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Asymmetric Hydrogenation

Efficient Asymmetric Hydrogenation of α-Acetamidocinnamates through a Simple, Readily Available Monodentate Chiral *H*-Phosphinate

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Abstract: An air-stable, simple (R_P)-mentylbenzylphosphinate, readily available in large quantities, can efficiently induce the rhodium-catalyzed asymmetric hydrogenation of α-acetamidocinnamates with high enantioselectivity (up to 99.6 % *ee*). Intramolecular hydrogen bonding plays an important role in this asymmetric induction.

The catalytic asymmetric hydrogenation by metals is one of the most useful methods to prepare optically pure compounds and has been studied extensively over the past half century.[1] High performance, simple operation, and ready availability of the catalyst are the three elements for an ideal asymmetric hydrogenation reaction. Because a chiral ligand is pivotal for the success of such reactions, a vast number of chiral ligands has been synthesized, and excellent performances of such ligand-based metal catalysts are known.[2] However, since the majority of the chiral ligands are phosphine-based ligands,[1] which are air-sensitive, an oxygen-free atmosphere is required for handling these compounds. Moreover, a complicated, tedious procedure is usually associated with the preparation of these ligands.[1] As a result, these ligands are often very expensive, which can hamper large-scale industrial applications.

H–P(O)Z^1Z^2 (Z = alky, aryl, or alkoxy groups) are air-stable compounds. They exist in equilibrium between P^V and P^{III} tautomeric structures[3] and recently have been shown to be effective and practically useful ligands for metal-catalyzed reactions [Eq. (1)].[3] Metal-catalyzed asymmetric reactions by using enantiomerically pure secondary phosphine oxides HP(O)R^1R^2 are also attracting attention.[4] Vries et al. first showed that imines and functionalized olefins can be asymmetrically hydrogenated with Rh and Ir by using chiral secondary phosphine oxides as ligands (up to 85 % *ee* of the product after 69 h).[5] Although these chiral secondary phosphine oxides have the advantage of being air and moisture stable, unfortunately, the performance (*ee*) demonstrated is inferior compared to the well-established chiral-phosphine-based systems.[1] Moreover, the preparation of these ligands by resolution of HP(O)R^1R^2 with chiral HPLC also limits its ready accessibility in large quantities.[6]

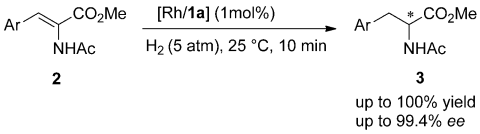
$$Z^1Z^2P(O)H \rightleftharpoons Z^1Z^2P(OH) \xrightarrow{M} Z^1Z^2P{-}OM \quad (1)$$

Diastereomerically pure (−)menthyl phosphinates **1** [(−)MenO]RP(O)H (Men = mentyl) with a single chiral phosphorus center are among the most readily available chiral phosphorus compounds, because they can be generated from easily accessible, non-expensive starting materials through a simple process [Eq. (2)].[7]

$$\begin{array}{l}(-)\text{MenOH} \xrightarrow{PCl_3} (-)\text{MenOPCl}_2 \xrightarrow{\text{RLi or RMgX}} \\ \text{RPCl}_2 + (-)\text{MenOH} \end{array} \xrightarrow[\text{recrystalization}]{H_2O} [(-)\text{MenO}]\text{RP(O)H} \quad (2)$$

1

Herein, we report that (R_P)-mentyl benzylphosphinate (**1 a**), an air- and moisture-stable chiral phosphinate that can be readily prepared in large scale by a well-established procedure starting from $PhCH_2MgCl$ and $(-)MenOPCl_2$,[8] is a high-performance chiral ligand for the rhodium-catalyzed asymmetric hydrogenation of α-acetamidocinnamates **2** to produce the chiral products **3** in high yields with high *ee* [Eq. (3)].



2 **3**

up to 100% yield
up to 99.4% *ee*

(3)

At the beginning, a series of chiral phosphinates [(−)MenO]RP(O)H **1 a–i** with different R groups was prepared (Figure 1)[6] and thoroughly investigated as ligands for the Rh-catalyzed asymmetric hydrogenation of methyl (*Z*)-α-acetamidocinnamate (**2 a**; Table 1). It was found that the *ee* of the

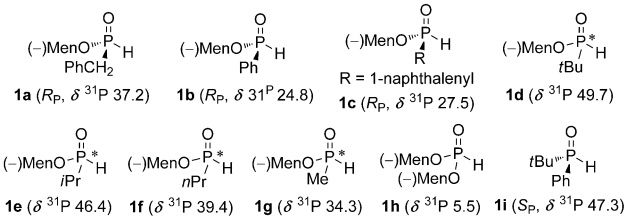


Figure 1. Chiral H–P(O)Z^1Z^2 **1** investigated.

