Bis(oxazoline) Ligands Containing Four and Five Spacer Atoms: Palladium Complexes and Catalytic Behavior

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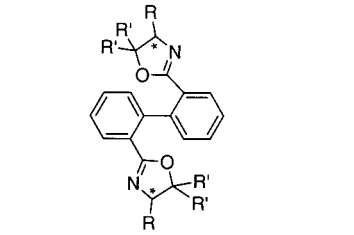
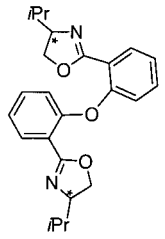
Chiral bis(oxazoline) ligands with biphenyl (**A**−**E**) and diphenyl ether and dibenzofuran (**F** and **G**, respectively) backbones were prepared, and their coordination chemistry to allyl palladium fragments was studied. The allylic complexes (**1L** and **2L**, **1** for the allyl and **2** for the 1,3-diphenylallyl) were characterized, both in the solid state and in solution. X-ray crystal structures were determined for complexes **1C** and **1F**. The ligands coordinate to palladium in a *N*,*N*-chelating way, giving monometallic complexes, except ligand **C**, which acts as a bridge between two metallic fragments, by *N*,*S*-coordination to palladium. Ligand **H**, with four sp^3 carbon spacers, did not react with several allylic starting materials. Complexes **1L** have been used as catalytic precursors in the model allylic alkylation reaction, producing up to 89% of enantiomeric excess. The catalytic behavior shown by these systems can be rationalized in terms of the coordination mode of the ligands toward the metal.

Introduction

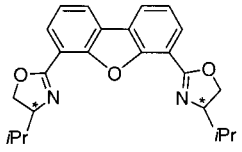
C_2 symmetrical bis(oxazolines) have received enormous interest in the past decade because of their efficiency in several metal-catalyzed processes.[1] The chirality source for most of these ligands is the heterocycle fragment, although in some of them, in addition to the oxazoline stereocenters, other chiral elements are present, such as *S*-[2a,b] or *P*-chiral atoms,[2c,d] ferrocene planar chirality,[3] and 1,3-dioxolane[4] or biaryl[5] backbones. It is important to note that few bis(oxazoline) ligands have been applied in the Pd-catalyzed allylic substitution reactions. The reported ligands contain zero-,[6] one-,[7] or two-carbon[8] spacer atoms between both heterocycle moieties, giving enantiomeric excesses up to 77, 97, and 86%, respectively, for the model allylic alkylation process, meaning *rac*-3-acetoxy-1,3-diphenyl-



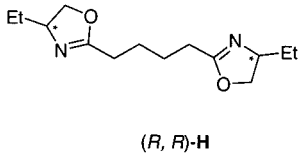
(*R, X*$_a$*, R*)-**A**, R = Et, R' = H
(*S, X*$_a$*, S*)-**B**, R = *i*Pr, R' = H
(*S, X*$_a$*, S*)-**C**, R = $(CH_2)_2$SMe, R' = Ph
(*S, X*$_a$*, S*)-**D**, R = $(CH_2)_2$-SO-Me, R' = Ph
(*S, X*$_a$*, S*)-**E**, R = $(CH_2)_2$-SO_2-Me, R' = Ph



(*S, S*)-**F**



(*S, S*)-**G**



(*R, R*)-**H**

Figure 1. Bis(oxazoline) ligands, (*R*,X_a,*R*)-**A**, (*S*,X_a,*S*)-**B**, (*S*,X_a,*S*)-**C**, (*S*,X_a,*S*)-**D**, (*S*,X_a,*S*)-**E**, (*S*,*S*)-**F**, (*S*,*S*)-**G**, and (*R*,*R*)-**H**.

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(1) (a) Ghosh, A. K.; Mathivanan, P.; Cappiello, J. *Tetrahedron: Asymmetry* **1998**, *9*, 1. (b) Braunstein, P.; Naud, F. *Angew. Chem., Int. Ed.* **2001**, *40*, 680.

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(3) Selected papers related to allylic substitution reactions: (a) Richards, C. J.; Locke, A. J. *Tetrahedron: Asymmetry* **1998**, *9*, 2377, and references therein. (b) Zhang, W.; Yoneda, Y.-i.; Kida, T.; Nakatsuji, Y.; Ikeda, I. *Tetrahedron: Asymmetry* **1998**, *9*, 3371. (c) Park, J.; Quan, Z.; Lee, S.; Han Ahn, K.; Cho, C.-W. *J. Organomet. Chem.* **1999**, *584*, 140. (d) Deng, W.-P.; Hou, X.-L.; Dai, L.-X.; Yu, Y.-H.; Xia, W. *Chem. Commun.* **2000**, 285.

(4) (a) Bedekar, A. V.; Andersson, P. G. *Tetrahedron Lett.* **1996**, *37*, 4073. (b) Harm, A. M.; Knight, J. G.; Stemp, G. *Synthesis* **1996**, 677. (c) Imai, Y.; Zhang, W.; Kida, T.; Nakatsuji, Y.; Ikeda, I. *Tetrahedron: Asymmetry* **1996**, *7*, 2453.

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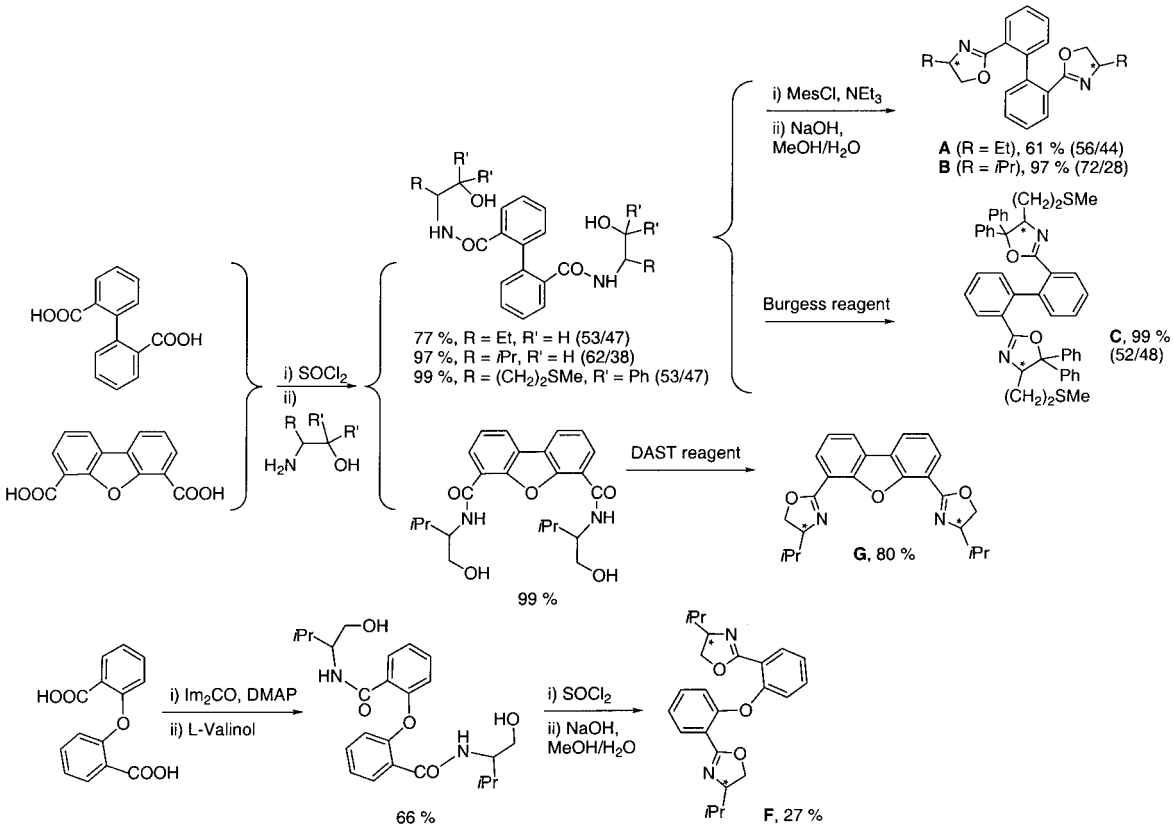
Scheme 1



1-propene with dimethyl malonate as nucleophile, under basic conditions.

Following our systematic research in the synthesis of bis(oxazolines) with different number of spacers between both heterocycles,[8] we planned to prepare ligands containing more than two carbon atoms (Figure 1) in order to apply them in catalytic allylic substitutions. During our study, two groups published works related to our ligands. One of them concerns ligands with an axis-unfixed biaryl backbone,[5,9] and the other describes the synthesis of ligand **G**,[10] although in both cases the catalytic applications are not allylic substitutions.

Here we describe the synthesis and characterization of allylic palladium complexes (**1L** for allyl = C_3H_5; **2L** for allyl = 1,3-Ph_2-C_3H_3), containing bis(oxazolines) with biphenyl (**A**−**E**), diphenyl ether (**F**), and benzofuran (**G**) backbones. Type-**1** complexes were used as catalytic precursors in the model allylic alkylation reaction, while **2L** complexes were prepared in order to compare the diastereomeric distribution of intermediate species and the enantioselectivity of the catalytic process.

Results and Discussion

Synthesis of Ligands. Bis(oxazoline) ligands **A**−**G**[11] (Figure 1) were prepared following the general methodology described in the literature for related compounds (see Experimental Section).[1] Bis(oxazolines) were prepared via bis(carboxiamides), which were obtained from the corresponding dicarboxylic acids[12] and enantiomerically pure 2-amino alcohols[13] (Scheme 1). After purification of these intermediate products, the activation of the hydroxyl group was optimized for each ligand, using methanesulfonyl chloride (MesCl), thionyl chloride, or Burgess (*N*-[(triethylammonio)sulfonyl]carbamate) or DAST ((diethylamino)sulfur trifluoride) reagent. When MesCl or $SOCl_2$ was used, the ring closure was further achieved by basic treatment in methanol/water medium. We prepared **G** from the corresponding bis(amide) in one step, an alternative method from that described by Kanemasa et al.[10] Ligands were prepared in good yields except **F**, containing the diphenyl ether backbone, which was isolated in 26% yield from its corresponding bis(amide) by treatment with $SOCl_2$ and sodium hydroxide methanolic solution. This last step was also carried out using Burgess or DAST reagent, but in both cases mixtures of bis(amide), mono-oxazoline, and bis(oxazoline) were obtained, which after purification by column chromatography, afforded lower yields than indicated above.

