Novel Binaphthalene–Amine Catalysts for the Asymmetric Epoxidation of Alkenes

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Abstract: We have prepared a range of binaphthalene-derived azepine derivatives containing alcohol functionality, and used them as catalysts in the asymmetric epoxidation of alkenes by Oxone, giving ee values of up to 81%. We have obtained evidence that points to the involvement of iminium ions in the reaction pathway, suggesting that the oxidizing species in the epoxidation reactions are in fact the corresponding oxaziridinium ions.

Key words: asymmetric, Oxone, epoxidation, alkene, epoxide

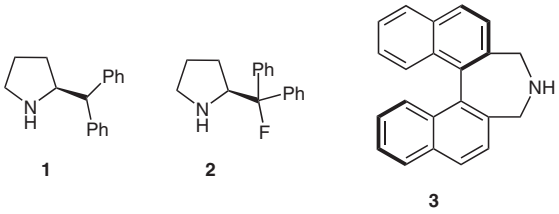

Figure 1

Nonracemic epoxides are important and highly versatile building blocks in asymmetric synthesis,[1] and the epoxide functionality is itself a part of the structure of many natural products and biologically active compounds.[2] Despite the development over the past few years of several methods for asymmetric epoxidation, access to chiral epoxides with high ee remains an important objective, perhaps because no single method is appropriate for all epoxide structures. Organocatalysis, that is, reactions carried out with substoichiometric quantities of organic molecules as catalysts, represents one of the most active areas of research in chemistry today.[3] Organic-molecule-catalysed reactions offer several notable advantages over the more traditional transition-metal-mediated processes; for example, reactions can often be carried out under wet and aerobic conditions, the catalysts are generally inexpensive and there are no associated toxicity problems. Currently, the most utilized types of chiral organocatalyst for the asymmetric epoxidation of alkenes are chiral dioxiranes, oxaziridines, and oxaziridinium salts.[4–6] More recently, amines have been shown to be effective mediators for the epoxidation of unfunctionalized alkenes.[7]

Chiral-amine-mediated epoxidation, reported independently by Aggarwal[8] and Yang,[9] has provided moderate enantioselectivities of up to 61% ee. These studies showed secondary amines to be better catalysts than the corresponding primary and tertiary amines. Chiral pyrrolidine analogues, such as **1** or **2**, were found to be effective mediators for the enantioselective epoxidation of alkene substrates (Figure 1). Surprisingly, no studies using chiral-binaphthalene-derived secondary amines have been reported to date.

With this in mind, we envisaged that the known chiral dihydroazepine **3** might prove to be an effective epoxidation catalyst due to its conformational rigidity; **3** has indeed been widely used in developing chiral species for asymmetric synthesis.[10] These include Hawkin's asymmetric stereoselective carbon–nitrogen bond formation,[11] Cram's asymmetric addition of organolithium reagents to aldehydes,[12] and chiral phase-transfer catalysts.[13]

Treatment of the known dibromo compound **4**[11] with allylamine and triethylamine as a base led to allyldihydroazepine **5** in good yield. Subsequent N-deallyllation of **5** using $Pd(OAc)_2$, Ph_3P, and *N*,*N*′-dimethylbarbituric acid (NDMBA) in dichloromethane, followed by treatment with concentrated hydrochloric acid, furnished the dihydroazepinium hydrochloride **6** in excellent yield (Scheme 1).

Ammonium salt **6** (5 mol%) was subsequently used as catalyst in the epoxidation of 1-phenylcyclohexene in the presence of Oxone (2 equiv), $NaHCO_3$ (5 equiv) in MeCN–H_2O (10:1), the conditions reported by Yang.[9] Disappointingly, **6** was found to be relatively unreactive and a poor chiral inducer, giving only 28% conversion into the 1*S*,2*S*-epoxide with 7% ee after two hours. Increasing the catalyst loading to 10 mol% failed to increase the rate of conversion.

