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PCN Pincer Palladium(II) Complex Catalyzed Enantioselective Hydrophosphination of Enones: Synthesis of Pyridine-Functionalized Chiral Phosphine Oxides as $NC_{sp^3}O$ Pincer Preligands

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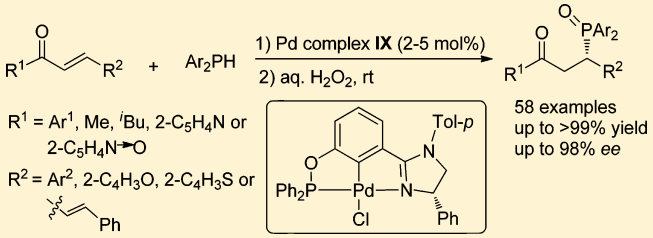
Supporting Information

ABSTRACT: A series of chiral PCN pincer Pd(II) complexes **VI**–**XIII** with aryl-based aminophosphine–imidazoline or phosphinite–imidazoline ligands were synthesized and characterized. They were examined as enantioselective catalysts for the hydrophosphination of enones. Among them, complex **IX**, which features a Ph_2PO donor as well as an imidazoline donor with (4*S*)-phenyl and *N*-Tol-*p* groups, was found to be the optimal catalyst. Thus, in the presence of 2–5 mol % of complex **IX** a wide variety of enones reacted smoothly with diarylphosphines to give the corresponding chiral phosphine derivatives in high yields with enantioselectivities of up to 98% ee. In particular, heteroaryl species such as 2-thienyl-, 2-furyl-, and 2-pyridinyl-containing enones that have a strong coordination ability to the Pd center were also appropriate substrates for the current catalytic system. For example, hydrophosphination of 2-alkenoylpyridines with diphenylphosphine followed by oxidation with H_2O_2 afforded the corresponding pyridine-functionalized chiral phosphine oxides in good yields with good to excellent enantioselectivities (10 examples, up to 95% ee). Furthermore, it had been demonstrated that the obtained pyridine-containing phosphine oxide acted as a tridentate ligand in the reaction with $PdCl_2$ to form an intriguing $NC_{sp^3}O$ pincer Pd(II) complex via C_{sp^3}–H bond activation, which to our knowledge is the first example of a chiral $DC_{sp^3}D'$ Pd pincer (D ≠ D′; D and D′ denote donor atoms such as P, N, etc.).



INTRODUCTION

Chiral phosphorus compounds have been extensively employed as ligands in organometallic chemistry and catalysis.[1] Therefore, the synthesis of these species has attracted great interest and catalytic enantioselective strategies have recently been developed.[2] Among them, the asymmetric addition of phosphorus nucleophiles such as secondary phosphines and phosphine oxides is one of the most efficient approaches to construct new carbon–phosphorus bonds and concurrently provide direct access to the chiral phosphanes.[2c,3] In particular, great progress has been achieved in the metal- or organo-catalyzed hydrophosphination of electron-deficient alkenes with secondary phosphines (conjugate addition of R_2PH to the alkenes) over the past decade. Successful examples include methacrylonitrile,[4] enones,[5] enals,[6] nitroalkenes,[7] α,β-unsaturated *N*-acylpyrroles,[8] unsaturated carboxylic and sulfonic esters,[9] and α,β-unsaturated imines.[10] Among the transition-metal catalysts for the above hydrophosphination, the CP palladacycle **A** and the PCP pincer Pd complex **B** (Chart 1), which are chiral cyclopalladated complexes, are found to be particularly effective. The former was developed by Leung's group and the latter by Duan's group.[11] Both **A** and **B** could catalyze hydrophosphination of several kinds of activated alkenes with diarylphosphines, producing the chiral phosphine derivatives with excellent enantioselectivities in all cases.[5,6d,7b,8−10] For example, in the hydrophosphination of β-substituted enones, complex **B** exhibited high levels of stereoselectivities (13 examples, 90–99% ees).[5b] Despite this impressive progress, the development of widely applicable catalysts is still of interest. Recently, we have also explored the application of pincer Pd(II) complexes in hydrophosphination, which is involved in the evaluation of the PCN Pd(II) pincers **I**–**IV** containing aryl-based aminophosphine–imidazoline or phosphinite–imidazoline ligands (Chart 1) in the asymmetric addition of diarylphosphines to β-aryl enones.[12,13] Among the four pincers utilized, complex **III** afforded the best result (up to 82% ee) in the addition of diphenylphosphine to chalcone and the other three complexes gave rather low ee values (0–30% ees) under the same reaction conditions. Thus, with complex **III** as the catalyst, moderate to excellent enantioselectivities could be obtained (13 examples, 40–94% ees). Overall, there is still room to improve the performance of complexes **I**–**IV** in catalysis, and this can be fulfilled through modifying the ligands. Meanwhile, the structural modification of these pincer Pd complexes is a relatively easy task. Consequently, we set out to further modify the PCN Pd(II) pincers and examine their potential in the hydrophosphination of enones with diarylphosphines. The results are given below.

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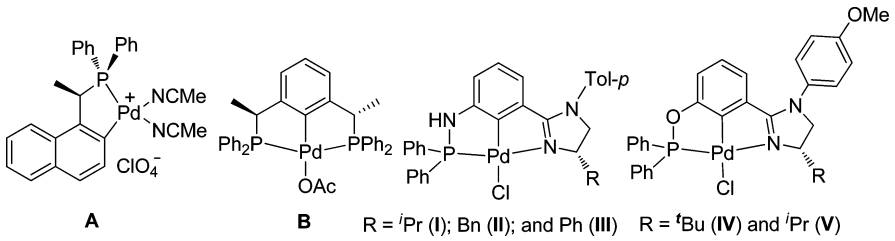
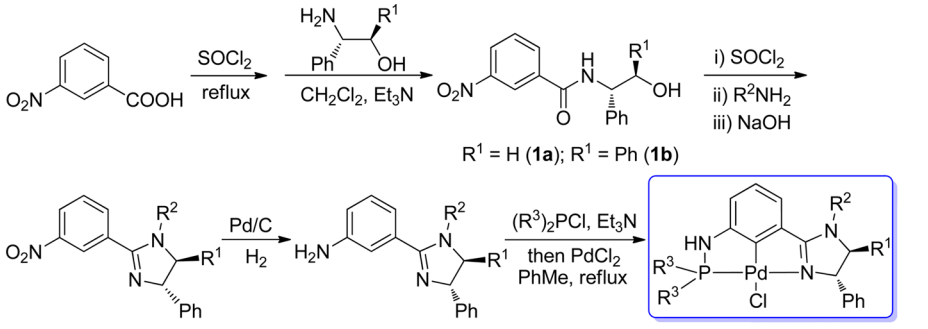
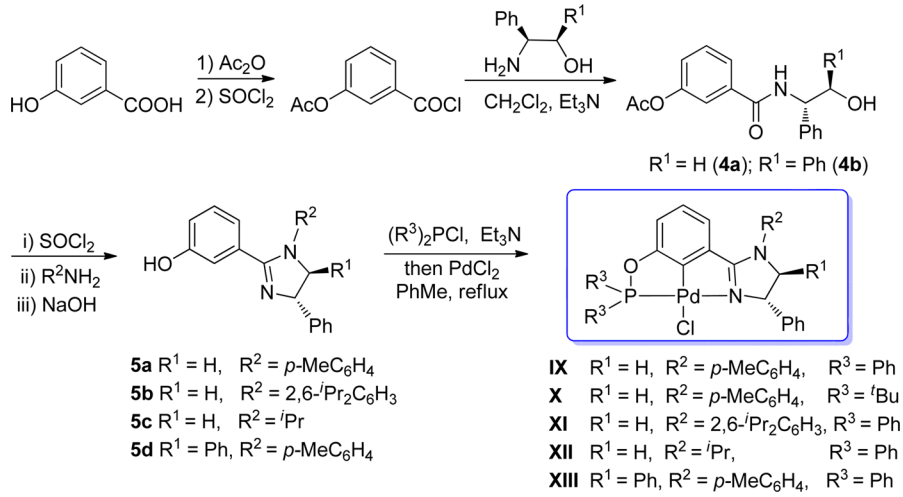
Chart 1



Scheme 1. Synthesis of the PCN Pincer Pd(II) Complexes VI–VIII with Aryl-Based Aminophosphine–Imidazoline Ligands



Scheme 2. Synthesis of the PCN Pincer Pd(II) Complexes IX–XIII with Aryl-Based Phosphinite–Imidazoline Ligands



RESULTS AND DISCUSSION

In our previous studies complex **III**, with a (4*S*)-phenyl substituent on the imidazoline ring, displayed higher enantioselectivity than complexes **I** and **II** with a (4*S*)-isopropyl or -benzyl group; therefore, the (4*S*)-phenyl group was used in the following investigations. Three new PCN pincer Pd(II) complexes with aminophosphine–imidazoline ligands, **VI–VIII** (Scheme 1),[12] and five complexes with phosphinite–imidazoline ligands, **IX–XIII** (Scheme 2),[14] were prepared according to the procedures previously reported by us. These complexes have different electronic and steric properties, which were realized by employing different chiral amino alcohols (for R^1), primary amines (for R^2) and dialkylchlorophosphines (for R^3). All of the new Pd complexes were well characterized by elemental analysis and ^1H, ^{13}C, and $^{31}P\{^1H\}$ NMR spectra. Additionally, an X-ray single-crystal analysis of complex **IX** confirmed the PCN pincer coordination mode (Figure 1).

With the expected pincer Pd(II) complexes in hand, they were first evaluated in the hydrophosphination of chalcones with diphenylphosphine under the optimized reaction conditions[12] previously established (for convenience of operation in the experiments, the phosphine adducts were oxidized to the corresponding phosphine oxides for analysis). In the series of Pd pincers possessing aminophosphine–imidazoline ligands, the bulky and more electron-rich $^tBu_2PNH$ donor in complex **VI** led to an obvious decrease in both yield and enanantioselectivity in comparison with complex **III** (Table 1, entry 1 vs 2). Complexes **VII** and **VIII** also did not provide better enantioselectivities (entries 3 and 4). The two complexes have a different NR^2 group or an additional (5*S*)-phenyl substitutent on the imidazoline ring in comparison with complex **III**. Gratifyingly,

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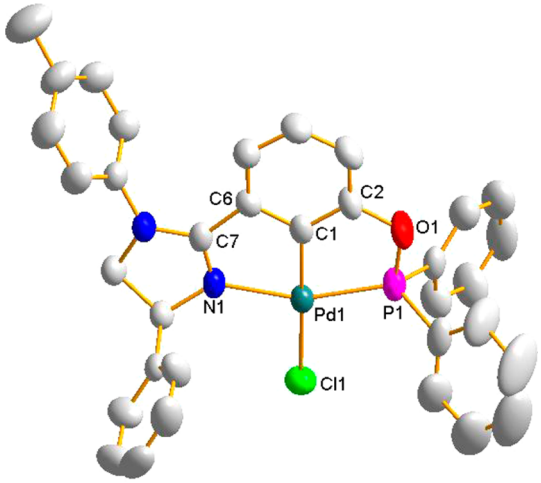
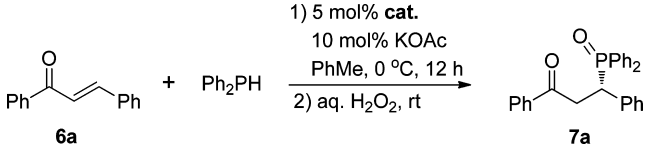


Figure 1. Molecular structure of the PCN pincer Pd(II) complex **IX**. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd(1)−C(1) 1.963(5), Pd(1)−P(1) 2.1978(12), Pd(1)−N(1) 2.098(3), Pd(1)−Cl(1) 2.3837(12); C(1)−Pd(1)−N(1) 78.92(18), C(1)−Pd(1)−P(1) 79.80(13), P(1)−Pd(1)−Cl(1) 101.51(5), N(1)−Pd(1)−Cl(1) 99.64(13), N(1)−Pd(1)−P(1) 158.60(13), C(1)−Pd(1)−Cl(1) 177.09(13).

Table 1. Evaluation of PCN Pincer Pd(II) Complexes VI−XIII in the Enantioselective Hydrophosphination of Chalcone with Diphenylphosphine[a]



entry	cat.	yield (%)[b]	ee (%)[c,d]
1	**III**	88[e]	82[e]
2	**VI**	16	18
3	**VII**	98	72
4	**VIII**	78	39
5	**IX**	99	92
6	**X**	20	33
7	**XI**	88	91
8	**XII**	83	84
9	**XIII**	92	52

[a]Hydrophosphination reactions were performed with Ph_2PH (0.2 mmol) and chalcone (0.3 mmol) in the presence of PCN pincer Pd complex (5 mol %) and KOAc base (10 mol %) in 2 mL of toluene at 0 °C for 12 h. [b]Isolated yield. [c]Determined by chiral HPLC. [d]The absolute configuration of the product was assigned to be *S* by comparison of optical rotation with that in refs 5b and 12. [e]Data from ref 12.

an almost quantitative yield with excellent enanantioselectivity was observed when complex **IX** was used as the catalyst (99% yield and 92% ee, entry 5). In contrast to complex **III**, complex **IX** contains a Ph_2PO instead of a Ph_2PNH donor group. Similarly, the $^tBu_2PO$ donor in complex **X** gave drastically decreased yield and enantioselectivity (entry 6 vs 5). Further changing NR^2 or R^1 substitutent on the imidazoline ring in the series of Pd pincers possessing phosphinite−imidazoline ligands also did not afford better results (entries 7−9). In general, the pincers **IX**−**XI** and **XIII** with phosphinite−imidazoline ligands gave better stereoselectivities than did the corresponding pincers **III** and **VI**−**VIII** with aminophosphine−imidazoline ligands. In addition, complex **IX** was found to be the optimal catalyst.

The hydrophosphination of a wide variety of enones with diphenylphosphine were then investigated using complex **IX** as the catalyst (Table 2). Both electron-withdrawing and electron-donating substituents on the aryl (R^1) attached to carbonyl group or *β*-aryl (R^2) in the *β*-aryl *α*,*β*-unsaturated aryl ketone substrates were tolerated, and all of them furnished high enantioselectivities (18 examples, 85−96% ees, entries 1−8 and 22−31). In fact, excellent enantioselectivities (≥90% ees) could be obtained in most cases (14 examples). The substituents include Br, F, NO_2, Me, and OMe. However, the enantioselectivities decreased drastically when the substituent was located on the ortho position of the *β*-aryl group (entry 12 vs 8 and entry 13 vs 7). The *β*-naphthyl enone was also an appropriate substrate for the current catalytic system (81% ee, entry 9). In the cases of *β*-heteroaryl species such as *β*-furyl and *β*-thienyl enones that may bind to the Pd center through the heteroatom, good stereocontrol could still be achieved (82% and 88% ee, respectively, entries 10 and 11). In addition, the enone substrates bearing an alkyl attached to the carbonyl group such as methyl (entries 14−21) or ^{i}Bu (entries 32 and 33) also afforded high levels of stereoselectivities. In particular, the ee values were invariably higher than 90% in the case of methyl enones (8 examples, 93−97% ees). In contrast, hydrophosphination did not occur when the *β* group was a *β*-alkyl such as cyclohexyl instead of a *β*-aryl. 2-Cyclohexen-1-one (a cyclic enone) also did not undergo hydrophosphination (data not shown in Table 2). When the catalyst loading was lowered to 2 mol %, excellent enantioselectivities could also be reached in some cases (entries 2, 14−16, 20, and 32). It was worth pointing out that in the reaction of 12 specific *β*-aryl enones, complex **IX** consistently provided better enantioselectivities than the very related complex **III**[12] under the same conditions. Although the results on hydrophosphination with diphenylphosphine were quite promising, the reactions of chalcone with bis(4-methylphenyl)- and bis(4-methoxyphenyl)-phosphines were somewhat disappointing and the corresponding products were isolated in a rather low yield (23% yield with 83% ee, entry 34) or with a rather low enantioselectivity (26% ee, entry 35).

On the other hand, pyridine-functionalized chiral phosphines are a type of important bidentate N,P ligand in organometallic chemistry and are widely used in asymmetric catalysis.[15] Therefore, in the following experiments pyridinyl was introduced into the enone substrates and hydrophosphination of 2-alkenoylpyridines was examined (Table 3). At first, the addition of diphenylphosphine to (*E*)-2-(3-phenylacryloyl)pyridine was carried out under the aforementioned optimized conditions. The reaction proceeded well to provide the desired product in a 95% yield, although the substrate has a strong coordination ability to the Pd catalyst and the enantioselectivity was just 78% ee (Table 3, entry 1). The results (especially the enantioselectivity) were inferior to those of chalcone (Table 2, entry 1), indicating that introduction of pyridinyl to the enone was unfavorable to the stereocontrol of the hydrophosphination. Pleasingly, lowering the temperature from 0 to −10 °C could increase the enantioselectivity to 89% ee (entry 2). A further decrease in temperature did not lead to a much improved ee value (90% ee), while the yield was reduced drastically (67% yield, entry 3). Then reactions of some other 2-alkenoylpyridines with diphenylphosphine were investigated at −10 °C (entries 4−12). The substrates that contain diverse *β*-aryl with an electron-withdrawing or -donating group such as bromo, nitro, methyl, and methoxy

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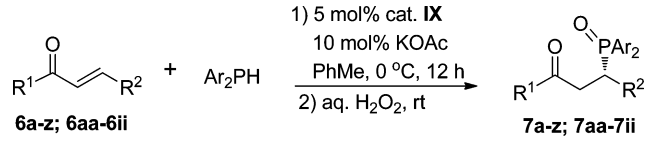
Table 2. Enantioselective Hydrophosphination of *β*-Aryl Enones with Diarylphosphines Catalyzed by the PCN Pincer Pd(II) Complex IX[a]



entry	R^1	R^2	Ar	product	yield (%)[b]	*ee* (%)[c,d]
1	Ph	Ph	Ph	**7a**	99(94[e])	92(89[e])
2	Ph	*p*-BrC_6H_4	Ph	**7b**	94[e]	91[e]
3	Ph	*m*-BrC_6H_4	Ph	**7c**	98	96
4	Ph	*p*-FC_6H_4	Ph	**7d**	92	92
5[f]	Ph	*p*-$O_2NC_6H_4$	Ph	**7e**	99(99[e])	95(82[e])
6	Ph	*m*-$O_2NC_6H_4$	Ph	**7f**	97	90
7	Ph	*p*-MeC_6H_4	Ph	**7g**	98(80[e])	94(86[e])
8	Ph	*p*-$MeOC_6H_4$	Ph	**7h**	92	86
9	Ph		Ph	**7i**	99	81
10	Ph		Ph	**7j**	59	82
11	Ph		Ph	**7k**	80	88
12	Ph	*o*-$MeOC_6H_4$	Ph	**7l**	>99	54
13	Ph	*o*-MeC_6H_4	Ph	**7m**	82	63
14	Me	Ph	Ph	**7n**	99(78[e])	97(92[e])
15	Me	*p*-BrC_6H_4	Ph	**7o**	90[e]	96[e]
16	Me	*p*-$O_2NC_6H_4$	Ph	**7p**	91[e]	97[e]
17	Me	*m*-$O_2NC_6H_4$	Ph	**7q**	98	96
18	Me	*p*-MeC_6H_4	Ph	**7r**	94	93
19	Me	*p*-FC_6H_4	Ph	**7s**	90	93
20	Me	*p*-ClC_6H_4	Ph	**7t**	97(75[e])	97(91[e])
21	Me	*p*-$MeOC_6H_4$	Ph	**7u**	66	96
22	*p*-$MeOC_6H_4$	Ph	Ph	**7v**	>99	95

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Table 2. continued

entry	R^1	R^2	Ar	product	yield (%)[b]	*ee* (%)[c,d]
23	*p*-$MeOC_6H_4$	*p*-$O_2NC_6H_4$	Ph	**7w**	>99(95[e])	94(84[e])
24	*p*-$MeOC_6H_4$	*p*-MeC_6H_4	Ph	**7x**	90	91
25	*p*-$MeOC_6H_4$	*m*-BrC_6H_4	Ph	**7y**	87	89
26	*p*-$MeOC_6H_4$	*p*-BrC_6H_4	Ph	**7z**	24	90
27	*p*-$MeOC_6H_4$	*p*-FC_6H_4	Ph	**7aa**	91	90
28	*p*-$NO_2C_6H_4$	Ph	Ph	**7bb**	99(98[e])	85(75[e])
29	*p*-$NO_2C_6H_4$	*p*-BrC_6H_4	Ph	**7cc**	98	88
30	*p*-BrC_6H_4	Ph	Ph	**7dd**	>99	92
31	*p*-BrC_6H_4	*p*-BrC_6H_4	Ph	**7ee**	99	92
32	^{i}Bu	*p*-$O_2NC_6H_4$	Ph	**7ff**	>99[e]	98[e]
33	^{i}Bu	Ph	Ph	**7gg**	47	80
34	Ph	Ph	*p*-MeC_6H_4	**7hh**	23	83
35	Ph	Ph	*p*-$MeOC_6H_4$	**7ii**	75	26

[a]Hydrophosphination reactions were performed with Ar_2PH (0.2 mmol) and *β*-aryl enones (0.3 mmol) in the presence of complex **IX** (5 mol %) and KOAc base (10 mol %) in 2 mL of toluene at 0 °C for 12 h. [b]Isolated yields. [c]Determined by chiral HPLC. [d]The absolute configurations of the products were assigned to be *S* by comparison of optical rotations with those in refs 5b and12 or by analogy. [e]Using 2 mol % of the catalyst **IX**. [f]The trivalent phosphine product without oxidation could be isolated in 80% yield.

uniformly afforded the corresponding chiral phosphine oxides in good yields and stereoselectivities (81−92% yields, 73−95% ees, entries 4 and 6−9). Even *β*-heteroaryl species such as *β*-furyl and *β*-thienyl could also be tolerated and good enantioselectivities were still obtained (82% ee, entries 10 and 11). However, the stereocontrol was rather bad when the *β*-aryl bears an ortho substitutent (38% ee, entry 5) or the *β*-aryl is a 2-naphthyl group (46% ee, entry 12). A similar phenomenon was observed in the cases of enones without a pyridinyl moiety (Table 2, entries 12 and 13).

