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## INVESTIGATIONS INTO THE NUCLEOPHILIC *meso*-SUBSTITUTION OF *F*-BODIPYs AND IMPROVEMENTS TO THE SYNTHESIS OF 4,4-DIFLUORO-4-BORA-3a,4a-DIAZA-*s*-INDACENE

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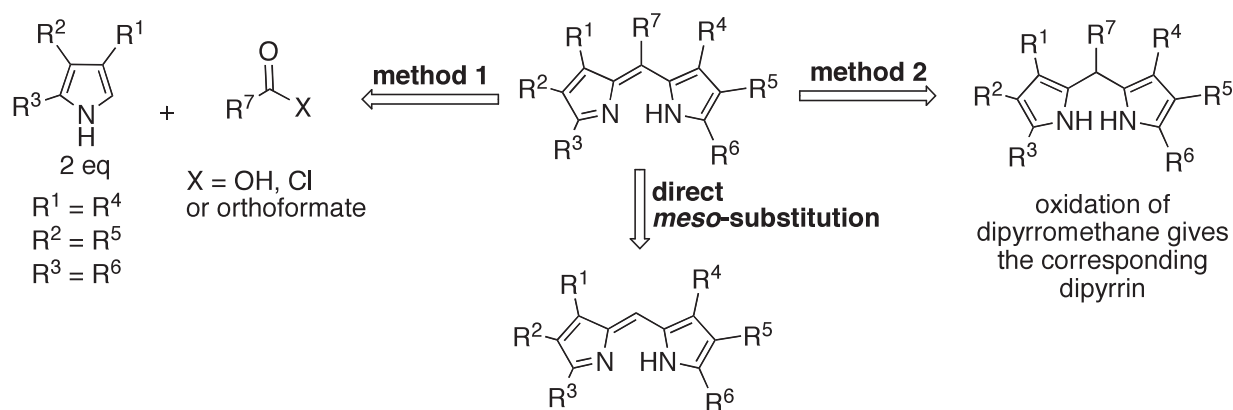
**Abstract** – A series of three *F*-BODIPYs, with varying levels of steric crowding about the *meso*-position were selected to investigate nucleophilic *meso*-substitution of *F*-BODIPYs. The synthesis of one of these *F*-BODIPYs, 4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (totally unsubstituted dipyrin skeleton), was optimized to give higher yields over routine literature procedures. This modified procedure involves oxidation of a dipyrromethane using *p*-chloranil, instead of DDQ, to give a dipyrin which is then trapped *in situ* as its BF<sub>2</sub> complex. Nucleophilic *meso*-alkylation of the series of *F*-BOIDPYs with *n*-butyllithium gave *meso*-butyl *F*-BODIPYs in moderate to good yields. This work represents a new, synthetically viable method for the synthesis of *meso*-alkylated *F*-BODIPYs. Extension of the nucleophilic substitution methodology to *meso*-arylation was possible. However, the reaction was unselective: substitution at boron, to give the boron-diaryl *C*-BOIDPYs, occurred preferentially to nucleophilic *meso*-substitution and thus a mixture of products was obtained.

## INTRODUCTION

Molecules containing the 4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (*F*-BODIPY) framework have wide applications as dyes, fluorescent probes in biological systems, and materials for incorporation into electroluminescent devices.<sup>1,2</sup> Both symmetrical and unsymmetrical *F*-BODIPYs are routinely synthesized in high yields from the isolated dipyrins free-bases or HX salts or by trapping the dipyrin *in situ*.<sup>3</sup> However, dipyrin free-bases and salts are historically difficult to manipulate and purify. Furthermore, there are only a few methods available to synthesize *meso*-substituted dipyrins.

To produce *meso*-substituted dipyrins (Figure 1), one can condense two equivalents of an  $\alpha$ -unsubstituted pyrrole with a carboxylic acid,<sup>4</sup> an acid chloride<sup>5</sup> or an orthoformate<sup>6</sup> (method 1) or

oxidize a 5-unsubstituted dipyrromethane to the corresponding *meso*-unsubstituted dipyrin (method 2).<sup>7</sup> The first method is limited to the synthesis of symmetrical dipyrins, while the second method is currently limited to the synthesis of dipyrins with *meso*-aryl substituents and it requires the synthesis of the dipyrromethane starting material. Dipyrins with *meso*-alkyl substituents can be synthesized from alkyl acid chlorides (method 1); however, the *meso*-alkyl dipyrins are generally unstable and are thus trapped *in situ* using boron trifluoride diethyletherate and then isolated as their corresponding *F*-BODIPYs, with overall yields often below 20%.<sup>8-11</sup>



