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Asymmetric Organocatalysis of Epoxidation by Iminium Salts under Non-Aqueous Conditions

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Abstract. Three iminium salts have been tested as catalysts for the asymmetric epoxidation of simple alkenes under non-aqueous conditions in various solvents, at varying temperatures, employing tetraphenylphosphonium monoperoxybisulfate (TPPP) as the stoichiometric oxidant. Enantiomeric excesses of up to 89% have been observed.

Keywords: Organocatalysis, catalysis, homogeneous, epoxidation

Introduction

Oxaziridinium salts, usually generated *in situ* from iminium salts and oxone, are useful electrophilic oxidants for alkene epoxidation.ⁱⁱ The first oxaziridinium salt was described by Lusinchi in 1976,ⁱⁱⁱ and over the last few years chiral iminium salts have been investigated as organocatalysts for the asymmetric epoxidation of alkenes by several groups (**1-5**) (Figure 1).^{iv} Armstrong and Yang have shown that even oxaziridinium salts generated *in situ* from chiral amines and aldehydes can mediate epoxidation;^v in these catalytic systems, however, catalyst loadings can be high.

Figure 1. Iminium salt systems for asymmetric epoxidation catalysis

We have reported the preparation of a number of enantiomerically pure chiral iminium salt epoxidation catalysts, in which the iminium unit is endocyclic and is conjugated with an aromatic ring.^{vi} In other published systems of this type, the exocyclic group attached to the nitrogen atom of the iminium salt is invariably methyl or ethyl, the asymmetric elements being sited elsewhere in the catalyst molecules. We reasoned that positioning of the controlling asymmetric elements in the exocyclic substituent at the iminium nitrogen atom would bring these enantiocontrolling elements of the catalyst nearer to the site of oxygen transfer, and might therefore increase the induced enantioselectivities. Three of our most successful and reactive catalysts, **6**, **7**, and **8**, are derived from 5-amino-2,2-dimethyl-4-phenyl-1,3-dioxane (acetoneamine) (Figure 2).

Figure 2. Iminium salts developed by Page and coworkers

X-Ray structure of 6

Figure 3

X-Ray structure of 7

Figure 4

Single crystal X-ray analyses of **6**^{vii} and **7**^{6b} (Figures 3 and 4 respectively) show that in both cases the six-membered acetal ring has a chair conformation, and the iminium unit is in an axial position, as might be expected given the lack of hindering 1,3-diaxial interactions and the potential operation of the gauche effect. It is interesting to note that the atropoisomer of the biphenyl unit in **6** possesses the same sense of asymmetry as is seen in the most successful isomer of the corresponding BINOL-derived catalyst **8**.

Catalysis of epoxidation by iminium salts has invariably been conducted using oxone as the stoichiometric oxidant. The use of oxone necessitates the presence of water as co-solvent in the epoxidation reactions, and this in turn prevents the reactions from being carried out at low temperatures. Oxone is a triple salt, and thus the quantity of inorganic byproduct is large. The addition of a base, typically sodium carbonate, to the reactions is also essential to prevent background (racemic) epoxidation. The organic co-solvent used has almost exclusively been acetonitrile, perhaps because of the degree of miscibility of water and acetonitrile; Lacour has, however, shown that dichloromethane may be used instead of acetonitrile if a crown ether is added to the mixture.^{viii}

We have recently shown that many of these drawbacks of iminium salt catalysis of epoxidation may be circumvented by the use of tetraphenylphosphonium monoperoxybisulfate (TPPP) as the stoichiometric oxidant.^{ix} TPPP is soluble in organic solvents such as dichloromethane and acetonitrile, and we have thus been able to report the development of the first non-aqueous conditions for the catalytic asymmetric epoxidation of simple alkenes mediated by iminium salts.^x These new conditions

eliminate the use of both water and added base, and therefore not only allow the epoxidation reactions to be carried out at low temperature, but also simplify the reaction and its work up. We have reported the optimum conditions for the epoxidation of *cis*-aryl substrates using catalyst **9**,^{xi} we have found, however, that these conditions (10 mol% catalyst, 2 equiv. TPPP, CHCl₃, –40 °C) provided relatively poor ees (when compared to the original oxone/MeCN/H₂O conditions) when using any of catalysts **6**, **7** or **8**.^{xii} We now report herein our findings concerning optimized conditions for asymmetric epoxidation using these three catalysts.

Results & Discussion

Several reactions using 1-phenylcyclohexene as test substrate were performed using dibenzazepinium catalyst **6** and dihydroisoquinolinium catalyst **7**. Reactions were conducted using 10 mol% catalyst over a range of temperatures, in acetonitrile, dichloromethane or a dichloromethane–acetonitrile (1:1) mixture. For comparison, the results obtained using oxone in aqueous acetonitrile at 0 °C are also included (Table 1).^{6b,6c}

Table 1: Catalytic asymmetric epoxidation of 1-phenylcyclohexene **10**

entry	solvent	catalyst	temp/°C	time/min	conv/% ^a	ee/% ^b
1	MeCN	6	–40	3	100	67
2	MeCN	6	0	3	100	58
3	MeCN	6	40	1	100	50
4	MeCN	6	80	3	100	47
5	MeCN	7	–40	60	42	43
6	MeCN	7	0	50	66	34
7	MeCN	7	40	5	89	30

