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Bis(perfluoroalkyl) Phosphino-Oxazoline: A Modular, Stable, Strongly π-Accepting Ligand for Asymmetric Catalysis

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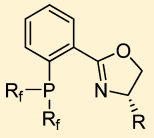
Supporting Information

ABSTRACT: A new class of stable, strongly π-accepting and modular bis-(perfluoroalkyl)-phosphine-oxazoline ligands (FOX) as CO mimics was prepared. It was demonstrated that these ligands, when coordinated to palladium catalysts, promote the asymmetric alkylation of monosubstituted allyl substrates with excellent regio- and enantioselectivity. Solid and solution structure analysis of the FOX-ligated Pd-allyl intermediate reveals that the combination of relative steric and strong *trans* influences presented by the $P(CF_3)_2$ moiety gave rise to the excellent selectivity.



- Chiral Ligands as CO mimics
- Strong π-acceptors
- Tunable Steric hinderances
- Air and moisture stablility
- Easy preparation

INTRODUCTION

Homogeneous asymmetric catalysis has grown enormously in recent years and has contributed significantly to the preparation of both chiral pharmaceuticals and bulk fine chemicals.[1] The design, synthesis and development of coordination chemistry of a few classes of chiral ligands,[2] such as BINAP[3] and its derivatives,[4] Josiphos,[5] and oxazoline ligands (BOX[6] and PHOX[7,8]) plays a critical role in the development of numerous asymmetric reactions and remains a field of intense research effort (Figure 1).[9] Typically, these ligands are good σ-donors, weak π-acceptors and often have a wide range of accessible steric and electronic properties for fine-tuning the reactivity and selectivity.[10] On the other hand, ligands that are moderate σ-donors and strong π-acceptors, such as CO, NO and PF_3, are much less frequently used in asymmetric reactions because these ligands cannot be modified. They are often used as ligands in metal complexes as starting materials and catalyst precursors.[11] We envisioned that if a family of sterically tunable new ligands that are electronically strong π-acceptors similar to CO could be created, it would be possible to develop new catalytic reactions that would find applications in organic synthesis and in the production of highly valuable pharmaceuticals and bulk chemicals.

Toward this end, inspired by the wide applications of the oxazoline ligands such as bisoxazolines (BOX), phosphine-oxazolines (PHOX)[7,13] and their derivatives,[8,14,15] we designed a new family of tunable bis(perfluoroalkyl) phosphino-oxazoline ligands (FOX). Perfluorinated alkyl phosphines $(R_f)_xPR_{(3-x)}$ have been known to be strongly π-accepting since 1960s.[12] It was anticipated that this strongly π-accepting phosphine would display significant ligand *trans* influence upon coordination to a transition metal center. The reduction of electron density at the transition metal center might destabilize its high oxidation states and make it more reactive. In addition, low electron density of the metal center enhances the Lewis acidic character of the catalyst, which can be advantageous for asymmetric catalysis.[15] Furthermore, the chirality on the oxazoline moiety required for asymmetric induction can be easily fine-tuned through modification of the substituents.

Herein, we report a facile three-step synthesis of bis-(perfluoroalkyll) phosphino- oxazoline ligands (FOX) and their applications in palladium-catalyzed asymmetric alkylation of monosubstituted allyl substrates with excellent regio- and enantioselectivity. A palladium(II) π-allyl intermediate was isolated and characterized by single crystal X-ray diffraction to explore the origins of high selectivity of the catalyst.

RESULTS AND DISCUSSION

Preparation of Bis(perfluoroalkyl) Phosphino-oxazoline Ligands. Our synthesis pathway toward ligands **3** and **6** is depicted in Scheme 1. Starting from commercially available 2-bromobenzoic acid, the oxazoline ring **2a**–**d** was formed by condensation with readily available chiral amino-alcohol and ring closure in the presence of TsCl and Et_3N. Lithium-bromide exchange of the resulting aryl bromide with *s*BuLi at −78 °C, followed by treatment with triphenylphosphite ($(PhO)_3P$),[16] gave the phosphite intermediates in high yields as determined by ^{31}P NMR spectroscopy, which were used without further purification. Treatment of the phosphite intermediates with Ruppert–Prakash reagent CF_3TMS or C_2F_5TMS in the presence of CsF provided the ligands **3a**–**h** in good to excellent 37–71% yields.[12i−l] Ferrocene-based ligands **6a**–**h** were prepared according to the analogous one-pot sequence in 30–51% yields. Ligands **6a**–**h** were obtained with high diastereoselectivity according to the ^{19}F and ^{31}P NMR spectroscopies of the crude reaction mixtures. The ligands were purified by flash column chromatography on silica gel.

The structures of ligands **3** and **6** were characterized by NMR and MS spectroscopy. Structure of ligand **6c** was further confirmed by single crystal X-ray diffraction (Figure 2).

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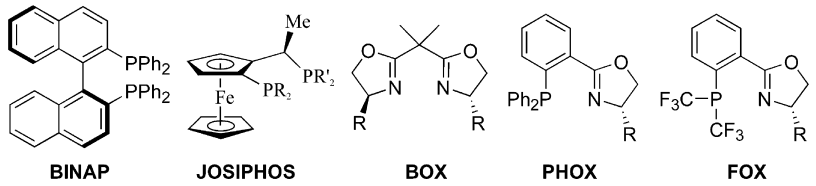
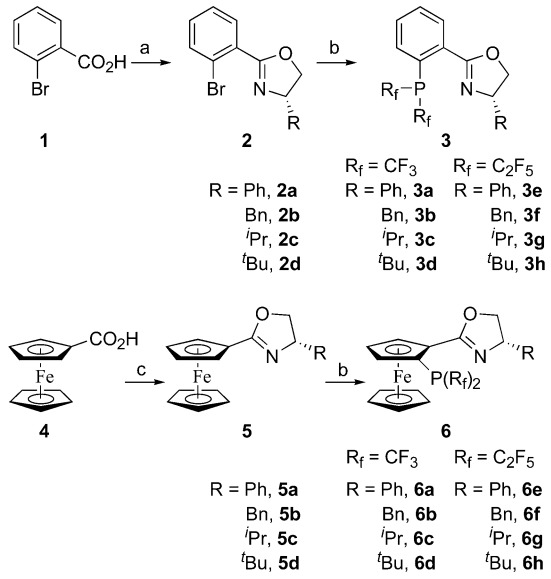


Figure 1. Chiral ligands for asymmetric catalysis.

Scheme 1. Synthesis of Bis(perfluoroalkyl)phosphino Oxazoline Ligands[a]



[a]Reagents and conditions: (a) (i) Amino alcohol, EDCI, HOBT, room temperature, 6 h; (ii) TsCl, Et_3N, room temperature, 12 h. (b) (i) *s*-BuLi, TMEDA, Et_2O, −78 °C for ligand **3** and *n*-BuLi, TMEDA, Et_2O, −78 °C for ligand **6**; (ii) $P(OPh)_3$, −100 °C to room temperature, 1 h; (iii) CF_3TMS/CsF, room temperature, overnight or C_2F_5TMS/CsF, 40 °C, overnight. (c) (i) $(COCl)_2$, room temperature, 2 h; amino-alcohol; then Et_3N, CH_2Cl_2, room temperature, 8 h; (ii) TsCl, Et_3N, room temperature, 12 h.

Notably, ligands **3** and **6** are air and moisture stable either as liquid or solid, or in deuterated chloroform for one week, as determined by ^{19}F NMR spectroscopy.

Comparison of the π-Accepting Properties of FOX Ligands with Phosphite and Phosphine. To compare the π-accepting properties of FOX ligands with phosphite and phenyl substituted phosphines, three *cis*-($\mathbf{L_2}$)molybdenum tetracarbonyl complexes were prepared, and IR spectra of these complexes were studied to determine ν(CO). Direct thermal substitution of ligand **3d**, phosphite oxazoline or PHOX with $Mo(CO)_6$ in refluxing toluene gave the tetracarbonyls **7**–**9** as pure crystalline solids in excellent yields. Complexes **7**–**9** are highly soluble in benzene and have been fully characterized by NMR, IR and element analyses. The analytical data are consistent with monomeric octahedral complexes. Structure of complex **8** was further confirmed by single crystal X-ray diffraction (Figure 3).

A comparison of ν(CO) from IR spectra of complexes **7**–**9** and several other known *cis*-$L_2Mo(CO)_4$ phosphine system is given in Table 1. As anticipated, the ν(CO) stretch frequency in complex **7** is much higher than those in complex **8** with posphite moiety and complex **9** or [(DPPE)$Mo(CO)_4$] with phosphine moiety, which indicates that ligands **3** are much

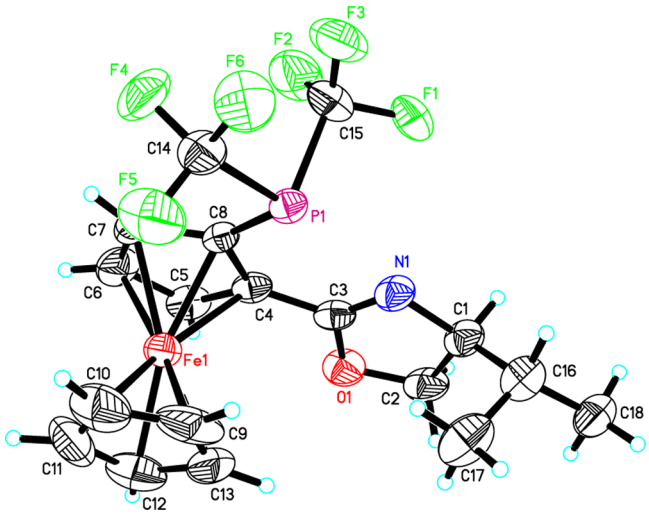


Figure 2. The ORTEP view of **6c**.

stronger π-acceptors than aryl-substituted phosphite and phosphine ligands. Interestingly, the ν(CO) stretch frequency in complex **7** is much lower than those in [$((CF_3)_2PCH_2CH_2P(CF_3)_2)Mo(CO)_4$] and [$(CF_3$-DIOP)$Mo(CO)_4$)], indicating that the synergistic effect of two perfluoroalkylphosphino groups on the ν(CO) of the Mo-complexes.

Palladium-Catalyzed Asymmetric Allylic Alkylation with FOX 3 or 6 as the Ligand. As a test ground for the effectiveness of our ligand design, we studied palladium-catalyzed asymmetric allylic alkylation of monosubstituted allyl substrates in the presence of ligand **3a**–**h** or **6a**–**h**. The palladium-catalyzed allylic alkylation reaction is one of the most thoroughly studied transition-metal-catalyzed reactions.[18] While excellent enantioselectivity for 1,3-disubstituted allyl substrates has been achieved, monosubstituted allyl substrates have been more challenging. Pioneering works by Hayashi, Pfaltz, Dai and Hou have shown that branched products were achieved only using catalysts with a few well-designed ligands.[19,20] These studies have shown that to achieve good regio- and enantioselectivity, a bidentate ligand with differentiated *trans* influences at the two coordination sites was of the utmost importance. In addition, a large group at the chiral ligand backbone is necessary to shield the less substituted terminal of the π-allylpalladium intermediate. As a result, the nucleophile attacks the more substituted position of the allylic intermediate that is *trans* to the stronger *trans*-directing coordination site to afford the branched product. In views of these previous observations, we reasoned that the strong π-accepting properties of FOX could provide even greater trans influence for the phosphorus coordination site and lead to high selectivity.

