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# Synthesis of salan (salalen) ligands derived from binaphthol for titanium-catalyzed asymmetric epoxidation of olefins with aqueous $H_2O_2$

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ABSTRACT

A series of chiral salan (salalen) ligands, easily prepared from the aldehyde derived from chiral binaphthol, are effective ligands for the titanium-catalyzed asymmetric epoxidation of olefins with aqueous $H_2O_2$ as the oxidant. One of the titanium–salan complexes was determined by X-ray crystallography.



## 1. Introduction

The asymmetric epoxidation of unfunctional olefins catalyzed by chiral complexes has proven to be one of the most useful reactions in organic synthesis, as the epoxides are highly useful intermediates and building blocks and they can be easily transformed into a large variety of compounds.[1] Among the reported methods, the most successful examples are the chiral metal–salen complexes and their derivatives.[2] Katsuki et al. developed a series of titanium–salan or titanium–salalen complexes which are able to catalyze the asymmetric epoxidation of olefins using aqueous hydrogen peroxide ($H_2O_2$) with high enantioselectivity.[3] Since $H_2O_2$ is inexpensive, safe, easy to handle, and the only by-product is water, this method has been determined to be a green process.[4]

Within this class of salalen and salan ligands developed by Katsuki, there are several ligands derived from chiral binaphthol. These ligands are very efficient not only in the asymmetric epoxidation of conjugated olefins,[3a] but also for a wide range of non-activated olefins.[3d] Their corresponding Nb–salan and Fe–salan complexes have been successfully applied to the asymmetric epoxidation of allylic alcohols,[5] asymmetric oxidation of sulfides,[6] and asymmetric oxidative coupling of 2-naphthols.[7] Most of these ligands were mainly synthesised from chiral diamines with 3-formyl-2-hydroxy-2′-phenyl-1, l′-binaphthyl (Fig. 1), however, the aldehyde is not easy to prepare from chiral binaphthol.[8] Therefore, efficient and easily available ligands are still in high demand. As a part of continuous interest in the asymmetric oxidation,[9] we herein report a series of salan (salalen) ligands, which can be easily prepared in good yield from chiral binaphthol, and can act as similar ligands in the titanium-catalyzed asymmetric epoxidation of olefins with $H_2O_2$ as an oxidant.

## 2. Results and discussion

The synthesis of aldehydes derived from binaphthol is the critical step in terms of synthesizing binaphthyl-type salan (salalen) ligands. The synthesis of aldehyde **4** or **5** starts from either (*R*)- or (*S*)-binaphthol according to a reported procedure (Scheme 1).[10] Treatment of binaphthol with $K_2CO_3$ and then iodomethane or benzyl bromide gave the mono-methyl (or benzyl) substituted binaphthyl ether. Compound **1** was protected as the MOM ether **2**. Successive treatment of **2** with *n*-butyllithium and *N*,*N*-dimethylformamide afforded aldehyde **3**, which was deprotected with hydrochloric acid to give the desired aldehyde **4** or **5**. After the condensation of (*R*)- or (*S*)-**4** (or **5**) with (*R*,*R*)- or (*S*, *S*)-1,2-cyclohexanediamine, salen ligands were obtained, which were then reduced by borohydride to give the corresponding salan ligands **6**–**9**. Salalen ligands **10** and **11** were synthesized from the aldehyde **4** according to the literature.[3a,11] The single crystal structures of ligand **7** and its corresponding Ti-complex were determined by X-ray crystallography (Fig. 2).[12]

With these salan (salalen) ligands **6**–**11** in hand, we initially explored their activities in the asymmetric epoxidation of styrene. The results are summarized in Table 1. First, salan ligand **6**, which was derived from (*R*,*R*)-1,2-cyclohexanediamine and (*S*)-binaphthol, was selected as the ligand in the asymmetric epoxidation of styrene with aqueous hydrogen peroxide as the oxidant. The styrene oxide was obtained in 78% yield and 80% ee with 3 equiv of $H_2O_2$ (Table 1, entry 3). A lesser amount of $H_2O_2$ led to low ee and yield (Table 1, entries 1 and 2). Ligand **8**, derived from (*R*,*R*)-diamine and (*R*)-binaphthol, only gave 2% yield of the product (Table 1, entry 5). It seems that salan ligands derived from the same configuration of diamine and binaphthol give rise to poor activity in the epoxidation reaction (Table 1, entries 5 and 6). Using salan ligand **7**, which contained a benzyloxy group, as the ligand for the epoxidation of styrene, the styrene oxide was obtained in 66% ee with an (*S*)-configuration (Table 1, entry 4). The salalen ligand **11** exhibited similar asymmetric induction

