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# Synthesis of dioxazaborocines from *N*-substituted-bis(2-hydroxyaryl)aminomethylamines

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**Abstract**

The preparation of a number of tripodal amines from aminoalkylation of 1,3-benzoxazines by phenols is presented. A series of ligands prepared in this manner were successfully coordinated to boron, giving dioxazaborocines. X-ray crystal structures of two analogues are reported. These compounds are capable of releasing borate ions and are therefore potentially biologically active.


*Keywords:* Boron; Boratrane; 1,3-Benzoxazine; Crystal structure; Dioxazaborocine

## 1. Introduction

Boron compounds capable of releasing borate ions have biocidal properties. In New Zealand, borate-based formulations including inorganic borates and borate esters are used as insecticides and timber preservatives for plantation softwoods, especially *Pinus radiata* [1]. Although organoboron compounds have been reported to be suitable substrates for wood preservation, only very simple examples have been tested [2]. For such an application, the release of the borate anion must be very slow but commensurate with the bio-efficiency required. In this regard, an extended organic moiety can provide considerable steric shielding of the inorganic part of the molecule, boron being shielded from polar solvents. This structural parameter, by design, should lead to products with better long-term biocidal activity compared with that of simple organoboron compounds used in wood treatment to date.

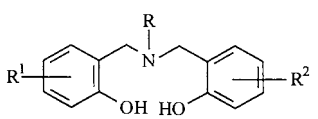


Fig. 1. Unsymmetrical tertiary amine.

A method for the preparation of *N*-substituted 3,4-dihydro-2*H*-1,3-benzoxazines by a Mannich-type condensation of a phenol with a primary amine and two equivalents of formaldehyde has been reported [3]. Burke et al. [4] found when a dihydro-1,3-benzoxazine (or a naphthoxazine) is treated with the phenol (or naphthol) from which the benzoxazine was derived, symmetrical products are obtained (Fig. 1; $R^1 = R^2$). In all other cases; however, the aminoalkylation of phenols or naphthols with 1,3-benzoxazines provides a route to unsymmetrically substituted tertiary amines (Fig. 1; $R^1 \neq R^2$). The success of the reaction depends largely on the structure of the primary amine used, on the temperature employed in the oxazine synthesis, and on the nucleophilicity at the active sites on the ring of the phenolic substrate [5–9]. We now report the coordination of boron to tertiary amines formed via these aminoalkylation reactions.

## 2. Results and discussion

Initially, it was anticipated that treatment of the tetradentate tertiary amine **2** with either boric acid or trimethyl borate would provide the novel boratrane **3** (Scheme 1). Naphthoxazines derived from straight-chain primary amines have been shown to aminoalkylate 2-naphthol [10]. It was not surprising, therefore,

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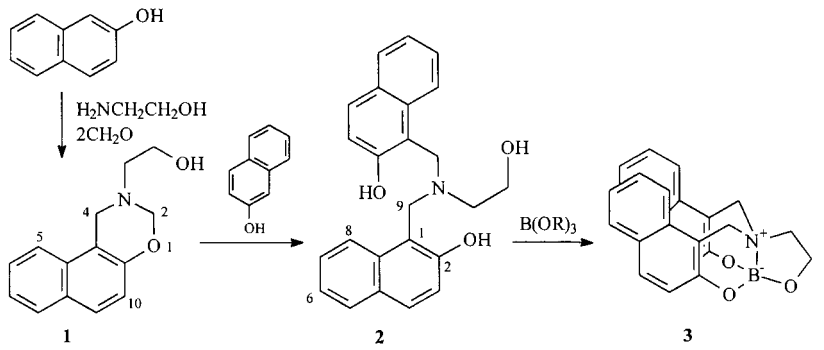
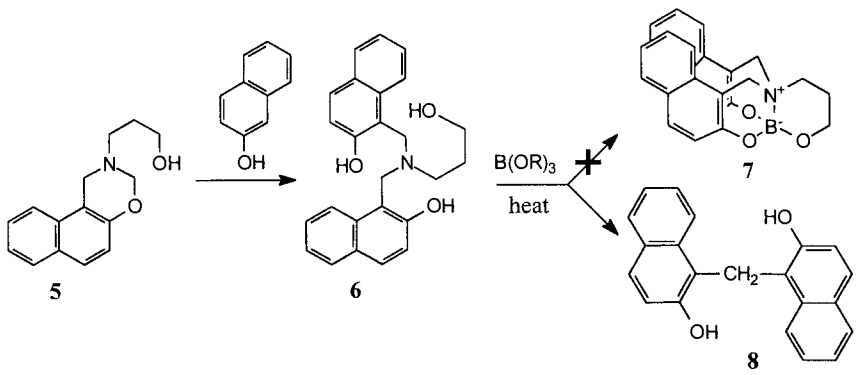



Scheme 1.

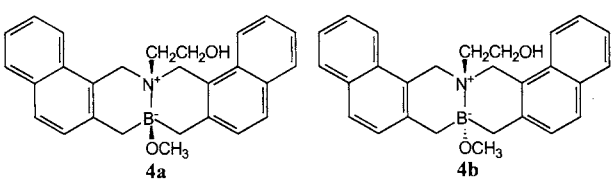



Scheme 2.

that the naphthoxazine **1** (prepared from 2-naphthol via a Mannich sequence using 2-aminoethanol) readily provided the biaryl tetradentate ligand *N*,*N*-(bis(1-naphthylmethyl)hydroxyethyl)amine (**2**).

Initial attempts to convert **2** into the [4.4.3.0]boratrane **3** (Scheme 1) involved refluxing a solution of the amine **2** with boric acid in a mixture of methanol and toluene.

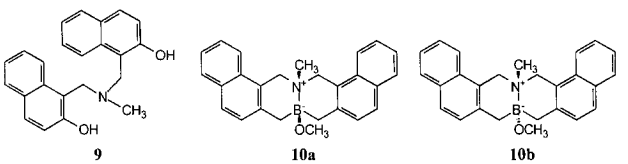
TLC analysis indicated that a mixture of products had formed after several hours. Furthermore, the $^{11}$B-NMR spectrum of this crude mixture contained several peaks, indicating that several boronato compounds were present. A small peak was observed at $\delta$ 4.66, which falls within the chemical shift range typical [11] of [4.4.3.0]boratranes; however, this was clearly a minor component. Column chromatography of the crude mixture on silica gel separated two major products, whose chemical shift in their $^{11}$B-NMR spectra corresponded to the largest peak ($\delta$ 2.23) in the spectrum of the crude mixture. Although both products exhibited very similar spectroscopic data overall, an obvious difference was observed in their $^{1}$H-NMR spectra. For one product, the pairs of doublets assigned to the axial and equatorial methylene protons occurred at $\delta$ 4.85 and 5.17, downfield relative to chemical shifts ($\delta$ 4.71, 4.87) of the doublets due to the analogous pair of methylene protons in the other product. Since both products were found to have the same molecular ion by mass spectrometry, it was concluded that they were stereoisomers **4a** and **4b**, having either *cis* or *trans* geometry about the B–N coordinate bond. These same two isomers were also the major products when a solution of the *N*-hydroxyethylamine **2** and trimethyl borate in DMF was heated under reflux for 12 h.




Although the more polar stereoisomer was formed in much higher yield than the other, it was not conclusive from the NMR data whether it had *cis* or *trans* geometry. To establish whether this lack of tetradentate coordination of boron could be attributable to consequential ring strain, a new ligand, *N*,*N*-(bis(1-naphthylmethyl)-3-hydroxypropyl)amine (**6**), analogous to the *N*-hydroxyethylamine used previously, was prepared (Scheme 2). In the expectation that the tricyclic [4.4.4.0] system **7** might form more readily than the [4.4.3.0] tricyclic congener **3**, the *N*-(3-hydroxypropyl)amine **6** was treated with boric oxide and methanol. However, a mixture was formed, from which the bis(2-hydroxynaphthyl)methane **8** was isolated as the major product.

To investigate whether the rate of deprotonation of the primary alcohol in the *N*-hydroxyethylamine **2** was too slow to allow cyclisation onto boron to give the desired [4.4.3.0]boratrane **3**, the methoxyboronato compound **4a** was treated with sodium hydride and the mixture then heated under reflux. It was hoped that attack of the deprotonated hydroxyethyl group at boron with elimination of the methoxy group would lead to the desired cyclised product. In the event this did not occur, and the methoxyboronato compound was recovered, together with some bis(2-hydroxy-1-naphthyl)methane (**8**) [1,12].

Since the tricyclic boratranes **3** and **7** could not be isolated when tertiary amines **2** and **6** bearing a hydroxyalkylated substituent on nitrogen were used, the boronation of the aminoalkyl-bridged naphthol **9** lacking hydroxylated groups on nitrogen was studied, in order to allow a more detailed study of the boron coordination geometry.



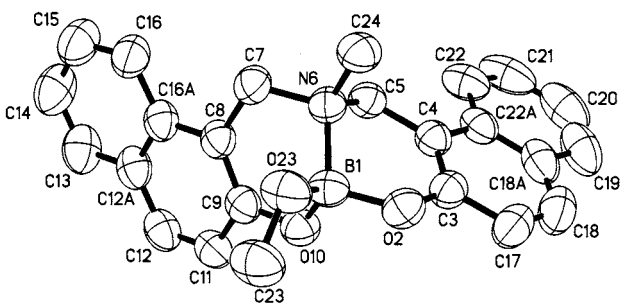
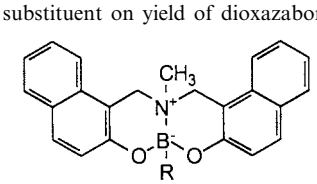




Fig. 2. The atomic arrangement in **10a**.

Table 1
Effect of boron substituent on yield of dioxazaborocine



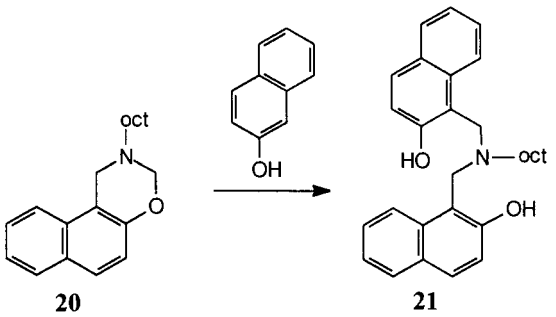

| R | Product | Yield (%) of *cis*-isomer |
|---|---|---|
| $OCH_3$ | **10** | 89 |
| $C_6H_5$ | **13** | 80 |
| $OCH_2CH_2OH$ | **14** | 75 |
| $OCH_2C_6H_5$ | **15** | 72 |
| $OC_9H_{19}$ | **16** | 64 |
| $OCH(CH_3)_2$ | **17** | 46 |
| $OC(CH_3)_3$ | **18** | >1 |
| $OC_6H_5$ | **19** | >1 |

Firstly, a solution of *N*,*N*-(bis(2-hydroxy-1-naphthylmethyl)methyl)amine (**9**) in a mixture of methanol and toluene was heated under reflux with boric oxide for several hours. The products isolated from this reaction were the *cis* and *trans* stereoisomers **10a** and **10b**. For these diastereoisomers the characteristic difference between the chemical shifts of the signals due to the equatorial and axial methylene protons was again observed. The major stereoisomer, again the more polar product, crystallised from acetone as colourless rhomboids suitable for X-ray crystallographic analysis, which enabled conclusive determination of the geometry at the ring junction. The crystal structure of **10a** (Fig. 2) showed the methoxy group at boron and the *N*-methyl substituent adopt a *cis* arrangement in the major product. The stereoisomeric minor product is therefore assumed to have *trans* geometry about this boron–nitrogen coordinate bond.

