# Biaryl-Bridged Salalen Ligands and Their Application in Titanium-Catalyzed Asymmetric Epoxidation of Olefins with Aqueous H<sub>2</sub>O<sub>2</sub>

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A series of biaryl-bridged salalen ligands together with their titanium complexes have been designed and synthesized. The Ti complexes could serve as highly efficient catalysts for

Introduction

Optically active epoxides are very important molecules in a broad range of chemical transformations; these compounds are mainly produced by a critical process involving catalyzed enantioselective epoxidation reactions of olefins.<sup>[1–3]</sup> Over the past three decades, many efforts have been devoted to the development of efficient catalysts for the enantioselective epoxidation of olefins. Many catalyst systems including chiral metal complexes<sup>[3-9]</sup> and organocatalvsts<sup>[10–15]</sup> have been successfully established. Indeed, high asymmetric induction for the asymmetric epoxidation of olefins clearly depends on the used oxidant. For example, NaOCl or PhIO was generally employed as oxidant in epoxidation reactions catalyzed by salen-Mn<sup>III</sup> complexes.[16-18] However, in terms of sustainability and atom efficiency, aqueous hydrogen peroxide is a desired choice of oxidant, only producing water as a byproduct.<sup>[19]</sup> In this context, the recent catalyst systems reported by Katsuki et al. are very successful, as they are able to catalyze the asymmetric epoxidation of olefins in high yield with high enantioselectivity by using titanium salalen or salan complexes as catalysts.<sup>[20-30]</sup> Moreover, other metal complexes based on salalen or salan ligands are effective catalysts in a number of asymmetric reactions.<sup>[31–39]</sup> The feature of these titanium complexes (salan or salalen) is that two Ti complex units are connected by two oxygen bridges. Based on their findings, Katsuki and Berkessel favored a mononuclear titanium complex as the real species responsible for the epoxidthe asymmetric epoxidation of a wide range of olefins, giving the corresponding epoxides with high *ee* values.

ation reaction.<sup>[24,28,29]</sup> As for another breakthrough in designing new ligands for asymmetry reaction, Ding and co-workers developed binuclear Ti–salen catalysts connected through organic linkages to dramatically enhance the catalytic activity and enantioselectivity for the cyanation of aldehydes.<sup>[40]</sup>

Inspired by this pioneering work and our early work in asymmetric reactions,<sup>[30,41]</sup> we decided to bridge two salalen ligands with a biaryl linker and to synthesize their corresponding di- $\mu$ -oxotitanium complexes. Delightedly, the dinuclear Ti complexes are found to serve as effective catalysts for the asymmetric epoxidation of a variety of olefins with high enantioselectivities.

## **Results and Discussion**

The synthetic route is illustrated in Scheme 1. The biarylbridged salalen ligands could be easily prepared from monoalkylated diamine II and 3,3'-diformyl-2,2-dihydroxy-1,1'-biphenyl or 3,3'-diformyl-2,2-dihydroxy-(*R*)-1,1'-binaphthyl according to the procedures for the synthesis of monomeric salalen ligands.<sup>[28,29]</sup> Based on this strategy, biaryl-bridged salalen ligands 1–4 were readily synthesized (Figure 1). A desired di- $\mu$ -oxotitanium complex could be formed with a standard procedure reported by Katsuki et al., which was confirmed by ESI-TOF MS (Figure 2). In



Scheme 1. The synthetic route for biaryl-bridge salalen ligands.

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Figure 1. Chiral salalen ligands 1-4.

addition, partial <sup>16</sup>O exchange with  $H_2^{18}O$  also demonstrates the existence of the oxygen bridge (Figure 3; Figures S4 and S5, Supporting Information).



Figure 2. Chiral salalen-Ti complexes.



Figure 3. HRMS of  $C_{52}H_{51}N_4O_6Ti_2$  with partial <sup>16</sup>O exchange with  $H_2^{18}O$ . Testing conditions: 20 equiv. of  $H_2^{18}O$  was added to the mixture of  $C_{52}H_{51}N_4O_6Ti_2$  (0.9 mg) and  $CH_2Cl_2$ , and then the mixture was stirred for 1 h.

