Conversion of *F*-BODIPYs to *Cl*-BODIPYs: Enhancing the Reactivity of *F*-BODIPYs

Travis Lundrigan and Alison Thompson*

Department of Chemistry, Dalhousie University, P.O. Box 15000, Halifax, NS, B3H 4R2, Canada

Alison.Thompson@dal.ca

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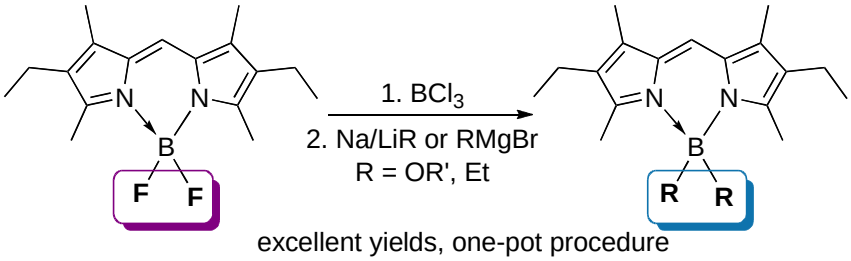


A new method for the synthesis of *Cl*-BODIPYs from *F*-BODIPYs is reported, merely requiring treatment of the *F*-BODIPY with boron trichloride. *Cl*-BODIPYs are exploited as synthetic intermediates generated in situ for the overall conversion of *F*-BODIPYs to *O*- and *C*-BODIPYs in high overall yields using a mild one-pot procedure. This route enables *F*-BODIPYs to be transformed into derivatives that are not accessible via the direct route, as demonstrated via the use of 1,3-propanediol.

Compounds containing the 4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (*F*-BODIPY) framework *F*-BODIPYs[1-3] are known for their high thermal and photochemical stability, chemical robustness, and chemically tunable fluorescence properties: they have wide application including as dyes, as probes or sensitizers in biological systems, and as materials for incorporation into devices.[4-6] However, studies in recent years have shown that the *F*-BODIPY unit is more modifiable, and not as chemically robust, as

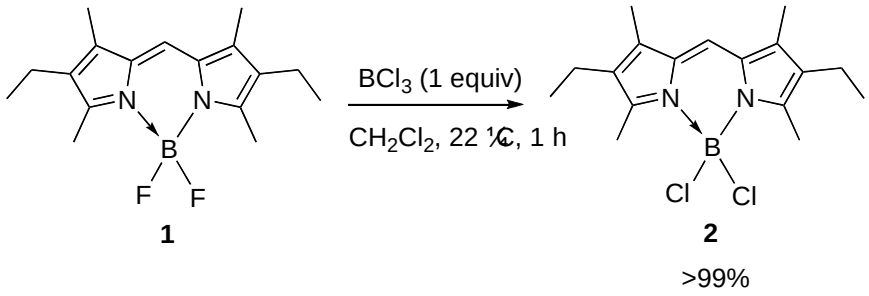
traditionally believed. Indeed, reaction under basic conditions leads to the removal of the BF_2 moiety, liberating the corresponding free-base dipyrrins.[7,8] Furthermore, treatment with acids of various strengths results in decomposition of *F*-BODIPYs.[9] Nucleophilic substitution of *F*-BODIPYs, usually under forcing conditions, has provided compounds bearing substituents other than fluorine at the boron center of the BODIPY core: this topic is under wide exploration,[10-13] with target compounds including aryl-, alkyl-, alkynyl-, alkoxy- and aryloxy-BODIPYs with exotic spectroscopic properties.

We have recently reported the synthesis of *Cl*-BODIPYs[14] in high yields through the treatment of free-base dipyrrins with BCl_3. Importantly, *Cl*-BODIPYs offer significant advantages over *F*-BODIPYs in terms of their utility as synthetic intermediates, courtesy of facile substitution at the boron center. Indeed, the weaker B–Cl bond strength makes the B–Cl bonds of *Cl*-BODIPYs substantially more labile than the corresponding B–F bonds of *F*-BODIPYs. Compared to *F*-BODIPYs, substitutions at the boron centre of *Cl*-BODIPYs proceed under milder conditions and require shorter reaction times to give high yielding BODIPY analogues that have been previously somewhat challenging to prepare from *F*-BODIPYs.[7]