**Figure 1.** Strategies for the Preparation of *meso*-Substituted Dipyrins

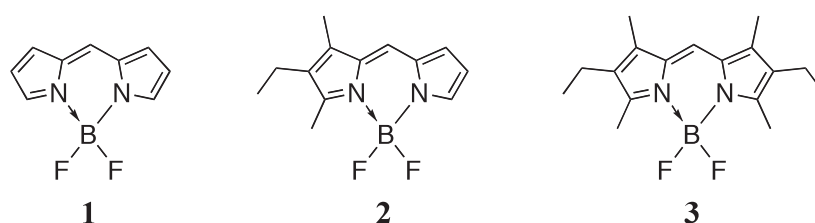
As shown in Figure 1, another potential strategy to *meso*-substituted dipyrins involves substitution of *meso*-unsubstituted dipyrins. However, examples of such direct *meso*-substitution of dipyrins or dipyrinato complexes are rare in the literature. *meso*-Cyano dipyrins can be directly generated from *meso*-unsubstituted dipyrins through cyanide anion attack at the *meso*-position to give the corresponding dipyrromethane, which can then be oxidized back to the dipyrin.<sup>12</sup> Oligopyrrolic bile pigments,<sup>13,14</sup> containing one or more dipyrin units, are reported to undergo *meso*-substitution in the presence of ethanethiole. A prodigiosin analogue,<sup>15</sup> which contains a dipyrin unit, was also reported to undergo photo-induced substitution with sulfur-based nucleophiles to give *meso*-substituted derivatives.

Direct *meso*-modification of *F*-BODIPYs has recently received interest and attempts at modification have utilized a *meso*-thioalkyl *F*-BODIPY as starting material.<sup>16</sup> The *meso*-thioalkyl substituent was shown to undergo nucleophilic substitution with amines,<sup>16,17</sup> and it was also coupled with aryl boronic acids, *via* the Liebeskind-Srögl cross-coupling reaction,<sup>18</sup> to generate other *meso*-substituted *F*-BODIPYs. Although this approach represents a great improvement in the synthesis of *meso*-aryl *F*-BODIPYs, it is limited to the generation of symmetrical derivatives as the *meso*-thioalkyl *F*-BODIPY is generated by the reaction of thiophosgene with two equivalents of a substituted pyrrole to give the corresponding dipyrrolthione, which is then alkylated and trapped as its  $\text{BF}_2$  complex.<sup>16</sup>

*meso*-Unsubstituted porphyrins and their metal complexes are susceptible to nucleophilic substitution at the *meso*-position, and the resulting intermediate is oxidized *in situ* to give *meso*-aryl and *meso*-alkyl substituted porphyrins.<sup>19,20</sup> Aryl and alkyl lithium reagents, with varying levels of functionalization, are the nucleophiles employed in these reactions. Interestingly, a small amount of a *meso*-butyl substituted BODIPY was isolated from the reaction of a *meso*-unsubstituted BODIPY with 2 equivalents of a perfluorinated aryl lithium reagent (prepared from reacting the perfluorinated bromobenzene with *n*-butyl lithium).<sup>21</sup> Based on this knowledge, we aimed to develop a methodology for the generation of *meso*-substituted *F*-BODIPYs *via* nucleophilic substitution at the *meso*-position of *meso*-unsubstituted *F*-BODIPYs.

## RESULTS AND DISCUSSION

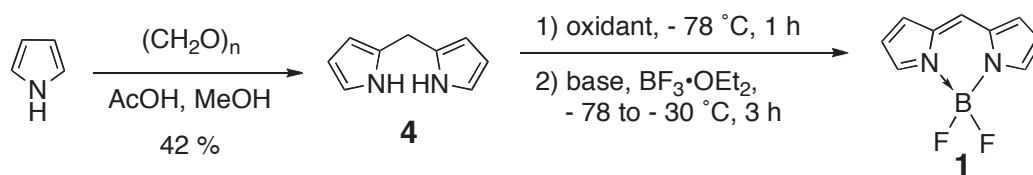
An ideal synthetic route for the synthesis of a *meso*-substituted *F*-BODIPY would be to begin with a chemically robust *meso*-unsubstituted *F*-BODIPY, which would undergo nucleophilic substitution at the *meso*-position. Three *F*-BODIPYs (Figure 2), containing examples with increasing steric crowding flanking the *meso*-position, were selected as test compounds to investigate a methodology for the nucleophilic *meso*-modification of *meso*-unsubstituted *F*-BODIPYs to give the corresponding *meso*-substituted *F*-BODIPYs.



**Figure 2.** *F*-BODIPY Test Compounds

*F*-BODIPYs **2** and **3** were synthesized from the corresponding dipyrrens using traditional methods.<sup>22</sup> The synthesis of *F*-BODIPY **1** has only very recently been reported.<sup>23-25</sup> One synthesis involves a four-step procedure from pyrrole, in 35 % overall yield.<sup>16,23,26</sup> The other two methods are one-pot reactions and involve trapping the unstable dipyrryn intermediate: both have reported yields under 10 %.<sup>24,25</sup> In order for this one-pot method for the preparation of **1** to be synthetically viable as a starting point for preparing derivatized *F*-BODIPYs, the yields needed to be increased.

The one-pot procedure involving the oxidation of an unsubstituted dipyrryn was selected for optimization.<sup>25</sup> The dipyrryn starting material (**4**) was synthesized using a literature method.<sup>27</sup> A series of trials were conducted in order to optimize the reaction conditions, the oxidant used in the dipyrryn formation reaction, and the base used in the *F*-BODIPY formation reaction. The results of these trials are outlined in Scheme 1.

