

1) Experimental procedure for transfer hydrogenation of benzil catalyzed by RuCl[(1*S*,2*S*)-*N*-*p*-toluenesulfonyl-1,2-diphenylethanediamine](η^6 -*p*-cymene)

A mixture of triethylamine 19.0 ml (136 mmol) and formic acid 8.7 ml (230 mmol) was added to benzil (**2a**) (11.0 g, 52.3 mmol) and RuCl[(1*S*,2*S*)-*N*-*p*-toluenesulfonyl-1,2-diphenylethanediamine](η^6 -*p*-cymene) (**1b**) (33.3 mg, 0.0523 mmol) and the mixture was degassed by freeze-thaw cycles. The mixture was stirred at 40 °C for 24 h, then triethylamine was evaporated with a vacuum pump and water (100 ml) was added. A precipitate formed was filtered and washed with 50 ml of water. The solid was dried under vacuum and recrystallized from ethanol at -40 °C to give enantiomerically pure (*R,R*)-hydrobenzoin (9.4g, 43.9 mmol). Isolated yield 84 %

2) Optical rotation data of hydrogenation products

(*R,R*)-1,2-Diphenylethanol, $[\alpha]_{\text{D}}^{25} +91.6$ (*c* 1.05 ethanol) (lit. $[\alpha]_{\text{D}}^{23} +95$ (*c* 0.87 ethanol), 99% ee (*R,R*), Wang Z.-M.; Sharpless, K. B. *J. Org. Chem.* **1994**, *59*, 8302–8303).

(*R,R*)-1,2-Bis(*p*-methylphenyl)ethanol, $[\alpha]_{\text{D}}^{25} +123.5$ (*c* 1.15 ethanol) (lit. $[\alpha]_{\text{D}}^{25} +107$ (*c* 1.16 ethanol), (*R,R*), Imuta, M.; Ziffer, H. *J. Org. Chem.* **1978**, *43*, 772–905).

(*R,R*)-1,2-Bis(*p*-methoxyphenyl)ethanol $[\alpha]_{\text{D}}^{27} +128.7$ (*c* 1.01) (lit. $[\alpha]_{\text{D}}^{25} +107$ (*c* 1.15 ethanol), (*R,R*), Imuta, M.; Ziffer, H. *J. Org. Chem.* **1978**, *43*, 772–905).

(*R,R*)-1,2-Bis(*p*-fluorophenyl)ethanol, $[\alpha]_{\text{D}}^{27} +53$ (*c* 1.10, ethanol) Absolute configuration was determined by X-ray crystal structural analysis of the salt with (*S,S*)-1,2-diaminocyclohexane

(1*R*,2*R*)-1,2-diphenyl-2-methoxyethanol, $[\alpha]_{\text{D}}^{27} +56.5$ (*c* 1.47, CHCl₃) (lit. $[\alpha]_{\text{D}}^{25} +53.3$ (*c* 1.50, CHCl₃), 100% ee (1*R*, 2*R*) Mizuno, M.; Kanai, M.; Iida, A.; Tomooka, K. *Tetrahedron* **1997**, *53*, 10699–10708).

3) Determination of the absolute configuration of the reaction products from racemic benzoin methyl ether (5)

Syn/anti ratio of 1,2-diphenyl-2-methoxyethanol formed was determined by ¹H NMR spectra in comparison to reported value.¹ The ee values of *syn* and *anti* isomers were determined by HPLC analysis using a Daicel Chiralcel OJ column. Major isomer, (1*R*,2*R*)-1,2-diphenyl-2-methoxyethanol was isolated by recrystallization from hexane and its absolute configuration was determined by optical rotation data.² [α]_D²⁷ +56.5 (*c* 1.47, CHCl₃) (lit. [α]_D²⁵ +53.3 (*c* 1.50, CHCl₃), (1*R*,2*R*)).

Absolute configurations of the minor products were determined on the basis of HPLC analysis in comparison to authentic sample. (1*R*,2*S*)-1,2-diphenyl-2-methoxyethanol was synthesized by diastereoselective reduction of (*S*)-benzoin methyl ether with LiAlH₄.³

(1) Shibata, I.; Yoshida, T.; Kawakami, T.; Baba, A.; Matsuda, H. *J. Org. Chem.* **1992**, *57*, 4049–4051.

(2) Mizuno, M.; Kanai, M.; Iida, A.; Tomooka, K. *Tetrahedron* **1997**, *53*, 10699–10708.)

(3) Davis, F. A.; Haque, M. S.; Przeslawski, R. M. *J. Org. Chem.* **1989**, *54*, 2021–2024.