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Highly Enantioselective Michael Addition of 2-Oxindole-3-carboxylate Esters to Nitroolefins Promoted by *Cinchona* Alkaloid-Thiourea-Brønsted Acid Cocatalysts

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Abstract: A highly efficient organocatalyzed Michael addition of 2-oxindole-3-carboxylate esters to nitroolefins using a *Cinchona* alkaloid-thiourea and an achiral Brønsted acid as cooperative organocatalysts is reproted that affords significantly improved enantioselectivity and diastereoselectivity. It also provides an efficient approach to the synthesis of spirooxindole derivatives with high enantioselectivity.

Keywords: nitroolefins; 2-oxindole-3-carboxylate esters; spirooxindoles; thiourea-Brønsted cocatalysis

Oxindole alkaloids bearing a quaternary carbon stereocenter, especially spirooxindoles, represent a prevalent scaffold found in natural products and biologically active compounds,[1] such as horsfiline, coerulescine, rychnophylline, spirotryprostatin A and B, CPC-1 and the orally bioavailable CRTH2 (DP2) receptor antagonist(Figure 1).

An impressive number of organocatalyzed asymmetric reactions have been developed based on the oxindole motif, including conjugate addition,[2] Henry reaction,[3] aldol reaction,[4] Mannich reaction,[5] alkylation,[6] cycloaddition[7] and domino reactions.[8] Among these reactions, asymmetric Michael additions are one of the most powerful tools in synthetic organic chemistry. The pioneering work on the Michael addition of oxindole to nitroolefin was undertaken by Barbas III,[2a,k] Shibasaki,[9] Cheng,[2b] Yuan[2c] and Zhou.[2d,e] Despite these advances, most of these strategies are limited to 3-alkyl- or 3-aryl-substituted oxindoles.[2–9] These limitations have renewed the impetus to develop alternative strategies for the asymmetric synthesis of versatile oxindole scaffolds.

In recent years, important contributions have been made to the development of bifunctional thiourea catalysts, which have been widely applied in the enantio-

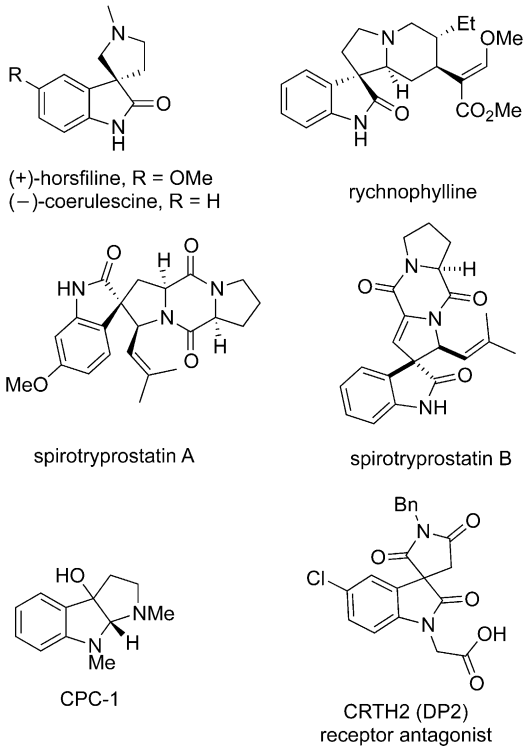
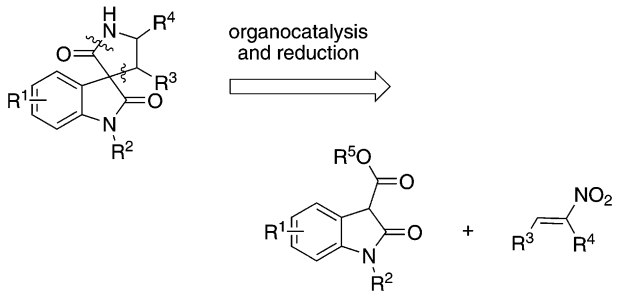


Figure 1. Examples of quaternary carbon-bearing oxindole alkaloids.



