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Masking and Demasking Strategies for the BF_2−BODIPYs as a Tool for BODIPY Fluorophores

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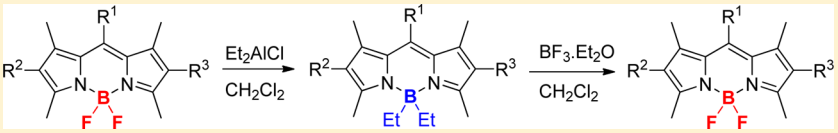
Supporting Information



ABSTRACT: An efficient and chemoselective route for transforming BF_2−BODIPYs to Et_2B-BODIPYs (masking) was developed using Et_2AlCl. The Et groups can be easily replaced with F atoms using $BF_3{\cdot}Et_2O$ in moist CH_2Cl_2 to regenerate the BF_2−BODIPYs (demasking). The masking−demasking strategy is very useful for synthesizing functionalized BODIPYs via nucleophilic and reductive reactions. The masking strategy was used to synthesize a BODIPY dimer by McMurry coupling of a formyl Et_2B−BODIPY, while a new BODIPY with an asymmetrically substituted B-center was synthesized using the demasking strategy.

INTRODUCTION

Due to good thermal and photochemical stabilities as well as tunable fluorescence properties, the dipyrromethene−BF_2 (4,4-difluoro-4-bora-3*a*,4*a*-diaza-s-indacene, BF_2−BODIPY) compounds are attractive precursors for various advanced materials. This aspect is highlighted in several elegant reviews including some recent ones on the chemistry and applications of the BODIPYs.[1] Functionalization of the BODIPY cores is important, as it would enable us to tune their spectral and electronic properties and expand their applications.[1,2] Unfortunately, due to the presence of the BF_2 unit, the BODIPYs are not amenable to nucleophilic and reductive reactions.[3] Masking the BF_2 unit by its conversion to the BR_2 unit (alkyl/alkenyl/alkynyl/aryl groups) can offset this limitation. Substitution of the F atoms at the B-center with alkyl/aryl groups has been used to improve the Stokes shift[4] and photostability,[5a,b] as well as to prevent the undesired micellar behavior of the BODIPYs.[5c−e] This is accomplished by reacting the BF_2−BODIPYs with hard nucleophiles like organo-Mg or organo-Li reagents, as the B−F bond is very strong.[3b,4,6a,b] However, these transformations, usually conducted at room temperature or even under refluxing conditions, proceed in low yields (≤60%).[3b,4] The high reactivity of the organo-Mg/Li reagents leads to degradation of the BODIPYs, accounting for the poor yields. In view of this, recently Thompson et al. developed an elegant synthesis of R_2B−BODIPYs in excellent yields by reacting different Grignard reagents with the BCl_2−BODIPYs, prepared separately or by *in situ* conversion of the BF_2−BODIPYs.[6c,d] However, chemoselective substitution of the F atoms by this route may not be possible with the BODIPYs containing more reactive electrophiles such as aldehyde, ester, etc.[7a,b] In addition, no strategy for reverting the BR_2−BODIPYs to the BF_2−BODIPYs (demasking) is known to date, although Gabbaï et al. reported substitution of the aryl and OH groups in BArF− and BROH−BODIPYs with Bu_4NF and KHF_2, respectively.[7c,d] Against the above backdrop, the aims of the present study were to (i) formulate an efficient method for selective alkylation at the BF_2 unit of the BODIPYs and (ii) convert the BR_2−BODIPYs to the BF_2− or BFR−BODIPYs. In particular, we wanted to use the R group in R_2B−BODIPYs as a masking agent so that they are amenable to nucleophilic and reductive reactions. The other aim was to utilize these protocols for the synthesis of some new BODIPY derivatives.

RESULTS AND DISCUSSION

Conversion of BF_2−BODIPYs to Et_2B−BODIPYs (Masking) and Its Application. It was envisaged that activation of the B−F bond would allow the alkylation at the B-center using soft nucleophiles under mild conditions to realize our objectives. $AlCl_3$ is a known activator of the B−F bond and has been specifically used to synthesize the B-alkoxy and B-aryloxy derivatives.[8a,b] Hence, we attempted the alkylation at the BF_2 moiety with the commercially available Et_2AlCl reagent that is a combination of the required B−F activator and a soft nucleophile. Consistent with our hypothesis, the reaction between Et_2AlCl and the commercially available BODIPY **1a** proceeded cleanly at 25 °C and was complete in 5 min to furnish the Et_2B derivative **3a** exclusively in 90% yield (Scheme 1). Lowering the reaction temperature (0 °C) increased the reaction time (30 min) without affecting the yield of **3a**. In comparison, reaction of **1a** with EtMgBr required longer time

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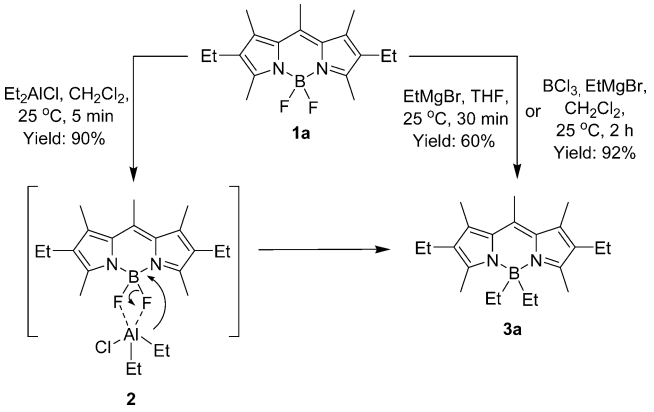
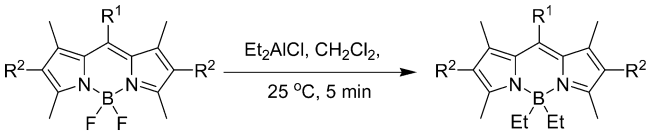
Scheme 1. Comparison of the Synthesis of 3a via Three Different Routes



(30 min) and furnished **3a** in 60% yield only. We also followed Thompson's method[6d] by reacting **1a** with BCl_3 followed by reaction with EtMgBr to obtain **3a** in a comparable yield (92%) as ours. However, as reported earlier,[6d] the reaction took a much longer time (2 h) compared to our new method. The reaction with Et_2AlCl is believed to proceed via the transition state **2** (Scheme 1) where the Al atom of the reagent gets coordinated with the F atoms of the BODIPY to make the B−F bond labile for the subsequent nucleophilic transfer of the Et group to the B center. Because of the less reactivity of the second Et group of Et_2AlCl, an excess (2.2 equiv) of the reagent was required to complete the reaction. Notably, use of 1 equiv of Et_2AlCl also furnished **3a** (40%) without any monoethyl compound. Our intention of synthesizing Et_2B−BODIPYs was merely to mask the BF_2 unit and not to develop a method of preparing R_2B−BODIPYs. Hence, we did not explore the reactions of other $(R/Ar)_2AlCl$ reagents, which are expected to take place in a similar fashion.

