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Enantioselective Arylation of 3-Carboxamide Oxindoles with Quinone Monoimines and Synthesis of Chiral Spirooxindole-benzofuranones

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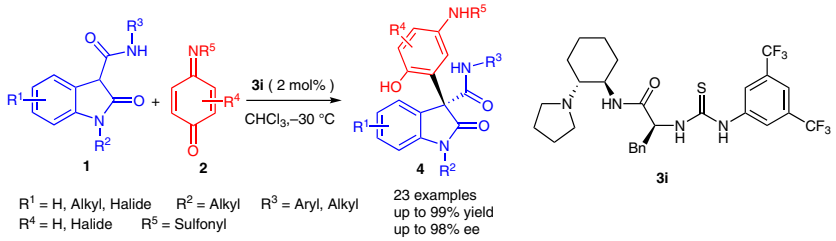

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Abstract A highly enantioselective arylation of 3-carboxamide oxoindoles with quinone monoimines is described. Various 3-aryl-3-carboxamide oxindoles with an all-carbon quaternary center were obtained in moderate to good yields (up to 99%) with moderate to good enantioselectivities (up to 98%) in the presence of a bifunctional thiourea-tertiary amine catalyst. The absolute configuration of one product was determined by an X-ray crystal structural analysis and the absolute configurations of the other products can be assigned by analogy. Moreover, several chiral spirooxindole-benzofuranones were synthesized from the 3-aryl-3-carboxamide oxindoles in moderate yields with moderate to good enantioselectivities.

Key words arylation, 3-carboxamide oxindoles, quinone monoimines, 3,3-disubstitutied oxindoles, spirooxindoles-benzofuranones

3,3-Disubstitutied oxindoles, which are frequently found in a variety of natural products and pharmaceutically relevant compounds, have drawn much attention from both synthetic and medicinal chemists.[1] Among these compounds, some 3-aryl-3,3-disubstituted oxindoles also exhibit important physiological activities (Figure 1).[2] Although many strategies for the construction of chiral 3,3-disubstituted oxoindoles have been established,[3,4] there are only a limited number of reports on the synthesis of chiral 3-aryl-3,3-disubstituted oxindoles.[5–8] Generally, enantioenriched 3-aryl-3,3-disubstituted oxindoles are prepared by asymmetric arylation of 3-monosubsituted oxindoles,[5] asymmetric arylation of isatin derivatives,[6] or asymmetric functionalization of 3-aryl-oxindoles.[7] Besides, Yuan and co-workers demonstrated an indirect asymmetric heteroarylation of 3-substituted oxindoles through conjugated addition followed by Paal–Knorr cyclization.[8]

As excellent electrophilic reagents, quinone derivatives have been widely used in asymmetric reactions to construct structurally diverse chiral compounds.[4i,4j,9,10] In recent years, our group has also been engaged in research on asymmetric reactions of quinone derivatives.[4i,10n–p] In a continuation of our interest in this area, herein we describe an enantioselective arylation of 3-carboxamide oxindoles with quinone monoimines catalyzed by a bifunctional thiourea-tertiary amine catalyst. This transformation enables easy access to various novel 3-aryl-3,3-disubstituted oxindoles in moderate to good yields (up to 99%) with moderate to good enantioselectivities (up to 98%). In addition, several chiral spirooxindole-benzofuranones were synthesized from the 3-aryl-3-carboxamide oxindoles in moderate yields with moderate to good enantioselectivities.

First, various chiral organocatalysts **3a–j** were tested in the arylation of 1-methyl-2-oxo-*N*-phenylindoline-3-carboxamide (3-amide oxindole) **1a** with quinone monoimine **2a** in dichloromethane at 0 °C. The results are summarized in Scheme 1. All the catalysts exhibited good activity and afforded the product with excellent yields in 10 minutes. The two cinchona alkaloids **3a** and **3b**, and thiourea-tertiary amine **3c** provided the product with poor *ee* values. When squaramide catalyst **3d** was used, slightly better enantioselectivity was obtained. A selection of cinchona alkaloids and L-amino acids incorporated in bifunctional thiourea-tertiary amines **3e–h** were then screened, in which **3g** delivered the best enantioselection (76% ee). (1*R*,2*R*)-Cyclohexane-1,2-diamine and L-phenylalanine incorporated thiourea-tertiary amine **3i** afforded the same *ee* value as **3g**. It is noteworthy that the racemic product was obtained with the cinconidine and D-phenylalanine incorporated catalyst **3j**, suggesting that the configuration of the two parts of the catalyst must be matched to achieve high