Our previous work with *Cl*-BODIPYs was grounded upon its reliance on the dipyrrin free-base[15,16] as starting material.[14] Many dipyrrins are not generally isolated in this free-base form due to instability, or as a consequence of protracted strategies used to prepare them. Consequently dipyrrins are often isolated as their HBr salts which are, unfortunately, unreactive with BCl_3. Alternative strategies to the dipyrrinato construct obviate the need to isolate dipyrrin free-bases, and it generates *F*-BODIPYs by trapping the free-base dipyrrins *in-situ* with $BF_3{\bullet}OEt_2$.[2] In these examples, an excess of $BF_3{\bullet}OEt_2$ and NEt_3 is required for *F*-BODIPY formation,[17] and this can result in the formation of a $BF_3{\bullet}NEt_3$ adduct that complicates purification, particularly on larger scales. These dipyrrins cannot be trapped as their *Cl*-BODIPYs since the overall procedure generally requires aqueous extractions and purification via chromatography, conditions that the *Cl*-BODIPY does not survive. Cognizant of these

synthetic challenges, we sought an alternate route for the synthesis of *Cl*-BODIPYs. Our ultimate goal was to determine facile substitution at the boron center of this structural unit so as to reveal a simple, mild route to a range of R-BODIPYs.

As the *F*-BODIPY construct is readily available both synthetically and commercially,[1,17] we investigated this construct as a source of dipyrrinato units for the synthesis of *Cl*-BODIPYs. In this work we demonstrate a new transformation involving the boron atom of *F*-BODIPYs. Indeed, the *F*-BODIPY **1** was stirred in anhydrous CH_2Cl_2 at room temperature and treated with one equiv BCl_3 (Scheme 1). The initial solution was bright orange with a green fluorescent hue: upon treatment with BCl_3 the solution became deep purple in colour. The reaction mixture was stirred for 1 h and then filtered through Celite. The resulting solution was concentrated *in vacuo* to give a quantitative yield of complex **2** as a pure solid, as identified by comparison of characterization data with the known compound.[14]



Scheme 1. Synthesis of *Cl*-BODIPY (**2**) from *F*-BODIPY (**1**)

The reaction occurred very rapidly, and attempts to monitor the reaction *via* ^{11}B NMR revealed that as soon as the BCl_3 was introduced to the solution of *F*-BODIPY, the *Cl*-BODIPY formed immediately (< 2 mins, the time it took to insert the sample into the NMR spectrometer and begin acquiring data). Consequently, the reaction was performed in an NMR tube using various stoichiometries of BCl_3 to enable the conversion of the *F*-BODIPY to the *Cl*-BODIPY to be monitored using ^{11}B resonances. As such, under inert atmosphere a solution of *F*-BODIPY **1** in CD_2Cl_2 was

placed in an NMR tube, which was then sealed with a septum. Aliquots of BCl_3 were added through the septum, as a 1.0 M solution in hexanes, and the sample was quickly shaken to ensure efficient mixing before NMR spectra were acquired. In each case, ^{11}B NMR data were acquired within 2 mins of the BCl_3 addition. The results are compiled as Figure 1. The starting material *F*-BODIPY (**1**) is represented as a triplet due to B–F coupling. After 0.5 equiv BCl_3 had been added, the intensity of the triplet due to the *F*-BODIPY decreased and a singlet corresponding to the *Cl*-BODIPY appeared: integration of the two signals revealed the two species to be present in essentially equal amounts, as expected after the addition of 0.5 equiv BCl_3. Upon the addition of 1.0 equiv BCl_3 complete conversion to the *Cl*-BODIPY was observed, with only the singlet apparent in the ^{11}B NMR spectrum.