Although the dioxazaborocines described so far are not tricyclic they are still expected to be susceptible to hydrolysis and release of boron, and therefore to have potential commercial application as biocides. Hence, the preparation of a range of analogous dioxazaborocines was investigated, since these analogues might have quite different physical and chemical properties and therefore show quite different biological activities. The three sites of derivatisation considered were the boron atom, the nitrogen atom, or the aromatic moiety.

### 2.1. Different boron substituents

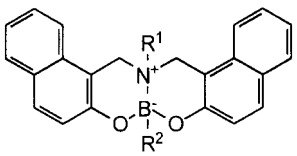
A series of experiments were undertaken in which a variety of potentially ligating co-solvents other than methanol were introduced. This work was intended to establish whether larger substituents could be attached at boron and, if so, how these substituents affect the physical and chemical properties (including stereochemistry) of the resulting dioxazaborocines. These experiments established that the nature of the co-solvent does indeed affect the isolated yield of the dioxazaborocine (Table 1). Bulky tertiary alcohols do not coordinate as efficiently as either secondary or primary alcohols. Irrespective of the size of the R group; however, in all cases the major product isolated was the *cis* stereoisomer, although the yield of the *trans* isomer increased when the substituent on boron became more bulky. For example, the *cis*:*trans* ratio was 32:1, 5:1 and 5:1, respectively, when either methanol or propan-2-ol or benzyl alcohol was employed. The observed increased yield of the *trans* isomer relative to the *cis* isomer is in agreement with the previous conclusions that bulky substituents on boron are not favoured energetically.




**20** **21**

Scheme 3.

Table 2
Effect of nitrogen and boron substituents on yield of dioxazaborocine




| $R^2$ | $R^1$ | Product | Yield (%) *cis*-isomer |
|---|---|---|---|
| $OCH_3$ | $CH_3$ | **10** | 89 |
| $OCH_2C_6H_5$ | $CH_3$ | **15** | 72 |
| $OC_9H_{19}$ | $CH_3$ | **16** | 64 |
| $OCH_3$ | *n*-octyl | **22** | 73 |
| $OCH_2C_6H_5$ | *n*-octyl | **23** | 43 |
| $OC_9H_{19}$ | *n*-octyl | **24** | >1 |

## 2.2. Different nitrogen substituents

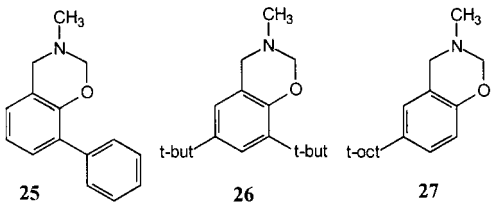
Having established which of these alcohols best coordinate boron, a series of experiments were then designed to determine how different substituents at nitrogen affect, (i) the subsequent coordination of the tridentate amines with boric oxide and various alcohols, and (ii) the stereochemistry of the resulting dioxazaborocine. Since the aminoalkylation reaction requires non-bulky groups on nitrogen, the aminomethyl-bridged naphthol **21** having a non-branching *N*-alkyl substituent was prepared, from *N*-octylnaphthoxazine **20** (Scheme 3). With *N*,*N*-(bis(2-hydroxy-1-naphthylmethyl)octyl)amine (**21**) in hand the coordination of boron and various alcohols was again investigated. This work established that a combination of small substituents at both boron and nitrogen resulted in the highest yielding reactions. Again, in all cases the *cis* stereoisomer was the major product isolated (Table 2).

All of the dioxazaborocines described so far have been derived from symmetrically substituted tertiary amines, in turn derived from 2-naphthol; this substrate had been selected because its highly nucleophilic C1 offers a reactive site for aminoalkylation. In terms of the preparation of a variety of dioxazaborocine analogues; however, the use of only 2-naphthol is rather limiting. Therefore, the preparation of analogues of the bis(2-hydroxynaphthyl)methylamine **9** having different aromatic moieties, in particular those derived from phenols, was investigated.

## 2.3. Different aromatic moieties

### 2.3.1. Symmetrically substituted

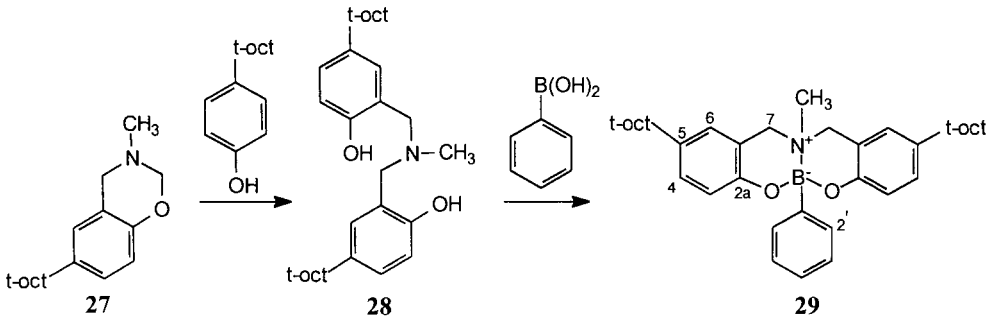
The aminoalkylation reaction proceeds most readily when the benzoxazine is electron deficient and the phenol that is to be aminoalkylated has an electron rich *ortho* position [13]. In order that a symmetrically substituted tertiary amine derived from phenol might be synthesised a series of experiments were undertaken to determine whether substituents on the aromatic rings of both the phenol and the aminoalkylating partner hindered reactivity, for either electronic or stereochemical reasons. Firstly, the benzoxazines **25**, **26**, **27** were prepared from 2-phenylphenol, 2,4-(1,1-dimethylethyl)-phenol, and 4-(1,1,3,3-tetramethylbutyl)phenol, respectively [for brevity of presentation, in the diagrams 2,4-(1,1-dimethylethyl) is depicted as *t*-butyl, and 4-(1,1,3,3-tetramethylbutyl) as *t*-octyl].




**25** **26** **27**

Subsequently, each of these benzoxazines was treated with the phenol from which it was derived (e.g. phenylbenzoxazine **25** was treated with 2-phenylphenol). In every case none of the tertiary amine aminoalkylation products precipitated from the reaction medium, even after several weeks. This was not unexpected given the steric shielding of the *ortho*-alkylated phenols compared with 2-naphthol. Analysis of each of the reactions by TLC indicated that only the tertiary amine **28** derived from 4-(1,1,3,3-tetramethylbutyl)phenol was formed, and could be separated by chromatography on silica gel. This amine was then converted into the symmetrical dioxazaborocine **29** by treatment with phenylboronic acid (Scheme 4).

Assignment of the geometry about the boron–nitrogen dative bond for the B-phenyl dioxazaborocine **29** by NMR analysis was difficult. Features of both the $^1H$- and the $^{13}C$-NMR spectra which had been used previously to distinguish the diastereoisomers having naphthyl moieties (i.e. naphthylmethyl pseudoboratranes) are apparently not applicable in systems where the pseudoboratrane is derived from a phenol (i.e. benzyl pseudoboratranes). The diagnostic difference in the chemical shifts for the diastereotopic $NCH_2$ protons, as observed for dioxazaborocines incorporating




Scheme 4.

naphthylmethyl rings (as opposed to benzyl rings), is due apparently to these methylene protons being deshielded by the diamagnetic ring current of the unsubstituted ring of the naphthylmethyl moiety. When this fused ring is absent, as is the present case for the benzyl-containing compounds, the methylene protons are not shifted to lower field because no such interaction can occur. Given that assignment of the stereochemistry of the dioxazaborocine **29** from its NMR data was inconclusive, it was gratifying that **29** could be crystallised and studied by X-ray crystallography. This analysis confirmed that the geometry about the boron–nitrogen bond was in fact *cis* (Fig. 3).

### 2.3.2. Unsymmetrically substituted

The aminoalkylation of phenols by benzoxazines derived from a different parent phenol leads to tertiary amines which are unsymmetrically substituted. Dioxazaborocine products derived from such unsymmetrically substituted tertiary amines do not have a $C_2$ axis (as was the case for the symmetrically substituted *cis*-dioxazaborocines discussed above). Therefore, the derived enantiomeric *cis*-dioxazaborocines exist, at least in principle, as a resolvable ($\pm$) pair (Fig. 4). This is the case for the dioxazaborocine **32** derived from tertiary amine **31** (Scheme 5).

Assignments of the NMR spectra of **31** and **32** were made after acquisition of both short-range HMQC and long-range COSY and HMBC 2D spectra. In the unsymmetrical dioxazaborocine **32** all of the methylene protons are in different environments, and therefore two sets of double doublets are observed, at $\delta$ 3.65, 3.91, and at $\delta$ 4.17, 4.26. The doublets at higher chemical shift are assigned to the axial and equatorial naphthylmethylene protons, consistent with the deshielding effect of the unsubstituted naphthyl ring shifting these signals to lower field. It is noteworthy that in this system all of the resonances due to methylene protons are at significantly lower field than those in the corresponding symmetrically substituted *cis*-dioxazaborocines having two naphthylmethyl substituents. This suggests that the fused ring of both naphthylmethyl substituents plays a significant role in deshielding both sets of methylene protons (see above). Furthermore, even the absence of one naphthyl ring, as in the unsymmetrical dioxazaborocine, decreases the deshielding of both sets of methylene protons; this observation is significant in terms of the potential biocidal application of these systems. In particular, the effects exerted by changes in the aromatic moieties of these dioxazaborocine systems may well be reflected in

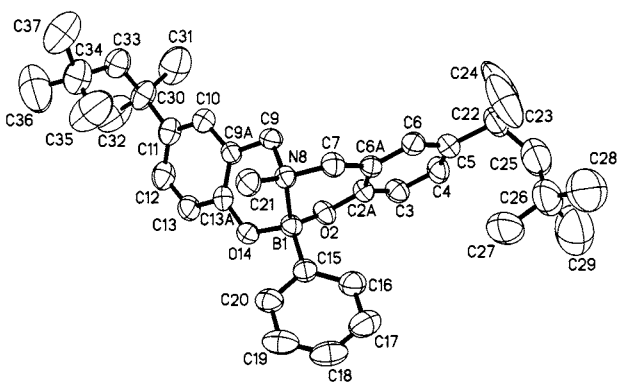



Fig. 3. The atomic arrangement in **29**.

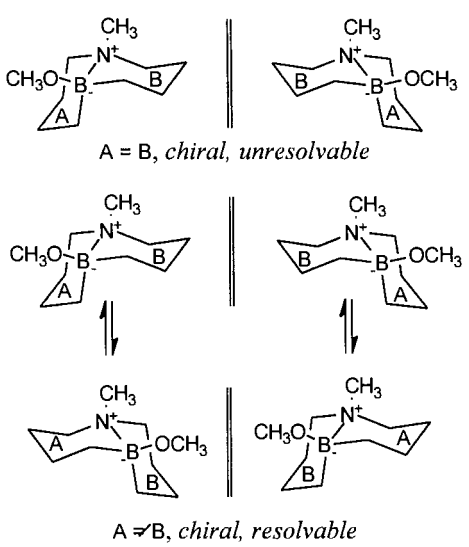
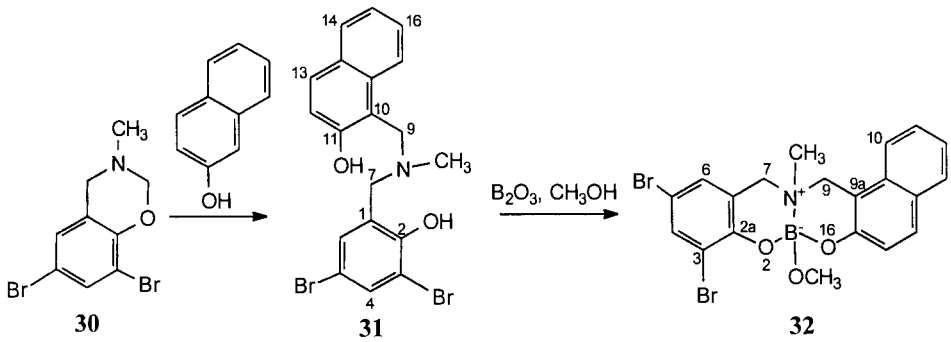



Fig. 4. Stereoisomeric dioxazaborocines.




