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Palladacycle-Catalyzed Asymmetric Hydrophosphination of Enones for Synthesis of C*- and P*-Chiral Tertiary Phosphines

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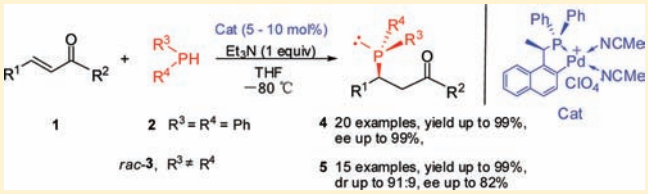
Supporting Information

ABSTRACT: A highly reactive and stereoselective hydrophosphination of enones catalyzed by palladacycles for the synthesis of C*- and P*-chiral tertiary phosphines has been developed. When Ph_2PH was employed as the hydrophosphinating reagent, a series of C*-chiral tertiary phosphines were synthesized (C*−P bond formation) in high yields with excellent enantioselectivities, and a single recrystallization provides access to their enantiomerically pure forms. When racemic secondary phosphines *rac*-$R^3(R^4)PH$ were utilized, a series of tertiary phosphines containing both C*- and P*-chiral centers were generated (C*−P* bond formation) in high yields with good diastereo- and enantioselectivities. The stereoelectronic factors involved in the catalytic cycle have been revealed.



INTRODUCTION

Apart from their well-established contributions to classic inorganic and organometallic chemistry, chiral phosphines have also played critical roles as valuable ligands in metal-based catalysis[1] as well as in organocatalysis.[2] Nevertheless, most of the important chiral phosphines are prepared predominantly either by the tedious resolution process or by use of the limited chiral pool.[3] Clearly, it is necessary to develop more efficient and practical methodologies for these chiral ligands. For obvious economic reasons, catalytic asymmetric transformations via C−P bond formation including cross-coupling[4] and hydrophosphination reactions for the efficient synthesis of chiral phosphines have recently attracted great interest. Among the catalytic methods, asymmetric hydrophosphination, the stereocontrolled addition of a P−H bond to unsaturated C−C bonds, is one of the most efficient and desired ways that provide direct, atom-economic, and "green" access to the targeted chiral phosphines.

Over the past decade, a few strategies for the synthesis of tertiary C*-chiral phosphines via hydrophosphination employing secondary phosphines have been reported. These include asymmetric hydrophosphination of Michael acceptors such as α,β-unsaturated esters, ketones, aldehydes, nitriles, etc., via transition-metal-catalyzed[5] or organocatalytic[6] processes. Among the transition-metal catalysts, several cyclopalladated complexes including pincer complexes have been demonstrated recently as efficient catalysts for these kinds of transformations.[7] In addition, tertiary C*-chiral phosphines have also been accessed by efficient allylic phosphination (substitution).[8] However, some of the reported methods suffered from drawbacks such as low stereoselectivity, low reactivity, and narrow substrate scope. More importantly, phosphine oxides, phosphine sulfides, or phosphine boranes were obtained as the final products. Conversion of these phosphine adducts to tertiary phosphines frequently involves strong reaction conditions and low yields. Therefore, it is our judgment that it is desirable to generate tertiary phosphines directly from a catalytic process.

Among chiral phosphines, P*-chiral phosphines have received increasing attention because they show great potential in asymmetric catalysis, particularly, as organocatalysts.[1c,4a] Catalytic approaches for the preparation of P*-chiral phosphines have been reported by the alkylation or arylation of secondary phosphines via cross-coupling pathways.[4a−j] P*-chiral phosphines have also been accessed by the hydrophosphination of activated olefins with *rac*-Ph(Me)PH, however, with low optical purity.[5b]

In a recent communication, we reported a C,N-palladacycle (*R*)-**A**-catalyzed asymmetric hydrophosphination of enones with Ph_2PH to form several keto-substituted C*-chiral tertiary phosphines.[7b] Herein, we report the evaluation of a series of palladacycles **A**−**F** for this reaction. The C,P-palladacycle (*R*)-**F** was found to be an improved catalyst, giving much enhanced reactivities, enantioselectivities, and a wider substrate scope for the asymmetric hydrophosphination reaction.

Furthermore, the same C,P-catalyst (*R*)-**F** can also be utilized for the efficient activation of racemic secondary phosphine (*rac*-**3**) to generate chiral tertiary phosphines with both C* and P* stereocenters (eq 1). To date, catalytic formation of the C*−P* bond with the simultaneous introduction of chirality at both carbon and phosphorus centers has not been reported.

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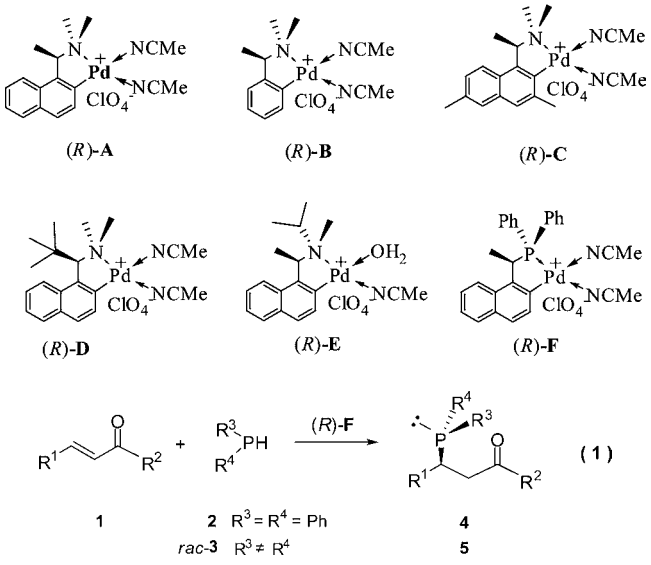
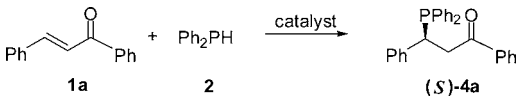


