CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.201102058

Asymmetric Synthesis of *cis*-4-Aminobenzopyran Derivatives Catalyzed by *N*,*N*′-Dioxide–Sc(OTf)$_3$ Complexes

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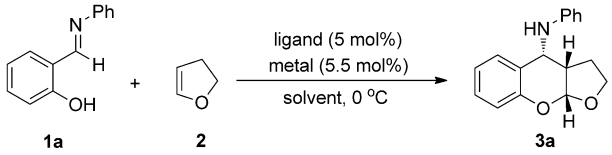
4-Aminobenzopyrans and related compounds are one of the common subunits of natural products,[1] which could also be used as drugs with antihypertensive and anti-ischemic properties, and as modulators of calcium and potassium channels, affecting the cardiac activity and blood pressure.[2–4] Therefore, considerable attention has been devoted to develop highly efficient methods for constructing this fused, cyclic structure. The reaction between salicylaldimines[5] and electron-rich alkenes has emerged as a powerful tool for the synthesis of multifunctional 4-aminobenzopyrans. Although diastereoselective reactions, catalyzed by various Lewis acids, have been widely developed,[6] catalytic asymmetric reactions to obtain enantiopure 4-aminobenzopyrans are relatively rare. Rueping and co-workers introduced chiral *N*-triflylphosphoramide-catalyzed asymmetric Mannich–ketalization reactions to access optically pure (3a,4-*trans*-3a,9a-*cis*)-4-aminotetrahydro-2*H*-furobenzopyrans and derivatives.[7,8] Recently, Fochi and co-workers used chiral phosphoric acid catalysts to obtain the corresponding (3a,4-*cis*-3a,9a-*cis*)-product with high diastereoselectivities, but only moderate *ee* values.[9] The search for new catalytic systems that achieve both excellent yields and stereoselectivities is highly desirable. Herein, we present asymmetric reactions of salicylaldimines with 2,3-dihydro-2*H*-furan (DHF) or 3,4-dihydro-*2H*-pyran (DHP) catalyzed by a chiral Lewis acid. Chiral *N*,*N*′-dioxide–Sc(OTf)$_3$ complexes[10,11] were found to be efficient catalysts for the stereoselective synthesis of (3a,4-*cis*-3a,9a-*cis*)-4-aminobenzopyran derivatives with up to 98% yield, >95:5 d.r., and 99% *ee*.

Initially, the model reaction of salicylaldimine **1a** with DHF was performed by screening metal salts with the ligand **L1**, derived from (*S*)-pipecolic acid (Table 1, entries 1–3). Sc(OTf)$_3$ gave the best results (52% yield, 60:40 d.r., 18% *ee*, Table 1, entry 1), and other metal sources, like In(OTf)$_3$ and Y(OTf)$_3$, resulted in poor selectivity or no reaction, respectively (Table 1, entries 2 and 3). Then, a series of *N*,*N*′- dioxides were synthesized by modifying the subunits of the amide and the amino acid (**L1**–**L7**). The combination of *N*,*N*′-dioxide with Sc(OTf)$_3$ showed that the amide moiety of the ligand had significant effect on both the yield and the stereoselectivity of the reaction (Table 1,

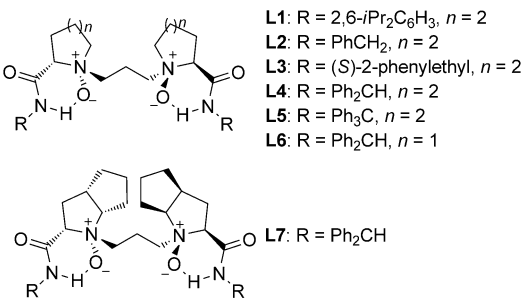
Table 1. Screening of the optimal reaction conditions.[a]



