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Palladium-catalyzed asymmetric allylation and complex formation involving *P,N*-bidentate derivatives of (*S*)-2-(anilinomethyl)pyrrolidine

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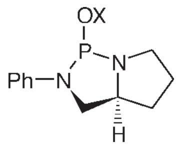
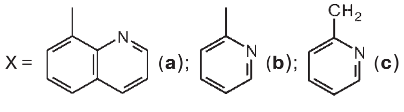
P,N-Bidentate (*S*)-2-(anilinomethyl)pyrrolidine derivatives and their complexes with rhodium(I) and palladium(II) were synthesized. It was demonstrated that these compounds can be used in the Pd-catalyzed asymmetric allylation for the synthesis of chiral methyl 2-phenyl-2-(2-phenyl-*o*-carboranyl-1)pent-4-enoate.

Key words: *P,N*-ligands, aminophosphites, palladiun, rhodium, asymmetric synthesis, allylation, carboranes.

Chiral *P,N*-heterobidentate compounds are among the most important ligands in the modern asymmetric catalysis.[1—3] Most of these systems contain the phosphine groups. However, *P,N*-hybrid ligands bearing the phosphite (amidophosphite) phosphorus center are finding ever increasing use due to their synthetic availability, the absence of oxidation-sensitive P—C bonds, and the pronounced π-acceptor character of the phosphorus center. The incorporation of the oxygen and/or nitrogen atoms into the first coordination sphere of the P atom allows the control over chemical stability of the ligand, its donor-acceptor properties, and steric requirements. Hence, *P,N*-bidentate derivatives of phosphorous acid have extensive applications in catalytic enantioselective allylation, coupled addition of organometallic reagents to enones, hydrogenation, and hydrosilylation.[1—8] In particular, *P,N*-bidentate ligands with the (2*R*,5*S*)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane core proved to be highly efficient in the copper-catalyzed Diels—Alder reactions,[9] palladium-catalyzed allylation and amination,[10—12] and the copper-catalyzed addition of diethylzinc to cyclohexenone.[12] However, all these systems involve nitrogen-containing quinoline or pyridine fragments[2,9—12] containing no additional chiral centers.



1a—c



In the present study, we report the synthesis of new ligands of this type bearing the imino or amino groups (the latter group contains the asymmetric carbon atom). The complex formation of these ligands with rhodium(I) and palladium(II) was examined. It was demonstrated that these ligands can be used in Pd-catalyzed allylation for the synthesis of optically active carborane derivatives.

Results and Discussion

New *P,N*-bidentate compounds **4a,b** were synthesized by the reactions of (*S*)-2-(anilinomethyl)pyrrolidine (**2**) with $P(NEt_2)_3$ followed by the addition of alcohol (**3a,b**) (Scheme 1).

Ligands **4a,b** are stable under a dry atmosphere and are readily soluble in most of organic media. The (*R*) configuration of the P*-stereogenic centers is evidenced by a pronounced analogy between the ^{13}C NMR spectroscopic parameters of the phosphorus-containing heterocyclic fragments of these ligands (see Experimental) and the corresponding spectroscopic parameters of **1a**.[10,12] In particular, the spin-spin coupling constants $^2J_{C(8),P}$,[13] which are of key importance in evaluating the absolute configuration of the asymmetric phosphorus atom, have rather close values (33.8, 38.2, and 33.2 Hz for **4a**, **4b**, and **1a**, respectively).[10—12] The (*R*) configuration of the P*-stereogenic center of ligand **1a** in the cationic com-

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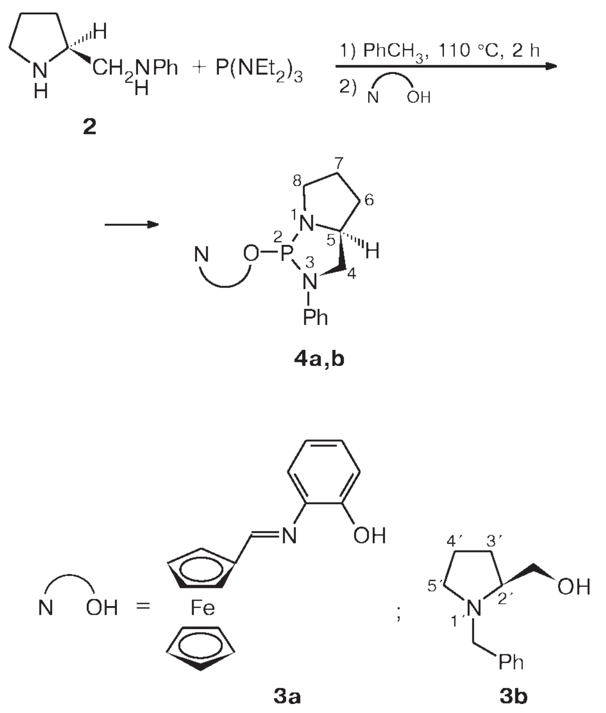
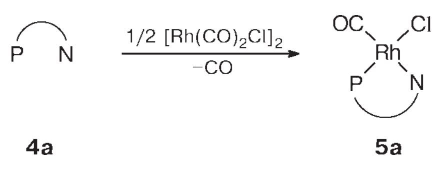
Scheme 1