RESULTS AND DISCUSSION

Selection of Catalysts. In our initial communication,[7b] we observed that (*R*)-**A** is an efficient catalyst for the hydrophosphination of aromatic enones with Ph_2PH. When (*R*)-**A** was used to activate the chiral secondary phosphine R^3R^4PH, however, unsatisfactory reactivity and enantioselectivity were observed. In order to select a better hydrophosphination catalyst for wider applications, we therefore screened a series of palladacycles (*R*)-**A**–**F** as catalysts (Table 1). All complexes are structurally similar with two coordination sites readily available for catalysis. Complexes **A**–**E** are C,N-cyclopalladated complexes, with similar electronic features originating from the σ-donating nitrogen and the π-accepting aromatic carbon. On the other hand, the C,P complex **F** is electronically designed to exhibit higher oxophilicity toward substrates because of the presence of both relatively soft carbon and phosporus donors. As reported earlier,[7b] (*R*)-**A** is indeed an efficient catalyst in this particular C–P bond formation reaction between Ph_2PH and the enone (entry 5). However, when complexes (*R*)-**B**–**E** were employed, the reaction proceeded at significantly slower rates. Furthermore, the resulting chemo- and stereoselectivities became unacceptable (entries 10–13). In particular, (*R*)-**B** gave numerous yet unidentified side products. These observations revealed that the catalytic properties of the C,N-cyclopalladated complexes are highly sensitive to minor structural modifications. To our delight, the C,P complex (*R*)-**F** was found to be an even better catalyst than (*R*)-**A** for this hydrophosphination reaction, with very high reactivity and excellent enantioselectivity (entry 14). Under optimal conditions, the reaction time was reduced noticeably from 24 to 2 h and the enantiomeric excess (ee) was improved from 77% to 98% (compared with that of entry 5). As expected, when the equally accessible (*S*)-**F** was employed as the catalyst for the reaction, the same enantioselectivity was achieved with reversal in the configuration from *S* to *R* at the chiral center (entry 15).[7b] The reaction was conveniently monitored by $^{31}P\{^1H\}$ NMR spectroscopy. The ee was determined from $^{31}P\{^1H\}$ NMR spectra of the derivatives, which resulted from treatment of the tertiary phosphine product with an enantiopure palladacycle (*R*)-**G** (Scheme 1).[5e,f,7b] The major diastereomer (R_C,S_C)-**6a** and minor diastereomer (R_C,R_C)-**6a** were characterized by X-ray crystallography. Thus, the absolute configuration of the major and minor enantiomers of **4** could be determined to be *S* and *R* by comparison, respectively.[7b]

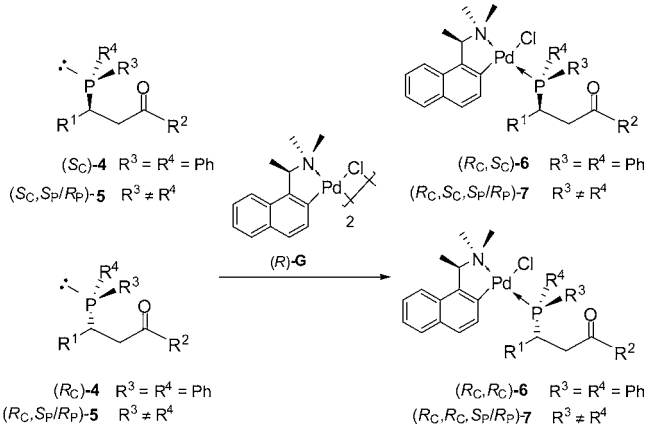
Table 1. Catalyst, Solvent, Temperature, and Base Effects on the Enantioselective Hydrophosphination of Enones with Ph_2PH[a]



entry	catalyst	solvent	*T* [°C]	*t* [h]	base	ee[b] (*S*) [%]
1	(*R*)-**A**	DCM	−80	24	Et_3N	62
2	(*R*)-**A**	acetone	−80	24	Et_3N	68
3	(*R*)-**A**	toluene	−80	24	Et_3N	68
4	(*R*)-**A**	$CHCl_3$	−40	24	Et_3N	49
5	(*R*)-**A**	THF	−80	24	Et_3N	77
6	(*R*)-**A**	THF	−40	24	Et_3N	74
7	(*R*)-**A**	THF	20	24	Et_3N	51
8	(*R*)-**A**	THF	−80 to +20	48[c]	DBU	27
9	(*R*)-**A**	THF	−80	2	^{t}BuOK	16
10	(*R*)-**B**	THF	−80	24	Et_3N	messy
11	(*R*)-**C**	THF	−80 to +20	48[c]	Et_3N	13
12	(*R*)-**D**	THF	−80 to +20	48[c]	Et_3N	38[d]
13	(*R*)-**E**	THF	−80 to +20	48[c]	Et_3N	15
14	(*R*)-**F**	THF	−80	2	Et_3N	98
15	(*S*)-**F**	THF	−80	2	Et_3N	98[d]

[a]Conditions: 0.35 mmol of Ph_2PH, 5 mol % catalyst, 1.0 equiv of *trans*-chalcone, and 0.5 equiv of base were reacted at the given temperature. The reaction was stopped after the indicated time with full conversion of Ph_2PH. [b]The ee was determined by $^{31}P\{^1H\}$ NMR; see the Supporting Information for details. [c]The reaction was stirred at −80 °C for 24 h and then gradually warmed to 20 °C for another 24 h. [d]The absolute configuration in this instance is *R*.

Scheme 1



Substrate Scope for Hydrophosphination with Ph_2PH. In order to evaluate the catalytic versatility of the C,P complex, a range of aromatic enones were screened for the asymmetric hydrophosphination reaction catalyzed by (*R*)-**F** using the established optimal conditions. The results are presented in Table 2. All of the reactions proceeded to full conversion of Ph_2PH smoothly under the given conditions, allowing the efficient transformation of a wide range of aromatic enones into chiral tertiary phosphines in nearly quantitative yields and excellent enantioselectivities. The process tolerates a broad

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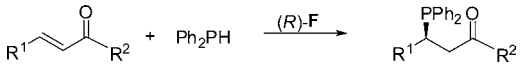
Table 2. Substrate Scope of the (*R*)-F-Catalyzed Enantioselective Hydrophosphination of Enones with Ph_2PH[a]



1 2 (*S*)-4

Entry	R^1	R^2	*t* [h]	4	Yield[b] [%]	*ee*[c](*S*) [%]
1	Ph	Ph	2	**4a**	99 (90)	98(>99)
2	4-$NO_2C_6H_4$	Ph	2	**4b**	99 (89)	98(>99)
3	3-$NO_2C_6H_4$	Ph	8	**4c**	99 (85)	96(>99)
4	4-BrC_6H_4	Ph	5	**4d**	99 (89)	98(>99)
5	4-ClC_6H_4	Ph	4	**4e**	99 (90)	98(>99)
6	4-FC_6H_4	Ph	5	**4f**	99 (91)	99(>99)
7	4-$CF_3C_6H_4$	Ph	2	**4g**	99 (91)	96(>99)
8	4-MeC_6H_4	Ph	12	**4h**	99 (90)	99(>99)
9	4-$MeOC_6H_4$	Ph	30	**4i**	99 (92)	99(>99)
10		Ph	30	**4j**	99 (90)	98(>99)
11	2-Naph	Ph	7	**4k**	99 (91)	99(>99)
12	2-Naph	4-FC_6H_4	7	**4l**	99 (89)	97(>99)
13	Ph	2-Naph	24	**4m**	98 (90)	98(>99)
14	Ph	4-BrC_6H_4	6	**4n**	99 (88)	96(>99)
15	Ph	4-ClC_6H_4	4	**4o**	99 (89)	97(>99)
16	Ph	4-FC_6H_4	6	**4p**	99 (90)	97(>99)
17	Ph	2-Pyridinyl	20	**4q**	99 (71)	92(>99)
18[d]	Ph	4-$MeOC_6H_4$	40	**4r**	98 (88)	98(>99)
19	4-FC_6H_4	4-ClC_6H_4	5	**4s**	99 (90)	97(>99)
20	4-ClC_6H_4	4-FC_6H_4	4	**4t**	99 (90)	98(>99)

