A Practical Method for the Large-Scale Synthesis of Diastereomerically Pure (2*R*,5*S*)- 3-Phenyl-2-(8-quinolinoxy)-1,3-diaza-2-phosphabicyclo-[3.3.0]-octane Ligand (QUIPHOS). Synthesis and X-ray Structure of Its Corresponding Chiral π-Allyl Palladium Complex

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The use of catalytic asymmetric reactions for the synthesis of highly enantiomerically enriched chiral compounds is of growing importance in organic chemistry and in the chemical industry at large.[1] In this area, the practical utility of a catalytic asymmetric method is closely tied to the accessibility of the catalyst and can be severely undermined if the process for preparation of the catalyst proves too costly or technically difficult for large-scale production. Over the past 30 years, a wide variety of organophosphorus ligands have been described and successfully used in various asymmetric reactions.[2] Nevertheless, few of these ligands have found industrial applications; the most famous of them are DIOP,[3] BINAP,[4] DIPAMP,[5] or DuPHOS.[6] In the past few years, the use of phosphine oxazoline ligands in palladium asymmetric reactions has attracted great interest.[7] However, the preparation of stable chiral ligands possessing a stereogenic phosphorus center via a large-scale synthesis has appeared to be difficult to envision.[8] Recently, we have described the straightforward synthesis of new chiral P-pyridine and quinoline phosphine ligands and their successful use in asymmetric palladium-catalyzed allylic substitution reactions leading to enantiomeric excesses (ee) up to 96%.[9,10] Thus, one of these (ligand **7**) has particularly focused our attention as a result of its easy access and its stability to air and moisture. This P,N ligand presents a chiral diazaphospholidine ring and a quinoloxy group bound to a stereogenic phosphorus atom; we propose the acronym QUIPHOS for **7**. Herein, we report an efficient, highly optimized procedure for the preparation of this ligand involving only three steps from commercial inexpensive precursors and the X-ray structure of its corresponding chiral π-allyl palladium complex **8** to prove unequivocally the stereochemistry of the P(III) atom and the ability of QUIPHOS to serve as a bidentate P, N ligand and to describe the sense of asymmetric induction observed in Pd(0) allylic substitution.

The first key step deals with the synthesis of chiral (*S*)-5-oxopyrrolidine-2-carboxanilide **2** from (L)-glutamic acid **1** and aniline according to a modified reported procedure.[11] This step has been improved on a large-scale synthesis (0.4 mol) using a Dean−Stark apparatus to eliminate the water produced during the reaction, increasing the chemical yield from 46% to 85% (69 g) after crystallization in methanol. The second significant improvement affecting the ligand synthesis was tied to the reduction of the previously mentioned diamide **2**. This reduction was conducted on a 0.35 mol scale. The hydrolysis step was controlled using the minimum required amount of 30% KOH solution (i.e., 4 equiv of water with respect to 1 equiv of $LiAlH_4$), leading after distillation of the crude product to a chemical yield up to 92% (57 g). Thus, this two-step sequence provides pure chiral (*S*)-2-anilinomethyl pyrrolidine **3** in a total 78% yield with respect to L-glutamic acid[12] (Scheme 1).

The synthesis of ligand **7** was accomplished under argon by exchange reaction in refluxing toluene between tris(dimethylamino)phosphine **4** (9.25 g, 56.8 mmol) and (*S*)-**3** (10 g, 56.8 mmol) for 2 h followed by addition of 8-hydoxyquinoline (8.23 g, 56.8 mmol). The reflux was maintained for 2 h, and crystallization overnight in toluene afforded diastereoselectively pure ligand **7** as a white solid stable to air and moisture in 98% yield (19.5 g) (Scheme 2).[13]

The synthesis of complex **8** was achieved by mixing an equimolar amount of bis(μ-chloro)bis(π-allyl)dipalladium

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(8) Although myriad examples of phosphines possessing carbon-centered chirality have been synthesized and applied in asymmetric catalysis, few P-chiral ligands have been investigated because of their inaccessibility. For a recent review, see: Petrusiewicz, K. M.; Zablocka, M. *Chem. Rev.* **1994**, *94*, 1375.

(9) (a) Brunel, J. M.; Constantieux, T.; Labande, A.; Lubatti, F.; Buono, G. *Tetrahedron Lett.* **1997**, *38*, 5971. (b) Constantieux, T.; Brunel, J. M.; Labande, A.; Buono, G. *Synlett* **1998**, 49. (c) Muchow, G.; Brunel, J. M.; Maffei, M.; Pardigon, O.; Buono, G. *Tetrahedron* **1998**, *54*, 10435.