Subsequently, we extended the above procedure to a variety of BODIPYs **1b−g** to obtain the corresponding Et_2B−BODIPYs **3b−g** in 80−90% yields (Scheme 2). The reactions

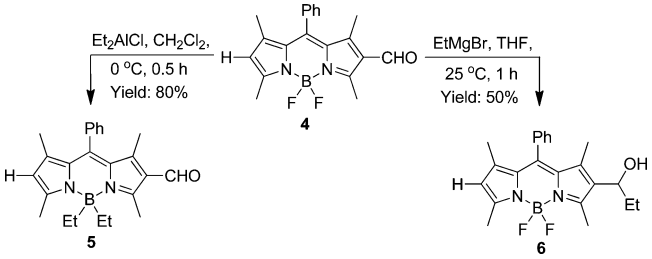
Scheme 2. Synthesis of the Dyes 3b−g from the Corresponding BF_2−BODIPYs



1b. R^1 = Me; R^2 = H
1c. R^1 = Ph; R^2 = H
1d. R^1 = Ph; R^2 = Et
1e. R^1 = *p*-MePh; R^2 = H
1f. R^1 = H; R^2 = Et
1g. R^1 = Me; R^2 = ^{t}Bu

were fast and proceeded without any alkylation at the pyrrole (viz. of **1b**, **1c**, **1e**) or the phenyl rings (viz. of **1c−e**) or at the *meso*-position (viz., of **1f**). This supported the proposed transition state. The chemoselectivity of the protocol was examined with the known 2-formyl BODIPY dye **4**.[6b] In this case also, the reaction of Et_2AlCl occurred exclusively at the B-center at 25 °C to furnish **5** in a moderate yield (40%). Lowering the reaction temperature to 0 °C increased the yield (80%) of **5** significantly (Scheme 3). In comparison, EtMgBr reacted selectively at the aldehyde function (both at 0 or 25

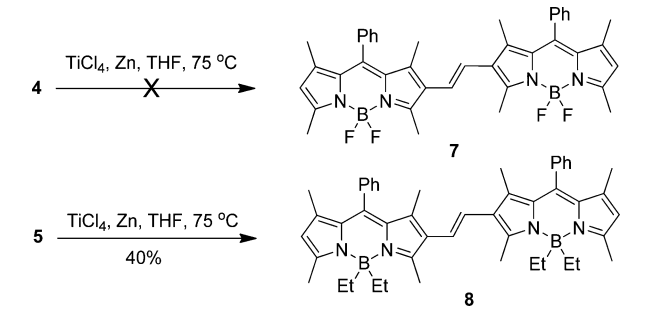
Scheme 3. Comparison of the Chemoselectivities of Et_2AlCl and EtMgBr



°C) to furnish the alcohol **6** in a moderate (50%) yield, without the formation of **5** (Scheme 3).[7a] On the other hand, Thompson's method[6d] (BCl_3/EtMgBr) furnished an unidentified fluorescent compound, but not **5** or **6**.

Next, we applied the new synthetic protocol for the synthesis of a novel BODIPY dimer. These dimers are of recent interest due to their unusual fluorescence and redox properties and other attributes such as charge delocalization, exciton coupling, etc. Previously, BODIPY dimers linked at α,[9] β,[10] and B-center[4b] were reported. The dimers, linked at the β-postiton through a small alkene spacer for an extended conjugation, are promising BODIPY candidates with new properties. Very recently, Bröring et al. have synthesized this type of dimers in low yields (~17%) using alkene metathesis.[11] We realized that the McMurry coupling of a formyl−BODIPY such as **4** may provide access to these molecules. However, due to the incompatibility of the BF_2 moiety under the reductive conditions, the McMurry coupling of **4** using various LVT reagents ($TiCl_4$/Zn, $TiCl_4$/Mg, $TiCl_4$/Li) and solvents[12] led to its complete degradation. Gratifyingly, reductive dimerization of the Et_2B−BODIPY dye **5** with $TiCl_4$/Zn/THF furnished the required compound **8** in a moderate (40%) yield (Scheme 4).

Scheme 4. McMurry Coupling of the Formyl−BODIPYs 4 and 5



Evidently, substitution of the F atoms of **4** increased its stability against the reducing agent, assisting the dimer formation. The *E*-geometry of the alkene moiety of **8** was confirmed from the doublets of the ^{13}C satellites (coupling constant ^3J = 15.0 Hz).

Photophysical Properties. The photophysical properties of the Et_2B−BODIPYs **3a−g** (Table S1, Supporting Information), as well as that (Table 1) of the monomer **5** and dimer **8**, were evaluated in CH_2Cl_2 solvent. The normalized absorption and emission spectra of **5** and **8** are shown in Figure 1. Consistent with the previous report by Ortiz et al.,[5b] the Et_2B−BODIPYs showed low fluorescence compared to the corresponding BF_2−BODIPYs. Replacement of the small F atoms at the B center with the bulky alkyl (Et) groups induced

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Table 1. Selected Optical Properties of 5 and 8 in CH_2Cl_2 at 25 °C

dye	λ_{abs} (nm)	λ_{em} (nm)	Stokes shift (cm^{-1})	Φ_F
5	492.0	516.0	945.4	0.02[a]
8	554.0	648.0	2618.4	0.06[b]

[a]Determined using Φ = 0.99 for **1b** in MeOH as the reference, λ_{exc} = 490 nm.[13a] [b]Determined using Φ = 0.913 for Rh 101 in EtOH as the reference, λ_{exc} = 550 nm.[13b]

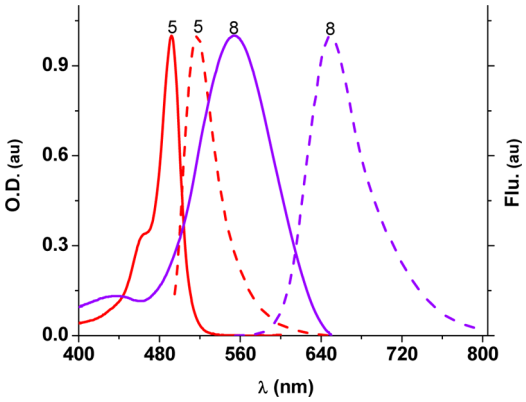

Figure 1. Normalized absorption (—) and fluorescence (- -) spectra of dyes **5** (red) and **8** (blue).

high steric hindrance, distorting the optimized excited-state geometries of the BODIPY chromophores. The lack of planarity enhances the internal conversion (nonradiative deactivation) to decrease the fluorescence drastically. Compound **5**, with a greenish yellow fluorescence (Φ_F = 2%), showed the longest-wavelength absorption (λ_{abs}) and emission (λ_{em}) maxima at 492 and 516 nm, respectively, with a small (945.4 cm^{-1}) Stokes shift, typical of the BODIPYs. Due to extended conjugation, the λ_{abs} and λ_{em} of the dimer **8** were red-shifted by 62 and 132 nm, respectively, compared to that of **5**. These amounted to a Stokes shift of 2618.4 cm^{-1} for the dimer **8** that is ~3-fold that of **5**. The dye **8** showed a red fluorescence, albeit with a low quantum yield (Φ_F = 6%).

