(4,4-Difluoro-4-bora-3a,4a,-diaza-s-indacen-3-yl)acetaldehyde: Synthesis and Chemical Properties

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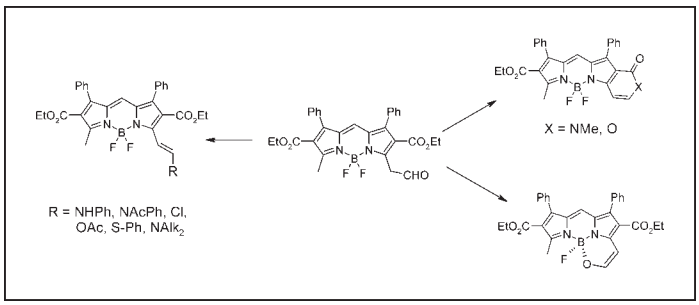

A reaction of 3,5-dimethylborondipyrromethene **3** with the DMF dimethylacetal gives rise to monoenamine **4**. The latter is converted to the corresponding aldehyde **5**. A considerable contribution of the enolic form of the aldehyde allows preparing numerous 3-vinyl substituted borondipyrromethenes and some heterocyclic derivatives. A reaction of the aldehyde **5** with tertiary aliphatic amines and the consecutive Hofmann-type decomposition of the intermediary quaternary salt give rise to the corresponding dialkylaminovinyl derivatives.

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INTRODUCTION

The 4,4-difluoro-4-boron-3a,4a-diazo-s-indacene (so-called borondipyrromethene (BODIPY))-derived dyes have both very intensive absorption bands in their ultraviolet-visible (UV-Vis) spectra and intensive fluorescence [1,2]. A low sensitivity of these properties of the BODIPY dyes toward both solvent polarity and the pH led to their numerous applications, such as labeling of proteins [3–5] and DNA [6]. To widen the range of the biochemical applications requiring deeply colored dyes, the extension of the chromophoric system of the BODIPY dyes by means of their peripheral functionalization is usually carried out. For example, the Knoevenagel reaction of the BODIPY involving methyl groups in 3- and 5-positions with aromatic aldehydes led to the corresponding monostyryl or distyryl derivatives [7–9]. The latter compounds exhibit absorption maxima at considerably longer wavelengths compared with the parent BODIPY. In this contribution, we report an efficient synthetic approach to the 3-vinyl substituted BODIPY dyes using the reactivity of the α-methyl groups. The obtained compounds are useful scaffolds that could be used in further structural and functional modifications of the dipyrromethene dyes.

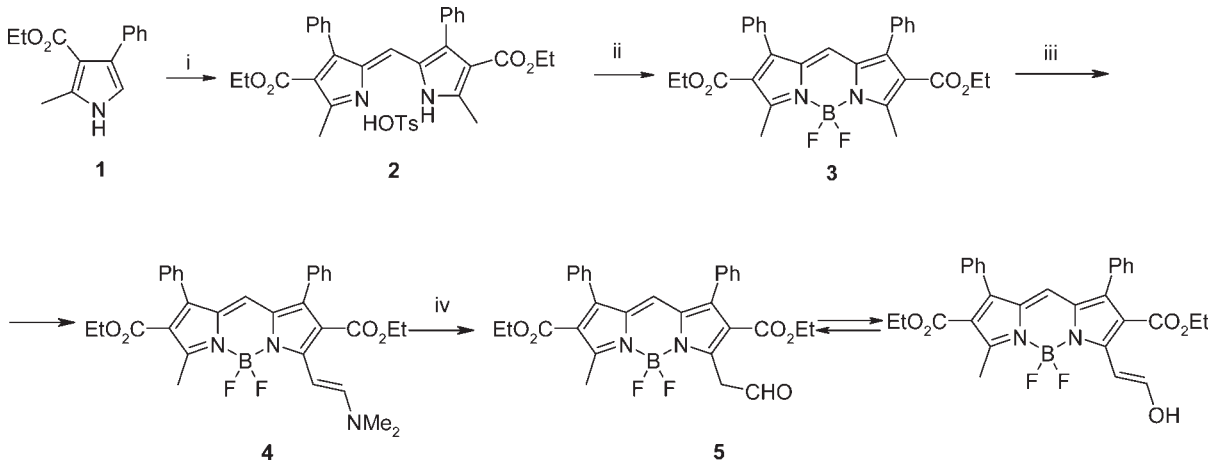
RESULTS AND DISCUSSION

As shown in Scheme 1, the condensation of the pyrrole **1** with trimethylorthoformate in the presence of *p*-toluenesulfonic acid leads to the dipyrromethene tosylate **2** in a 95% yield. Noteworthy, the preparation of hydrobromide of the dipyrromethene **2** from the pyrrole and triethyl orthoformate dissolved in the 50% HBr in acetic acid was reported in the literature [10], but no yield was given. Finally, the treatment of the tosylate **2** with $BF_3{\cdot}Et_2O$ and the Hünig's base gives rise to 84% of the BODIPY **3** that is used as the starting compound in our study.

A reaction of **3** with the DMF dimethylacetal in the presence of acetic anhydride in hot xylene results in 89% enamine **4** (Scheme 1). The fact that only one methyl group of **3** reacts even if a large excess of the DMF dimethylacetal is used reflects a decreased reactivity of the remaining methyl group of **4** on introduction of the electron donor enamine fragment.