Oxidation of the bis(thioether) **C** with hydrogen peroxide gave quantitatively the bis(sulfoxide) **D**. Further oxidation of **D** with *m*-CPBA (*meta*-chloroper-

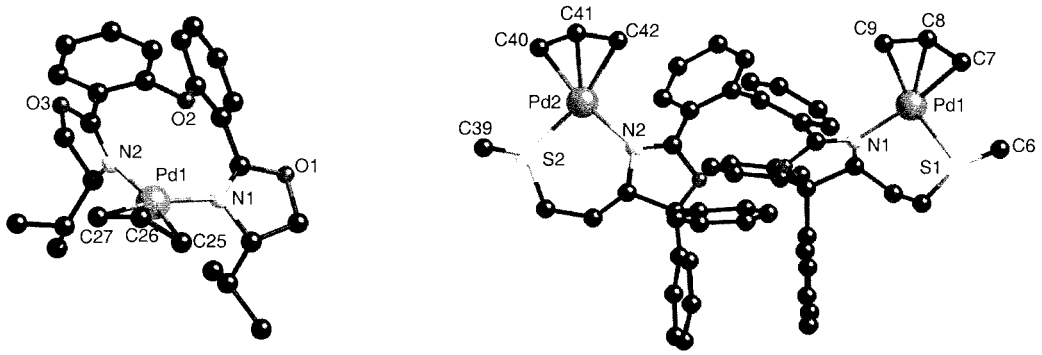
(9) Imai, Y.; Zhang, W.; Kida, T.; Nakatsuji, Y.; Ikeda, I. *Tetrahedron Lett.* **1997**, *38*, 2681

(10) (a) Kanemasa, S.; Oderaotoshi, Y.; Curran, D. P. *J. Org. Chem.* **1997**, *62*, 6454. (b) Kanemasa, S.; Oderaotoshi, Y.; Sakaguchi, S.-i.; Yamamoto, H.; Tanaka, J.; Wada, E.; Curran, D. P. *J. Am. Chem. Soc.* **1998**, *120*, 3074. (c) Kanemasa, S.; Oderaotoshi, Y.; Wada, E. *J. Am. Chem. Soc.* **1999**, *121*, 8675.

(11) Synthesis of **A** described in: Imai, Y.; Zhang, W.; Kida, T.; Nakatsuji, Y.; Ikeda, I. *J. Org. Chem.* **2000**, *65*, 3074.

(12) 1,1′-Biphenyl-2,2′-dicarboxilic acid is commercially available. See ref 1a for the synthesis of 4,6-dibenzofurandicarboxylic acid. See Experimental Section for the synthesis of 2,2′-bis(carboxy)diphenyl ether.

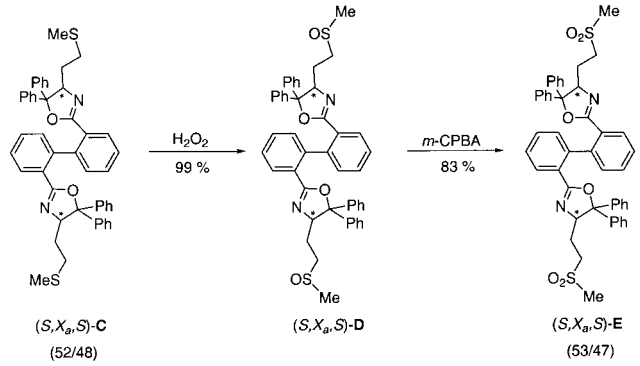
(13) L-Valinol and (*R*)-(+)-2-aminobutanol are commercially available. (*S*)-2-Amino-1,1-diphenyl-4-(methylthio)-1-butanol was prepared as described previously: Trentmann, W.; Mehler, T.; Martens, J. *Tetrahedron: Asymmetry* **1997**, *12*, 2033.



(*S,S*)- **1F** (*S,S*$_a$,*S*)- **1C**

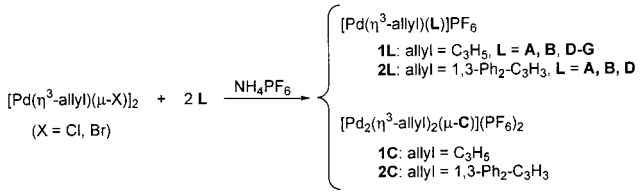
Figure 2. View of the molecular structures of complexes (*S,S*)-**1F** and (*S,S*$_a$,*S*)-**1C**. Hydrogen atoms and the hexafluorophosphate anion are omitted for clarity.

Scheme 2



(*S,X*$_a$,*S*)-**C** (52/48) (*S,X*$_a$,*S*)-**D** (*S,X*$_a$,*S*)-**E** (53/47)

Scheme 3



benzoic acid) led to the bis(sulfone) **E** with 83% yield (Scheme 2). **E** can also be obtained by treatment of **C** with an excess of *m*-CPBA (28 equivalents), but in lower yield (60%).

Bis(carboxiamides) and bis(oxazolines) containing the biphenyl backbone (**A**−**C** and **E**) were obtained as mixtures of two diastereomers because of the oxazoline stereocenters and the axial chirality, (*X,R*$_a$,*X*)-**L** and (*X,S*$_a$,*X*)-**L** (**L** = **A**−**C** and **E**; *X* and central label show the absolute configurations of carbon atoms and the biaryl axis, respectively). The low activation barrier between the two isomers with an axis-unfixed biaryl backbone[14] prevents the isolation of both compounds because the exchange is fast in solution. The diastereomeric ratio was determined by ^{1}H NMR spectroscopy (Schemes 1 and 2). The bis(sulfoxide) **D** has one more chiral center due to the stereogenic sulfur atom; therefore the number of isomers is higher than the other biphenyl compounds, showing six singlets (with similar relative integration) in the ^{1}H NMR spectrum for the *S*-methyl group (2.3−2.5 ppm). In this case, all the proton signals for each isomer could not be differentiated. Ligands **C** and **E** do not show preference for one of the isomers. In solution, both chloroform and acetone solutions at several temperatures (223−323 K), an equimolar isomeric mixture was observed.

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for (*S,S*$_a$,*S*)-1C and (*S,S*)-1F (with esd's in parentheses)

	(*S,S*)-**1F**	(*S,S*$_a$,*S*)-**1C**
Pd(1)−N(1)	2.127(5)	2.093(4)
Pd(1)−N(2)	2.107(5)	
Pd(1)−C(25)	2.113(8)	
Pd(1)−C(26)	2.059(13)	
Pd(1)−C(26′)	2.11(3)	
Pd(1)−C(27)	2.111(9)	
C(25)−C(26)	1.352(18)	
C(25)−C(26′)	1.41(3)	
C(26)−C(27)	1.306(19)	
N(1)−Pd(1)−N(2)	95.0(2)	
C(25)−Pd(1)−C(27)	69.3(4)	
Pd(2)−N(2)		2.097(4)
Pd(1)−S(1)		2.348(2)
Pd(2)−S(2)		2.334(2)
Pd(1)−C(7)		2.149(8)
Pd(1)−C(8)		2.097(12)
Pd(1)−C(9)		2.140(9)
Pd(2)−C(40)		2.092(7)
Pd(2)−C(41)		2.155(11)
Pd(2)−C(42)		2.155(8)
C(7)−C(8)		1.31(2)
C(8)−C(9)		1.336(18)
C(40)−C(41)		1.370(16)
C(41)−C(42)		1.343(14)
N(1)−Pd(1)−S(1)		92.73(15)
N(2)−Pd(2)−S(2)		94.25(13)
C(7)−Pd(1)−C(9)		68.9(5)
C(40)−Pd(2)−C(42)		68.4(4)

1,4-(Bis[(4*R*)-(4-ethyl-3,4-dihydrooxazol-2-yl)]butane, **H**, was synthesized by direct reaction between (*R*)-(+)-2-aminobutanol and adiponitrile, with a quantitative yield (see Experimental Section).

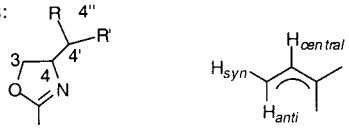
Synthesis of Allylic Complexes. 1L (allyl = C_3H_5, **L** = **A**−**G**) and **2L** (allyl = 1,3-Ph_2-C_3H_3, **L** = **A**−**D**) complexes were prepared from standard allyl halide dimer materials and the appropriate chiral ligand in the presence of ammonium hexafluorophosphate (Scheme 3), following the methodology previously described.[7a,8] Except for ligand **C**, **1L** and **2L** were obtained as monometallic complexes of general formula [Pd(η^3-allyl)(**L**)]PF_6, where the ligand is *N,N*-bonded to the metallic center. But **1C** and **2C** are bimetallic compounds, [Pd_2(η^3-allyl)$_2$(μ-(*N,S*-**C**))](PF_6)$_2$, where **C** bridges two "Pd allyl" fragments and acts as an *N,S*-donor for each palladium atom. Tests to obtain complexes containing

(14) (a) Desponds, O.; Schlosser, M. *Tetrahedron Lett.* **1996**, *37*, 47. (b) Tsue, H.; Fujimani, H.; Itakura, T.; Tsuchiya, R.; Kobayashi, K.; Takahashi, H.; Hirao, K.-i. *J. Chem. Soc., Perkin Trans. 1* **1999**, 3677.