Recently, we have shown that the amine analogues **7**–**9** of our previously reported iminium salt catalysts also catalyse the epoxidation of unfunctionalized alkenes (Figure 2).[14]

The poor reactivity of **6** may stem from the lack of a heteroatomic (e.g., O or F) group capable of stabilizing the active oxidizing species either inductively or through hy-

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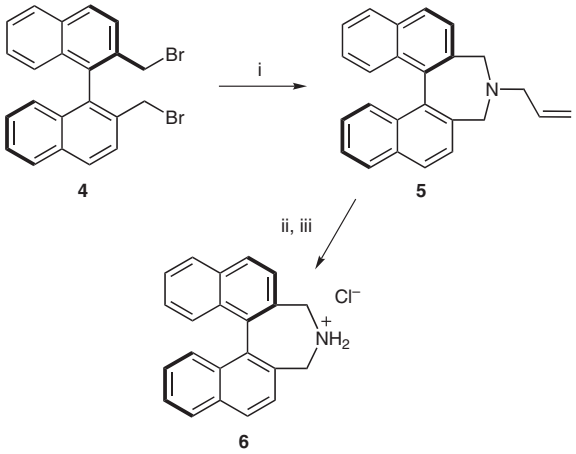


Scheme 1 *Reagents and conditions*: i: allylamine (1.7 equiv), Et_3N (3 equiv), THF, 55 °C, 3 h, 68%; ii: $Pd(OAc)_2$ (2 mol%), Ph_3P (0.1 equiv), NDMBA (1.5 equiv), CH_2Cl_2, 35 °C, 6 h; iii: HCl (1.1 equiv), 90%.

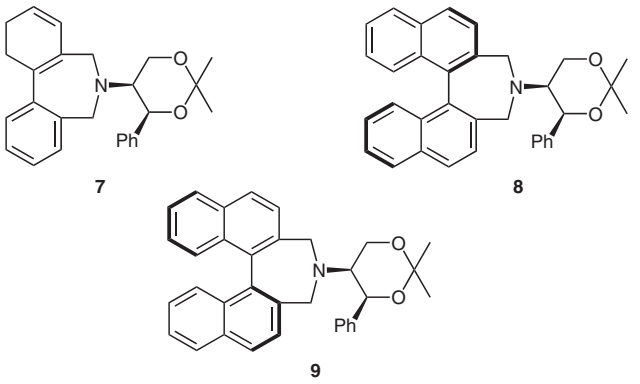
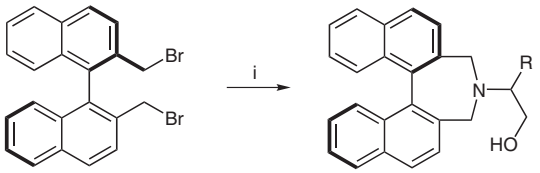


Figure 2

drogen bonding, as reported previously by Yang.[9] In order to investigate this structural motif further, we subsequently prepared a range of chiral binaphthalene-derived amino alcohols **10**–**14** from dibromo compound **4** (Scheme 2).

With amines **10**–**14** in hand, we tested them as catalysts (10 mol%) in the epoxidation of *E*-methylstilbene as substrate, again using the conditions of Yang [Oxone (2 equiv), $NaHCO_3$ (5 equiv), MeCN–H_2O (10:1), 0 °C, 5 h].

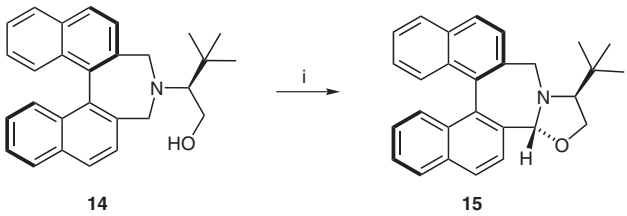


10 R = (*S*)-Me, 98%
11a R = (*S*)-Ph, 95%
11b R = (*R*)-Ph, 96%
12 R = (*S*)-*i*-Pr, 97%
13 R = (*S*)-*i*-Bu, 98%
14 R = (*S*)-*t*-Bu, 97%

Scheme 2 *Reagents and conditions*: i: amine (1.1 equiv), K_2CO_3 (3 equiv), MeCN, reflux, 16 h.