Treatment of the enamine **4** with TFA in water gives rise to the corresponding aldehyde **5**. The latter compound exists in a medium dependent equilibrium of two tautomeric forms. Thus, ^{1}H NMR spectrum of **5** recorded in $CDCl_3$ reveals characteristic peaks of CH_2 and aldehyde protons at 4.52 ppm and 9.82 ppm, respectively. The presence of the enolic form of **5** in $CDCl_3$ is, therefore, negligible and cannot be detected by means ^{1}H NMR. On the contrary, the DMSO-d_6 ^{1}H NMR spectrum of **5** shows both tautomeric forms in a 1:1 ratio. The latter manifests itself in two peaks of the CH_3 group at 2.76 and 2.81 ppm, one peak of the CH_2 group

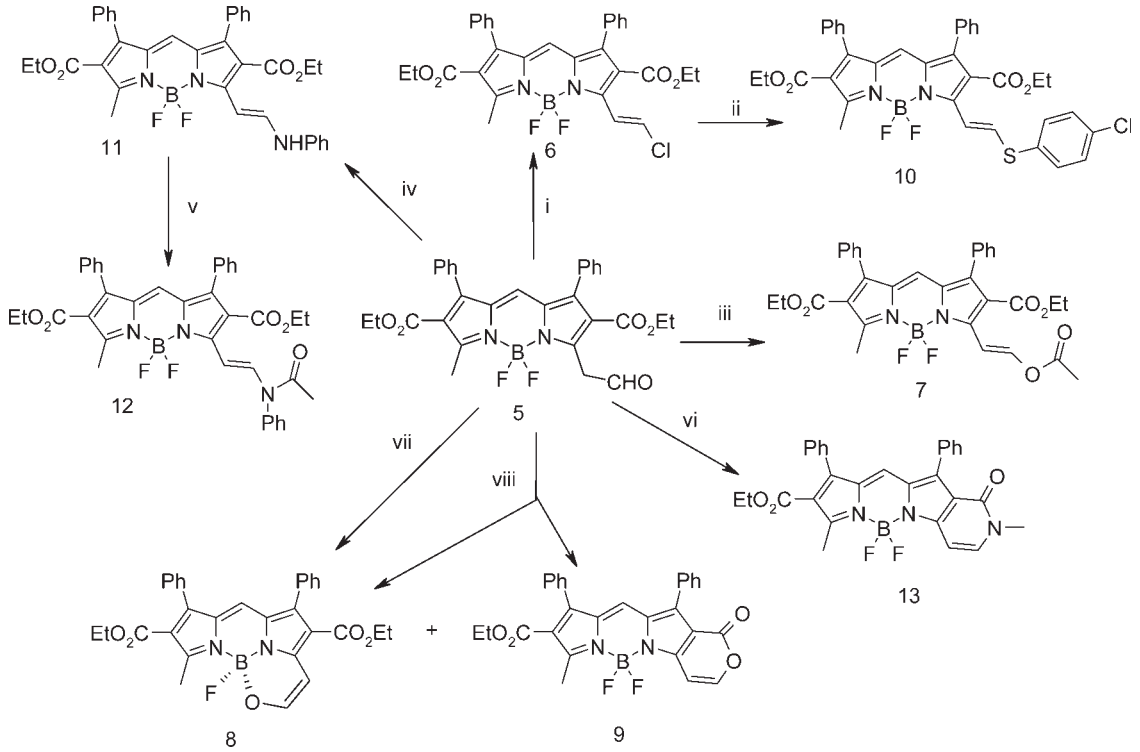
Scheme 1. Reagents and conditions. i, $CH(OCH_3)_3$, HOTs, room temperature; ii, BF_3*Et_2O, $EtN(i\text{-}Pr)_2$, room temperature; iii, $(CH_3O)_2CHN(CH_3)_2$, Ac_2O, o-xylene, reflux 1 min; iv, 30% TFA in water, reflux 1 min.



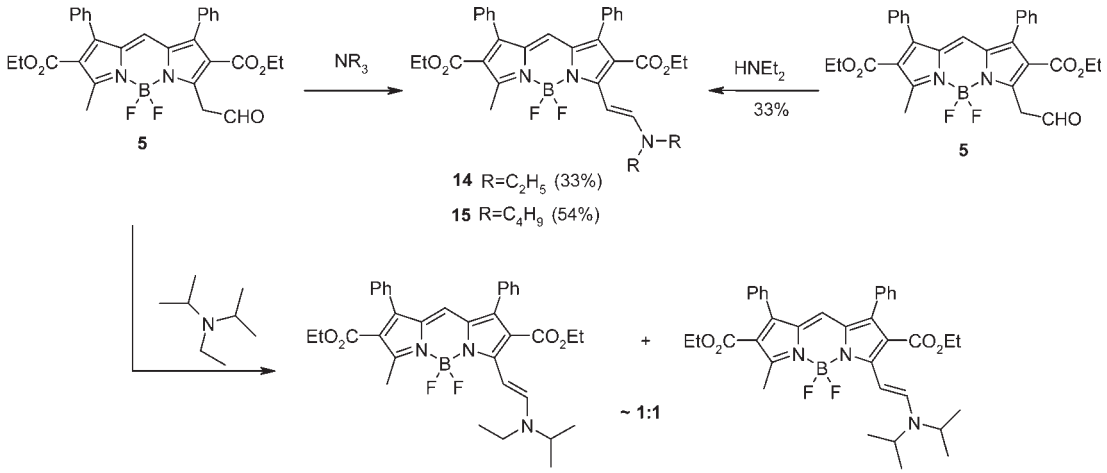
at 4.45 ppm, broad peaks of CH=CH at 6.46 and 8.09 ppm, two peaks of meso-protons at 6.7 and 6.98 ppm, and the aldehyde proton peak at 9.76 ppm.

