Asymmetric Ring Opening

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Asymmetric Ring-Opening of Cyclopropyl Ketones with Thiol, Alcohol, and Carboxylic Acid Nucleophiles Catalyzed by a Chiral *N,N′*-Dioxide–Scandium(III) Complex

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Abstract: *A highly efficient asymmetric ring-opening reaction of cyclopropyl ketones with a broad range of thiols, alcohols and carboxylic acids has been first realized by using a chiral N,N′-dioxide–scandium(III) complex as catalyst. The corresponding sulfides, ethers, and esters were obtained in up to 99% yield and 95% ee. This is also the first example of one catalytic system working for the ring-opening reaction of donor–acceptor cyclopropanes with three different nucleophiles, let alone in an asymmetric version.*

Cyclopropanes have proven to be powerful synthetic building blocks.[1] In particular, the ring-opening reactions of donor–acceptor (D-A) cyclopropanes[2–7] provide access to a myriad of functionalized carbon skeletons and have attracted extensive attention. Ring-opening reactions initiated by sulfur- and oxygen-containing nucleophiles have been found to be a very useful transformation in the synthesis of γ-thio and γ-oxy functionalized carbonyls.[8,9] For example, the (*S*)-proline and Ca(acac)$_2$-catalyzed racemic reaction with thiol nucleophiles were reported by Wang[7k] and Nolin,[7l] respectively. Moreover, the opening of 1-nitro-cyclopropanecarboxylates with phenols for synthesizing the norepinephrine reuptake inhibitor atomoxetine was developed by Charette.[7n] An intramolecular nucleophilic ring-opening dealkyoxycarbonylation of cyclopropane hemimalonate to the synthesis of γ-substituted butanolides under microwave irradiation was also documented by Kerr (Scheme 1 a).[7q] Although the reactions of D-A cyclopropanes with sulfur- and oxygen-containing nucleophiles have been developed, no examples of catalytic asymmetric ring-opening of D-A cyclopropanes with thiols, alcohols, or carboxylic acids have been reported to date. This could be assigned to the following reasons: i) For thiols, the strong coordination ability of sulfur atom to the central metal might poison the catalyst when a Lewis acid is used as catalyst; ii) For carboxylic acids, the reaction usually requires severe conditions because of their weak nucleophilic nature, which makes it difficult to balance the reactivity and stereocontrol. Furthermore, searching for a catalyst system that could work well on not only sulfur-containing nucleophiles but also oxygen-containing nucleophiles is challenging. As part of a program devoted to expanding new synthetic methods involving D-A cyclopropanes, we recently described an enantioselective ring-opening/cyclization of cyclopropyl ketones with primary amines using a chiral *N,N′*-dioxide–scandium(III) complex, and the corresponding 2,3-dihydropyrroles were obtained in excellent outcomes (Scheme 1 b).[10] In continuation of our studies on ring-opening of cyclopropyl ketones, herein we report our efforts on developing the catalytic asymmetric direct ring-opening reaction of cyclopropyl ketones with thiol, alcohol, and carboxylic acid nucleophiles catalyzed by a chiral *N,N′*-dioxide–scandium(III) complex[11] (Scheme 1 c).

Initially, cyclopropyl ketone **1a** and thiophenol **2e** were chosen as model substrates to optimize the reaction conditions. At first, various metal salts complexing with *N,N′*-dioxide L-PiPr$_3$ derived from (*S*)-pipecolic acid (Pi) were evaluated in the presence of LiCl in CHCl$_2$CHCl$_2$ at 60 °C (Table 1, entries 1–3). After 48 h, the complexes of Yb(OTf)$_3$ and Ni(ClO$_4$)$_2$·6 H$_2$O gave moderate yields and poor *ee* values (entries 1,2). To our delight, the L-PiPr$_3$-Sc(OTf)$_3$ complex was more effective at promoting the reaction, and the desired product **3ae** was obtained in 92% yield with 91% *ee*. The structure of the ligands were then investigated. It was found that the steric hindrance of the amide moieties, as well as the amino acid backbone of the ligands, influenced the reaction greatly. Decreasing the steric hindrance of amide substituent, or using (*S*)-proline derived L-PrPr$_3$ and L-ramipril derived L-RaPr$_3$ as ligands resulted in lower reactivity and poorer enantioselectivity (entries 4–6). When performed at 35 °C, the reaction could also occur and **3ae** was isolated in 80% yield with 92% *ee* after prolonging the reaction time to 96 h (entry 7). Other reaction conditions, such as solvent and additive, were also investigated, but no better results were obtained (see the Supporting Information for details). Therefore, the optimized conditions entailed the use of L-PiPr$_3$-Sc(OTf)$_3$ as catalyst and LiCl as additive in CHCl$_2$CHCl$_2$ at 60 °C for 48 h (entry 3).