Scheme 5.

the hydrolytic stability of these compounds, a significant factor when their potential use as a biocide is considered. With the information obtained from studying the symmetrically substituted naphthyl- and phenyldioxazaborocines, reasonable configurational assignments are now possible based on the observed chemical shifts of both methylene protons. These assignments were complemented by the observed chemical shifts of the signal due to the axial NMe carbon, which is shielded not only by the phenyl group at boron but also by the second ring of the naphthyl moiety. It follows that the absence of the shielding effect due to one naphthyl moiety, as in the unsymmetrical system **32**, leads to an axial Me resonance at a chemical shift which is the average of those observed in systems having two naphthyl rings and in systems having no naphthyl rings.

### 2.4. Nuclear Overhauser enhancement

The relative configuration of stereoisomeric dioxazaborocines could also be assigned on the basis of the nOe effect. Thus, irradiation of the OMe signal of **32** gave an nOe of 0.2% for the NMe protons; a complementary nOe of 0.7% was observed for the OMe protons after irradiating the NMe signal. These data establish that dioxazaborocine **32** is the *cis* stereoisomer. Furthermore, the nOe difference irradiation sequence is useful for assigning the signals to either an axial or equatorial methylene proton; when this sequence was used the doublets at $\delta$ 3.91 and 4.26 were present but the doublets at $\delta$ 3.65 and 4.17 were absent. Therefore, the signal at higher field in each pair is assigned to the axial methylene protons since they are closer to the NMe group than are the equatorial protons.

Repeating the preparation of selected pseudoboratranes at lower temperature, as opposed to the elevated temperature usually employed, established that the *cis* stereoisomers are formed under kinetic control and not thermodynamic control. Thus, only the *cis* isomer **15** forms at room temperature (r.t.), the *trans* isomer being detected only when the reaction is heated (xylenes) and then only in low yield.

### 2.5. X-ray crystal structure determinations of **10a** and **29**

Data were collected on a Siemens SMART diffractometer using 0.3° frames and profile fitting. Lorentz and polarisation corrections and absorption corrections were applied by the method of Blessing [14]. The structures were solved by direct methods, SHELXS97 [15], and refined by full-matrix least-squares, SHELXL97 [16]. All non-hydrogen atoms were allowed to assume anisotropic thermal motion. Hydrogen atoms were placed geometrically and allowed to ride on the carrier atom with 20% greater thermal parameter. Crystal data and refinement parameters are given in Table 3. The crystals of **29** were small and weakly diffracting, leading to a large fraction of weak data. As a result the final residual for this structure is higher than desirable. The structures of **10a** and **29** are depicted in Figs. 2 and 3, respectively, which also give the numbering schemes. Selected bond lengths are given in Tables 4 and 5. The B–N distances are long at 1.625(2) Å for **10a** and 1.674(5) Å for **29**, respectively. B–N distances can show considerable variation depending on the substituents on boron and nitrogen [17]. The shorter distance for **10a** is a reflection of the extra oxygen atom bonded to boron.

## 3. Conclusions

The coordination of boron to tertiary amines, prepared by Mannich chemistry using secondary amines, has been described. Investigation of the coordination of these tertiary amines to boron resulted in the unexpected isolation of some novel pseudoboratranes, which displayed surprising stability towards hydrolysis. Both X-ray crystallographic and NMR analyses established that the decalin-like central portion of these pseudoboratranes always prefers to adopt *cis* geometry about the B–N coordinate bond. The products isolated are

formed under kinetic control at r.t., and in high yield given the appropriate combination of substituents at boron and nitrogen.

Table 3
Data collection and processing parameters

| | **10a** | **29** |
|---|---|---|
| Formula | $C_{24}H_{22}BNO_3$ | $C_{37}H_{52}BNO_2$ |
| Molecular weight | 383.24 | 553.61 |
| Crystal system | Monoclinic | Monoclinic |
| Space group | $P2_1/n$ | $P2_1/c$ |
| $a$ (Å) | 10.7922(6) | 35.9770(3) |
| $b$ (Å) | 10.8486(6) | 7.1415910 |
| $c$ (Å) | 17.0269(10) | 13.0348(1) |
| $\beta$ (°) | 99.553(1) | 94.200(3) |
| $V$ (Å$^3$) | 1965.87(19) | 3340.01(6) |
| $Z$ | 4 | 4 |
| $D_{calc}$ (g cm$^{-3}$) | 1.295 | 1.101 |
| $F(000)$ | 808 | 1208 |
| $\mu$ (mm$^{-1}$) | 0.084 | 0.066 |
| Radiation Mo–$K_\alpha$ (monochromatic) $\lambda$ (Å) | 0.71073 | 0.71073 |
| Temperature (K) | 293 | 293 |
| Diffractometer | Siemens SMART | Siemens SMART |
| Scan technique | Area detector | Area detector |
| $2\theta$ (min–max) (°) | 2–26.3 | 1.7–25.1 |
| Reflections collected/unique | 11207/3971 $R_{int}$ 0.0168 | 16535/5883 $R_{int}$ |
| No. of observed reflections $I>2\sigma(I)$ | 2821 | 4199 |
| Crystal size (mm) | $0.56\times0.31\times0.25$ | $0.30\times0.20\times0.07$ |
| $A$ (min–max) | 0.954–0.979 | 0.981–0.995 |
| No. of variables in LS | 264 | 381 |
| Goodness of fit on $F^2$ | 1.033 | 2.108 |
| Function minimised | $\Sigma w(F_o^2-F_c^2)^2$ | $\Sigma w(F_o^2-F_c^2)^2$ |
| $R$ [a] (observed data) | 0.0431 | 0.1072 |
| $wR_2$ [b] (all data) | 0.1258 | 0.3211 |
| Difference map (min–max) (e Å$^{-3}$) | −0.17+0.13 | −0.46+1.13 |

[a] $R=\Sigma\|\|F_o|-|F_c\|\|/\Sigma|F_o|$.
[b] $wR_2=\{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; weight $=1.0/[\sigma^2(F_o^2)+a*P^2+b*P]$; $P=(F_o^2+2F_c^2)/3$.

Table 4
Selected bond lengths (Å) for **10a**

| | |
|---|---|
| B(1)–O(19) | 1.418(2) |
| B(1)–O(2) | 1.445(2) |
| B(1)–O(18) | 1.455(2) |
| B(1)–N(10) | 1.629(2) |
| O(2)–C(2A) | 1.3615(19) |
| C(2A)–C(8B) | 1.381(2) |
| C(8B)–C(9) | 1.503(2) |
| C(9)–N(10) | 1.4964(19) |
| N(10)–C(21) | 1.4940(19) |
| N(10)–C(11) | 1.4998(19) |
| C(11)–C(11A) | 1.509(2) |
| C(11A)–C(17A) | 1.374(2) |
| C(17A)–O(18) | 1.3624(19) |

Table 5
Selected bond lengths (Å) for **29**

| | |
|---|---|
| B(1)–O(14) | 1.444(5) |
| B(1)–O(2) | 1.455(5) |
| B(1)–C(15) | 1.608(6) |
| B(1)–N(8) | 1.674(5) |
| O(2)–C(2A) | 1.353(4) |
| C(2A)–C(6A) | 1.400(5) |
| C(6A)–C(7) | 1.499(5) |
| C(7)–N(8) | 1.497(4) |
| N(8)–C(37) | 1.492(5) |
| N(8)–C(9) | 1.490(4) |
| C(9)–C(9A) | 1.500(5) |
| C(9A)–C(13A) | 1.395(6) |
| C(13A)–O(14) | 1.362(4) |

## 4. Experimental

Melting points were determined on a Reichert–Kofler block and are uncorrected. Infrared spectra were recorded on a Perkin–Elmer 1000 or a Perkin–Elmer 1600 FTIR spectrometer. The spectra for solids were recorded as Nujol mulls or as a film on sodium chloride. NMR spectra were obtained using a Bruker AM400 spectrometer operating at 400.13 MHz for $^1$H, 100.62 MHz for $^{13}$C and 128.4 MHz for $^{11}$B nuclei. Unless otherwise stated, spectra were recorded in deuterochloroform using a 5 mm probe. $^{11}$B spectra were externally referenced to $Et_2O{\cdot}BF_3$. Low resolution mass spectra were recorded on a VG-7070 mass spectrometer operating at a nominal accelerating voltage of 70 eV. High resolution mass spectra were recorded at a nominal resolution of 5 000 or 10 000 as appropriate; all spectra were obtained by electron impact ionisation, using perfluorokerosene as the internal standard unless otherwise stated. Flash column chromatography was performed using Kieselgel 60 (230–400 mesh) silica gel and a silica:sample ratio (w/w) of ca. 30:1. Predistilled solvents were used in recrystallisation and purification of compounds by chromatographic techniques. All other reagents were used as obtained from commercial sources.

### *4.1. N-Hydroxyethyl-2,3-dihydro-1H-naphth[1,2-e][1,3]oxazine (**1**)*

To a solution of 2-naphthol (9.6 g, 66.6 mmol) and 2-hydroxyethylamine (4.13 g, 67.5 mmol) in methanol (30 ml) was added aqueous formaldehyde (37%w/w, 12.5 ml, 166.9 mmol) at r.t. and the mixture was heated under reflux with stirring for 12 h. The solvent was removed under reduced pressure, then dilute aqueous hydrochloric acid (2 mol l$^{-1}$) was added and the mixture extracted with dichloromethane. The aqueous phase was neutralised by the addition of solid sodium hydrogencarbonate, then extracted three times with dichloromethane. These organic extracts were washed

with water, dried, concentrated, and purified by flash column chromatography (dichloromethane; dichloromethane–methanol, 10:1) to afford **1** (14.34 g, 94%) as a yellow oil. (Found: $M^+$ 229.1097, $C_{14}H_{15}NO_2$ Calc.: 229.1103). $\nu_{max}$ 3400 (br, OH), 1625, 1598, 1515 (C=C aromatic), 1227, 1139, 1076 $cm^{-1}$ (C–O). $\delta_H$ 2.98 (t, *J* 5.2, 2H, H-2′), 3.71 (t, *J* 5.1, 2H, H-1′), 4.32 (s, 2H, H-4) 4.92 (s, 2H, H-2), 7.01 (d, *J* 9.0, 1H, H-10), 7.35 (td, *J* 7.52, 1.0, 1H, H-7), 7.46 (td, *J* 7.5, 1.2, 1H, H-6), 7.57 (d, *J* 8.5, 1H, H-5), 7.63 (d, *J* 8.9, 1H, H-9), 7.75 (d, *J* 8.0, 1H, H-8). $\delta_C$ 47.4 (C-1′), 53.9 (C-2′), 59.2 (C-4), 82.5 (C-2), 111.4 (C-4a), 118.5 (C-10), 120.9 (C-5), 123.5 (C-7), 126.6 (C-6), 128.2 (C-9), 128.6 (C-8), 128.9 (C-8a), 131.7 (C-4b), 151.7 (C-10a). *m*/*z* 230 (M + H, 9%), 229 (M, 66), 198 (M − $CH_2OH$, 43), 156 ($C_{11}H_8O$, 76), 128 (156 − CO, 100).

