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Chiral *N,N'*-Dioxide/Sc^{III} Complex-Catalyzed Asymmetric Ring-Opening Reaction of Cyclopropyl Ketones with Indoles

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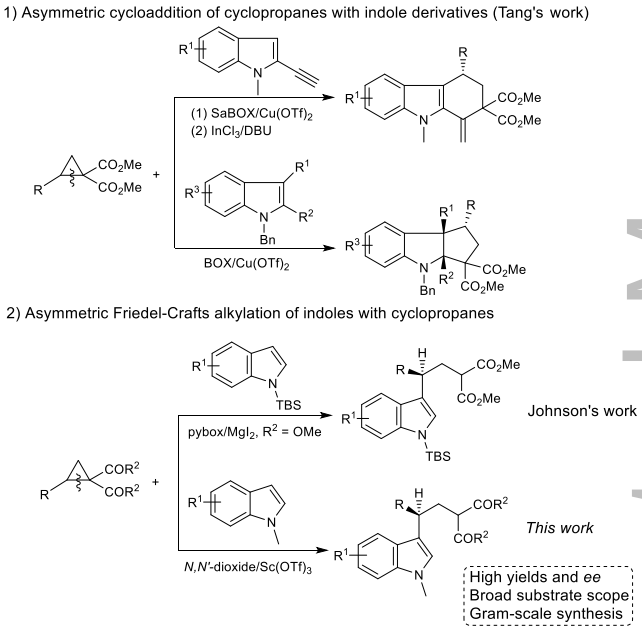
Abstract: The asymmetric ring-opening reaction of cyclopropyl ketones with indoles has been realized by using a *N,N'*-dioxide/scandium(III) complex as catalyst. The corresponding 3-alkylated indole derivatives were obtained in moderate to excellent yields with good *ee* values. Moreover, a possible transition state was proposed on the basis of experimental studies and X-ray of product.

Keywords: asymmetric catalysis; ring-opening reaction; D-A cyclopropanes; indoles; heterocycles

Donor-Acceptor (D-A) cyclopropanes are a kind of highly active cyclopropanes with both electron-withdrawing group and electron-donating group.[1] The ring-opening reaction of D-A cyclopropanes can provide a rapid access to a variety of cyclic or acyclic compounds by annulation or addition reactions.[2] The catalytic asymmetric ring-opening reactions of D-A cyclopropanes with heteroatom nucleophiles, such as nitrogen-,[3] sulfur-[4] and oxygen-containing[4a,5] nucleophiles, have been realized by using the chiral *N,N'*-dioxide/metal complexes[6] or chiral oxazoline/metal complexes. However, for the ring-opening reaction of D-A cyclopropanes with carbon nucleophiles, more challenges exist due to their weaker nucleophilic ability. The enol ethers are proved to be efficient carbon nucleophiles in the asymmetric [3+2] and [4+3] cycloaddition reactions of D-A cyclopropanes in the presence of oxazoline/Cu(II) complexes by Tang's and Waser's groups.[7-9] Besides, 2-naphthols were found to be another type of suitable C-nucleophiles to proceed [3+2] cyclopentannulation reaction with cyclopropanes in the presence of $Bi(OTf)_3$. Alternatively, a Friedel–Crafts-type addition to cyclopropanes took place when $Sc(OTf)_3$ was employed as the Lewis acid.[10a] Very recently, we accomplished the catalytic asymmetric ring-opening reaction of cyclopropyl ketones with β-naphthols using a *N,N'*-dioxide/scandium(III) complex as the chiral catalyst.[10b]



Scheme 1. Catalytic asymmetric ring-opening reaction of cyclopropanes with indoles.

On the other hand, indoles, as one kind of the most important heterocyclic compounds emerging in many research areas,[11] can also act as carbon nucleophiles in the ring-opening reaction of D-A cyclopropanes.[12] In the catalytic asymmetric version, Tang's group developed a BOX/Cu^{II} complex-catalyzed highly diastereo- and enantioselective annulation of indoles with D-A cyclopropanes.[13] The BOX/Cu^{II} complexes were also utilized to promote the [3+3] annulation of 2-alkynylindoles with D-A cyclopropanes.[14] As for the Friedel-Crafts alkylation of indoles with cyclopropanes to achieve ring-opened