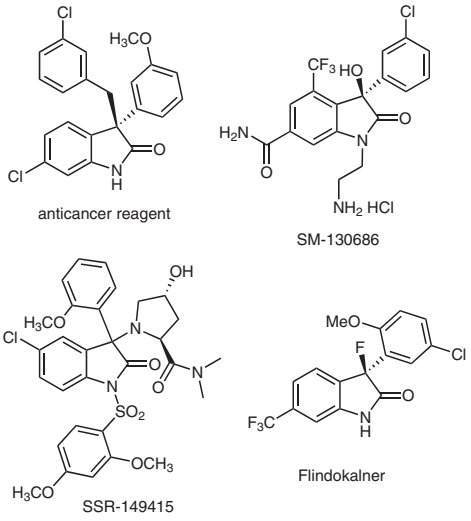
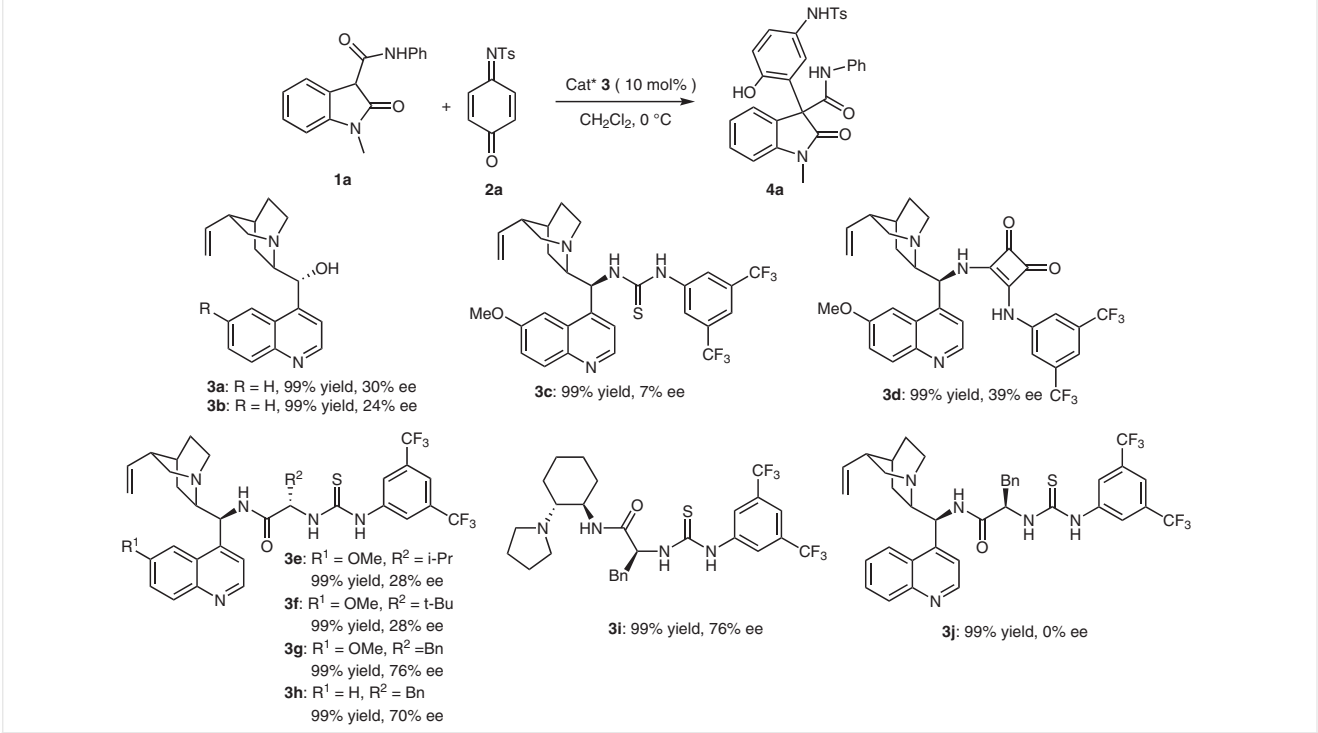


Figure 1 Representative examples of biologically active 3-aryl-3,3-disubstituted oxindoles

enantioselectivities. Hence **3i** was determined as the optimal catalyst for the reaction and used in the following investigations.

