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Asymmetric Epoxidation Using Iminium Salt Organocatalysts Featuring Dynamically Controlled Atropoisomerism

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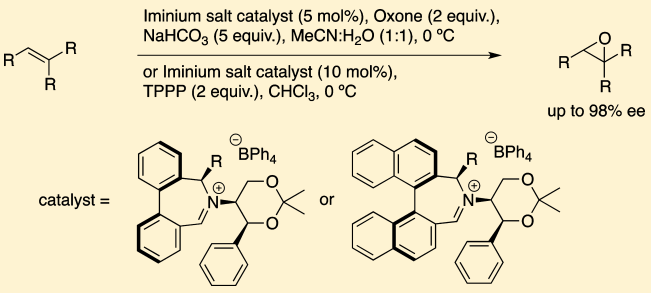
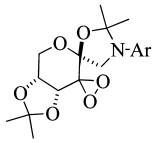
Supporting Information

ABSTRACT: Introduction of a pseudoaxial substituent at a stereogenic center adjacent to the nitrogen atom in binaphthyl- and biphenyl-derived azepinium salt organocatalysts affords improved enantioselectivities and yields in the epoxidation of unfunctionalized alkenes. In the biphenyl-derived catalysts, the atropoisomerism at the biphenyl axis is controlled by the interaction of this substituent with the chiral substituent at nitrogen.



INTRODUCTION

Epoxides are versatile building blocks widely used in synthesis.[1] The past 30 years have seen the development of many methodologies capable of efficient asymmetric epoxidation of various types of alkene.[2] Recently, asymmetric epoxidation using organocatalysts has received increasing attention. Chiral oxaziridines can be generated catalytically and are effective for asymmetric sulfur oxidation but are not generally useful for epoxidation.[3] Dioxiranes such as **1**,[4] and oxaziridinium salts such as **2**, first reported by Lusinchi,[5] have proven to be two of the most effective types of organocatalyst for asymmetric oxygen transfer to weakly nucleophilic substrates such as unfunctionalized alkenes.



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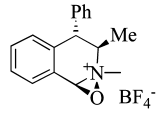

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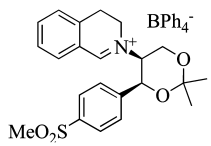

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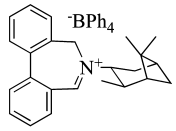

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We were the first to report enantioselective iminium salt epoxidation catalysts bearing an exocyclic chiral stereocontrolling group as a substituent on the nitrogen atom, such as dihydroisoquinolium salt **3**,[6] biphenylazepinium salts **4** and **5**,[7] and binaphthazepinium salt **6**.[8] High enantioselectivities are observed with arylalkene substrates, suggesting an interaction between the aryl unit of the substrate with the aryl groups of the catalysts. In some cases, the corresponding amines may be used as catalysts, generating the iminium species in situ.[9] These organocatalytic processes are typically driven using oxone as stoicheiometric oxidant but can also be driven by hydrogen peroxide,[10] bleach,[11] and even electrochemical methods.[12] We have also investigated the incorporation of simple chiral and achiral *N*-alkyl substituents into the binaphthazepinium ring, as in **7** and **8**, respectively.[13] Iminium salt catalysts containing a chiral nitrogen substituent can give increased enantiocontrol over those containing an achiral nitrogen substituent; in the case of the binaphthyl-derived systems, matched and mismatched effects are observed between the axial chirality of the binaphthyl unit and the chirality of the nitrogen substituent. In our hands, the dioxane core of (*S*,*S*)-(+)-acetonamine has provided catalysts generating excellent yields and induction of enantioselectivity in epoxidation reactions; this can be seen, for example, in a comparison of biphenylazepinium salts **4** and **5**,

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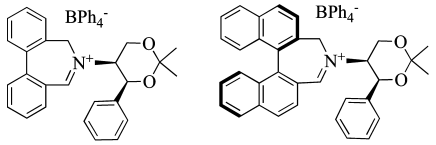
which induce 29% and 60% ee respectively when using 1-phenylcyclohexene as substrate under typical aqueous reaction conditions using oxone as reoxidant.[7] The effect of the controlled axial chirality of the binaphthyl unit can be seen in the epoxidation of the same substrate using catalyst **6**, which provides 91% ee.[8]



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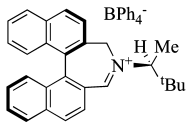

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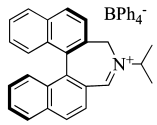

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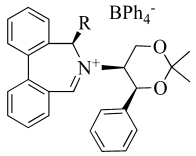
In considering further refinements to catalyst structure, we conjectured that the introduction of a further substituent at the methylene unit adjacent to the azepinium nitrogen atom in the biphenyl- and binaphthyl- derived catalysts, as in **9** and **10**, might provide increased enantiocontrol in the epoxidation process for two reasons. First, a substituent in this position was expected to provide additional steric control over any process occurring around the iminium double bond. Second, in the case of the biphenyl-derived catalysts **9**, the presence of a substituent at this position was also expected to affect the equilibrium position of the atropoisomerism around the biphenyl axis, perhaps driving it exclusively toward one rotamer; this was expected to influence the enantioselectivity in subsequent epoxidation, particularly as the related but configurationally stable binaphthyl unit exerts a very strong influence on enantiocontrol.



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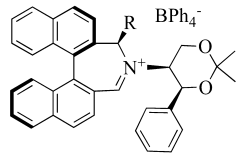

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RESULTS AND DISCUSSION

We chose for initial experimentation the (*S*,*S*)-acetonamine-derived biphenyl iminium salt catalyst **5**, which imparts good to high levels of enantiocontrol in asymmetric epoxidation. At −80 °C, four isomers can be seen in the NMR spectrum of **5**, corresponding to atropoisomerism about the biphenyl axis and to rotation around the exocyclic C−N bond.[14] We believe on the basis of NOESY experiments that the two major isomers correspond to a pair of isomers about the C−N bond, each having the *R* axial conformation; the ratio of the R_{ax} pair to the S_{ax} pair is then 89:11, and the ratio of the two pairs of observed C−N rotamers 83:17. The analogous binaphthyl system (see below) possesses a similar ratio of the two observed C−N rotamers of 88:12.

Substituents were introduced by addition of Grignard reagents (methyl, isopropyl, phenyl, benzyl) at −78 °C, generating pairs of diastereoisomeric amines **11**−**14** in each case, with diastereoisomeric ratios ranging from 5:1 to 11:1. We believe that the new substituent groups occupy a pseudoaxial position in each isomer,[15] the major isomer having an *R* axial chirality and the minor, *S*, so minimizing steric interaction with the large nitrogen substituent, in common with other systems of this type,[16] and with the nearby proton at C-3 of the adjacent aromatic ring, effects likely to be more pronounced for the larger substituents. The ^{1}H chemical shifts of the newly introduced methyl groups in **11** appear at 0.68 and 0.41 ppm, consistent with a pseudoaxial orientation.[16] A double stereochemical relay has thus taken place, where the chirality of the nitrogen substituent has controlled the atropoisomerism of the biphenyl axis, which has in turn controlled the stereochemistry of addition and asymmetry of the new substituents.

The major diastereoisomers, in each case the first eluting from silica gel chromatography, were treated with NBS to generate the iminium bromide salts, which underwent ion-exchange to generate the tetraphenyl borate iminium salts **15**−**18** in good to excellent yields as single diastereoisomers (Scheme 1). The new iminium double bonds are sited exclusively in the azepinium ring on the opposite side of the nitrogen atom from the newly introduced substituents, a result of loss of the one remaining more exposed, kinetically reactive pseudoaxial proton, again in common with other systems of this type.[16] It is thus the lesser substituted iminium bond regioisomers that were obtained, with complete retention of stereochemistry at the α-position in each instance. The ^{1}H chemical shift of the methyl group of **15** appears at 0.98 ppm, again as expected for a pseudoaxial orientation.[16]

A single-crystal X-ray structure of the methyl-substituted iminium salt **15** (Figure 1) indeed shows that the new methyl group occupies a pseudoaxial position, hindering the *si* face of the iminium unit, and also shows the relationship between the new asymmetric center (*R*) and the biphenyl axis (R_{ax}). Conformational control results from similar factors to those operating in **11**: avoidance of steric interaction between the new substituent and the nitrogen substituent, and between the new substituent and the hydrogen atom at the 3-position of the adjacent aromatic ring. The stereochemistry of each of **16**−**18** was assigned by analogy with that of **15**.

These new generation iminium salt catalysts were tested for their ability to induce enantiocontrol in the asymmetric epoxidation of 1-phenylcyclohex-1-ene using our standard aqueous reaction conditions with Oxone (2 equiv) as stoichiometric oxidant (water/acetonitrile (1:1), sodium carbonate (4 equiv), catalyst (5 mol %), Oxone (2 equiv)), and those inducing the highest enantiocontrol were then used in the epoxidation of several representative alkenes (Table 1).[17]

We were very pleased to observe generally increased enantiocontrol for the new generation catalysts, particularly catalyst **15**, containing an added methyl substituent and inducing up to 82% ee and 100% conversion, and catalyst **18**, containing a benzyl substituent and giving up to 77% ee and 100% conversion.

In order to investigate further the proposition that it is the atropoisomerism of the biphenyl axis that determines the stereochemistry of introduction of the added substituents, and to provide insight into the factors affecting the resulting induced enantioselectivity, we next investigated the corresponding binaphthyl-derived catalysts, which have a fixed axial chirality. One of the most enantioselective iminium salt catalysts reported to date is the binaphthyl-based iminium salt catalyst **6**,[8] a "matched" enantioselectivity system again

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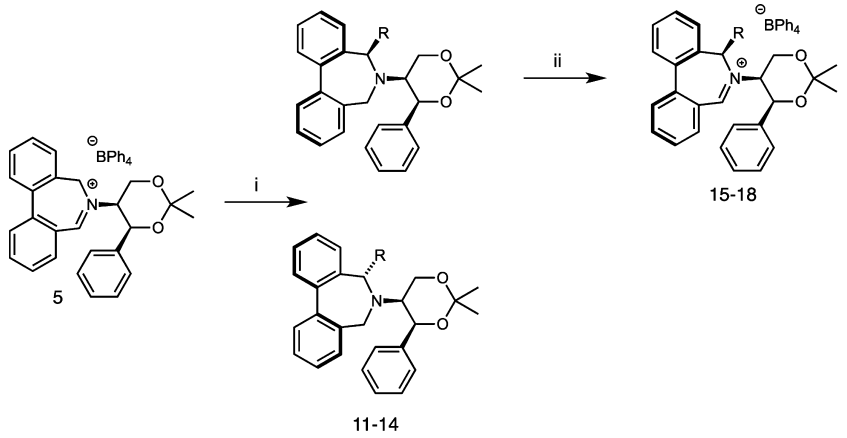
Scheme 1.



Reagents and conditions: (i) RMgX, THF, –78 °C to rt, 2 h; (ii) NBS, CH_2Cl_2, Δ, 30 min; $NaBPh_4$, MeCN, r.t., 10 min.