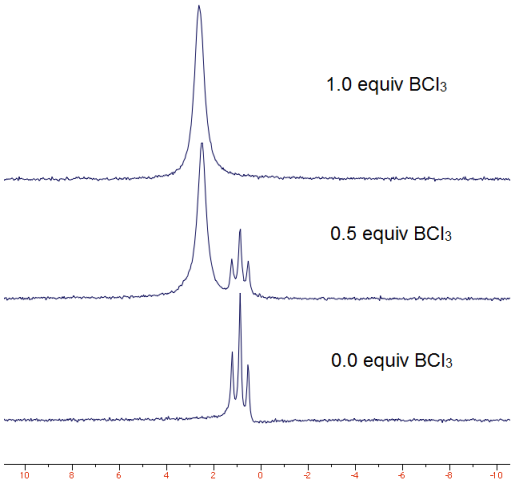
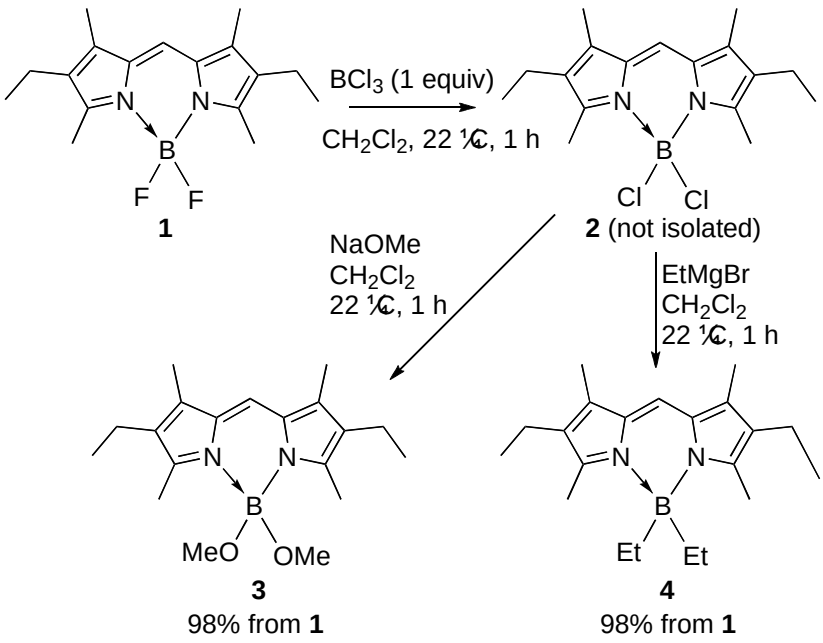


Figure 1. ^{11}B NMR Stack-Plot of *Cl*-BODIPY Formation. Bottom = *F*-BODIPY **1**; middle = *F*-BODIPY **1** and *Cl*-BODIPY **2** both present after the addition of 0.5 equiv BCl_3; top = only *Cl*-BODIPY **2** present after the addition of 1.0 equiv BCl_3.

Having successfully shown that the *Cl*-BODIPY **2** can easily be generated from its analogous *F*-BODIPY, we examined the utility of the *Cl*-BODIPY as a synthetic intermediate within a one-pot procedure. Knowing that boron substitutions of the *Cl*-BODIPY **2** occur under mild conditions, *F*-BODIPY **1** was treated with 1.0 equiv of BCl_3 in CH_2Cl_2 (Scheme 2). After 1 h solid NaOMe was

added to the solution under inert conditions and the reaction mixture was stirred for an hour. The solution was then washed with water and extracted with CH_2Cl_2. The organic layer was dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The *O*-BODIPY **3** was thus isolated in a 98% isolated yield from **1**. It should be noted that to convert the *F*-BODIPY **1** directly to the *O*-BODIPY **3**, the reaction requires elevated temperatures, typically reflux, and reaction times reaching 18 h:[7,12] when the *F*-BODIPY is treated with NaOMe at room temperature, only trace product is observed, supporting our discovery that the *Cl*-BODIPY intermediate is crucial to allow substitution at the boron center to proceed at room temperature within a short time-frame. The *C*-BODIPY **4** was also synthesized from *F*-BODIPY **1**, via the *Cl*-BODIPY intermediate. The initial step involving *Cl*-BODIPY formation was carried out in the same fashion, and the solution was then treated with EtMgBr, upon which the reaction mixture became bright orange rather than the dark purple colour of the *Cl*-BODIPY that had been formed in situ. After an hour the reaction mixture was washed with water and brine, and extracted with CH_2Cl_2. The organic layer was dried over anhydrous Na_2SO_4 and the resulting solution concentrated *in vacuo* to give the *C*-BODIPY **4** in a 98% isolated yield from **1**. Although treatment of *F*-BODIPY **1** with EtMgBr at room temperature also results in the formation of **4**, the yield is 67% compared to the 98% when using the *Cl*-BODIPY intermediate. Furthermore, proceeding via the *Cl*-BODIPY intermediate results in cleaner reactions: for example column chromatography is required to isolate/purify the *C*-BODIPY **4** prepared directly from the *F*-BODIPY at room temperature, but no such procedure is required after proceeding via the *Cl*-BODIPY.

