New biphenyl iminium salt catalysts for highly enantioselective asymmetric epoxidation: role of additional substitution and dihedral angle†

Philip C. Bulman Page,†a Christopher J. Bartlett,a Yohan Chan,a Steven M. Allin,b Michael J. McKenzie,c Jérôme Lacourd and Garth A. Jonesa

New biaryl iminium salt catalysts for enantioselective alkene epoxidation containing additional substitution in the heterocyclic ring are reported. The effects upon conformation and enantioselectivity of this additional substitution, and the influence of dihedral angle in these systems, has been investigated using a synthetic approach supported by density functional theory. Enantioselectivities of up to 97% ee were observed.

Introduction

Asymmetric epoxidation of alkenes to generate non-racemic chiral epoxides is an extremely powerful synthetic tool,1 and the development of effective organocatalytic systems for epoxidation has received considerable attention.2 The most successful organocatalytic methods for epoxidation are those utilizing dioxiranes and those utilizing oxaziridinium salts. Chiral ketones used as precursors to dioxiranes, such as those of Yang,3 Denmark,4 Armstrong,5 and especially Shi,6 have achieved high enantioselectivities, with observed enantiomeric excesses exceeding 97% in the best cases. Oxaziridinium salts, first reported by Lusinchi in 1976,7 are also reactive reagents for oxygen transfer to nucleophilic substrates such as sulfides and alkenes, and may be generated catalytically by use of iminium salts in the presence of a stoichiometric oxidant, typically Oxone.8 We have developed a range of catalysts based on biphenylazepinium (e.g. 1), binaphthylazepinium (e.g. 2) and dihydroisoquinolinium (e.g. 3) moieties containing a chiral appendage on the nitrogen atom for epoxidation reactions, with the most successful to date containing the 1,3-dioxane motif of (S,S)-acetonomine 4 (Fig. 1).9 We have also shown that alternative oxidants may be used in iminium salt-catalysed epoxidation reactions such as hydrogen peroxide,10 sodium hypochlorite,11 and electrochemically-generated oxidants.12 Amines have also been used as iminium precursors in related epoxidation processes by us13 and others.14

We reported the first very high enantioselectivities in the asymmetric epoxidation of alkenes using iminium salt catalysts, and we have developed non-aqueous conditions for these processes using tetraphenylphosphonium monoperoxysulfate (TPPP)15 as the oxidant.16 We have used the process in the syntheses of leveromakalim,17 (-)-lomatin, (+)-trans-khellactone,18 and scuteflorin19 utilizing catalysts 1 and 3.

We have shown that incorporation of a pseudo-axial substituent at the prochiral carbon atom α to the nitrogen atom in biaryl systems 1 and 2 affords higher enantioselectivities, with the addition of a methyl group found to have the greatest influence.20 It has also been reported that the level of enantiocontrol imparted by biaryl azepinium salt catalysts in the epoxidation of alkenes is in part correlated with the dihedral angle around the biphenyl axis in the iminium species,21 suggesting a parallel pattern of dihedral angles between the iminium parents and the putative derived oxaziridinium oxidative intermediates. It was further suggested that this angle is both larger and nearer to the optimum in the octahydrobiphenyl series than in the parent biphenyl series.

Fig. 1 Iminium salt catalysts.
Organic & Biomolecular Chemistry

Fig. 2 New biaryl catalysts.

We were interested to investigate this potential correlation between dihedral angles in the iminium species and in the oxaziridinium oxidative intermediates, and if any correlation might also be observed between dihedral angles and induced enantioselectivities. Consequently, geometry optimizations were carried out on oxaziridinium intermediates, as well as the iminium species, at the B3LYP/6-31G* level of theory. These calculations indeed suggest that there is little change in dihedral angles between the iminium and oxaziridinium species in the lowest energy conformations (vide infra).

We were interested to learn if related structural modifications would also improve the enantioselectivity of our other biaryl-containing catalysts. We report herein the design and use of new iminium salt catalysts combining both of these modifications (Fig. 2).

Results and discussion

Synthesis

To begin with, we focused on synthesis of the simpler 6,6'-dimethylbiphenyl backbone, with iminium salts 5Rax, 5Sax and 6Rax, 6Sax as targets. The synthesis of racemic bis-carboxaldehyde (±)-7 was achieved following literature procedures.21,22 Formation of the diazonium salt from 3-methylanthranilic acid followed by coupling of the radical generated in situ gave bis-acid (±)-8 in 58% yield. High concentration of the diazonium salt and careful temperature control are key factors to obtain an acceptable yield of (±)-8, as formation of the corresponding diazo compound, a bright yellow solid, competes with the desired reaction. We first used the racemic bis-acid, ultimately to access both diastereoisomers 5Rax and 5Sax in order to assess separately their potential as catalysts, in the expectation of finding ‘matched’ and ‘mismatched’ systems, and reasoning that separation of the diastereoisomers would be more practical on a larger scale than resolution of the bis-acid. Reduction of (±)-8 to the diol (±)-9 with lithium aluminium hydride proceeded in 96% yield. Oxidation of the two alcohol moieties of (±)-9 using PCC yielded the desired bis-carboxaldehyde (±)-7 in 87% yield. Reductive cycloamination of (±)-7 with enantiomerically pure (S,S)-acetalamine 4 gave diastereoisomers 10Rax, 10Sax, which were separated using silica gel column chromatography, in 49% and 26% yields respectively (Scheme 1).

Resolution of bis-acid (±)-8 using quinine following a literature procedure provided us with the means to prepare a single diastereoisomer of 10.22 By comparison of spectroscopic data and optical rotation, the amine diastereoisomer obtained from (+)-8Sax was found to be identical to 10Sax, allowing us to attribute the absolute configurations of 10Rax and 10Sax.

Oxidation of 10Rax, 10Sax separately using NBS followed by counter-ion exchange gave the corresponding tetraphenylborate iminium salts 5Rax and 5Sax in 61% and 83% yields respectively. Diastereoselective addition of methyl magnesium bromide gave 11Rax and 11Sax as single diastereoisomers, the methyl groups being introduced into a pseudo-axial position in each case, as we have previously observed,20 controlled by the axial chirality of the biphenyl backbone, and appearing in the 1H NMR spectra at high field (11Rax: 0.21 ppm; 11Sax: 0.14 ppm).

Oxidation of 11Rax, 11Sax and anion exchange gave α-methylated iminium salts 6Rax, 6Sax as single diastere- and regio-isomers in 28% and 32% yields over the three steps, respectively (Scheme 2), resulting from loss of the more accessible single remaining axial hydrogen atom in each case.20,23
The yield of the oxidation step was moderated by competing bromination of the methyl groups at the 6,6′ positions.