[a]Conditions: 0.30 mmol of Ph_2PH, 5 mol % (*R*)-**F**, 5 mL of THF, 1.0 equiv of enone, and 0.5 equiv of Et_3N were reacted at −80 °C, unless otherwise noted. [b]The yield was calculated from $^{31}P\{^1H\}$ NMR. In parentheses are the yields of isolated products after a single recrystallization. [c]The ee was determined by $^{31}P\{^1H\}$ NMR. In parentheses are the ee's after a single recrystallization. See the Supporting Information for details. [d]A total of 1.1 equiv of enone was used.

range of unprotected functional groups such as nitro and halogens (F, Cl, Br). Both electron-withdrawing- and electron-donating-group-substituted aromatic enones are suitable substrates. However, those bearing electron-withdrawing groups are more reactive than those bearing electron-donating groups. As far as the substituent on R^1 (R^1 = NO_2, for example) is concerned, the para-substituted enone showed the best reactivity and selectivity (entry 2, 98% ee) followed by the meta-substituted enone (entry 3, 96% ee) and the ortho-substituted enone (91% ee).[9] Those with a substituent on R^1 (entry 4) showed slightly better selectivities compared with those with the same substituent on R^2 (entry 14).

It is worth highlighting that all of these chiral tertiary phosphine products described in Table 2 could be purified efficiently to their enantiomerically pure forms (>99% ee) by a single recrystallization from acetone under a nitrogen atmosphere.

Selection of Secondary Phosphines. P*-chiral tertiary phosphines are configurationally stable at room temperature. The energy required to invert tertiary aryldialkylphosphines is in the range of 30−35 kcal mol^{-1}.[4a,10] This configurational stability makes it possible to synthesize P*-chiral tertiary phosphines. Encouraged by the excellent yields and selectivities achieved in Table 2, we explored the asymmetric hydrophosphination reaction employing the racemic secondary phosphines *rac*-**3** ($R^3 \neq R^4$) as hydrophosphinating reagents to stereoselectively generate tertiary phosphine products with both C*- and P*-chiral centers (Table 3).

In the presence of 10 mol % (*R*)-**F**, *rac*-Ph(Me)PH reacted with *trans*-chalcone quantitatively after 14 h at −80 °C, resulting in 87:13 dr (diastereomeric excess) and 71% ee. The ee was determined by the same method via derivatization with the enantiopure palladacycle (*R*)-**G** (Scheme 1). The major derivative (R_C,S_C,R_P)-**7a** was characterized by X-ray crystallography (Figure 1 and Table 4). Thus, the absolute configurations of the corresponding free phosphine product **5** at both phosphorus and carbon chiral centers could be determined to be *S* by comparison. It needs to be noted that the configuration at phosphorus in complex (R_C,S_C,R_P)-**7a** is *R*, and this apparent inversion of the configuration that occurs when the phosphine

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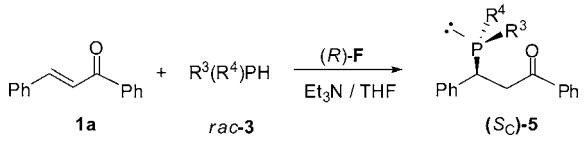
Table 3. Optimization of the Hydrophosphination Reaction between *trans*-Chalcone and *rac*-3[a]



1a rac-3 (S_C)-5

entry	R^3	R^4	time [h]	T [°C]	yield[b] [%]	dr[c]	ee[d] [%]
1	Ph	Me	14	−80	96	87:13	71
2	Ph	Me	12	−40	97	85:15	68
3	Ph	Me	5	−10	97	79:21	63
4	Ph	Me	5	0	97	77:23	62
5	Ph	Me	4	20	95	70:30	52
6	Ph	^{t}Bu	24	20	trace	-	-
7	Ph	Mes[e]	60	20	95	59:41	79

[a]Conditions: 0.36 mmol of *rac*-$R^3(R^4)$PH, 10 mol % (*R*)-**F**, 5 mL of THF, 1.2 equiv of *trans*-chalcone, and 1.0 equiv of Et_3N were reacted at the given temperature, unless otherwise noted. [b]The yield was calculated from $^{31}P\{^1H\}$ NMR. [c]dr was determined from $^{31}P\{^1H\}$ NMR of the crude products. [d]The ee (of the major diastereomer) was determined by $^{31}P\{^1H\}$ NMR; see the Supporting Information for details. For entries 1−5, the absolute configuration at phosphorus is *S*, and for entries 6 and 7, the absolute configuration at phosphorus is *R* according to the CIP rules. [e]Mes = 2,4,6-trimethylphenyl.

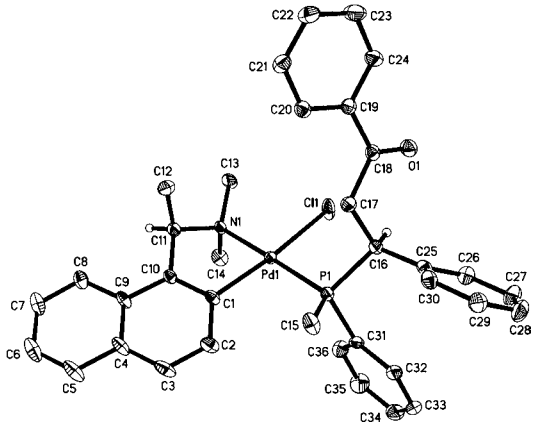


Figure 1. Molecular structure and absolute stereochemistry of the complex (R_C,S_C,R_P)-**7a** with 50% probability thermal ellipsoids shown. Hydrogen atoms except those on the chiral centers are omitted for clarity.

Table 4. Selected Bond Lengths (Å) and Angles (deg) of Complex (R_C,S_C,R_P)-7a

Pd1−C1	2.019(3)	Pd1−N1	2.142(2)
Pd1−P1	2.274(1)	Pd1−Cl1	2.371(1)
C15−P1	1.835(3)	C16−P1	1.869(3)
C18−O1	1.209(3)	C31−P1	1.816(3)
C1−Pd1−N1	81.3(1)	C1−Pd1−P1	97.8(1)
N1−Pd1−P1	178.6(1)	C1−Pd1−Cl1	170.6(1)
N1−Pd1−Cl1	89.6(1)	P1−Pd1−Cl1	91.2(1)
C25−C16−P1	115.8(2)	C17−C16−P1	106.1(2)
C15−P1−C16	101.7(2)	C16−P1−Pd1	109.4(1)
C31−P1−Pd1	110.7(1)	C15−P1−Pd1	121.8(1)

product is coordinated with the metal is merely a consequence of the Cahn−Ingold−Prelog (CIP) sequence rules.[11] The Pd−Cl bond is thermodynamically and kinetically stable,[12] and the phosphorus atom is exclusively coordinated with palladium trans to the σ-donating nitrogen. The five-membered ring is locked into a δ configuration, with the methyl group occupying an axial position at the chiral carbon center.