R	Amine	Yield/%	Ratio of diastereoisomers[a]	Iminium salt[b]	Yield/%
Me	**11**	74%	6:1	**15**	68%
iPr	**12**	72%	9:1	**16**	83%
Ph	**13**	85%	11:1	**17**	86%
Bn	**14**	73%	5:1	**18**	84%

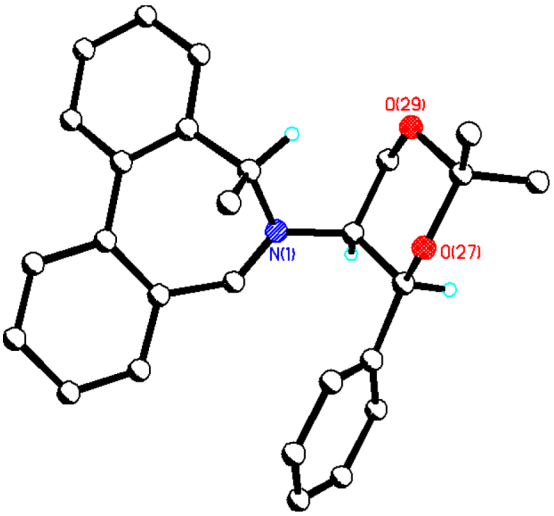
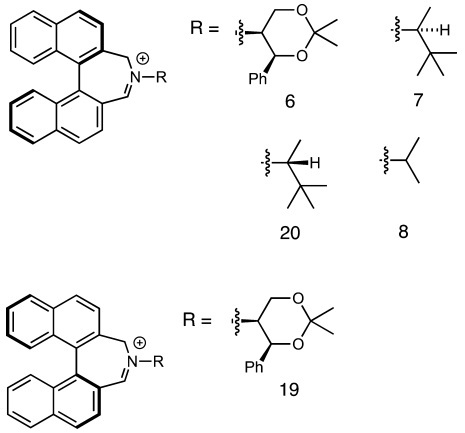


Figure 1. Single-crystal X-ray structure of **15**.



containing a nitrogen substituent derived from (*S*,*S*)-acetonamine, and having (R_{ax}) axial chirality. For this study, we decided to use two diastereoisomeric pairs of catalysts, our (*S*,*S*)-acetonamine-derived binaphthylazepinium salts **6** and **19**, and the (*S*)- and (*R*)- 3,3-dimethylbutylamine-derived binaphthylazepinium salts 7 and **20**,[18] as well as the isopropylamine-derived C_2-symmetric catalyst **8**.

Accordingly, we next introduced a methyl group substituent into these catalysts using chemistry similar to that used for the biphenyl series: The binaphthyl azepinium salts were treated with methylmagnesium bromide at −78 °C, generating the tertiary amines **21**−**25** in 68−99% yields. Unlike the biphenyl systems, however, all of the additions were completely diastereoselective (Scheme 2). The chemical shift of the newly introduced methyl groups are all at very high field (e.g., 0.12 ppm for **21**, derived from **6**), as expected for a pseudoaxial orientation. Single-crystal X-ray analysis of **21** clearly shows the expected pseudoaxial orientation of the methyl substituent and the R_{ax} axial chirality (Figure 2). Since both **21** and its S_{ax} diastereoisomer **22** incorporate the new methyl groups in a pseudoaxial orientation, it is clear that the chirality of the N-substituent plays little or no role in controlling the stereochemistry of addition of the Grignard reagent.

Oxidation of the amines and isolation of the azepinium tetrafluoroborate salts **26**−**30** were achieved as for the biphenyl salts in 64−72% yields as single diastereoisomers. As expected, the lesser substituted iminium bond regioisomers were obtained, with complete retention of stereochemistry at the α-position (Scheme 3). The chemical shifts of the newly introduced methyl substituents appeared far upfield in each case, again supporting a pseudoaxial orientation (e.g., **26**: 0.15 ppm; **27**: 0.75 ppm). Indeed, single crystal X-ray analysis of **27** clearly shows the axial orientation of the methyl substituent and the S_{ax} configuration of the binaphthyl unit (Figure 3).

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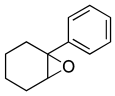
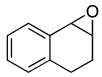
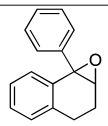
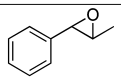
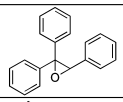
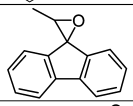
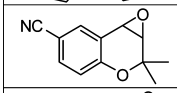
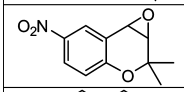
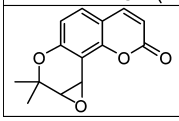
Table 1. Asymmetric Epoxidation of Alkenes Mediated by Biphenyl Catalysts[a]

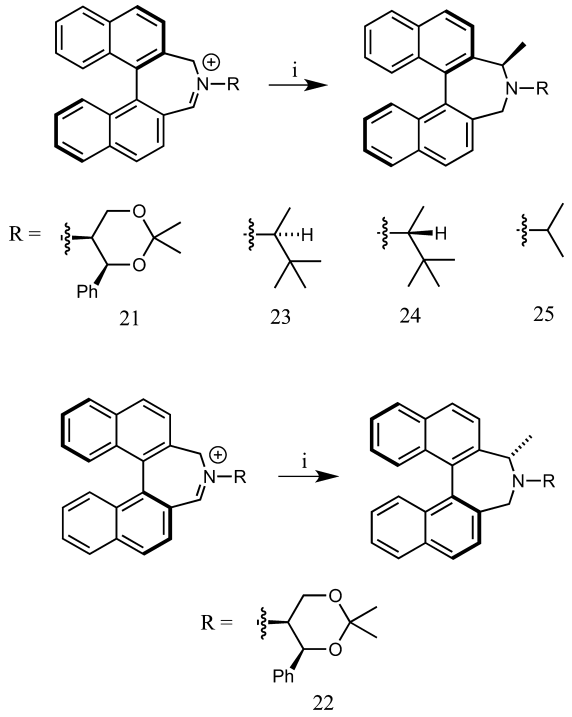
Epoxide	Catalyst	Conversion/%[b]	ee/%	Major enantiomer[c]
	**5**	100	60[d]	(−)-1*S*,2*S*
	15	100	82[d]	(−)-1*S*,2*S*
	16	100	64[d]	(−)-1*S*,2*S*
	17	100	63[d]	(−)-1*S*,2*S*
	18	100	77[d]	(−)-1*S*,2*S*
	**5**	93	52[e]	(−)-1*S*,2*R*
	15	95	64[e]	(−)-1*S*,2*R*
	18	100	49[e]	(−)-1*S*,2*R*
	**5**	90	41[f]	(+)-1*R*,2*S*
	15	100	78[f]	(+)-1*R*,2*S*
	18	91	76[f]	(+)-1*R*,2*S*
	**5**	100	16[e]	(−)-1*S*,2*S*
	15	100	31[e]	(−)-1*S*,2*S*
	**5**	100	18[f]	(+)-1*S*
	15	100	35[f]	(+)-1*S*
	**5**	100	38[f]	(+)-(*R*)
	15	100	40[f]	(+)-(*R*)
	**5**	90	56[f]	(−)-1*S*,2*S*
	15	100	36[f]	(−)-1*S*,2*S*
	**5**	100	66[f]	(−)-1*S*,2*S*
	15	100	45[f]	(−)-1*S*,2*S*
	**5**	100	66[f]	(+)-(3'*S*, 4'*S*)
	15	100	51[f]	(+)-(3'*S*, 4'*S*)

[a]Epoxidation conditions: iminium salt catalyst (5 mol %), Oxone (2 equiv), Na_2CO_3 (4 equiv), MeCN/H_2O (1:1), 0 °C; 1−12 h. [b]Conversions were evaluated from the ^1H NMR spectra by integration of the alkene and epoxide signals. [c]Absolute configurations of the major enantiomers were determined by comparison of optical rotation with those reported in the literature. [d]ee was determined using chiral stationary phase (CSP) GC. [e]ee was determined using ^1H NMR spectroscopy in the presence of europium(III) tris [3-(heptafluoropropylhydroxymethylene)-(+)-camphorate] as chiral shift reagent. [f]ee was determined using CSP HPLC.

The new salts were tested as catalysts in the epoxidation of a range of alkenes. Table 2 provides a comparison of the new methyl-substituted catalysts with their respective parent catalysts.

In almost every case for the "matched" systems, incorporation of the methyl substituent into the catalyst structure improved the levels of enantiocontrol imparted, in some cases dramatically, while the levels of enantiocontrol decreased on incorporation of the methyl substituent in the "mismatched" system **19**/**27**. The reactivity of the methyl-substituted catalysts was, however, decreased; conversions were generally lower for **28**/**29** than their parent nonmethylated catalysts **7**/**20**. Interestingly, incorporation of the methyl substituent into the C_2-symmetric isopropyl-substituted pair **8**/**30** had little effect

Scheme 2[a]



[a]Reagents and conditions: (i) MeMgBr, THF, −78 °C to rt, 12 h.

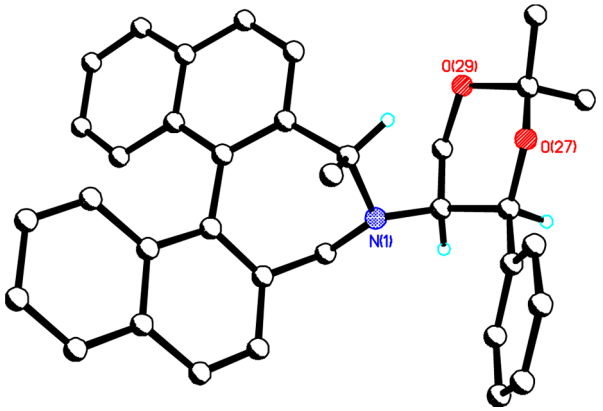


Figure 2. Single-crystal X-ray analysis of amine **21**.

on both enantioselectivity and reactivity in the epoxidation process. This suggests that the effect that the methyl group has on reactivity and enantioselectivity may be manifested through some interaction between itself and the chiral pendent amine, a discussion of which is presented below.

We have also developed nonaqueous conditions for the use of iminium salt catalysts,[19] which have proved particularly effective for epoxidation of cyclic *cis*-alkenes, and we have reported highly enantioselective syntheses of levcromakalim,[20] lomatin,[21] and scuteflorin A[22] using these conditions. Finally, we tested the new substituted biphenyl catalysts under these nonaqueous conditions and were again pleased to observe high levels of enantioselectivity and higher catalyst reactivity in several cases (Table 3).

Comparison with Table 1 shows that the biphenyl catalysts generally show reduced reactivity under the nonaqueous conditions, reaction times to completion are much increased, and indeed the binaphthyl-derived catalysts are insufficiently

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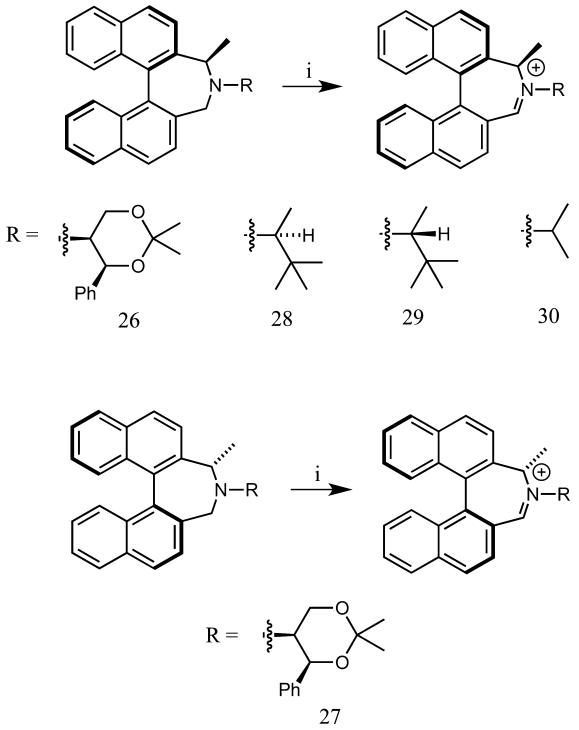
Scheme 3[a]



[a]Reagents and conditions: (i) NBS (1.1 equiv), CH_2Cl_2, rt, 10 min; $NaBPh_4$, EtOH, 1 h.

