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New Chiral Binaphthalene-Derived Iminium Salt Organocatalysts for Asymmetric Epoxidation of Alkenes

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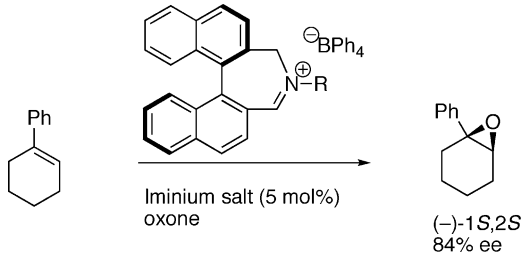

A series of binaphthalene-fused azepinium salts has been generated and used as organocatalysts in the asymmetric epoxidation of unfunctionalized alkenes, giving rise to ees of up to 84%.

Introduction

The development of catalytic asymmetric epoxidation of unfunctionalized alkenes is an ongoing synthetic endeavor due to the enormous synthetic versatility of epoxides. The chiral manganese salen complexes independently developed by Jacobsen and Katsuki can give remarkably high enantioselectivity for *cis*-alkenes.[1] However, *trans*-alkenes tend to be poor substrates. Recently, catalytic methods based on metal-free organic molecules (organocatalysis) have emerged as a powerful complement to metal- and biocatalysis.[2] From a practical point of view, the use of organocatalysis has the advantages that the catalysts are commonly inexpensive and stable, and hence some reactions can be performed under aerobic and even wet conditions. The practical advantages of organocatalysis, coupled with the need to improve enantioselectivity and extend the generality of application in terms of substrate structure, have spurred the development of organocatalytic asymmetric epoxidation methods.[3] Currently, the most utilized types of chiral organocatalyst for the asymmetric epoxidation of alkenes are chiral dioxiranes, oxaziridinium salts, oxaziridines, and amines.[4]

Chiral dioxiranes, derived *in situ* from the oxidation of chiral ketones by the triple salt oxone ($KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$), have emerged as one group of the most effective mediators of asymmetric epoxidation of alkenes.[5] Excellent enantioselectivities have been achieved with trisubstituted and *trans*-alkenes, while moderate to good selectivity is achieved for other alkenes.[6] The main limiting factor in chiral dioxirane-catalyzed epoxidation is the high catalyst loading required, presumably due to decomposition of the catalysts, for example through Baeyer–Villiger oxidation.[7]

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(1) For a review, see (a) Jacobsen, E. N.; Wu, M. H. in *Comprehensive Asymmetric Catalysis*; Jacobsen, E. N.; Pfaltz, A.; Yamamoto, H., Eds.; Springer: Berlin, 1999; Vol. 2, p649.

(2) See for example, Saeyad, J.; List, B. *Org. Biomol. Chem.* **2005**, *3*, 719; Dalko, P. I.; Moisan, L. *Angew. Chem., Int. Ed.* **2001**, *40*, 3726; Dalko, P. I.; Moisan, L. *Angew. Chem., Int. Ed.* **2004**, *43*, 5138.

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(5) Reviews: Frohn, M.; Shi, Y. *Synthesis* **2000**, 1979–2000; Shi, Y. *Acc. Chem. Res.* **2004**, *37*, 488; Yang, D. *Acc. Chem. Res.* **2004**, *37*, 497; Imashiro, R.; Seki, M. *J. Org. Chem.* **2004**, *69*, 4216; Li, W.; Fuchs, P. L. *Org. Lett.* **2003**, *5*, 2853; Jarvo, E. R.; Miller, S. J. *Tetrahedron* **2002**, *58*, 2481; Denmark, S. E.; Matsuhashi, H. J. *J. Org. Chem.* **2002**, *67*, 3479; Bortolini, O.; Fantin, G.; Fogagnolo, M.; Forlani, R.; Maietti, S.; Pedrini, P. *J. Org. Chem.* **2002**, *67*, 5802; Armstrong, A.; Hayter, B. R.; Moss, W. O.; Reeves, J. R.; Wailes, J. S. *Tetrahedron: Asymmetry* **2000**, *11*, 2057; Armstrong, A.; Moss, W.; Reeves, J. R. *Tetrahedron: Asymmetry* **2001**, *12*, 2779; Armstrong, A.; Tsuchiya, T. *Tetrahedron* **2006**, *62*, 257.

