

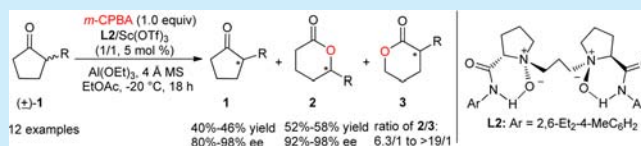
Regio- and Enantioselective Baeyer–Villiger Oxidation: Kinetic Resolution of Racemic 2-Substituted Cyclopentanones

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Supporting Information

ABSTRACT: A kinetic resolution of racemic 2-substituted cyclopentanones via highly regio- and enantioselective Baeyer–Villiger oxidation has been successfully developed. The reaction could afford the normal 6-substituted δ -lactones in up to 98% ee and >19/1 regioselectivity. Meanwhile, the unreacted ketones were recovered in excellent ee values (up to 98%). It represents the best results of the kinetic resolution of racemic 2-substituted cyclopentanones via nonenzymic asymmetric BV oxidation.



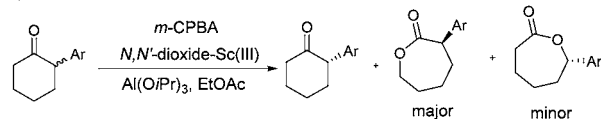
The Baeyer–Villiger (BV) oxidation¹ plays an important role in organic synthesis since it provides a straightforward access to esters or lactones from ketones. Especially, the asymmetric BV oxidation of substituted cyclic ketones is highly valuable for the synthesis of optically active lactones.^{2–7} Impressive results have been achieved for the asymmetric BV oxidations of prochiral cyclic ketones with biocatalysts,³ chiral metal complexes,⁴ or organocatalysts.⁵ Notably, the asymmetric BV oxidation of racemic 2-substituted cyclic ketones results in a kinetic resolution leading to optically active lactones and 2-substituted cyclic ketones. The related nonenzymatic catalytic system remains still elusive.⁶ In 1994, Bolm^{8a} and Strukul^{8b} reported the discovery of chiral bisoxazoline–Cu(II) and diphosphine–Pt(II) catalyzed asymmetric BV oxidation of 2-substituted cyclic ketones, respectively. Hitherto, the progress of this process is the chiral *N,N'*-dioxide–Sc(III) catalyzed BV oxidation of 2-arylcylohexanones by our group, and it is interesting to note that abnormal regioselectivity occurred in this case (Scheme 1a).⁹ Unfortunately, the kinetic resolution of 2-substituted cyclopentanones via asymmetric BV oxidation has

not been accomplished in these contexts, and the enantiomeric excess of the resulted δ -lactones was no less than 58% ee.^{8b} Herein, we would like to report an enantioselective BV oxidation and kinetic resolution of 2-substituted cyclopentanones. The regio- and enantioselectivity of the reaction are well addressed. In the presence of a chiral *N,N'*-dioxide–Sc(III) complex catalyst¹⁰ and additives, optically active δ -lactones generated preferentially from a normal CHR-group migration, and the unreactive 2-substituted cyclopentanones were recovered in high enantioselectivities (Scheme 1b).

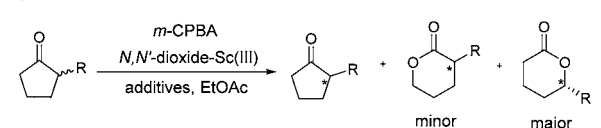
At the beginning, the catalytic system that is efficient for the asymmetric BV oxidation of 2-arylcylohexanones was subjected to the reaction of 2-phenylcyclopentanone **1a**. Although high enantioselectivities were achieved for both the normal δ -lactone **2a** and the abnormal δ -lactone **3a**, the regioselectivity (rs) and yield were poor (29% yield, 1/1.6 rs; Scheme 2). We then restarted to optimize the reaction conditions using 2-phenylcyclopentanone **1a** and *m*-chlorobenzoperoxoic acid (*m*-CPBA) as the model substrate and oxidant,¹¹ respectively. Performing the reaction in EtOAc at 0 °C without a catalyst afforded the racemic lactone **2a** in 25% yield as a single isomer (Table 1, entry 1), whereas only a trace amount of the products was observed in the presence of the chiral *N,N'*-dioxide **L1**–Sc(OTf)₃ complex catalyst (Table 1, entry 2). To improve the reactivity, the efficiency of additives was then examined. Delightedly, when the reaction was carried out with 1.0 equiv of Al(O^{*i*}Pr)₃ as the additive, the **L1**–Sc(OTf)₃ complex could give the δ -lactones in 17% yield. The ratio of the normal δ -lactone **2a** to the abnormal δ -lactone **3a** reached 5/1, and the ee value of the major δ -lactone **2a** was excellent (99% ee, Table 1, entry 3). The addition of 4 Å molecular sieves (MS) could further enhance the yield to 26% with the regio- and enantioselectivity maintained (Table 1, entry 4). Compar-

