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Enantioselective synthesis of 3-substituted 3-amino-2-oxindoles via amination with anilines

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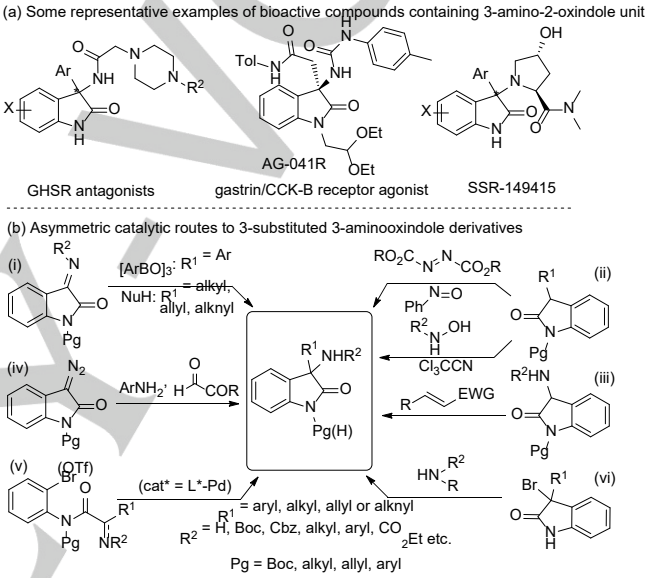
Abstract: A chiral *N,N'*-dioxide-nickel(II) complex-catalyzed asymmetric amination reaction of 3-bromo-3-substituted oxindoles with anilines was developed. A series of alkyl or aryl 3-amino-indolinones with quaternary stereocenters were obtained in high yields with excellent ee values in one step (up to 99 % yield, up to 96% ee). The method provided a readily route to optically active intermediates of 3-amino-2-oxindole-based bioactive compounds. Besides, a possible transition state model was proposed to elucidate the origin of the chirality induction based on the X-ray crystal structure of the catalyst and the adduct.

Oxindole skeleton bearing a stereogenic center at C3-position,[1] such as 3-substituted 3-aminooxindole units and the related represents a type of privileged structure, which presents in large amount of alkaloid natural products, pharmaceutical or agrochemical relevant compounds as well as synthetic biologically active molecules [2, 3] (Scheme 1a). Due to their great importance, much attention has been devoted to the efficient synthesis of optically active 3-substituted 3-aminooxindole derivatives by the use of chiral organocatalysts or chiral metal complex catalysts from various precursors (Scheme 1b), and several reviews have collected the advances in this area.[3]

In general, addition of isatin ketimines with various carbon-nucleophiles provided a straightforward route to different 3-substituted 3-aminooxindoles (path i).[4] Alternatively, amination of 3-substituted oxindoles with azodicarboxylates,[5] nitrosoarenes [6] or *N*-electrophiles [7] (path ii) enabled the introduction of nitrogen-containing functional group into C3-position. The transformations of 3-aminooxindoles (path iii),[8] 3-diazooxindoles (path iv),[9] and others [10] expanded the diversity of 3-substitution of 3-aminooxindoles. Also, Pd-catalyzed asymmetric intramolecular α-arylation of amide enolates [11] (path v) could directly construct the functionalized oxindoles. Last but not least, the amination of 3-substituted 3-bromooxindoles is a useful strategy to obtain this fascinating skeleton (path vi) with advantages as 3-substitution compatibility, N1-H free without protecting group, and readily modification to the target derivatives. Using indolines as the nucleophiles and chiral Box-Ni(II) complex catalyst, the Wang group realized asymmetric synthesis of *N*-tryptamine-related 3-alkyloxindole, a precursor for the total synthesis of (+)-psychotrimine.[12] However, the amination of 3-bromo-3-benzyl oxindole with anilines rendered the desired products with high yield but moderate enantioselectivity,[13] which might be due to the background reaction and amine-poisoning of the metal catalysts.