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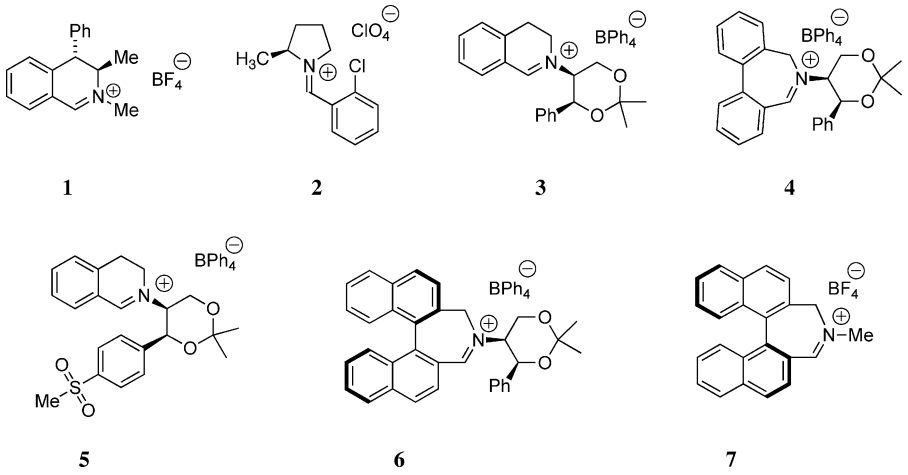

1 **2** **3** **4**

5 **6** **7**

FIGURE 1. Examples of chiral iminium salts from the literature.

Chiral oxaziridines have extensively been utilized by Davis[8] and ourselves[9] for the asymmetric oxidation of sulfides to sulfoxides. The use of chiral oxaziridines in the asymmetric epoxidation of alkenes is, however, less versatile, although the first (achiral) catalytic epoxidation using such reagents has recently been reported.[10] A close relative of oxaziridine-mediated epoxidation involves the use of oxaziridinium salts. Oxaziridinium salts generated *in situ* from iminium salts with oxone were shown by Lusinchi to be effective electrophilic oxidants for epoxidation of alkenes, rendering the development of catalytic processes possible.[11] The first enantiomerically pure iminium salt to be used in this way was **1**, with the controlling asymmetric centers sited in the saturated ring of a dihydroisoquinolinium salt, and was shown to catalyze epoxidation of alkenes, affording ees of up to about 40% (Figure 1).[12] Even exocyclic iminium salts such as **2**, derived from condensation of enantiopure pyrrolidine moieties with aromatic aldehydes, can afford moderate ees (up to 22%) with relatively high catalyst loadings necessary (up to 100 mol %), perhaps due to *in situ* hydrolysis of the iminium units.[13]

Recently, chiral secondary amines have been shown to catalyze the asymmetric epoxidation of alkenes, giving up to 66% ee.[14] Yang also screened a range of chiral secondary amines for catalytic activity.[15] These studies revealed the presence of an electron-withdrawing substituent (such as hydroxyl and fluorine groups) at the β-position to the amine group to be beneficial for catalytic activity.

Our own contribution has been to design chiral iminium salts that contain asymmetric centers in the exocyclic nitrogen substituent, based upon the reasoning that such designs would bring the enantiocontrolling asymmetric centers closer to the site of oxygen transfer and hence potentially increase enantioselectivity.[16] Accordingly, we have reported several series of catalysts including a number, e.g., **3**−**6**, that contain chiral moieties related to (4*S*,5*S*)-5-amino-2,2-dimethyl-4-phenyl-1,3-dioxane (acetonamine).

