Supporting Information for our Manuscript titled " Copper Ion-induced Activation and Asymmetric benzoylation of 1,2-Diols: Kinetic Chiral Molecular Recognition " by Yoshihiro Matsumura,* Toshihide Maki, Sachie Murakami, and Osamu Onomura

Measurement. ^1H NMR spectra were measured on a Varian Gemini 200, 300 or 500 spectrometer with TMS as an internal standard. Mass spectra were obtained on a JEOL IMS-DX 300 instrument. IR spectra were obtained on a Shimadzu FTIR-8100A.

Materials. All materials were reagent grade and used without further purification. Diols were prepared according to reported methods.

Monobenzoylation of *dl*-hydrobenzoin catalyzed by various metal ions (Table 1S).

Table 1S Lewis acid promoted monobenzoylation of *dl*-hydrobenzoin *)

run	metal	mol%	yield (%) of 2a
1	none	-	3
2	(CH ₃) ₂ SnCl ₂	1	95
3	PdCl ₂	20	35
4	NiCl ₂	20	9
5	CoCl ₂	20	31
6	ZnCl ₂	20	54
7	CuCl ₂	20	82

*) Complex was prepared in CH₂Cl₂. The reaction was carried out with complex (0.05 mmol), *dl*-hydrobenzoin (0.5 mmol), diisopropylethylamine (DIPEA, 1 mmol) and benzoyl chloride (0.5 mmol) in CH₂Cl₂ at 0°C.

Kinetic resolution of *dl*-hydrobenzoin with copper- chiral ligands complexes.

(*R*)-BINAP¹ for CuCl₂ was ineffective as a ligand for both the conversion and enantiomeric excess (ee) (run 2), and a tridentate ligand Ph-PyBOX¹ for CuCl₂ gave **2a** in high yield but the ee was disappointing (run 3). However, the use of (*R,R*)-Ph-BOX-CuCl₂¹ as a catalyst (5 mol%) fortunately gave almost optically pure (*S,S*)-**2a** (>99%ee) in 48% (run 4). On the other hand, (CH₃)₂SnCl₂ in the presence of (*R,R*)-Ph-BOX resulted in a low ee (run 5), while (*R,R*)-Ph-BOX-ZnCl₂ gave **2a** with 42%ee in which the enantiomerically enriched isomer was (*R,R*)-**2a** (run 6).

Table 2S. Kinetic resolution of dl-hydrobenzoin (dl-**1a**)^{a)}

run	chiral ligand ^{b)}	metal ion	hr	2a yield (%) ^{b)}	ee (%) ^{c)}
1 ^{d)}	2,2'-bipyridine	CuCl ₂	2	88	–
2	(R)-BINAP	CuCl ₂	14	27	2 (S,S)
3	(R,R)-Ph-PyBOX	CuCl ₂	7	46	8 (S,S)
4	(R,R)-Ph-BOX	CuCl ₂	2	48	> 99 (S,S)
5	(R,R)-Ph-BOX	Me ₂ SnCl ₂	7	41	8 (S,S)
6	(R,R)-Ph-BOX	ZnCl ₂	14	36	42 (R,R)

a) The reaction was carried out with catalyst (0.05 mmol), dl-hydrobenzoin (1mmol), diisopropylethylamine (DIPEA, 1 mmol) and benzoyl chloride (0.5 mmol) in CH₂Cl₂ at 0°C. b) Isolated yield based on dl-**1a**. c) Determined by CSP HPLC. d) 1.0 equiv. of PhCOCl was used.

(1) BINAP: 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl, (R,R)-Ph-PyBOX: [R-(R*,R*)]-2,6-bis(4,5-dihydro-4-phenyl-2-oxazolyl)pyridine, (R,R)-Ph-BOX: 2,2-isopropylidenebis[(4R)-4-phenyl-2-oxazoline]. All those ligands are commercially available.