With these Ti complexes in hand, their performance in the asymmetric epoxidation of styrene were initially evaluated by using  $H_2O_2$  as the oxidant and dichloromethane as the solvent. When 1 mol-% of complex Ti-1 was used as the catalyst, 88%ee was observed with 1 equiv. of H<sub>2</sub>O<sub>2</sub> (Table 1, Entry 1). Styrene oxide was obtained in 70% yield and 90% *ee* after increasing the amount of  $H_2O_2$  to 2 equiv. (Table 1, Entry 3). With complex Ti-2 as the catalyst, only 77% ee was achieved under the same conditions (Table 1, Entry 5). Unfortunately, complex Ti-3 was an inefficient catalyst, resulting in a trace amount of the product (Table 1, Entry 6). Complex Ti-4, derived from (1R,2R)-1,2-cyclohexanediamine and (R)-BINOL, provided considerable enantioselectivity, albeit with a low yield (Table 1, Entries 7 & 8). Interestingly, in situ generation of complex Ti-1 from ligand 1 and  $Ti(OiPr)_4$  showed comparable activity compared with pre-prepared complex Ti-1 (Table 1, Entry 4 vs. 3). Then the in situ generation of the active catalyst would be more practical and convenient.

Table 1. Screening of the catalysts and reaction conditions.

|                  |       | 30% H <sub>2</sub> O <sub>2</sub> / Ti<br>CH <sub>2</sub> Cl <sub>2</sub> , r.t., |   |                             |                          |                        |
|------------------|-------|---|---|-----------------------------|--------------------------|------------------------|
|                  | Entry | Complex (mol-%)   | H <sub>2</sub> O <sub>2</sub><br>[equiv.] | Yield<br>[%] <sup>[a]</sup> | ее<br>[%] <sup>[b]</sup> | Config. <sup>[c]</sup> |
| 1                |       | Ti-1 (1)  | 1.0                                       | 61                          | 88                       | S                      |
| 2                |       | Ti-1 (1)  | 1.5                                       | 62                          | 90                       | S                      |
| 3                |       | Ti-1 (1)  | 2.0                                       | 70                          | 90                       | S                      |
| 4 <sup>[d]</sup> |       | 1 and $Ti(O_iPr)_4(1)$  | 2.0                                       | 73                          | 88                       | S                      |
| 5                |       | Ti-2 (1)  | 2.0                                       | 67                          | 77                       | R                      |
| 6                |       | Ti-3 (1)  | 2.0                                       | trace                       | _                        | _                      |
| 7                |       | Ti-4 (1)  | 2.0                                       | 17                          | 81                       | S                      |
| 8                |       | Ti-4 (2)  | 2.0                                       | 50                          | 88                       | S                      |

[a] Determined by GC with *n*-nonane as internal standard. [b] Determined by GC with a CP-Chirasil-Dex CB chiral column (25 m  $\times 0.25$  mm). [c] The absolute configurations were assigned by comparing GC elution order with known literature data. [d] Reaction conditions: To a CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL) solution of ligand 1 and Ti-(OiPr)<sub>4</sub> (1 mol-%) stirred initially for 1 h was added one drop of H<sub>2</sub>O. The mixture was then stirred for 30 min, and styrene (0.1 mmol) and *n*-nonane (as internal standard) were added. Then, 30% aqueous hydrogen peroxide (0.2 mmol) was added into the mixture over 100 min. Finally, the mixture was stirred for 9 h.

Having established the optimal reaction system, a variety of olefins with different structures were explored with com-



plex Ti-1 as the catalyst, and the results are summarized in Table 2. To our delight, various styrene derivatives could be smoothly transformed into their epoxide derivatives in satisfactory yields and with >90% ee (Table 2, Entries 1–3). Substitution of styrene with electron-withdrawing groups such as chloride and bromide resulted in higher enantioselectivity than that observed with styrene. It is noteworthy that epoxidation of 2-vinylnaphthalene gave the corresponding epoxide in high enantioselectivity (99% ee; Table 2, Entry 4). Next, two 2,2-disubstituted chromene derivatives were examined in the asymmetric epoxidation with complex Ti-1 as catalyst. The epoxidation reactions proceeded smoothly with good chemical yield and high enantioselectivity (Table 2, Entries 6 & 8). Moreover, the catalytic system was also successfully applied to cis-olefins. 1,2-Dihydronaphthalene, cis- $\beta$ -methylstyrene, and (Z)-5-