We next turned our attention to the preparation of similar catalysts using the octahydrobinaphthyl backbone, where the iminium salt possesses large dihedral angles. Octahydrobinaphthyl-2,2′-bis-methanol 12 was obtained following literature procedures (Scheme 3). (R)-Binol was hydrogenated to (R)-octahydrobinol 13 using palladium on carbon under hydrogen pressure in 45% yield. Triflation of the phenolic hydroxyl moieties to give 14, followed by palladium-catalysed cycloamination to give 15, and reduction using lithium aluminium hydride gave (R)-octahydrobinaphthyl-1,1′-methanol 12 in 83% yield over the three steps.

Compound 12 was converted into the corresponding (R)-bis-carboxaldehyde 16 in quantitative yield. Tertiary amine 17 was, however, only obtained in 67% yield using the reductive cycloamination protocol. An alternative procedure consisting of displacing two bromide ions using (S,S)-acetonamine 4 was therefore used. Diol 12 was successfully bis-brominated to give 18 using phosphorus tribromide in 90% yield; double displacement with (S,S)-acetonamine 4 gave the desired amine 17 in an excellent 97% yield (Scheme 4).

Amine 17 was oxidized using NBS to afford iminium salt 19 in 73% yield. The corresponding α-methylated azepinium salt was obtained through a similar sequence to that described above, involving diastereoselective Grignard reagent addition to give 20 followed by oxidation and anion exchange to give 21 in 56% yield over the two steps. Again, the α-methylated iminium salt 21 was obtained as a single regio- and diastereoisomer with a pseudo-axial methyl group (Scheme 5).

Calculations

Geometry optimizations were carried out on a range of these iminium species and their putative derived oxaziridinium ions, at the B3LYP/6-31G* level using Gaussian 09 to determine the dihedral angles ϕ and θ in the lowest energy conformations. Both possible diastereoisomers were investigated in the case of each oxaziridinium ion. All stationary point structures were characterized by harmonic frequency analysis, and shown to be genuine energy minima (Tables 1 and 2). Cartesian co-ordinates of the optimized structures can be found in ESI.

For the oxaziridinium ions (Table 1), the calculations demonstrate a clear increase in dihedral angles upon moving from the biphenyl species (around 38°–42°) to the 6,6′-dimethylbiphenyl (around 54°–58°) and the octahydrobinaphthyl (around 55°–64°) species. Larger dihedral angles were also observed as expected in the binaphthyl species (around 54°–59°).

It is interesting to note that the pair of diastereoisomeric oxaziridinium ions in each case display similar dihedral angles, with the differences varying from 0.3° to 6.8° for ϕ and 0.1° to 3.7° for θ, the larger figures being observed for the octahydro species. Similar calculations carried out on the derived iminium ions suggest that similar dihedral angles also obtain for the iminium and derived oxaziridinium species; the calculations suggest that the dihedral angles differ by no more than 6.3° from those of the corresponding iminium species.

Incorporation of a methyl substituent at the prochiral carbon atom α- to the nitrogen atom in the heterocyclic ring does not, however, greatly affect the dihedral angles for either
Table 1: Dihedral angles calculated for oxaziridinium species

| Structure | $\phi/\theta$ | Structure | $\phi/\theta$ |
|-----------|--------------|-----------|--------------|
| ![Structure](image1) | $\phi = -40.1$ | $\theta = -41.3$ | $\phi = -37.9$ | $\theta = -40.4$ |
| ![Structure](image2) | $\phi = 38.9$ | $\theta = 41.7$ | $\phi = 39.4$ | $\theta = 40.8$ |
| ![Structure](image3) | $\phi = -38.7$ | $\theta = -39.2$ | $\phi = -37.7$ | $\theta = -39.7$ |
| ![Structure](image4) | $\phi = -58.5$ | $\theta = -54.8$ | $\phi = -56.4$ | $\theta = -54.0$ |
| ![Structure](image5) | $\phi = -58.1$ | $\theta = -54.0$ | $\phi = -56.0$ | $\theta = -53.9$ |
| ![Structure](image6) | $\phi = -57.8$ | $\theta = -54.7$ | $\phi = -56.3$ | $\theta = -54.4$ |
| ![Structure](image7) | $\phi = 56.3$ | $\theta = 55.0$ | $\phi = 57.5$ | $\theta = 54.7$ |
| ![Structure](image8) | $\phi = -57.7$ | $\theta = -53.9$ | $\phi = -55.6$ | $\theta = -54.3$ |
| ![Structure](image9) | $\phi = 57.2$ | $\theta = 54.9$ | $\phi = 57.5$ | $\theta = 54.3$ |
| ![Structure](image10) | $\phi = -63.0$ | $\theta = -58.3$ | $\phi = -57.3$ | $\theta = -54.6$ |
| ![Structure](image11) | $\phi = -63.8$ | $\theta = -57.6$ | $\phi = -57.0$ | $\theta = -54.9$ |

Table 2: Dihedral angles calculated for iminium species

| Structure | $\phi/\theta$ | Structure | $\phi/\theta$ |
|-----------|--------------|-----------|--------------|
| ![Structure](image12) | $\phi = -34.9$ | $\theta = -39.6$ | $\phi = -33.8$ | $\theta = -37.6$ |
| ![Structure](image13) | $\phi = -52.2$ | $\theta = -53.0$ | $\phi = -52.2$ | $\theta = -52.2$ |
| ![Structure](image14) | $\phi = -53.1$ | $\theta = -53.7$ | $\phi = -52.7$ | $\theta = -52.5$ |
| ![Structure](image15) | $\phi = 52.4$ | $\theta = 53.7$ | $\phi = 52.7$ | $\theta = 53.3$ |
| ![Structure](image16) | $\phi = -59.7$ | $\theta = -58.0$ | $\phi = -60.0$ | $\theta = -57.3$ |

Epoxidation reactions

Iminium salts $5\text{R}_{ax}$, $5\text{S}_{ax}$, $6\text{R}_{ax}$, $6\text{S}_{ax}$, $19$, and $21$ were used in the asymmetric epoxidation of a number of alkenes under optimized reaction conditions; and the results compared with known results from species $1$ and $30$ (Table 3). We have previously observed that the related binaphthyl catalysts $2$ and $31$ display somewhat different profiles of reactivity and selectivity from those of the biphenyl series, and these catalysts are therefore not included in this analysis.

