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

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Dedicated to Professor Henri Kagan on the occasion of his 80th birthday

ABSTRACT

A facile synthetic method toward 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.

1. Introduction

Oxindols are important heterocycles found in various naturally occurring compounds and biologically active molecules.[1] In particular, numerous methods have been reported for the enantioselective synthesis of oxindoles including Heck reaction,[2] cyanoamidation,[3] cycloaddition,[4] alkylation,[5] arylation,[6] 1,2-addition,[7] 1,4-addition,[8] hydroxylation,[9] fluorination,[10] rearrangement,[11] and addition to isatins.[12] In addition, enzyme-catalyzed asymmetric desymmetrization is known as an effective synthetic method for producing optically active oxindoles bearing a quaternary stereocenter at the 3-position,[13] but nonenzymic methods have not been reported. Recently, we have developed the 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.

2. Results and discussion

At first, 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). However, *N*-acetyloxindole **1b** gave the desired product **2b** with 9% yield and 63% ee (entry 2), and *N*-methoxymethyloxindole **1c** improved the enantioselectivity up to 99% ee although 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 a moderate yield while keeping 99% ee, *N*-(*p*-methylbenzyl)oxindole **1f** decreased both the chemical yield and the enantioselectivity (entries 5 and 6).

Next, we tried the transformation of monotosylated oxindole **2d** (Scheme 2). In the synthesis of **2d** using 1.2 equiv of tosyl chloride, the 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 conditions. The crude product of **3** was used for cyanation without further purification to give the compound **4** in 76% yield (over two steps). Chiral oxindole derivatives bearing 3-cyanomethyl group are known as useful synthetic intermediates.[3]

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 on 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*) (Fig. 1).

3. Conclusion

In summary, the enantioselective synthesis of oxindoles bearing a quaternary stereocenter at the 3-position was developed using the 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 a 3-cyanomethyl group via benzylation and cyanation. The absolute configuration of monotosylated oxindole **2d** was determined by the X-ray crystallographic analysis of the sulfonate ester **5**.

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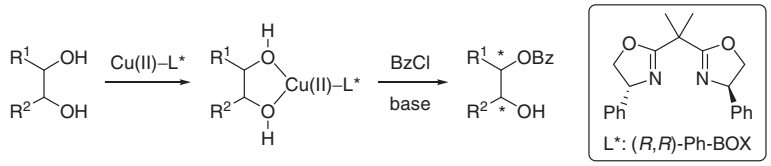
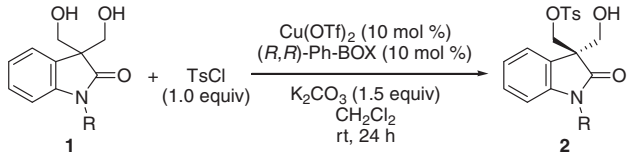


Scheme 1. Asymmetric benzoylation of 1,2-diols with Cu(II)–(*R*,*R*)-Ph-BOX.

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



1 2

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**	*p*-MeBn	**2f**	19	37

[a] Reaction conditions: 3,3-bis(hydroxymethyl)oxindole **1** (0.5 mmol), *p*-toluenesulfonyl chloride (0.5 mmol), K_2CO_3 (0.75 mmol), $Cu(OTf)_2$ (10 mol %), (*R*,*R*)-Ph-BOX (10 mol %), CH_2Cl_2 (2 mL), rt, 24 h.
[b] Isolated yield.
[c] Determined by HPLC.