Table 2. Selected ^{1}H NMR Data[a] (δ in ppm, 500 MHz, $CDCl_3$, 298 K) for A, B, 1A, 1B, 2A, and 2B

compd	H_3[b]	H_4	$H_{4'}$	$H_{4''}$	H_{anti}	H_{syn}	$H_{central}$
A[c]							
major (56%)	3.67 (t,7.2,1H) 4.17 (pt,7.4,1H)	4.04 (m,1H)	1.47 (m,2H)	0.82 (t,7.2,3H)			
minor (44%)	nd[d]	nd[d]	nd[d]	0.86 (t,7.2,3H)			
B[c]							
major (72%)	3.72 (t,7.8,1H) 4.11 (t,9.5,1H)	3.82 (m,1H)	1.67 (m,1H)	0.77 (d,6.5,3H) 0.78 (d,7.0,3H)			
minor (28%)	3.79 (m,2H)[e] 4.00 (t,7.3,1H)	3.79 (m,2H)[e]	1.62 (m,1H)	0.55 (m,6H)			
1A[f]							
major (72%)	3.91[e] (m,4H) 4.57 (t,9.0,2H)	3.91[e] (m,4H)	0.47(m,1H) 0.55(m,1H) 0.87(m,2H)	0.60 (t,7.2,3H) 0.73 (t,7.2,3H)	2.83 (d,12.0,1H) 3.22 (d,13.0,1H)	3.84 (d,7.0,1H) 4.05(dd, 6.7,1.7,1H)	5.68 (m,1H)
minor (28%)	4.41 (m,4H)	3.60 (m,2H)	0.87(m,2H) 1.26(m,2H)	0.85 (t,7.0,6H)	3.05 (d,12.5,2H)	4.17 (d,6.6,2H)	5.40 (m,1H)
1B							
major (71%)	4.11 (m,2H) 4.53 (m,2H)	3.72 (m,1H) 3.86 (m,1H)	0.74 (m,1H) 0.93 (m,1H)	0.31 (d,7.0,3H) 0.49 (d,6.5,3H) 0.61 (d,7.0,3H) 0.78 (d,6.5,3H)	2.79 (d,12.0,1H) 3.28 (d,13.0,1H)	3.89(dd, 7.2,1.5,1H) 3.99(dd, 7.0,2.0,1H)	5.65 (m,1H)
minor (29%)	nd[d]	nd[d]	0.85(m,2H)	nd[d]	3.00 (d,12.0,2H)	4.08 (d,6.0,2H)	5.42 (m,1H)
2A							
major	3.28 (pt,8.7,1H) 3.62(dd, 8.5,4.5,1H) 3.68(dd, 8.5,4.5,1H) 3.80 (pt,9.0,1H)	2.25(m,1H) 3.43(m,1H)	0.01(m,1H) 0.38(m,1H) 0.52(m,1H) 0.95(m,1H)	0.33 (t,7.2,3H) 0.82 (t,7.2,3H)	4.32 (d,10.5,1H) 5.43 (d,12.5,1H) [77.6,85.8][g]	-	6.20(dd, 12.5, 10.5,1H)
2B							
major	3.19 (t,9.0,1H) 3.73 (t,9.0,1H) 3.81 (dd, 8.7,4.2,1H) 3.91 (dd, 8.7,4.2,1H)	2.86(m,1H) 3.75(m,1H)	0.32(m,1H) 1.99(m,1H)	0.11 (d,6.5,3H) 0.40(m,6H) 0.93 (d,6.5,3H)	4.05 (d,9.5,1H) 5.47 (d,13.0,1H) [69.6,88.2][g]	-	6.07(dd, 13.0 9.5,1H)

[a] Multiplicity (b, broad; d, doublet; m, multiplet; s, singlet; t, triplet), coupling constants (in Hz), and relative integration in parentheses. [b] Hydrogen labels for oxazoline and allyl groups:



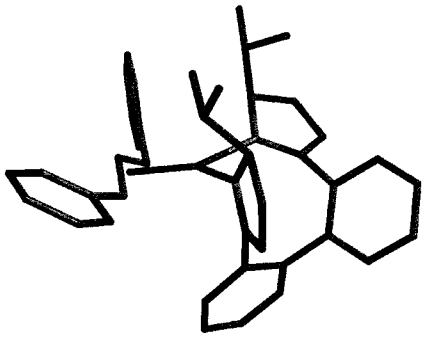
[c] Spectrum recorded at 250 MHz. [d] Not distinguished. [e] Protons **3** and **4** overlapped. [f] Spectrum recorded at 273 K. [g] ^{13}C NMR (62.9 MHz) chemical shifts in brackets.

the 1,3-diphenylallyl group with ligands **E** and **G** failed, probably due to steric hindrance (see below).

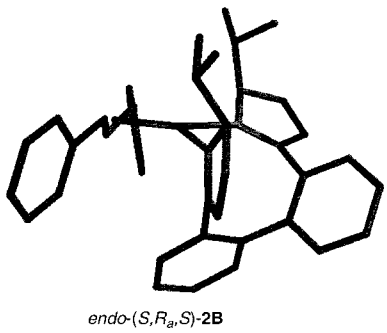
Reaction of **H** with several palladium precursors ($[Pd(\eta^3\text{-}C_3H_5)(\mu\text{-}Cl)]_2$, $[Pd(\eta^3\text{-}1,3\text{-}Ph_2\text{-}C_3H_3)(\mu\text{-}Cl)]_2$, or $[Pd(\eta^3\text{-}C_3H_5)(cod)]BF_4$) did not give allylic complexes containing the bis(oxazoline).

X-ray Structures. Suitable monocrystals for X-ray diffraction measurements were obtained from acetophenone dissolution of (S,X_a,S)-**1C** by slow diffusion of hexane and from chloroform dissolution of (S,S)-**1F** by slow diffusion of diethyl ether.

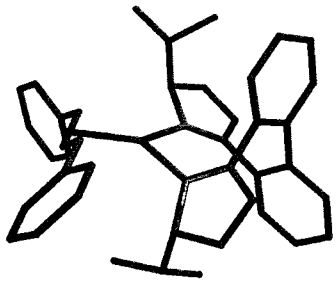
In (S,S)-**1F** (Figure 2), the palladium atom shows a distorted square-planar coordination, bonded to two nitrogen and two terminal allylic carbon atoms (Table 1), which are nearly coplanar (torsion angle N(1)−C(25)−C(27)−N(2) = 1.3°). The distance between palladium and the oxygen of the ether backbone is 2.95 Å, longer than a bond distance, but short enough to show the approximation between both atoms. The complex crystallized as a mixture of two isomers, depending on the relative position of the central allylic carbon atom and the oxygen of the ether backbone, *exo* and *endo*



exo-(*S*,R_a,*S*)-**2B**



endo-(*S*,R_a,*S*)-**2B**



(*S*,S_a,*S*)-**2B**

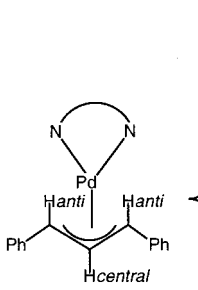
Figure 3. Calculated structures (PM3(tm)) for **2B** isomers.

isomers (carbon atom points in the same direction as oxygen, or in the opposite direction, respectively), in a ratio 0.63/0.37, respectively.

For (*S*,S_a,*S*)-**1C** (Figure 2), only the axial *S* isomer crystallized. The bis(oxazoline) ligand bridges two "Pd-allyl" fragments, where each palladium atom shows a distorted square-planar coordination, bonded to one nitrogen, one sulfur, and two terminal allylic carbon atoms. The metallic cycles are not equivalent, as observed by bond Pd−C allylic distances and bite angles (Table 1). The sulfur atoms, in each boat-six-membered metallic cycle, show *R* absolute configuration. In both palladium fragments, the allyl group exhibits an *exo* arrangement relative to the sulfur methyl group.

NMR Spectra. ^{1}H NMR spectra for complexes containing **A** and **B** ligands show the existence of several isomers in solution. For type-**1** complexes, two species ((*X*,R_a,*X*)- and (*X*,S_a,*X*)-**1L** (*X* = *R* for **A**; *X* = *S* for **B**)) are distinguished with a ratio ca. 70/30 (Table 2). This ratio does not change with the temperature (studied range 233−323 K), probably due to the high activation barrier between axial diastereomers. The ^{1}H NMR spectra for **2A** and **2B** at room temperature show mainly one species (ca. 90%), but other less intense signals can be distinguished. Therefore, for **2B** at 278 K, four species were differentiated (see below). The higher diatereomeric ratio shown by type-**2** compared to type-**1** complexes is due to the steric hindrance between the 1,3-diphenylallyl group and ligand.

Scheme 4



I-(*syn, syn* -**2B**) (84%):

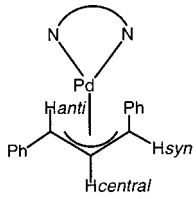
δ(H*central*): 6.12 ppm (dd, 13.0, 10.0 Hz)
δ(H*anti*): 5.53 ppm (d, 13.0 Hz)
δ(H*anti*): 4.11 ppm (d, 10.0 Hz)

II-(*syn, syn* -**2B**) (6%):

δ(H*central*): 6.47 ppm (dd, 12.5, 10.5 Hz)
δ(H*anti*): 5.02 ppm (d, 10.5 Hz)
δ(H*anti*): 4.75 ppm (d, 12.5 Hz)

III-(*syn, syn* -**2B**) (6%):

δ(H*central*): 6.67 ppm (pt, 11.2 Hz)
δ(H*anti*): 4.66 ppm (d, 2H,11.5 Hz)



IV-(*syn, anti* -**2B**) (4%):

δ(H*central*): 5.84 ppm (dd, 11.25, 7.75 Hz)
δ(H*syn*): 6.00 ppm (d, 7.75 Hz)
δ(H*anti*): 4.60 ppm (d, 11.25 Hz)

Comparing chemical shifts of the oxazoline protons of uncoordinated ligands, **A** and **B**, and major species of **1L** complexes, in addition to the loss of C_2 symmetry of the ligand upon coordination, as observed for other bis(oxazoline) complexes,[7,8] we observe that the ethyl and isopropyl protons ($H_{4'}$ and $H_{4''}$) are strongly influenced by the coordination to the metal. $H_{4'}$ and $H_{4''}$ protons (a half of them for **1B**) are shifted to higher fields than in free ligands. The signals distinguished for minor species point to a more symmetric complex. Therefore, for example, the two *syn* and two *anti* allylic protons are equivalent (Table 2).

In addition, when spectra for **1L** and **2L** complexes are compared, we observe that one of the H_4 protons for **2A** and **2B** is shifted to higher fields, while the other one is practically unchanged. A similar trend is also observed for H_3, $H_{4'}$, and $H_{4''}$ protons. This means that one oxazoline group is more influenced by the 1,3-diphenylallyl group than the other one. This asymmetry is also observed for the allyl group. The chemical shift difference between both H_{anti} protons is more than 1 ppm (4.32 and 5.43 ppm for **2A**; 4.05 and 5.47 ppm for **2B**). The difference is also important for ^{13}C chemical shifts (77.6 and 85.8 ppm for **2A**; 69.6 and 88.2 ppm for **2B**) (Table 2).

The calculated structures for (*S*,R_a,*S*)-**2B** (*endo* and *exo* isomers) and (*S*,S_a,*S*)-**2B**, by means of semiempirical PM3(tm) calculations (Figure 3), show that for the *S*-axial isomer one isopropyl group is closer to one of the allylic phenyl groups than the other one. While for *R*-axial isomers, both heterocycles are similarly influenced by the allylic phenyl groups. In solution, the Pd-allyl rotation can be fast, and consequently, both *exo* and *endo* *R*-axial isomers are not distinguished. In conclusion, the major species can be tentatively assigned to the *S*-axial isomer. This agrees with the NMR

Table 3. Chemical Shifts (ppm) of the S-Methyl Groups for Ligands C, D, and E and Their Allylic Complexes[a]

	C	D	E	1C	2C	1D	2D	1E
δ(S-*Me*)	1.94	2.33−2.46[b]	2.61 (55%) 2.67 (45%)	2.62	1.58 (68%)	2.36−2.42[b] 1.80 (32%)	2.34−2.46[b]	2.67 (56%) 2.74 (44%)

[a] Data from ^{1}H NMR spectra (250 MHz) recorded in $CDCl_3$ at room temperature. All signals are singlets. [b] Several singlets observed in this range.

