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Synthesis and spectroscopic properties of β,β' -dibenzo-3,5,8-triaryl-BODIPYs†

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Abstract

A series of β,β' -bicyclo-3,5-diaryl-BODIPYs were synthesized from the corresponding β,β' -bicyclo-3,5-diiodo-BODIPYs (**1a,b**) via Pd(0)-mediated Suzuki cross-coupling reactions in 82–92% yields. Subsequent aromatization with DDQ afforded the corresponding β,β' -dibenzo-aryl-BODIPYs, which showed red-shifted absorptions and emissions in the near-IR range. The dibenzo-appended BODIPYs showed characteristic ^1H -, ^{13}C -, ^{11}B - and ^{19}F -NMR shifts, and nearly planar conformations by X-ray crystallography.

Introduction

4,4-Difluoro-4-bora-3a,4a-diaza-*s*-indacene (known as BODIPY) dyes have attracted wide research interest in the last two decades, due to their remarkable properties, including large absorption extinction coefficients, narrow emission bandwidths, high fluorescence quantum yields, and ease of functionalization that enables the tuning of their physicochemical properties.¹ BODIPYs with specific functionalization and properties have been investigated for numerous applications, for example as imaging probes,² chemical sensors,³ photosensitizers,⁴ fluorescent switches⁵ and as energy transfer cassettes.⁶ The success of these applications relies on the synthesis of long-wavelength absorbing and emitting (ca. 600–800 nm) BODIPYs bearing functionalities for enhanced solubility and/or for conjugation to biomolecules. Strategies for achieving these goals include: (1) functionalization at the 3,5-positions with aryl,⁷ styryl^{7a,e,8} or arylethynyl^{7a,d,e,9} substituents, (2) replacement of the bridging *meso*-carbon with a nitrogen to generate aza-BODIPYs,¹⁰ (3) prevention of free rotation of BODIPY aryl substituents,¹¹ and (4) benzo-fusion to the β,β' -pyrrolic positions.^{12–15} The combination of two or more of these strategies can lead to BODIPYs with near-IR absorptions/emissions and enhanced quantum yields.

Among the BODIPYs with extended π -systems, those with aromatic ring fusion at the β,β' -pyrrolic positions are particularly attractive, because they induce large red-shifts (ca. 50 nm per annulated benzene ring), and generally enhance the planarity, hydrophobicity and cell permeability of the BODIPY platform. Current approaches to benzo-fused BODIPYs are outlined in Fig. 1. The Ono method¹³ (Route A) involves a retro Diels–Alder reaction from

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bicyclo-octadiene-fused precursors, requiring heating at 210–220 °C under reduced pressure for up to 2 h. Milder conditions were developed by Hao and Jiao¹⁴ (Route B, Fig. 1) from isoindole precursors, and by Ulrich and Ziesse¹⁵ (Route C) from 2-acylacetophenone precursors. Alternatively, benzo-fused BODIPYs are prepared from tetrahydroisoindole precursors (Route D) by reaction with DDQ in refluxing toluene, as we have recently reported.¹²

Various methods have been investigated for the functionalization of the 3,5-positions of BODIPYs,^{1,7} including metal mediated cross-coupling reactions,^{7,16} aromatic substitutions,^{7,16,17} Knoevenagel condensations,^{8,18} C–H arylations¹⁹ and radical arylations.²⁰ Among these, the Pd(0)-catalyzed Suzuki coupling reactions are particularly convenient³² due to the variety of commercially available boronic acids and the ready availability of 3,5-dichloro- and 3,5-dibromo-BODIPYs. Previously reported Suzuki couplings on 3,5-dichloro-BODIPYs require microwave irradiation, and produce the target BODIPYs in yields up to 68%.^{7a} In the case of 3,5-dibromo-BODIPYs, prolonged reflux in toluene produces the corresponding 3,5-diaryl-BODIPYs in yields ranging from 13% to 55%.^{4a,21} On the other hand, the more reactive 3,5-diiodo-BODIPYs have not been previously investigated in Suzuki cross-coupling reactions, although we have previously investigated their reactivity under Sonogashira cross-coupling reactions.^{9b} Herein we report the synthesis of β,β' -bicyclo-8-aryl-3,5-diiodo-BODIPYs from commercially available reagents, and investigate their functionalization by Pd(0)-catalyzed Suzuki reactions to afford β,β' -bicyclo-3,5,8-triaryl-BODIPYs in high yields. The optimized conditions were also applied for the synthesis of asymmetric BODIPYs. Furthermore, aromatization of the β,β' -bicyclo-3,5,8-triaryl-BODIPYs using DDQ, gave the corresponding β,β' -dibenzo-3,5,8-triaryl-BODIPYs in moderate yields. The structural and spectroscopic properties of the new BODIPYs were investigated.