We initially examined the reaction of (*E*)-cinnamyl acetate with dimethyl malonate in the presence of 4.0 mmol % $Pd(dba)_2$ and 4.0 mol % of various bis(perfluoroalkyl)-

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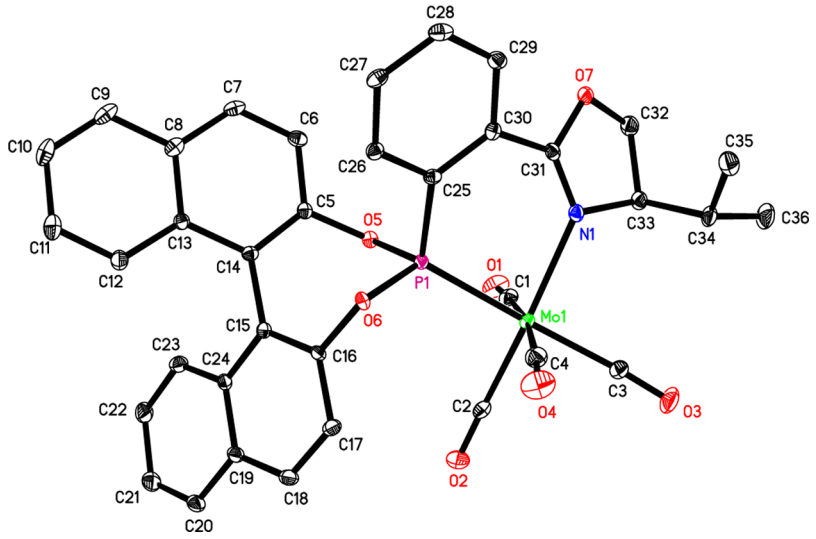
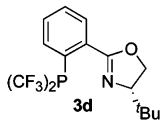
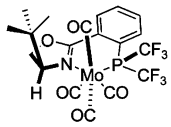
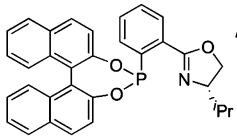
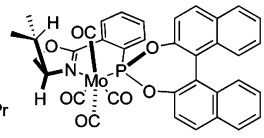
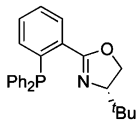
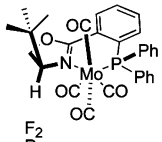
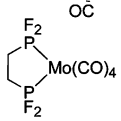
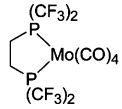
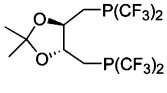
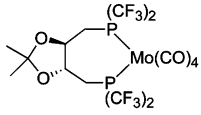
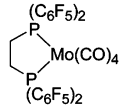
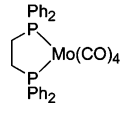


Figure 3. The ORTEP views of complex **8**.

Table 1. Comparison of ν(CO) Stretch Frequency in IR Spectra of *cis*-$L_2Mo(CO)_4$

Entry	Ligand	$L_2Mo(CO)_4$	ν_{CO} (cm^{-1})
1			**7** 2044
2			**8** 2027
3			**9** 2009
4			2087[17a]
5			2064[17b]
6			2073[17c]
7			2041[17d]
8			2020[17e]

phosphino oxazoline ligands using bis(trimethylsilyl)-acetamide (BSA) and 3.0 mol % LiOAc as the base. In general, sterically more hindered ligand gave higher regio- and enantioselectivity. For example, reactions catalyzed by the palladium complexes derived from ligand **3a–d** occurred to full conversion with 1/1–11.5/1 regioselectivity and 72–94% enantioselectivity (Table 2, entries 1–4). Similar trends were observed for the reactions in the presence of ligand **3e–h**, **6a–d** and **6e–h**. Reactions using ligand **3** gave similar enantioselectivity as those using **6**. However, the regioselectivity of the product was significantly higher when **3** was used as the ligand. For example, reaction of (*E*)-cinnamyl acetate with dimethyl malonate in the presence of 4.0 mmol % $Pd(dba)_2$ and 4.0 mol % of **3d** occurred to full conversion to give the product with 11.5/1 regioselectivity and 94% ee, while the same reaction using **6d** as the ligand gave the product with 4/1 regioselectivity and 93% ee (Table 2, entries 4 and 12). Reactions using bis-(pentafluoroethyl)phosphino-oxazoline derivatives as the ligand gave slightly higher enantioselectivity than those using bis(trifluoromethyl)phosphino-oxazoline derivatives as the ligand. However, the regioselectivity of the product using bis(pentafluoroethyl)phosphino-oxazoline derivatives as the ligand was slightly lower than those using bis(trifluoromethyl)-phosphino-oxazoline derivatives as the ligand (Table 2, entries 1–4 and 5–8). Thus, the best conditions were found to be using a combination of 4.0 mol % of $Pd(dba)_2$/**3d** as the catalyst (Table 2, entry 4). The absolute configuration of the product was assigned as (*S*) by comparison the measured optical rotations and HPLC retention times with the ones reported in literature. As a control, we also conducted an experiment with ^{t}Bu-PHOX as the ligand for the reaction of (*E*)-cinnamyl acetate with dimethyl malonate. Only the linear product was observed as determined by ^{1}H NMR spectroscopy of the crude product.

With the optimized reaction condition established, a series of monosubstituted allyl substrates were studied, and the results are summarized in Table 3. In general, reactions of both cinnamyl acetate or carbonate derivatives proceeded to full conversion within 8 h to provide the branched product in excellent regio- and enantioselectivity. For cinnamyl acetate or carbonate derivatives, we have determined that the regio- and enantioselectivity are moderately sensitive to electronic effects of the substrates. For example, reaction of 4-methoxy-substituted cinnamyl carboxylate gave the desired branched product in 92% ee and 19:1 branched:linear selectivity (Table 3, entry 7), while reaction of 4-chlorophenyl-substituted

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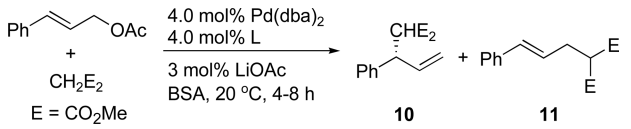
Table 2. Evaluation of the Effects of FOX Ligand in Palladium-Catalyzed Asymmetric Alkylation of Monosubstituted Allyl Substrate[a]



entry	ligand	time (h)	10:11[b]	ee (%)[c]
1	**3a**	8	1/1	72
2	**3b**	8	3.4/1	92
3	**3c**	8	5/1	88
4	**3d**	8	11.5/1	94
5	**3e**	8	0.58/1	88
6	**3f**	8	2.31/1	61
7	**3g**	8	2/1	60
8	**3h**	8	9/1	97
9	**6a**	4	0.64/1	77
10	**6b**	4	1/1	91
11	**6c**	4	1.4/1	87
12	**6d**	4	4/1	93
13	**6e**	4	1.4/1	72
14	**6f**	4	1.5/1	90
16	**6g**	4	2.5/1	86
16	**6h**	4	4.3/1	96

[a]Reagents and conditions: 4.0 mol % $Pd(dba)_2$, 4.0 mol % ligand, 0.5 mmol cinnamyl acetate, 1.5 mmol dimethyl malonate, 1.5 mol BSA, 3.0 mol %, 1,2-dichloroethane (2 mL), room temperature. [b]Determined by ^1H NMR spectroscopy of the crude. [c]Determined by HPLC.

substrate generated the product in 92% ee with slightly lower branched:linear selectivity of ~6:1 (Table 3, entry 11).

Reactions of sterically hindered 2-substituted cinnamyl acetates or carbonates occurred to give the branched product in slightly lower regio- and enantioselectivity than those *meta*- or *para*-substituted substrates. For example, reaction of 2-methoxy-substituted cinnamyl carboxylate gave the desired branched product in 64% ee and 13.3:1 branched:linear selectivity when **3d** was used as the ligand (Table 3, entry 18). The enantioselectivity was improved to 88% ee when **3h** was used as the ligand, but the regioselectivity was lowered slightly to 10/1 (Table 3, entry 19). In most cases, substrates with electron-withdrawing group on the phenyl ring generated the products with lower b/l ratios than those with electron-donating group. The one exception is the reaction of 3-methoxyl-substituted cinnamyl carbonate that occurred with high regio- and enantioselectivity (Table 3, entry 20). Since there is high regio- and enantioselectivity for the reaction of 3-(1′-naphthyl)-1-propen-3-yl acetate or carbonate, one would expect that sterically hindered substrates might give similar selectivity. In contrast, when 2-chloro- or 2-methoxy-substituted cinnamyl carbonate was used, much lower enantioselectivity was observed.

Typically, reactions using bis(pentafluoroethyl)phosphino-oxazoline derivatives as the ligand gave slightly higher enantioselectivity than those using bis(trifluoromethyl)-phosphino-oxazoline derivatives as the ligand. However, the regioselectivity of the product using bis(pentafluoroethyl)-phosphino-oxazoline derivatives as the ligand was slightly lower than those using bis(trifluoromethyl)phosphino-oxazoline derivatives as the ligand (Table 3, entries 1−2 or 3−4).

Importantly, Pd/FOX is an efficient catalyst not only for the asymmetric alkylation of cinnamyl substrates but also for branched substrates **13**. Good regio- and enantioselectivity were obtained with phenyl or 1-napththyl substrates (Table 3, entries 19−22). Few high regio- and enantioselective palladium-catalyzed allylic subsitutions of branched monosubstituted substrates have been reported. The current catalyst based on perfluoroalkyl phosphine ligand shows an advantage over the conventional phosphine ligands.

Reaction of 2-buten-3-yl acetate with dimethyl malonate under the optimized conditions occurred smoothly to give the linear product as the major product.

Comparison to Palladium Catalysts Containing Other Ligands. In general, linear products are favored for the palladium-catalyzed allylic alkylation. Only a few ligands with strong π-accepting properties have been designed to achieve high regio- and enantioselectivity for the allylic alkylation of monosubstituted allyl substrates. We then compared the selectivity of our Pd/Fox system with other previous reported palladium catalyst for the alkylation of of 3-(1′-naphthyl)-1-propen-3-yl acetate or 3-phenyl-1-propen-3-yl acetate. Excellent regio- and enantioselectivities were observed in the reaction with 3-(1′-naphthyl)-1-propen-3-yl acetate when Pfaltz's ligand **3i**,[19d] **3j**,[19e] Hou and Dai's ligand **3k**[19c] and our FOX ligand **3d** was used. The regioselectivities were much lower for other less sterically hindered substrates such as 3-phenyl-1-propen-3-yl acetate when **3i** or **3k** was used as the ligand. In contrast, reaction of 3-phenyl-1-propen-3-yl acetate with malonate in the presence of catalyst generated from ligand **3k** and **3d** occurred with excellent regio- and enantioselectivity.

