Diastereo- and Enantioselective Conjugate Addition of 3-Chlorooxindoles to Nitroalkenes Catalyzed by Binaphthyl-modified Organocatalyst

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Received December 24, 2014, Accepted January 9, 2015, Published online April 24, 2015

Keywords: Conjugate addition, 3-Chlorooxindoles, Asymmetric catalysis, Bifunctional organocatalysts

Oxindole derivatives have attracted considerable attention in organic synthesis and medicinal chemistry because of their prevalence in a number of natural and biologically active molecules.[1] Notably, 3,3-disubstituted oxindoles bearing a quaternary stereogenic center at position 3 are considered as crucial fragments of a number of natural products and medicinally important agents.[2] Therefore, the stereocontrolled synthesis of 3,3-disubstituted oxindole derivatives has become the subject of enormous interest over the past decades. Among the established strategies for the synthesis of chiral 3,3-disubstituted oxindoles, transition metal-catalyzed asymmetric reactions have been intensively studied.[3] Recently, a number of successful examples using various 3-monosubstituted oxindoles as nucleophiles reacting with diverse electrophiles to afford 3,3-disubstituted oxindoles have been reported.[4] However, there are a few reports for the synthesis of chiral 3-chloro-3-substituted oxindoles by the catalytic enantioselective C—C bond formation from 3-chlorooxindoles.[5] Although this method has been satisfied some extent as efficient process, new organocatalytic conjugate addition of 3-chlorooxindoles to nitroalkenes is highly desired.

As part of a research program related to the development of synthetic methods for the enantioselective construction of stereogenic carbon centers,[6] we recently reported enantioselective conjugate addition of active methylenes and methines using chiral organocatalysts.[7] Herein, we describe the enantioselective conjugate addition reaction of 3-chlorooxindoles to nitroalkenes catalyzed by binaphthyl-modified bifunctional organocatalysts bearing both central and axial chiral elements (Figure 1).

In an attempt to validate the feasibility of the organocatalytic enantioselective Michael addition of 3-chlorooxindoles, we investigated a reaction system with 3-chloroindolin-2-one (**1a**) with β-nitrostyrene (**2a**) in the presence of 10 mol% of catalyst in dichloromethane at room temperature. We first surveyed the effect of the structure of catalysts **I–VIII** on enantioselectivity (Table 1, entries 1–8). High yields and excellent enantioselectivities were observed for binaphthyl-derived squaramide catalyst **VIII** (93% ee, entry 8). A survey of the reaction media indicated that this reaction was highly solvent-dependent (entries 9–13). Among the solvents probed, the halogenated solvents gave the best results in the yields and enantiomeric excesses. The effective catalyst loading could be reduced to 5 mol% without compromising the yield or the enantioselectivity (entries 14–15). The

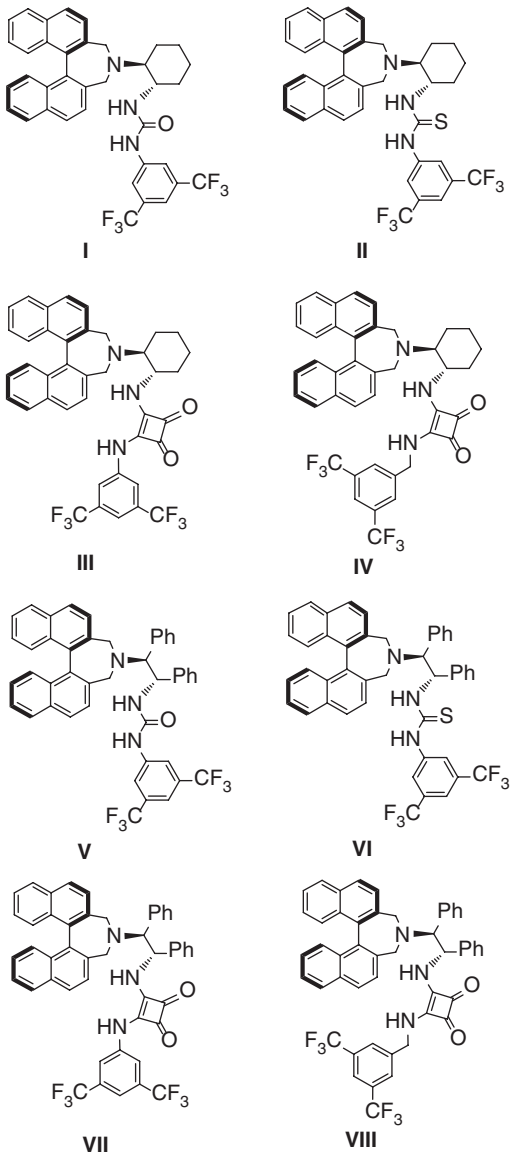
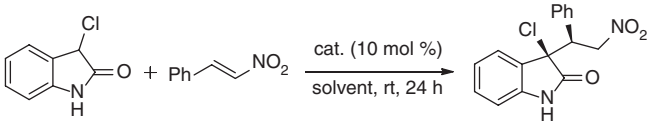