Earlier, Bröring et al. have also reported an enhanced Stokes shift with BODIPY dimers and suggested that geometry relaxation in the excited state may be responsible for this.[11] This was clearly substantiated by our theoretical calculations. For this, the geometries of the ground (S_0) and excited (S_1) states of the dye **8** were optimized by the density functional theory (DFT) (Figures 2 and 3). This revealed that its HOMO is spread over the whole molecule, indicating a remarkably high π-conjugation between the BODIPY moieties (Figure 2) and accounting for the large red shifts in its λ_{abs} and λ_{em}. Further, the two BODIPY moieties of **8** are not coplanar with their bridging ethylene moiety, and the calculated dihedral angle between them at the S_0 state revealed a highly twisted structure (Figures 3a and 3c). However, the S_1 excited state structure showed a significantly reduced dihedral angle, suggesting that the BODIPY moieties are more coplanar with the ethylene moiety (Figures 3b and 3c). This geometry relaxation on photoexcitation may impart a remarkable effect on the energy levels of the molecular orbitals to increase the Stokes shift considerably.[2b]

Regeneration of BF_2–BODIPYs from Et_2B–BODIPYs (Demasking) and Its Application. In search of a mild and selective method to regenerate the BF_2 moiety from the Et_2B precursors, a number of metal fluorides were unsuccessfully screened using **3a** as the model compound. Finally, **3a** could be converted to the BF_2–BODIPY **1a** in excellent (75%) yield within 15 min using $BF_3{\cdot}OEt_2$ (1.3 equiv) in moist CH_2Cl_2 (Scheme 5). We used commercial CH_2Cl_2 (Merck, GR) for the reactions, and the moisture content in the solvent was found to be 0.08–0.1% by Karl Fischer titration. Consistent with a previous report,[14] the yield decreased when the reaction was carried out in CH_2Cl_2 containing a higher concentration of H_2O. The conversion was confirmed from the disappearance of the ^1H NMR resonances [δ 0.28 (t) and δ 0.82 (q)] of the Et group and the appearance of the BF_2 triplet (δ 0.93, J = 33.5 Hz) in place of the broad singlet (δ 1.54) due to the Et_2B moiety in the ^{11}B NMR spectrum (Figures S1–S3, Supporting Information). Extension of the method to the other Et_2B–BODIPYs **3b–f** also furnished the corresponding BF_2–BODIPYs **1b–f** (70–85%) uneventfully (Scheme 5). The method was also effective with the BODIPY **3h** containing a dialkynyl-B moiety to obtain **1a** in 78% yield. However, the $-B(CH{=}CH_2)_2$ derivative **3i** and the dimer **8** degraded rapidly under the same reaction conditions, while Ph_2B–BODIPY **3j** was inert toward the reagent and the starting dye was recovered quantitatively even after exposure to the reagent for 1 h. This is consistent with the reported extraordinary stability of the Ar–B bonds in the Ar_2B–BODIPYs.[3a] We also tried fluorination of **3a**, **3i**, **3j**, and **8** with Bu_4NF.[7c] However, no reaction was observed with any of the compounds under the reported conditions. The demasking reaction with $BF_3{\cdot}OEt_2$ did not take place under an anhydrous condition, indicating that the reactive species is the *in situ* generated HF instead of BF_3. This was confirmed by the reaction of **3a** with aqueous HF that produced a mixture of EtFB dye **9** and **1a** along with some degraded products. Thus, $BF_3{\cdot}OEt_2$ in moist CH_2Cl_2 is a better reagent than aqueous HF for clean reactions with higher yields.

The importance of the BODIPY-based bi- or trimodal fluorophores has been highlighted earlier.[4] These types of molecules were previously synthesized by asymmetric substitutions at the B atom using a mixture of two different organo-Li reagents.[4d] However, this led to statistical mixtures of products comprised of the unwanted dyes, and the desired products were obtained in poor (~25%) yields. BODIPYs

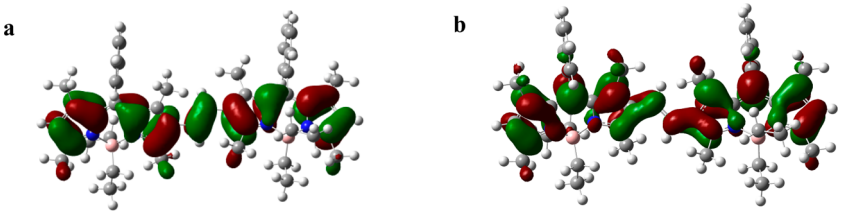

Figure 2. DFT-optimized structures of **8**: (a) HOMO and (b) LUMO.

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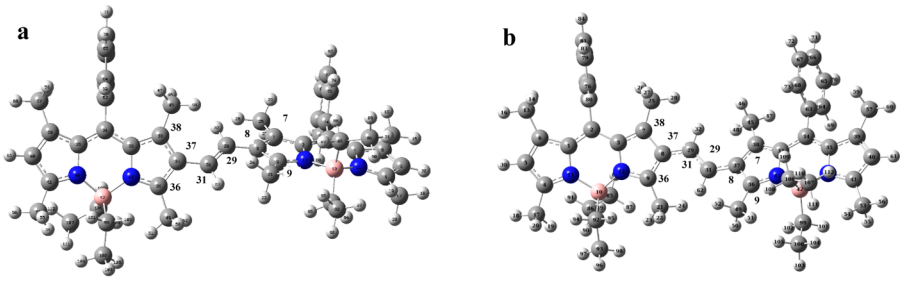
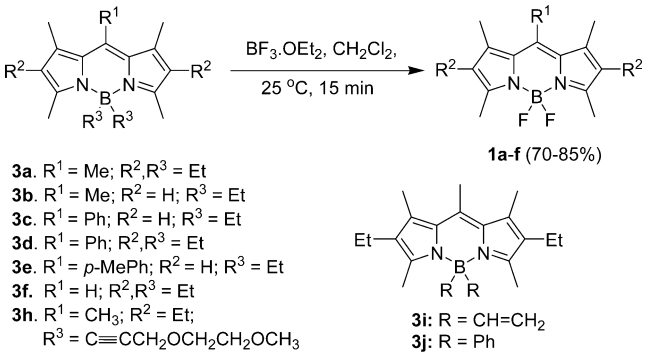


c

Dihedral angles	S_0 state	S_1 state
C38-C37-C31-C29	31.2°	18.8°
C36-C37-C31-C29	29.7°	18.1°
C7-C8-C29-C31	26.4°	16.3°
C9-C8-C29-C31	28.2°	16.2°

Figure 3. DFT-optimized structure of **8**: (a) S_0 state and (b) S_1 state. (c) Dihedral angles of the DFT-optimized S_0 and S_1 states of **8**.