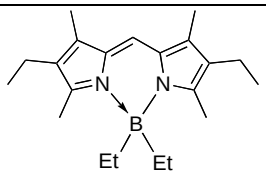
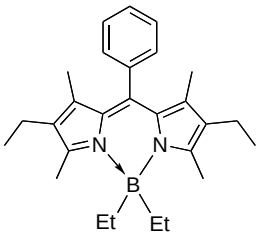
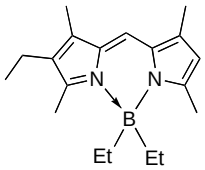
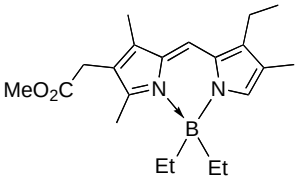
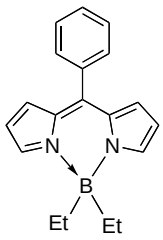


Scheme 2. Synthesis of *O*-BODIPY (**3**) and *C*-BODIPY (**4**) from *F*-BODIPY (**1**) using a *Cl*-BODIPY intermediate generated in situ using *F*-BODIPY **1**

To demonstrate the utility of this one-pot procedure, we expanded the scope of the dipyrrin ligands used (Table 1). Using a variety of dipyrrinato units with various substitutions around the pyrrolic rings as well as substitutions at the meso position we obtained high yields throughout. Compounds **4**-**6** (Table 1, entries 1-3) contain alkyl substituents around the pyrrolic rings, with both meso-H and meso-Ph substituents: reaction of the Grignard reagent at the meso position was not observed, and instead selective reaction at the boron centre occurred.[7,18] Compound **7** (Table 1, entry 4) contains a methyl alkanoate bound to one of the heterocycles: product(s) from the reaction of the Grignard reagent with the ester functional group were not isolated, although the yield for the preparation of **7** was only moderate, and the reaction mixture required filtration through a silica plug for pure **7** to be obtained. Compound **8** (Table 1, Entry 5) is completely unsubstituted on the pyrrolic rings, containing only a meso-Ph group, and was chosen to demonstrate the preferential reactivity of the Grignard reagent for substitution at boron as opposed to addition to the unsubstituted positions of the pyrrolic rings. *C*-BODIPYs were thus prepared from *F*-BODIPYs in one pot via *Cl*-BODIPYs

intermediates, and in high isolated yields. These yields are significantly higher than those typical for the direct derivatization of *F*-BODIPYs, demonstrating the overall efficiency of this new procedure.

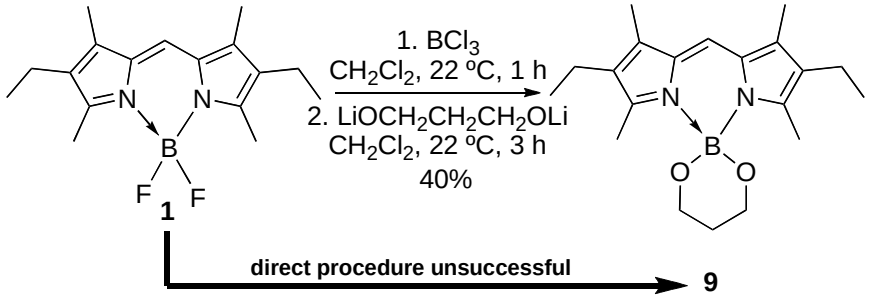
Table 1. Synthesis of *C*-BODIPYs from *F*-BODIPYs using *Cl*-BODIPY intermediates formed *in-situ*

entry	*C*-BODIPY product	yield (%)[a]
1	 **4**	98
2	 **5**	97
3	 **6**	99
4	 **7**	75
5	 **8**	99