Figure 1. Structures of organocatalysts.

Table 1. Optimization of the reaction conditions.[a]

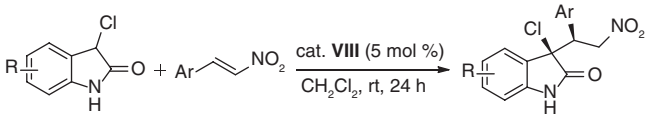


1a **2a** **3a**

Entry	Cat.	Solvent	Yield[b] (%)	dr[c]	ee[d] (%)
1	**I**	CH_2Cl_2	95	2:1	87
2	**II**	CH_2Cl_2	73	5:1	87
3	**III**	CH_2Cl_2	70	1.2:1	90
4	**IV**	CH_2Cl_2	52	3:1	91
5	**V**	CH_2Cl_2	54	3:1	78
6	**VI**	CH_2Cl_2	68	3:1	82
7	**VII**	CH_2Cl_2	73	20:1	92
8	**VIII**	CH_2Cl_2	85	14:1	93
9	**VIII**	$CHCl_3$	73	10:1	92
10	**VIII**	$ClCH_2CH_2Cl$	70	19:1	91
11	**VIII**	Et_2O	56	1.5:1	68
12	**VIII**	THF	trace	—	—
13	**VIII**	PhMe	trace	—	—
14[e]	**VIII**	CH_2Cl_2	83	13:1	93
15[f]	**VIII**	CH_2Cl_2	20	13:1	93

[a] Reaction conditions: 3-chlorooxindole (**1a**, 0.3 mmol), β-nitrostyrene (**2a**, 0.45 mmol), catalyst (0.03 mmol), solvent (3.0 mL) at room temperature.
[b] Isolated yield.
[c] Determined by ^{1}H NMR analysis.
[d] Enantiopurity was determined by HPLC analysis using Chiralcel OD-H column.
[e] 5 mol% catalyst loading.
[f] 2.5 mol% catalyst loading.

Table 2. Substrate scope.[a]



1 **2** **3**

Entry	**1**, *R*	**2**, Ar	Yield[b] (%)	dr[c]	ee[d] (%)
1	H	Ph	**3a**, 83	13:1	93
2	H	4-Me-Ph	**3b**, 85	10:1	90
3	H	4-OMe-Ph	**3c**, 71	8:1	89
4	H	4-F-Ph	**3d**, 84	10:1	90
5	H	3-F-Ph	**3e**, 79	11:1	95
6	H	2-F-Ph	**3f**, 77	8:1	94
7	H	2-NO_2-Ph	**3g**, 91	6:1	95
8	H	3-NO_2-Ph	**3h**, 64	12:1	97
9	H	2-furyl	**3i**, 90	8:1	91
10	H	2-thienyl	**3j**, 86	8:1	89
11	4-Cl	Ph	**3k**, 80	15:1	89
12	6-Cl	Ph	**3l**, 71	19:1	98