By a comparison of the respective reaction rates, Ph(Me)PH showed a lower reactivity than Ph_2PH for the hydrophosphination reaction, which indicates that an aromatic substituent at phosphorus facilitates the hydrophosphination process. At higher reaction temperatures, lower stereoselectivities were obtained. The reaction rate was significantly slower when the methyl group of the secondary phosphine was replaced by other sterically demanding substituents (entries 6 and 7).

Substrate Scope for Hydrophosphination with *rac*-Ph(Me)PH. On the basis of the reactivity and selectivity considerations, *rac*-Ph(Me)PH was selected as the hydrophosphinating agent for screening various substrates toward the asymmetric hydrophosphination reaction to be catalyzed by (*R*)-**F** (Table 5).

The results showed that the reaction proceeded smoothly, allowing the transformation of a range of aromatic enones and *rac*-Ph(Me)PH into functionalized tertiary phosphines with chiral centers at both phosphorus and carbon. The electronic properties of the substituents show a significant impact on the reactivity and selectivity. In general, those bearing election-withdrawing groups reacted much faster with lower selectivity, while those bearing electron-donating groups reacted slower with better selectivity.

Mechanism. On the basis of the experimental observations, a mechanism was proposed for the (*R*)-**F**-catalyzed asymmetric hydrophosphination of enones with secondary phosphines (Scheme 2). Free $PR^3(R^4)H$ having a high affinity to palladium gives the bis(phosphine) complex by displacement of the relatively weakly coordinated solvent (NCMe) on the original (*R*)-**F**. However, because of the strong π-accepting properties of the aromatic carbon donor, the P−Pd bond in the trans P−Pd−C moiety of the intermediate is weak and labile and readily undergoes the ligand redistribution process.

On the other hand, this readily available coordination position has shown significant oxophilicity. A number of stable complexes containing various trans O−Pd−C moieties, including some keto O−Pd−C species, have been isolated.[13] In comparison, the trans P−Pd−P moiety in the catalytic intermediate is more stable.[14] This renders acidification of the P−H bond in the reacting $PR^3(R^4)H$ facile. In the presence of Et_3N as the external base, the secondary phosphine on palladium is thus readily converted to the corresponding phosphido species $[Pd]P(R^3)(R^4)$, which rapidly undergoes inversion. The reactive phosphido intermediates then proceed to undergo the desired intramolecular 1,4-addition reaction with the activated enone at −80 °C to form the expected tertiary phosphines. The high stereoselectivity observed is attributed to the efficient control offered by the two projecting prochiral P-phenyl rings of the C,P-cyclopalladated catalyst. It should be noted that the significantly faster reaction rate observed with the C,P catalyst (*R*)-**F** compared to its C,N analogue (*R*)-**A** is, as designed, an electronic phenomenon. The phosphine product elimination process is clearly faster in a system involving the P−Pd−P species than those involving N−Pd−P bonds.

■ CONCLUSION

In summary, we have evaluated a series of palladacycles and found that the phosphapalladacycle (*R*)-**F** is a much improved

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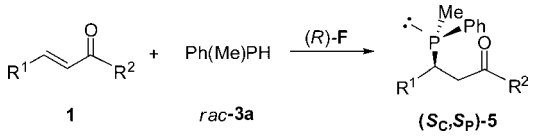
Table 5. Substrate Scope of the (*R*)-F-Catalyzed Stereoselective Hydrophosphination of Enones with *rac*-Ph(Me)PH[a]



Entry	R^1	R^2	*t*	**5**	Yield[b] [%]	*dr*[c]	*ee*[d] (S_C,S_P) [%]
1	Ph	Ph	14 h	**5a**	96	87:13	71
2	4-$NO_2C_6H_4$	Ph	5 h	**5b**	95	82:18	42
3	4-BrC_6H_4	Ph	12 h	**5c**	97	86:14	62
4	4-ClC_6H_4	Ph	6 h	**5d**	98	87:13	62
5	4-FC_6H_4	Ph	14 h	**5e**	96	88:12	66
6	4-$CF_3C_6H_4$	Ph	5 h	**5f**	98	85:15	39
7	4-$MeOC_6H_4$	Ph	6 d	**5g**	99	91:9	82
8		Ph	5 d	**5h**	95	91:9	75
9	2-Naph	Ph	30 h	**5i**	94	88:12	75
10	2-Naph	4-FC_6H_4	7 h	**5j**	95	87:13	74
11	Ph	2-Naph	30 h	**5k**	96	85:15	72
12	Ph	4-BrC_6H_4	14 h	**5l**	97	78:22	61
13	Ph	4-ClC_6H_4	8 h	**5m**	95	79:21	60
14	Ph	4-FC_6H_4	17 h	**5n**	96	87:13	72
15	4-FC_6H_4	4-ClC_6H_4	7 h	**5o**	95	83:17	57

[a]Conditions: 0.36 mmol of *rac*-Ph(Me)PH, 10 mol % (*R*)-**F**, 5 mL of THF, 1.2 equiv of enones, and 1.0 equiv of Et_3N were reacted at −80 °C, unless otherwise noted. [b]The yield was calculated from $^{31}P\{^1H\}$ NMR. [c]dr was determined from $^{31}P\{^1H\}$ NMR of the crude products. [d]The ee (of the major diastereomer) was determined by $^{31}P\{^1H\}$ NMR; see the Supporting Information for details.

catalyst for the powerful palladium(II)-catalyzed asymmetric hydrophosphination protocol. Furthermore, we also extended this reaction to allow the stereochemically challenging simultaneous formation of chirality at both carbon and phosphorus stereogenic centers. The resulting tertiary phosphine ligands can be coordinated directly onto other metal ions without the need for any tedious protection−deprotection sequence. This method should be applicable to the synthesis of a large range of functionalized chiral phosphine ligands containing carbon or phosphorus stereogenic centers, or both.