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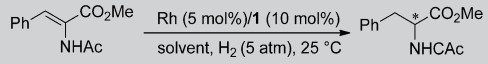
Table 1. Asymmetric hydrogenation catalyzed by Rh/**1**.[a]



2a **3a**

Entry	Ligand	Rh	Conditions	Yield [%][b]	*ee* [%] (config.)[c]
1	**1a**	–	CH_2Cl_2, 3 h	100	86.4 (*S*)
2	–[d]	$[Rh(cod)_2]OTf$	CH_2Cl_2, 3 h	83	86.0 (*S*)
3	–	–	CH_2Cl_2, 3 h[e]	100	81.6 (*S*)
4	–	–	CH_2Cl_2, 3 h[f]	100	84.7 (*S*)
5	–[g]	–	CH_2Cl_2, 3 h	99	4.3 (*R*)
6	–	$[Rh(cod)_2]BF_4$	CH_2Cl_2, 3 h	100	50.1 (*S*)
7	–	$[Rh(cod)Cl]_2$	CH_2Cl_2, 48 h	<1	–
8	–	$[Rh(C_2H_4)_2Cl]_2$	CH_2Cl_2, 72 h	5	–
9	**1b**	$[Rh(cod)_2]OTf$	CH_2Cl_2, 3 h	94	14.1 (*S*)
10	–[g]	–	CH_2Cl_2, 3 h	71	0.3 (*R*)
11	**1c**	–	CH_2Cl_2, 3 h	100	27.2 (S)
12	**1d**	–	THF, 40 h	80	13.6 (*S*)
13	**1e**	–	CH_2Cl_2, 3 h	100	86.1 (*S*)
14	–	–	CH_2Cl_2, 12 h[h]	37	46.1 (*S*)
15	–	–	toluene, 40 h	29	69.4 (*S*)
16	–	–	THF, 3 h	100	52.7 (S)
17	–	–	Et_2O, 3 h	100	60.2 (*S*)
18	–	–	acetone, 18 h	97	38.3 (*S*)
19	–	–	MeOH, 40 h	59	31.5 (*S*)
20	**1f**	–	CH_2Cl_2, 3 h	100	77.6 (*S*)
21	**1g**	–	CH_2Cl_2, 12 h	86	19.3 (*S*)
22	**1h**	–	CH_2Cl_2, 3 h	84	29.2 (*S*)
23	**1i**	–	CH_2Cl_2, 3 h	80	12.2 (*S*)

[a] Unless otherwise noted, reactions were conducted by using a 0.048 M solution of **2a**. [b] ^{1}H NMR yield. [c] Enantiomeric excesses were determined by chiral HPLC. The absolute configuration was determined by comparison with reported data.[7] [d] 5 mol% ligand. [e] 35 °C. [f] 20 atm of H_2. [g] **1** with R_P/S_P = 50:50 was used. [h] 0.1 equiv H_2O was added.