While catalyst **3** gives moderate enantioselectivity (up to 59% ee), catalyst **4**, incorporating a biphenyl structure, was found to be highly reactive, inducing complete epoxidation of alkenes within 1−10 min in aqueous acetonitrile at 0 °C; it is thus the most reactive iminium salt epoxidation catalyst discovered to date.[17] Lacour has reported the epoxidation of alkenes catalyzed by **4** but using an enantiomerically pure TRISPHAT counterion and a biphasic CH_2Cl_2/water solvent system.[18] Catalyst **5**, containing a *p*-methylsulfonyl group, excelled in the epoxidation of cyclic *cis*-alkenes, affording up to 97% ee.[19] We have also developed a range of azepinium salt catalysts containing a binaphthalene backbone and exocyclic *N*-isopinocampheyl or *N*-aminoacetal groups. In this group, catalyst **6** proved to be the most reactive and enantioselective, giving up to 95% ee.[20]

Some years ago, Aggarwal described a binaphthalene-fused azepinium salt catalyst **7**, prepared from dibromide **8**,[21] bearing

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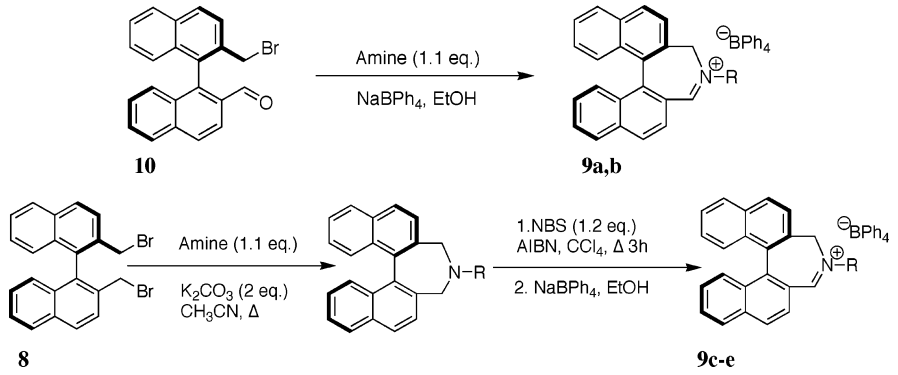
SCHEME 1



an achiral methyl group as the nitrogen substituent, which was reported to give up to 71% ee in the epoxidation of 1-phenylcyclohexene.[22] Other achiral nitrogen substituents in this system were claimed in the patent literature, together with reported ees for the epoxidation of 1-phenylcyclohexene mediated by the methyl-, ethyl-, and benzyl-substituted catalysts.[23] We conjectured that the enantioselectivity of these azepinium salt catalysts might be enhanced if a sterically bulkier group were added at the nitrogen atom, and we describe herein the synthesis of iminium salts **9a**−**e** and their use as organocatalysts in the epoxidation of several alkenes.

Results and Discussion

The required binaphthyl azepinium salts were readily prepared in good yields over two steps from bromoaldehyde **10** as we have described previously (**9a**, **9b**) by cyclocondensation with primary amines,[20] or from (*R*)-2,2′-bis(bromomethyl)[1,1′]-binaphthalene **8** (**9c**, **9d**, **9e**) by double displacement of bromide from **8** with primary amines followed by oxidation to the iminium species and cation exchange in good overall yields (Scheme 1, Table 1).

With these catalysts in hand, three alkene substrates were tested, initially with catalysts **9a** and **9b**, derived from *tert*-butylamine and 2,6-xylidene, respectively, under our standard aqueous conditions, using a 1:1 ratio of acetonitrile to water as solvent in the presence of Na_2CO_3 (Table 2).

As illustrated in Table 2, both catalyst **9a** and **9b** were relatively unreactive, leading for example to maximum conversions of 78% and 40%, respectively, when 1-phenylcyclohexene was used as a substrate (Table 2). Prolonged reaction times of up to 6 h did not improve the conversions. The poor reactivity of these catalysts is highlighted by the epoxidation of *trans*-α-methylstilbene and triphenylethylene, where extremely poor conversions to epoxides were observed. Catalyst **9a**, however, afforded an excellent 84% ee in the epoxidation of 1-phenylcyclohexene, so proving to be much more enantioselective than **9b** (40% ee).

Interestingly, when the reaction conditions were amended to those of Yang,[24] to use a 10:1 ratio of acetonitrile to water as solvent and slightly more acidic conditions (use of $NaHCO_3$ as base rather than Na_2CO_3), an increase in conversion was observed when using catalysts **9a** and **9b** and *trans*-α-methylstilbene as a substrate. These conditions, however, tend to produce diol products in some cases, presumably through *in situ* hydrolysis of the epoxides, an effect which is exacerbated by use of an increased proportion of water.