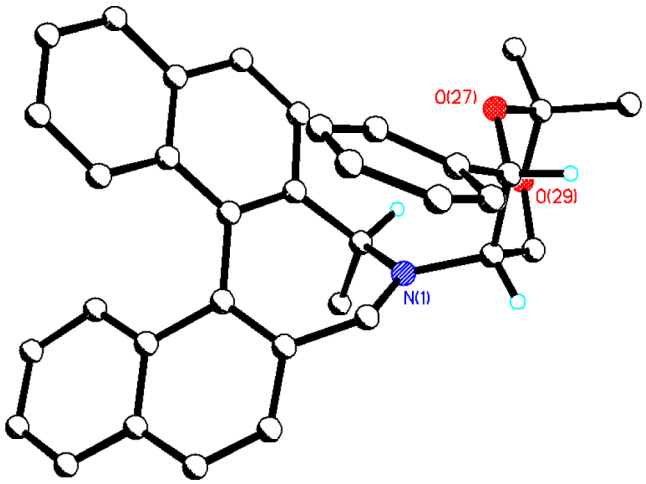


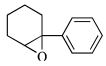
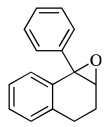
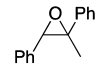
Figure 3. Single-crystal X-ray analysis of iminium salt **27**.

reactive to be effective under these conditions, with no observed conversion over 48 h.

There are a number of potential mechanisms by which the introduction of the new substituents could affect the enantioselectivity of the catalyzed epoxidation process.

In the case of the BINAP-based system, it has been suggested that the dihedral angle of the BINAP system is one of the controlling parameters determining enantioselectivity in epoxidation using these catalyst types.[18] Sandstrom has shown that the λ_{max} absorbance value of aromatic axially chiral species is dependent on the dihedral angle.[23] Examination of the CD spectra of our catalysts, however, shows that the λ_{max} values are almost identical in all cases, suggesting that the dihedral angle is the same for both the methylated species and the parent catalysts or that this method is insufficiently sensitive in our case. A change in the dihedral angle may therefore not be responsible for the observed increased enantioselectivities of the methylated catalysts.

Table 2. Asymmetric Epoxidation of Alkenes Mediated by Binaphthyl Catalysts[a]

Epoxide	Catalyst	Conversion/%[b]	ee/%[c,d]	Major enantiomer[e]
	**6**	99	91	(–)-1*S*,2*S*
	26	99	94	(–)-1*S*,2*S*
	19	99	79	(+)-1*R*,2*R*
	27	99	44	(+)-1*R*,2*R*
	8	99	75	(–)-1*S*,2*S*
	30	99	79	(–)-1*S*,2*S*
	20	99	75	(–)-1*S*,2*S*
	29	88	92	(–)-1*S*,2*S*
	7	99	74	(–)-1*S*,2*S*
	28	99	88	(–)-1*S*,2*S*
	**6**	99	94	(+)-1*R*,2*S*
	26	99	94	(+)-1*R*,2*S*
	19	80	57	(–)-1*S*,2*R*
	27	93	63	(–)-1*S*,2*R*
	8	99	85	(+)-1*R*,2*S*
	30	99	85	(+)-1*R*,2*S*
	20	80	85	(+)-1*R*,2*S*
	29	40	87	(+)-1*R*,2*S*
	7	99	83	(+)-1*R*,2*S*
	28	99	90	(+)-1*R*,2*S*
	**6**	99	49	(–)-1*S*,2*S*
	26	99	64	(–)-1*S*,2*S*
	19	40	49	(+)-1*R*,2*R*
	27	26	30	(+)-1*R*,2*R*
	8	99	53	(–)-1*S*,2*S*
	30	99	55	(–)-1*S*,2*S*
	20	18	52	(–)-1*S*,2*S*
	29	17	55	(–)-1*S*,2*S*
	7	56	44	(–)-1*S*,2*S*
	28	40	50	(–)-1*S*,2*S*

[a]Epoxidation conditions (**6**, **26**, **19**, **27**, **8**, **30**): iminium salt catalyst (5 mol %), Oxone (2 equiv), $NaHCO_3$ (5 equiv), $MeCN/H_2O$ (1:1), 0 °C, 17 min to 13 h. Epoxidation conditions (**20**, **29**, **7**, **28**): iminium salt catalyst (5 mol %), Oxone (1 equiv), 18-crown-6 (2.5 mol %), $NaHCO_3$ (4 equiv), dichloromethane/H_2O (3:2), 0 °C, 2 h. [b]Conversions were evaluated from the ^1H NMR spectra by integration of alkene and epoxide signals. [c]Enantiomeric excesses were determined by chiral HPLC using a Chiracel OD-H column. [d]Enantiomeric excesses were determined by ^1H NMR spectroscopy in the presence of europium(III) tris [3-(heptafluoropropylhydroxymethylene)-(+)-camphorate]. [e]Absolute configurations of the major enantiomers were determined by comparison of optical rotations with those reported in the literature.

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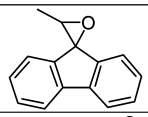
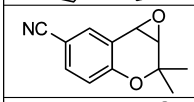
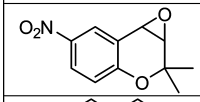
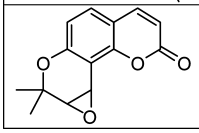
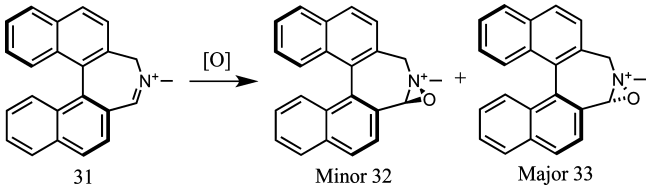
Table 3. Asymmetric Epoxidation of Alkenes Mediated by Biphenyl Catalysts under Nonaqueous Conditions.[a]

Epoxide	Catalyst	Conversion/%[b]	Reaction time (h)	ee/%[c]	Major enantiomer[d]
	**5**	100	22	69	(+)-(*R*)
	15	100	24	73	(+)-(*R*)
	**5**	90	20	97	(−)-1*S*,2*S*
	15	100	48	98	(−)-1*S*,2*S*
	**5**	<5	120	—	—
	15	74	120	94	(−)-1*S*,2*S*
	**5**	<5	120	—	—
	15	100	45	86	(+)-(3'*S*, 4'*S*)

[a]Epoxidation conditions: iminium salt catalyst (10 mol %), TPPP (2 equiv), $CHCl_3$, 0 °C. [b]Conversions were evaluated from the ^1H NMR spectra by integration of the alkene and epoxide signals. [c]ee was determined using chiral HPLC using a Chiracel OD-H column. [d]Absolute configurations of the major enantiomers were determined by comparison of optical rotation with those reported in the literature.

Generation of the purported oxaziridinium salt oxygen transfer agents from the iminium salt catalysts could take place at both faces of the iminium species, giving rise to diastereoisomeric pairs of oxaziridinium salts, each isomer of a pair potentially inducing different enantioselectivity from the other, and at different rates.[10] It is conceivable that the introduction of the new substituents could alter the ratio of these diastereoisomers and their reactivities by introducing steric hindrance at one face, thus altering the overall observed enantiocontrol. This effect on the ratio of diastereoisomers generated, however, could only arise if diastereoisomeric pairs of oxaziridinium salts are indeed generated from the parent catalysts. We have shown in a simpler system that only one diastereoisomer of the oxaziridinium salt is generated under the reaction conditions used here; furthermore, Houk has shown with a simpler N-Me system that the intermediate formed by the addition to **31** by Oxone, leading to the formation of the minor diastereoisomer **32**, was 8.1 kcal mol^{-1} higher in energy than the intermediate leading to the major diastereoisomer **33**, noting that the difference was due to steric repulsion between a monoperoxysulfate oxygen atom and the arene hydrogen atom at the 3 position (Scheme 4).[24]

Scheme 4



Although the barrier to rotation about the exocyclic C−N bond of the catalysts is similar, at about 11−12 kcal mol^{-1} in both the methylated and parent catalyst structures, as shown by VT-NMR experiments, the introduction of the new substituents is likely to alter the relative population of rotamers, and this could in turn affect the enantiocontrol in the catalyzed epoxidation process.[14] NOESY experiments performed at −80 °C suggest that in the parent systems conformations close to that shown in **34**, with the two indicated C−H bonds having a *syn*-periplanar relationship, are favored. Introduction of the methyl substituent significantly increases the proportion of conformations close to that shown in **35**, with the two indicated C−H bonds having an *anti*-periplanar relationship (Figure 4,

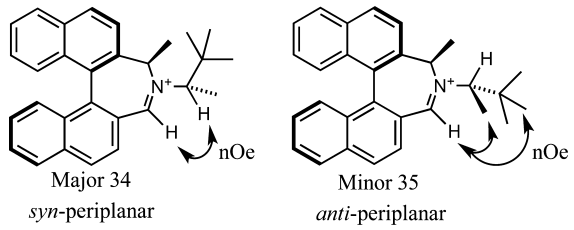


Figure 4. Illustration of the *syn*- and *anti*-periplanar rotamers **34**, **35**.

Table 4. Ratios of Rotamers about the Exocyclic C−N Bond for the Two Generations of Catalyst, Determined by NOESY at −80 °C

	syn-periplanar	*anti*-periplanar
6	88	12
26	60	40
19	72	28
27	61	39
7	100	0
28	80	20
8	100	0
30	100	0

Table 4). This arrangement would be expected to provide a less reactive catalyst, as there is greater steric bulk around the site of oxygen transfer (presumed to be on the opposite face from the new methyl substituents).

This model may also explain why little difference in enantioselectivity was observed between the two isopropylamine-derived catalysts **8** and **30**. In this case, there was no

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difference between the rotameric ratio, with both catalysts entirely favoring the *syn*-periplanar rotamers.

CONCLUSIONS

Stereocontrolled introduction of a substituent at a carbon atom adjacent to the nitrogen atom in binaphthyl- and biphenyl-derived azepinium salts affords new organocatalysts for asymmetric epoxidation, offering considerably improved enantioselectivities in many cases. The new substituent occupies a pseudoaxial position, and in the biphenyl-derived catalysts controls both the atropoisomerism at the biphenyl axis and the regiochemistry of introduction of the iminium double bond. We provide evidence to show that in the instances where the methyl substituent affects the reactivity and enantiocontrol demonstrated in the epoxidation process, it is by altering the ratio of sp^2N-sp^3C rotamers.