Scheme 5. Regeneration of the BF_2−BODIPYs from the BR_2−BODIPYs



containing a RFB moiety may be the appropriate precursors for constructing these fluorophores. Hence, we sought to examine if the present fluorination protocol for the R_2B−BODIPYs can selectively unmask only one of the Et groups to furnish the corresponding EtFB−BODIPYs. To this end, when **3a** was treated with 0.4 equiv of $BF_3{\cdot}OEt_2$, the monoethylated dye **9** was obtained in 40% yield along with the BF_2 product **1a** (5%) and recovered **3a** (47%). Thus, the effective yield of **9** was 75%, as the unreacted **3a** can be recycled for the same transformation to obtain another batch of **9**. The reproducibility of the reaction was high as confirmed by repeating it 2−3 times. Moreover, isolation of the products in our method was also much easier. Reaction of **9** with the Grignard reagent, prepared from 2,5-dioxaoct-7-yne,[3b] furnished **10** with two different substitutions at the B-center (Scheme 6).

CONCLUSIONS

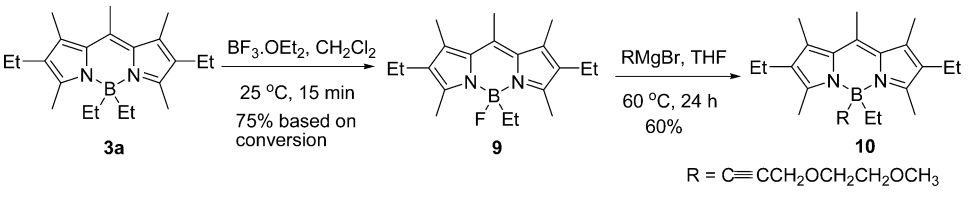
In short, we have developed an efficient and chemoselective protocol to substitute the F atoms of the BF_2−BODIPYs to the corresponding Et_2B−BODIPYs using Et_2AlCl. The importance of this method is illustrated by converting a Et_2B−BODIPY into a highly conjugated β-linked BODIPY dimer with a large Stokes shift. A rapid route of regenerating the BF_2−BODIPYs from the Et_2B−BODIPYs with $BF_3{\cdot}Et_2O$ also proceeded with high yield and can be used selectively for monofluorination. Taken together, these F-masking and unmasking strategies can be used for the syntheses of several functional molecules.

EXPERIMENTAL SECTION

Preparation of the Substrates. *Compound **3h**.*[5a] To a stirred solution of 2,5-dioxaoct-7-yne (4.08 mmol) in THF (10 mL) was added EtMgBr (4.1 mmol, 4.1 mL, 1.0 M in Et_2O). After heating the mixture at 60 °C for 2 h, **1a** (260 mg, 0.82 mmol) was added, and stirring continued for another 18 h. The resultant dark mixture was successively washed with aqueous saturated NH_4Cl (20 mL), H_2O (20 mL), and brine (20 mL) and dried. Removal of the solvent in vacuo followed by column chromatography of the residue (silica gel, hexane/EtOAc) furnished **3h** (256 mg, 62%). Red square crystals (benzene/hexane); mp: 154 °C; IR (solid): 2167, 2927 cm^{-1}; ^1H NMR: δ 1.00 (t, J = 7.6 Hz, 6H), 2.34 (s, 6H), 2.35 (q, J = 7.6 Hz, 4H), 2.66 (s, 6H), 2.59 (s, 3H), 3.34 (s, 6H), 3.55−3.49 (m, 4H), 3.65−3.59 (m, 4H), 4.16 (s, 4H); ^{13}C NMR: δ 13.8, 14.5, 14.9, 17.1, 17.3, 58.8, 59.5, 68.4, 71.6, 90.7, 129.9, 132.3, 134.2, 139.5, 151.5; ^{11}B NMR: δ −13.4 (s); EI-MS m/z (%): 506.3 (100) $[M]^+$. Anal. Calcd for $C_{30}H_{43}BN_2O_4$: C, 71.14; H, 8.56; N, 5.53%. Found: C, 71.11; H, 8.52; N, 5.51%.

*4,4-Divinyl-2,6-diethyl-1,3,5,7,8-pentamethyl-4-bora-3a,4a-diaza-s-indacene **3i**.*[5b] To a stirred solution of **1a** (100 mg, 0.31 mmol) in THF (20 mL) was added vinylmagnesium bromide (2.0 mmol, 2.0 mL, 1.0 M in THF), and the solution refluxed for 0.5 h. The resultant dark mixture was washed successively with aqueous saturated

Scheme 6. Synthesis of the BODIPY Dye 10 with an Asymmetrically Substituted B Center



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NH_4Cl (1 × 20 mL), H_2O (1 × 20 mL), and brine (1 × 20 mL) and dried. Removal of solvent in vacuo followed by column chromatography of the residue (silica gel, hexane/EtOAc) furnished **3i** (70 mg, 66%). Orange solid; ^1H NMR: δ: 0.92 (t, J = 7.5 Hz, 6H), 2.20 (s, 6H), 2.29 (s, 6H), 2.37 (q, J = 7.5 Hz, 4H), 2.58 (s, 3H), 4.91 (dd, J = 19.5 and 3.9 Hz, 2H), 5.32 (dd, J = 12.9 and 3.9 Hz, 2H), 6.38 (dd, J = 19.5 and 12.9 Hz, 2H); ^{13}C NMR: δ 15.1, 15.2, 15.5, 17.8, 17.9, 121.5, 131.1, 132.4, 132.9, 139.9, 150.5; EI-MS m/z (%): 334.3 (100) $[M]^+$. Anal. Calcd For $C_{22}H_{31}BN_2$: C, 79.04; H, 9.35; N, 8.38%. Found: C, 79.02; H, 9.71; N, 8.34%.