8	CH ₂ Cl ₂	6	−78	120	52	50
9	CH ₂ Cl ₂	6	−60	120	50	36
10	CH ₂ Cl ₂	6	−40	90	100	28
11	CH ₂ Cl ₂	6	0	10	100	26
12	CH ₂ Cl ₂	6	40	<5	100	23
13	CH ₂ Cl ₂	7	−78	480	15	23
14	CH ₂ Cl ₂	7	−40	120	70	37
15	CH ₂ Cl ₂	7	0	10	100	16
16	CH ₂ Cl ₂	7	40	25	75	0
17	CH ₂ Cl ₂ / MeCN	6	−78	360	100	70
18	CH ₂ Cl ₂ / MeCN	6 ^c	−78	24 h	85	70
19	CH ₂ Cl ₂ / MeCN	6	−40	30	100	53
20	CH ₂ Cl ₂ / MeCN	6	0	<5	100	51
21	CH ₂ Cl ₂ / MeCN	6	40	<5	100	43
22	CH ₂ Cl ₂ / MeCN	7	−78	480	35	45
23	CH ₂ Cl ₂ / MeCN	7	−40	120	83	46
24	CH ₂ Cl ₂ / MeCN	7	0	10	100	34
25	CH ₂ Cl ₂ / MeCN	7	40	10	100	25
26 ^d	MeCN / H ₂ O	6 ^c	0	5	100	60
27 ^d	MeCN / H ₂ O	7	0	10	100	41

^a Conversions were evaluated from the ¹H NMR spectra by integration of alkene and epoxide signals.
^b Enantiomeric excesses were determined by ¹H NMR spectroscopy in the presence of (+)-Eu(hfc)₃ (0.1 mol eq). ^c 2 mol% catalyst. ^d Conditions: Oxone (2 equiv), sodium carbonate (4 equiv), water-acetonitrile (1:1), 0 °C. ^e 5 mol% catalyst.

Generally, reduction in temperature resulted in increased enantiomeric excess. The increase in ee was accompanied by a decrease in reaction rate, and in some cases at −78 °C, the lowest temperature tested, little or no increase in epoxide conversion was observed even after extended reaction times. A comparison of reaction times shows that the biphenyl catalyst **6** is much the more reactive of the two

catalysts, providing complete conversion in acetonitrile at $-40\text{ }^{\circ}\text{C}$ in just 3 minutes, especially at lower temperatures, and is also much the more enantioselective, regardless of solvent.

The best selectivities were obtained when a mixture of solvents was employed. A 1:1 ratio of dichloromethane to acetonitrile allows the reaction mixture to remain homogeneous at $-78\text{ }^{\circ}\text{C}$ (acetonitrile freezes at $-45\text{ }^{\circ}\text{C}$), and under these conditions catalyst **6** has produced 1-phenylcyclohexene oxide **11** with 70% ee over six hours. Even when the catalyst loading was reduced to 2 mol%, we were able to observe 85% conversion after 24 hours, and the ee remained constant at 70%. In contrast, the dihydroisoquinolinium catalyst **7** is still rather unreactive at $-78\text{ }^{\circ}\text{C}$. Further, the levels of enantioselectivity observed for catalyst **7** under the new non-aqueous conditions do not exceed those obtained using the oxone-aqueous acetonitrile conditions. Again in contrast, however, in the case of the biphenyl catalyst **6**, reactivity is enhanced over, and selectivity is similar to, the aqueous oxone conditions. Catalyst **6** was therefore selected to screen a range of unfunctionalized alkenes (Table 2).

Table 2: Catalytic asymmetric epoxidation of unfunctionalized alkenes mediated by catalyst 6

entry	alkene	solvent	temp/ $^{\circ}\text{C}$	time/h	conv/% ^a	ee/% ^b	epoxide config ^c
1	 10	MeCN	-40	0.03	100	67	(-)-1S,2S
2		CH_2Cl_2	-78	2.0	52	50	(-)-1S,2S
3		CH_2Cl_2 / MeCN	-78	6.0	100	70	(-)-1S,2S
4	 12	MeCN	-40	1.0	50	40	(-)-1S,2S
5		CH_2Cl_2	-78	8.0	5	20	(-)-1S,2S
6		CH_2Cl_2	-40	6.0	100	50	(-)-1S,2S
7		CH_2Cl_2 / MeCN	-78	2.0	15	44	(-)-1S,2S
8		CH_2Cl_2 / MeCN	-40	2.0	86	50	(-)-1S,2S
9		MeCN	-40	1.0	78	60	(-)-R

10		CH ₂ Cl ₂	−78	8.0	<5	—	—
11	13	CH ₂ Cl ₂	−40	2.0	7	47	(−)-R
12		CH ₂ Cl ₂ /MeCN	−78	8.0	<5	—	—
13		CH ₂ Cl ₂ /MeCN	−40	1.0	30	29	(−)-R
14		CH ₂ Cl ₂ /MeCN	−40	24	63	22	(−)-R
15		MeCN	−40	0.2	100	14	(−)-1S,2S
16	14	CH ₂ Cl ₂	−40	4.0	100	39	(−)-1S,2S
17		CH ₂ Cl ₂ /MeCN	−40	2.0	100	33	(−)-1S,2S
18		MeCN	−40	1.0	100	22	(+)-1R,2S
19		CH ₂ Cl ₂	−40	3.0	100	7 ^d	(+)-1R,2S
20		CH ₂ Cl ₂ /MeCN	−40	0.7	100	65 ^d	(+)-1R,2S
21		CH ₂ Cl ₂ /MeCN	−78	5.0	100	64 ^d	(+)-1R,2S

^a Conversions were evaluated from the ¹H NMR spectra by integration of alkene and epoxide signals.^b Enantiomeric excesses were determined by ¹H NMR spectroscopy in the presence of (+)-Eu(hfc)₃ (0.1 mol eq).^c The absolute configurations of the major enantiomers were determined by correlation of optical rotation with those of known epoxides.^d Enantiomeric excesses were determined by chiral HPLC using a Chiracel OD-H column.