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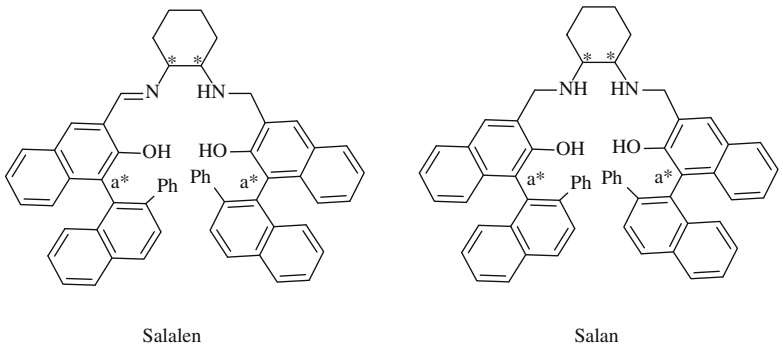
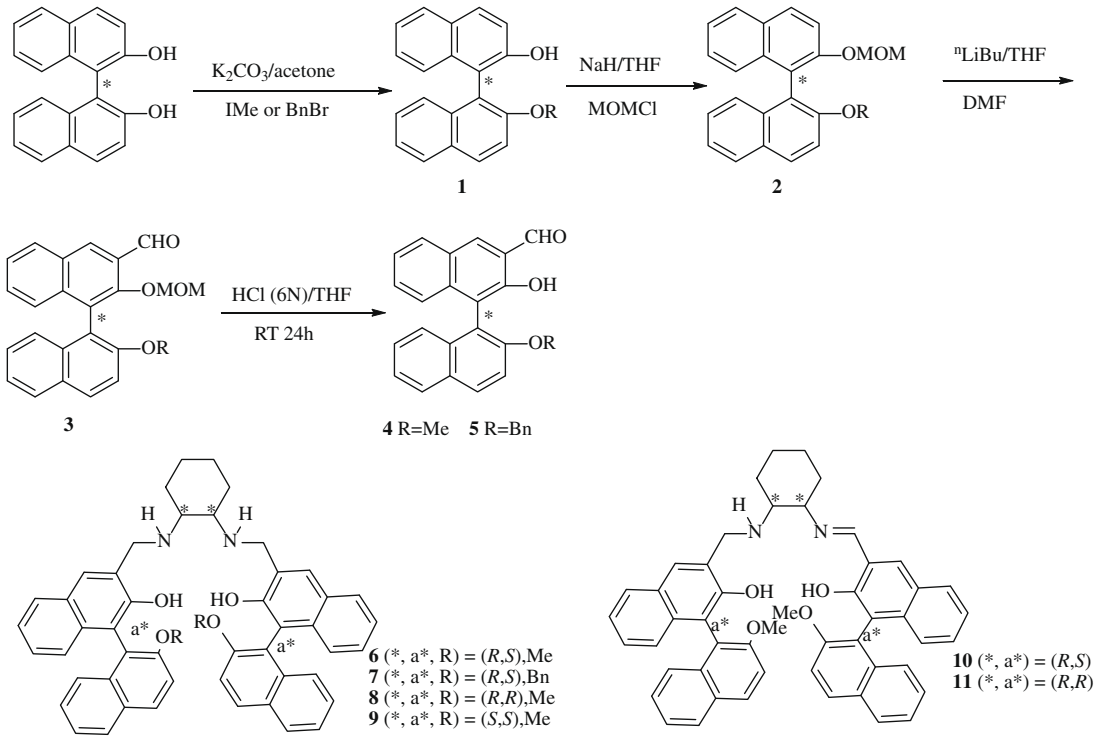



**Figure 1.** Binaphthol-derived salalen and salan ligands reported by Katsuki.




**Scheme 1.** Procedures for the synthesis of salan and salalen ligands **6**–**11**.

with salan ligand **6**, although the chiral backbone of the binaphthyl has the same configuration with the cyclohexanediamine. Based on all the results, it can be concluded that the configuration of the epoxide products is clearly dependent on the backbone of chiral diamine in both the salan or salalen ligands (Table 1, entries 3–8).