Scheme 1. An alternative approach to spirooxindoles.

selective Michael addition of malonate esters to nitroolefins.[10] However, to the best of our knowledge, ethyl 2-oxoindoline-3-carboxylate (easily derived from oxindole)[11] has been less used as a nucleophile in the organocatalysis field. As an alternative of the known protocols, variously substituted spirooxindole products could be obtained *via* the asymmetric Michael addition of ethyl 2-oxoindoline-3-carboxylates to nitroolefins using an organocatalyst (Scheme 1). Here, we wish to report a new valuable example of cooperative thiourea-Brønsted acid organocatalyzed Michael addition of 2-oxindole-3-carboxylates to nitroolefins which could be applied to the synthesis of spirooxindole derivatives.

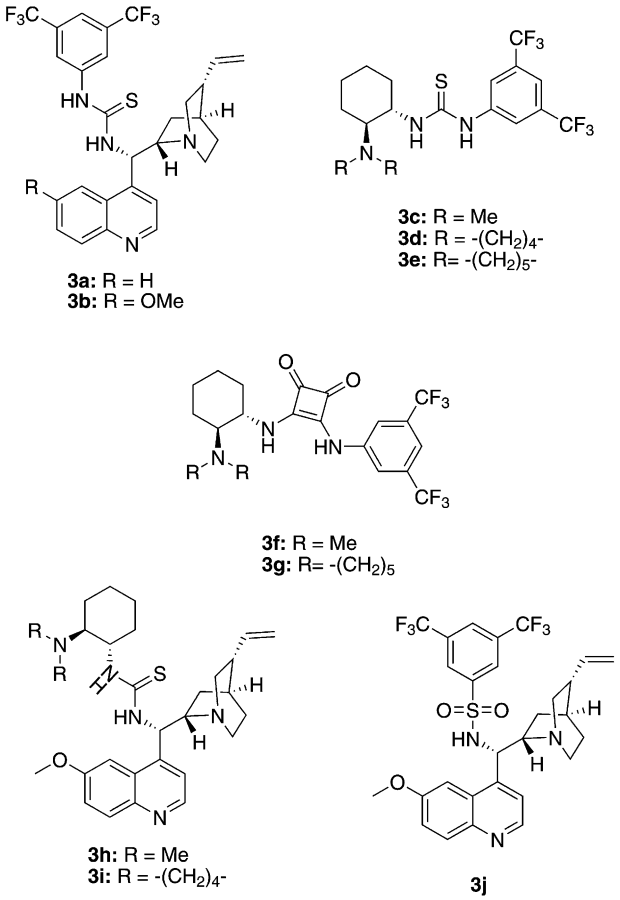


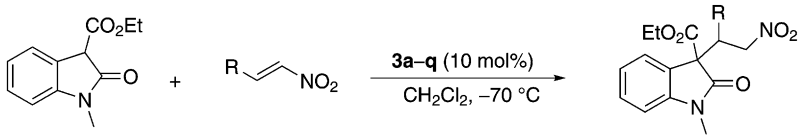
Figure 2. Screened catalysts.

A variety of catalysts **3a–3j** (Figure 2) was evaluated for the Michael addition of oxindole **1a** to nitroolefin **2a** and the results are summarized in Table 1. Use of catalysts **3a–3e** gave high yields (up to 99%) and enantiomeric excesses (*ee*) (up to 99%) when the reactions were performed in CH_2Cl_2 at −70 °C (Table 1, entries 1–5). Chiral squaramide derivatives **3f** and **3g** were also investigated but the results proved disappointing (entries 6 and 7). To further optimize the reaction conditions with the aim to improve the diastereoselectivity, multifunctional catalysts **3h** and **3i** derived from chiral *trans*-cyclohexane-1,2-diamine and *Cinchona* alkaloid thiourea were tested (entries 8 and 9). Unfortunately, both of them gave unsatisfactory results. Quinidine-derived sulfonamide **3j** also turned out to be a poor catalyst (entry 10). Examination of different solvents indicated that CH_2Cl_2 was the optimal choice (see the Supporting Information, Table 1).