Scheme 2 shows reactions of aldehyde **5** leading to a variety of vinyl derivatives. For example, heating of **5** in $POCl_3$ in the presence of *N*,*N*-diethylaniline results in the chlorovinyl compound **6**, whereas heating of **5** in acetic anhydride in the presence of catalytic amount of DMF gives rise to the enole acetate **7**. Interestingly, treatment of **5** with $BF_3{\cdot}Et_2O$ in toluene at room temperature leads to the intramolecular displacement of the fluorine with the enolic unit producing the cyclic structure **8**. ^{1}H NMR data show that the coupling constant of the ethylene protons in **8** is equal to 5.1 Hz, which is typical for the *cis*-configuration of the bond. This observation is in stark contrast with those for the noncyclic vynil

Scheme 2. Reagents and conditions. i, $POCl_3$, $PhN(Et)_2$, 90°C;ii, 4-ClC_6H_4SNa, DMF, room temperature; iii, Ac_2O, DMF, reflux 4 min; iv, $PhNH_2$, HOAc; v, Ac_2O, $N(Et)_3$; vi, $MeNH_2$, HOAc, toluene, reflux 2 min; vii, BF_3*Et_2O, toluene, room temperature; viii, HOAc, H_2SO_4, 100°C.



Scheme 3



derivatives shown in Scheme 2 in which the corresponding coupling constants are in the range of 12–16 Hz and characteristic of the *trans*-configuration of the double bond. ^{19}F NMR spectrum of **8** shows that the peak corresponding to its fluorine atom is shifted to the low field (−137.2 ppm) compared with that of **5** (−141.6 ppm). Mass spectrum of **8** (mw 524) recorded in the positive mode reveals cationic peak with *m*/*z* of 505 that corresponds to the loss of the remaining fluorine anion. The intermolecular displacement of the fluorine in BODIPYs with alkoxy and phenoxy groups in the presence of $AlCl_3$ has already been reported in the literature [11]. There are also reports on an intramolecular *O*-chelation of the boron atom in BODIPYs [12]. The described here compound **8** is the representative of unsymmetrically chelated BODIPYs recently reported in [13].

A mixture of cyclic structures **8** (28%) and **9** (22%) is obtained from the aldehyde **5** in hot acetic acid in the presence of sulfuric acid. The formation of the both cycles is also observed (TLC) while heating aldehyde **5** over 200°C.

The chlorine atom of the compound **6** is considerably reactive. Addition of bases, such as pyridine, triethylamine, carbonates etc., to **6** leads to the formation of tars. This observation can possibly be explained by the formation of the corresponding acetylene derivative and its polymerization. Similar tar formation is observed when a phenolate anion reacts with **6**. However, a reaction of **6** with a thiophenolate anion that is less basic but more nucleophilic gives rise to the sulfide **10**.

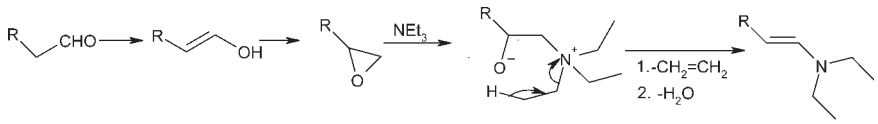
The aldehyde **5** reacts easily with aromatic amines. For example, a reaction of **5** with aniline gives rise to the anilinovinyl derivative **11** in a yield of 80%. The acylation of the latter compound leads to the corresponding acetanilide **12**. The derivatives of type **11** can also be obtained by the reaction of aniline with the enamine **4** and enole acetate **7**. However, reactions of **5** with primary aliphatic amines cannot be used for the preparation of the corresponding aminovinyl derivatives because of their follow-up cyclization to pyridones of type **13**. The pyridone **13** is easily obtained by the reaction of **5** with a methanol solution of methylamine in hot toluene in the presence of acetic acid (Scheme 2).

Attempting to carry out the reaction of **5** with different CH-acids in the presence of triethylamine led to a dye product. The structure of this dye does not depend on the structure of the CH-acid used as TLC and UV-Vis absorption spectra reveal. Further, analytical characterization of this new product confirms the structure of a diethylaminovinyl derivative **14** that is the result of a direct coupling of **5** and the triethylamine (Scheme 3). This reaction takes place after either 10–15 min of heating or 24 h of standing at room temperature of the reaction mixture in pyridine or dioxane. The enamine **14** can also be obtained by a reaction of **5** with diethylamine (Scheme 3).

A reaction of **5** with tributylamine proceeds in a similar way, giving rise to the dibutylamino-derivative **15**. The reaction results a chromatographically nonseparable mixture of two products if ethyldiisopropylamine is used. According to the ^{1}H NMR data, the mixture consists of equal amounts of diisopropylamino and ethylisopropylamino derivatives.