Scheme 1. Regio- and Enantioselective BV Oxidation of Racemic 2-Substituted Cyclohexanones and 2-Substituted Cyclopentanones

a): Previous work



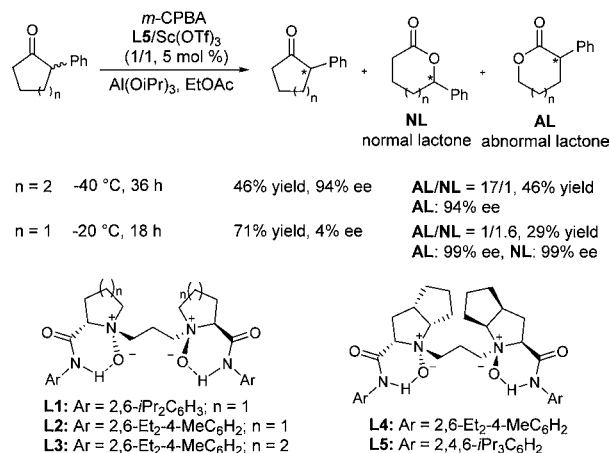
b): This work



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Scheme 2. Chiral N,N' -Dioxide–Sc(III) Complex Catalyzed Kinetic Resolution of Racemic 2-Phenyl Cyclic Ketones via Asymmetric BV Oxidation and N,N' -Dioxide Ligands Used in This Study



tively, a low yield was obtained in the presence of 4 Å MS without Al(O^{*i*}Pr)₃ (Table 1, entry 5).

Further optimization of the reaction conditions was then aimed at exploring the efficiency of other aluminum alkoxides as the additives (Table 1, entries 6–7). Fortunately, improved reactivity, as well as regio- and enantioselectivity, was observed when Al(OEt)₃ was employed as an additive (Table 1, entry 7). The 2-phenylcyclopentanone **1a** was recovered in 60% conversion with 40% ee, and δ -lactone **2a** was given in 99% ee. It is not possible to clearly rationalize the role of Al(OEt)₃ in the catalytic process at present. The primary IR spectrum of the mixture of Al(OEt)₃ and *m*-CPBA gives new peaks (see Supporting Information). We proposed that Al(OEt)₃ prior reacts with *m*-CPBA to generate an activate species which has enhanced the oxidative ability so that the reactivity was obviously improved. Next, the efficiency of other N,N' -dioxide ligands was explored (Scheme 2). When the ligand **L2** containing 2,6-diethyl-4-methylaniline was introduced, 56% conversion of the products with a 9.6/1 ratio of **2a** to **3a** was

achieved. The major δ -lactone **2a** was yielded in 98% ee, and the unreacted ketone **1a** was recovered in 44% yield with 90% ee (Table 1, entry 8).¹² As for the chiral backbone moiety, the N,N' -dioxide **L2** derived from L-proline acid exhibited superiority in enantiocontrol toward this reaction compared with the ones derived from (S)-pipecolic acid (**L3**) and (S)-ramipril acid (**L4**) (Table 1, entry 8 vs entries 9 and 10). The relationship between the enantioselectivity of the recovered ketone and the regioselectivity of the δ -lactones indicated that the two products primarily resulted from each enantiomer of the racemic ketone (entries 9 and 10). Therefore, the optimized conditions were identified as 5 mol % of the chiral N,N' -dioxide **L2**–Sc(OTf)₃ catalyst, Al(OEt)₃, and 4 Å MS as the additives in EtOAc at $-20\text{ }^{\circ}\text{C}$.

