Organic & Biomolecular Chemistry

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Cite this: *Org. Biomol. Chem.*, 2012, **10**, 236

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Asymmetric hydroxyamination of oxindoles catalyzed by chiral bifunctional tertiary amine thiourea: construction of 3-amino-2-oxindoles with quaternary stereocenters†

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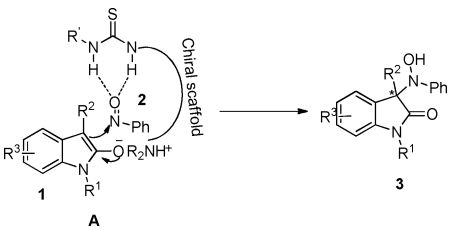
Received 18th August 2011, Accepted 26th September 2011
DOI: 10.1039/c1ob06413d

Chiral bifunctional tertiary amine thiourea was applied to catalyze the asymmetric hydroxyamination of 3-subsituted oxindoles with nitrosobenzene to construct 3-amino-2-oxindoles with quaternary stereocenters in good yields (up to 91%) and enantioselectivities (up to 90% ee).

Introduction

Optically active 3,3-disubstituted oxindole skeletons constitute important structural motifs in a variety of natural products and biologically active drugs.[1] Particularly, chiral 3-amino-2-oxindoles are versatile and useful building blocks for the preparation of natural products and candidate drugs, such as chartelline C and psychotrimine, as well as the potent gastrin/CCK-B receptor antagonist AG-041R, the effective anti-malarial drug candidate NITD609 and the vasopressin VIb receptor antagonist SSR-149415.[2] For the syntheses of those interesting structures, several asymmetric strategies have been developed for the synthesis of chiral quaternary 3-aminooxindoles, such as cyclization of *o*-chlorinated anilines,[3a] alkylation of 3-aminooxindoles,[3b] addition of imines derived from isatins,[3c,d] amination[3e–k] and hydroxyamination[3l] of oxindoles. Among them, hydroxyamination of 3-substituted oxindoles with nitrosobenzene is an important and straightforward way to access those interesting molecules. In 2010, Barbas and coworkers first reported dimeric quinidinine-catalyzed enantioselective aminoxylations of *N*-substituted 3-substituted 2-oxindoles with nitrosobenzene to give 3-hydroxyoxindole with good results.[4] By contrast, Chen and coworkers reported a *N*-nitroso aldol reaction of 3-substituted 2-oxindoles with nitrosobenzene catalyzed by *Cinchona* alkaloids, giving 3-amino-2-oxindoles in good to excellent yields (up to 100%) and moderate enantioselectivities (59–72% *ee*).[3l] Subsequently, Feng and coworkers developed an enantioselective hydroxyamination of 3-substituted 2-oxindoles with nitrosobenzene catalyzed by a chiral Lewis acid complex of $Sc(OTf)_3$/*N*,*N*-dioxide, and excellent results were obtained.[5] To date, there is only one metal-free catalytic asymmetric version of hydroxyamination of 3-substituted 2-oxindoles, which gives no more than 72% ee enantioselectivity.[3l] Considering the different catalytic mechanisms and features of metal catalysis and small molecule catalysis, it is still desirable to develop more and effective new organocatalytic protocols to achieve this transformation for the preparation of optically active 3-amino-2-oxindoles.

Recently, the development of chiral bifunctional thioureas as powerful hydrogen-bond-donating organocatalysts has received growing attention.[6] Among them, tertiary amine thioureas have been demonstrated effectively to activate both donors and acceptors simultaneously.[7,8a] Based on this concept and background, we envisioned that the tertiary amine group would activate the oxindoles **1** as a base to produce zwitterionic enolate **A**, while the thiourea group would direct the nitroso-group through two hydrogen bonds with the oxygen of the nitrosobenzene **2**. Thus, the synergistic interactions through chiral tertiary amine thiourea bifunctional catalysis would facilitate the zwitterionic enolate **A** to *N*-specific nucleophilic attack of nitrosobenzene **2** (Scheme 1). For our continuing interests in asymmetric catalysis[8] and further endeavors in the synthesis of structurally diverse oxindoles with quaternary stereocenters,[9] herein, we wish to report the first example of organocatalytic asymmetric hydroxyamination of oxindoles **1** with nitrosobenzene **2** catalyzed by tertiary amine thioureas, affording 3-amino-2-oxindoles **3** in satisfactory yields and enantioselectivities (up to 91 yield and 90% ee).



Scheme 1 Proposed transition state.