These olefins were less reactive than 1-phenylcyclohexene **10**, and therefore the majority of reactions were carried out at −40 °C. Generally, the dichloromethane/acetonitrile (1:1) conditions produced the best results in terms of both enantiomeric excesses and conversions. The best ee obtained was for 1-phenyl-3,4-dihydronaphthalene **15** at −40 °C in dichloromethane/acetonitrile (1:1), which in 40 min gave 100% conversion and 65% ee, a remarkable result given that 1-phenyl-3,4-dihydronaphthalene **15** gave the worst observed ee in dichloromethane (7%). Otherwise the difference in enantiomeric excesses between the three solvent systems was less dramatic than that observed in reactions of 1-phenylcyclohexene, but conversions differed quite significantly: all the experiments conducted in dichloromethane required longer reaction times, and in some cases still did not reach the conversion achieved in acetonitrile or dichloromethane-acetonitrile (1:1), even after several hours' reaction.

We have reported that the binaphthalene-derived catalyst **8** can provide ees of up to 95% when using our original aqueous oxone conditions.^{6d} We have also tested this catalyst under non-aqueous

conditions with TPPP as the stoichiometric oxidant (Table 3). Several substrates were epoxidized, using acetonitrile, dichloromethane or a mixture of the two solvents at either -40 or -78 °C. We observed a broadly similar level of selectivity in acetonitrile to those reactions carried out under the aqueous oxone conditions. The ee for α -methylstilbene oxide **16** is somewhat increased under these conditions (61% ee compared to 49% ee under the aqueous oxone system). Again, all of the experiments conducted in dichloromethane required longer reaction times, and, in the case of α -methylstilbene **16**, complete conversion to epoxide was not observed even after 24 hours. Reactions carried out at -78 °C afforded the epoxides with lower ees than were observed at -40 °C. Unlike catalysts **6** and **7**, catalyst **8** did not offer the highest enantiocontrol under the dichloromethane/acetonitrile (1:1) conditions, and a significant solvent effect was observed in each case; for example, the epoxidation of 1-phenyl-3,4-dihydronaphthalene **15** in dichloromethane afforded the epoxide with only 31% ee, but a significant increase in enantioselectivity was observed when the solvent was changed to acetonitrile, when 1-phenyl-3,4-dihydronaphthalene oxide **17** was produced in 89% ee.

Table 3: Epoxidation of several unfunctionalized alkenes using catalyst 8 and TPPP.^a

entry	alkene	Solvent	time (h)	yield (%) ^b	ee (%) ^c	epoxide config ^d
1	10	CH ₂ Cl ₂	10	71	70	(-)-1 <i>S</i> ,2 <i>S</i>
2		MeCN	7	81	89	(-)-1 <i>S</i> ,2 <i>S</i>
3		CH ₂ Cl ₂ /MeCN	8	69	75	(-)-1 <i>S</i> ,2 <i>S</i>
4		CH ₂ Cl ₂ /MeCN ^e	10	15 ^f	30	(-)-1 <i>S</i> ,2 <i>S</i>
5	15	CH ₂ Cl ₂	4	63	31 ^g	(+)-1 <i>R</i> ,2 <i>S</i>
6		MeCN	1	61	89 ^g	(+)-1 <i>R</i> ,2 <i>S</i>
7		CH ₂ Cl ₂ /MeCN	3	55	75 ^g	(+)-1 <i>R</i> ,2 <i>S</i>
8		CH ₂ Cl ₂ /MeCN ^e	10	38 ^f	67 ^g	(+)-1 <i>R</i> ,2 <i>S</i>
9		CH ₂ Cl ₂	24	70	57	(-)-1 <i>S</i> ,2 <i>S</i>
10		MeCN	14	74	77	(-)-1 <i>S</i> ,2 <i>S</i>

11		CH ₂ Cl ₂ /MeCN	14	76	68	(-)-1 <i>S</i> ,2 <i>S</i>
	18					
12		CH ₂ Cl ₂	24	65 ^f	58	(-)-1 <i>S</i> ,2 <i>S</i>
13		MeCN	24	66	61	(-)-1 <i>S</i> ,2 <i>S</i>
14	12	CH ₂ Cl ₂ /MeCN	24	71	58	(-)-1 <i>S</i> ,2 <i>S</i>

^a Epoxidation conditions: Iminium salt **3** (5 mol %), TPPP (2 eq), -40 °C; reactions were run to 100% conversion, evaluated from the ¹H NMR spectra by integration of alkene and epoxide signals, unless indicated otherwise. ^b Isolated yield. ^c Enantiomeric excesses were determined by ¹H-NMR spectroscopy with (+)-Eu(hfc)₃ (0.1 mol eq) as chiral shift reagent. ^d The absolute configurations of the major enantiomers were determined by correlation of optical rotation with those of known epoxides. ^e Reaction carried out at -78 °C. ^f Conversions, evaluated from the ¹H NMR spectra by integration of alkene and epoxide signals. ^g Enantiomeric excesses were determined by chiral HPLC using a Chiracel OD-H column.

In conclusion, dichloromethane-acetonitrile (1:1) appears to be the solvent of choice for catalysts **6** and **7** under the non-aqueous conditions described herein, and acetonitrile for catalyst **8**. The reasons for this remain unclear, but may be related to solvent polarity and catalyst solvation. Catalyst **8** remains one of the most selective iminium salt asymmetric catalyst of epoxidation so far discovered, providing up to 89% ee in epoxidations of 1-phenylcyclohexene and 1-phenyl-3,4-dihydronaphthalene.

