

Facile synthesis of optically active oxindols by copper-catalyzed asymmetric monotosylation of prochiral 1,3-diols

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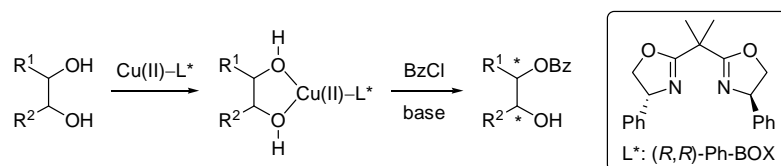
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Abstract. The facile synthetic method of optically active 3,3-disubstituted oxindoles with excellent enantioselectivity was achieved using chiral copper-catalyzed desymmetrization of prochiral 1,3-diols. The monotosylated product was transformed into oxindole derivatives efficiently.

Dedicated to Professor Dr. Henri Kagan on his 80th birthday

1. Introduction

Oxindols are important heterocycles found in various naturally occurring compounds and biologically active molecules.¹ Particularly, numerous methods have been reported for the enantioselective synthesis of oxindoles including Heck reaction², cyanoamidation³, cycloaddition⁴, alkylation⁵, arylation⁶, 1,2-addition⁷, 1,4-addition⁸, hydroxylation⁹, fluorination¹⁰, rearrangement¹¹, and addition to isatins¹². In addition, enzyme-catalyzed asymmetric desymmetrization was known as an effective synthetic method for optically active oxindoles bearing a quaternary stereocenter at the 3-position,¹³ but nonenzymic methods have not been reported. Recently, we have developed chiral copper-catalyzed kinetic resolution and desymmetrization of diols (Scheme 1).^{14,15} Herein, we would like to describe the efficient synthesis of optically active 3,3-disubstituted oxindoles using chiral copper-catalyzed asymmetric monotosylation^{15e} of prochiral 3,3-bis(hydroxymethyl)oxindoles.

Scheme 1. Asymmetric benzylation of 1,2-diols with Cu(II)–(*R,R*)-Ph-BOX**2. Results and Discussion**

First of all, the influence of *N*-protecting groups in 3,3-bis(hydroxymethyl)oxindoles **1** was examined in chiral copper-catalyzed desymmetrization with tosyl chloride (Table 1). The reaction using *N*-Boc oxindole **1a** did not proceed (entry 1). *N*-Acetyloxindole **1b** gave the desired product **2b** with 9% yield and 63% ee (entry 2). *N*-Methoxymethyloxindole **1c** improved enantioselectivity up to 99% ee though chemical yield was still low (entry 3). In the case of *N*-methyloxindole **1d**, the product **2d** was obtained in 75% yield and 98% ee (entry 4). Although *N*-benzyloxindole **1e** led to moderate yield keeping 99% ee, *N*-(*p*-methylbenzyl)oxindole **1f** decreased both chemical yield and enantioselectivity (entries 5-6).

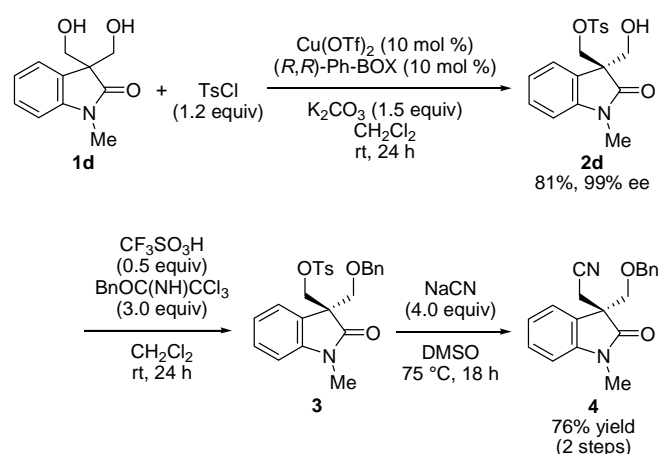
Table 1. Copper-catalyzed asymmetric monotosylation of 3,3-bis(hydroxymethyl)oxindoles ^a

entry	substrate	R	product	yield (%) ^b	ee (%) ^c
1	1a	Boc	2a	0	–
2	1b	Ac	2b	9	63
3	1c	MOM	2c	20	99
4	1d	Me	2d	75	98
5	1e	Bn	2e	54	99
6	1f	<i>p</i> -MeBn	2f	19	37