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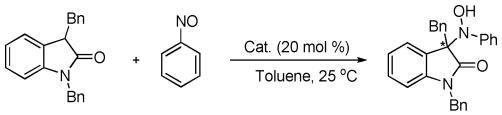
† Electronic supplementary information (ESI) available. See DOI: 10.1039/c1ob06413d

Table 1 Effect of bifunctional chiral organocatalysts[a]



Entry	Cat.	Time (h)	Yield (%)[b]	ee (%)[c]
1	**4a**	16	53	55
2	**4b**	15	63	55
3	**4c**	117	33	56
4	**4d**	15	69	64
5	**4e**	67	43	57
6	**4f**	**15**	**73**	**70**
7	**4g**	21	44	27
8	**4h**	24	14	30
9	**4i**	16	34	43
10	**4j**	17	72	35
11	**4k**	17	42	44
12	**4l**	17	65	–30
13	**4m**	17	61	–37

[a] All the reactions were performed using **1a** (0.2 mmol), **2** (0.22 mmol) and **4** (0.04 mmol) in toluene (1 ml). [b] Isolated yield after silica gel column chromatography. [c] Enantiomeric excess (ee) was determined by chiral HPLC.

Results and discussion

To validate our hypothesis, a series of catalysts with various substituents **4a–4m** (Fig. 1) was investigated and the reaction of oxindole **1a** with nitrosobenzene **2** was chosen as the model reaction, and the results are summarized in Table 1. All the catalysts tested could give the desired *N*-addition product **3a** in moderate yields (14–73%) and enantioselectivities (27–70% ee) in the presence of 20 mol% catalyst loading. Catalysts with cyclohexanediamine as chiral scaffold afforded better yields and enantioselectivities than those with diphenyldiamine scaffolds (Table 1, entries 1 *vs.* 7, 4 *vs.* 8, 6 *vs.* 9). The acidity of the N–H of the thiourea group has a positive effect on the catalytic activity. Catalysts **4d** and **4f** with 3,5-$(CF_3)_2$ substituents on the phenyl ring afforded better yields and enantioselectivities than those without substituents (Table 1, entries 4 *vs.* 3, 6 *vs.* 5). The substituents on the tertiary amine also have variable effects on the results. The *N*-methyl protected **4a** gave a lower yield than *N*-propyl **4b** with the same enantioselectivity (Table 1, entries 1 *vs.* 2). Cyclic substituents of the tertiary amine could increase the yields and enantioselectivities, and the six-membered ring is more

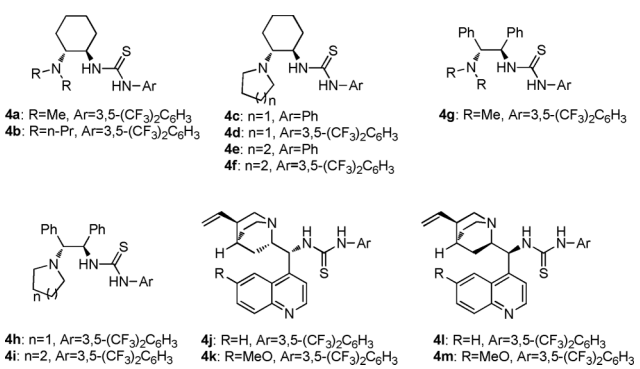
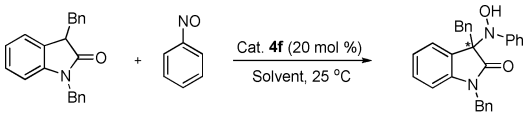


Fig. 1 Organocatalysts in this study.

Table 2 Screening of the solvents for the reaction[a]



Entry	Solvent	Time (h)	Yield (%)[b]	ee (%)[c]
1	Toluene	15	73	70
2	*o*-Xylene	17	65	62
3	*m*-Xylene	16	65	62
4	*p*-Xylene	16	70	61
5	Mesitylene	16	75	57
6	Chlorobenzene	16	60	65
7	*n*-Hexane	12	66	55
8	Cyclohexane	16	88	56
9	Ether	15	73	67
10	MTBE	16	78	66
11	DME	16	75	63
12	THF	16	55	61
13	1,4-Dioxane	16	81	61
14	DCM	16	44	58
15	EtOAc	16	60	56
16	Acetonitrile	16	90	28
17	DMA[d]	16	67	24
18	MeOH	2.3	87	7

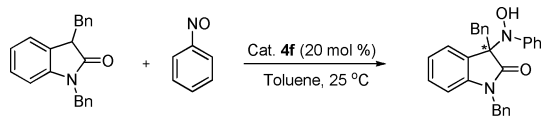
[a] All the reactions were performed using **1a** (0.2 mmol), **2** (0.22 mmol) and **4** (0.04 mmol) in solvent (1 ml). [b] Isolated yield after silica gel column chromatography. [c] Enantiomeric excess (ee) was determined by chiral HPLC. [d] *N*,*N*-Dimethylacetamide.

efficient than the five-membered one (Table 1, entries 6 *vs.* 4 *vs.* 1). *Cinchona* alkaloid-derived thioureas did not improve the results (Table 1, entries 10–13). Relatively, catalyst **4f** gave better yield and enantioselectivity (73% yield and 70% ee, Table 1, entry 6), and was selected for further optimization.

