

Supporting Information for our Manuscript titled

“Non-enzymatic Kinetic Resolution of 1,2-Diols Catalyzed by Organotin Compound“ (permanent Manuscript No.tol990390)

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(S)-4,4-dibromo-4,5-dihydro-3H-dinaphtho[2,1-c:1',2'-e]stannepin (A)

A was prepared according to ref 5 and 6 in the text.

General procedure for kinetic resolution of 1,2-diol (1a-e).

1,2-Diol (1 mmol) and 0.0025 mmol of catalyst **A** were dissolved in 5 mL of tetrahydrofuran (THF). After suspended 1.5 mmol of sodium carbonate, 0.5 mmol of benzoyl chloride was added at -10°C . The reaction mixture was stirred at -10°C for 14h. Then, the suspension was poured onto water and the organic portion was extracted three times with ethyl acetate. Combined organic layer was dried over magnesium sulfate. After remove of solvent, the residue was separated by silica gel column chromatography (n-hexane : ethyl acetate = 3 : 1). Optical yields were determined by CSP HPLC method.

1-phenyl-1,2-ethanediol (1a)¹: DAICEL Chiralcel OB (0.46 cm ϕ x 25cm), n-Hexane : Isopropanol = 9 : 1, wavelength: 254nm, flow rate: 1.0ml/min, retention time: 7min, 8min.

(S)-2-Benzoyloxy-1-phenylethanol (2a): $[\alpha]_{\text{D}}^{26} +8.5$ (c 1.0, MeOH); IR (KBr) 3480, 1709, 1451, 1318, 1281, 1096, 703, 698 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3) 2.35~3.0 (1H, m), 4.43 (1H, dd, $J=7.0, 11.0$ Hz), 4.55 (1H, dd, $J=4.0, 11.0$ Hz), 5.13 (1H, dd, $J=4.0, 7.0$ Hz), 7.25~7.65 (8H, m), 8.06 (2H, d, $J=7.0$ Hz); DAICEL Chiralcel OB (0.46 cm ϕ x 25cm), n-Hexane : Isopropanol = 9 : 1, wavelength : 254nm, flow rate: 1.0ml/min, retention time:13min, 25min, 78%ee.

(S)-2-Benzoyloxy-1-(2-naphthyl)ethanol (2b): white solid. mp $90-97^{\circ}\text{C}$; $[\alpha]_{\text{D}}^{21} +4.9$ (c 0.48, MeOH); IR (KBr) 2361, 2341 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3) 4.51 (1H, dd, $J= 8.0, 11.6$ Hz), 4.62 (1H, dd, $J= 3.6, 11.6$ Hz), 5.28 (1H, dd, $J= 3.6, 8.0$ Hz), 7.40~7.65 (6H, m), 7.81~8.09 (6H, m); DAICEL Chiralpak AS (0.46 cm ϕ x 25cm), n-Hexane : Isopropanol = 9:1, wavelength: 254nm, flow rate: 0.8ml/min., retention time: 16min, 19min, 64%ee; HRMS calcd for $\text{C}_{19}\text{H}_{16}\text{O}_3$ 292.1099, found 292.1129.

(S)-2-Benzoyloxy-1-(1-naphthyl)ethanol (2c): white solid; mp $99-103^{\circ}\text{C}$; $[\alpha]_{\text{D}}^{24} -6.5$ (c 0.5, MeOH); IR (KBr) 3510, 3404, 3059, 1705, 1722 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3) 4.51 (1H, dd, $J= 8.0, 11.6$ Hz), 4.63 (1H, dd, $J= 3.6, 11.6$ Hz), 5.28 (1H, dd, $J= 3.6, 8.0$ Hz), 7.37~7.54 (6H, m), 7.81~7.89 (4H, m), 8.02~8.06 (2H, m); DAICEL Chiralpak AS (0.46 cm ϕ x 25cm), n-Hexane : Isopropanol = 9:1, wavelength: 254nm, flow rate: 1.0ml/min., retention time:16min, 20min, 72%ee; HRMS calcd for $\text{C}_{19}\text{H}_{16}\text{O}_3$ 292.1099, found 292.1134.

(KBr) 3501, 2953, 2920, 2849, 1697 cm^{-1} . $^1\text{H-NMR}$ (CDCl_3)_0.88 (3H, t, $J= 6.5$ Hz), 4.23 (2H, s), 7.42~7.50 (2H, m), 7.55~7.60 (1H, m), 8.04~8.09 (2H, m); DAICEL Chiralpak AS (0.46 cm ϕ x 25cm), *n*-Hexane : Isopropanol = 98:2, wavelength: 254nm, flow rate: 1.0ml/min., retention time: 11min, 16min, 59%ee; HRMS calcd for $\text{C}_{19}\text{H}_{30}\text{O}_3$ 306.2195, found 306.2203.

(S)-1-Benzoyloxy-2-butanol (2e): colorless oil; $[\alpha]_{\text{D}}^{20} +3.7$ (c 1.0, MeOH); IR (neat) 3450, 2966, 2880, 1718 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3)_1.03 (3H, t, $J= 7.5$ Hz), 1.54~2.27 (2H, m), 3.92 (1H, dd, $J= 3.4, 6.8$ Hz), 4.24 (1H, dd, $J=6.8, 11.8$ Hz), 4.40 (1H, dd, $J= 3.4, 11.8$ Hz), 7.40~7.48 (2H, m), 7.54~7.58 (1H, m), 8.03~8.08 (2H, m); DAICEL Chiralcel OJ (0.46 cm ϕ x 25cm), *n*-Hexane : Isopropanol = 98:2, wavelength :254nm, flow rate: 1.0ml/min., retention time: 45min, 48min., 40%ee; HRMS calcd for $\text{C}_{11}\text{H}_{14}\text{O}_3$ 194.0943, found 194.0918.

All benzoylated products **2a-2e** were converted to corresponding diols by alkaline hydrolysis. Then the absolute configurations of the diols were confirmed by comparison of their specific rotation with authentic data (**1a**,¹ **1b**,² **1c**,³ **1d**,⁴ and **1e**²).

¹ See ref 7 in the text.

² Cho, B. T.; Chun, Y. S. *J. Org. Chem.* **1998**, *63*, 5280.

³ Miao, G.; Rossiter, B. E. *J. Org. Chem.* **1995**, *60*, 8424.