This observed increase in conversion may arise from the increase in substrate solubility with added organic solvent. Use of a 10:1 ratio of acetonitrile to water with Na_2CO_3 as base does not, however, produce a significant increase in conversion. The slightly acidic conditions might also be responsible for the increased conversion, as oxone is known to decompose at higher pH.[25] Despite the high enantioselectivity provided by catalyst **9a**, we abandoned its further use due to its poor reactivity, which perhaps results from high steric bulk at the nitrogen substituent.

We next screened catalysts **9c**−**e**, with a range of structural features in the nitrogen substituents but with less bulk than **9a** proximal to the azepinium ring, under these reaction conditions (Table 2). Catalysts **9c** and **9e** provide identical reactivity. Catalyst **9e** imparts higher enantioselectivities for most substrates than does catalyst **9c** and is similar in enantioselectivity to **9a** while providing much greater reactivity and thus providing the

TABLE 1. Preparation of Iminium Salt Catalysts from Dibromide 8 and Bromoaldehyde 10

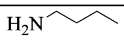
Amine	Catalyst Number	Yield (%)
	**9a**	60
	**9b**	71
	**9c**	72
	**9d**	59
	**9e**	79

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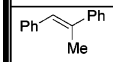
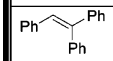
TABLE 2. Asymmetric Epoxidation of Alkenes with Catalysts 9a−e

Alkene	Catalyst	Conversion to epoxide [a]	Conversion to diol [a]	Yield of epoxide/% [b]	ee/% [c]	Configuration [d]
	**9a** [e]	78	—	54	84	(–)-1*S*,2*S*
	9b [e]	40	—	30	40	(–)-1*S*,2*S*
	9c [f]	83	17	67	72	(–)-1*S*,2*S*
	9d [f]	84	16	62	71	(–)-1*S*,2*S*
	9e [f]	89	11	73	82	(–)-1*S*,2*S*
	**9a** [e]	5	—	<5	-	—
	9b [e]	10	—	<5	-	—
	9a [f]	38	—	25	67	(–)-1*S*,2*S*
	9b [f]	70	—	47	16	(–)-1*S*,2*S*
	9c [f]	90	—	69	51	(–)-1*S*,2*S*
	9d [f]	90	—	65	48	(–)-1*S*,2*S*
	9e [f]	100	—	64	64	(–)-1*S*,2*S*
	**9a** [e]	4	—	<5	-	-
	9b [e]	5	—	<5	-	-
	9c [f]	90	—	74	25	(+)-*S*
	9d [f]	67	—	52	22	(+)-*S*
	9e [f]	90	—	71	28	(+)-*S*

[a] Conversions were evaluated from the ^{1}H NMR spectra by integration of alkene/diol/ epoxide signals. [b] Isolated yield. [c] Enantiomeric excesses were determined by ^{1}H NMR spectroscopy with Eu(hfc)$_3$ (10 mol %) as chiral shift reagent, or 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. [e] Epoxidation conditions: iminium salt (5 mol %), Oxone (2 equiv), Na_2CO_3 (4 equiv), MeCN:H_2O (1:1), 0 °C, 2 h. [f] Epoxidation conditions: iminium salt (5 mol %), Oxone (2 equiv), $NaHCO_3$ (5 equiv), MeCN:H_2O (10:1), 0 °C, 2 h.

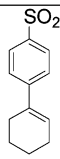
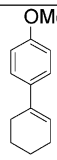
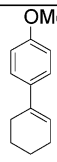
best balance of selectivity and reactivity, presumably resulting in part from the size and shape of the isopropyl nitrogen substituent. For example, 1-phenylcyclohexene and *trans*-α-methyl stilbene are epoxidized with 82% and 64% ee, respectively, using catalyst **9e** compared to 72% and 51% ee with catalyst **9c**. Catalyst **9d** was less enantioselective than **9c** and **9e**, affording similar enantioselectivities (up to 71% ee) to the catalyst **7** developed by Aggarwal.[22]

A number of other alkenes were next subjected to epoxidation mediated by catalyst **9e** (Table 3).