4,4-Diphenyl-2,6-diethyl-1,3,5,7,8-pentamethyl-4-bora-3a,4a-diaza-s-indacene ***3j***.[5b] To a stirred solution of **1a** (100 mg, 0.31 mmol) in THF (20 mL) was added PhMgBr (2.0 mL, 2.0 mmol, 1.0 M in THF), and stirring continued at 25 °C for 0.5 h. The resultant dark mixture was washed successively with aqueous saturated NH_4Cl (1 × 20 mL), H_2O (1 × 20 mL), and brine (1 × 20 mL) and dried. Removal of solvent in vacuo followed by column chromatography of the residue (silica gel, hexane/EtOAc) furnished **3j** (85 mg, 62%). Orange solid; ^1H NMR: δ 1.05 (t, J = 7.5, 6 H), 1.80 (s, 6 H), 2.42 (q, J = 7.5, 4 H), 2.44 (s, 6 H), 2.74 (s, 3 H), 7.28 (m, 10 H); ^{13}C NMR: δ 14.7, 14.8, 15.1, 17.5, 18.0, 125.5, 127.2, 128.1, 132.3, 132.4, 133.5, 133.7, 140.1, 151.2; EI-MS m/z (%): 434.3 (100) $[M]^+$.

2-Formyl-8-phenyl-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indecene ***4***.[6b] Compound **4** was synthesized in 90% yield as reported earlier.[6b] Red solid; mp: >300 °C; IR (solid): 1459, 1509, 1538, 1659, 2849, 2917 cm^{-1}; ^1H NMR: δ 1.41 (s, 3H), 1.63 (s, 3H), 2.60 (s, 3H), 2.81 (s, 3H), 6.14 (s, 1H), 7.24−7.29 (m, 2H), 7.49−7.54 (m, 3H), 9.99 (s, 1H); ^{13}C NMR: δ 11.4, 12.9, 14.7, 15.0, 29.6, 124.0, 126.1, 127.6, 128.3, 129.4, 129.5, 130.0, 133.4, 134.0, 142.8, 143.4, 147.3, 156.3, 161.6, 170.9, 185.9; ^{11}B NMR: δ 0.69 (t, J = 33.7 Hz). HRMS (ESI-TOF) m/z $[M + H]^+$ Calcd for $C_{20}H_{19}BF_2N_2O$: 353.1637. Found: 353.1604.

General Procedure for BF_2 to BEt_2 Conversion with Et_2AlCl (Masking). To a solution of **1a**−**g** (0.5 mmol) in dry CH_2Cl_2 (30 mL) was added Et_2AlCl (1.1 mmol, 1.1 mL, 1.0 M in hexane), and the mixture was stirred at 25 °C for 5 min. The mixture was treated with H_2O (10 mL), and the organic layer was separated, dried in vacuo and the residue column chromatographed (silica gel, hexane/EtOAc) to furnish **3a**−**g**.

2,4,4,6-Tetraethyl-1,3,5,7,8-pentamethyl-4-bora-3a,4a-diaza-s-indecene ***3a***.[5b] Yield: 152 mg (90%); red solid; mp: 104 °C; IR (solid): 1446, 1556, 2920, 2947 cm^{-1}; ^1H NMR: δ 0.28 (t, J = 7.5 Hz, 6H), 0.82 (q, J = 7.5 Hz, 4H), 1.04 (t, J = 7.5 Hz, 6H), 2.36 (s, 6H), 2.42−2.44 (m, 10H), 2.65 (s, 3H); ^{13}C NMR: δ 9.3, 14.0, 14.9, 15.1, 17.5, 17.7, 29.7, 131.3, 131.9, 132.2, 139.7, 148.2; ^{11}B NMR: δ 1.54 (s); Anal. Calcd for $C_{22}H_{35}BN_2$: C, 78.10; H, 10.43; N, 8.28%. Found: C, 78.25; H, 10.36; N, 8.43%.

4,4-Diethyl-1,3,5,7,8-pentamethyl-4-bora-3a,4a-diaza-s-indecene ***3b***. Yield: 120 mg (85%); red solid; mp: 183 °C; IR (solid): 1510, 1560, 2856, 2933 cm^{-1}; ^1H NMR: δ 0.29 (t, J = 7.6 Hz, 6H), 0.77 (q, J = 7.6 Hz, 4H), 2.43 (s, 12H), 2.61 (s, 3H), 6.05 (s, 2H); ^{13}C NMR: δ 9.1, 16.3, 16.9, 18.0, 121.7, 132.7, 136.3, 141.5, 149.9; ^{11}B NMR: δ 1.81 (s). HRMS (ESI-TOF) m/z $[M + H]^+$ Calcd for $C_{18}H_{27}BN_2$: 283.2345. Found: 283.2371. Anal. Calcd for $C_{18}H_{27}BN_2$: C, 76.60; H, 9.64; N, 9.93%. Found: C, 76.37; H, 9.64; N, 10.16%.

4,4-Diethyl-1,3,5,7-tetramethyl-8-phenyl-4-bora-3a,4a-diaza-s-indecene ***3c***. Yield: 144 mg (84%); red solid; mp: 134 °C; IR (solid): 1467, 1507, 1538, 2911 cm^{-1}; ^1H NMR: δ 0.42 (t, J = 7.6 Hz, 6H), 0.82 (q, J = 7.6 Hz, 4H), 1.33 (s, 6H), 2.46 (s, 6H), 5.98 (s, 2H), 7.25−7.29 (m, 2H), 7.42−7.48 (m, 3H); ^{13}C NMR: δ 9.2, 14.7, 16.4, 29.7, 121.6, 128.3, 128.4, 128.7, 128.9, 131.8, 136.6, 138.4, 142.3, 151.6; ^{11}B NMR: δ 2.20 (s). Anal. Calcd for $C_{23}H_{29}BN_2$: C, 80.23; H, 8.49; N, 8.14%. Found: C, 80.48; H, 8.62; N, 8.11%.

2,4,4,6-Tetraethyl-1,3,5,7-tetramethyl-8-phenyl-4-bora-3a,4a-diaza-s-indecene ***3d***.[6c] Yield: 160 mg (80%); red solid; mp: 138 °C; IR (solid): 1470, 1546, 2861, 2924 cm^{-1}; ^1H NMR: δ 0.40 (t, J = 7.5 Hz, 6H), 0.87 (q, J = 7.5 Hz, 4H), 0.97 (t, J = 7.5 Hz, 6H), 1.25 (s, 6H), 2.33 (q, J = 7.5 Hz, 4H), 2.44 (s, 6H), 7.27−7.30 (m, 3H), 7.43−7.45 (m, 2H); ^{13}C NMR: δ 9.3, 11.8, 14.0, 14.8, 17.5, 29.7, 128.1, 128.6, 128.8, 131.0, 132.2, 133.3, 137.5, 140.7, 150.0; ^{11}B NMR: δ 1.26 (s). Anal. Calcd for $C_{27}H_{37}BN_2$: C, 80.99; H, 9.31; N, 7.00%. Found: C, 81.01; H, 9.47; N, 6.79%.