A possible mechanism of the reaction of **5** with trialkylamines is depicted in Scheme 4. The enolic form of the aldehyde **5** undergoes cyclization to an oxirane intermediate, which reacts with the amine producing betaine. The following Hoffman-type decomposition of the quaternary salt leads to the consecutive elimination of the alkene and the water. To our knowledge, the reactions of acetaldehyde derivatives with trialkylamines leading

Scheme 4



to enamines or similar transformations have not been reported in the literature.

Optical properties. The cyclization of dipyrromethene **2** to boron dipyrromethene **3** leads to a bathochromic shift of the UV-Vis absorption maximum of **3** compared with **2** by 35 nm. Compound **3** has also a more intense UV-Vis absorption band when compared with **2** (Table 1). All vinyl derivatives prepared from **3** have their UV-Vis absorption maxima at longer wavelengths compared with the precursor. However, their absorption bands become broader than that of **3**. The smallest bathochromic shifts of the UV-Vis absorption maxima are observed for the chlorovinyl derivative **6** (29 nm) and enole acetates **7** (33 nm) and **9** (34 nm). Aminovinyl derivatives **4**, **11**, **14**, and **15** show significantly larger bathochromic shifts of their UV-Vis absorption maxima when compared with that of **3** ranging from 102 to 107 nm. However, the absorption intensities of the UV-Vis spectra of the aminovinyl derivatives show a twofold decrease while their absorption bands broaden.

The synthesized vinyl-substituted BODIPYs with the exception of the amino-derivatives exhibit high fluorescence quantum yields (φ = 0.73-1). The fluorescence quenching in enamines **4**, **14**, and **15** takes place seemingly *via* photoinduced electron transfer (PET) as it is described for some other amino-substituted BODIPYs [14,15]. In the case of aniline derivative **11**, the PET is much less pronounced (φ = 0.17). The PET quenching can be avoided by, e.g., acylation or cyclization into pyridone **13**. These structural modifications lead to the fluorescence increase. The largest Stokes shifts are observed for sulfide **10** and enamine **11** (1150 and 1400 cm^{-1}, respectively). The remaining vinyl derivatives show the Stokes shifts comparable with that of the starting BODIPY (500–700 cm^{-1}).

To sum up, the reported here BODIPY-3-acetaldehyde is a useful scaffold for the synthesis of 3-vinyl-substituted BODIPYs and some heterocycles having the BODIPYs core as the cycle component. The synthesized 3-vinyl-substituted BODIPYs can, in turn, be used for the further modification of BODIPYs.

Table 1

Optical properties of the synthesized dyes (in CH_2Cl_2).

	λ_{abs}, nm ($\varepsilon \cdot 10^{-4}$, M^{-1} cm^{-1})	fwhm, cm^{-1}	λ_{em}, nm (φ)	$\Delta\upsilon$, cm^{-1}
2	484 (10.9)	1200		
3	519 (12.2)	782	535 (0.98)	577
4	621 (6.0)	2385	659 (<0.001)	929
5	518 (12.4)	823	533 (0.97)	544
6	547 (10.3)	1013	566 (1)	516
7	552 (11.3)	791	569 (0.94)	541
8	579 (8.4)	901	598 (0.80)	549
9	553 (10.8)	921	574 (0.98)	662
10	584 (8.4)	1460	626 (0.84)	1149
11	626 (8.5)	1905	686 (0.17)	1397
12	580 (10.3)	1135	602 (0.83)	630
13	586 (9.5)	1146	614 (0.73)	778
14	622 (6.0)	2481	668 (<0.001)	1107

EXPERIMENTAL

Electronic absorption spectra were recorded on Shimadzu UV-3100 spectrophotometer. ^1H (300 MHz, 25°C, $Si(CH_3)_4$ as an internal standard) and ^{19}F NMR (188 MHz, $CFCl_3$ as internal standard) spectra were obtained with Varian VXR-300 instrument. LC/MS spectra were recorded using chromatography/mass spectrometric system that consists of high-performance liquid chromatograph ''Agilent 1100 Series'' equipped with diode-matrix and mass-selective detector ''Agilent LC\MSD SL.'' Purification by column chromatography was carried out with neutral silica gel 100 (70–230). Fluorescence spectra were recorded on a Solar CM 2203 fluorescence spectrophotometer. The relative fluorescent quantum yields (φ) were determined using Rhodamine 6G (φ = 0.95, EtOH) and indodicarbocyanine iodide (φ = 0.25, EtOH) as the references.