plex [Pd(allyl)(η^2-(PN))]$^+$ClO$_4^-$ has been established earlier by X-ray diffraction analysis.[10]

As part of our continuing studies, we examined the reactions of **4a,b** with [Rh(CO)$_2$Cl]$_2$. This starting complex was chosen because the IR and ^{31}P NMR spectra of chlorocarbonyl rhodium complexes with *P,N*-bidentate ligands have sensitive parameters, *viz.*, vibration frequencies ν(CO) and the spin-spin coupling constants $^1J_{\text{P,Rh}}$. These parameters allow the reliable estimation of the character of complex formation with the new ligand and the π-acceptor ability of the phosphorus center (see Refs. 14—16). Aminophosphoramidite **4a** forms chelate mononuclear complex **5a** as evidenced by its characteristic IR and ^{31}P NMR spectroscopic parameters[14] (Table 1, Scheme 2).

Scheme 2

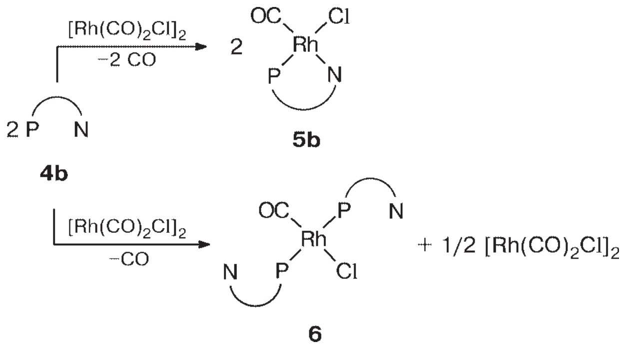


On the contrary, the complex formation of **4b** proceeded non-selectively to give complex **6** along with chelate compound **5b** (Scheme 3).

Table 1. Spectroscopic parameters of rhodium complexes **5a,b** (in CHCl$_3$)

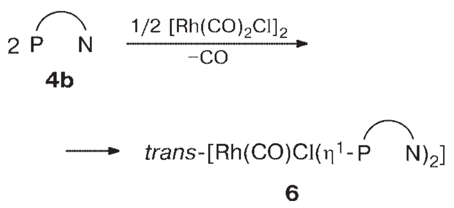
Compound	^{31}P NMR		IR, ν/cm^{-1}	
	δ_{P}	$^1J_{\text{P, Rh}}$/Hz	(CO)	(Rh—Cl)
5a	141.43	234.1	2017	292
5b	125.67	233.6	2012	293

Scheme 3



The IR and ^{31}P NMR spectra of the reaction solution in CHCl$_3$ have signals of both products, which were present in nearly equal amounts (Table 1) (54% of **5b** and 46% of **6**; ν(CO) 1996 cm, ν(Rh—Cl) 312 cm^{-1}; δ_{P} 124.68, $^1J_{\text{P,Rh}}$ = 180.4 Hz). The structure of **6**, proposed on the basis of the above-mentioned characteristic spectroscopic values,[14,17,18] was confirmed by its directed synthesis (Scheme 4).

Scheme 4

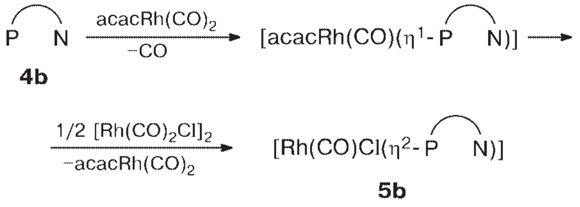


In particular, note the absence of noticeable coordination shifts $\Delta\delta_{\text{C}} = \delta_{\text{C}}(\text{complex}) - \delta_{\text{C}}(\text{ligand})$ of the signals from the carbon atoms at the amine nitrogen atom in complex **6** (see Experimental). This fact indicates that the peripheral amino groups are not bound to Rh$^{\text{I}}$.