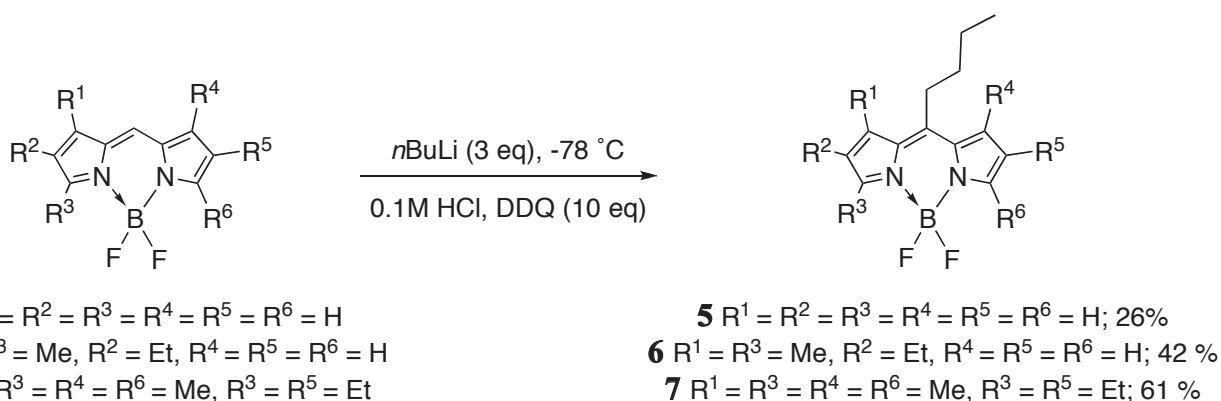


Trial	Oxidant	Base	Isolated Yield /%
1	DDQ	TEA	0
2		DIPEA	0.76
3		DBU	0.61
4-6	<i>p</i> -chloranil	DIPEA	10-29

**Scheme 1.** Optimization of the Synthesis of *F*-BODIPY **1**

The bases used in the *F*-BODIPY formation were explored first (Trial 1 through Trial 3), using DDQ as an oxidant to generate the dipyrryn. When triethylamine was used as a base, none of the desired unsubstituted *F*-BODIPY (**1**) was formed; however, when DIPEA or DBU were used, **1** was isolated in very low yield (Trials 2 and 3) in our hands, even though the literature reports indicate yields between 8 and 10% when using DIPEA.<sup>24,25</sup> DIPEA was thus selected as the base to use in further trials as it reproducibly gave the best yield (e.g. Trial 2). After the base for the *F*-BODIPY formation was selected, the oxidant for the dipyrryn formation was investigated. The isolated yield of the *F*-BODIPY **1** increased substantially when the oxidant was modified from DDQ to the milder *p*-chloranil (Trials 4-6). Using these modified conditions, the *F*-BODIPY **1** was generated in an average yield of 21% on a 100 mg scale.

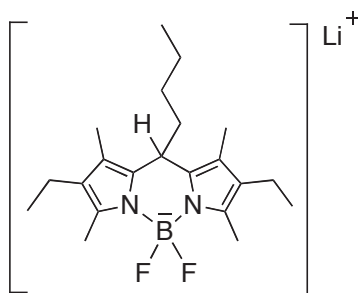
With *F*-BODIPYs **1**, **2** and **3** in hand, investigations proceeded regarding nucleophilic *meso*-substitution. Solutions of each compound were treated with *n*-butyllithium at -78 °C. The reaction mixture was slowly warmed to room temperature and then treated with DDQ. The *meso*-butyl substituted *F*-BODIPYs **5**, **6**,<sup>28</sup> and **7**<sup>28</sup> were isolated in moderate yields as shown in Scheme 2.



**Scheme 2.** *meso*-Butylation of *F*-BODIPYs **1**, **2**, and **3**

This transformation represents a new method for the synthesis of alkyl substituted *F*-BODIPYs in better yields than the existing published methods.<sup>8-11</sup> In the only previous example of the synthesis of a

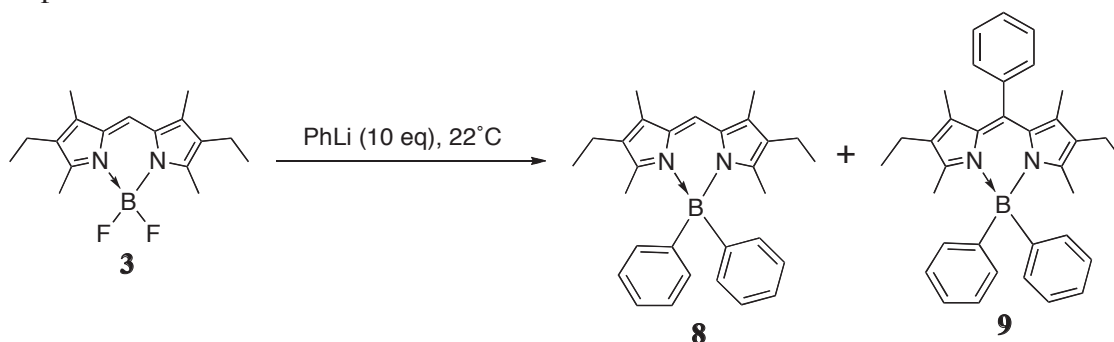
*meso*-butylated BODIPY from the *meso*-unsubstituted analogue, the authors speculated that a perfluorinated aryl lithium reagent (prepared from reacting the perfluorinated bromobenzene with *n*-butyl lithium) deprotonated the *meso*-position of the BODIPY, followed by reaction of the resultant monoanionic species with the residual *n*-butylbromide.<sup>21</sup> We postulate,<sup>28</sup> based on color changes during the course of the reaction, that the alkylation addition occurs by the nucleophilic attack of the *n*-butyl anion at the *meso*-position to give a charged dipyrromethane-type intermediate, as shown in Figure 3.