On the basis of the results, four additional nitroolefin substrates were examined using the catalyst **3d**. Unfortunately, the level of stereocontrol decreased obviously (entries 11–14). It is presumed that the distance between the two oxygen atoms of the dicarbonyl was shortened by the oxindole skeleton and catalyst **3d** bearing the pyrrolidine unit. Such a change may have led to a crowd-structure interaction. For this reason, two other suitable catalysts, **3b** and **3c**, were both employed on substrate **2c** with little modification. Gratifyingly, higher *ee*s (88% and 84%) were obtained with catalysts **3b** and **3c** than that with **3d** (entries 15 and 16). Inspired by previous reports of thiourea-Brønsted acid cooperative organocatalysis,[13] we also evaluated a number of Brønsted acids as co-catalysts in this reaction (entries 17–22). Rewardingly, the enantioselectivity increased to 96% when both **3b** (10 mol%) and benzoic acid (10 mol%) were employed, and the corresponding diastereoselectivity was improved as well. The result was almost unchanged upon decreasing the catalyst loading to 5 mol% (entry 23).

Encouraged by the above excellent results of substrate **2c** (Table 1, entry 22), we further examined the substrate generality with various substituted nitroolefins. As depicted in Table 2, nitroolefins **2b–2l** with either electron-donating or electron-withdrawing groups worked efficiently and afforded the corresponding products in excellent yields (91–99%) and high enantioselectivities (90–98%) with moderate to good diastereoselectivities (79:21 to 90:10) (Table 2, entries 2–12). However, use of 4-nitrostyrene **2m** resulted in decreased enantioselectivity (Table 2, entry 13), which may be due to a direct inhibitory effect on the formation of favourable hydrogen bonds by the nitro group of **2m**. Heteroaromatic nitroolefin **2n** also proved to be a feasible substrate generating

Table 1. Catalyst screening and reaction optimization.[a]



1a **2a:** R = Ph; **2b:** R = 4-MeO-C_6H_4; **2c:** R = 4-CH_3-C_6H_4; **2d:** R = 4-Br-C_6H_4; **2e:** R = 2-Br-C_6H_4 **4a–e**

Entry	**2**	Catalyst (mol%)	Additive (mol%)	Time [h]	Yield of **4** [%][b]	*dr*[c]	*ee* [%][d]
1	**2a**	**3a**	–	12	99 (**4a**)	80:20	85
2	**2a**	**3b**	–	12	99 (**4a**)	79:21	94
3	**2a**	**3c**	–	12	95 (**4a**)	78:22	97
4	**2a**	**3d**	–	12	99 (**4a**)	80:20	99
5	**2a**	**3e**	–	12	99 (**4a**)	72:28	82
6	**2a**	**3f**	–	12	95 (**4a**)	60:40	88
7	**2a**	**3g**	–	12	72 (**4a**)	67:33	40
8	**2a**	**3h**	–	12	99 (**4a**)	67:33	82
9	**2a**	**3i**	–	12	99 (**4a**)	77:23	91
10	**2a**	**3j**	–	12	78 (**4a**)	62:38	65
11	**2b**	**3d**	–	24	95 (**4b**)	67:33	73
12	**2c**	**3d**	–	12	99 (**4c**)	75:25	74
13	**2d**	**3d**	–	12	98 (**4d**)	80:20	82
14	**2e**	**3d**	–	12	98 (**4d**)	80:20	85
15	**2c**	**3b**	–	12	99 (**4c**)	81:19	88
16	**2c**	**3c**	–	12	99 (**4c**)	67:33	84
17	**2c**	**3b** (20)	$PhCO_2H$ (10)	24	99 (**4c**)	79:21	93
18	**2c**	**3b**	**$PhCO_2H$ (10)**	**24**	**99** (**4c**)	**84:16**	**96**
19	**2c**	**3b**	*o*-NO_2-$PhCO_2H$ (10)	24	94 (**4c**)	83:17	85
20	**2c**	**3b**	CH_3CO_2H (10)	24	99 (**4c**)	82:18	92
21	**2c**	**3b**	CCl_3CO_2H (10)	24	57 (**4c**)	84:16	89
22	**2c**	**3b**	CF_3CO_2H (10)	24	91 (**4c**)	81:19	87
23	**2c**	**3b** (5)	$PhCO_2H$ (5)	24	99 (**4c**)	81:19	94

