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Asymmetric N–H Insertion Reaction Cooperatively Catalyzed by Rhodium and Chiral Spiro Phosphoric Acids**

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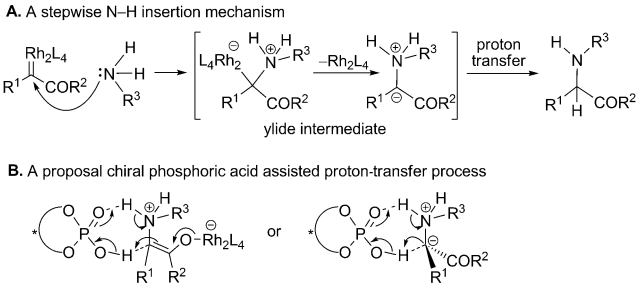
Nitrogen-containing organic compounds, such as α-amino acids and alkaloids, are important biologically active compounds, thus the development of efficient and enantioselective methods for the construction of carbon–nitrogen bonds is a fundamental goal in modern organic synthesis.[1] Transition-metal-catalyzed carbene insertion into N–H bonds is one of the most efficient methods to construct carbon–nitrogen bonds[2] and the development of asymmetric versions of the N–H insertion reaction has attracted considerable attention.[3] In initial studies, chiral dirhodium catalysts were tested in intramolecular[4] and intermolecular[5] N–H insertion reactions, however, only low to modest enantioselectivities (< 50 % *ee*) were achieved. Since these reports, other transition metals including copper and silver have been used as catalysts, and gave enantioselectivities up to 48 % *ee*.[6] Recently, we reported a highly enantioselective N–H insertion reaction (up to 98 % *ee*) using a copper complex with chiral spiro bisoxazoline ligands.[7] Subsequently, two other types of chiral copper catalysts have been developed, one with a planar chiral bipyridine ligand[8] and the other with a binol-derivative ligand,[9] and both of these catalysts give high enantioselectivities in N–H insertion reactions.

Although progress on copper-catalyzed asymmetric N–H insertion reactions has been substantial, they still have serious limitations. For instance, all the copper-catalyzed N–H insertion reactions require high catalyst loading (5–10 mol %) for satisfactory yields and enantioselectivities, thus more-efficient chiral catalysts are highly desirable. Because the activity of dirhodium(II) catalysts is usually superior to that of copper catalysts in nonenantioselective N–H insertion reactions,[10] the possibility of using dirhodium catalysts to achieve highly enantioselective N–H insertion reactions is an intriguing one. Recently, Saito et al.[11] reported that dirhodium(II) carboxylates and cinchona alkaloids cooperatively catalyze the asymmetric N–H insertion reactions of α-diazo-α-arylacetates with anilines. The combined catalysts exhibit excellent reactivity but only modest enantioselectivity (up to 71 % *ee*).



Scheme 1. Proposed mechanism for chiral phosphoric acid induced asymmetric N–H insertion.

It is generally accepted that the rhodium-catalyzed N–H insertion most likely proceeds via an ylide intermediate (Scheme 1 A).[2a] We speculated that the subsequent proton-transfer step could be facilitated by a chiral phosphoric acid[12] species via a seven-membered-ring transition state, and that, consequently, chiral induction could be accomplished in this step (Scheme 1 B). The groups of Yu[13] and Platz[14] have reported that either water or alcohols can assist proton transfer in O–H insertion reactions, as indicated by density functional theory calculations and ultrafast time-resolved IR spectroscopy studies. These studies stimulated our interest in exploring asymmetric N–H insertion in the presence of a proton-transfer catalyst. As part of our ongoing work on the development of asymmetric carbene insertion reactions,[15] we report herein the asymmetric N–H insertion reaction cooperatively catalyzed by dirhodium(II) carboxylates and chiral spiro phosphoric acids (SPAs).[16] Excellent reactivity and high enantioselectivity (up to 95 % *ee*) were achieved in the presence of as little as 0.1 mol % of catalyst.