To further explore the potential of PCN pincer Pd(II) complexes in the hydrophosphination, the enone substrates were extended to (*E*)-2-alkenoylpyridine *N*-oxides. Meanwhile, it was reported in the literature that the *N*-oxides afforded much higher enantioselectivities than the corresponding nonoxidized 2-alkenoylpyridines under some circumstances, such as in the Michael type reaction with indoles.[16] A brief survey of the pincer Pd complexes with aryl-based phosphinite−imidazoline ligands indicated that complex **IX** was still the most stereoselective catalyst for the reaction of (*E*)-2-(3-phenylacryloyl)-pyridine *N*-oxide, though the highest ee value was only 63% (Table 4, entries 1−5). Then hydrophosphination of several other 2-alkenoylpyridine *N*-oxides with diphenylphosphine was carried out (entries 6−17). In general the enantioselectivities were not very high, which might be caused by the weak and inappropriate coordination of pyridine N→O to the catalyst. Good stereocontrol could be achieved when the aryl (R) in the pyridine *N*-oxides was *p*-BrC_6H_4, *m*-$O_2NC_6H_4$, or *m*-$MeOC_6H_4$ (79−83% ees, entries 6, 10, and 13). Moderate enantioselectivities were observed in the cases of *p*-ClC_6H_4, *p*-$O_2NC_6H_4$, *p*-MeC_6H_4, *p*-$MeOC_6H_4$, and 2-furyl (55−77% ees, entries 8, 9, 11, 12, and 14). Similar to the above hydrophosphination, the introduction of an ortho substituent such as Br into the aryl resulted in greatly reduced enantioselectivity (entry 7 vs 6). (*E*)-2-(3-(2-Thienyl)acryloyl)pyridine and (*E*)-2-(3-(1-naphthyl)-acryloyl)pyridine *N*-oxides were also not appropriate substrates (21% and 9% ees, respectively, entries 15 and 17). Interestingly, in the case of (*E*,*E*)-2-(5-phenyl-2,4-pentadienoyl)pyridine *N*-oxide the expected 1,4-addition product was obtained in 77% yield with 72% ee and the 1,6-adduct was not isolated (entry 16).

To determine the absolute configurations of the catalytic products and illustrate the utility of the current method, the pyridine-functionalized phosphine oxide **7pp** was treated with $PdCl_2$ for complexation. After the mixture was stirred in CH_2Cl_2 at room temperature for 18 h, the chiral $NC_{sp^3}O$ pincer Pd(II) complex **8** was easily isolated, albeit in a modest yield (Scheme 3). The formation of this complex resulted from the expected coordinations of the pyridine nitrogen and phosphine oxide oxygen to Pd(II) as well as activation of the sp^3 C−H bond, which was somewhat unexpected. This interesting tridentate pincer type of bonding was unambiguously confirmed by X-ray single-crystal analysis (Figure 2). Notably, reports on

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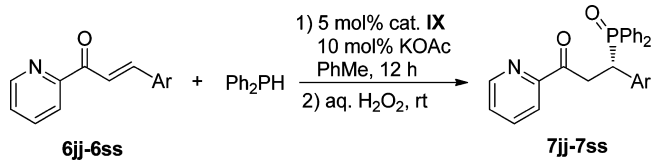
Table 3. Enantioselective Hydrophosphination of 2-Alkenoylpyridines with Diphenylphosphine Catalyzed by the PCN Pincer Pd(II) Complex IX[a]



entry	Ar	temp (°C)	product	yield (%)[b]	ee (%)[c,d]
1	Ph	0	**7jj**	95	78
2	Ph	-10	**7jj**	95	89
3	Ph	-20	**7jj**	67	90
4	*p*-BrC_6H_4	-10	**7kk**	92	87
5	*o*-BrC_6H_4	-10	**7ll**	74	38
6	*m*-BrC_6H_4	-10	**7mm**	86	85
7	*p*-$O_2NC_6H_4$	-10	**7nn**	90	88
8	*p*-MeC_6H_4	-10	**7oo**	81	73
9	*p*-$MeOC_6H_4$	-10	**7pp**	85	95
10		-10	**7qq**	87	82
11		-10	**7rr**	67	82
12		-10	**7ss**	55	46

[a]Hydrophosphination reactions were performed with Ph_2PH (0.2 mmol) and 2-alkenoylpyridines (0.3 mmol) in the presence of complex **IX** (5 mol %) and KOAc base (10 mol %) in 2 mL of toluene for 12 h. [b]Isolated yields. [c]Determined by chiral HPLC. [d]The absolute configuration of the product in entry 9 was determined to be *S* according to the X-ray crystal diffraction analysis of its complex with Pd(II) (vide infra). Those of the other products were assigned to be *S* by analogy.

the sp^3-carbometalated $DC_{sp^3}D$ (D and the undermentioned D′ denote donor atoms such as N, P, O, etc.) pincer Pd(II) complexes[17] remain rare, although the related aryl-based $DC_{sp^2}D$ pincers with sp^2-hybridized carbon have been studied extensively. Moreover, to the best of our knowledge, there has been no report on the chiral $DC_{sp^3}D$ and $DC_{sp^3}D'$ (D ≠ D′) Pd pincers. Thus, complex **8** represents the first example of the $DC_{sp^3}D'$ type. In addition, the X-ray single-crystal structure of complex **8** (Figure 2) showed clearly the *R*,*R* configurations of the two C stereocenters, including the newly formed center in this complex. On the basis of the X-ray results, the absolute configuration of the catalytic product **7pp** was assigned to be *S*. As a preliminary investigation, complex **8** was used as the catalyst for the hydrophosphination of chalcone with Ph_2PH under the same conditions as shown in Tables 1 and 2. It was found that complex **8** was an active but not stereoselective catalyst for the reaction, giving almost racemic product (2% ee) in 80% yield.

In addition to various enones, hydrophosphinations of *α*,*β*-unsaturated carboxylic esters and nitroalkenes with diphenylphosphine by using the PCN pincer Pd(II) complex **IX** as the catalyst were briefly investigated. It was found that no reaction occurred when the addition of Ph_2PH to *trans*-phenyl cinnamate was carried out in toluene at 0 °C or room temperature under conditions similar to those above. However, the reaction did occur with *tert*-amyl alcohol as the solvent at room temperature, giving the desired adduct in an 18% yield with 83% ee (Scheme 4). Finally, *trans*-*β*-nitrostyrene could react smoothly with diphenylphosphine in toluene at 0 °C to afford the expected product in 98% yield. Unfortunately, the ee value was only 14% (Scheme 5).

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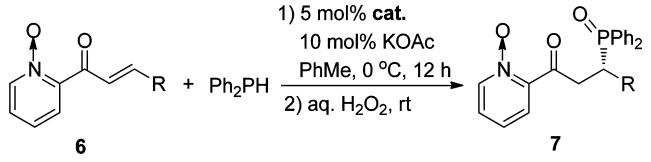
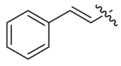
Table 4. Enantioselective Hydrophosphination of 2-Alkenoylpyridine *N*-Oxides with Diphenylphosphine Catalyzed by PCN Pincer Pd(II) Complexes[a]



entry	cat.	R	product	yield (%)[b]	ee (%)[c,d]
1	**IV**	Ph	**7jj'**	73	43
2	**V**	Ph	**7jj'**	63	28
3	**IX**	Ph	**7jj'**	82	63
4	**X**	Ph	**7jj'**	73	49
5	**XIII**	Ph	**7jj'**	92	47
6	**IX**	*p*-BrC_6H_4	**7kk'**	83	83
7	**IX**	*o*-BrC_6H_4	**7ll'**	54	18
8	**IX**	*p*-ClC_6H_4	**7tt**	55	68
9	**IX**	*p*-$O_2NC_6H_4$	**7nn'**	69	76
10	**IX**	*m*-$O_2NC_6H_4$	**7uu**	90	79
11	**IX**	*p*-MeC_6H_4	**7oo'**	81	59
12	**IX**	*p*-$MeOC_6H_4$	**7pp'**	65	77
13	**IX**	*m*-$MeOC_6H_4$	**7vv**	88	80
14	**IX**		**7qq'**	89	55
15	**IX**		**7rr'**	80	21
16	**IX**		**7ww**	77	72
17	**IX**		**7ss'**	80	9[e]

[a]Hydrophosphination reactions were performed with Ph_2PH (0.2 mmol) and 2-alkenoylpyridine *N*-oxides (0.3 mmol) in the presence of pincer Pd(II) complex (5 mol %) and KOAc (10 mol %) in 2 mL of toluene at 0 °C for 12 h. [b]Isolated yields. [c]Determined by chiral HPLC. [d]The absolute configurations of the products were assigned to be *S* by analogy. [e]The absolute configuration was assigned to be *R*.

On the basis of the literature reports[5b] and our previous results[12] on the pincer Pd(II) catalyzed hydrophosphination of enones, a plausible catalytic cycle for the current hydrophosphination is proposed in Scheme 6. First, the chloride in the PCN pincer Pd(II) complex **IX** was replaced by the acetate to afford the Pd-OAc complex in the presence of KOAc. Second, the transphosphination reaction occurred between the Pd-OAc complex and diarylphosphine, giving a Pd-PAr_2

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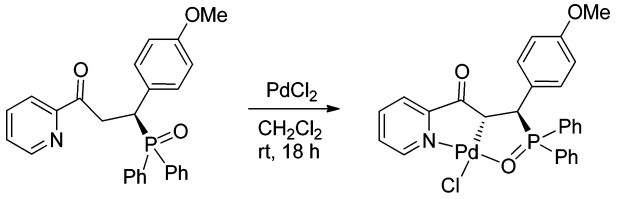
Scheme 3. Synthesis of the New Chiral $NC_{sp^3}O$ Pincer Pd(II) Complex 8 on the Basis of the Obtained Pyridine-Functionalized Phosphine Oxide 7pp



7pp **8** (35% yield)

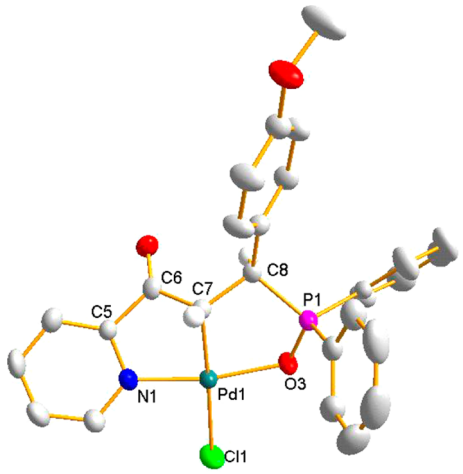


Figure 2. Molecular structure of the $NC_{sp^3}O$ pincer Pd(II) complex **8**. Hydrogen atoms, except for those on the two C stereocenters, are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd(1)−C(7) 2.040(3), Pd(1)−N(1) 2.007(3), Pd(1)−O(3) 2.076(2), Pd(1)−Cl(1) 2.3832(10); C(7)−Pd(1)−N(1) 81.76(13), C(7)−Pd(1)−O(3) 87.38(11), O(3)−Pd(1)−Cl(1) 95.09(7), N(1)−Pd(1)−Cl(1) 95.86(9), N(1)−Pd(1)−O(3) 168.77(10), C(7)−Pd(1)−Cl(1) 176.98(10).

intermediate. Then, nucleophilic attack of the diarylphosphido group on palladium at the enone produced an oxa-π-allylpalladium intermediate, which underwent protonolysis with acetic acid, leading to the formation of the phosphine adduct along with regeneration of the active pincer Pd-OAc catalyst. The possible stereochemical pathway for the formation of *S* product is also shown in Scheme 7. According to the X-ray single-crystal structure of complex **IX**, the central aryl ring, the imidazoline ring, and the two five-membered palladacycles are approximately coplanar. The Pd(II) center adopts a typical distorted-square-planar configuration. Thus, to minimize the unfavorable steric repulsions between the R^2 substituent at the β position (or the R^1 attached to carbonyl group) of the enone and the phenyl group on the imidazoline ring of the catalyst, the enone substrate approaches the Pd-PPh_2 intermediate with its *Si* face preferentially; this facial selectivity leads to the formation of *S* isomers.

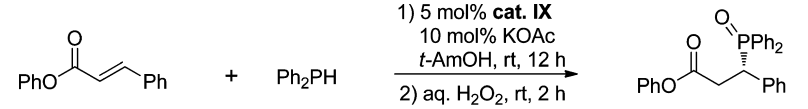
CONCLUSIONS

In summary, we have synthesized and fully characterized eight new chiral PCN pincer Pd(II) complexes. These complexes were found to be able to catalyze the enantioselective hydrophosphination of enones, of which complex **IX** displayed the best stereocontrol. By use of complex **IX** as the catalyst, the reactions of various enones with diphenylphosphine could easily afford the optically active phosphine derivatives in high yields with excellent enantioselectivities (up to 98% ee). In particular, heteroaryl-containing enones such as 2-alkenoylpyridines that may bind tightly to the catalyst were also tolerated, producing the corresponding pyridine-functionalized chiral phosphine oxides in good yields with good enantioselectivities. In addition, it was found that the obtained pyridine-functionalized phosphine oxide acted as a $NC_{sp^3}O$ pincer preligand in the reaction with $PdCl_2$, which illustrated preliminarily the utility of the current hydrophosphination. The formed pincer Pd(II) complex represented the first example of an sp^3-carbometalated chiral $DC_{sp^3}D'$ Pd pincer. Further efforts to optimize the synthetic procedure for the chiral $NC_{sp^3}O$ Pd pincers and synthesize complexes with other metals, including achiral ones, as well as their catalytic applications are currently in progress.

EXPERIMENTAL SECTION

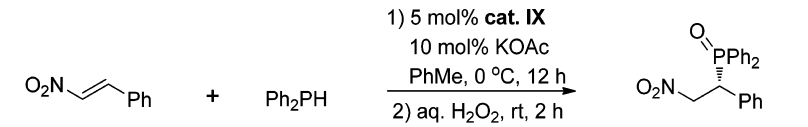
General Procedures. Solvents were dried with standard methods and freshly distilled prior to use if needed. 2-Acetylpyridine *N*-oxide,[18] 2-alkenoylpyridines and the corresponding *N*-oxides,[16] other enone substrates,[19] and bis(4-methoxyphenyl)phosphine[20] were prepared according to the literature methods. All other chemicals were used as purchased. NMR spectra were recorded with $CDCl_3$ as the solvent and TMS as an internal standard for ^1H and ^{13}C NMR and 85% H_3PO_4 as an external standard for $^{31}P\{^1H\}$ NMR. The ^1H and ^{13}C NMR spectra of the new compounds were assigned by using a combination of ^{13}C

Scheme 4. Enantioselective Hydrophosphination of *trans*-Phenyl Cinnamate with Diphenylphosphine Catalyzed by the PCN Pincer Pd(II) Complex IX



0.24 mmol (1.2 equiv.) 0.2 mmol 18% yield with 83% ee

Scheme 5. Enantioselective Hydrophosphination of *trans*-β-Nitrostyrene with Diphenylphosphine Catalyzed by the PCN Pincer Pd(II) Complex IX



0.3 mmol (1.5 equiv.) 0.2 mmol 98% yield with 14% ee

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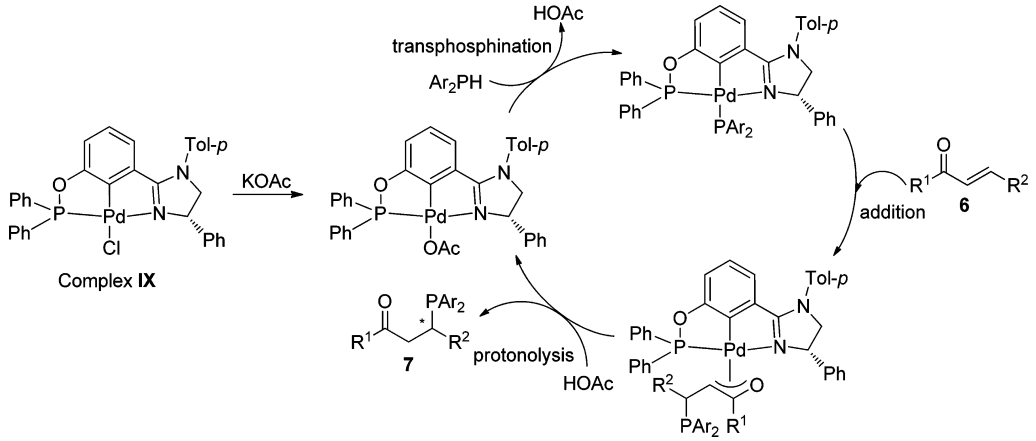
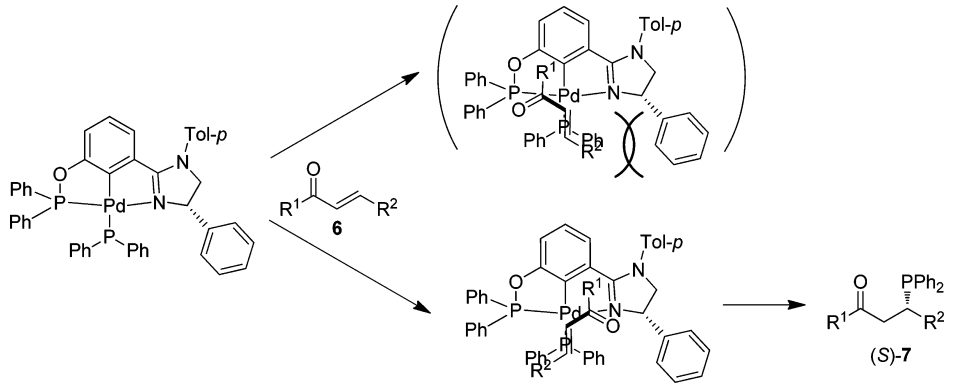
Scheme 6. Proposed Catalytic Cycle for the Hydrophosphination of Enones with Diarylphosphines Catalyzed by the PCN Pincer Pd(II) Complex IX



Scheme 7. Possible Stereochemical Pathway



DEPT (135°) and HSQC experiments if necessary. HRMS were determined on a Q-Tof Micro MS/MS System ESI spectrometer.

Synthesis of PCN Pincer Pd(II) Complexes VI–VIII with Aryl-Based Aminophosphine-Imidazoline Ligands. The complexes were synthesized according to the procedure previously reported by us.[12] The analytical data of the new compounds are given as follows.

*(S)-1-(2,6-Diisopropylphenyl)-2-(3-nitrophenyl)-4-phenyl-4,5-dihydro-1H-imidazole (**2b**).* Purified by column chromatography on silica gel with EtOAc/petroleum ether (1/30) as eluent; yellow solid (2.18 g, 5.10 mmol, 51% based on the 3-nitrobenzamido alcohol **1a**); mp 118–119 °C. $[\alpha]_D^{20}$ = −125° (*c* 0.100, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (s, 1H, Ar-H), 8.16 (dd, *J* = 1.0 and 8.2 Hz, 1H, Ar-H), 8.06 (d, *J* = 8.0 Hz, 1H, Ar-H), 7.47–7.40 (m, 5H, Ph-H), 7.34–7.28 (m, 2H, Ar-H and NAr-H), 7.17 (d, *J* = 7.8 Hz, 1H, NAr-H), 7.10 (d, *J* = 7.7 Hz, 1H, NAr-H), 5.49 (dd, 1H, *J* = 9.6 and 11.2 Hz, NCH), 4.29 (dd, *J* = 10.0 and 11.2 Hz, 1H, NC*H*H), 3.77 (app t, *J* = 9.5 Hz, 1H, NCH*H*), 3.38–3.31 (m, 1H, C*H*(CH_3)$_2$), 3.16–3.09 (m, 1H, C*H*(CH_3)$_2$), 1.29 (d, *J* = 6.8 Hz, 3H, CH(C*H*$_3$)$_2$), 1.07 (d, *J* = 6.6 Hz, 3H, CH(C*H*$_3$)$_2$), 1.05 (d, *J* = 6.5 Hz, 3H, CH(C*H*$_3$)$_2$), 0.91 (d, *J* = 6.8 Hz, 3H, CH(C*H*$_3$)$_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.2, 147.5, 147.4, 147.0, 144.1, 135.3, 134.7, 132.1, 129.1, 129.0, 128.8, 127.4, 126.8, 124.8, 124.7, 123.5, 68.0, 63.1, 28.15, 28.12, 25.7, 25.4, 23.2, 23.0. HRMS (positive ESI): $[M + H]^+$ calcd for $C_{27}H_{30}N_3O_2$ 428.2338, found 428.2330.

*(S,S)-2-(3-Nitrophenyl)-4,5-diphenyl-1-(p-tolyl)-4,5-dihydro-1H-imidazole (**2c**).* With EtOAc/petroleum ether (1/6) as eluent; yellow solid (3.73 g, 8.60 mmol, 86% based on the 3-nitrobenzamido alcohol **1b**); mp 52–53 °C. $[\alpha]_D^{20}$ = +233° (*c* 0.100, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.62 (s, 1H, Ar-H), 8.21 (dd, *J* = 3.2 and 8.2 Hz, 1H, Ar-H), 8.02 (d, *J* = 7.8 Hz, 1H, Ar-H), 7.49–7.27 (m, 11H, Ph-H and Ar-H), 6.89 (d, *J* = 8.2 Hz, 2H, NAr-H), 6.67 (d, *J* = 8.2 Hz, 2H, NAr-H), 5.17 (d, 1H, *J* = 7.4 Hz, NCH), 4.74 (d, *J* = 7.4 Hz, 1H, NCH), 2.18 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.5, 148.1, 143.0, 142.8, 140.1, 135.7, 135.0, 133.0, 129.9, 129.3, 129.2, 128.9, 128.1, 127.7, 126.9, 126.6, 124.9, 124.8, 124.2, 79.4, 78.7, 20.9. HRMS (positive ESI): $[M + H]^+$ calcd for $C_{28}H_{24}N_3O_2$ 434.1869, found 434.1866.