EXPERIMENTAL SECTION

General Experimental Details. Infrared spectra were acquired as nujol mulls or as thin films of their solution in dichloromethane on sodium chloride plates. Liquid samples were run neat.

^1H and ^{13}C NMR spectra were measured respectively at 400.13 and 100.62 MHz, or at 300.05 and 75.45 MHz, respectively. The solvent used for NMR spectroscopy was deuteriated chloroform unless stated otherwise, using tetramethylsilane as the internal reference. Chemical shifts are given in parts per million (ppm) and J values are given in hertz (Hz).

Optical rotation values were measured with instruments operating at λ = 589 nm, corresponding to the sodium D line at the temperatures indicated. The solvents used for these measurements were of spectrophotometric grade. The solutions for these measurements were prepared in volumetric flasks for maximum accuracy of the volume of solvent used.

Enantiomeric excesses were determined by either chiral shift proton NMR experiments, chiral gas chromatography flame ionization (GC–FID), or chiral high-performance liquid chromatography (chiral HPLC).

The chiral shift proton nuclear magnetic resonance spectra were recorded in deuteriated chloroform on an instrument operating at 400.13 MHz, in the presence of europium(III) tris [3-(heptafluoropropylhydroxymethylene)-(+)-camphorate], [(+)-Eu(hfc)$_3$], as the chiral shift reagent and tetramethylsilane as the internal standard.

The chiral columns used for the determination of enantiomeric excesses (ee) of nonracemic mixtures by chiral HPLC were Chiralcel OD-H and Eurocel 01-5 μm, operated on a Hitachi Elite LaChrome 2000 series instrument. Solvents used (hexane and 2-propanol) were of HPLC grade.

Reactions requiring anhydrous conditions were carried out under a nitrogen atmosphere unless otherwise stated, using glassware dried for 16 h at 150 °C. Reaction solvents were obtained commercially dry, except for the following light petroleum (bp 40–60 °C) was distilled from calcium chloride prior to use. Ethyl acetate was distilled over calcium sulfate or chloride. Dichloromethane was distilled over calcium hydride. Tetrahydrofuran was distilled under a nitrogen atmosphere from the sodium/benzophenone ketyl radical.

General Procedure for the Oxidation of Alkenes Using Chiral Iminium Salts under Aqueous Conditions. Sodium carbonate (4.0 equiv) was dissolved in water (1 mL) and acetonitrile (1 mL), and the suspension cooled to 0 °C. Oxone (2.0 equiv) was added and the mixture stirred for 10 min. The iminium salt catalyst (5 mol %) was added and the mixture stirred for a further 10 min. The alkene substrate (1 equiv) was added and the reaction progress followed using thin-layer chromatography. When the reaction was complete, diethyl ether (20 mL) was added. The mixture was washed twice with water and once with saturated brine and dried over $MgSO_4$. The solvents were removed under reduced pressure. The crude product was purified using column chromatography on silica gel (ethyl acetate/petroleum ether/triethylamine).

General Procedure for the Oxidation of Alkenes Using Chiral Iminium Salts under Nonaqueous Conditions. Tetraphenylphosphonium monoperoxysulfate (2 equiv) and the iminium salt catalyst (10 mol %) were dissolved in chloroform (10 mL) at −30 °C. The alkene substrate (1 equiv), dissolved in the minimum amount of chloroform, was added slowly with stirring, and the mixture stirred until the reaction was completion. Reaction progress was monitored by thin-layer chromatography. When the reaction was complete, diethyl ether (10 mL) was added. The mixture was filtered through Celite and washed with diethyl ether (2 × 10 mL), and the solvents were removed under reduced pressure. The crude product was purified using column chromatography on silica gel (ethyl acetate/petroleum ether/triethylamine).

General Procedure for the Addition of Grignard Reagents to Biphenyl Azepinium Salts. The azepinium salt was dissolved in anhydrous THF (30 mL per g of salt) under a nitrogen atmosphere and cooled to −78 °C. The Grignard reagent (10 equiv) was added dropwise over 5 min to the cold solution. The reaction mixture was stirred and allowed to reach ambient temperature over 2 h, cooled to 0 °C, and quenched with a saturated solution of ammonium chloride (2 mL per g of salt). The solvents were then removed under reduced pressure, and the residue was dissolved in dichloromethane (20 mL per g of salt). The mixture was washed twice with water, once with saturated brine, and dried over $MgSO_4$. The solution was filtered and silica gel added, and the solvent was removed under reduced pressure. The crude reaction mixture was purified by column chromatography on silica gel using ethyl acetate/petrol/triethylamine to yield the desired amine.

General Procedure for the Synthesis of Substituted Biphenyl Azepinium Tetraphenylborate Salts. A solution of *N*-bromosuccinimide (1.2 equiv) in CH_2Cl_2 (15 mL per g of NBS) was added to a solution of the amine in CH_2Cl_2 (15 mL per g of amine) and the reaction mixture heated under reflux for 2 h, allowed to cool to ambient temperature, extracted with water and saturated brine, and dried over $MgSO_4$. The solvent was removed under reduced pressure. The residue was then dissolved in ethanol and a solution of sodium tetraphenylborate (1 equiv) dissolved in the minimal amount of acetonitrile was added. The reaction mixture was stirred over 10 min, forming a yellow precipitate. The precipitate was collected by filtration and washed with cold ethanol to yield the product as a yellow crystalline solid.

6-(2,2-Dimethyl-4-phenyl-1,3-dioxan-5-yl)-5-methyl-6,7-dihydro-5*H*-dibenzo[*c*,*e*]azepine 11a and 11b. Prepared according to the general procedure from 6-(2,2-dimethyl-4-phenyl-1,3-dioxan-5-yl)-5*H*-dibenzo[*c*,*e*]azepinium tetraphenylborate **5** (1.0 g, 1.42 mmol) and methylmagnesium bromide (4.7 mL, 14.20 mmol, 10 equiv). The crude mixture was purified by column chromatography using 96:1:3 petroleum ether 40–60/ethyl acetate/triethylamine as eluent to give the desired compound as a pair of diastereoisomers **11a** and **11b**.

First eluting diastereoisomer (major) **11a**: colorless solid (0.36 g, 63%); ν_{max}(film) /cm^{-1} 3413, 3062, 3025, 2987, 2927, 2859, 2775, 2358, 1956, 1604, 1479, 1449, 1377, 1263, 1238, 1196, 1147, 1084, 956, 940, 852, 803, 755, 736, 695; $[\alpha]^{20}_D$ +30.3° (*c* 0.30, $CHCl_3$); δ_H (400 MHz; $CDCl_3$ 55 °C) 0.68 (3 H, d, *J* 7.0 Hz), 1.64 (3 H, s), 1.69 (3 H, s), 3.19 (1 H, q, *J* 4.1 Hz), 3.79 (2 H, s), 4.20 (1 H, dd, *J* 2.4 and 12.4 Hz), 4.32 (2 H, dd, *J* 4.8 and 12.3 Hz), 5.31 (1 H, s), 7.18–7.14 (2 H, m), 7.36–7.29 (3 H, m), 7.45–7.37 (5 H, m), 7.49 (1 H, dd, *J* 1.4 and 7.6 Hz), 7.53 (2 H, d, *J* 7.3 Hz); δ_C (100 MHz; $CDCl_3$ 55 °C) 19.6, 21.2, 29.1, 53.7, 58.6, 58.8, 63.2, 74.4, 99.4, 126.3, 126.6, 127.0, 127.1, 127.4, 127.6, 127.7, 127.8, 128.4, 128.5, 128.9, 138.1, 139.5, 140.4, 141.3, 141.4; *m*/*z* found (ESI) for $[M]^+$ 398.2168, $[C_{27}H_{29}NO_2]^+$ requires 399.2198.

Second eluting diastereoisomer (minor) **11b**: yellow oil (65 mg, 11%); ν_{max}(film) /cm^{-1} 2982, 2922, 2854, 1449, 1379, 1197, 1079, 854, 755, 698; $[\alpha]^{20}_D$ +69.0° (*c* 1.1, $CHCl_3$); δ_H (400 MHz; $CDCl_3$, 50 °C) 0.41 (3 H, d, *J* 7 Hz), 1.49 (3 H, s), 1.53 (3 H, s), 3.10 (1 H, q, *J* 2 Hz), 3.60 (1 H, d, *J* 12 Hz), 3.76 (1 H, q, *J* 7 Hz), 3.94 (1 H, d, *J* 12 Hz), 4.23 (2 H, dq, *J* 4 and 12 Hz), 5.26 (1 H, d, *J* 4 Hz), 6.92 (1 H, d, *J* 7 Hz), 7.14–7.30 (5 H, m), 7.31–7.36 (5 H, m), 7.42 (1 H, dd, *J* 2 and 8 Hz), 7.50 (2 H, dd, *J* 1 and 7 Hz); δ_C (100 MHz; $CDCl_3$, 50 °C)

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19.6, 23.5, 29.1, 51.2, 62.3, 62.6, 65.6, 73.9, 99.4, 126.2, 126.7, 126.8, 127.3, 127.4, 127.60, 127.63, 128.0, 128.9, 129.4, 129.5, 138.0, 139.3, 140.1, 141.2, 141.5; *m*/*z* found (ESI) for $[M + H]^+$ 400.2267, $[C_{27}H_{30}NO_2]^+$ requires 400.2277.

6-(2,2-Dimethyl-4-phenyl-1,3-dioxan-5-yl)-5-isopropyl-6,7-dihydro-5*H*-dibenzo[*c*,*e*]azepine 12. Prepared according to the general procedure from 6-(2,2-dimethyl-4-phenyl-1,3-dioxan-5-yl)-5*H*-dibenzo[*c*,*e*]azepinium tetraphenylborate **5** (0.50 g, 0.71 mmol) and isopropylmagnesium chloride (2 M in THF, 3.6 mL, 7.10 mmol, 10 equiv) The crude reaction mixture was purified by column chromatography using 96:1:3 petroleum ether 40−60/ethyl acetate/ /triethylamine as eluent to give the desired amine (0.22 g, 72%); ν_{max}(film) /cm^{-1} 3359, 3060, 2957, 2920, 2855, 2358, 2336, 1726, 1711, 1692, 1661, 1608, 1551, 1535, 1514, 1449, 1378, 1260, 1197, 1080, 850, 800, 754, 697. $[\alpha]^{20}_D$ +98.3° (*c* 0.96, $CHCl_3$). δ_H (400 MHz; $CDCl_3$) 0.02 (3 H, d, *J* 6 Hz, 0.57−0.68 (1 H, m), 0.73 (3 H, d, *J* 6 Hz), 1.54 (3 H, s), 1.59 (3 H, s), 2.97−3.02 (1 H, m), 3.28 (1 H, d, *J* 10 Hz), 3.57 (1 H, d, *J* 12 Hz), 4.19 (1 H, d, *J* 12 Hz), 4.34 (1 H, d, *J* 12 Hz), 4.43 (1 H, dd, *J* 12, 4 Hz), 5.19 (1 H, d, *J* 3 Hz), 6.23 (1 H, d, *J* 7 Hz), 7.00 (1 H, t, *J* 7 Hz), 7.14 (1 H, d, *J* 7.2 Hz), 7.18−7.33 (9 H, m), 7.36−7.42 (2 H, m). δ_C (100 MHz; $CDCl_3$) 19.3, 20.3, 21.1, 28.8, 34.4, 52.8, 63.4, 66.5, 75.4, 76.2, 99.6, 126.5, 126.7, 126.8, 127.0, 127.1, 127.4, 127.5, 127.9, 128.3, 128.7, 131.4, 138.2, 138.5, 139.2, 140.5, 141.6; *m*/*z* found (ESI) for $[M - H]^+$ 426.2439; $[C_{29}H_{32}NO_2]^+$ requires 426.2433.