Catalyst **9e** proved to be the most effective catalyst of this series, achieving >90% conversion for all substrates and moderate to good enantioselectivities (21−83% ee). Catalyst **9e** was also utilized in the epoxidation of a range of cycloalkenes incorporating groups with different electronic effects at the para-position of the aromatic ring (Table 2). Once again, we observed excellent conversions to epoxides and moderate enantioselectivities. Interestingly, all the cycloalkenes gave poorer enantioselectivities than 1-phenylcyclohexene and 1-phenyl-3,4-dihydronaphthalene. It is also unclear why alkenes containing a para-substituted electron-withdrawing (SO_2Me) group and alkenes containing an electron-donating (OMe) group both gave lower enantioselectivities than the parent 1-phenylcyclohexene.

Because of the slightly more acidic nature of the reaction mixture, hydrolysis of some of the epoxides to the corresponding diols occurs in some instances, particularly for 1-phenyl-3,4-dihydronaphthalene and *p*-methoxy-1-phenylcyclohexene substrates, where complete conversion to the corresponding diols is observed in 2 h. When 1-phenylcyclohexene was used as a substrate, we observed between 11 and 20% conversion to the

TABLE 3. Asymmetric Epoxidation of Alkenes with Catalyst 9e[a]

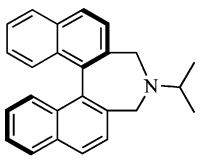
Alkene	Conversion to epoxide/% [b]	Conversion to diol/% [b]	Yield of epoxide/% [c]	ee/% [d]	Configuration [e]
	89	11	73	82	(–)-1*S*,2*S*
	100	—	85	64	(–)-1*S*,2*S*
	90	—	71	28	(+)-*S*
	100	—	75	22	(–)-*S*,*S*
	—	91	—	—	—
	90	—	68	83	(+)-1*R*,2*S* [f]
	94		83	27	(+)-1*R*,2*S* [f,g]
	100		80	21	(–)-1*S*,2*S*
	100		79	55	(–)-1*S*,2*S* [h]
	—	100	—	—	—
	100		63	66	(–)-1*S*,2*S* [f,h]
	80	20	60	65	(–)-1*S*,2*S*

[a] Epoxidation conditions: iminium salt (5 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/diol/epoxide signals. [c] Isolated yield. [d] Enantiomeric excesses were determined by ^1H NMR spectroscopy with $Eu(hfc)_3$ (10 mol %) as chiral shift reagent, or by chiral HPLC on a Chiralcel OD column, or by chiral GC on a Chiraldex B−DM column. [e] The absolute configurations of the major enantiomers were determined by comparison with literature values except where indicated. [f] Epoxidation conditions: iminium salt (5 mol %), Oxone (2 equiv), Na_2CO_3 (4 equiv), MeCN:H_2O (1:1), 0 °C, 2 h. [g] Reaction under Yang's conditions (footnote *a*) is capricious. [h] The absolute configurations of the major enantiomers were assigned by analogy with other examples on the basis of substrate and catalyst structure, and spectroscopic evidence.

diol. This hydrolysis of the epoxide products was obviated by use of our more basic epoxidation conditions (Oxone, Na_2CO_3, MeCN:H_2O (1:1)).

Recent studies by Lacour have shown biphenyl- and binaphthyl-derived tertiary azepines and their corresponding iminium salts both to be effective epoxidation catalysts in the presence of Oxone and sodium bicarbonate, leading to epoxides of almost identical enantioselectivities and configurations.[26] The amines were observed to perform best in terms of both enantioselectivity and conversion when monophasic 10:1 acetonitrile/water reaction conditions were used, while the iminium salts in some cases gave better results in biphasic 3:2 dichloromethane/water conditions in the presence of 18-crown-6, which presumably acts as a phase transfer catalyst.

We have therefore tested tertiary azepine **11** (5 mol %) as a catalyst in the epoxidation of *trans*-α-methylstilbene under these reaction conditions.



11

Interestingly, little epoxidation (9%) of the substrate was achieved over 2 h under the 10:1 acetonitrile:water conditions of Yang using $NaHCO_3$ as base. Addition of catalytic 18-crown-6 did not improve conversion (<5%) over the same reaction time; this procedure does not appear to have been previously tested. The biphasic 3:2 dichloromethane/water conditions developed by Lacour were also unsuccessful (<5% conversion) in this case. For comparison, the corresponding iminium salt catalyst **9e** gave 100% conversion under the 10:1 acetonitrile:water conditions at 0 °C over 2 h.

