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Synthesis of dioxazaborocines from *N*,*N*′-alkylbridged-bis(bis(2-hydroxybenzyl)aminomethyl)amines

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Abstract

The aminoalkylation of 2H-1,3-naphthoxazines by phenols has been used to prepare some tripodal amines. A series of these ligands were coordinated to boron, giving dioxazaborocines. The X-ray crystal structures of two dioxazaborocines are reported. These compounds are capable of releasing borate ions in vivo and are therefore potentially biologically active. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Boron; 2H-1,3-Naphthoxazine; Dioxazaborocine; Trien

1. Introduction

Dioxazaborocines derived from *N*-substituted-bis(2-hydroxybenzyl)aminomethyl amines have been described previously, and have been shown to adopt preferentially a *cis* geometry about the B–N coordinate bond [1,2]. Since both substituents R^1 and R^2 (Fig. 1) lie in the same plane, potentially they can be linked to a second biaryl-boroxazine moiety.

The resulting architecture, in which two biaryl-boroxazine moieties could be linked not only at boron (via an α,ω-diol) but also at nitrogen (via an α,ω-diamine), would enclose a macrocyclic centre. Such a cyclic array might coordinate metal ions, thereby offering the possibility of delivering both boron and, for example, copper(II), in vivo as complementary biocidal (wood preservative) components from a single carrier molecule. Moreover, the presence of a macrocycle might not be a necessary requirement for the chelation of ions; coordinating functionality appended from either nitrogen or boron separately could also provide potentially ligating species. In connection with these opportunities, we report herein the synthesis of dioxazaborocines from *N*,*N*′-alkylbridged-bis(bis(2-hydroxybenzyl)aminomethyl)amines.

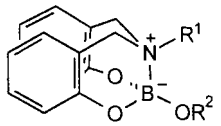

Fig. 1. Substituted dioxazaborocines.

2. Results and discussion

Two sites for potential chelation centres were considered; a bridge (R^1–R^1) between the nitrogen atoms of two dioxazaborocines (Fig. 1), and a bridge (R^2–R^2) between the two boron atoms.

Initially, it was necessary to establish whether the presence of an alkyl bridge between two tridentate bis(hydroxybenzyl)amine moieties allows boron coordination, since it had been established in earlier work that introduction of bulky substituents on boron was hindered when the substituent on nitrogen is also large [1]. Thus, bis(naphthoxazine) **1** was prepared [3] from 2-naphthol, aqueous formaldehyde and 1,2-diaminoethane (Scheme 1). Subsequent aminoalkylation of 2-naphthol by the bis(naphthoxazine) **1**, according to Burke et al. [4–9], resulted in the precipitation of the bis(tertiary amine) **2**, which was poorly soluble even in polar organic solvents such as DMSO. Attempted con-

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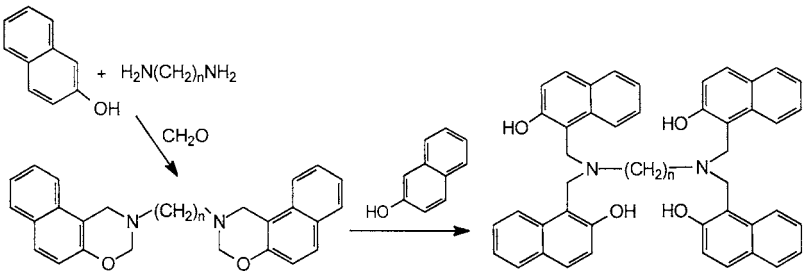


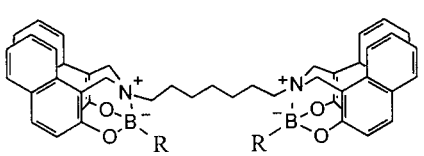
1: n = 2
3: n = 7

2: n = 2
4: n = 7

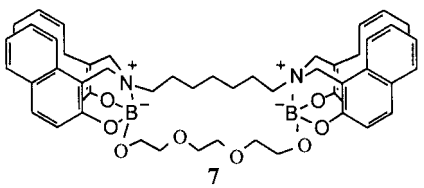
Scheme 1.

version of **2** into a pseudoboratrane (in which boron coordination is tridentate rather than tetradentate) [1] by treatment with boric acid in methanol resulted largely in the formation of bis(2-hydroxynaphthylmethyl)methane (from fragmentation of **2** to give 2-naphthol and an *ortho*-naphthoquinone methide). In order that the solubility of the bisamine might be improved, a primary α,ω-diamine with an extended hydrocarbon chain, 1,7-diaminoheptane, was then used instead of 1,2-diaminoethane. The derived bis(naphthoxazine) **3** was prepared and treated with 2-naphthol, affording the bisamine **4** having a C_7 linker. The ^{1}H-NMR spectrum of **4** included a signal at δ 4.10, typical of a benzylic methylene proton in a 2-hydroxy-1-naphthylmethylamine. In the ^{13}C-NMR spectrum the resonance due to the benzylic carbon C-9 was observed at a characteristic chemical shift of δ 53.1. The IR spectrum of this ditertiary bisamine **4** contains a rather weak series of bands, indicative of a symmetrical structure. Accurate mass measurement of the molecular ion (FAB^+ ionisation) was consistent with the required molecular formula. Compound **4** had improved solubility in organic solvents, allowing the synthesis of derived dioxazaborocines to be investigated.

In the event, the bis(dioxazaborocines) **5** and **6** were formed readily, using either a mixture of boric oxide and methanol or phenylboronic acid, respectively. Each of these pseudoboratranes was characterised fully by IR and NMR (2D COSY, HMQC, and HMBC experiments) spectroscopy, and by mass spectrometry. The bis(phenylboronato) compound **6** crystallised from xylene; its X-ray crystal structure (Fig. 2) showed that the *N*-heptyl bridge prefers to adopt a linear arrangement so that the bulky naphthylboronato appendages are at the greatest distance from each other.



5: R = OMe
6: R = Ph



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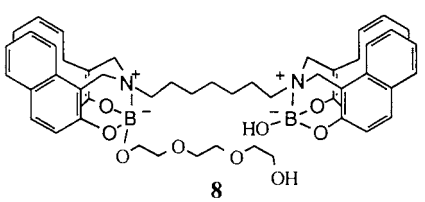
In view of the successful formation of the bis(B-methoxy) compound **5**, the α,ω-bisamine **4** appeared to be an attractive precursor of the bis(boronate) macrocycle **7**. However, attempts to prepare **7** from the reaction of **4** with boric acid and the α,ω-diol triethylene glycol were unsuccessful; instead the non-cyclised boronates **8** and **9** were isolated as the major products.