Experimental Section

General Experimental Detail. All infrared spectra were obtained using a Perkin-Elmer Paragon 1000 FT-IR spectrophotometer; thin film spectra were acquired using sodium chloride plates. All ¹H and ¹³C NMR spectra were measured at 250.13 and 62.86 MHz with a Bruker AC 250 MHz spectrometer or at 400.13 and 100.62 MHz with a Bruker DPX 400 MHz spectrometer, in deuteriochloroform solution unless otherwise stated, using TMS (tetramethylsilane) as the internal reference. Mass spectra were recorded using a Jeol-SX102 instrument utilizing electron-impact (EI), fast atom bombardment (FAB), and by the EPSRC national mass spectrometry service at the University

of Wales, Swansea, utilising electrospray (ES.). Analysis by GCMS utilized a Fisons GC 8000 series (AS 800), using a 15 m x 0.25 mm DB-5 column and an electron-impact low resolution mass spectrometer. Melting points were recorded using an Electrothermal-IA 9100 melting point instrument and are uncorrected. Optical rotation values were measured with an Optical Activity-polAAar 2001 instrument, operating at $\lambda=589$ nm, corresponding to the sodium D line, at the temperatures indicated. Microanalyses were performed on a Perkin Elmer Elemental Analyser 2400 CHN. All chromatographic manipulations used silica gel as the adsorbent. Reactions were monitored using thin layer chromatography (TLC) on aluminium-backed plates coated with Merck Kieselgel 60 F254 silica gel. TLC plates were visualised by UV radiation at a wavelength of 254 nm, or stained by exposure to an ethanolic solution of phosphomolybdic acid (acidified with concentrated sulphuric acid), followed by charring where appropriate. Reactions requiring anhydrous conditions were carried out using glassware dried overnight at 150 °C, under a nitrogen atmosphere unless otherwise stated. Reaction solvents were used as obtained commercially unless otherwise stated. Light petroleum (b.p. 40-60 °C) was distilled from calcium chloride prior to use. Ethyl acetate was distilled over calcium sulphate or chloride. Dichloromethane was distilled over calcium hydride. Tetrahydrofuran was distilled under a nitrogen atmosphere from the sodium/benzophenone ketyl radical or from lithium aluminium hydride. Enantiomeric excesses were determined either by proton nuclear magnetic resonance spectroscopy in the presence of europium (III) tris[3-(hepta-fluoropropylhydroxymethylene)-(+)-camphorate] as the chiral shift reagent (8-10 mg substrate and 3-5 mg (+)-Eu(hfc)₃), or by chiral HPLC using a Chiracel OD column on a TSP Thermo-Separating-Products Spectra Series P200 instrument, with a TSP Spectra Series UV100 ultra-violet absorption detector set at 254 nm and a Chromojet integrator. Epoxide configuration was determined by comparison of the sign of optical rotation to those reported in the literature.

**(+)-2-[(4*S*,5*S*)-2,2-Dimethyl-4-phenyl-1,3-dioxan-5-yl]-3,4-dihydroisoquinolinium
tetraphenylborate **6**^{vib}**

A solution of (+)-(4*S*,5*S*)-5-amino-2,2-dimethyl-4-phenyl-1,3-dioxane (acetanamine) (5.0 g, 24.2 mmol) in ethanol (50 mL), was added dropwise to 2-(2-bromoethyl)benzaldehyde (5.7 g, 26.6 mmol) with ice bath cooling. The reaction mixture was stirred overnight while attaining ambient temperature. A solution of sodium tetraphenylborate (9.2 g, 26.6 mmol) in acetonitrile (5 mL) was added in one portion, and the reaction mixture stirred for 5 minutes. The organic solvents were removed under reduced pressure, and ethanol (20 mL) added to the residue, followed by water (5 mL). The resulting yellow solid was collected by filtration, washed with additional ethanol (20 mL) followed by diethyl ether (20 mL), and recrystallized from acetone/diethyl ether. The product was isolated as a yellow crystalline solid (11.6 g, 75%), m.p. 169-170 °C; $[\alpha]_D^{20} +38.6$ (*c* 2.70, CH₃CN); $\nu_{\max}/\text{cm}^{-1}$ (nujol) 1637, 1603, 1571, 1480, 1266, 1202, 1166, 1108, 1073; δ_{H} (250 MHz; CD₃CN), 1.65 (3 H, s, CH₃), 1.94 (3 H, s, CH₃), [2.39-2.48 (1 H, m), 2.70-2.82 (1 H, m), Ar-CH₂], [3.25-3.40 (1 H, m), 3.81-3.97 (1 H, m), CH₂N], 4.06 (1 H, m, NCH), 4.30 (1 H, d, *J* 13.7 Hz upfield portion of an ABX system, N-CHCHH-O), 4.58 (1 H, dd, *J* 13.7, 3.1 Hz, downfield portion of an ABX system, N-CHCHH-O), 5.70 (1 H, d, *J* 2.8 Hz, Ph-CH), 6.81 (4 H, t, *J* 7.2 Hz, 4 x CH arom., *para* in BPh₄ group), 7.35-7.40 (6 H, m, 5 x CH arom., Ph gp., CH arom.), 7.46 (1 H, t, *J* 7.3 Hz, CH arom.), 7.65-7.74 (2 H, m, 2 x CH arom.), 8.92 (1 H, s, HC=N); δ_{C} (62.50 MHz; CD₃CN) 18.0 (CH₃), 24.1 (Ar-CH₂), 28.7 (CH₃), 51.6 (CH₂N), 61.4 (CH₂), 65.5 (NCH), 70.7 (Ph-CH), 104.9 (C quat.), 121.9 (8 x CH arom., *ortho* in BPh₄ gp.), 124.3 (C quat., arom.), 125.4 (2 x CH arom., *ortho* in Ph gp.), 125.7 (2 x CH arom., *meta* in Ph gp.), 128.1 (CH arom.), 128.5 (CH arom.), 128.6 (CH arom., *para* in Ph gp.), 128.0, (4 x CH arom., *para* in BPh₄ gp.), 134.4 (CH arom.), 135.8 (8 x CH arom., *meta* in BPh₄ gp.), 137.0 (C quat., arom., *ipso* in Ph gp.), 137.7 (C quat., arom.), 138.7 (CH arom.), 163.5 (4 x C quat., arom., *q*, *J* 196.40 Hz, C-B, *ipso* in BPh₄ gp.), 167.5 (HC=N); *m/z* 322.1809; C₂₁H₂₄NO₂ (cation) requires 322.1807.