Aqueous conditions using Oxone as oxidant and a mixture of acetonitrile and water as solvent gave the highest reactivities and enantioselectivities. Non-aqueous conditions using TPPP as oxidant and acetonitrile as solvent were less successful, however; for example, use of chloroform as solvent gave an ee lower than $5\%$. The enantioselectivity observed when 18-crown-6 and a biphasic system were used was also poor.

the iminium or oxaziridinium species (no more than about $2^\circ$). In the biphenyl cases $22$ and $23$, and the precursor iminium species $1$ and $30$, where interconversion between the atropoisomers is readily possible, the $S,S$-acetonamine unit induces a preference for the $R$-axial chirality in the biaryl unit. The methyl substituents in $23$ and $30$ occupy pseudo-axial positions, as is observed in the other methyl-substituted examples.
Table 3: Asymmetric epoxidation mediated by iminium salts 1, 5, 7a–b, 8a–b, 9, 10

| Substrate | Cat. | Time | Conv. % | ee % | Config. |
|-----------|------|------|---------|------|---------|
| Ph 1     | 5 min | 100 | 60° | (−)-(1R,2S) |
| Ph 30    | 0.5 h | 100 | 82° | (−)-(1R,2S) |
| Ph 5R     | 0.8 h | 99  | 87° | (−)-(1R,2S) |
| Ph 6R     | 1 h   | 99  | 92° | (−)-(1R,2S) |
| Ph 3S     | 1.8 h | 99  | 82° | (+)-(1R,2R) |
| Ph 6S     | 3 h   | 99  | 82° | (+)-(1R,2R) |
| Ph 19     | 0.6 h | 99  | 90° | (−)-(1R,2S) |
| Ph 19     | 1 h   | 99  | 92° | (−)-(1R,2S) |
| Ph 21     | 1.5 h | 99  | 96° | (−)-(1R,2S) |
| Ph 1a     | 3 min | 90  | 41° | (+)-(1R,2S) |
| Ph 30     | 0.5 h | 100 | 78  | (+)-(1R,2S) |
| Ph 5R     | 0.3 h | 99  | 89  | (+)-(1R,2S) |
| Ph 5R     | 0.3 h | 98  | 81  | (+)-(1R,2S) |
| Ph 6R     | 1 h   | 99  | 85  | (+)-(1R,2S) |
| Ph 5S     | 2 h   | 99  | 82  | (−)-(1R,2S) |
| Ph 6S     | 6 h   | 77  | 78  | (−)-(1R,2S) |
| Ph 19     | 0.7 h | 99  | 93  | (+)-(1R,2S) |
| Ph 21     | 3 h   | 87  | 97  | (+)-(1R,2S) |
| Ph 1a     | 5 min | 95  | 37  | (+)-(1R,2S) |
| Ph 6R     | 3 h   | 99  | 67  | (−)-(1R,2S) |
| Ph 5S     | 2 h   | 99  | 82  | (−)-(1R,2S) |
| Ph 6S     | 6 h   | 99  | 48  | (+)-(1R,2R) |
| Ph 19     | 1 h   | 99  | 60  | (−)-(1R,2S) |
| Ph 21     | 2 h   | 99  | 63  | (−)-(1R,2S) |
| Ph 21     | 18 h  | 80  | 69  | (−)-(1R,2S) |
| Ph 1a     | 5 min | 95  | 5   | (−)-(1R,2S) |
| Ph 5R     | 4.3 h | 99  | 17  | (−)-(1R,2S) |
| Ph 6R     | 6 h   | 99  | 39  | (−)-(1R,2S) |
| Ph 5S     | 6 h   | 99  | 8   | (+)-(1R,2R) |
| Ph 6S     | 6 h   | 99  | 10  | (+)-(1R,2R) |

Conditions: oxone® (2 equiv.), NaHCO₃ (5 equiv.), catalyst (5 mol%), MeCN: H₂O 10:1, 0 °C.  Conversions were evaluated from the ¹H NMR spectra by integration of the alkene and epoxide signals.  ee was determined using CSP HPLC using a Chiralcel OD-H column unless otherwise indicated.  Absolute configurations of the major enantiomers were determined by comparison of optical rotation with those reported in the literature.  ee was determined using CSP GC using a Chiralcel OJ-H column.  ee was determined using ¹H NMR spectroscopy in the presence of Eu(III) tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphorate] as chiral shift reagent.

From our results, it appears that observed enantioselectivities indeed increase for the trisubstituted alkenes from 37–60% ee for the simple biphenyl catalyst 1 (78–82% ee for the methylated derivative 30), with dihedral angles around 34–40°, to 60–93% ee for the matched 6,6'-dimethylbiphenyl catalyst 5R, with dihedral angles around 52–54°, and the octahydro naphtyl catalyst 19, with dihedral angles around 57–60° (69–97% ee for the methylated derivatives 6R and 21 respectively).

For catalysts 5 and 6, the ‘matched’ diastereoisomers, inducing higher enantioselectivities, are the (R)₃S₃ax and 6Rax, and the ‘mismatched’ ones are the (S)₃S₃ax and 6S₃ax, which are also generally less reactive. It is interesting to note that the relative stereochemistry of diastereoisomers 5Rax and 6Rax corresponds to that seen in the lowest energy atmosphere of the simple biphenyl analogue 1.

While the incorporation of a methyl substituent α to the nitrogen atom generally increases the enantiocontrol, it has a detrimental or no effect on the mismatched diastereoisomers 5S₃ax and 6S₃ax. The sense of stereochemical induction in the epoxidation process is controlled by the configuration of the biaryl backbone. Catalyst 6Rax with the added methyl group, is in most cases superior to catalyst 5Rax. The octahydropinaphthyl catalyst 21, with an additional methyl group, provides the highest enantioselectivities that we have seen for the epoxidation of 1-phenylecyclohexene, at 96% ee, and for 1-phenyl dihydronaphthalene, at 97% ee.

Conclusions

The results described herein provide further evidence that addition of additional methyl substituents adjacent to the nitrogen atom in the heterocyclic ring can provide improvements in enantioselectivities in the catalysed epoxidation reactions, with the α-methylated octahydropinaphthyl catalyst 21 giving the best results of this series; particularly noteworthy are the epoxidations of 1-phenylecyclohexene, at 96% ee, and of 1-phenyl dihydronaphthalene, at 97% ee.

Calculations clearly suggest a parallel pattern of dihedral angles between the iminium parents and the putative derived oxaaziridinium oxidative intermediates.

Experimental results also support the conjecture that some correlation may be observed between the dihedral angle found in the biaryl units of these iminium salt catalysts and the induced enantioselectivities in the catalysed epoxidation reactions. The 6,6'-dimethylbiphenyl catalysts 5 and 6 (dihedral angles around 52–54°) are superior to the simpler biphenyl species 1 and 30 (dihedral angles around 34–40°). The octahydrobipinaphthyl catalysts 19 and 21 (dihedral angles around 57–60°) induce generally similar enantioselectivities to the 6,6'-dimethylbiphenyl species, perhaps suggesting optimum dihedral angles of around 50–60° as one factor in the induction of enantioselectivities in the catalysed epoxidation reactions.