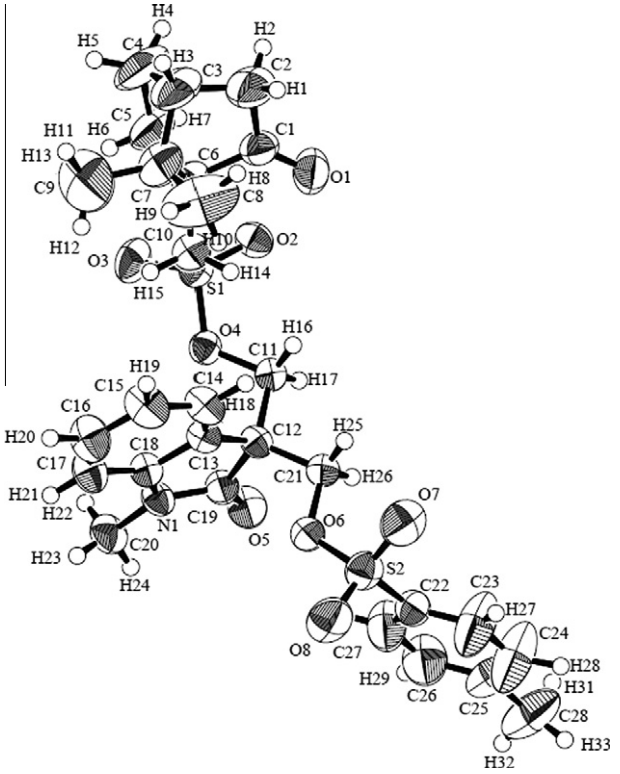


Figure 1. X-Ray crystal structure of (*R*)-(+)-3-((+)-10-camphorsulfonyloxymethyl)-1-methyl-3-(*p*-toluenesulfonyl)oxindole **5**.

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 the copper-catalyzed asymmetric monotosylation of 3,3-bis(hydroxymethyl)oxindoles

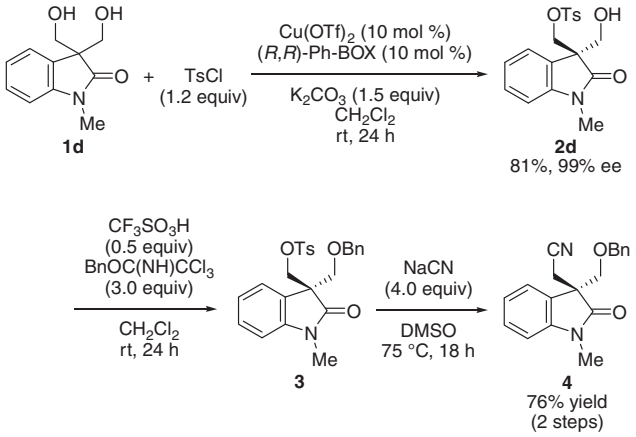
To a solution of $Cu(OTf)_2$ (0.05 mmol, 18.1 mg) and (*R*,*R*)-Ph-BOX (0.05 mmol, 16.7 mg) in CH_2Cl_2 (2 mL) were added 3,3-bis(hydroxymethyl)oxindoles **1e** (0.5 mmol, 89.6 mg), K_2CO_3 (0.75 mmol, 104 mg), and *p*-toluenesulfonyl chloride (0.6 mmol, 114 mg). After stirring for 24 h at room temperature, 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

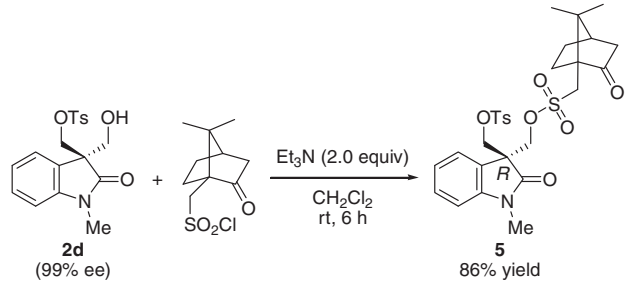
Yellow oil. IR (neat): 3400, 3020, 1760, 1720, 1640, 1470 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 8.23 (d, J = 8.1 Hz, 1H), 7.62 (d, J = 8.1 Hz, 1H), 7.42–7.10 (m, 6H), 4.46–4.38 (m, 2H), 3.93–3.81 (m, 2H), 2.63 (s, 3H), 2.45 (s, 3H), 2.04 (br s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.5, 170.4, 145.2, 140.5, 132.0, 129.9, 129.6, 127.9, 126.6, 125.5, 123.4, 116.8, 69.6, 64.6, 54.5, 26.6, 21.7. 63% ee (HPLC: Daicel chiralcel OG (4.6 mmφ, 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, $CHCl_3$). MS [HR-FAB(+)]: m/z calcd for $C_{19}H_{20}O_6NS$ $[M+H]^+$ 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, $CDCl_3$): 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). ^{13}C NMR (100 MHz, $CDCl_3$): 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, $CHCl_3$). MS [HR-FAB(+)]: m/z calcd for $C_{19}H_{22}O_6NS$ $[M+H]^+$ 392.1168, found 392.1193.