Table 4. Selected ^{1}H NMR Data[a] (δ in ppm, 500 MHz, 298 K) for 1F and 1G Complexes

compd	H_3[b]	H_4	$H_{4'}$	$H_{4''}$	H_{anti}	H_{syn}	$H_{central}$
1F ($CDCl_3$)	4.01 (pt,9.6,2H) 4.18 (t,9.4,1H) 4.33(m,1H)	3.89(m,1H) 4.06(m,1H)	2.18(m,2H)	0.83 (d,6.5,3H) 0.84 (d,6.5,3H) 0.92 (d,7.0,3H) 0.95 (d,7.5,3H)	2.08 (d,12.0,1H) 2.83 (d,12.5,1H)	3.57 (d,6.7,1H) 3.72 (d,6.4,1H)	5.25(m,1H)
1G (CD_3CN)							
major (90%)	4.57(m,2H) (t,8.5,2H) 4.75 (t,9.5,2H)	4.42(m,2H)	2.24(m,2H)	1.14 (d,7.0,6H) 1.21 (d,7.0,6H)	3.04(b,1H) 3.20(b,1H)	4.18(b,1H) 4.25(b,1H)	5.69(b,1H)
minor[c] (10%)	*d*	*d*	2.34(m,1H) *d*	0.69 (d,6.5,3H) 1.15 (d,6.5,3H) *d*	3.21 (d,12.0,1H) 3.36 (d,12.0,1H)	4.33 (d,6.5,1H) *d*	6.02(m,1H)

[a] Multiplicity (b, broad; d, doublet; m, multiplet; s, singlet; t, triplet), coupling constants (in Hz), and relative integration in parentheses. [b] For hydrogen labels for oxazoline and allyl groups, see footnotes of Table 2. [c] Data obtained from the ^{1}H NMR spectrum recorded at 273 K. [d] Signals overlapped by the major isomer.

differences observed for the major (*S*-axial isomer) and minor (*R*-axial isomer**) 1A** and **1B** species (see above).

At 278 K, the ^{1}H NMR spectrum for **2B** shows four species (**I**−**IV**) in a ratio 84/6/6/4. The existence of several isomers is in agreement with (i) the ligand axial chirality; (ii) the *exo* or *endo* relative position of the allyl group and ligand backbone; and/or (iii) the *syn* or *anti* arrangement of the phenylallyl groups. The three more abundant species correspond to *syn*,*syn* allylic complexes, as shown by the coupling constants of the allyl protons. However the minor species corresponds to a *syn*,*anti* allylic complex (Scheme 4). By NOESY experiments, exchange between one *syn* proton of the minor species (6.00 ppm) and one *anti* proton of the major compound (4.11 ppm) is observed. Then, selective terminal allylic opening is produced and both terminal allylic carbon atoms are electronically differentiated, because of the different hindrance between allyl and oxazoline fragments.

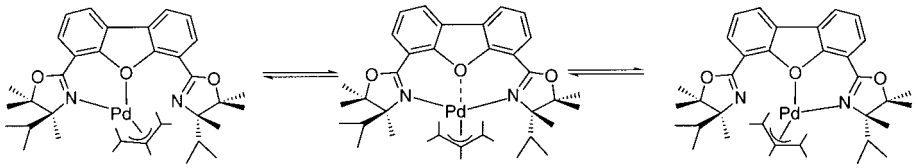
^{1}H NMR spectra for bimetallic **1C** and **2C** complexes, in chloroform-*d* and acetone-d_6 (studied temperature range 223−298 K), show broad signals, but two species are differentiated in a ratio of ca. 70/30 for both complexes. In these compounds several species are expected, due to the relative position between the allyl group and sulfur substituent and the different chiral sources: stereocenters (carbon and sulfur atoms) and axial backbone axis. However, the two species observed in solution are probably due to the axial chirality, because the allyl rotation and the configuration inversion of the sulfur atom exhibit lower activation energies than the interconversion between the axial diastereomers.

In contrast to ligand **C**, allylic complexes containing the bis(sulfoxide) **D** (**1D** and **2D**) and bis(sulfone) **E** (**1E**) are monometallic, as shown by their analytical data (FAB mass spectrometry, elemental analysis, and molar conductivity; see Experimental Section). Their ^{1}H NMR spectra prove the existence of several isomers in a similar ratio. These complexes can be bonded by the nitrogen or sulfur atom. Comparing the chemical shifts of the methyl substituent sulfur group in the free ligands **C**, **D**, and **E** and in the corresponding allylic complexes, we observe a relevant trend. When the sulfur atom is bonded to the metal (**1C** and **2C**), the methyl group is shifted to lower fields (1.94 vs 2.62 ppm, for **C** and **1C**, respectively) or to higher fields (1.94 vs 1.58 and 1.80 ppm, for **C** and **2C**, respectively) than free ligands (Table 3). In contrast, for complexes containing **D** and **E** ligands, no difference in chemical shifts is observed between free ligands and their palladium complexes (Table 3). Therefore, a bidentate *N*,*N*-coordination for **1D**, **2D**, and **1E** is proposed.

The ^{1}H NMR spectrum for **1F** shows the presence of only one species in solution (Table 4) in the temperature range studied (233−298 K), although in the solid state this compound crystallized as a mixture of two isomers (see above). Probably, a fast exchange between both isomers *exo*/*endo*-**1F** on the NMR time scale leads us to observe an averaged structure in solution.

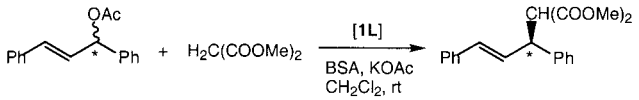
For **1G**, two species (ca. 9/1) are observed in the ^{1}H NMR spectra recorded at several temperatures (studied range 360−298 K; Table 4). The major species shows a C_2 symmetrical environment for ligand and allyl groups. At 273 K, a third species is distinguished (ratio 3.8/1.4/1). The two minor species do not show the C_2 symmetrical environment. Exchange signals (NOESY experiment) are observed among the three species. The isomers observed can be atributed to a *N*,*O*,*N*-tridentate

Scheme 5



VI V VII

Table 5. Results of Asymmetric Allylic Alkylation of *rac*-3-Acetoxy-1,3-diphenyl-1-propene with Dimethyl Malonate[a]



entry	precursor	time (days)	conv (%)[b]	ee (%)[c]	conf[d]
1	(*R*,*X*,*R*)-**1A**	7	100	86	*R*
2	(*S*,*X*,*S*)-**1B**	7	93	89	*S*
3	(*S*,*X*,*S*)-**1C**	1.5	100	45	*R*
4	(*S*,*X*,*S*)-**1D**	7	50	48.5	*R*
5	(*S*,*X*,*S*)-**1E**	7	0		
6	(*S*,*S*)-**1F**	2.5	100	89	*S*
7	(*S*,*S*)-**1G**	7	0		
8	Pd/(*R*,*R*)-**H**[e]	7	18	21	*R*

[a] Results determined from duplicate experiments. [b] Conversion percentage based on the substrate, determined by ^{1}H NMR spectroscopy. [c] Determined by HPLC on a Chiralcel-OD column. [d] Determined by optical rotation: Leutenegger, U.; Umbricht, G.; Fahrni, C.; Matt, P. V.; Pfaltz, A. *Tetrahedron* **1992**, *48*, 2143. [e] Catalyst generated under in situ conditions by reaction of 1 mol % of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ and 2.5 mol % of (*R*,*R*)-**H**.

complex (**V**, Scheme 5) and two *N*,*O*-bidentate species (**VI** and **VII**, Scheme 5).

Catalytic Results. The palladium/bis(oxazoline) systems described here were tested in the model allylic alkylation, between the racemic substrate *rac*-3-acetoxy-1,3-diphenyl-1-propene and dimethyl malonate, under basic Trost conditions.[15] The catalytic results are summarized in Table 5. The catalyses were run using allylic precursors **1L**, unless stated otherwise.

The highest activity was obtained with the bimetallic catalytic system, **1C**: total conversion of substrate was achieved in 1.5 days, but the asymmetric induction was moderate (45% ee, entry 3). When the thioether is oxidized (bis(sulfoxide) **D** and (bis)sulfone **E** ligands), the activity decreases drastically (entries 4 and 5). This catalytic behavior can be explained by the different coordination manner of the ligand toward the metal: **C** acts as an *N*,*S*-heterodonor, while **D** acts as an *N*,*N*-homodonor ligand. The nonactivity shown by **1E** is in agreement with the failed reactions when trying to obtain the 1,3-diphenylallyl complex.

Catalytic systems with ligands **A**, **B**, and **F** gave good enantioselectivities (entries 1, 2, and 6), up to 89% ee, the activity being higher for the Pd/**F** system than for Pd/**A** or Pd/**B** catalytic species (2.5 vs 7.0 days for total substrate conversion, respectively). In contrast, the Pd/**G** system was not active (entry 7). This behavior is in agreement with the unsuccessful attempts to synthesize the allyl palladium complex containing a 1,3-diphenylallyl group, as in the case of **E**. Probably, the steric hindrance between the ligand and the diphenylallyl group avoids the stabilization of the rigid ten-membered metallic cycle. The catalytic system containing the flexible methylenic ligand, Pd/**H**, gave very low activity and selectivity (entry 8). Although the number of spacer carbon atoms is the same as for biphenyl derivatives, this behavior is drastically different, because ligand **H** does not stabilize palladium allylic complexes.