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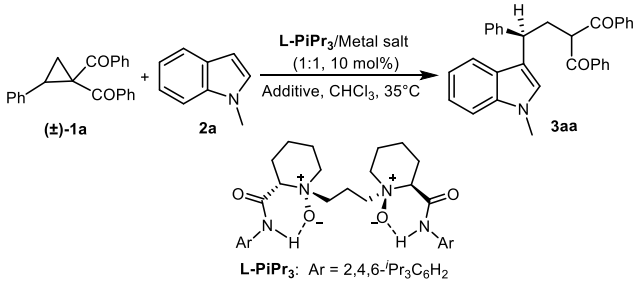
adduct, only Johnson described an asymmetric dynamic kinetic Friedel-Crafts alkylation promoted by pybox-MgI_2 complex in 2013.[15] The alkylation products were obtained in good yields with moderate to high enantioselectivities. To date, chiral oxazoline/metal (especially Cu (II)) complexes were the only efficient catalytic system for the ring-opening reaction of D-A cyclopropanes with carbon nucleophiles. As a consequence, developing new catalytic systems for the ring-opening reaction is meaningful. Herein, we reported our efforts in developing a chiral *N*,*N'*-dioxide/scandium(III) complex catalytic system for the highly enantioselective ring-opening reaction of cyclopropyl ketones with indoles, achieving optically active 3-alkylated indole derivatives in high yields with good enantioselectivities.

Our study began with the ring-opening of cyclopropyl ketone **1a** with *N*-methylindole **2a** as model reaction to optimize the reaction conditions, and the representative results were summarized in Table 1. Firstly, various metal salts complexing with (*S*)-pipecolic acid-derived *N*,*N'*-dioxide **L-PiPr3** were evaluated (Table 1, entries 1-6). Many metal salts, such as $Mg(OTf)_2$, $MgCl_2$, $Zn(OTf)_2$ and $Ni(OTf)_2$, can't or faintly promote the reaction (Table 1, entries 1-4). Delightedly, rare earth metal salts exhibit better catalytic abilities in this reaction, and scandium complexes were proven to be competent catalysts. Without additive, **L-PiPr3**/$Sc(OTf)_3$ complex gave the 3-alkylated indole product **3aa** with 70% *ee* but only in 19% yield (Table 1, entry 7). Fortunately, the of $MgCl_2$ to the reaction system could dramatically increase the yield to 84% and the enantioselectivity to 94% *ee* (Table 1, entry 8). Prolonging the reaction time to 5 days and increasing the concentration of indole to 0.5 mol/mL could effectively enhance the yield to 99% with the maintained enantioselectivity (94% *ee*, Table 1, entry 9). Therefore, the optimized conditions entail the use of the **L-PiPr3**/$Sc(OTf)_3$ complex (10 mol%) as the catalyst and the $MgCl_2$ (1 equiv) as an additive in $CHCl_3$ at 35 °C.

With the optimized conditions in hand, the substrate scope of the reaction was then evaluated. Firstly, a variety of cyclopropyl ketones were examined, and excellent level of enantioselectivity was achieved (Table 2). Cyclopropyl ketones with various substituents at different position of phenyl group R^1 converted efficiently to the corresponding products (80-99% yields, 85-94% *ee*, Table 2, entries 1-9). In addition, naphthyl-substituted substrates **1k** and **1l** were also tolerated, resulting the corresponding products **3ka** and **3la** in excellent yields and *ee* values (99% yield, 93-96% *ee*, Table 2, entries 10-11). Futhermore, the vinyl-substituted cyclopropyl ketone also transformed to the product **3ma** in 52% yield with 73% *ee* (Table 2, entry 12). Unfortunately, when aliphatic methyl substituted cyclopropyl ketone **1n** was applied in the reaction, no

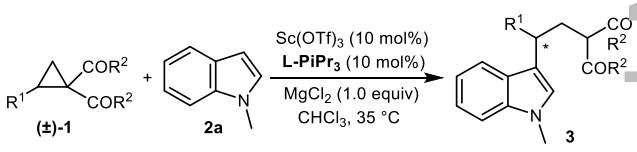
Table 1. Optimization of the reaction conditions.[a]



Entry	Metal salt	Additive	Yield [%][b]	*ee* [%][c]
1	$Mg(OTf)_2$	--	NR	--
2	$MgCl_2$	--	NR	--
3	$Zn(OTf)_2$	--	trace	--
4	$Ni(OTf)_2$	--	5	17
5	$Yb(OTf)_3$	--	62	20
6	$Y(OTf)_3$	--	31	56
7	$Sc(OTf)_3$	--	19	70
8[d]	$Sc(OTf)_3$	$MgCl_2$	84	94
9[d,e]	$Sc(OTf)_3$	$MgCl_2$	99	94

[a] Unless otherwise noted, all reactions were carried out with **1a** (0.22 mmol), **2a** (0.10 mmol), **L-PiPr3**/metal (1:1, 10 mol%) in $CHCl_3$ (0.5 mL) under nitrogen at 35°C for 3 days. [b] Yield of isolated product. [c] Determined by HPLC analysis on a chiral stationary phase. [d] Add $MgCl_2$ (1.0 equiv) to reaction system. [e] Prolong the reaction time to 5 days and decreasing the amount of $CHCl_3$ to 0.2 mL. OTf = trifluoromethansulfonate.