Isolation of the Palladium(II) π-Allyl Complex Ligated FOX Ligand 3d.[21] To probe the origin of the high selectivity, we prepared a palladium(II) π-allyl complex ligated by FOX ligand **3d**. Addition of **3d** to a solution of $[Pd(cinnamyl)Cl]_2$ in CH_2Cl_2 in the presence of $AgSbF_6$ formed $[Pd(\mathbf{3d})(\eta^3\text{-cinnamyl})]SbF_6$ **14**, which was characterized as a 2.7:1 ratio of *exo*/*endo* stereoisomers in solution at room temperature by NMR spectroscopic methods. The ratio of *exo*/*endo* stereoisomers was increased to 3.0/1 at 0 °C and 4.3/1 at −20 to −40 °C. Interestingly, single crystal X-ray diffraction analysis of **14** revealed that two *exo* isomers coexisted in the crystal, both of which have the phenyl group *trans* to $P(CF_3)_2$. In both isomers, Pd−C bonds *trans* to P (2.275 and 2.302 Å) are longer than those trans to N (2.129 and 2.112 Å), indicating stronger trans influence of the $P(CF_3)_2$ moiety (Figure 4).[22]

■ DISCUSSION

On the basis of the observation of solution and solid structure of the intermediate $[Pd(\mathbf{3d})(\eta^3\text{-cinnamyl})]SbF_6$ **14**, we proposed a working model to explain the high regio- and enantioselectivity of the Pd/Fox system for the allylic alkylation (Figure 5). Because of the steric effect of two trifluoromethyl groups, two diastereomeric π-allyl intermediates **exo-14** and **endo-14**, in which the less hindered terminal methylene group is positioned to the bis(trifluoromethyl)phosphino moiety, are formed when the substrate is oxidatively added to Pd(0)(**3d**) complex. The two isomers undergo fast isomerization that is much faster than the following nucleophilic substitution. Nucleophic attack of methyl malonate anion to **exo-14** leads to the (*S*)-isomer of the product, while attack to **endo-14** leads to the (*R*)-isomer. In addition, nucleophic attack of methyl malonate anion to **exo-14** is much fast than those to **endo-14**. The preferred product arises by reaction at the allylic C trans to

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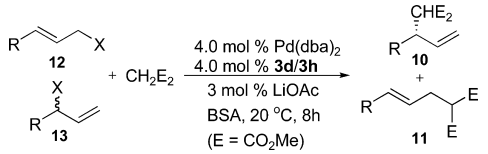
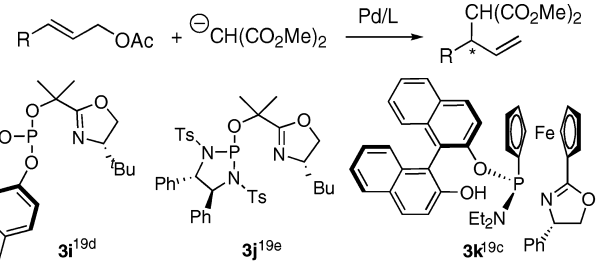
Table 3. Enantioselective Palladium-Catalyzed Asymmetric Alkylation of Monosubstituted Allyl Substrates[a]



entry	12 or 13	R	X	ligand	10/11[b]	ee (%)[c]	yield (%)[d]
1	**12a**	Ph	OAc	**3d**	92/8	93	97
2	**12a**	Ph	OAc	**3h**	90/10	97	98
3	**12b**	Ph	OCO_2Me	**3d**	92/8	92	96
4	**12b**	Ph	OCO_2Me	**3h**	86/14	95	98
5	**12c**	1-naphthyl	OAc	**3d**	96/4	94	95
6	**12d**	1-naphthyl	OCO_2Me	**3h**	91/9	96	98
7	**12e**	4-$MeOC_6H_4$	OAc	**3d**	95/5	92	96
8	**12f**	4-$MeOC_6H_4$	OCO_2Me	**3h**	93/7	94	96
9	**12g**	4-MeC_6H_4	OCO_2Me	**3d**	94/6	93	96
10	**12g**	4-MeC_6H_4	OCO_2Me	**3h**	92/8	95	98
11	**12h**	4-ClC_6H_4	OCO_2Me	**3d**	86/14	92	95
12	**12h**	4-ClC_6H_4	OCO_2Me	**3h**	82/18	96	97
13	**12i**	2-furan	OCO_2Me	**3d**	88/12	81	95
14	**12i**	2-furan	OCO_2Me	**3h**	88/12	87	95
15	**12j**	3-ClC_6H_4	OCO_2Me	**3d**	80/20	99.5	96
16	**12j**	3-ClC_6H_4	OCO_2Me	**3h**	83/17	99.6	97
17	**12k**	2-ClC_6H_4	OAc	**3d**	86/14	87	95
18	**12l**	2-$MeOC_6H_4$	OCO_2Me	**3d**	93/7	64	96
19	**12l**	2-$MeOC_6H_4$	OCO_2Me	**3h**	91/9	88	95
20	**12m**	3-$MeOC_6H_4$	OCO_2Me	**3d**	94/6	92	95
21	**13a**	Ph	OCO_2Me	**3h**	93/7	83	96
22	**13b**	Ph	OAc	**3d**	95/5	88	96
23	**13c**	1-naphthyl	OAc	**3d**	89/11	85	97

[a]Reagents and conditions: 4.0 mol % $Pd(dba)_2$, 4.0 mol % ligand, 0.5 mmol monosubstituted allyl substrate, 1.5 mmol dimethyl malonate, 1.5 mol BSA, 3.0 mol % LiOAc in 1,2-dichloroethane (2 mL), room temperature. [b]Determined by ^1H NMR spectroscopy of the crude. [c]Determined by HPLC. [d]Yields are for mixture of branch/linear isomers.

Table 4. Comparison of Regio- And Enantioselectivity of Pd/Fox System with Other Palladium Catalysts



	3i[19d]	**3j**[19e]	**3k**[19c]	**3d**
R = 1-naphthyl	87% B/L = 95/5, 94%ee	100% B/L = 98/2, 98%ee	97% (-43 °C) B/L = 99/1, 97% ee	95% B/L = 96/4, 94%ee
R = Ph	86% B/L = 76/24, 90% ee	100% B/L = 84/16, 94% ee	98% B/L = 95/5, 95% ee	97% B/L = 92/8, 93% ee

P of the *exo* or *endo* isomer because of the well-known *trans* influence of the ligand.

In the case of the branched substrates, both *syn* and *anti* η^3 π-allyl palladium intermediates are generated when the branched substrate is oxidatively added to Pd(0), and nucleophilic attack can take place either at the terminal or the internal position of the allyl fragment to give the linear (*E* or *Z*) or the branched product, respectively. The less stable *anti* intermediate generally undergoes isomerization to the more stable *syn* intermediate, and evantually an equilibrium is established. If the nucleophilic attack of the π-allyl palladium intermediates is slower than the isomerization, high regio- and enantioselectivity can be achieved. The high regio- and enantioselectivity in Pd/FOX system indicated the fast *syn*/*anti* equilibrium was established before the nucleophilic attack of the π-allyl intermediate.

■ CONCLUSION

In conclusion, we have introduced a new class of stable, strongly π-accepting and modular bis(perfluoroalkyl)-phosphine-oxazoline ligands (FOX) for asymmetric catalysis. We also showed that palladium complexes with these novel ligands effectively catalyzed the asymmetric alkylation of monosubstituted allyl substrates in good regioselectivity and excellent enantioselectivity. Crystal structure of palladium intermediate

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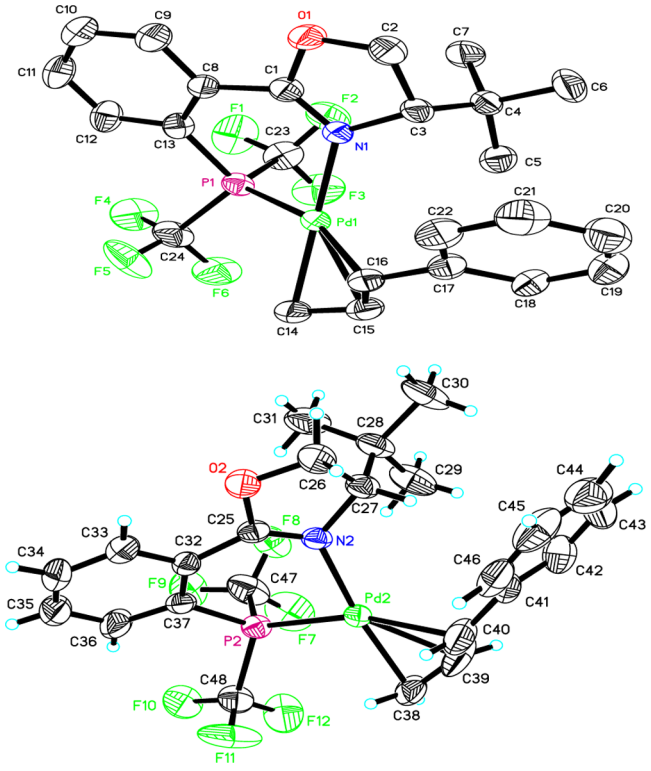

Figure 4. Crystal structure of the complex [Pd(**3d**)(cinnamyl)]SbF_6 **14**. Hydrogen atoms are omitted for clarity. Selected bond length [Å] and angles [°]: Pd1–C14 2.129 (5), Pd1–C15 2.180 (5), Pd1–C16 2.275 (5), C14–C15 1.389 (8), C15–C16 1.389 (9), Pd2–C38 2.112 (7), Pd2–C39 2.134 (7), Pd2–C40 2.302 (8), C38–C39 1.381 (12), C39–C40 1.273 (11); N1–Pd1–P1 87.65 (11), N2–Pd2–P2 87.88 (13), C14–C15–C16 119.7 (6), C34–C35–C36 120.7 (7).

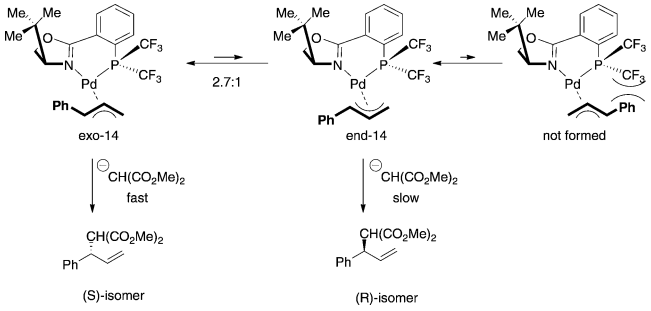

Figure 5. Working model for high selectivity in Pd-catalyzed allylic alkylation.