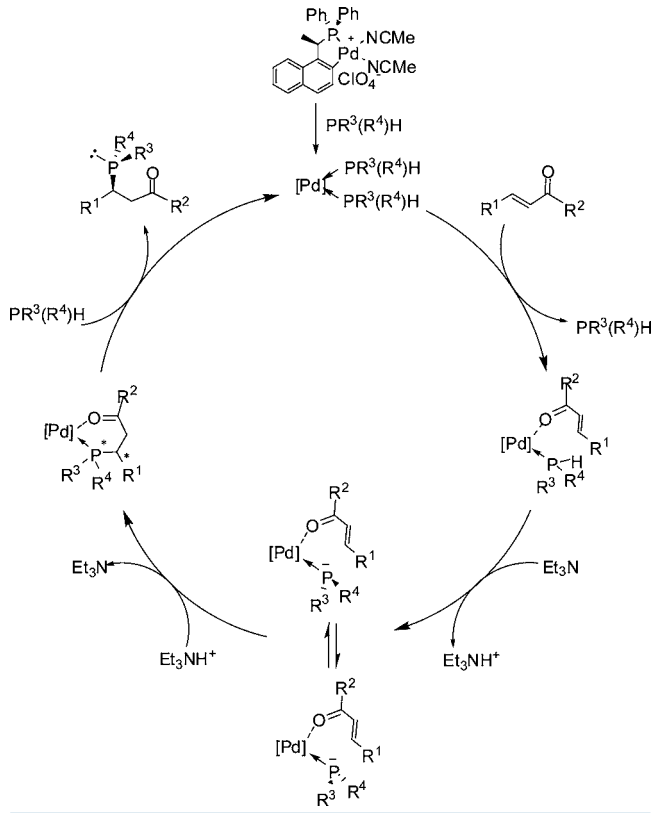
EXPERIMENTAL SECTION

All air-sensitive manipulations were performed under a positive pressure of nitrogen or argon using a standard Schlenk line. Solvents were degassed prior to use when necessary. Tetrahydrofuran (THF) was purchased from Tedia Co. (AR, stabilized with 0.02−0.03% BHT) and freshly distilled before use. A Low Temp PAIRSTIRRER PSL-1800 machine was used for controlling low temperatures for reactions. Column chromatography was conducted on silica gel 60 (Merck). NMR spectra were recorded on Bruker ACF 300, 400, and 500 spectrometers. Chemical shifts are reported in δ (ppm) referenced to an internal $SiMe_4$ standard (δ = 0 ppm) for ^1H NMR and chloroform-*d* (δ = 77.23 ppm) for ^{13}C NMR. The reaction was monitored by $^{31}P\{^1H\}$ NMR at room temperature immediately upon removal of an aliquot from the reaction mixture under inert conditions. Optical rotations were measured on the specified solution in a 0.1 dm cell at 20 °C with a Perkin-Elmer 341 polarimeter. Chiral palladacycles,[15,7e] enones[16] and racemic unsymmetrical phosphines[17] were prepared according to the literature.

Caution! *Perchlorate salts of metal complexes are potentially explosive compounds and should be handled with care.*

General Experimental Procedure for the Synthesis of C*-Chiral Phosphines. To a solution of Ph_2PH **2** (55.9 mg, 0.30 mmol, 1.0 equiv) in THF (5 mL) was added (*R*)-**F** (9.4 mg, 0.015 mmol, 5 mol %), and the solution was cooled to −80 °C. Subsequently,

Scheme 2. Proposed Catalytic Cycle



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aromatic enone **1** (0.30 mmol, 1.0 equiv) was added. Et_3N (15.2 mg, 0.15 mmol, 0.5 equiv) in THF (0.5 mL) was added dropwise. The solution was subsequently stirred at −80 °C. The reaction was monitored by $^{31}P\{^1H\}$ NMR. After the reaction was completed, the mixture was warmed to room temperature and the solution was evaporated by a vacuum pump to give the crude phosphine product **4** (air-sensitive) as a solid. The crude **4** was dissolved in 10 mL of dichloromethane (DCM) and filtered through a short silica gel column using a pipet fixed on a two-necked Schlenk flask protected by nitrogen or argon. The solvent was removed by a vacuum pump to give the product as a solid. A single recrystallization from acetone gave the enantiopure product **4**.

General Experimental Procedure for the Synthesis of C*- and P*-Chiral Phosphines. To a solution of *rac*-Ph(Me)PH **3a** (44.7 mg, 0.36 mmol, 1.0 equiv) in THF (5 mL) was added (*R*)-**F** (22.6 mg, 0.036 mmol, 10 mol %), and the solution was cooled to −80 °C. Subsequently, aromatic enone **1** (0.43 mmol, 1.2 equiv) was added. Et_3N (36.4 mg, 0.36 mmol, 1.0 equiv) in THF (0.5 mL) was added dropwise. The solution was subsequently stirred at −80 °C. The reaction was monitored by $^{31}P\{^1H\}$ NMR. After the reaction was completed, the mixture was warmed to room temperature, and the solution was evaporated by a vacuum pump to give the crude phosphine product **5** (air-sensitive).

Synthesis of (*S*)-4a. Crude (*S*)-**4a** was synthesized according to a general procedure (99% yield, 98% ee). Pure (*S*)-**4a** was obtained after purification as a solid (90% yield, >99% ee; air-sensitive). $[\alpha]_D^{20}$ = −152.5 (*c* = 1.2, CH_2Cl_2). ^{31}P NMR ($CDCl_3$, 121 MHz): δ 0.1. ^1H NMR ($CDCl_3$, 300 MHz): δ 3.07 (ddd, 1H, *J* = 17.3, 8.3, and 2.8 Hz, C*H*HCOPh), 3.58−3.69 (m, 1H, CH*H*COPh), 4.23−4.29 (m, 1H, PC*H*CH$_2$), 6.98−7.68 (m, 20H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 40.0 (d, 1C, $^1J_{PC}$ = 11.4 Hz, PCH), 42.6 (d, 1C, $^2J_{PC}$ = 22.1 Hz, *C*H$_2$COPh), 126.5−141.0 (m, 24C, Ar), 198.1 (d, 1C, $^3J_{PC}$ = 12.8 Hz, *C*OPh).

Synthesis of (*S*)-4b. Crude (*S*)-**4b** was synthesized according to a general procedure (99% yield, 98% ee). Pure (*S*)-**4b** was obtained after purification as a solid (89% yield, >99% ee; air-sensitive). $[\alpha]_D^{20}$ = −248.0 (*c* = 1.3, CH_2Cl_2).^{31}P NMR ($CDCl_3$, 121 MHz): δ 1.5. ^1H NMR ($CDCl_3$, 300 MHz): δ 3.19 (ddd, 1H, *J* = 17.8, 7.7, and 2.8 Hz, C*H*HCOPh), 3.60−3.71 (m, 1H, CH*H*COPh), 4.34−4.40 (m, 1H, PC*H*CH$_2$), 7.07−7.91 (m, 19H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 39.4 (d, 1C, $^1J_{PC}$ = 11.8 Hz, PCH), 42.4 (d, 1C, $^2J_{PC}$ = 22.0 Hz, *C*H$_2$COPh), 123.6−149.4 (m, 24C, Ar), 197.3 (d, 1C, $^3J_{PC}$ = 12.6 Hz, *C*OPh).