After evaluating the performance of the ligands obtained, we subsequently employed ligands **6** and **11** as the chiral ligands and investigated the scope of the substrates in the asymmetric epoxidation reaction. The results are summarized in Table 2. As can be seen from Table 2, the corresponding epoxides could be formed from olefins in good to excellent yields and ee. The substrate 6-cyano-2,2-dimethyl chromene can be oxidated to the epoxide with an excellent isolated yield and ee using **6** or **11** as the ligand (Table 2, entries 7 and 8). Styrene and the 4-halogen substituted styrene (Table 2, entries 1–6) can also be transformed to their corresponding epoxides in 61–84% yield and 73–80% ee with an (*S*)-configuration. The present system was also effective for the epoxidation of *cis*-β-methylstyrene, up to 80% ee was observed (Table 2, entries 9–10). When the same system was applied to epoxidation of non-conjugated olefin, the result was not as good as for the epoxidation of aromatic olefins (Table 2, entries 13–15).

## 3. Conclusion

Based on the pioneering studies by Katsuki, we have successfully designed and prepared a series of salan (salalen) ligands derived from chiral binaphthol in a facile way. These ligands are quite efficient in the enantioselective epoxidation of olefins, especially, for the reaction of 6-cyano-2,2-dimethyl chromene, up to 99% ee was achieved. Further improvements in the catalytic activity and substrate scope are now currently in progress.

## 4. Experimental

### 4.1. General remarks

The $^{1}H$ and $^{13}C$ NMR spectra were recorded on a Bruker Avance III 400 MHz spectrometer. Optical rotations were measured at 589 nm. ESI-MS was measured on a Waters ZQ-4000 MS. X-ray crystallographic data were collected on a Bruker SMART CCD1000 diffractometer with graphite- monochromated Mo Kα radiation ($\lambda$ = 0.71073 Å) at 298(2) K. High-resolution mass spectra (HRMS) were obtained on a Bruker Daltonics APEX II 47e FT-ICR

