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Catalytic asymmetric hydroxylative dearomatization of 2-naphthols: synthesis of lacinilene derivatives†

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An enantioselective hydroxylative dearomatization of 2-naphthols with oxaziridines has been accomplished using a N,N'-dioxide–scandium(III) complex catalyst. Various substituted *ortho*-quinols could be obtained in high yields (up to 99%) and enantioselectivities (up to 95 : 5 er). This methodology could be applied in the synthesis of bioactive lacinilenes in a gram-scale reaction. Based on the experimental investigations and previous work, a possible catalytic model was proposed.

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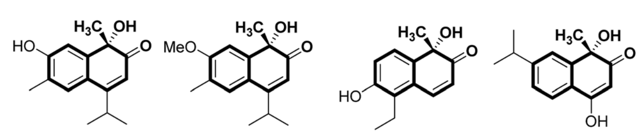
Introduction

Substituted *ortho*-quinols are essential structural motifs in a number of natural products and pharmaceuticals.[1] For instance, chiral lacinilene derivatives (Fig. 1), a series of phytoalexines isolated from cotton plants, have been utilized for inhibiting the growth of cotton bacterial pathogens, such as *Xanthomonas campestris* or *malvacearum*.[2] Studies have showed that the (*S*)-enantiomer of lacinilene C is more active than the (*R*)-enantiomer.[2c] While these biological activities provide a justification for the development of approaches to the synthesis of enantiomerically enriched lacinilene derivatives, novel catalytic enantioselective methods remain limited.[2b,d]

Optically active lacinilene derivatives in nature were proposed to be produced enzymically from the oxidation of dihydroxycadalenes, thus it is of practical interest to discover a catalytic asymmetric oxidative dearomatization route to the synthesis of these cadinanes.[3] Compared with other successful dearomatization events of phenols or naphthols,[4,5] controlling the chemo-, regio- and enantioselectivity of the asymmetric hydroxylative dearomatization is more difficult,[6] as there might be serious side reactions in the presence of oxidants including overoxidation of alkene functions, competitive *para*-oxidation and homocoupling.[6c,e] Additionally, the *ortho*-quinol product could undergo an unexpected α-ketol rearrangement, which enhances the difficulty of controlling the reactivity and selectivity.[6a,7] In this respect, only a few reports related to asymmetric hydroxylative dearomatization of phenols or naphthols have been reported. Asymmetric oxidative dearomatization of phenolate mediated by copper–sparteine–dioxygen complexes followed a [4 + 2] dimerization cascade, giving bicyclo[2.2.2] octenones as the final products.[6a] Several chiral hypervalent organoiodine compounds were developed for the asymmetric hydroxylative dearomatization of phenols and 1-naphthols.[6b–e] Taking these examples into account, we want to engage in discovering new enantioselective strategies for the synthesis of *ortho*-quinol moieties with improved efficiency and selectivity. Here, we present an efficient asymmetric hydroxylative dearomatization of 2-naphthols catalyzed by a chiral N,N'-dioxide–scandium(III) complex catalyst.[8] The process could be applied to the synthesis of various 1-hydroxy-1-alkyl-naphthalen-2-one derivatives including lacinilene C methyl ether and lacinilene D, in high to excellent yields and good enantioselectivities under mild reaction conditions (Scheme 1).



lacinilene C   lacinilene C ME   lacinilene D   cyclosorduriolone

Fig. 1 Representative active lacinilene derivatives bearing *ortho*-quinol structures.

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Results and discussion

We selected the hydroxylative dearomatization of 1-methylnaphthalen-2-ol **1a** as the model substrate using 3-phenyl-2-tosyl-1,2-oxaziridine **2a** as the oxidant which was proven to be chemoselective as a phase-transfer-catalyst under basic conditions (Table 1).[7a] Initially, the catalytic asymmetric reaction was performed with 10 mol% of chiral N,N'-dioxide L-**PiPr₂**–Sc(OTf)$_3$ complex in DCM at 30 °C, and the desired product **3a** could be obtained dominantly with 80 : 20 er while the α-ketol rearrangement byproduct **4a** was isolated in around one-fourth of