1a 2 3a

Entry	Ligand	Metal	Yield [%][b]	d.r.[c]	*ee* [%][c]
1	**L1**	Sc(OTf)$_3$	52	60:40	18
2	**L1**	In(OTf)$_3$	67	52:48	0
3	**L1**	Y(OTf)$_3$	n.r.[d]	–	–
4	**L2**	Sc(OTf)$_3$	58	74:26	25
5	**L3**	Sc(OTf)$_3$	65	75:25	40
6	**L4**	Sc(OTf)$_3$	86	79:21	62
7	**L5**	Sc(OTf)$_3$	75	66:34	21
8	**L6**	Sc(OTf)$_3$	86	81:19	62
9	**L7**	Sc(OTf)$_3$	79	74:26	35
10[e]	**L6**	Sc(OTf)$_3$	92	96:4	90
11[f]	**L6**	Sc(OTf)$_3$	83	85:15	58
12[e,g]	**L6**	Sc(OTf)$_3$	77	97:3	92
13[e,g,h]	**L6**	Sc(OTf)$_3$	97	97:3	97

[a] Unless otherwise noted, the reactions were performed with **1a** (0.1 mmol), **2** (12 μL, 1.2 equiv), ligand (5 mol%) and metal (5.5 mol%) in CH_2Cl_2 (0.5 mL) under nitrogen at 0°C for 48 h. [b] Isolated yield. [c] The *ee* and the d.r. values were determined by HPLC analysis (chiralcel AS-H); the d.r. value refers to *cis*:*trans*. [d] n.r. = no reaction. [e] $CHCl_3$ (0.5 mL) was used as the solvent. [f] CH_2ClCH_2Cl (0.5 mL) was used as the solvent. [g] Performed at −20°C. [h] 5 Å MS (5.0 mg) was added.



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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201102058.

entries 4–9). The introduction of diphenylmethyl groups into the amide moieties increased the yield and the *ee* value (86% yield with 62% *ee*; Table 1, entry 6). The reactivity and enantioselectivity significantly decreased when using *N,N′*-dioxides with larger or smaller sterically hindered amide moieties (Table 1, entries 4–5 and 7). *N,N′*-Dioxides derived from amino acids were also examined, and the ligand **L6**, derived from L-proline acid, and the ligand **L4**, derived from L-pipecolic acid, resulted in similar yield and enantioselectivity, but with slightly higher diastereoselectivity for **L6** (Table 1, entry 8 vs. 6). However, L-ramipril acid derived **L7** failed to control the enantioselectivity, giving a low *ee* value (Table 1, entry 9). In all these cases, the tetrahydropyran and tetrahydrofuran rings of the product were *cis*-fused, and (3a,4-*cis*-3a,9a-*cis*)-4-aminotetrahydrofurobenzopyran **3a** was isolated as the major diastereoisomer. With the best ligand **L6** in hand, the effect of solvents was further investigated (Table 1, entries 10–11). The results indicated that the reaction solvents played an important role in adjusting the enantioselectivity of the reaction. $CHCl_3$ was found to be the most suitable solvent for the reaction, affording the adduct **3a** in 92% yield and 96:4 d.r. with 90% *ee* (Table 1, entry 10). Subsequently, with decreasing the reaction temperature from 0 to −20°C, the reaction proceeded smoothly with a slight increase of enantioselectivity, whereas the reactivity was lower (Table 1, entry 12). It is worth noting that a significant increase of both the enantioselectivity and the yield was accomplished at −20°C by adding 5 Å molecular sieves (Table 1, entry 13). Other reaction conditions were also examined, but the results could not be improved (for details, see Supporting Information).

