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Binaphthalene-Derived Iminium Salt Catalysts for Highly Enantioselective Asymmetric Epoxidation

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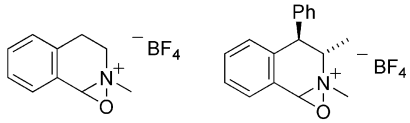
Enantiomerically enriched epoxides are useful intermediates that have found many applications in asymmetric synthesis, and development of efficient catalysts for asymmetric epoxidation has received considerable attention. In this manuscript we describe the design, preparation, and use of new highly selective iminium salt organocatalysts for asymmetric epoxidation, based around a chiral binaphthalene motif coupled with a chiral substituted dioxane moiety. The new catalysts have been tested in the catalytic asymmetric epoxidation of unfunctionalized alkenes, and provide up to 95 % *ee*.

Introduction

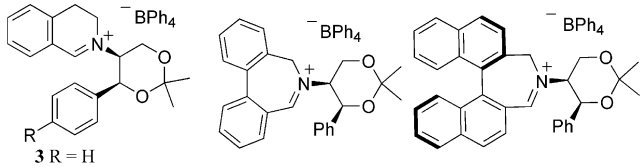
Enantiomerically enriched epoxides have found many applications in asymmetric synthesis,[1] and development of efficient catalysts for asymmetric epoxidation has received considerable attention.[2] Oxaziridinium salts such as **1**, generated from iminium salts and a stoichiometric oxidant, typically Oxone, are strong electrophilic oxidants for olefin epoxidation,[3] and have the advantage that they are "organocatalysts," no metal species being involved in the catalysed reaction.



1 **2**

Initially, enantiomeric excesses when employing enantiomerically pure oxaziridinium salts, for example **2**, ranged from low to moderate.[3–5] Our own approach to chiral iminium salt catalysts, which has led to several systems that afford epoxides with >90% *ee*,[6,7d] differs from previous investigations, where the exocyclic group attached to the nitrogen atom of the iminium salt has invariably been methyl or ethyl.

We reasoned that the attachment of asymmetric centres in an exocyclic substituent on the iminium nitrogen atom, as in **3**, would bring these controlling asymmetric elements of the catalyst nearer to the site of oxygen transfer, and might therefore increase the *ee* induced in an epoxidation reaction.[7] We[7b–7e] and others[8] have seen a certain success with our 5-amino-2,2-dimethyl-4-phenyl-1,3-dioxane-derived family of catalysts such **3**–**6**, some of which are extremely active, with catalyst loadings as low as 0.1 mol-%, and giving enantiomeric excesses of up to 97% in epoxidation reactions.



3 R = H
4 R = SO_2Me

5 **6**

Our standard conditions for the epoxidation reactions, optimized for 1-phenylcyclohexene as substrate, comprise typically 0.1 to 10 mol-% of the iminium salt, two equivalents of Oxone, and four equivalents of sodium carbonate in water/acetonitrile (1:1) at 0 °C. Blank reactions carried out in parallel under the same conditions, in the presence of Oxone, but without catalyst, gave no reaction over up to eight hours when four equivalents of sodium carbonate were present. Recently we have reported a successful alternative to these conditions, employing tetraphenylphosphonium mono-peroxysulfate (TPPP) as the stoichiometric oxidant; under these new conditions base is not required and water is not needed as a solvent, so allowing reactions to be performed at sub-zero temperatures.[7d] This system has afforded enantiomeric excesses of up to 97% and has allowed us to complete a highly enantioselective synthesis of levcromakalim.[7e]

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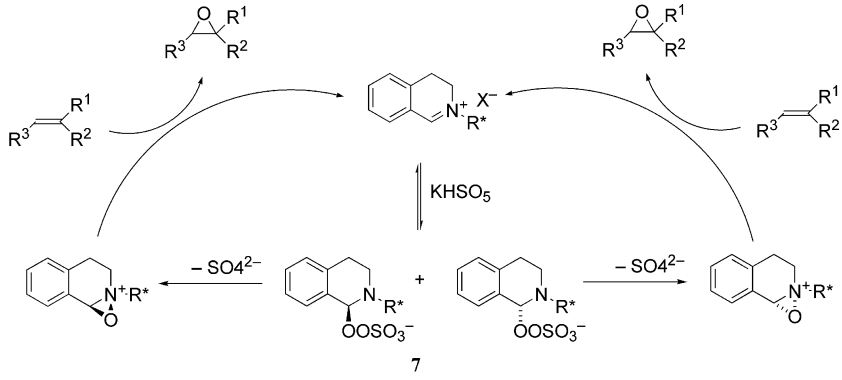


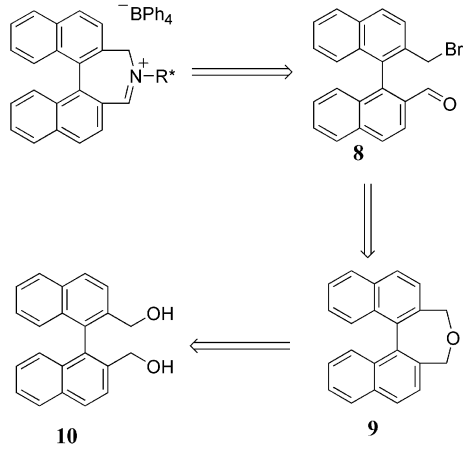
Scheme 1.

We have postulated a catalytic cycle for an oxaziridinium ion as the oxidative intermediate (Scheme 1) and have shown that this intermediate can be detected by ^{1}H NMR spectroscopy.[7f] We believe that the first stage involves the formation of an initial adduct **7**, uncharged at nitrogen, formed by (probably reversible) nucleophilic attack of the oxidant on the iminium salt. This is followed by irreversible expulsion of sulfate to give the oxaziridinium ion, which we suspect to be the rate-determining step under the reaction conditions. Oxygen may then be transferred to a substrate in a subsequent step. An interesting but complicating feature of these processes is that it is not one but two diastereoisomeric oxaziridinium salts that may be formed by attack of oxidant at the *si* or *re* face of the iminium species. Each may deliver the oxygen atom to either of the prochiral faces of the alkene substrate with a different degree of enantiocontrol, and the resulting oxaziridinium species may be in competition for the alkene substrate.

As a result of our research into the development of more selective iminium salt epoxidation catalysts we have reported our preliminary studies on a new family of catalyst, in which our original isoquinolinium/biphenyl moiety has been replaced by a binaphthalene structure fused to a seven-membered azepinium system, as in **6**.[6,9] We report here in full the preparation and use of several related catalysts, which contain a range of substituted 5-amino-2,2-dimethyl-4-phenyl-1,3-dioxanes and isopinocampheylamine moieties.

Results and Discussion

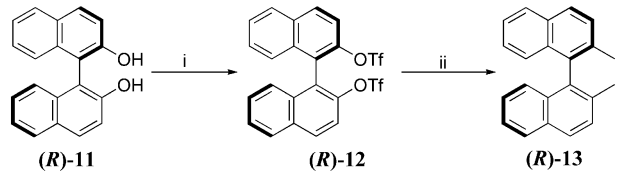
We envisaged that the mode of access to these catalysts would be by cyclocondensation of amines with the bromoaldehyde **8** as we have previously reported. This compound could be synthesized from the oxepine **9** by ring opening with bromine; synthesis of the oxepine **9** could in turn be accomplished by cyclization of the bis(hydroxymethyl) compound **10** (Scheme 2), a route used successfully by us for the synthesis of the corresponding biphenyl derivatives, the dibenzo[*c,e*]azepinium salts.[7c] Compound **10** is not commercially available, but several syntheses of **10**, in enantiomerically pure form, have been reported.[10–12] These generally involve a resolution at some point during the synthesis, but to avoid this, the synthesis can be achieved from commercially available enantiomerically pure (*R*)- or (*S*)-BINOL **11**. Generation of **10** has been described by Mazaleyrat from a dimethylbinaphthalene,[11] which in turn can be synthesized from BINOL.[9]



Scheme 2. Retrosynthetic analysis of the desired iminium salts.

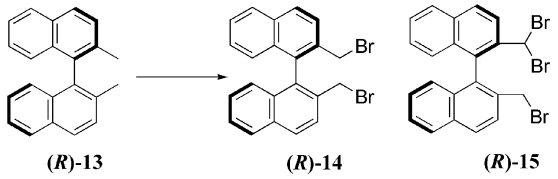
Using (*R*)-BINOL [(*R*)-**11**] in dichloromethane with trifluoromethanesulfonic anhydride, 4-(dimethylamino)pyridine, and 2,6-lutidine, the required product bis-triflate protected species **12** was produced in near-quantitative yield after four hours (Scheme 3).[13] Subsequent cross-coupling with methylmagnesium bromide and the nickel catalyst [$NiCl_2(dppp)_2$] afforded the (*R*)-dimethylated compound (*R*)-**13**, again in excellent yield (90%).[14]

Synthesis of the desired bis(bromomethyl)binaphthalene (*R*)-**14** has also been reported in the literature; the route involves the use of NBS in boiling carbon tetrachloride using benzoyl peroxide as the initiator, and afforded the product in 64% yield after 24 h (Scheme 4).[9] In our hands, however, this process was occasionally unreliable, and what we believe to be the tribromo compound (*R*)-**15** was sometimes formed as the major product, as indicated by the presence of a singlet proton signal at δ = 6.22 ppm and a double



Scheme 3. Formation of the (*R*)-bis-methylene compound (*R*)-**13**. Reagents and conditions: i: Tf_2O, DMAP (cat.), 2,6-lutidine, DCM, –30 °C to room temp., 99%; ii: MeMgBr, $NiCl_2(dppp)_2$, Et_2O, 12 h, 90%.

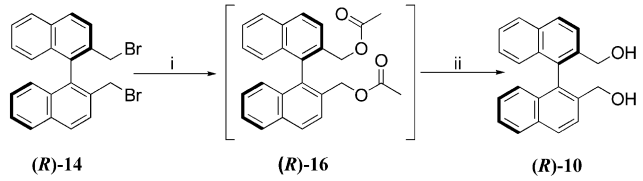
doublet at δ = 4.24 ppm in the ^1H NMR spectrum. This side product, formed under these reaction conditions, has also been noted by RajanBabu.[15]



Scheme 4. Bromination of (*R*)-**13** with NBS. Reagents and conditions: NBS (2 equiv.), solvent, heat or light.

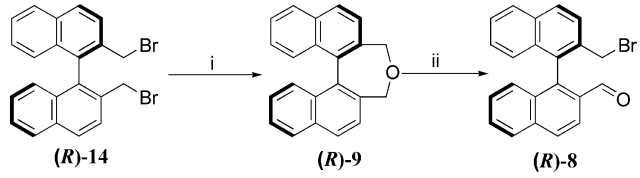
Slight modification of this procedure had a dramatic effect upon the yield of the reaction. Replacing the initiator with AIBN, removing the heat, and stirring at room temperature for 5 h under visible-light irradiation (150 W) afforded the desired compound (*R*)-**14** in up to 88% yield. Further modification by replacing the carcinogenic carbon tetrachloride solvent with cyclohexane did not alter the rate or yield of the reaction.

Conversion of the (*R*)-bis(bromomethyl)binaphthalene species (*R*)-**14** into the bis(hydroxymethyl)binaphthalene (*R*)-**10** required the formation of the intermediate diester (*R*)-**16** with potassium acetate and a catalytic amount of tetrabutylammonium bromide in DMF (Scheme 5). Subsequent hydrolysis with aqueous potassium hydroxide (1 M) afforded the (*R*)-bis(hydroxymethyl)binaphthalene (*R*)-**10** as colourless plates in 88% overall yield.



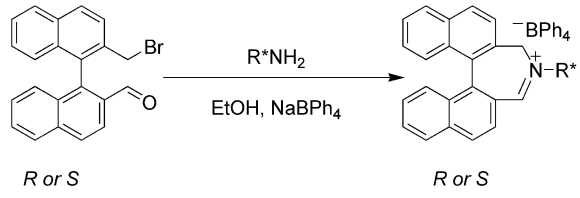
Scheme 5. Formation of the (*R*)-bis(hydroxymethyl) compound (*R*)-**10**. Reagents and conditions: i: KCO_2CH_3, Bu_4NBr (cat.), DMF, 80 °C, 20 h; ii: KOH (aq. 50%): 1,4-dioxane (1:1), Δ, 24 h, 88%.

Attempted cyclization of (*R*)-**10** to form the desired oxepine (*R*)-**9** under the conditions developed for the corresponding biphenyl derivative [HBr (aq. 24%), 100 °C, 1 h] was, however, unsuccessful.[7c] Increasing the concentration of the HBr or the reaction time had no effect, and complete recovery of the starting material was observed in each case. Fortunately, upon closer inspection of the Mazaleyrat paper,[11] we noted a brief comment that the bis(bromomethyl)binaphthalene (*R*)-**14** can be directly converted into the oxepine by heating in 1,4-dioxane/saturated sodium carbonate solution (Scheme 6). Indeed, cyclization under these conditions did occur, and the (*R*)-oxepine (*R*)-**9** was produced in 76% yield after 36 h. Ring opening of oxepine (*R*)-**9** using bromine in carbon tetrachloride under reflux afforded the (*R*)-bromoaldehyde (*R*)-**8** in 68% yield. Repeating the synthetic sequence with the (*S*)-enantiomer of BINOL produced the corresponding (*S*)-bromoaldehyde (*S*)-**8** in comparable yields. HPLC analysis of the two enantiomeric bromoaldehydes indicated that each retained greater than 99% *ee*.



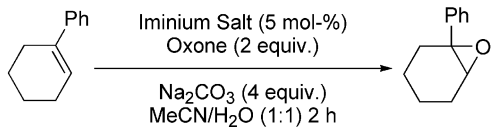
Scheme 6. Formation of (*R*)-bromoaldehyde (*R*)-**8**. Reagents and conditions: i: Na_2CO_3 (satd. aq.)/1,4-dioxane (1:1), reflux, 36 h, 76%; ii Br_2, CCl_4, reflux, 1 h, 68%.

With both enantiomers of the bromoaldehyde available, several new iminium salts **17**–**23** were synthesized by cyclocondensation with a range of amines under our standard conditions, by treatment of the bromoaldehydes with primary amines in ethanolic solution. Addition of sodium tetraphenylborate to the reaction mixture provides the iminium tetraphenylborate salts, which are generally highly crystalline (Scheme 7, Table 1).



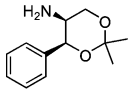
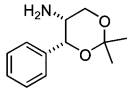
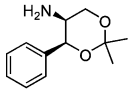
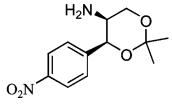
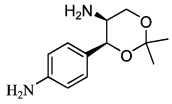
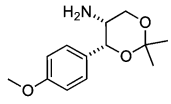
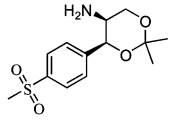
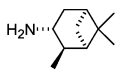
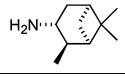
Scheme 7. Preparation of catalysts.

With the catalysts in hand, we were able to test their effectiveness in the epoxidation of our test substrate 1-phenylcyclohexene (Scheme 8, Table 2). Catalyst **6**, pairing the (*S*,*S*)-amine with the (R_{ax})-BINAP unit, showed the best reaction profile, providing the highest enantiomeric excesses (up to 91%), and was also the most reactive (complete conversion after just 20 min). Catalyst **17**, pairing the (*S*,*S*)-amine with the (S_{ax})-BINAP unit, and thus a diastereoisomer of **6**, shows poorer enantiomeric excess and poorer reactivity, presumably a result of a mismatch between the intrinsic enantiocontrol induced by the two components. The



Scheme 8.