Table 2. Asymmetric epoxidation of various olefins catalyzed by Ti complex Ti-1 and Ti-5.

|       | $\mathcal{A}^{R^2}$ | Complex (1 mol-  | %)                          |                               |                        |  |
|-------|---------------------|--|-----------------------------|-------------------------------|------------------------|--|
|       | $R^1 R^3$           | CH <sub>2</sub> Cl <sub>2</sub> , H <sub>2</sub> O <sub>2</sub><br>r.t., 9 h |                             | R <sup>1</sup> R <sup>3</sup> |                        |  |
| Entry | Substrate           | Complex  | Yield<br>[%] <sup>[a]</sup> | ee<br>[%] <sup>[b]</sup>      | Config. <sup>[c]</sup> |  |
| 1     |                     | Ti-1   | 70                          | 90                            | S                      |  |
| 2     | ci Ci               | Ti-1   | 68                          | 94                            | S                      |  |
| 3     | Br                  | Ti-1   | 74                          | 92                            | S                      |  |
| 4     |                     | . Ti- <b>1</b>   | 93 <sup>[d]</sup>           | 99                            | S                      |  |
| 5     |                     | Ti- <b>5</b>   | 60 <sup>[d]</sup>           | 66                            | S                      |  |
| 6     | NC                  | Ti- <b>1</b>   | 90 <sup>[d]</sup>           | 99                            | 3S,4S                  |  |
| 7     | Ľ_L₀L               | < Ti-5   | 87 <sup>[d]</sup>           | 98                            | 3S,4S                  |  |
| 8     | O <sub>2</sub> N    | Ti-1   | 80 <sup>[d]</sup>           | 99                            | 3 <i>S</i> ,4 <i>S</i> |  |
| 9     | $\land$             | Ti- <b>1</b>   | 89 <sup>[d,e]</sup>         | 97                            | 1S,2R                  |  |
| 10    |                     | Ti- <b>5</b>   | 90 <sup>[d,e]</sup>         | 94                            | 1S,2R                  |  |
| 11    | $\land$             | Ti- <b>1</b>   | 90                          | 96                            | 1S,2R                  |  |
| 12    |                     | Ti- <b>5</b>   | 56                          | 69                            | 1S,2R                  |  |
| 13    |                     | Ti-1   | 92 <sup>[d]</sup>           | 92                            | 2R,3S                  |  |
| 14    | $\bigcirc$          | Ti- <b>5</b>   | 88                          | 76                            | 2R,3S                  |  |
| 15    | $\bigwedge$         | Ti- <b>1</b>   | 10                          | 78                            | S                      |  |
| 16    | $\smile$            | Ti- <b>5</b>   | 12                          | 72                            | S                      |  |
| 17    | $\sim\sim\sim$      | ₩ Ti- <b>2</b> <sup>[f]</sup>  | 56                          | 61                            | R                      |  |

<sup>[</sup>a] Determined by GC analysis with *n*-nonane as internal standard. [b] Determined by GC with a CP-Chirasil-Dex CB chiral column (25 m  $\times 0.25$  mm) or HPLC with a Daicel chiral column. [c] The absolute configurations were assigned by comparing optical rotations and/or GC & HPLC elution order with known literature data. [d] Isolated yield. [e] Reaction at r.t. for 4 h. [f] Ti-2 (3 mol-%) as catalyst.

phenylpent-2-en-3-yne underwent the epoxidation with 97, 96, and 92% *ee*, respectively (Table 2, Entries 9, 11 and 13). Besides, a comparison experiment for the epoxidation of a mixture of *cis*- $\beta$ -methylstyrene and *trans*- $\beta$ -methylstyrene (*cis/trans* = 57:43) was also conducted, and the reaction of *trans*- $\beta$ -methylstyrene proved to be very sluggish (see the Supporting Information). The reaction of vinylcyclohexane proceeded with 78% *ee*, but the reaction was very slow (Table 2, Entry 15). The epoxidation of 1-octene gave 61% *ee* with 3 mol-% of complex Ti-**2** as catalyst (Table 2, Entry 17).