2-[3-Phenyl-4-carbethoxy-5-methylpyrrol-2-yl]methyliden-3-phenyl-4-carbethoxy-5-methylpyrrolium tosylate (2). Toluene-4-sulfonic acid (3.6 g, 21 mmol) was added to a stirred solution of pyrrole **1** (9.16 g, 40 mmol) in 20 mL trimethyl orthoformate at room temperature, and stirring was continued for 15 min. Then the mixture was diluted with benzene (50 mL), and the solid product was filtered. Yield 12.1 g (95%). mp 138–140°C. ^1H NMR ($CDCl_3$): δ 1.07(t, $^3J_{H,H}$ = 7.2 Hz, 6H, CH_2CH_3), 2.40 (s, 3H, CH_3), 2.85 (s, 6H, CH_3), 4.12 (q, $^3J_{H,H}$ = 7.2 Hz, 4H, CH_2CH_3), 6.82 (s, 1H, meso-CH), 7.09 (m, 4H, ArH), 7.27 (m, 8H, ArH), 7.91 (d, $^3J_{H,H}$ = 8.1 Hz, 2H, ArH), 13.82 (s, 2H, NH). Anal. calcd. for $C_{36}H_{36}N_2O_7S$: C,67.5; H, 5.62; N, 4.37. Found: C, 67.2; H, 5.65; N, 4.65.

1,7-Diphenyl-2,6-dicarbethoxy-3,5-dimethyl-4,4-difluoro-4-bora-3a,4a,-diaza-s-indacene (3). Diisopropylethylamine (14 mL, 80 mmol) was added dropwise to a stirred solution of compound **2** (12.8 g, 20 mmol) in $BF_3 \cdot Et_2O$ (50 mL) at room temperature The mixture was stirred for additional 20 min, followed by pouring into ice water (250 mL), and then was left for 2 h. The precipitate was filtered, air-dried, and recrystallized from hexane-toluene. Yield 8.7 g (84%). M.p. 217–218°C. ^1H NMR (DMSO-d_6): δ 1.03 (t, $^3J_{H,H}$ = 7.2 Hz, 6H, CH_2CH_3), 2.81 (s, 6H, CH_3), 4.08 (q, $^3J_{H,H}$ = 7.2 Hz, 4H, CH_2CH_3), 6.91 (s, 1H, meso-CH), 7.42 (s, 10H, ArH). Anal.

calcd. for $C_{29}H_{27}BF_2N_2O_4$: C, 67.4; H, 5.23; N, 5.43. Found: C, 67.5; H, 5.5; N, 5.5.

3-(2-Dimethylaminoethen-1-yl)-5-methyl-1,7-diphenyl-2,6-dicarbethoxy-4,4-difluoro-4-bora-3a,4a,-diaza-s-indacene (4). DMF dimethylacetal (3 g, 25 mmol) was added to a solution of compound **3** (2.58 g, 5 mmol), Ac_2O (6 mL) in o-xylene (15 mL), and the mixture was refluxed for 1 min. After cooling to room temperature, hexane (20 mL) was added, and the mixture was left overnight. The precipitate was filtered and washed with hexane. Yield 2.46 g (89%). M.p. 204–205°C. ^{1}H NMR (DMSO-d_6): δ 0.94 (t, 3H, CH_2CH_3), 1.01 (t, 3H, CH_2CH_3), 2.71 (s, 3H, CH_3), 3.08 (s, 3H, NCH_3), 3.29 (s, 3H, NCH_3), 4.06 (m, 4H, CH_2CH_3), 6.02 (d, $^3J_{H,H}$ = 12.9 Hz, 1H, CH), 6.30 (s, 1H, meso-CH), 7.25–7.44 (m, 10H, ArH), 8.19 (d, $^3J_{H,H}$ = 12.9 Hz, 1H, CH). Anal. calcd. for $C_{32}H_{32}BF_2N_3O_4$: C, 67.2; H, 5.6; N, 7.35. Found: C, 67.4; H, 5.4; N, 7.5.

(5-Methyl-1,7-diphenyl-2,6-dicarbethoxy-4,4-difluoro-4-bora-3a,4a,-diaza-s-indacen-3-yl)acetaldehyde (5). A mixture of enamine **4** (2.28 g, 4 mmol), water (12 mL), and trifluoroacetic acid (5 mL) was refluxed for 1 min. After cooling to room temperature, the product was filtered and recrystallized from acetonitrile. Yield 1.4 g (73%). M.p. 194–196°C. ^{1}H NMR ($CDCl_3$): δ 1.09 (m, 6H, CH_2CH_3), 2.92 (s, 3H, CH_3), 4.13 (m, 4H, CH_2CH_3), 4.52 (s, 2H, CH_2CHO), 6.98 (s, 1H, meso-CH), 7.28–7.39 (m, 10H, ArH), 9.82 (s, 1H, CHO). ^{19}F NMR ($CDCl_3$): δ −141.6 (m).

^{1}H NMR (DMSO-d_6) a mixture of tautomers: δ 1.01 (m, CH_2CH_3), 2.76 (s, CH_3), 2.81 (s, CH_3), 4.08 (m, CH_2CH_3), 4.45 (s, CH_2CHO), 6.46 (br.s, CH), 6.70 (s, meso-CH), 6.98 (s, meso-CH), 7.75 (m, ArH), 8.09 (br.s, CH), 9.76 (s, CHO). Anal. calcd. for $C_{30}H_{27}BF_2N_2O_5$: C, 66.2; H, 4.96 N, 5.15. Found: C, 66.4; H, 4.8; N, 5.1.

