Supporting information for

Lanthanide complexes combined with chiral Salen ligands: the application in the enantioselective epoxidation reaction of α,β-unsaturated ketones

Xuexiu Xia, Chengrong Lu, *a Bei Zhao, *a,b Yingming Yao a,b

Key Laboratory of Organic Synthesis of Jiangsu Province, a College of Chemistry, Chemical Engineering and Materials Science, b Dushu Lake Campus, Soochow University, Suzhou 215123 (P. R. China)
*Fax: +86-512-65880305; Tel: +86-512-65880305; E-mail: zhaobei@suda.edu.cn; yaoym@suda.edu.cn

Table of contents
The characterization data, NMR spectra and HPLC spectrum of 7a-7y S1-S25
The HPLC spectrum of compound 7e after recrystallization, X-Ray structure of 7e and the crystallographic parameter S26-27
General procedure for the synthesis of chiral Salen ligands S27-28
The NMR spectra of chiral ligands H2L1- H2L9 S28-34
General procedure for the synthesis of complex 8 and the characterization data S34
References S41
The NMR spectra and HPLC spectrum of compound 7a
The NMR spectra and HPLC spectrum of compound 7b
The NMR spectra and HPLC spectrum of compound 7c
The NMR spectra and HPLC spectrum of compound 7d
The NMR spectra and HPLC spectrum of compound 7e
The NMR spectra and HPLC spectrum of compound 7f
The NMR spectra and HPLC spectrum of compound 7g
The NMR spectra and HPLC spectrum of compound 7h
The NMR spectra and HPLC spectrum of compound 7i
The NMR spectra and HPLC spectrum of compound 7j
The NMR spectra and HPLC spectrum of compound 7k
The NMR spectra and HPLC spectrum of compound 71
The NMR spectra and HPLC spectrum of compound 7m.
The NMR spectra and HPLC spectrum of compound 7n
The NMR spectra and HPLC spectrum of compound 7o
The NMR spectra and HPLC spectrum of compound 7p
The NMR spectra and HPLC spectrum of compound 7q
The NMR spectra and HPLC spectrum of compound 7r
The NMR spectra and HPLC spectra of compound 7s
The NMR spectra and HPLC spectrum of compound 7t
The NMR spectra and HPLC spectrum of compound 7u

<Peak Table>

| Peak | Ret Time | Area   | Height | Area% |
|------|----------|--------|--------|-------|
| 1    | 8.058    | 42560095 | 3909010 | 48.991 |
| 2    | 8.473    | 38301670 | 3640175 | 51.009 |
| Total|          | 94601765 | 7449186 | 100.000 |

<Peak Table>

| Peak | Ret Time | Area   | Height | Area% |
|------|----------|--------|--------|-------|
| 1    | 8.117    | 1605693 | 153229 | 90.366 |
| 2    | 8.561    | 171193  | 14940  | 9.634  |
| Total|          | 1776886 | 168169 | 100.000 |
The NMR spectra and HPLC spectrum of compound 7v
The NMR spectra and HPLC spectrum of compound 7w
The NMR spectra and HPLC spectrum of compound 7x
The NMR spectra and HPLC spectrum of compound 7y
The HPLC spectrum of compound 7e after recrystallization

The HPLC spectrum of single crystal of 7e

The crystallographic parameter of 7e

| Compound | 7e |
|----------|----|
| Formula  | C_{16}H_{14}O_{3} |
| fw       | 29.02 |
| Temperature/K | 120.03 |
| Crystal system | monoclinic |
| Space group | C2 |
| a/Å       | 31.6601(8) |
| b/Å       | 5.7080(2)  |
| c/Å       | 15.2031(4) |
| α/°       | 90        |
| β/°       | 112.639(2) |
| $\gamma^\circ$ | 90 |
|----------------|----|
| Volume/Å$^3$   | 2535.75(13) |
| Z              | 8 |
| $\rho_{calc}$/g/cm$^3$ | 1.406 |
| $\mu$/mm$^{-1}$ | 1.151 |
| F(000)         | 1110 |
| Crystal size/mm$^3$ | 0.4 × 0.2 × 0.1 |
| Radiation      | CuKα ($\lambda = 1.54178$ Å) |

**General procedure for the synthesis of chiral salen ligands H$_2$L$^1$-H$_2$L$^9$**

**General procedure for the synthesis of ligands H$_2$L$^1$-H$_2$L$^6$**

![Chemical structure](image.png)

