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# Asymmetric Synthesis of Enaminophosphines via Palladacycle-Catalyzed Addition of $Ph_2PH$ to $\alpha,\beta$-Unsaturated Imines

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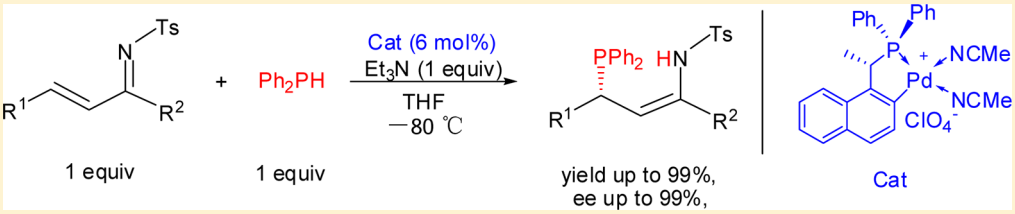
Supporting Information

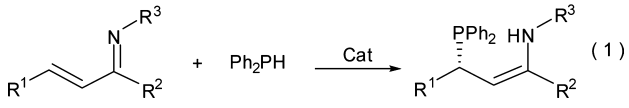



**ABSTRACT:** A highly reactive, chemo- and enantioselective addition of diphenylphosphine to $\alpha,\beta$-unsaturated imines catalyzed by a palladacycle has been developed, thus providing the access to a series of chiral tertiary enaminophosphines in high yields. A putative catalytic cycle has also been proposed.

## INTRODUCTION

Chiral phosphines, both as ligands[1] and as organocatalysts,[2] have played important roles in asymmetric transformations as well as touching other fields such as pharmaceuticals and agriculture.[3] Nevertheless, most chiral phosphines are prepared predominantly either via the tedious resolution process or by the use of a limited chiral pool.[3c,4] Recently, a few strategies for the catalytic synthesis of chiral phosphines via C−P bond formation have been reported and attracted great interest. These include the synthesis of chiral phosphines via cross-coupling[5] and hydrophosphination (the addition of a P−H bond to unsaturated C−C bonds) pathways. In particular, the asymmetric hydrophosphination of Michael acceptors such as conjugated esters, nitriles, enones, enals, and nitroalkenes, etc. via transition-metal-catalyzed[6] or organocatalytic[7] processes have been well studied, making it an active area of research. Among the transition-metal catalysts, several cyclopalladated complexes including pincer complexes have been recently utilized as efficient catalysts for this transformations.[8]

$\alpha,\beta$-Unsaturated imines have been well demonstrated as versatile synthetic building blocks in cycloaddition reactions such as [4 + 2], [3 + 2], [2 + 2], etc., as well as 1,2- and 1,4-addition reactions.[9] Many nucleophiles have been reported in the addition reactions involving $\alpha,\beta$-unsaturated imines.[9] However, to the best of our knowledge, secondary phosphines have never been reported to date as nucleophiles for the asymmetric addition to $\alpha,\beta$-unsaturated imines. In connection with our continuous interest in synthesis of chiral tertiary phosphines, herein, we report the first asymmetric addition of $Ph_2PH$ to $\alpha,\beta$-unsaturated ketimines catalyzed by a palladacycle for the construction of chiral tertiary enaminophosphines (chiral P,N-ligands) (eq 1).




(1)

## RESULTS AND DISCUSSION

Although the asymmetric addition of phosphine oxides or phosphites (addition of P(O)−H bond) to imines has been well studied,[10] the asymmetric addition of secondary phosphines (addition of P−H bond) to imines is unprecedented. We were interested in exploring the asymmetric addition of secondary phosphines to imines to prepare P,N-ligands. Initially, we used an aldimine (PhCH=NTs, Ts = tosyl) as the substrate for the hydrophosphination with $Ph_2PH$ in the presence of palladacycle (*S*)-**1** as the catalyst at −80 °C in THF. The result showed that $Ph_2PH$ can be successfully added to C=N double bonds; however, racemic addition products were obtained. Subsequently, we evaluated a ketimine (Ph(Me)C=NTs) instead of the aldimine under the same catalysis conditions only to find no reaction occurred. However, when a *N*-tosyl $\alpha,\beta$-unsaturated ketimine **6a** was utilized as the substrate under the same reaction conditions, to our delight, it showed excellent reactivity and enantioselectivity toward the asymmetric hydrophosphination reaction (1,4-addition). Further screening also showed that the reactivity decreased if the protecting group, $R^3$ = tosyl, was changed into a less electron withdrawing group such as phenyl and that messy products were generated if *N*-tosyl $\alpha,\beta$-unsaturated aldimine ($R^1$ = Ph, $R^2$ = H, $R^3$ = Ts) was employed as the substrate. Therefore, we focused on $\alpha,\beta$-unsaturated ketimines as the substrates with a

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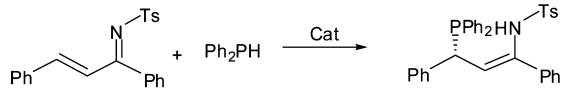
view of synthesizing a family of chiral P,N-ligands via 1,4-addition. The ketimine **6a** was chosen as the substrate for optimization of reaction conditions. The results from the screening of catalysts, temperature, and solvents are given in Table 1.