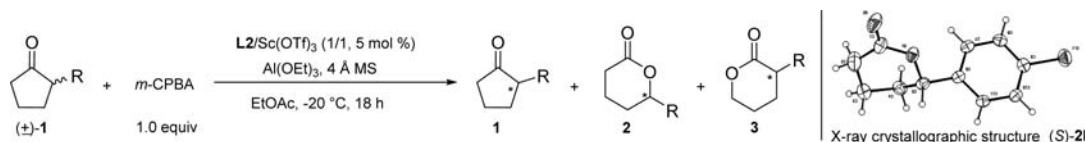
Under the optimal conditions (Table 1, entry 8), the asymmetric BV oxidation and kinetic resolution of a series of 2-substituted cyclopentanones **1** was examined. As shown in Table 2, the stereocontrol of the reaction was not sensitive to the electronic property of substituents on the phenyl ring of 2-arylcyclopentanones **1**. Generally, the normal δ -lactones **2** as the major products were obtained with a good to excellent ratio of **2** to **3** (6.3/1–>19/1 rs). Good to excellent enantiomeric excesses were achieved for the major products **2** (92–98% ee) and unreacted ketones **1** (80–98% ee; entries 1–11). The regioselectivity and reactivity were sensitive to the substituted position on 2-aryl group of the substrates rather than the electronic property. The substrates with 3-substituents on the phenyl ring afforded the lactones with decreased regioselectivity and were recovered partly in lower ee values compared with those containing 4-substituted ones (entries 2, 4, and 8 vs 3, 5, and 9). Especially, the racemic 2-([1,1'-biphenyl]-4-yl)cyclopentanone **1f** underwent the oxidation reaction well, affording the major δ -lactone **2f** in 98% ee with up to 13/1 ratio of **2f** to **3f**. And the unreacted ketone **1f** was isolated in 95% ee and 44% yield (entry 6). Moreover, 2-naphthyl substituted cyclopentanone **1k** was also tolerable, and the major product **2k** and unreacted ketone **1k** were obtained in 94% ee and 92% ee, respectively (entry 11). Besides, the absolute configuration of **2h** was determined to be *S* by X-ray analysis,¹³ and the recovered ketone **1d** was assigned as *R* by comparison of the

Table 1. Optimization of the Reaction Conditions for the Kinetic Resolution of Racemic 2-Phenylcyclopentanone **1a**

					conversion (%) ^b			ee (%) ^c		rs ^b
entry ^a	ligand	additive	MS		1a	2a + 3a		1a	2a	2a/3a
1	–	–	–		75	25 (2a)		–	–	–
2	L1	–	–		97	trace		–	–	–
3	L1	Al(O ^{<i>i</i>} Pr) ₃	–		83	17		4	99	5/1
4	L1	Al(O ^{<i>i</i>} Pr) ₃	4 Å MS		74	26		20	99	6.2/1
5	L1	–	4 Å MS		90	10		3	99	4.6/1
6	L1	Al(O ^{<i>i</i>} Bu) ₃	4 Å MS		87	13		8	99	5/1
7	L1	Al(OEt) ₃	4 Å MS		60	40		40	99	5.8/1
8	L2	Al(OEt) ₃	4 Å MS		44	56		90	98	9.6/1
9	L3	Al(OEt) ₃	4 Å MS		39	61		60	97	2.8/1
10	L4	Al(OEt) ₃	4 Å MS		31	69		70	97	2.3/1

^aUnless otherwise noted, all reactions were performed with **1a** (0.1 mmol), **L** (5 mol %), Sc(OTf)₃ (5 mol %), Al(OR)₃ (0.1 mmol), and 4 Å MS (30.0 mg) in EtOAc (1.0 mL) at $-20\text{ }^{\circ}\text{C}$, and then *m*-CPBA (0.1 mmol in 1.0 mL of EtOAc) was added at $-20\text{ }^{\circ}\text{C}$. The reaction mixture was stirred at $-20\text{ }^{\circ}\text{C}$ for 18 h. ^bThe conversion and the ratio of **2a/3a** were determined by ¹H NMR. ^cDetermined by chiral HPLC analysis.

Table 2. Substrate Scope for the Kinetic Resolution of Racemic 2-Substituted Cyclopentanones



entry ^a	a-I: R	yield (%) ^b		ee (%) ^c		rs ^d
		1	2 + 3	1	2	
1	a: Ph	42	53	90	98	9.6/1
2	b: 4-MeC ₆ H ₄	45	55	90	94	>19/1
3	c: 3-MeC ₆ H ₄	46	52	85	98	12/1
4	d: 4-MeOC ₆ H ₄	40	58	98 (R) ^e	94	15/1
5	e: 3-MeOC ₆ H ₄	43	56	80	92	7/1
6	f: 4-PhC ₆ H ₄	44	54	95	98	13/1
7	g: 4-FC ₆ H ₄	46	53	95	97	15.6/1
8	h: 4-ClC ₆ H ₄	46	53	92	97 (S) ^f	11.5/1
9	i: 3-ClC ₆ H ₄	41	56	87	98	6.3/1
10	j: 4-BrC ₆ H ₄	43	54	86	96	11/1
11	k: 2-naphthyl	44	56	92	94	9.5/1
12	l: benzyl	57	41	14	87 (62) ^g	1.33/1
13	d: 4-MeOC ₆ H ₄	42	55	90 (R)	95 ^h	13/1