*(S)-3-(1-(2,6-Diisopropylphenyl)-4-phenyl-4,5-dihydro-1H-imidazol-2-yl)aniline (**3b**).* With EtOAc/petroleum ether (1/5) as eluent; yellow solid (0.78 g, 1.96 mmol, 84% based on **2b**); mp 57–58 °C. $[\alpha]_D^{20}$ = −79° (*c* 0.100, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, *J* = 7.1 Hz, 2H, Ph-H), 7.38 (t, *J* = 7.6 Hz, 2H, Ph-H), 7.30–7.24 (m, 2H, Ar-H and Ph-H), 7.13 (dd, *J* = 1.5 and 7.7 Hz, 1H, NAr-H), 7.09–7.06 (m, 2H, NAr-H and Ar-H), 6.90 (t, *J* = 7.8 Hz, 1H, NAr-H), 6.68–6.66 (m, 1H, Ar-H), 6.60–6.57 (m, 1H, Ar-H), 5.40 (dd, *J* = 9.0 and 11.3 Hz, 1H, NCH), 4.19 (dd, *J* = 9.5 and 11.3 Hz, 1H, NC*H*H), 3.66 (app t, *J* = 9.3 Hz, 1H, NCH*H*), 3.53 (br s, 2H, NH_2), 3.39–3.32 (m, 1H, C*H*(CH_3)$_2$), 3.19–3.12 (m, 1H, C*H*(CH_3)$_2$), 1.26 (d, *J* = 6.9 Hz, 3H, CH(C*H*$_3$)$_2$), 1.05 (d, *J* = 6.6 Hz, 3H, CH(C*H*$_3$)$_2$), 1.03 (d, *J* = 6.5 Hz, 3H, CH(C*H*$_3$)$_2$), 0.92 (d, *J* = 6.8 Hz, 3H, CH(C*H*$_3$)$_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.5, 147.5, 147.1, 146.1, 144.8, 136.4, 131.0, 128.6, 128.5, 128.3, 127.1, 126.9, 124.5, 124.4, 118.8, 116.7, 115.7, 67.5, 63.2, 28.04, 28.02, 25.6, 25.3, 23.5, 23.3. HRMS (positive ESI): $[M + H]^+$ calcd for $C_{27}H_{32}N_3$ 398.2596, found 398.2594.

*(S,S)-3-(4,5-Diphenyl-1-(p-tolyl)-4,5-dihydro-1H-imidazol-2-yl)-aniline (**3c**).* With EtOAc/petroleum ether (1/2) as eluent; white solid (0.65 g, 1.61 mmol, 70% based on **2c**); mp 81–82 °C. $[\alpha]_D^{20}$ = +327° (*c* 0.100, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43–7.39 (m, 4H, Ph-H), 7.36–7.24 (m, 6H, Ph-H), 7.20 (t, *J* = 1.8 Hz, 1H, Ar-H), 7.06 (t, *J* = 7.7 Hz, 1H, Ar-H) 7.02–6.99 (m, 1H, Ar-H), 6.85 (d, *J* = 8.2 Hz, 2H, NAr-H), 6.70–6.67 (m, 1H, Ar-H), 6.65 (d, *J* = 8.2 Hz, 2H, NAr-H), 5.05 (d, *J* = 6.2 Hz, 1H, NCH), 4.69 (d, *J* = 6.2 Hz, 1H, NCH), 3.68 (br s, 2H, NH_2), 2.18 (s, 3H, CH_3). ^{13}C NMR (100 MHz,

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$CDCl_3$): δ 163.5, 146.4, 143.9, 143.7, 141.0, 134.1, 132.0, 129.4, 129.1, 128.7, 127.7, 127.4, 126.6, 126.5, 123.6, 119.5, 117.0, 115.7, 78.45, 78.37, 20.8. HRMS (positive ESI): $[M + H]^+$ calcd for $C_{28}H_{26}N_3$ 404.2127, found 404.2124.

*(S)-2-(4-Phenyl-1-(p-tolyl)-4,5-dihydro-1H-imidazol-2-yl)-6-((di-tert-butylphosphino)amino)phenylpalladium(II) Chloride (**VI**).* With CH_2Cl_2 as eluent; yellow solid (67.4 mg, 0.11 mmol, 22% based on **3a**); mp >290 °C. $[\alpha]_D^{20}$ = +148° (*c* 0.100, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, *J* = 7.5 Hz, 2H, Ph-H), 7.32 (t, *J* = 7.5 Hz, 2H, Ph-H), 7.24−7.15 (m, 5H, Ph-H and NAr-H), 6.64−6.56 (m, 2H, Ar-H), 5.99 (d, *J* = 7.5 Hz, 1H, Ar-H), 5.52 (dd, *J* = 3.8 and 10.7 Hz, 1H, NCH), 4.41 (app t, *J* = 10.2 Hz, 1H, NC*H*H), 4.22 (s, 1H, NH), 3.93 (dd, *J* = 3.8 and 9.7 Hz, 1H, NCH*H*), 2.39 (s, 3H, CH_3), 1.43 (d, *J* = 7.6 Hz, 9H, $C(CH_3)_3$), 1.39 (d, *J* = 7.6 Hz, 9H, $C(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.7 (d, J_{CP} = 2.2 Hz), 155.4 (d, J_{CP} = 18.5 Hz), 150.2 (d, J_{CP} = 2.6 Hz), 143.5, 137.9, 137.8, 135.0, 130.3, 128.4, 127.2, 126.8, 126.6, 124.2, 117.7, 111.1 (d, J_{CP} = 15.4 Hz), 64.3 (d, J_{CP} = 2.8 Hz), 63.3 (d, J_{CP} = 2.0 Hz), 38.2 (d, J_{CP} = 1.8 Hz), 37.9 (d, J_{CP} = 1.9 Hz), 28.36 (d, J_{CP} = 5.5 Hz), 28.30 (d, J_{CP} = 5.4 Hz), 21.2. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 139.1. Anal. Calcd for $C_{30}H_{37}ClN_3PPd$: C, 58.83; H, 6.09; N, 6.86. Found: C, 58.68; H, 6.23; N, 6.74.

*(S)-2-(1-(2,6-Diisopropylphenyl)-4-phenyl-4,5-dihydro-1H-imidazol-2-yl)-6-((diphenylphosphino)amino)phenylpalladium(II) Chloride (**VII**).* With CH_2Cl_2 as eluent; yellow solid (184.3 mg, 0.255 mmol, 51% based on **3b**); mp >290 °C. $[\alpha]_D^{20}$ = +199° (*c* 0.100, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 7.90−7.82 (m, 4H, PPh-H), 7.52 (d, *J* = 7.3 Hz, 2H, Ph-H), 7.44−7.32 (m, 9H, PPh-H and NAr-H), 7.25−7.20 (m, 3H, Ph-H), 6.64−6.57 (m, 2H, Ar-H), 5.65−5.61 (m, 2H, Ar-H and NCH), 4.81 (s, 1H, NH), 4.35 (app t, *J* = 10.6 Hz, 1H, NC*H*H), 3.80 (dd, *J* = 4.6 and 9.9 Hz, 1H, NCH*H*), 3.06−2.99 (m, 2H, C*H*$(CH_3)_2$), 1.24 (d, *J* = 6.9 Hz, 3H, CH(CH_3)$_2$), 1.06 (d, *J* = 6.8 Hz, 3H, CH(CH_3)$_2$), 0.97 (d, *J* = 6.9 Hz, 3H, CH(CH_3)$_2$), 0.93 (d, *J* = 6.8 Hz, 3H, CH(CH_3)$_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.7, 153.2 (d, J_{CP} = 24.3 Hz), 151.8, 147.9, 147.7, 143.8, 134.8, 134.2 (d, J_{CP} = 51.9 Hz), 133.5 (d, J_{CP} = 57.4 Hz), 133.2, 132.0 (d, J_{CP} =13.8 Hz), 131.9 (d, J_{CP} = 13.9 Hz), 131.0 (d, J_{CP} = 3.8 Hz), 129.7, 128.7 (d, J_{CP} = 11.5 Hz), 128.6 (d, J_{CP} = 8.9 Hz), 127.3, 126.4, 125.0, 124.8, 124.4, 117.6, 112.6 (d, J_{CP} = 18.2 Hz), 63.8, 63.7, 28.3, 28.2, 25.3, 24.2, 23.9, 23.7. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 91.4. Anal. Calcd for $C_{39}H_{39}ClN_3PPd$: C, 64.82; H, 5.44; N, 5.82. Found: C, 64.84; H, 5.58; N, 5.67.

*(S,S)-2-(4,5-Diphenyl-1-(p-tolyl)-4,5-dihydro-1H-imidazol-2-yl)-6-((diphenylphosphino)amino)phenylpalladium(II) Chloride (**VIII**).* With CH_2Cl_2 as eluent; yellow solid (72.9 mg, 0.10 mmol, 20% based on **3c**); mp >290 °C. $[\alpha]_D^{20}$ = +140° (*c* 0.100, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 7.87−7.77 (m, 4H, PPh-H), 7.43 (d, *J* = 7.2 Hz, 2H, Ph-H), 7.38−7.06 (m, 18H, PPh-H, Ph-H and NAr-H), 6.70−6.63 (m, 2H, Ar-H), 6.04 (d, *J* = 7.3 Hz, 1H, Ar-H), 5.36 (d, *J* = 5.4 Hz, 1H, NCH), 5.12 (s, 1H, NH), 4.74 (d, *J* = 5.4 Hz, 1H, NCH), 2.31 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.8 (d, J_{CP} = 2.8 Hz), 153.8 (d, J_{CP} = 24.3 Hz), 152.0, 143.2, 140.8, 138.0, 137.0, 134.9, 134.1 (d, J_{CP} = 52.6 Hz), 133.7 (d, J_{CP} = 54.1 Hz), 132.1 (d, J_{CP} = 13.6 Hz), 132.0 (d, J_{CP} = 13.5 Hz), 130.8 (d, J_{CP} = 3.7 Hz), 130.1, 129.1, 128.7 (d, J_{CP} = 10.0 Hz), 128.6 (d, J_{CP} = 11.4 Hz), 128.4, 127.6, 127.2, 126.5, 124.9, 118.1, 112.9 (d, J_{CP} = 18.3 Hz), 80.5 (d, J_{CP} = 3.3 Hz), 74.2, 21.2. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 91.5. Anal. Calcd for $C_{40}H_{33}ClN_3PPd$: C, 65.94; H, 4.57; N, 5.77. Found: C, 65.84; H, 4.58; N, 5.67.

Synthesis of PCN Pincer Pd(II) Complexes IX−XIII with Aryl-Based Phosphinite−Imidazoline Ligands. The complexes were synthesized according to the procedure previously reported by us.[14] The analytical data of the new compounds are given as follows.

*(S)-3-Acetoxy-N-(2-hydroxy-1-phenylethyl)benzamide (**4a**).* With EtOAc/petroleum ether (1/2) as eluent; white solid (2.51 g, 8.39 mmol, 84% based on 3-acetoxybenzoyl chloride); mp 119−120 °C. $[\alpha]_D^{20}$ = −21° (*c* 0.340, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, *J* = 8.0 Hz, 1H, Ar-H), 7.53 (t, *J* = 1.8 Hz, 1H, Ar-H), 7.41 (t, *J* = 8.0 Hz, 1H, Ar-H), 7.36−7.27 (m, 5H, Ph-H), 7.22 (ddd, *J* = 0.8, 2.2, and 8.1 Hz, 1H, Ar-H), 7.06 (d, *J* = 6.8 Hz, NH), 5.23−5.19 (m, 1H, C*H*NH), 3.92 (d, *J* = 5.2 Hz, 2H, CH_2OH), 2.58 (br s, 1H, OH), 2.30 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.5, 166.8, 150.8, 138.9, 135.7, 129.7, 128.9, 127.9, 126.7, 125.0, 124.5, 120.7, 66.2, 56.2, 21.1. HRMS (positive ESI): $[M + H]^+$ calcd for $C_{17}H_{18}NO_4$ 300.1236, found 300.1232; $[M + Na]^+$ calcd for $C_{17}H_{17}NNaO_4$ 322.1055, found 322.1099.

*(S)-3-(4-Phenyl-1-(p-tolyl)-4,5-dihydro-1H-imidazol-2-yl)phenol (**5a**).* With EtOAc/petroleum ether (2/1) as eluent; white solid (1.33 g, 4.05 mmol, 54% based on **4a**); mp 87−88 °C. $[\alpha]_D^{20}$ = +229° (*c* 0.464, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 7.41 (d, *J* = 7.2 Hz, 2H, Ph-H), 7.38−7.34 (m, 3H, Ar-H and Ph-H), 7.27 (t, *J* = 7.1 Hz, 1H, Ph-H), 6.94 (d, *J* = 8.0 Hz, 2H, NAr-H), 6.91 (t, *J* = 7.7 Hz, 1H, Ar-H), 6.67−6.64 (m, 3H, NAr-H and Ar-H), 6.60 (d, *J* = 7.6 Hz, 1H, Ar-H), 5.37 (dd, *J* = 7.6 and 10.8 Hz, 1H, NCH), 4.56 (dd, *J* = 9.4 and 10.8 Hz, 1H, NC*H*H), 3.83 (dd, *J* = 7.6 and 9.4 Hz, 1H, NCH*H*), 2.23 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.2, 157.9, 143.7, 139.1, 133.8, 130.3, 129.3, 129.1, 128.7, 127.4, 126.5, 122.8, 119.2, 118.3, 116.6, 65.8, 61.3, 20.8. HRMS (positive ESI): $[M + H]^+$ calcd for $C_{22}H_{21}N_2O$ 329.1654, found 329.1656.

*(S)-3-(1-(2,6-Diisopropylphenyl)-4-phenyl-4,5-dihydro-1H-imidazol-2-yl)phenol (**5b**).* With EtOAc/petroleum ether (2/0.3) as eluent; yellow solid (0.89 g, 2.23 mmol, 30% based on **4a**); mp 167−168 °C. $[\alpha]_D^{20}$ = +291° (*c* 0.100, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 7.89 (t, *J* = 1.8 Hz, 1H, Ar-H), 7.61 (d, *J* = 7.2 Hz, 2H, Ph-H), 7.48 (t, *J* = 7.7 Hz, 2H, Ph-H), 7.35 (t, *J* = 7.4 Hz, 1H, Ph-H), 7.23 (t, *J* = 7.7 Hz, 1H, NAr-H), 7.16 (dd, *J* = 1.6 and 7.7 Hz, 1H, NAr-H), 6.92 (dd, *J* = 1.6 and 7.6 Hz, 1H, NAr-H), 6.78 (t, *J* = 7.9 Hz, 1H, Ar-H), 6.61 (dd, *J* = 1.7 and 8.1 Hz, 1H, Ar-H), 6.30 (d, *J* = 7.7 Hz, 1H, Ar-H), 5.51 (dd, *J* = 9.8 and 11.5, 1H, NCH), 4.45 (dd, *J* = 9.8 and 11.5, 1H, NC*H*H), 3.60−3.50 (m, 2H, NCH*H* and C*H*$(CH_3)_2$), 2.88−2.81 (m, 1H, C*H*$(CH_3)_2$), 1.32 (d, *J* = 6.8 Hz, 3H, CH(CH_3)$_2$), 1.31 (d, *J* = 6.8 Hz, 3H, CH(CH_3)$_2$), 0.96 (d, *J* = 6.8 Hz, 3H, CH(CH_3)$_2$), 0.30 (d, *J* = 6.7 Hz, 3H, CH(CH_3)$_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.8, 158.0, 147.5, 146.9, 144.9, 134.7, 129.5, 128.7, 128.6, 127.3, 126.6, 124.7, 124.2, 118.3, 118.2, 117.5, 65.7, 63.1, 28.2, 28.0, 25.7, 25.3, 23.7, 22.5. HRMS (positive ESI): $[M + H]^+$ calcd for $C_{27}H_{31}N_2O$ 399.2436, found 399.2431.

*(S)-3-(1-Isopropyl-4-phenyl-4,5-dihydro-1H-imidazol-2-yl)phenol (**5c**).* With EtOAc/Et_3N (50/1) as eluent; yellow solid (0.92 g, 3.28 mmol, 44% based on **4a**); mp 45−46 °C. $[\alpha]_D^{20}$ = +86° (*c* 0.100, CH_2Cl_2). ^{1}HNMR (400 MHz, $CDCl_3$): δ 7.41 (d, *J* = 7.2 Hz, 2H, Ph-H), 7.36 (t, *J* = 7.6 Hz, 2H, Ph-H), 7.26−7.21 (m, 2H, Ph-H and Ar-H), 7.07 (t, *J* = 7.8 Hz, 1H, Ar-H), 6.71 (d, *J* = 7.5 Hz, 1H, Ar-H), 6.65 (dd, *J* = 1.8 and 8.2 Hz, 1H, Ar-H), 5.56 (br s, 1H, OH), 5.21 (dd, *J* = 8.4 and 11.4 Hz, 1H, NCH), 3.96 (dd, *J* = 9.8 and 11.4 Hz, 1H, NC*H*H), 3.87−3.80 (m, 1H, C*H*$(CH_3)_2$), 3.38 (app t, *J* = 9.1 Hz, 1H, NCH*H*), 1.14 (d, *J* = 6.7 Hz, 3H, CH(CH_3)), 0.92 (d, *J* = 6.6 Hz, 3H, CH(CH_3)). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.9, 158.7, 144.8, 130.3, 129.2, 128.6, 127.2, 126.4, 118.2, 117.2, 116.8, 65.2, 51.2, 46.6, 20.9, 19.7. HRMS (positive ESI): $[M + H]^+$ calcd for $C_{18}H_{21}N_2O$ 281.1654, found 281.1650.

*(S,S)-3-(4,5-Diphenyl-1-(p-tolyl)-4,5-dihydro-1H-imidazol-2-yl)-phenol (**5d**).* With EtOAc/petroleum ether (1/3) as eluent; white solid (1.28 g, 3.16 mmol, 42% based on **4b**); mp 136−137 °C. $[\alpha]_D^{20}$ = +588° (*c* 0.100, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 7.86 (t, *J* = 1.8 Hz, 1H, Ar-H), 7.49−7.33 (m, 10H, Ph-H), 6.96 (t, *J* = 7.9 Hz, 1H, Ar-H), 6.81 (d, *J* = 8.3 Hz, 2H, NAr-H), 6.78 (d, *J* = 7.6 Hz, 1H, Ar-H), 6.71 (dd, *J* = 1.7 and 8.1 Hz, 1H, Ar-H), 6.58 (d, *J* = 8.3 Hz, 2H, NAr-H), 5.16 (d, *J* = 5.5 Hz, 1H, NCH), 4.72 (d, *J* = 5.5 Hz, 1H, NCH), 2.16 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.3, 158.0, 143.7, 143.3, 139.8, 134.8, 130.7, 129.4, 129.34, 129.28, 128.9, 128.1, 127.6, 126.4, 126.3, 124.0, 119.5, 118.4, 116.9, 78.0, 76.6, 20.8. HRMS (positive ESI): $[M + H]^+$ calcd for $C_{28}H_{25}N_2O$ 405.1967, found 405.1965.

*(S)-2-(4-Phenyl-1-(p-tolyl)-4,5-dihydro-1H-imidazol-2-yl)-6-(diphenylphosphinoxy)phenylpalladium(II) Chloride (**IX**).* With CH_2Cl_2 as eluent; yellow solid (291.1 mg, 0.445 mmol, 81%); mp 248−249 °C. $[\alpha]_D^{20}$ = +187° (*c* 0.070, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 8.03−7.93 (m, 4H, PPh-H), 7.53 (dd, *J* = 1.3, 7.2 Hz, 2H, Ph-H), 7.46−7.43 (m, 6H, PPh-H), 7.36 (t, *J* = 7.5 Hz, 2H, Ph-H), 7.30−7.27 (m, 1H, Ph-H), 7.23 (d, *J* = 8.2 Hz, 2H, NAr-H), 7.18 (d, *J* = 8.2 Hz, 2H, NAr-H), 6.91 (d, *J* = 8.0 Hz, 1H, Ar-H), 6.78

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(dt, J = 1.1, 7.9 Hz, 1H, Ar-H), 6.24 (d, J = 7.6 Hz, 1H, Ar-H), 5.53 (dd, J = 4.4 and 10.9 Hz, 1H, NCH), 4.46 (dd, J = 9.8 and 10.9 Hz, 1H, NCH*H*), 4.01 (dd, J = 4.4 and 9.8 Hz, 1H, NCH*H*), 2.41 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.7, 162.5 (d, J_{CP} = 11.5 Hz), 151.8, 142.9, 138.3, 137.3, 135.4, 133.9 (d, J_{CP} = 51.8 Hz), 133.2 (d, J_{CP} = 53.7 Hz), 131.8, 131.7 (d, J_{CP} = 14.9 Hz), 131.6 (d, J_{CP} = 14.5 Hz), 130.5, 128.8 (d, J_{CP} = 11.3 Hz), 128.7, 127.6, 126.8, 126.7, 125.6, 121.4, 114.6 (d, J_{CP} = 16.6 Hz), 64.2 (d, J_{CP} = 3.4 Hz), 64.0 (d, J_{CP} = 2.6 Hz), 21.2. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 155.0. Anal. Calcd for $C_{34}H_{28}ClN_2OPPd{\cdot}0.75CH_2Cl_2$: C, 58.20; H, 4.15; N, 3.91. Found: C, 58.23; H, 4.52; N, 3.63.

*(S)-2-(4-Phenyl-1-(p-tolyl)-4,5-dihydro-1H-imidazol-2-yl)-6-(di-tert-butylphosphinoxy)phenylpalladium(II) Chloride (**X**).* With CH_2Cl_2 as eluent; yellow solid (175.4 mg, 0.286 mmol, 52%); mp 157−158 °C. $[\alpha]_D^{20}$ = +95° (c 0.100, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, J = 7.3 Hz, 2H, Ph-H), 7.34 (t, J = 7.5 Hz, 2H, Ph-H), 7.27−7.25 (m, 1H, Ph-H), 7.22 (d, J = 8.3 Hz, 2H, NAr-H), 7.17 (d, J = 8.3 Hz, 2H, NAr-H), 6.79 (d, J = 7.9 Hz, 1H, Ar-H), 6.72 (dt, J = 0.8 and 8.0 Hz, 1H, Ar-H), 6.19 (d, J = 7.5 Hz, 1H, Ar-H), 5.50 (dd, J = 4.0 and 10.8 Hz, 1H, NCH), 4.44 (app t, J = 10.3 Hz, 1H, NC*H*H), 3.95 (dd, J = 4.0 and 9.7 Hz, 1H, NCH*H*), 2.40 (s, 3H, CH_3), 1.45 (d, J = 4.4 Hz, 9H, $C(CH_3)_3$), 1.41 (d, J = 4.4 Hz, 9H, $C(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.5 (d, J_{CP} = 2.8 Hz), 164.8 (d, J_{CP} = 7.0 Hz), 151.3, 143.2, 138.1, 137.5, 135.5, 130.4, 128.5, 127.4, 126.8, 126.6, 124.9, 120.7, 113.6 (d, J_{CP} = 14.5 Hz), 64.2 (d, J_{CP} = 3.0 Hz), 63.5 (d, J_{CP} = 2.0 Hz), 39.4 (d, J_{CP} = 16.3 Hz), 39.3 (d, J_{CP} = 16.9 Hz), 27.75 (d, J_{CP} = 5.5 Hz), 27.69 (d, J_{CP} = 5.4 Hz), 21.2. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 210.3. Anal. Calcd for $C_{30}H_{36}ClN_2OPPd$: C, 58.74; H, 5.91; N, 4.57. Found: C, 58.71; H, 6.01; N, 4.35.