Taking into account all the aforesaid, we carried out the specific synthesis of chelate complex **5b** by the independent method using the exchange reaction developed by us earlier[19] for *P*-monodentate ligands (Scheme 5).

The intermediate complex [acacRh(CO)(η^1-(PN))] was identified[14] in the reaction solution without isolation by IR and ^{31}P NMR spectroscopy (ν(CO) 1990 cm^{-1}, ν(acac) 1580 and 1520 cm^{-1}; δ_{P} 131.12, $^1J_{\text{P,Rh}}$ = 247.2 Hz (in CHCl$_3$)).

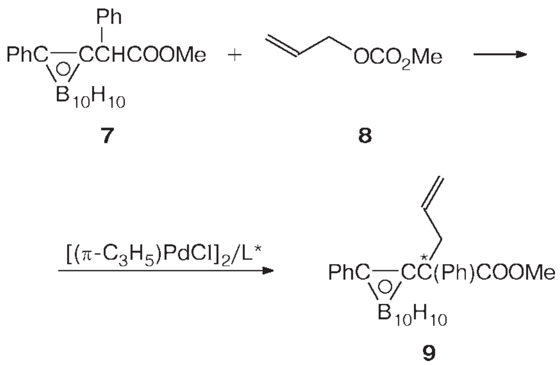
Scheme 5



The π-acceptor ability of the phosphorus center in ligands **4a,b** is substantially higher than that of traditional aminophosphines and is somewhat lower than that of aminophosphites as evidenced by the vibration frequencies ν(CO) and the spin-spin coupling constants $^1J_{\mathrm{P,Rh}}$ of **5a,b** (Table 1). These parameters are larger than the corresponding values for analogous complexes with aminophosphines (by 20—25 cm^{-1} and 65—70 Hz, respectively) but are smaller than those for complexes with aminophosphite derivatives (by 15—20 cm^{-1} and 30—50 Hz, respectively).[14—16]

It is known that the donor-acceptor ability of *P,N*-bidentate ligands has a substantial effect on the chemical and optical yields in various asymmetric catalytic reactions.[1—2] From this standpoint, complexes **4a,b** successfully fill the gap between the phosphine and phosphite systems.

Scheme 6



Reagents and conditions: 20 °C, 20 days, BSA, KOAc.

Table 2. Palladium-catalyzed allylation of **7** with prop-2-enyl methylcarbonate (**8**) using **4a,b**

Ligand	Solvent	Pd/L*	Yield of **9** (%)	*ee* (%)
4a	THF	1/2	—	—
4b	—	1/1	40	48
4b	—	1/2	44	48
4b	CH_2Cl_2	1/2	41	48
4b	Toluene	1/2	20	48

Previously,[20] we have performed for the first time the direct Pt-catalyzed asymmetric synthesis of compounds of the carborane series using the aminophosphite ligands. It was shown that methyl (2-phenyl-*o*-carboranyl-1)phenylacetate (**7**) reacts with prop-2-enyl methylcarbonate (**8**) in the presence of chiral *P,N*-bidentate aminophosphites to produce optically active allylation product **9** (see Scheme 6). The ligands utilized enabled us to prepare compound **9** with higher enantioselectivity compared to that achieved using the classical diphosphine ligands ((+)-DIOP and (+)-BINAP). This fact gave impetus to the use of ligands **4a,b** in the above-described reaction (Table 2). In the case of **4a** containing the *N*-donor center of the imine type, TLC analysis of the reaction mixture showed the absence of allylation product **9**. On the contrary, the use of ligand **4b** whose *N*-donor center is involved in the ring bearing the asymmetric carbon atom not only made it possible to prepare **9** but also proved to be much more efficient than aminophosphites employed earlier.[20] The optical yield of **9** (48% *ee*) achieved in the presence of **4b** is high for this type of allylation giving rise to a new asymmetric center at the carbon atom belonging to a nucleophile (this problem was considered in more detail in the study[20]). The use of toluene instead of THF or CH_2Cl_2 led to a twofold decrease in the chemical yield of **9**. It is known that the enantioselectivity of the Pd-catalyzed allylation depends on the nature of the solvent and the molar palladium to the chiral ligand ratio (Pd : L*).[21] However, in the reaction under examination, the optical yield was unaffected by variations in these conditions.

