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Direct synthesis of polymacrocyclic boron compounds. A convenient method for the synthesis of hemicarcerands

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Abstract

Six new hemicarcerand-like compounds have been synthesized *via* condensation reaction of 3-aminophenylboronic acid with 5,5′-methylene-bis(2-hydroxybenzencarbonyl) derivatives. The one-pot reaction constitutes an interesting approach to design molecular containers by direct synthesis in moderate yields. The strategy involves a self-assembly process through the formation of N–B coordinative bonds. The X-ray structural analysis for one derivative illustrates the inclusion of two benzene molecules within the cavity, showing in a first approximation the capability of the polymacrocyclic compounds to function as molecular receptors.

Keywords: Boron; Polymacrocycles; Self-assembly; Hemicarcerands; Schiff bases

1. Introduction

At the present, supramolecular chemistry is one of the most explored topics. One of the main goals is to improve the synthesis of molecular receptors, with the possibility to modulate the volume and periphery of the cavity in a predictable fashion [1]. In this context, the simplicity of the method used for the synthesis of calixarenes has allowed to perform an extensive exploration of these macrocycles as molecular receptors and molecular building blocks [2]. In order to improve their efficiency as molecular containers, several structural modifications have been realized in the calix base rims, e.g. the replacement of the phenol units by heteroaromatic rings [3] or the introduction of heteroatoms connecting the aromatic moieties [4].

Furthermore, double cone structures can be obtained by connecting two calix-like structures to provide systems with interesting properties in the molecular recognition area [5]. The coupling can take place through one single linker, or as many linkers as phenol rings are involved in the calixarene structure [6]. Although several synthetic methods have been described, coupling process between two calixarene units follows three well defined steps: (i) calixarene synthesis, (ii) functionalization of the groups located at the rims in either the lower or the upper part and (iii) coupling reaction between the calixarene units. The double cone structures can be carcerands or hemicarcerands, the difference being that carcerands permanently imprison guests during the cavitand shell closure, even at high temperatures. In the contrary, hemicarcerands contain portals that allow the entrance and egress of guest molecules [7].

Recently, we reported a method to prepare trimeric boron calix like compounds with a double cone conformation from 3-aminophenylboronic acid and salicylaldehyde derivatives [8]. In these compounds, the formation of N→B coordination bonds is a determinant factor for the rim closure and several structural analyses have been carried out in order to investigate the stability of the N–B coordination bonds [9]. Recently, dendrimeric compounds having a macrocyclic core containing N–B dative bonds within their structure have been reported [10]. It was shown that these molecules can be useful in the molecular

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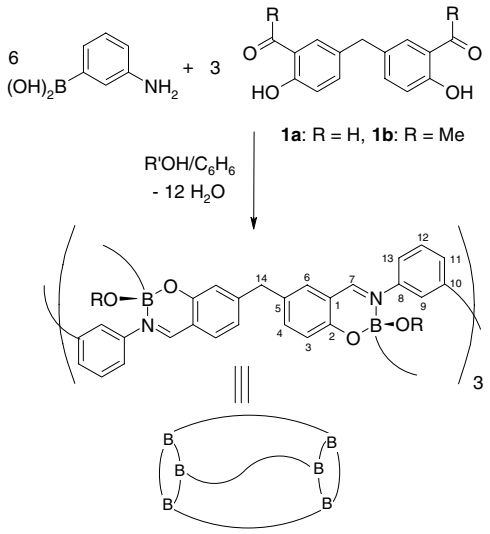
recognition towards small organic molecules in both the solid and the liquid state. Herein, we report on the preparation and structural characterization of doublecone boron-calix [3] arenes (hemicarcerands).

2. Results and discussion

We have first examined the reaction between 3-aminophenylboronic acid and 5,5′-methylene-bis(salicylaldehyde) (**1a**). This aldehyde was selected because it has been successfully employed in macrocyclic compound formation having a calix shape structure [11]. Additionally, 5,5′-methylene-bis(2-hydroxyacetophenone) (**1b**) has been synthesized and reacted with 3-aminophenylboronic acid in order to analyze if steric effects influence the cyclization process.