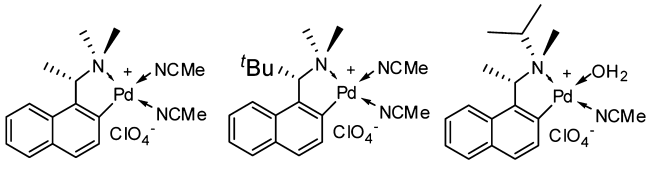
**Table 1. Screening of Conditions for the Enantioselective Hydrophosphination of an α,β-Unsaturated Ketimine with $Ph_2PH$[a]**



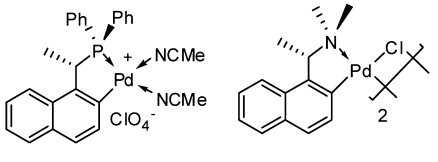

**6a** **7** **8a**

| entry | catalyst | solvent | temp (°C) | time (h) | yield[b] (%) | ee (*R*)[c] |
|---|---|---|---|---|---|---|
| 1 | (*S*)-**1** | THF | −80 | 2 | 99 | 95 |
| 2 | (*S*)-**1** | $CH_2Cl_2$ | −80 | 1 | 97 | 96 |
| 3 | (*S*)-**1** | acetone | −80 | 1 | 97 | 96 |
| 4 | (*S*)-**1** | toluene | −80 | 2 | trace | |
| 5 | (*S*)-**1** | $CHCl_3$ | −40 | 2 | 86 | 87 |
| 6 | (*S*)-**1** | NCMe | −40 | 2 | 91 | 95 |
| 7 | (*S*)-**1** | THF | −40 | 2 | 99 | 94 |
| 8 | (*S*)-**1** | THF | −20 | 2 | 76 | 80 |
| 9 | (*S*)-**1** | THF | 0 | 2 | 60 | 75 |
| 10 | (*S*)-**1** | THF | 20 | 5 | 50 | 75 |
| 11 | (*S*)-**2** | THF | −80 | 22 | 51 | 34 |
| 12 | (*S*)-**3** | THF | −80 | 71 | 83 | 50 |
| 13 | (*S*)-**4** | THF | −80 | 2 | 99 | 99 |

[a]Conditions: 0.20 mmol of $Ph_2PH$, 6 mol % of cat., 0.20 mmol of **6a**, 1.0 equiv of base, 5 mL of solvent were reacted at the given temperature. [b]Yield was calculated from $^{31}P\{^1H\}$ NMR of the crude product. [c]ee was determined from $^{31}P\{^1H\}$ NMR integration of the signals.




(*S*)-**1** (*S*)-**2** (*S*)-**3**




(*S*)-**4** (*S*)-**5**

The enantiomeric excess (ee) was determined from $^{31}P\{^1H\}$ NMR spectra of the derivative **9** formed by treating the corresponding enantiomerically enriched **8** with an enantiopure palladacycle complex **5**.[6e,f,8b,e,g] The single-crystal X-ray diffraction analysis of one such derivative, **9a** ($R^1$ = Ph, $R^2$ = Ph), revealed that the absolute configuration of the chiral carbon center of the major product is *R* (Figure 1). The results showed that the best ee was achieved in THF. Moderate to good enantioselectivities were observed when other solvents such $CH_2Cl_2$, acetone, $CHCl_3$, and NCMe were used. On the basis of previous studies,[8b,e,g] triethylamine was chosen as the base of choice to assist the reaction. When the reaction

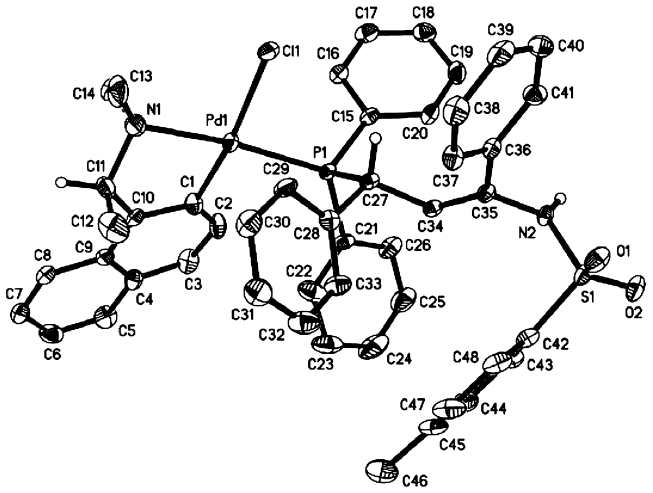



**Figure 1.** Molecular structure and absolute stereochemistry of the derivative complex (*R*,*R*)-**9a** with 50% probability thermal ellipsoids shown. Hydrogen atoms except those on the chiral center are omitted for clarity.

temperature was raised, the yield of 1,4-addition product decreased presumably due to the generation of 1,2-addition analogs (Table 1, entries 1, 7−10). Palladacycles (*S*)-**1**−**4**, which are structurally similar with two coordination sites readily available for catalysis, were screened as catalysts for the reaction. The results showed that (*S*)-**4** is the best one for the 1,4-addition providing 99% ee in quantitative yield. The yield decreased dramatically when the C,N-palladacycles (*S*)-**2** and (*S*)-**3** with a sterically demanding substituent on the chiral carbon or nitrogen center were employed as the catalyst.