With the optimal conditions established (Table 1, entry 13), various salicylaldimines **1a**–**1h**, substituted at the *N*-aryl ring, were examined, giving a wide range of *cis*-4-aminobenzopyrans in up to 98% yield with >95:5 d.r. and up to 99% *ee*. As shown in Table 2, the position of the substituent on the *N*-aryl ring of salicylaldimines had an evident effect on the enantioselectivities. Substrates with the substituent on the *para*-position afforded better results than those with the substituent on the *ortho*- or *meta*-position (Table 2, entries 2 and 3 vs. 4–8). The electronic effect of the substituent on the *N*-aryl ring of salicylaldimines had no evident influence on the stereoselectivities (Table 2, entries 4–8), and the best outcome of 99% *ee* with 94% yield was obtained for substrate **3h** with a 4-MeO substituent on the *N*-aryl ring (Table 2, entry 8). However, a dramatic decrease in enantioselectivities was observed for the salicylaldimines derived from substituted salicylaldehydes (for details, see Supporting Information). The only exception was substrate **1i** with a 4′-MeO substituent on the salicylaldehyde, giving the corresponding product **3i** in 85% yield with 91% *ee* (Table 2, entry 9). It is possible that the cause is the steric hindrance between the substrates and the ligand of the catalyst. We reasoned that chiral ligands with relative small steric hindrance might be suitable for these substrates. A series of chiral *N,N′*-dioxides with different amide subunits were then screened for the purpose of improving the outcome. Fortunately, the ligand **L3**, derived from L-pipecolic acid and (*S*)-2-phenylethanamine, was found suitable for substrates substituted on the salicylaldehyde moiety (Table 2, entries 10–13). The reactions of salicylaldimines **1j**–**1m** afforded the corresponding products smoothly with good enantioselectivities catalyzed by the *N,N′*-dioxide **L3**–$Sc(OTf)_3$ complex, although substrates with an electron-donating substituent were less reactive and larger amounts of DHF and longer reaction times were needed (Table 2, entries 12 and 13 vs. 10 and 11). It is worth pointing out that chiral match between the chiral amino acid backbone and phenylethanamine is crucial for the enantiodifferentiation in the process. The scandium complex of the ligand derived from D-pipecolic acid and (*S*)-2- phenylethanamine sharply decreased the enantioselectivity of the reactions. *cis*-4-Aminobenzpyran **3j** was obtained with only 10% *ee* (see Supporting Information). Moreover, to expand the synthetic utility of the reaction, various salicylaldimines with different *N*-aryl groups, such as a 4-methoxyphenyl (PMP) and a 4-fluorophenyl group, were subjected to the optimized reaction conditions (Table 2, entries 14–19). Pleasingly, excellent enantioselectivities were also observed for those salicylaldi-

Table 2. Scope of the substrates.[a,b]

1a-1s 2 3a-3s

Entry	R^1	R^2	Ligand	Yield [%][c]	*ee* [%][d]
1	H	H	**L6**	97 (**3a**)	97
2	H	2-Cl	**L6**	97 (**3b**)	82
3	H	3-Cl	**L6**	85 (**3c**)	85
4	H	4-Cl	**L6**	83 (**3d**)	97
5	H	4-F	**L6**	87 (**3e**)	97
6	H	4-CF_3	**L6**	87 (**3f**)	91
7	H	4-Me	**L6**	98 (**3g**)	95
8	H	4-MeO	**L6**	94 (**3h**)	99
9	4-MeO	H	**L6**	85 (**3i**)	93
10	5-Cl	H	**L3**	83 (**3j**)	92
11	5-Br	H	**L3**	81 (**3k**)	91
12[e]	5-Me	H	**L3**	92 (**3l**)	90
13	5-MeO	H	**L3**	84 (**3m**)	92
14	5-Cl	4-MeO	**L3**	86 (**3n**)	92
15	5-Br	4-MeO	**L3**	95 (**3o**)	93
16[e,f]	5-Me	4-MeO	**L3**	97 (**3p**)	91
17[e,f]	5-MeO	4-MeO	**L3**	96 (**3q**)	91
18	5-Cl	4-F	**L3**	96 (**3r**)	92
19	5-Me	4-F	**L3**	87 (**3s**)	90

[a] Unless otherwise noted, the reactions were performed with **1** (0.1 mmol), **2** (for details, see Supporting Information), 5 mol% of **L6**– or **L3**–Sc^{III} complex (1:1.1) and 5 Å MS (5.0 mg) in $CHCl_3$ (0.5 mL) under nitrogen at −20°C for 3–5 d. [b] The diastereomeric ratio was analyzed by ^1H NMR spectroscopy and all the values were >95:5. [c] Isolated yield. [d] Determined by HPLC analysis. [e] Performed at 0°C. [f] 20 Mol% of **L3**–Sc^{III} complex was used.