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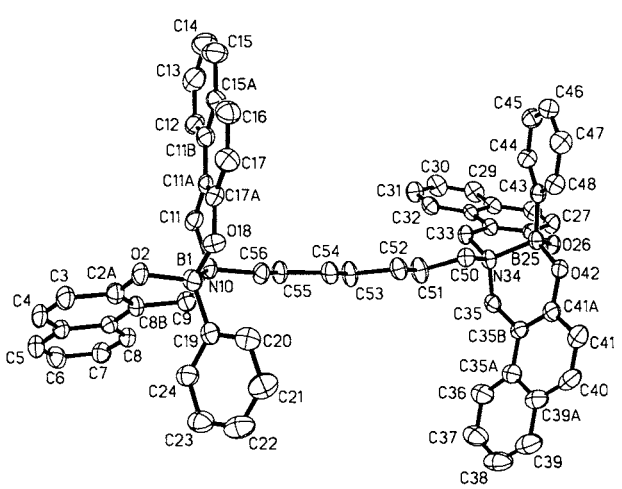


Fig. 2. The atomic arrangement in **6**.

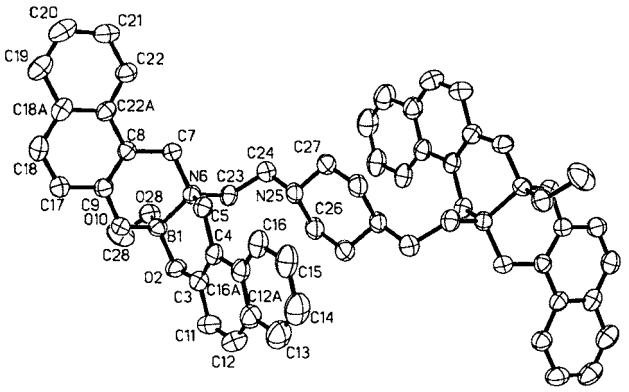
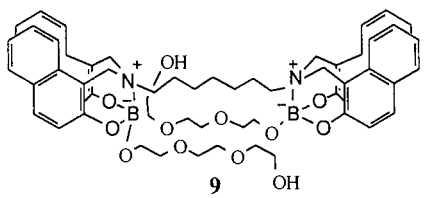


Fig. 3. The atomic arrangement in **11**.



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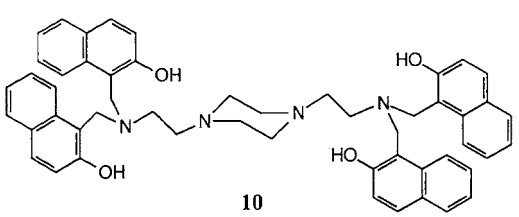
At this point, it had been established that dioxazaborocines could be synthesised from bis-*N*,*N*′-tridentate ligands. However, since the boronate linker chain in **8**/**9** did not cyclise, it was instead proposed that Lewis base functionality be included in the C_7 hydrocarbon chain bridging the two nitrogen atoms. Such potentially ligating sites could assist macrocyclisation by a template effect in the presence of an ionic species. Alternatively, even if macrocyclisation did not occur, these sites could still coordinate metal ions.

The coordinating power of triethylenetetramine (trien) with metals is well established [10]. Initially, available technical grade trien was treated with 2-naphthol and aqueous formaldehyde. After a few minutes a resinous material separated. Workup gave an oil, shown (^{1}H-NMR) to be a mixture of naphthoxazines. Treatment of this mixture with 2-naphthol resulted in the precipitation of a white solid **10**, which was heated under reflux in benzene with boric oxide and methanol. After workup a boronato species was isolated, but the usual spectroscopic methods of analysis did not establish its structure. However, crystallisation from xylene led to the characterisation of this compound as the bis(pseudoboratrane) **11**. Unexpectedly, the X-ray crystal structure of **11** (Fig. 3) showed that a piperazine ring is present in the bridging moiety.



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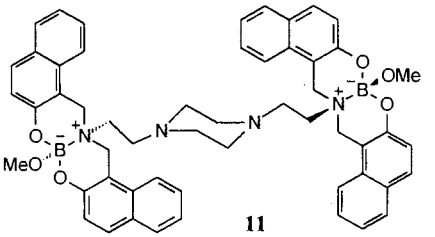

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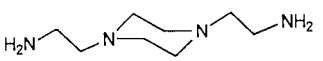
Subsequently, it was established by GC–MS that the technical grade trien used in this synthesis had contained (together with other amines) 18% of the amine **12** containing a piperazine ring, obviously derived from annulation of ethylene across the two secondary amine groups in trien. The isolation of bis(pseudoboratrane) **11** as a minor component from a mixture, which must have included related aminoalkylation products, in particular **13** (see below) derived from the major trien component of the technical grade triethylenetetramine, reflects serendipitous crystallisation of the piperazine from xylene. A sample of pure (by GC–MS) hydrated trien was then obtained and treated with 2-naphthol and aqueous formaldehyde, as described above. Again a resinous mixture of products separated within minutes. During acidic workup, compound **13** separated from the organic phase as a white solid. Although the NMR spectra for this compound were complicated due to the presence of both the naphthoxazine and the aminomethylnaphthyl aromatic moieties, complete assignments consistent with structure **13** were nevertheless achieved by a combination of short- and long-range 2D experiments. Clearly, not only the primary amines but also the secondary amines in trien had participated in Mannich-type reactions. Apparently, the 2-hydroxynaphthylmethyl substituents are either too bulky or too robust to undergo the aminoalkylation required to lead to the pseudoboratrane skeleton. Similarly, the tris(naphthoxazine) **14** prepared from tris(2-aminoethylamine) (tren) did not undergo aminoalkylation on treatment with 2-naphthol (three mol equivalents).