Experimental section

General procedure for the addition of methyl Grignard reagent to iminium salts

The iminium salt was dissolved in Et₂O (50 mL per g of iminium salt) under an atmosphere of N₂. The solution was cooled to −78 °C. A 3 molar solution of MeMgCl in THF (10 equiv.) was added dropwise over 10 min. After 1 h, cooling was ceased, and the mixture allowed to reach ambient temperature overnight. Saturated aqueous NH₄Cl (5 mL per g of iminium salt) and CH₂Cl₂ (2 × 50 mL per g of iminium salt) were added. The resulting mixture was transferred to a separating funnel, and brine (100 mL) added. The organic layer was collected and the aqueous layer washed with CH₂Cl₂ (2 × 50 mL per g of iminium salt). The combined organic layers were washed with
Organic & Biomolecular Chemistry

Water (2 × 100 mL per g of iminium salt) and brine (2 × 100 mL per g of iminium salt). The organic fraction was dried over MgSO₄, and evaporated to dryness under reduced pressure to yield the desired methyl azipines.

**General procedure for the synthesis of iminium salts from the corresponding azipines**

The azipine substrate was dissolved in CH₂Cl₂ (30 mL per g of azipine), and NBS (1.1 equiv.) added. The resulting bright yellow solution was stirred for 30 min at room temperature, after which time the solvent was switched to EtOH. To the ethanolic solution was added NaBPh₄ (1.1 equiv.) in the minimum amount of MeCN with stirring, which caused the iminium salt to precipitate. The solvent was switched to CH₂Cl₂ and the solution transferred to a separating funnel. The organic layer was washed with water (2 × 60 mL per g of azepine) and brine (30 mL per g of azipine). The crude product isolated after the removal of solvents was recrystallized from EtOH. The crystalline product was filtered off and washed with cold EtOH followed by Et₂O and hexane. The isolated iminium salt was left to dry under reduced pressure in an oven at 60 °C overnight.

6,6'-Dimethyl-2,2'-bis(carboxylic acid) (±)-8.¹ NaNO₂ (7.8 g, 0.11 mol) was added in one portion to an ice cold solution of 2-amino-3-methylbenzoic acid (17.0 g, 0.11 mol) in 2.45 M NaOH (60 mL). The mixture was stirred at 0 °C until it became homogeneous. An ice-cooled 4 M aqueous solution of HCl (240 mL) was added to the solution at a rate such that the temperature remained below 5 °C. The resulting orange solution of the diazonium salt was stirred at 0 °C for 20 min. Cu₂SO₄·5H₂O (24.0 g, 96 mmol) and water (75 mL) were added, and the resulting solution cooled in an ice-bath. When the solution had reached 5 °C, 30% w/v NH₄OH solution (47.5 mL) was added in one portion. A freshly prepared solution of NH₄OH, prepared from treatment of (NH₄OH)₂·H₂SO₄ (8.8 g, 53.5 mmol) with a 3 M ice-cold aqueous solution of NaOH (38 mL, 0.11 mol), was added to the resulting deep-blue solution. The solution was stirred for 20 min to cool to 0 °C. The diazonium salt prepared above was added to the copper solution in three equal portions of 50 mL. The temperature was maintained below 7 °C throughout the procedure. After the addition was complete, the resulting orange/red solution was heated under reflux for 30 min, and allowed to cool. After the red solution had attained ambient temperature, conc. HCl (37.5 mL) was added slowly and the mixture was allowed to stand overnight to provide for the complete precipitation of the product. The yellow/brown precipitate was removed by filtration using a Büchner funnel, washed with water and air-dried. The crude material was stirred in boiling EtOH (200 mL); any remaining bright yellow solid was removed by filtration, leaving a clear brown filtrate. Crystallization of the bis(carboxylic acid) (±)-8 was induced by the addition of water to the filtrate to yield light brown crystals (8.4 g, 55%); m.p. 226–230 °C (dec.); νmax(neat)/cm⁻¹ 2982, 2907, 2667, 2579, 1680, 1583, 1436, 1377, 1316, 1159, 962, 799, 768, 722; δH (500 MHz; d₆-DMSO) 1.81 (6 H, s), 7.31 (2 H, t, J = 7.5 Hz), 7.44 (2 H, d, J = 7.5 Hz), 7.71 (2 H, d, J = 7.5 Hz), 12.28 (2 H, broad); δC (125 MHz; d₆-DMSO) 19.8, 126.6, 127.3, 132.9, 136.0, 140.7, 168.1.

6,6'-Dimethyl-2,2'-bis(hydroxymethyl)biphenyl (±)-9.⁴ Compound (±)-8 (2.20 g, 8.2 mmol) was dissolved in Et₂O (30 mL) under a nitrogen atmosphere. The resulting pale yellow solution was cooled to 0 °C, and LiAlH₄ (0.93 g, 24.5 mmol) added slowly at a rate that just maintained the effervescence. The resulting suspension was heated under reflux for 1 h, after which time the reaction mixture was allowed to cool to room temperature. Solid Na₂SO₄ (6.0 g) was added to the suspension, which was cooled in an ice-bath and stirred for 5 min. Water (10 mL) was added dropwise to quench the excess LiAlH₄. The mixture was stirred for 30 min, filtered through a layered pad of Celite and Na₂SO₄, and the colourless filtrate concentrated under reduced pressure to yield (±)-9 as a colourless crystalline solid (1.91 g, 96%); νmax(neat)/cm⁻¹ 3254, 3064, 3017, 2935, 2880, 1679, 1592, 1458, 1378, 1239, 1211, 1163, 1028, 994, 902, 783, 760, 623; δH (500 MHz; CDCl₃) 1.86 (6 H, s), 3.19 (2 H, s), 4.08 (2 H, d, J = 11.5 Hz), 4.24 (2 H, d, J = 11.5 Hz), 7.24 (2 H, s, J = 7.5 Hz), 7.29 (2 H, t, J = 7.5 Hz), 7.34 (2 H, d, J = 7.5 Hz); δC (125 MHz; CDCl₃) 20.2, 63.1, 127.6, 128.0, 129.9, 136.1, 138.3, 138.5; m/z (HNES) found for [C₁₆H₁₈O₂ + Na⁺]⁺ 265.1200; [M + Na⁺]⁻ requires 265.1199.

6,6'-Dimethyl-1,1'-biphenyl-2,2'-bis(carboxaldehyde) (±)-7.²⁹ PCC (1.33 g, 62.0 mmol) was added in one portion to a solution of (±)-9 (0.50 g, 20.7 mmol) in CH₂Cl₂ (20 mL), producing a dark-orange solution. The solution was stirred vigorously for 3 h at room temperature. Et₂O (20 mL) and a spatula of Celite was added to the resulting black mixture, which was stirred for a further 30 min. The reaction mixture was filtered through a layered pad of Celite and silica gel. Solvents were removed under reduced pressure to yield compound (±)-7 as a colourless crystalline solid (0.43 g, 87%); m.p. 108–110 °C; δH (500 MHz; CDCl₃) 1.98 (6 H, s), 7.50 (2 H, t, J = 7.5 Hz), 7.59 (2 H, d, J = 7.5 Hz), 7.91 (2 H, d, J = 7.5 Hz), 9.60 (2 H, s); δC (125 MHz; CDCl₃) 19.7, 126.4, 128.6, 134.5, 135.9, 137.6, 140.0, 191.4; m/z (HNES) found for [C₁₆H₁₄O₂ + Na⁻]⁻ 256.1333; [M + NH₄⁺]⁻ requires 256.1332.