Table 1. Preparation of catalysts.[a]

Bromoaldehyde 8	Amine	Catalyst	% Yield[b]
(*R*)		**6**	66
(*S*)		*ent*-**6**	64
(*S*)		**17**	63
(*R*)		**18**	69
(*R*)		**19**	68
(*S*)		**20**	57
(*R*)		**21**	65
(*R*)		**22**	71
(*S*)		**23**	73

[a] Reaction conditions: a) amine (1 equiv.), (*R*)- or (*S*)-2′-(bromomethyl)-1,1′-binaphthalene-2-carboxaldehyde (1.10 equiv.), ethanol, 40 °C, 12 h; b) sodium tetraphenylborate (1.10 equiv.), acetonitrile, 5 min. [b] Isolated yield.

Table 2. Epoxidation of 1-phenylcyclohexene with catalysts **6**, *ent*-**6**, **17**–**23**.[a]

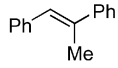
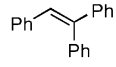
Catalyst	% Yield[b]	% *ee*[c]	Configuration[d]
6	69	91	(–)-1*S*,2*S*
ent-**6**	66	88	(+)-1*R*,2*R*
17	54	78	(+)-1*R*,2*R*
18	66	74	(–)-1*S*,2*S*
19	69	79	(–)-1*S*,2*S*
20	71[e]	80	(+)-1*R*,2*R*
21	70	76	(–)-1*S*,2*S*
22	40	53	(–)-1*S*,2*S*
23	44	58	(+)-1*R*,2*R*

[a] Epoxidation conditions: iminium salt (5 mol-%), Oxone (2 equiv.), Na_2CO_3 (4 equiv.), MeCN/H_2O (1:1), 0 °C, 2 h. [b] Isolated yield. [c] Enantiomeric excess determined by ^1H NMR spectroscopy with (+)-Eu(hfc)$_3$ (10 mol-%) as chiral shift reagent or by Chiral GC. [d] The absolute configuration of the major enantiomer was determined by comparison of the optical rotation with data reported in the literature. [e] Epoxidation conditions: iminium salt (5 mol-%), Oxone (2 equiv.), $NaHCO_3$ (5 equiv.), MeCN/H_2O (10:1), 0 °C, 2 h.

sense of induced enantiocontrol appears to be driven principally by the stereochemistry of the BINAP unit. The isopinocampheyl moiety offers poorer stereocontrol in the epoxidation process, and thus catalysts **22** and **23** produce epoxides with more moderate enantiomeric excesses.

The catalysts were next used in the epoxidation of a range of other alkenes under similar conditions (Table 3). Catalyst **20**, containing an electron-donating methoxy group, provided enantioselectivities similar to or higher than catalyst **6** for most substrates, an exception being when 1-phenylcyclohexene (**20**: 80% *ee*, cf. **6**: 91% *ee*) and 1-phenyl-3,4-dihydronaphthalene (**20**: 81% *ee*, cf. **6**: 95% *ee*) were used as substrates.

Table 3. Epoxidation of various alkenes using catalysts **6**, **18**–**21**.[a]

Alkene	Catalyst	Conv.[b]	% Yield[c]	% *ee*[d]	Config.[e]
	**6**	100	58	49	(–)-1*S*,2*S*
	18[f]	100	82	32	(–)-1*S*,2*S*
	20[f]	100	79	56	(+)-1*R*,2*R*
	21[f]	100	74	43	(–)-1*S*,2*S*
	**6**	100	60	12	(+)-*S*
	18[f]	92	73	6	(+)-*S*
	20[f]	100	70	20	(–)-*R*
	21[f]	100	79	9	(+)-*S*
	**6**	100	60	17	(+)-1*R*,2*S*
	18[g]	100	78	17	(+)-1*R*,2*S*
	19	100	77	13	(+)-1*R*,2*S*
	20[h]	100	70	15	(–)-1*S*,2*R*
	21	75	33	18	(+)-1*R*,2*S*
	**6**	100	66	95	(+)-1*R*,2*S*
	18[h]	94	79	69	(+)-1*R*,2*S*
	19	100	78	59	(+)-1*R*,2*S*
	20[i]	92	75	81	(–)-1*S*,2*R*
	21	80	63	68	(+)-1*R*,2*S*
	**6**	100	58	20	(–)-1*S*,2*S*
	18[f]	100	79	9	(–)-1*S*,2*S*
	20[f]	100	78	18	(+)-1*R*,2*R*
	21[f]	100	86	12	(–)-1*S*,2*S*

[a] Epoxidation conditions: iminium salt (5 mol-%), Oxone (2 equiv.), Na_2CO_3 (4 equiv.), MeCN/H_2O (1:1), 0 °C, 2 h. [b] Conversion evaluated from the ^1H NMR spectra by integration of alkene and epoxide peaks. [c] Isolated yield. [d] Enantiomeric excess determined by ^1H NMR spectroscopy with Eu(hfc)$_3$ (10 mol-%) as chiral shift reagent or by Chiral HPLC on a chiracel OD Column or by Chiral GC. [e] The absolute configuration of the major enantiomer was determined by comparison of the optical rotation with data reported in the literature. [f] Epoxidation conditions: iminium salt (5 mol-%), Oxone (2 equiv.), $NaHCO_3$ (5 equiv.), MeCN/H_2O (10:1), 0 °C, 2 h. [g] 3 h reaction time. [h] 4 h reaction time. [i] 5 h reaction time.

Due to poorer reactivity portrayed by catalysts **18**–**21** under our standard epoxidation conditions (1:1 acetonitrile/water, Na_2CO_3, Oxone), for example only 5–10% conversion typically being observed after six hours for stilbene substrates, we also utilized the reaction conditions developed by Yang[5] (10:1 acetonitrile/water, $NaHCO_3$, Oxone), which led typically to complete consumption of alkene in around two hours. Because of the more acidic nature of the reaction medium, however, hydrolysis of the epoxide products to the corresponding diols occurred in some cases, particularly for 1-phenyl-3,4-dihydronaphthalene, where complete conversion to the diol was observed in two hours. When 1-phenylcyclohexene was used as substrate, between 11% and 20% conversion to diol was observed. Hydrolysis to diol products was not observed under our standard conditions.

Catalyst **6** exhibited the highest degree of enantiocontrol, giving 95% *ee* for phenyl-1,2-dihydronaphthalene, one of the highest *ee* values ever reported for iminium salt-mediated epoxidation.

Several cycloalkenes of varying ring sizes were submitted to the asymmetric epoxidation reaction (Table 4). Reactions were carried out using just 1 mol-% of catalyst **6**. Again, good conversions to epoxides were achieved, and, interestingly, the five- and seven-membered ring cycloalkenes were less reactive than was 1-phenylcyclohexene. The reactions took almost five times as long to approach completion, and enantioselectivities were poorer than those observed for 1-phenylcyclohexene: 1-phenylcyclopentene oxide was formed in 55% *ee* and 1-phenylcycloheptene in 76% *ee*. This observation is difficult to explain, but presumably results from conformational effects in the cycloalkenes and stereoelectronic effects in the epoxidation transition states.

Table 4. Effect of ring size on the epoxidation of several cycloalkenes with catalyst **6**.[a]

Alkene	*t*/h	% Yield[b]	% *ee*[c]	Config.[d]
	5.0	52	55	(–)-1*S*,2*S*
	1.1	64	91	(–)-1*S*,2*S*
	5.0	57	76	(–)-1*S*,2*S*

[a] Conditions: Iminium salt (1 mol-%), Oxone (2 equiv.), Na_2CO_3 (4 equiv.), MeCN/H_2O (1:1), 0 °C. [b] Isolated yields. [c] Enantiomeric excesses were determined by ^{1}H NMR spectroscopy in the presence of (+)-Eu(hfc)$_3$ (10 mol-%). [d] The absolute configurations of the major enantiomers were determined by comparison of the optical rotation with data reported in the literature.

Using catalyst **6** we also conducted a catalyst loading study using as test substrate 1-phenylcyclohexene, with catalyst loadings ranging from 0.1 to 5 mol-% (Table 5). We were delighted and extremely surprised to observe a high level of asymmetric induction with very low catalyst loadings. We have previously reported that it is possible to use just 0.5 mol-% of catalyst, but a loss in enantioselectivity is commonly observed. In this case, however, catalyst loadings can be so low that effective epoxidation of 1.0 g of 1-phenylcyclohexene, with 68% yield and 88% *ee*, can be achieved using just 5 mg of catalyst (0.1 mol-%). This is an unprecedently low level of catalyst loading for an organocatalytic species.

Table 5. Catalyst loading study on the epoxidation of 1-phenylcyclohexene with catalyst **6**.[a]

Catalyst [mol-%]	Time [h]	% Yield[b]	% *ee*[c]	Configuration[d]
5.0	0.2	69	91	(–)-1*S*,2*S*
1.0	1.1	64	91	(–)-1*S*,2*S*
0.5	2.0	65	91	(–)-1*S*,2*S*
0.1	6.0	68	88	(–)-1*S*,2*S*

[a] Conditions: Oxone (2 equiv.), Na_2CO_3 (4 equiv.), MeCN/H_2O (1:1), 0 °C. [b] Isolated yields. [c] Enantiomeric excesses were determined by ^{1}H NMR spectroscopy in the presence of (+)-Eu(hfc)$_3$ (10 mol-%). [d] The absolute configurations of the major enantiomers were determined by comparison of the optical rotation with data reported in the literature.

Conclusions

Catalyst **6** is one of the most active iminium salt catalysts that we have discovered. It is also one of the most enantioselective iminium salt epoxidation catalysts ever reported, and is effective at remarkably low catalyst loading. Generally, organic catalysts require higher catalyst loadings, and a breakdown of the active species is sometimes observed. In the case of catalyst **6**, the enantioselectivity appears to be almost independent of catalyst loading, and decreasing the amount of catalyst merely increases the reaction time.

Experimental Section

(*R*)-1,1′-Binaphthalene-2,2′-diyl Bis(trifluoromethanesulfonate) (*R*)-12: [16](*R*)-**11** (3.00 g, 10.50 mmol) was dissolved in dichloromethane (60 mL), and the solution cooled to –30 °C and stirred at this temperature for 5 min. 4-(Dimethylamino)pyridine (0.51 g, 4.20 mmol), 2,6-lutidine (3.70 mL, 31.40 mmol) and triflic anhydride (5.30 mL, 31.40 mmol) were added. The resulting dark-brown mixture was allowed reach ambient temperature and stirred overnight. Silica gel was added to the solution and the solvent removed in vacuo. The product mixture, adsorbed onto silica gel, was transferred to a sintered glass funnel, and the material washed with hexane until the product had eluted. The solvent was removed in vacuo to give a colourless solid, which was crystallized from hexane to afford the product as colourless crystals (5.72 g, 99%); m.p. 76–78 °C. $[\alpha]_D^{20}$ = –147.7 (*c* = 1.01, $CHCl_3$), [ref.[16] +142.0 (*c* 1.04, $CHCl_3$), for (*S*)-enantiomer]. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.17–7.19 (m, 2 H, 2 C*H* arom., *binap*-3,-3′), 7.32–7.36 (m, 2 H, 2 C*H* arom., *binap*-7,-7′), 7.49–7.56 (m, 4 H, 4 C*H* arom., *binap*-8,-8′-9,9′), 7.94 (d, *J* = 8.2 Hz, 2 H, 2 C*H* arom., *binap*-4,-4′), 8.07 (d, *J* = 9.0 Hz, 2 H, 2 C*H* arom., *binap*-6,-6′) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 116.5 (q, *J* = 79.5 Hz, 2 *C*F_3, 2 *C* quat.), 119.3 (2 *C*H arom., *binap*-8,-8′), 123.5 (2 *C* quat., arom., *binap*-1,-1′), 126.8 (2 *C*H arom., *binap*-3,-3′), 127.3 (2 *C*H arom., *binap*-7,-7′), 128.0 (2 *C*H arom., *binap*-9,-9′), 128.4 (2 *C*H arom., *binap*-4,-

4′), 132.0 (2 *C*H arom., *binap*-6,-6′), 132.3 (2 *C* quat., arom., *binap*-5,-5′), 133.1 (2 *C* quat., arom., *binap*-10,-10′), 145.4 (2 *C* quat., arom., *binap*-2,-2′). MS (ES): *m*/*z* = 568.0316. $C_{22}H_{16}F_6NO_6S_2$ [M + NH_4]$^+$ calcd. 568.0323.

(*S*)-1,1′-Binaphthalene-2,2′-diyl Bis(trifluoromethanesulfonate [(*S*)-12]: Prepared in an identical manner to the (*R*)-enantiomer (*R*)-**12** above, from (*S*)-1,1′-binaphthalene-2,2′-diol (*S*)-**11** (3.00 g, 10.50 mmol). Colourless crystals (5.72 g, 99%), having almost identical spectroscopic data to (*R*)-**12**: m.p. 75–77 °C. $[\alpha]_D^{20}$ = +145.0 (*c* = 1.00, $CHCl_3$).

(*R*)-2,2′-Dimethyl-1,1′-binaphthalene [(*R*)-13]:[14] (*R*)-**12** (13.70 g, 24.87 mmol) and [1,3-bis(diphenylphosphanyl)propane]nickel(II) chloride (1.17 g, 1.79 mmol) were dissolved in anhydrous diethyl ether (100 mL). The reaction was cooled to –30 °C, and methylmagnesium bromide (3 M in Et_2O, 33.16 mL, 99.48 mmol) added dropwise over 30 min. The reaction was allowed to reach room temperature and stirred for 16 h. The resulting dark green reaction mixture was diluted with diethyl ether (100 mL) and filtered through a pad of Celite. The filtrate was washed with 35% aqueous hydrochloric acid (20 mL), water (100 mL) and brine (100 mL). Removal of the solvent under reduced pressure gave a reddish crude oil, which was purified by column chromatography, eluting with ethyl acetate/hexane (1:4), to give a colourless powder. Crystallization from methanol afforded the product as colourless crystals (6.32 g, 90%); m.p. 74–78 °C; [ref.[14] m.p. 67–71 °C]. $[\alpha]_D^{20}$ = –40.0 (*c* = 1.12, $CHCl_3$) [ref.[14] $[\alpha]_D^{20}$ = –35.6 (*c* = 1.00, $CHCl_3$)]. IR (film): ṽmax = 3053, 2246, 1594, 1506, 1422, 1379, 1351 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.09 (s, 6 H, 2 Ar-CH_3), 7.10 (dd, *J* = 8.5, 0.96 Hz, 2 H, 2 C*H* arom., *binap-3,-3′*), 7.23–7.28 (m, 2 H, 2 C*H* arom., *binap-7,-7′*), 7.42–7.46 (m, 2 H, 2 C*H* arom., *binap-8,-8′*), 7.56 (d, *J* = 8.5 Hz, 2 H, 2 C*H* arom., *binap-4,-4′*), 7.92–7.95 (m, 4 H, 4 C*H* arom., *binap-9,-9′* and *binap-6,-6′*) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.1 (2 *C*H_3, 2 Ar-*C*H_3), 124.9 (2 *C*H arom., *binap-7,-7′*), 125.7 (2 *C*H arom., *binap-8,-8′*), 126.1 (2 *C*H arom., *binap-4,-4′*), 127.3 (2 *C*H arom., *binap-9,-9′*), 127.8 (2 CH arom., *binap-6,-6′*), 128.8 (2 *C*H arom., *binap-3,-3′*), 132.2 (2 *C* quat., arom., *binap-5,-5′*), 132.8 (2 *C* quat., arom., *binap-10,-10′*), 134.3 (2 *C* quat., arom., *binap-2,-2′*), 135.2 (2 *C* quat., arom., *binap-1,-1′*); MS (EI): *m*/*z* = 282.1400. $C_{22}H_{18}$ [M$^+$] calcd. 282.1409 ppm.

(*S*)-2,2′-Dimethyl-1,1′-binaphthalene [(*S*)-13]: Prepared in an identical manner to the (*R*)-enantiomer (*R*)-**13** above from (*S*)-**12** (13.70 g, 24.87 mmol). Colourless crystals (6.32 g, 90%), having almost identical spectroscopic data to (*R*)-**13**: m.p. 72–74 °C. $[\alpha]_D^{20}$ = +38.0 (*c* = 1.00, $CHCl_3$).

(*R*)-2,2′-Bis(bromomethyl)-1,1′-binaphthalene [(*R*)-14]:[17] (*R*)-**13** (2.00 g, 7.08 mmol) was dissolved in cyclohexane (14 mL), and *N*-bromosuccinimide (2.77 g, 15.58 mmol) and azobis(isobutyronitrile) (0.12 g, 0.71 mmol) were added with stirring. The mixture was heated under reflux for 3 h, after which time complete disappearance of the starting material was observed by TLC. After cooling to room temperature, ethyl acetate (5 mL) and water (30 mL) were added to dissolve excess NBS and to allow trituration. The resulting suspension was stirred for 1 h, after which time precipitation had ceased. The mixture was filtered to afford the product as colourless solid (1.54 g, 50%); m.p. 180–183 °C [ref.[17] m.p. 171–174 °C]. $[\alpha]_D^{20}$ = +186.4 (*c* = 1.00, benzene) [ref.[17] $[\alpha]_D^{20}$ = +148.0 (*c* = 1.70, benzene)]. IR (film): ṽmax = 3049, 2360, 1506, 1432, 1211, 818, 759 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.17 (s, 4 H, 2 Ar-CH_2), 7.00 (d, *J* = 8.6, Hz, 2 H 2 C*H* arom., *binap-3,-3′*), 7.17–7.19 (m, 2 H, 2 C*H* arom., *binap-7,-7′*), 7.39–7.41 (m, 2 H, 2 C*H* arom., *binap-8,-8′*), 7.67 (d, *J* = 8.6 Hz, 2 H, 2 C*H* arom., *binap-4,-4′*), 7.85 (d, *J* = 8.2 Hz, 2 H, 2 C*H* arom., *binap-9,-9′*), 7.94 (d, *J* = 8.6 Hz, 2 H, 2 C*H* arom., *binap-6,-6′*) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.6 (2 Ar-*C*H_2), 126.87 (2 *C*H arom., *binap-7,-7′*), 126.88 (2 *C*H arom., *binap-8,-8′*), 127.1 (2 *C*H arom., *binap-4,-4′*), 127.8 (2 *C*H arom., *binap-9,-9′*), 128.2 (2 *C*H arom., *binap-6,-6′*), 129.9 (2 *C*H arom., *binap-3,-3′*), 132.5 (2 *C* quat., arom., *binap-5,-5′*), 133.3 (2 *C* quat., arom., *binap-10,-10′*), 134.1 (2 *C* quat., arom., *binap-2,-2′*), 134.2 (2 *C* quat., arom., *binap-1,-1′*). MS (EI): *m*/*z* = 437.9612. $C_{22}H_{16}Br_2$ [M$^+$] calcd. 437.9619 ppm.

(*S*)-2,2′-Bis(bromomethyl)-1,1′-binaphthalene [(*S*)-14]:[17] Prepared in an identical manner to the (*R*)-enantiomer (*R*)-**14** above, from (*S*)-**13** (2.00 g, 7.08 mmol). Colourless crystals (6.32 g, 90%), having almost identical spectroscopic data to (*R*)-**14**: m.p. 180–182 °C; [ref.[17] m.p. 181–182 °C]. $[\alpha]_D^{20}$ = –158.0 (*c* = 1.00, benzene); [ref.[17] $[\alpha]_D^{20}$ = –157.3 (*c* = 1.00, benzene)].

(*R*)-2,2′-Bis(hydroxymethyl)-1,1′-binaphthalene [(*R*)-10]:[11] A solution of (*R*)-**14** (3.50 g, 8.0 mmol) was dissolved in dimethylformamide (300 mL) and stirred at 80 °C with potassium acetate (3.75 g, 38.2 mmol) and tetrabutylammonium bromide (1.0 g) for 24 h. The mixture was cooled, diluted with brine (150 mL) and extracted with diethyl ether (3 × 100 mL). The organic solutions were combined and washed with brine (2 × 50 mL), dried ($MgSO_4$), and the solvents removed under reduced pressure to afford diacetate (*R*)-**16** as a pale yellow/brown oil, recrystallized from chloroform/hexane. Compound (*R*)-**16** (3.0 g, 7.5 mmol) was then hydrolysed in a boiling mixture of aqueous potassium hydroxide (50% in water) and 1,4-dioxane (1:1, 100 mL) for 24 h. The solution was cooled and extracted with diethyl ether (3 × 50 mL). The organic layers were combined and washed with brine (2 × 50 mL), and the solvents removed to give a crude yellow/brown oil which was crystallized from chloroform/hexane to give colourless crystals (2.10 g, 88%); m.p. 167–169 °C. $[\alpha]_D^{20}$ = +63.2 (*c* = 1.35, acetone) [ref.[11] $[\alpha]_D^{24}$ = –67.5 (*c* = 1.00, acetone) for (*S*)-enantiomer]. IR (film): ṽmax = 3384, 3057, 1648, 1507, 1428, 1216, 1013, 822 cm^{-1}. ^{1}H NMR (250 MHz. $CDCl_3$): δ = 3.26 (br. s, 2 H), 4.08 (d, *J* = 11.1 Hz, 2 H), 4.37 (d, *J* = 11.1 Hz, 2 H), 7.01 (d, *J* = 8.24 Hz, 2 H), 7.17–7.27 (m, 2 H), 1.92–2.02 (m, 2 H), 7.68 (d, *J* = 8.8 Hz, 2 H, 2), 7.89–8.00 (m, 4 H) ppm. ^{13}C NMR (100 MHz. $CDCl_3$): δ = 63.4, 126.3, 126.5, 126.7, 127.7, 128.5, 129.0, 133.5, 133.6, 134.7, 137.6. MS: *m*/*z* = 332.1650. $C_{22}H_{22}NO_2$ (M^+NH_4) calcd. 332.1651 ppm.

(*R*)-2,7-Dihydrodinaphtho[2,1-*c*;1′,2′-*e*]oxepine [(*R*)-9]:[12] (*R*)-**14** (1.16 g, 2.65 mmol) was suspended in a mixture of saturated aqueous sodium carbonate (40 mL) and 1,4-dioxane (40 mL). The mixture was heated under reflux for 36 h, cooled to room temperature, and extracted with diethyl ether (2 × 40 mL). The combined organic extracts were washed with brine (2 × 30 mL) and dried (Na_2SO_4), and the solvent removed in vacuo to give a yellow oil. The crude product was purified by flash column chromatography using ethyl acetate/light petroleum (0:100–5:95) as eluent to afford the product as a colourless solid (0.30 g, 81%); m.p. 184–186 °C; [ref.[12] m.p. 188–189 °C]. $[\alpha]_D^{20}$ = –551.2 (*c* = 1.00, $CHCl_3$). IR (film): ṽmax = 3049, 2959, 2923, 1594, 1507, 1463, 1367, 1237, 1195, 1057, 909, 828 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.12 (d, *J* = 11.3 Hz, 2 H, Ar-CH_2O), 4.56 (d, *J* = 11.3 Hz, 2 H, Ar-CH_2O), 7.19–7.25 (m, 2 H, 2 C*H* arom., *binap-3,-3′*), 7.41–7.47 (m, 4 H, 4 C*H* arom., *binap-7,-7′*, *binap-8,-8′*), 7.55 (d, *J* = 8.4 Hz, 2 H, 2 C*H* arom., *binap-4,-4′*), 7.89–7.94 (m, 4 H, 4 C*H* arom., *binap-6,-6′*, *binap-9,-9′*) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 67.5 (2 *C*H_2, 2 Ar-*C*H_2), 125.95 (2 CH arom., *binap-7,-7′*), 125.98 (2 *C*H arom., *binap-8,-8′*), 127.4 (2 *C*H arom., *binap-4,-4′*), 127.6 (2 *C*H arom., *binap-9,-9′*), 128.4 (2 *C*H arom., *binap-6,-6′*), 129.2 (2 *C*H arom., *binap-3,-3′*), 131.2 (2 *C* quat., arom., *binap-5,-5′*), 133.56

(2 *C* quat., arom., *binap-10,-10′*), 133.64 (2 *C* quat., arom., *binap-2,-2′*), 135.5 (2 *C* quat., arom., *binap-1,-1′*) ppm. MS (ESI): *m*/*z* = 314.1542. $C_{22}H_{20}NO$ [M + NH_4]$^+$ calcd. 314.1545.

(*S*)-2,7-Dihydrodinaphtho[2,1-*c*;1′,2′-*e*]oxepine [(*S*)-9]: Prepared in an identical manner to the (*R*)-enantiomer (*R*)-**9** above, from (*S*)-**14** (1.16 g, 2.65 mmol). Colourless crystals (0.30 g, 81%), having almost identical spectroscopic data to (*R*)-**9**: m.p. 184–186 °C. [*α*]$_D^{20}$ = +568.2 (*c* = 1.00, $CHCl_3$).

(*R*)-2′-Bromomethyl-1,1′-binaphthalene-2-carboxaldehyde [(*R*)-8]:[6] (*R*)-**9** (0.50 g, 1.69 mmol) was dissolved in cyclohexane, and the solution cooled to 0 °C. Bromine (0.31 g, 1.86 mmol) was added dropwise with stirring over 10 min. After stirring for a further 5 min at this temperature, the reddish coloured reaction mixture was heated under reflux for 1 h, becoming a pale yellow colour. The solvent was removed in vacuo, and the resulting yellow residue dissolved in diethyl ether (30 mL), and washed with saturated aqueous sodium carbonate (2 × 30 mL) and brine (2 × 30 mL). The combined organic extracts were dried (Na_2SO_4), and the solvent removed in vacuo to give a yellow oil. The crude product was purified by flash column chromatography using ethyl acetate/light petroleum (0:100) as eluent, to afford the product as a colourless solid (0.43 g, 68%); m.p. 150–152 °C; [ref.[6] m.p. 151–153 °C]. [*α*]$_D^{20}$ = +144.0 (*c* = 1.00, $CHCl_3$); [ref.[6] [*α*]$_D^{20}$ = +144.7 (*c* = 1.02, $CHCl_3$)]. IR (film): ṽmax = 3057, 2845, 2357, 1688, 1616, 1593, 1509, 1429, 1324, 1240, 1223, 1027, 909, 870, 821, 750, 730 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* = 4.01 (d, *J* = 10.1 Hz, 1 H, Ar-C*H*HBr), 4.26 (d, *J* = 10.1 Hz, 1 H, Ar-CH*H*Br), 6.95 (dd, *J* = 8.5, 0.8 Hz, 1 H, C*H* arom., *binap-7′*), 7.16–7.29 (m, 3 H, 3 C*H* arom., *binap-3,-8′-4′*), 7.40–7.46 (m, 1 H, C*H* arom., *binap-7*), 7.52–7.58 (m, 1 H, C*H* arom., *binap-8*), 7.65 (d, *J* = 8.6 Hz, 1 H, C*H* arom., *binap-4*), 7.87 (d, *J* = 8.4 Hz, 1 H, C*H* arom., *binap-6*), 7.93 (d, *J* = 8.4 Hz, 1 H, C*H* arom., *binap-6′*), 7.98 (d, *J* = 8.5 Hz, 1 H, C*H* arom., *binap-9*), 8.02 (d, *J* = 8.5 Hz, 1 H, C*H* arom., *binap-9′*), 8.14 (d, *J* = 8.6 Hz, 1 H, C*H* arom., *binap-3′*), 9.49 (d, *J* = 0.9 Hz, 1 H, C*H*O) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): *δ* = 31.9 (*C*H$_2$, Ar-*C*H$_2$), 122.4 (*C*H arom., *binap-3*), 126.6 (*C*H arom., *binap-7′*), 126.9 (*C*H arom., *binap-8′*), 127.0 (*C*H arom., *binap-4′*), 127.39 (*C*H arom., *binap-8*), 127.40 (2 *C*H arom., *binap-6′,9′*), 128.2 (*C*H arom., *binap-4*), 128.5 (*C*H arom., *binap-6*), 129.2 (*C*H arom., *binap-3′*), 129.3 (*C*H arom., *binap-7*), 129.9 (*C*H arom., *binap-9*), 132.41 (*C* quat., arom., *binap-5′*), 132.42 (*C* quat., arom., *binap-10′*), 132.5 (*C* quat., arom., *binap-2*), 133.0 (*C* quat., arom., *binap-5*), 133.6 (*C* quat., arom., *binap-2′*), 134.6 (*C* quat., arom., *binap-1′*), 136.3 (*C* quat., arom., *binap-10*), 141.6 (*C* quat., arom., *binap-1*), 191.8 (*C*HO) ppm. MS (ESI): *m*/*z* = 392.0643. $C_{22}H_{19}BrNO$ [M + NH_4]$^+$ calcd. 392.0650.

(*S*)-2′-(Bromomethyl)-1,1′-binaphthalene-2-carboxaldehyde [(*S*)-8]: Prepared in an identical manner to the (*R*)-enantiomer (*R*)-**8** above, from (*S*)-**9** (0.50 g, 1.69 mmol). Colourless crystals (0.22 g, 34%), having almost identical spectroscopic data to (*R*)-**8**: m.p. 153–154 °C. [*α*]$_D^{20}$ = –143.0 (*c* = 1.00, $CHCl_3$).

(2*S*)-Methyl 2-(*tert*-Butyloxycarbonylamino)-3-(4-hydroxyphenyl)-propanoate:[18] Triethylamine (9.63 mL, 69.06 mmol) was added to a cooled solution of L-tyrosine methyl ester hydrochloride salt (8.00 g, 34.53 mmol) in dichloromethane (100 mL) at 0 °C. The mixture was stirred for 30 min at 0 °C before a solution of *tert*-butyloxycarbonyl anhydride (8.29 g, 37.98 mmol) in dichloromethane (10 mL) was added dropwise. The mixture was stirred at room temperature for 16 h, transferred to a separating funnel and washed with 1 M citric acid (2 × 30 mL) and brine (2 × 30 mL). The organic solution was dried (Na_2SO_4), and the solvent removed under reduced pressure to give a colourless oil. Crystallization was achieved from dichloromethane to give colourless crystals (10.10 g, 99%); m.p. 102–103 °C. [*α*]$_D^{20}$ = +52.8 (*c* = 1.00, $CHCl_3$). IR (film): ṽmax = 3364 (OH), 2977, 1689 (C=O), 1614, 1515, 1444, 1366, 1225, 1166, 1058 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* = 1.43 [s, 9 H, $NCO_2C(CH_3)_3$], 2.98–3.04 (m, 2 H, Ar-C*H*$_2$, H3), 3.70 (s, 3 H, CO_2CH_3), 4.54 (q, *J* = 8.2 Hz, 1 H, C*H*N, H2), 5.13 (d, *J* = 8.4 Hz, 1 H, N*H*), 6.75 (d, *J* = 8.3 Hz, 2 H, 2 C*H* arom., H7, H8), 6.96 (d, *J* = 8.3 Hz, 2 H, 2 C*H* arom., H5, H6) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): *δ* = 28.3 [3 *C*H$_3$, $NCO_2C(CH_3)_3$], 37.5 (*C*H$_2$, Ar*C*H$_2$, C3), 52.4 (*C*H$_3$, CO_2CH_3), 54.4 (*C*H, *C*HN, C2), 80.4 [*C* quat., $NCO_2C(CH_3)_3$], 115.6 (2 *C*H arom., C7, C8), 127.1 (*C* quat., arom., *ipso* to C3 in Ar gp., C4), 130.3 (2 *C*H arom., C5, C6), 155.47 (*C* quat., *N*-Boc *C*=O), 155.53 (*C* quat., arom., *ipso* to OH in Ar gp., C9), 172.8 (*C* quat., C=O, CO_2CH_3) ppm. MS (FAB): *m*/*z* = 296.1496. $C_{15}H_{22}NO_5$ [M + H]$^+$ calcd. 296.1498.

(2*S*)-Methyl 2-(*tert*-Butyloxycarbonylamino)-3-(4-methoxyphenyl)-propanoate:[18] (2*S*)-Methyl 2-(*tert*-butyloxycarbonylamino)-3-(4-hydroxyphenyl)propanoate (9.90 g, 33.72 mmol) was dissolved in dimethylformamide (70 mL), and ground potassium hydroxide (2.31 g, 40.46 mmol) added. Iodomethane (2.52 mL, 40.46 mmol) was added dropwise at 0 °C. The reaction mixture was stirred at room temperature for 16 h, diluted with ethyl acetate (100 mL), and washed with water (6 × 50 mL) and brine (6 × 50 mL). The organic solution was dried (Na_2SO_4), and the solvent removed under reduced pressure to yield a colourless oil (9.38 g, 90%). IR (film): ṽmax = 3367, 2976, 1746 (C=O), 1715 (NC=O), 1612, 1514, 1441, 1366, 1249, 1167, 1034 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* = 1.34 [s, 9 H, $NCO_2C(CH_3)_3$], 2.92–2.97 (m, 2 H, Ar-C*H*$_2$, H3), 3.63 (s, 3 H, CO_2CH_3), 3.70 (s, 3 H, Ar*OCH*$_3$), 4.46 (q, *J* = 8.2 Hz, 1 H, C*H*N, H2), 4.95 (d, *J* = 8.2 Hz, 1 H, N*H*), 6.75 (d, *J* = 8.7 Hz, 2 H, 2 C*H* arom., H7, H8), 6.96 (d, *J* = 8.7 Hz, 2 H, 2 C*H* arom., H5, H6) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): *δ* = 28.3 [3 *C*H$_3$, $NCO_2C(CH_3)_3$], 37.4 (*C*H$_2$, Ar*C*H$_2$, C3), 52.2 (*C*H$_3$, CO_2CH_3), 54.6 (*C*H, *C*HN, C2), 55.2 (*C*H$_3$, Ar*OCH*$_3$), 79.8 [*C* quat., $NCO_2C(CH_3)_3$], 113.9 (2 *C*H arom., C7, C8), 127.9 (*C* quat., arom., *ipso* to C3 in Ar gp., C4), 130.3 (2 *C*H arom., C5, C6), 155.1 (*C* quat., *N*-Boc *C*=O), 158.6 (*C* quat., arom., *ipso* to OCH_3 in Ar gp., C9), 172.5 (*C* quat., C=O, CO_2CH_3) ppm. MS (FAB): *m*/*z* = 310.1651. $C_{16}H_{24}NO_5$ [M + H]$^+$ calcd. 310.1655.

(4*S*,5*R*)-Methyl 5-(4-Methoxyphenyl)-2-oxo-1,3-oxazolidine-4-carboxylate:[18] (2*S*)-Methyl 2-(*tert*-butyloxycarbonylamino)-3-(4-methoxyphenyl)propanoate (5.00 g, 16.26 mmol) was dissolved in acetonitrile (200 mL). Solutions of potassium persulfate (8.79 g, 32.51 mmol) in water (150 mL) and copper(II) sulfate (0.80 g, 3.21 mmol) in water (50 mL) were added. The reaction mixture was heated to 70 °C for 3 h under nitrogen, then cooled to room temperature before being extracted with ethyl acetate (3 × 70 mL). The combined organic extracts were dried (Na_2SO_4), and the solvent removed under reduced pressure to give a yellow oil. Column chromatography with ethyl acetate/light petroleum (1:1) afforded a colourless solid (1.03 g, 25%); m.p. 92–94 °C; [ref.[18] 94–96 °C]. [*α*]$_D^{20}$ = +85.2 (*c* = 1.00, $CHCl_3$); [ref.[18] [*α*]$_D^{20}$ = +83.5 (*c* = 1.15, $CHCl_3$)]. IR (film): ṽmax = 3314, 2954, 2841, 1762 (C=O), 1612, 1514, 1441, 1381, 1246, 1119, 1024, 921, 833, 735 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* = 3.74 (s, 3 H, CO_2CH_3), 3.76 (s, 3 H, Ar*OCH*$_3$), 4.24 (dd, *J* = 5.2, 0.6 Hz, 1 H, C*H*N, H4), 5.50 (d, *J* = 5.2 Hz, 1 H, Ar*CH*, H5), 6.75 (s, 1 H, N*H*), 6.85 (d, *J* = 8.6 Hz, 2 H, 2 C*H* arom., H9, H10), 7.27 (d, *J* = 8.6 Hz, 2 H, 2 C*H* arom., H7, H8) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): *δ* = 53.2 (*C*H$_3$, CO_2CH_3), 55.4 (*C*H$_3$, Ar*OCH*$_3$), 61.5 (*C*H, *C*HN, C4), 79.5 (*C*H, Ar*C*H, C5), 114.4 (2 *C*H arom., C9, C10), 127.1 (2 *C*H arom., C7, C8), 129.9 (*C* quat., arom., *ipso* to C5 in Ar gp., C6), 158.6 (*C* quat., N*C*=O, C2), 160.3 (*C* quat., arom., *ipso* to OCH_3 in Ar gp.,

C11), 170.3 (*C* quat., C=O, CO_2CH_3). MS (EI): *m*/*z* = 251.0799. $C_{12}H_{13}NO_5$ [M^+] calcd. 251.0794 ppm.

(4*R*,5*R*)-4-(Hydroxymethyl)-5-(4-methoxyphenyl)-1,3-oxazolidin-2-one:[18] (4*S*,5*R*)-Methyl 5-(4-methoxyphenyl)-2-oxo-1,3-oxazolidine-4-carboxylate (1.14 g, 4.55 mmol) was dissolved in ethanol (30 mL), and the solution cooled to 0 °C (external) using an ice bath. A solution of sodium borohydride (0.38 g, 10.01 mmol) in ethanol (5 mL) was added dropwise to the mixture. After the addition was complete the ice bath was removed and the reaction mixture stirred at room temperature for 55 min. The reaction mixture was cooled to 0 °C and concentrated hydrochloric acid (2 mL) added, followed by water (20 mL). The ethanol was removed under reduced pressure and the remaining aqueous mixture extracted with ethyl acetate (3 × 40 mL). The combined organic extracts were washed with brine (2 × 30 mL), dried (Na_2SO_4), and the solvents removed under reduced pressure to yield a colourless solid (0.95 g, 94%); m.p. 138–140 °C; [ref.[18] m.p. 140–142 °C]. $[\alpha]_D^{20}$ = +74.6 (*c* = 1.01, acetone); [ref.[18] $[\alpha]_D^{20}$ = +74.8 (*c* = 1.08, acetone)]. IR (nujol): ṽmax = 3239, 1725, 1614, 1514, 1459, 1376, 1251, 1174, 1062, 1016, 828 cm^{-1}. ^1H NMR (400 MHz, [D_6]acetone): δ = 3.76–3.80 (m, 3 H, C*H*N, H4 and CH_2OH, H6), 3.86 (s, 3 H, ArOCH_3), 5.35 (d, *J* = 5.3 Hz, 1 H, ArC*H*, H5), 7.01 (d, *J* = 8.6 Hz, 2 H, 2 C*H* arom., H10, H11), 7.41 (d, *J* = 8.6 Hz, 2 H, 2 C*H* arom., H8, H9) ppm. ^{13}C NMR (100 MHz, [D_6]acetone): δ = 56.0 (*C*H, *C*HN, C4), 63.1 (*C*H_3, ArO*C*H_3), 64.2 (*C*H_2, C6), 80.4 (*C*H, Ar*C*H, C5), 115.4 (2 *C*H arom., C10, C11), 128.7 (2 *C*H arom., C8, C9), 133.2 (*C* quat., arom., *ipso* to C5 in Ar gp., C7), 159.6 (*C* quat., N*C*=O, C2), 161.3 (*C* quat., arom., *ipso* to OCH_3 in Ar gp., C12) ppm. MS (EI): *m*/*z* = 223.0843. $C_{11}H_{13}NO_4$ [M^+] calcd. 223.0845.

(1*R*,2*R*)-(–)-2-Amino-1-(4-methoxyphenyl)propane-1,3-diol:[18] A mixture of (4*R*,5*R*)-4-(hydroxymethyl)-5-(4-methoxyphenyl)-1,3-oxazolidin-2-one (0.66 g, 2.95 mmol) and 1 M aqueous sodium hydroxide (30 mL) were heated under reflux for 45 min. The reaction mixture was cooled to room temperature and extracted with ethyl acetate (9 × 40 mL). The combined organic extracts were dried ($MgSO_4$) and the solvents removed under reduced pressure to afford a colourless solid, which was recrystallized from methanol/diethyl ether (0.51 g, 88%); m.p. 129–131 °C; [ref.[18] m.p. 132–134 °C]. $[\alpha]_D^{20}$ = –33.6 (*c* = 1.00, 2 M aq. HCl); [ref.[6] $[\alpha]_D^{20}$ = –28.3 (*c* = 1.06, 2 M aq. HCl)]. IR (nujol): ṽmax = 3339, 1619, 1584, 1517, 1459, 1377, 1253, 1064, 873 cm^{-1}. ^1H NMR (400 MHz, CD_3OD): δ = 2.89–2.93 (m, 1 H, C*H*N, H2), 3.30 (dd, *J* = 10.8, 4.2 Hz, 1 H, NCHC*H*H-O, H3), 3.43 (dd, *J* = 10.8, 4.2 Hz, 1 H, NCHC*H*H-O, H3′), 3.80 (s, 3 H, ArOCH_3), 4.50 (d, *J* = 7.2 Hz, 1 H, ArC*H*, H1), 6.93 (d, *J* = 8.7 Hz, 2 H, 2 C*H* arom., H7, H8), 7.29 (d, *J* = 8.7 Hz, 2 H, 2 C*H* arom., H5, H6) ppm. ^{13}C NMR (100 MHz, [D_6]acetone): δ = 55.7 (*C*H_3, ArO*C*H_3), 59.9 (*C*H, *C*HN, C2), 64.0 (*C*H_2, C3), 75.4 (*C*H, Ar*C*H, C1), 114.8 (2 *C*H arom., C7, C8), 128.8 (2 *C*H arom., C5, C6), 135.9 (*C* quat., arom., *ipso* to C1 in Ar gp., C4), 160.7 (*C* quat., arom., *ipso* to OCH_3 in Ar gp., C9) ppm. MS (FAB): *m*/*z* = 198.1127. $C_{10}H_{16}NO_3$ [M + H] calcd. 198.1130.

(2*S*)-2-(*tert*-Butyloxycarbonylamino)-3-(4-methoxyphenyl)propan-1-ol:[18] (2*S*)-Methyl 2-(*tert*-butyloxycarbonylamino)-3-(4-methoxyphenyl)propanoate (5.20 g, 16.91 mmol) was dissolved in dry diethyl ether (100 mL) under a nitrogen atmosphere, and the resulting solution cooled to 0 °C (external) using an ice bath. Lithium borohydride (1.47 g, 67.62) was added to the cooled reaction mixture in portions over 15 min. Methanol (40 mL) was added dropwise, and the reaction mixture stirred at room temperature overnight. The reaction mixture was diluted with ethyl acetate (100 mL), and saturated aqueous ammonium chloride added dropwise. The organic phase was separated and washed with water (2 × 20 mL) and brine (2 × 20 mL), dried (Na_2SO_4), and the solvent removed under reduced pressure to afford a colourless oil (4.75 g, 100%). $[\alpha]_D^{20}$ = –9.7 (*c* = 1.16, $CHCl_3$). IR (film): ṽmax = 3380 (OH), 2970, 1691 (NC=O), 1613, 1511, 1367, 1248, 1168, 1041, 912 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.33 [s, 9 H, $NCO_2C(CH_3)_3$], 2.69 (d, *J* = 6.9 Hz, 2 H, Ar-CH_2, H3), 3.44 (dd, *J* = 10.9, 5.0 Hz, 1 H, NCH-C*H*H-OH, H1), 3.54 (dd, *J* = 10.9, 4.0 Hz, 1 H, NCH-CH*H*-OH, H1′), 3.69 (s, 3 H, ArOCH_3), 3.74 (d, *J* = 4.0 Hz, 1 H, C*H*N, H2), 4.88 (d, *J* = 6.2 Hz, 1 H, N*H*), 6.75 (d, *J* = 8.6 Hz, 2 H, 2 C*H* arom., H7, H8), 7.05 (d, *J* = 8.6 Hz, 2 H, 2 C*H* arom., H5, H6) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.4 [3 *C*H_3, $NCO_2C(CH_3)_3$], 36.5 (*C*H_2, Ar*C*H_2, C3), 53.8 (*C*H, *C*HN, C2), 55.2 (*C*H_3, ArO*C*H_3), 63.9 (*C*H_2, *C*H_2OH, C1), 79.6 [*C* quat., $NCO_2C(CH_3)_3$], 113.9 (2 *C*H arom., C7, C8), 129.9 (*C* quat., arom., *ipso* to C3 in Ar gp., C4), 130.3 (2 *C*H arom., C5, C6), 156.3 (*C* quat., *N*-Boc *C*=O), 158.2 (*C* quat., arom., *ipso* to OCH_3 in Ar gp., C9) ppm. MS (FAB): *m*/*z* = 282.1710. $C_{15}H_{24}NO_4$ [M + H]$^+$ calcd. 282.1705.

(2*S*)-1-Acetoxy-2-*tert*-butyloxycarbonylamino-3-(4-methoxyphenyl)-propane:[18] (2*S*)-2-(*tert*-butyloxycarbonylamino)-3-(4-methoxyphenyl)propan-1-ol (4.80 g, 17.06 mmol) was dissolved in dichloromethane (50 mL), and the solution cooled to 0 °C. Acetic anhydride (1.94 mL, 20.60 mmol), *N*,*N*-diisopropylamine (3.60 mL, 20.60 mmol) and 4-(dimethylamino)pyridine (0.21 g, 1.72 mmol) were added. The reaction mixture was stirred at room temperature for 16 h. 1% aqueous HCl (40 mL) was added. The organic phase was separated and washed with 1% HCl (2 × 40 mL) and brine (2 × 40 mL). The organic solution was dried (Na_2SO_4) and the solvent removed under reduced pressure to yield a red oil (5.20 g, 94%). $[\alpha]_D^{20}$ = –8.8 (*c* = 1.00, $CHCl_3$). IR (film): ṽmax = 3360 (NH), 2973, 1706 (C=O), 1612, 1511, 1456, 1368, 1242, 1169, 1040, 916, 821, 735 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.34 [s, 9 H, $NCO_2C(CH_3)_3$], 2.00 (s, 3 H, CH_2-O-COCH_3), 2.63–2.74 (m, 2 H, Ar-CH_2, H3), 3.69 (s, 3 H, ArOCH_3), 3.92–3.96 (m, 3 H, C*H*N, H2 and NCHCH_2-O, H1), 4.58 (d, *J* = 6.8 Hz, 1 H, N*H*), 6.75 (d, *J* = 8.6 Hz, 2 H, 2 C*H* arom., H7, H8), 7.02 (d, *J* = 8.6 Hz, 2 H, 2 C*H* arom., H5, H6) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.9 (*C*H_3, O-CO-*C*H_3), 28.3 [3 *C*H_3, $NCO_2C(CH_3)_3$], 37.0 (*C*H_2, Ar*C*H_2, C3), 50.7 (*C*H, *C*HN, C2), 55.2 (*C*H_3, ArO*C*H_3), 65.0 (*C*H_2, NCH-*C*H_2-O, C1), 79.5 [*C* quat., $NCO_2C(CH_3)_3$], 114.0 (2 *C*H arom., C7, C8), 129.2 (*C* quat., arom., *ipso* to C3 in Ar gp., C4), 130.2 (2 *C*H arom., C5, C6), 155.3 (*C* quat., *N*-Boc *C*=O), 158.3 (*C* quat., arom., *ipso* to OCH_3 in Ar gp., C9), 170.9 (*C* quat., C=O); MS (EI): *m*/*z* = 323.1738. $C_{17}H_{25}NO_5$ [M^+] calcd. 323.1733 ppm.

(4*R*,5*R*)-4-(Acetoxymethyl)-5-(4-methoxyphenyl)-1,3-oxazolidin-2-one:[18] (2*S*)-1-Acetoxy-2-(*tert*-butyloxycarbonylamino)-3-(4-methoxyphenyl)propane (3.53 g, 10.92 mmol) was dissolved in acetonitrile (80 mL). Solutions of potassium persulfate (5.89 g, 21.83 mmol) in water (70 mL) and copper(II) sulfate (0.35 g, 2.16 mmol) in water (10 mL) were added. The reaction mixture was heated to 70 °C for 2.5 h under nitrogen, cooled to room temperature, and extracted with ethyl acetate (3 × 70 mL). The combined organic extracts were dried (Na_2SO_4), and the solvent removed under reduced pressure to yield a crude yellow oil. Column chromatography with ethyl acetate/petroleum ether (1:1) afforded a colourless solid (1.09 g, 38%); m.p. 99–100 °C. $[\alpha]_D^{20}$ = +55.8 (*c* = 1.29, $CHCl_3$). IR (film): ṽmax = 3328 (NH), 2958, 2839, 1745 (C=O), 1612, 1515, 1376, 1248, 1179, 1037, 917, 833, 732 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.00 (s, 3 H, O-CO-CH_3, H9), 3.72 (s, 3 H, ArOCH_3), 3.89–3.94 (m, 1 H, C*H*N, H4), 4.07 (dd, *J* = 11.5, 5.8 Hz, 1 H, NCH-C*H*H-O, H6), 4.19 (dd, *J* = 11.5, 4.6 Hz, 1 H, NCH-C*H*H-O, H6′), 5.13 (d, *J* = 6.2 Hz, 1 H, ArC*H*, H5),

6.83 (d, J = 8.7 Hz, 2 H, 2 C*H* arom., H13, H14), 6.95 (s, 1 H, N*H*), 7.21 (d, J = 8.7 Hz, 2 H, 2 C*H* arom., H11, H12) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.7 (*C*H$_3$, O-CO-*C*H$_3$, C9), 54.3 (*C*H$_3$, ArO*C*H$_3$), 58.1 (*C*H, *C*HN, C4), 63.4 (*C*H$_2$, NCH-*C*H$_2$-O, C6), 79.0 (*C*H, Ar*C*H, C5), 113.3 (2 *C*H arom., C13, C14), 126.5 (2 *C*H arom., C11, C12), 128.7 (*C* quat., arom., C10), 158.2 (*C* quat., N*C*=O, C2), 159.2 (*C* quat., arom., *ipso* to OCH$_3$ in Ar gp., C14), 169.8 (*C* quat., C=O, C8) ppm. MS (FAB): m/z = 266.1033. $C_{13}H_{16}NO_5$ [M + H]$^+$ calcd. 266.1029.

(4*R*,5*R*)-5-(Formylamino)-4-(4-methoxyphenyl)-2,2-dimethyl-1,3-dioxane:[7] (1*R*,2*R*)-(–)-2-Amino-1-(4-methoxyphenyl)propane-1,3-diol (0.63 g, 3.20 mmol) was dissolved in methanol (20 mL), and methyl formate (0.22 mL, 3.52 mmol) added followed by a solution of sodium methoxide (0.02 mL). The reaction mixture was stirred overnight and the solvent removed under reduced pressure. The crude product was dissolved in acetone (30 mL), and 2,2-dimethoxypropane (5 mL, 31 mmol) and scandium triflate (0.16 g, 0.31 mmol) added. The mixture was stirred overnight and the solvents removed under reduced pressure. The residue was dissolved in ethyl acetate and the solution washed with saturated aqueous sodium hydrogen carbonate (2 × 30 mL) and brine (2 × 30 mL), and dried (Na_2SO_4). The solvents were removed under reduced pressure to yield a crude yellow oil. Column chromatography with ethyl acetate/light petroleum (1:2) afforded the product as a colourless oil (0.75 g, 91%). $[\alpha]_D^{20}$ = –7.3 (c = 1.15, $CHCl_3$); [ref.[6] $[\alpha]_D^{20}$ = –2.7 (c = 1.20, $CHCl_3$)]. IR (film): ṽmax = 3302 (NH), 2988, 2871, 2243, 1673, 1512, 1378, 1247, 1196, 1083, 1036, 953, 836, 733, 628 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.54 (s, 3 H, C*H*$_3$, H7or H8), 1.58 (s, 3 H, C*H*$_3$, H7 or H8), 3.78 (s, 3 H, ArOC*H*$_3$), 3.87 (dd, J = 10.3, 1.8 Hz, 1 H, NCHC*H*H-O, H6), 4.23–4.27 (m, 2 H, NC*H*, H5 and NCHCH*H*-O, H6′), 5.16 (s, 1 H, Ar-C*H*, H4), 6.39 (d, J = 9.1 Hz, 1 H, N*H*), 6.87 (d, J = 8.7 Hz, 2 H, 2 C*H* arom., H12, H13), 7.23 (d, J = 8.7 Hz, 2 H, 2 C*H* arom., H10, H11), 7.97 (s, 1 H, NC*H*O) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.6 (*C*H$_3$, C7 or C8), 29.7 (*C*H$_3$, C7 or C8), 45.5 (*C*H, N*C*H, C5), 55.2 (*C*H$_3$, ArO*C*H$_3$), 64.6 (*C*H$_2$, C6), 71.4 (Ar-*C*H, C4), 99.7 (*C* quat., C2), 113.7 (2 *C*H arom., C12, C13), 126.5 (2 *C*H arom., C10, C11), 130.2 (*C* quat., arom., C9), 159.0 (*C* quat., arom., C14), 160.7 (N*C*HO, C15); MS (EI): m/z = 265.1318. $C_{14}H_{19}NO_4$ [M$^+$] calcd. 265.1314 ppm.

(4*R*,5*R*)-5-Amino-4-(4-methoxyphenyl)-2,2-dimethyl-1,3-dioxane:[7] (4*R*,5*R*)-5-(Formylamino)-4-(4-methoxyphenyl)-2,2-dimethyl-1,3-dioxane (0.49 g, 1.84 mmol) was dissolved in aqueous hydrazine hydrate (85%) (15 mL), and the solution heated under reflux for 3 h. The solution was cooled to room temperature and extracted with ethyl acetate (3 × 30 mL). The combined organic extracts were washed with water (2 × 30 mL) and brine (2 × 30 mL), and dried (Na_2SO_4), and the solvents were removed under reduced pressure to give the product as a colourless oil (0.41 g, 95%). $[\alpha]_D^{20}$ = –39.6 (c = 1.00, $CHCl_3$); [ref.[6] $[\alpha]_D^{20}$ = –28.9 (c = 1.08, $CHCl_3$)]. IR (film): ṽmax = 3372 (NH), 2987, 2937, 1609, 1512, 1458, 1375, 1246, 1192, 1046, 944, 860, 802 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.46 (s, 3 H, C*H*$_3$, H7 or H8), 1.48 (s, 3 H, C*H*$_3$, H7 or H8), 2.63 (dd, J = 3.8, 1.8 Hz, 1 H, NC*H*, H5), 3.74 (s, 3 H, ArOC*H*$_3$), 3.83 (dd, J = 11.7, 1.8 Hz, 1 H, NCHC*H*H-O, H6), 4.22 (dd, J = 11.7, 2.3 Hz, 1 H, NCHCH*H*-O, H6′), 4.99 (d, J = 1.6 Hz, 1 H, Ar-C*H*, H4), 6.85 (d, J = 8.9 Hz, 2 H, 2 C*H* arom., H12, H13), 7.18 (d, J = 8.9 Hz, 2 H, 2 C*H* arom., H10, H11) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.6 (*C*H$_3$, C7 or C8), 29.8 (*C*H$_3$, C7 or C8), 49.8 (*C*H, N*C*H, C5), 55.3 (*C*H$_3$, ArO*C*H$_3$), 66.0 (*C*H$_2$, C6), 73.5 (Ar-*C*H, C4), 99.2 (*C* quat., C2), 113.9 (2 *C*H arom., C10, C11), 126.9 (2 *C*H arom., C12, C13), 131.7 (*C* quat., arom., C9), 158.9 (*C* quat., arom., C14). MS (FAB): m/z = 238.1448. $C_{13}H_{20}NO_3$ [M + H]$^+$ calcd. 238.1443.

General Procedure for the Formation of Formyl-Protected 5-Amino-1,3-dioxanes from Amino Diols: The amino diol was dissolved in methanol (10 mL/g of aminodiol), and methyl formate (1.1 equiv.) and sodium methoxide (0.1 equiv.) were added. The mixture was stirred for 3.5 h and the solvent removed under reduced pressure. The crude yellow oil was dissolved with in acetone (50 mL/g of aminodiol), and 2,2-dimethoxypropane (10.0 equiv.) and camphorsulfonic acid (0.1 equiv.) were added. The mixture was stirred for up to 4 h and monitored by TLC. The solvents were removed under reduced pressure, and the residue was re-dissolved in ethyl acetate. The solution was washed with saturated aqueous sodium hydrogen carbonate (2 × 20 mL/g of aminodiol) and brine (2 × 20 mL/g of aminodiol), dried ($MgSO_4$), and the solvents were removed under reduced pressure.

(4*S*,5*S*)-5-(Formylamino)-2,2-dimethyl-4-phenyl-1,3-dioxane:[19] Prepared according to the general procedure from (1*S*,2*S*)-(+)-2-amino-1-phenylpropane-1,3-diol (5.00 g, 29.90 mmol). The product was isolated as a colourless oil (6.61 g, 94%). IR (film): ṽmax = 3295, 2990, 1668, 1505, 1381, 1200, 1089, 844, 700 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.49 (s, 3 H, C*H*$_3$, H7 or H8), 1.53 (s, 3 H, C*H*$_3$, H7 or H8), 3.80 (dd, J = 10.4, 1.6 Hz, 1 H, NCHC*H*H-O, H6), 4.19 (dd, J = 10.4, 1.6 Hz, 1 H, NCHC*H*H-O, H6′), 4.23 (s, 1 H, NC*H*, H5), 5.14 (s, 1 H, ArC*H*, H4), 7.16–7.28 (m, 5 H, 5 C*H* arom., Ph gp.), 7.89 (s, 1 H, NC*H*O) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.5 (*C*H$_3$, C7 or C8), 28.7 (*C*H$_3$, C7 or C8), 44.4 (*C*H, N*C*H, C5), 63.6 (*C*H$_2$, C6), 70.6 (Ar-*C*H, C4), 98.9 (*C* quat., C2), 124.2 (2 *C*H arom., C10, C11), 126.7 (*C*H arom., C14), 127.3 (2 *C*H arom., C12, C13), 137.0 (*C* quat., arom., C9), 159.5 (N*C*HO, C15) ppm.

(4*S*,5*S*)-5-(Formylamino)-2,2-dimethyl-4-(4-nitrophenyl)-1,3-dioxane:[7] Prepared according to the general procedure from (1*S*,2*S*)-(+)-2-amino-1-(4-nitrophenyl)propane-1,3-diol (3.00 g, 14.14 mmol). The product was isolated as a colourless oil (3.72 g, 94%). $[\alpha]_D^{20}$ = +7.0 (c = 1.43, $CHCl_3$); [ref.[6] $[\alpha]_D^{20}$ = +3.5 (c = 1.02, $CHCl_3$)]. IR (film): ṽmax = 2992, 1684, 1601, 1521, 1382, 1346, 1270, 1199, 1086, 856, 735 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.48 (s, 3 H, C*H*$_3$, H7 or H8), 1.54 (s, 3 H, C*H*$_3$, H7 or H8), 3.77 (dd, J = 12.2, 1.8 Hz, 1 H, NCHC*H*H-O, H6), 4.26 (dd, J = 12.2, 1.8 Hz, 1 H, NCHCH*H*-O, H6′), 4.35 (dd, J = 9.8, 1.8 Hz, 1 H, NC*H*, H5), 5.22 (d, J = 1.8 Hz, 1 H, ArC*H*, H4), 6.36 (d, J = 9.8 Hz, 1 H, N*H*), 7.44 (d, J = 8.9 Hz, 2 H, 2 C*H* arom., H12, H13), 7.86 (s, 1 H, NC*H*O), 8.12 (d, J = 8.9 Hz, 2 H, 2 C*H* arom., H10, H11) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.5 (*C*H$_3$, C7 or C8), 29.6 (*C*H$_3$, C7 or C8), 45.1 (*C*H, N*C*H, C5), 66.3 (*C*H$_2$, C6), 71.6 (Ar-*C*H, C4), 100.1 (*C* quat., C2), 123.7 (2 *C*H arom., C12, C13), 126.8 (*2 C*H arom., C10,11), 145.5 (*C* quat., arom., C9), 147.5 (*C* quat., arom., C14), 163.0 (N*C*HO, C15) ppm. MS (ESI): m/z = 298.1399. $C_{13}H_{20}N_3O_5$ [M + NH$_4$]$^+$ calcd. 298.1403.

(4*S*,5*S*)-5-(Formylamino)-2,2-dimethyl-4-[4-(methylthio)phenyl]-1,3-dioxane:[7] Prepared according to the general procedure from (1*S*,2*S*)-(+)-2-amino-1-(4-methylthiophenyl)-1,3-propandiol (5.00 g, 23.4 mmol). Colourless oil (5.50 g, 84%). $[\alpha]_D$ = +1.3 , c 1.27, $CHCl_3$). IR (film): ṽmax = 3315, 2988, 2362, 1667, 1494, 1380, 1197, 1084, 947. ^{1}H NMR (250 MHz. $CDCl_3$): δ = 1.54 (s, 3 H), 1.58 (s, 3 H), 2.45 (s, 3 H), 3.87 (dd, J = 7.5, 1.0 Hz, 1 H), 4.24 (dd, J = 7.5, 1.0 Hz, 1 H), 4.21–4.33 (m, 1 H), 5.16 (d, J = 1.3 Hz, 1 H), 6.27 (d, J = 5.8 Hz, 1 H), 7.20 (s, 4 H), 7.97 (s, 1 H) ppm. ^{13}C NMR (100 MHz. $CDCl_3$): δ = 15.8, 18.5, 29.7, 45.3, 64.6, 71.4, 99.7, 125.8, 126.6, 135.0, 137.8, 160.5; MS: m/z = 281.1081. $C_{14}H_{19}NO_3S$ [M$^+$] calcd. 281.1086 ppm.

(4*S*,5*S*)-5-(Formylamino)-2,2-dimethyl-4-[4-(methylsulfonyl)phenyl]-1,3-dioxane:[6] (4*S*,5*S*)-5-(Formylamino)-2,2-dimethyl-4-[4-(methylthio)phenyl]-1,3-dioxane (4.00 g, 14.2 mmol) was dissolved in dichloromethane (100 mL), and the solution cooled to 0 °C. A solution of *m*CPBA (2.2 eq, 7.03 g, 31.0 mmol) in chloroform (20 mL) was added dropwise over 10 min. The reaction was stirred for 2 h, washed with saturated aqueous sodium hydrogen carbonate (2 × 40 mL) and brine (2 × 40 mL), and dried ($MgSO_4$). The solvents were removed under reduced pressure to give a colourless oil. Crystallization from chloroform/diethyl ether gave the product as a colourless crystalline solid (3.80 g, 85%); m.p. 146–147 °C. $[\alpha]_D$ = –11.6 (*c* = 1.21, $CHCl_3$). IR (film): ṽmax = 3054, 2993, 1675, 1516, 1382, 1300, 1239, 1202, 1149, 1086, 948 cm^{-1}. $C_{14}H_{19}NO_5S$ (313.37): calcd. C 53.66, H 6.11, N 4.47; found C 52.68, H 6.12, N 4.33. ^1H NMR (400 MHz. $CDCl_3$): δ = 1.54 (s, 3 H), 1.57 (s, 3 H), 3.01 (s, 3 H), 3.82 (dd, *J* = 12.0, 2.0 Hz, 1 H), 4.33 (dd, *J* = 12.0, 1.6 Hz, 1 H), 4.37 (dd, *J* = 10.0, 1.6 Hz, 1 H), 5.25 (s, 1 H), 6.51 (d, *J* = 9.2 Hz, 1 H), 7.52 (d, *J* = 8.0 Hz, 2 H), 7.85 (d, *J* = 8.0 Hz, 2 H), 7.89 (s, 1 H) ppm. ^{13}C NMR (100 MHz. $CDCl_3$): δ = 18.9, 29.9, 44.8, 45.4, 64.9, 71.9, 100.4, 127.0, 127.5, 140.0, 145.0, 160.9. MS: *m*/*z* = 314.1058. $C_{14}H_{20}NO_5S$ [M⁺+H] calcd. 314.1062 ppm.

General Procedure for the Deprotection of Formamides with Hydrazine Hydrate: The formyl-protected acetonide was dissolved in aqueous hydrazine hydrate (85%) (20 mL/g of acetonide) and the solution heated under reflux for 3 h. The solution was allowed to reach ambient temperature and extracted with ethyl acetate (3 × 30 mL/g of acetonide). The combined organic layers were washed with water (2 × 30 mL/g of acetonide) and brine (2 × 30 mL/g of acetonide), dried (Na_2SO_4), and the solvents were removed under reduced pressure.

(4*S*,5*S*)-5-Amino-2,2-dimethyl-4-phenyl-1,3-dioxane:[19] Prepared according to the general procedure from (4*S*,5*S*)-5-(formylamino)-4-phenyl-2,2-dimethyl-1,3-dioxane (6.58 g, 28.1 mmol). The product was isolated as a yellow oil (5.39 g, 87% yield). $[\alpha]_D^{20}$ = +45.5 (*c* = 2.33, ethanol). IR (film): ṽmax = 3365 (NH), 2990, 1663, 1498, 1379, 1271, 1239, 1198, 1159, 1130, 1087, 1052, 945, 845, 740, 701 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.44 (s, 6 H, 2 C*H*$_3$), 2.64 (dd, *J* = 4.0, 2.0 Hz, 1 H, NC*H*, H5), 3.79 (dd, *J* = 12.0, 2.0 Hz, 1 H, NCHC*H*H-O, H6), 4.18 (dd, *J* = 12.0, 2.0 Hz, 1 H, NCHCH*H*-O, H6′), 4.98 (s, 1 H, PhC*H*, H4), 7.16–7.29 (m, 5 H, 5 C*H* arom., Ph gp.) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.6 (*C*H$_3$, C7 or C8), 29.7 (*C*H$_3$, C7 or C8), 49.6 (*C*H, NCH, C5), 65.9 (*C*H$_2$, C6), 73.7 (Ar-*C*H, C4), 95.0 (*C* quat., C2), 125.7 (2 *C*H arom., C10, C11), 127.4 (*C*H arom., C14), 128.4 (2 *C*H arom., C12, C13), 139.8 (*C* quat., arom., C9) ppm.

(4*S*,5*S*)-5-Amino-2,2-dimethyl-4-(4-nitrophenyl)-1,3-dioxane:[7] Prepared according to the general procedure from (4*S*,5*S*)-5-(formylamino)-2,2-dimethyl-4-(4-nitrophenyl)-1,3-dioxane (1.00 g, 3.57 mmol) except in that the reaction mixture was heated under reflux for 1 h. Column chromatography using ethyl acetate as an eluent gave a yellow oil (0.54 g, 60%). $[\alpha]_D^{20}$ = +91.6 (*c* = 0.83, $CHCl_3$); [ref.[6] $[\alpha]_D^{20}$ = +66.2 (*c* = 1.13, $CHCl_3$)]. IR (film): ṽmax = 3373 (NH), 2991, 2939, 1600, 1518, 1380, 1347, 1271, 1239, 1198, 1158, 1078, 946, 856 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.49 (s, 6 H, 2 C*H*$_3$, H7 H8), 2.79 (dd, *J* = 3.9, 2.0 Hz, 1 H, NC*H*, H5), 3.81 (dd, *J* = 12.3, 1.8 Hz, 1 H, NCHC*H*H-O, H6), 4.26 (dd, *J* = 12.3, 2.2 Hz, 1 H, NCHCH*H*-O, H6′), 5.12 (d, *J* = 1.6 Hz, 1 H, Ar-C*H*, H4), 7.44 (d, *J* = 10.5 Hz, 2 H, 2 C*H* arom., H12, H13), 8.16 (d, *J* = 10.5 Hz, 2 H, 2 C*H* arom., H10, H11) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.6 (*C*H$_3$, C7 or C8), 29.7 (*C*H$_3$, C7 or C8), 49.4 (*C*H, NCH, C5), 66.3 (*C*H$_2$, C6), 73.4 (Ar-*C*H, C4), 99.5 (*C* quat., C2), 123.6 (2 *C*H arom., C10, C11), 126.4 (2 *C*H arom., C12, C13), 147.2 (*C* quat., arom., C9), 147.3 (*C* quat., arom., C14) ppm. MS (FAB): *m*/*z* = 253.1186. $C_{12}H_{17}N_2O_4$ [M + H]⁺ calcd. 253.1188.

(4*S*,5*S*)-5-Amino-4-(4-aminophenyl)-2,2-dimethyl-1,3-dioxane: Prepared according to the general procedure from (4*S*,5*S*)-5-(formylamino)-4-(4-aminophenyl)-2,2-dimethyl-1,3-dioxane (2.0 g, 7.14 mmol). The product was obtained as a yellow oil (1.55 g, 98%). $[\alpha]_D^{20}$ = +62.0 (*c* = 1.13, $CHCl_3$). IR (film): ṽmax = 3361 (NH), 2990, 2939, 1614, 1518, 1380, 1272, 1239, 1198, 1157, 1127, 1050, 948, 849, 813 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.45 (s, 3 H, C*H*$_3$, H7 or H8), 1.46 (s, 3 H, C*H*$_3$, H7 or H8), 2.61 (dd, *J* = 2.3, 1.8 Hz, 1 H, NC*H*, H5), 2.67 (s, 4 H, 4 N*H*), 3.82 (dd, *J* = 12.8, 2.3 Hz, 1 H, NCHC*H*H-O, H6), 4.19 (dd, *J* = 12.8, 2.3 Hz, 1 H, NCHCH*H*-O, H6′), 4.93 (d, *J* = 1.8 Hz, 1 H, Ar-C*H*, H4), 6.64 (d, *J* = 8.5 Hz, 2 H, 2 C*H* arom., H12, H13), 7.03 (d, *J* = 8.5 Hz, 2 H, 2 C*H* arom., H10, H11) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.6 (*C*H$_3$, C7 or C8), 29.8 (*C*H$_3$, C7 or C8), 49.7 (*C*H, NCH, C5), 65.7 (*C*H$_2$, C6), 73.5 (Ar-*C*H, C4), 99.2 (*C* quat., C2), 115.1 (2 *C*H arom., C12, C13), 126.7 (2 *C*H arom., C10, C11), 129.3 (*C* quat., arom., C9), 145.8 (*C* quat., arom., C14) ppm. MS (FAB): *m*/*z* = 223.1445. $C_{12}H_{19}N_2O_2$ [M + H]⁺ calcd. 223.1441.

(4*S*,5*S*)-5-Amino-2,2-dimethyl-4-[4-(methylsulfonyl)phenyl]-1,3-dioxane:[7] Prepared according to the general procedure from (4*S*,5*S*)-5-(formylamino)-2,2-dimethyl-4-[4-(methylsulfonyl)phenyl]-1,3-dioxane (1.80 g, 5.8 mmol), isolated as a colourless oil, and crystallized from diethyl ether/ethyl acetate. Colourless crystals (1.59 g, 96%); m.p. 120–122 °C. $[\alpha]_D^{20}$ = +50.0 (*c* = 1.00, $CHCl_3$). $C_{13}H_{19}NO_4S$ (285.36): calcd. C 54.72, H 6.71, N 4.91; found C 54.64, H 6.69, N 4.83. IR (film): ṽmax = 3372, 2991, 1601, 1380, 1198, 1077, 949 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.56 (s, 6 H), 2.82–3.00 (m, 1 H), 3.06 (s, 3 H), 3.88 (dd, *J* = 11.6, 2.0 Hz, 1 H), 3.24 (dd, *J* = 11.6, 2.4 Hz, 1 H), 5.10–5.19 (m, 1 H), 7.55 (d, *J* = 8.0 Hz, 2 H), 7.95 (d, *J* = 8.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.0, 30.0, 44.9, 49.8, 66.8, 73.9, 99.9, 127.2, 127.9, 139.9, 146.6. MS: *m*/*z* = 285.1028. $C_{13}H_{19}NO_4S$ [M⁺] calcd. 285.1035 ppm.

(4*S*,5*S*)-5-Amino-2,2-dimethyl-4-[4-(methylthio)phenyl]-1,3-dioxane:[7] Prepared according to the general procedure from (4*S*,5*S*)-5-(formylamino)-2,2-dimethyl-4-[4-(methylthio)phenyl]-1,3-dioxane (1.50 g, 5.34 mmol). Colourless oil (1.28 g, 95%). $[\alpha]_D^{20}$ = +44.7 (*c* = 1.20, $CHCl_3$). IR (film): ṽmax = 3369, 2990, 1599, 1495, 1379, 1198, 1076, 947 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.53 (s, 3 H), 1.54 (s, 3 H), 2.47 (s, 3 H), 2.72 (q, *J* = 2.0 Hz, 1 H), 3.88 (dd, *J* = 12.0, 2.0 Hz, 1 H), 4.27 (dd, *J* = 12.0, 2.4 Hz, 1 H), 5.05 (d, *J* = 1.6 Hz, 1 H), 7.23–7.28 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.0, 18.6, 29.7, 49.6, 66.1, 73.5, 99.2, 126.4, 126.8, 136.6, 137.4. MS: *m*/*z* = 253.1137. $C_{13}H_{19}NO_2S$ [M⁺] calcd. 253.1137 ppm.

General Procedure for the Synthesis of Binaphthalene-Derived Iminium Salt Catalysts from (*R*)- or (*S*)-2′-Bromomethyl-1,1′-binaphthalene-2-carboxaldehyde (*R*)-8 or (*S*)-8 and Primary Amines: A solution of the amine in ethanol (10 mL/g of amine) was added dropwise to a solution of (*R*) or (*S*)-2′-bromomethyl-1,1′-binaphthalene-2-carboxaldehyde (*R*)-**8** or (*S*)-**8** (1.10 equiv. wrt amine) in ethanol (10 mL/g of carboxaldehyde) at 40 °C, and the mixture stirred at 40 °C overnight. The yellowish mixture was cooled to room temperature, and a solution of sodium tetraphenylborate (1.10 equiv.) in the minimum amount of acetonitrile added in one portion. The reaction mixture was stirred for 5 min. The solvents were removed under reduced pressure, the yellow residue was dissolved in dichloromethane (40 mL/g of amine), and the solution washed with water (2 × 30 mL/g of amine) and brine (2 × 30 mL/g of amine), and dried

(Na_2SO_4). The solvents were removed in vacuo. The yellow solid was recrystallized from ethanol, washed with cold ethanol followed by hexanes, and dried at 90 °C.

(R_{ax})-*N*-[(4*S*,5*S*)-2,2-Dimethyl-4-phenyl-1,3-dioxan-5-yl]-7*H*-dinaphtho[2,1-*c*;1′,2′-*e*]azepinium Tetraphenylborate (6): Prepared according to the general procedure from (+)-(4*S*,5*S*)-5-amino-2,2-dimethyl-4-phenyl-1,3-dioxane (0.15 g, 0.72 mmol). The product was isolated as yellow plates (0.39 g, 66%); m.p. 111–113 °C (dec.). $[\alpha]_D^{20}$ = –98.5 (*c* = 1.04, acetone). $C_{58}H_{50}BNO_2 \cdot 1.0H_2O$: calcd. C 84.73, H 6.13, N 1.71; found C 84.44, H 5.97, N 1.71. IR (film): ṽmax = 3055, 2986, 1626, 1610, 1593, 1548, 1478, 1450, 1382, 1266, 1203, 1110, 846, 817, 735, 704 cm^{-1}. ^1H NMR (400 MHz, [D$_6$]acetone): δ = 1.79 (s, 3 H), 1.85 (s, 3 H), 4.43 (d, *J* = 13.2 Hz, 1 H), 4.51 (d, *J* = 13.6 Hz, 1 H), 4.84–4.88 (m, 2 H), 5.96–6.00 (m, 2 H), 6.76 (t, *J* = 7.2 Hz, 4 H), 6.93 (t, *J* = 7.6 Hz, 8 H), 6.95–7.10 (m, 5 H), 7.18–7.32 (m, 2 H), 7.30–7.38 (m, 8 H), 7.41–7.49 (m, 3 H), 7.45–7.65 (m, 2 H), 7.75–7.83 (m, 1 H), 7.88 (d, *J* = 8.4 Hz, 1 H), 8.10 (d, *J* = 8.4 Hz, 1 H), 8.17 (d, *J* = 8.4 Hz, 1 H), 8.23 (dd, *J* = 8.4, 2.4 Hz, 1 H), 9.29 (s, 1 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]-acetone): δ = 19.3, 29.7, 57.0, 62.3, 68.4, 72.9, 102.1, 120.5, 122.7, 126.33, 126.4, 126.6, 127.3, 128.1, 128.2, 128.4, 129.1, 129.2, 129.9, 130.0, 130.1, 130.6, 130.7, 131.7, 132.2, 132.6, 132.9, 133.3, 135.3, 136.6, 137.4, 142.8, 165.3, 171.4 ppm. MS (FA$^+$): *m*/*z* (%) = 484 (100) [M$^+$], 320 (76), 293 (72), 277 (69), 265 (79), 252 (49), 165 (44), 133 (41). $C_{34}H_{30}NO_2$ (cation): calcd. 484.2271; found 484.2275.

(S_{ax})-*N*-[(4*R*,5*R*)-2,2-Dimethyl-4-phenyl-1,3-dioxan-5-yl]-7*H*-dinaphtho[2,1-*c*;1′,2′-*e*]azepinium Tetraphenylborate (*ent*-6): Prepared according to the general procedure from (–)-(4*R*,5*R*)-5-amino-2,2-dimethyl-4-phenyl-1,3-dioxane (0.16 g, 0.77 mmol). The product was isolated as yellow plates (0.40 g, 64%), having almost identical spectroscopic data to **6**; m.p. 109–112 °C (dec.). $[\alpha]_D^{20}$ = +95.3 (*c* = 1.01, acetone).

(S_{ax})-*N*-[(4*S*,5*S*)-2,2-Dimethyl-4-phenyl-1,3-dioxan-5-yl]-7*H*-dinaphtho[2,1-*c*;1′,2′-*e*]azepinium Tetraphenylborate 17:[6] Prepared according to the general procedure from (+)-(4*S*,5*S*)-5-amino-2,2-dimethyl-4-phenyl-1,3-dioxane (0.20 g, 0.97 mmol). The product was isolated as yellow plates (0.50 g, 64%); m.p. 218 °C (dec.). $[\alpha]_D^{20}$ = +360.4 (*c* = 1.10, acetone). $C_{58}H_{50}BNO_2 \cdot 1.0H_2O$: calcd. C 84.73, H 6.13, N 1.71; found C 84.33, H 6.06, N 1.64. IR (film): ṽmax = 3054, 2998, 1626, 1609, 1579, 1545, 1477, 1458, 1383, 1266, 1201, 1110, 840, 817, 733, 704 cm^{-1}. ^1H NMR (250 MHz; [D$_6$]acetone): δ = 1.72 (s, 3 H), 1.78 (s, 3 H), 4.23 (d, *J* = 13.4 Hz, 1 H), 4.31 (d, *J* = 13.9 Hz, 1 H), 4.73 (dd, *J* = 13.8, 3.0 Hz, 1 H), 4.90 (br. s, 1 H), 5.35 (d, *J* = 13.5 Hz, 1 H), 5.86 (d, *J* = 2.3 Hz, 1 H) 6.76 (t, *J* = 7.1 Hz, 4 H), 6.93 (t, *J* = 7.1 Hz, 8 H), 6.90–6.95 (m, 5 H), 7.17–7.25 (m, 8 H), 7.26–7.33 (m, 3 H), 7.40–7.48 (m, 1 H), 7.54–7.62 (m, 1 H), 7.72–7.82 (m, 1 H), 7.93 (dd, *J* = 8.6, 2.2 Hz, 2 H), 8.13 (d, *J* = 7.9 Hz, 1 H), 8.17 (d, *J* = 8.4 Hz, 1 H), 8.29 (dd, *J* = 8.6, 5.3 Hz, 2 H), 9.30 (s, 1 H) ppm. ^{13}C NMR (100 MHz; [D$_6$]acetone): δ = 19.1, 29.8, 57.3, 61.3, 67.0, 71.5, 100.6, 115.6, 121.9, 125.5, 125.7, 126.5, 126.9, 127.0, 127.3, 127.8, 127.9, 128.1, 128.7, 128.9, 129.3, 129.5, 130.6, 130.9, 131.1, 131.2, 132.0, 133.4, 133.7, 134.4, 141.1, 163.8, 170.8 ppm. MS (FAB$^+$): *m*/*z* (%) = 484 (100) [M$^+$], 320 (35), 292 (35), 277 (62), 265 (84), 252 (25), 165 (15), 133 (25). $C_{34}H_{30}NO_2$ (cation): calcd. 484.2271; found 484.2282.

(R_{ax})-*N*-[(4*S*,5*S*)-2,2-Dimethyl-4-(4-methylsulfonylphenyl)-1,3-dioxan-5-yl]-7*H*-dinaphtho[2,1-*c*;1′,2′-*e*]azepinium Tetraphenylborate (21): Prepared according to the general procedure from (4*S*,5*S*)-5-amino-4-(4-methylsulfonylphenyl)-2,2-dimethyl-1,3-dioxane (0.54 g, 1.89 mmol). The product was isolated as a yellow powder (1.08 g, 65%); m.p. 159–163 °C (dec.). $[\alpha]_D^{20}$ = –283.7 (*c* = 0.86, acetone). $C_{59}H_{52}BNO_4 \cdot H_2O$: calcd. C 78.74, H 6.04, N 1.56; found C 78.89, H 5.78, N 1.50. IR (film): ṽmax = 3050, 2953, 1617, 1532, 1512, 1461, 1376, 1301, 1248, 1203, 1098, 1030, 963, 818, 735 cm^{-1}. ^1H NMR (400 MHz, [D$_6$]acetone): δ = 1.70 (s, 3 H, CH_3, H7 or H8), 1.76 (s, 3 H, CH_3, H7 or H8), 2.85 (s, 3 H, SO_2CH_3), 4.30 (d, *J* = 13.8 Hz, 1 H, NCHC*H*HO, H6), 4.42 (d, *J* = 13.7 Hz, 1 H, ArC*H*HN), 4.75 (dd, *J* = 13.8, 3.2 Hz, 1 H, NCHCH*H*O, H6′), 4.82 (t, *J* = 3.2 Hz, 1 H, NC*H*, H5), 6.03 (br. s, 1 H, ArCH*H*N), 6.06 (d, *J* = 3.2 Hz, 1 H, ArC*H*, H4), 6.60–6.64 (m, 4 H, 4 C*H* arom., *para* in BPh_4 gp.), 6.87 (t, *J* = 7.3 Hz, 8 H, 8 C*H* arom., *ortho* in BPh_4 gp.), 6.87 (d, *J* = 8.7 Hz, 1 H, 2 C*H* arom., *binap*), 7.12–7.21 (m, 9 H, C*H* arom., *binap* and 8 C*H* arom., *meta* in BPh_4 gp.), 7.33–7.35 (m, 3 H, 3 C*H* arom., *binap*), 7.43 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1 H, *binap*), 7.61–7.69 (m, 5 H, 5 C*H* arom., *binap* and H10, H11, H12, H13), 7.82 (d, *J* = 8.5 Hz, 1 H, *binap*), 7.97 (d, *J* = 8.3 Hz, 1 H, *binap*), 8.05 (d, *J* = 8.4 Hz, 1 H, *binap*), 8.08 (d, *J* = 8.6 Hz, 1 H, *binap*), 8.14 (d, *J* = 8.6 Hz, 1 H, *binap*), 9.06 (s, 1 H, *H*C=N) ppm. ^{13}C NMR (100 MHz, [D$_6$]acetone): δ = 18.2 (*C*H$_3$, C7 or C8), 29.1 (*C*H$_3$, C7 or C8), 43.4 (*C*H$_3$, SO_2*C*H$_3$), 56.4 (*C*H$_2$, Ar*C*H$_2$N), 61.1 (*C*H$_2$, NCH*C*H$_2$O, C6), 66.9 (*C*H, N*C*H, C5), 71.5 (*C*H, Ar*C*H, C4), 101.1 (*C* quat., C2), 121.5 (4 *C*H arom., *para* in BPh_4 gp.), 125.0 (*C*H arom., *binap*), 125.1 (*C*H arom., *binap*), 125.21 (*C*H arom., *binap*), 125.26 (8 *C*H arom., *ortho* in BPh_4 gp.), 126.0 (*C* quat., arom.), 126.5 (2 *C*H arom., C12, C13), 126.8 (*C*H arom., *binap*), 127.1 (*C*H arom., *binap*), 127.3 (*C*H arom., *binap*), 127.9 (2 *C*H arom., C10, C11), 128.8 (*C*H arom., *binap*), 128.9 (*C*H arom., *binap*), 129.4 (*C*H arom., *binap*), 129.6 (*C*H arom., *binap*), 130.6 (*C*H arom., *binap*), 131.2 (*C* quat., arom.), 131.4 (*C* quat., arom.), 131.71 (*C*H arom., *binap*), 131.73 (*C* quat., arom.), 133.9 (*C* quat., arom.), 135.5 (*C* quat., arom.), 135.8 (*C* quat., arom.), 136.2 (8 *C*H arom., *meta* in BPh_4 gp.), 141.4 (*C* quat., arom.), 141.8 (*C* quat., arom.), 142.2 (*C* quat., arom.), 164.0 (4 *C* quat., arom., q, *J* = 49.1 Hz, 4 *C*-B *ipso* in BPh_4 gp.), 170.6 (H*C*=N) ppm. MS (ESI): *m*/*z* = 562.2044. $C_{35}H_{32}NO_4S$ (cation): calcd. 562.2047.

(R_{ax})-*N*-[(4*S*,5*S*)-2,2-Dimethyl-4-(4-nitrophenyl)-1,3-dioxan-5-yl]-7*H*-dinaphtho[2,1-*c*;1′,2′-*e*]azepinium Tetraphenylborate (18): Prepared according to the general procedure from (4*S*,5*S*)-5-amino-2,2-dimethyl-4-(4-nitrophenyl)-1,3-dioxane (0.40 g, 1.59 mmol). The product was isolated as a yellow powder (0.93 g, 69%); m.p. 144–146 °C (dec.). $[\alpha]_D^{20}$ = –360.0 (*c* = 1.00, acetone). $C_{58}H_{49}BN_2O_4 \cdot 2H_2O$: calcd. C 78.73, H 6.04, N 3.17; found C 78.21, H 5.55, N 3.17. IR (film): ṽmax = 3052, 2950, 1608, 1523, 1461, 1427, 1382, 1348, 1265, 1237, 1201, 1108, 1031, 851, 819, 735, 705 cm^{-1}. ^1H NMR (400 MHz, [D$_3$]acetonitrile): δ = 1.72 (s, 3 H, CH_3, H7 or H8), 1.82 (s, 3 H, CH_3, H7 or H8), 4.36 (d, *J* = 13.6 Hz, 1 H, NCHC*H*HO, H6), 4.42 (d, *J* = 13.3 Hz, 1 H, ArC*H*HN), 4.52 (t, *J* = 2.6 Hz, 1 H, NC*H*, H5), 4.72 (dd, *J* = 13.6, 2.6 Hz, 1 H, NCHCH*H*O, H6′), 5.15 (br. s, 1 H, ArCH*H*N), 5.79 (d, *J* = 2.6 Hz, 1 H, ArC*H*, H4), 6.60–6.64 (m, 5 H, C*H* arom., *binap* and 4 C*H* arom., *para* in BPh_4 gp.), 7.01 (t, *J* = 7.3 Hz, 8 H, 8 C*H* arom., *ortho* in BPh_4 gp.), 7.18 (ddd, *J* = 8.5, 6.8, 1.3 Hz, 1 H, C*H* arom., *binap*), 7.25–7.37 (m, 12 H, 4 C*H* arom., and 8 C*H* arom., *meta* in BPh_4 gp.), 7.45–7.58 (m, 4 H, 4 C*H* arom.), 7.72–7.800 (m, 2 H, 2 C*H* arom.), 7.95 (d, *J* = 8.1 Hz, 1 H, *binap*), 8.07 (d, *J* = 8.4 Hz, 1 H, *binap*), 8.15 (d, *J* = 8.8 Hz, 1 H, *binap*), 8.23 (d, *J* = 8.6 Hz, 1 H, *binap*), 9.32 (s, 1 H, *H*C=N) ppm. ^{13}C NMR (100 MHz, [D$_3$]acetonitrile): δ = 17.6 (*C*H$_3$, C7 or C8), 28.4 (*C*H$_3$, C7 or C8), 58.9 (*C*H$_2$, Ar*C*H$_2$N), 60.8 (*C*H$_2$, NCH*C*H$_2$O, C6), 65.3 (*C*H, N*C*H, C5), 70.4 (*C*H, Ar*C*H, C4), 101.0 (*C* quat., C2), 121.5 (4 *C*H arom., *para* in BPh_4 gp.), 123.0 (2 *C*H arom., C12, C13), 124.6 (*C*H arom., *binap*), 125.3 (8 *C*H arom., *ortho* in BPh_4 gp.), 125.6 (*C* quat., arom.), 125.7 (2 *C*H arom., C10, C11), 126.2 (*C*H arom., *binap*), 126.7 (*C*H arom., *binap*), 126.8 (*C*H arom., *binap*),

127.4 (*C*H arom., *binap*), 128.1 (*C*H arom., *binap*), 128.3 (*C*H arom., *binap*), 128.9 (*C*H arom., *binap*), 129.2 (*C*H arom., *binap*), 130.0 (*C* quat., arom.), 130.3 (*C*H arom., *binap*), 131.0 (*C* quat., arom.), 131.3 (*C*H arom., *binap*), 131.6 (*C* quat., arom.), 133.1 (*C* quat., arom.), 134.1 (*C* quat., arom.), 134.5 (*C*H arom., *binap*), 135.1 (*C* quat., arom.), 135.4 (8 *C*H arom., *meta* in BPh_4 gp.), 141.5 (*C* quat., arom.), 142.5 (*C* quat., arom.), 146.4 (*C* quat., arom.), 163.5 (q, J = 49.1 Hz, 4 *C* quat., arom., 4 *C*-B *ipso* in BPh_4 gp.), 168.9 (H*C*=N) ppm.