Since aminophosphite **4b** provided much higher enantioselectivity of the process, we investigated the structures of palladium catalysts including this ligand. For this purpose, we studied the reaction system [Pd(allyl)Cl]$_2$—**4b** in a solution of $CHCl_3$ by ^{31}P NMR spectroscopy. In the case of the molar ratio L* : Pd = 1 : 1, the spectrum has two singlets at δ_P 122.76 and 122.33 with equal intensities (the overall integral intensity is 65% of the total intensity of all ^{31}P signals in the spectrum), and these signals were assigned to the *exo* and *endo* isomers,[22] respectively, of the cationic complex $[\mathrm{Pd(allyl)}(\eta^2\text{-(PN)})]^+\mathrm{Cl}^-$ based on the characteristic δ_P value.[10] In addition, this spectrum shows a slightly broadened singlet at δ_P 117.36 (35% of the total ^{31}P intensity) attributed to $[\mathrm{Pd(allyl)}(\eta^1\text{-(PN)})_2]^+\mathrm{Cl}^-$.[23] When the molar ratio L* : Pd was increased to 2 : 1, this signal became the only one. No absorption bands ν(Pd—Cl) were observed in the long-wavelength region of the IR spectrum of the reaction solution, but the electrospray mass-spectrum had a peak of the characteristic ion at m/z (I_{rel} (%)): 937 [M – Cl]$^+$ (100).

Hence, the study of coordination of compound **4b** with rhodium(I) and palladium(II) demonstrated that **4b** is not sufficiently efficient as a chelating agent and is favorably disposed toward the *P*-monodentate bonding due, apparently, to high steric requirements of the peripheral amino group. Compound **4b** is similar in coordination ability to *P*-monodentate ligands. Nevertheless, it provides rather high enantioselectivity in palladium-catalyzed allylation thus offering advantages over more efficient chelating ligand **4a**. Apparently, this fact is associated with the specific requirements imposed upon the nature of the chiral phosphorus-containing ligand in allylation.

Experimental

The IR spectra were recorded in $CHCl_3$ solutions on SPECORD M-80 and Nicolet instruments in polyethylene cells and between CsI plates. The ^{31}P, ^{13}C, and ^{1}H NMR spectra were measured on a Bruker AMX-400 instrument. The ^{31}P NMR spectra were obtained at 161.98 MHz with 85% H_3PO_4 as the internal standard. The ^{13}C NMR spectra were recorded at 100.61 MHz relative to $CDCl_3$ (δ_C 76.91). The assignments of the signals in the ^{13}C NMR spectra were made using the DEPT method and the data published in the literature.[10—13] The ^{1}H NMR spectra were measured in $CDCl_3$ (400.13 MHz). The mass spectra (EI, 70 eV) were obtained on Varian MAT 311 and Kratos MS 890 instruments with direct injection. The electrospray mass spectra were recorded on a Micromass Bio II-ZS mass spectrometer. The optical rotation was measured on a Perkin Elmer 241 polarimeter. The optical yield of compound **8** was determined by HPLC on a Varian 5000 chromatograph (a chiral column (R, R) WHELK-01, hexane : Pr^iOH = 99 : 1, 1 mL min^{-1}, detection from absorbtion at 254 nm). Compounds **5a**,[24] **6**,[24] **7**,[20] and **8**[25] were synthesized according to procedures described previously. The ^{1}H NMR and mass spectra of **9** are identical with the data published earlier.[11]

All reactions were carried out under dry argon. The solvents were dried immediately before use according to known procedures.[26] Aminophosphine $P(NEt_2)_3$ was distilled immediately before use. Iminophenol **3a** was prepared according to a procedure described previously[27] and dried *in vacuo* (1 Torr, 3 h) before introduction into the reaction. (*S*)-2-(Anilinomethyl)pyrrolidine and amino alcohol **3b** were synthesized according to known procedures[10,28] and dried by azeotropic distillation with benzene followed by vacuum distillation (1 Torr) immediately before use. The starting $[Rh(CO)_2Cl]_2$, $acacRh(CO)_2$, and $[Pd(allyl)Cl]_2$ complexes were synthesized according to known procedures.[29—31] The course of the Pd-catalyzed reactions was monitored by TLC on Silufol UV 254 plates.