**(-)-2-[(4*S*,5*S*)-2,2-Dimethyl-4-phenyl-1,3-dioxan-5-yl]-5*H*-dibenzo[*c,e*]azepinium
tetraphenylborate **7**^{vic}**

A solution of (+)-(4*S*,5*S*)-5-amino-2,2-dimethyl-4-phenyl-1,3-dioxane (acetoneamine) (3.85 g, 18.8 mmol) in ethanol (40 mL) was added dropwise to an ice cooled solution of 2- (bromomethyl)biphenyl 2'-carboxaldehyde (5.7 g, 20.7 mmol) in ethanol (60 mL). The reaction mixture was stirred overnight while attaining ambient temperature. A solution of sodium tetraphenylborate (7.1 g, 20.7 mmol) in the minimum amount of acetonitrile (4 mL) was added in one portion, and the reaction mixture stirred for 5 minutes. The organic solvents were removed under reduced pressure, and ethanol (20 mL) added to the residue, followed by water (5 mL). The resulting yellow solid was collected by filtration and washed with ethanol (20 mL) followed by diethyl ether (20 mL). The product was isolated as yellow plates (9.00 g, 68%); m.p. 187-188 °C (dec.); $[\alpha]_D^{20}$ -44.0 (*c* 1.01, CH₃CN); Found C, 85.23; H, 6.52; N, 1.96. C₅₀H₄₆BNO₂ requires C, 85.34; H, 6.59; N, 1.99%; $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 3055, 3038, 2999, 1633, 1579, 1480, 1451, 1385, 1203, 1114, 848, 735, 706; $\delta_{\text{H}}(400 \text{ MHz; DMSO-d}_6, 115 \text{ }^\circ\text{C})$ 1.71 (3 H, s, CH₃), 1.74 (3 H, s, CH₃), 4.32 (1 H, d, *J* 21.8 Hz, upfield portion of an ABX system, N-CHCHH-O), 4.49 (1 H, d, *J* 21.6 Hz, Ar-CHHN), [4.68-4.77 (1 H, m, NCH), 4.72 (1 H, dd, *J* 5.2, 21.8 Hz, downfield portion of an ABX system, N-CHCHH-O, C6)], 5.15 (1 H, d, *J* 22.2 Hz, Ar-CHHN), 5.82 (1 H, d, *J* 4.1 Hz, Ar-CH), 6.75 (4 H, t, *J* 11.4 Hz, 4 x CH arom., *para* in BPh₄ gp.), 6.88 (8 H, t, *J* 11.5 Hz, 8 x CH arom., *ortho* in BPh₄ gp.), 7.11-7.16 (5 H, m, 5 x CH arom., Ph gp.), 7.20-7.25 (8 H, m, 8 x CH arom., *meta* in BPh₄ gp.), 7.55-7.63 (3 H, m, 3 x CH arom.), 7.64-7.69 (3 H, m, 3 x CH arom.), 7.92-7.94 (2 H, m, 2 x CH arom.), 9.03 (1 H, s, HC=N); $\delta_{\text{C}}(100 \text{ MHz; DMSO-d}_6, 120 \text{ }^\circ\text{C})$ 18.1 (CH₃), 28.4 (CH₃), 55.8 (Ar-CH₂N), 60.8 (CH₂), 66.1 (NCH), 70.5 (Ar-CH), 99.9 (C quat.), 120.4 (8 x CH arom., *ortho* in BPh₄ gp.), 124.1 (4 x CH arom., *para* in BPh₄ gp.), 124.2 (2 x CH arom., *meta* in Ph gp.), 124.2 (2 x CH arom., *ortho* in Ph gp.), 124.4 (CH arom., *para* in Ph gp.), 127.3 (C quat., arom.), 127.6 (CH arom.), 127.7 (CH arom.), 128.2 (CH arom.), 128.3 (CH arom.), 129.0 (CH arom.), 129.3 (CH arom. 6), 129.4 (CH arom.), 132.6 (C quat., arom.), 133.6 (CH arom.), 135.0 (8 x CH arom., *meta* in BPh₄ gp.), 135.2 (C quat., arom.), 140.5 (C quat., arom.), 163.3 (4 x C quat., arom., q, *J* 196.0 Hz, C-B *ipso* in BPh₄ gp.), 170.1 (HC=N); *m/z* 384.1968; C₂₆H₂₆NO₂ (cation) requires 384.1964.