In our initial study, we carried out the insertion of methyl α-diazo-α-phenylacetate (**3a**) into the N–H bond of *tert*-butyl carbamate ($BocNH_2$) in $CHCl_3$ at 25 °C using 1 mol % of $[Rh_2(OAc)_4]$ and 10 mol % of chiral SPAs **1** as the catalysts (Table 1). SPAs **1** were prepared by a simple condensation of $P(O)Cl_3$ with 6,6′-disubstituted-1,1′-spirobiindane-7,7′-diols **2**, followed by hydrolysis (Scheme 2).[17] Diols **2** were synthesized from spinol (1,1′-spirobiindane-7,7′-diol),[18] as described previously.[19] In the presence of (*R*)-**1a**, the N–H insertion reaction proceeded within 5 minutes to afford the insertion product in excellent yield with 11 % *ee* (Table 1, entry 2). Control experiments showed that the SPAs alone did not promote the insertion reaction.

A range of SPAs with various substituents at the 6 and 6′ positions were evaluated (Table 1, entries 3–9). All the tested SPAs afforded high yields in the N–H insertion reaction. SPA (*R*)-**1h**, which bears a 6,6′-di(naphth-2-yl) group, afforded the

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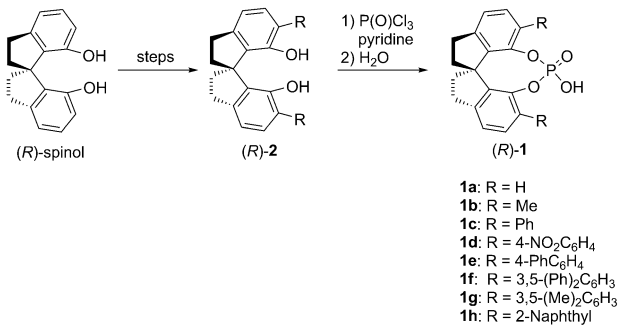
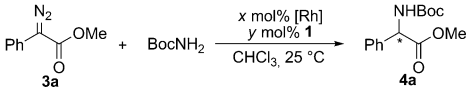


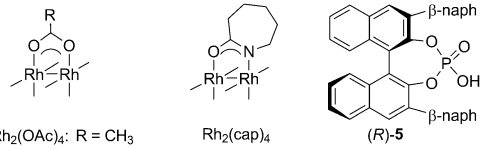
Scheme 2. Synthesis of chiral spiro phosphoric acids.

Table 1: N–H insertion reactions catalyzed by dirhodium(II) carboxylates and chiral spiro phosphoric acids: Optimization of reaction conditions.[a]



Entry	[Rh]	**1**	*x*/*y* [mol%]	*t* [min]	Yield [%][b]	*ee* [%][c]
1	$[Rh_2(OAc)_4]$	none	–	5	89	–
2	$[Rh_2(OAc)_4]$	(*R*)-**1a**	1:10	5	90	11
3	$[Rh_2(OAc)_4]$	(*R*)-**1b**	1:10	5	86	−9
4	$[Rh_2(OAc)_4]$	(*R*)-**1c**	1:10	5	94	50
5	$[Rh_2(OAc)_4]$	(*R*)-**1d**	1:10	5	90	18
6	$[Rh_2(OAc)_4]$	(*R*)-**1e**	1:10	5	94	6
7	$[Rh_2(OAc)_4]$	(*R*)-**1f**	1:10	5	94	10
8	$[Rh_2(OAc)_4]$	(*R*)-**1g**	1:10	5	91	49
9	$[Rh_2(OAc)_4]$	(*R*)-**1h**	1:10	5	92	67
10	$[Rh_2(cap)_4]$	(*R*)-**1h**	1:10	30	70	26
11	$[Rh_2(oct)_4]$	(*R*)-**1h**	1:10	1	78	56
12	$[Rh_2(piv)_4]$	(*R*)-**1h**	1:10	1	76	51
13	$[Rh_2(TFA)_4]$	(*R*)-**1h**	1:10	1	85	74
14	$[Rh_2(TPA)_4]$	(*R*)-**1h**	1:10	1	94	92
15	$[Rh_2(TPA)_4]$	(*R*)-**1h**	1:1	1	94	92
16	$[Rh_2(TPA)_4]$	(*R*)-**1h**	1:0.1	1	84	80
17	$[Rh_2(TPA)_4]$	(*R*)-**1h**	0.1:0.1	1	94	87
18	$[Rh_2(TPA)_4]$	(*R*)-**5**	1:1	1	97	−30