Preparation of (R,R)-Ph-BOX-CuCl₂

2,2-Isopropylidenebis[(4R)-4-phenyl-2-oxazoline] (1.0 mmol) and CuCl₂ (1.0 mmol) was stirred in CH₂Cl₂ (5 mL) for 2hrs. Remaining CuCl₂ was filtered off and the filtrate was evaporated under reduced pressure. The residue was re-crystallized from CH₂Cl₂ and afforded green crystals.

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

1,2-Diol (1mmol), diisopropylethylamine (DIPEA, 1 mmol) and 0.05 mmol of catalyst dissolved in 5 mL of CH₂Cl₂ were added benzoyl chloride at 0°C. The mixture was stirred until the benzoyl chloride was disappeared on TLC at 0°C. Then, the solution was poured onto water and extracted three portion of CH₂Cl₂. Combined organic layer was dried over magnesium sulfate. After remove of organic solvent, the residue was separated by silica gel column chromatography (*n*-Hexane : Ethyl acetate = 3 : 1). Optical yields were determined by SPCC HPLC method using DAICEL Chiralpak.

2a: White solid. m.p. 146-148°C. IR $\nu_{\max}$: 3472, 3034, 1721, 1453, 1273, 1113, 704cm⁻¹. ¹H-NMR (CDCl₃) δ 2.56-2.63(1H, br), 5.10(1H, d, *J*=7.3), 6.11(1H, d, *J*=7.3), 7.18-7.30(10H, m), 7.45-7.51(2H, m), 7.57-7.62(1H, m), 8.10-8.13(2H, m). HPLC: OJ column, *n*-Hexane : Isopropanol = 5 : 1, wavelength: 254nm, flow rate: 1.0ml/min, retention time: 13.2 min (for *S,S*-isomer) , 27.7 min (for *R,R*-isomer), >99.9%ee. [α]_D²⁸ -66.3 (c 1.00, MeOH).

2b: White solid. m.p. 185-187°C. IR $\nu_{\max}$: 3480, 3065, 1715, 1401, 1371, 1004, 710cm⁻¹. ¹H-NMR

(CDCl₃) δ 2.60(1H, d, $J=3.3$), 5.05(1H, dd, $J=3.3$, 7.3), 6.02(1H, d, $J=7.3$), 7.08-7.30(10H, m), 7.46-7.51(2H, m), 7.59-7.65(1H, m), 8.07-8.10(2H, m). HPLC: OD column, *n*-Hexane : Isopropanol = 5 : 1, wavelength: 254nm, flow rate: 1.0ml/min, retention time: 7.2 min (for *S,S*-isomer), 8.8 min (for *R,R*-isomer), >99.9%ee. $[\alpha]^{29}_{-84.5}$ (c 1.00, MeOH).

2c: White solid. m.p. 144-146°C. IR $\nu_{\max}$: 3472, 2923, 1721, 1450, 1271, 1111, 709cm⁻¹. ¹H-NMR (CDCl₃) δ 2.28(3H, s), 2.29(3H, s), 2.57(1H, d, $J=3.3$), 5.05(1H, dd, $J=3.3$, 7.6), 6.07(1H, d, $J=7.6$), 7.03-7.12(8H, m), 7.43-7.49(2H, m), 7.55-7.61(1H, m), 8.08-8.11(2H, m). HPLC: OJ column, *n*-Hexane : Isopropanol = 5 : 1, wavelength : 254nm, flow rate: 1.0ml/min, retention time: 8.6 min (for *S,S*-isomer) , 16.1 min (for *R,R*-isomer), 97%ee. $[\alpha]^{28}_{-100.6}$ (c 1.03, MeOH).

2d: White solid. m.p. 126-127°C. IR $\nu_{\max}$: 3488, 2957, 1715, 1514, 1271, 1111, 713cm⁻¹. ¹H-NMR (CDCl₃) δ : 2.56-2.61(1H, br), 3.74(3H, s), 3.76(3H, s), 5.02(1H, d, $J=7.8$), 6.03(1H, d, $J=7.8$), 6.73-6.80(4H, m), 7.08-7.18(4H, m), 7.42-7.50(2H, m), 7.55-7.61(1H, m), 8.08-8.12(2H, m). HPLC: OJ column, *n*-Hexane : Isopropanol = 1 : 1, wavelength : 254nm, flow rate: 1.0ml/min, retention time: 10.0 min (for *S,S*-isomer) , 15.3 min (for *R,R*-isomer), 98%ee. $[\alpha]^{28}_{-86.7}$ (c 1.00, MeOH).