Inspired by our previous works on catalytic asymmetric reactions with 3-bromo-3-substituted oxindoles,[14] we envisioned that chiral *N,N'*-dioxide-metal complex [15] developed by our group had potential to be an efficient catalyst for the enantioselective addition of anilines to 3-bromo-3-substituted oxindoles, overwhelming base-initiated racemic background reaction. Herein, we report our effort in developing a *N,N'*-dioxide/Ni(II) catalytic system[15] to promote asymmetric amination of 3-bromo-3-substituted oxindoles with various anilines, providing 3-alkyl or 3-aryl 3-aminooxindoles in good yields with high enantioselectivities. It enabled the easily accessible to the optically active key intermediates of AG-041R and others (Scheme 1a).



Scheme 1. Representative bioactive compounds and catalytic asymmetric synthesis of 3-substituted 3-amino oxindoles.

At the beginning of this study, 3-bromo-3-methylindolin-2-one (**1a**) and 4-methoxyaniline (**2a)** were selected as the model substrates to optimize the reaction conditions (Table 1). The reaction occurred well in the presence of one equivalent of $^{i}Pr_2NEt$ which was used to generate indol-2-one intermediate from **1a** (entry 1), indicating strong background reaction. Under this condition, a primary screening of chiral *N,N'*-dioxide ligands coordinated with $Ni(OTf)_2$ was carried out. Several frequently-used chiral *N,N'*-dioxide ligands were evaluated (See ESI for details), and the desired product **3aa** was obtained in high yield with more or less enantioselectivity (entries 2-4). The effect of base was investigated with the use of **L_2-Pi^{i}Pr$_2$** as the ligand in THF at 35 °C, and the results showed that $^{i}Pr_2NEt$ was better than

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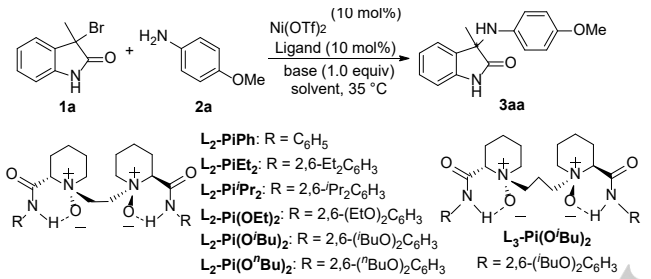
stronger organic base DMAP and inorganic base in terms of enantioselectivity (entries 4-6). Since the 2,6-substitutions on the amide units of the ligand had dramatic influence on the enantioselection, careful modification of the substituents showed that the *N,N'*-dioxide ligands containing 2,6-dialkoxy motifs[16] afforded a better enantioselectivity than the 2,6-dialkyl based ones (entries 7 and 8). Delightfully, the desired adduct **3aa** was obtained in 99% yield and 85% ee after switching the solvent to ethyl acetate and lowing the reaction temperature to 0 °C (entries 9 and 10). Reinvestigating the substructure of the chiral ligands confirmed that **L_2-Pi(O^{i}Bu)$_2$** with two-carbon linker was superior to the related **L_3-Pi(O^{i}Bu)$_2$** bearing three-carbon (entry 11). It was found that $Ni(BF_4)_2$•$6H_2O$ yielded comparable outcomes as $Ni(OTf)_2$ (entry 12), and the use of **L_2-Pi(O^{n}Bu)$_2$**/$Ni(BF_4)_2$ complex in the presence of ^{i}Pr$_2$NEt enabled the generation of the adduct **3aa** in 99% yield and 88% ee (entry 13).

Table 1. Optimization of the reaction conditions.