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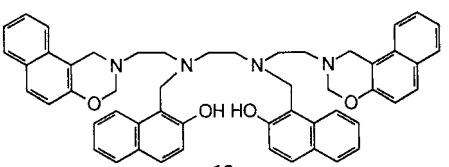

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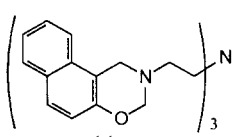

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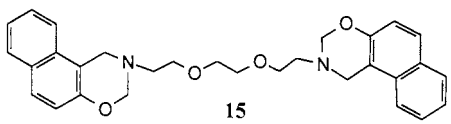
As an alternative to trien, 2,2′-(ethylenedioxy)-bis(ethylamine), was investigated as a bridging unit. This α,ω-diamine does not include the secondary amine groups, which had undergone Mannich-type reactions in trien, but instead includes Lewis base functionality (oxygen atoms) on the bridging moiety which might either assist cyclisation by a template effect, or themselves be potentially coordinating towards metal ions. The bis(naphthoxazine) **15** was therefore synthesised from 2-naphthol, aqueous formaldehyde, and 2,2′-(ethylenedioxy)bis(ethylamine) [1]. Subsequent aminoalkylation [4–9] of 2-naphthol with **15** occurred readily, affording the *N*,*N*′-(bis(2-hydroxy-1-naphthyl)-methyl)amine (**16**). Both the bis(naphthoxazine) **15** and its derived tertiary amine **16** had mass, IR, and NMR spectra which supported their proposed structures. Prior to attempting macrocyclisation using an α,ω-diol, the non-cyclised dioxazaborocine **17** was shown to be formed readily and in reasonable yield (46%) from the amine **16** and phenylboronic acid. Since the amine **16** includes oxygen atoms in the linker moiety, it was hoped that closure to a macrocycle might be assisted by a template effect in the presence of a suitable ion. However, attempted preparation of the cyclic dioxazaborocine species **18** by treatment of **17** with borax and triethylene glycol using high dilution conditions was unsuccessful. It is likely that ring closure is unfavourable in these attempted macrocyclisation reactions because of steric effects associated with the presence of large substituents on nitrogen.



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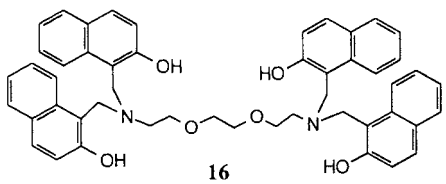

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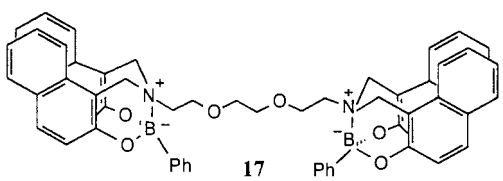

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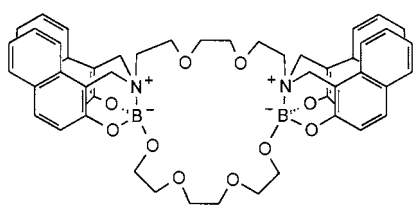

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Table 1
Data collection and processing parameters [a]

	6	**11**
Formula	$C_{87}H_{86}B_2N_2O_4$	$C_{70}H_{74}B_2N_4O_6$
Molecular weight	1245.20	1088.95
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a (Å)	11.7092(2)	12.2790(2)
b (Å)	15.6395(3)	10.9108(2)
c (Å)	19.6490(1)	21.7053(3)
α (°)	78.984(1)	
β (°)	78.891(1)	91.491(1)
γ (°)	85.983(1)	
V (Å^3)	3463.65(9)	2906.95(8)
Z	2	4
$D_{calc.}$ (g cm^{-3})	1.194	1.244
$F(000)$	1328	1160
μ (mm^{-1})	0.071	0.078
Radiation Mo–K$_\alpha$ (monochromatic) λ (Å)	0.71069	0.71069
Temperature (K)	203	203
Diffractometer	Siemens SMART	
Scan technique	Area detector	
2θ (min–max) (°)	2–50	3–50
Reflections collected/unique	23357/11821 [$R_{int} = 0.129$]	21525/5108 [$R_{int} = 0.0623$]
No. of observed reflections [$I > 2\sigma(I)$]	3980	3559
Crystal size (mm)	$0.11 \times 0.11 \times 0.10$	$0.41 \times 0.24 \times 0.20$
A (min–max)	0.992, 0.993	0.969, 0.085
Goodness-of-fit on F^2	0.886	0.978
Function minimised	$\Sigma w(F_o^2 - F_c^2)^2$	$\Sigma w(F_o^2 - F_c^2)^2$
R (observed data)	0.0584	0.0929
wR_2 (all data)	0.1410	0.3146
Difference map (min–max) (e Å^{-3})	+0.19 and −0.25	+0.31 and −0.29

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

2.1. X-ray crystal structure determinations of **6** and **11**

Data were collected on a Siemens SMART area detector diffractometer using 0.3° frames and covered a nominal sphere for **6** and a hemisphere for **11**. Lorentz, polarisation and an absorption correction [11] were applied. The structures were solved by direct methods using SHELXS-97 [12] and refined by full-matrix least-squares using SHELXL-97 [13]. Hydrogen atoms were included in calculated positions and allowed to ride on the carrier atom with 20% greater thermal parameter. Crystal data and refinement details are given in Table 1. The structures are depicted in Figs. 1 and 2. Selected bond lengths for **6** and **11** are given in Tables 2 and 3, respectively. There is known to be considerable variation in B–N bond lengths, dependent on the sub-

Table 2
Selected bond lengths (Å) for **6**

B(1)–O(18)	1.441(5)
B(1)–O(2)	1.465(5)
B(1)–C(19)	1.618(6)
B(1)–N(10)	1.654(5)
C(9)–N(10)	1.496(4)
N(10)–C(56)	1.505(4)
N(10)–C(11)	1.509(4)
B(25)–O(42)	1.465(5)
B(25)–O(26)	1.485(5)
B(25)–C(43)	1.590(6)
B(25)–N(34)	1.649(5)
C(33)–N(34)	1.499(4)
N(34)–C(50)	1.504(4)
N(34)–C(35)	1.510(4)

Table 3
Selected bond lengths (Å) for **11**

B(1)–O(19)	1.424(6)
B(1)–O(2)	1.451(6)
B(1)–O(18)	1.460(7)
B(1)–N(10)	1.640(6)
O(2)–C(2A)	1.357(6)
C(8B)–C(9)	1.503(7)
C(9)–N(10)	1.515(6)
N(10)–C(11)	1.503(6)
N(10)–C(21)	1.510(6)
C(11)–C(11A)	1.500(7)
C(17A)–O(18)	1.364(6)

stituents on boron and nitrogen [14]. The values found here (1.654(5) and 1.649(5) Å) for **6** and (1.640(6) Å) for **11** are not only comparable, but also typical of those in other molecules containing similar B–N interactions [14].

3. Experimental

Melting points were determined on a Reichert–Kofler block and are uncorrected. IR spectra were recorded on a Perkin–Elmer 1000 or a Perkin–Elmer 1600 FTIR spectrometer. The spectra for solids were recorded either 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. Unless otherwise stated spectra were recorded in deuteriochloroform using a 5 mm probe. 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 5000 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. Pre-distilled solvents were used during recrystallisation and purification of compounds by chromatographic techniques. All other reagents were used as obtained from commercial sources.