(10) It is noteworthy that compound **7** has been successfully used as ligand in an enantioselective copper-catalyzed Diels−Alder reaction of 3-acryloyl-1,3-oxazolidine-2-one with cyclopentadiene, leading to enantioselectivities up to 99%. Brunel, J. M.; Del Campo, B.; Buono, G. *Tetrahedron Lett.* **1998**, *39*, 9663.

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(12) Optical purity of **3** has been verified by ^{31}P NMR spectroscopy using (−)-dichloromenthyloxyphosphinite as chiral derivatizing agent. Thus, only one diastereomer was detected, indicating that no racemization about the stereogenic center occurred during the synthesis. For the method used, see: Brunel, J. M.; Faure, B. *Tetrahedron: Asymmetry* **1995**, *6*, 2353.

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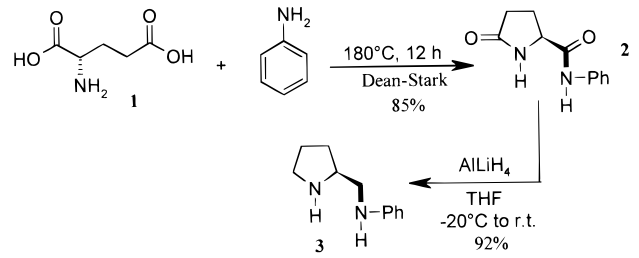
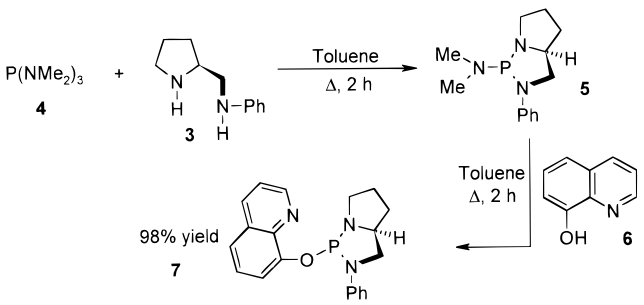
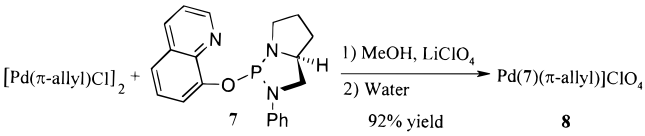
Scheme 1



Scheme 2



Scheme 3



and ligand **7** in methanol, followed by addition of $LiClO_4$. This mixture was stirred for 1 h, and water was added to afford a yellow precipitate. Crystallization from petroleum ether/$CHCl_3$ afforded the expected palladium complex **8** in 92% yield as pale yellow crystals stable to air and moisture (Scheme 3).[14] X-ray diffraction analysis led unambiguously to the determination of the proposed structure for **7** with *R* absolute configuration at the phosphorus (III) atom (Figure 1).[15] In comparison, complex **8** clearly demonstrates the bidentate chelating ability of ligand **7** toward Pd metal through, respectively, phosphorus and nitrogen atoms of the quinoline ring (distance Pd(1)−P(2) = 2.22 and Pd(1)−N(7) = 2.13 Å). The Pd−C bond lengths are significantly different from one another, the carbon atom trans to phosphorus

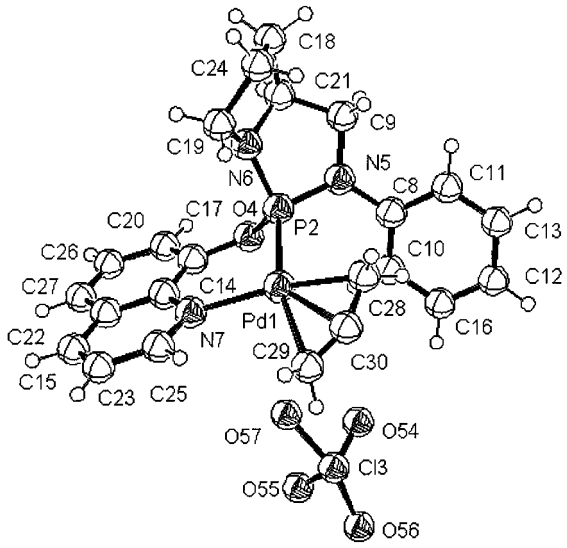
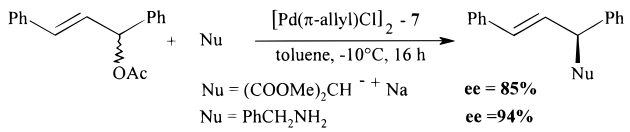