2e: White solid. m.p. 91-94°C. IR $\nu_{\max}$: 4550, 2939, 2862, 1718, 1603, 1453, 1281 cm⁻¹. ¹H-NMR (CDCl₃) δ : 1.22-1.50(4H, m), 1.70-1.82(2H, m), 2.08-2.21(2H, m), 3.70-3.81(1H, m), 4.82-4.91(1H, m), 7.41-7.45(2H, m), 7.53-7.61(1H, m), 8.05(2H, d, $J=9$). HPLC: OJ column, *n*-Hexane : Isopropanol = 30 : 1, wavelength: 254nm, flow rate: 1.0ml/min, retention time: 18.0 min (for *S,S*-isomer), 20.7 min (for *R,R*-isomer), 80%ee. $[\alpha]^{26}_{41.8}$ (c 1.34, MeOH).

2f: White solid. m.p. 73-74°C. IR $\nu_{\max}$: 4550, 3070, 2860, 1716, 1600, 1450, 1320, 718 cm⁻¹. ¹H-NMR (CDCl₃) δ 1.45-2.01(10H, m), 2.81(1H, s), 3.89-3.96(1H, m), 4.94-5.01(1H, m), 7.40-7.48(2H, m), 7.54-7.62(1H, m), 8.05(2H, d, $J=9$). HPLC: OJ column, *n*-Hexane : Isopropanol = 30 : 1, wavelength: 254nm, flow rate: 1.0ml/min, retention time: 14.0 min (for *S,S*-isomer), 16.5 min (for *R,R*-isomer), 84%ee. $[\alpha]^{23}_{35.9}$ (c 1.27, MeOH).

2g: Colorless oil. IR $\nu_{\max}$: 3480, 2970, 1719, 1455, 1284, 1116, 714cm⁻¹. ¹H-NMR (CDCl₃) δ ; 0.95-1.04(6H, m), 1.42-1.88(4H, m), 3.62-3.72(1H, m), 5.02-5.10(1H, m), 7.42-7.50(2H, m), 7.55-7.62(1H, m), 8.03-8.10 (2H, m). HPLC: AD column, *n*-Hexane : Isopropanol = 50 : 1, wavelength : 254nm, flow rate: 1.0ml/min, retention time: 23.0 min (for *R,R*-isomer) , 25.0 min (for *S,S*-isomer). 77%ee. $[\alpha]^{22}_{-22.4}$ (c 1.16, MeOH).

Table 3S Validity of 'selectivity' on acylating reagents

run	acylating reagents	product	yield (%)	ee (%)	selectivity
1	acetyl chloride	(S,S)- 6a	38	22	1.8
2	acetic anhydride	(S,S)- 6a	32	22	1.7
3	propionyl chloride	(S,S)- 7a	45	53	4.9
4	isobutyryl chloride	(S,S)- 8a	47	65	8.3
5	pivaloyl chloride	(S,S)- 9a	39	76	11.8

1) Isolated yield 2) Determined by HPLC

6a: White solid. m.p. 90-92°C. IR ν_{max} ; 3466, 3034, 1736, 1374, 1235, 1026, 700 cm^{-1} . $^1\text{H-NMR}$ (CDCl_3) δ 2.13(3H, s), 2.53(1H, d, $J=3.6$), 4.93(1H, dd, $J=3.6, 7.4$), 5.85(1H, d, $J=7.4$), 7.10-7.26(10H, m). HPLC: OD column, *n*-Hexane : Isopropanol = 9 : 1, wavelength : 254nm, flow rate: 1.0ml/min, retention time: 8.4 min (for *S,S*-isomer) , 12.5 min (for *R,R*-isomer), 22%ee. $[\alpha]^{28}_{\text{D}}$ -1.5 (c 1.02, MeOH).