3.1. 1,2-Bis(N,N′-(2,3-dihydro-1H-naphth[1,2-e]-[1,3]oxazine))ethane (*1*)

1,2-Diaminoethane (1.4 ml, 0.02 mol) and aqueous formaldehyde (37% w/w, 5.1 ml, 0.08 mol) were added to a solution of 2-naphthol (5.35 g, 0.04 mol) in methanol (30 ml). A precipitate separated within 1 min. This mixture was heated under reflux for 1 h before cooling, filtering off the precipitate and washing it with several portions of methanol. The crude product was recrystallised from dichloromethane to give **1** (7.10 g, 48%) as colourless plates, m.p. 188–9°C. (Found: $M^{+\bullet}$ 396.1844, $C_{26}H_{24}N_2O_2$. Calc.: 396.1838). ν_{max} 1622, 1595 (C=C aromatic), 1229, 1118 cm^{-1} (C–O). δ_H 3.08 (t, *J* 7.6, 4H, 2H-1′), 4.39 (s, 4H, 2H-4), 4.98 (s, 4H, 2H-2), 7.03 (d, *J* 8.9, 2H, 2H-10), 7.37 (t, *J* 7.2, 2H, 2H-7), 7.47 (td, *J* 8.2, 1.1, 2H, 2H-6), 7.59 (d, *J* 8.3, 2H, 2H-5), 7.64 (d, *J* 8.9, 2H, 2H-9), 7.76 (d, *J* 8.0, 2H, 2H-8). δ_C 48.0 2(C-4), 50.4 2(C-1′), 82.5 2(C-2), 111.7 2(C-4a), 118.5 2(C-10), 121.0 2(C-5), 123.5 2(C-7), 126.5 2(C-6), 128.1 2(C-9), 128.6 2(C-8), 129.0 2(C-8a), 131.8 2(C-4b), 151.9 2(C-10a). *m*/*z* (DEI^{+}) 396 (M, 4%), 240 (M–$C_{11}H_8O$, 10), 156 ($C_{11}H_8O$, 24), 128 (156-CO, 100).

3.2. 1,7-Bis(N,N′-(2,3-dihydro-1H-naphth[1,2-e][1,3]-oxazine))heptane (*3*)

A solution of 2-naphthol (5.01 g, 34.8 mmol) in methanol (30 ml) was treated with 1,7-diaminoheptane (2.50 g, 19.1 mmol) and aqueous formaldehyde (37% w/w, 5.7 ml, 76.5 mmol). This mixture was heated under reflux overnight before concentrating in vacuo. The crude residue was acidified (aqueous HCl, 2 mol l^{-1}, 20 ml) and extracted with dichloromethane (40 ml) to remove unreacted 2-naphthol. The aqueous phase was neutralised (solid $NaHCO_3$) and extracted with dichloromethane (3 × 40 ml). These combined organic extracts were washed with water, dried, and concentrated to give (^{1}H-NMR) an orange oil containing **3** and 1,7-diaminoheptane. Flash chromatography (dichloromethane) gave **3** as a yellow oil (3.54 g, 44%). (Found: M^{+}; 466.2629, $C_{31}H_{35}N_2O_2$. Calc.: 466.2620). ν_{max} 1738, 1625, 1599 (C=C aromatic), 1226, 1056 cm^{-1} (C–O). δ_H 1.34 (s, br, 10H, H-3′,4′,5′), 1.60 (t, *J* 6.4, 4H, H-2′), 2.78 (t, *J* 7.6, 4H, H-1′), 4.31 (s, 4H, 2H-4), 4.91 (s, 4H, 2H-2), 7.01 (d, *J* 8.8, 2H, 2H-10), 7.36 (t, *J* 7.2, 2H, 2H-7), 7.47 (td, *J* 8.4, 1.2, 2H, 2H-6), 7.61 (d, *J* 7.6, 2H, 2H-5), 7.63 (d, *J* 8.8, 2H, 2H-9), 7.75 (d, *J* 8.4, 2H, 2H-8). δ_C 27.2 (C-5′,4′), 28.2 (C-2′), 29.3 (C-3′),

47.8 2(C-4), 51.9 2(C-1′), 82.2 2(C-2), 118.9 2(C-4a), 118.5 2(C-10), 120.9 2(C-5), 123.3 2(C-7), 126.4 2(C-6), 127.9 2(C-9), 128.6 2(C-8), 128.9 2(C-8a), 131.8 2(C-4b), 151.9 2(C-10a). *m/z* 466 (M, <1%), 310 (M–$C_{11}H_8O$, 41), 156 ($C_{11}H_8O$, 78), 128 (156-CO, 100).

3.3. 2,7-Bis(*N*,*N*′-((2-hydroxy-1-naphthylmethyl)-heptyl)amine (**4**)

2-Naphthol (1.50 g, 10.4 mmol) was added to a solution of **3** (2.43 g, 5.2 mmol) in methanol (18 ml) at room temperature (r.t.). This mixture was stirred until a precipitate separated. The solid collected after filtration was washed with methanol to give the **4** (2.44 g, 62%) as a yellow solid, m.p. 134–5°C. (Found: $M+H^+$ 755.3865, $C_{51}H_{51}N_2O_4$. Calc.: 755.3849). ν_{max} 1622, 1597, 1562 (C=C aromatic), 1273, 1237 cm^{-1} (C–O). δ_H (DMSO-d_6) 0.86, 1.08, 1.62 (3s, br, 14H, H-1′-7′), 4.10 (s, br, 8H, 4CH_2N), 7.04 (d, *J* 8.2, 4H, H-3), 7.22 (t, br, 4H, 4H-6), 7.47 (t, br, 4H, 4H-7), 7.63 (d, *J* 8.2, 4H, 4H-4), 7.69 (d, *J* 7.5, 4H, 4H-5), 7.88 (d, *J* 7.8, 4H, 4H-8). δ_C (DMSO-d_6) 25.2 (C-4′), 26.5 (C-3′,5′), 28.1 (C-2′,6′), 48.8 (C-1′,7′), 53.1 4CH_2N, 113.7 4(C-1), 118.1 4(C-3), 122.2 4(C-6), 122.3 4(C-8), 126.1 4(C-7), 127.9 4(C-4a), 128.2 4(C-5), 128.8 4(C-4), 133.2 4(C-8a), 154.8 4(C-2). *m/z* (FAB^+) 755 (M + H, 2%), 599 (755-$C_{11}H_8O$, 2), 443 (599-$C_{11}H_8O$, 2), 157 ($C_{11}H_9O$, 21).