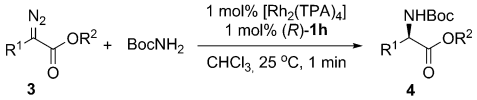
[a] Reaction conditions: [Rh]/**1**/**3**/$BocNH_2$ = 0.002*x*:0.002*y*:0.2:0.2 (mmol) in 3 mL of $CHCl_3$ at 25 °C. [b] Yield of the isolated product. [c] Determined by HPLC with a Chiralcel OJ-H column. Boc = *tert*-butyloxycarbonyl, naph = naphthyl.

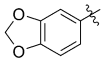


highest enantioselectivity (67% *ee*; Table 1, entry 9). Different dirhodium complexes were then studied with (*R*)-**1h** as a co-catalyst (Table 1, entries 10–14). Both the electronic and the steric properties of the ligands of the dirhodium complexes affected the reactivity and the enantioselectivity of the N–H insertion reactions. Carboxamidate ligated $[Rh_2(cap)_4]$ slowed the reaction and lowered both the yield and the *ee* value (Table 1, entry 10). $[Rh_2(TFA)_4]$, which has electron-deficient carboxylate ligands, improved the enantioselectivity to 74% *ee* (Table 1, entry 13). When we used $[Rh_2(TPA)_4]$, which contains bulky carboxylate ligands, the enantioselectivity was markedly improved to 92% *ee* with no accompanying decrease in reactivity or yield (Table 1, entry 14). Changing the rhodium/SPA ratio from 1:10 to 1:1 had almost no impact on either the reaction time or the enantioselectivity (Table 1, compare entries 14 and 15). Interestingly, even when the amount of SPA was reduced to 0.1 equivalents relative to $[Rh_2(TPA)_4]$, good yield and high enantioselectivity were still obtained (Table 1, entry 16). The reactivity of the cooperative catalysts was so high that 0.1 mol% of catalyst was sufficient to achieve a satisfactory outcome (entry 17). Thus, our preliminary results indicated that the combination of $[Rh_2(TPA)_4]$ and (*R*)-**1h** is an efficient catalytic system for the asymmetric N–H insertion reaction. For comparison, we also tested chiral phosphoric acid (*R*)-**5**,[12] which has a binaphthol scaffold, however, under identical reaction conditions only modest enantioselectivity was obtained (Table 1, entry 18). This result clearly shows that the spirobiindane backbone of the SPAs plays a crucial role in the chiral induction step.

Under the optimized reaction conditions, various α-aryl-α-diazoacetate substrates were investigated (Table 2, entries 1–12). Impressively, all the reactions were complete within 1 min under the mild reaction conditions, and the corresponding N–H insertion products were obtained in high yields (85–97%) with high enantioselectivities (90–95% *ee*). Compared to the chiral copper catalysts developed for the same reaction, the combination of $[Rh_2(TPA)_4]$ and (*R*)-**1h**

Table 2: N–H insertion reactions of various substrates catalyzed by $[Rh_2(TPA)_4]$ and chiral spiro phosphoric acid (*R*)-**1h**.[a]