Conclusions

Bis(oxazolines) containing axis-unfixed biphenyl (**A**−**E**) and diaryl ether (**F** and **G**) backbones have been prepared in order to study their coordination chemistry with allylic palladium starting materials. X-ray data and NMR spectra in several solvents and temperatures have allowed us to demonstrate the coordination of the ligands and the species present in solution. When only nitrogen atoms are present in the ligand as donor centers, *N*,*N*-bidentate monometallic complexes are obtained. But when thioether groups are involved (**C**), *N*,*S*-bidentate bimetallic complexes are stabilized. The Lewis basicity of the sulfur atom decreases when the thioether moiety is oxidized to the sulfoxide (**D**) and sulfone (**E**) derivatives. In these cases, *N*,*N*-bidentate complexes are again isolated. Type-**1** allylic precursors have been used in the model allylic alkylation reaction. The high enantiomeric excesses observed for biphenyl and diphenyl ether ligands (**A**, **B**, and **F**) is in agreement with the asymmetry produced in type-**2** intermediates, together with the high diastereomeric excesses observed for **2A** and **2B** complexes, because the enantioselectivity is controlled by the external attack of the soft nucleophile on the Pd(II)-allylic intermediate species. The nonactivity of catalytic systems Pd/**E** and Pd/**G** agrees with the nonstability of complexes bonded to the 1,3-diphenylallyl, probably due to steric hindrance between the chiral ligand and allyl group. Comparing the reactivity of bis(oxazolines) with four spacer atoms (biphenyl ligands **A**, **B**, and **H**), we can conclude that the rigidity of the aryl backbone allows the stabilization of monometallic allylic complexes and induces high enantioselectivity (ee up to 89%) in the allylic alkylation reaction, in contrast to the Pd/**H** system, which does not give allylic complexes and induces very low selectivity (ee = 21%).

Experimental Section

General Data. All compounds were prepared under a purified nitrogen atmosphere using standard Schlenk and vacuum-line techniques. The solvents were purified by standard procedures and distilled under nitrogen.[16] (*R*)-(+)-2-Aminobutanol (Fluka) and L-valinol (Aldrich) were used

(15) Trost, B. M.; Murphy, D. J. *Organometallics* **1985**, *4*, 1143.

(16) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon Press: Oxford, U.K., 1988.

without previous purification. (*S*)-2-Amino-1,1-diphenyl-4-(methylthio)-1-butanol,[17] ligand **B**,[5,9] ligand **G**,[10] $[Pd(\eta^3\text{-}C_3H_5)(\mu\text{-}Cl)]_2$,[18] and $[Pd(\eta^3\text{-}1,3\text{-}Ph_2\text{-}C_3H_3)(\mu\text{-}Cl)]_2$[7a] were prepared as described previously. NMR spectra were recorded on Varian XL-500 (^{1}H, standard $SiMe_4$), Varian Gemini (^{1}H, 200 MHz; ^{13}C, 50 MHz; standard $SiMe_4$), and Bruker DRX 250 (^{13}C, 62.9 MHz, standard $SiMe_4$) spectrometers, using $CDCl_3$ as solvent, unless stated otherwise. Chemical shifts are reported downfield from standards. IR spectra were recorded on a Nicolet 520 FT-IR spectrometer. FAB mass chromatograms were obtained on a Fisons V6-Quattro instrument. Enantiomeric excesses were determined by HPLC on a Waters Series 600 chromatograph (Chiralcel-OD chiral column) with a UV detector. Optical rotations were measured on a Perkin-Elmer 241MC spectropolarimeter. Conductivities were obtained on a Radiometer CDM3 conductimeter. Elemental analyses were carried out by the Serveis Cientifico-Tècnics de la Universitat de Barcelona in an Eager 1108 microanalyzer.

Synthesis of Ligands. 2,2′-Bis(carboxy)diphenyl Ether. Diphenyl ether (1.0 g, 11.8 mmol) dissolved in 7 cm^3 of THF was slowly added to a mixture of 10.3 cm^3 of *n*BuLi (ca. 1.6 M in hexane) and 4.2 cm^3 of TMEDA (23.3 mmol). The mixture was stirred at room temperature for 16 h. The reaction mixture was then poured over solid CO_2 in diethyl ether and stirred for 6 h at room temperature. The white solid obtained was filtered off, treated with 40 cm^3 of water, and acidified with a solution of 2 M HCl until pH = 3. The white product was filtered off, washed with water and cold ethanol, and dried under reduced pressure. Yield: 3.0 g (99%). ^{1}H NMR (200 MHz, CD_3COCD_3): δ 3.67 (bs, 1H), 5.61 (pdd, 8.0 Hz, 0.9 Hz, 1H), 5.93 (pt, 9 Hz, 1H), 6.22 (m, 1H), 6.66 (dd, 7.6 Hz, 1.8 Hz, 1H) ppm. ^{13}C NMR (50 MHz, CD_3COCD_3): δ 117.1, 120.9, 121.2, 129.7, 131.3, 153.8, 165 ppm. IR (KBr): 1699 (C═O), 1462 (C−O) cm^{-1}. Anal. Calcd for $C_{14}H_{10}O_5$: C, 65.11; H, 3.87. Found: C, 65.63; H, 4.07.

2,2′-Bis(carboxy chloride)diphenyl Ether. Dicarboxylic acid (1.0 g, 3.88 mmol) described above was treated with 7 cm^3 of $SOCl_2$. The mixture was heated at reflux temperature for 3 h. The solvent was then removed under reduced pressure, and the residue was washed with diethyl ether (3 × 15 cm^3), affording a white solid. Yield: 1.13 g (90%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 6.89 (pdd, 8.6 Hz, 1.2 Hz, 1H), 7.3 (pt, 7.8 Hz, 1H), 7.59 (pt, 7.9 Hz, 1H), 8.20 (pdd, 8 Hz, 1.6 Hz, 1H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ 119.6, 124.3, 125.1, 134.3, 135.9, 155.6, 163.7 ppm. IR (KBr): 1787 (C═O), 1442 (C−O) cm^{-1}. Anal. Calcd for $C_{14}H_8Cl_2O_2$: C, 60.24; H, 2.95; Cl, 25.77. Found: C, 60.11; H, 3.20; Cl, 26.00.

1,1′-Biphenyl-2,2′-dicarboxylic Acid Dichloride. One gram (4.10 mmol) of diphenic acid was treated with 7 cm^3 of $SOCl_2$. The mixture was heated at reflux temperature for 6 h. The solvent was then removed under reduced pressure, and the residue was washed with diethyl ether (3 × 15 cm^3), affording a white solid. Yield: 0.86 g (75%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.52 (t, 7.6 Hz, 1H), 8.05 (pdd, 7.6 Hz, 1.2 Hz, 1H), 8.43 (pdd, 7.7 Hz, 1.2 Hz, 1H) ppm. IR (KBr): 1701 (C═O), 1442 (C−O) cm^{-1}. Anal. Calcd for $C_{14}H_8Cl_2O_2$: C, 60.24; H, 2.95; Cl, 25.77. Found: C, 60.11; H, 3.20; Cl, 26.00.

***N,N*-Bis[(1*R*)-(1-ethyl-2-hydroxiethyl)]-1,1′-biphenyl-2,2′-dicarboxamide.** The diacid dichloride (1.1 g, 4 mmol) described above was dissolved in 20 cm^3 of THF in the presence of 1.11 g (8 mmol) of NEt_3. The mixture was cooled to 0 °C, and a solution of (*R*)-(+)-2-aminobutanol (0.71 cm^3, 8 mmol) in 10 cm^3 of THF was then added dropwise. The mixture was then stirred for 1 h at 0 °C and then warmed to room temperature. The resulting white solid was filtered off. From the filtrate, the solvent was removed, and the yellow residue was dissolved with dichloromethane and then washed with a 10% aqueous solution of ammonium chloride (3 × 5 cm^3) and water (5 × 10 cm^3). The organic phase was then dried over anhydrous sodium sulfate, and a yellow oil was separated after removing the solvent under reduced pressure. Yield: 1.19 g (78%). ^{1}H NMR (200 MHz, $CDCl_3$): δ *major* 0.73 (t, 6.5 Hz, 3H), 1.32 (m, 2H), 3.29 (m, 1H), 3.49 (m, 1H), 3.63 (m, 1H), 7.06 (m, 2H), 7.32 (m, 2H), 7.52 (m, 1H); *minor* 0.67 (t, 6.5 Hz, 3H), 1.32 (m, 2H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ *major* 9.3, 25.6, 53.8, 66.6, 126.9 (CH, Ph), 128.4 (CH, Ph), 128.5 (CH, Ph), 128.9, 130.5 (CH, Ph), 137.4, 169.5; *minor* 9.4, 23.6, 52.7, 137.6, 169.8 ppm. IR (KBr): 1636 (C═O), 1193 (C−O) cm^{-1}.

***N,N*-Bis[(1*S*)-(1-methylthioethyl-2,2-diphenyl-2-hydroxiethyl)]-1,1′-biphenyl-2,2′-dicarboxamide.** The diacid dichloride (1.1 g, 4 mmol) described above was dissolved in 20 cm^3 of THF in the presence of 1.11 g (8 mmol) of NEt_3. The mixture was cooled to 0 °C, and a solution (*S*)-2-amino-1,1-diphenyl-4-(methylthio)-1-butanol (2.29 g, 8 mmols) in 10 cm^3 of THF, was then added dropwise. The mixture was then stirred for 1 h at 0 °C and then warmed to room temperature. The resulting white solid was filtered off. From the filtrate, the solvent was removed and the yellow residue was dissolved with dichloromethane and then washed with water (5 × 10 cm^3 water). The organic phase was then dried over anhydrous sodium sulfate, and a yellow solid was separated after removing the solvent under reduced pressure. Yield: 3.11 g (99%). $[\alpha]_D^{25}$ −35 (*c* 0.9, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$): δ *major* 1.83 (m, 4H), 1.76 (s, 3H), 3.71 (pt, 6.2 Hz, 4H), 4.10 (m, 2H), 5.10 (m, 2H), 6.20 (d, 8.3 Hz, 2H), 7.53 (m, 24H), 8.25 (d, 9.2 Hz, 1H); *minor* 1.81 (s, 3H), 8.46 (d, 9.6 Hz, 1H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ *major* 15.2, 29.2, 30.9, 55.7, 80.6, 125.1 (CH, Ph), 125.3 (CH, Ph), 125.5 (CH, Ph), 126.6 (CH, Ph), 126.7 (CH, Ph), 127.1 (CH, Ph), 128.2 (CH, Ph), 128.3 (CH, Ph), 129.1 (CH, Ph), 135.6, 138.4, 144.8, 145.9, 170.7; *minor* 15.1, 29.6, 31.0, 55.6, 80.8, 134.9, 137.4, 144.6, 145.6, 170.2 ppm. IR (KBr): 1628 (C═O), 1248 (C−O) cm^{-1}. Anal. Calcd for $C_{48}H_{48}N_2O_4S_2$: C, 73.22; H, 6.27; N, 3.49; S, 7.71. Found: C, 73.40; H, 6.13; N, 3.67; S, 7.81.