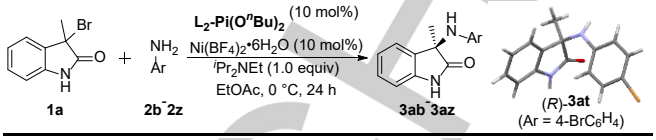


entry[a]	ligand	base	yield (%)[b]	ee (%)[c]
1	Without Ni(II)/ligand	^{i}Pr$_2$NEt	67	0
2	**L_2-PiPh**	^{i}Pr$_2$NEt	96	11
3	**L_2-PiEt$_2$**	^{i}Pr$_2$NEt	89	40
4	**L_2-Pi^{i}Pr$_2$**	^{i}Pr$_2$NEt	99	48
5	**L_2-Pi^{i}Pr$_2$**	DMAP	52	4
6	**L_2-Pi^{i}Pr$_2$**	Na_2CO_3	92	29
7	**L_2-Pi(OEt)$_2$**	^{i}Pr$_2$NEt	92	58
8	**L_2-Pi(O^{i}Bu)$_2$**	^{i}Pr$_2$NEt	90	58
9[d]	**L_2-Pi(O^{i}Bu)$_2$**	^{i}Pr$_2$NEt	97	82
10[d,e]	**L_2-Pi(O^{i}Bu)$_2$**	^{i}Pr$_2$NEt	99	85
11[d,e]	**L_3-Pi(O^{i}Bu)$_2$**	^{i}Pr$_2$NEt	74	44
12[d-f]	**L_2-Pi(O^{i}Bu)$_2$**	^{i}Pr$_2$NEt	99	86
13[d-f]	**L_2-Pi(O^{n}Bu)$_2$**	^{i}Pr$_2$NEt	99	88

[a] Unless otherwise noted, the reactions were carried out with $Ni(OTf)_2$/Ligand (10 mol%, 1:1), **1a** (0.1 mmol), 4-methoxyaniline **2a** (1.5 equiv), and base (1.0 equiv) in THF (0.1 M) at 35 °C for 16 hours. [b] Isolated yield. [c] Determined by HPLC. [d] In EtOAc. [e] At 0 °C for 24 hours. [f] $Ni(BF_4)_2$•$6H_2O$ was used.

With the optimized reaction conditions in hand, the substrate scope with anilines was then explored. As demonstrated in Table 2, various substituted anilines **2b-2z** performed the reaction with 3-bromo-3-methylindolinone **1a** smoothly to give the amination products **3ab–3az** in good yield (76-99%) with high enantioselectivity (86-96% ee). Generally, the position and electronic nature of substituents exhibited a little effect on the chiral control of the reaction. *Para*-substituted anilines (**2n**, **2q**, **2t**, **2v**, **2x** and **2z**) gave slightly higher enantioselectivity than *meta*- and *ortho*-substituted ones (**2l-2m**, **2o-2p**, **2r-2s**, **2u**, **2w** and **2y**).

Table 2. Substrate scope of anilines.



entry[a]	Ar	yield (%)[b]	ee (%)[c]
1	Ph	97 (**3ab**)	93
2[d]	3-MeC_6H_4	90 (**3ac**)	86
3	4-MeC_6H_4	98 (**3ad**)	88
4[d]	4-EtC_6H_4	99 (**3ae**)	88
5	4-^{i}PrC$_6$H$_4$	99 (**3af**)	90
6	2-$MeOC_6H_4$	90 (**3ag**)	92
7	4-$EtOC_6H_4$	97 (**3ah**)	86
8	4-CNC_6H_4	99 (**3ai**)	92
9	3-$NO_2C_6H_4$	92 (**3aj**)	92
10	4-$NO_2C_6H_4$	99 (**3ak**)	88
11	2-FC_6H_4	99 (**3al**)	92
12[d]	3-FC_6H_4	85 (**3am**)	92
13	4-FC_6H_4	99 (**3an**)	94
14	2-ClC_6H_4	99 (**3ao**)	88
15	3-ClC_6H_4	85 (**3ap**)	92
16	4-ClC_6H_4	92 (**3aq**)	95
17	2-BrC_6H_4	85 (**3ar**)	86
18	3-BrC_6H_4	89 (**3as**)	92
19	4-BrC_6H_4	99 (**3at**)	94 (*R*)
20[d]	2-IC_6H_4	76 (**3au**)	90
21	4-IC_6H_4	99 (**3av**)	94
22	2-$CF_3OC_6H_4$	86 (**3aw**)	92
23	4-$CF_3OC_6H_4$	99 (**3ax**)	96
24	3-$CF_3C_6H_4$	97 (**3ay**)	92
25	4-$CF_3C_6H_4$	99 (**3az**)	94

[a] Unless otherwise noted, the reactions were carried out with **1** (0.10 mmol), **2** (1.5 equiv), ^{i}Pr$_2$NEt (1.0 equiv), $Ni(BF_4)_2$•6H2O/**L_2-Pi(O^{n}Bu)$_2$** (1:1, 10 mol%) in EtOAc (0.1 M) at 0 °C for 24 hours. [b] Isolated yield of **3**. [c] The ee value of **3** was determined by HPLC analysis. [d] 48 hours.