[a] Reaction conditions: 3-chlorooxindoles (**1**, 0.3 mmol), nitroalkene (**2**, 0.45 mmol), catalyst **IV** (0.015 mmol), solvent (3.0 mL) at room temperature.
[b] Isolated yield.
[c] Determined by ^{1}H NMR analysis.
[d] Enantiopurity was determined by HPLC analysis using Chiralcel OD-H (**3a**), OF (**3h**), Chiralpak IB (**3b**, **3d**, **3g** , **3i**, and **3l**), IB-3 (**3e** and **3f**), IC (**3j** and **3k**), and ID (**3c**) columns.

absolute configuration of **3** was established by comparison of the optical rotation and chiral HPLC analysis with previously reported values.[5]

With the optimized conditions in hand, we proceeded to investigate the scope of the enantioselective conjugate addition of 3-chlorooxindoles with various nitroalkenes **2** in the presence of 5 mol% of binaphthyl-modified squaramide-tertiary amine catalyst **IV** in dichloromethane at room temperature (Table 2, entries 1–10). The corresponding Michael products **3a–3j** were formed in high yields (71–91%), high diastereoselectivities (6–19:1), and excellent enantioselectivities (89–95%). The substituents of the aromatic nitroalkenes had limited effects on the reaction efficiency. A chlorine atom substitution on the aryl ring of the 3-chlorooxindoles **1k–1l** provided corresponding products in high yields and high enantioselectivities (89–98%, entries 11–12).

In summary, we have developed highly efficient catalytic enantioselective Michael addition reactions of 3-chlorooxindoles to nitroalkenes using bifunctional organocatalyst. The desired Michael products were obtained in high yields and diasteroselectivities. Also, the excellent enantioselectivities were observed (89–95% ee). We believe that this method provides a practical entry to biologically useful chiral 3-chloro-3-substituted oxindoles.

Experimental

General. All commercial reagents and solvents were used without purification. TLC analyses were carried out on pre-coated silica gel plates with F_{254} indicator. Visualization was accomplished by UV light (254 nm), I_2, *p*-anisaldehyde, ninhydrin, and phosphomolybdic acid solution as an indicator. Purification of reaction products was carried out by flash chromatography using Merck silica gel 60 (Darmstadt, Germany, 230–400 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded on a Jeol ECS400 MHz NMR (Tokyo, Japan, 400 MHz for ^{1}H and 100 MHz for ^{13}C). Chemical shift values (δ) are reported in ppm relative to Me_4Si (δ 0.0 ppm). Optical rotations were measured on a JASCO-DIP-1000 digital polarimeter (Tokyo, Japan) with a sodium lamp. The enantiomeric excesses (ee) were determined by HPLC. HPLC analysis was performed on Younglin M9100 Series (Seoul, Korea), measured at 230 nm using the indicated chiral column.

Typical Procedure for the Michael Addition of 3-Chlorooxindole (1a) with β-Nitrostyrene (2a). To a solution of 3-chloroxindole (**1a**, 0.3 mmol, 50.3 mg) and catalyst **VIII** (0.015 mmol, 12.2 mg) in CH_2Cl_2 (3.0 mL) was added β-nitrostyrene (**2a**, 0.45 mmol, 67.1 mg). Reaction mixture

was stirred for 1 day at room temperature, concentrated, and purified by flash column chromatography (CH_2Cl_2:EtOAc = 20:1) to afford the Michael adduct (**3a**, 83 mg, 83%).