With **4f** as the optimal catalyst, the effect of the solvent was then investigated and the results are listed in Table 2. Solvents showed significant effects on the yields and enantioselectivities. In non-polar and less polar aprotic solvents such as toluene, alkanes and ethers, the reactions proceeded smoothly and gave moderate to good yields (44–88% yield) and enantioselectivities (Table 2, entries 1–15, 55–70% ee). In CH_3CN, the highest yield (90% yield) was obtained, but only 28% ee was detected (Table 2, entry 16). For more polar solvents, relatively lower enantioselectivities were observed, which may be due to the potential destruction of H-bonding interactions (Table 2, entries 16–18, 7–28% ee). The screening of solvents showed that toluene was a more suitable solvent for this conversion (Table 2, entry 1, 73% yield, 70% ee).

To further optimize the reaction conditions, the reaction temperature, substrate loading and the concentration of reactants were then screened, and the results are listed in Table 3. The reaction temperature affected the results dramatically. When the reaction was carried out at 0 °C, the enantioselectivity decreased to 61% ee (Table 3, entry 2). At the lower temperature of –20 °C, the yield and enantioselectivity both decreased obviously (34% yield, 39% ee, Table 3, entry 3). Excessive loading of nitrosobenzene **2** is unfavourable and the enantioselectivities decreased dramatically (Table 3, entries 4 and 5 *vs.* 1). By contrast, with excess 3-subsituted oxindoles **1a**, excellent yields were obtained (up to 99%) and the enantioselectivities slightly increased (up to 75% ee, Table 3, entries 6–8). The screening of the substrate loading showed that

Table 3 Optimization of the reaction conditions[a]



Entry	Solvent	**1a** : **2**	Conc. (mol L^{-1})	Time (h)	Yield (%)[b]	ee (%)[c]
1	Toluene	1 : 1.1	0.2	15	73	70
2[d]	Toluene	1 : 1.1	0.2	96	73	61
3[e]	Toluene	1 : 1.1	0.2	96	34	39
4	Toluene	1 : 2	0.2	24	36	37
5	Toluene	1 : 3	0.2	34	20	27
6	Toluene	2 : 1	0.2	6	79	75
7	Toluene	3 : 1	0.2	5	99	74
8	Toluene	4 : 1	0.2	5	99	75
9	Toluene	3 : 1	0.4	2	90	68
10	Toluene	3 : 1	0.3	2	95	72
11	Toluene	3 : 1	0.1	5	98	79
12	**Toluene**	**3 : 1**	**0.05**	**6**	**86**	**83**

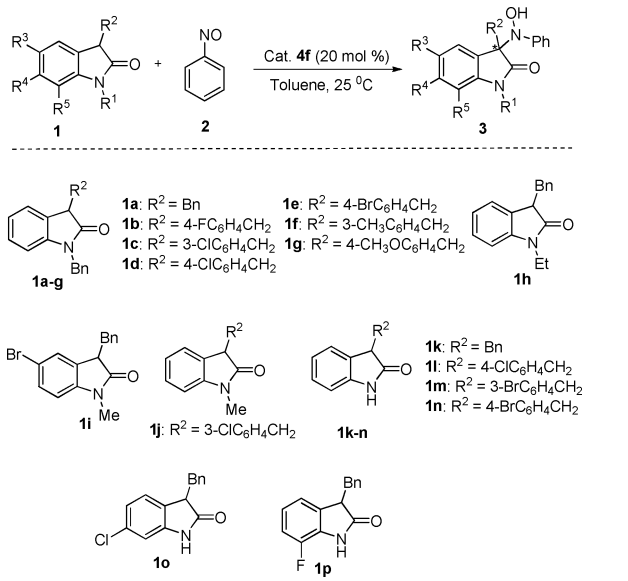
[a] Unless otherwise noted, reactions were performed with 0.2 mmol scale, 0.04 mmol **4f** in toluene at room temperature. [b] Isolated yield after silica gel column chromatography. [c] Enantiomeric excess (ee) was determined by chiral HPLC. [d] At 0 °C. [e] At –20 °C.