### 4.2. *N,N-(Bis(2-hydroxy-1-naphthylmethyl)-2-hydroxyethyl)amine (**2**)*

2-Naphthol (0.63 g, 4.4 mmol) was added to a solution of the 2*H*-1,3-benzoxazine **1** (1.0 g, 4.3 mmol) in methanol at r.t. This mixture was stirred until a precipitate separated. The solid collected after filtration was washed with methanol leaving **2** as yellow needles (1.38 g, 85%) (methanol–benzene), m.p. 133–5°C. (Found: $M^+$ 374.1754, $C_{24}H_{24}NO_3$. Calc.: 374.1756). $\nu_{max}$ 3152 (br, OH), 1626 (C=C aromatic), 1283, 1061, 1040 $cm^{-1}$. $\delta_H$ (DMSO-$d_6$) 2.89, 3.95 (2t, *J* 5.3, 4H, $NCH_2CH_2OH$), 4.39 (s, 4H, $2CH_2N$), 7.12 (d, *J* 8.9, 2H, 2H-3), 7.32 (t, *J* 7.6, 2H, 2H-6), 7.50 (t, *J* 6.9, 2H, 2H-7), 7.69 (d, *J* 8.8, 2H, 2H-4), 7.75 (d, *J* 8.4, 2H, 2H-5), 8.01 (d, *J* 8.8, 2H, 2H-8). $\delta_C$ (DMSO-$d_6$) 49.3 2(C-9), 55.3 $NCH_2CH_2OH$, 58.4 $NCH_2CH_2OH$, 113.7 2(C-1), 118.2 2(C-3), 122.2 2(C-6), 122.4 2(C-8), 126.1 2(C-7), 128.0 2(C-4a), 128.2 2(C-5), 128.7 2C(4), 128.9 2(C-8a), 154.7 2(C-2). *m*/*z* ($FAB^+$) 374 (M + H, 16%), 373 (M, 3), 342 (M − $CH_2OH$, 2).

Amine **2** (0.57 g, 1.58 mmol) and boric oxide (0.11 g, 1.58 mmol) in benzene and methanol (1:1, 5 ml) were placed in a flask fitted with a Dean–Stark water separator. The mixture was heated under reflux for 12 h, then concentrated in vacuo. Chromatography of the oily residue on silica gel (dichloromethane; dichloromethane–methanol, 10:1) gave, in order of decreasing polarity, *cis-N*-(2-hydroxyethyl)-1-methoxy-bis(naphthyl)[2,1-c:1,2-h]-10-aza-1-borabicyclooctane (**4a**) as thick needles (0.38 g, 58%), m.p. 221–2°C, and *trans-N*-(2-hydroxyethyl)-1-methoxy-bis(naphthyl)[2,1-c:1,2-h]10-aza-1-borabicyclooctane (**4b**) (0.03 g, 5%).

1. Compound **4a**: (Found: $M^+$ 413.1793, $C_{25}H_{24}BNO_4$. Calc.: 413.1798). $\nu_{max}$ 3453 (br OH), 1624, 1599 (C=C aromatic), 1264 1122, 1098, 1076, 1056 $cm^{-1}$ (C–O). $\delta_B$ 2.83. $\delta_H$ 3.42 (s, 3H, $OCH_3$), 3.46 (t, *J* 4.4, 2H, H-1′), 4.03 (t, *J* 4.4, 2H, H-2′), 4.71, 4.87 (2d, *J* 14.8, 4H, H-9,11), 7.16 (d, *J* 8.8, 2H, H-3,17), 7.31 (t, *J* 7.4, 2H, H-6,14), 7.42 (t, *J* 7.5, 2H, H-7,13), 7.61 (d, *J* 8.4, 2H, H-8,12), 7.70 (d, *J* 8.9, 2H, H-4,16), 7.76 (d, *J* 7.9, 2H, H-5,15). $\delta_C$ 49.6, $OCH_3$, 52.4 (br, C-2′), 55.0 (C-1′), 55.9 (C-9,11), 107.6 (C-8a,11a), 120.1 (C-8,12), 120.6 (C-3,17), 122.5 (C-6,14), 126.1 (C-7,13), 128.0 (C-4a,15a), 128.1 (C-5,15), 129.0 (C-4,16), 130.9 (C-8b,11a), 150.7 (C-2a,17a). *m*/*z* ($DEI^+$) 413 (M, 14%), 381 (M − $HOCH_3$, 34), 336 (381-$OCH_2CH_3$, 6), 256 (M − $C_{11}H_9O$, 100).
2. Compound **4b**: (Found: $M^+$ 413.1790, $C_{25}H_{24}BNO_4$. Calc.: 413.1798). $\nu_{max}$ 3450 (br OH), 1624, 1591 (C=C aromatic), 1250, 1078 $cm^{-1}$ (C–O). $\delta_H$ 3.27 (s, 3H, $OCH_3$), 3.35 (t, *J* 4.4, 2H, H-1′), 4.01 (t, *J* 4.4, 2H, H-2′), 4.85, 5.17 (2d, *J* 13.8, 4H, H-9,11), 7.26 (d, *J* 8.9, 2H, H-3,17), 7.35 (t, *J* 7.4, 2H, H-6,14), 7.53 (t, *J* 7.5, 2H, H-7,13), 7.71 (d, *J* 8.4, 2H, H-8,12), 7.75 (d, *J* 8.9, 2H, H-4,16), 7.77, d, *J* 7.9, 2H, H-5,15). $\delta_C$ 48.3 $OCH_3$, 51.9 (br, C-2′), 53.8 $(C\text{-}1')_2$, 56.7 (C-9,11), 107.9 (C-8a,11a), 120.3 (C-8,12), 120.8 (C-3,17), 122.5 (C-6,14), 126.2 (C-7,13), 128.1 (C-4a,15a), 128.1 (C-5,15), 128.0 (C-4,16), 131.0 (C-8b,11a), 152.0 C(2a, 17a). *m*/*z* ($DEI^+$) 413 (M, 10%), 381 (M − $HOCH_3$, 34), 336 (381-$OCH_2CH_3$, 5), 256 (M − $C_{11}H_9O$, 100).

### 4.3. *N-(3-Hydroxypropyl)-2,3-dihydro-1H-naphth-[1,2-e][1,3]oxazine (**5**)*

Aqueous formaldehyde (37%w/w, 2.6 ml, 34.4 mmol) was added to a solution of 2-naphthol (2.48 g, 17.2 mmol) and 3-hydroxypropylamine (1.30 g, 17.2 mmol) in methanol (18 ml) at r.t., and the mixture was heated under reflux with stirring for 12 h. The solvent was removed under reduced pressure, then dilute aqueous hydrochloric acid (2 mol $l^{-1}$, 15 ml) was added and the mixture extracted with dichloromethane (15 ml). The aqueous phase was neutralised by the addition of solid sodium hydrogencarbonate, then extracted three times with dichloromethane (15 ml). Workup and flash column chromatography (dichloromethane; dichloromethane–methanol, 10:1) afforded **5** (3.09 g, 79%) as a yellow oil. (Found: $M^+$ 243.1251, $C_{15}H_{17}NO_2$. Calc.: 243.1259). $\nu_{max}$ 3444 br (OH), 1622, 1599, 1519 (C=C aromatic), 1269, 1236 $cm^{-1}$ (C–O). $\delta_H$ 1.82 (p, *J* 5.2, 2H, $NCH_2\mathbf{C}H_2CH_2OH$), 2.98 (t, *J* 5.6, 2H, $NC\mathbf{H}_2CH_2CH_2OH$), 3.86 (t, *J* 5.5, 2H, $C\mathbf{H}_2OH$), 4.37 (s, 2H, H-4), 4.94 (s, 2H, H-2), 7.02 (d, *J* 8.9, 1H, H-10), 7.36 (t, *J* 7.7, 1H, H-7), 7.49 (t, *J* 7.4, 1H, H-6), 1.61 (d, *J* 8.4, 1H, H(5), 7.64 (d, *J* 8.9, 1H, H-9), 7.68 (d, *J* 8.8, 1H, H-8). $\delta_C$ 28.8 (C-2′), 47.4 (C-1′), 51.3 (C-3′), 63.5 (C-4), 82.0 (C-2), 111.5 (C-4a), 118.4 (C-10), 120.9 (C-5), 123.6 (C-7), 126.6 (C-6), 128.2 (C-9), 128.7 (C-8), 128.8 (C-8a), 131.8 (C-4b), 151.5 (C-10a). *m*/*z* 243 (M, 32%), 156 ($C_{11}H_8O$, 50), 128 (156-CO, 100).

### 4.4. N,N-(Bis(2-hydroxy-1-naphthylmethyl)-3-hydroxypropyl)amine (6)

2-Naphthol (1.12 g, 7.74 mmol) was added to a solution of the 2*H*-1,3-benzoxazine **5** (1.76 g, 7.74 mmol) in methanol (18 ml) at r.t. This mixture was stirred until a precipitate separated. The solid collected after filtration was washed with methanol, leaving **6** (2.0 g, 67%) as yellow crystals, m.p. 66–7°C. $\nu_{max}$ 3150, br, (OH), 1625 (C=C aromatic), 1062, 1039 $cm^{-1}$. (Found: $M^+$ 388.19328, $C_{25}H_{26}NO_3$. Calc.: 388.19127). $\delta_H$ 2.02 (t, *J* 5.2, 2H, $NCH_2CH_2CH_2OH$), 2.57 (p, *J* 5.2, 2H, $NCH_2CH_2CH_2OH$), 2.82 (t, *J* 5.2, 2H, $NCH_2CH_2CH_2OH$), 4.27 (s, 4H, 2H-9), 7.07 (d, *J* 8.8, 2H, 2H-3), 7.26 (td, *J* 7.8, 1.0, 2H, 2H-6), 7.46 (td, *J* 7.8, 1.0, 2H, 2H-7), 7.61 (d, *J* 8.8, 2H, 2H-4), 7.70 (d, *J* 7.9, 2H, 2H-5), 7.96 (d, *J* 8.6, 2H, 2H-8). $\delta_C$ ($CDCl_3$/DMSO-$d_6$) 28.6 (C-2′), 49.4 (C-9), 51.2, 59.9 (C-1′,2′,3′), 112.5 2(C-1), 118.1 2(C-3), 121.9 2(C-6), 126.0 2(C-7), 127.9 2(C-4a), 128.2 2(C-5), 128.7 2(C-4), 133.0 2(C-8a), 154.8 2(C-2). *m*/*z* ($FAB^+$) 388 (M, 60%), 157 ($C_{11}H_9O$, 42).