*(S)-2-(1-(2,6-Diisopropylphenyl)-4-phenyl-4,5-dihydro-1H-imidazol-2-yl)-6-(diphenylphosphinoxy)phenylpalladium(II) Chloride (**XI**).* With CH_2Cl_2 as eluent; yellow solid (111.4 mg, 0.154 mmol, 28%); mp 276−277 °C. $[\alpha]_D^{20}$ = +165° (c 0.100, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 8.04−7.96 (m, 4H, PPh-H), 7.53 (d, J = 7.3 Hz, 2H, Ph-H), 7.46−7.35 (m, 9H, PPh-H, NAr-H and Ph-H), 7.30−7.22 (m, 3H, Ph-H and NAr-H), 6.90 (d, J = 8.0 Hz, 1H, Ar-H), 6.71 (dt, J = 0.8 and 8.0 Hz, 1H, Ar-H), 5.82 (d, J = 7.7 Hz, 1H, Ar-H), 5.65 (dd, J = 4.8 and 11.3 Hz, 1H, NCH), 4.39 (app t, J = 10.7 Hz, 1H, NC*H*H), 3.83 (dd, J = 4.8 and 10.1 Hz, 1H, NCH*H*), 3.06−2.97 (m, 2H, $CH(CH_3)_2$), 1.24 (d, J = 6.8 Hz, 3H, $CH(CH_3)_2$), 1.05 (d, J = 6.8 Hz, 3H, $CH(CH_3)_2$), 0.99 (d, J = 6.9 Hz, 3H, $CH(CH_3)_2$), 0.91 (d, J = 6.8 Hz, 3H, $CH(CH_3)_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.5 (d, J_{CP} = 2.9 Hz), 162.5 (d, J_{CP} = 11.5 Hz), 151.9, 147.9, 147.6, 143.5, 135.2, 134.0 (d, J_{CP} = 51.8 Hz), 133.5 (d, J_{CP} = 53.2 Hz), 132.9, 131.8 (t, J_{CP} = 2.9 Hz), 131.7 (d, J_{CP} = 14.7 Hz), 131.6 (d, J_{CP} = 14.7 Hz), 130.0, 128.8 (d, J_{CP} = 11.7 Hz), 128.7, 127.5, 126.4, 125.6, 125.1, 124.5, 120.7, 114.8 (d, J_{CP} = 16.8 Hz), 64.0 (d, J_{CP} = 2.6 Hz), 63.6 (d, J_{CP} = 3.3 Hz), 28.32, 28.29, 25.3, 24.2, 23.9, 23.7. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 154.9. Anal. Calcd for $C_{39}H_{38}ClN_2OPPd$: C, 64.74; H, 5.29; N, 3.87. Found: C, 64.78; H, 5.65; N, 3.69.

*(S)-2-(1-Isopropyl-4-phenyl-4,5-dihydro-1H-imidazol-2-yl)-6-(diphenylphosphinoxy)phenylpalladium(II) Chloride (**XII**).* With CH_2Cl_2 as eluent; white solid (109.9 mg, 0.182 mmol, 33%); mp 259−260 °C. $[\alpha]_D^{20}$ = +222° (c 0.100, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 8.01−7.91 (m, 4H, PPh-H), 7.47−7.40 (m, 8H, PPh-H and Ph-H), 7.34−7.22 (m, 4H, Ph-H and Ar-H), 7.11 (t, J = 7.8 Hz, 1H, Ar-H), 7.01 (d, J = 8.0 Hz, 1H, Ar-H), 5.37 (dd, J = 4.8 and 11.4 Hz, 1H, NCH), 4.75−4.68 (m, 1H, $CH(CH_3)_2$), 4.14 (app t, J = 10.7 Hz, 1H, NC*H*H), 3.65 (dd, J = 4.8 and 10.0 Hz, 1H, NCH*H*), 1.31 (d, J = 6.6 Hz, 3H, $CH(CH_3)_2$), 1.28 (d, J = 6.6 Hz, 3H, $CH(CH_3)_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.3 (d, J_{CP} = 2.7 Hz), 162.8 (d, J_{CP} = 11.8 Hz), 151.8, 143.7, 136.0, 134.0 (d, J_{CP} = 51.4 Hz), 133.3 (d, J_{CP} = 53.4 Hz), 131.8, 131.7 (d, J_{CP} = 14.8 Hz), 131.6 (d, J_{CP} = 14.8 Hz), 128.8 (d, J_{CP} = 11.7 Hz), 128.6, 127.4, 126.7, 126.2, 119.9, 114.7 (d, J_{CP} = 16.9 Hz), 62.7 (d, J_{CP} = 2.2 Hz), 53.4 (d, J_{CP} = 3.6 Hz), 46.7, 21.4, 20.2. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 154.6. Anal. Calcd for $C_{30}H_{28}ClN_2OPPd$: C, 59.52; H, 4.66; N, 4.63. Found: C, 59.49; H, 4.95; N, 4.50.

*(S,S)-2-(4,5-Diphenyl-1-(p-tolyl)-4,5-dihydro-1H-imidazol-2-yl)-6-(diphenylphosphinoxy)phenylpalladium(II) Chloride (**XIII**).* With CH_2Cl_2 as eluent; yellow solid (124.4 mg, 0.171 mmol, 31%); mp 154−155 °C. $[\alpha]_D^{20}$ = +111° (c 0.100, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 8.04−7.94 (m, 4H, PPh-H), 7.44−7.27 (m, 17H, PPh-H, Ph-H and NAr-H), 7.17−7.04 (m, 3H, Ph-H), 6.95 (d, J = 8.0 Hz, 1H, Ar-H), 6.80 (t, J = 7.6 Hz, 1H, Ar-H), 6.23 (d, J = 7.7 Hz, 1H, Ar-H), 5.40 (d, J = 5.6 Hz, 1H, NCH), 4.78 (d, J = 5.6 Hz, 1H, NCH), 2.31 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.6 (d, J_{CP} = 2.9 Hz), 162.7 (d, J_{CP} = 11.5 Hz), 152.1, 142.9, 140.6, 138.4, 136.6, 135.6, 133.8 (d, J_{CP} = 52.4 Hz), 133.5 (d, J_{CP} = 53.4 Hz), 131.9 (d, J_{CP} = 1.6 Hz), 131.73 (d, J_{CP} = 14.7 Hz), 131.66 (d, J_{CP} = 14.7 Hz), 130.3, 129.1, 128.9, 128.8 (d, J_{CP} = 12.1 Hz), 128.6, 127.8, 127.2, 126.6, 125.8, 121.5, 114.7 (d, J_{CP} = 16.9 Hz), 80.0 (d, J_{CP} = 3.5 Hz), 74.2 (d, J_{CP} = 2.1 Hz), 21.2. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 154.8. Anal. Calcd for $C_{40}H_{32}ClN_2OPPd{\cdot}0.2CH_2Cl_2$: C, 64.68; H, 4.37; N, 3.75. Found: C, 65.18; H, 4.52; N, 3.63.

General Procedure for the Enantioselective Hydrophosphination of Enones with Diarylphosphines. A mixture of pincer Pd catalyst (5 mol %) and KOAc (2.0 mg, 10 mol %) in toluene (2 mL) was stirred for 30 min at 0 °C under a N_2 atmosphere. Then diphenylphosphine (37.2 mg, 0.2 mmol) was added, and stirring was continued for another 30 min. After addition of enone (0.3 mmol), the resulting mixture was stirred for an additional 12 h at 0 °C and then directly oxidized with H_2O_2 aqueous solution (30%, 60 μL). After this mixture was stirred at room temperature for 2 h, saturated $Na_2S_2O_3$ aqueous solution was added. The organic layer was separated and the aqueous phase extracted with CH_2Cl_2. The combined organic phases were dried (Na_2SO_4), and the volatiles were removed under reduced pressure. Purification by column chromatography on silica gel provided the chiral phosphine oxide products. For the reactions of 2-alkenoylpyridine N-oxides, a mixture of CH_2Cl_2 and acetone (1/1) was used as eluent. For the other enones, CH_2Cl_2/acetone (10/1) was used as eluent unless otherwise stated.

*(S)-3-(Diphenylphosphinyl)-1,3-diphenylpropan-1-one (**7a**).*[5b,12] White solid (81.3 mg, 99%). The enantiomeric excess was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol (85/15) and flow rate 0.2 mL/min and detected at a UV wavelength of 228 nm. Retention times: 30.5 min (major), 36.6 min, 92% ee. $[\alpha]_D^{20}$ = −150° (c 0.200, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 8.00−7.96 (m, 2H), 7.85 (d, J_{HH} = 7.5 Hz, 2H), 7.53−7.43 (m, 6H), 7.40−7.33 (m, 5H), 7.25−7.22 (m, 2H), 7.17−7.10 (m, 3H), 4.47 (ddd, J_{HH} = 9.8 and 2.1 Hz, J_{HP} = 7.1 Hz, 1H, PC*H*CH$_2$), 4.03 (ddd, J_{HH} = 18.1 and 10.4 Hz, J_{HP} = 4.3 Hz, 1H, PCHC*H*H), 3.38 (ddd, J_{HH} = 18.1 and 2.1 Hz, J_{HP} = 11.3 Hz, 1H, PCHCH*H*).

*(S)-3-(4-Bromophenyl)-3-(diphenylphosphinyl)-1-phenylpropan-1-one (**7b**).*[5b,12] White solid (92.0 mg, 94%). The enantiomeric excess was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol (95/5) and flow rate 0.5 mL/min and detected at a UV wavelength of 228 nm. Retention times: 27.9 min (major), 42.8 min, 91% ee. $[\alpha]_D^{20}$ = −153° (c 0.200, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 7.99−7.94 (m, 2H), 7.83 (d, J_{HH} = 7.8 Hz, 2H), 7.53−7.47 (m, 7H), 7.39 (app t, J_{HH} = 7.8 Hz, 3H), 7.31−7.26 (m, 5H), 4.43 (app t, J = 7.7 Hz, 1H, PC*H*CH$_2$), 3.96 (ddd, J_{HH} = 18.0 and 10.4 Hz, J_{HP} = 4.0 Hz, 1H, PCHC*H*H), 3.35 (dd, J = 18.1 and 10.7 Hz, 1H, PCHCH*H*).

*(S)-3-(3-Bromophenyl)-3-(diphenylphosphinyl)-1-phenylpropan-1-one (**7c**).*[5b] White solid (95.9 mg, 98%). The enantiomeric excess was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol (90/10) and flow rate 0.5 mL/min and detected at a UV wavelength of 228 nm. Retention times: 16.5 min (major), 20.8 min, 96% ee. $[\alpha]_D^{20}$ = −156° (c 0.264, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 7.99−7.94 (m, 2H), 7.84 (d, J_{HH} = 7.2 Hz, 2H), 7.53−7.45 (m, 7H), 7.41−7.24 (m, 6H), 7.23 (d, J_{HH} = 7.2 Hz, 1H), 7.02 (t, J_{HH} = 7.9 Hz, 1H), 4.42 (ddd, J_{HH} = 9.8 and 2.4 Hz, J_{HP} = 7.0 Hz, 1H, PC*H*CH$_2$), 3.96 (ddd, J_{HH} = 18.2 and 10.3 Hz, J_{HP} = 4.4 Hz, 1H, PCHC*H*H), 3.39 (ddd, J_{HH} = 18.2 and 2.4 Hz, J_{HP} = 11.2 Hz, 1H, PCHCH*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.3 (d, J_{CP} = 12.9 Hz), 138.4 (d, J_{CP} = 5.5 Hz), 136.2, 133.5, 132.9 (d, J_{CP} = 5.8 Hz), 132.2 (d, J_{CP} = 2.7 Hz), 131.7 (d, J_{CP} = 2.7 Hz), 131.6 (d, J_{CP} = 25.0 Hz), 131.3 (d, J_{CP} = 8.5 Hz), 130.9 (d, J_{CP} = 8.9 Hz), 130.6 (d, J_{CP} = 19.8 Hz), 130.2 (d, J_{CP} = 2.5 Hz), 129.8 (d, J_{CP} = 1.8 Hz),

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129.0 (d, J_{CP} = 11.2 Hz), 128.6, 128.4, 128.3 (d, J_{CP} = 12.0 Hz), 128.1, 122.2 (d, J_{CP} = 2.2 Hz), 40.9 (d, J_{CP} = 67.9 Hz), 38.9. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 33.9.

*(S)-3-(Diphenylphosphinyl)-3-(4-fluorophenyl)-1-phenylpropan-1-one (**7d**).* White solid (78.8 mg, 92%); mp 245−246 °C. The enantiomeric excess was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol (90/10) and flow rate 0.4 mL/min and detected at a UV wavelength of 228 nm. Retention times: 16.0 min (major), 20.7 min, 92% ee. $[\alpha]_D^{20}$ = −147° (*c* 0.270, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 8.00−7.95 (m, 2H), 7.83 (d, J_{HH} = 7.3 Hz, 2H), 7.54−7.45 (m, 6H), 7.40−7.34 (m, 5H), 7.29−7.25 (m, 2H), 6.84 (t, J_{HH} = 8.7 Hz, 2H), 4.45 (ddd, J_{HH} = 10.1 and 2.3 Hz, J_{HP} = 6.8 Hz, 1H, PC*H*CH_2), 3.97 (ddd, J_{HH} = 18.1 and 10.5 Hz, J_{HP} = 4.3 Hz, 1H, PCHC*H*H), 3.36 (ddd, J_{HH} = 18.1 and 2.4 Hz, J_{HP} = 10.8 Hz, 1H, PCHCH*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.6 (d, J_{CP} = 13.4 Hz), 161.9 (dd, J_{CP} = 2.8 Hz, J_{CF} = 244 Hz), 136.3, 133.5, 132.1 (d, J_{CP} = 2.7 Hz), 131.9 (d, J_{CP} = 33.6 Hz), 131.7 (dd, J_{CP} = 6.4 Hz, J_{CF} = 3.3 Hz), 131.6 (d, J_{CP} = 2.6 Hz), 131.4 (dd, J_{CP} = 5.8 Hz, J_{CF} = 7.9 Hz), 131.2 (d, J_{CP} = 8.6 Hz), 130.91 (d, J_{CP} = 28.0 Hz), 130.88 (d, J_{CP} = 9.0 Hz), 129.0 (d, J_{CP} = 11.1 Hz), 128.6, 128.2 (d, J_{CP} = 11.7 Hz), 128.1, 115.2 (dd, J_{CP} = 1.6 Hz, J_{CF} = 21.3 Hz), 40.3 (d, J_{CP} = 69.0 Hz), 39.1. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 34.1. HRMS (positive ESI): $[M + H]^+$ calcd for $C_{27}H_{23}FO_2P$ 429.1420, found 429.1416.

*(S)-3-(Diphenylphosphinyl)-3-(4-nitrophenyl)-1-phenylpropan-1-one (**7e**).*[5b,12] White solid (90.2 mg, 99%). The enantiomeric excess was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol (70/30) and flow rate 0.3 mL/min and detected at a UV wavelength of 228 nm. Retention times: 21.6 min (major), 33.5 min, 95% ee. $[\alpha]_D^{20}$ = −254° (*c* 0.200, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 8.02−7.97 (m, 4H), 7.84 (d, J_{HH} = 7.8 Hz, 2H), 7.60−7.48 (m, 8H), 7.42−7.36 (m, 3H), 7.32−7.29 (m, 2H), 4.57 (ddd, J_{HH} = 9.7 and 2.2 Hz, J_{HP} = 6.7 Hz, 1H, PC*H*CH_2), 4.03 (ddd, J_{HH} = 18.4 and 10.6 Hz, J_{HP} = 4.3 Hz, 1H, PCHC*H*H), 3.43 (ddd, J_{HH} = 18.4 and 2.2 Hz, J_{HP} = 10.5 Hz, 1H, PCHCH*H*).

(S)-3-(Diphenylphosphino)-3-(4-nitrophenyl)-1-phenylpropan-1-one.[5a,d] According to the general procedure, the reaction was stirred at 0 °C for 12 h, and then the solvent was removed under vacuum. The residue was directly purified by column chromatography on silica gel in a glovebox under nitrogen with petroleum ether/EtOAc (5/1) as eluent to afford the trivalent phosphine as the product. White solid (70.3 mg, 80%). ^1H NMR (300 MHz, $CDCl_3$): δ 7.98 (d, J_{HH} = 8.5 Hz, 2H), 7.78 (d, J_{HH} = 7.7 Hz, 2H), 7.71−7.66 (m, 2H), 7.54−7.49 (m, 1H), 7.43−7.31 (m, 7H), 7.21−7.14 (m, 5H), 4.48−4.42 (m, 1H, PC*H*CH_2), 3.73 (ddd, J_{HH} = 17.6 and 11.2 Hz, J_{HP} = 4.2 Hz, 1H, PCHC*H*H), 3.27 (ddd, J_{HH} = 17.6 and 2.5 Hz, J_{HP} = 7.6 Hz, 1H, PCHCH*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.1 (d, J_{CP} = 12.5 Hz), 149.2 (d, J_{CP} = 8.2 Hz), 146.3 (d, J_{CP} = 2.6 Hz), 135.68 (d, J_{CP} = 109.6 Hz), 135.65 (d, J_{CP} = 109.9 Hz), 135.1, 133.7 (d, J_{CP} = 20.5 Hz), 133.3 (d, J_{CP} = 19.3 Hz), 129.9, 129.7 (d, J_{CP} = 7.2 Hz), 129.3, 129.0 (d, J_{CP} = 7.5 Hz), 128.6, 128.3 (d, J_{CP} = 7.3 Hz), 127.9, 123.4, 41.8 (d, J_{CP} = 21.4 Hz), 40.0 (d, J_{CP} = 13.3 Hz). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 0.8.

*(S)-3-(Diphenylphosphinyl)-3-(3-nitrophenyl)-1-phenylpropan-1-one (**7f**).*[21] White solid (88.4 mg, 97%); mp 248−249 °C. The enantiomeric excess was determined on a Daicel Chiralpak AD-H column with hexane/2-propanol (70/30) and flow rate 1.0 mL/min and detected at a UV wavelength of 228 nm. Retention times: 15.8 min (major), 28.1 min, 90% ee. $[\alpha]_D^{20}$ = −185° (*c* 0.270, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 8.17 (d, J_{HH} = 1.7 Hz, 1H), 8.02−7.95 (m, 3H), 7.86−7.79 (m, 3H), 7.57−7.48 (m, 6H), 7.42−7.28 (m, 6H), 4.58 (ddd, J_{HH} = 10.1 and 2.2 Hz, J_{HP} = 6.9 Hz, 1H, PC*H*CH_2), 4.05 (ddd, J_{HH} = 18.4 and 10.7 Hz, J_{HP} = 4.3 Hz, 1H, PCHC*H*H), 3.44 (ddd, J_{HH} = 18.4 and 2.3 Hz, J_{HP} = 10.5 Hz, 1H, PCHCH*H*).

*(S)-3-(Diphenylphosphinyl)-1-phenyl-3-(p-tolyl)propan-1-one (**7g**).*[5b,12] White solid (83.2 mg, 98%). The enantiomeric excess was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol (85/15) and flow rate 0.2 mL/min and detected at a UV wavelength of 228 nm. Retention times: 29.1 min (major), 41.3 min, 94% ee. $[\alpha]_D^{20}$ = −151° (*c* 0.200, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 7.99−7.94 (m, 2H), 7.84 (d, J_{HH} = 7.4 Hz, 2H), 7.52−7.47 (m, 6H), 7.39−7.33 (m, 3H), 7.28−7.25 (m, 4H), 6.95 (d, J_{HH} = 7.9 Hz, 2H), 4.45 (ddd, J_{HH} = 9.9 and 2.3 Hz, J_{HP} = 7.0 Hz, 1H, PC*H*CH_2), 3.99 (ddd, J_{HH} = 18.1 and 10.5 Hz, J_{HP} = 4.3 Hz, 1H, PCHC*H*H), 3.36 (ddd, J_{HH} = 18.1 and 2.3 Hz, J_{HP} = 11.2 Hz, 1H, PCHCH*H*), 2.20 (s, 3H, CH_3).

*(S)-3-(Diphenylphosphinyl)-3-(4-methoxyphenyl)-1-phenylpropan-1-one (**7h**).* White solid (81.1 mg, 92%); mp 227−228 °C. The enantiomeric excess was determined on a Daicel Chiralpak AD-H column with hexane/2-propanol (60/40) and flow rate 1.0 mL/min and detected at a UV wavelength of 228 nm. Retention times: 21.3 min (major), 30.5 min, 86% ee. $[\alpha]_D^{20}$ = −127° (*c* 0.252, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 8.00−7.94 (m, 2H), 7.83 (d, J_{HH} = 7.2 Hz, 2H), 7.52−7.46 (m, 6H), 7.38−7.24 (m, 7H), 6.69 (d, J_{HH} = 8.6 Hz, 2H), 4.43 (ddd, J_{HH} = 10.0 and 2.3 Hz, J_{HP} = 7.0 Hz, 1H, PC*H*CH_2), 3.97 (ddd, J_{HH} = 18.0 and 10.5 Hz, J_{HP} = 4.3 Hz, 1H, PCHC*H*H), 3.68 (s, 3H, OCH_3), 3.34 (ddd, J_{HH} = 18.0 and 2.4 Hz, J_{HP} = 10.9 Hz, 1H, PCHCH*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.8 (d, J_{CP} = 13.4 Hz), 158.6 (d, J_{CP} = 2.2 Hz), 136.5, 133.3, 132.2 (d, J_{CP} = 23.5 Hz), 132.0 (d, J_{CP} = 2.5 Hz), 131.4 (d, J_{CP} = 2.7 Hz), 131.28 (d, J_{CP} = 8.3 Hz), 131.26 (d, J_{CP} = 16.7 Hz), 131.0 (d, J_{CP} = 8.9 Hz), 130.9 (d, J_{CP} = 5.8 Hz), 128.9 (d, J_{CP} = 11.3 Hz), 128.5, 128.11 (d, J_{CP} = 11.7 Hz), 128.10, 127.8 (d, J_{CP} = 5.6 Hz), 113.8 (d, J_{CP} = 1.8 Hz), 55.1, 40.2 (d, J_{CP} = 69.7 Hz), 39.1. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 34.3. HRMS (positive ESI): $[M + H]^+$ calcd for $C_{28}H_{26}O_3P$: 441.1620, found 441.1620.