**Figure 3.** Postulated Alkylation Intermediate

The decrease in yield of the *meso*-butyl *F*-BODIPYs with decreasing substitution about the *F*-BODIPY is likely due to a decrease in the stability of boron-containing dipyrromethane-type intermediate with decreasing substitution, analogous to that of the corresponding dipyrin series.<sup>29</sup> Isolated yields of the *meso*-butylated *F*-BODIPYs **5**, **6** and **7** increased with increasing substitution from 26%, for the least substituted, to 61%, for the most substituted. Nevertheless, this strategy provides a reasonable and reliable route to *meso*-butyl substituted *F*-BODIPYs.

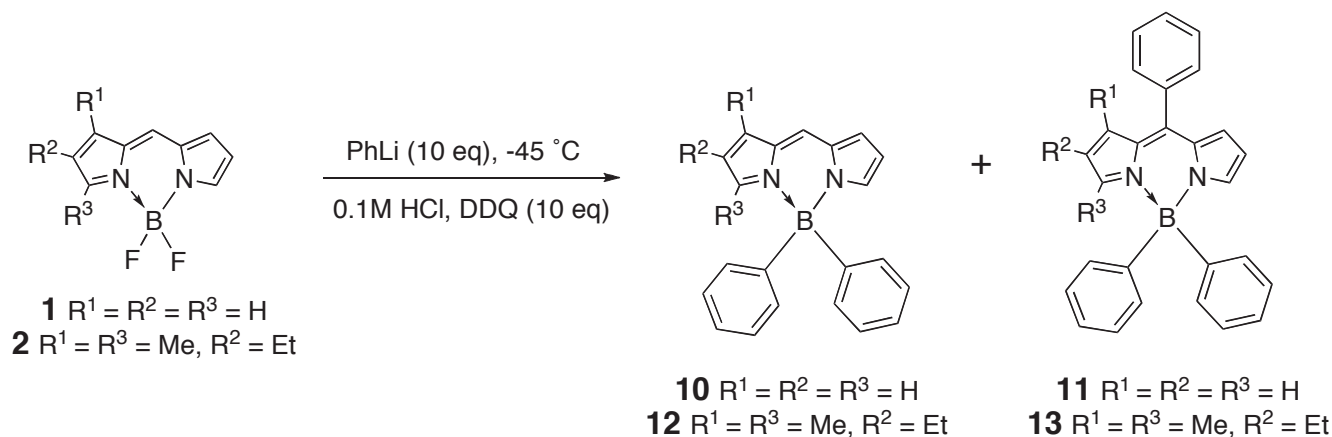
We also investigated the *meso*-arylation of the *F*-BODIPYs **1**, **2** and **3**. We have previously reported that when the *F*-BODIPY **3** is treated phenyllithium the *meso*-phenyl product was not produced; however, the *B*-diphenyl *C*-BODIPY **8** was isolated in 22% yield.<sup>28</sup> Interestingly, when the reaction with 10 eq phenyllithium was conducted at room temperature, in the absence of DDQ, a mixture of the *C*-BODIPY **8** and the *C*-BODIPY **9**, with the desired *meso*-phenyl substituent, were generated as shown in Scheme 3. Presumably the substitution at boron is accompanied/followed by nucleophilic attack and then elimination at the *meso*-position.



**Scheme 3.** *meso*-Arylation of *F*-BODIPY **2** at Room Temperature

Integration of the corresponding peaks in the  $^1\text{H}$  NMR spectrum, from the reaction carried out at room temperature, showed BODIPY **8** and BODIPY **9** to be isolated in a 0.2:1.0 ratio. The absence of *F*-BODIPY material in the reaction mixture indicates that nucleophilic attack at the boron centre appears to occur preferentially to nucleophilic attack at the *meso*-position in the case of the aryllithium reagent. This reactivity has been exploited to synthesize *C*-BODIPYs from *meso*-substituted *F*-BODIPYs although the products are generally isolated in yields below 50%.<sup>30</sup> The absence of DDQ in this reaction also indicates that this transformation may be occurring through an alternate mechanism than the analogous *meso*-alkylation. Color observations are not useful in this case because the phenyllithium reagent itself is a red color and obscures any loss of color due to the dipyrinato construct.