[Pd(**3d**)(cinnamyl)]SbF_6 reveals that the combination of relative steric and strong *trans* influence presented by $P(CF_3)_2$ gives rise to the excellent selectivity. The easy preparation, stability toward air and moisture and strong π-accepting properties of FOX ligands are especially appealing. Expanding the scope of the ligands for a variety of reactions is under investigation.

EXPERIMENTAL SECTION

General Information. All reactions were performed under Ar atmosphere using oven-dried glassware. Solvents were distilled under Ar atomosphere before use. Diethyl ether and dioxane were distilled from sodium benzophenone ketal. 1,2-Dichloroethane and dichloromethane were distilled from calcium hydride. Commercially available reagents were used as received without further purification. ^{1}H, ^{13}C, ^{19}F, ^{31}P NMR spectra were recorded on 300 (or 400), 100.5, 376, 121 (or 162) MHz spectrometer. ^{1}H NMR and ^{13}C NMR chemical shifts were determined relative to internal standard TMS at δ 0.0, and ^{19}F NMR chemical shifts were determined relative to $CFCl_3$ as internal standard. ^{31}P NMR spectra were referenced to an external 85% H_3PO_4 signal (0.0 ppm). All reactions were monitored by TLC, ^{19}F NMR or ^{31}P NMR spectroscopy. Flash column chromatograph was performed on silica gel (300–400 mesh) unless otherwise stated.

General Procedure for the Synthesis of Ligands 3 and 6. *Method A.* A solution of *s*-BuLi in cyclohexane (1.5 M, 11.3 mL, 16.9 mmol) was added to a vigorously stirred suspension of the corresponding aryl oxazoline (14.0 mmol) in anhydrous diethyl ether (25 mL) at −78 °C under argon. The reaction mixture was stirred at −78 °C for 15 min, and TMEDA (2.2 mL, 17 mmol) was added. The mixture was cooled to −100 °C in a diethyl ether/dry ice/liquid nitrogen bath for 15 min before $P(OPh)_3$ (3.8 mL in 5 mL anhydrous diethyl ether, 17 mmol) was added slowly over 5 min. The reaction mixture was allowed to warm to room temperature over 2 h. The reaction was monitored by ^{31}P NMR spectroscopy until there was no change in the peak corresponding to $P(OPh)_3$.[22] TMSCl (30 mmol) was added, and the mixture was stirred for 2 h at room temperature. The mixture was filtrated under argon, and the solvent was evaporated under reduced pressure. Dioxane (40 mL) was added, followed by the addition of CsF (4.5 g, 29 mmol) and $TMSCF_3$ (4.5 mL, 29.0 mmol).[12i] If the starting material was not completely converted to the corresponding bis(trifluoromethyl)phosphine ligand after 8 h as monitored by ^{31}P NMR spectroscopy, $TMSCF_3$ (6.3 mL, 51 mmol) was added in one portion. The reaction was stirred at room temperature and monitored by ^{19}F and ^{31}P NMR spectroscopy. The solvent was evaporated in vacuo, and the residue was purified by column chromatography (petroleum ether/CH_2Cl_2 = 5/1) to give the desired ligand.

Method B. TMEDA (1.7 mL, 13 mmol) and a solution of *n*-BuLi in hexane (5.2 mL, 2.5 M, 13 mmol) was added to a vigorously stirred suspension of the corresponding chiral oxazolinylferrocene (10 mmol) in anhydrous diethyl ether (25 mL) at −78 °C under argon. The reaction mixture was stirred at −78 °C for 30 min and at 0 °C for 2 h. The mixture was cooled to −100 °C in a diethyl ether/dry ice/liquid nitrogen bath for 15 min before $P(OPh)_3$ (3.84 mL in 5 mL anhydrous diethyl ether, 13 mmol) was added slowly over 5 min and then warmed to room temperature. The reaction mixture was stirred at room temperature for 2 h until there was no change in the peak corresponding to $P(OPh)_3$ as monitored by ^{31}P NMR spectroscopy.[22] The solvent was evaporated in vacuo, and diether ether (50 mL) was added followed by addition of CsF (3.4 g, 22 mmol) and $TMSCF_3$ (3.4 mL, 22 mmol). If the starting material was not completely converted to the corresponding bis(trifluoromethyl)phosphine ligand after 8 h as monitored by ^{31}P NMR spectroscopy, $TMSCF_3$ (4.3 mL, 28 mmol) was added in one portion.[12i] The reaction was stirred at room temperature and monitored by ^{19}F and ^{31}P NMR spectroscopy. The solvent was evaporated in vacuo, and the residue was purified by column chromatography (petroleum ether/CH_2Cl_2 = 5/1) to give the desired ligand.

(S)-2-(2-(Bis(trifluoromethyl)phosphino)phenyl)-4-phenyl-4,5-dihydrooxazole ***3a***. The product was prepared according to the method A as a colorless liquid in 61% yield (3.4 g): $[\alpha]_D^{30.4}$ = −68.4 (*c* 0.9895, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.26 (t, *J* = 8.8 Hz, 1 H), 4.83 (dd, *J* = 10.4, 8.4 Hz, 1 H), 5.48 (t, *J* = 9.6 Hz, 1 H), 7.25–7.37 (m, 5 H), 7.58–7.63 (m, 2 H), 7.97–8.02 (m, 2 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 70.3, 75.6, 126.6, 127.8, 128.8, 129.7, 129.8, 131.5, 131.6, 133.1 (d, *J* = 25.5 Hz), 134.0, 141.3, 163.6 (d, *J* = 2.9 Hz) ppm; ^{31}P NMR (81 MHz) δ −3.91 (m) ppm; ^{19}F NMR (376 MHz) δ −52.0 (dq, *J* = 75.6, 47.8, 7.5 Hz, 6 F) ppm; MS (ESI) *m*/*z* (%) 392.1 [M + H]$^+$, 391.1 [M]$^+$; HRMS (MALDI-FT) *m*/*z* [M + H]$^+$ Calcd for $C_{17}H_{13}NOF_6P$ 392.0634, found 392.0637; IR (KBr) ν = 3066, 3032, 2971, 2905, 1652, 1175, 1125 cm^{-1}.

(S)-4-Benzyl-2-(2-(bis(trifluoromethyl)phosphino)phenyl)-4,5-dihydrooxazole ***3b***. The product was prepared according to the method A as a colorless liquid in 57% yield (3.2 g): $[\alpha]_D^{28.6}$ = +2.6 (*c* 0.9450, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.76 (dd, *J* = 14.0, 8.4 Hz, 1

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H, CH_2), 3.22 (dd, J = 14.0, 5.6 Hz, 1 H, CH_2), 4.16 (t, J = 8.2 Hz, 1 H), 4.38 (t, J = 9.0 Hz, 1 H), 5.48 (m, 1 H), 7.30−7.33 (m, 3 H), 7.36−7.40 (m, 2 H), 7.60−7.65 (m, 2 H), 7.96−7.99 (m, 1 H), 8.05−8.08 (m, 1 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 41.4, 68.1, 72.9, 126.7, 128.6, 129.3, 129.35, 129.4, 131.4, 131.5, 133.1 (d, J = 25.5 Hz), 133.9, 137.6, 162.8 (d, J = 3.0 Hz) ppm; ^{31}P{^{1}H} NMR (81 MHz) δ −5.28 (sept, J = 69 Hz) ppm; ^{19}F{^{1}H} NMR (376 MHz) δ −52.0 (app d, J = 68.9 Hz, 6 F) ppm; MS (ESI) m/z (%) 406.4 [M + H]$^+$, 405.1 [M]$^+$; HRMS (MALDI-FT) m/z [M + H]$^+$ Calcd for $C_{18}H_{15}NOF_6P$ 406.0790, found 406.0799; IR (KBr) ν = 3065, 3029, 2927, 2855, 1655, 1177, 1125 cm^{-1}.

(S)-2-(2-(Bis(trifluoromethyl)phosphino)phenyl)-4-isopropyl-4,5-dihydrooxazole ***3c***. The product was prepared according to the method A as a colorless liquid in 65% yield (3.2 g): $[\alpha]_D^{29.3}$ = −5.0 (c 1.2920, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.97 (dd, J = 28.0, 6.4 Hz, 6 H), 1.83 (m, 1 H), 4.18 (m, 2 H), 4.48 (m, 1 H), 7.57−7.64 (m, 2 H), 7.94−7.97 (m, 1 H), 7.99−8.01 (m, 1 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.4, 32.6, 71.4, 73.0, 129.0 129.04, 131.1, 131.6, 132.6 (d, J = 23.0 Hz), 133.5, 162.0 (d, J = 3.7 Hz) ppm; ^{31}P NMR (81 MHz) δ −5.06−2.53 (m) ppm; ^{19}F NMR (376 MHz) δ −51.8 (dq, J = 64.1, 57.8, 8.2 Hz, 6 F) ppm; MS (ESI) m/z (%) 358.5 [M + H]$^+$, 357.1 [M]$^+$; HRMS (MALDI-FT) m/z [M + H]$^+$ Calcd for $C_{14}H_{15}NOF_6P$ 358.0790, found 358.0796; IR (KBr) ν = 2965, 2934, 2910, 2877, 1657, 1366, 1177, 1126 cm^{-1}.

(S)-2-(2-(Bis(trifluoromethyl)phosphino)phenyl)-4-tert-butyl-4,5-dihydrooxazole ***3d***. The product was prepared according to the method A as a colorless liquid in 71% yield (3.8 g): $[\alpha]_D^{30.3}$ = +6.8 (c 1.3260, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.98 (s, 9 H), 4.16 (t, J = 12.2 Hz, 1 H), 4.26 (t, J = 15.0 Hz, 1 H), 4.41 (t, J = 12.4 Hz, 1 H), 7.56−7.63 (m, 2 H), 7.92−7.80 (m, 2 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.8, 33.8, 69.8, 76.8, 129.2 129.3, 131.2, 131.3, 132.8 (d, J = 23.5 Hz), 133.7, 162.1 (d, J = 3.8 Hz) ppm; ^{31}P{^{1}H} NMR (81 MHz) δ −2.81 (m) ppm; ^{19}F{^{1}H} NMR (376 MHz) δ −52.0 (dq, J = 75.8, 61.8, 7.5 Hz, 6 F) ppm; MS (ESI) m/z (%) 372.4 [M + H]$^+$, 371.1 [M]$^+$; HRMS (MALDI-FT) m/z [M + H]$^+$ Calcd for $C_{15}H_{17}NOF_6P$ 372.0947, found 372.0945; IR (KBr) ν = 2961, 2908, 2872, 1658, 1177, 1126 cm^{-1}.