To a THF solution of 30 mmol substituted phenol and 45 mmol MgCl$_2$, 90 mmol Et$_3$N was added, and the mixture was continued to stir for 30 min at the room temperature. Then, the mixture was shifted to an oil bath and added 180 mmol Paraformaldehyde, the mixture was refluxed at 75 °C overnight. Finally, Cooled to room temperature, The reaction is quenched by hydrochloric acid. The crude product was extracted with ethyl acetate (3×50 mL). The combined organic layers were washed with NaHCO$_3$ (3×20 mL) and brine (3×20 mL) in turn and dried over Na$_2$SO$_4$. After removing solvent in vacuo, the crude product disubstituted salicylaldehyde A was purified by column chromatography using eluent of ethyl acetate to petroleum ether 1:10.

The (1S, 2S)-1,2-diaminocyclohexane (10 mmol) was added to the ethanol solution of disubstituted salicylaldehyde A. The mixture was stirred for 5 h and the yellow solid product was separated and collected by vacuum filtration without recrystallization.

**The synthesis of ligand H$_2$L$^7$**

![Chemical structure](image.png)

4-tert-Butylphenol (20 mmol) and 1-adamantanol (20 mmol) were dissolved in dichloromethane (DCM) at the room temperature. The sulfuric acid H$_2$SO$_4$ (1.5 mL) was added dropwise to the mixture and stir for 30 min. The reaction is quenched by NaOH solution (2M). The organic layer was dried over Na$_2$SO$_4$. The crude product was concentrated and purified by column chromatography using eluent of ethyl acetate to petroleum ether 1:20.

The procedure for the synthesis of disubstituted salicylaldehyde C is similar to that of A. The following procedure for the synthesis of H$_2$L$^7$ is similar to the above method.
The (1S, 2S)-diphenyl-1,2-ethanediamine (10 mmol) was added to the ethanol solution of disubstituted salicyaldehyde $A$. The mixture was stirred for 5 h and the yellow solid product was separated and collected by vacuum filtration without recrystallization.

The $^1$H NMR and $^{13}$C NMR spectra of ligand $H_2L^1$
The $^1$H NMR and $^{13}$C NMR spectrum of ligand $H_2L^2$

The $^1$H NMR and $^{13}$C NMR spectrum of ligand $H_2L^3$
The $^1$H NMR and $^{13}$C NMR spectrum of ligand $H_2L^4$

The $^1$H NMR and $^{13}$C NMR spectrum of ligand $H_2L^5$
The $^1$H NMR and $^{13}$C NMR spectrum of ligand $H_2L^6$
The $^1$H NMR and $^{13}$C NMR spectrum of ligand $\text{H}_2\text{L}^7$
The $^1$H NMR and $^{13}$C NMR spectrum of ligand $H_2L^8$

The $^1$H NMR and $^{13}$C NMR spectrum of ligand $H_2L^9$
The $^1$H NMR spectrum of complex 8

The characterization data of complex 8

$^1$H NMR (400 MHz, C$_6$D$_6$) δ 8.10 (s, 1H, CH), 7.91 (s, 2H, CH), 7.60 (m, 3H, CH), 6.95 (m, 6H, Ar-H), 6.68 (m, 4H, Ar-H), 6.45 (s, 2H, Ar-H), 3.67 (m, 6H, CH), 2.77 (m, 36H, CH$_3$), 1.77 (m, 6H, CH), 1.57 (m, 8H, CH), 1.41 (m, 4H, CH), 1.01 (m, 6H, CH).

The elemental analysis of complex 8

| Complex 8   | color       | RE (%) | C (%) | H (%) | N (%) |
|-------------|-------------|--------|-------|-------|-------|
| L$_3^{1}$La$_2$ | yellow     | Found  | 19.786| 61.240| 6.265 | 5.621 |
|             |            | calcd  | 19.530| 61.582| 6.234 | 5.906 |

References

(1) Qian, Q.; Tan, Y.; Zhao, B.; Feng, T.; Shen, Q.; Yao, Y. Org. Lett. 2014, 16, 4516-4519.
(2) Zeng, C.; Yuan, D.; Zhao, B.; Yao, Y. Org. Lett. 2015, 17, 2242-2245.
(3) Bin, W.; Shoufang, W.; Chungu, X.; Wei, S. *Chem. Eur. J.* **2012**, *18*, 7332-7335.