*(S)-3-(Diphenylphosphinyl)-3-(naphthalen-1-yl)-1-phenylpropan-1-one (**7i**).*[21] White solid (91.2 mg, 99%); mp 225−226 °C. The enantiomeric excess was determined on a Daicel Chiralpak AD-H column with hexane/2-propanol (70/30) and flow rate 1.0 mL/min and detected at a UV wavelength of 228 nm. Retention times: 19.2 min (major), 23.7 min, 81% ee. $[\alpha]_D^{20}$ = −179° (*c* 0.218, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 8.40 (s, 1H), 8.05−8.00 (m, 2H), 7.91−7.87 (m, 2H), 7.81−7.77 (m, 2H), 7.58−7.42 (m, 9H), 7.36−7.32 (m, 1H), 7.27−7.23 (m, 2H), 7.17−7.07 (m, 3H), 4.53 (ddd, J_{HH} = 9.8 and 2.3 Hz, J_{HP} = 6.7 Hz, 1H, PC*H*CH_2), 4.19 (ddd, J_{HH} = 17.9 and 10.4 Hz, J_{HP} = 4.4 Hz, 1H, PCHC*H*H), 3.52 (ddd, J_{HH} = 17.9 and 2.4 Hz, J_{HP} = 11.1 Hz, 1H, PCHCH*H*).

*(S)-3-(Diphenylphosphinyl)-3-(furan-2-yl)-1-phenylpropan-1-one (**7j**).* White solid (47.2 mg, 59%); mp 194−195 °C. The enantiomeric excess was determined on a Daicel Chiralpak AD-H column with hexane/2-propanol (70/30) and flow rate 0.9 mL/min and detected at a UV wavelength of 228 nm. Retention times: 17.7 min (major), 29.3 min, 82% ee. $[\alpha]_D^{20}$ = −72° (*c* 0.124, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 7.92−7.87 (m, 4H), 7.60−7.45 (m, 7H), 7.42−7.35 (m, 4H), 7.16 (s, 1H), 6.16−6.15 (m, 1H), 6.08−6.06 (m, 1H), 4.73 (ddd, J_{HH} = 10.4 and 2.6 Hz, J_{HP} = 7.8 Hz, 1H, PC*H*CH_2), 3.94 (ddd, J_{HH} = 18.0 and 10.7 Hz, J_{HP} = 4.6 Hz, 1H, PCHC*H*H), 3.42 (ddd, J_{HH} = 18.0 and 2.7 Hz, J_{HP} = 10.0 Hz, 1H, PCHCH*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.4 (d, J_{CP} = 12.4 Hz), 149.0 (d, J_{CP} = 6.7 Hz), 141.8 (d, J_{CP} = 2.9 Hz), 136.2, 133.4, 132.2 (d, J_{CP} = 2.7 Hz), 131.9 (d, J_{CP} = 2.6 Hz), 131.4 (d, J_{CP} = 26.3 Hz), 131.32 (d, J_{CP} = 8.8 Hz), 131.28 (d, J_{CP} = 9.2 Hz), 130.4 (d, J_{CP} = 29.4 Hz), 128.9 (d, J_{CP} = 11.6 Hz), 128.6, 128.3 (d, J_{CP} = 11.8 Hz), 128.2, 110.7 (d, J_{CP} = 2.7 Hz), 108.8 (d, J_{CP} = 5.9 Hz), 36.5, 35.9 (d, J_{CP} = 70.2 Hz). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 32.8. HRMS (positive ESI): $[M + H]^+$ calcd for $C_{25}H_{22}O_3P$ 401.1307, found 401.1303.

*(S)-3-(Diphenylphosphinyl)-1-phenyl-3-(thien-2-yl)propan-1-one (**7k**).* Pale yellow solid (67.0 mg, 80%); mp 219−220 °C. The enantiomeric excess was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol (90/10) and flow rate 1.0 mL/min and detected at a UV wavelength of 228 nm. Retention times: 9.5 min (major), 12.0 min, 88% ee. $[\alpha]_D^{20}$ = −121° (*c* 0.139, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 7.98−7.93 (m, 2H), 7.87−7.85 (m, 2H), 7.61−7.49 (m, 6H), 7.41−7.32 (m, 5H), 7.04−7.00 (m, 2H), 6.79 (dd, J_{HH} = 3.6 and 5.0 Hz, 1H), 4.83 (ddd, J_{HH} = 10.1 and 2.3 Hz, J_{HP} = 7.6 Hz, 1H, PC*H*CH_2), 3.97 (ddd, J_{HH} = 18.0 and 10.4 Hz, J_{HP} = 4.2 Hz, 1H, PCHC*H*H), 3.35 (ddd, J_{HH} = 18.0 and 2.4 Hz, J_{HP} = 10.3 Hz, 1H, PCHCH*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.4 (d, J_{CP} = 12.6 Hz), 137.6 (d, J_{CP} = 6.4 Hz), 136.3, 133.5, 132.2

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(d, J_{CP} = 2.5 Hz), 131.7 (d, J_{CP} = 2.7 Hz), 131.5 (d, J_{CP} = 19.3 Hz), 131.3 (d, J_{CP} = 8.5 Hz), 131.1 (d, J_{CP} = 8.8 Hz), 130.6 (d, J_{CP} = 13.0 Hz), 129.0 (d, J_{CP} = 11.3 Hz), 128.6, 128.24 (d, J_{CP} = 11.6 Hz), 128.19, 127.4 (d, J_{CP} = 6.5 Hz), 126.8 (d, J_{CP} = 2.3 Hz), 124.9 (d, J_{CP} = 2.7 Hz), 39.9, 36.5 (d, J_{CP} = 70.5 Hz). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 33.3. HRMS (positive ESI): $[M + H]^+$ calcd for $C_{25}H_{22}O_2PS$ 417.1078, found 417.1077.

*(S)-3-(Diphenylphosphinyl)-3-(2-methoxyphenyl)-1-phenylpropan-1-one (**7l**).*[5b,12] Colorless oil (87.7 mg, >99%). The enantiomeric excess was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol (95/5) and flow rate 0.6 mL/min and detected at a UV wavelength of 228 nm. Retention times: 31.1 min (major), 40.4 min, 54% ee. $[\alpha]_D^{20}$ = −65° (*c* 1.300, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 8.05−8.00 (m, 2H), 7.86 (d, J_{HH} = 7.5 Hz, 2H), 7.63 (d, J_{HH} = 7.6 Hz, 1H), 7.56−7.50 (m, 3H), 7.48−7.29 (m, 7H), 7.21−7.16 (m, 2H), 6.89 (app t, J_{HH} = 7.4 Hz, 1H), 6.53 (d, J_{HH} = 8.2 Hz, 1H), 5.16 (ddd, J_{HH} = 10.1 and 2.5 Hz, J_{HP} = 7.3 Hz, 1H, PC*H*CH_2), 4.08 (ddd, J_{HH} = 17.2 and 10.5 Hz, J_{HP} = 5.4 Hz, 1H, PCHC*H*H), 3.46 (s, 3H, OCH_3), 3.40 (ddd, J_{HH} = 18.0 and 2.5 Hz, J_{HP} = 10.1 Hz, 1H, PCHCH*H*).

*(S)-3-(Diphenylphosphinyl)-1-phenyl-3-(o-tolyl)propan-1-one (**7m**).* Colorless oil (69.6 mg, 82%). The enantiomeric excess was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol (85/15) and flow rate 0.3 mL/min and detected at a UV wavelength of 228 nm. Retention times: 19.8 min (major), 28.9 min, 63% ee. $[\alpha]_D^{20}$ = −139° (*c* 0.302, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 8.03−7.98 (m, 2H), 7.84 (d, J_{HH} = 7.2 Hz, 2H), 7.78 (d, J_{HH} = 7.6 Hz, 1H), 7.59−7.53 (m, 3H), 7.48 (t, J_{HH} = 7.4 Hz, 1H), 7.38−7.31 (m, 3H), 7.24−7.14 (m, 5H), 7.05 (t, J_{HH} = 7.5 Hz, 1H), 6.90 (d, J_{HH} = 7.5 Hz, 1H), 4.68 (ddd, J_{HH} = 9.8 and 2.3 Hz, J_{HP} = 7.2 Hz, 1H, PC*H*CH_2), 4.08 (ddd, J_{HH} = 18.2 and 10.3 Hz, J_{HP} = 4.4 Hz, 1H, PCHC*H*H), 3.40 (ddd, J_{HH} = 18.2 and 2.3 Hz, J_{HP} = 11.1 Hz, 1H, PCHCH*H*), 2.06 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.9 (d, J_{CP} = 13.5 Hz), 137.4 (d, J_{CP} = 6.2 Hz), 136.3, 134.3 (d, J_{CP} = 5.8 Hz), 133.4, 132.30, 132.27 (d, J_{CP} = 2.6 Hz), 131.7 (d, J_{CP} = 8.3 Hz), 131.6 (d, J_{CP} = 2.8 Hz), 131.3, 131.0 (d, J_{CP} = 9.4 Hz), 130.1, 129.0 (d, J_{CP} = 11.2 Hz), 128.8, 128.6, 128.1, 127.8 (d, J_{CP} = 11.7 Hz), 127.1 (d, J_{CP} = 2.4 Hz), 126.2 (d, J_{CP} = 2.5 Hz), 39.8, 36.1 (d, J_{CP} = 68.3 Hz), 19.7. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 34.9. HRMS (positive ESI): $[M + H]^+$ calcd for $C_{28}H_{26}O_2P$ 425.1670, found 425.1669.

*(S)-4-(Diphenylphosphinyl)-4-phenylbutan-2-one (**7n**).*[12] White solid (69.0 mg, 99%). The enantiomeric excess was determined on a Daicel Chiralpak AD-H column with hexane/2-propanol (70/30) and flow rate 0.5 mL/min and detected at a UV wavelength of 228 nm. Retention times: 20.6 min (major), 32.7 min, 97% ee. $[\alpha]_D^{20}$ = −146° (*c* 0.200, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 7.96−7.91 (m, 2H), 7.57−7.50 (m, 3H), 7.45−7.41 (m, 2H), 7.36−7.22 (m, 5H), 7.18−7.13 (m, 3H), 4.22 (ddd, J_{HH} = 10.2 and 2.8 Hz, J_{HP} = 7.2 Hz, 1H, PC*H*CH_2), 3.34 (ddd, J_{HH} = 17.9 and 10.2 Hz, J_{HP} = 5.3 Hz, 1H, PCHC*H*H), 2.94 (ddd, J_{HH} = 17.9 and 2.8 Hz, J_{HP} = 11.2 Hz, 1H, PCHCH*H*), 1.96 (s, 3H, $COCH_3$).

*(S)-4-(4-Bromophenyl)-4-(diphenylphosphinyl)butan-2-one (**7o**).*[5b,12] White solid (76.9 mg, 90%). The enantiomeric excess was determined on a Daicel Chiralpak AD-H column with hexane/2-propanol (70/30) and flow rate 1.0 mL/min and detected at a UV wavelength of 228 nm. Retention times: 12.7 min (major), 33.6 min, 96% ee. $[\alpha]_D^{20}$ = −164° (*c* 0.200, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 7.94−7.89 (m, 2H), 7.58−7.51 (m, 3H), 7.49−7.44 (m, 2H), 7.39−7.35 (m, 1H), 7.30−7.26 (m, 4H), 7.21−7.18 (m, 2H), 4.18 (ddd, J_{HH} = 10.0 and 2.7 Hz, J_{HP} = 7.0 Hz, 1H, PC*H*CH_2), 3.27 (ddd, J_{HH} = 18.1 and 10.2 Hz, J_{HP} = 5.0 Hz, 1H, PCHC*H*H), 2.91 (ddd, J_{HH} = 18.2 and 2.7 Hz, J_{HP} = 10.9 Hz, 1H, PCHCH*H*), 1.97 (s, 3H, $COCH_3$).

*(S)-4-(Diphenylphosphinyl)-4-(4-nitrophenyl)butan-2-one (**7p**).*[12] White solid (71.6 mg, 91%). The enantiomeric excess was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol (70/30) and flow rate 0.4 mL/min and detected at a UV wavelength of 228 nm. Retention times: 16.6 min (major), 23.5 min, 97% ee. $[\alpha]_D^{20}$ = −210° (*c* 0.200, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, J_{HH} = 8.7 Hz, 2H), 7.96−7.91 (m, 2H), 7.61−7.54 (m, 3H), 7.52−7.45 (m, 4H), 7.40−7.36 (m, 1H), 7.31−7.28 (m, 2H), 4.34 (ddd, J_{HH} = 10.0 and 2.7 Hz, J_{HP} = 6.9 Hz, 1H, PC*H*CH_2), 3.35 (ddd, J_{HH} = 18.5 and 10.4 Hz, J_{HP} = 4.8 Hz, 1H, PCHC*H*H), 2.99 (ddd, J_{HH} = 18.5 and 2.7 Hz, J_{HP} = 10.8 Hz, 1H, PCHCH*H*), 2.00 (s, 3H, $COCH_3$).

*(S)-4-(Diphenylphosphinyl)-4-(3-nitrophenyl)butan-2-one (**7q**).*[12] White solid (77.1 mg, 98%). The enantiomeric excess was determined on a Daicel Chiralpak AD-H column with hexane/2-propanol (70/30) and flow rate 0.5 mL/min and detected at a UV wavelength of 228 nm. Retention times: 24.0 min (major), 45.7 min, 96% ee. $[\alpha]_D^{20}$ = −180° (*c* 0.200, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, J_{HH} = 1.9 Hz, 1H), 7.99−7.96 (m, 3H), 7.71 (d, J_{HH} = 7.0 Hz, 1H), 7.62−7.55 (m, 3H), 7.49−7.44 (m, 2H), 7.36 (app t, J_{HH} = 8.0 Hz, 2H), 7.29−7.24 (m, 2H), 4.33 (ddd, J_{HH} = 10.2 and 2.8 Hz, J_{HP} = 7.2 Hz, 1H, PC*H*CH_2), 3.35 (ddd, J_{HH} = 18.6 and 10.2 Hz, J_{HP} = 5.0 Hz, 1H, PCHC*H*H), 2.99 (ddd, J_{HH} = 18.6 and 2.8 Hz, J_{HP} = 10.7 Hz, 1H, PCHCH*H*), 2.00 (s, 3H, $COCH_3$).

*(S)-4-(Diphenylphosphinyl)-4-(p-tolyl)butan-2-one (**7r**).* White solid (68.1 mg, 94%); mp 194−195 °C. The enantiomeric excess was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol (90/10) and flow rate 0.8 mL/min and detected at a UV wavelength of 228 nm. Retention times: 10.3 min (major), 12.9 min, 93% ee. $[\alpha]_D^{20}$ = −106° (*c* 0.168, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 7.91 (t, J_{HH} = 8.7 Hz, 2H), 7.55−7.46 (m, 5H), 7.33 (d, J_{HH} = 7.4 Hz, 1H), 7.27−7.23 (m, 2H), 7.17 (d, J_{HH} = 6.9 Hz, 2H), 6.96 (d, J_{HH} = 7.7 Hz, 2H), 4.19 (ddd, J_{HH} = 10.0 and 2.6 Hz, J_{HP} = 7.4 Hz, 1H, PC*H*CH_2), 3.29 (ddd, J_{HH} = 17.7 and 10.2 Hz, J_{HP} = 5.2 Hz, 1H, PCHC*H*H), 2.91 (ddd, J_{HH} = 17.8 and 2.6 Hz, J_{HP} = 11.1 Hz, 1H, PCHCH*H*), 2.22 (s, 3H, CH_3), 1.94 (s, 3H, $COCH_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 205.5 (d, J_{CP} = 13.0 Hz), 136.7 (d, J_{CP} = 2.2 Hz), 132.5 (d, J_{CP} = 5.9 Hz), 132.0 (d, J_{CP} = 2.4 Hz), 131.4 (d, J_{CP} = 2.6 Hz), 131.3 (d, J_{CP} = 8.6 Hz), 131.0 (d, J_{CP} = 8.8 Hz), 130.7 (d, J_{CP} = 11.5 Hz), 129.6 (d, J_{CP} = 5.6 Hz), 129.1, 128.92 (d, J_{CP} = 13.0 Hz), 128.86 (d, J_{CP} = 11.2 Hz), 128.1 (d, J_{CP} = 11.7 Hz), 43.6, 40.6 (d, J_{CP} = 68.7 Hz), 30.6, 21.0. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 33.8. HRMS (positive ESI): $[M + H]^+$ calcd for $C_{23}H_{24}O_2P$ 363.1514, found 363.1511.

*(S)-4-(Diphenylphosphinyl)-4-(4-fluorophenyl)butan-2-one (**7s**).* White solid (65.9 mg, 90%); mp 210−211 °C. The enantiomeric excess was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol (90/10) and flow rate 0.8 mL/min and detected at a UV wavelength of 228 nm. Retention times: 10.6 min (major), 12.8 min, 93% ee. $[\alpha]_D^{20}$ = −131° (*c* 0.222, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 7.95−7.90 (m, 2H), 7.59−7.51 (m, 3H), 7.47−7.42 (m, 2H), 7.37−7.24 (m, 5H), 6.86 (t, J_{HH} = 8.6 Hz, 2H), 4.21 (ddd, J_{HH} = 10.1 and 2.8 Hz, J_{HP} = 7.1 Hz, 1H, PC*H*CH_2), 3.28 (ddd, J_{HH} = 18.0 and 10.3 Hz, J_{HP} = 5.1 Hz, 1H, PCHC*H*H), 2.91 (ddd, J_{HH} = 18.1 and 2.8 Hz, J_{HP} = 10.9 Hz, 1H, PCHCH*H*), 1.96 (s, 3H, $COCH_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 205.2 (d, J_{CP} = 12.7 Hz), 161.9 (dd, J_{CP} = 2.4 Hz, J_{CF} = 244 Hz), 132.1 (d, J_{CP} = 2.7 Hz), 131.8 (d, J_{CP} = 19.2 Hz), 131.65 (t, J_{CP} = 2.6 Hz), 131.56 (d, J_{CP} = 2.8 Hz), 131.232 (dd, J_{CP} = 5.4 Hz, J_{CF} = 7.9 Hz), 131.229 (d, J_{CP} = 8.5 Hz), 130.9 (d, J_{CP} = 8.8 Hz), 130.8 (d, J_{CP} = 13.3 Hz), 129.0 (d, J_{CP} = 11.3 Hz), 128.2 (d, J_{CP} = 11.7 Hz), 115.3 (dd, J_{CP} = 1.8 Hz, J_{CF} = 21.5 Hz), 43.7, 40.2 (d, J_{CP} = 68.7 Hz), 30.6. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 33.5. HRMS (positive ESI): $[M + H]^+$ calcd for $C_{22}H_{21}FO_2P$ 367.1263, found 367.1265.

*(S)-4-(4-Chlorophenyl)-4-(diphenylphosphinyl)butan-2-one (**7t**).*[12] White solid (74.3 mg, 97%). The enantiomeric excess was determined on a Daicel Chiralpak AD-H column with hexane/2-propanol (70/30) and flow rate 1.0 mL/min and detected at a UV wavelength of 228 nm. Retention times: 11.1 min (major), 30.8 min, 97% ee. $[\alpha]_D^{20}$ = −160° (*c* 0.200, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 7.94−7.89 (m, 2H), 7.59−7.51 (m, 3H), 7.49−7.44 (m, 2H), 7.39−7.35 (m, 1H), 7.30−7.24 (m, 4H), 7.14 (d, J_{HH} = 8.4 Hz, 2H), 4.19 (ddd, J_{HH} = 10.0 and 2.8 Hz, J_{HP} = 7.0 Hz, 1H, PC*H*CH_2), 3.28 (ddd, J_{HH} = 18.1 and 10.3 Hz, J_{HP} = 5.0 Hz, 1H, PCHC*H*H), 2.91 (ddd, J_{HH} = 18.1 and 2.8 Hz, J_{HP} = 10.9 Hz, 1H, PCHCH*H*), 1.97 (s, 3H, $COCH_3$).

*(S)-4-(Diphenylphosphinyl)-4-(4-methoxyphenyl)butan-2-one (**7u**).* White solid (49.9 mg, 66%); mp 184−185 °C. The enantiomeric

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excess was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol (90/10) and flow rate 0.6 mL/min and detected at a UV wavelength of 228 nm. Retention times: 19.2 min (major), 24.2 min, 96% ee. $[\alpha]_D^{20}$ = −111° (*c* 0.248, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94−7.89 (m, 2H), 7.53−7.43 (m, 5H), 7.35−7.32 (m, 1H), 7.27−7.21 (m, 4H), 6.70 (d, J_{HH} = 8.6 Hz, 2H), 4.18 (ddd, J_{HH} = 10.1 and 2.7 Hz, J_{HP} = 7.3 Hz, 1H, PC*H*CH_2), 3.70 (s, 3H, OCH_3), 3.28 (ddd, J_{HH} = 17.7 and 10.4 Hz, J_{HP} = 5.3 Hz, 1H, PCHC*H*H), 2.90 (ddd, J_{HH} = 17.8 and 2.7 Hz, J_{HP} = 10.8 Hz, 1H, PCHCH*H*), 1.94 (s, 3H, $COCH_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 205.6 (d, J_{CP} = 13.0 Hz), 158.6 (d, J_{CP} = 2.3 Hz), 132.0 (d, J_{CP} = 2.8 Hz), 131.9, 131.4 (d, J_{CP} = 2.7 Hz), 131.3 (d, J_{CP} = 8.4 Hz), 131.0 (d, J_{CP} = 8.8 Hz), 130.7 (d, J_{CP} = 5.7 Hz), 128.9 (d, J_{CP} = 11.2 Hz), 128.1 (d, J_{CP} = 11.7 Hz), 127.6 (d, J_{CP} = 5.6 Hz), 113.8 (d, J_{CP} = 1.4 Hz), 55.1, 43.6, 40.2 (d, J_{CP} = 69.2 Hz), 30.7. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 33.9. HRMS (positive ESI): $[M + H]^+$ calcd for $C_{23}H_{24}O_3P$ 379.1463, found 379.1465.