(*S*)-[(4*S*,5*S*)-2,2-Dimethyl-4-phenyl-1,3-dioxan-5-yl]-3*H*-4-azepinium cyclohepta[2,1-*a*;3,4-*a'*]dinaphthalene tetraphenylborate 8^{xia}

A solution of (+)-(4*S*,5*S*)-5-amino-2,2-dimethyl-4-phenyl-1,3-dioxane (acetanamine) (0.15 g, 0.72 mmol) in ethanol (2 mL) was added dropwise to a solution of (*R*)-2-bromomethyl-[1,1']binaphthalenyl 2'-carboxaldehyde (0.30 g, 0.79 mmol) in warm (35 °C) ethanol (3 mL). The reaction mixture was stirred overnight while attaining ambient temperature. A solution of sodium tetraphenylborate (0.27 g, 0.79 mmol) in acetonitrile (1 mL) was added in one portion, and the reaction mixture stirred for 5 minutes. The organic solvents were removed under reduced pressure, and ethanol added to the residue (1 mL), followed by water (0.5 mL). The resulting solid was collected by filtration and washed with ethanol (2 mL) followed by hexane (5 mL). The product was isolated as a yellow solid (0.39 g, 66%); m.p. 111-113 °C (dec.); $[\alpha]_D^{20}$ -398.5 (*c* 1.04, acetone); Found: C, 84.44; H, 5.97; N, 1.71. C₅₈H₅₀BNO₂•1.0H₂O requires C, 84.73; H, 6.13; N, 1.71%; $\nu_{\max}(\text{film})$ /cm⁻¹ 3055, 2986, 1626, 1610, 1593, 1548, 1478, 1450, 1382, 1266, 1203, 1110, 846, 817, 735, 704; $\delta_{\text{H}}(400 \text{ MHz; acetone-d}_6)$ 1.79 (3 H, s, CH₃), 1.85 (3 H, s, CH₃), 4.43 (1 H, d, *J* 13.2 Hz, Ar-CHHN), 4.51 (1 H, d, *J* 13.6 Hz, upfield portion of an ABX system, N-CHCHH-O), 4.86 (2 H, m, downfield portion of an ABX system, N-CHCHH-O, & NCH), 5.98 (2 H, m, Ar-CH & Ar-CHHN), 6.76 (4 H, t, *J* 7.2 Hz, 4 x CH arom., *para* in BPh₄ gp.), 6.93 (8 H, t, *J* 7.6 Hz, 8 x CH arom., *ortho* in BPh₄ gp.), 6.95-7.10 (5 H, m, 5 x CH arom., Ph gp.), 7.18-7.32 (2 H, m, 2 x CH arom.), 7.34 (8 H, m, 8 x CH arom., *meta* in BPh₄ gp.), 7.45 (3 H, m, 3 x CH arom.), 7.45-7.65 (2 H, m, 2 x CH arom.), 7.78 (1 H, m, CH arom.), 7.88 (1 H, d, *J* 8.4 Hz, CH arom.), 8.10 (1 H, d, *J* 8.4 Hz, CH arom.), 8.17 (1 H, d, *J* 8.4 Hz, CH arom.), 8.23 (1 H, dd, *J* 8.4, 2.4 Hz, CH arom.), 9.29 (1 H, s, HC=N); $\delta_{\text{C}}(100 \text{ MHz; acetone-d}_6)$ 19.3 (CH₃), 29.7 (CH₃), 57.0 (Ar-CH₂N), 62.3 (CH₂), 68.4 (NCH), 72.9 (Ar-CH), 102.1 (C quat.), 120.5 (C quat., arom.), 122.7 (4 x CH arom., *para* in BPh₄ gp.), 126.3 (CH arom., *para* in Ph gp.) 126.4 (8 x CH arom., *ortho* in BPh₄ gp.), 126.6 (C quat., arom.), 127.3 (C quat., arom.), 128.1 (CH arom.), 128.2 (CH arom.), 128.4 (2 x CH arom., *ortho* in Ph gp.), 129.1 (2 x CH arom., *meta* in Ph gp.), 129.2 (2 x CH arom.), 129.9 (2 x CH arom.), 130.0 (CH arom.), 130.1 (CH arom.), 130.6 (CH arom.), 130.7 (CH arom.), 131.7 (CH arom.),

132.2 (C quat., arom.), 132.6 (C quat., arom.), 132.9 (CH arom.), 133.3 (C quat., arom.), 135.3 (C quat., arom.), 136.6 (C quat., arom.), 137.4 (8 x CH arom., *meta* in BPh₄ gp.) 142.8 (C quat., arom., *ipso* in Ph gp.), 165.3 (4 x C quat., q, *J* 196.0 Hz, arom., C-B *ipso* in BPh₄ gp.), 171.4 (HC=N); *m/z* 484.2275; C₃₄H₃₀NO₂ (cation) requires 484.2277.

Tetraphenylphosphonium monoperoxysulfate^{ix}

Oxone triple salt (2 KHSO₅:KHSO₄:K₂SO₄) (15.0 g, 48.8 mmol with respect to KHSO₅) was dissolved in deionized water (300 ml), and the solution stirred at 10–15 °C (water bath). A solution of tetraphenylphosphonium chloride (15.0 g, 40.0 mmol) in distilled dichloromethane (300 ml) was added over 5 min, and the mixture stirred for an additional 30 min. The organic layer was separated, and the solvent removed under reduced pressure at room temperature. The colourless residue, the crude salt, was transferred to a fritted glass funnel and washed with distilled water (2 x 75 ml). The solid was dissolved in dichloromethane (180 ml), and the solution dried (MgSO₄). Hexane was added until cloudiness developed, and the flask was placed in the freezer (–20 °C) overnight, producing a colourless precipitate of the salt about 85% pure in peroxide (15.4 g, 70%). ¹H (250 MHz; CDCl₃) 7.62–7.65 (8 H, m), 7.76–7.81 (8 H, m), 7.88–7.92 (4 H, m), 8.92 (1 H, s).