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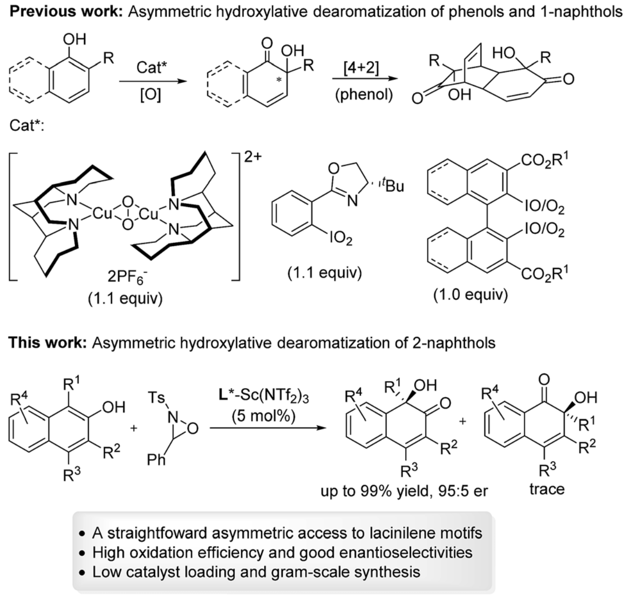
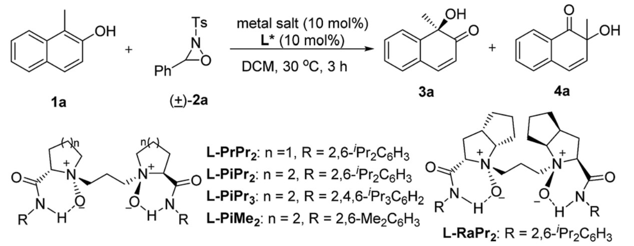


Scheme 1 Catalytic asymmetric hydroxylative dearomatization of phenols and naphthols.

Table 1 Optimization of the reaction conditions[a]



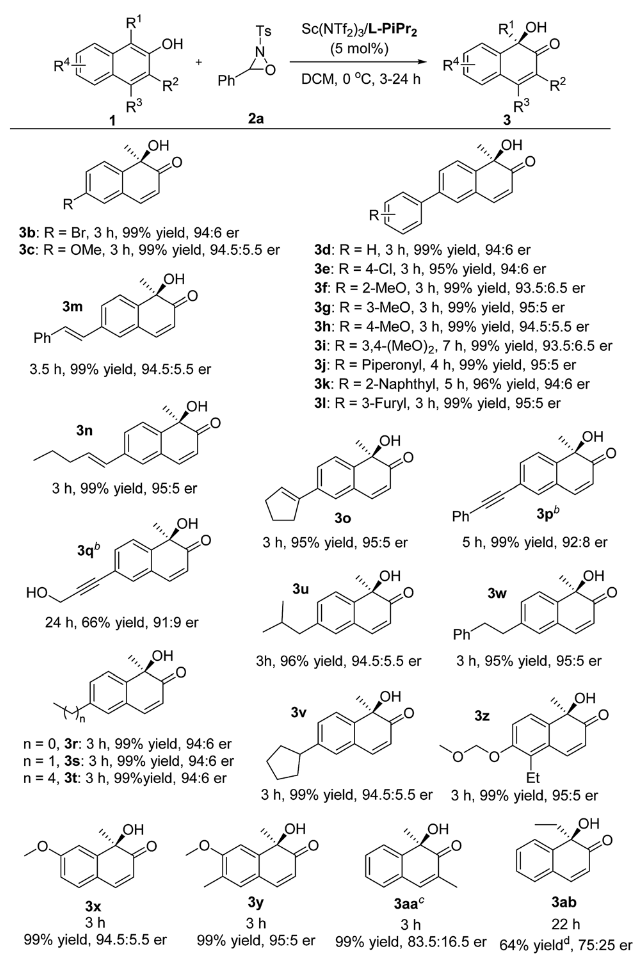
Entry	Metal salt	L*	Yield[b] (%)	Ratio (3a/4a)[c]	er (3a)[c]
1	$Sc(OTf)_3$	**L-PiPr$_2$**	96	73 : 27	80 : 20
2	$Sc(OTf)_3$	**L-PrPr$_2$**	99	79 : 21	63 : 37
3	$Sc(OTf)_3$	**L-RaPr$_2$**	99	75 : 25	53.5 : 46.5
4	$Sc(OTf)_3$	**L-PiMe$_2$**	90	>95 : 5	60 : 40
5	$Sc(OTf)_3$	**L-PiPr$_3$**	96	89 : 11	73 : 27
6	$Sc(NTf_2)_3$	**L-PiPr$_2$**	99	>95 : 5	92 : 8
7[d]	$Sc(NTf_2)_3$	**L-PiPr$_2$**	99	>95 : 5	95 : 5
8[e]	$Sc(NTf_2)_3$	**L-PiPr$_2$**	86	>95 : 5	93.5 : 6.5
9[d,f]	$Sc(NTf_2)_3$	**L-PiPr$_2$**	99	>95 : 5	94.5 : 5.5