With optimal conditions established for the asymmetric 1,4-addition catalyzed by (*S*)-**4**, a range of α,β-unsaturated ketimines were screened for the reaction. The results are presented in Table 2. All of the reactions proceeded to full conversion of $Ph_2PH$ under the given conditions, thus allowing the efficient transformation of a wide range of α,β-unsaturated ketimines into corresponding chiral tertiary enaminophosphines in excellent yields and enantioselectivities. The process tolerates a broad range of functional groups such as halogens (F, Cl, Br) and heterocycles (thienyl). Substrates bearing both electron-withdrawing and electron-donating groups are also suitable as substrates. Nevertheless, those bearing electron-withdrawing groups are more reactive than those bearing electron-donating groups. As far as the substituent on $R^1$ is concerned, the *p*- and *m*-substituted α,β-unsaturated ketimines showed excellent enantioselectivity (entries 2 and 3), while the *o*-substituted one showed lowest enantioselectivity. The cross-conjugated azatriene **6o** with two C=C double bonds (entry 15) showed good reactivity and selectivity toward the hydrophosphination in the presence of 1 equiv of $Ph_2PH$. However, in the presence of 2 equiv of $Ph_2PH$ under the same reaction conditions, only the monoaddition product was observed with the excess $Ph_2PH$ intact. The other substrates bearing aliphatic substituent we tried showed low efficiency for this kind of reaction.[11] Palladacycle (*S*)-**4** was therefore a highly efficient catalyst for this asymmetric hydrophosphination scenario and generated the chiral P,N-ligands in excellent yields (95−99%) and ee's (70−99%) while tolerating a wide range of ketimine substrates.

On the basis of experimental results and observations, a mechanism was proposed for the (*S*)-**4**-catalyzed asymmetric


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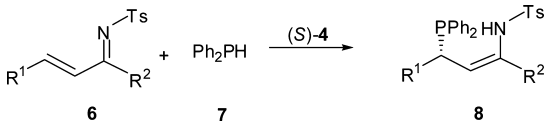
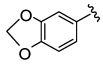
**Table 2. Substrate scope of the (*S*)-4-Catalyzed Enantioselective Hydrophosphination of *α,β*-Unsaturated Ketimines with $Ph_2PH$[a]**




6 7 8

| Entry | $R^1$ | $R^2$ | *t* [h] | **8** | Yield[b] [%] | ee(*R*)[c] [%] |
|---|---|---|---|---|---|---|
| 1 | Ph | Ph | 2 | **8a** | 99 | 99 |
| 2 | 4-$ClC_6H_4$ | Ph | 2 | **8b** | 96 | 92 |
| 3 | 3-$ClC_6H_4$ | Ph | 2 | **8c** | 96 | 95 |
| 4 | 2-$ClC_6H_4$ | Ph | 2 | **8d** | 95 | 70 |
| 5 | 4-$FC_6H_4$ | Ph | 2 | **8e** | 97 | 97 |
| 6 | 4-$BrC_6H_4$ | Ph | 2 | **8f** | 94 | 91 |
| 7 | 4-$CF_3C_6H_4$ | Ph | 2 | **8g** | 95 | 96 |
| 8 | 4-$MeC_6H_4$ | Ph | 2 | **8h** | 97 | 96 |
| 9 | 4-$MeOC_6H_4$ | Ph | 7 | **8i** | 98 | 97 |
| 10 |  | Ph | 2 | **8j** | 99 | 99 |
| 11 | 2-Naph | Ph | 2 | **8k** | 97 | 92 |
| 12 | Ph | 4-$MeC_6H_4$ | 5 | **8l** | 98 | 99 |
| 13 | Ph | 4-$BrC_6H_4$ | 2 | **8m** | 95 | 96 |
| 14 | Ph | 2-thienyl | 2 | **8n** | 97 | 95 |
| 15 | Ph | -(*E*)-CH=CHPh | 2 | **8o** | 97 | 91 |

[a]Conditions: 0.20 mmol of $Ph_2PH$, 6 mol % of (*S*)-**4**, 5 mL of THF, 1.0 equiv of **6**, 1.0 equiv of $Et_3N$ were reacted at −80 °C, unless otherwise noted. [b]Isolated yield. [c]ee was determined from $^{31}P\{^1H\}$ NMR; see the Supporting Information for details.

hydrophosphination of *α,β*-unsaturated ketimines with $Ph_2PH$ (Scheme 1). Free $Ph_2PH$ by virtue of its high affinity to palladium readily yields the bis-phosphine complex by displacement of the relatively weakly coordinated solvent (NCMe) on (*S*)-**4**. However, due to the strong *π*-accepting properties of the aromatic carbon donor of the palladacycle and strong trans effect, the P−Pd bond of the coordinated diphenylphosphine in the *trans* P−Pd−C moiety of the intermediate is labile, thus allowing for *α,β*-unsaturated ketimines to coordinate to palladium. In comparison, the P−Pd bond involving the diphenylphosphine in the *trans* P−Pd−P moiety is significantly more stable. In the presence of $Et_3N$ as the external base, the acidified secondary phosphine coordinated on palladium is readily converted to the corresponding phosphido species [Pd]P(Ph)Ph, which is very reactive and undergoes the desired intramolecular 1,4-addition at −80 °C to form the tertiary enaminophosphines. It is indeed interesting to note that instead of the expected iminophosphine products what were finally obtained in the asymmetric hydrophosphination of *α,β*-unsaturated ketimines were the enaminophosphine products. Our previous work on stoichiometric palladacycle-promoted hydroamination of ethynylphosphines had shown an instance wherein the iminophosphine ligand could be transformed to the enamino form upon complexation with palladium.[12]