***N,N*-Bis[(1*S*)-(1-isopropyl-2-hydroxiethyl)]-2,2′-dicarboxamidediphenyl Ether.** 2,2′-Bis(carboxy chloride)diphenyl ether (1.1 g, 4.45 mmol) and 1.58 g (9.80 mmol) of carbonyldiimidazole were dissolved with 35 cm^3 of THF. After stirring for 30 min at room temperature, a mixture of 1.01 g (9.80 mmol) of L-valinol and 0.011 g (0.090 mmols) of DMAP ((dimethylamino)pyridine) in 80 cm^3 of THF was slowly added. The mixture was stirred at room temperature for 18 h and then heated at 50 °C for 1 h. The solvent was removed under reduced pressure, and the residue was dissolved in 40 cm^3 of dichloromethane. Extractions with 2 M HCl (3 × 5 cm^3), aqueous saturated $NaHCO_3$ (3 × 5 cm^3), and water (3 × 5 cm^3) were carried out. The organic extracts were dried over anhydrous sodium sulfate and filtered off, and the solvent was removed under reduced pressure. The residue was chromatographied over SiO_2 using ethyl acetate/hexane (1/5) as eluent, affording the bisamide as a yellow oil. Yield: 1.25 g (66%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.82 (d, 6.6 Hz, 3H), 0.99 (d, 6.6 Hz, 3H), 1.84 (m, 1H), 3.64 (m, 2H), 3.89 (m, 1H), 6.86 (d, 8 Hz, 1H), 7.23 (t, 7.2 Hz, 1H), 7.41 (t, 7.9 Hz, 1H), 7.63 (d, 8.8 Hz, 1H), 8.01 (dd, 7.7 Hz, 1.9 Hz, 1H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): 18.0, 18.4, 28.1, 55.9, 61.6, 117.7, 123.4, 124.9, 130.4, 131.5, 152.4, 164.2 ppm. IR (KBr): 1758 (C═O), 1198 (C−O) cm^{-1}.

2,2′-Bis[(4*R*)-(4-ethyl-3,4-dihydrooxazol-2-yl)]-1,1′-biphenyl, (*R*,*R*)-A. *N*,*N*-Bis[(1*R*)-(1-ethyl-2-hydroxiethyl)]-1,1′-biphenyl-2,2′-dicarboxamide (0.440 g, 1.1 mmol), NEt_3 (0.96 cm^3, 4.84 mmol), and mesylate chloride (0.46 cm^3, 2.42 mmol) were dissolved in 10 cm^3 of dichloromethane at 0 °C. The mixture was warmed to room temperature and stirred for 2 h. The mixture was diluted with 10 cm^3 of dichloromethane and poured into a saturated aqueous solution of ammonium chloride. The aqueous phase was extracted with dichloro-

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methane (3 × 20 cm^3), and the combined organic phases were successively washed with an aqueous solution of sodium chloride (3 × 10 cm^3) and water (3 × 10 cm^3) and finally dried over anhydrous sodium sulfate. The mixture was filtered off, and the solvent was removed under reduced pressure, affording the crude bis(mesylate) as an oil, which was used in the next reaction without further purification. The corresponding bis(mesylate) was treated with a methanolic solution (50% in weight) of sodium hydroxide (10 equiv) for 4 days at room temperature. The product was extracted with dichloromethane (3 × 10 cm^3). The organic phase was dried over anhydrous sodium sulfate and filtered off, and the solvent was removed under reduced pressure, affording an oil, which was chromatographed over SiO_2 using ethyl acetate/hexane (1/5) as eluent, giving the bisoxazoline as a yellow oil. Yield: 0.23 g (61%). $[\alpha]_D^{25}$ +132.5 (*c* 1.1, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$): δ *major* 0.82 (t, 7.2 Hz, 3H), 1.47 (m, 2H), 3.67 (t, 7.2 Hz, 1H), 4.04 (m, 1H), 4.17 (pt, 7.4 Hz, 1H), 7.39 (m, 3H), 7.79 (d, 6.2 Hz, 1H); *minor* 0.86 (t, 7.2 Hz, 3H), 7.82 (d, 7 Hz, 1H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ *major* 8.9, 27.3, 66.7, 71.3, 125.9, 128.2, 128.5, 128.9, 129.3, 140.3, 163.1; *minor* 9.2, 27.7, 66.9 ppm. IR (NaCl): 1663 (C═N) cm^{-1}.

2,2′-Bis{(4*S*)-[4-(2-methylthio)propyl-3,3-diphenyl-3,4-dihydrooxazol-2-yl]}-1,1′-biphenyl, (*S,S*)-C. *N,N*-Bis[(1*S*)-(1-methylthioethyl-2,2-diphenyl-2-hydroxiethyl)]-1,1′-biphenyl-2,2′-dicarboxamide (0.78 g, 1 mmol) and 0.48 g (2 mmol) of Burgess reagent were dissolved in 15 cm^3 of THF. The mixture was stirred for 8 h at room temperature, until total consumption of the biscarboxamide) (monitored by TLC; eluent, hexane/ethyl acetate, 1/1). The mixture was then filtered off and the filtrate filtered over silica (1% of NEt_3). The solvent was removed under reduced pressure, affording a yellow solid. Yield: 0.71 g (99%). $[\alpha]_D^{25}$ −11.1 (*c* 1, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ *major* 1.28 (m, 4H), 1.94 (s, 6H), 2.43 (t, 7.2 Hz, 4H), 3.88 (dd, 10.7 Hz, 3.3 Hz, 2H), 6.64 (d, 7.2 Hz, 2H), 6.76 (d, 7.2 Hz, 2H), 7.05 (t, 8 Hz, 4H), 7.36 (m, 22H), 7.98 (dd, 7 Hz, 1.4 Hz, 1H); *minor* 1.95 (s, 6H), 4.80 (dd, 10.6 Hz, 3.5 Hz, 2H), 8.11 (d, 7.3 Hz, J = 1.9 Hz, 1H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ *major* 14.6, 30.4, 32.7, 71.8, 91.6, 126.0, 126.9, 128.4, 128.8, 130.1, 139.1, 140.8, 141.2, 142.8, 164.0; *minor* 13.2, 32.9, 71.4, 91.3 ppm. IR (KBr): 1653 (C═N) cm^{-1}. Anal. Calcd for $C_{48}H_{44}N_2O_2S_2$: C, 77.39; H, 5.95; N, 3.76; S, 8.61. Found: C, 77.20; H, 6.00; N, 3.33; S, 8.94. MS (FAB positive): *m*/*z* 747 ($[M + 2]^+$).

2,2′-Bis{(4*S*)-[4-(2-methylsulfoxide)propyl-3,3-diphenyl-3,4-dihydrooxazol-2-yl]}-1,1′-biphenyl, (*S,S*)-D. (*S, S*)-**C** (0.4 g, 0.53 mmol) in 5 cm^3 of acetone was treated with 0.15 cm^3 of 33% H_2O_2 (1.60 mmol) in 7 cm^3 of acetone. The mixture was stirred at room temperature for 3 h and washed with water (3 × 10 cm^3). The organic phase was dried over anhydrous sodium sulfate and filtered off, and the solvent was removed under reduced pressure, affording a yellow solid. Yield: 0.38 g (93%). $[\alpha]_D^{25}$ −158 (*c* 1, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.04 (m, 2H), 1.69 (m, 2H), 2.33 (s, 6H), 2.34 (s, 6H), 2.38 (s, 6H), 2.39 (s, 6H), 2.44 (s, 6H), 2.46 (s, 6H), 2.59 (m, 4H), 4.62 (dd, 7.9 Hz, 3.6 Hz, 1H), 4.75 (m, 1H), 6.75 (m, 2H), 6.97 (d, 6.7 Hz, 2H), 7.25 (m, 22H), 7.94 (m, 1H), 8.09 (dd, 6.8 Hz, 1.8 Hz, 1H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ 26.8, 51.7, 52.0, 52.7, 52.9, 72.4, 72.6, 73.6, 73.8, 92.3, 92.7, 124.9, 125.1, 126.1, 126.3, 128.8, 129.9, 127.0, 127.2, 127.3, 127.6, 128.2, 128.4, 128.5, 129.3, 129.5, 138.6, 139.3, 142.1, 142.3, 143.5, 162.4 ppm. IR (KBr): 1651 (C═N), 1044 (S═O) cm^{-1}. Anal. Calcd for $C_{48}H_{44}N_2O_4S_2$: C, 74.20; H, 5.71; N, 3.61; S, 8.25. Found: C, 74.24; H, 5.78; N, 3.61; S, 8.23. MS (FAB positive): *m*/*z* 778 ($[M + 2]^+$).

2,2′-Bis{(4*S*)-[4-(2-methylsulfone)propyl-3,3-diphenyl-3,4-dihydrooxazol-2-yl]}-1,1′-biphenyl, (*S,S*)-E. *m*-CPBA (1.18 g, 13.7 mmol) in 20 cm^3 of dichloromethane was slowly added at 0 °C to a solution of (*S,S*)-**D** (0.81 g, 1.0 mmol) in 7 cm^3 of dichloromethane. The mixture was then warmed at room temperature and stirred for 2 days (monitored by TLC). The mixture was successively washed with saturated aqueous solutions of sodium hydrogen sulfite (3 × 10 cm^3), sodium hydrogen carbonate (3 × 10 cm^3), and water (3 × 10 cm^3). The organic phase was dried over anhydrous sodium sulfate and filtered off, and the solvent was removed under reduced pressure, affording a yellow solid, which was recrystallized from dichloromethane and hexane. Yield: 0.67 g (83%). ^{1}H NMR (250 MHz, $CDCl_3$): δ *major* 0.89 (m, 2H), 1.71 (m, 2H), 2.64 (s, 6H), 2.71 (m, 2H), 2.89 (m, 2H), 4.70 (dd, 11.8 Hz, 3.7 Hz, 2H), 6.79 (d, 6.7 Hz, 2H), 6.97 (d, 6.7 Hz, 2H), 7.25 (m, 22H), 7.99 (dd, 7.6 Hz, 1.3 Hz, 2H); *minor* 2.67 (s, 6H), 4.80 (dd, 10.7 Hz, 3.8 Hz, 2H), 8.09 (dd, 6.8 Hz, 1.8 Hz, 2H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ *major* 25.7, 39.9, 50.7, 71.4, 91.5, 124.9, 125.1, 126.1, 126.3, 128.8, 129.9, 127.0, 127.2, 127.4, 127.6, 128.2, 129.3, 129.5, 138.4, 141.1, 141.4, 142.2, 161.7; *minor* 25.6, 39.7, 50.9, 70.4, 91.8, 138.3, 162.1 ppm. IR (KBr): 1644 (C═N), 1297 (S═O), 1131 (S═O) cm^{-1}. Anal. Calcd for $C_{48}H_{44}N_2O_6S_2$: C, 71.28; H, 5.44; N, 3.46; S, 7.92. Found: C, 72.02; H, 5.23; N, 3.32; S, 8.03. MS (FAB positive): *m*/*z* 810 ($[M + 2]^+$).