[a] Unless otherwise noted, the reactions were performed with L*/Sc(III) (1 : 1, 10 mol%), **1a** (0.10 mmol) and **2a** (2.0 equiv.) in DCM (1.0 mL) under N_2 at 30 °C for 3 h. [b] Isolated yield by silica gel chromatography. [c] Determined by chiral HPLC analysis. [d] 5 mol% catalyst loading at 0 °C. [e] 1 mol% catalyst loading at 0 °C for 4 h. [f] **2a** (1.5 equiv.) was used.

a 96% total yield (Table 1, entry 1). The evaluation of the structure of the *N*,*N*′-dioxides showed that **L-PiPr$_2$** was the optimal ligand in terms of the enantioselectivity albeit ligand **L-PiMe$_2$** and **L-PiPr$_3$** improved the yield of the desired product **3a** (entries 2–5). Fortunately, changing the counterion of the scandium salt from $^-$OTf to $^-$NTf$_2$ could suppress the α-ketol rearrangement, delivering the quinol **3a** in a 99% yield with 92 : 8 er (Table 1, entry 6). Further optimization of the reaction conditions, such as decreasing the temperature and the catalyst loading to 5 mol%, resulted in slightly improved enantioselectivity with maintained efficiency (entry 7). Lowering the catalyst loading to 1 mol% or the amount of the oxidant **2a** decreased either the yield or the selectivity a little (entries 8 and 9). We therefore chose the reaction conditions in Table 1, entry 7 for further studies.

We next explored the substrate scope of 2-naphthols (Table 2). The introduction of bromo or methoxyl groups at the C6-position of 2-naphthols had no obvious effect on the result. The 6-aryl substituted 2-naphthol derivatives **1d–1l** tethering various electron-donating and electron-withdrawing substituents could undergo the transformations smoothly, providing the products **3d–3l** in 95–99% yield and 93.5 : 6.5–95 : 5 er. It was noteworthy that 6-alkenyl and alkynyl substituted substrates **1m–1q** were compatible with the reaction conditions, and no aminohydroxylation of the unsaturated carbon–carbon bond occurred, giving the hydroxylative dearomatization products **3m–3q** in good to excellent yields and enantioselectivities.[9]

Table 2 Substrate scope for 2-naphthols[a]



[a] Reaction conditions: the same as entry 7 in Table 1. [b] 10 mol% catalyst loading. [c] L-PiEt$_2$–Sc(OTf)$_3$ (1 : 1, 5 mol%). [d] Total yield of **3ab** and **4ab**, **3ab**/**4ab** = 87 : 13.