Results and discussion

Syntheses

β,β' -Bicyclo-3,5-diiodo-BODIPYs **1a,b** were synthesized from tetrahydroisoindole **2**²² as shown in Scheme 1. The methoxy groups were introduced on the 8-aryl group of **1b** with the aim to enhance the solubility of the targeted dibenzo-BODIPYs. The acid-catalyzed condensation of **2** with benzaldehyde or 3,5-dimethoxybenzaldehyde, in the presence of *n*Bu₄NI, gave dipyrromethanes **3a** and **3b** in 95 and 86% yields, respectively.¹² Basic hydrolysis followed by acidic work-up produced the corresponding carboxylic acids, which were iodinated and oxidized in one step, using iodine in aqueous methanol, to produce the corresponding 3,5-diiodo-dipyrromethenes **4a,b**. Complexation of **4a** and **4b** with BF₃·Et₂O under basic conditions gave BODIPYs **1a** and **1b**, in 40–42% overall yield from **3a,b** (4 steps). A crystal of BODIPY **1a** suitable for X-ray crystallography analysis was obtained and the structure is shown in Fig. 2. The mean of four C–I bonds in two independent molecules is 2.063 Å, these long bonds favor palladium(0) insertion in the Suzuki cross-coupling reactions. The plane of the *meso*-phenyl ring is nearly orthogonal to be central C₃N₂B best plane, forming a dihedral angle of 86.9° (average of two) with it.

The DDQ aromatization of BODIPYs **1a,b** and of dipyrromethenes **4a,b** was attempted under similar conditions to those previously reported for 3,5-di(ethoxycarbonyl)-BODIPYs,¹² using 9 equiv. DDQ in refluxing toluene. However, no β,β' -dibenzo-BODIPYs were produced, likely due to the instability of the C–I bonds under these conditions. Therefore, the reactivity of 3,5-diiodo-BODIPYs **1a,b** under Pd(0)-catalyzed Suzuki reactions was investigated prior to DDQ aromatization, as shown in Scheme 2. Among the Pd(0)-mediated cross-couplings previously investigated for the functionalization of halogenated BODIPYs, the Suzuki reaction is particularly attractive due to the ease of preparation of boronic acids and the variety of commercially available reagents, the ease of removal of boronic acids after reaction completion, and the relatively mild reaction conditions.²³ Therefore we decided to investigate the reactivity of 3,5-diiodo-BODIPYs **1a,b** under Suzuki conditions, and optimize the reactions conditions to produce the targeted 3,5-di-functionalized BODIPYs **5a–f** in high yields.

Three different palladium catalysts, Pd(PPh₃)₄,^{7a} Pd(OAc)₂/PPh₃²⁴ and Pd(PPh₃)₂ Cl₂^{9b} were first employed in the coupling of BODIPY **1a** with phenylboronic acid, using toluene as the solvent and K₂CO₃ as the base. After 8 h reflux in toluene the 3,5-diphenyl-BODIPY **5a** was isolated in 45%, 35% and 52% yields, respectively. These moderate yields led us to investigate Pd(dppf)Cl₂ as the catalyst,^{25,26} since Pd(0)–bidentate ligand complexes are more reactive in the oxidative addition of aryl iodide. Using Pd(dppf)Cl₂ as the catalyst, BODIPY **5a** was obtained from **1a** in 73%, after only 2 h reflux in toluene and in the presence of K₂CO₃. The reaction was further optimized using a co-solvent system consisting of toluene and THF in 1 : 1 ratio,^{21b} and under these conditions BODIPY **5a** was obtained in 85% yield. The optimized conditions were then used for the coupling of other boronic acids (4-nitrophenyl, 4-cyanophenyl-, 4-(trifluoromethyl)phenyl- and 4-(benzyloxycarbonyl)phenyl-²⁷ boronic acids) and the products from these reactions, BODIPYs **5b–f** were isolated consistently in high yields, as summarized in Table 1. The highest yield (92%) was obtained for **5f** due to the enhanced solubility of **1b** and **5f** in organic solvents.