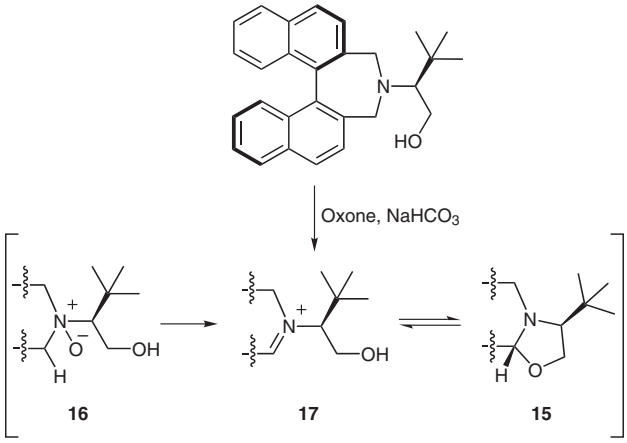
Curiously, all but amines **12** and **14** failed to show any catalytic activity. Catalyst **14** gave only 16% conversion into the (–)-1*S*,2*S*-epoxide, with 40% ee, but catalyst **12** proved to be more reactive and enantioselective, giving 88% conversion into the (–)-1*S*,2*S*-epoxide, with 45% ee. The ^1H NMR spectroscopic analysis of the crude mixture revealed that the amines decomposed under these reaction conditions. We were puzzled by the difference in reactivity of these structurally similar amines, and so embarked on an investigation of the decomposition pathways of these amines, which inhibit their catalytic activities.

We discovered that amine **14** is converted into the diastereomerically pure oxazolidine **15** when submitted to the epoxidation reaction conditions [Oxone (2 equiv), $NaHCO_3$ (5 equiv), MeCN–H_2O (10:1)]. The same oxazolidine **15** is also partially formed when a chloroform solution of amine **14** is allowed to stand at room temperature overnight (Scheme 3).



Scheme 3 *Reagents and conditions*: i: Oxone (2 equiv), $NaHCO_3$ (5 equiv), MeCN–H_2O (10:1), 5 h.

Oxazolidine formation was also observed when using amines **12** and **13**, but not amines **10** or **11**. At this stage, we rationalize that the formation of the oxazolidine product **15** arises from cyclization of an iminium salt formed under the reaction conditions. We postulate that, under our reaction conditions, amine **14** is initially oxidized to the corresponding *N*-oxide **16**.[15] Subsequent loss of hydoxide leads to the iminium salt **17**. This iminium salt is presumably in equilibrium with the oxazolidine **15** under the reaction conditions (Scheme 4). The stereochemistry of **15** was established by NOE experiments.

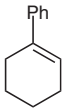
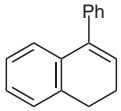
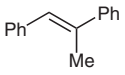
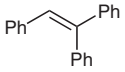
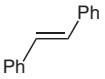
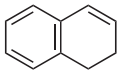


Scheme 4

A potential explanation for the difference in reactivity exhibited within the group of amines **10**–**14** towards the epoxidation of alkenes lies in the competition between the oxidation of the iminium salt to the oxaziridinium species (the active oxidant) and the oxazolidine formation.

With amine **12** being the most reactive in this series, a number of other alkenes were next subjected to epoxidation mediated by this catalyst (Table 1).

Table 1 Asymmetric Epoxidation of Alkenes with Amine **12**[a]

Alkene	Conversion (%)	ee (%)	Configuration[b–d]
	90 (10)[e]	81	(–)-1*S*,2*S*
	62	80	(+)-1*R*,2*S*[g]
	88	45	(–)-1*S*,2*S*[f]
	47	28	(+)-*S*[f]
	65	17	(–)-1*S*,2*S*[f]
	44	47	(+)-1*R*,2*S*[g]

[a] Epoxidation conditions: amine (10 mol%), Oxone (2 equiv), $NaHCO_3$ (5 equiv), MeCN–H_2O (10:1), 0 °C, 2 h, unless otherwise indicated.
[b] Conversions were evaluated from the ^1H NMR spectra by integration of alkene, dio, and epoxide signals.
[c] Enantiomeric excesses were determined by chiral HPLC on a Chiralcel OD column, or by chiral GC on a Chiraldex B-DM column.
[d] The absolute configurations of the major enantiomers were determined by comparison with literature values except where indicated.
[e] The numbers in parentheses refers to the percentage conversion into diol.
[f] Reaction time: 5 h.
[g] Epoxidation conditions: iminium salt (5 mol%), Oxone (2 equiv), Na_2CO_3 (4 equiv), MeCN–H_2O (1:1), 0 °C, 5 h.