Synthesis of ligands 4a,b (general procedure). (*S*)-2-(Anilinomethyl)pyrrolidine (1.377 g, 8.5 mmol) and $P(NEt_2)_3$ (2.12 g, 8.5 mmol) were dissolved in toluene (20 mL). The reaction mixture was heated with intense stirring, refluxed for 2 h, and cooled to ~20 °C. Then **3a** (2.593 g, 8.5 mmol) or **3b** (1.624 g, 8.5 mmol) was added. The solution was again heated to boiling with intense stirring and refluxed for 2.5 h. The solvent was evaporated (together with $HNEt_2$) to approximately one-half of the initial volume, and the resulting solution was concentrated *in vacuo* (10 Torr) at 50 °C for 1 h. The red oil that formed in the synthesis of **4a** was dissolved in a minimum volume of benzene and the product was precipitated with a high excess of heptane. The precipitate was separated by centrifugation, washed with hexane (10 mL), and dried *in vacuo* (1 Torr, 2 h). The colorless oil that formed in the synthesis of **4b** was dissolved in hexane, the solution was filtered, the filtrate was concentrated *in vacuo* (40 Torr), and the product was dried *in vacuo* (1 Torr, 50 °C, 1 h).

(2*R*,5*S*)-2-{2´-[(Ferrocenylideno)amino]phenoxy}-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane (4a), orange powder, m.p. 89—90 °C, the yield was 72%. Found (%): C, 66.30; H, 5.78; N, 7.89. $C_{28}H_{28}FeN_3OP$. Calculated (%): C, 66.02; H, 5.54; N, 8.25. ^{31}P NMR ($CDCl_3$), δ: 125.96. ^{13}C NMR ($CDCl_3$), δ: 162.07 (s, CH=); 145.84—114.97 (C_{Ar}); 80.49 (s, C_{Fc}-*ipso*); 70.84, 70.79, 68.70, and 68.43 (all s, C_{Fc}); 69.06 (s, C_{Fc}—Cp); 62.38 (d, C(5), $^2J_{C,P}$ = 8.4 Hz); 53.80 (d, C(4), $^2J_{C,P}$ = 7.4 Hz); 47.61 (d, C(8), $^2J_{C,P}$ = 33.8 Hz); 31.49 (s, C(6)); 26.32 (d, C(7), $^3J_{C,P}$ = 3.9 Hz). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 509 $[M]^+$ (5), 305 $[HOC_6H_4NCHFc]^+$ (100), 205 $[M - OC_6H_4NCHFc]^+$ (78).

(2*R*,5*S*,2´*S*)-2-[(1´-Bezylpyrrolidin-2´-yl)methoxy]-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane (4b), colorless transparent oil, $[\alpha]_D^{20}$ −219.0 (*c* 1, CH_2Cl_2), the yield was 86%. Found (%): C, 70.11; H, 7.93; N, 10.40. $C_{23}H_{30}N_3OP$. Calculated (%): C, 69.85; H, 7.65; N, 10.63. ^{31}P NMR ($CDCl_3$), δ: 121.57. ^{13}C NMR ($CDCl_3$), δ: 145.29—113.95 (C_{Ar}); 64.53 (d, CH_2O, $^2J_{C,P}$ = 5.7 Hz); 63.0 (d, C(2´), $^3J_{C,P}$ = 2.4 Hz); 62.56 (d, C(5), $^2J_{C,P}$ = 8.7 Hz); 58.87 (s, C(5´)); 54.33 (d, C(4), $^2J_{C,P}$ = 7.0 Hz); 54.0 (s, CH_2Ph); 47.94 (d, C(8), $^2J_{C,P}$ = 38.2 Hz); 31.29 (s, C(6)); 28.0 (s, C(3´)); 25.52 (d, C(7), $^3J_{C,P}$ = 3.5 Hz); 22.14 (s, C(4´)). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 395 $[M]^+$ (1), 304 $[M - CH_2Ph]^+$ (28), 91 $[CH_2Ph]^+$ (100).

Solution of the $[Rh(CO)_2Cl]_2$—4b reaction system for spectral analysis. A solution of **4b** (0.048 g, 0.12 mmol) in $CHCl_3$ (1.5 mL) was added dropwise with continuous stirring to a solution of $[Rh(CO)_2Cl]_2$ (0.023 g, 0.06 mmol) in $CHCl_3$ (1.5 mL) at 20 °C. The reaction mixture was stirred for 1 h and then the sample for analysis was taken.