Comparison experiments between biaryl-bridged complex Ti-1 and nonbridged complex Ti-5 reported by Berkessel were performed under the same reaction conditions. In the case of 2-vinylnaphthalene, complex Ti-1 led to a 93% yield and 99% ee (Table 2, Entry 4). However, only 66% ee was observed with complex Ti-5 (Table 2, Entry 5).<sup>[42]</sup> For the epoxidation of 2,2-disubstituted chromene derivatives and 1,2-dihydronaphthalene, both catalysts showed similar activity and enantioselectivity (Table 2, Entries 6 & 7 and 9 & 10). When complexes Ti-1 and Ti-5 were used to catalyze the epoxidation of cis- $\beta$ -methylstyrene or (Z)-5-phenylpent-2-en-3-yne, the ee values were 96 and 69% or 92 and 76%, respectively (Table 2, Entries 11 & 12 and 13 & 14). We also tested nonconjugated olefins such as vinylcyclohexane, and the epoxide yield was quite low with both catalysts (Table 2, Entries 15 & 16). Based on the above results, complex Ti-1 has great advantages in the epoxidation of terminal aromatic olefins such as 2-vinylnaphthalene. It can also efficiently catalyze the asymmetric epoxidation of cis- $\beta$ -methylstyrene, affording the enantioenriched epoxide in 96% ee. As for the improvement in the ee values in some examples, the reason may be ascribed to the larger steric hindrance of complex Ti-1 at the biaryl substituent site compared with the Ph group of Ti-5.

#### Conclusions

In conclusion, we have developed a biaryl-bridged salalen titanium complex that exhibited high enantioselectivity in the epoxidation of a range of olefins with aqueous hydrogen peroxide as the oxidant. The intramolecular dinuclear Ti catalyst possessing a biaryl bridge is highly efficient for the reaction of terminal aromatic olefins. Further studies on asymmetric catalysis and the mechanism of metal complexes bearing the biaryl-bridged salalen or salan ligands are in progress.

## **Experimental Section**

**Procedure for the Synthesis of Ligands 1–4:** Under an argon atmosphere, 3,3'-diformyl-2,2'-dihydroxy-1,1'-biphenyl (121 mg, 0.5 mmol) and *N*-(3-phenyl-2-hydroxybenzyl)-(1*R*,2*R*)-1,2-diaminocyclohexane (296 mg, 1 mmol) were dissolved in ethanol (15 mL), and the mixture was heated at reflux overnight. The mixture was cooled and filtered. Then the residue was washed with cooled ethanol and dried under vacuum at 40 °C. Ligand 1 was obtained as a yellow powder (203 mg, 51% yield). Data for ligand 1:  $[a]_{D}^{20} = -135.7$  (c = 0.47, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 13.57$  (s, 2 H), 8.45 (s, 2 H), 7.57–6.80 (m, 22 H), 4.08 (d, J =

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13.6 Hz, 2 H), 3.89 (d, J = 13.6 Hz, 2 H), 3.09–3.03 (m, 2 H), 2.76–2.71 (m, 2 H), 2.21–2.18 (m, 2 H), 1.79–1.20 (m, 14 H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 166.0$ , 158.4, 155.0, 138.6, 134.6, 131.3, 129.7, 129.4, 129.2, 128.0, 127.4, 126.7, 125.7, 123.7, 119.0, 118.7, 118.5, 73.4, 61.4, 50.2, 34.0, 29.9, 24.3 ppm. HRMS (ESI): calcd. for C<sub>52</sub>H<sub>55</sub>N<sub>4</sub>O<sub>4</sub> [M + H]<sup>+</sup> 799.4223, found799.4213.

**Procedure for the Synthesis of Complex Ti-1:**  $Ti(OiPr)_4$  (2.6 mmol) was added to a solution of salalen ligand 1 (1.2 mmol) in dried dichloromethane (3.5 mL) under an argon atmosphere, and the solution was stirred at room temperature for 5 h. Then a few drops of H<sub>2</sub>O were added, and the resultant mixture was stirred overnight. Volatiles were removed under reduced pressure, and the residue was washed with diethyl ether (3 × 3 mL) to give desired complex Ti-1 in a 90% yield.  $C_{52}H_{50}N_4O_6Ti_2$ ·CH<sub>2</sub>Cl<sub>2</sub>·H<sub>2</sub>O: calcd. C 62.06, H 5.31, N 5.46; found C 62.06, H 5.56, N 5.37. HRMS (ESI): calcd. for  $C_{52}H_{51}N_4O_6Ti_2$  [M + H]<sup>+</sup> 923.2774; found 923.2770.