With the optimized conditions established, the substrate scope of thiol nucleophiles was explored. As shown in Table 2, a wide range of thiols including aromatic and aliphatic

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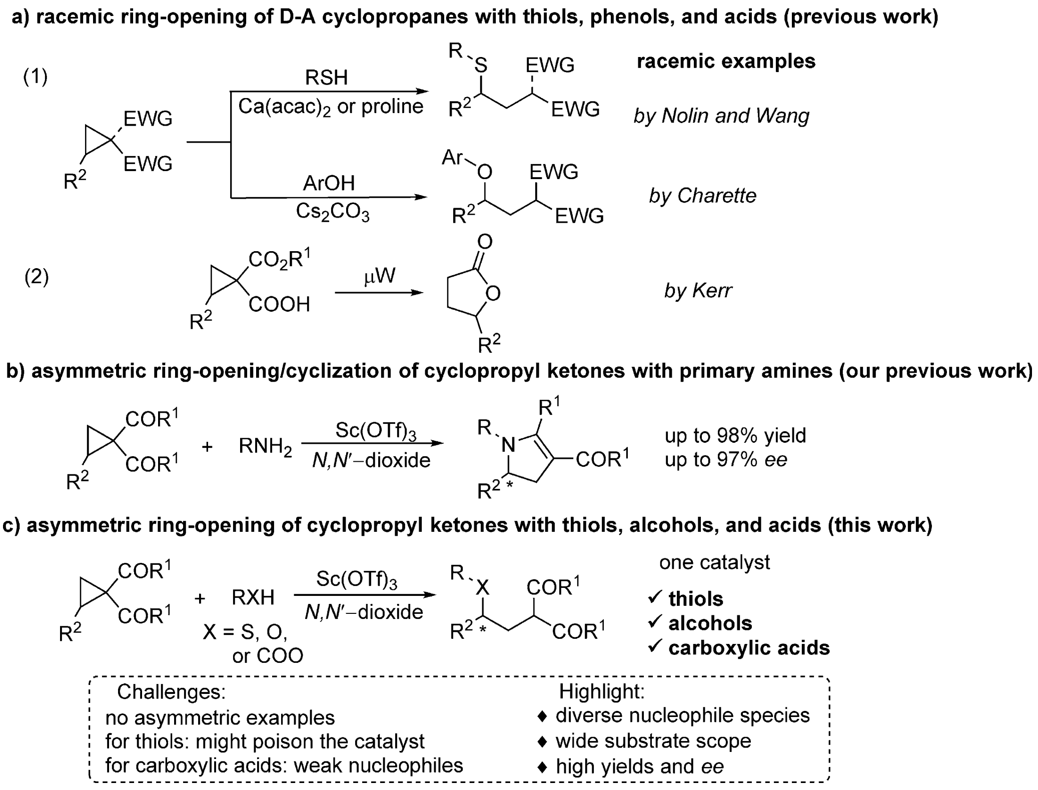
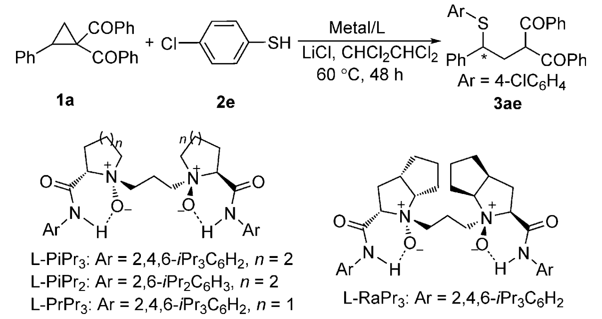


Scheme 1. Ring-opening reactions of D-A cyclopropanes with nucleophiles.