### 4.5. N,N-(bis(2-hydroxy-1-naphthylmethyl)-methyl)amine (9)

Aqueous formaldehyde (37%w/w, 3.5 ml, 0.46 mol) was added to a solution of 2-naphthol (3.24 g, 0.023 mol) and methylamine (2.8 ml, 0.23 mol) in methanol (30 ml) at r.t., and the mixture was heated under reflux with stirring for 12 h. The solvent was removed under reduced pressure, then dilute aqueous hydrochloric acid (2 mol $l^{-1}$, 15 ml) was added and the mixture extracted with dichloromethane (15 ml). The aqueous phase was neutralised by the addition of solid sodium hydrogencarbonate, then extracted three times with dichloromethane (15 ml). Workup and flash column chromatography (dichloromethane; dichloromethane–methanol, 10:1) afforded *N*-methyl-2,3-dihydro-1H-naphth[1,2-e][1,3]oxazine (3.98 g, 100%) as yellow crystals, m.p. 67–8°C (EtOH) (Ref. [5] 67–8°C). 2-Naphthol (2.70 g, 0.019 mol) was added to *N*-methyl-2,3-dihydro-1*H*-naphth[1,2-e][1,3]oxazine (3.78 g, 0.019 mol) to give **9** (6.38 g, 98%) as yellow crystals, m.p. 145–6°C (Ref. [5] 147–8°C). $\nu_{max}$ 1623, 1514 (C=C aromatic), 1260, 1239 (C–O), 745 $cm^{-1}$. $\delta_H$ 2.45 (s, 3H, $NCH_3$), 4.23 (br, 2H, OH), 4.34 (s, 4H, 2H-9), 7.01 (d, *J* 8.8, 2H, 2H-3), 7.29 (t, *J* 7.1, 2H, 2H-6), 7.50 (t, *J* 7.1, 2H, 2H-7), 7.61 (d, *J* 8.9, 2H, 2H-4), 7.73 (d, *J* 8.0, 2H, 2H-5), 7.99 (d, *J* 8.6, 2H, 2H-8). $\delta_C$ 41.3 $NCH_3$, 53.2 2(C-9), 118.5 2(C-1), 121.5 2(C-3), 122.7 2(C-6), 126.7 2(C-7), 128.6 2(C-4a), 128.8 2(C-5), 129.7 2(C-4), 133.3 2(C-8a), 155.0 2(C-2).

Amine **9** (1.1 g, 3.2 mmol) and boric oxide (0.2 g, 3.2 mmol) in benzene and methanol (1:1, 5 ml) were placed in a flask fitted with a Dean–Stark water separator. The mixture was heated under reflux for 12 h, then concentrated in vacuo. Chromatography on silica gel (dichloromethane; dichloromethane–methanol, 10:1) gave, in order of decreasing polarity, *cis*-*N*-methyl-1-methoxy-bis(naphthyl)[2,1-c:1,2-h]-10-aza-1-borabicyclooctane (**10a**) (1.1 g, 89%) as colourless needles, m.p. 225°C (dec.), and *trans*-*N*-methyl-1-methoxy-bis(naphthyl)[2,1-c:1,2-h]-10-aza-1-borabicyclooctane (**10b**) (8 mg, 3%) as colourless cubes.

1. Compound **10a**: (Found: $M^+$ 383.1693, $C_{24}H_{22}BNO_3$. Calc.: 383.1693). $\nu_{max}$ 1625, 1599 (C=C aromatic), 1247, 1214, 1135–1012 $cm^{-1}$ (m, C–O). $\delta_B$ 2.09. $\delta_H$ 2.90 (s, 3H, $NCH_3$), 3.47 (s, 3H, $OCH_3$), 4.42, 4.56 (2d, *J* 14.8, 4H, H-9,11), 7.19 (d, *J* 8.5, 2H, H-3,17), 7.30 (t, *J* 7.8, 2H, H-6,14), 7.42 (t, *J* 8.3, 2H, H-7,13), 7.46 (d, *J* 8.3, 2H, H-8,12), 7.70 (d, *J* 8.9, 2H, H-4,16), 7.75 (d, *J* 8.0, 2H, H-5,15). $\delta_C$ 44.7 $NCH_3$, 50.2 $OCH_3$, 56.8 (C-9,11), 107.2 (C-8a,11a), 120.1 (C-8,12), 121.4 (C-3,17), 123.0 (C-6,14), 126.6 (C-7,13), 128.5 (C-4a,15a), 128.8 (C-5,15), 129.8 (C-4,16), 131.2 (C-8b,11a), 151.3 (C-2a,17a). *m*/*z* 383 (M, 23%), 351 ($M - HOCH_3$, 6), 336 ($351 - CH_3$, 4), 226 ($M - C_{11}H_9O$, 100).
2. Compound **10b**: (Found: $M^+$ 383.1682, $C_{24}H_{22}BNO_3$. Calc.: 383.1693). $\nu_{max}$ 1628 (C=C aromatic), 1467 (br, B–O), 1089 $cm^{-1}$ (C–O). $\delta_H$ 2.75 (s, 3H, $NCH_3$), 3.25 (s, 3H, $OCH_3$), 4.53, 4.85 (2d, *J* 13.8, 4H, H-9,11), 7.29 (d, *J* 8.9, 2H, H-3,17), 7.36 (td, *J* 7.0, 0.9, 2H, H-6,14), 7.52 (td, *J* 8.3, 1.2, 2H, H-7,13), 7.63 (d, *J* 8.4, 2H, H-8,12), 7.76 (d, *J* 8.9, 2H, H-4,16), 7.82 (d, *J* 8.0, 2H, H-5,15). $\delta_C$ 43.3 $NCH_3$, 49.5 $OCH_3$, 58.9 (C-9,11), 108.0 (C-8a,11a), 120.3 (C-8,12), 121.7 (C-3,17), 123.0 (C-6,14), 126.6 (C-7,13), 128.6 (C-4a,15a), 128.8 (C-5,15), 129.7 (C-4,16), 131.5 (C-8b,11a), 152.1 (C-2a,17a). *m*/*z* ($DEI^+$) 383 (M, 24%), 351 ($M - HOCH_3$, 10), 336 ($351 - CH_3$, 4), 226 ($M - C_{11}H_9O$, 100).

### 4.6. Cis-N-methyl-1-phenyl-bis(naphthyl)[2,1-c:1,2-h]-10-aza-1-borabicyclooctane (13)

Amine **9** (0.13 g, 0.38 mmol) and phenylboronic acid (0.05 g, 0.41 mmol) in benzene (5 ml) were placed in a flask fitted with a Dean–Stark water separator. The mixture was heated under reflux for 12 h, then concentrated in vacuo. Flash chromatography on silica gel (dichloromethane; dichloromethane–methanol, 10:1) gave **13** (0.13 g, 80%) as microneedles, m.p. > 330°C. (Found: $M^+$ 429.1903, $C_{29}H_{24}BNO_2$. Calc.: 429.1900). $\nu_{max}$ 1624, 1599 (C=C aromatic), 1244, 1202, 1095, 1086, 1044 $cm^{-1}$ (C–O). $\delta_B$ 3.33. $\delta_H$ 2.85 (s, 3H, $NCH_3$), 4.32, 4.70 (2d, *J* 14.8, 4H, H-9,11), 7.25 (m, 5H, H-3′,4′,5′,3,17), 7.35 (t, *J* 7.3, 2H, H-6,14), 7.46 (t, *J* 7.0, 2H, H-7,13), 7.50 (d, *J* 8.4, 2H, H-8,12), 7.64 (d, *J* 7.9, 2H, H-2′,6′), 7.78 (d, *J* 8.9, 2H, H-4,16), 7.83 (d, *J* 8.0, 2H, H-5,15). $\delta_C$ 45.8 ($NCH_3$), 56.6 (C-9,11), 106.9

(C-8a,11a), 119.9 (C-8,12), 121.4 (C-3,17), 122.8 (C-6,14), 126.5 (C-7,13), 127.2 127.8, (C-Ph), 128.3 (C-4a,15a), 128.7 (C-5,15), 129.9 (C-4,16), 131.1 (C-8b,11a), 133.0 (C-1′) 151.6 (C-2a,17a). *m/z* ($DEI^+$) 553 (M, 14%), 538 ($M-CH_3$, 30), 496 ($M-(CH_3)_3C$, 2), 482 ($M-(CH_3)_3CCH_2$, 42), 476 ($M-C_6H_5$, 100).

### 4.7. Cis-N-methyl-1-(2-hydroxyethoxy)-bis-(naphthyl)[2,1-c:1,2-h]-10-aza-1-borabicyclooctane (**14**)

Amine **9** (0.20 g, 0.59 mmol), boric oxide (0.02 g, 0.3 mmol), and ethane-1,2-diol (0.02 g, 0.3 mmol) in benzene (5 ml) were placed in a flask fitted with a Dean–Stark water separator. The mixture was heated under reflux for 12 h, then concentrated in vacuo. Flash column chromatography on silica gel (dichloromethane; dichloromethane–methanol, 10:1) afforded **14** (0.18 g, 75%) as colourless rhomboids, m.p. 221–2°C. (Found: $M^+$ 459.1995, $C_{30}H_{26}BNO_3$. Calc.: 459.2006). $\nu_{max}$ 3445 (br, OH), 1625, 1560 (C=C aromatic), 1271, 1247, 1156, 1098, 1045 $cm^{-1}$ (C–O). $\delta_H$ 2.97 (s, 3H, $NCH_3$), 3.67 (s, 2H, H-2′), 3.81 (s, 2H, H-1′), 4.48, 4.60 (2d, *J* 14.8, 4H, H-9,11), 7.17 (d, *J* 8.9, 2H, H-3,17), 7.33 (t, *J* 7.4, 2H, H-6,14), 7.45 (t, *J* 6.7, 2H, H-7,13), 7.50 (d, *J* 8.4, 2H, H-8,12), 7.72 (d, *J* 8.9, 2H, H-4,16), 7.78 (d, *J* 8.0, 2H, H-5,15). $\delta_C$ 44.9 $NCH_3$, 56.9 (C-2′), 63.8 (C-1′), 64.1 (C-9,11), 107.2 (C-8a,11a), 120.2 (C-8,12), 121.3 (C-3,17), 123.2 (C-6,14), 126.7 (C-7,13), 128.6 (C-4a,15a), 128.9 (C-5,15), 130.0 (C-4,16), 131.2 (C-8b,11a), 151.1 (C-2a, 17a). *m/z* ($DEI^+$) 413 (M, 30%), 369 ($M-C_2H_4O$, 22), 352 ($M-OCH_2H_2OH$, 16), 212 (100).

Amine **9** (0.22 g, 0.53 mmol) and boric oxide (0.03 g, 0.32 mmol) in toluene (5 ml) and benzyl alcohol (0.07 g, 0.53 mmol) were placed in a flask fitted with a Dean–Stark water separator. The mixture was heated under reflux for 12 h, then concentrated in vacuo. Chromatography of the oily residue on silica gel (dichloromethane; dichloromethane–methanol, 10:1) gave, in decreasing order of polarity, cis-*N*-methyl-1-benzyloxy-bis(naphthyl)[2,1-c:1,2-h]-10-aza-1-borabicyclooctane (**15a**) (0.17 g, 73%) as colourless plates, m.p. 218–9°C (acetone), and *trans*-*N*-methyl-1-benzyloxy-bis(naphthyl)[2,1-c:1,2-h]-10-aza-1-borabicyclooctane (**15b**) (0.04 g, 17%) as colourless plates, m.p. 160–1°C (acetone).