(S)-2-(2-(Bis(pentafluoroethyl)phosphino)phenyl)-4-phenyl-4,5-dihydrooxazole ***3e***. The product was prepared according to the method A as a colorless liquid in 41% yield (2.8 g): $[\alpha]_D^{24.2}$ = 13.3 (c 0.3400, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.31 (t, J = 8.7 Hz, 1 H), 4.84 (t, J = 9.0 Hz, 1 H), 5.50 (t, J = 9.0 Hz, 1 H), 7.34−7.44 (m, 5 H), 7.62 (dt, J = 7.2, 19.2 Hz, 2 H), 8.01 (t, J = 6.6 Hz, 1 H), 8.17 (t, J = 7.5 Hz, 1 H) ppm; ^{13}C NMR (75.45 MHz, $CDCl_3$) δ 70.8, 75.3, 126.6, 127.7, 128.7, 130.2, 130.3, 130.7, 132.5, 135.8 (d, J = 33.3 Hz), 136.6, 141.6, 163.6 ppm; ^{31}P NMR (121.5 MHz) δ −7.7 to −9.6 (m) ppm; ^{19}F NMR (282.3 MHz) δ −110.1 (m, 4 F), −82.0 (m, 6 F) ppm; MS (ESI) m/z (%) 492.0 [M + H]$^+$, 491.1 [M]$^+$; HRMS (MALDI-FT) m/z [M + H]$^+$ Calcd for $C_{19}H_{13}NOF_{10}P$ 492.0570, found 492.0576.

(S)-4-Benzyl-2-(2-(bis(pentafluoroethyl)phosphino)phenyl)-4,5-dihydrooxazole ***3f***. The product was prepared according to the method A as a colorless liquid in 37% yield (2.6 g): $[\alpha]_D^{24.2}$ = +8.0 (c 0.3150, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.77 (dd, J = 13.6, 8.4 Hz, 1 H, CH_2), 3.20 (dd, J = 13.6, 5.6 Hz, 1 H, CH_2), 4.17 (t, J = 7.2 Hz, 1 H), 4.38 (t, J = 8.4 Hz, 1 H), 4.64−4.72 (m, 1 H), 7.22−7.33 (m, 5 H), 7.54 (dt, J = 22.8, 7.6 Hz, 2 H), 7. 86 (t, J = 5.6 Hz, 1 H), 8.09 (d, J = 7.6 Hz, 1 H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 41.4, 68.6, 72.4, 126.6, 128.5, 129.3, 129.9, 130.0, 130.6, 132.4, 135.7 (d, J = 32.4 Hz), 136.5, 137.5, 162.6 ppm; ^{31}P{^{1}H} NMR (161.9 MHz) δ −8.8 to −10.5 (m) ppm; ^{19}F{^{1}H} NMR (376 MHz) δ −110 (m, 4 F), −81.5 (m, 6 F) ppm; MS (ESI) m/z (%) 506.0 [M + H]$^+$, 505.1 [M]$^+$; HRMS (MALDI-FT) m/z [M + H]$^+$ Calcd for $C_{20}H_{15}NOF_{10}P$ 506.0726, found 506.0733.

(S)-2-(2-(Bis(pentafluoroethyl)phosphino)phenyl)-4-isopropyl-4,5-dihydrooxazole ***3g***. The product was prepared according to the method A as a colorless liquid in 45% yield (2.9 g): $[\alpha]_D^{28.2}$ = −16.3 (c 0.3650, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.83 (dd, J = 20.8, 6.8 Hz, 6 H), 1.70 (m, 1 H), 4.02 (m, 2 H), 4.28 (m, 1 H), 7.40 (dt, J = 25.6, 7.6 Hz, 2 H), 7.75 (t, J = 5.6 Hz, 1 H), 7.95 (t, J = 7.2 Hz, 1 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.2 (d, J = 1.1 Hz), 18.3 (d, J = 1.9 Hz), 32.7, 70.8, 73.5, 129.9 130.0, 130.3, 132.3, 136.0 (d, J = 33.2 Hz), 136.5, 161.9 ppm; ^{31}P NMR (162 MHz) δ −9.2 to −10.9 (m) ppm; ^{19}F NMR (376 MHz) δ −110 (m, 4 F), −81.6 (m, 6 F) ppm; MS (ESI) m/z (%) 458.0 [M + H]$^+$, 457.1 [M]$^+$; HRMS (MALDI-FT) m/z [M + H]$^+$ Calcd for $C_{16}H_{15}NOF_{10}P$ 458.0726, found 458.0712.

(S)-2-(2-(Bis(pentafluoroethyl)phosphino)phenyl)-4-tert-butyl-4,5-dihydrooxazole ***3h***. The product was prepared according to the method A as a colorless liquid in 47% yield (3.1 g): $[\alpha]_D^{22.8}$ = −19.6 (c 0.3300, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.95 (s, 9 H), 4.11 (t, J = 8.0 Hz, 1 H), 4.22 (t, J = 8.4 Hz, 1 H), 4.34 (t, J = 8.8 Hz, 1 H), 7.52 (dt, J = 27.2, 7.6 Hz, 2 H), 7.86 (t, J = 6.4 Hz, 1 H), 8.05 (d, J = 8.0 Hz, 1 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.8(d, J = 1.5 Hz), 34.1, 69.3, 77.4, 130.0, 130.1, 130.3, 132.4, 136.1 (d, J = 34.3 Hz), 136.7, 161.8 ppm; ^{31}P{^{1}H} NMR (162 MHz) δ −8.8 to −10.5 (m); ^{19}F{^{1}H} NMR (376 MHz) δ −109.9 (m, 4 F), −81.6 (d, J = 13.9 Hz, 3 F), −81.5 (d, J = 20.7 Hz, 3 F) ppm; MS (ESI) m/z (%) 472.1 [M + H]$^+$, 471.1 [M]$^+$; HRMS (MALDI-FT) m/z [M + H]$^+$ Calcd for $C_{17}H_{17}NOF_{10}P$ 472.0883, found 472.0882.

[(S,Sp)-4,5-Dihydro-4-phenyl-2-oxazolyl]-(2-(bis(trifluoromethyl)-phosphino)-ferrocene ***6a***. The product was prepared according to the method B as an orange solid in 39% yield (1.9 g): mp 103−105 °C; $[\alpha]_D^{28.6}$ = −157.9 (c 0.2155, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 4.21 (t, J = 7.8 Hz, 1 H), 4.34 (s, 5 H), 4.71 (s, 2 H), 4.75 (d, J = 8.7 Hz, 1 H), 5.15 (s, 1 H), 5.30 (d, J = 10.8 Hz, 1 H), 7.30 (m, 3 H), 7.39 (m, 2 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 69.9, 71.5, 73.4, 73.9, 73.93, 74.1 (m), 75.0, 76.6 (d, J = 23.0 Hz), 126.4, 127.6, 128.8, 142.5, 165.4 (d, J = 3.8 Hz) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ −50.57 (dq, J = 74.9, 8.2 Hz, 3 F), −55.44 (dq, J = 60.6, 8.2 Hz, 3 F) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ −6.97 (m) ppm; MS (MALDI) m/z (%) 500.0 [M + H]$^+$, 499.0 [M]$^+$. Anal. Calc. for $C_{21}H_{16}F_6FeNOP$, Calcd: C, 50.53; H, 3.23; N, 2.81. Found: C, 50.59; H, 3.12; N, 2.72.

[(S,Sp)-4,5-Dihydro-4-(phenylmethyl)-2-oxazolyl]-(2-(bis-(trifluoromethyl)phosphino)-ferrocene ***6b***. The product was prepared according to the method B as an orange solid in 40% yield (2.05 g): mp 77−79 °C; $[\alpha]_D^{28.6}$ = −145.3 (c 0.1760, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 2.74 (d, J = 5.1 Hz, 1 H), 2.92 (d, J = 13.5 Hz, 1 H), 3.95 (t, J = 6.3 Hz, 1 H), 4.06 (s, 5 H), 4.12 (m, 1 H), 4.49 (d, J = 17.1 Hz, 2 H), 4.88 (s, 1 H), 7.18 (s, 5 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 40.1, 66.7, 70.3, 72.1, 72.6, 72.62, 72.9 (m), 75.9 (d, J = 15.2 Hz), 125.6, 127.5, 128.8, 136.5, 163.3 (d, J = 4.6 Hz) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ −50.43 (dd, J = 74.3, 8.5 Hz, 3 F), −55.07 (dd, J = 59.9, 7.1 Hz, 3 F) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ −6.83 (m) ppm; MS (MALDI) m/z (%) 514.0 [M + H]$^+$, 513.0 [M]$^+$. Anal. Calc. for $C_{22}H_{18}F_6FeNOP$, Calcd: C, 51.49; H, 3.54; N, 2.73. Found: C, 51.46; H, 3.41; N, 2.58.

[(S,Sp)-4,5-dihydro-4-(1-methylethyl)-2-oxazolyl]-(2-(bis-(trifluoromethyl)phosphino)-ferrocene ***6c***. The product was prepared according to the method B as an orange solid in 51% yield (2.4 g): mp 45−46 °C; $[\alpha]_D^{29.1}$ = −209.3 (c 0.1865, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 0.98 (d, J = 6.6 Hz, 3 H), 1.02 (d, J = 6.6 Hz, 3 H), 1.80 (m, 1 H), 4.02 (m, 1 H), 4.09 (m, 1 H), 4.29 (s, 5 H), 4.34 (m, 1 H), 4.64 (s, 2 H), 5.02 (s, 1 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 17.4, 31.6, 69.4, 70.3, 71.5, 71.9, 72.1 (d, J = 3.8 Hz), 72.6 (m), 76.6 (d, J = 25.0 Hz), 162.3 (d, J = 4.6 Hz) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ −50.46 (dq, J = 74.3, 8.2 Hz, 3 F), −54.85 (dq, J = 58.7, 8.2 Hz, 3 F) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ −10.98 (m) ppm; MS (MALDI) m/z (%) 466.0 [M + H]$^+$, 465.0 [M]$^+$. Anal. Calc. for $C_{18}H_{18}F_6FeNOP$, Calcd: C, 46.48; H, 3.90; N, 3.01. Found: C, 46.78; H, 3.85; N, 3.02.

[(S,Sp)-4-(1,1-Dimethylethyl)-4,5-dihydro-2-oxazolyl]-(2-(bis-(trifluoromethyl)-phosphino)-ferrocene ***6d***. The product was prepared according to the method B as an orange solid in 32% yield (1.5 g): mp 104−106 °C; $[\alpha]_D^{29.1}$ = −241.5 (c 0.1780, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 0.91 (s, 9 H), 3.94 (t, J = 8.7 Hz, 1 H), 4.19 (m, 1 H), 4.28 (s, 5 H), 4.33 (m, 1 H), 4.64 (s, 2 H), 4.91 (s, 1 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 24.8, 32.7, 68.0, 70.2, 71.8, 71.9, 72.6 (m), 75.3 (d, J = 3.7 Hz), 77.8 (d, J = 25.0 Hz), 162.4

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(d, J = 4.6 Hz) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ −50.46 (dq, J = 73.1, 8.2 Hz, 3 F), −55.53 (dq, J = 56.8, 8.2 Hz, 3 F) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ −6.01 (m) ppm; MS (MALDI) m/z (%) 480.1 $[M + H]^+$, 479.1 $[M]^+$. Anal. Calc. for $C_{19}H_{20}F_6FeNOP$, Calcd: C, 47.62; H, 4.21; N, 2.92. Found: C, 47.68; H, 4.36; N, 2.97.