When *F*-BODIPY **1** and *F*-BODIPY **2** were treated with phenyllithium, mixtures of *meso*-unsubstituted *C*-BODIPYs and *meso*-phenyl *C*-BODIPYs were isolated in yields of 10% and 6%, respectively (Scheme 4).



**Scheme 4.** *meso*-Arylation of *F*-BODIPYs **1** and **2**

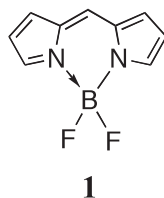
The reaction of the *F*-BODIPY **1** with phenyllithium resulted in two products, which could not be fully characterized. The mass spectrum (ESI<sup>+</sup>) the mixture indicated the formation of a mixture of *C*-BODIPY **10** and *C*-BODIPY **11**, as shown in Scheme 4. A comparison of the relative integrations of the pyrrolic hydrogen peaks in the proton NMR spectrum of the product indicated that *C*-BODIPY **10** and *C*-BODIPY **11** were present in a 1 to 0.6 ratio. The reaction of *F*-BODIPY **2** with phenyllithium gave the *C*-BODIPY **12** and the *C*-BODIPY **13** in a 1 to 0.7 ratio. Under the same conditions, the *meso*-arylated *C*-BODIPY **9** could not be isolated. This indicates that steric factors play a role in *meso*-arylation, with low temperature *meso*-arylation being favored when the *meso*-position is not blocked by nearby substituents; however, *B*-arylation is favored over *meso*-arylation in all cases when using phenyllithium. To conclude, as the interest in and possible applications of BODIPYs grows, methods for the direct modification of *F*-BODIPYs will be needed. In order to investigate the *meso*-modification of *F*-BODIPYs we optimized a reported synthesis<sup>24,25</sup> of the totally unsubstituted *F*-BODIPY such that **1** can now be

routinely isolated in 20-30% yield. We have also developed a synthetically viable, alternative method for the production of *meso*-butylated *F*-BODIPYs by exploiting the nucleophilic attack of *n*-butyllithium at the *meso*-position of *F*-BODIPYs. Expansion of this methodology to other alkyllithium reagents is currently under investigation. *meso*-Arylation, using the same method, was not successful as nucleophilic attack at the boron centre was more favorable to nucleophilic attack at the *meso*-position and mixtures of products were isolated.

## EXPERIMENTAL

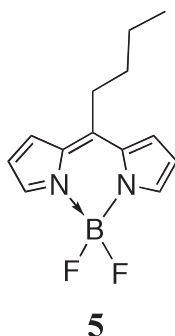
All  $^1\text{H}$  NMR (500 MHz),  $^{13}\text{C}$  NMR (125 MHz), and  $^{11}\text{B}$  NMR (160 MHz) spectra were recorded using a Bruker Avance AV-500 spectrometer.<sup>31</sup> Chemical shifts are expressed in parts per million (ppm) using the solvent signal [ $\text{CDCl}_3$  ( $^1\text{H}$  7.26 ppm;  $^{13}\text{C}$  71.16 ppm)] as an internal reference for  $^1\text{H}$  and  $^{13}\text{C}$  and  $\text{BF}_3\cdot\text{OEt}_2$  as an external reference for  $^{11}\text{B}$ . Splitting patterns are indicated as follows: br, broad; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. All coupling constants (*J*) are reported in Hertz (Hz). Mass spectra were obtained using ion trap time-of-flight (ESI) instruments. Column chromatography was performed using 230-400 mesh ultra pure silica or 150 mesh Brockmann III activated, basic aluminum oxide, as indicated. Spectral data for compounds **1**,<sup>23-25</sup> **2**,<sup>3,22,28,31</sup> **3**,<sup>22,28</sup> **4**,<sup>27</sup> **6**,<sup>28</sup> **7**,<sup>28</sup> and **8**<sup>28</sup> have been previously reported in the literature.