1. Compound **15a**: (Found: $M^+$ 459.2014, $C_{30}H_{26}BNO_3$. Calc.: 459.2006). $\nu_{max}$ 1622, 1598 (C=C aromatic), 1264, 1244, 1082, 1052 $cm^{-1}$ (C–O). $\delta_B$ 2.24. $\delta_H$ 2.85 (s, 3H, $NCH_3$), 4.35, 4.50 (2d, *J* 14.7, 4H, H-9,11), 4.83 (s, 2H, H-1′), 7.10 (m, 2H, H-3′,7′), 7.18 (m, 5H, H-3,17,4′,5′,6′), 7.27 (td, *J* 7.0, 1.9, 2H, H-6,14), 7.38 (m, 4H, H-7,8,12,13), 7.66 (d, *J* 8.9, 2H, H-4,16), 7.72 (d, *J* 8.0, 2H, H-5,15). $\delta_C$ 44.7 $NCH_3$, 56.7 (C-9,11), 64.1 (C-1′), 107.2 (C-8a,11b), 120.1 (C-8,12), 121.4 (C-3,17), 123.0, 126.6 (C-4′,5′,6,14?), 126.6 (C-7,13), 127.8 (C-3′), 128.4 (C-4a,15a), 128.8 (C-5,15), 129.8 (C-4,16), 131.2 (C-8b,11a), 141.9 (C-2′), 151.3 (C-2a,17a). *m/z* ($DEI^+$) 459 (M, 29%), 351 ($M-C_6H_5CH_2OH$, 20), 336 ($351-CH_3$, 9), 302 ($M-C_{11}H_9O$, 100).
2. Compound **15b**: (Found: $M^+$ 459.2025, $C_{30}H_{26}BNO_3$. Calc.: 45.2006). $\nu_{max}$ 1624, 1599 (C=C aromatic), 1247, 1140, 1056, 1029 $cm^{-1}$ (C–O). $\delta_B$ 2.15. $\delta_H$ 2.75 (s, 3H, $NCH_3$), 4.54, 4.92 (2d, *J* 13.8, 4H, H-9,11), 4.64 (s, 2H, H-1′), 6.98 (m, 2H, H-3′,7′), 6.99 (m, 3H, H-4′,5′,6′), 7.26 (d, *J* 8.9, 1.9, 2H, H-3,17), 7.36 (td, *J* 7.4, 2H, H-6,14), 7.50 (td, *J* 7.6, 1.2, 2H, H-7,13), 7.61 (d, *J* 8.3, 2H, H-8,12), 7.74 (d, *J* 8.9, 2H, H-4,16), 7.81 (d, *J* 8.4, 2H, H-5,15). $\delta_C$ 43.2 $NCH_3$, 58.6 (C-9,11), 63.7 (C-1′), 108.1 (C-8a,11b), 120.3 (C-8,12, 121.7 (C-3,17), 123.1, 126.5, (C-4′,5′,6,14), 126.7 (C-7,13), 127.7 (C-3′), 128.6 (C-4a,15a), 128.9 (C-5,15), 129.8 (C-4,16), 131.4 (C-8b,11a), 142.0 (C-2′), 152.0 (C-2a,17a). *m/z* 459 (M, 31%), 351 ($M-C_6H_5CH_2OH$, 26), 336 ($351-CH_3$, 6), 302 ($M-C_{11}H_9O$, 100).

### 4.8. Cis-N-methyl-1-nonoxy-bis(naphthyl)[2,1-c:1,2-h]-10-aza-1-borabicyclooctane (**16**)

Amine **9** (0.21 g, 0.51 mmol) and boric oxide (0.02 g, 0.51 mmol) in benzene (5 ml) and nonan-1-ol (0.1 g, 0.51 mmol) were placed in a flask fitted with a Dean–Stark water separator. The mixture was heated under reflux for 12 h, then concentrated in vacuo. Flash column chromatography on silica gel (dichloromethane; dichloromethane–methanol, 10:1) gave **16** (0.16 g, 64%) as a yellow oil. (Found: $M^+$ 495.2955, $C_{32}H_{38}BNO_3$. Calc.: 495.2945). $\nu_{max}$ 1624, 1580 (C=C aromatic), 1248, 1157, 1097, 1042, 1029 $cm^{-1}$ (C–O). $\delta_H$ 0.94 (t, *J* 7.2, 3H, H-9′), 1.14 (m, 12H, H-3′-8′), 1.14 (t, *J* 7.2, 2H, H-2′), 2.89 (s, 3H, $NCH_3$), 3.69 (t, *J* 6.6, 2H, H-1′), 4.41, 4.54 (2d, br, *J* 14.0, 4H, H-9,11), 7.18 (d, *J* 7.2, 2H, H-3,17), 7.27 (t, *J* 7.1, 2H, H-6,14), 7.41 (t, *J* 6.7, 2H, H-7,13), 7.46 (d, *J* 8.2, 2H, H-8,12), 7.68 (d, *J* 8.9, 2H, H-4,16), 7.74 (d, *J* 8.0, 2H, H-5,15). $\delta_C$ 14.1 (C-9′), 22.6 (C-8′), 26.0 (C-7′), 29.2 (C-6′), 29.3 (C-5′), 29.6 (C-4′), 31.8 (C-3′), 32.2 (C-2′), 44.7 $NCH_3$, 56.8 (C-1′), 62.0 (C-9,11), 107.3 (C-8a,11a), 120.1 (C-8,12), 121.6 (C-3,17), 123.0 (C-6,14), 126.6 (C-7,13), 128.5 (C-4a,15a), 128.9 (C-5,15), 129.8 (C-4,16), 131.3 (C-8b,11a), 151.6 (C-2a,17a). *m/z* 495 (M, 30%), 351 ($M-C_9H_{19}OH$, 30), 338 ($M-C_{11}H_9O$, 100).

Amine **9** (0.26 g, 0.75 mmol) and boric oxide (0.03 g, 0.38 mmol) in benzene (5 ml) and propan-2-ol (0.2 g, 3.3 mmol) were placed in a flask fitted with a Dean–Stark water separator. The mixture was heated under reflux for 12 h, then concentrated in vacuo. Chromatography on silica gel (dichloromethane; dichloromethane–methanol, 10:1) gave, in decreasing order of

polarity, cis-*N*-methyl-1-(1-methylethoxy-bis(naphthyl)-[2,1-c:1,2-h]-10-aza-1-borabicyclooctane (**17a**) (0.14 g, 46%) as small colourless needles, m.p. 225–6°C (acetone), and trans-*N*-methyl-1-(1-methylethoxy)-bis(-naphthyl)[2,1-c:1,2-h]-10-aza-1-borabicyclooctane (**17b**) (0.03 g, 9%) as colourless crystals, m.p. 184–5°C (acetone).

1. Compound **17a**: (Found: $M^+$ 411.2010, $C_{26}H_{26}BNO_3$. Calc.: 411.2006). $\nu_{max}$ 1625, 1599 (C=C aromatic), 1271 (B–O), 1248, 1181, 1098, 1043 $cm^{-1}$ (C–O). $\delta_B$ 1.91. $\delta_H$ 0.83 (d, *J* 6.1, 6H, $OCH(CH_3)_2$), 2.68 (s, 3H, $NCH_3$), 4.13 (d, *J* 6.1, 1H, $OCH(CH_3)_2$) 4.48, 4.86 (2d, *J* 13.7, 4H, H-9,11), 7.24 (d, *J* 8.9, 2H, H-3,17), 7.34 (t, *J* 7.1, 2H, H-6,14), 7.51 (t, *J* 8.3, 2H, H-7,13), 7.63 (d, *J* 8.3, 2H, H-8,12), 7.74 (d, *J* 8.9, 2H, H-4,16), 7.81 (d, *J* 8.2, 2H, H-5,15). $\delta_C$ 25.1 $OCH(CH_3)_2$, 42.6 $NCH_3$, 58.5 (C-9,11), 62.9 $OCH(CH_3)_2$, 108.2 (C-8a,11b), 120.3 (C-8,12), 121.7 (C-3,17), 122.9 (C-6,14), 126.6 (C-7,13), 128.2 (C-4a,15a), 128.9 (C-5,15), 129.6 (C-4,16), 131.5 (C-8b,11a), 152.4 (C-2a,17a). *m*/*z* 411 (M, 30%), 351 ($M-(CH_3)_2CHOH$, 28), 254 ($M-C_{11}H_9O$, 100).
2. Compound **17b**: (Found: $M^+$ 411.2000, $C_{26}H_{26}BNO_3$. Calc.: 411.2006). $\nu_{max}$ 1623, 1598 (C=C aromatic), 1263 (B–O), 1244, 1089, 1058 $cm^{-1}$ (C–O). $\delta_B$ 1.95. $\delta_H$ 1.11 (d, *J* 6.1, 6H, $OCH(CH_3)_2$), 2.90 (s, 3H, $NCH_3$), 4.13 (h, *J* 6.1, 1H, $OCH(CH_3)_2$), 4.41, 4.53 (2d, *J* 14.5, 4H, H-9,11), 7.17 (d, *J* 8.8, 2H, H-3,17), 7.30 (td, *J* 7.4, 1.2, 2H, H-6,14), 7.43 (t, *J* 6.0, 2H, H-7,13), 7.46 (d, *J* 8.3, 2H, H-8,12), 7.69 (d, *J* 8.8, 2H, H-4,16), 7.76 (d, *J* 8.0, 2H, H-5,15). $\delta_C$ 25.4 $OCH(CH_3)_2$, 44.7 $NCH_3$, 56.6 (C-9,11), 63.7 $OCH(CH_3)_2$, 107.3 (C-8a,11b), 120.1 (C-8,12), 121.7 (C-3,17), 122.9 (C-6,14), 126.6 (C-7,13), 128.5 (C-4a,15a), 128.8 (C-5,15), 129.7 (C-4,16), 131.3 (C-8b,11a), 151.7 (C-2a,17a). *m*/*z* 411 (M, 30%), 351 ($M-(CH_3)_2CHOH$, 25), 255 ($M-C_{11}H_8O$, 44), 254 ($M-C_{11}H_9O$, 100).

### 4.9. N-Octyl-2,3-dihydro-1H-naphth[1,2-e][1,3]oxazine (20)

Aqueous formaldehyde (37%w/w, 3.5 ml, 47 mmol) was added to a solution of 2-naphthol (3.37 g, 23 mmol) and *n*-octylamine (3.9 ml, 23 mmol) in methanol (30 ml) at r.t., and the mixture was heated under reflux with stirring for 12 h. The solvent was removed under reduced pressure, then dilute aqueous hydrochloric acid (2 mol $l^{-1}$, 15 ml) was added and the mixture extracted with dichloromethane (15 ml). Workup and flash chromatography (dichloromethane; dichloromethane–methanol, 10:1) afforded **20** (1.43 g, 21%) as a yellow oil. (Found: $M^+$ 297.2082, $C_{20}H_{27}NO$. Calc.: 297.2093). $\nu_{max}$ 1625, 1500 (C=C aromatic), 1227, 1140 $cm^{-1}$ (C–O). $\delta_H$ 0.87 (td, *J* 8.7, 3.3, 3H, H-8′), 1.25 (m, 10H, H-3′-7′), 1.56 (t, *J* 7.1, 2H, H-2′), 2.73 (t, *J* 7.4, 2H, H-1′), 4.25 (s, 2H, H-4), 4.86 (s, 2H, H-2), 6.99 (d, *J* 8.9, 1H, H-10), 7.27 (t, *J* 6.2, 1H, H-7), 7.39 (t, *J* 6.9, 1H, H-6), 7.54 (2d, *J* 8.4, 2H, H-5,9), 7.68 (d, *J* 8.5, 1H, H-8). $\delta_C$ 14.0 (C-8′), 22.5 (C-7′), 27.1 (C-6′), 28.2 (C-5′), 29.2 (C-4′), 29.4 (C-3′), 31.7 (C-2′), 47.7 (C-1′), 51.9 (C-1), 82.0 (C-3), 111.8 (C-4a), 118.4 (C-10), 120.8 (C-5), 123.2 (C-7), 126.2 (C-6), 127.7 (C-9), 128.5 (C-8), 128.8 (C-8a), 131.8 (C-4b), 151.8 (C-10a). *m*/*z* 297 (M, 72%), 296 (M − H, 100), 198 ($M-C_7H_{15}$, 40), 156 ($C_{11}H_8O$, 68), 128 (156 − CO, 84).