4,4-Diethyl-1,3,5,7-tetramethyl-8-(p-tolyl)-4-bora-3a,4a-diaza-s-indecene ***3e***. Yield: 148 mg (83%); red solid; mp: 152 °C; IR (solid): 1470, 1546, 2859, 2927 cm^{-1}; ^1H NMR: δ 0.42 (t, J = 7.5 Hz, 6H), 0.86 (q, J = 7.5 Hz, 4H), 1.37 (s, 6H), 2.43 (s, 3H), 2.46 (s, 6H), 5.98 (s, 2H), 7.15 (d, J = 8.1 Hz, 2H), 7.27 (d, J = 8.1 Hz, 2H); ^{13}C NMR: δ 9.1, 14.8, 16.3, 21.4, 29.7, 121.5, 128.3, 129.4, 132.0, 133.5, 138.1, 138.5, 142.7, 151.5; HRMS (ESI-TOF) m/z $[M + H]^+$ Calcd for $C_{24}H_{31}BN_2$: 359.2658. Found: 359.2633. Anal. Calcd for $C_{24}H_{31}BN_2$: C, 80.45; H, 8.72; N, 7.82%. Found: C, 80.23; H, 8.50; N, 7.63%.

2,4,4,6-Tetraethyl-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indecene ***3f***.[6c] Yield: 146 mg (90%); red solid; IR (solid): 1469, 1510, 1538, 2922 cm^{-1}; ^1H NMR: δ 0.30 (t, J = 7.5 Hz, 6H), 0.82 (q, J = 7.5 Hz, 4H), 1.06 (t, J = 8.0 Hz, 6H), 2.18 (s, 6H), 2.38−2.43 (m, 10H), 6.98 (s, 1H); ^{13}C NMR: δ 9.2, 9.3, 13.7, 14.8, 17.7, 29.7, 119.2, 130.9, 131.7, 132.4, 150.9; ^{11}B NMR: δ 2.55 (s); EI-MS m/z (%): 324.3 (100) $[M]^+$. Anal. Calcd for $C_{21}H_{33}BN_2$: C, 77.77; H, 10.26; N, 8.64%. Found: C, 77.44; H, 10.41; N, 8.40%.

2,6-Di-(tert-Butyl)-4,4-diethyl-1,3,5,7,8-pentamethyl-4-bora-3a,4a-diaza-s-indecene ***3g***. Yield: 171 mg (87%); red solid; mp: 122 °C; IR (solid): 1537, 2920, 2947 cm^{-1}; ^1H NMR: δ 0.31 (t, J = 7.5 Hz, 6H), 0.81 (q, J = 7.5 Hz, 4H), 1.42 (s, 18H), 2.47 (s, 6H), 2.54 (s, 6H), 2.62 (s, 3H); ^{13}C NMR: δ 9.7, 18.1, 18.4, 20.9, 30.0, 32.3, 33.0, 132.2, 133.9, 136.3, 139.6, 148.4; ^{11}B NMR: δ 2.55 (s). HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{26}H_{43}BN_2$: 395.3597. Found: 395.3564. Anal. Calcd for $C_{26}H_{43}BN_2$: C, 79.17; H, 10.99; N, 7.10%. Found: C, 79.45; H, 10.85; N, 6.75%.

2-Formyl-4,4-diethyl-1,3,5,7-tetramethyl-8-phenyl-4-bora-3a,4a-diaza-s-indecene ***5***. To a cooled solution (0 °C) of **4** (176 mg, 0.5 mmol) in dry CH_2Cl_2 (30 mL) was added Et_2AlCl (5.0 mmol, 5.0 mL, 1.0 M in hexane) and the mixture stirred for 0.5 h at 0 °C. Subsequent workup as above followed by column chromatography of the residue (silicagel, hexane/EtOAc) furnished **5** (149 mg, 80%). Red-brown solid; mp: 130 °C; IR (solid): 1506, 1546, 1660, 2881, 2941 cm^{-1}; ^1H NMR: δ 0.44 (t, J = 7.6 Hz, 6H), 0.82−0.95 (m, 4H), 1.36 (s, 3H), 1.60 (s, 3H), 2.51 (s, 3H), 2.74 (s, 3H), 6.12 (s, 1H), 7.24−7.29 (m, 2H), 7.47−7.51 (m, 3H), 9.95 (s, 1H); ^{13}C NMR: δ 9.0, 11.4, 14.8, 15.0, 16.7, 29.8, 124.7, 125.7, 128.2, 128.9, 129.0, 130.2, 134.7, 135.6, 139.9, 142.8, 143.9, 152.7, 157.7, 186.0; ^{11}B NMR: δ 2.61 (s). Anal. Calcd for $C_{24}H_{29}BN_2O$: C, 77.42; H, 7.85; N, 7.52%. Found: C, 77.48; H, 8.13; N, 7.53%.

BF_2 to BEt_2 Conversion via the Grignard Route. *Route 1*. To a stirred solution of **1a** (159 mg, 0.5 mmol) in THF (30 mL) was added EtMgBr (2.0 mmol, 2.0 mL, 1.0 M in Et_2O), and stirring continued at 25 °C for 0.5 h. The resultant dark mixture was successively washed with aqueous saturated NH_4Cl (1 × 20 mL), H_2O (1 × 20 mL), and brine (1 × 20 mL) and dried. Removal of solvent in vacuo followed by column chromatography of the residue (silica gel, hexane/EtOAc) furnished **3a** (101 mg, 60%).

Route 2 (in the Presence of BCl_3). To a stirred solution of **1a** (159 mg, 0.5 mmol) in CH_2Cl_2 (30 mL) was added BCl_3 (0.5 mmol, 0.5 mL, 1.0 M in hexane), and stirring continued at 25 °C for 1.0 h. To this was added EtMgBr (1.0 mmol, 1.0 mL, 1.0 M in Et_2O) followed by stirring for another 1 h at 25 °C. The resultant dark mixture was washed successively with aqueous saturated NH_4Cl (1 × 20 mL), H_2O (1 × 20 mL), and brine (1 × 20 mL) and dried. Removal of solvent in vacuo followed by column chromatography of the residue (silica gel, hexane/EtOAc) furnished **3a** (155 mg, 92%).