Table 2. Scope of the cyclopropyl ketone.[a]



Entry	R^1, R^2	Yield [%][b]	*ee* [%][c]
1	4-MeC_6H_4, Ph (**1b**)	99 (**3ba**)	91 (*R*)
2	4-FC_6H_4, Ph (**1c**)	99 (**3ca**)	89 (*R*)
3	4-ClC_6H_4, Ph (**1d**)	94 (**3da**)	93 (*R*)
4	4-BrC_6H_4, Ph (**1e**)	95 (**3ea**)	89 (*R*)
5	3-MeC_6H_4, Ph (**1f**)	95 (**3fa**)	86 (*R*)
6	3-$MeOC_6H_4$, Ph (**1g**)	99 (**3ga**)	85 (*R*)
7	3-ClC_6H_4, Ph (**1h**)	80 (**3ha**)	93 (*R*)
8	3-BrC_6H_4, Ph (**1i**)	84 (**3ia**)	94 (*R*)
9	2-MeC_6H_4, Ph (**1j**)	99 (**3ja**)	91 (*R*)
10	1-Naphthyl, Ph (**1k**)	99 (**3ka**)	96 (*R*)
11	2-Naphthyl, Ph (**1l**)	99 (**3la**)	93 (*R*)
12	Vinyl, Ph (**1m**)	52 (**3ma**)	73 (*R*)
13	Me, Ph (**1n**)	0	--
14	Ph, 4-FC_6H_4 (**1o**)	97 (**3oa**)	94 (*R*)
15	Ph, 4-MeC_6H_4 (**1p**)	86 (**3pa**)	86 (*R*)
16	Ph, 4-$MeOC_6H_4$ (**1q**)	77 (**3qa**)	92 (*R*)

[a] Unless otherwise noted, the reactions were performed with **1** (0.22 mmol), **2a** (0.10 mmol), **L-PiPr3**/$Sc(OTf)_3$ (1:1, 10 mol%), $MgCl_2$ (1.0 equiv) in $CHCl_3$ (0.2 mL) under nitrogen at 35 °C. [b] Yield of isolated product. [c] Determined by HPLC analysis on a chiral stationary phase.

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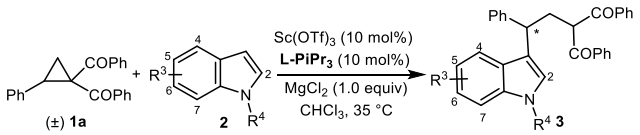
product was detected (Table 2, entry 13). Investigation of carbonyl substituent R^2 revealed that electron-withdrawing groups on the phenyl group had little influence on the reaction, but the electron-donating substituents would led to a reduced yield or enantioselectivity (Table 2, entries 14-16).

Table 3. Scope of the indole substrate.[a]