*(S)-3-(Diphenylphosphinyl)-1-(4-methoxyphenyl)-3-phenylpropan-1-one (**7v**).*[5b] White solid (87.7 mg, >99%). The enantiomeric excess was determined on a Daicel Chiralpak AD-H column with hexane/2-propanol (60/40) and flow rate 0.7 mL/min and detected at a UV wavelength of 228 nm. Retention times: 26.0 min (major), 36.7 min, 95% ee. $[\alpha]_D^{20}$ = −154° (*c* 0.200, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01−7.96 (m, 2H), 7.83 (d, J_{HH} = 8.9 Hz, 2H), 7.53−7.31 (m, 8H), 7.26−7.07 (m, 5H), 6.84 (d, J_{HH} = 8.9 Hz, 2H), 4.47 (ddd, J_{HH} = 9.9 and 2.3 Hz, J_{HP} = 6.8 Hz, 1H, PC*H*CH_2), 3.98 (ddd, J_{HH} = 17.9 and 10.4 Hz, J_{HP} = 4.3 Hz, 1H, PCHC*H*H), 3.81 (s, 3H, OCH_3), 3.32 (ddd, J_{HH} = 17.9 and 2.3 Hz, J_{HP} = 11.3 Hz, 1H, PCHCH*H*).

*(S)-3-(Diphenylphosphinyl)-1-(4-methoxyphenyl)-3-(4-nitrophenyl)propan-1-one (**7w**).*[12] White solid (96.6 mg, >99%). The enantiomeric excess was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol (70/30) and flow rate 0.6 mL/min and detected at a UV wavelength of 228 nm. Retention times: 13.9 min (major), 20.7 min, 94% ee. $[\alpha]_D^{20}$ = −245° (*c* 0.200, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02−7.97 (m, 4H), 7.82 (d, J_{HH} = 8.8 Hz, 2H), 7.58−7.47 (m, 7H), 7.40−7.36 (m, 1H), 7.31−7.27 (m, 2H), 6.86 (d, J_{HH} = 8.8 Hz, 2H), 4.57 (ddd, J_{HH} = 10.6 and 2.0 Hz, J_{HP} = 6.9 Hz, 1H, PC*H*CH_2), 3.98 (ddd, J_{HH} = 18.1 and 10.6 Hz, J_{HP} = 6.5 Hz, 1H, PCHC*H*H), 3.83 (s, 3H, OCH_3), 3.36 (ddd, J_{HH} = 18.1 and 2.0 Hz, J_{HP} = 10.4 Hz, 1H, PCHCH*H*).

*(S)-3-(Diphenylphosphinyl)-1-(4-methoxyphenyl)-3-(p-tolyl)-propan-1-one (**7x**).* White solid (81.8 mg, 90% yield); mp 234−235 °C. The enantiomeric excess was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol (90/10) and flow rate 0.5 mL/min and detected at a UV wavelength of 228 nm. Retention times: 23.7 min (major), 41.3 min, 91% ee. $[\alpha]_D^{20}$ = −146° (*c* 0.380, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99−7.94 (m, 2H), 7.82 (d, J_{HH} = 8.9 Hz, 2H), 7.51−7.46 (m, 5H), 7.36−7.32 (m, 1H), 7.27−7.23 (m, 4H), 6.94 (d, J_{HH} = 7.9 Hz, 2H), 6.83 (d, J_{HH} = 8.9 Hz, 2H), 4.45 (ddd, J_{HH} = 9.8 and 2.3 Hz, J_{HP} = 6.9 Hz, 1H, PC*H*CH_2), 3.94 (ddd, J_{HH} = 17.9 and 10.5 Hz, J_{HP} = 4.4 Hz, 1H, PCHC*H*H), 3.80 (s, 3H, OCH_3), 3.29 (ddd, J_{HH} = 17.8 and 2.4 Hz, J_{HP} = 11.2 Hz, 1H, PCHCH*H*), 2.19 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.2 (d, J_{CP} = 13.5 Hz), 163.6, 136.5 (d, J_{CP} = 2.6 Hz), 132.9 (d, J_{CP} = 5.7 Hz), 132.3 (d, J_{CP} = 18.8 Hz), 131.9 (d, J_{CP} = 2.6 Hz), 131.33 (d, J_{CP} = 16.9 Hz), 131.32 (d, J_{CP} = 2.0 Hz), 131.29 (d, J_{CP} = 8.6 Hz), 131.0 (d, J_{CP} = 8.8 Hz), 130.4, 129.7 (d, J_{CP} = 5.7 Hz), 129.6, 129.0 (d, J_{CP} = 1.8 Hz), 128.9 (d, J_{CP} = 11.1 Hz), 128.1 (d, J_{CP} = 11.7 Hz), 113.6, 55.5, 40.6 (d, J_{CP} = 69.2 Hz), 38.6, 21.0. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 34.4. HRMS (positive ESI): $[M + H]^+$ calcd for $C_{29}H_{28}O_3P$ 455.1776, found 455.1774.

*(S)-3-(3-Bromophenyl)-3-(diphenylphosphinyl)-1-(4-methoxyphenyl)propan-1-one (**7y**).* White solid (90.4 mg, 87%); mp 198−199 °C. The enantiomeric excess was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol (90/10) and flow rate 0.4 mL/min and detected at a UV wavelength of 228 nm. Retention times: 31.1 min (major), 37.1 min, 89% ee. $[\alpha]_D^{20}$ = −143° (*c* 0.276, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00−7.95 (m, 2H), 7.83 (d, J_{HH} = 8.9 Hz, 2H), 7.53−7.46 (m, 6H), 7.38−7.21 (m, 5H), 7.01 (t, J_{HH} = 7.9 Hz, 1H), 6.84 (d, J_{HH} = 8.9 Hz, 2H), 4.43 (ddd, J_{HH} = 9.8 and 2.3 Hz, J_{HP} = 6.9 Hz, 1H, PC*H*CH_2), 3.92 (ddd, J_{HH} = 18.0 and 10.4 Hz, J_{HP} = 4.3 Hz, 1H, PCHC*H*H), 3.80 (s, 3H, OCH_3), 3.32 (ddd, J_{HH} = 18.0 and 2.4 Hz, J_{HP} = 11.1 Hz, 1H, PCHCH*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.7 (d, J_{CP} = 13.0 Hz), 163.8, 138.5 (d, J_{CP} = 5.6 Hz), 132.8 (d, J_{CP} = 5.8 Hz), 132.2 (d, J_{CP} = 2.6 Hz), 131.69 (d, J_{CP} = 28.3 Hz), 131.66 (d, J_{CP} = 2.6 Hz), 131.3 (d, J_{CP} = 8.4 Hz), 130.9 (d, J_{CP} = 8.9 Hz), 130.6, 130.4, 130.2 (d, J_{CP} = 2.4 Hz), 129.7 (d, J_{CP} = 1.8 Hz), 129.3, 129.0 (d, J_{CP} = 11.4 Hz), 128.4 (d, J_{CP} = 5.7 Hz), 128.2 (d, J_{CP} = 11.8 Hz), 122.2 (d, J_{CP} = 2.2 Hz), 113.7, 55.5, 40.9 (d, J_{CP} = 68.0 Hz), 38.4. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 34.1. HRMS (positive ESI): $[M + H]^+$ calcd for $C_{28}H_{25}BrO_3P$ 519.0725, found 519.0723.

*(S)-3-(4-Bromophenyl)-3-(diphenylphosphinyl)-1-(4-methoxyphenyl)propan-1-one (**7z**).*[21] White solid (24.9 mg, 24%); mp 245−246 °C. The enantiomeric excess was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol (90/10) and flow rate 0.5 mL/min and detected at a UV wavelength of 228 nm. Retention times: 23.7 min (major), 32.8 min, 90% ee. $[\alpha]_D^{20}$ = −161° (*c* 0.122, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99−7.94 (m, 2H), 7.82 (d, J_{HH} = 8.9 Hz, 2H), 7.53−7.52 (m, 5H), 7.39−7.35 (m, 1H), 7.30−7.26 (m, 6H), 6.84 (d, J_{HH} = 8.9 Hz, 2H), 4.44 (ddd, J_{HH} = 9.1 and 2.2 Hz, J_{HP} = 6.6 Hz, 1H, PC*H*CH_2), 3.92 (ddd, J_{HH} = 17.9 and 10.6 Hz, J_{HP} = 4.2 Hz, 1H, PCHC*H*H), 3.81 (s, 3H, OCH_3), 3.28 (ddd, J_{HH} = 17.9 and 2.2 Hz, J_{HP} = 10.8 Hz, 1H, PCHCH*H*).

*(S)-3-(Diphenylphosphinyl)-3-(4-fluorophenyl)-1-(4-methoxyphenyl)propan-1-one (**7aa**).* White solid (83.4 mg, 91% yield); mp 240−241 °C. The enantiomeric excess was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol (90/10) and flow rate 0.5 mL/min and detected at a UV wavelength of 228 nm. Retention times: 23.4 min (major), 29.2 min, 90% ee. $[\alpha]_D^{20}$ = −128° (*c* 0.232, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01−7.96 (m, 2H), 7.82 (d, J_{HH} = 8.9 Hz, 2H), 7.53−7.45 (m, 5H), 7.38−7.33 (m, 3H), 7.29−7.24 (m, 2H), 6.85−6.81 (m, 4H), 4.46 (ddd, J_{HH} = 9.2 and 2.2 Hz, J_{HP} = 6.7 Hz, 1H, PC*H*CH_2), 3.94 (ddd, J_{HH} = 17.9 and 10.6 Hz, J_{HP} = 4.2 Hz, 1H, PCHC*H*H), 3.80 (s, 3H, OCH_3), 3.29 (ddd, J_{HH} = 17.9 and 2.3 Hz, J_{HP} = 10.8 Hz, 1H, PCHCH*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.0 (d, J_{CP} = 13.4 Hz), 163.8, 161.8 (dd, J_{CP} = 2.4 Hz, J_{CF} = 244 Hz), 132.1 (d, J_{CP} = 2.8 Hz), 131.9 (d, J_{CP} = 40.2 Hz), 131.8 (dd, J_{CP} = 5.5 Hz, J_{CF} = 3.2 Hz), 131.5 (d, J_{CP} = 2.7 Hz), 131.3 (dd, J_{CP} = 5.8 Hz, J_{CF} = 7.9 Hz), 131.2 (d, J_{CP} = 8.6 Hz), 130.92 (d, J_{CP} = 33.0 Hz), 130.86 (d, J_{CP} = 8.9 Hz), 130.4, 129.4, 129.0 (d, *J* = 11.2 Hz), 128.2 (d, *J* = 11.7 Hz), 115.2 (dd, J_{CP} = 1.6 Hz, J_{CF} = 21.4 Hz), 113.7, 55.5, 40.3 (d, J_{CP} = 69.1 Hz), 38.6. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 34.4. HRMS (positive ESI): $[M + H]^+$ calcd for $C_{28}H_{25}FO_3P$ 459.1525, found 459.1526.

*(S)-3-(Diphenylphosphinyl)-1-(4-nitrophenyl)-3-phenylpropan-1-one (**7bb**).*[5b] White solid (90.2 mg, 99%). The enantiomeric excess was determined on a Daicel Chiralpak AD-H column with hexane/2-propanol (60/40) and flow rate 1.0 mL/min and detected at a UV wavelength of 228 nm. Retention times: 36.0 min (major), 47.8 min, 85% ee. $[\alpha]_D^{20}$ = −142° (*c* 0.200, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (d, J_{HH} = 8.6 Hz, 2H), 8.00−7.95 (m, 4H), 7.54−7.43 (m, 5H), 7.37−7.33 (m, 3H), 7.26−7.09 (m, 5H), 4.42 (ddd, J_{HH} = 10.2 and 2.8 Hz, J_{HP} = 7.0 Hz, 1H, PC*H*CH_2), 4.01 (ddd, J_{HH} = 18.1 and 9.2 Hz, J_{HP} = 4.1 Hz, 1H, PCHC*H*H), 3.45 (ddd, $_{HH}$ = 18.1 and 2.8 Hz, J_{HP} = 10.7 Hz, 1H, PCHCH*H*).

*(S)-3-(4-Bromophenyl)-3-(diphenylphosphinyl)-1-(4-nitrophenyl)-propan-1-one (**7cc**).*[21] White solid (104.7 mg, 98%); mp 246−247 °C. The enantiomeric excess was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol (85/15) and flow rate 0.5 mL/min and detected at a UV wavelength of 228 nm. Retention times: 40.4 min (major), 57.7 min, 88% ee. $[\alpha]_D^{20}$ = −138° (*c* 0.420, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, J_{HH} = 8.9 Hz, 2H), 7.99−7.94 (m, 4H), 7.56−7.48 (m, 5H), 7.41−7.37 (m, 1H), 7.32−7.25 (m, 6H), 4.40 (ddd, J_{HH} = 10.0 and 2.7 Hz, J_{HP} = 7.0 Hz, 1H, PC*H*CH_2), 3.95 (ddd, J_{HH} = 18.4 and 10.0 Hz, J_{HP} = 5.0 Hz, 1H, PCHC*H*H), 3.43 (ddd, J_{HH} = 18.4 and 2.7 Hz, J_{HP} = 10.4 Hz, 1H, PCHCH*H*).

*(S)-1-(4-Bromophenyl)-3-(diphenylphosphinyl)-3-phenylpropan-1-one (**7dd**).*[5b] White solid (97.4 mg, >99%). The enantiomeric excess was determined on a Daicel Chiralpak AD-H column with hexane/2-propanol (60/40) and flow rate 0.7 mL/min and detected at a UV wavelength of 228 nm. Retention times: 29.7 min (major), 44.4 min,

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92% ee. $[\alpha]_D^{20}$ = −145° (*c* 0.200, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 7.97−7.95 (m, 2H), 7.69 (d, J_{HH} = 8.6 Hz, 2H), 7.53−7.43 (m, 7H), 7.37−7.32 (m, 3H), 7.26−7.08 (m, 5H), 4.43 (ddd, J_{HH} = 10.3 and 2.5 Hz, J_{HP} = 6.9 Hz, 1H, PC*H*CH_2), 3.95 (ddd, J_{HH} = 18.0 and 10.3 Hz, J_{HP} = 4.6 Hz, 1H, PCHC*H*H), 3.35 (ddd, $_{HH}$ = 18.0 and 2.5 Hz, J_{HP} = 11.0 Hz, 1H, PCHCH*H*).

*(S)-1,3-Bis(4-bromophenyl)-3-(diphenylphosphinyl)propan-1-one (**7ee**).*[21] White solid (112.5 mg, 99%); mp 261−262 °C. The enantiomeric excess was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol (85/15) and flow rate 0.7 mL/min and detected at a UV wavelength of 228 nm. Retention times: 10.8 min (major), 13.6 min, 92% ee. $[\alpha]_D^{20}$ = −137° (*c* 0.292, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 7.98−7.93 (m, 2H), 7.68 (d, J_{HH} = 8.6 Hz, 2H), 7.54−7.47 (m, 7H), 7.39−7.35 (m, 1H), 7.31−7.24 (m, 6H), 4.40 (ddd, J_{HH} = 10.0 and 2.5 Hz, J_{HP} = 6.8 Hz, 1H, PC*H*CH_2), 3.89 (ddd, J_{HH} = 18.1 and 10.4 Hz, J_{HP} = 4.6 Hz, 1H, PCHC*H*H), 3.33 (ddd, J_{HH} = 18.1 and 2.5 Hz, J_{HP} = 10.7 Hz, 1H, PCHCH*H*).

*(S)-1-(Diphenylphosphinyl)-5-methyl-1-(4-nitrophenyl)hexan-3-one (**7ff**).*[12] White solid (86.7 mg, >99%). The enantiomeric excess was determined on a Daicel Chiralpak AD-H column with hexane/2-propanol (70/30) and flow rate 1.0 mL/min and detected at a UV wavelength of 228 nm. Retention times: 16.7 min (major), 55.9 min, 98% ee. $[\alpha]_D^{20}$ = −155° (*c* 0.200, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, J_{HH} = 8.6 Hz, 2H), 7.96−7.92 (m, 2H), 7.60−7.54 (m, 3H), 7.52−7.46 (m, 4H), 7.39−7.36 (m, 1H), 7.30−7.26 (m, 2H), 4.36 (ddd, J_{HH} = 9.8 and 2.6 Hz, J_{HP} = 6.8 Hz, 1H, PC*H*CH_2), 3.31 (ddd, J_{HH} = 18.4 and 10.2 Hz, J_{HP} = 4.8 Hz, 1H, PCHC*H*H), 2.92 (ddd, J_{HH} = 18.4 and 2.6 Hz, J_{HP} = 11.0 Hz, 1H, PCHCH*H*), 2.09 (d, J_{HH} = 6.9 Hz, 2H), 1.90 (heptet, J_{HH} = 6.8 Hz, 1H), 0.70 (d, J_{HH} = 6.8 Hz, 3H), 0.66 (d, J_{HH} = 6.8 Hz, 3H).

*(S)-1-(Diphenylphosphinyl)-5-methyl-1-phenylhexan-3-one (**7gg**).* White solid (36.7 mg, 47%); mp 169−170 °C. The enantiomeric excess was determined on a Daicel Chiralpak AD-H column with hexane/2-propanol (70/30) and flow rate 1.0 mL/min and detected at a UV wavelength of 228 nm. Retention times: 8.6 min (major), 12.8 min, 80% ee. $[\alpha]_D^{20}$ = −89° (*c* 0.124, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 7.96−7.91 (m, 2H), 7.58−7.50 (m, 3H), 7.45−7.40 (m, 2H), 7.35−7.27 (m, 3H), 7.26−7.21 (m, 2H), 7.18−7.10 (m, 3H), 4.26 (ddd, J_{HH} = 9.9 and 2.8 Hz, J_{HP} = 7.0 Hz, 1H, PC*H*CH_2), 3.31 (ddd, J_{HH} = 17.8 and 10.1 Hz, J_{HP} = 5.3 Hz, 1H, PCHC*H*H), 2.86 (ddd, J_{HH} = 17.8 and 2.8 Hz, J_{HP} = 11.4 Hz, 1H, PCHCH*H*), 2.07 (d, J_{HH} = 7.0 Hz, 2H), 1.97−1.85 (m, 1H), 0.68 (d, J_{HH} = 6.6 Hz, 3H), 0.64 (d, J_{HH} = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.5 (d, J_{CP} = 12.4 Hz), 135.6 (d, J_{CP} = 5.4 Hz), 132.1 (d, J_{CP} = 2.7 Hz), 131.57 (d, J_{CP} = 17.3 Hz), 131.54 (d, J_{CP} = 2.8 Hz), 131.3 (d, J_{CP} = 8.7 Hz), 130.9 (d, J_{CP} = 9.0 Hz), 130.6 (d, J_{CP} = 11.7 Hz), 129.8 (d, J_{CP} = 5.6 Hz), 129.0 (d, J_{CP} = 11.5 Hz), 128.3 (d, J_{CP} = 1.9 Hz), 128.1 (d, J_{CP} = 11.9 Hz), 127.2 (d, J_{CP} = 2.4 Hz), 52.4, 43.0, 40.9 (d, J_{CP} = 68.5 Hz), 24.5, 22.2 (d, J_{CP} = 25.3 Hz), 20.7. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 35.0. HRMS (positive ESI): $[M + H]^+$ calcd for $C_{25}H_{28}O_2P$ 391.1827, found 391.1828.

*(S)-3-(Bis(4-methylphenyl)phosphinyl)-1,3-diphenylpropan-1-one (**7hh**).* With CH_2Cl_2/EtOAc (10/1) as eluent; white solid (20.0 mg, 23%); mp 203−205 °C. The enantiomeric excess was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol (90/10) and flow rate 1.0 mL/min and detected at a UV wavelength of 228 nm. Retention times: 6.9 min (major), 9.4 min, 83% ee. $[\alpha]_D^{20}$ = −117° (*c* 0.165, CH_2Cl_2). ^1H NMR(400 MHz, $CDCl_3$): δ 7.86−7.82 (m, 4H), 7.51−7.47 (m, 1H), 7.40−7.30 (m, 8H), 7.17−7.03 (m, 5H), 4.42 (ddd, J_{HH} = 9.9 and 2.2 Hz, J_{HP} = 7.1 Hz, 1H, PC*H*CH_2), 4.00 (ddd, J_{HH} = 18.1 and 10.4 Hz, J_{HP} = 4.2 Hz, 1H, PCHC*H*H), 3.37 (ddd, J_{HH} = 18.1 and 2.2 Hz, J_{HP} = 11.1 Hz, 1H, PCHCH*H*), 2.38 (s, 3H, CH_3), 2.26 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.8 (d, J_{CP} = 13.4 Hz), 142.4 (d, J_{CP} = 2.5 Hz), 141.7 (d, J_{CP} = 2.6 Hz), 136.4, 136.2 (d, J_{CP} = 5.5 Hz), 133.3, 131.2 (d, J_{CP} = 8.7 Hz), 131.0 (d, J_{CP} = 9.3 Hz), 129.9 (d, J_{CP} = 5.7 Hz), 129.6 (d, J_{CP} = 11.6 Hz), 128.9 (d, J_{CP} = 33.4 Hz), 128.8 (d, J_{CP} = 12.0 Hz), 128.5, 128.3 (d, J_{CP} = 1.4 Hz), 128.1, 127.9 (d, J_{CP} = 28.1 Hz), 126.9 (d, J_{CP} = 2.1 Hz), 41.2 (d, J_{CP} = 68.7 Hz), 39.1, 21.55, 21.47. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 34.8. HRMS (positive ESI): $[M + H]^+$ calcd for $C_{29}H_{28}O_2P$: 439.1827, found 439.1829.

*(S)-3-(Bis(4-methoxyphenyl)phosphinyl)-1,3-diphenylpropan-1-one (**7ii**).*[5b,12] White solid (70.6 mg, 75%). The enantiomeric excess was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol (60/40) and flow rate 0.6 mL/min and detected at a UV wavelength of 228 nm. Retention times: 9.6 min (major), 17.2 min, 26% ee. $[\alpha]_D^{20}$ = −31° (*c* 0.116, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 7.89−7.83 (m, 4H), 7.49 (t, J_{HH} = 7.4 Hz, 1H), 7.38−7.30 (m, 6H), 7.18−7.11 (m, 3H), 7.00 (dd, J_{HH} = 8.8 and 2.1 Hz, 2H), 6.74 (dd, J_{HH} = 8.8 and 2.2 Hz, 2H), 4.37 (ddd, J_{HH} = 9.9 and 2.2 Hz, J_{HP} = 7.3 Hz, 1H, PC*H*CH_2), 3.98 (ddd, J_{HH} = 18.1 and 10.3 Hz, J_{HP} = 4.5 Hz, 1H, PCHC*H*H), 3.82 (s, 3H, OCH_3), 3.73 (s, 3H, OCH_3), 3.40 (ddd, J_{HH} = 18.1 and 2.4 Hz, J_{HP} = 11.3 Hz, 1H, PCHCH*H*).