Figure 1. Structure of **8**, showing labeling scheme. Selected bond distances (Å): Pd1−P2, 2.216(2); Pd1−N7, 2.125(6); Pd1−C28, 2.05(1); Pd1−C29, 2.230(9); Pd1−C30, 2.09(2); P2−O4, 1.648(4); N7−C25, 1.32(2); N7−C14, 1.384(8); P2−N6, 1.62-(5); P2−N5, 1.686(5); C17−O4, 1.393(8); C29−C30, 1.17(3); C30−C28, 1.20(3). Selected bond angles (deg): P2−Pd1−N7, 91.3(2); P2−Pd1−C28, 101.5(3); P2−Pd1−C29, 164.7(3); P2−Pd1−C30, 134.6(6); N7−Pd1−C28, 167.0(3); N7−Pd1−C29, 102.6(3); N7−Pd1−C30, 133.9(6); C28−Pd1−C29, 65.0(4); C28−Pd1−C30, 33.8(7); C29−Pd1−C30, 31.3(6); Pd1−P2−O4, 103.4(2); Pd1−P2−N5, 123.7(2); Pd1−P2−N6, 124.8(2); O4−P2−N5, 99.6(3); O4−P2−N6, 107.3(3); N5−P2−N6, 94.8(3); C29−C28−C30, 13.6(7); Pd1−C30−C328, 71.6(8); Pd1−C29−C30, 81.2(8).

Scheme 4



displaying the expected longer distance (Pd(1)−C(29) = 2.230(9) Å) as compared to its partner trans to nitrogen (Pd(1)−C(28) = 2.05(1) Å). This is an expression of the higher trans influence of the phosphine ligand.[16] The plane of the allyl ligand is tilted 29.4° from the perpendicular to the plane Pd−N−P. The sums of angles around N_5 and N_6 atoms (respectively 351.4° and 346.8°) showed in both cases a nonplanar configuration. Furthermore, the observed torsion angle C9−N5−C8−C11 of 13.8° suggests a reduced electronic interaction by decreasing the overlap of the nitrogen lone pair orbital with the π-aromatic system. The efficiency of this ligand in asymmetric palladium-catalyzed reactions (Scheme 4) could result from the unique conformation adopted by the allylic system as a result of the steric hindrance of the pyrrolidine ring. Thus, the asymmetric induction observed could be apprehended from the transition state **11** in which the nucleophilic attack may occur predominantly at the alkyl terminus trans to the better p-acceptor (P ≫ N) (Scheme 5).

In conclusion, we have reported a practical procedure for the large-scale synthesis (up to 0.5 mol) of an efficient chiral quinoline diazaphospholidine ligand **7** (QUIPHOS), as well as the first X-ray structure of the corresponding

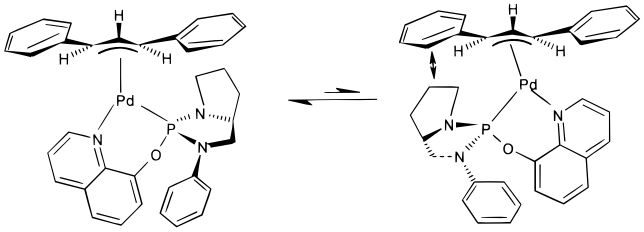
(13) The synthesis of the (2*S*,5*R*) enantiomer of ligand **7** may be envisionned according to the same experimental procedure using commercially available D-glutamic acid. For application of L- and D-glutamic acid in asymmetric synthesis, see: Coppola, G. M.; Shuster, H. F. *Asymmetric Synthesis*; Wiley-Interscience: New York, 1987; p 216.

(14) Ligand **7** is not prone to oxidation, and a sample has been stored for 1 year at room temperature in air without any alteration of the product.