6-(2,2-Dimethyl-4-phenyl-1,3-dioxan-5-yl)-5-phenyl-6,7-dihydro-5*H*-dibenzo[*c*,*e*]azepine 13. Prepared according to the general procedure from 6-(2,2-dimethyl-4-phenyl-1,3-dioxan-5-yl)-5*H*-dibenzo[*c*,*e*]azepinium tetraphenylborate **5** (0.50 g, 0.71 mmol) and phenylmagnesium chloride (3.2 mL, 7.10 mmol, 10 equiv). The crude reaction mixture was purified by column chromatography using 96:1:3 petroleum ether 40−60/ethyl acetate/triethylamine as eluent to give the desired amine (0.28 g, 85%): ν_{max}(film)/cm^{-1} 3343, 2987, 2988, 2854, 2366, 1656, 1638, 1598, 1479, 1444, 1371, 1343, 1322, 1265, 1240, 1197, 1176, 1150, 1136, 1801, 1064, 1026, 1008, 955, 921, 876, 852, 780, 763, 733, 697, 657, 610; $[\alpha]^{20}_D$ +46 (*c* 1.03, $CHCl_3$); δ_H (400 MHz; $CDCl_3$) 1.58 (3 H, s), 1.64 (3 H, s), 3.08 (1 H, q, *J* 3 Hz), 3.80 (1 H, d, *J* 12 Hz), 4.07 (1 H, d, *J* 12 Hz), 4.33 (2 H, d. *J* 2 Hz), 5.28 (1 H, d, *J* 3 Hz), 5.49 (1 H, s), 6.29 (2 H, d, *J* 7 Hz), 6.62 (2 H, t, *J* 8 Hz), 6.70 (1 H, t, *J* 7 Hz), 6.88 (1 H, d, *J* 7 Hz), 7.00 (1 H, dt, *J* 8, 1 Hz), 7.10 (1 H, dt, *J* 8, 1 Hz), 7.15 (1 H, dd, *J* 7, 1 Hz), 7.20−7.38 (9 H, m); δ_C (100 MHz; $CDCl_3$) 18.9, 29.5, 54.1, 59.9, 63.4, 67.9, 74.5, 99.4, 124.5, 126.1, 126.4, 126.5, 126.8, 127.1, 127.3, 127.37, 127.39, 128.2, 128.6, 129.1, 130.9, 137.7, 139.7, 140.4, 140.8, 145.5; *m*/*z* found (ESI) for $[M]^+$ 461.2355, $[C_{32}H_{31}NO_2]^+$ requires 461.2355.

6-(2,2-Dimethyl-4-phenyl-1,3-dioxan-5-yl)-5-benzyl-6,7-dihydro-5*H*-dibenzo[*c*,*e*]azepine 14a and 14b. Prepared according to the general procedure from 6-(2,2-dimethyl-4-phenyl-1,3-dioxan-5-yl)-5*H*-dibenzo[*c*,*e*]azepinium tetraphenylborate **5** (0.50 g, 0.71 mmol) and benzylmagnesium chloride (2.0 M in THF, 3.5 mL, 7.10 mmol, 10 equiv). The crude mixture was purified by column chromatography using 96:1:3 petroleum ether 40−60/ethyl acetate/ triethylamine as eluent to give the desired compound as a pair of diastereoisomers **14a** and **14b**.

First eluting diastereoisomer (major) **14a**: colorless solid (0.21 g, 0.45 mmol, 60%): ν_{max}(film)/cm^{-1} 3414, 3060, 3024, 2989, 2935, 2856, 2359, 2339, 1602, 1495, 1481, 1450, 1379, 1348, 1309, 1263, 1237, 1198, 1177, 1147, 1080, 1029, 952, 852, 800, 778, 755, 736, 698, 668; $[\alpha]^{20}_D$ −11.8 (*c* 1.02, $CHCl_3$); δ_H (400 MHz; $CDCl_3$ 55 °C) 1.63 (3 H, s), 1.72 (3 H, s), 1.89−1.83 (1 H, m), 2.20 (1 H, dd, *J* 5.6 and 12.8 Hz), 3.00 (1 H, s), 3.78 (1 H, d, *J* 11.2 Hz), 3.94 (1 H, d, *J* 11.2 Hz), 4.17 (1 H, d, *J* 12.4 Hz), 4.24 (1 H, dd, *J* 4.4 and 12.4 Hz), 4.53 (1 H, dd, *J* 6.0 and 9.6 Hz), 5.28 (1 H, d, *J* 3.2 Hz), 6.63 (1 H, d, *J* 7.2 Hz), 6.68 (2 H, d, *J* 7.6 Hz), 7.01−7.09 (4 H, m), 7.26−7.34 (3 H, m), 7.35−7.40 (3 H, m), 7.43−7.47 (2 H, m), 7.52−7.54 (3 H, m); δ_C (100 MHz; $CDCl_3$ 55 °C) 19.4, 29.4, 43.0, 54.2, 60.9, 63.8, 68.3, 74.3, 99.5, 125.3, 126.2, 126.8, 127.1, 127.1, 127.4, 127.6, 127.8, 127.9, 128.0, 128.2, 129.18, 129.21, 130.9, 137.9, 138.8, 139.0, 140.4, 141.6. *m*/*z* found (ESI) for $[M - H]^+$ 474.2426, $[C_{33}H_{32}NO_2]^+$ requires 474.2433.

Second eluting diastereoisomer (minor) **14b**: yellow oil (0.045 g, 13%); ν_{max}(film)/cm^{-1} 3062, 3026, 2990, 2921, 1603, 1496, 1450, 1380, 1199, 1080, 909, 756, 736, 698; $[\alpha]^{20}_D$ +89 (*c* 1.2, $CHCl_3$); δ_H (400 MHz; $CDCl_3$) 1.47 (3 H, s, C^7H_3), 1.50 (3 H, s, C^8H_3), 1.76 (1 H, dd, *J* 8 and 12 Hz, $C^{11}HH$), 1.99 (1 H, dd, *J* 8 and 12 Hz, $C^{11}HH$), 3.09 (1 H, q, *J* 4 Hz, NC^5H), 3.58 (1 H, d, *J* 12 Hz, $NC^{10}HH$), 3.88 (1 H, dd, *J* 6.4 and 8.8 Hz, $NC^{10}HH$), 4.03 (1 H, d, *J* 12 Hz, OC^4HH), 4.24 (2 H, d, *J* 4 Hz, OC^4HH), 5.23 (1 H, d, *J* 4 Hz, OC^6HPh), 6.46−6.52 (2 H, m Ar−C*H*), 6.90 (2 H, t, *J* 8 Hz, Ar-C*H*), 6.95−7.01 (3 H, m, Ar-C*H*), 7.14 (1 H, td, *J* 1.3 and 7.5 Hz, Ar-C*H*), 7.18−7.26 (2 H, m, Ar-C*H*), 7.27−7.36 (4 H, m, Ar-C*H*), 7.38−7.44 (4 H, d, *J* 8 Hz, Ar-H); δ_C (100 MHz; $CDCl_3$,) 19.6, 29.1, 44.3, 51.3, 62.9, 63.2, 73.7, 73.8, 99.4, 125.5, 126.2, 126.8, 127.0, 127.7, 127.82, 127.84, 127.86, 128.8, 129.1, 129.1, 129.6, 131.0, 137.8, 139.2, 139.3, 140.3, 141.5. *m*/*z* found (ESI) for $[M + H]^+$ 476.2573, $[C_{33}H_{34}NO_2]^+$ requires 476.2590.

6-(2,2-Dimethyl-4-phenyl-1,3-dioxan-5-yl)-5-methyl-5*H*-dibenzo[*c*,*e*]azepinium Tetraphenylborate 15. Prepared according to the general procedure from 6-(2,2-dimethyl-4-phenyl-1,3-dioxan-5-yl)-5-methyl-6,7-dihydro-5*H*-dibenzo[*c*,*e*]azepine **11a** (0.16 g, 0.40 mmol), *N*-bromosuccinimide (0.09 g, 0.48 mmol, 1.2 equiv), and sodium tetraphenylborate (0.14 g, 0.40 mmol, 1 equiv) to give the desired tetraphenylborate azepinium salt as a yellow powder (0.20 g, 68%): ν_{max}(film)/cm^{-1} 3054, 3002, 2884, 2160, 1629, 1386, 1201, 1109, 735, 704; $[\alpha]^{20}_D$ −62.9 (*c* 0.96, $CHCl_3$); δ_H (400 MHz; $(CD_3)_2SO$, 80 °C) 0.98 (3 H, d, *J* 7 Hz), 1.73 (3 H, s), 1.76 (3 H, s), 4.45 (1 H, dd, *J* 14, 1 Hz), 4.77 (1 H, dd, *J* 14, 3 Hz), 4.87 (1 H, dd, *J* 3, 1 Hz), 5.77 (1 H, q, *J* 7 Hz), 5.87 (1 H, d, *J* 3 Hz), 6.79−6.85 (4 H, m), 6.95 (8 H, t, *J* 8 Hz), 7.08−7.15 (3 H, m), 7.23−7.32 (11 H, m), 7.52 (2 H, sextuplet, *J* 7, 2 Hz), 7.66−7.74 (2 H, m), 7.81 (1 H, dd, *J* 8, 1 Hz), 7.93 (1 H, dt, *J* 7, 2 Hz), 7.96 (1 H, dd, *J* 8, 1 Hz), 9.33 (1 H, s); δ_C (100 MHz; $(CD_3)_2SO$) 14.8, 18.5, 29.2, 54.8, 62.1, 67.2, 70.2, 100.5, 121.6, 125.0, 125.3, 125.38, 125.42, 125.5, 128.0, 128.4, 128.8, 129.0, 129.6, 129.9, 130.4, 130.6, 134.1, 135.1, 135.7, 136.0, 136.6, 137.5, 140.9, 162.6, 163.3, 163.9, 164.6, 170.4; *m*/*z* found (ESI) for [iminium cation]$^+$ 398.2115, $[C_{27}H_{28}NO_2]^+$ requires 398.2120.