[(S,Sp)-4,5-Dihydro-4-phenyl-2-oxazolyl]-(2-(bis-(pentafluoroethyl)phosphino)-ferrocene ***6e***. The product was prepared according to the method B as an orange solid in 38% yield (2.3 g): $[\alpha]_D^{22.5}$ = 3.3 (c 0.8050, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 4.10 (t, J = 8.4 Hz, 1 H), 4.29 (s, 5 H), 4.64 (s, 1 H), 4.70 (s, 2 H), 5.18 (m, 2 H), 7.17−7.34 (m, 5 H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 69.8, 71.6, 73.3, 73.34, 73.8, 74.9, 75.4, 76.3, 77.3, 126.5, 127.5, 128.7, 142.2, 165.7 ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ −113.6 to −109.3 (m, 3 F), −106.0 (dd, J = 52.2, 299.2 Hz, 1 F), −82.4 (t, J = 17.8 Hz, 3 F), −81.8 (s, 3 F) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ −1.39 to 0.39 (m) ppm; MS (MALDI) m/z (%) 600.1 $[M + H]^+$, 599.0 $[M]^+$; HRMS (MALDI-FT) m/z $[M + H]^+$ Calcd for $C_{23}H_{17}F_{10}{}^{54}FeNOP$ 598.0279, found 598.0279.

[(S,Sp)-4,5-Dihydro-4-(phenylmethyl)-2-oxazolyl]-(2-(bis-(pentafluoroethyl)phosphino)-ferrocene ***6f***. The product was prepared according to the method B as an orange liquid in 30% yield (1.8 g): $[\alpha]_D^{24.2}$ = −34.1 (c 0.2800, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.74 (dd, J = 7.6, 13.6 Hz, 1 H), 3.07 (dd, J = 4.8, 13.6 Hz, 1 H), 4.02 (t, J = 8.0 Hz, 1 H), 4.20 (s, 5 H), 4.30 (t, J = 9.2 Hz, 1 H), 4.42 (m, 1 H), 4.59 (s, 1 H), 4.77 (s, 1 H), 5.08 (s, 1 H), 7.21−7.32 (m, 5 H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 41.0, 67.4, 71.3, 71.5, 72.9, 73.4, 75.2, 76.8, 77.2, 126.5, 128.3, 129.7, 137.4, 164.4 (d, J = 3.8 Hz) ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ −109.0 (m, 3F), −104.4 to −105.6 (dd, J = 54.4, 297.5 Hz, 1 F), −82.0 (s, 3 F), −81.6 (s, 3 F) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ −0.83 (m) ppm; MS (MALDI) m/z (%) 614.1 $[M + H]^+$, 613.0 $[M]^+$; HRMS (MALDI-FT) m/z $[M + H]^+$ Calcd for $C_{24}H_{19}F_{10}{}^{54}FeNOP$ 612.0435, found 612.0442.

[(S,Sp)-4,5-dihydro-4-(1-methylethyl)-2-oxazolyl]-(2-(bis-(pentafluoroethyl)phosphino)-ferrocene ***6g***. The product was prepared according to the method B as an orange solid in 40% yield (2.3 g): $[\alpha]_D^{22.7}$ = −52.7 (c 0.0.3900, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 0.92 (d, J = 6.3 Hz, 3 H), 0.98 (d, J = 6.9 Hz, 3 H), 1.75 (m, 1 H), 3.96−4.07 (m, 2 H), 4.26 (s, 5 H), 4.32 (t, J = 8.1 Hz, 1 H), 4.60 (s, 1 H), 4.69 (s, 1 H), 5.10 (s, 1 H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 18.0, 18.4, 32.5, 70.2, 71.4, 72.3, 72.7 (d, J = 4.0 Hz), 73.3, 75.0, 76.8, 77.1, 163.7 (d, J = 4.0 Hz) ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ −109.4 to −113.6 (m, 3F), −104.8 to −106.1 (dd, J = 52.2, 297.8 Hz, 1 F), −82.4 (t, J = 17.8 Hz, 3 F), −82.0 (s, 3 F) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ −1.4 to 0.37 (m) ppm; MS (MALDI) m/z (%) 566.1 $[M + H]^+$, 565.0 $[M]^+$; HRMS (MALDI-FT) m/z $[M + H]^+$ Calcd for $C_{20}H_{19}F_{10}{}^{54}FeNOP$ 564.0435, found 564.0447.

[(S,Sp)-4-(1,1-Dimethylethyl)-4,5-dihydro-2-oxazolyl]-(2-(bis-(pentafluoroethyl)-phosphino)-ferrocene ***6h***. The product was prepared according to the method B as an orange solid in 40% yield (2.3 g): $[\alpha]_D^{22.8}$ = −110.8 (c 0.1350, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 0.95 (s, 9 H), 3.87 (dd, J = 7.9, 10.2 Hz, 1 H), 4.12 (t, J = 8.4 Hz, 1 H), 4.25−4.31 (m, 6 H), 4.62 (s, 1 H), 4.69 (app t, J = 2.4 Hz, 1 H), 5.04 (s, 1 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 25.8, 29.7, 33.5, 68.8, 71.4, 72.6 (d, J = 3.3 Hz), 73.1, 75.0, 76.2, 77.5, 163.2 ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ −109.3 to −113.2 (m, 3 F), −104.7 to −105.9 (dd, J = 53.6, 299.5 Hz, 1 F), −82.4 (t, J = 17.8 Hz, 3 F), −81.9 (s, 3 F) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ −0.63 to −1.81 (m) ppm; MS (MALDI) m/z (%) 580.1 $[M + H]^+$, 579.1 $[M]^+$. Anal. Calc. for $C_{21}H_{20}F_{10}FeNOP$, Calcd: C, 43.55; H, 3.48; N, 2.42. Found: C, 43.69; H, 3.85; N, 2.20.

General Procedure for the Pd-Catalyzed Allylic Alkylation of 12 or rac-13.[19c] $Pd(dba)_2$ (11 mg, 0.020 mmol) and ligand (***S***)-**3d** or (***S***)-**3h** (0.020 mmol) were dissolved in dry $(CH_2Cl)_2$ (2.0 mL) and then stirred for 30 min at room temperature under an atmosphere of argon. To this solution were successively added **12** or ***rac*-13** (0.5 mmol), dimethylmalonate (0.17 mL, 1.5 mmol), *N*,*O*-bis-(trimethylsilyl)acetamide (BSA) (0.37 mL, 1.5 mmol), and lithium acetate (1.0 mg, 0.015 mmol). The mixture was stirred at room temperature and monitored by TLC. After the disappearance of the starting material **12** or **13**, the mixture was diluted with CH_2Cl_2 (20 mL) and washed twice with ice-cold saturated aqueous ammonium chloride. The organic phase was dried over anhydrous Na_2SO_4 and then concentrated under reduced pressure. The regioselectivity of the reaction was determined by ^{1}H NMR spectroscopy of the crude product. The residue was purified by preparative TLC (EtOAc/petroleum ether = 1/15) to give the crude product. The enantiomeric purities were determined by chiral HPLC after purification with comparison to those of the racemic product that was obtained by the palladium-catalyzed allylic alkylation using (*rac*)-BINAP as the ligand.

Dimethyl-3-phenyl-1-butene-4,4-dicarboxylate ***10a*** *and* ***10b*** *(Table 3, entries 1−4, 21−23).*[19c] Eluent: petroleum ether/ethyl acetate = 15/1. 122 mg (98%, combined yield of **10a** and **11a**): $[\alpha]_D^{29.3}$ = −29.8 (c 1.0160, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.50 (s, 3 H), 3.75 (s, 3 H), 3.88 (d, J = 11.0 Hz, 1 H), 4.10 (dd, J = 11.0, 8.1 Hz, 1 H), 5.09 (d, J = 10.2 Hz, 1 H), 5.13 (d, J = 17.1 Hz, 1 H), 6.0 (ddd, J = 17.1, 10.2, 8.1 Hz, 1 H), 7.21−7.32 (m, 5 H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 49.7, 52.3, 52.5, 57.3, 116.6, 127.1, 127.7, 128.6, 137.8, 139.9, 167.8, 168.2 ppm; HPLC (chiralcel OD-H column, 214 nm, 99/1 hexane/isopropanol, flow = 0.7 mL/min) t_R = 12.85 (**R**), 13.92 (**S**) min.

Dimethyl-3-(1′-naphthyl)-1-butene-4,4-dicarboxylate ***10c*** *and* ***10d*** *(Table 3, entries 5−6 and 24).*[19c] Eluent: petroleum ether/ethyl acetate = 15/1. 146 mg (98%, combined yield of **10c** and **11c**): $[\alpha]_D^{28.3}$ = −35.8 (c 0.8025, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.39 (s, 3 H), 3.79 (s, 3 H), 4.17 (d, J = 10.9 Hz, 1 H), 5.04 (dd, J = 10.9, 8.1 Hz, 1 H), 5.11 (d, J = 10.2 Hz, 1 H), 5.16 (d, J = 17.1 Hz, 1 H), 6.08 (ddd, J = 17.1, 10.2, 8.1 Hz, 1 H), 7.37−7.57 (m, 4 H), 7.74 (d, J = 7.4 Hz, 1 H), 7.84 (d, J = 8.0 Hz, 1 H), 8.24 (d, J = 8.6 Hz, 1 H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 44.0, 52.3, 52.5, 56.9, 117.0, 123.2, 124.3, 125.1, 125.6, 126.1, 127.6, 128.8, 131.3, 134.0, 136.0, 137.5, 167.7, 168.3 ppm; HPLC (chiralcel OD column, 220 nm, 97/3 hexane/isopropanol, flow = 0.7 mL/min) t_R = 8.98 (**R**), 9.75 (**S**) min.

Dimethyl-3-(4′-methoxyphenyl)-1-butene-4,4-dicarboxylate ***10e*** *and* ***10f*** *(Table 3, entries 7−8).*[19c] Eluent: petroleum ether/ethyl acetate = 15/1. 134 mg (96%, combined yield of **10e** and **11e**): $[\alpha]_D^{28.7}$ = −23.6 (c 0.4635, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.50 (s, 3 H), 3.74 (s, 3 H), 3.78 (s, 3 H), 4.06 (dd, J = 10.7, 8.0 Hz, 1 H), 5.05−5.12 (m, 2 H), 5.98 (ddd, J = 17.1, 10.2, 8.0 Hz, 1 H), 6.83 (d, J = 6.7 Hz, 1 H), 7.15 (d, J = 6.7 Hz, 1 H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 48.8, 52.3, 52.4, 55.1, 57.4, 113.8, 113.9, 116.1, 128.8, 138.0, 158.5, 167.8, 168.1 ppm; HPLC (chiralcel OD column, 220 nm, 90/10 hexane/isopropanol, flow = 0.7 mL/min) t_R = 9.35 (**R**), 10.48 (**S**) min.