### 4.10. N,N-(Bis(2-hydroxy-1-naphthylmethyl)octyl)amine (21)

2-Naphthol (0.34 g, 2.4 mmol) was added to a solution of the 2*H*-1,3-benzoxazine **20** (0.70 g, 2.4 mmol) in methanol and benzene (2:1, 12 ml) at r.t. This mixture was stirred until a precipitate separated. The solid collected after filtration was washed with methanol leaving **21** (0.80 g, 75%) as yellow rhomboids, m.p. 133–4°C (dichloromethane–methanol). (Found: $M^+$ 442.2744, $C_{30}H_{36}NO_2$. Calc.: 442.2746). $\nu_{max}$ 3160 (br, OH), 1626, 1581 (C=C aromatic), 1279, 1264, 1238 $cm^{-1}$ (C–O). $\delta_H$ ($CDCl_3$, DMSO-$d_6$) 0.84 (t, *J* 7.2, 3H, H-8′), 1.24 (m, 10H, H-5′-7′), 1.78 (t, br, 2H, H-2′), 2.67 (t, *J* 7.6, 2H, H-1′), 4.24 (s, 2H, $2CH_2N$) 7.06 (d, *J* 8.8, 2H, 2H-3), 7.28 (t, *J* 7.2, 2H, 2H-6), 7.47 (t, *J* 7.2, 2H, 2H-7), 7.61 (d, *J* 8.8, 2H, 2H-4), 7.71 (d, *J* 8.0, 2H, 2H-5), 7.96 (d, *J* 8.8, 2H, 2H-8). $\delta_C$ (DMSO-$d_6$) 13.3 (C-8′), 21.7 (C-7′), 25.2 (C-6′), 26.6 (C-5′), 28.3 (C-4′), 28.5 (C-3′), 30.9 (C-2′), 49.0 (C-1′), 53.7 $CH_2N$, 112.4 2(C-1), 117.7 2(C-3), 120.9 2(C-6), 121.6 2(C-8), 125.6 2(C-7), 127.6 2(C-4a), 127.8 2(C-5), 128.3 2(C-4), 132.7 2(C-8a), 154.6 2(C-2). *m*/*z* ($FAB^+$) 442 (M + H, 70%), 285 ($M-C_{11}H_8O$, 16), 157 ($C_{11}H_9O$, 100).

### 4.11. Cis-N-octyl-1-methoxy-bis(naphthyl)[2,1-c:1,2-h]-10-aza-1-borabicyclooctane (22)

Amine **20** (0.20 g, 0.45 mmol), boric oxide (0.02 g, 0.23 mmol) in toluene (5 ml) and methanol (1:1, 5 ml) were placed in a flask fitted with a Dean–Stark water separator. The mixture was heated under reflux for 12 h, then concentrated in vacuo. Flash column chromatography on silica gel (dichloromethane; dichloromethane–methanol, 10:1) gave **22** (0.16 g, 73%) as colourless fine needles, m.p. 222–3°C (acetone). (Found: $M^+$ 481.2784, $C_{31}H_{36}BNO_3$. Calc.: 481.2788). $\nu_{max}$ 1624, 1599 (C=C aromatic), 1246, 1199, 1094, 1045 $cm^{-1}$ (C–O). $\delta_H$ 0.83 (t, *J* 7.2, 2H, H-8′), 1.20 (m, 10H, H-3′-7′), 1.75 (t, br, 2H, H-2′), 3.32 (t, *J* 7.2, 2H, H-1′), 3.45 (s, 3H, $OCH_3$), 4.52 (s, 4H, H-9,11), 7.21 (d, *J* 8.2, 2H, H-3,17), 7.31 (t, *J* 7.6, 2H, H-6,14), 7.44 (t, *J* 7.6, 2H, H-7,13), 7.53 (d, *J* 8.4, 2H, H-8,12), 7.71 (d, *J* 8.9, 2H, H-4,16), 7.77 (d, *J* 8.1, 2H, H-5,15). $\delta_C$ 14.0 (C-8′),

21.1 (C-7′), 22.5 (C-6′), 26.9 (C-5′), 29.0 (C-4′), 31.6 (C-3′), 50.2 $OCH_3$, 51.8 (br, C-1′), 53.4 (C-9,11), 107.4 (C-8a,11a), 120.0 (C-8,12), 121.5 (C-3,17), 123.0 (C-6,14), 126.6 (C-7,13), 128.6 (C-4a,15a), 128.9 (C-5,15), 129.8 (C-4,16), 131.4 (C-8b,11a), 151.5 (C-2a,17a). *m/z* ($DEI^+$) 481 (M, 32%), 450 ($M - OCH_3$, 4), 324 ($M - C_{11}H_9O$, 90), 226 (100).

### 4.12. Cis-N-octyl-1-benzyloxy-bis(naphthyl)-[2,1-c:1,2-h]-10-aza-1-borabicyclooctane (23)

Amine **20** (0.20 g, 0.45 mmol), boric oxide (0.02 g, 0.23 mmol) in benzene (5 ml), and benzyl alcohol (0.05 g, 0.45 mmol) were placed in a flask fitted with a Dean–Stark water separator. The mixture was heated under reflux for 12 h, then concentrated in vacuo. Flash column chromatography on silica gel (dichloromethane; dichloromethane–methanol, 10:1) yielded **23** (0.11 g, 43%) as colourless crystals, m.p. 220–1°C (acetone). (Found: $M^+$ 557.5377, $C_{37}H_{40}BNO_3$. Calc.: 557.5379). $\nu_{max}$ 1624, 1599 (C=C aromatic), 1246, 1198, 1093, 1045 $cm^{-1}$ (C–O). $\delta_B$ 3.73. $\delta_H$ 0.80 (t, *J* 7.2, 3H, H-8″), 1.16 (m, 10H, H-3″-7″), 1.65 (t, br, 2H, H-2″), 3.09 (t, br, 2H, H-1″), 4.35, 4.50 (2d, *J* 14.7, 4H, H-9,11), 4.83 (s, 2H, H-1′), 7.26 (m, *J* 7.2, 5H, H-4′,5′,6′,3,17), 7.31 (t, *J* 7.0, 2H, H-6,14), 7.43 (td, *J* 7.0, 0.9, 2H, H-7,13), 7.52 (d, *J* 8.4, 2H, H-8,12), 7.63 (d, *J* 7.9, 2H, H-3′,7′), 7.75 (d, *J* 8.9, 2H, H-4,16), 7.79 (d, *J* 8.1, 2H, H-5,15). $\delta_C$ 14.1 (C-8″), 21.1 (C-7″), 22.4 (C-6″), 26.9 (C-5″), 28.9 (C-4″), 29.7 (C-3″), 31.5 (C-2″), 51.6, br (C-1″), 54.8 (C-9,11), 64.1 (C-1′), 107.1 (C-8a,11a), 119.9 (C-8,12), 121.7 (C-3,17), 122.9 (C-6,14), 126.7 (C-7,13), 127.4, 127.8 (C-3′,4′,5′,6′,7′), 128.5 (C-4a,15a), 129.0 (C-5,15), 130.0 (C-4,16), 131.3 (C-8b,11a), 133.2 (C-2′), 151.6, (C-2a,17a). *m/z* ($DEI^+$) 557 (M, 20%), 449 ($M - C_6H_5CH_2OH$, 25), 400 ($M - C_{11}H_9O$, 100).

### 4.13. N-Methyl-2,3-dihydro-1H-8-phenylbenz-[1,2-e][1,3]oxazine (25)

Aqueous formaldehyde (37%w/w, 4.5 ml, 0.06 mol) was added to a solution of 2-phenylphenol (3.93 g, 0.023 mol) and methylamine (3.4 ml, 0.027 mol) in methanol (18 ml) at r.t., and the mixture was heated under reflux with stirring for 12 h. The solvent was removed under reduced pressure, then dilute aqueous hydrochloric acid (2 mol $l^{-1}$, 15 ml) was added and the mixture extracted with dichloromethane (15 ml). The aqueous phase was neutralised by the addition of solid sodium hydrogencarbonate, then extracted three times with dichloromethane (15 ml). Workup and flash chromatography (dichloromethane; dichloromethane–methanol, 10:1) afforded **25** (4.21 g, 81%) as colourless crystals, m.p. 87–8°C. (Found: $M^+$ 225.11535, $C_{15}H_{15}NO$. Calc.: 225.11536). $\nu_{max}$ 1465, 1430 (C=C aromatic), 1229, 1201 $cm^{-1}$ (C–O). $\delta_H$ 2.62 (s, 3H, $NCH_3$), 4.01 (s, 2H, H-4), 4.80 (s, 2H, H-2), 6.94 (m, 2H, H-4′,5?), 7.12 (2d, *J* 7.5, 1H, H-7?), 7.29 (t, *J* 7.5, 1H, H-6), 7.38 (t, *J* 7.5, 2H, H-3′,5′?), 7.54 (d, *J* 7.2, 2H, H-2′,6′). $\delta_C$ 39.8 $NCH_3$, 52.5 (C-4), 83.9 (C-2), 120.1 (C-4a), 120.3 (C-5), 126.9 (C-6,7?), 128.0 (C-2′,6′?), 129.0 (C-4′?), 129.4 (C-3′,5′?), 138.0 (C-1′), 150.6 (C-8a). *m/z* 225 (M, 67%), 182, ($M - CH_3N{=}CH_2$, 100).

### 4.14. N-Methyl-2,3-dihydro-1H-6,8-bis(1,1-dimethylethyl)benz[1,2-e][1,3]oxazine (26)

Aqueous formaldehyde (37%w/w, 4.0 ml, 0.032 mol) was added to a solution of 2,4-(1,1-dimethylethyl)-phenol (6.07 g, 0.029 mol) and methylamine (5.0 ml, 0.065 mol) in methanol (30 ml) at r.t., and the mixture was heated under reflux with stirring for 12 h. The solvent was removed under reduced pressure, then dilute aqueous hydrochloric acid (2 mol $l^{-1}$, 15 ml) was added and the mixture extracted with dichloromethane (15 ml). Workup and flash chromatography (dichloromethane; dichloromethane–methanol, 10:1) gave **26** (5.33 g, 69%) as a colourless oil. (Found: $M^+$ 261.20894, $C_{17}H_{27}NO$. Calc.: 261.20926). $\nu_{max}$ 1231 (C–O) 941 $cm^{-1}$. $\delta_H$ 1.28, 1.38 (s, 18H, $2C(CH_3)_3$), 2.58 (s, 3H, $NCH_3$), 3.95 (s, 2H, H-4), 4.76 (s, 2H, H-2), 6.79 (d, *J* 2.2, 1H, H-5), 7.15 (d, *J* 2.2, 1H, H-7). $\delta_C$ 29.6, 31.5, $2C(CH_3)_3$, 34.2, 34.8 $2C(CH_3)_3$, 39.8 $NCH_3$, 53.0 (C-4), 83.0 (C-2), 118.7 (C-4a), 121.8, 121.9 (C-5,7), 136.5 (C-8), 142.0 (C-6), 150.2 (C-8a). *m/z* 261 (M, 52%) 246 ($M - CH_3$, 16), 203 ($246 - CH_3N{=}CH_2$, 100).