(*R*)-3-chloro-3-((*S*)-2-nitro-1-phenylethyl)indolin-2-one (3a). $[\alpha]_D^{27} = -172.16$ (c = 1, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-d) δ 7.79 (s, 1H), 7.31 (td, *J* = 15.6, 1.4 Hz, 1H), 7.28–7.24 (m, 1H), 7.19–7.15 (m, 2H), 7.05 (td, *J* = 14.8, 1.4 Hz, 1H), 6.99–6.97 (m, 2H), 6.9 (d, *J* = 8 Hz, 1H), 6.79 (d, *J* = 8Hz, 1H), 5.67 (dd, *J* = 13.4, 3.8 Hz, 1H), 5.15 (dd, *J* = 13.2, 11.2 Hz, 1H), 4.29 (dd, *J* = 11, 3.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.86, 139.92, 132.64, 131.16, 129.50, 129.17, 128.97, 128.67, 127.25, 126.06, 123.47, 110.81, 75.62, 66.13, 50.72; the ee value was 93%, t_R (major) = 29.4 min, t_R (minor) = 21.9 min (Chiralcel OD-H, λ = 230 nm, Hex/*i*-PrOH 95/5, flow rate = 1.0 mL/min).

(*R*)-3-chloro-3-((*S*)-2-nitro-1-(*p*-tolyl)ethyl)indolin-2-one (3b). $[\alpha]_D^{22} = -88.08$ (c = 1, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-d) δ 7.82 (s, 1H), 7.30 (td, *J* = 15.6, 1.2 Hz, 1H), 7.06 (td, *J* = 15.6, 1 Hz, 1H), 6.98–6.93 (m, 3H), 6.85 (d, *J* = 8 Hz, 2H), 6.79 (d, *J* = 8, 1H), 5.64 (dd, *J* = 13.2, 3.6 Hz, 1H), 5.12 (dd, *J* = 13.2, 11.6 Hz, 1H), 4.26 (dd, *J* = 11.4, 3.8 Hz, 1H), 2.26 (s, 3H); the ee value was 90%, t_R (major) = 17.8 min, t_R (minor) = 13.8 min (Chiralcel IB, λ = 230 nm, Hex/*i*-PrOH 95/5, flow rate = 1.0 mL/min).

(*R*)-3-chloro-3-((*S*)-1-(4-methoxyphenyl)-2-nitroethyl) indolin-2-one (3c). $[\alpha]_D^{22} = -93.76$ (c = 0.5, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-d) δ 7.03 (td, *J* = 15.4, 1.2 Hz, 1H), 7.17 (s, 1H), 7.07 (td, *J* = 15.2, 1.2 Hz, 1H), 7.00–6.96 (m, 1H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.75 (d, *J* = 8 Hz, 1H), 6.68 (d, *J* = 8.8 Hz, 2H), 5.62 (dd, *J* = 9.4, 3.4 Hz, 1H), 5.09 (dd, *J* = 13, 11.8 Hz, 1H), 4.27 (dd, *J* = 11.6, 3.6 Hz, 1H), 3.74 (s, 3H). The ee value was 89%, t_R (major) = 35.1 min, t_R (minor) = 32.9 min (Chiralcel ID, λ = 230 nm, Hex/*i*-PrOH 95/5, flow rate = 1.0 mL/min).

(*R*)-3-chloro-3-((*S*)-1-(4-fluorophenyl)-2-nitroethyl)indolin-2-one (3d): $[\alpha]_D^{23} = -90.92$ (c = 1, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-d) δ 7.97 (s, 1H), 7.33 (td, *J* = 15.4, 1.4 Hz, 1H), 7.08 (td, *J* = 15.6, 1 Hz, 1H), 6.98–6.94 (m, 3H), 6.89–6.81 (m, 3H), 5.65 (dd, *J* = 13.2, 3.6 Hz, 1H), 5.09 (dd, *J* = 13.2, 11.2 Hz, 1H), 4.30 (dd, *J* = 11.4, 3.4 Hz, 1H); the ee value was 90%, t_R (major) = 22.4 min, t_R (minor) = 16.8 min (Chiralcel IB, λ = 230 nm, Hex/*i*-PrOH 95/5, flow rate = 1.0 mL/min).