2,2′-Bis[(4*S*)-(4-isopropyl-3,4-dihydrooxazol-2-yl)]-1,1′-diphenyl ether, (*S,S*)-F. $SOCl_2$ (1.2 cm^3, 17 mmol) was added to a solution of 0.300 g (0.70 mmols) of the appropriate bis(amide) in 10 cm^3 of dichloromethane at 0 °C. The mixture was warmed to room temperature and then refluxed for 3 h. At room temperature, 15 cm^3 of dichloromethane was added, and the mixture was extracted with saturated aqueous solutions of sodium hydrogen carbonate (3 × 10 cm^3), sodium chloride (3 × 10 cm^3), and water (3 × 10 cm^3). The organic phase was dried over anhydrous sodium sulfate and filtered off, and the solvent was removed under reduced pressure, affording a yellow solid. This bis(amide) chloride was treated with a methanolic solution (50% in weight) of sodium hydroxide (10 equiv) for 5 h at reflux of solvent. The organic phase was dried over anhydrous sodium sulfate and filtered off, and the solvent was removed under reduced pressure, affording an oil, which was chromatographed over SiO_2 using ethyl acetate/hexane (1/1) as eluent, giving the bisoxazoline as a yellow oil. Yield: 0.76 g (27%). ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.83 (d, 6.7 Hz, 3H), 0.92 (d, 6.8 Hz, 3H), 1.76 (m, 1H), 3.99 (m, 2H), 4.26 (m, 1H), 6.87 (d, 8.2 Hz, 1H), 7.10 (t, 7.5 Hz, 1H), 7.34 (m, 1H), 7.83 (dd, 8.0 Hz, 7.5 Hz, 1H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ 16.9, 17.7, 31.5, 69.1, 71.1, 118.4, 119.2, 122.0, 130.3, 130.9, 154.4, 161.2 ppm. IR (NaCl): 1652 (C═N) cm^{-1}.

1,4-Bis[(4*R*)-(4-ethyl-3,4-dihydrooxazol-2-yl)]butane, (*R,R*)-H. Adiponitrile (1.00 g, 9.20 mmol), 2.70 g (32 mmol) of (*R*)-(+)-2-aminobutanol, and 8.2 mg (0.06 mmol) of zinc dichloride were dissolved in 30 cm^3 of toluene and refluxed for three weeks (reaction monitored by GC). Then the solvent was removed under reduced pressure, and the oil obtained was dissolved in 25 cm^3 of dichloromethane. The organic phase was washed with water, dried over anhydrous sodium sulfate, and filtered off and the solvent removed under reduced pressure. Yield: 2.30 g (99%). ^{1}H NMR (300 MHz, $CDCl_3$): 0.93 (t, 7.3 Hz, 3H), 1.43 (m, 1H), 1.56 (m, 1H), 1.67 (m, 2H), 2.29 (m, 2H), 3.83 (t, 9.7 Hz, 1H), 4.01 (m, 1H), 4.26 (m, 1H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ 8.8, 24.6, 26.3, 27.5, 66.2, 70.7, 165.8 ppm. IR (KBr): 1666 (C═N) cm^{-1}.

Synthesis of Complexes. Type-**1** and type-**2** allylic complexes were prepared following the methodology previously described.[7a,8]

(η^3-Allyl)-{2,2′-bis[(4*R*)-(4-ethyl-3,4-dihydrooxazol-2-yl)]-1,1′-biphenyl-*N,N*}palladium(II) Hexafluorophosphate, (*R,X,R*)-1A. Starting materials were 64 mg (0.18 mmol) of $[Pd(\eta^3\text{-}C_3H_5)(\mu\text{-}Cl)]_2$, 128 mg (0.37 mmol) of (*R,X,R*)-**A**, and 43 mg of NH_4PF_6 (0.26 mmol) of NH_4PF_6. Yield: 219 mg (93%). IR (KBr): 1644 (st, C═N), 843 (st, P−F) cm^{-1}. Anal. Calcd for $C_{25}H_{29}F_6N_2O_2PPd$: C, 46.89; H, 4.71; N, 4.36. Found: C, 47.19; H, 4.95; N, 4.35. Mp: 139 °C. MS (FAB positive): *m*/*z* 495 ($[M - PF_6]^+$).

(η^3-Allyl)-{2,2′-bis[(4*S*)-(4-isopropyl-3,4-dihydrooxazol-2-yl)]-1,1′-biphenyl-*N,N*}palladium(II) Hexafluorophosphate, (*S,X,S*)-1B. Starting materials were 64 mg (0.18 mmol) of [Pd(η^3-C_3H_5)(μ-Cl)]$_2$, 132 mg (0.35 mmol) of (*S,X,S*)-**B**, and 41.5 mg (0.25 mmol) of NH_4PF_6. Yield: 213 mg (91%). IR (KBr): 1645 (st, C═N), 842 (st, P−F) cm^{-1}. Anal. Calcd for $C_{27}H_{33}F_6N_2O_2PPd$: C, 48.48; H, 5.11; N, 4.19. Found: C, 49.00; H, 5.26; N, 4.27. Mp: 140 °C. MS (FAB positive): *m/z* 523 ([M − PF_6]$^+$).

Bis(η^3-allyl)-μ-{2,2′-bis{(4*S*)-[4-(2-methylthio)propyl-3,3-diphenyl-3,4-dihydrooxazol-2-yl]}-1,1′-biphenyl-*N,S*}-dipalladium(II) Bis(hexafluorophosphate), (*S,X,S*)-1C. Starting materials were 0.252 g (0.55 mmol) of [Pd(η^3-C_3H_5)(μ-Br)]$_2$, 0.313 g (0.42 mmol) of (*S,X,S*)-**C**, and 0.169 g (1.04 mmol) of NH_4PF_6. Yield: 0.222 g (99%). IR (KBr): 1635 (st, C═N), 839 (st, P−F) cm^{-1}. Anal. Calcd for $C_{54}H_{54}F_{12}N_2O_2S_2P_2Pd_2$: C, 48.70; H, 4.09; N, 2.10; S, 4.80. Found: C, 48.33; H, 4.05; N, 2.05; S, 4.29. Mp: 187 °C. Molar conductivity (acetonitrile): 188 Ω^{-1} cm^2 mol^{-1}. MS (FAB positive): *m/z* 1184 ([M − PF_6]$^+$).

(η^3-Allyl)-{2,2′-bis{(4*S*)-[4-(2-ethylmethylsulfinyl)-3,3-diphenyl-3,4-dihydrooxazol-2-yl]}-1,1′-biphenyl-*N,N*}-palladium(II) Hexafluorophosphate, (*S,X,S*)-1D. Starting materials were 36 mg (0.080 mmol) of [Pd(η^3-C_3H_5)(μ-Br)]$_2$, 124 mg (0.16 mmol) of (*S,X,S*)-**D**, and 39 mg (0.24 mmol) of NH_4PF_6. Yield: 166 mg (98%). IR (KBr): 1640 (st, C═N), 1035 (st, S═O), 842 (st, P−F) cm^{-1}. Anal. Calcd for $C_{51}H_{49}F_6N_2O_4S_2PPd$: C, 57.22; H, 4.58; N, 2.61; S, 5.98. Found: C, 57.46; H, 5.01; N, 2.65; S, 5.65. Mp: 160 °C. Molar conductivity (acetonitrile): 133 Ω^{-1} cm^2 mol^{-1}. MS (FAB positive): *m/z* 923 ([M − PF_6]$^+$).

(η^3-Allyl)-{2,2′-bis{(4*S*)-[4-(2-ethylmethylsulfonyl)-3,3-diphenyl-3,4-dihydrooxazol-2-yl]}-1,1′-biphenyl-*N,N*}-palladium(II) Hexafluorophosphate, (*S,X,S*)-1E. Starting materials were 35 mg (0.08 mmol) of [Pd(η^3-C_3H_5)(μ-Br)]$_2$, 126 mg (0.15 mmol) of (*S,X,S*)-**E**, and 38 mg (0.23 mmol) of NH_4PF_6. Yield: 150 mg (87%). IR (KBr): 1638 (st, C═N), 1305 (st, S═O), 1131 (st, S═O), 844 (st, P−F) cm^{-1}. Anal. Calcd for $C_{51}H_{49}F_6N_2O_6S_2PPd$: C, 55.56; H, 4.44; N, 2.54; S, 5.80. Found: C, 55.10; H, 4.35; N, 2.25; S, 5.70. Mp: 165 °C. Molar conductivity (acetonitrile): 140 Ω^{-1} cm^2 mol^{-1}. MS (FAB positive): *m/z* 956 ([M − PF_6]$^+$).

(η^3-Allyl)-{2,2′-bis[(4*S*)-(4-isopropyl-3,4-dihydrooxazol-2-yl)]diphenyl ether-*N,N*}palladium(II) Hexafluorophosphate, (*S,S*)-1F. Starting materials were 65 mg (0.14 mmol) of [Pd(η^3-C_3H_5)(μ-Br)]$_2$, 112 mg (0.28 mmol) of (*S, S*)-**F**, and 35 mg (0.21 mmol) of NH_4PF_6. Yield: 140 mg (73%). IR (KBr): 1650 (st, C═N), 849 (st, P−F) cm^{-1}. Anal. Calcd for $C_{27}H_{33}F_6N_2O_3PPd$: C, 47.34; H, 4.82; N, 4.09. Found: C, 47.57; H, 5.02; N, 4.05. MS (FAB positive): *m/z* 539 ([M − PF_6]$^+$).

(η^3-Allyl)-{2,2′-bis[(4*S*)-(4-isopropyl-3,4-dihydrooxazol-2-yl)]-4,6-dibenzofuran-*N,N*}palladium(II) Hexafluorophosphate, (*S,S*)-1G. Starting materials were 67 mg (0.15 mmol) of [Pd(η^3-C_3H_5)(μ-Br)]$_2$, 114 mg (0.29 mmol) of (*S, S*)-**G**, and 36 mg (0.22 mmol) of NH_4PF_6. Yield: 199 mg (99%). IR (KBr): 1653 (st, C═N), 843 (st, P−F) cm^{-1}. Anal. Calcd for $C_{27}H_{31}F_6N_2O_3PPd$: C, 47.47; H, 4.54; N, 4.70. Found: C, 47.63; H, 4.02; N, 4.82. Mp: 165 °C. MS (FAB positive): *m/z* 537 ([M − PF_6]$^+$).