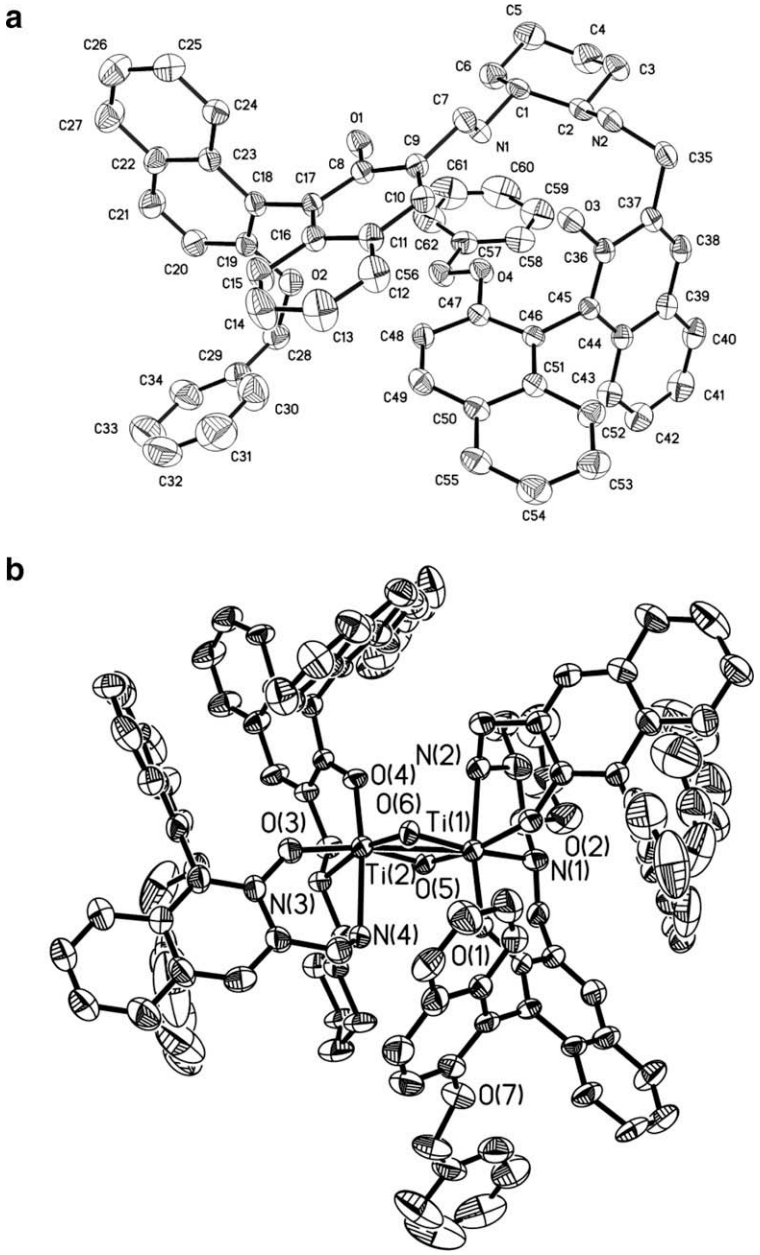



**Figure 2.** (a) X-Ray crystal structure of salan ligand **7**; (b) X-ray crystal structure of Ti complex of salan ligand **7** (hydrogen atoms are omitted for clarity, with thermal ellipsoids drawn at the 50% probability level).

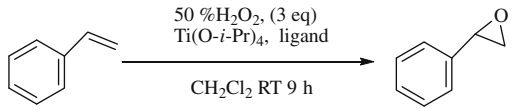
mass spectrometer. FT-IR spectroscopy was carried out on a NICOLET NEX-US 670 with a spectral range of 4000–400 $cm^{-1}$. GC analyses were performed on an Agilent 6820 instrument with a CP-Chirasil-Dex CB Capillary column or Waters–Breeze (2487 Dual-λ Absorbance Detector and 1525 Binary HPLC Pump with chiral OD column to determine the enantiomeric excesses. Column chromatography was generally performed on silica gel (200–300 mesh) and TLC inspections were on silica gel GF254 plates.

Solvents were of analytical grade and used as received. (*R*,*R*)- or (*S*,*S*)-1,2-cyclohexanediamine, (*R*)- or (*S*)-binaphthol, iodomethane, benzyl bromide, *n*-butyllithium, *N*,*N*,*N*′,*N*′-tetramethylethylenediamine, *N*,*N*-dimethylformamide, and all the olefins were purchased from the commercial sources and were used as received. The 3-formyl-2-hydroxy-2′-methoxy-1, l′-binaphthyl, 3-formyl-2-hydroxy-2′-benzyloxy-1, and l′-biphenyl were synthesized according to the reported procedure from (*R*)- or (*S*)-binaphthol.[10]

### 4.2. Preparation of salan ligands 6–9

Ligand **6**: Under argon atmosphere, a mixture of (*R*,*R*)-1,2-cyclohexanediamine (45.6 mg, 0.4 mmol) and (*S*)-**4** (262.4 mg, 0.8 mmol) in absolute ethanol (10 mL) was refluxed for about 10 h to yield a yellow precipitate. The crude product was filtered at room temperature and washed with ice-cold ethanol to afford pure salen ligand as a yellow solid in 89% yield (261 mg). Mp 140–144 °C; $^1$H NMR($CDCl_3$): $\delta$ 13.11 (s, 2H), 8.46 (s, 2H), 8.01–7.49 (m, 10H), 7.35–7.23 (m, 6H), 7.08–6.97 (m, 6H), 3.80 (s, 6H), 2.50–2.38 (m, 2H), 2.15–2.00 (m, 2H), 1.60 (s, 2H), 1.20–1.02 (m, 4H); $^{13}$C NMR($CDCl_3$): $\delta$ 165.31, 155.21, 154.55, 135.48, 133.99, 133.38, 129.87, 129.57, 129.01, 128.25, 128.20, 127.57, 126.66, 125.12, 124.91, 123.76, 123.29, 120.71, 119.07, 114.36, 73.22, 57.17, 32.99, 24.33; ESI-MS: *m*/*z*: calcd for $C_{50}H_{42}N_2O_4$: 734.31 found: 735.82 $[M+H]^+$.