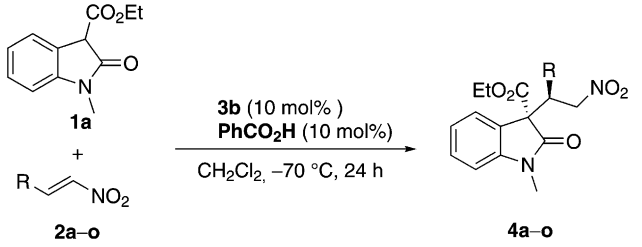
[a] Unless otherwise noted, reactions were performed with oxindoles **1a** (0.1 mmol) and nitroolefins **2** (2.0 equiv.) in the presence of 10 mol% catalyst **3** in 2 mL of CH_2Cl_2.
[b] Isolated yields.
[c] Determined by ^{1}H NMR or HPLC analysis.
[d] Determined by chiral HPLC analysis for the major diastereomer.

the desired product **4n** (Table 2, entry 14) with high yield (95%) and good enantioselectivity (86%). Furthermore, the reaction was found to proceed smoothly with an alkyl-substituted nitroolefin, giving **4o** in 90% yield with high enantioselectivity (82/94% *ee*) but poor diastereoselectivity (60:40).

To further expand the substrate scope, a series of oxindoles **1b–1k** and nitroolefin **2g** were examined (Table 3). The processes were highly efficient for all the cases with different substituents on the aromatic ring (**1b–1f**) and ester carboxylate (**1g**) oxindoles, affording products **4p–4u** with high yields and enantioselectivities (Table 3, entries 1–6). It is worth noting that *N*-Bn and *N*-MOM protecting groups had no influence on the enantioselectivity (Table 3, entries 7 and 8). Use of unprotected oxindole **1k** also led to an excellent yield and a good enantioselectivity (Table 3, entry 10). However, when the protecting group on the nitrogen atom was CO_2Et, the yield decreased significantly under our optimized conditions (Table 3, entry 9).

The benzoic acid additive played an important role in this process due to its enforcement effect in the enantioselectivities and diastereoselectivities. Schreiner,[13b] Najera,[13c] Jacobsen,[13d,e] and Wang[2i,3] also reported similar cooperative catalysis systems. Schreiner found that hydrogen-bonding interactions were formed in the bifunctional thiourea and Brønsted acid cooperative system using NMR techniques. Similar ^{1}H NMR experiments were also reproduced in our system (see the Supporting Information, Figure 1). We envisaged that the tertiary amine of thiourea **3b** may be protonated by the weak Brønsted acid which was similar to organic ion-pair formation.[14] The protonated catalyst **3b** may result in a slower deprotonation of the 1,3-dicarbonyl moiety leading to the improvement of the enantioselectivity in this reaction. Unfortunately, no clear evidence colud explain wheth-

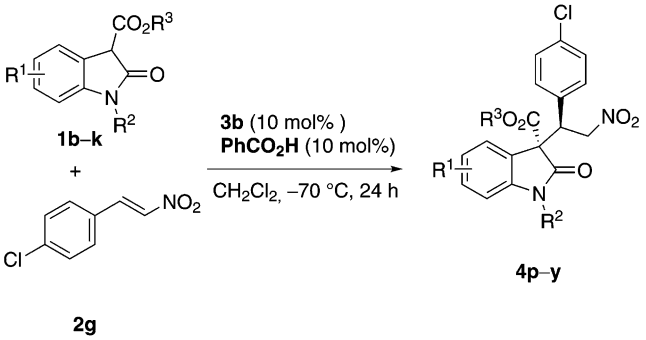
Table 2. Asymmetric Michael addition of ethyl 1-methyl-oxoindoline-3-carboxylate to a series of nitroolefins.[a]