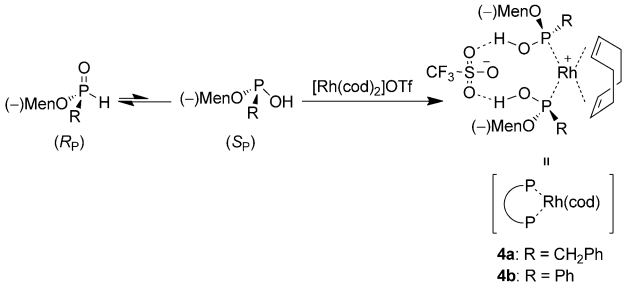
product strongly depends on the structure of the R group, that is, a tiny change on R can dramatically change the *ee*. Interestingly, benzylphosphinate **1a** (entry 1) and isopropylphosphinate **1e** (entry 13) gave the highest selectivity (ca. 86.4% *ee*), followed by *n*-propylphosphinate **1f** (77.6% *ee*), whereas an aryl group (entry 9, Ph, **1b** and entry 11, 1-naphthyl, **1c**) gave a low *ee* of the product. Both the bulky *tert*-butylphosphinate **1d** (entry 12) and the small methylphosphinate **1g** (entry 21) only gave a low selectivity. Surprisingly, using 5 mol% of **1a** (Rh/P = 1:1) also led to a similar selectivity of 86.0% *ee* (entry 2). The selectivity slightly decreased when the reaction was conducted at 35 °C (entry 3), whereas a higher pressure of hydrogen (entry 4) did not improve the *ee*. The choice of the rhodium complex also strongly affected the reaction. Thus, the *ee* decreased when $[Rh(cod)_2]BF_4$ was used (entry 6), and the reduction hardly progressed with $[Rh(cod)Cl]_2$ (entry 7) or $[Rh(C_2H_4)_2Cl]_2$ (entry 8). Solvents also greatly affected the results. Among the solvents investigated (entries 13–19), CH_2Cl_2 gave the best results, whereas the commonly used solvent methanol only gave a low *ee* of the product. Water lowered both the reactivity and enantioselectivity of the reaction; thus, in the presence of 0.1 equivalents of H_2O (entry 14), the reduction product was obtained in only 37% yield with 46.1% *ee*, even after 12 hours. Finally, the chiral secondary phosphine ligand **1i**, which performed best in the literature,[5a] only gave 12.2% *ee* (entry 23).

Although the chiral P(O)H group is assumed to play an essential role in this asymmetric induction, the contribution of the chiral menthoxy auxiliary cannot be ruled out. Dimenthoxy phosphite **1h** gave 29.2% *ee* of the product under the optimized reaction conditions (entry 22). In addition, the hydrogenation of **2a** by using **1a** (**1b**) with R_P/S_P = 50:50 was conducted (entries 5 and 10). The enantioselectivity was low, leading to the product in 4.3% *ee* (0.3% *ee*), showing that the asymmetric induction is predominantly influenced by the chiral phosphorus center and that the contribution of the chiral menthoxy auxiliary is small.

With these preliminary results in hand, we decided to investigate the reaction. Since the formation of metallic rhodium was observed in these reactions, we felt that there might be a problem with the current system in generating the catalyst. Thus, probably owing to the relatively low ligating ability of [(−)MenO]RP(O)H compared to a phosphine R_3P, the combination of the rhodium complex $[Rh(cod)_2]OTf$ with (MenO)RP(O)H might not readily produce the expected active Rh/L system, which catalyzes the asymmetric hydrogenation. Consequently, the remaining nonligated rhodium may also catalyze the hydrogenation, resulting in a decrease in enantioselectivity of the product.

This indeed was true. As confirmed by ^{31}P NMR spectroscopy, a mixture of **1b** (0.062 mmol) and $[Rh(cod)_2]OTf$ (0.031 mmol) in CD_2Cl_2 (0.5 mL) at room temperature only slowly reacted to produce a new complex, which was observed in the ^{31}P NMR spectrum at δ = 122.3 ppm (d, J_{P-Rh} = 206.2 Hz) and was assigned to complex **4b**, as described later (Figure 2). As followed by ^{31}P NMR spectroscopy, the completion of this reaction required more than two days (time, yield of **4b**: 40 min, 11%; 14 h, 75%; 48 h, 97%). Ligand **1a** reacted similarly. Interestingly, in the above reaction of **1a** (**1b**) with $[Rh(cod)_2]OTf$, only one cod was replaced by two phosphinate ligands **1a** (**1b**) to give **4a** (**4b**) exclusively (Scheme 1). Thus, further replacement of cod in **4a** by **1a** was not observed at room temperature, even when a large amount of **1a** (5 equiv to Rh) was used.

The resulting complexes **4a** and **4b** were only slightly soluble in toluene. Taking advantage of this low solubility in toluene, good crystals of **4b** that are suitable for X-ray analysis were isolated in 95% yield.



Scheme 1. Formation of rhodium complexes **4a** and **b**.