[a]isolated yields

To further demonstrate that the advantageous use of *Cl*-BODIPYs as in situ intermediates we selected a transformation that is unsuccessful for *F*-BODIPYs. The reaction of a meso-aryl *F*-BODIPY with alcohols is ameliorated in the presence of $AlCl_3$: the reaction is postulated to proceed via in situ formation of a chelate involving B–F–Al coordination.[19] Such Lewis acid activation of the B–F bonds allowed a range of *O*-BODIPYs to be prepared in low-good yields: the reactions did not occur in the absence of $AlCl_3$. The reactions proceeded well with alkyl and aryl alcohols, as well as several diols to provide cyclic analogues. However, attempted substitution of the fluoro substitituents with 1,3-propanediol did not provide the corresponding cyclic derivative at boron. We thus probed the utility of our method involving in situ generation of *Cl*-BODIPYs, for the overall conversion of *F*-BODIPYs using 1,3-propanediol.

We thus reacted *F*-BODIPY **1** with BCl_3, to form **2** in situ. The lithium dienolate of 1,3-propanediol was then added in a stoichiometric amount, and the desired cyclic *O*-BODIPY **9** was subsequently isolated in 40% yield (Scheme 3) for the two-step, one-pot transformation: reaction of *Cl*-BODIPY **2** with 1,3-propanediol was unfruitful, and so the dienolate was used in the one-pot procedure. Attempted reaction of *F*-BODIPY **1** with the dienolate was unsuccessful, demonstrating the advantage of proceeding via the *Cl*-BODIPY using our one-pot procedure.



Scheme 3. Preparation of cyclic *O*-BODIPY **9**.

A new synthetic method has been developed for the quantitative conversion of *F*-BODIPYs into the recently discovered *Cl*-BODIPYs. We have also demonstrated how the *Cl*-BODIPY can be used as

a synthetic intermediate in a one-pot procedure for the formation of BODIPY derivatives via substitution at the boron center. Taking advantage of the increased reactivity of the *Cl*-BODIPY over the *F*-BODIPY, we have successfully synthesized *O*-BODIPYs and *C*-BODIPYs from the corresponding *F*-BODIPYs, and have employed *F*-BODIPY starting materials with various substitutions around the dipyrrinato backbone. The one-pot conversion of *F*-BODIPYs to other BODIPYs was accomplished in excellent yields using mild conditions and shorter reaction times than the traditional methods reported for boron substitutions of *F*-BODIPYs. It is anticipated that this new one-pot method, via *Cl*-BODIPYs, will have widespread utility in the facile synthesis of various BODIPYs from *F*-BODIPYs, compounds that are routinely available commercially and synthetically.

Experimental Section

1,3,5,7-Tetramethyl-2,6-diethyl-8-*H*-4,4'-dichloro-bora-3a,4a-diaza-*s*-indacene (2)[14]

F-BODIPY **1**[17] (50 mg) was treated with 1 equiv BCl_3 in anhydrous CH_2Cl_2 and the reaction mixture was stirred for 1 h. The reaction mixture was filtered over Celite and the solution was concentrated in vacuo to give the title compound **2** (55 mg, >99%). δ_H (500 MHz, THF-d_8) 7.34 (1H, s), 2.69 (6H, s), 2.43 (4H, q, J = 7.6), 2.21 (6H, s), 1.07 (6H, t, J = 7.6); δ_C (125 MHz, THF-d_8) 157.0, 138.3, 133.7, 132.3, 120.3, 18.0, 14.6, 14.4, 9.1; δ_B (160 MHz, THF-d_8) 2.39 (s). NMR data matches that previously reported.[14]

1,3,5,7-Tetramethyl-2,6-diethyl-8-*H*-4,4'-dimethoxy-bora-3a,4a-diaza-*s*-indacene (3)[14]

F-BODIPY **1**[17] (50 mg) was treated with 1 equiv BCl_3 in anhydrous CH_2Cl_2 and the reaction mixture was stirred for 1 h. Solid $NaOCH_3$ (2 equiv) was added to the reaction mixture and stirring was continued for another hour. The mixture was then washed with brine (15 mL) and the organic layer was dried over Na_2SO_4. The solution was then concentrated in vacuo to give the title compound **3** (53 mg, 98%). δ_H (500 MHz, $CDCl_3$) 6.90 (1H, s), 2.84 (6H, s), 2.47 (6H, s), 2.38 (4H, q, J=7.5), 2.17 (6H, s),