Entry	R^1, R^2	Product	Yield [%]	*ee* [%]
1	C_6H_5, Me (**3a**)	**4a**	94	92 (*R*)
2	4-$MeOC_6H_4$, Me (**3b**)	**4b**	88	90
3	4-MeC_6H_4, Me (**3c**)	**4c**	90	90 (*R*)
4	4-ClC_6H_4, Me (**3d**)	**4d**	92	92 (*R*)
5	4-PhC_6H_4, Me (**3e**)	**4e**	90	94
6	3-$MeOC_6H_4$, Me (**3f**)	**4f**	94	92
7	3-MeC_6H_4, Me (**3g**)	**4g**	97	91
8	3-ClC_6H_4, Me (**3h**)	**4h**	85	91
9	2-$MeOC_6H_4$, Me (**3i**)	**4i**	92	95
10	2-ClC_6H_4, Me (**3j**)	**4j**	93	91 (*R*)
11	 , Me (**3k**)	**4k**	94	90
12	2-Naphthyl, Me (**3l**)	**4l**	89	91
13[b]	Me, Bn (**3m**)	**4m**	99	50 (*R*)

[a] The reaction conditions and analysis method were the same as those described in Table 1, entry 15. All reactions were complete within 1 min. [b] (*R*)-**1g**, instead of (*R*)-**1h**, was used. Bn = benzyl.

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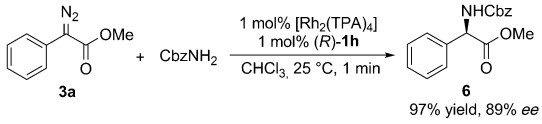
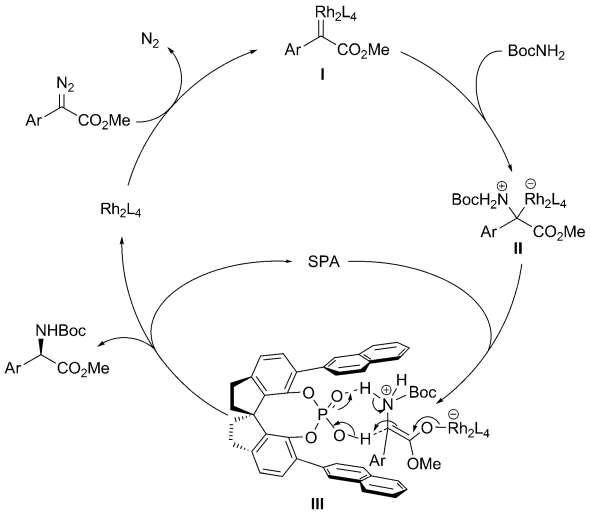
has obvious advantages, including lower catalyst loading and higher yields. Additionally, in the reaction of α-diazopropionate **3m**, the copper catalyst gives 1,2-H migration rather than N–H insertion,[8] whereas $[Rh_2(TPA)_4]$/(*R*)-**1g** afforded the N–H insertion product almost quantitatively, albeit with only moderate enantioselectivity (Table 2, entry 13).

Similar to the N–H insertion reaction of $BocNH_2$, the reaction of $CbzNH_2$ exhibited high yield and high enantioselectivity under the optimized reaction conditions (Scheme 3). In contrast, the N–H insertions of acetamide and 4-methylbenzenesulfonamide afforded racemic products.



Scheme 3. Cbz = benzyloxycarbonyl.



Scheme 4. Proposed N–H insertion mechanism.

We performed additional experiments to improve our understanding of the mechanism of the chiral induction. First, a sodium salt of (*R*)-**1h** was prepared and used to catalyze the N–H insertion reaction of **3a** with $BocNH_2$. The insertion reaction proceeded smoothly in 96% yield, however, only 7% *ee* was achieved. This result demonstrated that the acidic hydrogen of SPA was critical for chiral induction. In 1992 McKervey et al.,[20] and Pirrung and Zhang[21] reported the synthesis and use of a chiral dirhodium(II) phosphate complex for asymmetric carbene transformations. To rule out the formation of a chiral rhodium(II) phosphate species by a simple ligand exchange in our system, a ^{31}P NMR study was performed. The ^{31}P NMR spectrum of a $CDCl_3$ solution of (*R*)-**1h** did not change when 0.5 equivalents of $[Rh_2(TPA)_4]$ was introduced at room temperature, thus indicating that there was no coordination of (*R*)-**1h** to rhodium. The addition of 0.5 equivalents of (*R*)-**1h** to a $CDCl_3$ solution of $BocNH_2$ had no effect on the ^{13}C NMR and FTIR signals of the carbonyl group of $BocNH_2$. This result implies that the activation of $BocNH_2$ through the formation of a hydrogen bond with (*R*)-**1h** was unlikely.