3.4. *N*,*N*′-Bis(cis-heptyl-1-methoxy-bis(naphthyl)-[2,1-c:1,2-h]-10-aza)-1-borabicyclodecane (**5**)

2,7-Bis(*N*,*N*′-((2-hydroxy-1-naphthylmethyl)heptyl)-amine (**4**) (0.23 g, 0.3 mmol) and boric oxide (0.02 g, 0.3 mmol) in 1:1 methanol–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 (chloroform; 9:1 chloroform–methanol) gave **5** (0.1 g, 45%) as micro-crystals, m.p. 185–6°C (xylene). (Found: $M^{+\bullet}$ 834.4063, $C_{53}H_{52}B_2N_2O_6$. Calc.: 834.4011). ν_{max} 1624, 1599 (C=C aromatic), 1247, 1212, 1134, 1092, 1051 cm^{-1} (C–O). δ_H 1.18, 1.26, 1.56, 1.67 (m, 10H, H-2′,3′,4′,5′,6′), 3.26 (t, br, *J* 6.4, 4H, H-1′,7′), 3.44 (s, 6H, 2OCH_3), 4.48 (s, 8H, 2H-9,11), 7.20 (d, *J* 8.9, 4H, 2H-3,17), 7.33 (t, *J* 7.32, 4H, 2H-6,14), 7.46 (t, *J* 8.0, 4H, 2H-7,13), 7.52 (d, *J* 8.3 4H, 2H-8,12), 7.72 (d, *J* 8.9, 4H, 2H-4,16), 7.78 (d, *J* 8.0, 4H, 2H-5,15). δ_C 20.9 (C-4′), 26.6 (C-3′,5′), 28.7 (C-2′,6′), 50.2 OCH_3, 51.8 br, 2(C-9,11), 53.2 (C-1′,7′), 107.3 2(C-8a,11b), 120.1, 2(C-8,12), 121.5 2(C-3,17), 123.1 2(C-6,14), 126.7 2(C-7,13), 128.6 2(C-4a,15a), 128.9 2(C-5,15), 130.0 2(C-4,16), 131.3 2(C-8b,11a), 151.5 2(C-2a,17a). *m/z* (FAB^+) 834 (M, 2%), 803 (M–MeO, 3), 521 (5), 536 (10).

3.5. *N*,*N*′-Bis(cis-heptyl-1-phenyl-bis(naphthyl)-[2,1-c:1,2-h]-10-aza)-1-borabicyclodecane (**6**)

A solution of 2,7-bis(*N*,*N*′-((2-hydroxy-1-naphthylmethyl)heptyl)amine (**4**) (0.28 g, 0.38 mmol), and phenylboronic acid (0.10 g, 0.75 mmol) in DMF (5 ml) was heated under reflux for 12 h, then concentrated in vacuo. Flash column chromatography on silica gel (dichloromethane) gave **6** (0.15 g, 43%) as yellow micro-crystals, m.p. 213–4°C (xylene). (Found: $M^{+\bullet}$ 926.4440, $C_{63}H_{56}B_2N_2O_4$. Calc.: 926.4426). ν_{max} 1624, 1599 (C=C aromatic), 1246, 1198, 1093, 1045 cm^{-1} (C–O). δ_H 1.00 (m, br, 6H, H-3′,4′,5′), 1.50 (m, br, 4H, 2H-2′,6′), 2.98, s, 4H, br, H-1′,7′), 4.31, 4.59 (2d, *J* 15.2, 8H, 2H-9,11), 7.18 (t, *J* 7.4, 6H, 2H-3″,4″,5″), 7.25 (d, *J* 8.2, 4H, 2H-3,17), 7.33 (t, *J* 7.4, 4H, 2H-6,14), 7.43 (t, *J* 7.4, 4H, 2H-7,13), 7.48 (d, *J* 8.4, 4H, 2H-8,12), 7.59 (dd, *J* 8.0, 1.2, 4H, 2H-2″,6″), 7.75 (d, *J* 8.9, 4H, 2H-4,16), 7.80 (d, *J* 7.9, 4H, 2H-5,15). δ_C 20.9 (C-4′), 26.4 (C-3′,5′), 28.6 (C-2′,6′), 51.5 br, 2(C-9,11), 54.5 (C-1′,7′), 107.0 2(C-8a,11b), 119.9 2(C-8,12), 121.7 2(C-3,17), 123.0 2(C-6,14), 126.7 2(C-7,13), 127.4 2(C-3″,5″), 128.0 2(C-4″), 128.6 2(C-4a,15a), 129.0 2(C-5,15), 130.1 2(C-4,16), 130.4 2(C-1″), 131.3 2(C-8b,11a), 133.2 2(C-2″,6″), 151.9 2(C-2a,17a). *m/z* (FAB^+) 926 (M, 5%), 849 (M–C_6H_5, 9), 769 (M–$C_{11}H_9O$, 4), 693 (849-$C_{11}H_8O$, 6), 615 (692-C_6H_6, 10).

A solution of **4** (0.30 g, 0.4 mmol) in toluene (5 ml) was added to a suspension of boric oxide (0.04 g, 0.8 mmol) in toluene (5 ml). This mixture was heated to just below reflux temperature and then a solution of tetraethylene glycol (0.30 g, 2.0 mmol) in toluene (20 ml) was added slowly from a syringe pump during 9 h. When the addition was complete the mixture had become homogeneous. After a further hour, the mixture was concentrated. Chromatography of the oily residue on silica gel (dichloromethane) gave, in decreasing order of polarity, *N*,*N*′-bis(*cis*-heptyl-1-hydroxyethyl-1′-hydroxy-bis(naphthyl)[2,1-c:1,2-h]-10-aza-1-borabicyclodecane (**8**) (0.09 g, 23%) as colourless crystals, and *N*,*N*′-bis(*cis*-heptyl-1-tetraol-bis(naphthyl)[2,1-c:1,2-h]-10-aza)-1-borabicyclodecane (**9**) (0.07 g, 16%) as colourless crystals, m.p. 168–9°C.

Compound **8**: (Found: M^+; 939.4623, $C_{57}H_{61}B_2N_2O_9$. Calc.: 939.4563). ν_{max} 3453, br, OH; 1624, 1599 (C=C aromatic), 1271 (B–O), 1247, 1183, 1093 cm^{-1} (C–O). δ_H 1.12, 1.22, 1.66, m, 10H, H(2′,3′,4′,5′,6′); 3.30, m, 4H, H(1′,7′); 3.53 (t, *J* 4.6, 10H, OCH_2CH_2O), 3.84 (t, *J* 4.6, 2H, $BOCH_2CH_2O$), 4.48 (s, 8H, 2H-9,11), 7.14, d, *J* 9.0, 4H, 2H-3,17), 7.30 (t, *J* 7.2, 4H, 2H-6,14), 7.43 (t, *J* 8.1, 4H, 2H-7,13), 7.50 (d, br, *J* 7.6 4H, 2H-8,12), 7.68 (d, *J* 8.9, 4H, 2H-4,16), 7.74 (d, *J* 8.1, 4H, 2H-5,15). δ_C 20.8 (C-4′), 26.5 (C-3′,5′), 28.6 (C-2′,6′), 51.5 2(br, C-9,11), 53.1, 53.5, 69.8, 70.0, 72.3 (C-1′,7′,$BOCH_2CH_2OCH_2CH_2OCH_2CH_2$-OH), 107.2 2(C-8a,11b), 120.1 2(C-8,12), 121.3 2(C-

3,17), 123.1 2(C-6,14), 126.7 2(C-7,13), 128.6 2(C-4a,15a), 128.8 2(C-5,15), 129.8 2(C-4,16), 131.3 2(C-8b,11a), 151.3 2(C-2a,17a). *m/z* (FAB$^+$) 939 (M, $<1\%$) 806 (M–$C_6H_{13}O_3$, 1), 789 (M–$C_6H_{12}O_3$–H_2O, 2), 633 (789-$C_{11}H_8O$, 5).