**Table 1**
Asymmetric epoxidation of styrene with various ligands/Ti[a]



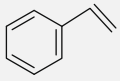
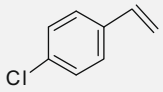
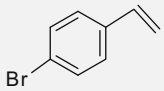
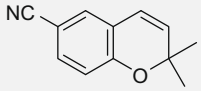
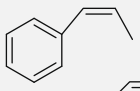
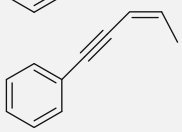
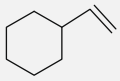
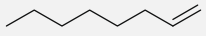

| Entry | Ligand | Yield[b] (%) | ee[c] (%) | Config.[d] |
|---|---|---|---|---|
| 1[e] | **6** | 15 | 64 | (*S*) |
| 2[f] | **6** | 30 | 70 | (*S*) |
| 3 | **6** | 78 | 80 | (*S*) |
| 4 | **7** | 70 | 66 | (*S*) |
| 5 | **8** | 2 | 40 | (*S*) |
| 6 | **9** | 5 | 52 | (*R*) |
| 7 | **10** | 23 | 72 | (*S*) |
| 8 | **11** | 75 | 79 | (*S*) |

[a] Reaction was carried out at room temperature for 9 h with 10 mol % of ligand and Ti(O-*i*-Pr)$_4$, styrene (0.1 mmol), 50% $H_2O_2$ (0.3 mmol).
[b] Determined by GC analysis. *n*-Nonane was used as the internal standard.
[c] Determined by GC analysis with a CP-Chirasil-Dex CB chiral column (25 m × 0.32 mm).
[d] The absolute configurations were assigned by comparing the GC elution order with known literature data.
[e] 1.5 equiv of $H_2O_2$.
[f] 2.0 equiv of $H_2O_2$.

This salen ligand was dissolved in methanol/THF (1:1) 40 mL, followed by the addition of $NaBH_4$ (165 mg). After stirring overnight, the reaction was quenched with aqueous $NH_4Cl$ and the reaction mixture was extracted with ethyl acetate. The organic phase was dried over anhydrous $Na_2SO_4$ and concentrated with a rotary evaporator purified by column chromatography (petroleum ether/ethyl acetate = 3:1) to give ligand **6** (247 mg, 94%) as a pale solid. Mp 142–144 °C; $^1$H NMR ($CDCl_3$): $\delta$ 7.95–7.52 (m, 6H), 7.58–7.00 (m, 16H), 4.20–4.15 (m, 4H), 3.74 (s, 6H), 2.48–2.39 (m, 2H), 2.16–1.98 (m, 2H), 1.58–1.40 (m, 2H), 1.20–1.00 (m, 4H); $^{13}$C NMR ($CDCl_3$): $\delta$ 155.12, 153.29, 133.92, 133.84, 129.56, 129.29, 128.17, 128.01, 127.63, 127.48, 126.31, 125.88, 125.84, 125.24, 124.72, 123.49, 122.92, 118.90, 116.72, 114.12, 60.50, 56.76, 50.58, 31.30, 24.46; $[\alpha]_D^{20} = -134.7$ (*c* 0.0170, $CH_2Cl_2$). HRMS(ESI-MS): *m*/*z*: calcd for $C_{50}H_{46}N_2O_4$: 738.3530, found: 739.3537 $[M+H]^+$.