7a: White solid. m.p. 100-102°C. IR ν_{max} ; 3480, 3034, 1740, 1454, 1199, 1080, 700 cm^{-1} . $^1\text{H-NMR}$ (CDCl_3) δ 1.13(3H, t, $J=7.5$), 2.42(2H, q, $J=7.5$), 2.55(1H, d, $J=3.3$), 4.93(1H, dd, $J=3.3, 7.5$), 5.86(1H, d, $J=7.5$), 7.10-7.26(10H, m). HPLC: OD column, *n*-Hexane : Isopropanol = 5 : 1, wavelength: 254nm, flow rate: 1.0ml/min, retention time: 5.9 min (for *S,S*-isomer) , 7.7 min (for *R,R*-isomer). 53%ee. $[\alpha]^{22}_{\text{D}}$ -4.2 (c 0.62, MeOH).

8a: White solid. m.p. 105-106°C. IR ν_{max} ; 3464, 2974, 1740, 1454, 1199, 1159, 767, 700 cm^{-1} . $^1\text{H-NMR}$ (CDCl_3) δ ; 1.16(6H, dd, $J=2.2, 7.1$), 2.50(1H, d, $J=3.6$), 2.64(1H, sep, $J=7.1$), 4.94(1H, dd, $J=3.6, 6.9$), 5.85(1H, d, $J=6.9$), 7.10-7.25(10H, m). HPLC: OJ column, *n*-Hexane : Isopropanol = 5 : 1, wavelength: 254nm, flow rate: 1.0ml/min, retention time: 7.5 min (for *S,S*-isomer) , 10.1 min (for *R,R*-isomer), 65%ee. $[\alpha]^{22}_{\text{D}}$ 1.7 (c 1.00, MeOH).

9a: White solid. m.p. 108-110°C. IR ν_{max} ; 3480, 2973, 1727, 1455, 1282, 1153, 702 cm^{-1} . $^1\text{H-NMR}$ (CDCl_3) δ 1.21(9H, s), 2.42-2.47(1H, br), 4.94(1H, d, $J=6.8$), 5.84(1H, d, $J=6.8$), 7.1-7.29(10H, m). HPLC: OJ column, *n*-Hexane : Isopropanol = 5 : 1, wavelength: 254nm, flow rate: 1.0ml/min, retention time: 6.8 min (for *S,S*-isomer) , 10.1 min (for *R,R*-isomer), 76%ee. $[\alpha]^{28}_{\text{D}}$ -1.4 (c 1.00, MeOH).

Desymmetrization of *meso*-1a

5: White solid. IR ν_{max} ; 3553, 3032, 1700, 1450, 1273, 1111, 706 cm^{-1} . $^1\text{H-NMR}$ (CDCl_3) δ ; 1.22(1H, d, $J=3.9$), 5.15(1H, dd, $J=3.6, 5.9$), 6.16(1H, d, $J=5.7$), 7.22-7.33(10H, m), 7.45-7.51(2H, m), 7.57-7.62(1H, m), 8.10-8.13(2H, m). HPLC: OJ column, *n*-Hexane : Isopropanol = 5 : 1, wavelength: 254nm, flow rate: 1.0ml/min, retention time: 10.4 min (major), 16.0 min. 94%ee. $[\alpha]^{24}_{\text{D}}$ -35.3 (c=1.00, CHCl_3).

Plausible Reaction Mechanism

Scheme 1S shows our proposed mechanism why (*S,S*)-**1a** was highly resolved by (*R,R*)-Ph-box-CuCl₂. Possibly, benzoyl chloride can approach more easily to alkoxide **B(S,S)**, which is generated from (*S,S*)-**1a** with (*R,R*)-Ph-box-CuCl₂, than to alkoxide **B(R,R)**, which is generated from (*R,R*)-**1a** with (*R,R*)-Ph-box-CuCl₂, since a transition state **B'(S,S)** from **B(S,S)** may be less crowded than a transition state **B'(R,R)** from **B'(S,S)**.

Scheme 1S