Entry	R	Yield of **4** [%][b]	*dr*[c]	*ee* [%][d]
1	C_6H_5 (**2a**)	99 (**4a**)	88:12	97
2[e]	4-MeO-C_6H_4 (**2b**)	98 (**4b**)	79:21	90
3	4-CH_3-C_6H_4 (**2c**)	99 (**4c**)	84:16	96
4	4-Br-C_6H_4 (**2d**)	98 (**4d**)	87:13	96
6	2-Br-C_6H_4 (**2e**)	99 (**4e**)	85:15	97
5	3-Br-C_6H_4 (**2f**)	99 (**4f**)	87:13	96
7	4-Cl-C_6H_4 (**2g**)	99 (**4g**)	89:11	98
8	2-Cl-C_6H_4 (**2h**)	99 (**4h**)	86:14	97
9	2,4-Cl_2-C_6H_3 (**2i**)	99 (**4i**)	82:18	94
10	2-naphthyl (**2j**)	97 (**4j**)	86:14	93
11	4-F-C_6H_4 (**2k**)	91 (**4k**)	92:08	97
12	4-CF_3-C_6H_4 (**2l**)	98 (**4l**)	90:10	94
13	4-NO_2-C_6H_4 (**2m**)	93 (**4m**)	89:11	72
14	2-furanyl (**2n**)	95 (**4n**)	67:33	86
15[f]	*n*-Pr (**2o**)	90 (**4o**)	60:40	82/94[g]

[a] Unless otherwise noted, reactions were performed with oxindoles **1a** (0.1 mmol) and nitroolefins **2a–2o** (2.0 equiv.) in the presence of 10 mol% catalyst **3b** and 10 mol% benzoic acid in 2 mL of CH_2Cl_2.
[b] Isolated yields.
[c] Determined by ^{1}H NMR or HPLC analysis.
[d] Determined by chiral HPLC analysis for the major diastereomer. The absolute configuration was determined by X-ray analysis of the major diastereomer **4e** (see the Supporting Information). The other major diastereomers were assigned accordingly.[12]
[e] Performed for 36 h.
[f] Performed at −60 °C for 36 h.
[g] The *ee* value of the minor diastereomer.

Table 3. Substrate scope of asymmetric Michael additions of a variety of oxindoles with nitroolefin **2g**.[a]



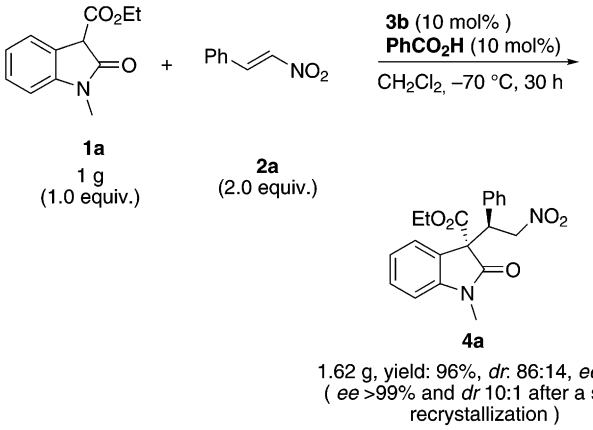
Entry	R^1, R^2, R^3	Yield [%][b]	*dr*[c]	*ee* [%][d]
1	5-OMe, Me, Et (**1b**)	99 (**4p**)	95:5	97
2	5-Cl, Me, Et (**1c**)	99 (**4q**)	82:18	94
3	7-Cl, Me, Et (**1d**)	99 (**4r**)	81:19	95
4	5-Br, Me, Et (**1e**)	98 (**4s**)	80:20	94
5	5-F, Me, Et (**1f**)	99 (**4t**)	84:16	95
6	H, Me, *i*-Bu (**1g**)	98 (**4u**)	86:14	95
7	H, Bn, Et (**1h**)	96 (**4v**)	67:33	93
8	H, MOM, Et (**1i**)	96 (**4w**)	78:22	95
9	H, CO_2Et, Et (**1j**)	48 (**4x**)	n.d.[e]	n.d.[e]
10	H, H, Et (**1k**)	99 (**4y**)	70:30	79

[a] Unless otherwise noted, reactions were performed with oxindoles **1a–k** (0.1 mmol) and nitroolefin **2g** (2.0 equiv.) in the presence of 10 mol% catalyst **3b** and 10 mol% benzoic acid in 2 mL of CH_2Cl_2.
[b] Isolated yields.
[c] Determined by ^{1}H NMR or HPLC analysis.
[d] Determined by chiral HPLC analysis for the major diastereomer.
[e] Not determined.