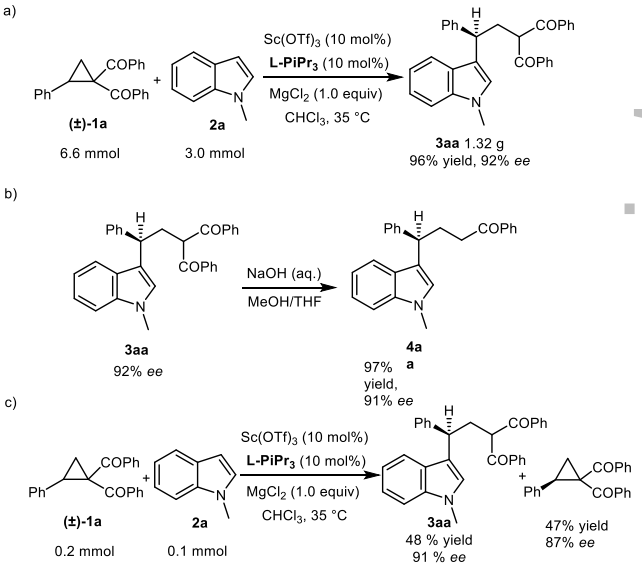


Entry	R^3, R^4	Yield [%][b]	*ee* [%][c]
1	H, H	67 (**3ad**)	84 (*R*)
2	H, TBS	56 (**3ae**)	96 (*R*)
3	2-Me, CH_3	90 (**3af**)	96 (*R*)
4	4-Me, CH_3	63 (**3ag**)	94 (*R*)
5	4-Br, CH_3	53 (**3ah**)	95 (*R*)
6	5-Me, CH_3	99 (**3ai**)	91 (*R*)
7	5-MeO, CH_3	80 (**3aj**)	94 (*R*)
8	5-Cl, CH_3	79 (**3ak**)	86 (*R*)
9	5-F, CH_3	78 (**3al**)	91 (*R*)
10	6-Me, CH_3	95 (**3am**)	91 (*R*)
11	6-Cl, CH_3	78 (**3an**)	92 (*R*)
12	7-Me, CH_3	99 (**3ao**)	90 (*R*)
13	7-Cl, CH_3	88 (**3ap**)	91 (*R*)

[a] Unless otherwise noted, the reactions were performed with **1a** (0.22 mmol), **2** (0.10 mmol), **L-PiPr3**/$Sc(OTf)_3$ (1:1, 10 mol%), $MgCl_2$ (1.0 equiv) in $CHCl_3$ (0.2 mL) under nitrogen at 35 °C. [b] Yield of isolated product. [c] Determined by HPLC analysis on a chiral stationary phase.

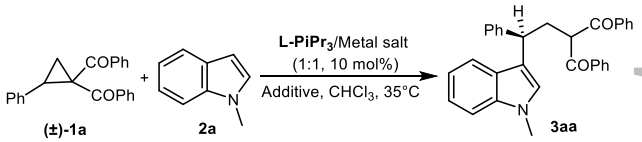
Subsequently, various indoles **2** were investigated by reacting with cyclopropyl ketone **1a** (Table 3). Indole **2d** without protection and *N*-TBS-indole **2e** proceeded the reaction in lower activities but still good enantioselectivities (Table 3, entries 1-2). When the *N*-methyl-2-methy-indole **2f** was subjected to the reaction, the corresponding product **3af** was obtained in 90% yield with 96% *ee* (Table 3, entry 3). Indoles with substitutions at C4-position converted to the desired product with good enantioselectivities but in lower yields(63-53% yields; 94-95% *ee*, Table 3, entries 4-5), probably due to the steric hindrance between the substrate and the ligand. In comparison, indoles (**2i**-**2p**) bearing substituents attached on C5-, C6-, and C7-position, mostly behaved well in the current system (78-99% yields, 86-94% *ee*, Table 3, entries 6-13), indicating that the electronic effect has little effect on the reaction. The absolute configuration of **3aa** was determined to be (*R*) by X-ray crystallography, and the configurations of others were also assigned to be (*R*) by comparing the circular dichroism spectrum with that of **3aa**.

To evaluate the synthetic potential of this methodology, a gram-scale synthesis of **3aa** was carried out. In the optimal conditions, 6.6 mmol cyclopropyl ketone **1a** reacted smoothly with 3 mmol *N*-methylindole **2a**, affording 1.32 g (96% yield) of the product **3aa** in 92% *ee* (Scheme 2). Furthermore, the product **3aa** could be readily transformed to mono carbonyl product **4a** upon treatment with NaOH in a mixed solvent of methanol and tetrahydrofuran. When 2.0 equiv of cyclopropyl ketone **1a** reacted with **2a**, the product **3aa** was obtained in 48% yield with 91% *ee* after 5 days, and the unreacted cyclopropyl ketone **1a** was recovered in 47% yield with 87% *ee*, revealing that a kinetic resolution process was invovled in our catalytical system.



Scheme 2. a) Scale-up reaction. b) Product transformation. c) Kinetic resolution of **1a** with **2a**

Table 4. Control experiment.[a]



Entry	Metal salt	Additive	Yield [%][b]	*ee* [%][c]
1	$Sc(OTf)_3$	$Mg(OTf)_2$	75	17
2	$Sc(OTf)_3$	$MgSO_4$	49	50
3	$Sc(OTf)_3$	$nBu_4N^+Cl^-$	23	98
4	$Sc(OTf)_3$	NaCl	21	82
5	$ScCl_3 \cdot 6H_2O$	--	52	97
6	$ScCl_3 \cdot 6H_2O$	$Mg(OTf)_2$	49	86

[a] Unless otherwise noted, the reactions were performed with **1a** (0.22 mmol), **2** (0.10 mmol), **L-PiPr3**/metal salt (1:1, 10 mol%), additive (1.0 equiv) in $CHCl_3$ (0.2 mL) under nitrogen at 35 °C. [b] Yield of isolated product. [c] Determined by HPLC analysis on a chiral stationary phase.