General Procedure for the Asymmetric Epoxidation of the Olefins: To a stirred solution of catalyst Ti-1 (0.9 mg, 1 mol-%) in dichloromethane (0.5 mL) was added styrene (0.1 mmol) and *n*-nonane (as internal standard); 30% aqueous hydrogen peroxide (0.2 mmol) was added in five equal portions over 100 min. After stirring for 9 h, the mixture was dried with Na<sub>2</sub>SO<sub>4</sub>, and the yield and the *ee* values were determined by GC-6820 with a CP-Chirasil-Dex CB chiral column (25 m × 0.25 mm). To get the isolated yields, the reactions were carried out on 0.2-mmol scale. The reactions were monitored by TLC. After the reaction, the corresponding epoxides were obtained after column chromatography on silica gel.

**Supporting Information** (see footnote on the first page of this article): General methods and characterization data, copies of the NMR, GC, and HPLC spectra.

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- [1] O. A. Wong, Y. Shi, Chem. Rev. 2008, 108, 3958–3987.
- [2] B. S. Lane, K. Burgess, Chem. Rev. 2003, 103, 2457–2473.
- [3] Q. H. Xia, H. Q. Ge, C. P. Ye, Z. M. Liu, K. X. Su, Chem. Rev. 2005, 105, 1603–1662.
- [4] W. Zhang, J. L. Loebach, S. R. Wilson, E. N. Jacobsen, J. Am. Chem. Soc. 1990, 112, 2801–2803.
- [5] R. Irie, K. Noda, Y. Ito, N. Matsumoto, T. Katsuki, *Tetrahedron Lett.* **1990**, *31*, 7345–7348.
- [6] A. U. Barlan, A. Basak, H. Yamamoto, Angew. Chem. 2006, 118, 5981–5984; Angew. Chem. Int. Ed. 2006, 45, 5849–5852.
- [7] W. Zhang, A. Basak, Y. Kosugi, Y. Hoshino, H. Yamamoto, Angew. Chem. 2005, 117, 4463–4465; Angew. Chem. Int. Ed. 2005, 44, 4389–4391.
- [8] W. Zhang, H. Yamamoto, J. Am. Chem. Soc. 2007, 129, 286– 287.
- [9] E. M. McGarrigle, D. G. Gilheany, Chem. Rev. 2005, 105, 1563–1602.
- [10] Y. Shi, Acc. Chem. Res. 2004, 37, 488-496.
- [11] D. Yang, Acc. Chem. Res. 2004, 37, 497-505.
- [12] X. J. Lu, Y. Liu, B. F. Sun, B. Cindric, L. Deng, J. Am. Chem. Soc. 2008, 130, 8134–8135.
- [13] T. Ooi, D. Ohara, M. Tamura, K. Maruoka, J. Am. Chem. Soc. 2004, 126, 6844–6845.