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



Entry	Metal	L	Yield [%][b]	*ee* [%][c]
1	$Ni(ClO_4)_2\cdot 6H_2O$	L-PiPr$_3$	42	8
2	$Yb(OTf)_3$	L-PiPr$_3$	51	36
3	$Sc(OTf)_3$	L-PiPr$_3$	92	91
4	$Sc(OTf)_3$	L-PiPr$_2$	75	79
5	$Sc(OTf)_3$	L-RaPr$_3$	68	88
6	$Sc(OTf)_3$	L-PrPr$_3$	56	77
7[d]	$Sc(OTf)_3$	L-PiPr$_3$	80	92

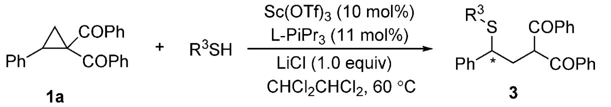
[a] Unless otherwise noted, all reactions were carried out with **1a** (0.25 mmol), **2a** (0.1 mmol), L-metal (1.1:1, 10 mol%), and LiCl (0.1 mmol) in $CHCl_2CHCl_2$ (0.5 mL) under nitrogen at 60°C for 48 h. [b] Yield of isolated product. [c] Determined by chiral HPLC analysis on a chiral stationary phase. [d] At 35°C for 96 h. OTf = trifluoromethanesulfonate.

substituents were suitable substrates for the reaction. Generally, thiophenols showed higher reactivities and gave better yields than aliphatic substituted ones. In respect to the stereoselectivities, neither the steric hindrance nor the electronic nature of the substituents at the aromatic ring of thiolphenols had any obvious influence on enantioselectivities (entries 1–9). Moreover, heteroaromatic and naphthyl-substituted thiols were also suitable substrates, giving the desired acyclic products **3aj**–**3al** in 74–98% yields with 90–91% *ee* (entries 10–12). The aliphatic thiols, including primary, acyclic, and cyclic secondary thiols exhibited high levels of asymmetric induction, affording the corresponding sulfides **3am**–**3ar** in 90–95% *ee* (entries 13–18). It is particularly noteworthy that tertiary substituted *tert*-butyl mercaptan was also compatible, and the product **3as** was obtained in 86% *ee*, albeit with a moderate yield (55%, entry 19). Furthermore, when the reaction of **1a** with **2e** was carried out on a gram scale, the corresponding product **3ae** was accomplished in 83% yield with 94% *ee* (entry 20).

Subsequently, the substrate scope of cyclopropyl ketones was examined, and the results are listed in Table 3. Cyclopropyl ketones with either electron-rich or electron-poor substituted aryl R^1 at the 2-position could be efficiently converted to the corresponding products in good yields (62–94%) with excellent *ee* (90–95%, entries 1–9). When naphthyl-substituted substrate was injected to the reaction, the opening product **3ke** was obtained in 92% yield with 88% *ee* (entry 10). The electronic nature of the substituent at the *para* position of the benzoyl group had no obvious effect on the reactivities and enantioselectivities of this reaction (entries 11, 12). The 2-phenyl-cyclopropane-1,1-dimethylketones, 2-methyl-cyclopropane-1,1-diphenylketones, and 2-phenyl-cyclopropane-1,1-dicarboxylic acid diesters were also investigated, but no ring-opening products were observed.[12]

Encouraged by the results obtained from thiols, we extended this catalytic system to the ring-opening reactions of cyclopropyl ketones with oxygen-containing nucleophiles. Aliphatic alcohols proceeded smoothly to give the corresponding products in good yields (65–94%) with excellent enantiomeric excesses (90–92%; Table 4, entries 1–8). Extending the carbon chains of alcohols had no obvious influence on the enantioselectivities (entries 1–4). Besides the acyclic substituted alcohols, cyclic substituted alcohols also performed well in this catalytic system, giving the opening

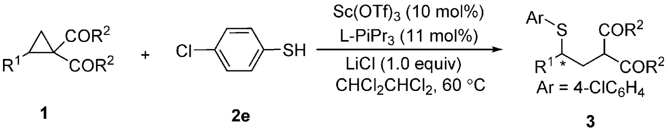
Table 2: Substrate scope for thiols.[a]



Entry	R^3	3	Yield [%][b]	*ee* [%][c]
1	Ph	**3aa**	94	92
2	4-MeC$_6$H$_4$	**3ab**	97	91
3	4-MeOC$_6$H$_4$	**3ac**	95	89
4	4-FC$_6$H$_4$	**3ad**	84	91
5[d]	4-ClC$_6$H$_4$	**3ae**	92	91 (*R*)
6	4-BrC$_6$H$_4$	**3af**	90	92
7	3-ClC$_6$H$_4$	**3ag**	90	93
8	2-ClC$_6$H$_4$	**3ah**	83	92
9	2-MeC$_6$H$_4$	**3ai**	95	92
10	1-naphthyl	**3aj**	98	90
11	2-naphthyl	**3ak**	95	91
12	2-thienyl	**3al**	74	90
13[e]	Et	**3am**	78	95
14	Bn	**3an**	94	95
15[e]	EtO$_2$CCH$_2$CH$_2$	**3ao**	69	95
16[f]	*i*Pr	**3ap**	79	90
17[e]	cyclopentyl	**3aq**	89	93
18[e]	cyclohexyl	**3ar**	90	91
19[f]	*t*Bu	**3as**	55	86
20[g]	4-ClC$_6$H$_4$	**3ae**	83	94