Dimethyl-3-(4′-methylphenyl)-1-butene-4,4-dicarboxylate ***10g*** *(Table 3, entries 9 and 10).*[19c] Eluent: petroleum ether/ethyl acetate = 15/1. 128 mg (98%, combined yield of **10g** and **11g**): $[\alpha]_D^{29.0}$ = −31.7 (c 1.3040, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.30 (s, 3 H), 3.51 (s, 3 H), 3.73 (s, 3 H), 4.07 (dd, J = 10.9, 8.2 Hz, 1 H), 5.07 (d, J = 9.4 Hz, 1 H), 5.11 (d, J = 17.0 Hz, 1 H), 5.98 (ddd, J = 17.1, 9.4, 8.2 Hz, 1 H), 7.10 (s, 4 H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 17.3, 45.6, 48.6, 48.8, 53.6, 112.6, 124.0, 125.6, 132.9, 133.2, 134.3, 164.1, 164.5 ppm; HPLC (chiralcel OD-H column, 214 nm, 99/1 hexane/isopropanol, flow = 0.7 mL/min) t_R = 10.82 (**R**), 11.79 (**S**) min.

Dimethyl-3-(4′-chlorophenyl)-1-butene-4,4-dicarboxylate ***10h*** *(Table 3, entries 11 and 12).*[19c] Eluent: petroleum ether/ethyl acetate = 15/1. 137 mg (97%, combined yield of **10h** and **11h**): $[\alpha]_D^{31.1}$ = −19.6 (c 1.6160, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.52 (s, 3 H), 3.74 (s, 3 H), 3.81 (d, J = 11.2 Hz, 1 H), 4.07 (dd, J = 11.2, 8.0 Hz, 1 H), 5.09−5.13 (m, 2 H), 5.90 (dt, J = 8.9, 17.7 Hz, 1 H), 7.16 (d, J = 8.4 Hz, 2 H), 7.26 (d, J = 8.8 Hz, 2 H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 48.9, 52.5, 52.6, 57.1, 117.0, 127.4, 128.6, 128.8, 129.3, 130.0, 137.2, 167.6, 167.9 ppm; HPLC (chiralcel OD column, 220 nm, 99/1 hexane/isopropanol, flow = 0.7 mL/min) t_R = 16.38 (**R**), 20.91 (**S**) min.

Dimethyl-3-(2′-furanyl)-1-butene-4,4-dicarboxylate ***10i*** *(Table 3, entries 13 and 14).*[23] Eluent: petroleum ether/ethyl acetate = 15/1. 113 mg (95%, combined yield of **10i** and **11i**): $[\alpha]_D^{29.3}$ = −39.6 (c 0.9065, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.63 (s, 3 H), 3.73 (s,

3 H), 3.86 (d, J = 9.9 Hz, 1 H), 4.20 (dd, J = 9.6, 9.0 Hz, 1 H), 5.15 (d, J = 4.8 Hz, 1 H), 5.18 (d, J = 12.0 Hz, 1 H), 5.91 (ddd, J = 18.3, 9.9, 8.4, Hz 1 H), 6.10 (d, J = 3.0 Hz, 1 H), 6.28 (m, 1 H), 7.33 (m, 1 H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 43.2, 52.5, 52.6, 55.4, 106.4, 110.2, 118.1, 134.6, 141.8, 152.9, 167.7, 167.72 ppm; HPLC (chiralcel OJ-H column, 220 nm, 95/5 hexane/isopropanol, flow = 0.7 mL/min) t_R = 16.80 (**S**), 17.99 (**R**) min.

Dimethyl-3-(3′-chlorophenyl)-1-butene-4,4-dicarboxylate ***10j*** *(Table 3, entries 15 and 16).* Eluent: petroleum ether/ethyl acetate = 15/1. 137 mg (97%, combined yield of **10i** and **11i**): $[\alpha]_D^{29.3}$ = −21.2 (c 0.4135, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.53 (s, 3 H), 3.74 (s, 3 H), 3.82 (d, J = 11.2 Hz, 1 H), 4.06 (dd, J = 10.8, 8.4 Hz, 1 H), 5.10 (m, 2 H), 5.91 (m, 1 H), 7.11 (dd, J = 6.8, 2.0 Hz, 1 H), 7.21 (m, 3 H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 44.5, 47.8, 47.9, 52.3, 112.5, 121.6, 122.6, 123.3, 125.1, 126.9, 132.3, 137.3, 162.8, 163.1 ppm; HPLC (chiralcel AD-H column, 214 nm, 99/1 hexane/isopropanol, flow = 0.7 mL/min) t_R = 14.60 (**S**), 15.97 (**R**) min.

Dimethyl-3-(2′-chlorophenyl)-1-butene-4,4-dicarboxylate ***10k*** *(Table 3, entry 17).* Eluent: petroleum ether/ethyl acetate = 15/1. 134 mg (95%, combined yield of **10k** and **11k**): $[\alpha]_D^{30.3}$ = −36.9 (c 0.9330, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.54 (s, 3 H), 3.74 (s, 3 H), 4.02 (d, J = 10.5 Hz, 1 H), 4.65 (t, J = 9.0 Hz, 1 H), 5.10 (m, 2 H), 5.93 (dt, J = 17.7, 8.9 Hz, 1 H), 6.14 (ddd, J = 17.0, 10.1, 8.6 Hz, 1 H), 7.16 (m, 1 H), 7.22 (dd, J = 1.5, 7.8 Hz, 2 H), 7.36 (d, J = 7.8 Hz, 1 H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 45.6, 52.4, 52.5, 55.8, 117.6, 126.9, 128.1, 128.5, 129.5, 130.0, 136.0, 137.4, 168.0, 169.2 ppm; HPLC (chiralcel OD-H column, 214 nm, 99/1 hexane/isopropanol, flow = 0.7 mL/min) t_R = 14.12 (**R**), 17.22 (**S**) min.

Dimethyl-3-(2′-methoxyphenyl)-1-butene-4,4-dicarboxylate ***10l*** *(Table 3, entry 18 and 19).* Eluent: petroleum ether/ethyl acetate = 15/1. 132 mg (95%, combined yield of **10l** and **11l**): $[\alpha]_D^{27.1}$ = −33.2 (c 1.050, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.47 (s, 3 H), 3.73 (s, 3 H), 3.83 (s, 3 H), 4.17 (d, J = 10.8 Hz, 1 H), 4.32 (dd, J = 10.8, 8.4 Hz, 1 H), 5.02 (m, 2 H), 6.09 (dq, J = 10.0, 8.0 Hz, 1 H), 6.84 (m, 2 H), 7.14 (m, 2 H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 45.9, 52.1, 52.2, 55.2, 55.3, 110.9, 116.6, 120.5, 127.9, 128.1, 129.2, 136.8, 157.0, 168.0, 168.5 ppm; HPLC (chiralcel OD-H column, 214 nm, 995/5 hexane/isopropanol, flow = 0.7 mL/min) t_R = 8.87 (**R**), 9.83 (**S**) min.

Dimethyl-3-(3′-methoxyphenyl)-1-butene-4,4-dicarboxylate ***10m*** *(Table 3, entry 20).*[24] Eluent: petroleum ether/ethyl acetate = 15/1. 132 mg (95%, combined yield of **10m** and **11m**): $[\alpha]_D^{29.3}$ = −31.1 (c 0.6195, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.56 (s, 3 H), 3.77 (s, 3 H), 3.82 (s, 3 H), 3.90 (d, J = 10.8 Hz, 1 H), 4.12 (dd, J = 10.8, 8.3 Hz, 1 H), 5.12 (d, J = 10.4 Hz, 1 H), 5.17 (dt, J = 1.3, 16.9 Hz, 1 H), 6.00 (ddd, J = 17.2, 10.1, 8.3 Hz, 1 H), 6.78−6.81 (m, 2 H), 6.85 (d, J = 7.8 Hz, 1 H), 7.25 (td, J = 7.8, 1.0 Hz, 1 H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 49.7, 52.4, 52.5, 55.0, 57.1, 112.3, 113.6, 116.6, 120.0, 129.5, 137.5, 141.4, 159.6, 167.7, 168.0 ppm; HPLC (chiralcel OD-H column, 214 nm, 99/1 hexane/isopropanol, flow = 0.7 mL/min) t_R = 18.69 (**R**), 20.59 (**S**) min

General Procedure for the Preparation of Pd(3d)(cinnamyl)-SbF_6 Complex.[25] KCl (1.40 g, 18.8 mmol) was added to a solution of $PdCl_2$ (1.76 g, 10.0 mmol) in 18 mL of deionized water. A red-brown solution was formed after 5 min. Eighteen milliliters of deionized water and cinnamyl chloride (5.0 g, 33 mmol) was added. The mixture was stirred at room temperature for 24 h. A green-yellow solid $[Pd(cinnamyl)Cl]_2$ was filtered and used without further purification (2.5 g, 96.5%).