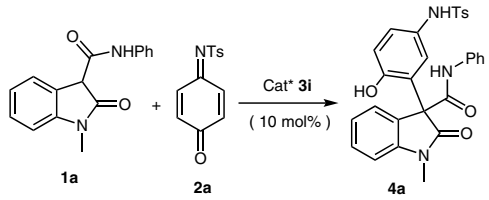
Subsequently, the other conditions were optimized. First, various solvents were screened and chloroform was found to be the most favorable solvent for the reaction (Table 1, entry 5). The reaction was then performed at lower temperatures and clear increases in enantioselection were observed (entries 8 and 9). A slightly higher *ee* value was obtained when the reaction was performed in 2 mL of chloroform (entry 10). To our delight, reducing the catalyst loading to 5 and 2 mol% did not result in a decrease in enantioselection (entries 11 and 12).

Having established the optimal reaction conditions, the scope of the reaction was examined. The results are summarized in Table 2. First, a range of 3-carboxamide oxindoles bearing various substituents on the aromatic ring of the amide were tested in the reaction with quinone monoimine **2a**. Generally, for 3-carboxamide oxindoles with *para*-substituents on the *N*-phenyl group, the reactions proceeded smoothly to afford the corresponding products in good yields with good *ee* values (entries 2–6). Several substrates with *ortho*-substituents on the *N*-phenyl group also provided the products in good yields with good *ee* values (entries 7–9). However, much lower enantioselectivity was obtained with *ortho*-methoxy substrate **1j** (entry 10). Two 3-carboxamide oxindoles with *meta*-substituents on the *N*-phenyl group gave the products with good *ee* values but lower yields (entries 11 and 12). *N*-Benzyl 3-carboxamide oxindole **1m** provided the product in moderate yield with moderate *ee* value (entry 13), while *N*-cyclohexyl 3-carboxamide oxindole **1n** gave rise to excellent *ee* value but rather



Scheme 1 Evaluation of the chiral catalysts in enantioselective arylation of 1-methyl-2-oxo-*N*-phenylindoline-3-carboxamide (**1a**) with quinone monoimine **2a**. Unless otherwise specified, the reactions were carried out with **1a** (0.10 mmol), **3a** (0.12 mmol) and chiral catalyst **2** (0.01 mmol) in solvent (1 mL) at 0 °C for 10 minutes. Isolated yield based on **1a**. Enantiomeric excess was determined by HPLC analysis on a chiral stationary phase.

Table 1 Optimization of the Conditions[a]



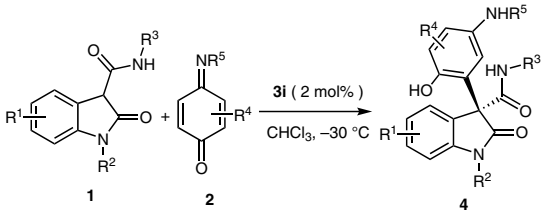
Entry	Solvent	*T* (°C)	Time (min.)	Yield (%)[b]	*ee* (%)[c]
1	CH_2Cl_2	0	10	99	76
2	THF	0	10	99	75
3	CH_3CN	0	10	99	9
4	toluene	0	10	99	71
5	$CHCl_3$	0	10	95	88
6	DCE	0	10	99	72
7	$CHCl_2CH_2Cl$	0	10	99	80
8	$CHCl_3$	–10	30	88	89
9	$CHCl_3$	–30	60	82	93
10[d]	$CHCl_3$	–30	60	80	96
11[d,e]	$CHCl_3$	–30	60	80	95
12[d,f]	$CHCl_3$	–30	60	80	95