The synthesis of salan ligands **7**–**9** was according to the same procedure as mentioned above.Ligand **7**: mp 184–188 °C; $^1$H NMR ($CDCl_3$): $\delta$ 7.95–7.65 (m, 6H),7.49 (s, 2H), 7.35–6.80 (m, 24H), 4.99 (s, 4H), 4.15–4.05 (m, 4H), 2.52–2.45 (m, 2H), 2.19–2.01 (m, 2H), 1.52–1.43 (m, 2H), 1.30–0.87 (m, 4H); $^{13}$C NMR($CDCl_3$): $\delta$ 154.21, 153.44, 137.78, 134.05, 133.94, 129.64, 129.40, 128.16, 128.06, 127.95, 127.57, 127.31, 127.19, 126.71, 126.51, 125.91, 125.81, 125.41, 124.92, 123.83, 122.91, 120.57, 116.79, 116.34, 71.27, 60.03, 50.07,46.24, 30.49, 24.13; $[\alpha]_D^{20} = -51.1$ (*c* 0.0300, $CH_2Cl_2$). HRMS(ESI-MS): *m*/*z*: calcd for $C_{62}H_{54}N_2O_4$: 890.4156, found: 891.4167 $[M+H]^+$.Ligand **8**: mp 142–146 °C; $^1$H NMR ($CDCl_3$): $\delta$ 7.98–7.65 (m, 6H), 7.58–7.00 (m, 16H), 4.20–4.08 (m, 4H), 3.72 (s, 3H),3.67 (s, 3H), 2.48–2.40 (m, 2H), 2.17–2.00 (m, 2H), 1.65–1.58 (m, 2H), 1.20–1.00 (m, 4H); $^{13}$C NMR ($CDCl_3$): $\delta$ 155.08, 153.19, 133.92, 133.80, 129.60, 129.30, 128.22, 128.13, 127.59, 127.42, 126.53, 125.90, 125.69, 125.11, 124.68, 123.57, 122.94, 118.96,

**Table 2**
Asymmetric epoxidation of various olefins[a]

| Entry | Substrate | Time (h) | Ligand | Yield[b] (%) | ee[c] (%) | Config.[d] |
|---|---|---|---|---|---|---|
| 1 |  | 9 | **6** | 78 | 80 | (*S*) |
| 2 | | | **11** | 61 | 79 | (*S*) |
| 3 |  | 9 | **6** | 82 | 73 | (*S*) |
| 4 | | | **11** | 73 | 76 | (*S*) |
| 5 |  | 9 | **6** | 84 | 75 | (*S*) |
| 6 | | | **11** | 70 | 71 | (*S*) |
| 7 |  | 6 | **6** | 90[e] | 98[f] | (3*S*,4*S*) |
| 8 | | | **11** | 92[e] | 99[f] | (3*S*,4*S*) |
| 9 |  | 24 | **6** | 70 | 73 | (2*R*,3*S*) |
| 10 | | 24 | **11** | 95 | 80 | (2*R*,3*S*) |
| 11 |  | 24 | **6** | 97[e] | 82[f] | (2*R*,3*S*) |
| 12 | | 24 | **11** | Trace | - | - |
| 13 |  | 18 | **6** | 75 | 67 | (*S*) |
| 14 | | | **11** | 50 | 51 | (*S*) |
| 15 |  | 24 | **6** | 23 | 44 | (*R*) |

[a] Reaction was carried out at room temperature with ligand **6** or **11** (10 mol %) and Ti(O-*i*-Pr)$_4$, olefin (0.1 mmol), 50% $H_2O_2$ (0.3 mmol).
[b] Determined by GC analysis. *n*-Nonane was used as the internal standard.
[c] Determined by GC with a CP-Chirasil-Dex CB chiral column (25 m × 0.32 mm).
[d] The absolute configurations were assigned by comparing the specific rotations and/or GC and HPLC elution order with known literature data.
[e] Yields of isolated product by column chromatography on silica gel.
[f] Determined by HPLC with a OD-column.

116.64, 114.18, 60.40, 56.82, 50.14, 30.60, 24.31; $[\alpha]_D^{20} = +36.75$ (*c* 0.0090, $CH_2Cl_2$). HRMS(ESI-MS): *m*/*z*: calcd for $C_{50}H_{46}N_2O_4$: 738.3530, found: 739.3536 $[M+H]^+$.Ligand **9**: mp 141–144 °C; $^1H$ NMR ($CDCl_3$):$\delta$ 7.98–7.65 (m, 6H), 7.52–7.00 (m, 16H), 4.20–4.05 (m, 4H), 3.72–3.65 (m, 6H), 2.48–2.40 (m, 2H), 2.17–2.00 (m, 2H), 1.65–1.58 (m, 2H), 1.20–1.00 (m, 4H); $^{13}C$ NMR ($CDCl_3$): $\delta$ 155.07, 153.22, 133.92, 133.80, 129.58, 129.40, 128.38, 128.12, 127.96, 127.40, 126.52, 125.88, 125.71, 125.12, 124.68, 123.56, 122.93, 119.01, 116.66, 114.19, 60.09, 56.82, 50.16, 30.60, 24.31; $[\alpha]_D^{20} = -31.3$ (*c* 0.0073, $CH_2Cl_2$). HRMS(ESI-MS): *m*/*z*: calcd for $C_{50}H_{46}N_2O_4$: 738.3530, found: 739.3540 $[M+H]^+$.