(η^3-1,3-Diphenylallyl)-{2,2′-bis[(4*R*)-(4-ethyl-3,4-dihydrooxazol-2-yl)]-1,1′-biphenyl-*N,N*}palladium(II) Hexafluorophosphate, (*R,X,R*)-2A. Starting materials were 116 mg (0.17 mmols) of [Pd(η^3-1,3-Ph_2-C_3H_3)(μ-Cl)]$_2$, 121 mg (0.35 mmol) of (*R,X,R*)-**A**, and 85 mg of NH_4PF_6 (0.52 mmol) of NH_4PF_6. Yield: 0.228 g (89%). IR (KBr): 1626 (st, C═N), 842 (st, P−F) cm^{-1}. Anal. Calcd for $C_{37}H_{37}F_6N_2O_2PPd$: C, 56.03; H, 5.03; N, 3.53. Found: C, 55.97; H, 5.54; N, 3.72. Mp: 187 °C. MS (FAB positive): *m/z* 647 ([M − PF_6]$^+$).

(η^3-1,3-Diphenylallyl)-{2,2′-bis[(4*S*)-(4-isopropyl-3,4-dihydrooxazol-2-yl)]-1,1′-biphenyl-*N,N*}palladium(II) Hexafluorophosphate, (*S,X,S*)-2B. Starting materials were 70 mg (0.10 mmol) of [Pd(η^3-1,3-Ph_2-C_3H_3)(μ-Cl)]$_2$, 79 mg (0.21 mmol) of (*S,X,S*)-**B**, and 51.3 mg (0.31 mmol) of NH_4PF_6. Yield: 146 mg (85%). IR (KBr): 1637 (st, C═N), 841 (st, P−F) cm^{-1}. Anal. Calcd for $C_{39}H_{41}F_6N_2O_2PPd$: C, 56.99; H, 4.99; N, 3.41. Found: C, 56.75; H, 4.95; N, 3.41. Mp: 198 °C. MS (FAB positive): *m/z* 675 ([M − PF_6]$^+$).

Bis(η^3-1,3-diphenylallyl)-μ-{2,2′-bis{(4*S*)-[4-(2-methylthio)propyl-3,3-diphenyl-3,4-dihydrooxazol-2-yl]}-1,1′-biphenyl-*N,S*}dipalladium(II) Bis(hexafluorophosphate), (*S,X,S*)-2C. Starting materials were 0.326 g (0.49 mmol) of [Pd(η^3-1,3-Ph_2-C_3H_3)(μ-Cl)]$_2$, 0.364 g (0.49 mmol) of (*S,X,S*)-**C**, and 0.239 g (1.46 mmol) of NH_4PF_6. Yield: 0.720 g (93%). IR (KBr): 1626 (st, C═N), 839 (st, P−F) cm^{-1}. Anal. Calcd for $C_{78}H_{70}F_{12}N_2O_2S_2P_2Pd_2{\cdot}2C_4H_{10}O$: C, 57.32; H, 4.28; N, 1.71; S, 3.91. Found: C, 58.00; H, 4.85; N, 1.74; S, 3.57. Mp: 153 °C. Molar conductivity (acetonitrile): 198 Ω^{-1} cm^2 mol^{-1}.

(η^3-1,3-Diphenylallyl)-{2,2′-bis{(4*S*)-[4-(2-ethylmethylsulfinil)-3,3-diphenyl-3,4-dihydrooxazol-2-yl]}-1,1′-biphenyl-*N,N*}palladium(II) Hexafluorophosphate, (*S,X,S*)-2D. Starting materials were 56 mg (0.084 mmol) of [Pd(η^3-1,3-Ph_2-C_3H_3)(μ-Cl)]$_2$, 130 mg (0.17 mmol) of (*S,X,S*)-**D**, and 41 mg (0.25 mmol) of NH_4PF_6. Yield: 203 mg (99%). IR (KBr): 1656 (st, C═N), 1036 (st, S═O), 840 (st, P−F) cm^{-1}. Anal. Calcd for $C_{63}H_{57}F_6N_2O_4S_2PPd$: C, 61.94; H, 4.67; N, 2.29; S, 5.24. Found: C, 61.35; H, 5.25; N, 2.87; S, 5.21. Mp: 152 °C. Molar conductivity (acetonitrile): 159 Ω^{-1} cm^2 mol^{-1}. MS (FAB positive): *m/z* 1075 ([M − PF_6]$^+$).

Crystallography. A prism yellow crystal of (*S,S$_a$,S*)-**1C** and block colorless crystal of (*S,S*)-**1F** were selected and mounted on a Bruker SMART CCD area detector single-crystal diffractometer with graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å) operating at room temperature. Crystal data are summarized in Table 6.

(*S,S$_a$,S*)-1C. Preliminary unit cell constants were calculated with a set of 45 narrow frame (0.3° in ω) scans. A total of 1271 frames of data were collected using the phi-omega scan method. A total of 10 565 reflections were assumed as observed applying the condition $I \geq 2\sigma(I)$. The first 50 frames were recollected at the end of data collection to monitor for decay. The crystal used for the diffraction study showed no decomposition during data collection. Absorption corrections were applied using the SADABS program[19] (maximum and minimum transmission coefficients 1.000 and 0.729). The structure was solved by direct methods using the SHELXS-97 computer program[20] for crystal structure determination and refined by full-matrix least-squares method on F^2, with the SHELXL-97 computer program,[21] to give R1 = 0.0633, wR2 = 0.1337 for $I > 2\sigma(I)$ and R1 = 0.0860, wR2 = 0.1444 for all data [R1 = $\sum||F_o| - |F_c||/\sum|F_o|$ and wR2 = $\{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$]. A total of 13 663 reflections were included in the refinement, and no restraints were applied to the 687 parameters. Hydrogen atoms were included in calculated positions and refined in riding mode. The weighting scheme employed was $w = [\sigma^2(F_o^2 + (0.0535P)^2 + 6.0245P]$ and $P = (|F_o|^2 + 2|F_c|^2)/3$.

(*S,S*)-1F. Preliminary unit cell constants were calculated with a set of 45 narrow frame (0.3° in ω) scans. A total of 1271 frames of data were collected using the phi-omega scan method. A total of 5838 reflections were assumed as observed applying the condition $I \geq 2\sigma(I)$. The first 50 frames were recollected at the end of data collection to monitor for decay. The crystal used for the diffraction study showed no decomposition during data collection. Absorption corrections were applied using the SADABS program[19] (maximum and minimum transmission coefficients 1.000 and 0.585). The structure was

(19) Sheldrick, G. M. *SADABS* program, a program for empirical absorption correction of area detector data; University of Göttingen: Germany, 1996.

(20) Sheldrick, G. M. *SHELXS-97*, a computer program for crystal structure determination; University of Göttingen: Germany, 1997.

(21) Sheldrick, G. M. *SHELXL-97*, a computer program for crystal structure refinement; University of Göttingen: Germany, 1997.

Table 6. Crystal Data for Complexes (*S*,*S*$_a$,*S*)-1C and (*S*,*S*)-1F

	(*S*,*S*$_a$,*S*)-**1C**	(*S*,*S*)-**1F**
empirical formula	$C_{54}H_{53}F_{12}N_2O_2P_2S_2Pd_2$	$C_{27}H_{33}F_6N_2O_3PPd\cdot CHCl_3$
fw	1328.84	804.29
cryst dimens, mm	0.40 × 0.30 × 0.30	0.40 × 0.30 × 0.30
temperature, K	298(2)	298(2)
cryst syst	orthorombic	orthorombic
space group	$P2_12_12_1$	$P2_12_12_1$
a, Å	10.8055(2)	8.4776(2)
b, Å	10.9429(2)	11.5467(3)
c, Å	47.0396(7)	39.9906(9)
α, deg	90	90
β, deg	90	90
γ, deg	90	90
V, Å^3	5562.13(17)	3523.06(15)
Z	4	4
density (calcd), g cm^{-3}	1.587	1.516
abs coeff, mm^{-1}	0.862	0.862
F(000)	2676	1624
θ range for data collection	0.87−28.32°	1.13−28.29°
no. of reflns collected	39 004	19 885
no. of ind reflns	13663 [R_{int} = 0.0467]	8748 [R_{int} = 0.0557]
final *R* indices [$I>2\sigma(I)$]	R1 = 0.0633, wR2 = 0.1337	R1 = 0.0674, wR2 = 0.1376
R indices (all data)	R1 = 0.0860, wR2 = 0.1444	R1 = 0.1138, wR2 = 0.1610
GOF on F^2	1.104	1.122
absolute struct param	−0.01(3)	0.01(5)
largest diff peak and hole, e Å^{-3}	0.631 and −0.630	0.681 and −0.878

solved by direct methods using the SHELXS-97 computer program[20] for crystal structure determination and refined by full-matrix least-squares method on F^2, with the SHELXL-97 computer program,[21] to give R1 = 0.0674, wR2 = 0.1376 for $I > 2\sigma(I)$ and R1 = 0.1138, wR2 = 0.1610 for all data [R1 = $\sum||F_o| - |F_c||/\sum|F_o|$ and wR2 = $\{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$]. A total of 8748 reflections were included in the refinement, and no restraints were applied to the 425 parameters. Hydrogen atoms were included in calculated positions and refined in the riding mode. The weighting scheme employed was $w = [\sigma^2(F_o^2 + (0.0675P)^2 + 1.2857P]$ and $P = (|F_o|^2 + 2|F_c|^2)/3$.

General Procedure for Palladium-Catalyzed Allylic Alkylation. The precursor (0.02 mmol of complex of type **1**) was dissolved in 2 cm^3 of CH_2Cl_2. *rac*-1,3-Diphenyl-2-propenyl acetate (252 mg, 1 mmol), dissolved in 2 cm^3 of CH_2Cl_2, was added, followed by dimethyl malonate (396 mg, 3 mmol), BSA (610 mg, 3 mmol), and a catalytic amount of KOAc. The mixture was stirred at room temperature until the substrate had been totally consumed (unless stated otherwise), monitored by TLC (eluent: hexane/ethyl acetate, 4/1). The solution was then diluted with diethyl ether, filtered over Celite, and washed successively with an aqueous solution of ammonium chloride (10%) and water (2 × 10 cm^3). The organic phase was dried over anhydrous Na_2SO_4 and filtered off, and the solvent removed under reduced pressure. The product was purified by column chromatography (SiO_2; ethyl acetate), followed by heating treatment at 130 °C under vacuum. The enantiomeric excesses were determined by HPLC on a Chiralcel OD column, using hexane/*i*PrOH, 99/1, as eluent, in a flow of 0.3 cm^3/min and a pressure of 10 bar.

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