Grignard Reaction with the Aldehyde 4. *2-(1-Ethanol)-4,4-difluoro-1,3,5,7-tetramethyl-8-phenyl-4-bora-3a,4a-diaza-s-indecene* ***6***.[7a] To a stirred solution of **4** (176 mg, 0.5 mmol) in THF (30 mL) at 25 °C was added EtMgBr (1.0 mmol, 1.0 mL, 1.0 M in Et_2O). After stirring for 1 h, the resultant dark mixture was treated with aqueous saturated NH_4Cl (1 × 20 mL), the organic layer separated, and the aqueous portion extracted with Et_2O (3 × 5 mL). The combined organic extracts were washed with H_2O (1 × 20 mL) and brine (1 × 20 mL), dried, and concentrated in vacuo to obtain a residue, which on column chromatography (silica gel, hexane−EtOAc) furnished **6** (96 mg, 50%). Red solid; mp: 167 °C; IR (solid): 1460,

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1510, 1536, 2917, 3574 cm^{-1}; ^1H NMR: δ 0.87 (t, J = 7.5 Hz, 3H), 1.37 (s, 3H), 1.42 (s, 3H), 1.60−1.65 (m, 1H), 1.79−1.83 (m, 1H), 2.50 (s, 3H), 2.63 (s, 3H), 4.01 (s, 1H), 4.62 (t, J = 7.5 Hz, 1H), 6.09 (s, 1H), 7.38−7.41 (m, 2H), 7.58−7.61 (m, 3H); ^{13}C NMR: δ 10.0, 11.3, 13,0, 13.6, 30.3, 67.8, 120.9, 128.2, 129.0, 129.3, 130.8, 130.9, 133.9, 135.2, 139.6, 141.8, 142.2, 154.1, 155.3; ^{11}B NMR: δ 0.79 (t, J = 33.7 Hz). Anal. Calcd for $C_{22}H_{25}BF_2N_2O$: C, 69.13; H, 6.59; N, 7.33%. Found: C, 69.47; H, 6.69; N, 7.31%.

General Procedure for BR_2 to BF_2 Conversion (Demasking). To a solution of **3a−f** and **3h** (0.5 mmol) in CH_2Cl_2 (30 mL) was added $BF_3{\cdot}Et_2O$ (0.5 mmol, 125 μL), and the mixture was stirred at 25 °C for 15 min. The mixture was treated with aquueous saturated $NaHCO_3$ (10 mL); the organic was layer separated, washed with H_2O (10 mL), and dried in vacuo; and the residue was column chromatographed (silica gel, hexane/EtOAc) to furnish **1a** from both **3a** and **3h** and **1b−f** from **3b−f**, respectively.

*HF-Mediated Demasking of **3a**.* To a solution of **3a** (170 mg, 0.5 mmol) in CH_2Cl_2 (30 mL) was added aqueous HF (48%, 2 mmol, 36 μL), and the mixture was stirred at 25 °C for 15 min. Aqueous saturated $NaHCO_3$ (10 mL) was added to the mixture, and the organic layer was separated, washed with H_2O (10 mL), and dried in vacuo. The residue was column chromatographed (silica gel, hexane/EtOAc) to furnish **9** (15 mg, 9%) and **1a** (34 mg, 21%).

*2,6-Diethyl-4,4-difluoro-1,3,5,7,8-pentamethyl-4-bora-3a,4a-diaza-s-indecene **1a**.*[5b,15a] Yield: 120 mg (75%); red needles (CH_2Cl_2/cyclohexane); mp: 208 °C (lit.[15a] mp 207−208 °C); IR (solid): 1474, 1541, 2929, 2963 cm^{-1}; ^1H NMR: δ 1.03 (t, J = 7.6 Hz, 6H), 2.32 (s, 6H), 2.67 (s, 3H), 2.37 (q, J = 7.6 Hz, 4H), 2.48 (s, 6H), 2.59 (s, 3H); ^{13}C NMR: δ 12.2, 14.2, 14.8, 16.7, 17.0, 131.5, 132.2, 136.3, 139.8, 151.6; ^{11}B NMR: δ 0.93 (t, J = 33.5 Hz). HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{18}H_{25}BF_2N_2$: 319.2157. Found: 319.2123.

*4,4-Difluoro-1,3,5,7,8-pentamethyl-4-bora-3a,4a-diaza-s-indecene **1b**.*[5b,15a] Yield: 92 mg (70%); red needles (CH_2Cl_2/cyclohexane); mp: 256 °C (lit.[15a] mp 254−257 °C); IR (solid): 1506, 1552, 2854, 2920 cm^{-1}; ^1H NMR: δ 2.40 (s, 6H), 2.52 (s, 6H), 2.56 (s, 3H), 6.05 (s, 2H); ^{13}C NMR: δ 14.4, 16.3, 17.3, 121.2, 132.0, 141.0, 141.4, 153.6; ^{13}C NMR: δ 14.3, 16.3, 17.2, 121.1, 132.0, 140.9, 141.4, 153.5; ^{11}B NMR: δ 0.60 (t, J = 33.7 Hz); EI-MS m/z (%): 262.0 (100) $[M]^+$.

*4,4-Difluoro-1,3,5,7-tetramethyl-8-phenyl-4-bora-3a,4a-diaza-s-indecene **1c**.*[15b] Yield: 138 mg (85%); red amorphous solid; mp: 178 °C; IR (solid): 1470, 1505, 1537, 2926 cm^{-1}; ^1H NMR: δ 1.36 (s, 6H), 2.54 (s, 6H), 5.97 (s, 2H), 7.25−7.28 (m, 2H), 7.44−7.48 (m, 3H); ^{13}C NMR: δ 14.2, 14.5, 121.2, 127.9, 128.5, 128.9, 129.1, 131.4, 134.9, 141.7, 143.1, 155.4; ^{11}B NMR: δ 0.77 (t, J = 33.7 Hz). HRMS (ESI-TOF) m/z $[M + H]^+$ Calcd for $C_{19}H_{19}BF_2N_2$: 325.1687. Found: 325.1660.

*2,6-Diethyl-4,4-difluoro-1,3,5,7-tetramethyl-8-phenyl-4-bora-3a,4a-diaza-s-indecene **1d**.*[6c,15c] Yield: 148 mg (78%); orange needles (CH_2Cl_2/cyclohexane); mp: 185 °C (lit.[15c] mp: 185−186 °C); ^1H NMR: δ 1.09 (t, J = 7.6 Hz, 6H), 1.48 (s, 6H), 2.31 (q, J = 7.6 Hz, 4H), 2.87 (s, 6H), 7.01−7.06 (m, 2H), 7.29−7.37 (m, 3H); ^{13}C NMR: δ 11.6, 12.5, 14.6, 17.1, 128.3, 128.7, 129.0, 130.8, 132.7, 135.8, 138.4, 140.2, 153.7; ^{11}B NMR: δ 0.80 (t, J = 33.7 Hz); EI-MS m/z (%): 380.0 (100) $[M]^+$.