### 4-Bora-3a,4a-diaza-s-indacene (1)

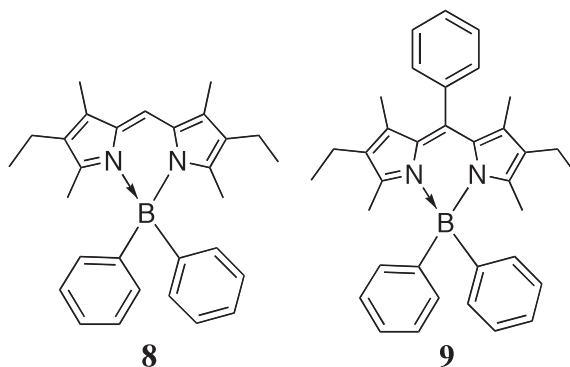


Following a modified literature procedure,<sup>25</sup> a suspension of 2,3,5,6-tetrachloro-*p*-benzoquinone (174 mg, 0.71 mmol) in DCM (7.5 mL) under a nitrogen atmosphere was added drop-wise to a stirred solution of di(1*H*-pyrrol-2-yl)methane<sup>27</sup> (100 mg, 0.68 mmol) in DCM (7.5 mL) at -80 °C under nitrogen. Once the addition was complete, the solution was stirred at -80 °C for 1 h. Diisopropylethylamine (0.71 mL, 4.08 mmol) was added drop-wise to the reaction mixture followed by  $\text{BF}_3\cdot\text{OEt}_2$  (0.68 mL, 6.12 mmol) and the reaction mixture was stirred for 3 h while warming to -30 °C. The reaction mixture was filtered through celite and the solvent was removed *in vacuo*. The crude solid was purified over silica gel eluting with 50% DCM in hexanes. The combined fractions were concentrated *in vacuo* and then purified over silica gel eluting with 15% ethyl acetate in hexanes and the combined fractions were then concentrated *in vacuo* to give **1** as a red solid (30 mg, 23%).  $\delta_{\text{H}}$  (500 MHz,  $\text{CDCl}_3$ ) 7.90 (s, 2H), 7.42 (s, 1H), 7.16 (d, *J* = 4.0, 2H), 6.55 (d, *J* = 4.5, 2H);  $\delta_{\text{C}}$  (125 MHz,  $\text{CDCl}_3$ ) 145.2, 135.0, 131.5 (q, *J* = 2), 131.4, 118.9 (q, *J* = 2);  $\delta_{\text{B}}$  (160 MHz,  $\text{CDCl}_3$ ) 0.15 (t, *J* = 30); *m/z* ESI<sup>+</sup> found 215.0564 [ $\text{M}+\text{Na}$ ]<sup>+</sup> calculated for  $\text{C}_9\text{H}_7\text{BF}_2\text{N}_2\text{Na}$  215.0568.  $^{13}\text{C}$  NMR data matches that previously reported.<sup>23-25</sup>



**8-Butyl-4-bora-3a,4a-diaza-s-indacene (5)**

*n*-Butyllithium (1.9 mL of a 1.6 M solution in hexanes, 3.1 mmol) was slowly added under a nitrogen atmosphere to a round-bottom flask containing a solution of **1** (60 mg, 0.31 mmol) in THF (10 mL) at -78 °C. The solution was stirred while slowly warming to -30 °C. At -30 °C, methanol (2 mL) was added drop-wise followed by a 0.1 M aqueous solution of HCl (2 mL) and the mixture was stirred for 10 min. The mixture was removed from the cooling bath and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (541 mg, 2.4 mmol) was added and the reaction mixture was stirred for 3 h at room temperature. The reaction mixture was diluted with DCM (75 mL) and water (150 mL). The layers were separated and the organic layer was washed with water (3 x 150 mL). The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed *in vacuo*. The crude solid was dissolved in DCM and the solution was filtered through a pad of silica eluting with DCM. Purification over silica gel eluting with 50% DCM in hexanes gave **5** as an orange solid (20 mg, 26%). δ<sub>H</sub> (500 MHz, CDCl<sub>3</sub>) 7.85 (s, 2H), 7.27-7.28 (m, 2H), 6.53-6.54 (m, 2H), 2.95-2.92 (m, 2H), 1.81-1.75 (m, 2H), 1.47 (sextet, *J* = 7.5, 2H), 0.97 (t, *J* = 7.5, 3H); δ<sub>C</sub> (125 MHz, CDCl<sub>3</sub>) 151.4, 143.4, 135.3, 127.9, 118.1, 36.1, 31.3, 23.3, 13.9; δ<sub>B</sub> (160 MHz, CDCl<sub>3</sub>) 0.02 (t, *J* = 30); *m/z* ESI<sup>+</sup> found 271.1178 [M+Na]<sup>+</sup> calculated for C<sub>13</sub>H<sub>15</sub>BF<sub>2</sub>N<sub>2</sub>Na 271.1194.

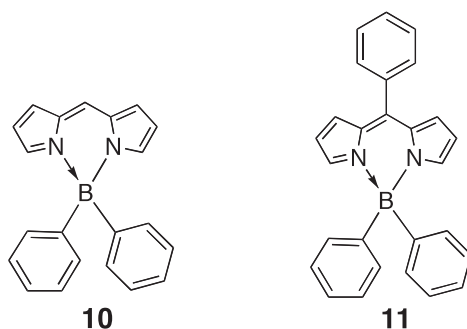
**4,4-Diphenyl-1,3,5,7-tetramethyl-2,6-diethyl-8-*H*-4-bora-3a,4a-diaza-s-indacene (8) and 4,4-diphenyl-1,3,5,7-tetramethyl-2,6-diethyl-8-phenyl-4-bora-3a,4a-diaza-s-indacene (9)**