Synthesis of (*S*)-4c. Crude (*S*)-**4c** was synthesized according to a general procedure (99% yield, 96% ee). Pure (*S*)-**4c** was obtained after purification as a solid (85% yield, >99% ee; air-sensitive). $[\alpha]_D^{20}$ = −230.3 (*c* = 1.0, CH_2Cl_2). ^{31}P NMR ($CDCl_3$, 161 MHz): δ 0.3. ^1H NMR ($CDCl_3$, 400 MHz): δ 3.20 (ddd, 1H, *J* = 17.8, 7.8, and 2.7 Hz, C*H*HCOPh), 3.63−3.71 (m, 1H, CH*H*COPh), 4.35−4.39 (m, 1H, PC*H*CH$_2$), 7.07−7.97 (m, 19H, Ar). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 39.8 (d, 1C, $^1J_{PC}$ = 13.0 Hz, PCH), 41.9 (d, 1C, $^2J_{PC}$ = 21.8 Hz, *C*H$_2$COPh), 121.6−148.2 (m, 24C, Ar), 197.3 (d, 1C, $^3J_{PC}$ = 12.6 Hz, *C*OPh).

Synthesis of (*S*)-4d. Crude (*S*)-**4d** was synthesized according to a general procedure (99% yield, 98% ee). Pure (*S*)-**4d** was obtained after purification as a solid (89% yield, >99% ee; air-sensitive). $[\alpha]_D^{20}$ = −164.2 (*c* = 1.7, CH_2Cl_2). ^{31}P NMR ($CDCl_3$, 161 MHz): δ−0.7. ^1H NMR ($CDCl_3$, 400 MHz): δ 3.07 (ddd, 1H, *J* = 17.2, 7.6, and 2.4 Hz, C*H*HCOPh), 3.53−3.61 (m, 1H, CH*H*COPh), 4.20−4.25 (m, 1H, PC*H*CH$_2$), 7.00−7.68 (m, 19H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 39.4 (d, 1C, $^1J_{PC}$ = 11.8 Hz, PCH), 42.3 (d, 1C, $^2J_{PC}$ = 21.2 Hz, *C*H$_2$COPh), 120.3−140.2 (m, 24C, Ar), 197.8 (d, 1C, $^3J_{PC}$ = 12.6 Hz, *C*OPh).

Synthesis of (*S*)-4e. Crude (*S*)-**4e** was synthesized according to a general procedure (99% yield, 98% ee). Pure (*S*)-**4e** was obtained after purification as a solid (90% yield, >99% ee; air-sensitive). $[\alpha]_D^{20}$ = −208.7 (*c* = 1.2, CH_2Cl_2). ^{31}P NMR ($CDCl_3$, 121 MHz): δ 0.0. ^1H NMR ($CDCl_3$, 300 MHz): δ 3.07 (ddd, 1H, *J* = 17.4, 7.9, and 2.8 Hz, C*H*HCOPh), 3.52−3.63 (m, 1H, CH*H*COPh), 4.20−4.27 (m, 1H, PC*H*CH$_2$), 7.02−7.68 (m, 19H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 39.4 (d, 1C, $^1J_{PC}$ = 11.8 Hz, PCH), 42.4 (d, 1C, $^2J_{PC}$ = 22.0 Hz, *C*H$_2$COPh), 128.1−139.6 (m, 24C, Ar), 197.8 (d, 1C, $^3J_{PC}$ = 12.6 Hz, *C*OPh).

Synthesis of (*S*)-4f. Crude (*S*)-**4f** was synthesized according to a general procedure (99% yield, 99% ee). Pure (*S*)-**4f** was obtained after purification as a solid (91% yield, >99% ee; air-sensitive). $[\alpha]_D^{20}$ = −145.0 (*c* = 1.0, CH_2Cl_2). ^{31}P NMR ($CDCl_3$, 162 MHz): δ−0.9. ^1H NMR ($CDCl_3$, 400 MHz): δ 3.06 (ddd, 1H, *J* = 17.6, 8.0, and 2.8 Hz, C*H*HCOPh), 3.54−3.62 (m, 1H, CH*H*COPh), 4.21−4.26 (m, 1H, PC*H*CH$_2$), 6.71−7.68 (m, 19H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 39.3 (d, 1C, $^1J_{PC}$ = 11.4 Hz, PCH), 42.5 (d, 1C, $^2J_{PC}$ = 22.3 Hz, *C*H$_2$COPh), 115.2−162.7 (m, 24C, Ar), 198.0 (d, 1C, $^3J_{PC}$ = 13.0 Hz, *C*OPh). ^{19}F NMR ($CDCl_3$, 376.5 MHz): δ −116.4.

Synthesis of (*S*)-4g. Crude (*S*)-**4g** was synthesized according to a general procedure (99% yield, 96% ee). Pure (*S*)-**4g** was obtained after purification as a solid (91% yield, >99% ee; air-sensitive). $[\alpha]_D^{20}$ = −156.4 (*c* = 1.1, CH_2Cl_2). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 0.2. ^1H NMR ($CDCl_3$, 400 MHz): δ 3.14 (ddd, 1H, *J* = 17.6, 8.0, and 2.8 Hz, C*H*HCOPh), 3.60−3.69 (m, 1H, CH*H*COPh), 4.30−4.35 (m, 1H, PC*H*CH$_2$), 7.05−7.70 (m, 19H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 40.0 (d, 1C, $^1J_{PC}$ = 12.7 Hz, PCH), 42.2 (d, 1C, $^2J_{PC}$ = 21.4 Hz, *C*H$_2$COPh), 123.0−145.5 (m, 25C, Ar), 197.6 (d, 1C, $^3J_{PC}$ = 12.3 Hz, *C*OPh). ^{19}F NMR ($CDCl_3$, 376.5 MHz): δ −62.4.

Synthesis of (*S*)-4h. Crude (*S*)-**4h** was synthesized according to a general procedure (99% yield, 99% ee). Pure (*S*)-**4h** was obtained after purification as a solid (90% yield, >99% ee; air-sensitive). $[\alpha]_D^{20}$ = −169.3 (*c* = 1.1, CH_2Cl_2). ^{31}P NMR ($CDCl_3$, 121 MHz): δ −0.3. ^1H NMR ($CDCl_3$, 300 MHz): δ 2.13 (s, 3H, C*H*$_3$O), 3.03 (ddd, 1H, *J* = 17.4, 8.4, and 3.0 Hz, C*H*HCOPh), 3.52−3.63 (m, 1H, CH*H*COPh), 4.20−4.26 (m, 1H, PC*H*CH$_2$), 6.85−7.67 (m, 19H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.2 (s, 1C, *C*H$_3$O), 39.5 (d, 1C, $^1J_{PC}$ = 11.3 Hz, PCH), 42.5 (d, 1C, $^2J_{PC}$ = 22.1 Hz, *C*H$_2$COPh), 128.1−137.8 (m, 24C, Ar), 198.2 (d, 1C, $^3J_{PC}$ = 12.7 Hz, *C*OPh).