Synthesis of complex 5b by the exchange reaction. A solution of ligand **4b** (0.142 g, 0.36 mmol) in $CHCl_3$ (10 mL) was added dropwise with continuous stirring to a solution of $acacRh(CO)_2$ (0.093 g, 0.36 mmol) in $CHCl_3$ (10 mL) at 20 °C. The solution was stirred for 0.5 h to obtain the [acacRh(CO)(h^1-(PN))] complex. Then a solution of $[Rh(CO)_2Cl]_2$ (0.070 g, 0.18 mmol) in $CHCl_3$ (10 mL) was added dropwise and the mixture was stirred for 1 h. The solvent was distilled off *in vacuo* (40 Torr) and the recovered $acacRh(CO)_2$ was extracted from the solid residue with hexane (4×15 mL). The reaction product was dried *in vacuo* (1 Torr) for 1 h.

((2*R*,5*S*)-2-{2´-[(Ferrocenylideno)amino]phenoxy}-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane-P,N)carbonylchlororhodium (5a),[24] orange-brown powder, m.p. 148—149 °C, the yield was 89%. Found (%): C, 51.82; H, 4.36; N, 6.39. $C_{29}H_{28}ClFeN_3O_2PRh$. Calculated (%): C, 51.55; H, 4.18; N, 6.22.

((2*R*,5*S*,2´*S*)-2-[(1´-Bezylpyrrolidin-2´-yl)methoxy]-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane-P,N)carbonylchlororhodium (5b), pale-brown powder, m.p. 127—129 °C, the yield was 86%. Found (%): C, 51.61; H, 5.21; N, 7.25. $C_{24}H_{30}ClN_3O_2PRh$. Calculated (%): C, 51.31; H, 5.38; N, 7.48.

***trans*-Di((2*R*,5*S*,2´*S*)-2-[(1´-Bezylpyrrolidin-2´-yl)methoxy]-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane-P,N)carbonylchlororhodium (6)**,[24] pale-brown powder, m.p. 112—114 °C, the yield was 94%. Found (%): C, 58.75; H, 6.51; N, 9.02. $C_{47}H_{60}ClN_6O_3P_2Rh$. Calculated (%): C, 58.97; H, 6.32;

N, 8.78. ^{13}C NMR (CDCl$_3$), δ: 143.84—115.82 (C$_{\text{Ar}}$); 66.24 (s, CH$_2$O); 62.99 (s, C(2´)); 61.05 (s, C(5)); 59.44 (s, C(5´)); 55.75 (s, C(4)); 54.54 (s, CH$_2$Ph); 48.83 (d, C(8), $^2J_{\text{C,P}}$ = 9.6 Hz); 30.68 (s, C(6)); 28.44 (s, C(3´)); 25.80 (s, C(7)); 22.42 (s, C(4´)).

The Pd$^{\text{II}}$ complexes with ligand **4b** were prepared according to the following general procedure. A solution of **4b** (0.048 g, 0.12 mmol) in CHCl$_3$ (1.5 mL) was added dropwise with stirring to a solution of [Pd(allyl)Cl]$_2$ (0.022 g, 0.06 mmol) or (0.011 g, 0.03 mmol) CHCl$_3$ (1.5 mL) at 20 °C. The reaction mixture was stirred for 1 h and then a sample for spectral analysis was taken.

Palladium-catalyzed allylation of ester 7 with carbonate 8 (general procedure). A solution of [(p-C$_3$H$_5$)PdCl]$_2$ (3.7 mg, 0.01 mmol) and the ligand (0.02 mmol) in THF or CH$_2$Cl$_2$ (4 mL) was stirred for 20 min. Then ester **7** (185 mg, 0.5 mmol), carbonate **8** (0.12 mL, 1 mmol), BSA (*N*,*O*-bis(trimethylsilyl)acetamide) (0.15 mL, 0.6 mmol), and anhydrous KOAc (3 mg, 0.03 mmol) were added. The resulting homogeneous solution was kept at ~20 °C for 20 days. After evaporation of the major portion of the solvent, the residue was dissolved in ether (30 mL) and washed with a 5 % solution of HCl (2×20 mL), a saturated solution of NaHCO$_3$ (20 mL), and water. The ethereal layer was dried with Na$_2$SO and the ether was removed under reduced pressure. The yellow oil that obtained was chromatographed on a plate (17×23 cm) with a SiO$_2$ layer using a 7 : 1 light petroleum—EtOAc mixture as the eluent. The eluent was removed under reduced pressure. Allylation product **9** was obtained as a yellow oil

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