6-(2,2-Dimethyl-4-phenyl-[1,3]dioxan-5-yl)-5-isopropyl-5*H*-dibenzo[*c*,*e*]azepinium Tetraphenylborate 16. Prepared according to the general procedure from 6-(2,2-dimethyl-4-phenyl-1,3-dioxan-5-yl)-5-isopropyl-6,7-dihydro-5*H*-dibenzo[*c*,*e*]azepine **12** (0.15 g, 0.35 mmol), *N*-bromosuccinimide (0.08 g, 0.42 mmol, 1.2 equiv), and sodium tetraphenylborate (0.12 g, 0.35 mmol, 1 equiv) to give the desired tetraphenylborate azepinium salt as a yellow powder (0.22 g, 83%): ν_{max}(film) /cm^{-1} 3385, 2964, 2926, 2359, 2339, 1714, 1636, 1557, 1455, 1385, 1201, 1079, 960, 841, 763, 752, 700, 667; $[\alpha]^{20}_D$ −8.1 (*c* 0.64, $CHCl_3$); δ_H (400 MHz; $(CD_3)_2SO$, 80 °C) 0.44 (3 H, d, *J* 6 Hz), 0.99 (3 H, d, *J* 6 Hz), 1.47−1.56 (1 H, m), 1.69 (3 H, s), 1.70 (3 H, s), 4.62 (1 H, d, *J* 14 Hz), 4.76 (1 H, dd, *J* 14, 3 Hz), 4.81−4.83 (1 H, m), 5.83 (1 H, d, *J* 2 Hz), 6.75−6.83 (5 H, m), 6.89 (1 H, t, *J* 7 Hz), 6.92 (9 H, t, *J* 7 Hz), 7.19−7.26 (8 H, m), 7.38 (2 H, t, *J* 7 Hz), 7.44−7.50 (2 H, m), 7.58 (1 H, d, *J* 8 Hz), 7.63−7.69 (1 H, m), 7.75−7.79 (1 H, m), 7.96 (2 H, d, *J* 4 Hz), 8.11 (1 H, d, *J*, 8 Hz), 9.63 (1 H, s); δ_C (100 MHz; $(CD_3)_2SO$) 18.7, 19.2, 19.4, 26.2, 29.0, 61.5, 68.0, 70.7, 80.1, 100.9, 115.4, 121.7, 124.7, 125.1, 125.40, 125.43, 125.47, 125.51, 126.9, 128.0, 128.1, 128.9, 129.1, 129.6, 129.7, 130.3, 130.4, 130.6, 133.2, 135.3, 135.4, 135.8, 136.2, 141.2, 162.6, 163.3, 164.0, 164.6, 169.3; *m*/*z* found (ESI) for [iminium cation]$^+$ 426.2438, $[C_{29}H_{32}NO_2]^+$ requires 426.2433.

6-(2,2-Dimethyl-4-phenyl-1,3-dioxan-5-yl)-5-phenyl-5*H*-dibenzo[*c*,*e*]azepinium Tetraphenylborate 17. Prepared according to the general procedure from 6-(2,2-dimethyl-4-phenyl-1,3-dioxan-5-yl)-5-phenyl-6,7-dihydro-5*H*-dibenzo[*c*,*e*]azepine **13** (0.14 g, 0.30 mmol), *N*-bromosuccinimide (0.07 g, 0.36 mmol, 1.2 equiv), and sodium tetraphenylborate (0.10 g, 0.30 mmol, 1 equiv) to yield the desired tetraphenylborate azepinium salt as a yellow powder (0.20 g, 86%): ν_{max}(film) /cm^{-1} 3057, 3024, 2921, 2360, 1628, 1595, 1448, 1260, 1086, 1027, 800, 756, 698; $[\alpha]^{20}_D$ −21.2 (*c* 0.98, $CHCl_3$); δ_H (400 MHz; $(CD_3)_2SO$, 80 °C) 1.77 (3 H, s, 1.88 (3 H, s), 4.66 (1 H, d, *J* 14 Hz), 4.88 (1 H, dd, *J* 14, 3 Hz), 5.11 (1 H, s), 5.93 (1 H, d, *J* 2 Hz), 6.48−6.54 (2 H, m), 6.80 (3 H, t, *J* 7 Hz), 6.93 (11 H, t, *J* 7 Hz),

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6.98−7.03 (3 H, m), 7.08 (2 H, d, *J* 7 Hz), 7.20−7.26 (8 H, m), 7.46−7.53 (2 H, m), 7.56−7.69 (7 H, m), 7.88 (1 H, d, *J* 8 Hz), 9.66 (1 H, s); δ_C (100 MHz; $(CD_3)_2SO$) 18.7, 29.2, 60.9, 66.8, 70.3, 73.0, 100.1, 101.1, 115.3, 121.6, 124.4, 125.2, 125.36, 125.40, 125.43, 125.5, 127.8, 127.9, 128.6, 129.1, 129.2, 129.5, 130.5, 130.6, 130.7, 133.2, 134.76, 134.82, 135.4, 135.7, 136.27, 136.3, 140.8, 162.6, 163.2, 163.9, 164.6, 170.7; *m*/*z* found (ESI) for [iminium cation]$^+$ 460.2271, $[C_{32}H_{30}NO_2]^+$ requires 460.2276.

5-Benzyl-6-(2,2-dimethyl-4-phenyl-1,3-dioxan-5-yl)-5-benzyl-5*H*-dibenzo[*c*,*e*]azepinium Tetraphenylborate 18. Prepared according to the general procedure from 6-(2,2-dimethyl-4-phenyl-1,3-dioxan-5-yl)-5-phenyl-6,7-dihydro-5*H*-dibenzo[*c*,*e*]azepine **14a** (0.17 g, 0.35 mmol), *N*-bromosuccinimide (0.08 g, 0.43 mmol, 1.2 equiv,) and sodium tetraphenylborate (0.12 g, 0.35 mmol, 1 equiv) to yield the desired tetraphenylborate azepinium salt as a yellow powder (0.24 g, 84%): ν_{max}(film) /cm^{-1} 3372, 2960, 2359, 1708, 1639, 1619, 1448, 1383, 1260, 1201, 1083, 1027, 799, 751, 700. $[\alpha]^{20}_D$ −18.5 (*c* 1.06, $CHCl_3$); δ_H (400 MHz; $(CD_3)_2SO$, 80 °C) 1.65 (3 H, s), 1.67 (3 H, s), 2.53 (2 H, d, *J* 8 Hz), 3.52 (1 H, d, *J* 14 Hz), 4.46 (1 H, dd, *J* 14, 3 Hz), 4.73−4.77 (1 H, m), 5.68 (1 H, t, *J* 8 Hz), 5.78 (1 H, d, *J* 3 Hz), 6.80 (4 H, t, *J* 7 Hz), 6.83−6.88 (2 H, m), 6.89 (1 H, d, *J* 7 Hz), 6.93 (8 H, t, *J* 7 Hz), 6.98−7.04 (3 H, m), 7.17−7.28 (13 H, m), 7.32 (1 H, dt, *J* 7, 1 Hz), 7.47 (1 H, dt, *J* 7, 1 Hz), 7.68 (1 H, d, *J* 8 Hz), 7.84 (1 H, dt, *J* 8, 1 Hz), 8.02−8.08 (3 H, m), 8.10 (1 H, d, *J* 8 Hz), 9.54 (1 H, s); δ_C (100 MHz; $(CD_3)_2SO$) 18.4, 29.1, 32.9, 61.3, 67.9, 70.3, 100.6, 121.6, 124.9, 125.36, 125.39, 125.43, 125.5, 127.6, 128.1, 128.9, 129.0, 129.2, 129.89, 129.94, 130.0, 130.2, 130.5, 134.1, 135.2, 135.3, 137.2, 141.3, 162.6, 163.3, 163.9, 164.6, 170.4; *m*/*z* found (ESI) for [iminium cation]$^+$ 474.2427, $[C_{33}H_{32}NO_2]^+$ requires 474.2433.

General Procedure for the Addition of Methyl Grignard Reagent to Binaphthyl Azepinium Salts. A solution of methylmagnesium bromide in diethyl ether (3M, 10 equiv) was added dropwise with stirring to a solution of iminium salt in THF (50 mL per g of iminium salt) at −78 °C. After being stirred at −78 °C for 1 h, the mixture was allowed to reach ambient temperature overnight. Saturated aqueous ammonium chloride (5 mL per g of iminium salt) was added, and the organic solvents removed under reduced pressure. The mixture was dissolved in ethyl acetate and filtered and the organic layer separated and washed with water (2 × 60 mL per g of iminium salt) and brine (50 mL per g of iminium salt). The organic layer was dried over magnesium sulfate, and the solvents were removed under reduced pressure to give the crude azepine, which was purified using flash column chromatography on silica gel, typically eluting with 5:1 light petroleum/ethyl acetate buffered with 2% triethylamine.

General Procedure for the Synthesis of Methyl-Substituted Binaphthylazepinium Tetraphenylborate Salts. *N*-Bromosuccinimide (1.1 equiv) was added to a solution of the azepine substrate in dichloromethane (30 mL per g of azepine). The resulting yellow solution was stirred for 10 min. The organic layer was separated, washed with water (2 × 60 mL per gram of azepine) and brine (30 mL), and dried over magnesium sulfate. The solvents were removed under reduced pressure, and the resulting crude yellow/orange foam redissolved in ethanol (60 mL per gram of azepine). A solution of sodium tetraphenylborate (1.1 equiv) in a minimum amount of acetonitrile was added, resulting in the formation of an orange precipitate. The solvents were removed under reduced pressure to yield the crude iminium salt as an orange-brown foam, which was recrystallized from ethanol and washed with cold ethanol followed by hexane and diethyl ether. The fine orange powder was dried in a vacuum oven at 60 °C overnight.

(R_{ax})-4-((4*S*,5*S*)-2,2-Dimethyl-4-phenyl-1,3-dioxan-5-yl)-3-methyl-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]azepine 21. Prepared according to the general procedure from (R_{ax})-*N*-[(4*S*,5*S*)-5-(4-phenyl-2,2-dimethyl-1,3-dioxanyl)]-7*H*-dinaphtho[2,1-*c*;1′,2′-*e*]-azepinium tetraphenylborate **6** (1.20 g, 1.49 mmol) and isolated as a colorless solid (510 mg, 68%): mp 200−201 °C dec; $[\alpha]^{20}_D$ −152.35 (*c* 0.68, $CHCl_3$); ν_{max} (neat)/cm^{-1} 3044, 2987, 2857, 1496, 1448, 1378, 1196, 1144, 1101, 1078, 1016, 952, 907, 850, 818, 767, 749, 727, 697; δ_H (400 MHz; $CDCl_3$) 0.12 (3 H, d, *J* 6.9 Hz), 1.50 (3 H, s), 1.59 (3 H, s), 2.87 (1 H, s), 3.52 (1 H, d, *J* 11.5 Hz), 3.72 (1 H, d, *J* 11.4 Hz), 3.97 (1 H, d, *J* = 12.4 Hz), 4.19 (1 H, dd, *J* 12.4 Hz, 3.6 Hz), 4.44 (1 H, q, *J* 6.8 Hz), 5.12 (1 H, s), 7.06−7.33 (13 H, m), 7.72−7.80 (4 H, m); δ_C (75 MHz; $CDCl_3$) 19.2, 21.1, 29.3, 54.1, 59.9, 60.1, 63.9, 72.3, 99.4, 125.09, 125.14, 125.3, 125.6, 126.3, 126.7, 127.4, 127.5, 127.6, 127.8, 127.9, 128.2, 128.4, 128.6, 128.9, 131.9, 132.0, 132.6, 132.8, 133.1, 135.0, 136.4, 140.0, 140.3; *m*/*z* found (ESI) for [M + H]$^+$ 500.2576, $[C_{35}H_{34}NO_2]^+$ requires 500.2584.