In order to explore the role of magnesium chloride in this system, several control experiments and HRMS analysis were conducted (Table 4). When the

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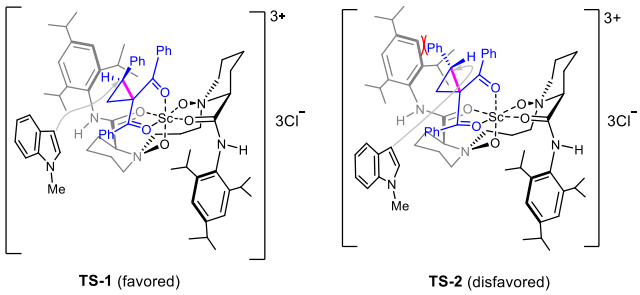

Scheme 3. Proposed transition model.

anion of additive was changed from Cl^- to OTf^- or SO_4^{2-}, both yield and *ee* value of the product decreased sharply (Table 4, entries 1-2). Switching the cation of additive to nBu_4N^+ or Na^+, the yield the decreased but the enantioselectivity was still excellent (Table 4, entries 3-4). These two control experiments indicated that both magnesium cation and chloride anion are critical for high yield and high enantioselectivity in this reation[16]. Moreover, when $ScCl_3{\cdot}6H_2O$/**L-PiPr$_3$** was used as catalyst, the corresponding product **3aa** were obtained in 52% yield with 97% *ee* value (Table 4, entry 5), suggesting that counteranion exchange might exist during the preparation of catalyst. HRMS analysis confirmed this assumption. A mixture of ligand **L-PiPr$_3$**, $Sc(OTf)_3$ and $MgCl_2$ shown an ionic peak at *m/z* 847.4476, 849.4464 {[**L-PiPr$_3$** + Sc^{3+} + $2Cl^-$]$^+$ *m/z* calcd 847.4484, 849.4455}. Besides, in the mixture of ligand **L-PiPr$_3$**, $Sc(OTf)_3$, $MgCl_2$, and **1a**, the characteristic signals of [**L-PiPr$_3$** + Sc^{3+}+ Cl^- + **1a**]$^{2+}$ at *m/z* 569.3047, 569.8102 (*m/z* calcd 569.3049, 569.8065) were also observed. Based on the above studies, the absolute configuration of products, and our previous work,[17] a possible transition state model was proposed. As shown in Scheme 3, the oxygen atoms of ligand and cyclopropyl ketone **1a** coordinate with the Sc^{III} to form an octahedral complex, which could distinguish the two different configurations of cyclopropyl ketone and selectively activated (*S*)-**1a** via coordination (**TS-1**), then indole attacked (*S*)-**1a** from the the direction with small steric hindrance to deliver (*R*)-configured product. In comparation, the coordination of (*R*)-**1a** with *N*,*N*′-dioxide/scandium(III) complex is much less efficient due to the steric repulsion between the 2,4,6-diisopropylphenyl group of the ligand and the phenyl group of cyclopropyl ketone (in TS-2). Therefore, (*R*)-**1a** was less active under optimized conditions and could be recovered in high enantioselectivity. With regards to the role of counteranion, we envisoned that the Lewis acidity of metal species is responsible for the observed reactivity and more acidic $ScCl_3$ exhibited a higher reactivity than $Sc(OTf)_3$ in the reaction. Moreover, the electrostatic attraction between *N*,*N*′-dioxide-$Sc^{(III)}$ complex with Cl^- provided a more suitable chiral enviroment for recognizating (*R*)-**1a**, which was in consist with experimental results.

In summary, a chiral *N*,*N*′-dioxide/scandium(III) complex was proved to be efficient for the highly enantioselective ring-opening reaction of cyclopropyl ketones with indoles. A series of 3-alkylated indole derivatives were obtained in high to excellent yields with high *ee* values. Further exploration of the catalyst system for other asymmetric reactions is currently under investigation.

Experimental Section

N,*N*′-Dioxide ligand **L-PiPr$_3$** (0.01 mmol), $Sc(OTf)_3$ (0.01 mmol), $MgCl_2$ (0.10 mmol) and cyclopropyl ketone **1a** (0.22 mmol) were stirred in $CHCl_3$ (0.2 mL) at 35 °C under N_2 atmosphere for 0.5 h. Then, indole **2a** (0.10 mmol) was added and the mixture was stirred at 35 °C for 5 days. The reaction mixture was purified by flash chromatography (petroleum: ethyl acetate = 10:1) on silica gel to afford the desired product as a yellow solid in 99% yield with 94% *ee*.

Acknowledgements

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