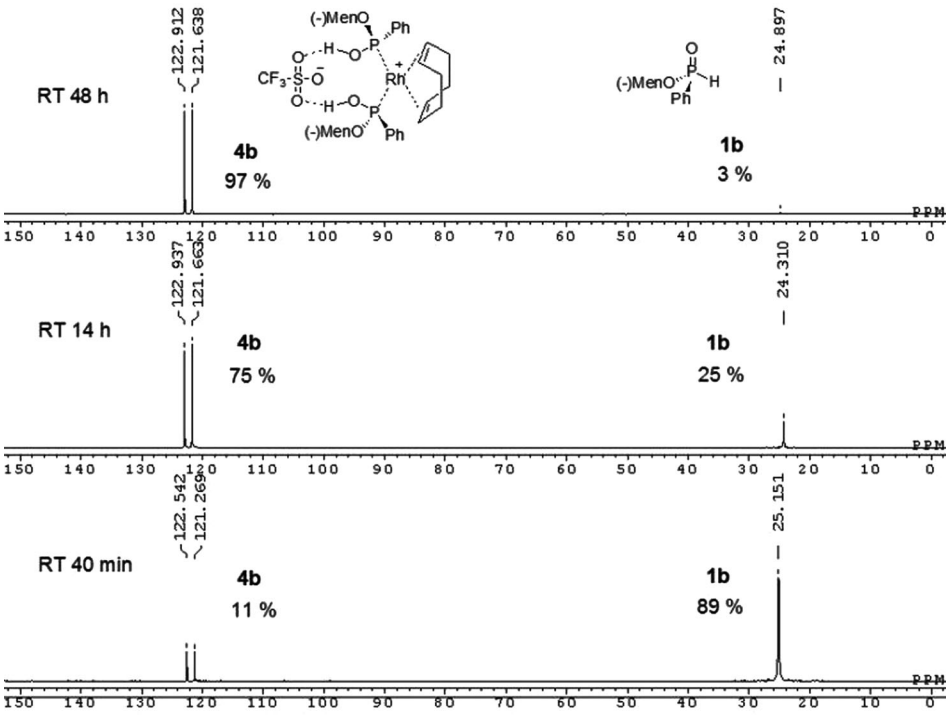


Figure 2. The reaction between **1b** and $[Rh(cod)_2]OTf$ in CD_2Cl_2 followed by ^{31}P NMR spectroscopy.

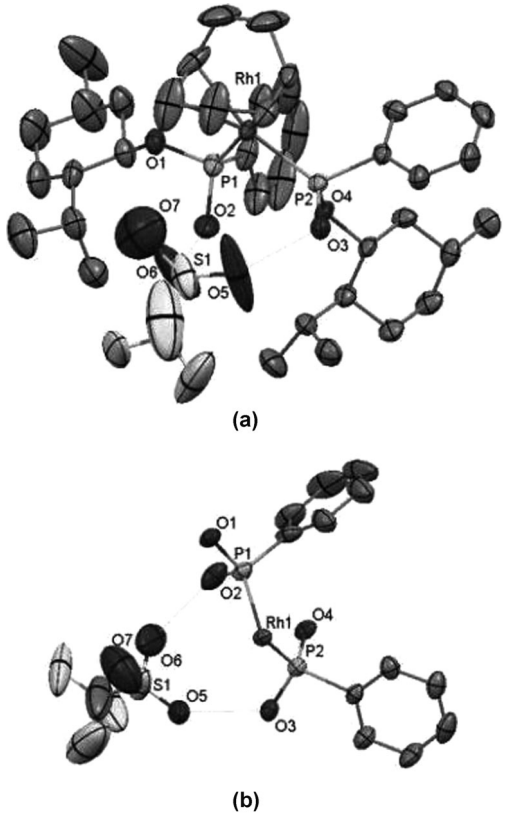
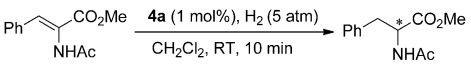


Figure 3. Rhodium complex **4b**. a) H atoms have been omitted for clarity. b) H atoms, 1,5-cyclooctadiene, and menthol groups have been omitted for clarity. Selected bond lengths [Å] and angles [°]: P1–Rh1 2.2580(13), P2–Rh1 2.2558(13), P1–O1 1.621(4), P1–O2 1.580(5), P2–O3 1.592(4), P2–O4 1.598(4), O2–O6 2.550, O3–O5 2.568, S1–O5 1.386(7), S1–O6 1.311(11), S1–O7 1.602(15); O1-P1-O2 105.1(2), O3-P2-O4 106.6(2), P1-Rh1-P2 90.77(5).