(*R*)-3-chloro-3-((*S*)-1-(3-fluorophenyl)-2-nitroethyl)indolin-2-one (3e). $[\alpha]_D^{28} = -113.92$ (c = 1, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-d) δ 7.92 (s, 1H), 7.33 (td, *J* = 15.6, 1 Hz, 1H), 7.19–7.14 (m, 1H), 7.07 (td, *J* = 15, 1 Hz, 1H), 7.00–6.95 (m, 1H), 6.91 (d, *J* = 8 Hz, 1H), 6.84–6.79 (m, 2H), 5.67 (dd, *J* = 13.4, 3.4 Hz, 1H), 5.10 (dd, *J* = 13.4, 11.4 Hz, 1H), 4.29 (dd, *J* = 11.6, 3.6 Hz, 1H); the ee value was 95%, t_R (major) = 122.1 min, t_R (minor) = 102.7 min (Chiralcel IB-3, λ = 230 nm, Hex/*i*-PrOH 99/1, flow rate = 1.0 mL/min).

(*R*)-3-chloro-3-((*S*)-1-(2-fluorophenyl)-2-nitroethyl)indolin-2-one (3f). $[\alpha]_D^{23} = -70.92$ (c = 1, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-d) δ 8.08 (s, 1H), 6.98–6.92 (m, 2H), 6.88 (d, *J* = 8 Hz, 1H), 6.54 (d, *J* = 7.6 Hz, 1H), 7.36–7.29 (m, 3H), 7.12 (td, *J* = 15.4, 1 Hz, 1H), 5.75 (dd, *J* = 14, 4 Hz, 1H), 5.16 (dd, *J* = 13.8, 11 Hz, 1H), 4.64 (dd, *J* = 11, 3.8 Hz, 1H); the ee value was 94%, t_R (major) = 27.4 min, t_R (minor) = 20.2 min (Chiralcel IB-3, λ = 230 nm, Hex/*i*-PrOH 95/5, flow rate = 1.0 mL/min).

(*R*)-3-chloro-3-((*S*)-2-nitro-1-(2-nitrophenyl)ethyl)indolin-2-one (3g). $[\alpha]_D^{23} = -91.16$ (c = 1, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-d) δ 8.49 (s, 1H), 7.88 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.80–7.78 (m, 1H), 7.68 (td, *J* = 15.6, 1.4 Hz, 1H), 7.57 (td, *J* = 15.6, 1.2 Hz, 1H), 7.29 (dd, *J* = 8, 1.2 Hz, 1H), 6.96 (d, *J* = 4 Hz, 1H), 6.86 (td, *J* = 15.2, 0.8 Hz, 1H), 6.26 (d, *J* = 7.6 Hz, 1H), 5.82 (dd, *J* = 14, 3.6 Hz, 1H), 5.28 (dd, *J* = 10.6, 3.4 Hz, 1H), 5.17 (dd, *J* = 13.8, 10.6 Hz, 1H); the ee value was 95%, t_R (major) = 68.0 min, t_R (minor) = 55.0 min (Chiralcel IB, λ = 230 nm, Hex/*i*-PrOH 95/5, flow rate = 1.0 mL/min).

(*R*)-3-chloro-3-((*S*)-2-nitro-1-(3-nitrophenyl)ethyl)indolin-2-one (3h). $[\alpha]_D^{23} = -102.40$ (c = 1, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-d) δ 7.68 (s, 1H), 7.31 (td, *J* = 15.4, 1 Hz, 1H), 7.10–7.05 (m, 2H), 6.97 (d, *J* = 7.6 Hz, 1H), 6.80–6.77 (m, 2H), 6.57 (d, *J* = 7.2 Hz, 1H), 6.48–6.47 (m, 1H), 5.65 (dd, *J* = 13.2, 3.6 Hz, 1H), 5.12 (dd, *J* = 13.2, 11.6 Hz, 1H), 4.28 (dd, *J* = 11.6, 3.6 Hz, 1H); the ee value was 97%, t_R (major) = 78.0 min, t_R (minor) = 107.3 min (Chiralcel OF, λ = 230 nm, Hex/*i*-PrOH 95/5, flow rate = 1.0 mL/min).