^a Reaction conditions: 3,3-bis(hydroxymethyl)oxindole **1** (0.5 mmol), *p*-toluenesulfonyl chloride (0.5 mmol), K₂CO₃ (0.75 mmol), Cu(OTf)₂ (10 mol %), (*R,R*)-Ph-BOX (10 mol %), CH₂Cl₂ (2 mL), rt, 24 h. ^b Isolated yield. ^c Determined by HPLC.

Then, we tried the transformation of monotosylated oxindole **2d** (Scheme 2). In the synthesis of **2d** using 1.2 equiv of tosyl chloride, chemical yield and enantioselectivity were improved to give the product in 81% yield and 99% ee. Monotosylated oxindole **2d** was benzylated with benzyl 2,2,2-trichloroacetimidate under acidic condition. The crude product of **3** was used for cyanation without further purification to give the compound **4** with 76% yield (2 steps). The chiral oxindole derivatives bearing 3-cyanomethyl group are known as useful synthetic intermediates.³

Scheme 2. Transformation of (*R*)-(+)-3-hydroxymethyl-1-methyl-3-(*p*-toluenesulfonyloxymethyl)-oxindole **2d**



The absolute configuration of **2d** was determined by X-ray crystallographic analysis.¹⁶ Monotosylated oxindole **2d** was treated with (+)-10-camphorsulfonyl chloride, giving the sulfonate ester **5**, which was recrystallized from diethyl ether to provide fine crystals after purification with silica gel column chromatography (Scheme 3). Then, the X-ray crystallographic analysis of the sulfonate ester **5** proved that the newly generated stereogenic center was *R* (Figure 1).

Scheme 3. Synthesis of (*R*)-(+)-3-((+)-10-camphorsulfonyloxymethyl)-1-methyl-3-(*p*-toluenesulfonyloxymethyl)oxindole **5**

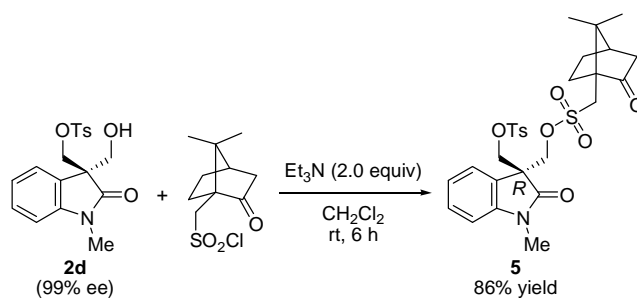
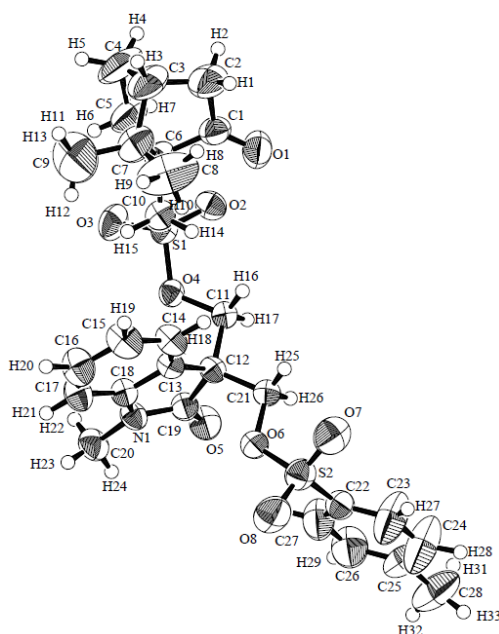


Figure 1. X-ray crystal structure of (*R*)-(+)-3-((+)-10-camphorsulfonyloxymethyl)-1-methyl-3-(*p*-toluenesulfonyloxymethyl)oxindole **5**.