[a] Unless otherwise specified, the reactions were carried out with **1a** (0.10 mmol), **2a** (0.12 mmol) and chiral catalyst **3i** (0.01 mmol) in solvent (1 mL).
[b] Yield of isolated product based on **1a**.
[c] Enantiomeric excess was determined by HPLC analysis on a chiral stationary phase.
[d] The reaction was performed in $CHCl_3$ (2 mL).
[e] 0.005 mmol of **3i** was used.
[f] 0.002 mmol of **3i** was used.

lower yield (entry 14). Moreover, 5-methyl-3-carboxamide oxindole **1o** was also investigated in the reaction with **2a** and moderate yield as well as moderate *ee* value was delivered (entry 15). 5-Chloro-3-carboxamide oxindole **1p** resulted in moderate yield but good enantioselectivity (entry 16). Excellent yields and excellent enantioselectivities were obtained with 1-ethyl-3-carboxamide oxindole **1q** (entry 17) and 1-allyl-3-carboxamide oxindole **1r** (entry 18). Finally, some other quinone monoimines were subjected in reaction with 3-carboxamide oxindole **1a**. Changing the N-substituent to Ns led to a considerable decrease in both yield and enantioselection (entry 19). However, good yield and good *ee* value were obtained with *N*-(4-methoxybenzene)sulfonyl quinone monoimine (entry 20). Reaction of 3-chloroquinone monoimine with **1a** afforded the product in good yield with moderate enantioselectivity (entry 21). Unfortunately, changing the N-substituent of the quinone monoimine to benzoyl led to an inseparable mixture (entry 22). Reaction of *N*-free 3-carboxamide oxindole **1s** with quinone monoimine **2a** also failed to give the desired product (entry 23).

Furthermore, a gram-scale reaction of 3-carboxamide oxoindole **1a** with quinone monoimine **2a** was performed. The reaction proceeded smoothly to give the product without any loss in yield or enantioselection (Scheme 2).

Table 2 Enantioselective Arylation of 3-Carboxamide Oxindoles **1** with Quinone Monoimine **2**[a]



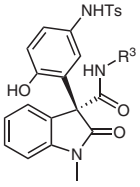
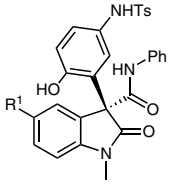
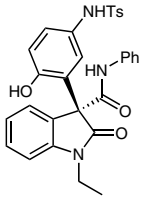
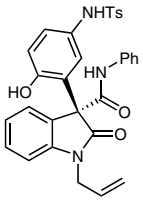
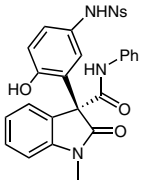
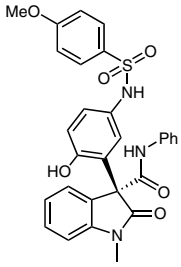
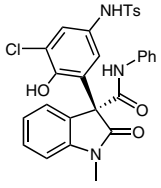
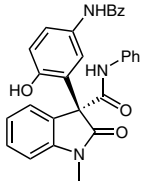
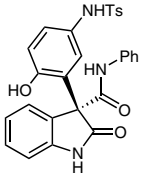
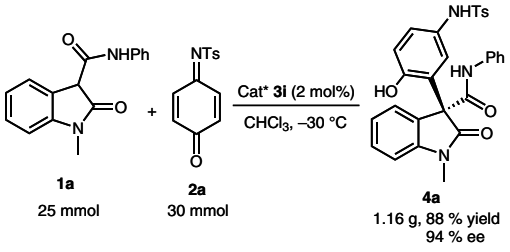
Entry	4	Yield (%)[b]	ee (%)[c]
1	 **4a**: R^3 = Ph	80	95
2	**4b**: R^3 = 4-FC_6H_4	93	92
3	**4c**: R^3 = 4-ClC_6H_4	99	85
4	**4d**: R^3 = 4-BrC_6H_4	87	88
5	**4e**: R^3 = 4-MeC_6H_4	99	94
6	**4f**: R^3 = 4-$MeOC_6H_4$	92	98
7	**4g**: R^3 = 2-FC_6H_4	92	94
8	**4h**: R^3 = 2-ClC_6H_4	87	89
9	**4i**: R^3 = 2-MeC_6H_4	93	94
10	**4j**: R^3 = 2-$MeOC_6H_4$	90	60
11	**4k**: R^3 = 3-BrC_6H_4	54	98
12	**4l**: R^3 = 3-$MeOC_6H_4$	77	93
13	**4m**: R^3 = Bn	80	80
14	**4n**: R^3 = Cyclohexyl	57	98
15	 **4o**: R^1 = Me	75	73
16	**4p**: R^1 = Cl	75	92
17	 **4q**	95	94