3-(2-Chloroethen-1-yl)-5-methyl-1,7-diphenyl-2,6-dicarbethoxy-4,4-difluoro-4-bora-3a,4a,-diaza-s-indacene (6). A mixture of aldehyde **5** (270 mg, 0.5 mmol), $POCl_3$ (1 mL, 11 mmol), and *N*,*N*-diethylaniline (150 mg, 1 mmol) was heated at 90–95°C for 45 min. After cooling to room temperature, the mixture was poured into ice water, the precipitate was filtered and washed with hot ethanol. Yield 200 mg (71%). M.p. 186–187°C. ^{1}H NMR ($CDCl_3$): δ 0.99 (t, 3H, CH_2CH_3), 1.01 (t, 3H, CH_2CH_3), 2.93 (s, 3H, CH_3), 4.14 (m, 4H, CH_2CH_3), 6.93 (s, 1H, meso-CH), 7.25–7.40 (m, 10H, ArH), 7.53 (d, $^3J_{H,H}$ = 13.5 Hz,1H, CH), 7.68 (d, $^3J_{H,H}$ = 13.5 Hz, 1H, CH). ^{19}F NMR ($CDCl_3$): δ −141.4 (m). Anal. calcd. for $C_{30}H_{26}BClF_2N_2O_4$: C, 64.0; H, 4.62; N, 4.98. Found: C, 63.7; H, 4.4; N, 5.1.

3-(2-Acetoxyethen-1-yl)-5-methyl-1,7-diphenyl-2,6-dicarbethoxy-4,4-difluoro-4-bora-3a,4a,-diaza-s-indacene (7). A mixture of aldehyde **5** (270 mg, 0.5 mmol), Ac_2O (1.3 mL), and DMF (35 mg, 0.5 mmol) was heated at reflux for 4 min. After cooling to room temperature, the mixture was diluted with i-PrOH (3 mL), and the precipitate was filtered. Yield 240 mg (82%). M.p. 209–210°C. ^{1}H NMR ($CDCl_3$): δ 1.04 (m, 6H, CH_2CH_3), 2.25 (s, 3H, $COCH_3$), 2.93 (s, 3H, CH_3), 4.13 (m, 4H, CH_2CH_3), 6.90 (s, 1H, meso-CH), 7.11 (d, $^3J_{H,H}$ = 13.5 Hz,1H, CH), 7.26–7.39 (m, 10H, ArH), 8.68 (d, $^3J_{H,H}$ = 13.5 Hz, 1H, CH). ^{19}F NMR ($CDCl_3$): δ −142.5 (m). Anal. calcd. for $C_{32}H_{29}BF_2N_2O_6$: C, 65.5; H, 4.95; N, 4.78. Found: C, 65.7; H, 4.8; N, 5.0.

9b-Fluoro-9-methyl-5,7-diphenyl-4,8-dicarbethoxy-1-oxa-9a,9c-diaza-9b-bora-cyclopenta[e]acenaphtylene (8). $BF_3{\cdot}Et_2O$ (500 mg, 3.5 mmol) was added to a solution of aldehyde **5** (270 mg, 0.5 mmol) in toluene (5 mL) at room temperature. The mixture was allowed for stand for 45 min, followed by addition of water (5 mL). The organic layer was separated, washed with water, dried over Na_2SO_4, and then evaporated to dryness. The residue was purified by column chromatography on silica gel (eluent hexane:EtOAc, 4:1). Yield 150 mg (58%). M.p. 167–168°C. ^{1}H NMR(DMSO-d_6): δ 1.01 (t, 3H, CH_2CH_3), 1.15 (t, 3H, CH_2CH_3), 2.87 (s, 3H, CH_3), 4.06 (q, 2H, CH_2CH_3), 4.17 (q, 2H, CH_2CH_3), 6.69 (d, $^3J_{H,H}$ = 5.1 Hz, 1H, CH), 6.88 (s, 1H, meso-CH), 7.40–7.52 (m, 10H, ArH), 7.72 (d, $^3J_{H,H}$ = 5.1 Hz, 1H, CH). ^{19}F NMR ($CDCl_3$): δ −137.2 (m). LS-MS: *m*/*z* 505 $[M\text{-}19(F)]^+$. Anal. calcd. for $C_{30}H_{26}BFN_2O_5$: C, 68.7; H, 4.94; N, 5.34. Found: C, 68.5; H, 4.9; N, 5.1.

2-Carbethoxy-3,7-dimetyl-1,9-diphenyl-4,4-difluoro-7-oxa-3a,4a-diaza-4-bora-cyclopenta[b]fluoren-8-on (9). A solution of aldehyde **5** (300 mg, 0.55 mmol), H_2SO_4 (98 mg, 1 mmol) in AcOH (3 mL) was heated at 100°C for 30 min. After cooling to room temperature, the mixture was poured into water. The precipitate was filtered and air dried. The crude product was purified by column chromatography on silica gel (eluent hexane-EtOAc, 4:1) to give **8** (80 mg), and **9** (60 mg) in 28% and 22% yield, respectively. mp 234–235°C. ^{1}H NMR ($CDCl_3$): δ 1.11 (t, 3H, CH_2CH_3), 2.99 (s, 3H, CH_3), 4.18 (q, 2H, CH_2CH_3), 6.96 (d, $^3J_{H,H}$ = 5.7 Hz, 1H, CH), 7.23 (s, 1H, meso-CH), 7.33–7.55 (m, 11H, ArH, CH), ^{19}F NMR ($CDCl_3$): δ −143.6 (m). Anal. calcd. for $C_{28}H_{21}BF_2N_2O_4$: C, 67.5; H, 4.21; N, 5.62. Found: C, 67.4; H, 4.4; N, 5.76.