The X-ray crystal structure clearly shows that two phosphinate ligands **1b**, in their P^{III} tautomer form, coordinate to Rh in a *cis* fashion (Figure 3). Interestingly, the two ligands are linked by two hydrogen bonds with $CF_3SO_3^-$. It is worth noting that the geometry at the phosphorus atom is S_P with complete retention of its original geometry. This clearly confirms the stereochemistry of the chiral P(O)H compound when it ligates to the metal in its P^{III} tautomer form.[9]

Moreover, the X-ray structure also helps in understanding the effects of the counter anion of the rhodium complex and the solvent on the enantioselectivity of the reaction. Thus, in the presence of $CF_3SO_3^-$, two hydrogen bonds connect the chiral phosphorus ligands, making these two monodentate ligands behave like a bidentate ligand that rigidly ligates rhodium, which improves the enantioselectivity.[10] The ligated structure might be retained in CH_2Cl_2 or toluene, but in methanol or THF this kind of hydrogen bonding can be destroyed and, consequently, the enantioselectivity of the product decreases.

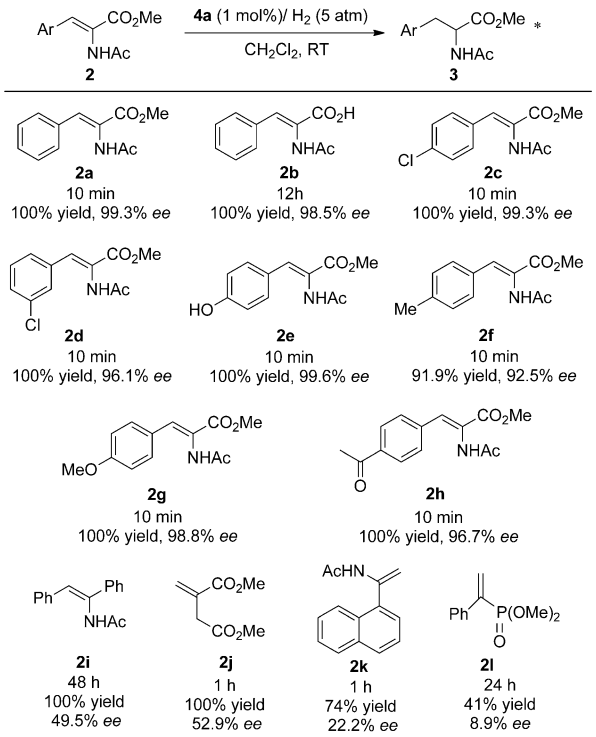
To our delight, compared to the in situ generated catalyst described above, complex **4a** showed excellent catalytic activity in the asymmetric hydrogenation of α-acetamidocinnamates to produce the corresponding chiral products in high yields with high enantioselectivities. Thus, the enantioselective hydrogenation of **2a** in CH_2Cl_2 (0.048 M) by using **4a** (1 mol%) was complete within 10 min to quantitatively yield **3a** with 94.8% *ee* [Eq. (4)].[11] Interestingly, the enantioselectivity of the product constantly increased under more dilute conditions and reached up to 99.3% *ee* with a 0.008 M concentration of **2a**.[12]



(4)

0.048 M, 94.8% *ee*; 0.016 M, 96.7% *ee*; **0.008 M, 99.3% *ee***

Under similar reaction conditions, analogues of **2a** were readily hydrogenated to give the corresponding products in excellent yields and enantioselectivities (Scheme 2). Although a longer reaction time was required compared to other substrates, owing to its low solubility, the asymmetric hydrogenation of an acid, (*Z*)-α-acetamidocinnamic acid (**2b**), gave a quantitative yield of the product with 98.5% *ee* after 12 h.[13] Substrates with electron-donating groups, such as chloro, hydroxyl, methyl, or methoxyl, and an electron-withdrawing



Scheme 2. Asymmetric hydrogenation catalyzed by **4a**.

group, such as acetyl, all reacted quickly to produce the hydrogenation products in high yields with high enantioselectivities. However, substrates such as **2i–l** only gave a moderate to low *ee* under similar conditions, indicating the necessity for further optimizations of the catalyst (Scheme 2).