Compounds **2a**–**2c** were synthesized in moderate yields using 5,5′-methylene-bis(salicylaldehyde) as starting material (Scheme 1). The reactions were carried out under reflux conditions in an alcohol/benzene solvent mixture (1:1 ratio, alcohol used: methanol, ethanol and propanol for **2a**–**2c**, respectively). In order to efficiently remove the byproduct water, the reaction was performed using a Dean-Stark trap to separate part of the azeotropic benzene–water mixture. Upon cooling the crude solution, yellow powders were precipitated from the reaction media, which after filtration and drying gave the solid products. In the case of compound **2a** yellow crystals, which were suitable for X-ray diffraction analysis, formed upon cooling.

All three compounds are insoluble in most organic solvents and only well soluble in DMSO and DMF. Furthermore, high melting points (>350 °C) were observed, suggesting a good thermal stability of the polymacrocycles.



Scheme 1. Synthesis of the hemicarcerand-like boron compounds.

Initially, the structure was deduced by FAB^+ mass spectrometry. The molecular ions observed ($m/z = 1458$, 1542 and 1626) were consistent with hemicarcerand boron compounds (**2a**–**2c**, respectively), having either MeO, EtO or PrO groups attached to the boron atoms. In all three cases, the IR spectrum showed a strong band at 1628 cm^{-1}, attributed to the stretching frequency of the C=N groups. Moreover, no bands were observed in the region for OH groups, indicating the alcoholysis of the B–OH groups to B–OR.

In all three cases the NMR analysis showed only one set of signals, so that molecular structures are symmetric in solution or a rapid fluxion process is occurring averaging the signals. The ^1H NMR spectra showed single signals at $\delta = 8.70$, 8.91 and 8.90 ppm for the imine hydrogen of **2a**, **2b** and **2c**, respectively, while in the ^{13}C NMR spectra the signals for the carbon atoms of the same group were observed at $\delta = 163.4$, 162.7 and 162.4 ppm for **2a**–**2c**, respectively. The ^{11}B NMR spectra showed broad signals at $\delta = 3.0$, 1.8 and 3.3 ppm, for **2a**–**2c**, respectively, in agreement with the chemical shifts observed for similar species having boron atoms in tetracoordinated geometry [8].

An X-ray diffraction analysis of compound **2a** gives further evidence for the hemicarcerand structure obtained (Fig. 1). The X-ray analysis permitted to establish unambiguously the structural arrangement and the conformation of this molecule. The overall structure of **2a** consists of two double cone-like fragments which are connected by three methylene linkers. All three bis(salicylidene) fragments present in the molecule have *trans* configuration.

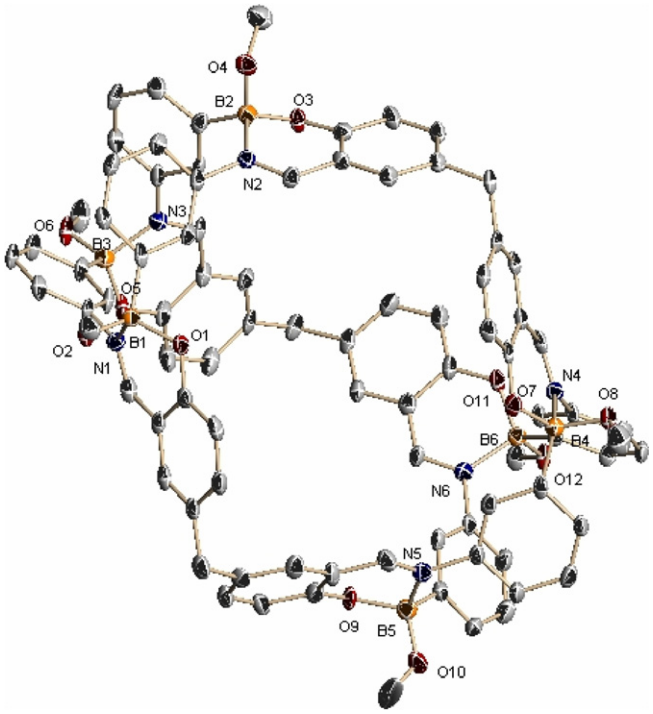


Fig. 1. ORTEP-like plot for compound **2a**, thermal ellipsoids are shown with 50% probability level.