*(S)-3-(Diphenylphosphinyl)-3-phenyl-1-(pyridin-2-yl)propan-1-one (**7jj**).* With CH_2Cl_2/acetone (5/1) as eluent; pale yellow solid (77.7 mg, 95%); mp 188−190 °C. The enantiomeric excess was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol (80/20) and flow rate 1.0 mL/min and detected at a UV wavelength of 228 nm. Retention times: 7.5 min (major), 9.4 min, 89% ee. $[\alpha]_D^{20}$ = −133° (*c* 0.303, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 8.61 (dd, J_{HH} = 0.6 and 4.7 Hz, 1H), 8.02−7.97 (m, 2H), 7.83 (d, J_{HH} = 7.8 Hz, 1H), 7.73−7.69 (m, 1H), 7.52−7.46 (m, 5H), 7.41−7.23 (m, 6H), 7.14−7.08 (m, 3H), 4.49−4.35 (m, 2H), 3.61−3.54 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.8 (d, J_{CP} = 13.5 Hz), 152.7, 149.0, 136.7, 135.8 (d, J_{CP} = 5.8 Hz), 132.1 (d, J_{CP} = 31.2 Hz), 131.9 (d, J_{CP} = 2.7 Hz), 131.5 (d, J_{CP} = 8.5 Hz), 131.4 (d, J_{CP} = 2.6 Hz), 131.14 (d, J_{CP} = 26.2 Hz), 131.12 (d, J_{CP} = 8.8 Hz), 130.0 (d, J_{CP} = 5.4 Hz), 128.8 (d, J_{CP} = 11.1 Hz), 128.2 (d, J_{CP} = 1.9 Hz), 128.1 (d, J_{CP} = 11.7 Hz), 127.3, 127.0 (d, J_{CP} = 2.3 Hz), 121.8, 41.5 (d, J_{CP} = 68.2 Hz), 38.2. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 33.7. HRMS (positive ESI): $[M + H]^+$ calcd for $C_{26}H_{23}NO_2P$ 412.1466, found 412.1469.

*(S)-3-(4-Bromophenyl)-3-(diphenylphosphinyl)-1-(pyridin-2-yl)-propan-1-one (**7kk**).* Pale yellow solid (90.3 mg, 92%); mp 219−221 °C. The enantiomeric excess was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol (90/10) and flow rate 1.0 mL/min and detected at a UV wavelength of 228 nm. Retention times: 17.0 min (major), 20.4 min, 87% ee. $[\alpha]_D^{20}$ = −146° (*c* 0.163, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 8.61 (d, J_{HH} = 4.5 Hz, 1H), 8.00−7.96 (m, 2H), 7.83 (d, J_{HH} = 7.8 Hz, 1H), 7.73 (t, J_{HH} = 7.6 Hz, 1H), 7.55−7.50 (m, 5H), 7.42−7.20 (m, 8H), 4.44−4.32 (m, 2H), 3.55−3.48 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.7 (d, J_{CP} = 13.5 Hz), 152.6, 149.0, 136.8, 135.0 (d, J_{CP} = 5.8 Hz), 132.0 (d, J_{CP} = 2.9 Hz), 131.64 (d, J_{CP} = 3.5 Hz), 131.60 (d, J_{CP} = 5.1 Hz), 131.4 (d, J_{CP} = 8.5 Hz), 131.3 (d, J_{CP} = 1.9 Hz), 131.0 (d, J_{CP} = 8.8 Hz), 130.9 (d, J_{CP} = 30.7 Hz), 128.9 (d, J_{CP} = 11.4 Hz), 128.3 (d, J_{CP} = 11.7 Hz), 127.4, 121.8, 121.1 (d, J_{CP} = 3.2 Hz), 41.0 (d, J_{CP} = 68.0 Hz), 38.1. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 33.1. HRMS (positive ESI): $[M + H]^+$ calcd for $C_{26}H_{22}BrNO_2P$ 490.0572, found 490.0573.

*(S)-3-(2-Bromophenyl)-3-(diphenylphosphinyl)-1-(pyridin-2-yl)-propan-1-one (**7ll**).* With CH_2Cl_2/acetone (5/1) as eluent; pale yellow solid (72.7 mg, 74%); mp 102−105 °C. The enantiomeric excess was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol (80/20) and flow rate 1.0 mL/min and detected at a UV wavelength of 228 nm. Retention times: 8.1 min (major), 10.8 min, 38% ee. $[\alpha]_D^{20}$ = −53° (*c* 0.221, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 8.62 (dd, J_{HH} = 0.5 and 4.6 Hz, 1H), 8.14−8.08 (m, 2H), 7.91−7.88 (m, 1H), 7.83 (d, J_{HH} = 7.8 Hz, 1H), 7.74−7.70 (m, 1H), 7.59−7.56 (m, 3H), 7.42−7.17 (m, 8H), 6.99−6.95 (m, 1H), 5.10 (ddd, J_{HH} = 10.6 and 3.0 Hz, J_{HP} = 7.2 Hz, 1H, PC*H*CH_2), 4.30 (ddd, J_{HH} = 17.5 and 11.0 Hz, J_{HP} = 6.0 Hz, 1H, PCHC*H*H), 3.69 (ddd, J_{HH} = 17.8 and 3.1 Hz, J_{HP} = 9.6 Hz, 1H, PCHCH*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.5 (d, J_{CP} = 13.5 Hz), 152.6, 148.9, 136.8, 135.6 (d, J_{CP} = 5.1 Hz), 132.5 (d, J_{CP} = 1.7 Hz), 132.2 (d, J_{CP} = 2.7 Hz), 131.7 (d, J_{CP} = 8.6 Hz), 131.54 (d, J_{CP} = 2.7 Hz), 131.52 (d, J_{CP} = 72.1 Hz), 131.2 (d, J_{CP} = 9.4 Hz), 130.7 (d, J_{CP} = 4.1 Hz), 130.6 (d, J_{CP} = 66.6 Hz), 128.9 (d, J_{CP} = 11.2 Hz), 128.5 (d, J_{CP} = 2.3 Hz), 127.8 (d, J_{CP} = 11.9 Hz), 127.7 (d, J_{CP} = 2.4 Hz), 127.3, 126.4 (d, J_{CP} = 7.4 Hz), 121.8, 40.1 (d, J_{CP} = 67.1 Hz), 38.9. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 34.1. HRMS (positive ESI): $[M + H]^+$ calcd for $C_{26}H_{22}BrNO_2P$ 490.0572. found 490.0573.

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*(S)-3-(3-Bromophenyl)-3-(diphenylphosphinyl)-1-(pyridin-2-yl)-propan-1-one (**7mm**).* Pale yellow solid (84.2 mg, 86%); mp 210−213 °C. The enantiomeric excess was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol (90/10) and flow rate 1.0 mL/min and detected at a UV wavelength of 228 nm. Retention times: 15.4 min (major), 23.0 min, 85% ee. $[\alpha]_D^{20} = -120°$ (*c* 0.090, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 8.62 (dd, J_{HH} = 0.6 and 4.6 Hz, 1H), 8.01−7.95 (m, 2H), 7.85−7.83 (m, 1H), 7.75−7.71 (m, 1H), 7.53−7.48 (m, 5H), 7.43−7.37 (m, 3H), 7.33−7.27 (m, 3H), 7.23−7.21 (m, 1H), 7.01 (t, J_{HH} = 7.8 Hz, 1H), 4.43−4.30 (m, 2H), 3.60−3.53 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.5 (d, J_{CP} = 13.2 Hz), 152.6, 149.0, 138.3 (d, J_{CP} = 5.4 Hz), 136.8, 133.0 (d, J_{CP} = 5.5 Hz), 132.1 (d, J_{CP} = 2.6 Hz), 131.7 (d, J_{CP} = 33.4 Hz), 131.65 (d, J_{CP} = 2.5 Hz), 131.5 (d, J_{CP} = 8.4 Hz), 131.1 (d, J_{CP} = 8.8 Hz), 130.7 (d, J_{CP} = 28.9 Hz), 130.1 (d, J_{CP} = 2.6 Hz), 129.7 (d, J_{CP} = 2.0 Hz), 128.9 (d, J_{CP} = 11.4 Hz), 128.5 (d, J_{CP} = 5.4 Hz), 128.2 (d, J_{CP} = 11.7 Hz), 127.4, 122.1 (d, J_{CP} = 2.4 Hz), 121.8, 41.4 (d, J_{CP} = 67.6 Hz), 38.0. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 33.3. HRMS (positive ESI): $[M + H]^+$ calcd for $C_{26}H_{22}BrNO_2P$ 490.0572, found 490.0574.

*(S)-3-(Diphenylphosphinyl)-3-(4-nitrophenyl)-1-(pyridin-2-yl)-propan-1-one (**7nn**).* Pale yellow solid (81.9 mg, 90%); mp 207−209 °C. The enantiomeric excess was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol (90/10) and flow rate 1.0 mL/min and detected at a UV wavelength of 228 nm. Retention times: 34.1 min (major), 46.2 min, 88% ee. $[\alpha]_D^{20} = -191°$ (*c* 0.199, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 8.63 (dd, J_{HH} = 1.4 and 4.7 Hz, 1H), 8.03−7.98 (m, 4H), 7.84−7.82 (m, 1H), 7.76−7.72 (m, 1H), 7.56−7.52 (m, 7H), 7.45−7.37 (m, 2H), 7.33−7.30 (m, 2H), 4.58−4.41 (m, 2H), 3.58 (ddd, J_{HH} = 18.0 and 2.0 Hz, J_{HP} = 9.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.4 (d, J_{CP} = 13.2 Hz), 152.4, 149.1, 146.8 (d, J_{CP} = 2.8 Hz), 144.1 (d, J_{CP} = 5.7 Hz), 136.9, 132.3 (d, J_{CP} = 2.7 Hz), 131.9 (d, J_{CP} = 2.7 Hz), 131.4 (d, J_{CP} = 49.0 Hz), 131.3 (d, J_{CP} = 8.5 Hz), 130.9 (d, J_{CP} = 8.9 Hz), 130.8 (d, J_{CP} = 5.4 Hz), 130.4 (d, J_{CP} = 45.7 Hz), 129.0 (d, J_{CP} = 11.5 Hz), 128.4 (d, J_{CP} = 11.8 Hz), 127.6, 123.3 (d, J_{CP} = 1.8 Hz), 121.8, 41.8 (d, J_{CP} = 66.2 Hz), 38.1. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 32.6. HRMS (positive ESI): $[M + H]^+$ calcd for $C_{26}H_{22}N_2O_4P$ 457.1317, found 457.1318.

*(S)-3-(Diphenylphosphinyl)-1-(pyridin-2-yl)-3-(p-tolyl)propan-1-one (**7oo**).* Pale yellow solid (68.8 mg, 81%); mp 213−215 °C. The enantiomeric excess was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol (80/20) and flow rate 1.0 mL/min and detected at a UV wavelength of 228 nm. Retention times: 7.4 min (major), 9.8 min, 73% ee. $[\alpha]_D^{20} = -112°$ (*c* 0.111, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 8.61 (d, J_{HH} = 4.6 Hz, 1H), 8.00−7.95(m, 2H), 7.82 (d, J_{HH} = 7.8 Hz, 1H), 7.70 (t, J_{HH} = 7.6 Hz, 1H), 7.54−7.50 (m, 5H), 7.40−7.34 (m, 2H), 7.29−7.25 (m, 2H), 7.21−7.19 (m, 2H), 6.93 (d, J_{HH} = 7.9 Hz, 2H), 4.47−4.31 (m, 2H), 3.56 (ddd, J_{HH} = 17.7 and 2.0 Hz, J_{HP} = 12.8 Hz, 1H), 2.19 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.9 (d, J_{CP} = 13.6 Hz), 152.8, 149.0, 136.7, 136.5 (d, J_{CP} = 2.5 Hz), 132.5 (d, J_{CP} = 5.7 Hz), 132.3 (d, J_{CP} = 21.8 Hz), 131.8 (d, J_{CP} = 2.5 Hz), 131.5 (d, J_{CP} = 8.5 Hz), 131.33 (d, J_{CP} = 2.8 Hz), 131.32 (d, J_{CP} = 16.2 Hz), 131.2 (d, J_{CP} = 8.7 Hz), 129.8 (d, J_{CP} = 5.6 Hz), 128.9 (d, J_{CP} = 1.9 Hz), 128.7 (d, J_{CP} = 11.1 Hz), 128.1 (d, J_{CP} = 11.6 Hz), 127.2, 121.8, 41.0 (d, J_{CP} = 68.7 Hz), 38.3, 21.1. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 33.6. HRMS (positive ESI): $[M + H]^+$ calcd for $C_{27}H_{25}NO_2P$ 426.1623, found 426.1624.

*(S)-3-(Diphenylphosphinyl)-3-(4-methoxyphenyl)-1-(pyridin-2-yl)propan-1-one (**7pp**).* Pale yellow solid (75.2 mg, 85%); mp 206−208 °C. The enantiomeric excess was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol (80/20) and flow rate 1.0 mL/min and detected at a UV wavelength of 228 nm. Retention times: 9.9 min (major), 13.0 min, 95% ee. $[\alpha]_D^{20} = -146°$ (*c* 0.086, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 8.61 (d, J_{HH} = 4.2 Hz, 1H), 8.01−7.96 (m, 2H), 7.83 (d, J_{HH} = 7.8 Hz, 1H), 7.73−7.69 (m, 1H), 7.53−7.48 (m, 5H), 7.41−7.34 (m, 2H), 7.30−7.23 (m, 4H), 6.67 (d, J_{HH} = 8.6 Hz, 2H), 4.44−4.30 (m, 2H), 3.69 (s, 3H, OCH_3), 3.56−3.50 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.0 (d, J_{CP} = 13.8 Hz), 158.5 (d, J_{CP} = 2.3 Hz), 152.8, 149.0, 136.7, 132.3 (d, J_{CP} = 31.9 Hz), 131.8 (d, J_{CP} = 2.4 Hz), 131.5 (d, J_{CP} = 8.6 Hz), 131.3 (d, J_{CP} = 2.7 Hz), 131.2 (d, J_{CP} = 8.7 Hz), 131.0 (d, J_{CP} = 5.5 Hz), 128.8 (d, J_{CP} = 11.1 Hz), 128.1 (d, J_{CP} = 11.6 Hz), 127.6 (d, J_{CP} = 5.8 Hz), 127.3, 121.8, 113.6 (d, J_{CP} = 1.7 Hz), 55.1, 40.6 (d, J_{CP} = 69.1 Hz), 38.3. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 33.6. HRMS (positive ESI): $[M + H]^+$ calcd for $C_{27}H_{25}NO_3P$ 442.1572, found 442.1573.

*(S)-3-(Diphenylphosphinyl)-3-(furan-2-yl)-1-(pyridin-2-yl)propan-1-one (**7qq**).* Pale yellow solid (69.9 mg, 87%); mp 149−151 °C. The enantiomeric excess was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol (80/20) and flow rate 1.0 mL/min and detected at a UV wavelength of 228 nm. Retention times: 9.7 min (major), 12.7 min, 82% ee. $[\alpha]_D^{20} = -76°$ (*c* 0.105, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 8.64 (d, J_{HH} = 4.6 Hz, 1H), 7.92−7.87 (m, 3H), 7.76 (t, J_{HH} = 7.6 Hz, 1H), 7.62−7.38 (m, 9H), 7.14 (s, 1H), 6.16 (t, J_{HH} = 2.9 Hz, 1H), 6.08 (t, J_{HH} = 3.2 Hz, 1H), 4.74 (ddd, J_{HH} = 14.1 and 3.0 Hz, J_{HP} = 11.1 Hz, 1H, PC*H*CH_2), 4.24 (ddd, J_{HH} = 18.5 and 10.9 Hz, J_{HP} = 5.5 Hz, 1H, PCHC*H*H), 3.67 (ddd, J_{HH} = 18.5 and 3.0 Hz, J_{HP} = 9.9 Hz, 1H, PCHCH*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.5 (d, J_{CP} = 12.5 Hz), 152.7, 149.3 (d, J_{CP} = 6.5 Hz), 149.0, 141.7 (d, J_{CP} = 2.9 Hz), 136.8, 132.0 (d, J_{CP} = 2.5 Hz), 131.8 (d, J_{CP} = 2.7 Hz), 131.6 (d, J_{CP} = 46.6 Hz), 131.51 (d, J_{CP} = 8.8 Hz), 131.50 (d, J_{CP} = 8.9 Hz), 130.6 (d, J_{CP} = 49.6 Hz), 128.7 (d, J_{CP} = 11.6 Hz), 128.2 (d, J_{CP} = 11.6 Hz), 127.4, 121.9, 110.7 (d, J_{CP} = 2.8 Hz), 108.8 (d, J_{CP} = 5.9 Hz), 36.2 (d, J_{CP} = 70.0 Hz), 36.0. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 32.3. HRMS (positive ESI): $[M + H]^+$ calcd for $C_{24}H_{21}NO_3P$ 402.1259, found 402.1263.

*(S)-3-(Diphenylphosphinyl)-1-(pyridin-2-yl)-3-(thien-2-yl)propan-1-one (**7rr**).* With CH_2Cl_2/acetone (5/1) as eluent; white solid (55.7 mg, 67%); mp 176−178 °C. The enantiomeric excess was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol (80/20) and flow rate 1.0 mL/min and detected at a UV wavelength of 228 nm. Retention times: 8.9 min (major), 11.5 min, 82% ee. $[\alpha]_D^{20} = -110°$ (*c* 0.100, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 8.62 (d, J_{HH} = 4.5 Hz, 1H), 7.99−7.94 (m, 2H), 7.87 (d, J_{HH} = 7.8 Hz, 1H), 7.75−7.70 (m, 1H), 7.63−7.58 (m, 2H), 7.51−7.49 (m, 3H), 7.42−7.39 (m, 2H), 7.35−7.31 (m, 2H), 7.02−6.97 (m, 2H), 6.79−6.77 (m, 1H), 4.85−4.80 (m, 1H, PC*H*CH_2), 4.33 (ddd, J_{HH} = 18.2 and 10.8 Hz, J_{HP} = 5.1 Hz, 1H, PCHC*H*H), 3.58 (ddd, J_{HH} = 18.3 and 2.7 Hz, J_{HP} =10.0 Hz, 1H, PCHCH*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.4 (d, J_{CP} = 13.0 Hz), 152.6, 149.0, 137.6 (d, J_{CP} = 6.5 Hz), 136.7, 132.0 (d, J_{CP} = 2.5 Hz), 131.68 (d, J_{CP} = 12.7 Hz), 131.65 (d, J_{CP} = 2.8 Hz), 131.5 (d, J_{CP} = 8.7 Hz), 131.3 (d, J_{CP} = 8.8 Hz), 130.7 (d, J_{CP} = 7.8 Hz), 128.8 (d, J_{CP} = 11.4 Hz), 128.2 (d, J_{CP} = 11.7 Hz), 127.40 (d, J_{CP} = 4.9 Hz), 127.38, 126.7 (d, J_{CP} = 2.5 Hz), 124.8 (d, J_{CP} = 2.9 Hz), 121.8, 39.2, 36.9 (d, J_{CP} = 70.1 Hz). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 32.7. HRMS (positive ESI): $[M + H]^+$ calcd for $C_{24}H_{21}NO_2PS$ 418.1031, found 418.1032.

*(S)-3-(Diphenylphosphinyl)-3-(naphthalen-1-yl)-1-(pyridin-2-yl)-propan-1-one (**7ss**).* With CH_2Cl_2/acetone (5/1) as eluent; pale yellow solid (51.1 mg, 55%); mp 156−158 °C. The enantiomeric excess was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol (80/20) and flow rate 1.0 mL/min and detected at a UV wavelength of 228 nm. Retention times: 8.1 min (major), 10.7 min, 46% ee. $[\alpha]_D^{20} = -57°$ (*c* 0.106, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 8.60 (d, J_{HH} = 4.3 Hz, 1H), 8.10−8.05 (m, 4H), 7.71−7.60 (m, 4H), 7.52−7.51 (m, 3H), 7.43−7.32 (m, 6H), 7.08−7.04 (m, 1H), 6.97−6.93 (m, 2H), 5.48−5.42 (m, 1H, PC*H*CH_2), 4.46 (ddd, J_{HH} = 18.1 and 9.8 Hz, J_{HP} = 6.5 Hz, 1H, PCHC*H*H), 3.87 (ddd, J_{HH} = 18.2 and 3.0 Hz, J_{HP} = 10.9 Hz, 1H, PCHCH*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.9 (d, J_{CP} = 12.6 Hz), 152.6, 148.9, 136.6, 133.5, 132.7 (d, J_{CP} = 5.3 Hz), 132.2, 132.1, 132.0, 131.7 (d, J_{CP} = 8.3 Hz), 131.2 (d, J_{CP} = 2.0 Hz), 131.0, 130.8 (d, J_{CP} = 9.2 Hz), 128.8 (d, J_{CP} = 11.1 Hz), 128.6, 127.7 (d, J_{CP} = 11.7 Hz), 127.3, 125.8, 125.4, 125.1, 122.9, 121.7, 39.6, 34.8 (d, J_{CP} = 68.5 Hz). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 33.8. HRMS (positive ESI): $[M + H]^+$ calcd for $C_{30}H_{25}NO_2P$ 462.1623. Found: 462.1624.

*(S)-2-(3-(Diphenylphosphinyl)-3-phenylpropionyl)pyridine N-Oxide (**7jj'**).*[21] White solid (69.8 mg, 82%); mp 169−170 °C. The enantiomeric excess was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol (70/30) and flow rate 1.0 mL/min and detected at a UV wavelength of 228 nm. Retention times: 18.0 min (major), 23.6 min, 63% ee. $[\alpha]_D^{20} = -49°$ (*c* 0.896, CH_2Cl_2).