### 4.15. N-Methyl-2,3-dihydro-1H-6-(1,1,3,3-tetramethyl-butyl)benz[1,2-e][1,3]oxazine (27)

Aqueous formaldehyde (37%w/w, 3.7 ml, 50 mmol) was added to a solution of 4-(1,1,3,3-tetramethyl-butyl)phenol (5.13 g, 25 mmol) and methylamine (25%v/v 3.5 ml, 25 mmol) in methanol (30 ml) at r.t., and the mixture was heated under reflux with stirring for 12 h. The solvent was removed under reduced pressure, then dilute aqueous hydrochloric acid (2 mol $l^{-1}$, 15 ml) was added and the mixture extracted with dichloromethane. Workup and flash chromatography (dichloromethane; dichloromethane–methanol, 10:1) afforded **27** (0.15 g, 23%) as a colourless oil. (Found: $M^+$ 261.20887, $C_{17}H_{27}NO$. Calc.: 261.20926). $\nu_{max}$ 1501 (C=C aromatic), 1236, 1136 (C–O), 937, 821 $cm^{-1}$. $\delta_H$ 0.69 (s, 9H, $C(CH_3)_3$), 1.32 (s, 6H, $C(CH_3)_2$), 1.67 (s, 2H, $CH_2$) 2.59 (s, 3H, $NCH_3$), 3.93 (s, 2H, H-4), 4.76 (s, 2H, H-2), 6.69 (d, *J* 8.6, 1H, H-8), 6.91 (d, *J* 2.0, 1H, H-5), 7.12 (dd, *J* 8.6, 2.2, 1H, H-7). $\delta_C$ 31.5 $C(CH_3)_2$, 31.7 $C(CH_3)_3$, 32.3 $C(CH_3)_3$, 37.9 $C(CH_3)_2$, 39.8 $NCH_3$, 52.8 $CH_2$, 57.0 (C-4), 83.7 (C-2), 115.4 (C-8), 118.6 (C-4a), 125.0, 125.4 (C-5,7), 142.2 (C-6), 151.1 (C-8a). *m/z* 261 (M, 28%), 190 ($M - C_5H_{11}$, 100), 147 ($190 - CH_3N{=}CH_2$, 54).

### 4.16. N,N-(Bis(2-hydroxy-5-(1,1,3,3-tetramethylbutyl)phenyl-1-methyl)methyl)amine (28)

A mixture of the 2*H*-1,3-benzoxazine **27** (1.24 g, 4.7 mmol) and 4-(1,1,3,3-tetramethylbutyl)phenol (0.98 g, 4.7 mmol) in methanol (12 ml) was stirred at r.t. overnight, after which time only starting materials were present (TLC). The mixture was left standing at r.t. for 3 weeks. Flash chromatography afforded **28** (0.48 g, 10%) as a pale yellow oil. (Found: $M^+$ 467.37465, $C_{31}H_{49}NO_2$. Calc.: 467.37633). $\nu_{max}$ 1503 (C=C aromatic), 1263 (C–O), 821 $cm^{-1}$. $\delta_H$ (DMSO-$d_6$) 0.68 (s, 18H, 2C($CH_3$)$_3$), 1.32 (s, 12H, 2C($CH_3$)$_2$), 1.66 (s, 4H, 2$CH_2$), 2.27 (s, 3H, $NCH_3$), 3.77 (s, 4H, 2H-9), 6.76 (d, *J* 8.4, 2H, 2H-3), 7.03 (d, *J* 2.3, 2H, 2H-6), 7.13 (dd, *J* 8.4, 2.4, 2H, 2H-4). $\delta_C$ (DMSO-$d_6$) 31.7 2C($CH_3$)$_2$, 31.5 2C($CH_3$)$_3$, 32.2 2C($CH_3$)$_3$, 37.9 2C($CH_3$)$_2$, 40.6 $NCH_3$, 57.1 2$CH_2$, 59.5 2(C-9), 115.4 2(C-3), 120.9 2(C-1), 126.9, 127.8 2(C-4/6?), 140.8 2(C-5), 153.9 2(C-2). *m*/*z* 467 (M, 4%), 452 (M − $CH_3$, 1), 396 (M − $C_5H_{11}$, 10).

### 4.17. Cis-N-methyl-1-phenyl-bis(5,11-(1,1,3,3-tetramethylbutyl)phenyl)[1,2-c:2,1-h]-8-aza-1-borabicyclooctane (29)

Amine **28** (0.48 g, 1.0 mmol) and phenylboronic acid (0.13 g, 1.1 mmol) in toluene (5 ml) were placed in a flask fitted with a Dean–Stark water separator. The mixture was heated under reflux for 12 h, then concentrated in vacuo. Flash column chromatography on silica gel (dichloromethane; dichloromethane–methanol, 10:1) gave **29** (0.37 g, 66%) as colourless flattened needles, m.p. 278–9°C (acetone). (Found: $[M + H]^+$ 554.4104, $C_{37}H_{53}BNO_2$. Calc.: 553.4091). $\nu_{max}$ 1504 (C=C aromatic), 1291, 1263, 1244, 1195, 1048 $cm^{-1}$ (C–O). $\delta_B$ 3.87. $\delta_H$ 0.80 (s, 18H, 2C($CH_3$)$_3$), 1.33 (s, 12H, 2C($CH_3$)$_2$), 1.68 (s, 4H, 2C$H_2$), 2.59 (s, 3H, $NCH_3$) 3.84, 4.21 (2d, *J* 14.4, 4H, H-7,9), 6.88 (sd, *J* 2.0, 2H, H-6,10), 6.96 (d, *J* 8.4, 2H, H-3,13), 7.18 (td, *J* 7.6, 1.6, 3H, H-3′,4′,5′), 7.23 (d, *J* 8.4, 2H, H-4,12), 7.56 (dd, *J* 8.0, 1.2, 2H, H-2′,6′). $\delta_C$ 31.4 2C($CH_3$)$_2$, 31.8 2C($CH_3$)$_3$, 32.4 2C($CH_3$)$_3$, 37.9 2C($CH_3$)$_2$, 44.7 $NCH_3$, 57.2 ($CH_2$,C-7,9), 115.4 (C-6a,9a), 118.5 (C-3,13), 124.3 (C-6,10), 127.2 (C-3′,4′,5′), 127.6 (C-4, 12), 127.7 (C-1′), 133.3 (C-2′,6′), 140.8 (C-5,11), 151.3 (C-2a,13a). *m*/*z* ($DEI^+$) 553 (M, 14%), 538 (M − $CH_3$, 2), 496 (M − $C_4H_9$, 2), 482 (M − $CH_2C(CH_3)_3$, 42), 476 (M − $C_6H_5$, 100).

### 4.18. N-Methyl-2,3-dihydro-1H-6,8-dibromobenzyl-[1,2-e][1,3]oxazine (30)

Aqueous formaldehyde (37%w/w, 1.7 ml, 23 mmol) was added to a solution of 2,4-dibromophenol (2.63 g, 10.4 mmol) and methylamine (25%v/v, 1.4 ml, 11.5 mmol) in methanol (25 ml) at r.t., and the mixture was heated under reflux with stirring for 12 h. The solvent was removed under reduced pressure, then dilute aqueous hydrochloric acid (2 mol $l^{-1}$, 15 ml) was added and the mixture extracted with dichloromethane. Workup and flash chromatography (dichloromethane, dichloromethane–methanol, 10:1) afforded **30** (1.62 g, 51%) as yellow crystals, m.p. 77–6°C (acetone) (Ref. [9] 78–9°C). $\nu_{max}$ 1558 (C=C aromatic), 1237, 1152 (C–O), 891 $cm^{-1}$. $\delta_H$ 2.58 (s, 3H, $NCH_3$), 3.87 (s, 2H, H-4), 4.89 (s, 2H, H-2), 6.96 (s, 1H, H-5), 7.42 (s, 1H, H-7). $\delta_C$ 39.8 $NCH_3$, 49.7 (C-4), 83.8 (C-2), 110.9 (C-8), 112.0 (C-4a), 123.4 (C-6), 129.2 (C-5), 133.2 (C-7), 160.1 (C-8a).

### 4.19. N-((2-Hydroxy-3,5-dibromo-1-methylbenzyl)-N-(2-hydroxy-1-naphthylmethyl)methyl)amine (31)

2-Naphthol (0.74 g, 5.2 mmol) was added to a solution of the 2*H*-1,3-benzoxazine **30** (1.58 g, 5.2 mmol) in methanol–dichloromethane (1:1, 30 ml) at r.t. The mixture was stirred until a precipitate separated. The solid collected after filtration was washed with methanol, leaving **31** (1.89 g, 81%) as yellow plates, m.p. 174–5°C (dichloromethane–methanol) (Ref. [4] 174°C). (Found: $M^+$ 450.9616, $C_{19}H_{17}^{79,81}Br_2NO_2$. Calc.: 450.9606). $\nu_{max}$ 1625, 1575, 1520 (C=C aromatic), 1283 $cm^{-1}$ (C–O). $\delta_H$ 2.23 (s, 3H, $NCH_3$), 3.74 (s, 2H, H-9), 4.07 (s, 2H, H-7), 7.02 (d, *J* 2.3, 1H, H-5), 7.16 (d, *J* 8.9, 1H, H-12), 7.22 (t, *J* 7.1, 1H, H-15), 7.37 (d, *J* 2.4, 1H, H-3), 7.42 (td, *J* 8.4, 1.1, 1H, H-16), 7.39 (t, *J* 8.8, 1H, H-14), 7.67 (d, *J* 7.8, 1H, H-13), 7.87 (d, *J* 8.5, 1H, H-17). $\delta_C$ 40.1 $NCH_3$, 50.3 (C-9), 58.2 (C-7), 109.0, 109.6 (C-2/4?), 112.3 (C-10), 117.2 (C-12), 121.1 (C-17), 121.6 (C-15), 124.5 (C-6), 125.9 (C-16), 127.4 (C-13a), 127.7 (C-14), 128.8 (C-13), 129.5 (C-5), 132.6 (C-3), 133.0 (C-17a), 153.1 (C-1), 153.8 (C-11). *m*/*z* ($DEI^+$) 451 (M, 5%), 295 (M − $C_{11}H_8O$, 40), 156 ($C_{11}H_8O$, 60), 128 (156 − CO, 100).

### 4.20. N-Methyl-1-methoxy-3,5-dibromophenyl[1,2-c]-naphthyl[1,2-h]-8-aza-1-borabicyclooctane (32)

Amine **31** (0.55 g, 1.2 mmol) and boric oxide (0.04 g, 0.6 mmol) in benzene and methanol (5 ml) were placed in a flask fitted with a Dean–Stark water separator. The mixture was heated under reflux for 12 h, then concentrated in vacuo. Flash column chromatography on silica gel (chloroform, chloroform–methanol, 10:1) afforded **32** (0.51 g, 85%) as colourless plates, m.p. 128–9°C (acetone). (Found: $M^+$ 490.9719, $C_{20}H_{18}B^{79,81}Br_2NO_3$. Calc.: 490.9726). $\nu_{max}$ 1624, 1599 (C=C aromatic), 1213, 1136, 1098, 1075, 1051, 1026 $cm^{-1}$ (C–O). $\delta_H$ 2.60 (s, 3H, $NCH_3$), 3.31 (s, 3H, $OCH_3$), 3.65, 3.91 (2d, *J* 15.0, 2H, H-7), 4.17, 4.26 (2d, *J* 14.8, 2H, H-9), 6.77 (d, *J* 2.2, 1H, H-6), 7.00 (d, *J* 9.0, 1H, H-15), 7.20 (td, *J* 5.4, 2.6, 1H, H-12), 7.31 (m, 1H,

H-10), 7.30 (m, 1H, H-11), 7.44 (d, *J* 2.2, 1H, H-4), 7.55 (d, *J* 8.9, 1H, H-14), 7.62 (d, *J* 8.0, 1H, H-13). $\delta_C$ 44.0 $NCH_3$, 50.0 $OCH_3$, 56.3 (C-9), 57.6 (C-7), 106.7 (C-9a), 110.7 (C-5), 114.0 (C-3), 119.5 (C-6a), 120.0 (C-10), 121.1 (C-15), 123.2 (C-12), 126.7 (C-10), 128.4 (C-13a), 128.7 (C-4), 129.9 (C-14), 130.9 (C-9b), 134.7 (C-6), 149.6 (C-2a), 150.8 (C-15a). *m*/*z* ($DEI^+$) 491 (M, 24%), 459 ($M - HOCH_3$, 12), 334 ($M - C_{11}H_9O$, 100).

## 5. Supplementary material

The crystal structures have been allocated the following deposition numbers at the Cambridge Crystallographic Data Centre; CCDC 132002 for **10a**, and CCDC 132003 for **29**.

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