

## Supporting Information

### Asymmetric Transfer Hydrogenation of Aryl Ketones Catalyzed by Salt-free Two Samarium Centers Supported by a Chiral Multidentate Alkoxy Ligand

Kouji Ohno, Yasutaka Kataoka, and Kazushi Mashima\*

*Department of Chemistry, Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan*

**General Procedure.** All manipulations involving air- and moisture-sensitive organometallic compounds were carried out by using the standard Schlenk techniques under an argon atmosphere. THF was dried over sodium benzophenone ketyl and then distilled prior to use. Ethanol was distilled from magnesium ethoxide. 2-Propanol was purified by distillation after drying over calcium hydride. (1*R*,5*R*)-3-Aza-3-benzyl-1,5-dihydroxy-1,5-diphenylpentane, (*R*)-**1**, was prepared according to the literature procedure.<sup>1</sup> LnI( $\eta^8$ -cyclooctatetraene)(thf)<sub>n</sub> (**3a**: Ln = La, n = 3; **3b**: Ln = Ce, n = 3; **3c**: Ln = Pr, n = 3; **3d**: Ln = Nd, n = 2; **3e**: Ln = Sm, n = 1) were prepared by our reported procedure.<sup>2</sup> (*R*)-Styrene oxide was purchased from Axros. Column chromatography was conducted by using silica gel 60 (Merck 9385 230-400 mesh). Nuclear magnetic resonance [<sup>1</sup>H (300 MHz)] spectra were measured on a Varian MERCURY300-C/H. Other spectra were recorded by the use of the following instruments: optical rotation, JASCO DIP-370; HPLC, JASCO PU-980 pumping system, JASCO UV-970 UV/vis detector, JASCO CO-1560 column thermostat, DAICEL CHIRALCEL OD 0.46 mm  $\phi$  x 25 cm chiral column.

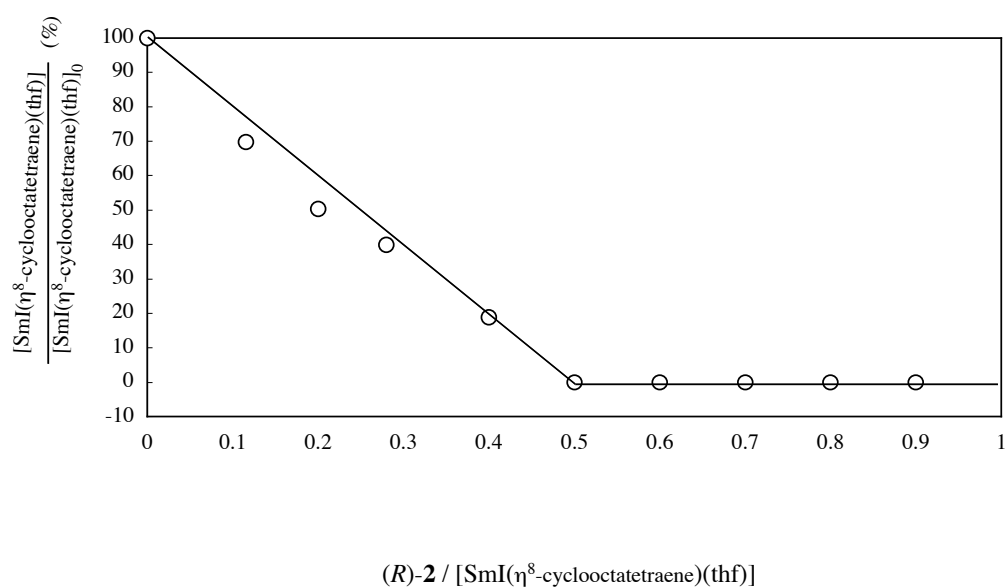
**Synthesis of (*R,R,R,R*)-*N,N,N',N'*-tetra(2-hydroxy-2-phenylethyl)-1,3-xylylene diamine **R**-(2).** To a solution of *m*-xylylenediamine (1.0 mL, 7.8 mmol) in ethanol (2.0 mL) at 0 °C was added a solution of (*R*)-(+)-styrene oxide (3.6 mL, 31.3 mmol) in ethanol (4.0 mL). The reaction mixture was stirred for 1 h at 0 °C, and then refluxed for 4 h. After removal of the solvent under reduced pressure, the resulting oil was purified by column chromatography (silica gel, hexane : ethyl acetate = 3 : 1 with 3% triethyl amine), to afford (*R*)-**2** as a pale yellow oil (2.35 g, 3.9 mmol, 50% yield).