As illustrated in Table 1, amine **12** is an effective catalyst for the enantioselective epoxidation of a range of substrates. While the conversions into epoxides are moderate to good (44–100%), enantioselectivities of up to 81% were obtained with 1-phenylcyclohexene oxide. This amine catalyst, while being less reactive, is comparable in enantioselectivity to our previously reported *N*-isopropyl-substituted iminium salt catalyst **18** (Figure 3), which afforded up to 83% ee.[16] It is noteworthy that amine **12** induced epoxidation of 1,2-dihydronaphthalene with higher ee (47%) than all other reported binaphthalene-derived amines and iminium salts to date.

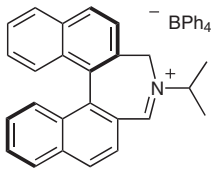


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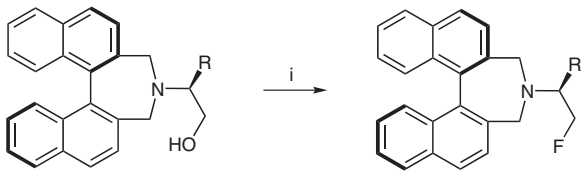
Figure 3

An interesting observation during the course of the epoxidation was that the reaction changed from colourless to intense yellow, conceivably indicating the formation of the corresponding iminium salt, which is generally a yellow solid. After the completion of the epoxidation reaction, the yellow residue was triturated in diethyl ether, and the sample analysed by ^1H NMR spectroscopy and mass spectrometry. We observed the iminium signal at around δ = 10 ppm ($CDCl_3$), while the mass spectrum revealed almost a 100% molecular ion corresponding to the iminium salt, supporting our postulation that iminium salts are generated in situ and are the active catalysts mediating the epoxidation reactions.

With the aim of improving the reactivity of our amines and inhibiting the oxazolidine formation, we next prepared the fluorine-containing amines **19** and **20** in one step from amines **12** and **14**. A wide variety of fluorinating reagents is available;[17] diethylaminosulfur trifluoride (DAST) is widely used to mediate the direct conversion of alcohols into fluorides in high yields.[18] Treatment of amines **12** and **14** in dichloromethane with DAST at room temperature for five hours afforded fluorinated products **19** and **20** respectively, albeit in low yields (28–30%), along with other unidentified byproducts. Improved yields were obtained when bis(2-methoxyethyl)aminosulfur trifluoride (Deoxofluor) was used as the fluorinating reagent (Scheme 5).



12 R = *i*-Pr
14 R = *t*-Bu

19 R = *i*-Pr, 66%
20 R = *t*-Bu, 60%

Scheme 5 *Reagents and conditions*: i: Deoxofluor (1.05 equiv), CH_2Cl_2, 0 °C to r.t., 24 h.

We subsequently tested amines **19** and **20** (10 mol%) in the epoxidation of *trans*-α-methylstilbene. Surprisingly, no conversion into epoxide was observed using these amines after five hours. Changing the reaction conditions to the biphasic dichloromethane/water (3:2) conditions in the presence of 18-crown-6, developed by Lacour, also failed.[14]

Recently, Lacour reported a range of enantiopure doubly bridged biphenyl azepines and azepinium salts as cata-

lysts for the asymmetric epoxidation of alkenes, affording ee of up to 85% ee.[15,19] Lacour observed that some amines were effective catalysts, while others showed no catalytic activity at all, and subsequently identified a decomposition pathway involving *N*-oxide formation and Cope elimination that presumably inhibited the catalytic activities of some of the amines.[19] The catalytic activity of one of these amines could be restored by the addition of NBS (5 mol%) to the amine prior to addition of the substrates and other reagents, presumably by in situ formation of the iminium species. In our hands, addition of a catalytic amounts of NBS (10 mol%) to amines **19** and **20** in dichloromethane (1 mL) for ten minutes prior to the addition of water (0.5 mL), the substrate, 18-crown-6, Oxone, and $NaHCO_3$, failed to give any epoxide after a reaction time of five hours.

In conclusion, we have prepared a range of binaphthalene-derived azepines containing alcohol functionality and used them as catalysts in the asymmetric epoxidation of alkenes. Amine **12** exhibited the best reactivity and enantioselectivity profile, giving ee values of up to 81%. We have also identified a reaction pathway involving the formation of oxazolidines, which presumably retards the catalytic activity of these amines. We have obtained limited spectroscopic evidence that points to the involvement of iminium ions in the reaction pathway, suggesting that the oxidizing species in the epoxidation reactions are in fact the corresponding oxaziridinium ions.

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