A solution of $AgSbF_6$ (0.352 g, 1.03 mmol) in methanol (4.0 mL) was added to a solution of ligand **4** (0.3 g, 1.05 mmol) and complex **21** (0.26 g, 0.5 mmol) in CH_2Cl_2 (10 mL). After being stirred at room temperature for 1 h in the dark, the solution was filtered through a short plug of Celite. The solid was washed with CH_2Cl_2 (5.0 mL × 3). The filtrates were combined and concentrated in vacuo. The residue was purified by recrystallization with $CHCl_3$ and pentane to give slightly yellow crystals (**14**, 0.40 g, 91.5%): mp 224−226 °C; $[\alpha]_D^{28.5}$ = −134.9 (c 0.1120, $CHCl_3$); IR ν_{max} solid 2965.7, 1618.9, 1586.3, 1571.4, 1192.2, 1150.0, 656.4 cm^{-1}; ^{1}H NMR (75% isomer, $CDCl_3$, 400 MHz) δ 0.53 (s, 9 H), 2.86 (dd, J = 9.2, 2.8 Hz, 1 H), 3.16 (*anti* to central, *trans* to N, d, J = 11.6 Hz, 1 H), 4.17 (*syn* to central, *trans* to N, d, J = 6.8 Hz, 1 H), 4.19 (t, J = 9.2 Hz, 1H), 4.39 (dd, J = 9.2, 2.8 Hz, 1 H), 6.15 (*trans* to P, d, J = 14.0, 10.4 Hz, 1 H), 6.38 (central, ddd, J = 19.2, 12.0, 7.2 Hz, 1H), 7.46−7.55 (aryl region, m, 3 H), 7.80−7.91 (aryl region, m, 4 H), 8.09 (t, J = 8.8 Hz, 1 H), 8.42 (t, J = 6.8 Hz, 1 H) ppm; ^{19}F NMR (75% isomer, 376 MHz, $CDCl_3$) δ −56.19 (dq, J = 89.5, 7.1 Hz, 3 F), −56.19 (dq, J = 101.1, 7.1 Hz, 3 F) ppm; ^{1}H NMR (25% isomer, $CDCl_3$, 400 MHz) δ 0.83 (s, 9 H), 2.94 (d, J = 8.4 Hz, 1 H), 3.46 (anti to central, trans to N, d, J = 12.0 Hz, 1 H), 3.74 (syn to central, trans to N, d, J = 9.2 Hz, 1 H), 4.21 (m, 1 H), 4.36 (m, 1 H), 5.58 (trans to P, t, J = 12.4 Hz, 1 H), 6.31 (central, m, 1 H), 7.46−7.55 (aryl region, m, 3 H), 7.66 (d, J = 6.0 Hz, 2 H), 7.80−7.91 (aryl region, m, 2 H), 8.07 (m, 1 H), 8.42 (m, 1 H) ppm; ^{19}F NMR (25% isomer, 376 MHz, $CDCl_3$) δ −55.57 (dq, J = 89.1, 7.1 Hz, 3 F), −52.14 (dq, J = 95.5, 7.1 Hz, 3 F) ppm; ^{31}P NMR (both major isomers, 81 MHz, $CDCl_3$) δ 35.4 (m, 1H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 24.2, 33.7, 69.9, 72.4, 111.3, 111.5, 112.77, 112.8, 113.4, 113.42, 130.0, 131.2, 133.9, 134.1, 135.2, 135.3, 135.7, 165.1(d, J = 2.2 Hz, C=N) ppm. Anal. Calc. for $C_{24}H_{25}F_{12}NOPPdSb$ (830.60) Calcd: C, 34.70; H, 3.03; N, 1.69. Found: C, 34.52; H, 3.19; N, 1.47.

General Procedure for Preparation of Mo-Complexes 7, 9.[12c] In the dark, a mixture of $Mo(CO)_6$ (0.10 g, 0.38 mmol) and ligand **3d** or (*S*)-4-*tert*-butyl-2-2(diphenylphosphino)phenyl)-4,5-dihydrooxazoline (^{t}BuPHOX) (0.30 mmol) in toluene (3.0 mL) was refluxed for 2−3 h. The reaction was monitored by ^{19}F NMR or ^{31}P NMR spectroscopy. After the disappearance of the peak corresponding to the ligand, the solvent was removed in vacuo. The residue was dissolved in petroleum ether and filtered through filter paper. The filtrates were concentrated and gave the Mo complexes as red solids.

General Procedure for Preparation of Mo-Complex 8.[26] In a Schlenk flask, to a Et_2O solution (5 mL) of (4*S*)-2-(2-(dinaphtho[2,1′-*d*:1′,2′-*f*][1,3,2]dioxoaphosphenpin-4-yl)phenyl)-4-isopropyl-4,5-dihydrooxazole (0.13 g, 0.49 mmol) at −80 °C was added dropwise a precooled solution of *s*-BuLi (0.38 mL, 1.3 M in cyclohexane). The mixture was stirred for 10 min, and $ClP(NEt_2)_2$ (0.10 g, 0.49 mmol) was added slowly. The mixture was allowed to warm up to room temperature and was stirred for 1−2 h. The volatiles were removed in vacuo, and toluene (10 mL) was added. The solution was filtered through a pad of Celite. ^{31}P NMR spectrum of the crude product showed a single resonance at δ 97.4 ppm. (*R*)-binapthol (0.49 mmol, 0.14 g) was then added, and the mixture was heated under reflux for 12 h. After cooling to room temperature, the solvent was removed, and the residue was washed twice with pentane and diethyl ether. The solid was dissolved in toluene (10 mL), and the solution was filtered through a short plug of Celite. ^{31}P NMR spectrum of the solution showed a single resonance at δ 199.9 ppm. $Mo(CO)_6$ (0.133 g, 0.500 mmol) was added, and the reaction mixture was heated under reflux for 1−2 h. After cooling to room temperature, the mixture was filtered, and the solvent was removed in vacuo. The residue was purified by recrystallization with CH_2Cl_2 and pentane to give the desired Mo complex as a slightly orange crystals (0.28 g, 80.3%).

Complex 7 (0.15 g, 86.3%): mp 87−88 °C; $[\alpha]_D^{28.8}$ = +270.4 (c 0.0620, $PhCH_3$); IR ν_{max} solid 2970.5, 2900.4, 2872.4, 2043.8, 1941.6, 1918.4, 1900.2, 1874.6, 1878.7, 1862.9 cm^{-1}; ^{1}H NMR (C_6D_6, 400 MHz) δ ^{1}H NMR (400 MHz, C_6D_6) δ 0.65 (s, 9 H), 3.35 (dd, J = 9.2, 8.0 Hz, 1 H), 3.64 (dd, J = 8.4, 2.4 Hz, 1 H), 3.69 (dd, J = 9.6, 2.0 Hz, 1 H), 6.82−6.91 (m, 2 H), 7.72 (m, 1 H), 7.94 (t, J = 7.2 Hz, 1 H) ppm; ^{13}C NMR (100 MHz, C_6D_6) δ 25.7, 35.5, 67.9, 86.3 (d, J = 2.8 Hz), 132.1, 132.12, 132.25, 132.34, 132.5 (m), 133.0 (d, J = 1.9 Hz), 166.7 (d, J = 5.5 Hz), 204.3 (d, J = 8.8 Hz, CO), 205.7 (d, J = 8.7 Hz, CO), 211.0 (d, J = 41.2 Hz, CO), 215.1 (d, J = 10.2 Hz, CO) ppm; ^{31}P{^{1}H} NMR (162 MHz) δ 66.17 (sept, J = 79.2 Hz); ^{19}F{^{1}H} NMR (376 MHz) δ −37.18 (dq, J = 80.1, 2.2 Hz, 3 F), −33.71 (dq, J = 79.0, 8.3 Hz, 3 F) ppm. Anal. Calc. for $C_{19}H_{16}F_6MoNO_5P$ (580.97) Calcd: C, 39.40; H, 2.78; N, 2.42. Found: C, 39.45; H, 2.59; N, 2.05.

Complex 9 (0.16 g, 89.6%): mp 157 °C; $[\alpha]_D^{28.9}$ = +537.5 (c 0.0465, $PhCH_3$); IR ν_{max} solid 2960.8, 2009.5, 1942.6, 1909.3, 1893.6, 1846.4 cm^{-1}; ^{1}H NMR (C_6D_6, 400 MHz) δ ^{1}H NMR (400 MHz, C_6D_6) δ 0.45 (s, 9 H), 3.35 (m, 1 H), 3.68 (m, 2 H), 6.69 (t, J = 7.6 Hz, 1 H), 6.77 (dt, J = 8.4, 0.8 Hz, 1 H), 6.87 (t, J = 8.0 Hz, 1 H), 6.96 (m, 3 H), 7.04 (m, 3 H), 7.35 (m, 2 H), 7.58 (m, 2 H), 7.93 (dq, J =

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4.0, 1.6 Hz, 1 H) ppm; ^{13}C NMR (100 MHz, C_6D_6) δ 26.0, 34.9, 68.2, 83.6 (d, J = 2.8 Hz), 128.4, 128.5, 128.7, 128.8, 129.7 (t, J = 1.4 Hz), 129.8, 130.3 (d, J = 2.1 Hz), 131.9, 131.97, 131.98, 132.0, 133.0, 133.1, 134.0, 134.2, 134.4, 137.0, 137.3, 168.6 (d, J = 0.9 Hz), 207.3 (d, J = 8.4 Hz, CO), 210.0 (d, J = 9.2 Hz, CO), 216.6 (d, J = 33.8 Hz, CO), 220.8 (d, J = 7.4 Hz, CO) ppm; ^{31}P{^{1}H} NMR (162 MHz) δ 35.6 ppm. Anal. Calc. for $C_{29}H_{26}MoNO_5P$ (597.06) Calcd: C, 58.49; H, 4.40; N, 2.35. Found: C, 58.59; H, 4.31; N, 2.16.

Complex 8 (0.28 g, 80.3%): $[\alpha]_D^{29.5}$ = −212.7 (c 0.1525, $CHCl_3$); IR ν_{max} solid 2961.3, 2921.0, 2869.8, 2027.4, 1922.0, 1871.3 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.64 (d, J = 6.8 Hz, 3 H), 0.94 (d, J = 6.8 Hz, 3 H), 2.69 (dq, J = 6.8, 3.2 Hz, 1 H), 4.16 (m, 1 H), 4.30 (m, 2 H), 6.55 (d, J = 8.8 Hz, 1 H), 7.06 (t, J = 7.6 Hz, 1 H), 7.16 (m, 4 H), 7.33 (m, 4 H), 7.57 (d, J = 8.8 Hz, 1 H), 7.71 (d, J = 8.8 Hz, 1 H), 7.78 (d, J = 8.0 Hz, 1 H), 7.89 (d, J = 8.0 Hz, 1 H), 8.00 (dd, J = 9.2 Hz, 1 H),8.04 (dd, J = 4.4, 7.6 Hz, 1 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.1, 19.3, 29.8, 66.9, 81.0 (d, J = 209 Hz), 122.5, 123.5 (d, J = 2.3 Hz), 123.9 (d, J = 3.7 Hz, ArC), 125.8 (d, J = 3.0 Hz), 126.8, 126.9, 127.7, 127.9, 128.7, 128.8 (d, J = 1.5 Hz), 128.97, 129.0, 129.2, 129.23, 129.3, 130.3, 131.5, 131.7, 131.8 (d, J = 3.8 Hz, ArC), 131.9, 132. 5, 132.6 (d, J = 1.5 Hz), 133.37 (d, J = 1.5 Hz, ArC), 133.4 (d, J = 2.3 Hz, ArC), 148.9 (d, J = 3.2 Hz, ArC), 149.7 (d, J = 11.1 Hz, ArC), 164.5 (d, J = 3.0 Hz, C═N), 205.4 (d, J = 13.4 Hz, CO), 206.9 (d, J = 10.4 Hz, CO), 214.4 (d, J = 51.3 Hz, CO), 217.1 (d, J = 11.9 Hz, CO) ppm; ^{31}P{^{1}H} NMR (162 MHz) δ 199.9 ppm. Anal. Calc. for $C_{36}H_{26}MoNO_7P$ (713.05) Calcd: C, 60.77; H, 3.68; N, 1.97. Found: C, 60.72; H, 3.83; N, 1.56.

■ ASSOCIATED CONTENT

Supporting Information

Proton and carbon NMR spectra of novel reported compounds **3a−h**, **6a−h**, **10a−m**, CIF files of single crystals **6c**, **8**, and **14** as well as HPLC spectra for **10a−m**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ NOTE ADDED AFTER ASAP PUBLICATION

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