 133.0, 131.9, 131.8 (d, $^2J_{P-C}$ = 15.1 Hz), 131.6 (d, $^2J_{P-C}$ = 17.3 Hz), 128.8 (d, $^3J_{P-C}$ = 11.7 Hz), 128.7 (d, $^3J_{P-C}$ = 11.5 Hz), 128.2, 125.5, 121.1, 115.0, 114.3 (d, $^3J_{P-C}$ = 16.7 Hz), 66.3, 55.6, 30.1, 18.8, 14.6; IR (KBr) ν 3428, 3054, 2954, 2921, 2867, 1564, 1531, 1523, 1463, 1437, 1295, 1250, 1226, 1109, 1019, 895, 872, 838, 796, 746, 690 cm^{-1}; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 155.4. Anal. Calcd for $C_{31}H_{30}ClN_2O_2PPd \cdot 0.5CH_2Cl_2$ (677.90): C, 55.81; H, 4.61; N, 4.13. Found: C, 55.90; H, 4.51; N, 3.99.

2-((*S*)-4-Isopropyl-1-(4-methoxyphenyl)-4,5-dihydro-1*H*-imidazole-2-yl)-6-(diisopropylphosphinoxy)phenylchloropalladium(II) (3b): 140.4 mg, 45% yield; pale yellow solids; mp 240−241 °C; $[\alpha]_D^{20}$ +66 (*c* 0.174, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, J = 8.4 Hz, 2H, NAr), 6.94 (d, J = 8.4 Hz, 2H, NAr), 6.72 (d, J = 7.7 Hz, 1H, Ar-H), 6.68 (t, J = 7.6 Hz, 1H, Ar-H), 6.05 (d, J = 7.3 Hz, 1H, Ar-H), 4.38−4.34 (m, 1H, NCH), 3.97 (app t, J = 10.5 Hz, 1H, NC*H*H), 3.86 (s, 3H, OCH_3), 3.75 (dd, J = 6.0, 9.9 Hz, 1H, NCH*H*), 2.82−2.74 (m, 1H, C*H*(CH_3)$_2$), 2.48−2.38 (m, 2H, PC*H*(CH_3)$_2$), 1.44 (dd, J = 1.4, 7.2 Hz, 3H, PCH(C*H*$_3$)$_2$), 1.39 (dd, J = 1.5, 7.1 Hz, 3H, PCH(C*H*$_3$)$_2$), 1.35−1.24 (m, 6H, PCH(C*H*$_3$)$_2$), 0.94 (d, J = 6.8 Hz, 3H, C*H*$_3$CHCH$_3$), 0.91 (d, J = 7.0 Hz, 3H, CH_3CHC*H*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4 (d, $^3J_{P-C}$ = 2.7 Hz), 163.9 (d, $^2J_{P-C}$ = 7.9 Hz), 159.0, 150.2, 135.8, 133.1, 128.2, 125.0, 120.6, 114.9, 113.3 (d, $^3J_{P-C}$ = 15.0 Hz), 66.1 (d, $^3J_{P-C}$ = 2.1 Hz), 55.6 (d, $^4J_{P-C}$ = 3.4 Hz), 55.5, 30.0, 29.0 (d, $^1J_{P-C}$ = 24.6 Hz), 28.9 (d, $^1J_{P-C}$ = 24.4 Hz), 18.7, 17.5 (d, $^2J_{P-C}$ = 5.8 Hz), 17.3 (d, $^2J_{P-C}$ = 6.3 Hz), 17.0, 16.5, 14.6; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 202.6; IR (KBr) ν 3432, 2958, 2871, 2831, 1569, 1534, 1513, 1462, 1439, 1297, 1251, 1164, 1030, 873, 838, 788, 687 cm^{-1}. Anal. Calcd for $C_{25}H_{34}ClN_2O_2PPd$ (567.40): C, 52.92; H, 6.04; N, 4.94. Found: C, 53.11; H, 6.00; N, 4.79.

2-(*S*)-4-Isopropyl-1-phenyl-4,5-dihydro-1*H*-imidazole-2-yl)-6-(diphenylphosphinoxy)phenylchloropalladium(II) (3c): 163.1 mg, 49% yield; pale yellow solids; mp 255−256 °C; $[\alpha]_D^{20}$ +99 (*c* 0.164, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) 8.06−8.01 (m, 4H, Ph-H), 7.51−7.35 (m, 9H, Ph-H), 7.25−7.24 (m, 1H, Ph-H), 7.19−7.14 (m, 1H, Ph-H), 6.89 (d, J = 8.0 Hz, 1H, Ar-H), 6.75 (t, J = 7.7 Hz, 1H, Ar-H), 6.17 (d, J = 7.7 Hz, 1H, Ar-H), 4.72−4.42 (m, 1H, NCH), 4.07 (app t, J = 10.6 Hz, 1H, NC*H*H), 3.84 (dd, J = 5.6, 9.9 Hz, 1H, NCH*H*), 2.88−2.80 (m, 1H, C*H*(CH_3)$_2$), 0.95 (d, J = 6.8 Hz, 3H, C*H*$_3$CHCH$_3$), 0.94 (d, J = 7.0 Hz, 3H, CH_3CHC*H*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 162.6, 151.3, 140.4, 135.7, 133.7 (d, $^1J_{P-C}$ = 52.3 Hz), 133.4 (d, $^1J_{P-C}$ = 53.3 Hz),131.9,131.8 (d, $^2J_{P-C}$ =15.1 Hz), 131.6 (d, $^2J_{P-C}$ =14.7 Hz), 129.8, 128.9 (d, $^3J_{P-C}$ = 11.6 Hz), 128.8 (d, $^3J_{P-C}$ = 11.7 Hz), 127.8, 126.6, 125.5, 121.2, 114.4 (d, $^3J_{P-C}$ = 16.8 Hz), 66.4, 55.3, 30.0, 18.8, 14.6; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 155.1; IR (KBr) ν 3449, 3050, 2955, 2917, 2869, 1565, 1532, 1498, 1434, 1298, 1225, 1107, 1023, 996, 871, 794, 749, 696 cm^{-1}. Anal. Calcd for $C_{30}H_{28}ClN_2OPPd \cdot 0.75CH_2Cl_2$ (669.10): C, 55.20; H, 4.44; N, 4.19. Found: C, 55.40; H, 4.34; N, 4.03.

2-((*S*)-4-Isopropyl-1-*p*-tolyl-4,5-dihydro-1*H*-imidazole-2-yl)-6-(diphenylphosphinoxy)phenylchloropalladium(II) (3d): 170.3 mg, 50% yield; pale yellow solids; mp 275−276 °C; $[\alpha]_D^{20}$ +110 (*c* 0.166, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 8.05−8.00 (m, 4H, Ph-H), 7.51−7.43 (m, 6H, Ph-H), 7.22 (d, J = 8.1 Hz, 2H, NAr), 7.13 (d, J = 8.1 Hz, 2H, NAr), 6.88 (d, J = 8.0 Hz, 1H, Ar-H), 6.74 (dt, J = 0.9, 7.8 Hz, 1H, Ar-H), 6.16 (d, J = 7.7 Hz, 1H, Ar-H), 4.45−4.40 (m, 1H, NCH), 4.02 (app t, J = 10.6 Hz, 1H, NC*H*H), 3.79 (dd, J = 5.7, 10.0 Hz, 1H, NCH*H*), 2.85−2.80 (m, 1H, C*H*(CH_3)$_2$), 2.41 (s, 3H, CH_3), 0.94 (d, J = 6.8 Hz, 3H, C*H*$_3$CHCH$_3$), 0.93 (d, J = 7.1 Hz, 3H, CH_3CH-C*H*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 162.5 (d, $^2J_{P-C}$ = 11.5 Hz), 151.2, 137.9, 137.7, 135.7, 133.8 (d, $^1J_{P-C}$ = 52.1 Hz),

133.4 (d, $^1J_{P-C}$ = 53.4 Hz), 131.9, 131.8 (d, $^2J_{P-C}$ = 14.7 Hz), 131.6 (d, $^2J_{P-C}$ = 14.7 Hz), 130.4, 128.8 (d, $^3J_{P-C}$ = 11.6 Hz), 128.7 (d, $^3J_{P-C}$ = 11.6 Hz), 126.5, 125.5, 121.2, 114.3 (d, $^3J_{P-C}$ = 16.9 Hz), 66.4, 55.4, 30.1, 21.2, 18.8, 14.6; $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$) δ 154.6; IR (KBr) ν 3448, 3044, 2952, 2917, 2864, 1565, 1533, 1437, 1232, 1106, 1038, 1019, 874, 792, 697 cm^{-1}. Anal. Calcd for $C_{31}H_{30}ClN_2OPPd \cdot 0.25CH_2Cl_2$ (640.66): C, 58.59; H, 4.80; N, 4.37. Found: C, 58.48; H, 4.79; N, 4.32.

2-((*S*)-4-Benzyl-1-(4-methoxyphenyl)-4,5-dihydro-1*H*-imidazole-2-yl)-6-(diphenylphosphinoxy)phenylchloropalladium(II) (3e): 176.6 mg, 47% yield; pale yellow solids; mp 226−227 °C; $[\alpha]_D^{20}$ +161 (*c* 0.102, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 8.10−8.02 (m, 4H, Ph-H), 7.52−7.49 (m, 6H, Ph-H), 7.40 (d, *J* = 6.6 Hz, 2H, Ph-H), 7.26−7.17 (m, 4H, Ph and NAr), 6.90−6.84 (m, 3H, Ar and NAr), 6.72 (t, *J* = 79 Hz, 2H, Ph and Ar-H), 5.97 (d, *J* = 7.7 Hz, 1H, Ar-H), 4.74−4.69 (m, 1H, NCH), 4.03 (app t, *J* = 10.3 Hz, 1H, NC*H*H), 3.82 (s, 3H, OCH_3), 3.75 (dd, *J* = 5.1, 10.0 Hz, 1H, NCH*H*), 3.46 (dd, *J* = 3.4, 13.5 Hz, 1H, C*H*HPh), 3.18 (dd, *J* = 7.6, 13.5 Hz, 1H, CH*H*Ph); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1 (d, $^3J_{P-C}$ = 3.0 Hz), 162.4 (d, $^2J_{P-C}$ = 11.3 Hz), 159.1, 151.3, 137.5, 135.6, 133.6 (d, $^1J_{P-C}$ = 52.3 Hz), 133.4 (d, $^1J_{P-C}$ = 53.1 Hz), 132.3, 131.9 (virtual t, $^4J_{P-C}$ = 2.5 Hz), 131.7 (d, $^2J_{P-C}$ = 14.8 Hz), 131.6 (d, $^2J_{P-C}$ = 14.7 Hz), 130.1, 128.9 (d, $^3J_{P-C}$ = 11.7 Hz), 128.7 (d, $^3J_{P-C}$ = 11.7 Hz), 128.2, 126.3, 125.6, 121.0, 114.8, 114.4 (d, $^3J_{P-C}$ = 16.8 Hz), 62.3 (d, $^3J_{P-C}$ = 2.5 Hz), 59.3 (d, $^4J_{P-C}$ = 3.5 Hz), 55.5, 41.0; $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$) δ 154.8; IR (KBr) ν 3448, 3054, 2931, 1567, 1534, 1509, 1439, 1336, 1292, 1248, 1181, 1106, 1028, 871, 791, 747, 697 cm^{-1}. Anal. Calcd for $C_{35}H_{30}ClN_2O_2PPd \cdot 0.25CH_2Cl_2$ (704.70): C, 60.08; H, 4.36; N, 3.98. Found: C, 59.88; H, 4.34; N, 3.88.

2-((*S*)-4-*tert*-Butyl-1-(4-methoxyphenyl)-4,5-dihydro-1*H*-imidazole-2-yl)-6-(diphenylphosphinoxy)phenylchloropalladium(II) (3f): 178.6 mg, 50% yield; pale yellow solids; mp 138−140 °C; $[\alpha]_D^{20}$ +92 (*c* 0.242, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 8.07−8.00 (m, 4H, Ph-H), 7.51−7.44 (m, 6H, Ph-H), 7.16 (d, *J* = 7.1 Hz, 2H, NAr), 6.93 (d, *J* = 8.9 Hz, 2H, NAr), 6.87 (d, *J* = 8.0 Hz, 1H, Ar-H), 6.74 (dt, *J* = 0.9, 7.9 Hz, 1H, Ar-H), 6.11 (d, *J* = 7.7 Hz, 1H, Ar-H), 4.13 (dd, *J* = 3.3, 9.4 Hz, 1H, NCH), 4.00−3.93 (m, 2H, NCH_2), 3.84 (s, 3H, OCH_3), 1.11 (s, 9H, $C(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1 (d, $^3J_{P-C}$ = 3.2 Hz), 162.4 (d, $^2J_{P-C}$ = 11.3 Hz), 159.2, 150.7, 135.5, 133.8 (d, $^1J_{P-C}$ = 51.7 Hz), 133.2 (d, $^1J_{P-C}$ = 54.6 Hz), 132.8, 131.9 (d, $^4J_{P-C}$ = 2.6 Hz), 131.8 (d, $^2J_{P-C}$ = 14.6 Hz),131.7 (d, $^2J_{P-C}$ = 14.5 Hz), 128.8 (virtual t, $^3J_{P-C}$ = 11.1 Hz), 128.3, 125.5, 121.0, 114.9, 114.2 (d, $^3J_{P-C}$ = 17.0 Hz), 69.0 (d, $^3J_{P-C}$ = 2.8 Hz), 58.3 (d, $^4J_{P-C}$ = 2.9 Hz), 55.6, 36.0, 26.4; $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$) δ 155.1; IR (KBr) ν 3052, 2956, 2924, 2851, 1565, 1528, 1507, 1465,1438, 1367, 1328, 1287, 1249, 1181, 1108, 1034, 1010, 979, 873, 836, 790, 745, 694 cm^{-1}. Anal. Calcd for $C_{32}H_{32}ClN_2O_2PPd \cdot CH_2Cl_2$(734.34): C, 53.97; H, 4.67; N, 3.81. Found: C, 53.77; H, 4.83; N, 3.68.

Procedure for the Synthesis of PCN Pincer Chloronickel Complex 4a. To a stirred solution of **2a** (143 mg, 0.46 mmol) and triethylamine (77 μL, 0.55 mmol) in toluene (20 mL) was added diphenylchlorophosphine (0.55 mmol) under N_2 atmosphere at rt. The resultant mixture was refluxed for 3 h. $NiCl_2(THF)_{0.28}$ (114 mg, 0.76 mmol) was then added, and the reaction mixture was refluxed for another 12 h. After cooling, filtration, and evaporation, the residue was purified by preparative TLC on silica gel plates eluting with ethyl acetate and petroleum ether (1:1) to afford the corresponding PCN pincer Ni(II) complex **4a**.

2-((*S*)-4-iIsopropyl-1-(4-methoxyphenyl)-4,5-dihydro-1*H*-imidazole-2-yl)-6-(diphenylphosphinoxy)phenylchloronickel(II) (4a): 111.8 mg, brown solids; 41% yield; mp 147−148 °C; $[\alpha]_D^{20}$ +162 (*c* 0.112, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 8.08−8.02 (m, 4H, Ph-H), 7.54−7.42 (m, 6H, Ph-H), 7.18 (d, *J* = 8.8 Hz, 2H, NAr), 6.94 (d, *J*=8.8 Hz, 2H, NAr), 6.73−6.67 (m, 2H, Ar-H), 6.02 (d, *J* = 7.2 Hz, 1H, Ar-H), 4.20−4.16 (m, 1H, NCH), 4.02 (app t, *J* = 10.5 Hz, 1H, NC*H*H), 3.85 (s, 3H, OCH_3), 3.81 (dd, *J* = 4.6, 10.0 Hz, 1H, NCH*H*), 2.66−2.62 (m, 1H, C*H*$(CH_3)_2$), 0.98 (d, *J* = 6.8 Hz, 3H, C*H*$_3$CHCH$_3$), 0.89 (d, *J* = 7.0 Hz, 3H, CH_3CHCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 163.8 (d, $^2J_{P-C}$ = 15.3 Hz), 159.1, 149.4 (d, $^2J_{P-C}$ = 35.8 Hz), 137.1, 132.8 (d, $^1J_{P-C}$ = 46.5 Hz), 132.5 (d, $^1J_{P-C}$ = 47.8 Hz), 132.4, 131.8 (d, $^2J_{P-C}$ = 12.8 Hz), 131.7 (d, $^2J_{P-C}$ = 12.8 Hz), 131.5 (virtual t, $^4J_{P-C}$ =3.1 Hz), 128.7 (d, $^3J_{P-C}$ = 10.9 Hz), 128.6 (d, $^3J_{P-C}$ = 10.8 Hz), 127.9, 125.7, 119.8, 114.8, 113.3 (d, $^3J_{P-C}$ = 13.5 Hz), 64.3, 56.1, 55.6, 30.4, 18.7, 14.5; $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$) δ 149.0; IR (KBr) ν 3444, 3054, 2955, 2925, 2867, 1567, 1537, 1511, 1438, 1291, 1250, 1107, 1026, 870, 838, 793, 747, 696 cm^{-1}. Anal. Calcd for $C_{31}H_{30}ClNiN_2O_2P \cdot 0.5CH_2Cl_2$ (630.17): C, 60.04; H, 4.96; N, 4.45. Found: C, 60.72; H, 5.05; N, 4.40.

Procedure for the Synthesis of PCN Pincer Iodopalladium Complex 5e. To a stirred solution of methanol (20 mL) and dichloromethane (30 mL) were added **3e** (158.4 mg, 0.24 mmol) and potassium iodide (800 mg, 4.8 mmol) under air at room temperature. After it was stirred for 24 h at that temperature, the reaction mixture was filtered through a pad of Celite, and then the filtrate was concentrated under reduced pressure. Purification by silica gel chromatography (dichloromethane) gave yellow solids of **5e** in 87% yield (156.5 mg).

2-((*S*)-4-Benzyl-1-(4-methoxyphenyl)-4,5-dihydro-1*H*-imidazole-2-yl)-6-(diphenylphosphinoxy)phenyliodopalladium(II) (5e): mp 226−227 °C; $[\alpha]_D^{20}$ +114 (*c* 0.214, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 8.12−8.00 (m, 4H, Ph-H), 7.52−7.46 (m, 6H, Ph-H), 7.42 (d, *J* = 7.0 Hz, 2H, Ph-H), 7.25−7.20 (m, 4H, Ph and NAr), 6.94 (d, *J* = 8.0 Hz, 1H, Ar-H), 6.86 (d, *J* = 8.0 Hz, 2H, NAr), 6.75 (t, *J* = 7.8 Hz, 2H, Ph and Ar-H), 5.98 (d, *J* = 7.6 Hz, 1H, Ar-H), 4.74−4.69 (m, 1H, NCH), 3.97 (app t, *J* = 10.2 Hz, 1H, NC*H*H), 3.82 (s, 3H, OCH_3), 3.82−3.79 (m, 1H, NCH*H*), 3.49 (dd, *J* = 2.5, 13.3 Hz, 1H, C*H*HPh), 3.09 (dd, *J* = 8.2, 13.3 Hz, 1H, CH*H*Ph); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 161.8 (d, $^2J_{P-C}$ = 12.2 Hz), 159.2, 154.8, 137.5, 135.6, 133.5 (d, $^1J_{P-C}$ = 54.0 Hz), 133.2 (d, $^1J_{P-C}$ = 54.7 Hz), 132.6 (virtual t, $^2J_{P-C}$ = 14.2 Hz), 132.2, 132.0 (d, $^4J_{P-C}$ = 2.3 Hz), 131.9 (d, $^4J_{P-C}$ = 2.3 Hz), 130.0, 128.8 (d, $^3J_{P-C}$ = 11.6 Hz), 128.7 (d, $^3J_{P-C}$ = 11.5 Hz), 128.3, 126.4, 125.7, 120.9, 114.8, 114.6 (d, $^3J_{P-C}$ = 17.2 Hz), 63.4, 59.2 (d, $^4J_{P-C}$ = 3.5 Hz), 55.5, 41.4; $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$) δ 154.8; IR (KBr) ν 3444, 3055, 2927, 2851, 1567, 1532, 1511, 1439, 1288, 1247, 1179, 1108, 1031, 867, 788, 747, 706 cm^{-1}. Anal. Calcd for $C_{35}H_{30}IN_2O_2PPd \cdot C_4H_{10}O$ (849.04): C, 55.17; H, 4.75; N, 3.30. Found: C, 55.45; H, 4.26; N, 3.32.

General Procedure for Suzuki−Miyaura Coupling Reaction. A 10 mL Schlenk flask was charged with 1-iodo-2-methoxynaphthalene (0.2 mmol), 1-naphthaleneboronic acid (0.3 mmol), pincer complex (5 mol %), CsF (0.93 mmol), and toluene (4 mL). The mixture was stirred at 80 °C for 15 h under N_2. After the mixture was cooled, solvent was removed on a rotary evaporator, and the product was isolated by thin-layer chromatography. The purified product was identified by ^1H and ^{13}C NMR spectra and melting point comparison with the literature data. The ee value of the product was determined by HPLC on a chiral stationary phase [Daicel Chiralpak AD-H column, *n*-hexane−*i*-PrOH, 98:2, 0.25 mL/min, 254 nm; t_R = 20.46 min (minor) and 23.93 min (major)].

X-ray Diffraction Studies. Crystals of **3a**, **3b**, **3c**, **3d**, and **4a** were obtained by recrystallization from CH_2Cl_2−petroleum ether at ambient temperature, those of **3f** from CH_2Cl_2−*n*-hexane, and those of **3e** and **5e** from CH_2Cl_2−ethyl acetate at ambient temperature. The data of **3a**, **3c**, **3d**, **3e**, and **4a** were collected with a Rigaku-IV imaging plate area detector, and those of **3f**, **3b**, and **5e** were collected on a Rigaku Saturn 724 CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at ambient temperature. The diffraction data were corrected for Lorentz and polarization factors. The structures were solved by direct methods, expanded using Fourier techniques, and refined by full-matrix least-squares methods. The nonhydrogen atoms were refined anisotropically, and the hydrogen

atoms were included but not refined. Their raw data were corrected, and the structures were solved using the SHELXL-97 program.[28] CCDCs 762184, 762185, 762186, 762187, 762188, 769635, 764938, and 764939 contain the crystallographic data for complexes **3a**−**f**, **4a**, and **5e**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

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Supporting Information Available: Tables and figures giving crystallographic data of complexes **3b**−**e** and **5e**, investigations on the catalytic reaction, figures giving ^{1}H NMR and ^{13}C NMR spectra of all the new compounds, and CIF files giving crystallographic data for all the pincer complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

(28) Sheldrick, G. M. *SHELXL-97*, Program for Refinement of Crystal Structure; University of Göttingen: Germany, 1997.