On the basis of the aforementioned experiments and analysis, we propose a preliminary N–H insertion reaction mechanism shown in Scheme 4. First, treatment with the dirhodium complex results in decomposition of the diazo compound to generate a rhodium carbene intermediate (**I**), which reacts with the $BocNH_2$ to generate an ylide (**II**). The SPA assists proton transfer via a seven-membered-ring intermediate (**III**) to form the N–H insertion product, and the dirhodium catalyst and chiral SPA are simultaneously regenerated. The chiral induction occurs in the proton-transfer step. The dirhodium catalyst is most likely involved in the proton-transfer step, considering its strong influence on the enantioselectivity of the reaction (see Table 1, entries 9–14). According to this mechanism, the chiral SPA acts as a proton-transfer shuttle. We believe this new model for enantioselective proton-transfer catalysis will help the design of additional reactions. More detailed investigations into the precise reaction mechanism are underway in our laboratory.

In summary, an asymmetric N–H insertion reaction catalyzed cooperatively by dirhodium(II) complexes and chiral SPAs with high yield and high enantioselectivity was developed. This entirely new type of enantioselective N–H insertion catalyst system is expected to have further applications in asymmetric X–H bond insertion reactions.

Experimental Section

A typical procedure for asymmetric N–H insertion: $[Rh_2(Ph_3CCO_2)_4]\cdot 0.5CH_2Cl_2$ (2.7 mg, 0.002 mmol, 1 mol%) and (*R*)-**1h** (1.2 mg, 0.002 mmol, 1 mol%) were introduced into an oven-dried Schlenk tube in an argon-filled glovebox. After $CHCl_3$ (2 mL) was injected into the Schlenk tube, the mixture was stirred at 25°C. A solution of methyl α-diazo-α-phenylacetate **3a** (35.2 mg, 0.2 mmol) and $BocNH_2$ (23.4 mg, 0.2 mmol) in $CHCl_3$ (1 mL) was added to the mixture in one portion by a syringe. The color of the diazo compound disappeared immediately after the addition. The reaction mixture was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 8:1) to give methyl 2-(*tert*-butoxycarbonylamino)-2-phenylacetate **4a** as a white solid. Yield: 94%, white solid, m.p.: 104–105°C. 92% *ee* [HPLC conditions: Chiralcel OJ-H column, *n*-hexane/*i*-propanol = 90:10, flow rate = 1.0 mL min^{-1}, wavelength = 220 nm, t_R = 9.78 min (*S*), t_R = 12.93 min (*R*)]. $[\alpha]_D^{28} = -113$ (c = 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.38–7.30 (m, 5H, ArH), 5.54 (brs, 1H, NH), 5.32 (d, J = 7.2 Hz, 1H, CH), 3.72 (s, 3H, OCH_3), 1.43 ppm (s, 9H, $C(CH_3)_3$).

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[1] A. K. Yudin, *Catalyzed Carbon-Heteroatom Bond Formation*, Wiley-VCH, Weinheim, **2011**.
[2] For reviews, see: a) M. P. Doyle, M. A. McKervey, T. Ye, *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds*,