Furthermore, electron-poor anilines (**2i-2z**) obtained better results than electron-rich anilines (**2b**-**2h**), which might be due to the decreased background reaction. In addition, the absolute configuration of the product **3at** was determined to be *R* by X–ray crystallography.[17] The absolute configurations of other products

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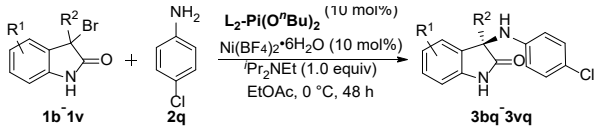
3 were assigned as the same by comparison with the Cotton effect in the CD spectra with **3at** (see ESI for details). In comparison, alkylamine resulted in low enantioselectivity but secondary amines obtained moderate enantioselectivity (see ESI for details).

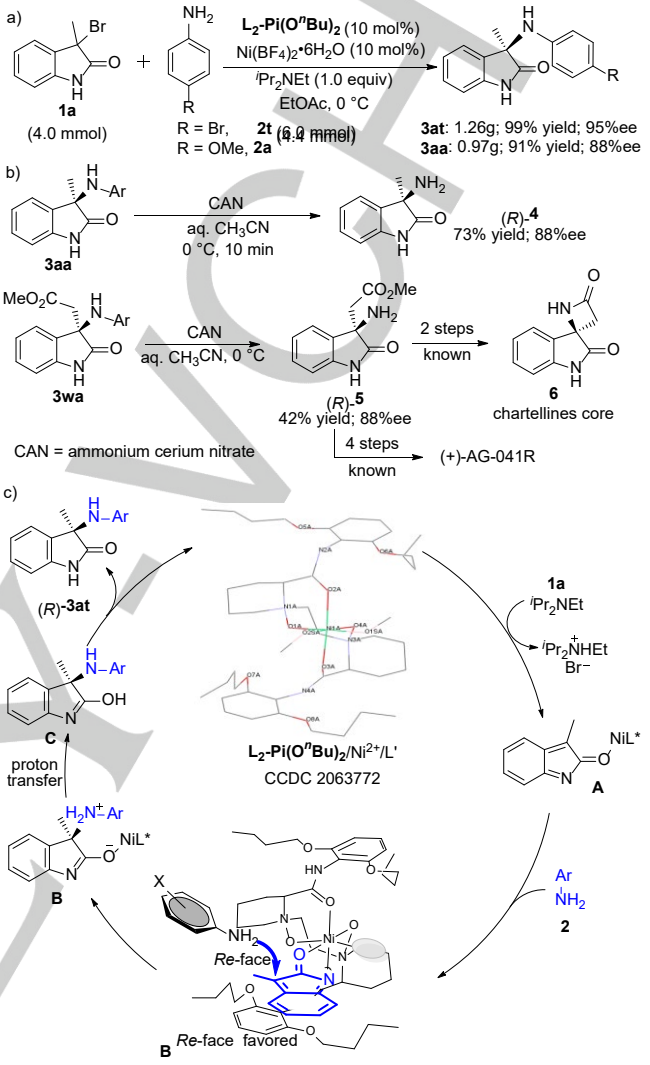
Table 3. Substrate scope of oxindoles.



entry[a]	R^1	R^2	yield (%)[b]	ee (%)[c]
1[d]	H	allyl	98 (**3bq**)	94
2[d]	H	Bn	99 (**3cq**)	90
3[d]	H	4-Me$C_6H_4CH_2$	96 (**3dq**)	90
4	H	3,4-(MeO)$_2C_6H_3CH_2$	99 (**3eq**)	86
5	H	4-F$C_6H_4CH_2$	90 (**3fq**)	88
6	H	4-Cl$C_6H_4CH_2$	82 (**3gq**)	88
7	H	4-Br$C_6H_4CH_2$	84 (**3hq**)	90
8	H	4-CN$C_6H_4CH_2$	83 (**3iq**)	86
9	H	furan-2-ylmethyl	99 (**3jq**)	94
10	H	thiophen-2-ylmethyl	99 (**3kq**)	92
11	4-Cl	Me	96 (**3lq**)	88
12	4-Br	Me	95 (**3mq**)	86
13[d]	5-Me	Me	99 (**3nq**)	94
14[d]	5-MeO	Me	99 (**3oq**)	92
15[d]	5-F	Me	92 (**3pq**)	96
16[d]	5-Cl	Me	96 (**3qq**)	93
17	5-Br	Me	99 (**3rq**)	92
18[d]	5-I	Me	95 (**3sq**)	92
19	6-Cl	Me	86 (**3tq**)	82
20[d]	6-Br	Me	90 (**3uq**)	80
21	H	C_6H_5	97 (**3vq**)	94
22[d]	H	CH_2CO_2Me	99 (**3wq**)	96
23[d,e]	H	CH_2CO_2Me	97 (**3wa**)	88