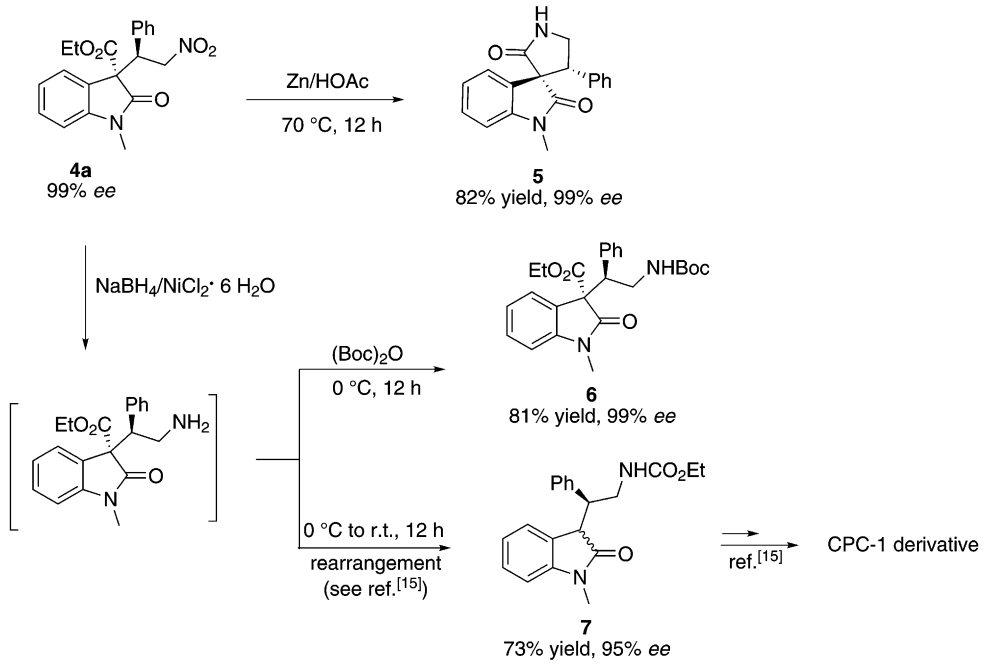
er the hydrogen-bonding interactions occurred in our ^{1}H NMR experiments.

To further investigate the potential applications of this method, the asymmetric Michael addition of substrate **1a** to nitroolefin **2a** on a gram-scale was examined. The desired product **4a** was obtained with 96% yield, 86:14 *dr*, and 95% *ee* (Scheme 2).

The compound **4a** could be converted into spirooxindole derivative **5** with 99% *ee* in one step using Zn/HOAc reduction under heated conditions. In addition, reduction of the nitro group was readily accomplished with $NaBH_4/NiCl_2{\cdot}6H_2O$. However, the unprotected amine led to epimerization at the C-3 position by an easy rearrangement reaction under neutral or basic conditions. The mechanism of rearrangement and conversion of compound **7** to CPC-1 derivative were reported by Zhang.[15] Finally, the Boc-protected product **6** was obtained with 99% *ee* by treatment with $(Boc)_2O$ at 0 °C (Scheme 3).



Scheme 2. The asymmetric Michael addition of **1a** to **3a** on a gram scale.



Scheme 3. Synthesis of spirooxindole derivatives from compound **4a**.

In conclusion, we have developed a highly efficient organocatalyzed Michael addition reaction of 2-oxindole-3-carboxylates to nitroolefins. When a *Cinchona* alkaloid-thiourea and a weak Brønsted acid were used as cooperative organocatalysts, both enantioselectivity and diastereoselectivity were improved. This catalytic system displayed broad substrate scope and gave the corresponding adducts in high yields (up to 99%) with high enantioselectivities (up to 98%) and good diastereoselectivities (up to 95:5). This new strategy will be applicable to other asymmetric catalytic systems as well as efficient construction of biologically active spirooxindoles.

Experimental Section

General Procedure

To a solution of oxindole **1** (1.0 equiv., 0.1 mmol), catalyst **3b** (10 mol%) and benzoic acid (10 mol%) in dry CH_2Cl_2 (1.5 mL) was added nitroolefin **2** (2.0 equiv.) in dry CH_2Cl_2 (0.5 mL) at −70 °C under a nitrogen atmosphere. After the reaction was finished, the mixture was purified directly by flash column chromatography to afford the product **4**.

Acknowledgements

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