(+)-(R)-6-{[(4S,5S)-2,2-Dimethyl-4-phenyl-1,3-dioxan-5-yl]-1,11-dimethyl-6,7-dihydro-5H-dibenzo[cd]azepine 10Rax and (+)-(S)-6-{[(4S,5S)-2,2-dimethyl-4-phenyl-1,3-dioxan-5-yl]-1,11-dimethyl-6,7-dihydro-5H-dibenzo[cd]azepine 10Sax. Amine 4 (2.70 g, 12.9 mmol) was added to a solution of (±)-7 (2.81 g, 11.8 mmol) in MeOH (160 mL). After stirring for 5 min, NaBH₄/CN (1.62 g, 25.8 mmol) and glacial acetic acid (1 mL) were added. The solution was stirred for 24 h at room temperature. A 1 M aqueous solution of NaOH (20 mL) was added, followed by Et₂O (100 mL). The organic layer was collected, and the aqueous layer extracted with Et₂O (2 × 30 mL). The organic fractions were combined, washed with brine, and dried over Na₂SO₄. The solvents were removed under reduced pressure to yield a crude oil that was purified by flash column chromatography, eluting with light petroleum/EtOAc (10:1), buffered with 2% TEA, to give the desired compound as a mixture of
diasteroisomers [First eluting 10Rax as a colourless crystalline solid (1.18 g, 49%); and second eluting 10Sax as a colourless foam (0.62 g, 26%)].

First eluting amine 10Rax: [α]D +54.9 (c = 0.97, CDCl3); νmax (neat)/cm⁻¹ 2990, 2934, 2860, 1452, 1378, 1308, 1263, 1236, 1200, 1172, 1150, 1075, 1027 953, 852, 787, 749, 727, 698; δH (400 MHz; CDCl3) 1.58 (3 H, s), 1.64 (3 H, s), 2.11 (6 H, s), 2.65 (1 H, d, J = 1.9 Hz), 3.16 (2 H, d, J = 12.1 Hz), 3.67 (2 H, d, J = 12.1 Hz). 4.12–4.21 (2 H, m), 5.10 (1 H, d, J = 6.3 Hz), 6.98–7.02 (2 H, m), 7.14–7.18 (4 H, m), 7.24–7.36 (5 H, m); δC (100 MHz; CDCl3) 19.3, 20.0, 29.3, 50.2, 60.1, 61.9, 75.3, 99.3, 126.4, 126.7, 126.9, 127.5, 129.0, 135.4, 136.7, 138.6, 140.5; m/z found for [C28H30NO2 + H]+ 414.2431; [M + H]+ requires 414.2448.

Second eluting amine 10Sax: [α]D +121.0 (c = 1.07, CDCl3); νmax (neat)/cm⁻¹ 2990, 2939, 2859, 1497, 1452, 1378, 1322, 1263, 1198, 1168, 1140, 1076 1024, 1001, 952, 853, 787, 750, 722, 697, 665; δH (400 MHz; CDCl3) 1.46 (3 H, s), 1.49 (3 H, s), 2.12 (6 H, s), 3.01 (1 H, br), 3.31 (2 H, d, J = 12.5 Hz), 3.46 (2 H, d, J = 12.4 Hz), 3.92 (1 H, d, J = 12.4 Hz), 4.13 (1 H, d, J = 12.4 Hz), 5.13 (1 H, d, J = 3.0 Hz), 6.80–7.02 (2 H, m), 7.16–7.27 (4 H, m), 7.33 (2 H, t, J = 7.6 Hz), 7.45 (2 H, d, J = 7.6 Hz); m/z found for [C28H30NO2 + H]+ 414.2425; [M + H]+ requires 414.2428.

(–)(R)ax-6-(4S,5S)-2,2-Dimethyl-4-phenyl-1,3-dioxan-5-yl)-1,11-dimethyl-5H-dibenzo[c,e]azepin-6-ium tetraphenylborate 5Rax:
Prepared according to the general procedure from 10Rax (1.10 g, 2.66 mmol). The title compound 11Rax was isolated as a colourless foam (0.27 g, 94%). νmax (neat)/cm⁻¹ 3059, 2991, 2921, 2859, 1593, 1497, 1432, 1378, 1256, 1239, 1201, 1156, 1079, 1029, 955, 910, 885, 853, 787, 744, 700; δH (400 MHz; CDCl3) 0.21 (3 H, d, J = 7.2 Hz), 1.56 (3 H, s), 1.63 (3 H, s), 2.07 (3 H, s), 2.13 (3 H, s), 2.91 (1 H, d, J = 6.0 Hz, 3.9 Hz), 3.35 (1 H, d, J = 11.4 Hz), 3.52 (1 H, d, J = 11.4 Hz), 4.08 (1 H, d, J = 12.3 Hz, 2.1 Hz), 4.22 (1 H, d, J = 12.0 Hz, 4.0 Hz), 4.33 (1 H, d, J = 7.0 Hz), 5.15 (1 H, d, J = 3.5 Hz), 6.81 (1 H, t, J = 4.4 Hz), 6.86 (1 H, d, J = 6.7 Hz, 2.0 Hz), 7.09–7.15 (4 H, m), 7.20–7.38 (5 H, m); δC (100 MHz; CDCl3) 19.2, 19.3, 19.4, 21.0, 29.1, 54.0, 59.7, 60.0, 63.2, 74.2, 99.3, 126.0, 126.4, 126.8, 127.4, 127.6, 128.5, 128.7, 135.9, 136.9, 138.9, 139.2, 140.3, 141.3; m/z (HESI) found for [C28H30NO2 + H]+ 428.2582; [M + H]+ requires 428.2584.