^aUnless otherwise noted, the reactions were performed with **1** (0.1 mmol), **L2** (5 mol %), Sc(OTf)₃ (5 mol %), Al(OEt)₃ (0.1 mmol, 16.2 mg), and 4 Å MS (30.0 mg) in EtOAc (1.0 mL) at -20 °C, and then *m*-CPBA (0.1 mmol in 1.0 mL of EtOAc) was added at -20 °C. The reaction mixture was stirred at -20 °C for 18 h. ^bIsolated yield. ^cDetermined by chiral HPLC analysis. ^dThe regioselectivity of **2/3** was determined by ¹H NMR. ^eThe absolute configuration of **1d** was confirmed to be *R* by comparison of the optical rotation with this reported in the literature. ^fThe absolute configuration of **2h** was determined to be *S* by X-ray analysis. ^gThe ee of the δ-lactone **3l** was 62%. ^hUsing 3.0 mmol of **1d** as the substrate.

optical rotation with the literature.¹⁴ It indicated that the (S)-ketone preferred to be oxidized to δ-lactone **2** in the asymmetric catalytic system and the migration proceeded with retention of configuration at the migrating carbon atom. Optically active 2-arylcyclopentanones did not racemize under the asymmetric catalytic system but suffered slight racemization by column chromatography via silica at higher temperature.¹² When 2-benzylcyclopentanone **1l** was subjected to the BV oxidation, the regioselectivity and reactivity decreased obviously. The corresponding mixed δ-lactones **2l** and **3l** were obtained with 1.33/1 rs, as well as 87% and 62% ee, respectively. As a result, the unreacted ketone **1l** was recovered with only 14% ee (entry 12).¹⁵ Furthermore, by treatment of 3.0 mmol of the racemic **1d**, the product **2d** was produced smoothly in 55% yield with up to 95% ee and 13/1 rs, and the unreacted ketone **1d** was recovered in 42% yield with 90% ee, which showed the synthetic utility of the catalytic system (entry 13).

Next, the catalytic system was explored for the BV oxidations of the racemic 2-phenylcyclobutanone **4** and 2-phenylcyclohexanone **7**.¹⁶ The product distribution and enantioselectivities changed obviously. As shown in Figure 1, the BV oxidation of

the racemic 2-phenylcyclobutanone **4** gave the mixed γ-lactones **5** and **6** with only 1.33/1 rs. The normal lactone **5** and the unreacted ketone **4** were isolated in 50% and 42% ee, respectively. The racemic 2-phenylcyclohexanone **7** generated the abnormal ε-lactone **9** slightly more than the normal ε-lactone **8**. The normal ε-lactone **8** and the unreacted ketone **7** were isolated in low ee values, albeit ε-lactone **9** was given in 93% ee. It was proposed that the different ring strain and conformations of the 2-substituted cyclic ketones, and the steric hindrance created by a chiral catalyst as well, would account for the migratory aptitude in the circumstances.

In summary, we have successfully developed a highly regio- and enantioselective BV oxidation of racemic 2-substituted cyclopentanones using the highly efficient *N,N'*-dioxide-Sc^{III} complex catalyst. The asymmetric BV oxidation could afford the desired δ-lactones in 87–98% ee and moderate to good regioselectivities. Moreover, the kinetic resolution process gave optically active ketones in excellent ee (up to 98%). To the best of our knowledge, it represents the best example of the kinetic resolution of 2-substituted cyclopentanones via nonenzymatic asymmetric BV oxidation to date. Further study on the reaction mechanism and extensive exploration of the methodology to other cyclic ketones are underway.

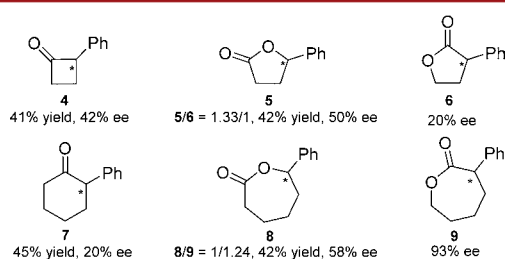


Figure 1. Asymmetric BV oxidations of the racemic 2-phenylcyclobutanone **4** and 2-phenylcyclohexanone **7**.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures, spectral and analytical data for the products. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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- (11) Using H₂O₂ or TBHP as the oxidant, no BV product was observed.
- (12) The optically active 2-arylcyclopentanones suffer slow racemization by column chromatography on silica gel at high temperature.
- (13) CCDC 998771 (2h) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.ac.uk/data_request/cif.
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- (15) The BV reaction of 2-methylcyclopentanone was tested, but the method of determination of the ee value is not established.
- (16) Under the optimal reaction conditions, no BV product was observed for 2-phenylcycloheptanone.