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^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (d, J_{HH} = 6.5 Hz, 1H), 8.01−7.96 (m, 2H), 7.55−7.51 (m, 3H), 7.47−7.43 (m, 2H), 7.37−7.33 (m, 1H), 7.27−7.22 (m, 3H), 7.15−7.05 (m, 7H), 4.44 (ddd, J_{HH} = 12.8 and 4.0 Hz, J_{HP} = 8.9 Hz, 1H, PC*H*CH_2), 4.06 (ddd, J_{HH} = 18.0 and 10.8 Hz, J_{HP} = 8.0 Hz, 1H, PCHC*H*H), 3.73 (ddd, J_{HH} = 18.0 and 4.0 Hz, J_{HP} = 8.6 Hz, 1H, PCHCH*H*).

*(S)-2-(3-(4-Bromophenyl)-3-(diphenylphosphinyl)propionyl)-pyridine N-Oxide (**7kk'**).*[21] Pale yellow solid (84.0 mg, 83%); mp 208−209 °C. The enantiomeric excess was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol (70/30) and flow rate 1.0 mL/min and detected at a UV wavelength of 228 nm. Retention times: 20.9 min (major), 32.5 min, 83% ee. $[\alpha]_D^{20}$ = −69° (*c* 0.828, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, J_{HH} = 6.4 Hz, 1H), 7.99−7.94 (m, 2H), 7.55−7.47 (m, 5H), 7.40−7.36 (m, 1H), 7.31−7.21 (m, 5H), 7.19−7.06 (m, 4H), 4.42 (ddd, J_{HH} = 12.2 and 3.7 Hz, J_{HP} = 8.8 Hz, 1H, PC*H*CH_2), 4.06 (ddd, J_{HH} = 18.0 and 10.8 Hz, J_{HP} = 7.3 Hz, 1H, PCHC*H*H), 3.71 (ddd, J_{HH} = 18.0 and 3.7 Hz, J_{HP} = 8.8 Hz, 1H, PCHCH*H*).

*(S)-2-(3-(2-Bromophenyl)-3-(diphenylphosphinyl)propionyl)-pyridine N-Oxide (**7ll'**).*[21] Pale yellow oil (55.0 mg, 54%). The enantiomeric excess was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol (70/30) and flow rate 1.0 mL/min and detected at a UV wavelength of 228 nm. Retention times: 16.0 min (major), 26.0 min, 18% ee. $[\alpha]_D^{20}$ = −15° (*c* 0.941, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06−8.02 (m, 3H), 7.73−7.70 (m, 1H), 7.53−7.52 (m, 3H), 7.31−7.16 (m, 5H), 7.13−7.07 (m, 3H), 7.02−6.98 (m, 2H), 6.90−6.85 (m, 1H), 5.01 (ddd, J_{HH} = 12.0 and 4.2 Hz, J_{HP} = 8.0 Hz, 1H, PC*H*CH_2), 3.91 (ddd, J_{HH} = 19.4 and 11.0 Hz, J_{HP} = 8.3 Hz, 1H, PCHC*H*H), 3.76 (ddd, J_{HH} = 16.9 and 4.2 Hz, J_{HP} = 7.4 Hz, 1H, PCHCH*H*).

*(S)-2-(3-(4-Chlorophenyl)-3-(diphenylphosphinyl)propionyl)-pyridine N-Oxide (**7tt**).*[21] White solid (50.9 mg, 55%); mp 210−212 °C. The enantiomeric excess was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol (70/30) and flow rate 1.0 mL/min and detected at a UV wavelength of 228 nm. Retention times: 19.2 min (major), 28.5 min, 68% ee. $[\alpha]_D^{20}$ = −98° (*c* 0.832, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (d, J_{HH} = 6.5 Hz, 1H), 7.99−7.94 (m, 2H), 7.56−7.46 (m, 5H), 7.40−7.36 (m, 1H), 7.31−7.27 (m, 3H), 7.19−7.06 (m, 6H), 4.43 (ddd, J_{HH} = 12.4 and 3.8 Hz, J_{HP} = 8.7 Hz, 1H, PC*H*CH_2), 4.05 (ddd, J_{HH} = 18.0 and 10.8 Hz, J_{HP} = 7.4 Hz, 1H, PCHC*H*H), 3.71 (ddd, J_{HH} = 18.0 and 3.8 Hz, J_{HP} = 8.7 Hz, 1H, PCHCH*H*).

*(S)-2-(3-(Diphenylphosphinyl)-3-(4-nitrophenyl)propionyl)-pyridine N-Oxide (**7nn'**).*[21] Pale yellow solid (65.0 mg, 69%); mp 197−198 °C. The enantiomeric excess was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol (60/40) and flow rate 1.0 mL/min and detected at a UV wavelength of 228 nm. Retention times: 20.6 min (major), 41.8 min, 76% ee. $[\alpha]_D^{20}$ = −104° (*c* 0.818, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (d, J_{HH} = 6.4 Hz, 1H), 8.01−7.97 (m, 4H), 7.58−7.50 (m, 5H), 7.45−7.38 (m, 3H), 7.32−7.28 (m, 4H), 7.17 (t, J_{HH} = 7.4 Hz, 1H), 4.59 (ddd, J_{HH} = 11.2 and 3.4 Hz, J_{HP} = 8.6 Hz, 1H, PC*H*CH_2), 4.20 (ddd, J_{HH} = 18.2 and 10.8 Hz, J_{HP} = 6.7 Hz, 1H, PCHC*H*H), 3.79 (ddd, J_{HH} = 18.4 and 3.4 Hz, J_{HP} = 9.1 Hz, 1H, PCHCH*H*).

*(S)-2-(3-(Diphenylphosphinyl)-3-(3-nitrophenyl)propionyl)-pyridine N-Oxide (**7uu**).*[21] Pale yellow solid (85.0 mg, 90%); mp 214−215 °C. The enantiomeric excess was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol (60/40) and flow rate 0.8 mL/min and detected at a UV wavelength of 228 nm. Retention times: 17.3 min (major), 28.2 min, 79% ee. $[\alpha]_D^{20}$ = −117° (*c* 0.994, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (d, J_{HH} = 6.4 Hz, 1H), 8.02−7.96 (m, 3H), 7.90 (d, J_{HH} = 1.9 Hz, 1H), 7.76 (d, J_{HH} = 7.0 Hz, 1H), 7.58−7.50 (m, 5H), 7.40−7.27 (m, 6H), 7.17−7.13 (m, 1H), 4.59 (ddd, J_{HH} = 12.0 and 3.6 Hz, J_{HP} = 8.7 Hz, 1H, PC*H*CH_2), 4.16 (ddd, J_{HH} = 18.2 and 10.7 Hz, J_{HP} = 6.9 Hz, 1H, PCHC*H*H), 3.80 (ddd, J_{HH} = 18.4 and 3.6 Hz, J_{HP} = 9.1 Hz, 1H, PCHCH*H*).

*(S)-2-(3-(Diphenylphosphinyl)-3-(4-methylphenyl)propionyl)-pyridine N-Oxide (**7oo'**).*[21] Pale yellow solid (71.5 mg, 81%); mp 185−187 °C. The enantiomeric excess was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol (70/30) and flow rate 1.0 mL/min and detected at a UV wavelength of 228 nm. Retention times: 17.3 min (major), 26.6 min, 59% ee. $[\alpha]_D^{20}$ = −74° (*c* 0.730, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, J_{HH} = 6.5 Hz, 1H), 7.99−7.94 (m, 2H), 7.54−7.46 (m, 5H), 7.38−7.34 (m, 1H), 7.28−7.24 (m, 3H), 7.08 (d, J_{HH} = 4.6 Hz, 2H), 7.03−7.01 (m, 2H), 6.89 (d, J_{HH} = 7.9 Hz, 2H), 4.41 (ddd, J_{HH} = 13.1 and 4.0 Hz, J_{HP} = 10.7 Hz, 1H, PC*H*CH_2), 4.03 (ddd, J_{HH} = 18.0 and 10.7 Hz, J_{HP} = 8.0 Hz, 1H, PCHC*H*H), 3.71 (ddd, J_{HH} = 17.7 and 3.9 Hz, J_{HP} = 8.6 Hz, 1H, PCHCH*H*), 2.20 (s, 3H, CH_3).

*(S)-2-(3-(Diphenylphosphinyl)-3-(4-methoxyphenyl)propionyl)-pyridine N-Oxide (**7pp'**).*[21] Pale yellow solid (59.0 mg, 65%); mp 196−198 °C. The enantiomeric excess was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol (70/30) and flow rate 1.0 mL/min and detected at a UV wavelength of 228 nm. Retention times: 23.2 min (major), 34.0 min, 77% ee. $[\alpha]_D^{20}$ = −112° (*c* 0.418, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (d, J_{HH} = 6.5 Hz, 1H), 7.99−7.94 (m, 2H), 7.55−7.44 (m, 5H), 7.38−7.34 (m, 1H), 7.28−7.24 (m, 3H), 7.10−7.04 (m, 4H), 6.63 (d, J_{HH} = 8.6 Hz, 2H), 4.39 (ddd, J_{HH} = 12.7 and 3.9 Hz, J_{HP} = 9.0 Hz, 1H, PC*H*CH_2), 4.01 (ddd, J_{HH} = 17.8 and 11.0 Hz, J_{HP} = 7.8 Hz, 1H, PCHC*H*H), 3.73−3.65 (m, 4H, PCHCH*H* and OCH_3).

*(S)-2-(3-(Diphenylphosphinyl)-3-(3-methoxyphenyl)propionyl)-pyridine N-Oxide (**7vv**).*[21] Pale yellow oil (80.3 mg, 88%). The enantiomeric excess was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol (70/30) and flow rate 1.0 mL/min and detected at a UV wavelength of 228 nm. Retention times: 19.5 min (major), 28.7 min, 80% ee. $[\alpha]_D^{20}$ = −104° (*c* 0.492, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, J_{HH} = 6.5 Hz, 1H), 8.00−7.95 (m, 2H), 7.54−7.45 (m, 5H), 7.38−7.33 (m, 1H), 7.28−7.23 (m, 3H), 7.11−7.08 (m, 2H), 6.99 (t, J_{HH} = 7.9 Hz, 1H), 6.72 (d, J_{HH}= 7.4 Hz, 1H), 6.67−6.62 (m, 2H), 4.43 (ddd, J_{HH} = 13.2 and 4.1 Hz, J_{HP} = 10.7 Hz, 1H, PC*H*CH_2), 4.06 (ddd, J_{HH} = 18.0 and 10.8 Hz, J_{HP} = 8.2 Hz, 1H, PCHC*H*H), 3.72 (ddd, J_{HH} = 17.8 and 4.1 Hz, J_{HP} = 8.6 Hz, 1H, PCHCH*H*), 3.60 (s, 3H, OCH_3).

*(S)-2-(3-(Diphenylphosphinyl)-3-(furan-2-yl)propionyl)pyridine N-Oxide (**7qq'**).*[21] Pale yellow oil (74.0 mg, 89%). The enantiomeric excess was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol (60/40) and flow rate 1.0 mL/min and detected at a UV wavelength of 228 nm. Retention times: 11.9 min (major), 17.0 min, 55% ee. $[\alpha]_D^{20}$ = −20° (*c* 0.947, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, J_{HH} = 6.4 Hz, 1H), 7.90−7.85 (m, 2H), 7.55−7.43 (m, 6H), 7.40−7.30 (m, 4H), 7.23−7.19 (m, 1H), 7.11 (s, 1H), 6.17 (dd, J_{HH} = 1.9 and 3.2 Hz, 1H), 6.05 (t, J_{HH} = 3.2 Hz, 1H), 4.75 (ddd, J_{HH} = 14.8 and 4.6 Hz, J_{HP} = 10.3 Hz, 1H, PC*H*CH_2), 3.96 (ddd, J_{HH} = 18.2 and 10.1 Hz, J_{HP} = 8.6 Hz, 1H, PCHC*H*H), 3.78 (ddd, J_{HH} = 18.1 and 4.6 Hz, J_{HP} = 8.6 Hz, 1H, PCHCH*H*).

*(S)-2-(3-(Diphenylphosphinyl)-3-(thien-2-yl)propionyl)pyridine N-Oxide (**7rr'**).*[21] Pale yellow solid (70.0 mg, 80%); mp 167−168 °C. The enantiomeric excess was determined on a Daicel Chiralpak AD-H column with hexane/2-propanol (60/40) and flow rate 1.0 mL/min and detected at a UV wavelength of 228 nm. Retention times: 33.2 min (major), 56.2 min, 21% ee. $[\alpha]_D^{20}$ = −22° (*c* 0.644, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (d, J_{HH} = 6.4 Hz, 1H), 7.98−7.93 (m, 2H), 7.57−7.52 (m, 5H), 7.43−7.39 (m, 1H), 7.34−7.28 (m, 3H), 7.23−7.20 (m, 1H), 7.16−7.12 (m, 1H), 7.01−6.99 (m, 1H), 6.85 (t, J_{HH} = 2.6 Hz, 1H), 6.77 (dd, J_{HH} = 3.6, 5.0 Hz, 1H), 4.81 (ddd, J_{HH} = 13.8 and 3.9 Hz, J_{HP} = 10.6 Hz, 1H, PC*H*CH_2), 4.00 (ddd, J_{HH} = 17.9 and 10.8 Hz, J_{HP} = 7.4 Hz, 1H, PCHC*H*H), 3.72 (ddd, J_{HH} = 17.7 and 4.0 Hz, J_{HP} = 8.0 Hz, 1H, PCHCH*H*).

*(S,E)-2-(3-(Diphenylphosphinyl)-5-phenyl-4-pentenoyl)pyridine N-Oxide (**7ww**).*[21] Pale yellow oil (70.0 mg, 77%). The enantiomeric excess was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol (60/40) and flow rate 1.0 mL/min and detected at a UV wavelength of 228 nm. Retention times: 11.8 min (major), 16.7 min, 72% ee. $[\alpha]_D^{20}$ = −67° (*c* 0.917, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, J_{HH} = 6.3 Hz, 1H), 7.94−7.89 (m, 2H), 7.79−7.74 (m, 2H), 7.53−7.41 (m, 7H), 7.33−7.29 (m, 1H), 7.24−7.13 (m, 6H), 6.30 (dd, *J* = 15.9, 4.3 Hz, 1H), 6.08 (ddd, *J* = 14.9, 9.1, 5.7 Hz, 1H), 4.20−4.12 (m, 1H, PC*H*CH_2), 3.76 (ddd, J_{HH} = 17.7 and 10.0 Hz, J_{HP} = 8.0 Hz, 1H, PCHC*H*H), 3.61 (ddd, J_{HH} = 17.5 and 4.0 Hz, J_{HP} = 9.8 Hz, 1H, PCHCH*H*).

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*(R)-2-(3-(Diphenylphosphinyl)-3-(naphthalen-1-yl)propionyl)-pyridine N-Oxide (**7ss'**).*[21] Pale yellow oil (75.8 mg, 80%). The enantiomeric excess was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol (60/40) and flow rate 1.0 mL/min and detected at a UV wavelength of 228 nm. Retention times: 9.3 min, 13.6 min (major), 9% ee. $[\alpha]_D^{20}$ = +4° (*c* 0.984, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15−8.10 (m, 2H), 8.01 (d, J_{HH} = 6.4 Hz, 1H), 7.86−7.83 (m, 1H), 7.74 (d, J_{HH} = 8.5 Hz, 1H), 7.62−7.59 (m, 5H), 7.39 (t, J_{HH} = 7.6 Hz, 1H), 7.28−7.15 (m, 4H), 7.08−6.92 (m, 4H), 6.73 (t, J_{HH} = 7.6 Hz, 1H), 6.65−6.62 (m, 1H), 5.48 (ddd, J_{HH} = 13.6 and 4.6 Hz, J_{HP} = 10.4 Hz, 1H, PC*H*CH$_2$), 4.10 (ddd, J_{HH} = 14.2 and 7.1 Hz, J_{HP} = 3.3 Hz, 1H, PCHC*H*H), 3.95 (ddd, J_{HH} = 17.2 and 4.6 Hz, J_{HP} = 7.0 Hz, 1H, PCHCH*H*).

(S)-Phenyl 3-(Diphenylphosphinyl)-3-phenylpropanoate (Product in Scheme 4).[9a] With CH_2Cl_2/MeOH (100/1) as eluent. white solid (15.0 mg, 18%); mp 176−177 °C. The enantiomeric excess was determined on a Daicel Chiralpak IC-3 column with hexane/2-propanol (80/20) and flow rate 1.0 mL/min and detected at a UV wavelength of 228 nm. Retention times: 24.9 min (major), 32.6 min, 83% ee. $[\alpha]_D^{20}$ = −56° (*c* 0.116, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01−7.97 (m, 2H), 7.59−7.46 (m, 5H), 7.37−7.11 (m, 11H), 6.68 (d, J_{HH} = 7.6 Hz, 2H), 4.15 (ddd, J_{HH} = 11.5 and 3.6 Hz, J_{HP} = 8.2 Hz, 1H), 3.37 (ddd, J_{HH} = 18.0 and 11.5 Hz, J_{HP} = 6.7 Hz, 1H), 3.27 (ddd, J_{HH} = 16.2 and 3.6 Hz, J_{HP} = 8.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.0 (d, J_{CP} = 17.8 Hz), 149.3, 133.6 (d, J_{CP} = 5.6 Hz), 131.2 (d, J_{CP} = 2.6 Hz), 130.6 (d, J_{CP} = 2.7 Hz), 130.4 (d, J_{CP} = 8.6 Hz), 130.1 (d, J_{CP} = 8.9 Hz), 129.5 (two peaks), 128.8 (d, J_{CP} = 5.3 Hz), 128.2, 128.0 (d, J_{CP} = 11.2 Hz), 127.4 (d, J_{CP} = 1.3 Hz), 127.1 (d, J_{CP} = 11.8 Hz), 126.5 (two peaks), 124.8, 120.3, 42.2 (d, J_{CP} = 67.5 Hz), 34.0. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 32.4.

(R)-(2-Nitro-1-phenylethyl)diphenylphosphine Oxide (Product in Scheme 5).[7b,22] With CH_2Cl_2/acetone (40/1) as eluent. white solid (68.9 mg, 98%). The enantiomeric excess was determined on a Daicel Chiralpak AD-H column with hexane/2-propanol (70/30) and flow rate 0.5 mL/min and detected at a UV wavelength of 228 nm. Retention times: 20.4 min (major), 34.6 min, 14% ee. $[\alpha]_D^{20}$ = −40° (*c* 0.200, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (app t, J_{HH} = 9.7 and 8.1 Hz, 2H), 7.63−7.60 (m, 3H), 7.46−7.40 (m, 3H), 7.29−7.20 (m, 7H), 5.14−5.07 (m, 1H, PC*H*CH$_2$), 4.76 (ddd, J_{HH} = 13.8 and 5.8 Hz, J_{HP} = 3.2 Hz, 1H, PCHC*H*H), 4.44−4.34 (m, 1H, PCHCH*H*).

Synthesis of the New Chiral NC$_{sp^3}$O Pincer Pd(II) Complex 8. To a stirred solution of the adduct **7pp** (73.0 mg, 0.16 mmol) obtained from hydrophosphination of (*E*)-2-(3-(*p*-methoxyphenyl)-acryloyl)pyridine in CH_2Cl_2 (2 mL) was added $PdCl_2$ (35.2 mg, 0.20 mmol, 1.2 equiv). After it was stirred at room temperature for 18 h, the reaction mixture was filtered through Celite. Evaporation of the solvent gave a residue, which was purified by column chromatography on silica gel with CH_2Cl_2/acetone (3/1) as eluent to afford the NCO pincer Pd(II) complex **8** as pale yellow solids (33.7 mg, 35%). In addition, 28% of the starting **7pp** was recovered.

Data for complex **8** are as follows. Mp: 173−174 °C. $[\alpha]_D^{20}$ = −301° (*c* 0.102, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.09 (d, J_{HH} = 5.4 Hz, 1H), 7.95−7.91 (m, 1H), 7.85−7.80 (m, 2H), 7.64−7.58 (m, 5H), 7.55−7.50 (m, 2H), 7.46−7.43 (m, 3H), 6.87 (dd, *J* = 8.6 and 1.9 Hz, 2H), 6.70 (d, J_{HH} = 8.6 Hz, 2H), 5.14 (dd, J_{HH} = 10.0 Hz, J_{HP} = 4.0 Hz, 1H, PCHC*H*), 4.87 (dd, J_{HH} = 10.0 Hz, J_{HP} = 16.8 Hz, 1H, PC*H*CH), 3.75 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.9 (d, J_{CP} = 14.0 Hz), 159.1 (d, J_{CP} = 3.1 Hz), 157.5, 151.5, 139.3, 133.6 (d, J_{CP} = 2.4 Hz), 133.2 (d, J_{CP} = 2.7 Hz), 133.1 (d, J_{CP} = 8.8 Hz), 131.8 (d, J_{CP} = 9.7 Hz), 129.8 (d, J_{CP} = 5.3 Hz), 128.98 (d, J_{CP} = 97.0 Hz), 128.95 (d, J_{CP} = 12.1 Hz), 128.4 (d, J_{CP} = 11.7 Hz), 127.2, 125.4 (d, J_{CP} = 3.3 Hz), 124.9 (d, J_{CP} = 90.6 Hz), 122.6, 114.0 (d, J_{CP} = 2.1 Hz), 56.2, 55.3, 48.1 (d, J_{CP} = 73.0 Hz). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 73.1. Anal. Calcd for $C_{27}H_{23}ClNO_3PPd\cdot0.5H_2O$: C, 54.84; H, 4.09; N, 2.37. Found: C, 54.61; H, 4.20; N, 2.08.

X-ray Diffraction Studies. Crystals of complexes **IX** and **8** (CCDC file nos. 980604 and 1007292, respectively) were obtained by recrystallization from CH_2Cl_2/petroleum ether and acetone/*n*-hexane, respectively, at ambient temperature. The data were collected on an Oxford Diffraction Gemini E diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.7107 Å) at ambient temperature. The structure was solved by direct methods using the SHELXS-97 program, and all non-hydrogen atoms were refined anisotropically on F^2 by the full-matrix least-squares technique, which used the SHELXL-97 crystallographic software package.[23] The hydrogen atoms were included but not refined. Details of the crystal structure determination are summarized in Table S1 in the Supporting Information.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

A table giving crystallographic details for the pincer Pd(II) complexes **IX** and **8**, figures giving NMR spectra of the new compounds **2**−**5** and the pincer Pd(II) complexes **VI**−**XIII** and **8** and NMR spectra of the catalysis products as well as their chiral HPLC spectra, and CIF files giving crystallographic data for complexes **IX** and **8**. 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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