Compound **9**: (Found: M$^+$; 1070.5233, $C_{63}H_{72}B_2N_2O_{12}$. Calc.: 1070.5271). ν_{max} 3445 (br, OH), 1623, 1599 (C=C aromatic), 1271 (B–O), 1247, 1182–1029 cm^{-1} (C–O). δ_H 1.16, 1.24, 1.57 (m, 10H, H-2′,3′,4′,5′,6′); 3.34 (m, 24H, H-1′,7′,2CH_2OCH_2-CH_2OCH_2CH_2OH), 3.85 (t, *J* 4.8, 4H, 2BOCH_2CH_2O), 4.47, 4.54 (2d, *J* 15.0, 8H, 2H-9,11), 7.17 (d, *J* 8.7, 4H, 2H-3,17), 7.31 (t, *J* 7.2, 4H, 2H-6,14), 7.44 (t, *J* 8.0, 4H, 2H-7,13), 7.51 (d, *J* 9.0, 4H, 2H-8,12), 7.69 (d, *J* 9.0, 4H, 2H-4,16), 7.75, (d, *J* 8.0, 4H, 2H-5,15). δ_C 20.8 (C-4′), 26.5 (C-3′,5′), 28.6 (C-2′,6′), 51.5 2(br, C-9,11), 53.2, 61.0, 61.5, 69.8, 69.9, 70.0, 72.3 C-1′,7′, 2BOCH_2CH_2OCH_2CH_2OCH_2CH_2OH), 107.5 2(C-8a,11b), 120.1 2(C-8,12), 121.3 2(C-3,17), 123.0 2(C-6,14), 126.7 2(C-7,13), 128.5 2(C-4a,15a), 128.8 2(C-5,15), 129.7 2(C-4,16), 131.3 2(C-8b,11a), 151.3 2(C-2a,17a). *m/z* (FAB$^+$) 1071 (M, 1%), 939 (M–$C_6H_{12}O_3$, 2), 920 (M-939-H–H_2O, 1), 789 (939-$C_6H_{12}O_3$–H_2O, 5), 763 (920-$C_{11}H_9O$, 10).

3.6. (13,13′-Piperazine-(N,N,N‴,N‴-tetra((2-hydroxynaphthyl)methyl))ethane)amine (**10**)

To a stirred solution of 2-naphthol (1.85 g, 12.8 mmol) and triethylenetetramine (technical grade, 60%, 0.94 g, 5.4 mmol) in methanol (12 ml) at r.t. was added aqueous formaldehyde (37% w/v, 2.0 ml, 25.7 mmol). After a few minutes the mixture had become resinous and after 30 min the mixture was diluted with dichloromethane (30 ml), transferred to a separating funnel and acidified (aqueous HCl, 2 mol l^{-1}, 12 ml). The dichloromethane phase was separated and the aqueous phase extracted twice. The aqueous phase was then neutralised (solid $NaHCO_3$) and extracted with dichloromethane. These dichloromethane extracts were washed with water, dried and concentrated in vacuo leaving a light brown residue. A solution of this residue in 1:1 methanol–benzene (15 ml) was treated with 2-naphthol (1.60 g, 11.0 mmol) and stirred at r.t. for 2 h. The colourless solid that precipitated was filtered off and washed with methanol, leaving **10** (0.48 g, 13%) as a colourless solid, m.p. 145–6°C. (Found: C, 77.60; H, 6.73; N, 7.54; $C_{50}H_{50}N_4O_4$. Calc.: C, 77.84; H, 6.54; N, 7.27%). ν_{max} 1621, 1597 (C=C aromatic), 1219 cm^{-1} (C–O). δ_H (DMSO-d_6) 1.90, 2.43 (2s, br, 16H, 2H-11,12,14), 4.02 (s, 8H, 2H-9), 7.00 (d, *J* 8.8, 4H, 4H-3), 7.12 (t, *J* 7.7, 4H, 4H-6), 7.21 (t, *J* 7.6, 4H, 4H-7), 7.66, 7.71 (d, *J* 8.4, 4H, 4H-4,5), 7.85 (d, *J* 8.5, 4H, 4H-8), 10.32 (s, br, 4H, 4OH). δ_C (DMSO-d_6) 48.0 2(C-9), 48.5, 51.3, 54.0 2(C-11,12,14), 114.0 4(C-1), 118.2 4(C-3), 122.1 4(C-6), 122.7 4(C-8), 126.0 4(C-7), 127.9 4(C-4a), 128.1 4(C-5), 128.9 4(C-4), 133.5 4(C-8a), 154.6 4(C-2).

3.7. N′,N″-Bis(N,N‴-(1-methoxynaphthyl[2,1-c:1,2-h]-10-aza)-1-borabicyclodecane)ethylene-21,21′-piperazine (**11**)

A solution of **10** (0.40 g, 0.52 mmol) and boric oxide (0.04 g, 0.8 mmol) in a mixture of 1:1 methanol–benzene (5 ml) was heated under reflux for 12 h, then concentrated in vacuo. Flash column chromatography on silica gel (chloroform; 9:1 chloroform–methanol) gave **11** (0.10 g, 39%) as a colourless solid. (Found: M$^+$; 877.4339, $C_{54}H_{55}B_2N_4O_6$. Calc.: 877.4308). ν_{max} 1626, 1600 (C=C aromatic), 1273 (B–O), 1248, 1212, 1135, 1091, 1045 cm^{-1} (C–O). δ_H ($CDCl_3$, DMSO-d_6) 2.11, 2.69, 3.45 (3s, br, 16H, 4NCH_2CH_2N), 3.48 (s, 6H, 2OCH_3), 4.63, 4.83 (2d, *J* 14.7, 8H, 2H-9,11), 7.06 (d, *J* 8.8, 4H, 2H-3,17), 7.29 (t, *J* 7.4, 4H, 2H-6,14), 7.40 (t, *J* 7.5, 4H, 2H-7,13), 7.60 (d, br, 4H, 2H-8,12), 7.69 (d, *J* 8.9, 4H, 2H-4,16), 7.75 (d, *J* 8.0, 4H, 2H-5,15). δ_C ($CDCl_3$, DMSO-d_6) 47.2 NCH_2CH_2N-(CH_2CH_2)$_2$NCH_2CH_2N), 48.0 2 × OCH_3, 49.9 (NCH_2CH_2N(CH_2CH_2)$_2$NCH_2CH_2N), 50.6 4(C-9), 106.9 2(C-8a,11b), 119.2 2(C-8,12), 121.3 2(C-3,17), 125.0 2(C-6,14), 126.6 2(C-7,13), 126.9 2(C-5,15), 127.6 2(C-4,16), 129.7 2(C-8b,11a), 149.3 2(C-2a,17a). *m/z* (FAB$^+$) 877 (M, 10%), 845 (M–MeOH, 1), 719 (M–$C_{11}H_{10}O$, 2), 689 (845-$C_{11}H_8O$, 2), 533 (689-$C_{11}H_8O$, 4).

3.8. Triethylenetetramine-N′,N″-(bis(2-hydroxy-naphthyl)methyl)-N,N‴-bis(2,3-dihydro-1H-naphthyl-[1,2-e][1,3]oxazine) (**13**)

A solution of 2-naphthol (5.0 g, 34.0 mmol) in methanol was added to a solution of triethylenetetramine hydrate (2.52 g, 17.0 mmol) in methanol (12 ml) under nitrogen at 0°C, followed by aqueous formaldehyde (37% w/w, 5.2 ml, 70.0 mmol). When all of the formalin had been added a precipitate separated. After 30 min the resinous mixture was diluted with aqueous hydrochloric acid (2 mol l^{-1}, 20 ml) and dichloromethane (20 ml). The dichloromethane phase was separated and the aqueous phase extracted again with dichloromethane (an emulsion which formed separated on standing). The aqueous phase was neutralised and extracted with dichloromethane. This organic phase was extracted with aqueous sodium hydroxide (2 mol l^{-1}) to ensure no 2-naphthol remained. The combined organic phases were then washed, dried and concentrated, leaving a purple oil which formed a voluminous foam on pumping in vacuo. This extract contained a mixture (TLC) that could not be separated by flash chromatography. Therefore, the mixture was dissolved in methanol (12 ml), treated with 2-naphthol,

and stirred at r.t. overnight. The colourless solid that precipitated was filtered off and washed with methanol, leaving **13** (0.7 g, 5%) as a colourless solid, m.p. 150–1°C. (Found: $M+H^+$ 795.3889, $C_{52}H_{51}N_4O_4$. Calc.: 795.3910). ν_{max} 1620, 1599 (C=C aromatic), 1223 cm^{-1} (C–O). δ_H (DMSO-d_6) 2.57 (s, br, 12H, H-11,12,23), 3.89 (s, 4H, br, H-4), 3.92 (s, 4H, br, H-14), 4.54 (s, 4H, br, H-2), 6.78 (d, *J* 8.8, 2H, 2H-17), 6.84 (d, *J* 8.8, 2H, 2H-10), 7.04 (t, *J* 7.3, 2H, 2H-22?), 7.16 (t, *J* 7.1, 4H, 2H-7,21), 7.27 (s, br, 4H, 2H-6,5), 7.48 (d, *J* 8.2, 4H, 2H-9,18), 7.56 (d, *J* 8.0, 4H, 2H-8,19), 7.72 (d, *J* 8.4, 2H, 2H-20?). δ_C (DMSO-d_6) 46.7 (C-4), 48.4, 50.1 (C-12,23), 50.7 (C-14), 51.5 (C-11), 81.8 (C-2), 111.8 2(C-10), 113.3 2(C-15), 118.2 2(C-10), 118.4 2(C-17), 121.2 2(C-5), 122.2 2(C-20,22), 123.2 2(C-7), 126.0 2(C-21), 126.3 2(C-6), 127.5 2(C-9), 127.9 2(C-18a), 128.2 2(C-8,19,8a?), 128.6 2(C-18), 131.4 2(C-4b), 134.0 2(C-22a), 151.3 2(C-10a), 155.2 2(C-16). *m*/*z* (FAB^+) 795 (M + H, 1%), 639 (795-$C_{11}H_8O$, 1), 483 (639-$C_{11}H_8O$, 1).

*3.9. Tris(N,N,N-ethyl(2,3-dihydro-1H-naphth[1,2-e]-[1,3]oxazine)) (**14**)*

Reaction (as for **13**) of 2-naphthol (three mol equivalents) with tris(2-aminoethyl)amine gave **14** (70%) as an orange oil (foams in vacuo). (Found: $M^{+\bullet}$ 651.3380, $C_{42}H_{43}N_4O_3$. Calc.: 651.3335). ν_{max} 1625, 1598, 1516 (C=C aromatic), 1227, 1140 cm^{-1} (C–O). δ_H 2.80, s, br, 3H(2′)$_2$; 2.92, s, br, 3H(1′)$_2$; 4.28, s, 3H(4)$_2$; 4.86, s, 3H(2)$_2$; 6.99, d, *J* 8.9, 3H(10); 7.33, td, *J* 8.0, 1.0, 3H(7); 7.43, td, *J* 8.2, 1.2, 3H(6); 7.53, d, *J* 8.6, 3H(5); 7.61, d, *J* 8.9, 3H(9); 7.74, d, *J* 8.2, 3H(8). δ_C 29.7, 3C(1′)$_2$; 48.1, 3C(2′)$_2$; 53.5, 3C(4)$_2$; 82.5, 3C(2)$_2$; 111.8, 3C(4a); 118.5, 3C(10); 121.0, 3C(5); 123.4, 3C(7); 126.5, 3C(6); 128.0, 3C(9); 128.6, 3C(8); 128.9, 3C(8a); 131.8, 3C(4b); 151.8, 3C(10a). *m*/*z* 651 (2, M^+); 495 (2, M–$C_{11}H_8O$); 339 (2, 495-$C_{11}H_8O$), 156 (60, $C_{11}H_8O$); 128 (100, 156-CO).