3-[2-(4-Chlorophenylsulfanyl)ethen-1-yl)-5-methyl-1,7-diphenyl-2,6-dicarbethoxy-4,4-difluoro-4-bora-3a,4a,-diaza-s-indacene (10). An ethanol solution of sodium *p*-chlorotiophenolate (consisted of *p*-chlorotiophenole (54 mg, 0.37 mmol), NaOH (15 mg, 0.37 mmol) and EtOH (1 mL)) was added to a solution of compound **6** (160 mg, 0.28 mmol) in DMF (2 mL). The mixture was left for 30 min at room temperature followed by pouring into 10% aqueous NH_4Cl, and then the precipitate was filtered. The wet product was dissolved in EtOAc, dried over Na_2SO_4, and evaporated to dryness. The residue was recrystallized from cyclohexane. Yield 140 mg (74%). M.p.125–126°C. ^{1}H NMR (DMSO-d_6): δ 0.90 (t, 3H, CH_2CH_3), 1.03 (t, 3H, CH_2CH_3), 2.79 (s, 3H, CH_3), 4.08 (m, 4H, CH_2CH_3), 6.89 (s, 1H, meso-CH), 7.05 (d, $^3J_{H,H}$ = 15.9 Hz, 1H, CH), 7.42 (m, 10H, ArH), 7.59 (s, 4H, ArH), 8.08 (d, $^3J_{H,H}$ = 15.9 Hz, 1H, CH). Anal. calcd. for $C_{36}H_{30}BClF_2N_2O_4S$: C, 64.5; H, 4.48; N, 4.18. Found: C, 64.7; H, 4.6; N, 4.1.

3-(2-Phenylaminoethen-1-yl)-5-methyl-1,7-diphenyl-2,6-dicarbethoxy-4,4-difluoro-4-bora-3a,4a,-diaza-s-indacene (11). a. A mixture of aldehyde **5** (130 mg, 0.24 mmol), aniline (35 mg, 0.38 mmol), and acetic acid (2 mL) was heated to 80°C. After cooling to room temperature, the precipitate was filtered. Yield 120 mg (81%).

b. A mixture of enamine **4** (570 mg, 1 mmol), aniline (130 mg, 1.4 mmol), and acetic acid (3 mL) was refluxed for 20 min. After cooling to room temperature, the precipitate was filtered. Yield 360 mg (58%).

M.p.217–218°C. ^{1}H NMR (DMSO-d_6): δ 0.88 (t, 3H, CH_2CH_3), 1.01 (t, 3H, CH_2CH_3), 2.76 (s, 3H, CH_3), 4.06 (m, 4H, CH_2CH_3), 6.46 (s, 1H, meso-CH), 6.68 (d, $^3J_{H,H}$ = 13.2 Hz, 1H, CH), 7.15 (m, 3H, ArH), 7.34–7.44 (m, 12H, ArH), 8.81 (dd, $^3J_{H,H}$ = 13.5 Hz, $^3J_{H,H}$=13.2 Hz,1H, CH), 10.96 (d, $^3J_{H,H}$ = 13.5 Hz, 1H, NH). ^{19}F NMR (DMSO-d_6): δ −140.8

(m). Anal. calcd. for $C_{36}H_{32}BF_2N_3O_4$: C, 69.8; H, 5.16; N, 6.78. Found: C, 69.7; H, 5.4; N, 7.1.

3-(2-Acetanilidoethen-1-yl)-5-methyl-1,7-diphenyl-2,6-dicarbethoxy-4,4-difluoro-4-bora-3a,4a,-diaza-s-indacene (12). A solution of compound **10** (200 mg, 0.32 mmol), Ac_2O (0.5 g, 4.9 mmol), and triethylamine (15 mg, 0.15 mmol) in acetonitrile (2 mL) was refluxed for 1 min. After cooling to room temperature, the mixture was poured into water and allowed to stand for 30 min. The product was filtered and recrystallized from EtOH. Yield 120 mg (56%). M.p. 145–146°C. ^{1}H NMR (DMSO-d_6): δ 1.01 (m, 6H, CH_2CH_3), 1.99 (s, 3H, $COCH_3$), 2.69 (s, 3H, CH_3), 4.08 (m, 4H, CH_2CH_3), 5.93 (d, $^3J_{H,H}$ = 14.7 Hz, 1H, CH), 6.78 (s, 1H, meso-CH), 7.38–7.48 (m, 12H, ArH), 7.64 (m, 3H, ArH), 8.93 (d, $^3J_{H,H}$ = 14.7 Hz, 1H, CH). Anal. calcd. for $C_{38}H_{34}BF_2N_3O_5$: C, 70.0; H, 5.14; N, 6.35. Found: C, 69.9; H, 5.1; N, 6.1.