(15) X-ray structure of palladium complex **8**. A pale yellow crystal ($0.4 \times 0.3 \times 0.2$ mm^3) grown from petroleum ether and chloroform by a diffusion method was used for data collection. $C_{23}H_{26}O_5N_3P_1Pd_1{\cdot}ClO_4$; M_r = 561.85; orthorhombic; space group $P2_12_12_1$; a = 8.918(1), b = 15.531(1), c = 17.569(1) Å; α = 90.000(1)°, β = 90.000(1)°, γ = 90.000-(1)°; V = 2433.4(6) Å^3; d_{calcd} = 1.250 g cm^{-3}. All of the measurements were made on a Rigaku diffractometer with Mo Kα radiation. Cell constants and the orientation matrix for data collection were obtained from a least-squares refinement using setting angles of 30 reflections in the range θ = 1−25° for Z = 4. A total of 2695 reflections were collected at T = 298 K and R = 0.052 for the refined structure. The standards were measured after every 120 reflections. Among the first 200 pairs of reflections, the signs of the corresponding calculated differences established that the molecule is described with the correct absolute configuration *R* at the phosphorus atom. Moreover, it has been verified that crystallization does not occur to provide individual crystals of different stereoisomers of complex **8**.

(16) For a review, see: Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335−422.

Scheme 5



11 ***exo*** **12** ***endo***

chiral π-allyl palladium complex **8**. Further studies to use ligand **7** in various catalytic asymmetric reactions are currently under investigation.

Experimental Section

Materials and Methods. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on Bruker AC100, AC200, and AC400 spectrometers. The chemical shifts (ppm) were determined relative to Me_4Si (^{1}H and ^{13}C) and 85% H_3PO_4 (^{31}P). IR spectra were recorded on a Perkin-Elmer 1720X FT-IR spectrometer. Toluene and tetrahydrofuran (THF) were distilled from sodium/benzophenone ketyl immediately prior to use.

(*S*)-5-Oxopyrrolidine-2-carboxanilide (2). In a 500 mL round-bottomed flask fitted with a Dean−Stark apparatus, a mixture of L-glutamic acid (60 g, 0.4 mol) and aniline (350 mL) was stirred at 195−200 °C. After 30 min, the mixture became clear, and the water formed was removed by azeotropic distillation. Stirring was maintained for 4 h. Excess of aniline was then recovered at 60−70 °C under reduced pressure distillation. The hot oily residue was swirled with acetone (250 mL) to lead to the formation of a brown solid, which was collected by filtration and dissolved in hot methanol (200 mL). The solution was slowly cooled to room temperature to afford crystalline optically pure (*S*)-5-oxopyrrolidine-2-carboxanilide as white needles in 85% yield (69 g): mp 189.0 °C; $[\alpha]^{20}_D$ +18.0 (*c* 1.0, MeOH); ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.00 (tdd, 1H, J = 9.7,-12.3, 4.3 Hz), 2.18 (td, 2H, J = 9.7, 14.4 Hz), 2.31 (tdd, 1H, J = 9.7, 12.3, 8.5 Hz), 4.19 (dd, 1H, J = 8.5, 4.3 Hz), 7.06 (t, 1H, J = 7.5 Hz), 7.32 (t, 2H, J = 7.5 Hz), 7.63 (d, 2H, J = 7.5 Hz), 7.92 (s, 1H, D_2O exchangeable), 10.06 (s, 1H, D_2O exchangeable); ^{13}C NMR (25.18 MHz, DMSO-d_6) δ 25.3, 29.3, 56.4, 119.3, 123.5, 128.8, 138.8, 171.3, 177.5. Anal. Calcd for $C_{11}H_{12}N_2O_2$: C, 64.70; H, 5.88; N, 13.72. Found: C, 64.85; H, 5.74; N, 13.46.