3. Conclusion

In summary, the enantioselective synthesis of oxindoles bearing a quaternary stereocenter at the 3-position was developed using copper-catalyzed asymmetric monotosylation of prochiral 1,3-diols. The reaction with *N*-methyl oxindole **1d** led to excellent yield and enantioselectivity. The tosylated product was readily converted to the oxindole derivatives bearing 3-cyanomethyl group via benzylaition and

cyanation. The absolute configuration of monotosylated oxindole **2d** was determined by the X-ray crystallographic analysis of the sulfonate ester **5**.

4. Experimental

4.1. General

All melting points are not corrected. IR spectra were obtained with Shimadzu FT-IR-8100 and expressed in cm^{-1} . ^1H and ^{13}C NMR spectra were taken with Varian Gemini 300 or JEOL JNM-AL 400, and chemical shift values are expressed in ppm relative to internal TMS. Abbreviations are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. High-resolution mass spectra (HRMS) were recorded with JEOL JMS-700N spectrometer. Specific rotations were measured with JASCO DIP-1000. All reagents and solvents were used as received without further purification. The products were isolated by silica gel column chromatography with Merck silica gel 60.

4.2. General procedure of Copper-catalyzed asymmetric monotosylation of 3,3-bis(hydroxymethyl)oxindoles

To a solution of $\text{Cu}(\text{OTf})_2$ (0.05 mmol, 18.1 mg) and (*R,R*)-Ph-BOX (0.05 mmol, 16.7 mg) in CH_2Cl_2 (2 mL) were added 3,3-bis(hydroxymethyl)oxindoles **1e** (0.5 mmol, 89.6 mg), K_2CO_3 (0.75 mmol, 104 mg), and *p*-toluenesulfonyl chloride (0.6 mmol, 114 mg). After stirring for 24 h at room temperature, water (10 mL) was added. The resulting mixture was extracted with AcOEt. The combined organic layers were washed with brine, and then dried over MgSO_4 . Concentration and purification through silica gel column chromatography gave the product.

4.2.1 (+)-1-Acetyl-3-hydroxymethyl-3-(*p*-toluenesulfonyloxymethyl)oxindole (2b). Yellow oil. IR (neat): 3400, 3020, 1760, 1720, 1640, 1470 cm^{-1} . ^1H -NMR (300 MHz, CDCl_3): δ 8.30-8.15 (m, 1H), 7.62 (d, $J = 7.5$ Hz, 1H), 7.42-7.10 (m, 6H), 4.41 (bs, 2H), 3.88-3.81 (m, 2H), 2.72-2.56 (m, 3H), 2.59 (s, 3H), 2.04 (bs, 1H). ^{13}C -NMR (100 MHz, CDCl_3): δ 176.5, 170.4, 145.2, 132.0, 129.9, 129.6, 128.9, 127.9, 125.9, 125.5, 123.4, 116.8, 69.6, 64.6, 54.5, 26.6, 21.7. 63% ee (HPLC: Daicel chiralcel OG (4.6 mm ϕ , 250 mm), *n*-Hexane : Isopropanol = 10 : 1, 254 nm, 1.0 ml/min, 64 min and 77 min (enriched)).

$[\alpha]_D^{19} + 47.0$ (*c* 1.0, CHCl₃). MS [HR-FAB(+)]: *m/z* calcd for C₁₉H₂₀O₆NS [M+H]⁺ 390.1011, found 390.1044.

4.2.2 (+)-3-Hydroxymethyl-1-methoxymethyl-3-(*p*-toluenesulfonyloxymethyl)oxindole (2c).