(*R*)-**2**: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 35 °C):  $\delta$  7.35-7.18 (m, 24H, phenyl proton), 4.72 (dd, *J* = 9.9, 3.4 Hz, 4H, -CH<sub>2</sub>-CH(OH)-Ph), 3.99 (d, *J* = 13.5 Hz, 2H, Ph-CHH-N-), 3.70 (d, *J* = 13.5 Hz, 2H, Ph-CHH-N-). 2.79 (dd, *J* = 13.3, 3.4 Hz, 4H, -N-CHH-CH(OH)Ph), 2.78 (dd, *J* = 13.3, 9.9 Hz, 4H, -N-CHH-CH(OH)Ph). MS (FAB): *m/z* 617 (M<sup>+</sup>), 509 (M<sup>+</sup>-PhCHOH), 360 (M<sup>+</sup>-N(CH<sub>2</sub>CH(OH)Ph)<sub>2</sub>), 105 (M<sup>+</sup>-

(N(CH<sub>2</sub>CH(OH)Ph)<sub>2</sub>)<sub>2</sub>). *R<sub>f</sub>* 0.80 (hexane : ethyl acetate = 1 : 1). [ $\alpha$ ]<sub>D</sub><sup>25</sup> -88.5 (*c* 1.0, MeOH). HRMS: calcd for [C<sub>40</sub>H<sub>44</sub>N<sub>2</sub>O<sub>4</sub>] 617.8083, found 617.8111.