(S_{ax})-4-((4*S*,5*S*)-2,2-Dimethyl-4-phenyl-1,3-dioxan-5-yl)-3-methyl-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]azepine 22. Prepared according to the general procedure from (S_{ax})-*N*-[(4*S*,5*S*)-5-(4-phenyl-2,2-dimethyl-1,3-dioxanyl)]-7*H*-dinaphtho[2,1-*c*;1′,2′-*e*]-azepinium tetraphenylborate **19** (390 mg, 0.49 mmol) and isolated as a colorless foam (210 mg, 78%): $[\alpha]^{20}_D$ +227.1 (*c* 0.93, acetone); ν_{max} (neat)/cm^{-1} 2991, 2920, 1714, 1596, 1498, 1449, 1378, 1221, 1197, 1079, 1014, 854, 819, 768, 752, 698; δ_H (400 MHz; acetone-D_6) 0.15 (3 H, d, *J* 7.1 Hz), 1.38 (3 H, s), 1.51 (3 H, s), 3.28 (1 H, m), 3.55 (1 H, d, *J* 11.4 Hz), 4.00- 4.19 (2 H, m), 4.26 (1 H, d, *J* 11.4 Hz), 4.37 (1 H, dd, *J* 12.4, 3.5 Hz), 5.38 (1 H, d, *J* 4.0 Hz), 7.09 (1 H, d, *J* 8.3 Hz), 7.17−7.29 (4 H, m), 7.33−7.41 (4 H, m), 7.45 (1 H, ddt, *J* 8.7, 6.7, 1.1 Hz), 7.57−7.61 (3 H, m), 7.78 (1 H, d, *J* 8.3 Hz), 7.90 (1 H, d, *J* 8.3 Hz), 8.00 (1 H, d, *J* 8.2 Hz), 8.04 (1 H, d, *J* 8.3 Hz); δ_C (75 MHz; acetone-D_6) 19.3, 22.78, 28.83, 52.1, 62.89, 63.93, 66.8, 74.3, 99.6, 126.1, 126.4, 126.5, 126.6, 126.9, 127.2, 127.8, 128.1, 128.3, 129.1, 129.2, 129.3, 129.9, 132.7, 133.0, 133.7, 133.9, 134.0, 135.7, 137.5, 140.8, 141.7; *m*/*z* found (ESI) for [M + H]$^+$ 500.2577, $[C_{35}H_{34}NO_2]^+$ requires 500.2584.

(R_{ax})-4-((4*S*,5*S*)-2,2-Dimethyl-4-phenyl-1,3-dioxan-5-yl)-3-methyl-3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]azepinium Tetraphenylborate 26. Prepared according to the general procedure from (R_{ax})-4-((4*S*,5*S*)-2,2-dimethyl-4-phenyl-1,3-dioxan-5-yl)-3-methyl-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]azepine **21** (480 mg, 0.96 mmol) and isolated as an orange-yellow powder (542 mg, 69%: mp 127−128 °C dec; $[\alpha]^{20}_D$ −302.5 (*c* 1.05, acetone); ν_{max} (neat)/cm^{-1} 3055, 2983, 2358, 2335, 1633, 1612, 1580, 1551, 1464, 1426, 1380, 1262, 1238, 1201, 1164, 1111, 1031, 958, 857, 816, 749, 733, 702, 668, 631, 611; δ_H (300 MHz; acetonitrile-d_3) 1.00 (3 H, d, *J* 7.1 Hz), 1.69 (3 H, s), 1.76 (3 H, s), 4.35 (1 H, dd, *J* 13.8, 1.1 Hz), 4.44 (1 H, td, *J* 2.9, 1.1 Hz), 4.73 (1 H, dd, 13.8, 3.0 Hz), 5.61 (1 H, q, *J* 6.9 Hz), 5.67 (1 H, d, *J* 2.9), 6.47 (1 H, t, *J* 7.5 Hz), 6.67 (2 H, t, *J* 7.8 Hz), 6.81−6.89 (5 H, m), 6.95−7.06 (10 H, m), 7.16−7.24 (1 H, m), 7.25−7.37 (11 H, m), 7.55 (1 H, ddd, *J* 8.1, 6.8, 1.1 Hz), 7.73 (2 H, ddd, *J* 7.9, 4.9, 1.7 Hz), 8.01 (1 H, d, *J* 8.2 Hz), 8.02 (1 H, d, *J* 8.3 Hz), 8.12 (1 H, d, *J* 8.3 Hz), 8.21 (1 H, d, *J* 8.5 Hz), 9.31 (1 H, s); δ_C (75 MHz; acetonitrile-d_3) 13.8, 18.0, 28.9, 62.0, 68.4, 69.7, 71.1, 101.2, 122.0, 124.8, 124.9, 125.82−125.93 (8C, 8 × *CH arom*), 126.2, 126.4, 127.1, 127.2, 127.9, 128.1, 128.5, 128.7, 129.0, 129.49, 129.50, 131.0, 131.9, 132.0, 133.0, 134.0, 135.8, 135.9, 136.0, 138.9, 142.1, 164.1 (4 C, q, *J* = 49.0 Hz), 169.2; *m*/*z* found (ESI) for [iminium cation]$^+$ 498.2415, $[C_{35}H_{32}NO_2]^+$ requires 498.2428.

(S_{ax})-4-((4*S*,5*S*)-2,2-Dimethyl-4-phenyl-1,3-dioxan-5-yl)-3-methyl-3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]azepinium Tetraphenylborate 27. Prepared according to the general procedure from (S_{ax})-4-((4*S*,5*S*)-2,2-dimethyl-4-phenyl-1,3-dioxan-5-yl)-3-methyl-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]azepine **22** (170 mg, 0.34 mmol) and isolated as bright yellow powder (201 mg, 72%): mp 203−205 °C dec; $[\alpha]^{20}_D$ +421.4 (*c* 0.99, acetone); ν_{max} (neat)/cm^{-1} 3054, 2986, 1631, 1611, 1586, 1554, 1464, 1426, 1379, 1240, 1198, 1120, 1086, 1048, 1030, 952, 834, 821, 753, 733, 701, 672; δ_H (400 MHz; acetone-d_6) 0.75 (1 H, d, *J* 7.1 Hz), 1.73 (3 H, s), 1.74 (3 H, s), 4.29 (1 H, d, *J* 13.9 Hz), 4.88 (1 H, dd, *J* 13.9, 2.9 Hz), 5.01 (1 H, t, *J* 2.7 Hz), 6.02 (1 H, d, *J* 2.9 Hz), 6.05 (1 H, q, *J* 7.1 Hz), 6.78 (4 H, t, *J* 7.2 Hz), 6.93−7.04 (11 H, m), 7.24−7.46 (13 H, m), 7.59 (1 H, t, *J* 7.2 Hz), 7.75−7.81 (2 H, m), 7.95 (1 H, d, *J* 8.6 Hz), 8.12 (1 H, d, *J* 8.2 Hz), 8.17 (1H, d, *J* 8.2 Hz), 8.28 (1 H, d, *J* 8.6 Hz), 8.29 (1 H, d, *J* 8.3 Hz), 9.47 (1 H, s); δ_C (75 MHz; acetone-d_6) 12.4, 17.9, 28.6, 61.8, 68.8, 69.2, 71.8, 101.0, 121.5, 125.3, 125.5, 126.6, 127.1, 127.19, 127.25, 127.29, 128.2, 128.3, 128.7, 128.8, 129.0, 129.3, 129.4, 129.6, 131.0, 131.7, 131.8, 132.9, 134.0, 135.9, 139.6, 141.8, 164.3 (4 C, q, *J* = 49.0 Hz), 176.2; *m*/*z* found (ESI) for [iminium cation]$^+$ 498.2413, $[C_{35}H_{32}NO_2]^+$ requires 498.2428.

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(3*R*, R_{ax})-4-((*R*)-3,3-Dimethylbutan-2-yl)-3-methyl-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]azepine 24. Prepared according to the general procedure from **20** (0.50 g, 0.72 mmol), and isolated as a colorless foam, (0.29 g, 99%): $[\alpha]^{21}_{D}$ −291.3 (*c* = 1.03, $CHCl_3$); ν_{max} (neat)/cm^{-1} 3046, 2953, 2912, 2860, 1739, 1505, 1469, 1455, 1377, 1364, 1325, 1313, 1248, 1218, 1199, 1166, 1147, 1110, 1071, 997, 815; (400 MHz; acetone-d_6) 0.51 (3 H, d, *J* 7.1 Hz), 0.98 (1 H, d, *J* 7.1 Hz), 1.04 (9 H, s), 2.73 (1 H, q, *J* 6.9 Hz), 3.29 (1 H, d, *J* 10.8 Hz), 3.70 (1 H, d, *J* 10.8 Hz), 4.11 (1 H, q, *J* 7.0 Hz), 7.25−7.32 (2 H, m), 7.35 (1 H, d, *J* 8.4 Hz), 7.41−7.51 (3 H, m), 7.59 (1 H, d, *J* 8.3 Hz), 7.64 (1 H, d, *J* 8.3 Hz), 7.98−8.08 (4 H, m); δ_C (100 MHz; acetone-d_6) 10.5, 22.5, 27.7, 35.8, 49.4, 70.2, 73.0, 125.4, 125.5, 125.8, 125.9, 127.0, 127.1, 127.9, 128.4, 128.6, 128.9, 129.0, 129.1, 132.0, 132.1, 132.3, 133.1, 133.2, 135.3, 136.8, 140.3; *m*/*z* found (ESI) for $[M + H]^+$ 394.2531, $[C_{29}H_{32}N]^+$ requires 394.2529.

(3*R*, R_{ax})-4-((*S*)-3,3-Dimethylbutan-2-yl)-3-methyl-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]azepine 23. Prepared according to the general procedure from **7** (0.50 g, 0.72 mmol), and isolated as a yellow foam (0.29 g, 99%): $[\alpha]^{20}_{D}$ −185.6 (*c* = 0.97, $CHCl_3$); ν_{max} (neat)/cm^{-1} 2950, 2920, 1688, 1505, 1458, 1431, 1388, 1364, 1321, 1245, 1226, 1217, 1206, 1173, 1158, 1137, 1080, 1006, 863, 817; (400 MHz; acetone-d_6) 0.52 (3 H, d, *J* 7.1 Hz), 1.00 (9 H, s), 1.10 (1 H, d, *J* 7.0 Hz) 2.63 (1 H, q, *J* 7.0 Hz), 3.65 (1 H, d, *J* 10.9 Hz), 3.68 (1 H, d, *J* 11.0 Hz), 4.26 (1 H, q, *J* 7.1 Hz), 7.25−7.31 (3 H, m), 7.40 (1 H, d, *J* 8.6 Hz), 7.44−7.51 (2 H, m), 7.57 (1 H, d, *J* 8.4 Hz), 7.67 (1 H, d, *J* 8.3 Hz), 7.99−8.05 (4 H, m); δ_C (100 MHz; acetone-d_6) 11.6, 22.6, 27.1, 36.8, 57.5, 59.9, 69.6, 126.3, 126.4, 126.6, 126.7, 127.9, 128.0, 129.2, 129.3, 129.5, 129.6, 129.9, 130.5, 132.8, 133.0, 133.8, 134.1, 134.2, 136.1, 137.2, 140.8; *m*/*z* found (ESI) for $[M + H]^+$ 394.2530, $[C_{29}H_{32}N]^+$ requires 394.2529.