Crystals suitable for X-ray analysis were obtained for BODIPYs **5a**, **5b**, **5c**, **5d** and **5e** and these are shown in Fig. 3. In BODIPY **5a**, the central C₃N₂B ring is nearly planar, with mean deviation 0.014 Å. Its 8-(*meso*)-phenyl ring forms a dihedral angle of 79.8° with the central ring, and its 3,5-phenyl rings form an average dihedral angle of 56.2° with the central ring. The molecule of **5b** lies on a crystallographic twofold axis, and the central ring is slightly twisted from planarity about that axis, with the off-axis C atoms lying alternately 0.076 Å off the best plane, and the N atoms 0.072 Å. The *meso*-phenyl group forms a dihedral angle of 60.4° with the central best plane, and the 3,5-phenyl groups 47.2°. In BODIPY **5c**, the central ring is non-planar, with the B atom lying 0.238 Å out of the C₃N₂B best plane. The *meso*-phenyl group forms a dihedral angle of 72.8° with the central plane, and the 3,5-phenyl groups an average of 61.0° with the central plane. In BODIPY **5d**, the central C₃N₂B ring is fairly planar, with mean deviation 0.022 Å. The *meso*-phenyl ring forms a dihedral angle of 74.4° with the central plane, and the 3,5-phenyl groups an average of 52.9° with it. In BODIPY **5e**, the central C₃N₂B ring is also fairly planar, with mean deviation 0.017 Å. The *meso*-phenyl group forms a dihedral angle of 82.4° with the central

plane, and the 3,5-phenyl rings an average of 59.8° with it. While **1a** and **5c** are also dichloromethane solvates, the larger 3,5-substituents in BODIPY **5e** form a cavity, which allows the solvent molecule to nest inside it, as shown in Fig. 3.

The aromatizations of BODIPYs **5a–f** were then investigated, using 9 equiv. of DDQ in refluxing toluene for 30 minutes,¹² and the reactions were monitored by TLC and UV-Vis (Scheme 2). The dibenzo-BODIPYs **6a–f** were isolated in moderate yields (32–54%), as summarized in Table 1. The lowest yield was obtained for the 3,5-dinitrophenyl-substituted BODIPY **6b**, due to the strong electron-withdrawing character of the nitro groups, and its reduced solubility compared with the other BODIPYs. Polar byproducts were observed in all the reactions, likely as a result of BODIPY oxidation and/or radical polymerization processes. Such polar compounds were the major products obtained from the DDQ aromatization of BODIPYs bearing electron-donating groups at the 3,5-positions, such as *p*-methoxyphenyl or thienyl groups.

BODIPYs **6a**, **6b** and **6c** were characterized by X-ray crystallography, as shown in Fig. 4. BODIPY **6a** has a similar twisted conformation to that seen in **5b**, although in this case the molecule has only approximate C_2 symmetry rather than lying on a crystallographic axis. The B and *meso* C atoms lie an average of only 0.011 Å from the C_3N_2B best plane, while twisting about the C–B vector causes the other four atoms to lie alternately an average of 0.045 Å out of plane. The *meso*-phenyl group forms a dihedral angle of 68.3° with the central plane, and the 3,5-phenyls an average of 60.6°. The central ring of BODIPY **6b** has a similar non-planar conformation to that of **5c**, with the B atom lying 0.223 Å out of the plane of the other five atoms. The *meso*-phenyl ring forms a dihedral angle of 76.8° with the central plane, and the 3,5-diphenyls a mean dihedral angle of 57.2° with it. The central ring of both independent molecules of BODIPY **6c** has a similar conformation to that of **5c** and **6b**, with the B atom lying 0.244 Å (mean of two) out of the plane of the other five atoms. The *meso*-phenyl group forms a mean dihedral angle of 82.2° with the central plane, and the 3,5-diphenyls a mean (of four) dihedral angle of 50.2° with it.