Table 2 (continued)

Entry	4	Yield (%)[b]	ee (%)[c]
18	 **4r**	95	96
19	 **4s**	63	84
20	 **4t**	93	94
21	 **4u**	99	8
22	 **4v**	N. D.	–
23	 **4w**	N. D.	–

[a] Unless otherwise specified, the reactions were carried out with **1** (0.10 mmol), **2** (0.12 mmol) and **3i** (0.002 mmol) in $CHCl_3$ (2 mL) at –30 °C for 1 hour.
[b] Isolated yield based on **1**.
[c] The *ee* values were determined by using chiral HPLC.
[d] The absolute configuration of **4q** was determined by an X-ray crystal structural analysis and the absolute configurations of the other products were assigned by analogy.



Scheme 2 Gram-scale reaction of 3-carboxamide oxindole **1a** with quinone monoimine **2a**

The absolute (*S*)-configuration of product **4q** was determined by an X-ray crystal structural analysis (Figure 2). Consequently, the absolute configurations of the other products can be assigned by analogy.

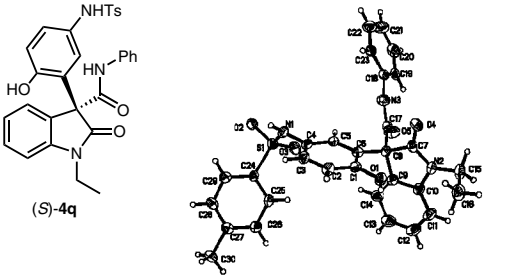
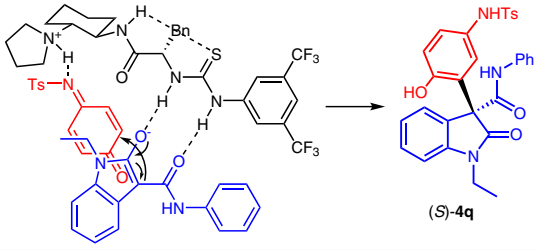


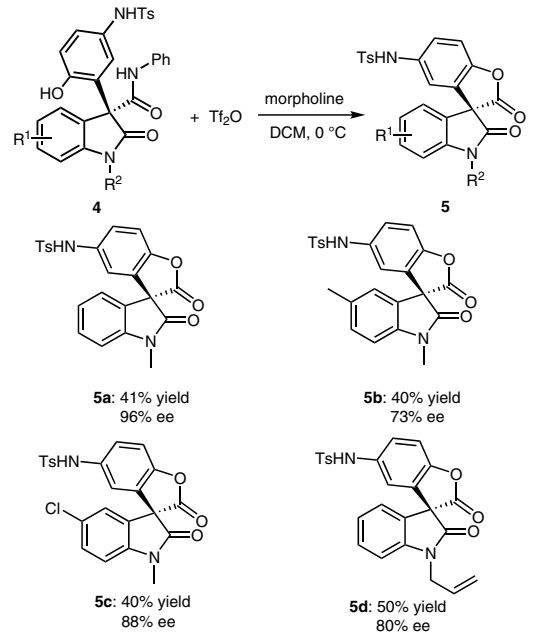
Figure 2 X-ray crystal structure of (*S*)-**4q**

Although detailed structural and mechanistic studies remain to be carried out, based on the absolute configuration of the product **4q**, we proposed a plausible transition-state model for the reaction (Scheme 3).[11] First, the 3-carboxamide oxindole is deprotonated by the bifunctional thiourea-tertiary amine catalyst. The protonated tertiary amine of the catalyst then activates the quinone monoimine by H-bonding. Meanwhile, the thiourea moiety of the catalyst is connected with the enolate generated by deprotonated 3-carboxamide oxindole through H-bonding. Finally, the enolate attacks the quinone monoimine from the *Si*-face followed by simultaneous aromatization to produce (*S*)-**4q**.