Synthesis of (*S*)-4i. Crude (*S*)-**4i** was synthesized according to a general procedure (99% yield, 99% ee). Pure (*S*)-**4i** was obtained after purification as a solid (92% yield, >99% ee; air-sensitive): $[\alpha]_D^{20}$ = −178.5 (*c* = 1.3, CH_2Cl_2). ^{31}P NMR ($CDCl_3$, 161 MHz): δ −1.4. ^1H NMR ($CDCl_3$, 400 MHz): δ 3.03 (ddd, 1H, *J* = 17.1, 7.9, and 2.6 Hz, C*H*HCOPh), 3.53−3.62 (m, 1H, CH*H*COPh), 3.63 (s, 3H, C*H*$_3$O), 4.18−4.23 (m, 1H, PC*H*CH$_2$), 6.60−7.68 (m, 19H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 39.1 (d, 1C, $^1J_{PC}$ = 11.0 Hz, PCH), 42.7 (d, 1C, $^2J_{PC}$ = 22.4 Hz, *C*H$_2$COPh), 55.3 (s, 1C, *C*H$_3$O), 113.9−158.2 (m, 24C, Ar), 198.3 (d, 1C, $^3J_{PC}$ = 13.0 Hz, COPh).

Synthesis of (*S*)-4j. Crude (*S*)-**4j** was synthesized according to a general procedure (99% yield, 98% ee). Pure (*S*)-**4j** was obtained after purification as a solid (90% yield, >99% ee; air-sensitive): $[\alpha]_D^{20}$ = −195.6 (*c* = 0.9, CH_2Cl_2). ^{31}P NMR ($CDCl_3$, 121 MHz): δ −0.7. ^1H NMR ($CDCl_3$, 300 MHz): δ 3.00 (ddd, 1H, *J* = 17.1, 7.8, and 2.7 Hz, C*H*HCOPh), 3.48−3.59 (m, 1H, CH*H*COPh), 4.15−4.21 (m, 1H, PC*H*CH$_2$), 5.74 (dd, 2H, *J* = 5.4 and 1.5 Hz, C*H*$_2$O$_2$), 6.45−7.68 (m, 18H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 39.8 (d, 1C, $^1J_{PC}$ = 11.2 Hz, PCH), 42.8 (d, 1C, $^2J_{PC}$ = 22.7 Hz, *C*H$_2$COPh), 100.9 (s, 1C, *C*H$_2$O$_2$), 108.3−147.6 (m, 24C, Ar), 198.1 (d, 1C, $^3J_{PC}$ = 12.8 Hz, COPh).

Synthesis of (*S*)-4k. Crude (*S*)-**4k** was synthesized according to a general procedure (99% yield, 99% ee). Pure (*S*)-**4k** was obtained after purification as a solid (91% yield, >99% ee; air-sensitive): $[\alpha]_D^{20}$ = −229.0 (*c* = 1.1, CH_2Cl_2). ^{31}P NMR ($CDCl_3$, 161 MHz): δ −0.7. ^1H NMR ($CDCl_3$, 400 MHz): δ 3.15 (ddd, 1H, *J* = 17.4, 8.2, and 2.7 Hz, C*H*HCOPh), 3.70−3.78 (m, 1H, CH*H*COPh), 4.42−4.47 (m, 1H, PC*H*CH$_2$), 6.99−7.68 (m, 22H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 40.0 (d, 1C, $^1J_{PC}$ = 11.7 Hz, PCH), 42.6 (d, 1C, $^2J_{PC}$ = 22.4 Hz, *C*H$_2$COPh), 125.5−138.7 (m, 28C, Ar), 197.9 (d, 1C, $^3J_{PC}$ = 12.3 Hz, *C*OPh).

Synthesis of (*S*)-4l. Crude (*S*)-**4l** was synthesized according to a general procedure (99% yield, 97% ee). Pure (*S*)-**4l** was obtained after purification as a solid (89% yield, >99% ee; air-sensitive): $[\alpha]_D^{20}$ = −153.3 (*c* = 0.8, CH_2Cl_2). ^{31}P NMR ($CDCl_3$, 162 MHz): δ −0.8. ^1H NMR ($CDCl_3$, 400 MHz): δ 3.11 (ddd, 1H, *J* = 17.2, 8.0, and 2.8 Hz, C*H*HCOPh), 3.64−3.72 (m, 1H, CH*H*COPh), 4.39−4.43 (m, 1H, PC*H*CH$_2$), 6.90−7.70 (m, 21H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz):

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δ 41.2 (d, 1C, $^1J_{PC}$ = 12.8 Hz, PCH), 46.5 (d, 1C, $^2J_{PC}$ = 21.7 Hz, CH_2COPh), 115.6−138.6 (m, 28C, Ar), 196.5 (d, 1C, $^3J_{PC}$ = 12.4 Hz, COPh). ^{19}F NMR ($CDCl_3$, 376.5 MHz): δ −105.2.

Synthesis of (*S*)-4m. Crude (*S*)-**4m** was synthesized according to a general procedure (98% yield, 98% ee). Pure (*S*)-**4m** was obtained after purification as a solid (90% yield, >99% ee; air-sensitive). $[\alpha]_D^{20}$ = −145.8 (*c* = 1.1, CH_2Cl_2). ^{31}P NMR ($CDCl_3$, 121 MHz): δ 0.1. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.21 (ddd, 1H, *J* = 16.9, 8.2, and 2.8 Hz, C*H*HCOPh), 3.70−3.81 (m, 1H, CH*H*COPh), 4.27−4.33 (m, 1H, PC*H*CH_2), 6.97−8.15 (m, 22H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 40.3 (d, 1C, $^1J_{PC}$ = 11.4 Hz, PCH), 42.7 (d, 1C, $^2J_{PC}$ = 22.2 Hz, CH_2COPh), 124.0−140.8 (m, 28C, Ar), 198.1 (d, 1C, $^3J_{PC}$ = 13.2 Hz, COPh).

Synthesis of (*S*)-4n. Crude (*S*)-**4n** was synthesized according to a general procedure (99% yield, 96% ee). Pure (*S*)-**4n** was obtained after purification as a solid (88% yield, >99% ee; air-sensitive). $[\alpha]_D^{20}$ = −120.6 (*c* = 1.0, CH_2Cl_2). ^{31}P NMR ($CDCl_3$, 121 MHz): δ 0.1. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.02 (ddd, 1H, *J* = 17.1, 8.4, and 3.0 Hz, C*H*HCOPh), 3.49−3.60 (m, 1H, CH*H*COPh), 4.18−4.25 (m, 1H, PC*H*CH_2), 6.98−7.63 (m, 19H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 40.2 (d, 1C, $^1J_{PC}$ = 11.6 Hz, PCH), 42.6 (d, 1C, $^2J_{PC}$ = 22.2 Hz, CH_2COPh), 126.6−140.8 (m, 24C, Ar), 197.2 (d, 1C, $^3J_{PC}$ = 12.8 Hz, COPh).