BODIPYs **1a** and **1b** were also subjected to unsymmetric functionalization, using two different boronic acids, as shown in Scheme 3. Reaction of BODIPY **1a** with one equivalent of (4-(benzyloxycarbonyl)phenyl)boronic acid in the presence of Pd(dppf)Cl₂ and K₂CO₃, produced mixtures of the di- and mono-substituted products **6e** and **7a**, along with unreacted **1a**. While short reaction times gave low yields of **7a** (5% after 30 minutes), long reaction times favored the reduction of **7a** to the corresponding α -free BODIPY. On the other hand, the reaction of **1a** with three equivalents of boronic acid afforded the targeted iodo-BODIPY **7a** in 42% yield, after 30 minutes reaction time. After quick work up and purification, BODIPY **7a** was subjected to a second Suzuki cross-coupling reaction in the presence of five equivalents of 4-(trifluoromethyl)phenylboronic acid for 15 minutes, affording BODIPY **8a** in 95% yield. BODIPY **1b** reacted under similar conditions giving BODIPY **8b** in 40% yield over two steps. The aromatization of unsymmetrical BODIPYs **8a** and **8b** using 9 equivalents of DDQ in refluxing toluene for 30 minutes, gave BODIPYs **9a** and **9b** in 54% and 51% yield, respectively.

Spectroscopy

All BODIPYs were characterized by ^1H , ^{11}B , ^{13}C and ^{19}F NMR, HRMS, and by UV-Vis and fluorescence spectrophotometry (see ESI† for the spectra). The products from the Suzuki cross-coupling reactions, the β,β' -bicyclo-3,5,8-triaryl-BODIPYs **5a–f** and **8a,b** showed the characteristic ^1H and ^{13}C chemical shifts for the 3,5-aryl groups in the ranges 7.0–8.5 ppm and 120–155 ppm, respectively. After aromatization to the corresponding β,β' -dibenzo-BODIPYs, the chemical shifts for the 3,5-aryl groups shifted only slightly. However, the ^1H and ^{13}C chemical shifts for the fused benzene rings characteristically appeared within the aromatic region. Differences were also seen in the ^{11}B and ^{19}F NMR spectra of the BODIPYs that are diagnostic of the formation of the Suzuki and the β,β' -dibenzo products, as shown in Table 2. All BODIPYs showed a triplet in ^{11}B -NMR with *ca.* $J_{\text{BF}} = 32$ Hz, as previously observed. In ^{19}F -NMR the isotopes ^{11}B ($I = 3/2$, 80%) and ^{10}B ($I = 3$, 20%) split the BF_2 signals into a quartet ($J_{11\text{BF}} = 32$ Hz) and septet ($J_{10\text{BF}} = 10$ Hz), respectively.²⁸ The signals in ^{11}B -NMR shifted downfield from *ca.* 0.5 ppm for the β,β' -bicyclo-3,5-diiodo-BODIPYs to about 0.8 ppm for the β,β' -bicyclo-3,5,8-triaryl-BODIPYs and about 1.7 ppm for the β,β' -dibenzo-3,5,8-triaryl-BODIPYs. Similarly in ^{19}F -NMR the signals shifted downfield, from the β,β' -bicyclo-3,5-diiodo-BODIPYs to the corresponding Suzuki products and the final β,β' -dibenzo-BODIPYs. These changes are likely due to interactions of the 3,5-aryl groups with the BF_2 unit, and to the extension of π -conjugation in the case of the β,β' -dibenzo-BODIPYs.

The spectroscopic properties of BODIPYs **1a,b**, **5a–f**, **6a–f**, **8a,b** and **9a,b** in THF, namely their maximum absorption and emission wavelengths, molar extinction coefficients, Stokes shifts, and fluorescence quantum yields, were investigated and are summarized in Table 3. Fig. 5 and 6 show the normalized absorption and emission spectra of selected BODIPYs, respectively (additional spectra can be found in the ESI†). The BODIPYs show characteristic absorption and emission spectra, with high molar absorption coefficients ($\log \epsilon = 4.63\text{--}5.00$) and Stokes-shifted narrow emission bands. The strong absorption bands are due to the $S_0\text{--}S_1$ ($\pi\text{--}\pi^*$) transition, and the shoulders at lower wavelength are due to the 0–1 vibrational transition. The 3,5-diiodo-BODIPYs **1a** and **1b** show the lowest quantum yields due to the heavy atom effect,²⁹ and their absorption and emission bands are close to the previously reported *meso*-free 3,5-diiodo-BODIPYs,^{9b} while their Stokes shifts are smaller due to the presence of the *meso*-aryl group. The β,β' -bicyclo-3,5,8-triaryl-BODIPYs show higher quantum yields and larger Stokes shifts than the starting **1a,b**, in the ranges of 0.35–0.52 and 26–39 nm, respectively. Among them, BODIPY **5b** bearing two nitro groups showed the most red-shifted absorption and emission bands, and the largest Stokes shift. On the other hand, the fluorescence quantum yields were lowest for **5b** with two nitro groups and highest for **5d** bearing two trifluoromethyl groups. *p*-Nitrophenyl groups have been reported to partially quench the fluorescence of BODIPYs *via* intramolecular photoinduced electron transfer,³⁰ due to the very strong electron-withdrawing effect of the nitro group. The trifluoromethylphenyl groups likely reduce photoinduced electron transfer, and the presence of a trifluoromethyl at the 8-position of BODIPYs was previously reported to induce high