2-Carbethoxy-3,7-dimetyl-1,9-diphenyl-4,4-difluoro-3a,4a,7-triaza-4-bora-cyclopenta[b]fluoren-8-on (13). A mixture of aldehyde **5** (200 mg, 0.37 mmol), acetic acid (22 mg, 0.37 mmol), 27% methanol solution of methylamine (100 mg), and toluene (3 mL) was refluxed for 2 min. After cooling to room temperature, the precipitate was filtered. Yield 80 mg (42%). M.p. 273–274°C. ^{1}H NMR (DMSO-d_6): δ 1.04 (t, 3H, CH_2CH_3), 2.85 (s, 3H, CH_3), 3.43 (s, 3H, NCH_3), 4.10 (q, 2H, CH_2CH_3), 6.58 (d, $^3J_{H,H}$ = 6.9 Hz, 1H, CH), 7.11 (s, 1H,meso-CH), 7.47 (m, 8H, ArH), 7.64 (m, 2H, ArH), 7.84 (d, $^3J_{H,H}$ = 6.9 Hz, 1H, CH).^{19}F NMR (DMSO-d_6): δ −141.6 (m). LS-MS: *m*/*z* 511 $[M]^+$. Anal. calcd. for $C_{29}H_{24}BF_2N_3O_3$: C, 68.1; H, 4.69; N, 8.22. Found: C, 68.4; H, 4.6; N, 7.96.

3-(2-Diethylaminoethen-1-yl)-5-methyl-1,7-diphenyl-2,6-dicarbethoxy-4,4-difluoro-4-bora-3a,4a,-diaza-s-indacene (14). a. A solution of aldehyde **5** (270 mg, 0.5 mmol) and triethylamine (150 mg, 1.5 mmol) in dioxane (3 mL) was allowed to stand for 24 h at room temperature. The reaction mixture was purified by column chromatography on silica gel (eluent CH_2Cl_2) to give the pure product. Yield 100 mg (33%).

b. A solution of aldehyde **5** (136 mg, 0.25 mmol), diethylamine (91 mg, 1.25 mmol), and acetic acid (60 mg, 1 mmol) in methanol (2 mL) was heated at reflux for 5 min. After cooling to room temperature, the product was filtered and purified by column chromatography (eluent hexane-EtOAc, 3:2). Yield 50 mg (33%).

M.p. 188–189°C. ^{1}H NMR (DMSO-d_6): δ 0.92 (t, 3H, CH_2CH_3), 0.99 (t, 3H, CH_2CH_3), 1.25 (t, 6H, NCH_2CH_3), 2.71 (s, 3H, CH_3), 3.49 (q, 4H, NCH_2CH_3), 4.03 (m, 4H, CH_2CH_3), 6.10 (d, $^3J_{H,H}$ = 12.9 Hz, 1H, CH), 6.28 (s, 1H, meso-CH), 7.30–7.44 (m, 10H, ArH), 8.25 (d, $^3J_{H,H}$ = 12.9 Hz, 1H, CH). ^{19}F NMR (DMSO-d_6): δ −141.1 (m). Anal. calcd. for $C_{34}H_{36}BF_2N_3O_4$: C, 68.1; H, 6.0; N, 7.01. Found: C, 67.9; H, 5.9; N, 7.1.

3-(2-Dibuthylaminoethen-1-yl)-5-methyl-1,7-diphenyl-2,6-dicarbethoxy-4,4-difluoro-4-bora-3a,4a,-diaza-s-indacene (15). The product was prepared using tributylamine analogously to **14**. Yield 180 mg (54 %). M.p. 179–180°C. ^{1}H NMR (DMSO-d_6): δ 0.97 (m, 12H, CH_2CH_3+$N(CH_2)_3CH_3$), 1.39 (m, 4H, CH_2), 1.65 (m, 4H, CH_2), 2.7 (s, 3H, CH_3), 3.44 (q, 4H, NCH_2), 4.04 (m, 4H, CH_2CH_3), 6.11 (d, $^3J_{H,H}$ = 13.2 Hz, 1H, CH), 6.27 (s, 1H, meso-CH), 7.30–7.42 (m, 10H, ArH), 8.23 (d, $^3J_{H,H}$ = 13.2 Hz, 1H, CH). Anal. calcd. for $C_{38}H_{45}BF_2N_3O_4$: C, 69.6; H, 6.87; N, 6.41. Found: C, 69.9; H, 6.9; N, 6.2.

Reaction of aldehyde 5 with ethyldiisopropylamine. A solution of aldehyde **5** (270 mg, 0.5 mmol), ethyldiisopropylamine (130 mg, 1 mmol) in dioxane (3 mL) was allowed to stand for 24 h at room temperature. The reaction mixture was purified by column chromatography on silica gel (eluent CH_2Cl_2) to give 110 mg of the mixture of two dyes. ^{1}H NMR ($CDCl_3$): δ 0.88 (t, 6H, CH_2CH_3), 1.07 (t, 6H, CH_2CH_3), 1.36 (m, 21H, $CH(CH_3)_2$ + NCH_2CH_3), 2.86 (s, 6H, CH_3), 3.47 (q, 2H, NCH_2CH_3), 3.75 (m, 2H, $CH(CH_3)_2$), 4.01–4.11 (m, 8H, CH_2CH_3), 4.28 (m, 1H, $CH(CH_3)_2$), 6.31 (d, $^3J_{H,H}$ = 13.5 Hz, 1H, CH), 6.43 (m, 3H, meso-CH + CH), 7.25–7.44 (m, 20H, ArH), 8.57 (d, $^3J_{H,H}$ = 13.5 Hz, 1H, CH), 8.69 (d, $^3J_{H,H}$ = 13.5 Hz, 1H, CH).

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