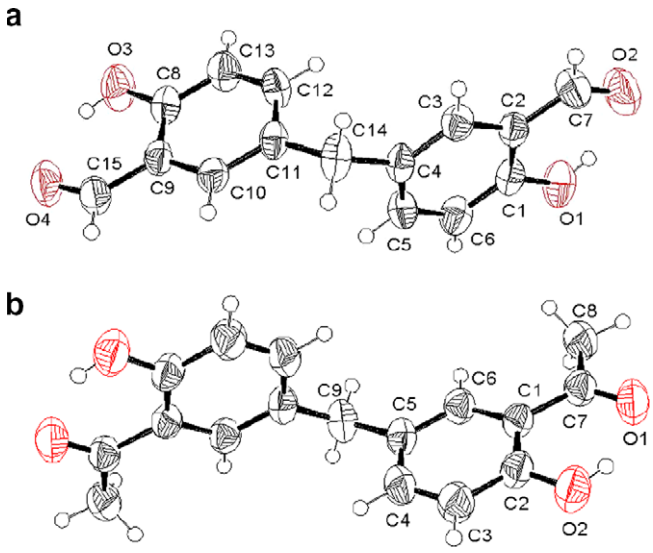


Fig. 2. ORTEP-like plot for ligands 1**a** and **1b**, thermal ellipsoids are shown with 50% probability level. In both cases a *trans* disposition for the carbonyl fragments is observed.

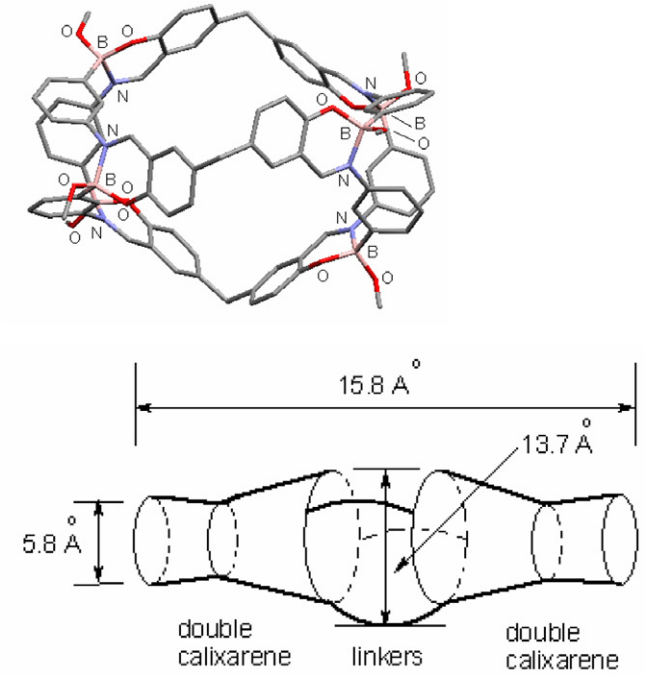


Fig. 3. Stick model of compound **2a** (top). Schematic representation of the hemicarcerand showing the size of the compound (bottom).

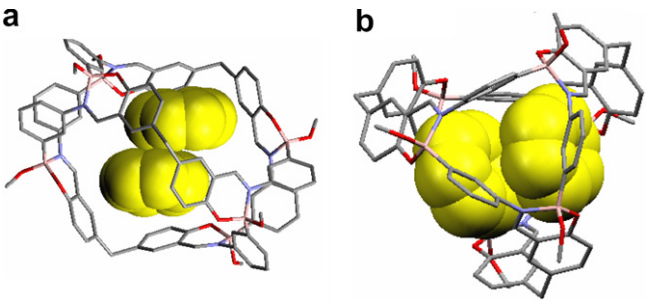


Fig. 4. Schematic representation of the hemicarcerand containing two benzene molecules included in its interior, (a) lateral view and (b) top view.

The same configuration is observed in the solid state for ligands **1a** and **1b** (see Fig. 2). The molecules of **2a** possess pseudo D_3 symmetry with the three fold axis passing through the center of the rims formed by the three arylboronic acid moieties. This observation is in accordance with the fact that only one set of signals was observed in the NMR studies.

In compound **2a**, each boron atom has a *pseudo* tetrahedral environment and is connected to two oxygen atoms, one carbon atom and one nitrogen atom. The reaction can be considered as diastereoselective since that all six boron atoms included in the polymacrocycle have the same configuration (all *R* or all *S*), which is a determinant factor for the final conformation of the hemicarcerand. In addition, the N→B coordination bonds are oriented in the same direction at each extreme of the polymacrocycle. The B–N bonds have an average distance of 1.624(12) Å, which is similar to other boronates [8]. All six MeO groups are located at the outside of the cavity. In its interior only aromatic electronic density is present and the cavity can be considered as hydrophobic. The size of the hemicarcerand can be estimated from the distance between the ring centers at the extremes of the overall structure (15.8 Å) and the distance between the central $–CH_2–$ linkers 13.7 Å (Fig. 3) [12].

The crystal structure is a clathrate having several solvent molecules included in the unit cell (composition: **2a** · $8C_6H_6$ · $4CH_3OH$ · H_2O). Nonetheless, the cavity of the compound is occupied by only two benzene molecules, showing the capability of this hemicarcerand compound to act as molecular receptor (Fig. 4). The two benzene molecules included are stacked showing π–π interactions with a distance between the aromatic centroids of 3.6 Å. The three linkers present in the molecule give rise to the formation of three portals, which are big enough to allow the free passage of solvent molecules into its interior or vice versa. As a consequence, crystalline material of this compound is easily transformed to porous material owing to the fast evaporation of the solvent molecules. In fact, the crystallographic study was realized at 100 K using the capillary technique to avoid the decomposition of the crystals. From the elemental analysis, no evidence for the presence of benzene molecules was found, indicating the fast remotion of the solvent from the cavity through the portals after treatment under vacuum (see Section 4) [13].

When using ligand **1b** instead of **1a** for the condensation with 3-aminophenylboronic acid the polymacrocyclic compounds **3a**–**3c** were formed. All three reactions were carried out in a refluxing alcohol/benzene solvent mixture (1:1 ratio) to favor the alcoholysis reaction. Mass spectrometry showed that hemicarcerand-like structures were obtained, since for all three compounds the molecular ion was

observed. Additionally, the IR spectra shown bands at 1622, 1625 and 1621 cm^{-1} for **3a**–**3c**, respectively, corresponding to the stretching band of the C=N moiety. Although the reaction conditions were not modified, the yields are considerable diminished (≈20% less) in comparison with derivatives **2a**–**c**. This should be a consequence of steric effects existing between the methyl groups of the azomethine moiety and the aromatic rings of the aryl boronate fragment.

3. Conclusions

In summary, this report has shown that the combination of 3-aminophenylboronic acid and 5,5′-methylene-bis(2-hydroxybenzencarbonyl) derivatives is a very convergent strategy for the synthesis of hemicarcerands. Additionally, this approach shows the versatility that boron compounds with N→B coordination bonds have in the construction of polymacrocycles with a well-defined conformation. Due to the possibility to construct and modulate the cavity of this type of molecules by changing the linkers (–CH_2– groups) [11] within the calixarene structures; at present, we are preparing systems with different linkers, in order to explore their influence on the formation of similar hemicarcerand compounds. At the same time, analogous compounds having large alkyl groups attached to the boron atoms are prepared in order to increase the solubility and explore the potential of this type of structures for molecular recognition.

4. Experimental

4.1. Reagents and materials

All reagents and solvents used were obtained from Aldrich and used without further purification. Ligands **1a** and **1b** were synthesized according to a literature procedure [11].

4.2. Instrumentation

Nuclear magnetic resonance (NMR) data were obtained on Varian Gemini 200 and Varian VXR-400 instruments. As standard references were used TMS (internal, ^1H, $\delta = 0.00$ ppm, ^{13}C, $\delta = 0.0$ ppm) and $BF_3 \cdot OEt_2$ (external, ^{11}B, $\delta = 0.0$ ppm). 2D COSY, HMQC and NOESY experiments have been carried out for the unambiguous assignment of the ^1H and ^{13}C NMR spectra. All chemical shifts are stated in ppm and coupling constants are reported in Hz. Assignments for the ^1H and ^{13}C NMR peaks are according to the numbering shown in Scheme 1. Infrared spectra have been recorded on a Bruker Vector 22 FT-IR spectrophotometer. Mass spectra were obtained with a Jeol JMS 700 equipment. Elemental analyses were carried out on a Perkin–Elmer Series II 2400 Instrument. Melting points were determined with a Büchi B-540 digital apparatus.

4.3. X-ray analysis

X-ray diffraction studies were performed on a Bruker-APEX diffractometer with a CCD area detector, Mo Kα-radiation, $\lambda = 0.71073$ Å, graphite monochromator. Frames were collected at $T = 100$ K. The measured intensities were reduced to F^2 and corrected for absorption with SADABS (SAINT-NT). Corrections were made for Lorentz and polarization effects. Structure solution, refinement and data output were carried out with the SHELXTL-NT program package [14]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrically calculated positions using a riding model. The high R value observed for **2a** is occasioned by solvent molecule disorder.

Crystal data for **1a**: $C_{15}H_{12}O_4$, Monoclinic, space group $P2(1)/c$, $a = 7.8125(14)$, $b = 11.725(2)$, $c = 13.238(2)$ Å, $\beta = 94.631(3)$, $V = 1208.7(4)$ $Å^3$, $T = 293$ K, $Z = 4$, μ(Mo Kα) = 0.71073 mm^{-1}, 10454 reflections measured, 1890 unique, ($R_{int} = 0.02$), R_1 [$I > 2\sigma I$] = 0.0483, $wR_2 = 0.1140$ for all data.

Crystal data for **1b**: $C_{17}H_{16}O_4$, Monoclinic, space group $C2/c$, $a = 26.428(6)$, $b = 5.2293(11)$, $c = 10.053(2)$ Å, $\beta = 94.516(4)$, $V = 1385.0(5)$ $Å^3$, $T = 273$ K, $Z = 4$, μ(Mo Kα) = 0.71073 mm^{-1}, 6182 reflections measured, 1217 unique, ($R_{int} = 0.02$), R_1 [$I > 2\sigma I$] = 0.0443, $wR_2 = 0.1248$ for all data.

Crystal data for **2a**: $C_{87}H_{72}B_6N_6O_{12} \cdot 8C_6H_6 \cdot 4CH_3OH \cdot H_2O$: Triclinic, space group $P\bar{1}$, $a = 17.745(4)$, $b = 18.325(4)$, $c = 21.303(5)$ Å, $\alpha = 95.454(4)$, $\beta = 100.584(4)$, $\gamma = 116.258(3)°$, $V = 5983(2)$ $Å^3$, $T = 100$ K, $Z = 2$, μ(Mo Kα) = 0.71073 mm^{-1}, 48243 reflections measured, 16633 unique, ($R_{int} = 0.07$), R_1 [$I > 2\sigma I$] = 0.1078, $wR_2 = 0.2898$ for all data.

4.4. Synthesis

4.4.1. Ligand 1a

White powder, yield 48% (3.47 g). IR (KBr) ν_{max}: 1655 (*s*, *C=O*); CI-EM *m/z* (%): 256 (M^+, 98), 227 (74), 199 (17), 181 (21), 169 (13), 152 (15), 135 (25), 122 (14), 107 (10), 77 (11); ^1H NMR (200 MHz, $CDCl_3$)δ: 10.85 (2H, *s*, OH), 9.78 (2H, *s*, H-8), 7.3 (2H, *dd*, $J = 8.4$, 2.2, H-4), 7.20 (2H, *s*, H-6), 6.89 (2H, *d*, $J = 8.4$, H-3), 3.9 (2H, *s*, H-7); ^{13}C NMR (50 MHz, $CDCl_3$) δ: C-8 (196.2), C-2 (160.2), 137.6 (C-4), 133.6 (C-6), 131.9 (C-5), 120.5 (C-1), 118.1 (C-3), 39.7 (C-7).

4.4.2. Ligand *1b*

White powder, yield 10% (1.22 g); mp 143 °C, IR (KBr)ν_{max}: 1643 (*s*, *C=O*); MS-CI *m/z* (%): 284 (M^+, 79), 269 (63), 241 (35), 223 (16), 197 (25), 181 (12), 165 (35), 149 (10), 136 (50), 121 (100), 105 (4), 93 (15), 77 (5); ^1H NMR (200 MHz, $CDCl_3$) δ: 12.20 (2H, *s*, OH), 7.49 (2H, *d*, $J = 2.2$, H-6), 7.27 (2H, *dd*, $J = 8.6$, 2.2, H-4), 6.92 (2H, *d*, $J = 8.6$, H-3), 3.90 (2H, *s*, H-7), 2.60 (6H, *s*, H-9); ^{13}C NMR (50 MHz, $CDCl_3$)δ: 204.1 (C-8), 160.9 (C-2), 137.1

(C-4), 131.0 (C-5), 130.3 (C-6), 119.6 (C-1), 118.8 (C-3), 40.3 (C-7), 27.0 (C-9).

*4.4.3. Compound **2a** was synthesized from 5,5′-methylene-bis(salicylaldehyde) (0.97 mmol) and 3-aminophenylboronic acid monohydrated (1.94 mmol)*

The reagents were dissolved in a methanol/benzene mixture (1:1 ratio) that was brought to reflux. After 30 min under stirring, part of the solvent and the water formed through the condensation reaction were removed using a Dean-Stark trap. After standing overnight, yellow crystals were obtained in 85 % (0.45 g) yield. M.p. >350 °C; MS-FAB *m/z* (%): 1458 (24) [M^+], 1427 (38) [$(M\text{-}OMe)^+$]; IR (KBr) $\nu_{max} = 1628\ cm^{-1}$ (C=N); ^{1}H NMR (400 MHz, DMSO-d_6): $\delta = 8.70$ (s, 6H; H-7), 7.62 (d, $J = 8.2$, 6H; H-4), 7.57 (s, 6H; H-6), 7.36 (d, $J = 7.7$, 6H; H-11), 7.18 (d, $J = 7.7$, 6H; H-13), 6.93 (d, $J = 8.2$, 6H; H-3), 6.87 (t, $J = 7.7$, 6H; H-12), 6.57 (s, 6H; H-9), 4.05 (s, 6H; H-14), 3.16 (s, 18H; OMe); ^{13}C NMR (100 MHz, DMSO-d_6), $\delta = 163.4$ (C-7), 159.2 (C-2), 147.8 (C-8), 136.1 (C-4), 134.2 (C-11), 133.3 (C-5), 132.5 (C-6), 129.2 (C-9), 127.6 (C-12), 123.3 (C-13), 119.7 (C-1), 117.3 (C-3), 50.6 (OMe), 40.4 (C-14); ^{11}B NMR (64 MHz, DMSO-d_6), $\delta = 3.0$ (br, $h_{1/2} = 1370$ Hz). Elemental Anal. Calc. for $C_{87}H_{72}B_6N_6O_{12}$(1458.57): C, 71.64; H, 4.97; N, 5.76. Found: C, 71.12; H, 4.78; N, 5.56%.

Compounds **2b**–**2c** and **3a**–**3c** were synthesized using the same procedure as described above for **2a**.

*4.4.4. Compound **2b***

Yellow powder, yield 57% (0.28 g); m.p. >350 °C; IR (KBr) ν_{max}: 1628 (C=N, *s*); FAB-MS *m/z* (%): 1542 (M^+, 9), 1497 (11), 1427 (3), 919 (8), 766 (11), 613 (14), 460 (20), 391(15), 307 (100), 289 (71); ^{1}H NMR (400 MHz, DMSO-d_6)δ: 8.91 (6H, *s*, H-7), 7.76 (6H, *s*, H-9), 7.70 (6H, *dt*, $J = 6.2$, 2.5 Hz, H-11), 7.50 (6H, *d*, $J = 2.2$ Hz, H-6), 7.41 (6H, *t*, $J = 6.2$ Hz, H-12), 7.28 (6H, *dd*, $J = 8.4$, 2.2 Hz, H-4), 6.95 (6H, *dt*, $J = 6.2$, 2.5 Hz, H-13), 6.91 (6H, *d*, $J = 8.4$ Hz, H-3), 3.91 (6H, *s*, H-14), 3.43 (12H, *q*, $J = 7$ Hz, H-15), 1.05 (18H, *t*, $J = 7$ Hz, H-16); ^{13}C NMR (100 MHz, DMSO-d_6)δ: 162.7 (C-7), 158.2 (C-2), 146.9 (C-8), 133.3 (C-4), 132.4 (C-11), 131.7 (C-5), 131.7 (C-6), 128.3 (C-9), 126.7 (C-12), 122.4 (C-13), 118.9 (C-1), 116.4 (C-3), 55.9 (C-15), 40.7 (C-14), 18.6 (C-16); ^{11}B NMR (64 MHz, DMSO-d_6) δ: 1.8 ppm ($h_{1/2} = 2{,}496$ Hz). Elemental Anal. Calc. for $C_{93}H_{84}B_6N_6O_{12}$(1542.67): C, 72.41; H, 5.48; N, 5.44. Found: C, 71.60; H, 5.03; N, 5.35%.

*4.4.5. Compound **2c***

Yellow powder, yield 48% (0.25 g); m.p. >350 °C; IR (KBr) ν_{max} 1628 (C=N, *s*) cm^{-1}; FAB-MS *m/z* (%): 1626 (M^+, 4), 1584 (4), 1568 (12), 1526 (9), 1483 (34), 1159 (15), 1022 (13), 714 (12), 708 (13), 468 (14), 441 (21), 229 (100); ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.90 (6H, *s*, H-7), 7.76 (6H, *s*, H-9), 7.72–7.66 (6H, *m*, H-11), 7.72–7.66 (6H, *m*, H-13), 7.50 (6H, *d*, $J = 2.2$, H-6), 7.41 (6H, *t*, $J = 8.2$, H-12), 7.29 (6H, *dd*, $J = 8.2$, 2.2, H-4), 6.91 (6H, *d*, $J = 8.2$, H-3), 3.91 (6H, *s*, H-14), 3.33 (12H, *t*, $J = 7.2$, H-15), 1.41 (12H, *sex*, $J = 7.2$, H-16), 0.83 (18, *t*, $J = 7.2$, H-17); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 162.4 (C-7), 158.2 (C-2), 146.9 (C-8), 133.3 (C-4), 132.4 (C-11), 131.7 (C-5), 131.7 (C-6), 128.3 (C-9), 126.7 (C-12), 122.5 (C-13), 118.9 (C-1), 116.4 (C-3), 62.4 (C-15), 40.3 (C-14), 25.7 (C-16), 10.6 (C-17); ^{11}B NMR (64 MHz, DMSO-d_6) δ: 3.3 ppm ($h_{1/2} = 4{,}032$ Hz). Elemental Anal. Calc. for $C_{99}H_{96}B_6N_6O_{12}$(1626.76): C, 73.09; H, 5.94; N, 5.16. Found: C, 72.45; H, 5.21; N, 5.05%.

*4.4.6. Compound **3a***

Yellow powder, yield 64% (0.31 g); m.p. 335 °C; IR (KBr) ν_{max}: 1622 (C=N, *m*) cm^{-1}; MS-FAB *m/z* (%): 1542 (M^+, 5), 1509 (12), 1461 (10), 1282 (8), 1166 (10), 1030 (7), 928 (10), 835 (13), 815 (35), 559 (21), 541 (10), 407 (100), 285 (75), 229 (11); ^{1}H NMR (400 MHz, DMSO-d_6)δ: 7.76 (6H, *s*, H-9), 7.69 (6H, *d*, $J = 2.2$, H-6), 7.60 (6H, *d*, $J = 7.7$, H-11), 7.37 (6H, *t*, $J = 7.7$, H-12), 7.28 (6H, *dd*, $J = 8.4$, 2.2 Hz, H-4), 7.01 (6H, *d*, $J = 7.7$, H-13), 6.87 (6H, *d*, $J = 8.4$, H-3), 3.91 (6H, *s*, H-14), 3.26 (18H, *s*, OMe), 2.63 (18H, *s*, H-15); ^{13}C NMR (100 MHz, DMSO-d_6)δ: 174.3 (C-7), 158.8 (C-2), 147.1 (C-8), 136.4 (C-4), 134.7 (C-11), 131.7 (C-5), 130.6 (C-6), 130.6 (C-9), 127.5 (C-12), 121.8 (C-13), 119.7 (C-1), 117.5 (C-3), 40.8 (OMe), 38.3 (C-14), 27.8 (C-15); ^{11}B NMR (64 MHz, DMSO-d_6)δ: 3.2 ppm ($h_{1/2} = 4160$ Hz). Elemental Anal. Calc. for $C_{93}H_{84}B_6N_6O_{12}$(1542.67): C, 72.41; H, 5.48; N, 5.44. Found: C, 70.34; H, 5.36; N, 5.16%.