[a] Unless otherwise noted, all reactions were carried out with **1a** (0.25 mmol), **2a** (0.1 mmol), L-PiPr$_3$-Sc(OTf)$_3$ (1.1:1, 10 mol%), and LiCl (0.1 mmol) in CHCl$_2$CHCl$_2$ (0.5 mL) under nitrogen at 60°C for 48 h. [b] Yield of isolated product. [c] Determined by chiral HPLC analysis on a chiral stationary phase. [d] The absolute configuration of **3ae** was determined to be *R* by X-ray crystallographic analysis of the corresponding sulfone **6**. [e] Reaction time was 72 h. [f] Reaction time was 96 h. [g] The reaction was carried out on a gram scale.

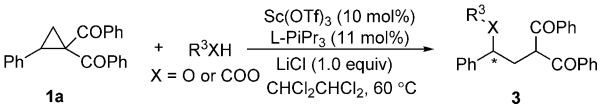
Table 3: Substrate scope for cyclopropyl ketones.[a]



Entry	R^1	R^2	3	Yield [%][b]	ee [%][c]
1	4-MeC$_6$H$_4$	Ph	**3be**	83	91
2	3-MeC$_6$H$_4$	Ph	**3ce**	94	93
3	3-MeOC$_6$H$_4$	Ph	**3de**	90	94
4	2-MeC$_6$H$_4$	Ph	**3ee**	93	91
5[d]	4-FC$_6$H$_4$	Ph	**3fe**	88	93
6[d]	4-ClC$_6$H$_4$	Ph	**3ge**	80	90
7[d]	4-BrC$_6$H$_4$	Ph	**3he**	76	92
8[d]	3-ClC$_6$H$_4$	Ph	**3ie**	62	95
9[e]	3,4-Cl$_2$C$_6$H$_3$	Ph	**3je**	68	92
10	2-naphthyl	Ph	**3ke**	92	88
11	Ph	4-MeC$_6$H$_4$	**3le**	87	95
12	Ph	4-FC$_6$H$_4$	**3me**	85	95

[a] Reaction conditions were the same as that in Table 2. [b] Yield of isolated product. [c] Determined by chiral HPLC analysis on a chiral stationary phase. [d] Reaction time was 96 h. [e] Reaction time was 168 h.

Table 4: Substrate scope for alcohols and carboxylic acids.[a]



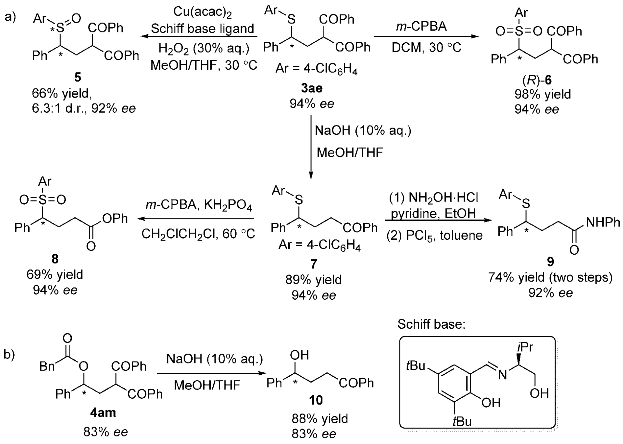
Entry	R^3	X	3 or 4	Yield [%][b]	*ee* [%][c]
1	Me	O	**4aa**	69	91
2	Et	O	**4ab**	78	92
3	*n*-Pr	O	**4ac**	65	92
4	*n*-octanyl	O	**4ad**	78	91
5	Bn	O	**4ae**	60	90
6	cyclobutyl	O	**4af**	72	92
7	cyclopentyl	O	**4ag**	94	92
8[d]	cyclohexyl	O	**4ah**	78	91
9[e]	Ph	O	**4ai**	62	50
10[f]	Me	COO	**4aj**	90	76
11[f]	Et	COO	**4ak**	90	77
12[f]	*n*-heptyl	COO	**4al**	98	82
13[f]	Bn	COO	**4am**	99	83
14[f]	Ph	COO	**4an**	96	69
15[f,g]	cyclohexyl	COO	**4ao**	99	72