(S_{ax})-*N*-[(4*R*,5*R*)-4-(4-Methoxyphenyl)-2,2-dimethyl-1,3-dioxan-5-yl]-7*H*-dinaphtho[2,1-*c*;1′,2′-*e*]azepinium Tetraphenylborate (20): Prepared according to the general procedure, method 1, from (4*R*,5*R*)-5-amino-4-(4-methoxyphenyl)-2,2-dimethyl-1,3-dioxane (0.30 g, 1.26 mmol). The product was isolated as a yellow powder (0.60 g, 57%); m.p. 199–200 °C (dec.). $[\alpha]_D^{20}$ = +353.5 (c = 0.86, acetone). $C_{59}H_{52}BNO_3$: calcd. C 84.98, H 6.29, N 1.68; found C 84.59, H 6.28, N 1.80. IR (film): ṽmax = 3053, 2969, 1611, 1548, 1512, 1463, 1379, 1305, 1255, 1201, 1110, 1031, 961, 817, 737, 707, 612 cm^{-1}. ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 1.79 (s, 3 H, CH_3, H7 or H8), 1.84 (s, 3 H, CH_3, H7 or H8), 3.57 (s, 3 H, ArOCH_3), 4.41 (d, J = 13.5 Hz, 1 H, NCH-C*H*H-O, H6), 4.54 (d, J = 13.2 Hz, 1 H, ArC*H*H-N), 4.64 (t, J = 3.1 Hz, 1 H, NC*H*, H5), 4.79 (dd, J = 13.5, 3.1 Hz, 1 H, NCH-CH*H*-O, H6′), 5.87–5.88 (m, 2 H, ArC*H*, H4 and ArCH*H*-N), 6.57 (d, J = 8.7 Hz, 2 H, 2 C*H* arom., H12, H13), 6.74–6.79 (m, 4 H, 4 C*H* arom., *para* in BPh_4 gp.), 6.92 (t, J = 7.2 Hz, 8 H, 8 C*H* arom., *ortho* in BPh_4 gp.), 7.00 (d, J = 8.7 Hz, 1 H, C*H* arom., *binap*), 7.19 (d, J = 8.7 Hz, 2 H, 2 C*H* arom., H10, H11), 7.27–7.31 (m, 1 H, C*H* arom., *binap*), 7.33–7.37 (m, 8 H, 8 C*H* arom., *meta* in BPh_4 gp.), 7.43–7.49 (m, 2 H, 2 C*H* arom., *binap*), 7.53–7.61 (m, 2 H, 2 C*H* arom., *binap*), 7.77–7.83 (m, 2 H, 2 C*H* arom., *binap*), 8.11 (dd, J = 8.2, 0.6 Hz, 1 H, C*H* arom., *binap*), 8.20 (dd, J = 8.4, 0.8 Hz, 1 H, C*H* arom., *binap*), 8.23 (d, J = 8.6 Hz, 1 H, C*H* arom., *binap*), 8.26 (d, J = 8.6 Hz, 1 H, C*H* arom., *binap*), 9.09 (s, 1 H, *H*C=N) ppm. ^{13}C NMR (100 MHz, [D$_6$]acetone): δ = 18.9 (*C*H$_3$, C7 or C8), 29.9 (*C*H$_3$, C7 or C8), 55.5 (*C*H$_3$, ArO*C*H$_3$), 58.2 (*C*H$_2$, Ar*C*H$_2$N), 61.9 (*C*H$_2$, NCH-*C*H$_2$-O, C6), 68.3 (*C*H, N*C*H, C5), 72.4 (*C*H, Ar*C*H, C4), 101.6 (*C* quat., C2), 114.8 (2 *C*H arom., C12, C13), 122.3 (4 *C*H arom., *para* in BPh_4 gp.), 126.1 (8 *C*H arom., *ortho* in BPh_4 gp.), 126.3 (2 *C*H arom., C10, C11), 127.1 (*C* quat., arom., *binap-2*), 127.2 (2 *C*H arom., *binap*), 127.7 (*C*H arom., *binap*), 127.8 (*C*H arom., *binap*), 128.1 (*C*H arom., *binap*), 128.7 (*C*H arom., *binap*), 128.9 (*C* quat., arom., C9), 129.65 (*C*H arom., *binap*), 129.70 (*C*H arom., *binap*), 130.2 (*C*H arom., *binap*), 130.3 (*C*H arom., *binap*), 131.4 (*C*H arom., *binap*), 131.8 (*C* quat., arom., *binap-10*), 132.2 (*C* quat., arom., *binap-5′*), 132.5 (*C*H arom., *binap*), 132.8 (*C* quat., arom., *binap-10′*), 134.8 (*C* quat., arom., *binap-5*), 136.3 (*C* quat., arom., *binap-2′*), 136.5 (*C* quat., arom., *binap-1′*), 137.1 (8 *C*H arom., *meta* in BPh_4 gp.), 142.5 (*C* quat., arom., *binap-1*), 160.4 (*C* quat., arom., C14), 164.9 (4 *C* quat., arom., q, J = 49.1 Hz, 4 *C*-B *ipso* in BPh_4 gp.), 170.7 (H*C*=N) ppm. MS (ESI): m/z = 514.2386. $C_{35}H_{32}NO_3$ (cation): calcd. 514.2377.

(–)-(R_{ax})-*N*-[(1*R*,2*R*,3*R*,5*S*)-2,6,6-trimethylbicyclo[3.1.1]hept-3-yl]-7*H*-dinaphtho[2,1-*c*;1′,2′-*e*]azepinium Tetraphenylborate (22):[6] Prepared according to the general procedure from (–)-isopinocampheylamine (0.25 g, 1.6 mmol). The product was isolated as yellow plates (0.82 g, 73%), m.p. 219–221 °C (dec). $[\alpha]_D^{20}$ = –318.8 (c = 1.37, acetone). $C_{48}H_{48}BN{\cdot}0.5H_2O$: calcd. C 88.61, H 6.91, N 1.85; found C 88.22, H 6.81, N 1.79. IR (nujol): ṽ = 3055, 2997, 1629, 1612, 1588, 1551, 1155, 818, 734, 706 cm^{-1}. ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 1.10 (s, 3 H), 1.21 (d, J = 6.8 Hz, 3 H), 1.32 (s, 3 H), 1.53 (d, J = 10.4 Hz, 1 H), 2.01–2.08 (m, 1 H), 2.15–2.17 (m, 1 H) 2.39–2.45 (m, 1 H), 2.63–2.70 (m, 3 H), 4.80 (dd, J = 13.6, 1.2 Hz, 1 H) 5.06 (q, J = 7.6 Hz, 1 H), 5.48 (d, J = 14.0 Hz, 1 H) 6.73 (t, J = 8.0 Hz, 4 H), 6.88 (t, J = 8.0 Hz, 8 H), 7.06 (d, J = 8.4 Hz, 1 H), 7.27 (t, J = 8.0 Hz, 8 H), 7.45–7.49 (m, 3 H), 7.56–7.63 (m, 1 H), 7.77–7.80 (m, 1 H), 7.99 (d, J = 8.8 Hz, 1 H), 8.03 (d, J = 8.4 Hz, 1 H), 8.08 (d, J = 8.4 Hz, 1 H), 8.20 (d, J = 8.4 Hz, 1 H), 8.26 (d, J = 8.4 Hz, 1 H), 8.31 (d, J = 8.4 Hz, 1 H), 9.62 (s, 1 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]acetone): δ = 20.3, 23.9, 28.8, 34.1, 35.2, 40.6, 42.1, 42.6, 48.6, 54.2, 75.6, 122.7, 126.5, 127.2, 127.6, 128.2, 128.3, 128.6, 129.1, 130.0, 130.1, 130.2, 130.6, 130.8, 131.6, 132.8, 132.9, 133.1, 133.3, 135.2, 135.4, 136.7, 137.5, 142.8, 165.4, 170.8 ppm. MS (ES$^+$): m/z = 430 (100) [M$^+$], 355 (30), 154 (15), 119 (13). $C_{32}H_{32}N$ (cation): calcd. 430.2535; found 430.2540.

(+)-(S_{ax})-*N*-[(1*R*,2*R*,3*R*,5*S*)-2,6,6-trimethylbicyclo[3.1.1]hept-3-yl]-7*H*-dinaphtho[2,1-*c*;1′,2′-*e*]azepinium Tetraphenylborate (23): [6]Prepared according to the general procedure from (–)-isopinocampheylamine (0.25 g, 1.6 mmol). The product was isolated as yellow plates (0.82 g, 73%), m.p. 225–227 °C (dec). $[\alpha]_D^{20}$ = +359.1 (c = 1.31, acetone). $C_{48}H_{48}BN{\cdot}0.5H_2O$: calcd. C 88.61, H 6.91, N 1.85; found C 88.38, H 6.86, N 1.80.IR (nujol): ṽ = 3053, 2996, 1627, 1610, 1580, 1549, 1206, 750, 705 cm^{-1}. ^{1}H NMR (400 MHz, [D$_6$]-acetone): δ = 0.84 (d, J = 4.0 Hz, 3 H), 1.13 (s, 3 H), 1.32 (s, 3 H), 1.51 (d, J = 8.0 Hz, 1 H), 2.00–2.08 (m, 1 H), 2.13–2.23 (m, 1 H) 2.31–2.39 (m, 1 H), 2.64–2.71 (m, 1 H), 2.75–2.81 (m, 2 H), 4.80 (dd, J = 13.6, 1.2 Hz, 1 H) 5.14 (q, J = 7.6 Hz, 1 H), 5.50 (d, J = 14.0 Hz, 1 H) 6.74 (t, J = 8.0 Hz, 4 H), 6.89 (t, J = 8.0 Hz, 8 H), 7.06 (d, J = 8.4 Hz, 1 H), 7.33 (t, J = 8.0 Hz, 8 H), 7.40–7.51 (m, 3 H), 7.72–7.76 (m, 1 H), 7.77–7.80 (m, 1 H), 7.94 (d, J = 8.8 Hz, 1 H), 7.99 (d, J = 8.4 Hz, 1 H), 8.08 (d, J = 8.4 Hz, 1 H), 8.20 (d, J = 8.4 Hz, 1 H), 8.24 (d, J = 8.4 Hz, 1 H), 8.29 (d, J = 8.4 Hz, 1 H), 9.72 (s, 1 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]acetone): δ = 19.4, 23.4, 28.5, 33.8, 35.1, 40.2, 41.6, 42.3, 48.2, 54.7, 75.4, 122.2, 125.9, 126.0, 126.0, 126.1, 126.1, 126.4, 127.8, 127.9, 128.00, 128.0, 128.1, 128.6, 129.5, 129.6, 130.2, 130.3, 131.2, 132.3, 137.0, 137.1, 142.4, 164.9, 171.2 ppm. MS (FAB$^+$): m/z = 430 (100) [M$^+$], 294 (55), 277 (52), 265 (61), 263 (32), 252 (20).$C_{32}H_{32}N$ (cation): calcd. 430.2535; found 430.2536.

Representative Epoxidation Procedure: Oxone (0.77 g, 1.26 mmol) was added to an ice-cooled solution of sodium carbonate (0.26 g, 2.52 mmol) in water (2.1 mL) with stirring, and the resulting foaming solution stirred for 5–10 min, so that most of the initial effervescence subsided. A solution of the iminium salt **6** (0.5 mol-%, 0.0025 g, 0.0032 mmol) in acetonitrile (1.05 mL) was added, followed by a solution of 1-phenylcyclohexene (0.10 g, 0.63 mmol) in acetonitrile (1.05 mL). The suspension was stirred until the substrate was completely consumed by TLC (2.0 h). The reaction mixture was diluted with ice-cooled diethyl ether (20 mL), immediately followed by the addition of water (20 mL). The aqueous phase was extracted with diethyl ether (4 × 20 mL) and the combined organic extracts were washed with brine and dried ($MgSO_4$). Filtration and evaporation of the solvents furnished a light brown residue. Column chromatography, eluting with ethyl acetate/light petroleum (1:99) afforded pure 1-phenylcyclohexene oxide as a colourless oil [0.071 g, 65%, 91% *ee*, (–)-1*S*,2*S*]. Colourless oil. IR (neat): ṽmax = 3084, 1602, 1495, 1446, 1359, 1249, 1173, 1132, 1079, 1030, 993, 974 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.22–1.35 (m, 1 H), 1.53–1.64 (3H m), 1.99–2.06 (m, 2 H) 2.16–2.18 (m, 1 H), 2.26–2.32 (m, 1 H), 3.10 (t, J = 2.0 Hz, 1 H), 7.28–7.44 (m, 5 H) ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 19.8, 20.1, 24.7, 28.2, 60.1, 61.8, 125.3, 127.1, 128.2, 142.8 ppm.

***trans*-Stilbene Oxide:**[6,20] Colourless solid. IR (nujol): ṽ = 1601, 1492, 1284, 1176, 1157, 1094, 1072, 1025 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.84 (s, 2 H), 7.28–7.37 (m, 10 H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 63.3, 126.0, 128.6, 129.3, 137.6 ppm.

1,2-Dihydronaphthalene Oxide:[6,21] Colourless oil. IR (neat): ν̃max = 3059, 3028, 2930, 2850, 1602, 1493, 1316, 1129, 1088, 1030, 964 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.65–1.73 (m, 1 H), 2.30–2.36 (m, 1 H), 2.45 (dd, J = 15.6, 5.6 Hz, 1 H), 2.67–2.74 (m, 1 H), 3.65 (t, J = 4.0 Hz, 1 H), 3.78 (d, J = 4.4 Hz, 1 H), 7.01 (d, J = 7.2 Hz, 1 H), 7.10–7.20 (m, 2 H), 7.33 (d, J = 7.2 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.2, 24.8, 55.2, 55.6, 126.5, 128.8, 128.8, 129.9, 132.9, 137.1 ppm.

1-Phenylcyclohept-1-ene Oxide:[6,22] Colourless oil. IR (neat): ν̃max = 3084, 1602, 1494, 1445, 1358, 1255, 1166, 1128, 1088, 1030, 964, 855, 738 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.50–1.85 (m, 6 H), 1.90–2.20 (m, 2 H), 2.38–2.50 (m, 2 H), 3.04 (q, J = 3.8 Hz, 1 H), 7.25–7.40 (m, 5 H) ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 24.9, 25.5, 29.9, 31.7, 33.9, 63.4, 65.8, 125.4, 127.3, 128.5, 142.0 ppm.

***trans*(α-Methyl)stilbene Oxide:**[6,23] Colourless oil. IR (neat): ν̃max = 3061, 1602, 1495, 1449, 1381, 1279, 1157, 1118, 1065, 1027, 980 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.46 (s, 3 H), 3.96 (s, 1 H), 7.30–7.46 (m, 10 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.1, 63.5, 67.5, 125.6, 126.9, 127.7, 127.9, 128.6, 129.2, 136.4, 142.8 ppm.

Triphenylethylene Oxide:[6,24] Colourless oil which slowly solidified. IR (neat): ν̃max = 3062, 3030, 2957, 2925, 2856, 1605, 1596, 1499, 1471, 1448, 1262, 1221, 741, 698, 621 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 4.40 (s, 1 H), 7.10–7.47 (m, 15 H) ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 68.0, 68.3, 126.3, 126.8, 127.5, 127.6, 127.7, 127.8 128.0, 128.2, 128.6, 135.42, 135.9, 141.1 ppm.

1-Phenyl-3,4-dihydronaphthalene Oxide:[6,25] Pale yellow solid. IR (nujol): ν̃ = 1602, 1486, 1307, 1155, 1074, 1042, 953 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.10 (td, J = 5.8, 13.7 Hz, 1 H), 2.49–2.60 (m, 1 H), 2.77 (dd, J = 5.6, 15.5 Hz, 1 H), 2.98–3.06 (m, 1 H), 3.71 (d, J = 3.1 Hz, 1 H), 7.11–7.31 (m, 4 H), 7.45–7.61 (m, 5 H) ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 22.1, 25.4, 60.9, 63.0, 126.0, 127.7, 127.9, 128.1, 128.2, 128.6, 129.8, 135.0, 137.5, 138.8 ppm.

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