Phenyllithium (4.6 mL of a 1.8 M solution in di-*n*-butyl ether, 8.2 mmol) was slowly added under a nitrogen atmosphere to a round-bottom flask containing a solution of **3** (250 mg, 0.82 mmol) in diethyl ether (15 mL) at 25 °C. The solution was allowed to stir at room temperature for 18 h. Methanol (5 mL)



was added drop-wise and the reaction mixture was concentrated *in vacuo* to give an orange oil. The crude oil was purified over silica gel eluting with 4% EtOAc in hexanes to give a mixture of **8** and **9** as an orange solid (28 mg **8**, 7%, and 142 mg **9**, 29%).  $\delta_{\text{H}}$  (500 MHz,  $\text{CDCl}_3$ ) 7.49-7.47 (m, 3H, **9**), 7.42-7.40 (m, 4H, **9**), 7.36-7.34 (m, 2H, **9**), 7.30-7.16 (m, 8.5H, **8** and **9**), 7.13 (s, 0.20H, **8**), 2.33 (q,  $J = 7.0$ , 0.84H, **8**), 2.22 (m,  $J = 7$ , 5H, **8** and **9**), 1.77-1.76 (m, 6.7H, **8** and **9**), 1.31 (s, 6H, **9**), 0.99 (t,  $J = 7$ , 1.3H, **8**), 0.90 (t,  $J = 7$ , 6H, **9**);  $\delta_{\text{C}}$  (125 MHz,  $\text{CDCl}_3$ ) 154.0, 153.1, 140.8, 137.1, 135.4, 134.1, 133.9, 133.8, 132.9, 131.6, 130.9, 129.0, 128.9, 128.5, 127.28, 127.26, 125.7, 125.6, 119.5, 19.5, 17.7, 17.5, 14.9, 14.7, 14.5, 12.1, 9.5;  $\delta_{\text{B}}$  (160 MHz,  $\text{CDCl}_3$ ) -0.34 (broad s);  $m/z$  ESI<sup>+</sup>  $[\text{M}+\text{Na}]^+$  443.3, 519.3. Although this mixture could not be separated, assignments are based on those of a pure sample of the C-BODIPY **8**.<sup>28</sup>

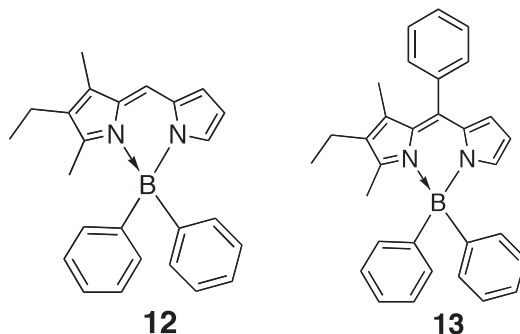
**4,4-Diphenyl-8H-4-bora-3a,4a-diaza-s-indacene (10) and 4,4-diphenyl-8-phenyl-4-bora-3a,4a-diaza-s-indacene (11)**



Phenyllithium (0.65 mL of a 1.8 M solution in di-*n*-butyl ether, 1.2 mmol) was slowly added under a nitrogen atmosphere to a round-bottom flask containing a solution of **1** (56 mg, 0.29 mmol) in THF (11 mL) at  $-45\text{ }^{\circ}\text{C}$ . The solution was stirred for 30 min and then the cooling bath was removed and the mixture was stirred at room temperature for 1 h. A 0.1 M aqueous solution of HCl (4 mL) was added drop-wise and the reaction mixture was stirred for 5 min. 2,3-Dichloro-5,6-dicyano-*p*-benzoquinone (658 mg, 10 mmol) was added and the reaction mixture was stirred for 1 h at room temperature. The reaction mixture was filtered through a pad of Brockman III neutral alumina, dried over  $\text{Na}_2\text{SO}_4$ , and concentrated *in vacuo* to give a brown oil. The crude oil was filtered through silica gel eluting with 15% EtOAc in hexanes and the combined fractions were concentrated *in vacuo* to give an orange solid. Purification over silica using a gradient of 1% EtOAc in hexanes to 3% EtOAc in hexanes, and concentration *in vacuo* gave a mixture of **10** (3.4 mg, 4 %) and **11** (2.1 mg, 2%) as an orange solid.  $\delta_{\text{H}}$  (500 MHz,  $\text{CDCl}_3$ ) 7.55-7.54 (m, 1H), 7.52-7.51 (m, 0.5H), 7.50-7.49 (m, 0.5H), 7.40-7.39 (m, 0.5H), 7.31 (d,  $J = 4$ , 0.50H), 7.25-7.17 (m, 4H), 7.13-7.11 (m, 2H), 7.07-7.01 (m, 6H), 6.91-6.87 (m, 2H), 6.59 (d,  $J = 4.5$ , 0.5H), 6.53 (d of d,  $J = 2.0, 4.0$ , 1H), 6.40 (d of d,  $J = 1.5, 4.0$ , 0.5H);  $\delta_{\text{C}}$  (125 MHz,  $\text{CDCl}_3$ ) 145.9, 144.5, 136.9, 135.0, 132.8, 132.4, 131.4, 130.6, 129.8, 129.3, 129.2, 128.4, 128.1, 127.6, 127.2, 127.1, 126.4, 126.0, 125.3, 121.2, 117.92, 117.86;  $\delta_{\text{B}}$  (160 MHz,  $\text{CDCl}_3$ ) 0.80 (broad s);  $m/z$  ESI<sup>+</sup> found 331.1375  $[\text{M}+\text{Na}]^+$

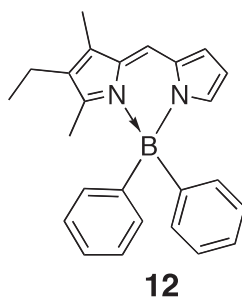
calculated for  $C_{21}H_{17}BN_2Na$  331.1382 (**10**) and found 407.1675  $[M+Na]^+$  calculated for  $C_{27}H_{21}BN_2Na$  407.1695 (**11**).