General procedure for catalytic asymmetric epoxidation of simple alkenes mediated by iminium salts using tetraphenylphosphonium monoperoxysulfate

Tetraphenylphosphonium monoperoxysulfate (2 equiv. with respect to the alkene) was dissolved in the desired mixture of solvents (2 mL per 0.1 g TPPP) and the solution cooled to the required temperature. A solution of the iminium salt (10 mol% with respect to the alkene) in the solvent (0.5 mL per 0.1 g TPPP) was cooled to the same temperature as the solution containing TPPP and added to it dropwise over 15–20 min; the temperature of the reaction vessel was monitored to minimize the increase in temperature during the addition. A solution of the alkene in the reaction solvent (0.5 mL per 0.1 g TPPP) was added dropwise. The mixture was stirred at the reaction temperature until the alkene

was completely consumed according to tlc. Diethyl ether (pre-cooled to the reaction temperature) (20 mL per 0.1 g TPPP) was added to induce precipitation of the remaining oxidant, and the mixture filtered through Celite. The solvents were removed, diethyl ether (40 mL per 0.1 g oxidant) was added to the residue, and the solution passed through a short pad of silica gel to remove catalyst residues. The solvents were removed to give the epoxide. If the reaction does not reach completion the epoxide can be separated from the alkene by column chromatography, eluting with ethyl acetate/light petroleum (1:99).

(–)-(1*S*,2*S*)-1-Phenylcyclohex-1-ene oxide 11 (Table 3, entry 2, 89% ee, determined by 250 MHz ¹H-NMR by addition of (+)-Eu(hfc)₃ (4 mg) to the epoxide (10 mg) in CDCl₃. Integration of the epoxide CH (originally at 3.10 ppm, before addition of the chiral shift reagent) at 4.01 ppm (Major) and 3.85 ppm (Minor) gave an ee of 89% in favour of the (–)-(1*S*,2*S*) enantiomer, lit.^{xiii} [α]_D²⁴ –119.6 (c 1.85, C₆H₆). Prepared according to the general procedure from 1-phenylcyclohex-1-ene **10** (0.079 g, 0.5 mmol). Colourless oil (0.07 g, 81%); $\nu_{\max}$ (neat)/cm^{–1} 3084, 1602, 1495, 1446, 1359, 1249, 1173, 1132, 1079, 1030, 993, 974; δ_{H} (250 MHz; CDCl₃) [1.22-1.35 (1 H, m), 1.53-1.64 (3 H m), 1.99-2.06 (2 H, m) 2.16-2.18 (1 H, m), 2.26-2.32 (1 H, m) 4 x CH₂], 3.10 (1 H, t, *J* 2.0 Hz, CH), 7.28-7.44 (5 H, m, arom., Ph gp.); δ_{C} (62.5 MHz; CDCl₃) [19.8, 20.1, 24.7, 28.2 (4 x CH₂), 60.1 (C quat., C1), 61.8 (CH) 125.3 (2 x CH arom., *ortho* in Ph gp.), 127.1 (CH arom., *para* in Ph gp.), 128.2 (2 x CH arom., *meta* in Ph gp.), 142.8 (C quat., arom., *ipso* in Ph gp.).

(–)-(1*S*,2*S*)-1-Phenylcyclohept-1-ene oxide (Table 3, entry 10, 77% ee determined by 250 MHz ¹H-NMR by addition of (+)-Eu(hfc)₃ (4 mg) to the epoxide (10 mg) in CDCl₃. Integration of the epoxide CH (originally at 3.04 ppm, before addition of the chiral shift reagent) at 4.06 ppm (Major) and 3.84 ppm (Minor) gave an ee of 77% in favour of the (–)-(1*S*,2*S*) enantiomer). Prepared according to the general procedure from 1-phenylcyclohept-1-ene **18** (0.086 g, 0.5 mmol). Colourless oil (0.07 g, 74%); $\nu_{\max}$ (neat)/cm^{–1} 3084, 1602, 1494, 1445, 1358, 1255, 1166, 1128, 1088, 1030, 964, 855, 738; δ_{H} (250

MHz; CDCl₃) 1.50-1.85 (6 H, m, 3 x CH₂), 1.90-2.20 (2 H, m, CH₂), 2.38-2.50 (2 H, m, CH₂), 3.04 (1 H, q, *J* 3.8 Hz, CH), 7.25-7.40 (5 H, m, 5 x CH arom., Ph gp.); δ_C(62.5 MHz; CDCl₃) 24.9 (CH₂), 25.5 (CH₂), 29.9 (CH₂), 31.7 (CH₂), 33.9 (CH₂), 63.4 (CH), 65.8 (C quat.), 125.4 (2 x CH arom., *ortho* in Ph gp.), 127.3 (CH arom., *para* in Ph gp.), 128.5 (2 x CH arom., *meta* in Ph gp.), 144.0 (C quat., arom., *ipso* in Ph gp.).

(–)-(S,S)-*trans*-Stilbene oxide (Table 2, entry 16, 39% ee determined by 250 MHz ¹H-NMR by addition of (+)-Eu(hfc)₃ (6 mg) to the epoxide (10 mg) in CDCl₃. Integration of the epoxide CH (originally at 3.84 ppm, before addition of the chiral shift reagent) at 4.74 ppm (Major) and 4.54 ppm (Minor) gave an ee of 39% in favour of the (–)-(S,S) enantiomer, lit.^{xiv} (99% ee) [α]_D²⁵ +361.0 (c 2.05, CH₃C₆H₆) for (+)-(R,R) enantiomer). Prepared according to the general procedure from *trans*-stilbene **14** (0.09 g, 0.5 mmol). Colourless solid (0.082 g, 84%); mp 66-67 °C, (lit.^{xv} mp 61-63 °C). ν_{max}(nujol)/cm^{–1} 1601, 1492, 1284, 1176, 1157, 1094, 1072, 1025; δ_H(400 MHz; CDCl₃) 3.84 (2 H, s, 2 x CH), 7.28-7.37 (10 H m, 10 x CH arom., 2 x Ph gp.); δ_C(100 MHz; CDCl₃) 63.3 (2 x CH), 126.0 (4 x CH, arom., *ortho* in 2 x Ph gp.), 128.6 (2 x CH, arom., *para* in 2 x Ph gp.), 129.3 (4 x CH, arom., *meta* in 2 x Ph gp.), 137.6 (2 x C quat., arom., *ipso* in 2 x Ph gp.).