[a-c] See the condition in entry 20, Table 2. [d] 24 hours.[e] **2a** instead of **2q**.

Subsequently, we turned attention to the scope of oxindoles **1** (Table 3). A variety of 3-allyl, 3-alkyl, and 3-aryl oxindoles reacted with **2q** smoothly to generate the products (**3bq-3kq**, **3vq-3wq**) with good yields (82-99%) and enantioselectivity (86-96% ee). Then substrates with substituents on the oxindole ring at C4, C5, and C6 positions were examined. Almost all of them could give satisfactory results (**3lq-3sq**, 92-99% yields, 86-96% ee) except the C6-substituted oxindoles **1t-1u** exhibited slightly reduced enantioselectivity (**3tq**, 86% yield, 82% ee and **3uq**, 90% yield, 80% ee). Unfortunately, C7-substituted oxindoles exhibited poor reactivity, yielding racemic product(see ESI for details).



Scheme 2. (a) Gram-scale synthesis; (b) further transformations; (c) Proposed catalytic cycle and favorable transition state.

To demonstrate the practicality of this transformation, two scale-up experiments of oxindole **1a** were performed with **2t** (6.0 mmol) or **2a** (4.4 mmol) under the optimized reaction conditions, providing the desired product **3at** in 99% yield with 95% ee, and the product **3aa** in 91% yield with 88% ee (Scheme 2a). Moreover, removal of the *p*-methoxyphenyl (PMP) group [6b,18] was carried out under conventional conditions to give 3-amino-3-methyloxindole (*R*)-**4** and 2-(3-amino-2-oxoindolin-3-yl)acetate (*R*)-**5** in good yield without loss of enantioselectivity (Scheme 2b). The compound **5** could be converted into (+)-AG-041R and spiro-β-lactam **6** by following the reported literature procedure.[4n, 5d]

The enantiocontrol of this amination reaction was considered based on the X-ray crystal structure of the the catalyst [17] and the outcome of this reaction process (Scheme 2c). The indol-2-one generated *in situ* in the assistant of ^{i}Pr$_2$NEt, could be activated after coordinating to the *N,N'*- dioxide/Ni^{II} complex to form **A**. As shown in **B** where the aniline conducts nucleophilic addition, the

Si-face of the indol-2-one is shielded by downward amide unit of the ligand, and the addition of aniline occurs preferentially from the *Re*-facial, yielding the (*R*)-product as the major isomer.

In summary, a direct and efficient enantioselective synthesis of 3-substituted 3-amino oxindoles was realized by developing a chiral nickel complex catalytic system for addition reaction of 3-bromo-3-substituted oxindoles with anilines. A wide range of 3-aminooxindoles with 3-alkyl or 3-aryl substitution was readily available in excellent yield and enantioselectivity, including key intermediates of the bioactive molecules. Further application of the chiral catalysts to other enantioselective synthesis are ongoing in our laboratory.

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Keywords: oxindoles • amination • asymmetric catalysis • *N,N'*-dioxides • nickel

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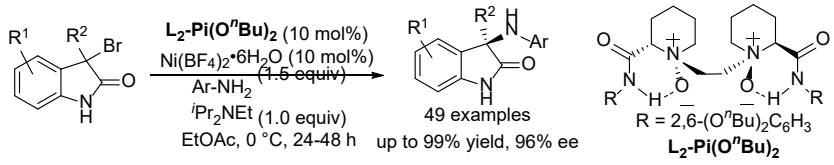

Lewis acid catalyzed asymmetric synthesis of phenylamino-3-indolin-2-ones via amination reaction of 3-bromo-3-substituted oxindoles with anilines.