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Wiley, New York, **1998**, chap. 8; b) Z.-H. Zhang, J.-B. Wang, *Tetrahedron* **2008**, *64*, 6577 – 6605.
[3] For a review, see: C. J. Moody, *Angew. Chem.* **2007**, *119*, 9308 – 9310; *Angew. Chem. Int. Ed.* **2007**, *46*, 9148 – 9150.
[4] C. F. García, M. A. McKervey, T. Ye, *Chem. Commun.* **1996**, 1465 – 1466.
[5] R. T. Buck, C. J. Moody, A. G. Pepper, *ARKIVOC* **2002**, *viii*, 16 – 33.
[6] S. Bachmann, D. Fielenbach, K. A. Jørgensen, *Org. Biomol. Chem.* **2004**, *2*, 3044 – 3049.
[7] B. Liu, S.-F. Zhu, W. Zhang, C. Chen, Q.-L. Zhou, *J. Am. Chem. Soc.* **2007**, *129*, 5834 – 5835.
[8] E. C. Lee, G. C. Fu, *J. Am. Chem. Soc.* **2007**, *129*, 12066 – 12067.
[9] Z.-R. Hou, J. Wang, P. He, J. Wang, B. Qin, X.-H. Liu, L.-L. Lin, X.-M. Feng, *Angew. Chem.* **2010**, *122*, 4873 – 4876; *Angew. Chem. Int. Ed.* **2010**, *49*, 4763 – 4766.
[10] For selected rhodium-catalyzed nonenantioselective N–H insertion reactions, see: a) T. N. Salzmann, R. W. Ratcliffe, B. G. Christensen, F. A. Bouffard, *J. Am. Chem. Soc.* **1980**, *102*, 6161 – 6163; b) C. J. Moody, L. Ferris, D. Haigh, E. Swann, *Chem. Commun.* **1997**, 2391 – 2392; c) C. Bolm, A. Kasyan, K. Drauz, K. Günther, G. Raabe, *Angew. Chem.* **2000**, *112*, 2374 – 2376; *Angew. Chem. Int. Ed.* **2000**, *39*, 2288 – 2290; d) F. A. Davis, T. Fang, R. Goswami, *Org. Lett.* **2002**, *4*, 1599 – 1602; e) H. Matsushita, S.-H. Lee, K. Yoshida, B. Clapham, G. Koch, J. Zimmermann, K. D. Janda, *Org. Lett.* **2004**, *6*, 4627 – 4629; f) J. R. Davies, P. D. Kane, C. J. Moody, *J. Org. Chem.* **2005**, *70*, 7305 – 7316; g) X. Zhang, Z. Sui, *Tetrahedron Lett.* **2006**, *47*, 5953 – 5955; h) D. Lecerclé, S. Gabillet, J.-M. Gomis, F. Taran, *Tetrahedron Lett.* **2008**, *49*, 2083 – 2087; i) O. Pavlyuk, H. Teller, M. C. McMills, *Tetrahedron Lett.* **2009**, *50*, 2716 – 2718; j) B. Shi, A. J. Blake, W. Lewis, I. B. Campbell, B. D. Judkins, C. J. Moody, *J. Org. Chem.* **2010**, *75*, 152 – 161.
[11] H. Saito, T. Uchiyama, M. Miyake, M. Anada, S. Hashimoto, T. Takabatake, S. Miyairi, *Heterocycles* **2010**, *81*, 1149 – 1155.
[12] For reviews on the development of chiral phosphoric acids as Brønsted acid catalysts, see: a) T. Akiyama, *Chem. Rev.* **2007**, *107*, 5744 – 5758; b) M. Terada, *Chem. Commun.* **2008**, 4097 – 4112.
[13] Y. Liang, H.-L. Zhou, Z.-X. Yu, *J. Am. Chem. Soc.* **2009**, *131*, 17783 – 17785.
[14] J. Xue, H. L. Luk, M. S. Platz, *J. Am. Chem. Soc.* **2011**, *133*, 1763 – 1765.