mines **1n**–**1s**. Generally, electron-withdrawing substituents, such as a Cl or Br group, slightly enhanced the reactivity, while electron-donating substituents, such as a MeO or a Me group, diminished the reactivity (Table 2 entries 16 and 17 vs. 14 and 15, entry 19 vs. 18).[12]

The absolute configuration of the major product **3j** was unambiguously determined to be (3a*S*, 4*R*, 9a*R*) by a single-crystal X-ray diffraction study (Figure 1).[13]

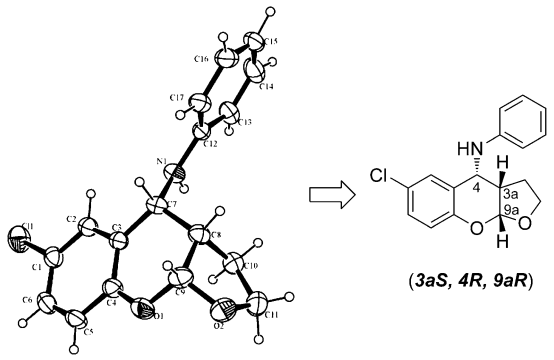
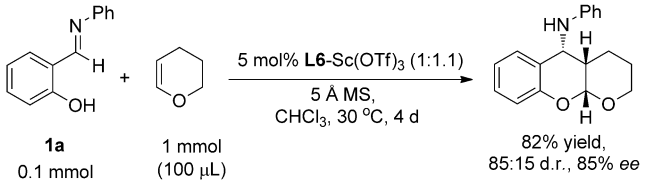


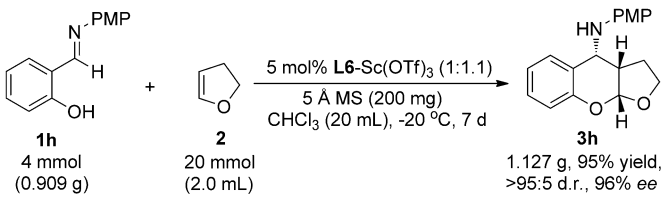
Figure 1. X-ray structure of the product **3j**.

To further evaluate the synthetic potential of this catalyst system, the reaction between salicylaldimine **1a** and 3,4-dihydro-2*H*-pyran (DHP) was examined (Scheme 1). DHP was tolerated in terms of yield and enantioselectivity, providing the corresponding (4a,5-*cis*-4a,9a-*cis*)-adduct as major isomer in 82% yield, 85:15 d.r., and 85% *ee* under mild conditions.



Scheme 1. The reaction of salicylaldimine **1a** with DHP.

A sub-gram synthesis of *cis*-4-aminobenzopyran derivative **3h** was carried out with **1h** and DHF (Scheme 2). The reaction proceeded smoothly to give the product **3h** in 95% yield, >95:5 d.r. and 96% *ee* with 5 mol% catalyst loading.



Scheme 2. Scaled-up version of the reaction.

In connection with the *N*-triflylphosphoramide catalyzed reaction,[7] the difference in stereoselectivity might be due to the activation model of the catalysts. Often, the *cis*-product was obtained as the major product in the presence of a Lewis acid, such as $LiBF_4$,[6b] $InCl_3$,[6d] and I_2.[6g] The model **C1** (Figure 2) could help to explain the mechanism. A six-membered ring, formed with a Lewis acid and including both the nitrogen and oxygen of the salicylaldimine, leads to the formation of (3a,4-*cis*-3a,9a-*cis*)-**3**. However, an arrangement as shown in **C2** is more likely to proceed through a single hydrogen activation of the imine in Rueping's report to yield (3a,4-*trans*-3a,9a-*cis*)-**3**.