Colorless oil. IR (neat): 3400, 2940, 1730, 1620 cm⁻¹. ¹H-NMR (400 MHz, CDCl₃): δ 7.61 (d, *J* = 8.3 Hz, 2H), 7.38-7.29 (m, 4H), 7.10-7.02 (m, 2H), 5.15-5.05 (m, 2H), 4.46 (d, *J* = 9.3 Hz, 1H), 4.37 (d, *J* = 9.3 Hz, 1H), 3.87 (d, *J* = 11.7 Hz, 1H), 3.79 (d, *J* = 11.7 Hz, 1H), 3.25 (s, 3H), 2.44 (s, 4H). ¹³C-NMR (100 MHz, CDCl₃): δ 176.6, 145.0, 142.2, 132.1, 129.8, 129.4, 127.9, 126.0, 124.0, 123.5, 110.1, 71.2, 69.6, 64.1, 56.1, 54.0, 21.6. 99% ee (HPLC: Daicel chiralcel OJ-H (4.6 mmφ, 250 mm), *n*-Hexane : Isopropanol = 5 : 1, 254 nm, 1.0 ml/min, 39 min and 43 min (enriched)). $[\alpha]_D^{20} + 6.8$ (*c* 1.0, CHCl₃). MS [HR-FAB(+)]: *m/z* calcd for C₁₉H₂₂O₆NS [M+H]⁺ 392.1168, found 392.1193.

4.2.3 (R)-(+)-3-Hydroxymethyl-1-methyl-3-(*p*-toluenesulfonyloxymethyl)oxindole (2d). White solid of mp 119-120 °C. IR (neat): 3350, 3060, 1720, 1620 cm⁻¹. ¹H-NMR (400 MHz, CDCl₃): δ 7.67 (d, *J* = 8.3 Hz, 2H), 7.38-7.23 (m, 4H), 7.07 (t, *J* = 7.8 Hz, 1H), 6.87 (d, *J* = 7.8 Hz, 1H), 4.48 (d, *J* = 9.8 Hz, 1H), 4.28 (d, *J* = 9.8 Hz, 1H), 3.85 (d, *J* = 9.2 Hz, 1H), 3.72 (d, *J* = 9.2 Hz, 1H), 3.19 (s, 3H), 2.54 (bs, 1H), 2.44 (s, 3H). ¹³C-NMR (100 MHz, CDCl₃): δ 175.5, 145.0, 143.8, 132.2, 129.8, 129.2, 127.9, 126.5, 124.1, 123.1, 108.6, 69.6, 63.8, 53.2, 26.3, 21.6. 99% ee (HPLC: Daicel chiralcel OG (4.6 mmφ, 250 mm), *n*-Hexane : Isopropanol = 10 : 1, 254 nm, 1.0 ml/min, 92 min (enriched) and 98 min). $[\alpha]_D^{22} + 17.2$ (*c* 1.0, CHCl₃). MS [HR-FAB(+)]: *m/z* calcd for C₁₈H₂₀O₅NS [M+H]⁺ 362.1062, found 362.1062.

4.2.4 (+)-1-Benzyl-3-hydroxymethyl-3-(*p*-toluenesulfonyloxymethyl)oxindole (2e). White solid of mp 123-124 °C. IR (neat): 3400, 3010, 17610, 1610 cm⁻¹. ¹H-NMR (300 MHz, CDCl₃): δ 7.62 (d, *J* = 8.4 Hz, 1H), 7.34-7.15 (m, 10H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.70 (d, *J* = 7.5 Hz, 1H), 4.99 (d, *J* = 15.9 Hz, 1H), 4.83 (d, *J* = 15.9 Hz, 1H), 4.52 (d, *J* = 9.3 Hz, 1H), 4.41 (d, *J* = 9.3 Hz, 1H), 3.92 (d, *J* = 11.1 Hz, 1H), 3.80 (d, *J* = 11.1 Hz, 1H), 2.47 (brs, 1H), 2.43 (s, 3H). ¹³C-NMR (100 MHz, CDCl₃): δ 175.7, 144.9, 143.0, 135.0, 132.1, 129.8, 129.1, 128.8, 127.9, 127.6, 126.9, 126.5, 123.9, 123.1, 109.6, 69.8, 64.0, 53.5, 43.7, 21.6. 99% ee (HPLC: Daicel chiralcel OG (4.6 mmφ, 250 mm), *n*-Hexane :