Spirooxindoles[12] and spirobenzofuranones[13] are privileged scaffolds for drug development. Herein, we demonstrated the utility of this methodology for easy access to spirooxindole-benzofuranones. As can be seen in Scheme 4, several 3-aryl 3,3-disubstituted oxindoles **4** were treated with trifluoromethanesulfonic anhydride in the presence of morpholine. Spirooxindole-benzofuranones **5a–c** were prepared in moderate yields without loss in enantioselection. Surprisingly, the enantioselectivity of **5d** cannot be retained in the process of transformation. However, the reason is still unclear.



Scheme 3 Plausible reaction mechanism



Scheme 4 Synthesis of spirooxindole-benzofuranones

In conclusion, we have developed an asymmetric arylation of 3-carboxamide oxindoles with quinone monoimines catalyzed by a bifunctional thiourea-tertiary amine to construct a series of chiral 3-aryl 3,3-disubstituted oxindoles in moderate to good yields (up to 99%) with moderate to good enantioselectivities (up to 98%).[14,15] The absolute configuration of one product was determined by an X-ray crystal structural analysis and the absolute configurations of the other products were assigned by analogy. Moreover, several spirooxindole-benzofuranones were prepared from the products in moderate yields with moderate to good enantioselectivities.

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0037-1611782.

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(14) **Enantioselective Arylation of 2-Oxoindoline-3-carboxamide 1 with Quinone Monoimine 2; General Procedure:** 2-Oxoindoline-3-carboxamide **1** (0.10 mmol) and catalyst **3i** (0.002 mmol, 2 mol%) were dissolved in $CHCl_3$ (2 mL) in a flame-dried vial equipped with a magnetic stirring bar. After stirring for 30 minutes at –30 °C, quinone monoimine **2** (0.12 mmol, 1.2 equiv) was added. The reaction mixture was stirred at –30 °C until no starting material was detected by TLC. The mixture was subjected to chromatography (silica gel, petroleum ether/EtOAc, 2:1) to afford the desired product **4**.

(15) **3-(2-Hydroxy-5-(4-methylphenylsulfonamido)phenyl)-1-methyl-2-oxo-*N*-phenylindoline-3-carboxamide (4a):** Yield: 0.042 g (80%); white solid; mp 169.0–171.5 °C; 95% ee, HPLC condition: Chiralpak Ic-H (*n*-hexane/ethanol: 70:30, 1.0 mL/min, t_{major} = 7.476 min, t_{minor} = 9.122 min); $[\alpha]_D^{20}$ = +25.2 (*c* 1.50, CH_2Cl_2). ^{1}H NMR (300 MHz, DMSO-d_6): δ = 9.81 (s, 1 H), 9.67 (s, 1 H), 9.27 (s, 1 H), 7.55 (d, *J* = 8.0 Hz, 2 H), 7.45 (d, *J* = 7.9 Hz, 2 H), 7.33 (q, *J* = 7.5 Hz, 3 H), 7.19 (d, *J* = 7.9 Hz, 2 H), 7.16–6.98 (m, 4 H), 6.96–6.81 (m, 2 H), 6.58 (d, *J* = 8.5 Hz, 1 H), 3.22 (s, 3 H), 2.32 (s, 3 H). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 175.33, 164.48, 152.71, 143.96, 143.28, 138.39, 136.97, 129.79, 129.48, 129.16, 128.83, 128.63, 127.14, 126.56, 125.70, 124.54, 123.58, 122.94, 122.76, 120.51, 116.80, 108.88, 63.38, 27.13, 21.44. HRMS (ESI): *m*/*z* [M+Na]$^+$ calcd. for $C_{30}H_{27}N_3O_5SNa^+$: 550.1402; found: 550.1407.