In conclusion, we have prepared a range of novel chiral binaphthalene-derived catalysts achiral at the nitrogen atom and utilized them in the asymmetric epoxidation of unfunctionalized alkenes. The *N*-isopropyl-substituted catalyst **9e** proved to be the most reactive and enantioselective, affording up to 83% ee and is superior in enantioselection to the *N*-methyl analogue **7** for a range of alkene substrates. Appropriate choice of reaction conditions allows for the successful epoxidation of relatively unreactive substrates and for the isolation of sensitive epoxides without hydrolysis. Catalyst **9e** is also more reactive than the corresponding tertiary azepine **11**.

Experimental Procedures

General Procedure for the Synthesis of Iminium Salt Catalysts. Method 1: From (*R*)-2′-(Bromomethyl)[1,1′]binaphthalene-2-carboxaldehyde and Primary Amines. A solution of the amine in ethanol (10 mL per gram of amine) was added dropwise to a solution of (*R*)-2′-(bromomethyl)[1,1′]binaphthalenyl-2-carboxaldehyde **(10)** (1.1 equiv with respect to (wrt) amine) in ethanol (10 mL per gram of carboxaldehyde) at 40 °C. The reaction mixture was stirred at 40 °C overnight. The yellowish mixture was left to cool to room temperature before addition of a solution of sodium tetraphenylborate (1.10 equiv) in the minimum amount of acetonitrile in one portion. The reaction mixture was stirred for a further 5 min, and the solvents were removed under reduced pressure. The yellow residue was dissolved in dichloromethane (40 mL per gram of amine) and washed with water (2 × 30 mL per gram of amine) and brine (2 × 30 mL per gram of amine), the organic phase was dried (Na_2SO_4), and the solvents were removed *in vacuo*. The yellow solid was recrystallized from ethanol, washed with ethanol followed by hexanes, and dried at 90 °C.

(*R*)-*N*-2,6-Dimethylphenyl-7*H*-dinaphtho[2,1-*c*;1′,2′-*e*]azepinium Tetraphenylborate (9b). Prepared according to the general procedure, method 1, from 2,6-dimethylaniline (0.103 g, 0.85 mmol), but heated under reflux for 16 h. The product was isolated as yellow powder (0.53 g, 79%), mp 211−214 °C; $[\alpha]^{20}_D = -725.0$ (*c* 0.96, acetone); Found: C, 89.68; H, 6.03; N, 1.85. $C_{54}H_{44}BN \cdot 0.3\ H_2O$ requires C, 89.69; H, 6.21; N, 1.94%; ν_{max} (film)/cm^{-1} 3052, 1608, 1583, 1544, 1505, 1426, 1416, 1378, 1265, 1168, 1032, 817; ^{1}H NMR (400 MHz, d_6-DMSO): δ 1.33 (3H, s), 2.43 (3H, s), 5.42 (2H, s), 6.77−6.81 (4H, m), 6.93 (8H, t, J = 7.4 Hz), 7.09 (1H, d, J = 8.6 Hz), 7.17−7.25 (9H, m), 7.35 (1H, ddd, J = 8.5 Hz, 6.9 Hz, 1.3 Hz), 7.45−7.47 (2H, m), 7.52−7.54 (2H, m), 7.56 (1H, ddd, J = 8.0 Hz, 6.8 Hz, 1.0 Hz), 7.82 (1H, d, J = 8.4 Hz), 7.86(1H, ddd, J = 8.1 Hz, 5.9 Hz, 2.0 Hz), 8.14 (1H, d, J = 8.1 Hz), 8.21 (1H, d, J = 8.7 Hz), 8.29 (2H, d, J = 8.6 Hz), 8.47 (1H, d, J = 8.7 Hz), 9.80 (1H, s); ^{13}C NMR (100 MHz, d_6-DMSO): δ 16.5, 17.7, 59.9, 121.5, 125.3, 126.1, 126.7, 126.9, 126.9, 127.1, 127.4, 127.9, 128.7, 128.8, 128.9, 129.3, 129.4, 129.5, 130.6, 130.7, 130.7, 131.2, 131.3, 131.4, 132.1, 133.0, 133.3, 135.2, 135.5, 136.2, 141.5, 143.0, 163.3, 173.1; *m*/*z* 398.1911; $C_{30}H_{24}N$ (cation) requires 398.1909.