Synthesis of (*S*)-4o. Crude (*S*)-**4o** was synthesized according to a general procedure (99% yield, 97% ee). Pure (*S*)-**4o** was obtained after purification as a solid (89% yield, >99% ee; air-sensitive): $[\alpha]_D^{20}$ = −144.0 (*c* = 1.0, CH_2Cl_2). ^{31}P NMR ($CDCl_3$, 121 MHz): δ 0.0. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.02 (ddd, 1H, *J* = 17.1, 8.6, and 2.9 Hz, C*H*HCOPh), 3.50−3.61 (m, 1H, CH*H*COPh), 4.18−4.25 (m, 1H, PC*H*CH_2), 6.97−7.60 (m, 19H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 40.1 (d, 1C, $^1J_{PC}$ = 11.7 Hz, PCH), 42.4 (d, 1C, $^2J_{PC}$ = 22.3 Hz, CH_2COPh), 126.6−140.8 (m, 24C, Ar), 196.9 (d, 1C, $^3J_{PC}$ = 12.7 Hz, COPh).

Synthesis of (*S*)-4p. Crude (*S*)-**4p** was synthesized according to a general procedure (99% yield, 97% ee). Pure (*S*)-**4p** was obtained after purification as a solid (90% yield, >99% ee; air-sensitive). $[\alpha]_D^{20}$ = −138.9 (*c* = 0.9, CH_2Cl_2). ^{31}P NMR ($CDCl_3$, 121 MHz): δ 0.1. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.02 (ddd, 1H, *J* = 17.1, 8.1, and 3.0 Hz, C*H*HCOPh), 3.52−3.63 (m, 1H, CH*H*COPh), 4.20−4.26 (m, 1H, PC*H*CH_2), 6.89−7.70 (m, 19H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 40.1 (d, 1C, $^1J_{PC}$ = 11.6 Hz, PCH), 42.5 (d, 1C, $^2J_{PC}$ = 22.3 Hz, CH_2COPh), 115.6−167.5 (m, 24C, Ar), 196.5 (d, 1C, $^3J_{PC}$ = 12.9 Hz, COPh). ^{19}F NMR ($CDCl_3$, 282.4 MHz): δ −105.3.

Synthesis of (*S*)-4q. Crude (*S*)-**4q** was synthesized according to a general procedure (99% yield, 92% ee). Pure (*S*)-**4q** was obtained after purification as a solid (71% yield, >99% ee; air-sensitive). $[\alpha]_D^{20}$ = −133.0 (*c* = 1.0, CH_2Cl_2). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 0.6. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.30 (ddd, 1H, *J* = 17.6, 7.7, and 3.2 Hz, C*H*HCOPh), 3.98−4.06 (m, 1H, CH*H*COPh), 4.27−4.32 (m, 1H, PC*H*CH_2), 6.96−8.55 (m, 19H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 40.1 (d, 1C, $^1J_{PC}$ = 17.6 Hz, PCH), 41.6 (d, 1C, $^2J_{PC}$ = 22.0 Hz, CH_2COPh), 122.0−153.4 (m, 24C, Ar), 199.9 (d, 1C, $^3J_{PC}$ = 12.7 Hz, COPh).

Synthesis of (*S*)-4r. Crude (*S*)-**4r** was synthesized according to a general procedure (98% yield, 98% ee). Pure (*S*)-**4r** was obtained after purification as a solid (88% yield, >99% ee; air-sensitive). $[\alpha]_D^{20}$ = −150.6 (*c* = 0.9, CH_2Cl_2). ^{31}P NMR($CDCl_3$, 161 MHz): δ −0.5. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.01 (ddd, 1H, *J* = 17.2, 8.4, and 2.8 Hz, C*H*HCOPh), 3.55−3.63 (m, 1H, CH*H*COPh), 3.73 (s, 3H, CH_3O), 4.23−4.28 (m, 1H, PC*H*CH_2), 6.73−7.68 (m, 19H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 40.1 (d, 1C, $^1J_{PC}$ = 11.4 Hz, PCH), 42.5 (d, 1C, $^2J_{PC}$ = 22.0 Hz, CH_2COPh), 55.6 (s, 1C, CH_3O), 113.8−163.6 (m, 24C, Ar), 196.6 (d, 1C, $^3J_{PC}$ = 12.8 Hz, COPh).

Synthesis of (*S*)-4s. Crude (*S*)-**4s** was synthesized according to a general procedure (99% yield, 97% ee). Pure (*S*)-**4s** was obtained after purification as a solid (90% yield, >99% ee; air-sensitive). $[\alpha]_D^{20}$ = −133.9 (*c* = 0.6, CH_2Cl_2). ^{31}P NMR ($CDCl_3$, 121 MHz): δ −0.2. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.03 (ddd, 1H, *J* = 17.2, 8.0, and 2.8 Hz, C*H*HCOPh), 3.47−3.55 (m, 1H, CH*H*COPh), 4.18−4.22 (m, 1H, PC*H*CH_2), 6.72−7.60 (m, 18H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 39.4 (d, 1C, $^1J_{PC}$ = 11.7 Hz, PCH), 42.5 (d, 1C, $^2J_{PC}$ = 22.6 Hz, CH_2COPh), 115.2−162.8 (m, 24C, Ar), 196.9 (d, 1C, $^3J_{PC}$ = 12.8 Hz, COPh). ^{19}F NMR ($CDCl_3$, 282.4 MHz): δ −116.3.

Synthesis of (*S*)-4t. Crude (*S*)-**4t** was synthesized according to a general procedure (99% yield, 98% ee). Pure (*S*)-**4t** was obtained after purification as a solid (90% yield, >99% ee; air-sensitive). $[\alpha]_D^{20}$ = −172.7 (*c* = 0.9, CH_2Cl_2). ^{31}P NMR ($CDCl_3$, 121 MHz): δ 0.0. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.04 (ddd, 1H, *J* = 17.4, 7.8, and 2.7 Hz, C*H*HCOPh), 3.47−3.58 (m, 1H, CH*H*COPh), 4.18−4.24 (m, 1H, PC*H*CH_2), 6.92−7.72 (m, 18H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 39.5 (d, 1C, $^1J_{PC}$ = 12.0 Hz, PCH), 42.4 (d, 1C, $^2J_{PC}$ = 22.1 Hz, CH_2COPh), 115.7−167.6 (m, 24C, Ar), 196.3 (d, 1C, $^3J_{PC}$ = 12.7 Hz, COPh). ^{19}F NMR ($CDCl_3$, 282.4 MHz): δ −104.9.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data in CIF format, general information, experimental section, NMR spectra, and X-ray data. This material is available free of charge via the Internet at http://pubs.acs.org.

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