1.06 (6H, t, *J*=7.5); δ_C (125 MHz, $CDCl_3$) 154.9, 134.6, 133.8, 131.2, 118.4, 49.3, 17.5, 14.9, 12.3, 9.5; δ_B (160 MHz, $CDCl_3$) 2.66 (s). NMR data matches that previously reported.[14]

General Procedure for the Synthesis of *C*-BODIPYs (GP1)

The *F*-BODIPY (50 mg) was dissolved in anhydrous dichloromethane (10 mL) and 1 equiv BCl_3 was added drop-wise from a 1.0 M solution in anhydrous hexanes. The reaction was stirred for an hour to allow in situ formation of the *Cl*-BODIPY to occur. The *Cl*-BODIPY was then reacted with 2 equiv EtMgBr using a 3.0 M solution in anhydrous diethyl ether. Stirring was continued for another hour. Upon completion of the reaction, the mixture was washed with brine (15 mL) and the organic layer was dried over Na_2SO_4. The solution was then concentrated in vacuo to obtain the BODIPY product.

1,3,5,7-Tetramethyl-2,6-diethyl-8-*H*-4,4'-diethyl-bora-3a,4a-diaza-*s*-indacene (4)[14]

Using **GP1**, compound **4** was synthesized from the corresponding *F*-BODIPY.[17] Bright orange solid (52 mg, 98%). δ_H (500 MHz, $CDCl_3$) 6.99 (1H, s), 2.44-2.39 (10H, m, 2x(CH_3+CH_2)), 2.18 (6H, s), 1.06 (6H, t, *J*=7.6), 0.82 (4H, q, *J*=7.6), 0.31 (6H, t, *J*=7.6); δ_C (125 MHz, $CDCl_3$) 151.1, 132.6, 131.8, 131.1, 119.4, 17.9, 15.0, 13.9, 9.43, 9.40 (one signal obscured); δ_B (160 MHz, $CDCl_3$) 2.50 (s). NMR data matches that previously reported.[14]

1,3,5,7-Tetramethyl-2,6-diethyl-8-phenyl-4,4'-diethyl-bora-3a,4a-diaza-*s*-indacene (5)

Using **GP1**, compound **5** was synthesized from the corresponding *F*-BODIPY.[17] Bright orange solid (52 mg, 97%). δ_H (500 MHz, $CDCl_3$) 7.44 (3H, br app s), 7.29-7.28 (2H, m), 2.44 (6H, s), 2.32 (4H, q, *J*=7.1), 1.25 (6H, s), 0.97 (6H, t, *J*=7.1), 0.87 (4H, q, *J*=7.3), 0.41 (6H, t, *J*=7.0); δ_C (125 MHz, $CDCl_3$) 150.2, 140.9, 137.7, 133.4, 132.4, 131.1, 129.0, 128.8, 128.3, 29.9, 17.6, 15.0, 14.1, 12.0, 9.6; δ_B (160 MHz, $CDCl_3$) 1.85 (s). NMR data matches that previously reported.[14]

1,3,5,7-Tetramethyl-2-ethyl-8-*H*-4,4'-diethyl-bora-3a,4a-diaza-*s*-indacene (6)

Using **GP1**, compound **6** was synthesized from the corresponding *F*-BODIPY.[17] Bright orange solid (53 mg, 99%). δ_H (500 MHz, $CDCl_3$) 7.02 (1H, s), 6.02 (1H, s), 2.42 (8H, 2xCH_3+CH_2), 2.25 (3H, s),

2.19 (3H, s), 1.06 (3H, t, *J*=7.6), 0.81 (4H, qd, *J*=3.2, 7.6), 0.32 (6H, t, *J*=7.6); δ_C (125 MHz, $CDCl_3$) 153.0, 151.4, 135.2, 133.3, 133.1, 133.0, 132.0, 120.1, 118.3, 17.9, 16.3, 14.9, 14.0, 11.3, 9.4, 9.3 (one signal obscured); δ_B (160 MHz, $CDCl_3$) 2.85 (s); Mp 128-130 °C; HRMS (APCI) *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{30}BN_2$ 297.2497; Found 297.2491.