General Procedure for the Synthesis of Iminium Salt Catalysts. Method 2: From (*R*)-2,2′-Bis(bromomethyl)[1,1′]binaphthalene (8) and Primary Amines. The primary amine (1.1 equiv) was added to a nitrogen-purged stirred solution of (*R*)-2,2′-bis(bromomethyl)[1,1′]binaphthalene **(8)** and potassium carbonate (3 equiv) in acetonitrile (10 mL per gram of dibromide) at room temperature. The reaction mixture was heated under reflux overnight or until disappearance of starting material was observed by TLC. The mixture was diluted with dichloromethane (40 mL per gram of dibromide) and washed with water (2 × 30 mL per gram of dibromide) and brine (2 × 30 mL per gram of dibromide). The organic phase was separated and dried (Na_2SO_4). *N*-Bromosuccinimide (1.2 equiv) was added to the resulting crude amine product in dichloromethane, and the mixture was heated under reflux for 3 h, after which time the reaction mixture was allowed to cool to room temperature. The solvent was removed *in vacuo* and the residue redissolved in ethanol. A solution of sodium tetraphenylborate (1.1 equiv) in a minimum amount of acetonitrile was added in one portion. The resulting mixture was stirred for 5 min, after which the solvents were removed *in vacuo*. The yellow residue was dissolved in dichloromethane (40 mL per gram of dibromide) and washed with water (2 × 30 mL per gram of dibromide) and brine (2 × 30 mL per gram of dibromide), the organic phase was dried (Na_2SO_4), and the solvents were removed *in vacuo*. The yellow solid was recrystallized from ethanol, washed with ethanol followed by hexanes, and dried at 90 °C.

(*R*)-*N*- Isopropyl-7*H*-dinaphtho[2,1-*c*;1′,2′-*e*]azepinium Tetraphenylborate (9e). Prepared according to the general procedure, method 2, from isopropylamine (1.5 g, 3.41 mmol). The product isolated as yellow powder (1.58 g, 71%); mp 159−162 °C; $[\alpha]^{20}_D = -440.0$ (*c* 0.65, acetone); Found: C, 87.59; H, 6.38; N, 2.23. $C_{49}H_{42}BN \cdot 1.0\ H_2O$ requires C, 87.36; H, 6.58; N, 2.08%; ν_{max} (film)/cm^{-1} 3050, 2994, 1947, 1637, 1585, 1552, 1472, 1427, 1374, 1263, 1133, 1031, 959, 845, 818, 738, 707; ^{1}H NMR (400 MHz, d_6-acetone): δ 1.53 (3H, d, J = 6.6 Hz), 1.56 (3H, d, J = 6.6 Hz), 4.59−4.67 (2H, m), 5.37 (1H, d, J = 13.7 Hz), 6.57−6.63 (4H, m), 6.77 (8H, t, J = 7.3 Hz), 6.94 (1H, d, J = 8.8 Hz), 7.16−7.26 (9H, m), 7.29−7.40 (2H, m), 7.45 (1H, ddd, J = 7.0 Hz, 6.8 Hz, 1.0 Hz), 7.67 (1H, ddt, J =6.4 Hz, 3.3 Hz, 1.6 Hz), 7.87 (1H, d, J = 8.4 Hz), 7.91 (1H, d, J = 8.6 Hz), 7.97 (1H, d, J = 8.2 Hz), 8.09 (1H, d, J = 8.3 Hz) 8.14 (1H, d, J = 8.5 Hz), 8.20 (1H, d, J

(26) Gonçalves, M. H.; Martinez, A.; Grass, S.; Page, P. C. B.; Lacour, J. *Tetrahedron Lett.* **2006**, *47*, 5297.

= 8.7 Hz), 9.31 (1H, s); ^{13}C NMR (100 MHz, d_6-acetone): δ 20.9, 21.1, 53.9, 66.7, 122.3, 126.1, 126.7, 127.0, 127.8, 128.1, 128.5, 129.6, 129.7, 130.1, 130.2, 130.7, 131.1, 132.1, 131.8, 132.4, 132.5, 132.8, 134.7, 135.3, 136.2, 137.0, 137.4, 164.9, 168.2; *m*/*z* 336.1755; $C_{25}H_{22}N$ (cation) requires 336.1752.