3.0 equiv. of **1a** to **2** was a suitable molecular ratio. Furthermore, the concentration of nitrosobenzene **2** also affected the yields and enantioselectivities, and the lower concentration resulted in a slight improvement in enantioselectivity (entries 7 *vs.* 9–12). Good yield and enantioselectivity were obtained at 0.05 M concentration (86% yield, 83% ee, Table 3, entry 12). Based on the above screenings, the recommended reaction conditions of 3.0 equiv. **1a** and 1.0 equiv. **2** in toluene with 20 mol% catalyst **4f** at 25 °C were established.

Under the optimal conditions, the scopes of the substrates were finally investigated, and the results are listed in Table 4. The effects of substituents at the C3 position of *N*-benzyl-substituted oxindoles **1a–g** were evaluated first, and the yields ranged from 71% to 89% and the enantioselectivities ranged from 77% ee to 83% ee (Table 4, entries 1–7). The electronic features and position of the substituents on the C3-subsituted aromatic ring slightly affected the enantioselectivities; both electron-withdrawing (Table 4, entries 2–5) and electron-donating groups (Table 4, entries 6, 7) at the *meta*- (Table 4, entries 3, 6) or *para*-position (Table 4, entries 2, 4, 5, 7) in the aromatic ring at the C3 position gave good yields and enantioselectivities (up to 89% yield and 83% ee), whereas *meta*-substituted groups in the aromatic ring of C3-substituents afforded higher yields than the ones with *para*-substituted groups (Table 4, entries 3 *vs.* 4, entries 13 *vs.* 14). *N*-Ethyl oxindole **1h** and *N*-methyl oxindoles **1i** and **1j** gave moderate to good yields and good enantioselectivities (51–89% yield, 75–81% ee, Table 4, entries 8–10). This optimized protocol was then expanded to *N*-unsubstituted oxindoles **1k–p**, and good yields and enantioselectivities were obtained (71–91% yield, 76–90% ee, Table 4, entries 11–16). Particularly, C3-benzyl-substituted *N*-unprotected oxindoles **1k** gave the corresponding 3-amino-2-oxindoles in the highest enantioselectivity (90% ee, Table 4, entry 11).

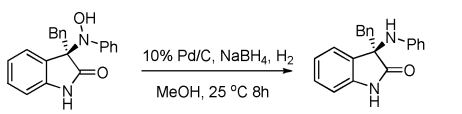
The hydroxyamination product **3k** could easily transformed into 3-amino oxindole **5k** in 71% yield and 92% ee (Scheme 2).

Table 4 Enantioselective hydroxyamination of oxindoles[a]



Entry	Substrate	Time (h)	Product	Yield (%)[b]	ee (%)[c,e]
1	**1a**	6	**3a**	86	83
2	**1b**	5	**3b**	75	80
3	**1c**	5	**3c**	87	81
4	**1d**	6	**3d**	71	82
5	**1e**	4	**3e**	83	80
6	**1f**	7	**3f**	89	77
7	**1g**	9	**3g**	71	77
8	**1h**	11	**3h**	51	81
9	**1i**	5	**3i**	85	75
10	**1j**	5	**3j**	89	77
11[d]	**1k**	3	**3k**	86	90
12[d]	**1l**	3	**3l**	85	82
13[d]	**1m**	3	**3m**	91	82
14[d]	**1n**	2	**3n**	84	76
15[d]	**1o**	1.5	**3o**	71	86
16[d]	**1p**	1.5	**3p**	71	78

[a] All the reactions were performed using **1a** (0.6 mmol), **2** (0.2 mmol) and **4f** (0.04 mmol) in toluene (4 ml) at room temperature. [b] Isolated yield after silica gel column chromatography. [c] Enantiomeric excess (ee) was determined by chiral HPLC. [d] Isolated yield after filtration. [e] The configuration (*R*) was determined by comparison of the rotation of **1k**, **1l** and **1n** with the literature.[3l,5]



Scheme 2 Cleavage of N–O bond.

Conclusions

In conclusion, we have presented an efficient regioselective and enantioselective bifunctional chiral thiourea–tertiary amine-catalyzed hydroxyamination of C3-subsituted oxindoles. 3-Amino-2-oxindoles with chiral quaternary stereocenters were obtained in good yields and enantioselectivities (up to 91% yield, up to 90% ee) for a series of C3-subsituted oxindoles, the best results for metal-free catalytic hydroxyamination to date. Further investigations of the mechanism and other variants of

enantioselective hydroxyamination reaction are underway in our laboratory.

Acknowledgements

We are grateful for financial support from National Natural Science Foundation of China (No. 20802075 and No.21042006).

Notes and references

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