*4,4-Difluoro-1,3,5,7-tetramethyl-8-(p-tolyl)-4-bora-3a,4a-diaza-s-indecene **1e**.*[15d] Yield: 126 mg (75%); red amorphous solid; mp: 183 °C; IR (solid): 1467, 1507, 1538, 2911 cm^{-1}; ^1H NMR: δ 1.39 (s, 6H), 2.42 (s, 3H), 2.54 (s, 6H), 5.96 (s, 2H), 7.14 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H); ^{13}C NMR: δ: 14.4, 14.5, 21.4, 121.0, 127.7, 129.7, 131.6, 131.9, 138.8, 142.1, 143.1, 155.2; ^{11}B NMR: δ: 0.77 (t, J = 33.7 Hz). HRMS (ESI-TOF) m/z $[M + H]^+$ Calcd for $C_{20}H_{21}BF_2N_2$: 339.1844. Found: 339.1819.

*2,6-Diethyl-4,4-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indecene **1f**.*[6c] Yield: 121 mg (80%); red solid; ^1H NMR: δ 1.06 (t, J = 7.6 Hz, 6H), 2.16 (s, 6H), 2.36 (q, J = 7.6 Hz, 4H), 2.49 (s, 6H), 6.95 (s, 1H); ^{13}C NMR: δ 9.4, 12.5, 14.6, 17.3, 118.5, 131.6, 132.4, 136.6, 154.6; ^{11}B NMR: δ: 0.77 (t, J = 33.7 Hz); EI-MS m/z (%): 304.2 (100) $[M]^+$.

*McMurry Coupling of **5**.* A mixture of $TiCl_4$ (0.8 mmol, 88 μL) and Zn (105 mg, 1.6 mmol) in dry THF (20 mL) was refluxed for 3 h. After cooling, **5** (100 mg, 0.26 mmol) in dry THF (5 mL) was added into it, and the mixture was refluxed for another 2 h. The mixture was diluted with EtOAc (10 mL), treated with aqueous saturated K_2CO_3 (10 mL), and passed through Celite. The organic layer was separated and concentrated in vacuo, and the residue was column chromatographed (alumina, hexane/EtOAc) to furnish **8** (38 mg, 40%). Red solid; mp: >300 °C; IR (solid): 1610, 2861, 2921 cm^{-1}; ^1H NMR: δ 0.43 (t, J = 7.5 Hz, 12H), 0.86 (q, J = 7.5 Hz, 8H), 1.33 (s, 6H), 1.40 (s, 6H), 2.47 (s, 6H), 2.55 (s, 6H), 5.99 (s, 2H), 6.35 (s, 2H), 7.25−7.29 (m, 4H), 7.43−7.47 (m, 6H); ^{13}C NMR: δ: 9.3, 13.2, 14.8, 15.4, 16.4, 29.7, 121.8, 123.1, 128.4, 128.7, 128.8, 129.3, 131.6, 132.1, 133.6, 136.8, 138.4, 142.0, 151.3, 151.7; HRMS (ESI-TOF) m/z $[M + H]^+$ Calcd for $C_{48}H_{58}B_2N_4$: 713.4926. Found: 713.4905. Anal. Calcd for $C_{48}H_{58}B_2N_4$: C, 80.90; H, 8.20; N, 7.86%. Found: C, 80.79; H, 8.20; N, 7.68%.

Synthesis of BODIPY 10 with Asymmetrically Substituted B.
*4-Fluoro-1,3,5,7,8-pentamethyl-2,4,6-triethyl-4-bora-3a,4a-diaza-s-indecene **9**.* To a solution of **3a** (170 mg, 0.5 mmol) in CH_2Cl_2 (30 mL) was added $BF_3{\cdot}Et_2O$ (0.2 mmol, 50 μL), and the mixture was stirred at 25 °C for 15 min. Aqueous saturated $NaHCO_3$ (10 mL) was added, and the organic layer was separated, washed with H_2O (10 mL), and concentrated in vacuo. Column chromatography of the residue (silica gel, hexane/EtOAc) furnished **9** (65 mg, 75% based on conversion). Red solid; mp: 153 °C; ^1H NMR: δ 0.28 (t, J = 7.6 Hz, 3H), 0.64 (q, J = 7.6 Hz, 2H), 1.01 (t, J = 7.6 Hz, 6H), 2.32 (s, 6H), 2.41 (q, J = 7.6 Hz, 4H), 2.45 (s, 6H), 2.60 (s, 3H); ^{13}C NMR: δ 8.5, 8.6, 12.7, 12.8, 14.3, 15.0, 17.2, 29.7, 128.5, 131.7, 131.9, 133.9, 139.8, 150.6; EI-MS m/z (%): 327.7 (20) $[M - 1]^+$, 309.5 (100) $[M - 19]^+$. Anal. Calcd for $C_{20}H_{30}BFN_2$: C, 73.17; H, 9.21; N, 8.53%. Found: C, 73.43; H, 9.58; N, 8.38%.

*Compound **10**.* To a stirred solution of 2,5-dioxaoct-7-yne (2.04 mmol) in THF (10 mL) was added EtMgBr (2.04 mmol, 2.04 mL, 1 M in Et_2O). After heating the mixture at 60 °C for 2 h, **9** (130 mg, 0.40 mmol) was added, and stirring continued at 60 °C for another 18 h. The resultant dark mixture was thoroughly washed successively with aqueous saturated NH_4Cl (20 mL), H_2O (20 mL), and brine (20 mL) and dried. Removal of the solvent in vacuo followed by column chromatography of the residue (silica gel, hexane/EtOAc) furnished **10** (101 mg, 60%). Red solid; ^1H NMR: δ 0.19 (t, J = 7.6 Hz, 3H), 0.75 (q, J = 7.6 Hz, 2H), 1.02 (t, J = 7.6 Hz, 6H), 2.33 (s, 6H), 2.42 (q, J = 7.6 Hz, 4H), 2.58 (s, 6H), 2.60 (s, 3H), 3.36 (s, 3H), 3.51−3.57 (m, 2H), 3.63−3.69 (m, 2H), 4.20 (s, 2H); ^{13}C NMR: δ: 1.0, 8.3, 13.9, 14.6, 15.0, 17.4, 29.7, 58.9, 59.7, 68.2, 71.8, 131.3, 132.1, 132.6, 139.7, 150.0. HRMS (ESI-TOF) m/z $[M + H]^+$ Calcd for $C_{26}H_{39}BN_2O_2$: 423.3183. Found: 423.3193.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Photophysical data, ^1H and ^{13}C NMR spectra of all compounds, and computational data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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