(*R*)-*N*-Isopropyl-2,7-dihydrodinaphtho[2,1-*c*;1′,2′-*e*]azepine (11). *N*-Isopropylamine (0.24 g, 4.09 mmol) was added to a nitrogen-purged stirred solution of (*R*)-2,2′-bis(bromomethyl)[1,1′]binaphthalene **(8)** (1.50 g, 3.41 mmol) and potassium carbonate (1.41 g, 10.22 mmol) in acetonitrile (10 mL) at room temperature. The reaction mixture was heated under reflux overnight. The mixture was diluted with dichloromethane (40 mL) and washed with water (2 × 30 mL) and brine (2 × 30 mL). The organic phase was separated and dried (Na_2SO_4), and the solvent was removed *in vacuo* to afford a yellow residue. Purification by column chromatography using EtOAc/petroleum ether (50:50) as eluent afforded the product as colorless solid (1.03 g, 89%). A pure sample was obtained by trituration in acetone (1−2 mL) for 5 min and collecting the colorless crystals by filtration; mp 158−159 °C; $[\alpha]^{20}_D$ = −491.8 (*c* 0.98, acetone); υ_{max} (film)/cm^{-1} 3048, 2965, 2806, 1507, 1460, 1376, 1122, 1032, 908, 816, 748; ^{1}H NMR (400 MHz, $CDCl_3$): 1.05 (3H, d, *J* = 6.4 Hz), 1.19 (3H, d, *J* = 6.3 Hz), 2.64−2.71 (1H, septet), 3.17 (2H, d, *J* = 12.4 Hz), 3.82 (2H, d, *J* = 12.4 Hz), 7.15−7.19 (2H, m), 7.34−7.40 (4H, m), 7.50 (2H, d, *J* = 8.2 Hz), 7.85 (4H, d, *J* = 8.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): 21.3, 21.9, 52.3, 52.9, 125.4, 125.7, 127.5, 128.0, 128.3, 128.3, 131.3, 133.1, 133.3, 135.0; *m*/*z* 337.1826; $C_{25}H_{23}N$ requires 337.1831.

General Procedure for Asymmetric Epoxidation. Method 1. Sodium carbonate (4 equiv wrt alkene) was dissolved in water (1.7 mL), and the mixture was cooled to 0 °C. Oxone (2 equiv) was added as a solid to the cooled mixture, and the resulting slurry was vigorously stirred at 0 °C for 5 min. To the mixture was added a solution of the catalyst (5 mol % wrt alkene) in acetonitrile (0.85 mL), followed by a solution of the alkene (0.5 mmol) in acetonitrile (0.85 mL). The reaction mixture was stirred at 0 °C until complete conversion of the substrate was observed by TLC. Diethyl ether at 0−5 °C (20 mL) was added to the reaction mixture, followed by water at 0−5 °C (20 mL). The aqueous phase was extracted with diethyl ether (2 × 20 mL), the combined organic extracts were washed with brine (2 × 20 mL) and dried (Na_2SO_4), and the solvent was removed *in vacuo*. Pure epoxides were obtained by column chromatography using petroleum ether (40−60 °C) as eluent.

Method 2. A mixture of alkene (0.4 mmol) and catalyst (5 mol %) was dissolved in acetonitrile (1 mL) and water (0.1 mL) and the mixture cooled to 0 °C. A mixture of Oxone (0.492 g, 0.8 mmol, 2 equiv) and sodium hydrogen carbonate (0.168 g, 5 equiv, 2 mmol) was added as a solid in one portion to the mixture with vigorous stirring. The mixture was stirred at 0 °C until complete conversion of the alkene was observed by TLC. Diethyl ether (10 mL) was added, and the reaction mixture was filtered through a pad of mixed $MgSO_4$ and sodium bisulfite. The solvent was removed *in vacuo*. Pure epoxides were obtained by column chromatography using petroleum ether (40−60 °C) as eluent.

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Supporting Information Available: Full experimental detail, ^{1}H and ^{13}C NMR spectra for synthesized compounds, hplc/gc/NMR traces for ee measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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