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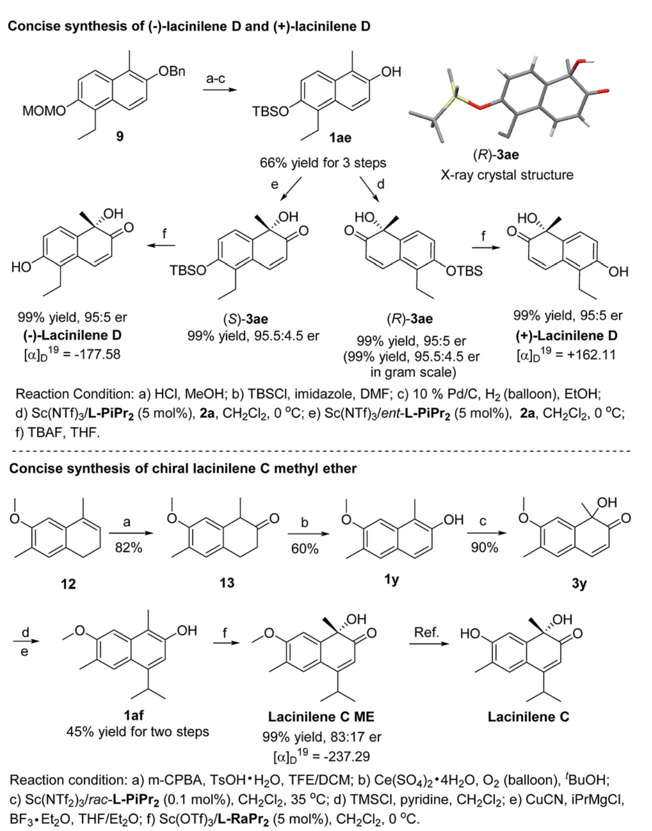
Additionally, 6-alkyl substituted 2-naphthols **3r–3w** bearing methyl, ethyl, and butyl groups were well tolerated, accomplishing the asymmetric hydroxylative reaction with the outcomes of 95–99% yield and 94 : 6–95 : 5 er. The installation of substituents to the 5- and 7-positions did not influence the reaction efficiency (**3x–3z**). The MOM-protected substrate **1z** could deliver the desired product **3z** with good results without any deprotection process occurring under the reaction conditions. However, the increase of steric hindrance at the *ortho*-position of 2-naphthol was harmful as a consequence (**3aa** and **3ab**).

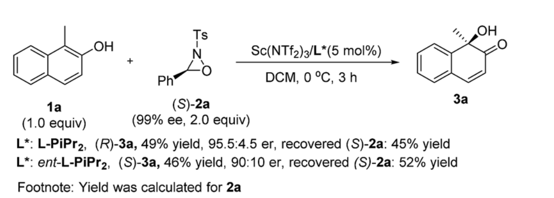
To show the synthetic utility of the current catalyst system, asymmetric synthesis of bioactive lacinilenes was carried out (Scheme 2). Initially, the direct deprotection of the product **3z** under acidic conditions formed the optically active lacinilene D, but an aromatization side product 1-ethyl-5-methylnaphthalene-2,6-diol was obtained.[2d,10] It was anticipated that the TBS protecting group could be easily removed under neutral conditions, which might avoid the occurrence of the aromatization process. As expected, the TBS-substituted 2-naphthol **1ae** could be easily synthesized from **9** in 66% yield after 3 steps, which was further enantioselectively oxidized into the product **3ae** in quantitative yield and 95 : 5 er, even when it was performed at the gram scale. The absolute configuration of **3ae** from L-**PiPr₂**–Sc(NTf₂)₃ complex catalysis was determined to be (*R*) by X-ray crystal diffraction analysis.[11] For the benefit of the further differential biological activity study on each enantiomer of the chiral lacinilenes,[2c] (*S*)-lacinilene D was synthesized using an *ent*-L-**PiPr₂**–Sc(NTf₂)₃ complex with a comparable result of 99% yield and 95 : 5 er. Next, the synthesis of optically active lacinilene C methyl ether was explored. The synthetic route began from 1,2-dihydronaphthalene **12**, which could be easily accessed from 2-methoxytoluene through a four-step protocol.[2d] Subsequent two-step oxidation could afford the 2-naphthol derivative **1y** in 49% yield, which underwent hydroxylative dearomatization catalyzed by 0.1 mol% of the Sc(NTf₂)₃/*rac*-L-**PiPr₂** complex to produce racemic lacinilene **3y** in 90% yield.[2d] After trimethylsilylation and copper catalyzed 1,4-addition/aromatization, 2-naphthol **1af** could be attained in 45% yield after two steps. By treatment with oxaziridine **2a** in the presence of Sc(OTf)₃/L-**RaPr₂**, chiral lacinilene C methyl ether could be obtained in quantitative yield and 83 : 17 er, which could further transform to lacinilene C according to the literature.[2b]