1,3,6-Trimethyl-2-(2-methoxy-2-oxoethyl)-7-ethyl-8-*H*-4,4'-diethyl-bora-3a,4a-diaza-*s*-indacene (7)

Using **GP1**, compound **7** was synthesized from the corresponding *F*-BODIPY.[17] The crude material was filtered through a plug of silica eluting with CH_2Cl_2 to isolate the product. Bright orange solid (40 mg, 75%). δ_H (500 MHz, $CDCl_3$) 7.16 (1H, s), 7.15 (1H, s), 3.67 (3H, s), 3.45 (2H, s), 2.62 (2H, q, *J*=7.6), 2.38 (3H, s), 2.24 (3H, s), 2.07 (3H, s), 1.17 (3H, t, *J*=7.6), 0.84 (2H, dq, *J*=7.4, 14.5), 0.46 (2H, dq, *J*=7.4, 14.6), 0.32 (6H, t, *J*=7.6); δ_C (125 MHz, $CDCl_3$) 171.8, 153.4, 140.8, 139.4, 135.7, 133.4, 132.0, 124.0, 121.74, 121.71, 52.2, 30.6, 18.0, 16.4, 13.6, 10.3, 9.9, 9.0 (one signal obscured); δ_B (160 MHz, $CDCl_3$) 1.83 (s); decomposition >110 ºC °C; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{21}H_{31}BN_2NaO_2$ 377.2371; Found 377.2354.

8-Phenyl-4,4'-diethyl-bora-3a,4a-diaza-*s*-indacene (8)

Using **GP1**, compound **8** was synthesized from the corresponding *F*-BODIPY.[17] Bright orange solid (53 mg, 99%). δ_H (500 MHz, $CDCl_3$) 7.61-7.59 (2H, m), 7.57-7.45 (5H, m), 6.85 (2H, d, *J*=4.3), 6.54 (2H, dd, *J*=1.5, 4.3), 0.67 (4H, q, *J*=7.3), 0.50 (6H, t, *J*=7.3); δ_C (125 MHz, $CDCl_3$) 146.6, 142.1, 135.2, 134.4, 130.5, 130.0, 128.2, 127.3, 117.2, 29.8, 8.9; δ_B (160 MHz, $CDCl_3$) 1.38 (s); Mp 118-120 °C. HRMS (APCI) *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{22}BN_2$ 289.1871; Found 289.1871.

1,3,5,7-Tetramethyl-2,6-diethyl-8-*H*-4,4'-propane-1,3-bis(olate)-bora-3a,4a-diaza-*s*-indacene (9)

F-BODIPY **1**[17] (50 mg) was treated with 1 equiv BCl_3 in anhydrous CH_2Cl_2 and the reaction mixture was stirred for 1 h. A solution of $LiO(CH_2)_3OLi$ (1 equiv) in $CH_2Cl_2$was added to the reaction mixture, and stirring was then continued for another three hours. The mixture was then washed with brine (15

mL) and the organic layer was dried over Na_2SO_4. The solution was then concentrated *in vacuo*. The crude material was purified over silica eluting with 50:50 hexanes:ethyl acetate. The product was isolated as an orange solid (22 mg, 40%). δ_H (500 MHz, $CDCl_3$) 6.90 (1H, s), 4.04 (4H, t, *J*=5.8), 2.54 (6H, s), 2.36 (4H, q, *J*=7.6), 2.12 (6H, s), 1.93 (2H, dt, *J*=5.9, 11.9), 1.02 (6H, t, *J*=7.6); δ_C (125 MHz, $CDCl_3$) 153.7, 136.2, 133.3, 131.0, 119.0 59.9, 28.2, 17.5, 14.9, 13.5, 9.6; δ_B (160 MHz, $CDCl_3$) 1.55 (s); Decomposition > 105 °C. LRMS (ESI+) *m/z*: $[M + H]^+$ 257.2 (deprotected during ionization to give the free-base dipyrrins[17]).

Acknowledgements

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Supporting Information

General experimental procedures and copies of NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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