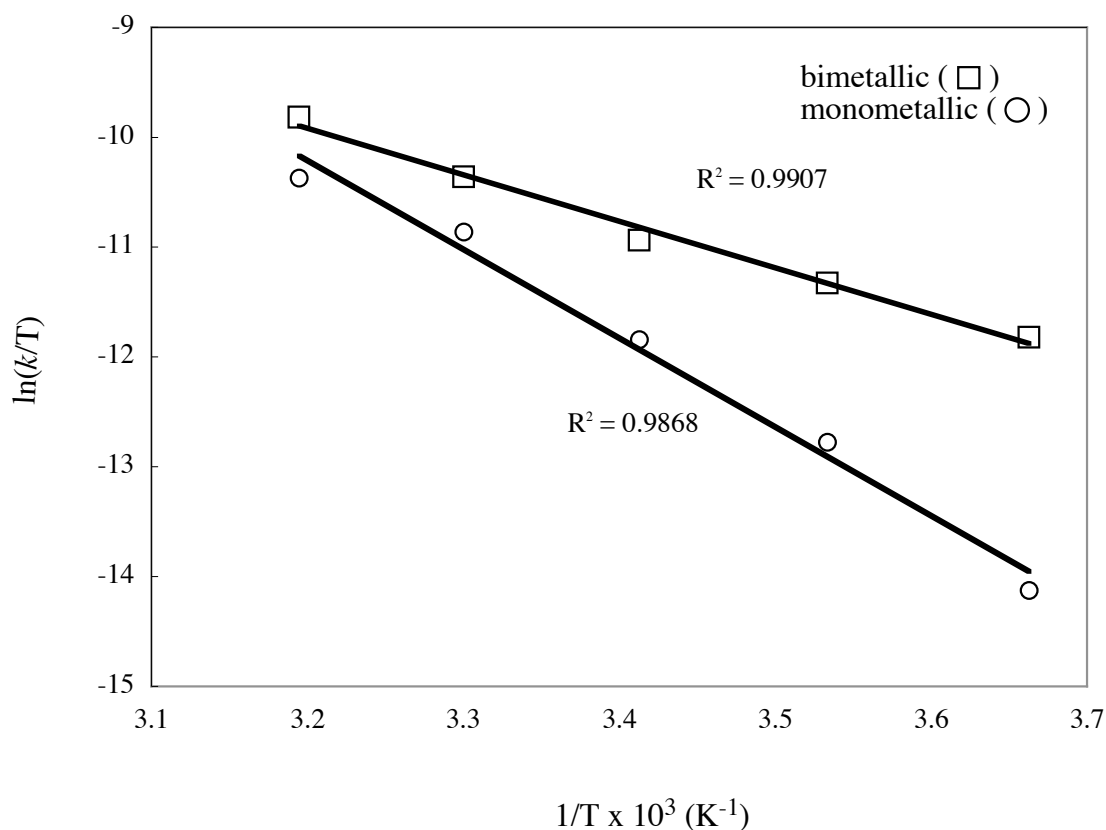
**Preparation of Catalysts and Asymmetric Transfer Hydrogenation of Aryl Ketones:** Typical procedure for the synthesis of lanthanoid catalysts and asymmetric transfer hydrogenation of aryl ketones is as follows: In a 20 mL Schlenk, SmI( $\eta^8$ -cyclooctatetraene)(thf) (**3e**) (17.3 mg, 38.2  $\mu$ mol) and (*R*)-**2** (8.0 mg, 23.8  $\mu$ mol) was solved in THF (2.0 mL). After the reaction mixture was stirred at room temperature for 1 h, 2-propanol (1.5 mL, 500 equivalents relative to **3e**) and acetophenone (0.09 mL, 763  $\mu$ mol, 20 equivalents relative to **3e**) were added. The resulting reaction mixture was stirred at 25 °C for 24 h and quenched with H<sub>2</sub>O, and then organic compounds were extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layer was dried over MgSO<sub>4</sub>, filtered, and the solvent was removed under reduced pressure. The resulting oil purified by K ugelrohr distillation to afford (*R*)-1-phenylethanol in 95% ee and >99% conversion (934 mg, 763  $\mu$ mol). Conversion was determined by <sup>1</sup>H NMR spectroscopy, and enantioselectivity was determined by HPLC (eluent: Hexane / 2-propanol = 95 / 5, detector: 254 nm, flow rate: 0.5mL / min: (*R*) *t* = 16.8 min, (*S*) *t* = 19.9 min). Absolute configuration was assigned by comparison of literature value.<sup>3</sup>

**Procedures of UV-visible Titration:** An absorption band at 581 nm of **3e** in THF was monitored by UV-vis spectroscopy. Solutions of (*R*)-**2** with various concentration (24-240  $\mu$ M) in THF were added to a solution of **3e** (240  $\mu$ M) in THF. Results are shown in Figure S1, where vertical axis indicated molar ratio of [SmI( $\eta^8$ -cyclooctatetraene)(thf)] and horizontal axis indicated the molar ratio of [(*R*)-**2**] in per [SmI( $\eta^8$ -cyclooctatetraene t)(thf)]. When 2 equiv of **3e** were allowed to react with (*R*)-**2** in THF, chromophore at 581 nm disappeared.



**Figure S1.** UV-visible titration of **3e** in THF by (*R*)-**2**

**Kinetic Study:** Asymmetric transfer hydrogenations of acetophenone were conducted at 0, 10, 20, 30 and 40 °C. Conversions were determined by the <sup>1</sup>H NMR spectroscopy of the reaction mixtures after aqueous work up. The observed rate constants were determined from the slope of first-order plots of  $-\ln([\text{acetophenone}]/[\text{acetophenone}]_0)$  versus time (sec). Eyring plot is shown in Figure S2.



**Figure S2.** Eyring Plots of  $\ln(k/T)$  vs  $1/T \times 10^3$

## References

- (1) Evans, D. A.; Nelson, S. G.; Gagne, M. R.; Muci, A. R. *J. Am. Chem. Soc.* **1993**, *115*, 9800.
- (2) (a) Mashima, K.; Takaya, H. *Tetrahedron Lett.* **1989**, *30*, 3697. (b) Mashima, K.; Nakayama, Y.; Nakamura, A.; Kanehisa, N.; Kai, Y.; Takaya, H. *J. Organomet. Chem.* **1994**, *473*, 85.
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