(5S,11bRax)-6-(4S,5S)-2,2-Dimethyl-4-phenyl-1,3-dioxan-5-yl)-1,11-dimethyl-5H-dibenzo[c,e]azepin-6-ium tetraphenylborate 5Sax:
Prepared according to the general procedure from 5Sax (0.80 g, 0.97 mmol). The title compound 11Sax was isolated as a colourless foam (0.23 g, 99%). νmax (neat)/cm⁻¹ 3059, 2991, 2921, 2859, 1593, 1497, 1432, 1378, 1245, 1239, 1201, 1156, 1079, 1029, 955, 910, 885, 853, 787, 744, 700; δH (400 MHz; CDCl3) 0.14 (3 H, d), 1.47 (3 H, s), 1.50 (3 H, s), 2.05 (3 H, s), 2.14 (3 H, s), 3.02 (1 H, d, J = 6.5 Hz, 4.1 Hz), 3.31 (1 H, d, J = 11.3 Hz), 3.63 (1 H, q, J = 7.1 Hz), 3.90 (1 H, d, J = 11.3 Hz), 4.01 (1 H, d, J = 12.3 Hz, 2.4 Hz), 4.15 (1 H, d, J = 12.3 Hz, 4.0 Hz), 5.20 (1 H, d, J = 4.2 Hz), 6.65–6.71 (1 H, m), 6.95 (1 H, d, J = 6.6 Hz, 2.1 Hz), 7.02–7.07 (2 H, m), 7.15–7.24 (3 H, m), 7.32 (2 H, t, J = 7.7 Hz), 7.46 (2 H, t, J = 7.1 Hz); δC (125 MHz; chloroform-d) 19.4, 19.5, 19.6, 22.3, 29.0, 50.9, 62.2, 63.1, 67.0, 73.7, 99.0, 126.0, 126.5, 126.7, 126.3, 127.2, 127.4, 127.6, 128.5, 128.9, 135.4, 136.3, 136.6, 138.1, 138.9, 140.0, 148.8; m/z (HESI) found for [C28H30NO2 + H]+ 428.2579; [M + H]+ requires 428.2584.
(1 H, s); δC (100 MHz; DMSO) 14.9, 19.3, 19.9, 20.0, 29.9, 62.0, 65.9, 67.4, 70.8, 101.0, 122.2, 125.2, 125.9, 126.5, 127.5, 128.3, 128.7, 128.8, 129.7, 131.1, 132.0, 132.1, 136.2, 136.4, 137.7, 138.8, 139.2, 140.2, 164.0; m/z found for [C\textsubscript{29}H\textsubscript{32}NO\textsubscript{2}]\textsuperscript{+}: 426.2435; iminium cation requires 426.2428.

(+)-(5S,11bS)-6-(4S,5S)-2,2-Dimethyl-4-phenyl-1,3-dioxan-5-yl)-1,5,11-trimethyl-5H-dibenzo[e,c]azepin-6-ium tetraphenylborate (6S\textsubscript{ax}). Prepared according to the general procedure from 11S\textsubscript{ax} (0.25 g, 0.58 mmol). The title compound 6S\textsubscript{ax} was isolated as a pale yellow powder (0.14 g, 32%). 

Compound 6S\textsubscript{ax} was synthesized from (+)-(5S,11bS)-6-(4S,5S)-2,2-Dimethyl-4-phenyl-1,3-dioxan-5-yl)-1,5,11-trimethyl-5H-dibenzo[e,c]azepin-6-ium tetraphenylborate (6S\textsubscript{ax}). Prepared according to the general procedure from 11S\textsubscript{ax} (0.25 g, 0.58 mmol). The title compound 6S\textsubscript{ax} was isolated as a pale yellow powder (0.14 g, 32%).

The vessel was heated to 80 °C and maintained at a pressure of 2.4 atm. of CO for 48 h. The reaction mixture was transferred to a round-bottomed flask, and solvents were removed under reduced pressure to yield an oily residue. This crude residue was purified by column chromatography, eluting with light petroleum/EtOAc (5:1). Compound 15 was obtained as a colourless crystalline solid (5.9 g, 88%); m.p. = 119-121 °C; [\alpha]\textsubscript{D}\textsuperscript{29} = -29.6 (c = 1.03, CHCl\textsubscript{3}), lit.\textsuperscript{29} [\alpha]\textsubscript{D}\textsuperscript{29} = -60.3 (c = 1.00, CHCl\textsubscript{3}); υ\textsubscript{max}(neat)/cm\textsuperscript{-1} 2947, 2870, 2836, 1746, 1441, 1410, 1249, 1202, 1182, 1138, 1048, 926, 872, 926, 872, 853, 834, 806, 763, 699, 644; δ\textsubscript{C} (300 MHz; CDCl\textsubscript{3}) 1.75 (8 H, m), 2.28 (2 H, dt, J = 6.0 Hz, 17.4 Hz), 2.43 (2 H, dt, J = 6.0, 17.7 Hz), 2.86 (4 H, t, J = 6.0 Hz), 7.16 (2 H, d, J = 8.6 Hz), 7.23 (2 H, d, J = 8.6 Hz); δ\textsubscript{C} (75 MHz; CDCl\textsubscript{3}) 22.2, 22.3, 27.4, 29.3, 118.1, 118.2 (q, J = 322 Hz), 127.1, 130.9, 138.3, 139.7, 144.4.

(-)-(R\textsubscript{a})-5,5′,6,6′,7,7′,8,8′-Octahydro-1,1′-binaphthyl-2,2′-bis(carboxylate) (15).\textsuperscript{28} DMSO (90 mL), MeOH (36.0 mL, 1.56 mol) and Hüning's base (13.4 mL, 137 mmol) were added to 14 (1.50 g, 17.9 mmol), Pd(OAc)\textsubscript{2} (0.61 g, 4.7 mmol) and dppp (1.11 g, 4.70 mmol) under an argon atmosphere. The vessel was sealed with a gas manifold and pressurised with CO (g) at 2 bar followed by evacuation of the atmosphere until the orange solution just began to boil. The cycle was repeated five times. During the cycles, the solution turned to opaque black.

The vessel was heated to 80 °C and maintained at a pressure of 2.4 atm. of CO for 48 h. The reaction mixture was transferred to a round-bottomed flask, and solvents were removed under reduced pressure to yield an oily residue. This crude residue was purified by column chromatography, eluting with light petroleum/EtOAc (5:1). Compound 15 was obtained as a colourless crystalline solid (5.9 g, 88%); m.p. = 119-121 °C; [\alpha]\textsubscript{D}\textsuperscript{29} = -29.6 (c = 1.03, CHCl\textsubscript{3}), lit.\textsuperscript{29} [\alpha]\textsubscript{D}\textsuperscript{29} = -60.3 (c = 1.00, CHCl\textsubscript{3}); υ\textsubscript{max}(neat)/cm\textsuperscript{-1} 2947, 2870, 2836, 1746, 1441, 1410, 1249, 1202, 1182, 1138, 1048, 926, 872, 926, 872, 853, 834, 806, 763, 699, 644; δ\textsubscript{C} (300 MHz; CDCl\textsubscript{3}) 1.75 (8 H, m), 2.28 (2 H, dt, J = 6.0 Hz, 17.4 Hz), 2.43 (2 H, dt, J = 6.0, 17.7 Hz), 2.86 (4 H, t, J = 6.0 Hz), 7.16 (2 H, d, J = 8.6 Hz), 7.23 (2 H, d, J = 8.6 Hz); δ\textsubscript{C} (75 MHz; CDCl\textsubscript{3}) 22.2, 22.3, 27.4, 29.3, 118.1, 118.2 (q, J = 322 Hz), 127.1, 130.9, 138.3, 139.7, 144.4.
8.8 Hz); δC (75 MHz; CDCl3) 22.7, 23.2, 27.6, 29.8, 62.9, 127.2, 128.9, 134.8, 135.7, 137.6, 138.3.

(+)(R,R)-5',6',6',7',7',8,8'-Octahydro-1',1'-binaphthyl-2,2'-bis-(carbaldehyde) 16.21 Compound 12 [0.11 g, 0.34 mmol] was dissolved in CH2Cl2 (20 mL) and PCC (0.22 g, 1.02 mmol) added in one portion. The resulting dark orange solution was stirred for 2 h, and celite added followed by Et3O (20 mL). The mixture was stirred for 30 min and filtered through a layered pad of silica gel and Celite. The desired compound was eluted with Et3O. Solvents were then removed to furnish compound 16 as a colourless crystalline solid (0.18 g, 97%). m.p. 129–131 °C; [α]20 –+110.4 (c = 0.83, CHCl3), lit.27 [α]20 +27.7 (c = 0.72, CHCl3); vmax(neat)/cm−1 2928, 2832, 1451, 1377, 1291, 1267, 1237, 1194, 1172, 1147, 1074, 1053, 1017, 939, 989, 852, 829, 810, 753, 723, 700, 654, 640, 628; δH (300 MHz; CDCl3) 1.46–1.57 (2 H, m, 1.57 [3 H, s], 1.62 [3 H, s], 1.67–1.82 (6 H, m), 2.13 [2 H, dt, J = 5.9 Hz, 11.5 Hz], 2.58–2.65 (3 H, m), 2.75–2.86 (4 H, m), 3.07 [2 H, d, J = 12.2 Hz], 4.17 [2 H, m], 5.07 [1 H, d, J = 3.1 Hz]. 6.89 [2 H, d, J = 7.6 Hz]. 7.30 [5 H, m]; δC (75 MHz; CDCl3) 19.1, 22.7, 22.9, 27.6, 29.4, 29.6, 52.7, 59.8, 61.8, 75.0, 99.1, 126.0, 126.7, 127.6, 128.2, 133.6, 135.0, 136.0, 138.4, 140.4; m/z (HNES) found for [C34H39NO2 +H] +: 494.3039; [M + H]+: requires 494.3039.

(−)-(R,R)-4-((4S,5S)-2,2-Dimethyl-4-phenyl-1,3-dioxan-5-yl)-8,9,10,11,12,13,14,15-octahydro-3H-dianthophan[2,1-c1',1'−e]azepine-4-ium tetraphenylborate 19. Prepared according to the general procedure from 17 (1.47 g, 2.98 mmol) and NBS (0.58 g, 3.28 mmol). Ion exchange was performed with NaBPh4 (1.12 g, 3.28 mmol). The title compound 19 was isolated as a fine, pale-yellow crystalline solid (1.51 g, 63%). m.p. 195–199 °C; [α]20 −331.9 (c = 1.01, acetone); vmax(neat)/cm−1 3053, 2982, 2936, 2864, 1615, 1577, 1479, 1450, 1280, 1304, 1263, 1235, 1198, 1107, 1083, 1010, 954, 941, 904, 835, 763, 746, 731, 701, 660, 623, 609; δH (400 MHz; aceton-d6, 50 °C) 1.35–1.41 [1 (H, m), 1.45–1.56 [1 (H, m), 1.67 [3 (H, s), 1.70 [3 (H, s), 1.67–1.83 (6 H, m), 2.01–2.06 (1 H, m), 2.24 [1 (H, J = 7.5 Hz), 2.53–2.62 (1 H, m), 2.70–3.01 (5 H, m), 4.12 [1 (H, J = 13.2 Hz)]. 4.21 [2 (H, d, J = 13.7 Hz), 4.41 [1 (H, t, J = 2.6 Hz), 4.63 [1 (H, d, d, J = 13.7 Hz, 3.0 Hz)], 5.18 [1 (H, d, J = 13.7 Hz), 5.74 [1 (H, d, J = 3.0 Hz), 6.75 [4 (H, t, J = 7.2 Hz)], 6.89 [8 (H, t, J = 7.4 Hz), 7.06–7.21 (6 H, m), 7.23–7.40 (11 H, m), 8.73 [1 (H, s), 1.47 [75 (H, s); acetone-d6] 18.0, 21.6, 21.9, 22.0, 22.1, 27.4, 27.5, 28.9, 29.2, 29.8, 56.7, 60.1, 66.0, 71.3, 100.8, 121.6, 124.9, 125.0, 125.3, 125.8, 128.1, 128.8, 129.1, 129.4, 130.4, 133.5, 134.5, 136.28, 136.32, 137.7, 139.1, 139.9, 140.9, 145.0, 164.3, 169.7; m/z (HNES) found for [C34H39NO2 +H] +: 492.2895; iminium cation requires 492.2897.
General procedure for the formation of racemic epoxides

The alkene was dissolved in CH2Cl2 (10 mL per g of alkene) and the solution cooled to 0 °C. A solution of m-CPBA (2 equiv.) in CH2Cl2 (10 mL per g of alkene), dried over MgSO4, was filtered into the solution of alkene. The reaction was allowed to proceed for 2 h at 0 °C until complete conversion of the alkene was observed by TLC, or for up to 6 h. The reaction mixture was then diluted with EtO (10 mL) and the resulting suspension filtered through a pad of mixed Na2SO3 and MgSO4. The solvents were removed under reduced pressure, and analytically pure samples of the epoxide were obtained by means of flash column chromatography or preparative TLC, typically eluting with light petroleum/EtOAc (99 : 1), containing 2% TEA. The major enantiomer was identified by [α]D20 measurements and comparison with the literature; enantioselectivities were determined either by chiral HPLC, or by 1H NMR spectroscopy in the presence of a resolving agent.

Method B: A mixture of water (1 mL), MeCN (1 mL) and NaHCO3 (100 mg, 1.2 mmol) was cooled in an ice-bath at 0 °C. Oxone® (370 mg, 0.6 mmol) was added. After the effervescence had subsided, the catalyst (5 mol%) was added, followed after 1 min, by the alkene (0.3 mmol). The mixture was stirred at 0 °C until complete conversion of the alkene was observed by TLC, or for up to 6 h. The reaction mixture was diluted with EtO (10 mL per 0.10 g of substrate), and the resulting suspension filtered through a pad of mixed Na2SO3 and MgSO4. The solvents were removed under reduced pressure, and analytically pure samples of the epoxide were obtained by either flash column chromatography or preparative TLC, eluting with light petroleum/EtOAc (99 : 1), containing 2% TEA. The major enantiomer was identified by [α]D20 measurements and comparison with the literature; enantioselectivities were determined either by chiral HPLC, or by 1H NMR spectroscopy in the presence of a resolving agent.

Method C: A mixture of water (0.8 mL) and NaHCO3 (67 mg, 0.80 mmol) was cooled in an ice-bath at 0 °C. Oxone® (132.0 mg, 0.21 mmol) was added, and the solution stirred until the effervescence had ceased. The alkene (0.20 mmol) was dissolved in CH2Cl2 (0.5 mL) and added. A solution of the catalyst (5 mol%) and 18-crown-6 (1 mg, 2.5 mol%) in CH2Cl2 (0.7 mL) was cooled to 0 °C, and added with stirring. The reaction mixture was vigorously stirred, typically for 2 h at 0 °C. CH2Cl2 (10 mL) and water (10 mL), both cooled to around 0 °C, were added. The organic layer was collected and dried over MgSO4. The solvents were removed under reduced pressure, and analytically pure samples of the epoxide were obtained by either column chromatography or preparative TLC, eluting with light petroleum/EtOAc (99 : 1), containing 2% TEA. The major enantiomer was identified by [α]D20 measurements; enantioselectivities were determined either by chiral HPLC, or by 1H NMR spectroscopy in the presence of a resolving agent.

Tetraphenylphosphonium monoperoxysulfate

Tetraphenylphosphonium chloride (15.0 g, 40 mmol) was dissolved in CH2Cl2 (200 mL), and the solution cooled to 10 °C. A solution of Oxone® (15.0 g, 48 mmol) in deionised water (300 mL) was cooled to 10 °C, and added over a period of 5 min. The resulting biphasic mixture was stirred vigorously

**General procedures for catalytic asymmetric epoxidation of alkenes with Oxone® mediated by iminium salts under aqueous conditions**

**Method A:** Oxone® (2 equiv.) and NaHCO3 (5 equiv.) were added with stirring to a solution of the catalyst (5 mol%) in MeCN (1 mL) and water (0.1 mL) at 0 °C. After 5 min, alkene (3 mmol) dissolved in MeCN (1 mL), was added. The mixture was stirred at 0 °C until complete conversion of the alkene was observed by TLC, or for up to 6 h. The reaction mixture was then diluted with EtO (10 mL) and the resulting suspension filtered through a pad of mixed Na2SO3 and MgSO4. The solvents were removed under reduced pressure, and analytically pure samples of the epoxide were obtained by means of flash column chromatography or preparative TLC, typically eluting with light petroleum/EtOAc (99 : 1), containing 2% TEA. The major enantiomer was identified by [α]D20 measurements and comparison with the literature; enantioselectivities were determined either by chiral HPLC, or by 1H NMR spectroscopy in the presence of a resolving agent.
for 1 h. The organic layer was separated, and the solvents were removed under reduced pressure at room temperature. The crude colourless solid was washed with deionised water (3 × 80 mL). The solid was re-dissolved in CH₂Cl₂ (150 mL) and dried over MgSO₄. Hexane was added until a solid precipitate just began to form, and the flask placed in a freezer overnight.

The resulting colourless crystalline solid was collected by filtration (12.87 g, 71%); ν<sub>max</sub>(neat)/cm⁻¹ 3210, 3060, 1586, 1484, 1435, 1262, 1226, 1162, 1106, 1058, 1041, 996, 721; δ<sub>H</sub> (400 MHz; CDCl₃) 7.58–7.69 (8 H, m), 7.71–7.80 (8 H, m), 7.82–7.86 (4 H, m), 9.18 (1 H, s). The oxygen content, typically 94% peroxide, was estimated by comparing the integrals of the aromatic and hydroxyl signals.

General procedure for catalytic asymmetric epoxidation of alkenes with TPPP mediated by iminium salts under non-aqueous conditions

A solution of alkene was cooled to the required temperature, and TPPP was added in one portion with stirring over 2 min. The reaction was stirred until complete consumption of the starting alkene had been observed, or until it was judged that no further conversion was occurring, by TLC. Et₂O, cooled to 0 °C, was added to precipitate out TPPP and its reduced by-products. The suspension was filtered through a thin pad of celite and silica gel to yield the desired epoxide. If column chromatography was required, it was typically performed eluting with light petroleum/EtOAc (99 : 1), containing 2% TEA. The major enantiomer was identified by [α]<sub>D</sub> measurements and comparison to the literature; enantiorecognition was determined by either chiral HPLC, or by 1H NMR spectroscopy in the presence of a resolving agent.

(E)-Methylstilbene oxide.³⁰ Isolated as a colourless crystalline solid: ν<sub>max</sub>(neat)/cm⁻¹ 3061, 1601, 1495, 1449, 1370, 1278, 1156, 1117, 1065, 1026, 980; δ<sub>H</sub> (300 MHz; CDCl₃) 1.46 (3 H, s), 3.95 (1 H, s), 7.30–7.45 (10 H, m). HPLC conditions-hexane/2-propanol (80 : 20), oven temp 20 °C, column Chiracel OD-H 01 250 × 4.6 mm, 5 μm particle size, flow rate 1 mL min⁻¹, 254 nm: t<sub>r</sub> 4.00 min (−)-(1S,2S), 6.92 min (+)-(1R,2R).

Dihydronaphthalene oxide.¹⁶ Isolated as a colourless oil: ν<sub>max</sub>(neat)/cm⁻¹ 3058, 3028, 2931, 2850, 1602, 1492, 1314, 1129, 1088, 1031, 965; δ<sub>H</sub> (400 MHz; CDCl₃) 1.65–1.84 (1 H, m), 2.33–2.42 (1 H, m), 2.52 (1 H, dd, J = 15.5 Hz, 5.5 Hz), 2.67–2.85 (1 H, m), 3.71–3.80 (1 H, m), 3.81–3.89 (1 H, m), 7.05 (1 H, d, J = 7.2 Hz), 7.18–7.35 (2 H, m), 7.40 (1 H, d, J = 7.1 Hz).

Triphenylethylene oxide.¹⁶ Isolated as a colourless crystalline solid: ν<sub>max</sub>(neat)/cm⁻¹ 3011, 3031, 2956, 2924, 2857, 1604, 1595, 1498, 1471, 1448, 1262, 1220, 741, 699; δ<sub>H</sub> (400 MHz; CDCl₃) 4.42 (1 H, s), 7.13–5.50 (15H, m). HPLC conditions-hexane/2-propanol (90 : 10), oven temp 20 °C, column Chiracel OD-H 01 250 × 4.6 mm, 5 μm particle size, flow rate 1 mL min⁻¹, 254 nm: t<sub>r</sub> 4.26 min (+)-(S), 7.47 min (−)-(R).

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