(−)-(3*R*, R_{ax})-4-Isopropyl-3-methyl-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]azepine 25. Prepared according to the general procedure from **8** (0.70 g, 1.07 mmol), and isolated as a colorless crystalline solid (0.32 g, 85%): $[\alpha]^{20}_{D}$ −375.3 (*c* = 1.02, $CHCl_3$); ν_{max} (neat)/cm^{-1} 3044, 2958, 2802, 1594, 1505, 1458, 1363, 1317, 1243, 1164, 1101, 1057, 979, 948, 862, 810, 767, 749, 699, 674, 628; δ_H (300 MHz; $CDCl_3$) 0.50 (3 H, d, *J* 7.2 Hz), 1.05 (3 H, d, *J* 6.5 Hz), 1.13 (3 H, d, *J* 6.7 Hz), 3.12 (1 H, sept, *J* 6.6 Hz), 3.44 (1 H, d, *J* 10.5 Hz), 3.64 (1 H, d, *J* 10.5 Hz), 4.23 (1H, q, *J* 7.2 Hz), 7.26 (3 H, m), 7.38 (1 H, dd, *J* 8.6, 0.9 Hz), 7.46 (2 H, m), 7.61 (1 H, d, *J* 8.4 Hz), 7.66 (1 H, d, *J* 8.3 Hz), 8.01 (4 H, m); δ_C (75 MHz; $CDCl_3$) 18.9, 21.2, 24.5, 53.1, 57.0, 60.0, 126.3, 126.4, 126.6, 126.7, 127.9, 128.0, 129.2, 129.3, 129.4, 129.66, 129.73, 130.4, 132.8, 133.0, 133.87, 133.93, 134.1, 135.8, 137.2, 141.0; *m*/*z* found (ESI) for $[M + H]^+$ 352.2064, $[C_{26}H_{26}N]^+$ 352.2060.

(−)-(3*R*,R_{ax})-4-((*R*)-3,3-Dimethylbutan-2-yl)-3-methyl-3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]azepin-4-ium Tetraphenylborate 29. Prepared according to the general procedure from (3*R*,R_{ax})-4-((*R*)-3,3-dimethylbutan-2-yl)-3-methyl-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]azepine **24** (0.25 g, 0.64 mmol) and isolated as a fine yellow powder (0.33 g, 72%): mp 108−109 °C dec; $[\alpha]^{20}_{D}$ −324.00 (*c* = 1.00, acetone); ν_{max} (neat)/cm^{-1} 3054, 2981, 1610, 1585, 1557, 1464, 1425, 1373, 1120, 1089, 1032, 817, 731, 702, 666, 611; δ_H (400 MHz; acetone-d_6) 0.97 (9 H, s), 1.29 (3 H, d, *J* 7.1 Hz), 1.80 (3 H, s), 4.59 (1 H, q, *J* 6.9 Hz), 5.88 (1 H, q, *J* 7.1 Hz), 6.74 (4 H, t, *J* 7.1 Hz), 6.89 (8 H, t, *J* 7.4 Hz), 7.06 (1 H, d, *J* 8.6 Hz), 7.25−7.35 (11 H, m), 7.42 (1 H, m), 7.56 (1 H, ddd, *J* 8.1, 6.8, 1.1 Hz), 7.77 (1 H, ddd, *J* 8.1, 6.8, 1.2 Hz), 7.82 (1 H, d, *J* 8.5 Hz), 8.04 (1 H, d, *J* 8.6 Hz), 8.07 (1 H, d, *J* 8.2 Hz), 8.19 (1 H, d, *J* 8.3 Hz), 8.26 (1 H, d, *J* 8.4 Hz), 8.33 (1 H, d, *J* 8.5 Hz), 9.67 (1 H, s); δ_C (75 MHz; acetone-d_6) 12.2, 14.7, 26.5, 35.8, 62.1, 81.8, 122.3, 126.1, 126.6, 128.0, 128.1, 128.2, 128.3, 128.9, 129.5, 129.8, 130.1, 130.4, 131.0, 131.7, 132.1, 132.8, 133.3, 134.6, 136.9, 137.2, 140.7, 142.7, 165.3 (4 C, q, *J* = 49.0 Hz), 171.6; *m*/*z* found (ESI) for [iminium cation]$^+$ 392.2370, $[C_{29}H_{30}N]^+$ requires 392.2373.

(−)-(3*R*,11cR_a)-4-((*S*)-3,3-Dimethylbutan-2-yl)-3-methyl-3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]azepin-4-ium Tetraphenylborate 28. Prepared according to the general procedure from **23** (0.27 g, 0.69 mmol) and isolated as a fine orange-yellow powder (0.31 g, 64%): mp 131−132 °C dec; $[\alpha]^{20}_{D}$ −259.56 (*c* = 0.90, acetone); ν_{max} (neat)/cm^{-1} 3056, 2986, 1612, 1587, 1552, 1478, 1426, 1381, 1261, 1119, 1088, 1032, 960, 817, 732, 702, 670, 632, 611; δ_H (400 MHz; acetone-d_6) 1.18 (9 H, s), 1.33 (3 H, d, *J* 6.9 Hz), 1.74 (3 H, br s), 4.55 (1 H, br s), 5.89 (1 H, q, *J* 7.0 Hz), 6.73 (4 H, t, *J* 7.2 Hz), 6.88 (8 H, t, *J* 7.4 Hz), 7.07 (1 H, d, *J* 8.6 Hz), 7.29 (9 H, m), 7.45 (2 H, m), 7.55 (1 H, ddd, *J* 8.0, 6.8, 1.1 Hz), 7.78−7.80 (1 H, m), 7.85 (1 H, br s), 8.06 (1 H, d, *J* 8.2 Hz), 8.10 (1 H, br s), 8.21 (1 H, d, *J* 8.3 Hz), 8.22 (1 H, d, *J* 8.5 Hz), 8.34 (1 H, d, *J* 8.6 Hz), 9.52 (1 H, br s); δ_C (75 MHz; MeCN-d_3) 13.6, 26.1, 35.7, 80.6, 121.5, 125.3, 125.7, 127.2, 127.3, 128.1, 128.7, 129.0, 129.3, 129.8, 129.9, 130.8, 131.5, 132.0, 132.7, 133.9, 135.9, 136.3, 141.6, 164.3 (4 C, q, *J* = 49.0 Hz); *m*/*z* found (ESI) for [iminium cation]$^+$ 392.2372; $[C_{29}H_{30}N]^+$ requires 392.2373.

(−)-(3*R*,R_{ax})-4-Isopropyl-3-methyl-3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]azepin-4-ium Tetraphenylborate 30. Prepared according to the general procedure from **25** (0.32 g, 0.92 mmol) and isolated as a bright yellow powder (0.43 g, 71%): mp 209.0−218.3 °C dec; $[\alpha]^{20}_{D}$ −358.38 (*c* = 0.99, acetone); ν_{max} (neat)/cm^{-1} 2053, 1652, 1591, 1578, 1552, 1474, 1461, 1524, 1376, 1359, 1262, 1211, 1134, 1109, 1045, 1030, 969, 867, 823, 796, 746, 735, 702; δ_H (300 MHz; DMSO-d_6) 1.05 (3 H, d, *J* 7.1 Hz), 1.44 (3 H, d, *J* 6.5 Hz), 1.57 (3 H, d, *J* 6.5 Hz), 4.57 (1 H, sept, *J* 6.5 Hz), 5.90 (1 H, q, *J* 7.1 Hz), 6.76 (4 H, t, *J* 7.2 Hz), 6.90 (8 H, t, *J* 7.3 Hz), 6.97 (1 H, d, *J* 8.5 Hz), 7.17 (8 H, m), 7.26 (1 H, ddd, *J* 8.2, 6.8, 1.3 Hz), 7.34 (1 H, d, *J* 8.6 Hz), 7.45 (1 H, ddd, *J* 8.0, 6.8, 1.2 Hz), 7.53 (1 H, ddd, *J* 8.0, 6.8, 1.0 Hz), 7.76 (1 H, ddd, *J* 8.0, 6.8, 1.0 Hz), 7.90 (1 H, d, *J* 8.5 Hz), 8.07 (2 H, m), 8.23 (2 H, t, *J* 8.6 Hz), 8.36 (1 H, d, *J* 8.6 Hz), 9.52 (1 H, s); δ_C (75 MHz; DMSO) 14.3, 19.4, 20.0, 60.2, 66.7, 121.7, 125.5, 125.8, 126.6, 126.7, 126.9, 127.0, 127.1, 128.0, 128.7, 129.0, 129.2, 129.3, 130.2, 131.3, 131.4, 132.0, 133.3, 134.7, 135.0, 135.8, 140.2, 140.4, 163.6 (4 C, q, *J* = 49.0 Hz), 167.5; *m*/*z* found (ESI) for [iminium cation]$^+$ 350.1904, $[C_{26}H_{24}N]^+$ requires 350.1903.

Crystallographic Data. X-ray diffraction studies for **15**, **21**, and **27** were performed at 93K using a Rigaku MM007/Mercury diffractometer (confocal optics Mo Kα radiation). Intensity data were collected using ω steps accumulating area detector frames spanning at least a hemisphere of reciprocal space for all structures (data were integrated using CrystalClear). All data were corrected for Lorentz, polarization, and long-term intensity fluctuations. Absorption effects were corrected on the basis of multiple equivalent reflections. Structures were solved by direct methods and refined by full-matrix least-squares against F^2 (SHELXTL). Hydrogen atoms were assigned riding isotropic displacement parameters and constrained to idealized geometries.[25]

15: $C_{51}H_{48}BNO_2$, *M* = 717.71, orthorhombic, space group *P*2(1)2(1)2(1), *a* = 11.283(2) Å, *b* = 15.681(3) Å, *c* = 22.336(5) Å, *U* = 3951.9(13) Å^3, *Z* = 4, D_c = 1.206 Mg m^{-3}, μ = 0.072 mm^{-1}. Of 25306 measured data, 5313 were unique to give R_1= 0.0535 and wR_2 = 0.1053, GOF= 0.960.

21: $C_{35}H_{33}NO_2$, *M* = 717.71, orthorhombic, space group *P*2(1)-2(1)2(1), *a* = 11.198(3) Å, *b* = 12.171(3) Å, *c* = 19.804(5) Å, *U* = 2699.0(11) Å^3, *Z* = 4, D_c = 1.230 Mgm^{-3}, μ = 0.075 mm^{-1}. Of 17103 measured data, 4914 were unique to give R_1= 0.0526 and wR_2 = 0.1188, GOF = 0.978.

27·3CH$_2$Cl$_2$: $C_{62}H_{58}BNO_2Cl_6$, *M* = 1072.60, orthorhombic, space group *P*2(1)2(1)2(1), *a* = 11.458(2) Å, *b* = 17.247(3) Å, *c* = 27.663(6) Å, *U* = 5466.5(19) Å^3, *Z* = 4, D_c = 1.303 Mg m^{-3}, μ = 0.359 mm^{-1}. Of 34687 measured data, 9884 were unique to give R_1= 0.1056 and wR_2 = 0.2036, GOF = 0.882.

■ ASSOCIATED CONTENT

Supporting Information

^{1}H and ^{13}C NMR spectra; chromatograms and spectra for ee determination by GC, HPLC, and NMR techniques; X-ray data for **15**, **21**, **27**, including CIF files. This information is available free of charge *via* the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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