[a] Reaction conditions were similar to that in Table 2 except the reaction time was 96 h. [b] Yield of isolated product. [c] Determined by chiral HPLC analysis on a chiral stationary phase. [d] Reaction time was 168 h. [e] Reaction time was 48 h. [f] **1a** (0.4 mmol), L-PiPr$_3$-Sc(OTf)$_3$ (1:1, 5 mol%), 24 h. [g] L-PiPr$_3$-Sc(OTf) (1:1, 10 mol%), 48 h.

products **4af–4ah** in 72–94% yields with 91–92% *ee* (entries 6–8). A yield of 62% with 50% *ee* was observed when phenol was tested (entry 9). Carboxylic acids could also participate in this reaction and they generated the opening products in excellent yields with moderate to good enantioselectivities (Table 4, entries 10–15). Extending the alkyl length of carboxylic acids slightly improved the results (entries 10–12). An 83% enantiomeric excess was obtained when phenylacetic acid was employed (entry 13). A moderate *ee* (69%) and excellent yield (96%) were observed when aromatic substituted benzoic acid was applied (entry 14). Notably, the reaction could be extended to cyclic substituted acids, such as cyclohexane carboxylic acid, and the corresponding product **4ao** was isolated in nearly quantitative yield with 72% *ee* (entry 15).

To evaluate the synthetic potential of this method, several transformations were carried out. The sulfide product **3ae** could be efficiently transformed into sulfoxide **5** by using aqueous H$_2$O$_2$ (30%) as an oxidant in the presence of copper–Schiff base.[13] Meanwhile, **3ae** could also be transformed to sulfone **6** using *m*-CPBA as an oxidant through an oxidation process. The absolute configuration of **6** was unambiguously confirmed as *R* by X-ray diffraction analysis.[14] In the presence of aqueous NaOH, one benzoyl group of **3ae** could be removed, giving γ-sulfide mono-carbonyl compound **7**. Baeyer–Villiger oxidation of **7** proceeded with *m*-CPBA to afford γ-sulfonyl ester **8** in 69% yield with 94% *ee*. Furthermore, amide **9** could be easily achieved from **7** through an oximation/Beckmann rearrangement sequence (Scheme 2a). The ester **4am** also could be efficiently converted to chiral γ-hydroxyl ketone **10** in 88% yield with maintained enantioselectivity by treatment with aqueous NaOH (Scheme 2b).

In summary, we have realized the first catalytic asymmetric ring-opening reaction of cyclopropyl ketones with



Scheme 2. a) Elaboration of a ring-opening product; b) transformation of ester to γ-hydroxyl ketone.

thiols, alcohols, and carboxylic acids by using a chiral N,N'-dioxide–scandium(III) complex, offering a novel access to a variety of chiral sulfides, ethers, and esters in moderate to excellent yields (up to 99 %) and excellent enantioselectivities (up to 95 % *ee*). The process proceeded under mild conditions and the ring-opening products could be efficiently converted to a series of γ-substituted carbonyl compounds. This is also the first example of one catalytic system working for the catalytic asymmetric ring-opening reaction of D-A cyclopropanes with three different nucleophiles. Further studies on related reactions are underway.

Experimental Section

Conditions: Sc(OTf)$_3$ (0.01 mmol), N,N'-dioxide ligand L-PiPr$_3$ (0.011 mmol), LiCl (0.1 mmol) and cyclopropyl ketone **1a** (0.25 mmol) were stirred in CH$_2$Cl$_2$ (0.5 mL) at 35 °C for 0.5 h under nitrogen atmosphere. After removing CH$_2$Cl$_2$ in vacuum, CHCl$_2$CHCl$_2$ (0.5 mL) and substrate **2e** (0.1 mmol) were added. The reaction was stirred at 60 °C for 48 h, and then directly purified by flash chromatography on silica gel (petroleum ether/ethyl ether = 15:1) to afford the desired product **3ae** (92 % yield, 91 % *ee*).

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Keywords: asymmetric catalysis · cyclopropyl ketones · nucleophiles · ring opening · scandium catalysts

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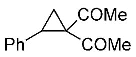
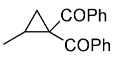
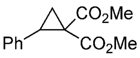


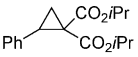
1n



1o



1p



1q

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[14] CCDC 1056523 (**6**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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