Isopropanol = 10 : 1, 254 nm, 1.0 ml/min, 60 min and 65 min (enriched)). [α]²²_D + 29.5 (*c* 1.0, CHCl₃). MS [HR-FAB(+)]: *m/z* calcd for C₂₄H₂₄O₅NS [M+H]⁺ 438.1375, found 438.1375.

4.2.5 (-)-3-Hydroxymethyl-1-(*p*-methylbenzyl)-3-(*p*-toluenesulfonyloxymethyl)oxindole (2f).

Yellow oil. IR (neat): ν 3360, 2920, 1700, 1620, 1470 cm⁻¹. ¹H-NMR (300 MHz, CDCl₃): δ 7.60 (d, *J* = 8.1 Hz, 1H), 7.18-7.06 (m, 9H), 6.98 (t, *J* = 7.8 Hz, 1H), 6.69 (d, *J* = 7.8 Hz, 1H), 4.93 (d, *J* = 15.6 Hz, 1H), 4.74 (d, *J* = 15.6 Hz, 1H), 4.52 (d, *J* = 9.6 Hz, 1H), 4.40 (d, *J* = 9.6 Hz, 1H), 3.90-3.72 (m, 2H), 2.42 (s, 3H), 2.29 (s, 3H), 1.50 (bs, 1H). ¹³C-NMR (100 MHz, CDCl₃): δ 175.7, 144.9, 143.0, 137.3, 132.1, 131.9, 129.8, 129.5, 129.1, 127.9, 126.8, 123.9, 123.0, 109.7, 69.8, 63.9, 53.5, 43.5, 21.6, 21.0. 37% ee (HPLC: Daicel chiralcel AS (4.6 mm ϕ , 250 mm), *n*-Hexane : Isopropanol = 10 : 1, 254 nm, 1.0 ml/min, 17 min and 26 min (enriched)). [α]¹⁹_D -0.8 (*c* 0.9, CHCl₃). MS [HR-FAB(+)]: *m/z* calcd for C₂₅H₂₆O₅NS [M+H]⁺ 452.1532, found 452.1525.

4.3. Transformation of (R)-(+)-3-hydroxymethyl-1-methyl-3-(*p*-toluenesulfonyloxymethyl)oxindole (2d)

4.3.1. (R)-(+)-3-Benzyloxymethyl-3-cyanomethyl-1-methyloxindole (4). To a solution of **2d** (0.8 mmol) in CH₂Cl₂ (3 mL) was added BnOC(NH)CCl₃ (2.4 mmol) at 0 °C. Then, CF₃SO₃H (0.4 mmol) in CH₂Cl₂ (1 mL) was added slowly at 0 °C, and the reaction mixture was stirred at room temperature for 24 h. Saturated NH₄Cl was added and the resulting mixture was extracted with AcOEt. The combined organic layers were dried over MgSO₄ and filtration and concentration gave the crude product of (R)-3-benzyloxymethyl-1-methyl-3-(*p*-toluenesulfonyloxymethyl)oxindole **3**, which was used without further purification.