(*R*)-3-chloro-3-((*R*)-1-(furan-2-yl)-2-nitroethyl)indolin-2-one (3i). $[\alpha]_D^{23} = -73.12$ (c = 1, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-d) δ 8.15 (s, 1H), 7.30 (td, *J* = 15.6, 1.0 Hz, 1H), 7.25–7.24 (m, 1H), 7.04 (td, *J* = 15, 1 Hz, 1H), 6.87 (d, *J* = 8 Hz, 1H), 6.80 (d, *J* = 8 Hz, 1H), 6.29–6.23 (m, 2H), 5.64 (dd, *J* = 13.6, 3.6 Hz, 1H), 5.16 (dd, *J* = 13.8, 11 Hz, 1H), 4.44 (dd, *J* = 11.2, 3.6 Hz, 1H); the ee value was 91%, t_R (major) = 19.9 min, t_R (minor) = 17.4 min (Chiralcel IB, λ = 230 nm, Hex/*i*-PrOH 95/5, flow rate = 1.0 mL/min).

(*R*)-3-chloro-3-((*R*)-2-nitro-1-(thiophen-2-yl)ethyl)indolin-2-one (3j). $[\alpha]_D^{22} = -82.92$ (c = 1, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-d) δ 8.10 (s, 1H), 7.35 (td, *J* = 15.6, 1.4 Hz, 1H), 7.19–7.17 (m, 1H), 7.08 (td, *J* = 15.4, 1.2 Hz, 1H), 6.95 (d, *J* = 7.2 Hz, 1H), 6.87–6.80 (m, 3H), 5.70 (dd, *J* = 13, 3.4 Hz, 1H), 5.02 (dd, *J* = 13.2, 11.2 Hz, 1H), 4.63 (dd, *J* = 11.2, 3.2 Hz, 1H); the ee value was 89%, t_R (major) = 20.8 min, t_R (minor) = 19.2 min (Chiralcel IC, λ = 230 nm, Hex/*i*-PrOH 95/5, flow rate = 1.0 mL/min).

(*R*)-3,4-dichloro-3-((*S*)-2-nitro-1-phenylethyl)indolin-2-one (3k). $[\alpha]_D^{28} = -86.72$ (c = 1, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-d) δ 7.98 (s, 1H), 7.24–7.10 (m, 5H), 6.97–6.95 (m, 2H), 6.63 (dd, *J* = 7.4, 1.2 Hz, 1H), 5.51 (dd, *J* = 13.6, 3.2 Hz, 1H), 5.38 (dd, *J* = 13.4, 11.8 Hz, 1H), 4.56 (dd, *J* = 11.6, 3.2 Hz, 1H); the ee value was 89%, t_R (major) = 12.8 min, t_R (minor) = 15.3 min (Chiralcel IC, λ = 230 nm, Hex/*i*-PrOH 95/5, flow rate = 1.0 mL/min).

(*R*)-3,6-dichloro-3-((*S*)-2-nitro-1-phenylethyl)indolin-2-one (3l). $[\alpha]_D^{24} = -280.64$ (c = 0.25, CH_2Cl_2); ^{1}H NMR (400

MHz, Chloroform-d) δ 7.34 (s, 1H), 7.32–7.21 (m, 3H), 7.04–7.02 (m, 2H), 7.00 (dd, J = 8.2, 1.8 Hz, 1H), 6.80 (d, J = 2 Hz, 1H), 6.69 (d, J = 8 Hz, 1H), 5.67 (dd, J = 13.2, 3.6 Hz, 1H), 5.12 (dd, J = 13.6, 11.2 Hz, 1H), 4.24 (dd, J = 10.8, 3.6 Hz, 1H); the ee value was 98%, t_R (major) = 125.6 min, t_R (minor) = 115.4 min (Chiralcel IB, λ = 230 nm, Hex/*i*-PrOH 99/1, flow rate = 1.0 mL/min).

Acknowledgment. This research was supported by Soonchunhyang University Research Fund.

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