It is worth noting that the present study also demonstrates one of the few examples of efficient asymmetric hydrogenation reactions based on monodentate ligands without using a 1,1′-bi-2-naphthol (BINOL) auxiliary. Before 2000, most of the efficient phosphine ligands reported for asymmetric hydrogenations were chelating bidentate phosphorus ligands.[14] Although the first monodentate phosphorous ligand has been reported by Knowles in the 1960 s in his initial work on asymmetric hydrogenations,[1e] the progress for the development of an efficient monodentate phosphorous ligand was slow.[15]

In summary, the asymmetric hydrogenation with a chiral *H*-phosphinate as ligand was investigated. Rhodium complexes **4a** and **4b** were easily prepared by the reaction of [Rh(cod)$_2$]OTf with two simple, readily available chiral *H*-phosphinates **1a** and **1b**. Complex **4a** efficiently catalyzed the asymmetric hydrogenation of α-acetamidocinnamates, giving high enantioselectivities (up to 99.6% *ee*). The reaction proceeded smoothly under mild conditions (5 atm H_2, RT, 1 mol% catalyst loading). These results show the potential of chiral *H*-phosphinates as efficient ligands in asymmetric hydrogenation reactions.

Experimental Section

Preparation of 4a and b

Compound **1a** (0.183 g, 0.62 mmol) or **1b** (0.174 g, 0.62 mmol) and [Rh(cod)$_2$]OTf (145.2 mg, 0.31 mmol) were dissolved in toluene (4 mL) in a glove box and stirred at room temperature until **1a** or **1b** disappeared (as indicated by ^{31}P NMR analysis) and a large number of orange crystals precipitated. The crystals were filtered off and washed with a small amount of toluene. The filtrate and the toluene washing were concentrated and recrystallized again. All the crystals were collected and dried under vacuum. **4a**: 0.285 g, 94% isolated yield. **4b**: 0.28 g, 95% isolated yield.

General hydrogenation procedure

Compound **4a** or **b** (0.3 mg, 0.00048 mmol) and substrate **2** (10.5 mg, 0.048 mmol) were dissolved in CH_2Cl_2 (6 mL) in a vial in the glove box. The mixture was charged with H_2 (5 atm) and stirred at room temperature for 10 min. The solvent was evaporated and the residue was purified by a short silica gel column to give the corresponding hydrogenation product, which was then analyzed by chiral HPLC to determine the *ee*.

CCDC 956594 (**4b**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

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Keywords: asymmetric catalysis · *H*-phosphinates · hydrogenation · rhodium

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[10] Such hydrogen bonding between a ligand and the anion of rhodium (TfO^-) has never been recognized before; however, the importance of hydrogen bonding has been noticed, see: a) A. J. Sandee, A. M. van der Burg, J. N. H. Reek, *Chem. Commun.* **2007**, 864 – 866; b) A. C. Laungani, B. Breit, *Chem. Commun.* **2008**, 844 – 846; c) Y. Li, Y. Feng, Y.-M. He, F. Chen, J. Pan, Q.-H. Fan, *Tetrahedron Lett.* **2008**, *49*, 2878 – 2881; d) J. Meeuwissen, M. Kuil, A. M. van der Burg, A. J. Sandee, J. N. H. Reek, *Chem. Eur. J.* **2009**, *15*, 10272 – 10279; e) J. Meeuwissen, J. N. H. Reek, *Nat. Chem.* **2010**, *2*, 615 – 621; f) Y. Liu, C. A. Sandoval, Y. Yamaguchi, X. Zhang, Z. Wang, K. Kato, K. Ding, *J. Am. Chem. Soc.* **2006**, *128*, 14212 – 14213.

[11] The hydrogenation of **2a** in CH_2Cl_2 (0.048 M) by using **4b** (5 mol%) was complete with 10 min to give **3a** with 14.1% *ee*. The hydrogenation of **2a** in THF (0.048 M) by using **4a** (5 mol%) produced **3a** in 94% yield with 44.7% *ee*.

[12] We assume that the intramolecular hydrogen bonds between P(OH) and TfO^- must be more stable in a more dilute solutions, which may lead to the improvement of the enantioselectivity.

[13] Compound **2b** is poorly soluble in CH_2Cl_2, and the mixture remained as a suspension in the first few hours.

[14] a) P. W. N. M. van Leeuwen, P. C. J. Kamer, C. Claver, O. Pàmies, M. Diéguez, *Chem. Soc. Rev.* **2011**, *111*, 2077 – 2118; b) Ref. [1h].

[15] Only in recent years, by using BINOL as the source of chirality, a number of monodentate ligands have been synthesized (see ref. [3a] and [6]). Other chiral monodentate ligands were also reported (see ref. [1g] and [9c]).

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