**4,4-Diphenyl-1,3-dimethyl-2-ethyl-8H-4-bora-3a,4a-diaza-s-indacene (12) and 4,4-diphenyl-1,3-dimethyl-2-ethyl-8-phenyl-4-bora-3a,4a-diaza-s-indacene (13)**



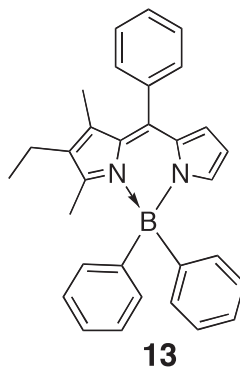
Phenyllithium (2.2 mL of a 1.8 M solution in di-*n*-butyl ether, 4.0 mmol) was slowly added under a nitrogen atmosphere to a round-bottom flask containing a solution of **2** (100 mg, 0.40 mmol) in THF (15 mL) at  $-45\text{ }^{\circ}\text{C}$ . The solution was stirred for 30 min and then the cooling bath was removed and the mixture was stirred at room temperature for 1 h. A 0.1 M aqueous solution of HCl (5 mL) was added drop-wise and the reaction mixture was stirred for 5 min. 2,3-Dichloro-5,6-dicyano-*p*-benzoquinone (908 mg, 10 mmol) was added and the reaction mixture was stirred for 1 h at room temperature. The reaction mixture was filtered through a pad of Brockmann III neutral alumina, dried over  $Na_2SO_4$ , and concentrated *in vacuo* to give a brown oil. The crude oil was purified over silica gel eluting with 2% EtOAc in hexanes to give a mixture of **12** and **13** as a bright orange solid. The mixture was purified over silica gel eluting with a gradient of hexanes to 2% EtOAc in hexanes. Concentration *in vacuo* gave a mixture of **12** and **13** as a bright orange solid (14 mg **12**, 10% and 10 mg **13**, 6%). The crude mixture of **12** and **13** was again purified over silica eluting with a gradient of hexanes to 2% EtOAc in hexanes. Concentration of the pure fractions *in vacuo* gave **12** as an orange solid and **13** as an orange solid.

**4,4-Diphenyl-1,3-dimethyl-2-ethyl-8 H-4-bora-3a,4a-diaza-s-indacene (12)**



$\delta_{\text{H}}$  (500 MHz,  $\text{CDCl}_3$ ) 7.29 (s, 1H), 7.23-7.14 (m, 11H), 6.89 (d of d,  $J = 1.0, 4.0$ , 1H), 6.31 (d of d,  $J = 1.0, 4.0$ , 1H), 2.41 (q,  $J = 7.5$ , 2H), 2.26 (s, 3H), 1.84 (s, 3H), 1.06 (t,  $J = 7.5$ , 3H);  $\delta_{\text{C}}$  (125 MHz,  $\text{CDCl}_3$ ) 139.6, 138.0, 136.1, 134.2, 133.3, 132.0, 127.4, 126.0, 124.3, 123.6, 114.9, 105.6, 17.7, 15.0, 14.7, 9.6 (1 C missing);  $\delta_{\text{B}}$  (160 MHz,  $\text{CDCl}_3$ ) 0.19 (broad s);  $m/z$  ESI<sup>+</sup> found 387.1985  $[\text{M}+\text{Na}]^+$  calculated for  $\text{C}_{25}\text{H}_{25}\text{BN}_2\text{Na}$  387.2003.

#### 4,4-Diphenyl-1,3-dimethyl-2-ethyl-8-phenyl-4-bora-3a,4a-diaza-s-indacene (13)



$\delta_{\text{H}}$  (500 MHz,  $\text{CDCl}_3$ ) 7.48-7.46 (m, 3H), 7.39-7.37 (m, 2H), 7.28-7.23 (m, 8H, overlaps with  $\text{CHCl}_3$  solvent signal), 7.21-7.17 (m, 3H), 6.36 (d of d,  $J = 1.0, 4.0$ , 1H), 6.24 (d of d,  $J = 1.0, 4.0$ , 1H), 2.34 (q,  $J = 7.5$ , 2H), 1.85 (s, 3H), 1.50 (s, 3H), 1.00 (t,  $J = 7.5$ , 3H);  $\delta_{\text{C}}$  (125 MHz,  $\text{CDCl}_3$ ) 160.3, 142.4, 139.2, 139.0, 135.6, 135.4, 134.2, 133.5, 133.3, 129.2, 128.9, 128.3, 127.4, 125.9, 124.1, 114.6, 17.6, 15.3, 14.7, 12.7 (1 C missing);  $\delta_{\text{B}}$  (160 MHz,  $\text{CDCl}_3$ ) - 0.09 (broad s);  $m/z$  ESI<sup>+</sup> found 463.2288  $[\text{M}+\text{Na}]^+$  calculated for  $\text{C}_{31}\text{H}_{29}\text{BN}_2\text{Na}$  463.2316.

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