(+)-(1R,2S)-1-Phenyl-3,4-dihydronaphthalene oxide 17 (Table 3, entry 6, 89% ee determined by chiral HPLC using a Chiracel OD column using a flow rate of 1.0 mL per min and a solvent ratio of 90:10 (hexane:IPA). Retention times: 9.37 (–)-(1S,2R) (Minor); 12.40 (+)-(1R,2S) (Major) gave an ee of 89% in favour of the (+)-(1R,2S) enantiomer, lit.^{xv} (95% ee) [α]_D²⁵ –42.8 (c 0.95, CHCl₃) for (–)-(1S,2R) enantiomer). Prepared according to the general procedure from 1-phenyl-3,4-dihydronaphthalene **15** (0.10 g, 0.5 mmol). Pale yellow solid (0.068 g, 61%); mp 104-106 °C, (lit.^{xvi} mp 94-97 °C); ν_{max}(nujol)/cm^{–1} 1602, 1486, 1307, 1155, 1074, 1042, 953; δ_H(250 MHz; CDCl₃) 2.10 (1 H, td, *J* 5.8 and 13.7 Hz, CHH), 2.49-2.60 (1 H, m, CHH), 2.77 (1 H, dd, *J* 5.6 and 15.5 Hz, CHH), 2.98-3.06 (1 H, m, CHH), 3.71 (1 H, d, *J* 3.1 Hz), 7.11-7.31 (4 H, m, 4 x CH arom.), 7.45-7.61 (5 H, m, 5 x

CH arom. Ph gp.); δ_{C} (62.5 MHz; CDCl_3) 22.1 (CH_2), 25.4 (CH_2), 60.9 (C quat.), 63.0 (CH) [126.0, 127.7, 127.9, 128.1, 128.2, 128.6, 129.8 (9 x CH, arom.), 135.0, 137.5, 138.8 (3 x C quat., arom.).

(–)-(R)-Triphenylethylene oxide (Table 2, entry 9, 60% ee determined by 250 MHz ^1H -NMR by addition of (+)-Eu(hfc)₃ (6 mg) to the epoxide (10 mg) in CDCl_3 . Integration of the epoxide CH (originally at 4.40 ppm, before addition of the chiral shift reagent) at 4.59 ppm (Major) and 4.46 ppm (Minor) gave an ee of 60% in favour of the (–)-(R) enantiomer, lit.^{xv} (97% ee) [α_{D}^{25} –43.2 (c 0.82, EtOH)]. Prepared according to the general procedure from triphenylethylene **13** (0.13 g, 0.5 mmol). Colourless oil which slowly solidified (0.081 g, 63%), mp 66–67 °C, (lit. mp 75 °C); ν_{max} (neat)/ cm^{-1} 3062, 3030, 2957, 2925, 2856, 1605, 1596, 1499, 1471, 1448, 1262, 1221, 741, 698, 621; δ_{H} (250 MHz; CDCl_3) 4.40 (1 H, m, CH), 7.10–7.47 (15 H, m, 15 x CH arom., 3 x Ph gp.); δ_{C} (62.5 MHz; CDCl_3) 68.0 (CH), [68.3 (C quat., Ph_2C), 126.3, 126.8, 127.5, 127.6, 127.7, 127.8 128.0, 128.2, 128.6 (15 x CH, arom.), 135.42, 135.9, 141.1 (3 x C quat., arom.) 3 x Ph gp.].

(–)-(1S,2S)-trans-(α -Methyl)-stilbene oxide 16 (Table 3, entry 13, 61% ee determined by 250 MHz ^1H -NMR by addition of (+)-Eu(hfc)₃ (6 mg) to the epoxide (10 mg) in CDCl_3 . Integration of the epoxide CH (originally at 3.96 ppm, before addition of the chiral shift reagent) at 4.34 ppm (Major) and 4.24 ppm (Minor) gave an ee of 61% in favour of the (–)-(1S,2S) enantiomer, lit.^{xv} (96% ee) [α_{D}^{25} +113.9 (c 0.90, EtOH) for (+)-(1R,2R) enantiomer]). Colourless oil; ν_{max} (neat)/ cm^{-1} 3061, 1602, 1495, 1449, 1381, 1279, 1157, 1118, 1065, 1027, 980; δ_{H} (400 MHz; CDCl_3) 1.46 (3 H, s, C3), 3.96 (1 H, s), 7.30–7.46 (10 H, m, 10 x CH arom., 2 x Ph gp.); δ_{C} (100 MHz; CDCl_3) 17.1 (CH_3), 63.5 (C quat.), 67.5 (CH), [125.6, 126.9, 127.7, 127.9, 128.6, 129.2 (10 x CH, arom.), 136.4, 142.8 (2 x C quat., arom.) 2 x Ph gp.].

General procedure for the formation of racemic epoxides

The alkene was dissolved in CH₂Cl₂ (10 ml/g) and the solution cooled using an ice bath. A solution of *m*-CPBA (2 eq.) in CH₂Cl₂ (10 ml/g, pre-dried over MgSO₄) was added. The reaction was allowed to reach ambient temperature and stirred until complete consumption of the substrate was observed by tlc. Saturated aqueous NaHCO₃ (10 ml/g) was added and the layers separated. The organic layer was washed with saturated aqueous NaOH (1.0 M, 10 ml/g) and dried (MgSO₄). The solvents were removed under reduced pressure, and the residue purified by column chromatography, typically eluting with ethyl acetate/light petroleum (1:99), to give the pure epoxide.

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