- [14] X. W. Wang, C. M. Reisinger, B. List, J. Am. Chem. Soc. 2008, 130, 6070–6071.
- [15] C. M. Reisinger, X. W. Wang, B. List, Angew. Chem. 2008, 120, 8232–8235; Angew. Chem. Int. Ed. 2008, 47, 8112–8115.
- [16] T. Katsuki, Coord. Chem. Rev. 1995, 140, 189-214.
- [17] T. Katsuki, J. Mol. Catal. A 1996, 113, 87-107.
- [18] Y. N. Ito, T. Katsuki, Bull. Chem. Soc. Jpn. 1999, 72, 603-619.
- [19] I. W. C. E. Arends, Angew. Chem. 2006, 118, 6398–6400; Angew. Chem. Int. Ed. 2006, 45, 6250–6252.
- [20] K. Matsumoto, Y. Sawada, B. Saito, K. Sakai, T. Katsuki, Angew. Chem. 2005, 117, 5015–5019; Angew. Chem. Int. Ed. 2005, 44, 4935–4939.
- [21] Y. Sawada, K. Matsumoto, S. Kondo, H. Watanabe, T. Ozawa, K. Suzuki, B. Saito, T. Katsuki, *Angew. Chem.* **2006**, *118*, 3558– 3560; *Angew. Chem. Int. Ed.* **2006**, *45*, 3478–3480.
- [22] K. Matsumoto, Y. Sawada, T. Katsuki, Synlett 2006, 3545-3547.
- [23] Y. Sawada, K. Matsumoto, T. Katsuki, Angew. Chem. 2007, 119, 4643–4645; Angew. Chem. Int. Ed. 2007, 46, 4559–4561.
- [24] S. Kondo, K. Saruhashi, K. Seki, K. Matsubara, K. Miyaji, T. Kubo, K. Matsumoto, T. Katsuki, *Angew. Chem.* 2008, 120, 10349–10352; *Angew. Chem. Int. Ed.* 2008, 47, 10195–10198.
- [25] K. Matsumoto, T. Oguma, T. Katsuki, Angew. Chem. 2009, 121, 7568–7571; Angew. Chem. Int. Ed. 2009, 48, 7432–7435.
- [26] H. Egami, T. Katsuki, Angew. Chem. 2008, 120, 5249–5252; Angew. Chem. Int. Ed. 2008, 47, 5171–5174.
- [27] H. Egami, T. Oguma, T. Katsuki, J. Am. Chem. Soc. 2010, 132, 5886–5895.
- [28] A. Berkessel, M. Brandenburg, E. Leitterstorf, J. Frey, J. Lex, M. Schäfer, Adv. Synth. Catal. 2007, 349, 2385–2391.
- [29] A. Berkessel, M. Brandenburg, M. Schäfer, Adv. Synth. Catal. 2008, 350, 1287–1294.
- [30] D. L. Xiong, M. Wu, S. F. Wang, F. W. Li, C. G. Xia, W. Sun, *Tetrahedron: Asymmetry* 2010, 21, 374–378.
- [31] K. Matsumoto, B. Saito, T. Katsuki, Chem. Commun. 2007, 3619–3627.
- [32] H. Egami, T. Katsuki, J. Am. Chem. Soc. 2007, 129, 8940-8941.
- [33] T. Yamaguchi, K. Matsumoto, B. Saito, T. Katsuki, Angew. Chem. 2007, 119, 4813–4815; Angew. Chem. Int. Ed. 2007, 46, 4729–4731.
- [34] K. Matsumoto, T. Yamaguchi, T. Katsuki, *Chem. Commun.* 2008, 1704–1706.
- [35] H. Shitama, T. Katsuki, Angew. Chem. 2008, 120, 2484–2487; Angew. Chem. Int. Ed. 2008, 47, 2450–2453.
- [36] H. Egami, T. Katsuki, J. Am. Chem. Soc. 2009, 131, 6082-6083.
- [37] B. Saito, H. Egami, T. Katsuki, J. Am. Chem. Soc. 2007, 129, 1978–1986.
- [38] B. Saito, T. Katsuki, Angew. Chem. 2005, 117, 4676–4678; Angew. Chem. Int. Ed. 2005, 44, 4600–4602.
- [39] K. Suyama, Y. Sakai, K. Matsumoto, B. Saito, T. Katsuki, Angew. Chem. 2010, 122, 809–811; Angew. Chem. Int. Ed. 2010, 49, 797–799.
- [40] During the preparation of this manuscript, Prof. Kuiling Ding developed an intramolecular di-μ-oxotitanium complex for the enantioselective cyanation of aldehydes: Z. P. Zhang, Z. Wang, R. Z. Zhang, K. L. Ding, *Angew. Chem.* **2010**, *122*, 6898–6902; *Angew. Chem. Int. Ed.* **2010**, *49*, 6746–6750.
- [41] a) M. Wu, B. Wang, S. F. Wang, C. G. Xia, W. Sun, Org. Lett.
  2009, 11, 3622–3625; b) W. Sun, H. W. Wang, C. G. Xia, J. W. Li, P. Q. Zhao, Angew. Chem. 2003, 115, 1072–1074; Angew. Chem. Int. Ed. 2003, 42, 1042–1044; c) Z. Li, Z. H. Tang, X. X. Hu, C. G. Xia, Chem. Eur. J. 2005, 11, 1210–1216; d) Q. G. Cheng, F. G. Deng, C. G. Xia, W. Sun, Tetrahedron: Asymmetry 2008, 19, 2359–2362.
- [42] For the epoxidation of 2-vinylnaphthalene by Katsuki et al., 83% ee was obtained with a salalen–Ti complex generated in situ. See ref.<sup>[24]</sup>

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