## ■ CONCLUSION

In summary, we have successfully developed a protocol for the highly reactive asymmetric addition of $Ph_2PH$ to *α,β*-unsaturated ketimines catalyzed by a palladacycle. Broad functional group tolerance is exhibited, and a wide range of substrates can be efficiently converted into the desired products in high yields with excellent chemo- and enantioselectities. This method allows for the synthesis of a series of chiral tertiary enaminophosphines (chiral P, N-ligands) which are potentially useful for catalysis. A putative catalytic cycle has also been proposed.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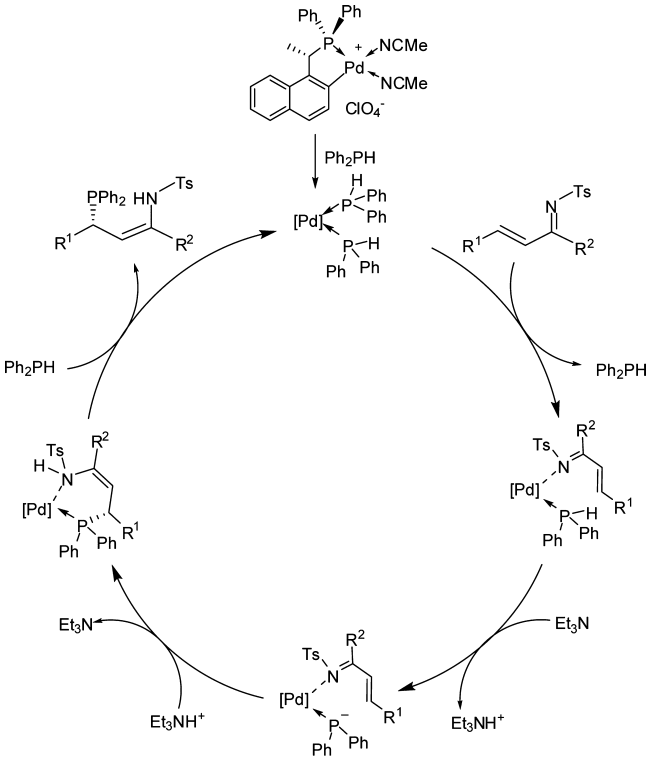
**Scheme 1. Proposed Catalytic Cycle**



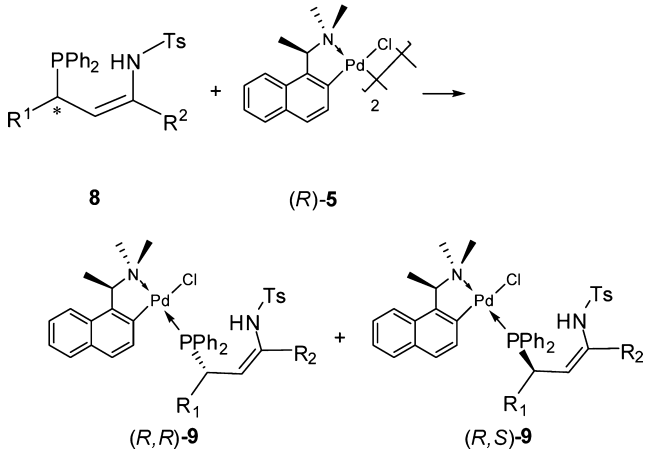
## EXPERIMENTAL SECTION

All air-sensitive manipulations were performed under a positive pressure of nitrogen or argon using standard Schlenk line. Solvents were degassed prior to use when necessary. THF was freshly distilled before use. Column chromatography was conducted on silica gel 60. $^1$H NMR (300, 400, 500 MHz) spectra were recorded in $CDCl_3$ [using $SiMe_4$ ($\delta$ = 0 ppm) as an internal standard]. $^{13}$C NMR (75, 100, 125 MHz) spectra were recorded in $CDCl_3$ [using $CDCl_3$ ($\delta$ = 77.23 ppm) as an internal standard]. $^{13}$C multiplicities were assigned using a DEPT sequence, where appropriate HMQC experiments were carried out to aid assignment. $^{31}$P NMR (100, 162, 202 MHz) were recorded in $CDCl_3$ [using 80% $H_3PO_4$ ($\delta$ = 0 ppm) as an external standard]. The following abbreviations are used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Optical rotations were measured on the specified solution in a 0.1 dm cell at 20 °C with a polarimeter. HRMS (ESI) were recorded on a time-of-flight (TOF) LC/MS instrument. Chiral palladacycles (*S*)-**1**,[13] (*S*)-**2**,[14] (*S*)-**3**,[14] (*S*)-**4**,[8e,15] (*S*)-**5**,[16] and $\alpha,\beta$-unsaturated ketimines[17] were prepared according to the literature.

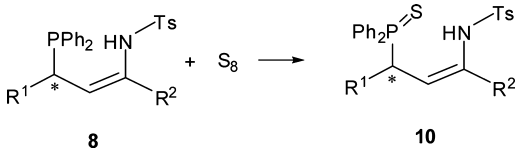
**Caution!** Perchlorate salts of metal complexes are potentially explosive compounds and should be handled with care.

**General Experimental Procedure for Synthesis of Chiral Tertiary Phosphines 7.** To a solution of $Ph_2PH$ **7** (50 mg, 0.27 mmol) in degassed THF (5 mL) was added (*S*)-**4** (10.1 mg, 0.016 mmol). The solution was stirred at room temperature for 5 min and then was cooled to −80 °C before the addition of $\alpha,\beta$-unsaturated ketimines **6** (1 equiv) followed by dropwise addition of $Et_3N$ (27 mg, 0.27 mmol) in THF (0.5 mL). The solution was subsequently stirred at −80 °C, and the reaction was monitored by $^{31}$P{$^1$H} NMR. Upon completion, the reaction setup was warmed to room temperature and solvent removed under reduced pressure to give the crude product. $CH_2Cl_2$ (10 mL) was added to the solids, and the solution was filtered directly through a short silica gel column using a Pasteur pipet fixed on a nitrogen purged two-neck Schlenk flask (in order to remove the catalyst and phosphine oxides, if any). Solvent is removed from the filtrate under reduced pressure to give the chiral tertiary enaminophosphines **8** as the desired product.

For determination of ee, **8** was coordinated with complex **5** quantitatively to give the corresponding diastereomers **9** the ratios of which were then determined by $^{31}$P{$^1$H} NMR.[18]



For the convenience of characterizing the addition product **8** (air-sensitive), it was transformed into **10** via sulfurization.[18]



**(*R*)-Ph(PPh$_2$)CHCH=C(Ph)NHTs (8a).** Compound **8a** was synthesized according to the general procedure (146 mg, 99% yield, ee = 99%). The sulfurized derivative **10a** was characterized as: mp 160−162 °C; $[\alpha]^{20}_D$ = +21.2 (*c* 0.5, $CH_2Cl_2$); $^{31}$P NMR ($CDCl_3$, 162 MHz) $\delta$ 50.4; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 2.37 (s, 3H, PhC*H*$_3$), 4.38 (t, 1H, *J* = 10.8 Hz, PC*H*), 6.17 (t, 1H, *J* = 11.6 Hz, PCHC*H*), 6.22 (s, 1H, N*H*), 6.84−7.46 (m, 24H, Ar); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 21.8 (s, 1C, PhCH$_3$), 47.1 (d, 1C, $J_{CP}$ = 49.0 Hz, PCH), 112.8 (s, 1C, PCHCH), 143.7 (s, 1C, CH=*C*N) (the remaining signals of aromatic carbons could not be distinguished); HRMS (ESI) calcd for $C_{34}H_{31}NO_2PS_2$ $[M + H]^+$ 580.1534, found 580.1548.

**(*R*)-4-ClPh(PPh$_2$)CHCH=C(Ph)NHTs (8b).** Compound **8b** was synthesized according to the general procedure (151 mg, 96% yield, ee = 92%). The sulfurized derivative **10b** was characterized as: mp 158−160 °C; $[\alpha]^{20}_D$ = +24.5 (*c* 0.5, $CH_2Cl_2$); $^{31}$P NMR ($CDCl_3$, 121 MHz) $\delta$ 50.9; $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ 2.39 (s, 3H, PhC*H*$_3$), 4.34 (t, 1H, *J* = 10.8 Hz, PC*H*), 6.11 (t, 1H, *J* = 11.1 Hz, PCHC*H*), 6.23 (s, 1H, N*H*), 6.76−7.46 (m, 23H, Ar); $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$ 21.8 (s, 1C, PhCH$_3$), 46.6 (d, 1C, $J_{CP}$ = 48.8 Hz, PCH), 111.7 (s, 1C, PCHCH), 143.9 (s, 1C, CH=CN) (the remaining signals of aromatic carbons could not be distinguished); HRMS (ESI) calcd for $C_{34}H_{30}NO_2PS_2Cl$ $[M + H]^+$ 614.1144, found 614.1143.

**(*R*)-3-ClPh(PPh$_2$)CHCH=C(Ph)NHTs (8c).** Compound **8c** was synthesized according to the general procedure (151 g, 96% yield, ee = 95%). The sulfurized derivative **10c** was characterized as: mp 160−163 °C; $[\alpha]^{20}_D$ = +16.7 (*c* 0.5, $CH_2Cl_2$); $^{31}$P NMR ($CDCl_3$, 121 MHz) $\delta$ 51.2; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 2.39 (s, 3H, PhC*H*$_3$), 4.32 (t, 1H, *J* = 10.8 Hz, PC*H*), 6.08 (t, 1H, *J* = 11.6 Hz, PCHC*H*), 6.22 (s, 1H, N*H*), 6.75−7.40 (m, 23H, Ar); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 21.8 (s, 1C, PhCH$_3$), 47.0 (d, 1C, $J_{CP}$ = 48.0 Hz, PCH), 111.4 (s, 1C, PCHCH), 144.0 (s, 1C, CH=CN) (the remaining signals of aromatic carbons could not be distinguished); HRMS (ESI) calcd for $C_{34}H_{30}NO_2PS_2Cl$ $[M + H]^+$ 614.1144, found 614.1132.

**(*R*)-2-ClPh(PPh$_2$)CHCH=C(Ph)NHTs (8d).** Compound **8d** was synthesized according to the general procedure (149 mg, 95% yield, ee = 70%). The sulfurized derivative **10d** was characterized as: mp 190−192 °C; $[\alpha]^{20}_D$ = +75.5 (*c* 0.5, $CH_2Cl_2$); $^{31}$P NMR ($CDCl_3$, 162 MHz) $\delta$ 51.6; $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$ 2.39 (s, 3H, PhC*H*$_3$), 5.17 (t, 1H, *J* = 10.8 Hz, PC*H*), 6.17 (s, 1H, N*H*), 6.23 (t, 1H, *J* = 11.1 Hz,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PCHCH), 6.81−7.51 (m, 23H, Ar); $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$ 21.8 (s, 1C, PhCH$_3$), 41.5 (d, 1C, $J_{CP}$ = 49.5 Hz, PCH), 111.7 (s, 1C, PCHCH), 143.6 (s, 1C, CH=CN) (the remaining signals of aromatic carbons could not be distinguished); HRMS (ESI) calcd for $C_{34}H_{30}NO_2PS_2Cl$ $[M + H]^+$ 614.1144, found 614.1144.

**(*R*)-4-FPh(PPh$_2$)CHCH=C(Ph)NHTs (8e).** Compound **8e** was synthesized according to the general procedure (148 mg, 97% yield, ee = 97%). The sulfurized derivative **10e** was characterized as: mp 176−178 °C; $[\alpha]^{20}_D$ = +33.9 (*c* 0.6, $CH_2Cl_2$); $^{31}$P NMR ($CDCl_3$, 162 MHz) $\delta$ 50.5 (d, 1P, $J_{PF}$ = 5.0 Hz); $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 2.40 (s, 3H, PhCH$_3$), 4.36 (t, 1H, *J* = 10.8 Hz, PCH), 6.11 (t, 1H, *J* = 11.6 Hz, PCHCH), 6.12 (s, 1H, NH), 6.79−7.47 (m, 23H, Ar); $^{19}$F NMR ($CDCl_3$, 282 MHz) $\delta$ −114.9 (d, 1F, $J_{FP}$ = 6 Hz); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 21.8 (s, 1C, PhCH$_3$), 46.4 (d, 1C, $J_{CP}$ = 49.0 Hz, PCH), 112.2 (s, 1C, PCHCH), 143.9 (s, 1C, CH=CN) (the remaining signals of aromatic carbons could not be distinguished); HRMS (ESI) calcd for $C_{34}H_{30}NO_2PS_2F$ $[M + H]^+$ 598.1440, found 598.1438.

**(*R*)-4-BrPh(PPh$_2$)CHCH=C(Ph)NHTs (8f).** Compound **8f** was synthesized according to the general procedure (159 mg, 94% yield, ee = 91%). The sulfurized derivative **10f** was characterized as: mp 167−169 °C; $[\alpha]^{20}_D$ = +20.4 (*c* 0.5, $CH_2Cl_2$); $^{31}$P NMR ($CDCl_3$, 162 MHz) $\delta$ 50.1; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 2.39 (s, 3H, PhCH$_3$), 4.32 (t, 1H, *J* = 10.8 Hz, PCH), 6.09 (t, 1H, *J* = 11.2 Hz, PCHCH), 6.20 (s, 1H, NH), 6.70−7.46 (m, 23H, Ar); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 21.8 (s, 1C, PhCH$_3$), 46.7 (d, 1C, $J_{CP}$ = 49.0 Hz, PCH), 111.6 (s, 1C, PCHCH), 143.9 (s, 1C, CH=CN) (the remaining signals of aromatic carbons could not be distinguished); HRMS (ESI) calcd for $C_{34}H_{30}NO_2PS_2Br$ $[M + H]^+$ 658.0639, found 658.0638.

**(*R*)-4-CF$_3$Ph(PPh$_2$)CHCH=C(Ph)NHTs (8g).** Compound **8g** was synthesized according to the general procedure (158 mg, 95% yield, ee = 96%). The sulfurized derivative **10g** was characterized as: mp 146−149 °C; $[\alpha]^{20}_D$ = +34.3 (*c* 0.6, $CH_2Cl_2$); $^{31}$P NMR ($CDCl_3$, 162 MHz) $\delta$ 51.1 (d, 1P, $J_{PF}$ = 3 Hz); $^1$H NMR ($CDCl_3$,300 MHz) $\delta$ 2.39 (s, 3H, PhCH$_3$), 4.41 (t, 1H, *J* = 10.5 Hz, PCH), 6.17 (t, 1H, *J* = 11.4 Hz, PCHCH), 6.22 (s, 1H, NH), 6.83−7.60 (m, 23H, Ar); $^{19}$F NMR ($CDCl_3$, 282 MHz) $\delta$ −62.5 (d, 1F, $J_{FP}$ = 3.0 Hz); $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$ 21.8 (s, 1C, PhCH$_3$), 47.2 (d, 1C, $J_{CP}$ = 48.0 Hz, PCH), 111.0 (s, 1C, PCHCH), 124.8 (d, 1C, $J_{CF}$ = 1.5 Hz, $C_6H_4CF3$), 144.0 (s, 1C, CH=CN) (the remaining signals of aromatic carbons could not be distinguished); HRMS (ESI) calcd for $C_{35}H_{30}NO_2PS_2F_3$ $[M + H]^+$ 648.1408, found 648.1407.

**(*R*)-4-MePh(PPh$_2$)CHCH=C(Ph)NHTs (8h).** Compound **8h** was synthesized according to the general procedure (147 mg, 97% yield, ee = 96%). The sulfurized derivative **10h** was characterized as: mp 117−118 °C; $[\alpha]^{20}_D$ = +13.5 (*c* 0.5, $CH_2Cl_2$); $^{31}$P NMR ($CDCl_3$, 121 MHz) $\delta$ 50.9; $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$ 2.28 (s, 3H, PCHPhCH$_3$), 2.39 (s, 3H, $SO_2$PhCH$_3$), 4.38 (t, 1H, *J* = 10.8 Hz, PCH), 6.11 (s, 1H, NH), 6.11 (t, 1H, *J* = 11.1 Hz, PCHCH), 6.72−7.47 (m, 23H, Ar); $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$ 21.1 (s, 1C, PCHPhCH$_3$), 21.7 (s, 1C, $SO_2$PhCH$_3$), 46.6 (d, 1C, $J_{CP}$ = 48.8 Hz, PCH), 113.1 (s, 1C, PCHCH), 143.6 (s, 1C, CH=CN) (the remaining signals of aromatic carbons could not be distinguished); HRMS (ESI) calcd for $C_{35}H_{33}NO_2PS_2$ $[M + H]^+$ 594.1690, found 594.1724.

**(*R*)-4-MeOPh(PPh$_2$)CHCH=C(Ph)NHTs (8i).** Compound **8i** was synthesized according to the general procedure (153 mg, 98% yield, ee = 97%). The sulfurized derivative **10i** was characterized as: mp 216−217 °C; $[\alpha]^{20}_D$ = +19.1 (*c* 0.5, $CH_2Cl_2$); $^{31}$P NMR ($CDCl_3$, 121 MHz) $\delta$ 51.0; $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$ 2.40 (s, 3H, PhCH$_3$), 3.77 (s, 3H, PhOCH$_3$), 4.36 (t, 1H, *J* = 11.1 Hz, PCH), 6.06 (s, 1H, NH), 6.09 (t, 1H, *J* = 11.1 Hz, PCHCH), 6.63−7.32 (m, 23H, Ar); $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$ 21.9 (s, 1C, PhCH$_3$), 46.3 (d, 1C, $J_{CP}$ = 49.5 Hz, PCH), 55.4 (s, 1C, PhOCH$_3$), 113.6 (s, 1C, PCHCH), 159.0 (s, 1C, CH=CN) (the remaining signals of aromatic carbons could not be distinguished); HRMS (ESI) calcd for $C_{35}H_{33}NO_3PS_2$ $[M + H]^+$ 610.1640, found 610.1638.

**(*R*)-CH$_2$(1,3-2OPh)(PPh$_2$)CHCH=C(Ph)NHTs (8j).** Compound **8j** was synthesized according to the general procedure (158 mg, 99% yield, ee = 99%). The sulfurized derivative **10j** was characterized as: mp 196−197 °C; $[\alpha]^{20}_D$ = +23.5 (*c* 0.5, $CH_2Cl_2$); $^{31}$P NMR ($CDCl_3$, 202 MHz) $\delta$ 50.3; $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 2.40 (s, 3H, PhCH$_3$), 4.31 (t, 1H, *J* = 10.5 Hz, PCH), 5.91 (s, 2H, OCH$_2$O), 6.02 (t, 1H, *J* = 11.5 Hz, PCHCH) 6.14 (s, 1H, NH),, 6.46−7.48 (m, 22H, Ar); $^{13}$C NMR ($CDCl_3$, 162 MHz) $\delta$ 21.8 (s, 1C, PhCH$_3$), 46.7 (d, 1C, $J_{CP}$ = 64.8 Hz, PCH), 101.1 (s, 1C, OCH$_2$O), 112.8 (s, 1C, PCHCH), 147.4 (s, 1C, CH=CN) (the remaining signals of aromatic carbons could not be distinguished); HRMS (ESI) calcd for $C_{35}H_{31}NO_4PS_2$ $[M + H]^+$ 624.1432, found 624.1423.

**(*R*)-NaphPh(PPh$_2$)CHCH=C(Ph)NHTs (8k).** Compound **8k** was synthesized according to the general procedure (157 mg, 97% yield, ee = 92%). The sulfurized derivative **10k** was characterized as: mp 161−163 °C; $[\alpha]^{20}_D$ = +10.9 (*c* 0.5, $CH_2Cl_2$); $^{31}$P NMR ($CDCl_3$, 121 MHz) $\delta$ 51.0; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 2.32 (s, 3H, PhCH$_3$), 4.54 (t, 1H, *J* = 10.4 Hz, PCH), 6.09 (s, 1H, NH), 6.24 (t, 1H, *J* = 11.2 Hz, PCHCH), 6.91−7.48 (m, 26H, Ar); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 21.8 (s, 1C, PhCH$_3$), 47.4 (d, 1C, $J_{CP}$ = 49.0 Hz, PCHPh), 112.8 (s, 1C, PCHCH), 143.9 (s, 1C, CH=CN) (the remaining signals of aromatic carbons could not be distinguished); HRMS (ESI) calcd for $C_{38}H_{33}NO_2PS_2$ $[M + H]^+$ 630.1690, found 630.1688.

**(*R*)-Ph(PPh$_2$)CHCH=C(4-MePh)NHTs (8l).** Compound **8l** was synthesized according to the general procedure (149 mg, 98% yield, ee = 99%). The sulfurized derivative **10l** was characterized as: mp 160−162 °C; $[\alpha]^{20}_D$ = +18.8 (*c* 0.6, $CH_2Cl_2$); $^{31}$P NMR ($CDCl_3$, 162 MHz) $\delta$ 50.6; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 2.39 (s, 6H, $SO_2$PhCH$_3$; PhCH$_3$), 4.41 (t, 1H, *J* = 10.4 Hz, PCH), 6.11 (t, 1H, *J* = 11.2 Hz, PCHCH), 6.12 (s, 1H, NH), 6.81−7.31 (m, 23H, Ar); $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$ 21.6 (s, 1C, $SO_2$PhCH$_3$), 21.8 (s, 1C, PhCH$_3$), 47.1 (d, 1C, $J_{CP}$ = 36.0 Hz, PCH), 112.4 (s, 1C, PCHCH), 143.7 (s, 1C, CH=CN) (the remaining signals of aromatic carbons could not be distinguished); HRMS (ESI) calcd for $C_{35}H_{33}NO_2PS_2$ $[M + H]^+$ 594.1690, found 594.1670.

**(*R*)-Ph(PPh$_2$)CHCH=C(4-BrPh)NHTs (8m).** Compound **8m** was synthesized according to the general procedure (161 mg, 95% yield, ee = 96%). The sulfurized derivative **10m** was characterized as: mp 159−161 °C; $[\alpha]^{20}_D$ = +9.8 (*c* 0.6, $CH_2Cl_2$); $^{31}$P NMR ($CDCl_3$, 121 MHz) $\delta$ 51.2; $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 2.43 (s, 3H, PhCH$_3$), 4.35 (t, 1H, *J* = 10.8 Hz, PCH), 6.10 (t, 1H, *J* = 10.8 Hz, PCHCH), 6.27 (s, 1H, NH), 6.81−7.54 (m, 23H, Ar); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 21.8 (s, 1C, PhCH$_3$), 47.2 (d, 1C, $J_{CP}$ = 48.4 Hz, PCH), 111.2 (s, 1C, PCHCH), 143.9 (s, 1C, CH=CN) (the remaining signals of aromatic carbons could not be distinguished); HRMS (ESI) calcd for $C_{34}H_{30}NO_2PS_2Br$ $[M + H]^+$ 658.0639, found 658.0643.

**(*R*)-Ph(PPh$_2$)CHCH=C(2-thienyl)NHTs (8n).** Compound **8n** was synthesized according to the general procedure (145 mg, 97% yield, ee = 95%). The sulfurized derivative **10n** was characterized as: mp 188−190 °C; $[\alpha]^{20}_D$ = +14.3 (*c* 0.5, $CH_2Cl_2$); $^{31}$P NMR ($CDCl_3$, 121 MHz) $\delta$ 33.0; $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$ 2.34 (s, 3H, PhCH$_3$), 5.10 (t, 1H, *J* = 10.8 Hz, PCH), 5.90 (s, 1H, NH), 6.14 (t, 1H, *J* = 11.1 Hz, PCHCH), 6.74−7.60 (m, 22H, Ar); $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$ 21.8 (s, 1C, PhCH$_3$), 46.9 (d, 1C, $J_{CP}$ = 64.5 Hz, PCH), 117.5 (s, 1C, PCHCH), 143.4 (s, 1C, CH=CN) (the remaining signals of aromatic carbons could not be distinguished); HRMS (ESI) calcd for $C_{32}H_{29}NO_2PS_3$ $[M + H]^+$ 586.1098, found 586.1111.

**(*R*)-Ph(PPh$_2$)CHCH=C[(*E*)-CH=CHPh]NHTs (8o).** Compound **8o** was synthesized according to the general procedure (149 mg, 97% yield, ee = 91%). The sulfurized derivative **10o** was characterized as: mp 179−181 °C; $[\alpha]^{20}_D$ = +42.7 (*c* 1.1, $CH_2Cl_2$); $^{31}$P NMR ($CDCl_3$, 121 MHz) $\delta$ 50.3; $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$ 2.35 (s, 3H, PhCH$_3$), 4.75 (t, 1H, *J* = 10.8 Hz, PCH), 5.99 (s, 1H, NH), 6.57−7.86 (m, 27H, Ar, =CH); $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$ 21.7 (s, 1C, PhCH$_3$), 47.4 (d, 1C, $J_{CP}$ = 49.7 Hz, PCH), 120.6 (d, 1C, $J_{CP}$ = 12.1 Hz, PCHCH), 143.7 (s, 1C, CH=CN) (the remaining signals of aromatic and vinyl carbons could not be distinguished); HRMS (ESI) calcd for $C_{36}H_{33}NO_2PS_2$ $[M + H]^+$ 606.1684, found 606.1690.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

$^1$H, $^{13}$C, and $^{31}$P NMR spectra for compounds **10a−o**; $^{31}$P NMR spectra of **9a−o** for determining ee; X-ray crystallo-


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graphic data of (*R*,*R*)-**9a**. 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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(18) For more details, see the Supporting Information.