After stirred at room temperature for 10 min, the mixture of NaCN (3.2 mmol) and crude product **3** was stirred at 75 °C for 18 h. Then, cold water and ether were added at room temperature. The resulting mixture was extracted with ether and the aqueous layer was treated with 20% FeSO₄. The combined organic layers were washed with cold water and brine, and dried over MgSO₄. Concentration and purification through silica gel column chromatography gave (R)-(+)-3-benzyloxymethyl-3-

cyanomethyl-1-methyloxindole **4** in 76% yield (2 steps). Yellow oil. IR (neat): 2250, 1620, 1260 cm^{-1} . $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 7.38-6.92 (m, 9H), 4.50 (d, $J = 2.7$ Hz, 2H), 3.80 (d, $J = 9.0$ Hz, 1H), 3.62 (d, $J = 9.0$ Hz, 1H), 3.23 (s, 3H), 3.04 (d, $J = 16.5$ Hz, 1H), 2.76 (d, $J = 16.5$ Hz, 1H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 175.0, 143.5, 137.3, 129.4, 128.4, 128.2, 127.8, 127.5, 124.3, 123.1, 116.2, 108.6, 73.7, 72.2, 49.8, 26.5, 22.2. $[\alpha]_{\text{D}}^{22} +16.7$ (c 0.36, CH_2Cl_2). MS [HR-EI(+)]: m/z calcd for $\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_2$ $[\text{M}]^+$ 306.1368, found 306.1368.

4.3.2. (R)-(+)-3-((+)-10-Camphorsulfonyloxymethyl)-1-methyl-3-(p-toluenesulfonyloxymethyl)-oxindole (5). To a solution of **2d** (0.5 mmol) in CH_2Cl_2 (3 mL) was added triethylamine (1.0 mmol) and (+)-10-camphorsulfonyl chloride (0.6 mmol) and the mixture was stirred at room temperature for 6 h. Then, saturated NaHCO_3 was added, and the resulting mixture was extracted with ethyl acetate. The combined organic layers were dried over MgSO_4 and concentration and purification through silica gel column chromatography gave (R)-(+)-3-((+)-10-camphorsulfonyloxymethyl)-1-methyl-3-(p-toluenesulfonyloxymethyl)oxindole **5** in 86% yield. This product was recrystallized from diethyl ether, and X-ray crystallographic analysis was conducted. Colorless plates of mp 109-110 $^\circ\text{C}$. IR (neat): 2960, 1750, 1710, 1610, 1360, 1180 cm^{-1} . $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 7.68 (d, $J = 8.4$ Hz, 2H), 7.37-7.31 (m, 4H), 7.09-7.04 (m, 1H), 6.87-6.84 (m, 1H), 4.57 (d, $J = 9.9$ Hz, 1H), 4.41 (d, $J = 9.9$ Hz, 1H), 4.34 (d, $J = 9.6$ Hz, 1H), 4.18 (d, $J = 9.6$ Hz, 1H), 3.39 (d, $J = 15.0$ Hz, 1H), 3.21 (s, 3H), 2.84 (d, $J = 15.0$ Hz, 1H), 2.45 (s, 3H), 2.37-2.17 (m, 2H), 2.07 (t, $J = 4.5$ Hz, 1H), 2.01-1.93 (m, 1H), 1.87 (d, $J = 18.6$ Hz, 1H), 1.47-1.31 (m, 2H), 1.01 (s, 3H), 0.80 (s, 3H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 213.7, 172.5, 145.2, 143.8, 131.9, 129.9, 129.6, 127.9, 125.3, 124.8, 123.1, 108.6, 77.2, 69.4, 68.8, 57.6, 51.7, 47.9, 47.2, 42.6, 42.3, 26.8, 26.5, 24.7, 21.6, 19.54, 19.49. $[\alpha]_{\text{D}}^{22} + 24.0$ (c 0.5, CHCl_3). MS [HR-FAB(+)]: m/z calcd for $\text{C}_{28}\text{H}_{34}\text{O}_8\text{NS}_2$ $[\text{M}+\text{H}]^+$ 576.1720, found 576.1752.

Acknowledgments

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(16) Crystallographic data for (*R*)-(+)-3-((+)-10-camphorsulfonyloxymethyl)-1-methyl-3-(*p*-toluene-sulfonyloxymethyl)oxindole **5** was deposited in the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 767295. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK; fax: +44(0) 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk.