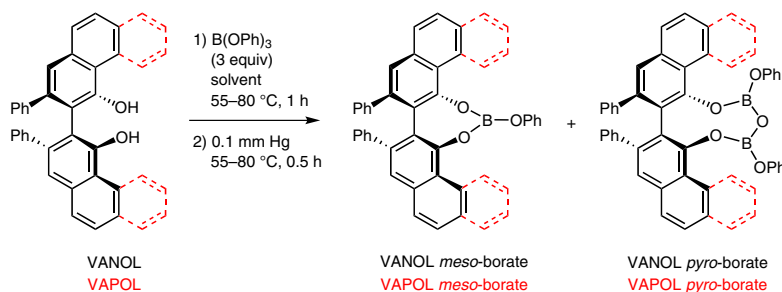


# The Nature of *meso*- and *pyro*-Borate Precatalysts to the VANOL and VAPOL BOROX Catalysts

Wenjun Zhao  
Xiaopeng Yin  
Anil K. Gupta  
Xin Zhang  
William D. Wulff\*

Department of Chemistry, Michigan State University,  
East Lansing, MI 48824, USA  
wulff@chemistry.msu.edu



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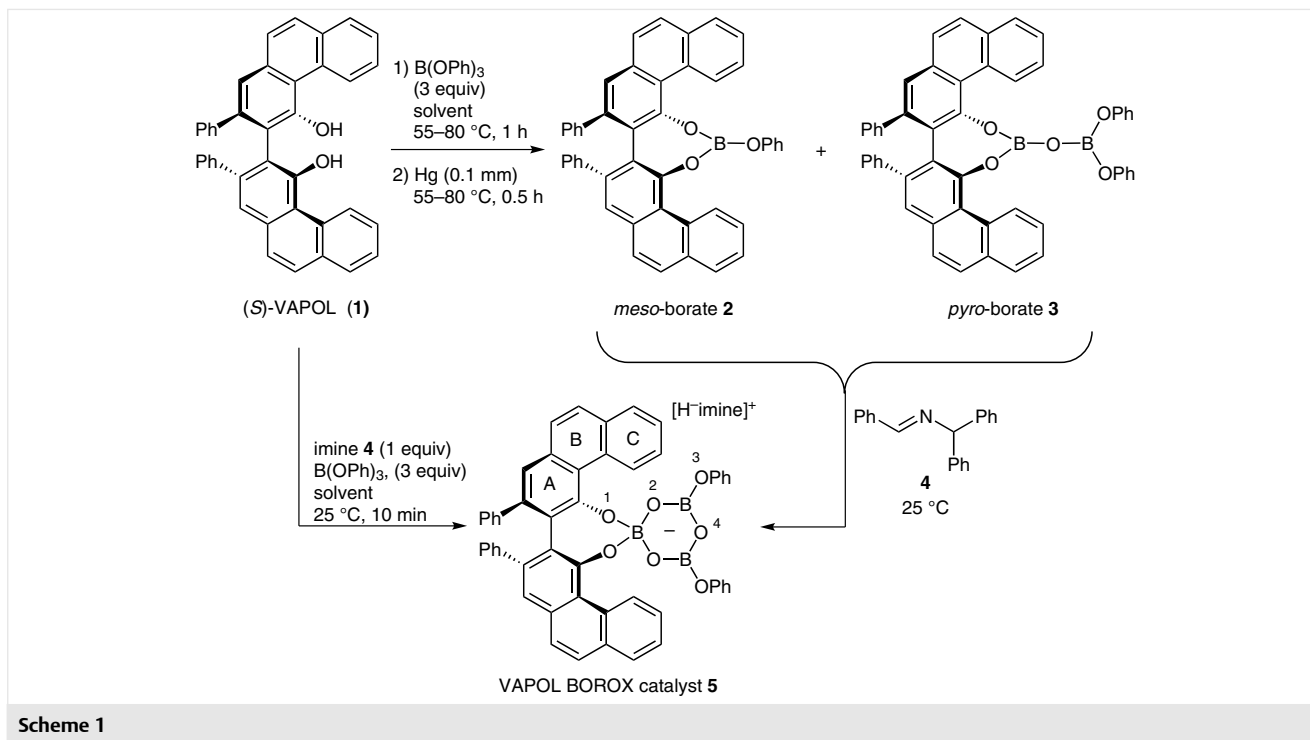
**Abstract** The structures of the *meso*- and *pyro*-borate esters generated by treatment of the VANOL and VAPOL ligands with triphenylborate have been revisited. These species were previously identified as precatalysts that could be in situ converted into VANOL and VAPOL BOROX catalysts by an imine substrate. The complete assignment of all protons for both the *meso*- and *pyro*-borate esters of both ligands was aided by the <sup>1</sup>H NMR spectrum of each generated from pentadeuterophenol. There were significant differences between the chemical shifts for certain protons in the *meso*- and *pyro*-borate species in both the VANOL and VAPOL derivatives. Optimized structures for the *meso*-borates and two different isomers of the *pyro*-borates were determined by DFT calculations for each ligand. For each ligand the cyclic *pyro*-borate was found to be lower in energy than the corresponding linear *pyro*-borate at the B3LYP/6-311+G(d,p) level of theory. The structures of the cyclic *pyro*-borate esters were more consistent with the observed <sup>1</sup>H NMR chemical shifts than the linear *pyro*-borates for each ligand and thus the structures of the *pyro*-borates esters of VANOL and VAPOL have been re-assigned as the cyclic isomers.

**Key words** *meso*- and *pyro*-borate esters, VANOL and VAPOL ligands, VANOL and VAPOL BOROX Catalysts, imine substrate

We have found that chiral BOROX catalysts derived from the VAPOL (and VANOL) ligand are effective catalysts for a number of asymmetric reactions including *cis*-aziridinations,<sup>1</sup> *trans*-aziridinations,<sup>2</sup> heteroatom Diels–Alder reactions,<sup>3</sup> aza-Cope rearrangements,<sup>4</sup> three-component Ugi reactions,<sup>5</sup> and quinoline reductions.<sup>6</sup> The BOROX catalysts were originally prepared from a precatalyst which was generated by heating the VAPOL ligand with three equivalents of B(OPh)<sub>3</sub> for one hour followed by removing all volatiles at the same temperature at 0.133 mbar (Scheme 1).<sup>1,7</sup> The precatalyst was previously determined to be a mixture of two compounds that were identified as the *meso*-borate **2** and the *pyro*-borate **3**.<sup>8</sup> The BOROX catalyst was then generated

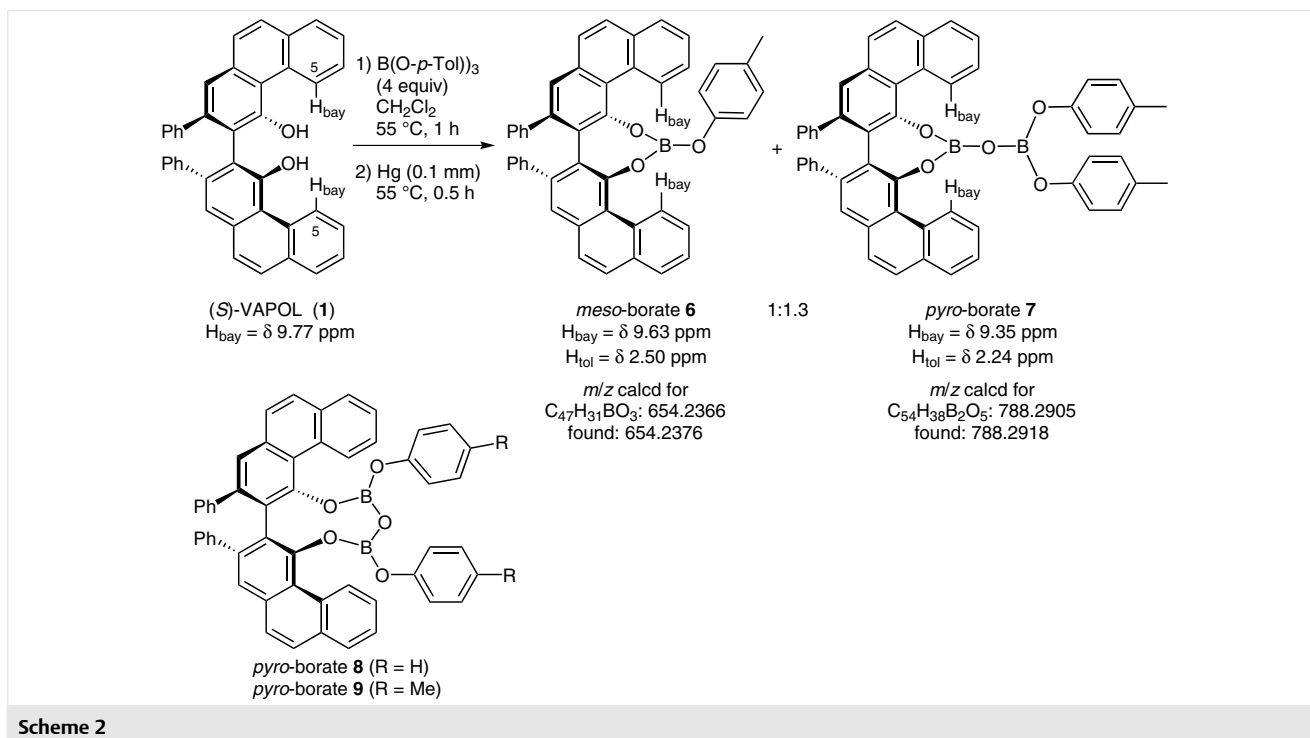
by treating the precatalyst mixture with an imine **4** at room temperature.<sup>9</sup> The overall yield of the BOROX catalyst **5** can be quite high since B(OPh)<sub>3</sub> is not removed under the conditions for the generation of the precatalyst. Later it was found that generation of the precatalyst is not necessary as the treatment of the VAPOL ligand with imine **4** and B(OPh)<sub>3</sub> leads to the formation of the BOROX catalyst **5** in less than ten minutes at room temperature.<sup>7</sup>

The ratio of the *meso*-borate **2** to the *pyro*-borate **3** varies depending on conditions and can range from 10:1 in favor of the *meso*-borate **2** to 1:20 in favor of the *pyro*-borate **3**.<sup>8</sup> Under the conditions indicated in Scheme 1 the ratio is typically ca. 1:4 in favor of **3**.<sup>8</sup> Neither species could be obtained in completely pure form by crystallization or by silica gel chromatography since they are hydrolytically sensitive and thus were characterized as mixtures.<sup>8</sup> One of the distinctive NMR handles that can be used to characterize these compounds is the bay proton on carbon 5 (Scheme 2) of each of the phenanthrene rings which for VAPOL appears as a doublet at  $\delta = 9.79$  ppm (CDCl<sub>3</sub>) which is well outside the range of the normal aromatic protons due to the diamagnetic anisotropy present in phenanthrenes. Since the precatalyst consists of a mixture of *meso*- and *pyro*-borates and since all of the protons in each molecule are aromatic, analysis of the <sup>1</sup>H NMR spectrum was quite challenging. The assignment of the bay protons to the *meso*- and *pyro*-borates was made by an analysis of the precatalyst mixture prepared from *tris-p*-tolyl borate (Scheme 2).<sup>8</sup> Under the conditions shown in Scheme 2, a 1:1.3 mixture of borates was formed, and the VAPOL ligand was completely consumed. A different ratio of borates **6** and **7** was obtained by heating VAPOL with four equivalents of B(*O-p*-Tol)<sub>3</sub> and one equivalent of H<sub>2</sub>O in toluene at 80 °C for one hour and then removal of all volatiles at 80 °C for 0.5 hours which gave a 1:8.4 ratio of **6/7**. This allowed for a correlation of the two different methyl protons of the tolyl group with a particular



bay proton. The integration of the bay proton at  $\delta = 9.63$  ppm against the tolyl methyl group at  $\delta = 2.50$  ppm was found to be 1:1.8 for **6** (1:1.5 expected), and the integration

of bay proton at  $\delta = 9.35$  ppm against the tolyl methyl group at  $\delta = 2.24$  ppm was found to be 1:3.5 for **7** (1:3.0 expected). High resolution mass spectroscopic analysis of the 1:1.3



mixture of **6/7** revealed two parent ions with an intensity ratio of 1:1.3, and the calculated mass for each ion matched that expected for the two borates. There was not any evidence to definitively distinguish between the isomeric *pyro*-borates **7** and **9** (or **3** and **8**). A tentative assignment of the *pyro*-borate as the linear structure **3** rather than the cyclic structure **8** was made on the basis of the  $^{11}\text{B}$  NMR spectrum. Three coordinate borate esters present a broad absorption at  $\delta = 16\text{--}18$  ppm and for a 1:8 mixture of **6/7** this broad absorption appeared as two equal peaks that were slightly separated. The linear *pyro*-borate **3** would be expected to have two different borons, and the symmetric cyclic *pyro*-borate **8** would be expected to have a single boron. However, since the presence of other borate esters including  $\text{B}(\text{OPh})_3$  could not be rigorously excluded, assignment of the *pyro*-borate ester as the linear isomer **3** on this basis can only be classified as tentative.

In our original publication all of the protons for the *meso*-borate **2** and the *pyro*-borate **3** were not assigned from the mixture of the two.<sup>8</sup> A subsequent effort to do so began with a consideration of the  $^1\text{H}$  NMR spectrum of 1:4.3 mixture of **2/3** (Figure 1). There is at most a trace of the free VAPOL ligand remaining, and thus essentially all of the VAPOL is incorporated into two  $\text{C}_2$ -symmetrical species since both bay protons in each species appears as one doublet rather than two. The other two protons that stand out from the rest of the aromatic protons are the two doublets at  $\delta = 6.49$  and 6.64 ppm (Figure 1). Based on the chemical shifts, one possibility for these protons is that they are the *ortho* hydrogens in the phenoxy groups in the borate esters **2** and **3**. However, while the integration of the absorptions at  $\delta = 6.49$  to that at  $\delta = 9.33$  ppm is 4:2 and consistent with the structure **3**, the integration of the absorptions at  $\delta = 6.64$  to that at  $\delta = 9.60$  ppm is also 4:2 and thus not consistent with structure **2**.

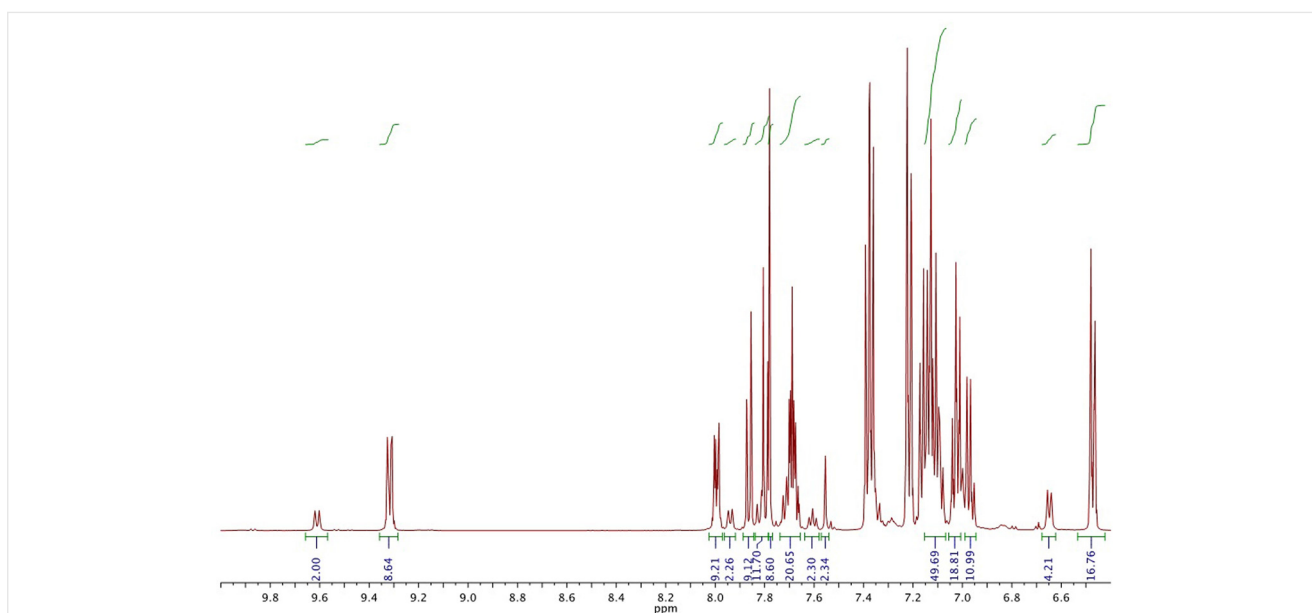
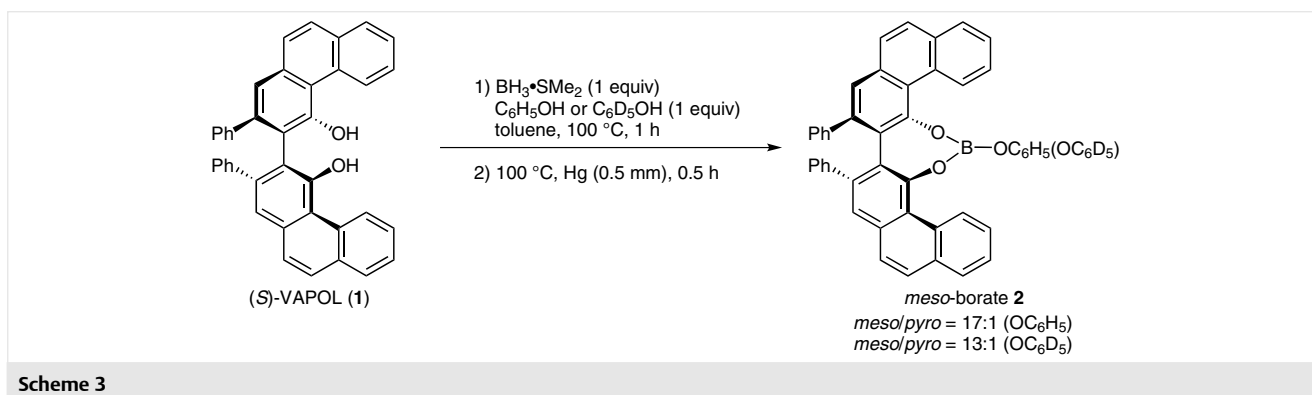


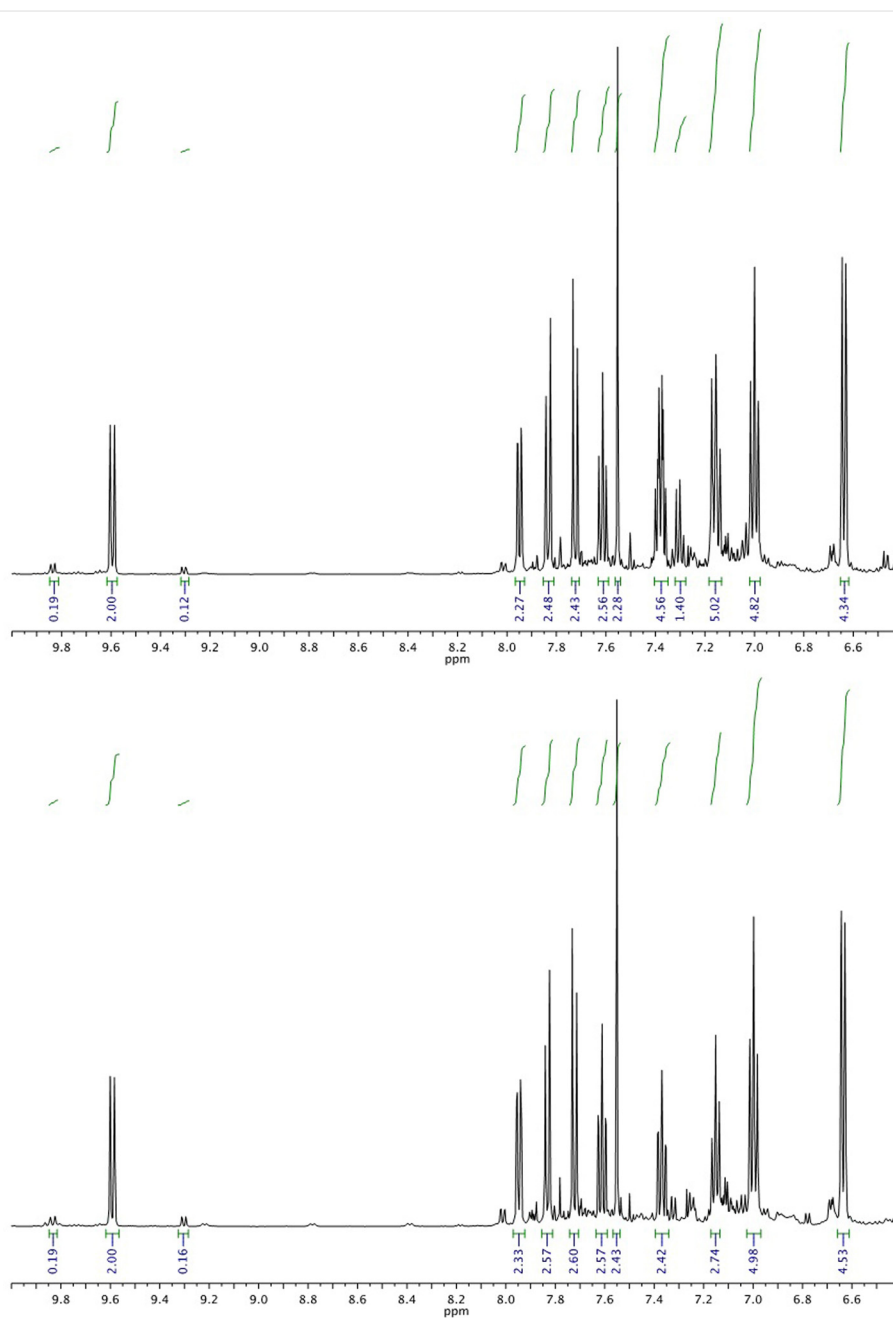
Figure 1  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ) of a 1:4.3 mixture of *meso*-borate **2** to *pyro*-borate **3**



Scheme 3

If these are in fact the *ortho* hydrogens of the phenoxy groups, then one would have to conclude that the spectral data would likely be most consistent with a mixture of the linear and cyclic *pyro*-borates **3** and **8**. This prompted a series of new NMR experiments that would lead to a complete assignment of all of the protons in the two borate species and to the reassignment of the linear *pyro*-borate species **3** as the cyclic *pyro*-borate **8**.

We have found that cleaner formation of the *meso*-borate **2** can be achieved by heating VAPOL with one equivalent of  $\text{BH}_3\text{-SMe}_2$  complex and one equivalent of phenol in toluene at  $100^\circ\text{C}$  and then removal of all volatiles at the same temperature under vacuum (Scheme 3).<sup>10</sup> This gives a 17:1 mixture of *meso*-/*pyro*-borate esters. This greatly simplifies the aromatic region of the  $^1\text{H}$  NMR spectrum as shown in Figure 2 (a). To even further simplify the aromatic



**Figure 2** (a) Top:  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ) of *meso*-borate **2** (*meso*/*pyro* = 17:1) prepared from VAPOL as shown in Scheme 3 from  $\text{C}_6\text{H}_5\text{OH}$ . (b) Bottom:  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ) of *meso*-borate **2** (*meso*/*pyro* = 13:1) prepared from VAPOL as shown in Scheme 3 from  $\text{C}_6\text{D}_5\text{OH}$ .

region, the *meso*-borate **2** was prepared in the same way but with pentadeuterophenol to remove the three protons of the phenoxy group from the mix (Figure 2, b). The most interesting fact emerging from the two spectra in Figure 2 is that the doublet at  $\delta = 6.64$  ppm is not from the *ortho* proton in the phenoxy group of *meso*-borate **2**. Since it is a doublet integrating to four protons, it can only be assigned to the *ortho* protons of the two phenyl groups in the 2- and 2'-positions of the VAPOL ligand. By subtraction of the two spectra, the protons of the phenoxy group in *meso*-borate **2** can thus be assigned as a doublet at  $\delta = 7.16$  ppm, a triplet at  $\delta = 7.30$  ppm, and a triplet at  $\delta = 7.39$  ppm.

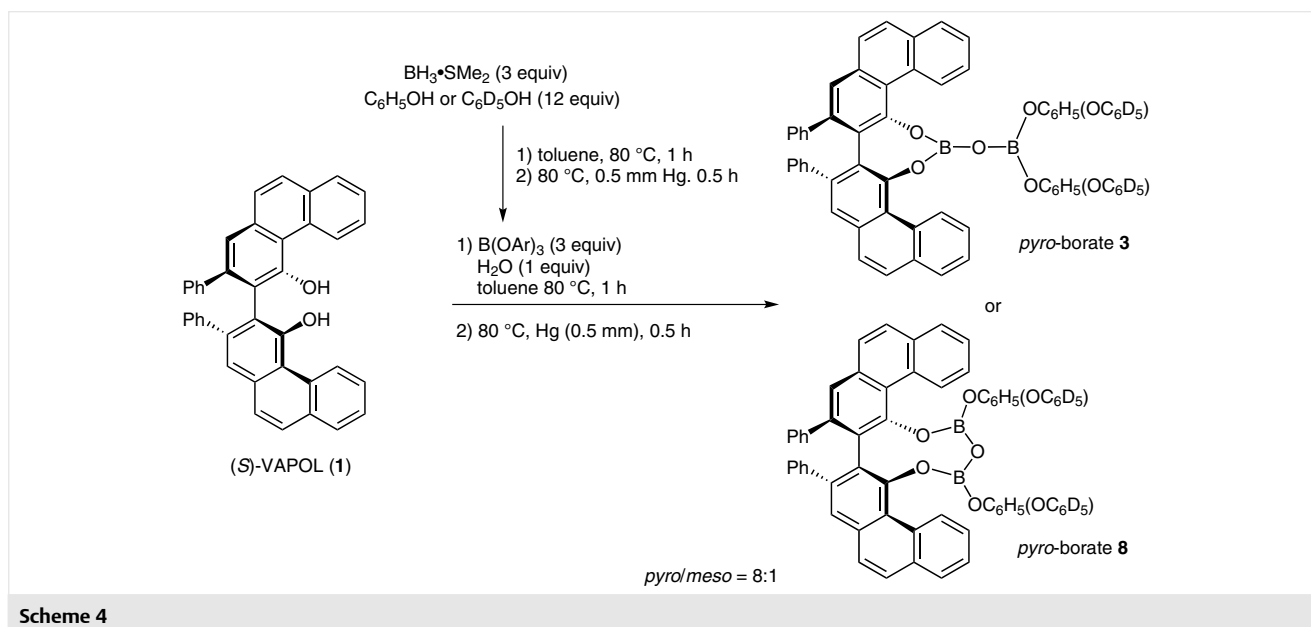
The *pyro*-borate complex of VAPOL could be prepared as an 8:1 mixture with the *meso*-borate **2** from  $\text{BH}_3\cdot\text{SMe}_2$  and phenol as indicated in Scheme 4. In this case, three equivalents of  $\text{B}(\text{OAr})_3$  is freshly prepared by heating three equivalents of  $\text{BH}_3\cdot\text{SMe}_2$  and 12 equivalents of phenol at  $80^\circ\text{C}$  for one h, and then the volatiles and excess phenol are removed at  $80^\circ\text{C}$  under vacuum for 0.5 hours.<sup>11</sup> Then the VAPOL ligand and one equivalent of water are added and the mixture heated at  $80^\circ\text{C}$  for one hour, and then the volatiles were removed at  $80^\circ\text{C}$  under vacuum. This procedure gives an 8:1 mixture of *pyro*-/*meso*-borates and the spectra for this mixture prepared from  $\text{C}_6\text{H}_5\text{OH}$  and  $\text{C}_6\text{D}_5\text{OH}$  are shown in Figures 3 (a) and (b), respectively. Water is added since the formation of a B–O–B linkage requires one equivalent of water. Note that when commercial  $\text{B}(\text{OPh})_3$  is used to prepare the pyroborate, the addition of water is usually not necessary since commercial  $\text{B}(\text{OPh})_3$  is usually partially hydrolyzed to the point that the formation of both *pyro*-borates and BOROX catalysts (Scheme 1) are facile.<sup>7</sup> Since the original assignment of the *pyro*-borate was only tentatively

made as the linear isomer **3**, both the linear and cyclic structures **3** and **8** need to be considered going forward.

In contrast to the situation for the *meso*-borate **2**, the most upfield doublet at  $\delta = 6.49$  ppm in the *pyro*-borate is lost when the *pyro*-borate is prepared from  $\text{C}_6\text{D}_5\text{OH}$  (Figures 3, a vs. 3, b). From the difference of Figures 3 (a) and (b), the protons from the phenoxy group in the *pyro*-borate can be identified as a doublet at  $\delta = 6.49$ , triplet at  $\delta = 6.99$ , and a triplet at  $\delta = 7.05$  ppm. A doublet integrating to four protons for the *ortho* hydrogens of the phenyl group in the *pyro*-borate can only reside in the multiplet at  $\delta = 7.09$ – $7.18$  (Figure 3, b). Thus it is interesting to note that the *ortho* hydrogens of the phenyl and phenoxy groups switch places in the *meso*- and *pyro*-borates. The *ortho* hydrogens of the phenyl group move from  $\delta = 6.64$  ppm in the *meso*-borate to  $\delta = 7.09$ – $7.18$  ppm in the *pyro*-borate.

In contrast, the *ortho* hydrogens of the phenoxy group move from  $\delta = 7.16$  ppm in the *meso*-borate to  $\delta = 6.49$  in the *pyro*-borate.

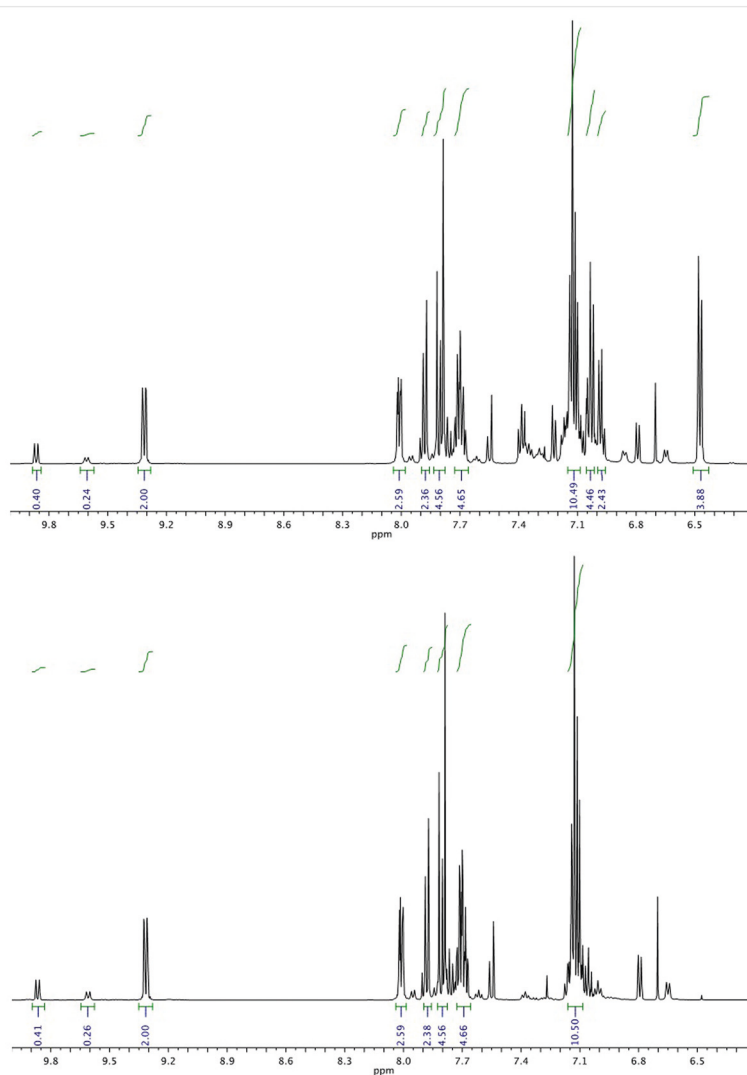
In order to gain some insight into the chemical shifts observed for the *meso*- and *pyro*-borates, energy-minimized structures of VAPOL and its borates were determined at the B3LYP/6-31G(d) level of theory for VAPOL, the *meso*-borate **2**, both isomers of the *pyro*-borates **3** and **8**, and the minimized structures are shown in Figure 4. The lowest-energy structure in the gas phase for the VAPOL ligand was found to have a dihedral angle of  $81.1^\circ$  between the two phenanthrene rings. The crystal structure of five different forms of VAPOL have been determined, and all have dihedral angles in the range of  $73.0$ – $88.5^\circ$ .<sup>12</sup> The first issue of note is that of the two isomeric *pyro*-borates, the cyclic *pyro*-borate **8** is significantly more stable (5.63 kcal/mol) than the linear *pyro*-borate **3**. A unique feature among the



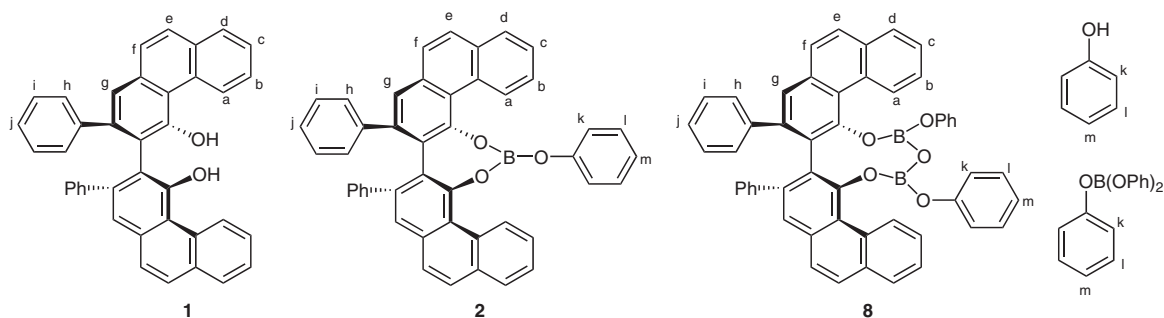
Scheme 4

structures is that the cyclic *pyro*-borate **8** has an *ortho* hydrogen of each phenoxy group pointing directly at the central ring of each of the phenanthrene ring systems. The distance of  $d = 4.555 \text{ \AA}$  is in the range of that expected for a CH- $\pi$  interaction as defined by the standard practice of measuring the distance from the carbon bearing the hydrogen to the centroid of the arene ring with which it interacts.<sup>13–15</sup> This would explain the upfield shift of the *ortho* hydrogens of the phenoxy hydrogens of the *pyro*-borate species ( $\delta = 6.49 \text{ ppm}$ ) relative to those of the *meso*-borate **2** ( $\delta = 7.16 \text{ ppm}$ ) if the *pyro*-borate existed as the cyclic structure **8**. Neither the linear *pyro*-borate species **3** nor the *meso*-borate **2** have any potential CH- $\pi$  interactions with distances less than  $5.5 \text{ \AA}$ .

Thus the computational and  $^1\text{H}$  NMR studies both indicate that the better assignment for the *pyro*-borate species is the cyclic structure **8** rather than the linear structure **3**. The  $^{11}\text{B}$  NMR spectrum of the 8:1 mixture of *pyro*-/*meso*-borates shown in Figure 3 (a) reveals a broad peak at  $\delta = 16.33 \text{ ppm}$  with a smaller shoulder peak at  $\delta = 18.26 \text{ ppm}$  (see Supporting Information). This is not necessarily taken as evidence that the *pyro*-borate contains two different borons since the shoulder peak could be due to the presence of other unidentified three-coordinate borates. Instead, the assignment is made as the cyclic *pyro*-borate **8** on the basis of all of the other evidence gathered in the present study. The assignment of all of the protons for the *meso*-borate **2** and the *pyro*-borate **8** are presented in Table 1 along with those for phenol and triphenylborate for comparison. The *ortho* hydrogens ( $\text{H}_k$ ) of the phenoxy groups in  $\text{B}(\text{OPh})_3$  are



**Figure 3** (a) Top:  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ) of *pyro*-borate **3** or **8** (*meso*/*pyro* = 1:8) prepared from VAPOL as shown in Scheme 4 from  $\text{C}_6\text{H}_5\text{OH}$ . (b) Bottom:  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ) of *pyro*-borate **3** or **8** (*meso*/*pyro* = 1:8) prepared from VAPOL as shown in Scheme 4 from  $\text{C}_6\text{D}_5\text{OH}$ .

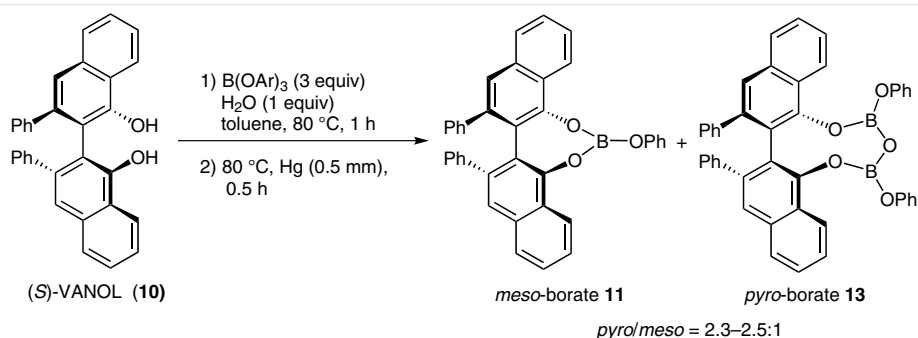
**Table 1**  $^1\text{H}$  NMR Data for VAPOL, VAPOL Borates **2** and **8**, Phenol, and Triphenylborate<sup>a</sup>

	VAPOL <b>1</b>	VAPOL <i>meso</i> -borate <b>2</b>	VAPOL <i>pyro</i> -borate <b>8</b>	Phenol	B(OPh) <sub>3</sub>
H <sub>a</sub>	9.79	9.60	9.33	–	–
H <sub>b</sub>	7.72	7.37	7.68–7.74	–	–
H <sub>c</sub>	7.67	7.61	7.68–7.74	–	–
H <sub>d</sub>	7.98	7.95	8.01	–	–
H <sub>e(f)</sub>	7.72	7.72	7.82	–	–
H <sub>f(e)</sub>	7.86	7.83	7.88	–	–
H <sub>g</sub>	7.48	7.55	7.80	–	–
H <sub>h</sub>	6.72	6.64	7.09–7.18	–	–
H <sub>i</sub>	7.00	7.00	7.09–7.18	–	–
H <sub>j</sub>	7.11	7.15	7.09–7.18	–	–
H <sub>k</sub>	–	7.16	6.49	6.85	7.15
H <sub>l</sub>	–	7.39	7.05	7.26	7.33
H <sub>m</sub>	–	7.30	6.99	6.95	7.11

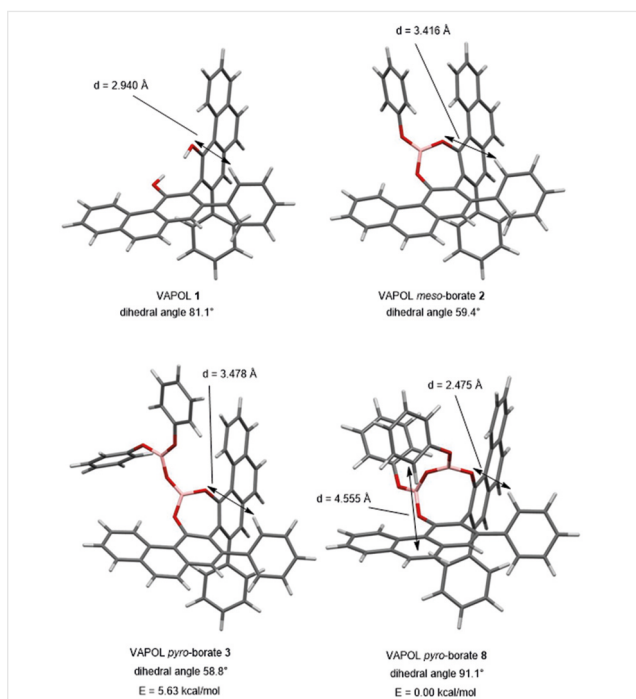
<sup>a</sup> CDCl<sub>3</sub> as solvent.

at  $\delta = 7.15$  ppm and thus the *ortho*-phenoxy protons in the *meso*-borate **2** at  $\delta = 7.16$  ppm are in a 'normal' position for an aryl borate ester. It is the *ortho* hydrogens of the phenoxy groups of the *pyro*-borate **8** that are anomalous with a chemical shift of  $\delta = 6.49$  ppm and as illustrated in the structures in Figure 4, and this can be accounted for by the CH– $\pi$  interaction with the central ring of the phenanthrene unit.

With regard to the chemical shift of the *ortho* hydrogens of the phenyl group (H<sub>h</sub>), the chemical shift of H<sub>h</sub> in the *meso*-borate **2** ( $\delta = 6.64$  ppm) is very close to those of the free VAPOL ligand **1** ( $\delta = 6.72$  ppm). In contrast, the chemical shift of H<sub>h</sub> in the *pyro*-borate **8** is shifted downfield to 7.09–7.18 ppm. The two phenyl groups in VAPOL **1** and in the *meso*-borate **2** are close to parallel and are within the  $\pi$ – $\pi$  stacking distance (3.4–3.6 Å). The phenyl rings are offset such that the *ortho* hydrogens of these phenyl groups

**Scheme 5**





**Figure 4** B3LYP/6-31G(d) optimized structures for VAPOL, the VAPOL *meso*-borate **2**, the VAPOL linear *pyro*-borate **3**, and the VAPOL cyclic *pyro*-borate **8**. The relative energies were calculated at the B3LYP/6-311+G(d,p) level of theory. The structures are visualized by the Mercury program (C, gray; O, red; B, pink; H, white).

should be shielded which is consistent with their upfield shifts. The phenyl groups  $H_h$  in the *pyro*-borate complex **8** are also nearly parallel at a distance of 3.77 Å and are also offset. However, these protons are deshielded and appear at  $\delta = 7.09$ –7.18 ppm.

An investigation of the structures in Figure 4 leads to a possible explanation of this deshielding of the  $H_h$  protons in complex **8**. The protons  $H_h$  are within H-bonding distance of O1 of the *pyro*-borate bridge with an O–H distance of 2.457 Å.<sup>16</sup> This distance is uniquely short for complex **8** as this distance is ca. 0.5–1.0 Å larger for all other structures. Such an H-bonding interaction would be expected to lead to deshielding, and an observed shift of ca. 0.5 ppm relative to the *meso*-borate **2** would be consistent with this expectation.

A similar type of NMR and computational analysis was carried out on the *meso*- and *pyro*-borates of VANOL, and the results essentially mirrored those obtained with the *meso*- and *pyro*-borates of VAPOL. In this way the *pyro*-borate of VANOL was reassigned as the cyclic *pyro*-borate **13** (Scheme 5) rather than its linear isomer. The details of this analysis can be found in the Supporting Information.

We have determined the complete assignments of the <sup>1</sup>H NMR signals for the *meso*-borates and *pyro*-borates of the vaulted biaryl ligands VANOL and VAPOL. This spectroscopic analysis coupled with computational studies has led

to the reassignment of the *pyro*-borates of both ligands as the cyclic isomers as opposed the linear isomers. This new information concerning the structures of the *pyro*-borates esters of VANOL and VAPOL shed some light on understanding how the mixtures of *meso*- and *pyro*-borates are transformed by the presence of an amine or imine base into boroxinate (BOROX) catalysts due to the similarity between the structures of the cyclic *pyro*-borates and the catalysts suggesting that the cyclic *pyro*-borates on the pathway to the boroxinates and this possibility should serve to stimulate experiments to test this possibility.

## Acknowledgment

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## Supporting Information

Supporting information for this article is available online at <http://dx.doi.org/10.1055/s-0034-1378707>. Included are experimental procedures, <sup>1</sup>H NMR and <sup>11</sup>B NMR spectra of compounds **2**, **8**, **11**, and **13** and pdb files for DFT energy-minimized structures for **1–3**, **8**, **10–13**.

## Primary Data

Primary data for this article are available online at <http://www.thieme-connect.com/products/ejournals/journal/10.1055/s-00000083> and can be cited using the following DOI: 10.4125/pd0067th.

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- (10) **Preparation of VAPOL-*meso*-borate 2 (Procedure A)**  
To a flame-dried 25 mL Schlenk flask equipped with a stir bar and flushed with nitrogen was added (*R*)-VAPOL (**1**, 54 mg, 0.10 mmol, 1.0 equiv), phenol (9.4 mg, 0.10 mmol, 1.0 equiv), dry toluene (2 mL), and  $\text{BH}_3\text{-SMe}_2$  (2 M in toluene, 0.10 mmol, 1.0 equiv). The flask was sealed, and the resulting mixture was stirred at 100 °C for 1 h. The volatiles were then carefully removed via high vacuum and left under high vacuum at 100 °C for 0.5 h. The residue was dissolved in ca. 0.7 mL  $\text{CDCl}_3$  and transferred to a quartz NMR tube and was subjected to  $^1\text{H}$  NMR and  $^{11}\text{B}$  NMR analysis. To locate the five aromatic protons in the phenol moiety in the *meso*-borate **2**, procedure A described above was repeated with phenol-2,3,4,5,6- $d_5$  (10 mg, 0.10 mmol, 1.0 equiv), and the resultant *meso*-borate **2** was subjected to  $^1\text{H}$  NMR and  $^{11}\text{B}$  NMR analysis. The ratio of *meso*-/*pyro*-borates with phenol was 17:1 and with the pentadeuterophenol was 13:1.  
**Spectral Data for 2 (from Phenol, Figure 2, a)**  
 $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 6.64 (dd, 4 H,  $J$  = 8.3, 1.0 Hz), 7.00 (t, 4 H,  $J$  = 7.8 Hz), 7.13–7.18 (m, 4 H), 7.30 (tt, 1 H,  $J$  = 1.1, 7.5 Hz), 7.35–7.40 (m, 4 H), 7.55 (s, 2 H), 7.61 (ddd, 2 H,  $J$  = 7.8, 7.0, 1.0 Hz), 7.72 (d, 2 H,  $J$  = 9.0 Hz), 7.83 (d, 2 H,  $J$  = 8.5 Hz), 7.95 (dd, 2 H,  $J$  = 7.8, 1.2 Hz), 9.60 (d, 2 H,  $J$  = 8.5 Hz).  
**Spectral Data for 2 (from Pentadeuterophenol, Figure 2, b)**  
 $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 6.64 (dd, 4 H,  $J$  = 8.3, 1.0 Hz), 7.00 (t, 4 H,  $J$  = 7.8 Hz), 7.15 (t, 2 H,  $J$  = 7.3 Hz), 7.37 (ddd, 2 H,  $J$  = 8.7, 7.0, 1.4 Hz), 7.55 (s, 2 H), 7.61 (ddd, 2 H,  $J$  = 7.8, 7.0, 1.0 Hz), 7.72 (d, 2 H,  $J$  = 9.0 Hz), 7.83 (d, 2 H,  $J$  = 8.5 Hz), 7.95 (dd, 2 H,  $J$  = 7.8, 1.2 Hz), 9.59 (d, 2 H,  $J$  = 8.5 Hz).
- (11) **Preparation of *pyro*-Borate 8 (Procedure B)**  
To a flame-dried 25 mL Schlenk flask equipped with a stir bar and flushed with nitrogen was added phenol (113 mg, 1.20 mmol, 12.00 equiv), dry toluene (2 mL), and  $\text{BH}_3\text{-SMe}_2$  (2 M in toluene, 150  $\mu\text{L}$ , 0.300 mmol, 3.00 equiv). The flask was sealed, and the resulting mixture was stirred at 80 °C for 1 h. The volatiles were then carefully removed via high vacuum and left under high vacuum at r.t. for 0.5 h yielding a white solid. To this solid was added VAPOL (54 mg, 0.10 mmol, 1.0 equiv), dry toluene (2 mL), and  $\text{H}_2\text{O}$  (1.8  $\mu\text{L}$ , 0.10 mmol, 1.0 equiv). The mixture was stirred at 80 °C for 1 h. The volatiles were carefully removed via high vacuum and left under high vacuum at 80 °C for 0.5 h. The residue was then dissolved in ca. 0.7 mL  $\text{CDCl}_3$  and transferred to a quartz NMR tube, and the *pyro*-borate **8** was subjected to  $^1\text{H}$  NMR and  $^{11}\text{B}$  NMR analysis. To locate the five aromatic protons in the phenol moiety in **8**, the procedure B described above was repeated with phenol-2,3,4,5,6- $d_5$  (120 mg, 1.20 mmol, 12.00 equiv). The ratio of *pyro*-/*meso*-borates with phenol was 8:1 and with the pentadeuterophenol was 8:1.  
**Spectral Data for 8 (from Phenol, Figure 3, a)**  
 $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 6.49 (d, 4 H,  $J$  = 7.8 Hz), 6.99 (tt, 2 H,  $J$  = 7.2, 1.3 Hz), 7.05 (t, 4 H,  $J$  = 7.8 Hz), 7.09–7.18 (m, 10 H), 7.68–7.74 (m, 4 H), 7.80 (s, 2 H), 7.82 (d, 2 H,  $J$  = 9.0 Hz), 7.88 (d, 2 H,  $J$  = 9.0 Hz), 8.01 (dd, 2 H,  $J$  = 7.3, 2.0 Hz), 9.29–9.34 (m, 2 H).  
**Spectral Data for 8 (from Pentadeuterophenol, Figure 3, b)**  
 $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.09–7.18 (m, 10 H), 7.68–7.74 (m, 4 H), 7.80 (s, 2 H), 7.81 (d, 2 H,  $J$  = 9.0 Hz), 7.88 (d, 2 H,  $J$  = 9.0 Hz), 8.01 (dd, 2 H,  $J$  = 7.3, 2.0 Hz), 9.29–9.34 (m, 2 H).
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