### 4.3. Preparation of salalen ligands 10 and 11

The synthesis of salalen ligands **10** and **11** was according to the modular procedure for salalen ligands from (*R*)- or (*S*)-**4**.[3a,11]Ligand **10**: mp 176–180 °C; $^1H$ NMR ($CDCl_3$): $\delta$ 12.99 (s, 1H), 8.61 (s, 1H), 8.02–7.62 (m, 8H), 7.40–6.94 (m, 14H), 4.30–4.20 (m, 2H), 3.70 (s, 6H), 3.22–3.02 (m, 1H), 2.85–2.75 (m, 1H), 2.11–2.08 (m, 1H), 1.80–1.50 (m, 4H), 1.45–1.15 (m, 3H); $^{13}C$ NMR ($CDCl_3$): $\delta$ 166.07, 155.02, 154.25, 135.51, 133.92, 133.76, 133.70, 133.42, 129.70, 129.47, 129.33, 128.79, 128.24, 128.07, 127.53, 127.34, 126.90, 126.50, 126.22, 125.80, 125.32, 125.07, 124.86, 124.60, 123.58, 123.44, 123.27, 122.79, 120.56, 118.60, 117.40, 116.74, 114.25, 114.12, 67.97, 61.62, 56.82, 56.79, 51.10, 33.80, 30.08, 25.61, 24.35, 24.20; $[\alpha]_D^{20} = -71.8$ (*c* 0.0442, $CH_2Cl_2$); HRMS(ESI-MS): *m*/*z*: calcd for $C_{50}H_{46}N_2O_4$: 736.3374, found: 737.3379 $[M+H]^+$.Ligand **11**: mp 164–168 °C; $^1H$ NMR ($CDCl_3$):$\delta$ 13.03 (s, 1H), 8.49 (s, 1H), 8.02–7.65 (m, 8H), 7.45–7.00 (m, 14H), 4.30–4.17 (m, 2H),3.70–3.65 (m, 6H), 3.20–3.08 (m, 1H), 2.78–2.76 (m, 1H), 2.11–1.80 (m, 4H), 1.75–1.17 (m, 4H); $^{13}C$ NMR ($CDCl_3$): $\delta$ 166.01, 155.06, 155.03, 154.20, 135.51, 133.90, 133.74, 133.69, 133.42, 129.71, 129.47, 129.32, 128.77, 128.24, 128.07, 127.53, 127.39, 126.90, 126.49, 126.24, 125.79, 125.32, 125.05, 124.83, 124.60, 123.58, 123.48, 123.28, 122.79, 120.56, 118.61, 117.38, 116.74, 114.25, 114.14, 67.97, 61.64, 56.80, 56.76, 51.10, 33.80, 30.08, 25.60, 24.35, 24.20; $[\alpha]_D^{20} = -294.5$ (*c* 0.0047, $CH_2Cl_2$); HRMS(ESI-MS): *m*/*z*: calcd for $C_{50}H_{44}N_2O_4$: 736.3374, found: 737.3372 $[M+H]^+$.

### 4.4. Typical procedure for the asymmetric epoxidation of olefins

To a stirred solution of ligand **6** (10 μmol) in dichloromethane was added dropwise a solution of Ti (O-*i*-Pr)$_4$ (10 μmol) in dichloromethane (0.5 mL) at room temperature. After the mixture had been stirred for 30 min, a drop of water was added and the resultant mixture was stirred for 30 min. Then the reaction mixture was stirred at room temperature for 9 h after styrene (0.1 mmol), *n*-nonane (as an internal standard) and 50% aqueous hydrogen peroxide (0.3 mmol) were added. After the epoxidation reaction, anhydrous $Na_2SO_4$ was added. The yield and the ee were determined by GC analysis without further manipulations.

## Acknowledgment

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12. CCDC 740842 (salan ligand **7**) and CCDC 754008 (Ti complex of salan ligand **7**) contain the supplementary crystallographic data for this Letter. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.