*4.4.7. Compound **3b***

Yellow powder, yield 38% (0.20 g); m.p. 306–310 °C; IR (KBr) ν_{max}, 1625 (C=N, *s*) cm^{-1}; MS-FAB *m/z* (%): 1626 (M^+, 3), 1581 (10), 1467 (54), 1402 (44), 1245 (87), 1169 (65), 963 (77), 831 (96), 789 (95), 621 (100), 562 (79); ^{1}H NMR (400 MHz, DMSO-d_6)δ: 7.77 (6H, *s*, H-9); 7.68 (6H, *d*, $J = 2.2$, H-6), 7.61 (6H, *d*, $J = 7.4$, H-11), 7.37 (6H, *t*, $J = 7.4$, H-12), 7.25 (6H, *dd*, $J = 8.4$, 2.2, H-4), 7.0 (6H, *t*, $J = 7.4$, H-13), 6.87 (6H, d, $J = 8.4$, H-3), 3.9 (6H, s, H-14), 3.2 (12H, q, $J = 7.0$, H-16), 2.63 (18H, *s*, H-15), 1.05 (18H, *t*, $J = 7.0$, H-17); ^{13}C NMR (100 MHz, DMSO-d_6)δ:171.8 (C-7), 158.9 (C-2), 145.1 (C-8), 136.0 (C-4), 131.8 (C-5), 130.2 (C-6), 129.0 (C-9), 127.7 (C-12), 121.8 (C-13), 119.7 (C-1), 118.6 (C-3), 55.9 (C-16), 38.3 (C-14), 27.52 (C-15), 16.92 (C-17); ^{11}B NMR (64 MHz, DMSO-d_6)δ: 2.9 ppm ($h_{1/2} = 3840$ Hz). Elemental Anal. Calc. for $C_{99}H_{96}B_6N_6O_{12}$(1626.76): C, 73.09; H, 5.94; N, 5.16. Found: C, 72.07; H, 5.77; N, 4.67%.

*4.4.8. Compound **3c***

Yellow powder, yield 30% (0.12 g); m.p. 270 °C; IR (KBr) ν_{max} 1621 (C=N, *s*) cm^{-1}; MS-FAB *m/z* (%): 1710 (M^+,4), 1652 (10), 1178 (12), 1068 (13), 866 (13), 736 (31), 622 (10), 620 (15), 289 (16), 154 (100); ^{1}H NMR (400 MHz, DMSO-d_6)δ: 7.82 (6H, *s*, H-9), 7.71 (6H, *d*, $J = 2.0$, H-6), 7.63 (6H, *d*, $J = 7.2$, H-11), 7.39 (6H, *dd*, $J = 7.2$, 7.2, H-12), 7.26 (6H, *dd*, $J = 8.4$, 2.0, H-4), 7.01

(6H, *dd*, $J = 7.2$, 2.4, H-13), 6.88-6.85 (6H, *m*, H-3), 3.90 (6H, *s*, H-14), 3.49 (12H, *t*, $J = 7.4$, H-16), 2.60 (18H, *s*, H-15), 1.41 (12H, *sex*, $J = 7.4$, H-17), 0.83 (18H, *t*, $J = 7.4$, H-18); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 172.4 (C-7), 158.8 (C-2), 142.5 (C-8), 136.6 (C-4), 133.4 (C-11), 132.1 (C-5), 131.8 (C-6), 128.1 (C-9), 127.0 (C-12), 122.8 (C-13), 117.2 (C-1), 116.6 (C-3), 63.1 (C-16), 38.9 (C-14), 28.31 (C-15), 26.3 (C-17), 17.71 (C-18); ^{11}B NMR (64 MHz, DMSO-d_6)δ: 3.6 ppm ($h_{1/2} = 4288$ Hz). Elemental Anal. Calc. for $C_{105}H_{108}B_6N_6O_{12}$ (1710.85): C, 73.71; H, 6.36; N, 4.91. Found: C, 73.24; H, 5.93; N, 4.70%.

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Appendix A. Supplementary material

CCDC 642298, 642299 and 295968 contain the supplementary crystallographic data for **1a**, **1b** and **2a** respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.07.035.

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[13] For all six compounds, elemental analyses were performed after exposure of the solid material to high vacuum (2 h).

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