*3.10. N,N′-13,13′-(Ethylenedioxy)-bis(ethyl(N,N′-bis-(2,3-dihydro-1H-naphthyl[1,2-e][1,3]oxazine))) (**15**)*

A solution of 2-naphthol (5.45 g, 37.8 mmol) in methanol was treated with 2,2′-(ethylenedioxy)-bis(ethylamine) (2.8 ml, 19.1 mmol) and aqueous formaldehyde (37% w/w, 5.7 ml, 76.5 mmol). This mixture was heated under reflux overnight before concentrating in vacuo. The crude residue was acidified (aqueous HCl, 2 mol l^{-1}) and extracted with dichloromethane to remove unreacted 2-naphthol. The aqueous phase was neutralised and extracted with dichloromethane (3 × 40 ml). These combined organic extracts were washed with water, dried, and concentrated to give an orange oil containing (^{1}H-NMR) **15** and 2,2′-(ethylenedioxy)bis(ethylamine). Flash chromatography (dichloromethane; 10:1 dichloromethane–methanol) gave **15** (10.4 g, 56%) as a colourless solid, m.p. 213–4°C. (Found: $M^{+\bullet}$ 484.2359, $C_{30}H_{32}N_2O_4$. Calc.: 484.2362). ν_{max} 1624, 1598 (C=C aromatic), 1226, 1180–1100 cm^{-1} (br, C–O). δ_H 3.01 (t, *J* 5.4, 4H, 2H-11), 3.59 (s, 4H, 2H-14), 3.67 (t, *J* 5.4, 4H, 2H-12), 4.36 (s, 4H, 2H-4), 4.93 (s, 4H, 2H-2), 7.01 (d, *J* 8.8, 2H, 2H-10), 7.31 (td, *J* 7.9, 1.0, 2H, 2H-7), 7.42 (td, *J* 8.3, 1.1, 2H, 2H-6), 7.57 (d, *J* 8.6, 2H, 2H-5), 7.60 (d, *J* 9.1, 2H, 2H-9), 7.72 (d, *J* 8.0, 2H, 2H-8). δ_C 48.2 2(C-4), 51.6, 69.9, 70.4 2(C-11,12,14), 82.6 2(C-2), 111.8 2(C-4a), 118.5 2(C-7), 120.9 2(C-5), 123.4 2(C-7), 126.4 2(C-6), 127.9 2(C-9), 128.6 2(C-8), 128.9 2(C-8a), 131.8 2(C-4b), 151.8 2(C-10a). *m*/*z* (DEI^+) 484 (M, 1%), 328 ($C_{11}H_8O$, 6), 300 (328-CO, 1), 156 ($C_{11}H_8O$, 66), 128 (156-CO, 100).

*3.11. 13,13′-(Ethylenedioxy)bis(ethylamino)-N,N′-(bis-(2-hydroxy-1-naphthyl)methyl)amine (**16**)*

2-Naphthol (2.1 g, 14.4 mmol) was added to a solution of the 2*H*-1,3-benzoxazine **15** (3.5 g, 7.2 mmol) in 1:1 methanol–benzene (18 ml) at rt. This mixture was stirred until a precipitate separated. The solid collected after filtration was washed with methanol to give **16** (4.2 g, 88%) as a colourless solid, m.p. 128–9°C. (Found: $M+H^+$ 773.3595, $C_{56}H_{49}N_2O_6$. Calc.: 773.3591). ν_{max} 3181, br, OH; 1627 (C=C aromatic), 1331, 1286, 1235 cm^{-1} (C–O). δ_H ($CDCl_3$, DMSO-d_6) 3.27 (s, 6H, 3CH_2CH_2O), 3.43 (t, *J* 5.4, 6H, 3CH_2CH_2O), 4.01 (s, 8H, 4CH_2N), 6.78 (d, *J* 8.8, 4H, 4H-3), 6.98 (t, *J* 7.1, 4H, 4H-6), 7.16 (t, *J* 7.2, 4H, 4H-7), 7.33 (d, *J* 8.8, 4H, 4H-4), 7.42 (d, *J* 7.8, 4H, 4H-5), 7.70 (d, *J* 8.5, 4H, 4H-8). δ_C (DMSO-d_6) 49.8 4(CH_2O), 52.0, 68.3, 69.5 (*C*H_2N, 2(N*C*H_2*C*H_2O*C*H_2), 112.8 4(C-1), 117.9 4(C-3), 121.3 4(C-6), 121.9 4(C-8), 125.8 4(C-7), 127.8 4(C-4a), 128.0 4(C-5), 128.6 4(C-4), 132.9 4(C-8a), 154.6 4(C-2). *m*/*z* (FAB^+) 773 (M + H, 1%), 617 (773-$C_{11}H_8O$, 1), 461 (614-$C_{11}H_8O$, 4).

*3.12. N,N′-(21,21′-Ethylene-dioxy)-bis(ethylene(N,N′-(1-phenyl-naphthyl)[2,1-c:1,2-h]-10-aza)-1-bora-bicyclodecane) (**17**)*

Amine **16** (0.5 g, 0.6 mmol) and phenylboronic acid (0.16 g, 1.3 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 (chloroform; 9:1 chloroform–methanol) gave **17** (0.26 g, 46%) as a colourless solid, m.p. 220–221°C. (Found: M^+; 944.4184, $C_{62}H_{54}B_2N_2O_6$. Calc.: 944.4168). ν_{max} 1625 (C=C aromatic), 1130–1035 (C–O) cm^{-1}. δ_H 3.09 3.15, 3.44 (3s, br, 12H, 2(NCH_2-CH_2OCH_2), 4.50, 4.72 (2d, 8H, *J* 15.1, 2H-9, 11), 7.23–31 (m, 14H, 2H-3,17,6,14,3″,4″,5″), 7.39 (t, *J* 7.4, 4H, 2H-7,13), 7.45 (d, *J* 8.2, 4H, 2H-8,12), 7.64 (d, *J*

7.3, 4H, 2H-2″,6″), 7.74 (d, *J* 8.9, 4H, 2H-4,16), 7.78 (d, *J* 8.1, 4H, 2H-5,15). δ_C 54.1, 65.2, 70.4 2(N*C*H_2-*C*H_2O*C*H_2, C-9,11), 107.5 2(C-8a,11b), 120.0 2(C-8,12), 121.7 2(C-3,17), 122.9 2(C-6,14), 126.5 2(C-7,13), 127.5 2(C-3″,5″), 128.1 2(C-4″), 128.3 2(C-5a?), 128.6 2(C-4a?), 129.0 2(C-4,16), 131.3 2(C-8b,11a), 133.2 2(C-2″,6″), 151.7 2(C-2a,17a). *m*/*z* 944 (M, 6%), 867 (M–C_6H_5, 7), 789 (867-C_6H_6, 4), 633 (789-$C_{11}H_8O$, 10).

4. Supplementary material

The crystal structures have been allocated the following deposition numbers at the Cambridge Crystallography Data Centre: CCDC 132630 for **6**, and CCDC 132631 for **11**.

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