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



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

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, $CDCl_3$): 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 (br s, 1H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 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, $CHCl_3$). MS [HR-FAB(+)]: m/z calcd for $C_{18}H_{20}O_5NS$ $[M+H]^+$ 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, $CDCl_3$): 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), 3.94–3.78 (m, 2H), 2.56 (br s, 1H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 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)). $[\alpha]_D^{22} = +29.5$ (c 1.0, $CHCl_3$). MS [HR-FAB(+)]: m/z calcd for $C_{24}H_{24}O_5NS$ $[M+H]^+$ 438.1375, found 438.1375.

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

Yellow oil. IR (neat): 3360, 2920, 1700, 1620, 1470 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.60 (d, J = 8.1 Hz, 1H), 7.28–7.06 (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), 4.79 (d, J = 15.6 Hz, 1H), 4.52 (d, J = 9.6 Hz, 1H), 4.40 (d, J = 9.6 Hz, 1H), 3.90–3.77 (m, 2H), 2.50 (br s, 1H), 2.42 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.7, 144.9, 143.0, 135.0, 132.1, 129.8, 129.1, 128.8, 127.9, 127.6, 126.8, 126.5, 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 mmφ, 250 mm), *n*-hexane/isopropanol = 10:1, 254 nm, 1.0 mL/min, 17 min and 26 min (enriched)). $[\alpha]_D^{19} = -0.8$ (c 0.9, $CHCl_3$). MS [HR-FAB(+)]: m/z calcd for $C_{25}H_{26}O_5NS$ $[M+H]^+$ 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 CH_2Cl_2 (3 mL) was added $BnOC(NH)CCl_3$ (2.4 mmol) at 0 °C. Then, CF_3SO_3H (0.4 mmol) in CH_2Cl_2 (1 mL) was added slowly at 0 °C, and the reaction mixture was stirred at room temperature for 24 h. Saturated NH_4Cl was added and the resulting mixture was extracted with AcOEt. The combined organic layers were dried over $MgSO_4$, 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 stirring 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% $FeSO_4$. The combined organic layers were washed with cold water and brine, and dried over $MgSO_4$. Concentration and purification through silica gel column chromatography gave (*R*)-(+)-3-benzyloxymethyl-3-cyanomethyl-1-methyloxindole **4** in 76% yield (two steps). Yellow oil. IR (neat): 2250, 1620, 1260 cm^{-1}. ^1H 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}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. $[\alpha]_D^{22} = +16.7$ (c 0.36, CH_2Cl_2). MS [HR-EI(+)]: m/z calcd for $C_{19}H_{18}N_2O_2$ $[M]^+$ 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) were 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 °C. IR (neat): 2960, 1750, 1710, 1610, 1360, 1180 cm^{-1}. ^1H 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}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.

$[\alpha]_D^{22} = +24.0$ (c 0.5, $CHCl_3$). MS [HR-FAB(+)]: m/z calcd for $C_{28}H_{34}O_8NS_2$ $[M+H]^+$ 576.1726, found 576.1752.

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16. Crystallographic data for (*R*)-(+)-3-((+)-10-camphorsulfonyloxymethyl)-1-methyl-3-(*p*-toluenesulfonyloxymethyl)oxindole **5** were 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.