(*S*)-2-Anilinomethyl Pyrrolidine (3). In a 1 L glass reactor under argon fitted with a condenser and mechanical stirrer was slowly added in dry THF (500 mL) at −10 °C 40.0 g of lithium aluminum hydride (1.05 mol). This suspension was allowed to rise to 0 °C and (*S*)-5-oxopyrrolidine-2-carboxanilide (71.4 g, 0.35 mol) was slowly added in portions to maintain a gentle bubbling. After stirring overnight at room temperature, the suspension was heated for 1 h under reflux. After the mixture cooled to 0 °C, the excess of lithium aluminum hydride was decomposed by careful addition of 30% KOH solution (75 mL). This solution was then stirred overnight at room temperature. The inorganic salts were filtered off and washed with CH_2Cl_2 (2 × 50 mL). The solvents were removed under vaccuum, and the oily residuewas purified by distillation to afford the desired (*S*)-2-anilinomethyl pyrrolidine in 92% yield (56.6 g): bp 92.0 °C (0.1 mmHg); $[\alpha]^{20}_D$ +19.2 (*c* 1.0, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.43 (tdd, 1H, J = 8.9, 12.3, 6.7 Hz), 1.72 (m, 3H), 1.89 (dddd, 1H, J = 12.3, 8.9, 6.7, 5.3 Hz), 2.91 (td, 2H, J = 6.5, 1.9 Hz), 2.94 (br dd, 1H, J = 11.9, 7.7 Hz), 3.15 (br dd, 1H, J = 11.9, 4.5 Hz), 3.35 (dddd, 1H, J = 7.7, 6.7, 5.3, 4.5 Hz), 4.10 (br s, 1H), 6.62 (dd, 2H, J = 8.6, 1.0 Hz,), 6.62 (tt, 1H, J = 7.3, 1.0 Hz), 7.16 (ddt, 2H, J = 8.6, 7.3, 2.1 Hz); ^{13}C NMR (25.18 MHz, $CDCl_3$) δ 25.7, 29.5, 46.5, 48.6, 57.6, 112.9, 117.2, 129.1, 148.5. Anal. Calcd for $C_{11}H_{16}N_2$: C, 74.00; H, 9.09; N, 15.90. Found: C, 75.08; H, 9.12; N, 15.81.

(2*R*,5*S*)-3-Phenyl-2-(8-quinolinoxy)-1,3-diaza-2-phosphabicyclo[3.3.0]octane (7) (QUIPHOS). To a 250 mL two-necked round-bottomed flask containing 100 mL of dry toluene were added under argon tris(dimethylamino)phosphine **(4)** (9.25 g, 56.8 mmol) and (*S*)-2-anilinomethyl pyrrolidine **(3)** (10.0 g, 56.8 mmol). The solution was heated to reflux, and the reaction was monitored by ^{31}P NMR spectroscopy. After 2 h and cooling to room temperature, 8-hydroxyquinoline (8.23 g, 56.8 mmol) was introduced under argon. The solution was then heated to reflux, and this temperature maintained for 2 h. After completion of the reaction, the solution was allowed to rise to room temperature overnight. White needles stable to air and moisture were obtained after crystallization affording 16.3 g of the expected ligand. Evaporation of the solvent and a second crystallization of the crude residue in toluene led to another 3.2 g of ligand **7**, 98% yield (19.5 g): mp 135 °C; $[\alpha]^{20}$ −45.6 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.54 (dq, 1H, J = 11.5, 6.7 Hz), 1.84 (dtt, 2H, J = 7.3, 7.3, 6.5 Hz), 1.93 (dq, 1H, J = 11.5, 6.5 Hz), 3.28 (ddd, 1H, J = 8.7, 6.5 Hz, J_{P-H} = 5.9 Hz), 3.45 (ddd, 1H, J = 10.2, 7.3 Hz, J_{P-H} = 7.3 Hz), 3.78 (dd, 1H, J = 8.7, 6.5 Hz), 3.83 (m, 1H), 3.90 (q, 1H, J = 6.5 Hz), 6.86 (t, 1H, J = 7.3 Hz), 7.13 (d, 2H, J = 7.8 Hz), 7.18 (d, 1H, J = 7.5 Hz), 7.22 (dd, 2H, J = 7.8, 7.3 Hz), 7.35 (dd, 1H, J = 8.3, 4.1 Hz), 7.37 (t, 1H, J = 7.5 Hz), 7.46 (d, 1H, J = 7.5 Hz), 8.12 (dd, 1H, J = 8.3, 1.6 Hz), 8.89 (dd, 1H, J = 4.1, 1.6 Hz); ^{13}C NMR (100.33 MHz, $CDCl_3$) δ 26.6 (d, J_{P-C} = 5.0 Hz), 32.0, 48.0 (d, J_{P-C} = 33.2 Hz), 53.7, 65.6 (d, J_{P-C} = 9.1 Hz), 115.5 (d, J_{P-C} = 14.1 Hz), 119.1, 119.6, 121.2, 121.9, 126.9, 129.1, 129.7, 135.8, 142.2, 145.7 (d, J_{P-C} = 15.1 Hz), 148.9, 151.8; ^{31}P NMR (40.5 MHz, $CDCl_3$) δ 128.6. Anal. Calcd for $C_{20}H_{20}N_3OP$: C, 72.07; H, 0.6.00; N, 12.61; P, 9.30. Found: C, 72.0; H, 5.93; N, 12.44; P, 9.40.

[Pd(7)(π-allyl)]ClO_4 (8). A mixture of bis(μ-chloro)bis(π-allyl)dipalladium (558 mg, 1.52 mmol) and ligand **7** (1.10 g, 3.06 mmol) was placed in anhydrous MeOH (30 mL) under argon in a 50 mL two-necked round-bottomed flask. The solution was stirred at room temperature, and the solids almost dissolved after 1 h, giving an orange solution. After small amount of insoluble solids was filtered off, $LiClO_4 \cdot 3H_2O$ (1.62 g, 15.3 mmol) in 6 mL of methanol was added, and the mixture was kept stirring at room temperature for 2 h. Water (100 mL) was added until no more yellow precipitates were formed. [Pd(**7**)(π-allyl)]-ClO_4 (**8**) was obtained by filtration, washed with water, and dried in vacuo. For a single-crystal X-ray analysis, the product was recrystallized from petroleum ether/$CHCl_3$ giving **8** as pale yellow crystals in 92% yield: mp 142 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.88 (dq, J = 11.5, 6.7 Hz, 1H, H_{18a}), 1.94 (dtt, J = 7.3, 7.3, 6.5 Hz, 2H, H_{24}), 2.15 (dq, J = 11.5, 6.5 Hz, 1H, H_{18b}), 2.74 (br s, 1H, H_{28a}), 2.93 (ddd, J = 10.2, 7.3 Hz, J_{P-H} = 7.3 Hz, 1H, H_{19a}), 3.13 (d, J = 11.8 Hz, 1H, H_{28b}), 3.61 (dd, J = 8.7, 6.5 Hz, 1H, H_{9a}), 3.80 (m, 1H, H_{19b}), 4.02 (dd, J = 8.7, 6.5 Hz, 1H, H_{9b}), 4.28 (dd, J = 12.5 Hz, J_{P-H} = 14.4 Hz, 1H, H_{29a}), 4.47 (q, J = 6.5 Hz, 1H, H_{21}), 5.00 (dd, J = 7.6 Hz, J_{P-H} = 7.3 Hz, 1H, H_{29b}), 5.81 (tt, J = 12.5, 7.6 Hz, 1H, H_{30}), 6.98 (t, J = 7.3 Hz, 1H, H_{13}), 7.08 (d, J = 7.9 Hz, 2H, H_{16}, H_{12}), 7.28 (dd, J = 7.9, 7.3 Hz, 2H, H_{10}, H_{16}), 7.34 (d, J = 7.5 Hz, 1H, H_{20}), 7.65 (t, J = 7.5 Hz, 1H, H_{26}), 7.74 (dd, J = 8.3, 4.1 Hz, 1H, H_{23}), 7.82 (d, J = 7.5 Hz, 1H, H_{27}), 8.56 (d, J = 8.3 Hz, 1H, H_{15}), 9.58 (d, J = 4.1 Hz, 1H, H_{25}); ^{13}C NMR (100.33 MHz, $CDCl_3$) δ 26.7 (d, J_{P-C} = 4.0 Hz, C_{24}), 31.1 (s, C_{18}), 48.9 (d, J_{P-C} = 22.0 Hz, C_{19}), 49.5 (br s, C_{28}), 54.5 (s, C_9), 61.7 (s, C_{21}), 87.7 (d, J_{P-C} = 38.1 Hz, C_{29}), 116.9 (d, J_{P-C} = 8.1 Hz, C_{11}, C_{12}), 122.4 (s, C_{16}), 122.8 (s, C_{26}), 123.8 (s, C_{23}), 124.7 (d, J_{P-C} = 10.0 Hz, C_{30}), 125.8 (s, C_{20}), 128.3 (s, C_{26}), 129.4 (s, C_{10}, C_{13}), 131.2 (s, C_{22}), 136.0 (s, C_{15}), 141.4 (s, C_{14}), 141.7 (d; J_{P-C} = 12.0 Hz, C_8), 145.9 (s, C_{25}), 162.3 (s, C_{17}); ^{31}P NMR (40.5 MHz, $CDCl_3$) δ 128.05. Anal. Calcd for $C_{23}H_{25}N_3O_5ClPPd$: C, 46.30; H, 4.19; N, 7.04; Cl, 5.95; P, 5.20; Pd, 17.85. Found: C, 46.82; H, 4.17; N, 7.40; Cl, 6.02; P, 5.18; Pd, 18.1.

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