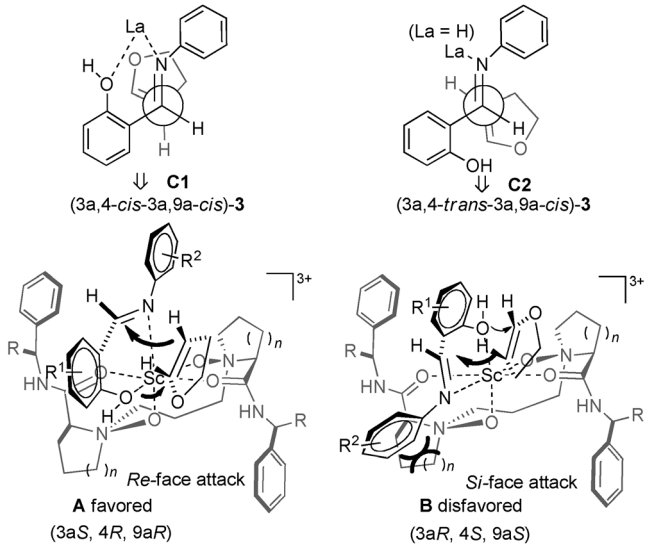


Figure 2. Proposed catalytic model.

The enantiodiscrimination of salicylaldimine in the reaction process can be rationalized according to Figure 2. In the presence of the scandium catalyst, the salicylaldimine coordinates to the central metal in a bidentate manner. In combination with the absolute configuration of the product **3j**, we postulate that the steric hindrance between the *N*-aryl group of the imine and one azacycle of the ligand makes intermediate **B** unfavorable. It would thus appear that DHF readily attacks the *Re*-face of the imine, followed by a fast ketalization step to afford the (3a*S*, 4*R*, 9a*R*)-product (Figure 2, **A**). It can also be seen that when substrates substituted on the salicylaldehyde moiety were used, the use of less sterically hindered ligand **L3** (R = Me) is sufficient to give good selectivity.

In conclusion, we have developed chiral *N*,*N*′-dioxide–Sc-$(OTf)_3$ complexes for the asymmetric reactions of DHF and DHP with salicylaldimine derivatives. This method enables efficient access to a variety of optically pure *cis*-4-aminobenzopyrans in excellent outcomes (up to 98% yield, >95:5 d.r., up to 99% *ee*). Moreover, the broad substrate scope and the facile procedure demonstrated the potential of the catalytic system. Further application of the catalyst in other reactions is currently underway.

Experimental Section

Typical experimental procedure: *N,N'*-Dioxide **L6** (3.2 mg, 0.005 mmol), scandium triflate (2.6 mg, 0.0055 mmol), salicylaldimine **1a** (19.7 mg, 0.1 mmol) and 5 Å molecular sieves (5.0 mg) were stirred in a dry reaction tube in $CHCl_3$ (0.5 mL) under nitrogen at 25 °C for 1 h. Then, 2,3-dihydro-2*H*-furan (12 μL, 0.12 mmol) was added at −20 °C and the system was stirred for 3 d. The process was monitored by TLC. After salicylaldimine **1a** was consumed, the reaction mixture was purified by flash chromatography (petroleum ether/ethyl acetate = 10:1) on silica gel to afford the desired product **3a** as white solid (27.0 mg, 97% yield).

Acknowledgements

We appreciate the National Natural Science Foundation of China (Nos. 20732003, 21021001 and 20872097), and the National Basic Research Program of China (973 Program: 2010CB833300) for financial support. We also thank Sichuan University Analytical & Testing Centre for NMR and X-ray analysis.

Keywords: aminobenzopyrans · dioxides · enantioselectivity · salicylaldimines · scandium

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[12] A 20 mol% catalyst loading was needed. With 5 mol% catalyst loading, the reactivity was too low to afford the desired products in satisfying results.

[13] CCDC 831655 (**3j**) contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Date Centre via www.ccdc.cam.ac.uk/data_request/cif.

Received: July 5, 2011
Published online: November 3, 2011