[15] For O–H insertions, see: a) C. Chen, S.-F. Zhu, B. Liu, L.-X. Wang, Q.-L. Zhou, *J. Am. Chem. Soc.* **2007**, *129*, 12616 – 12617; b) S.-F. Zhu, C. Chen, Y. Cai, O.-L. Zhou, *Angew. Chem.* **2008**, *120*, 946 – 948; *Angew. Chem. Int. Ed.* **2008**, *47*, 932 – 934; c) S.-F. Zhu, Y. Cai, H.-X. Mao, J.-H. Xie, Q.-L. Zhou, *Nat. Chem.* **2010**, *2*, 546 – 551; d) S.-F. Zhu, X.-G. Song, Y. Li, Y. Cai, Q.-L. Zhou, *J. Am. Chem. Soc.* **2010**, *132*, 16374 – 16376; for S–H insertion, see: e) Y.-Z. Zhang, S.-F. Zhu, Y. Cai, H.-X. Mao, Q.-L. Zhou, *Chem. Commun.* **2009**, 5362 – 5364; for Si–H insertion, see: f) Y.-Z. Zhang, S.-F. Zhu, L.-X. Wang, Q.-L. Zhou, *Angew. Chem.* **2008**, *120*, 8624 – 8626; *Angew. Chem. Int. Ed.* **2008**, *47*, 8496 – 8498; for recent asymmetric X–H insertions reported by other groups, see: g) T. C. Maier, G. C. Fu, *J. Am. Chem. Soc.* **2006**, *128*, 4594 – 4595; h) Y. Yasutomi, H. Suematsu, T. Katsuki, *J. Am. Chem. Soc.* **2010**, *132*, 4510 – 4511; i) R. Sambasivan, Z. T. Ball, *J. Am. Chem. Soc.* **2010**, *132*, 9289 – 9291; j) H. Saito, R. Iwai, T. Uchiyama, M. Miyake, S. Miyairi, *Chem. Pharm. Bull.* **2010**, *58*, 872 – 874.
[16] For a recent review on cooperative catalysis, see: a) M. Rueping, R. M. Koenigs, I. Atodiresei, *Chem. Eur. J.* **2010**, *16*, 9350 – 9365; Hu et al. have used chiral binaphthyl phosphoric acids as Brønsted acid catalysts to influence the stereochemical outcome of carbon – carbon bond-forming reactions of oxonium or ammonium ylides generated by rhodium acetate, see: b) W.-H. Hu, X.-F. Xu, J. Zhou, W.-J. Liu, H.-X. Huang, J. Hu, L.-P. Yang, L.-Z. Gong, *J. Am. Chem. Soc.* **2008**, *130*, 7782 – 7783; c) J. Jiang, H.-D. Xu, J.-B. Xi, B.-Y. Ren, F.-P. Lv, X. Guo, L.-Q. Jiang, Z.-Y. Zhang, W.-H. Hu, *J. Am. Chem. Soc.* **2011**, *133*, 8428 – 8431.
[17] During the preparation of this manuscript, three groups reported the preparation of chiral spiro phosphoric acids using a similar procedure, see: a) F.-X. Xu, D. Huang, C. Han, W. Shen, X.-F. Lin, Y.-G. Wang, *J. Org. Chem.* **2010**, *75*, 8677 – 8680; b) I. Čorić, S. Müller, B. List, *J. Am. Chem. Soc.* **2010**, *132*, 17370 – 17373; c) C.-H. Xing, Y.-X. Liao, J. Ng, Q.-S. Hu, *J. Org. Chem.* **2011**, *76*, 4125 – 4131.
[18] For the preparation and resolution of spinol, see: a) V. B. Birman, A. L. Rheingold, K.-C. Lam, *Tetrahedron: Asymmetry* **1999**, *10*, 125 – 131; b) J.-H. Zhang, J. Liao, X. Cui, K.-B. Yu, J. Zhu, J.-G. Deng, S.-F. Zhu, L.-X. Wang, Q.-L. Zhou, L.-W. Chung, T. Ye, *Tetrahedron: Asymmetry* **2002**, *13*, 1363 – 1366.
[19] Y. Yang, S.-F. Zhu, H.-F. Duan, C.-Y. Zhou, L.-X. Wang, Q.-L. Zhou, *J. Am. Chem. Soc.* **2007**, *129*, 2248 – 2249.
[20] N. McCarthy, M. A. McKevery, T. Ye, M. McCann, E. Murphy, M. P. Doyle, *Tetrahedron Lett.* **1992**, *33*, 5983 – 5986.
[21] M. C. Pirrung, J. Zhang, *Tetrahedron Lett.* **1992**, *33*, 5987 – 5990.

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