To elucidate the stereochemical course of the oxidation process, some control experiments were conducted (Scheme 3). The optically pure oxaziridine (*S*)-**2a** reacted with 2-naphthol **1a** in the presence of the Sc(NTf₂)₃/L-**PiPr₂** complex, affording the (*R*)-quinol **3a** in 49% yield and 95.5 : 4.5 er with the recovered oxaziridine (*S*)-**2a** in 45% yield.[12d] Using *ent*-L-**PiPr₂** as the ligand, (*S*)-quinol **3a** was obtained in 46% yield and 90 : 10 er with the recovered oxaziridine (*S*)-**2a** in 52% yield. This indicates that the chiral matched and mis-matched effect between chiral ligand and chiral oxaziridine was not obvious in this case compared to previous reports,[12] and there might be negligible interaction between the chiral catalyst and oxaziridine.

To probe into the interaction between the catalysts and 2-naphthol, ^{1}H NMR analysis of the mixture of components was carried out (see ESI† for details). The chemical shift of 1-methyl 2-naphthol **1a** remained nearly unchanged after Sc(NTf₂)₃ was added. There was an obvious high-field shift for most signals of **1a** after mixing with the Sc(NTf₂)₃/L-**PiPr₂** catalyst. This indicates that the chiral catalyst makes the 2-naphthol reactive for hydroxylative reactions. Based on these results and our previous study on the chiral *N*,*N*′-dioxide–metal complex catalysts,[8,13] we suggested an enantioselective catalytic model as shown in Fig. 2. The ligand L-**PiPr₂** binds to the scandium(III) center *via* four oxygens to form a polycyclic octahedral metal complex catalyst. The 2-naphthol coordinates to the metal center at one of the vacant sites, with its *Re*-face shielded by one amide unit of the ligand. Therefore, **2a** preferably attacked the α-position of 2-naphthol from the *Si*-face to generate the corresponding *R*-configured product **3ae** and imine byproduct. If a substituent was introduced into the C3 or C4 positions of 2-naphthol, the steric hindrance discrimination between the two sides of the



Scheme 2 Concise synthesis of chiral lacinilene C methyl ether, (−)-lacinilene D and (+)-lacinilene D.



Scheme 3 Control experiments.

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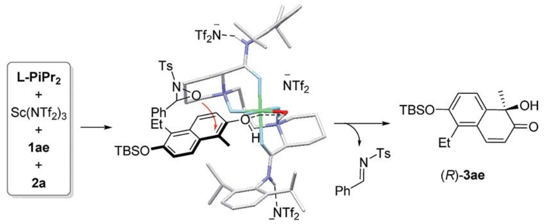

Fig. 2 Proposed enantioselective catalytic model.

hydroxyl group decreases, thus it is difficult to control the face-selection. As a result, the enantioselectivity for the generation of product **3aa** and lacinilene C methyl ether is lower than that for the others.

Conclusions

In summary, we have described a highly chemo- and enantioselective hydroxylative dearomatization of 2-naphthol derivatives with oxaziridine catalyzed by a chiral *N*,*N*′-dioxide–$Sc(NTf_2)_3$ complex catalyst. The desired substituted *ortho*-quinols with one quaternary carbon stereogenic center were afforded with high enantioselectivities and reactivity (up to 99% yield and 95 : 5 er). The α-ketol rearrangement byproducts were efficiently suppressed. This new procedure has been successfully applied to the catalytic asymmetric synthesis of the phytoalexines lacinilenes. The application of the *N*,*N*′-dioxide/metal catalyst system in the synthesis of other bioactive molecules will be explored.

Acknowledgements

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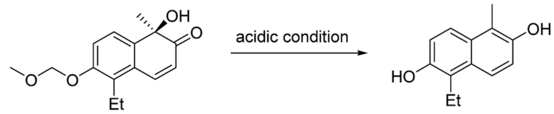

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