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fluorescence quantum yields.³¹ The introduction of a 8-(3,5-dimethoxy)phenyl group in place of a 8-phenyl caused negligible shifts in the absorption and emission wavelengths, and slightly decreased the quantum yield, probably because of increased non-radiative decay to the ground state.³²

The β,β' -dibenzo-BODIPYs showed 77–89 nm red-shifts in the absorption and emission bands, compared with their corresponding β,β' -bicyclo-BODIPYs, due to decrease in the HOMO–LUMO gap, and slightly smaller Stokes shifts. The fluorescence quantum yields were in general higher for the β,β' -dibenzo-BODIPYs compared with the corresponding β,β' -bicyclo-BODIPYs, in agreement with previous observations,¹² except in the case of the 3,5-dinitrophenyl-BODIPY **6b**, which showed the lowest quantum yield of all 3,5,8-triaryl-BODIPYs. The spectroscopic properties of the unsymmetrical BODIPYs **8a,b** and **9a,b** were similar to those of symmetric **5d–f** and **6d–f**, respectively, in agreement with previous observations.²⁰

The functionalized near-IR β,β' -dibenzo-3,5,8-triaryl-BODIPYs are important platforms for further derivatization, for example by reduction of the nitro groups³³ or by ester cleavage,^{7b,9b,34} to enable their conjugation to proteins for fluorescence labelling, and other applications.

Conclusions

Two β,β' -bicyclo-3,5-diiodo-BODIPYs (**1a,b**) bearing either a *meso*-phenyl or a *meso*-3,5-dimethoxyphenyl group were synthesized from a tetrahydroisindole precursor. The functionalization of **1a,b** via Suzuki cross-coupling reactions, using Pd(dppf)Cl₂ in 1 : 1 toluene/THF, in the presence of K₂CO₃ and an arylboronic acid (aryl = phenyl, 4-nitrophenyl, 4-cyanophenyl, 4-(trifluoromethyl)-phenyl- and 4-(benzyloxycarbonyl)phenyl) gave the corresponding β,β' -bicyclo-3,5,8-triaryl-BODIPYs in 82–92% yields. Unsymmetrically-substituted 3,5-diaryl-BODIPYs were also prepared using two consecutive Suzuki cross-coupling reactions, in 40% yield. DDQ aromatization of these compounds produced the corresponding β,β' -dibenzo-3,5,8-triaryl-BODIPYs in 32–56% yields. The dibenzo-BODIPYs showed characteristic ¹H and ¹³C-NMR chemical shifts for the fused benzene rings in the aromatic region. Furthermore, characteristic downfield shifts were observed for the BF₂ group in the ¹¹B and ¹⁹F-NMR spectra. The β,β' -dibenzo-3,5,8-triaryl-BODIPYs showed 77–89 nm red-shifted absorptions and fluorescence emissions compared with the corresponding β,β' -bicyclo-BODIPYs, smaller Stokes shifts, and in general higher quantum yields. The 3,5-(*p*-nitrophenyl) groups caused the largest red-shifts in the absorption and emission bands, and the largest Stokes shifts, although they partially quenched the fluorescence of the BODIPYs via intramolecular photoinduced electron transfer. On the other hand, the 3,5-(*p*-trifluoromethylphenyl) groups induced the highest fluorescence quantum yields among this series of BODIPYs.

Experimental section

General

^1H , ^{11}B , ^{13}C and ^{19}F NMR spectra were measured on a 400 MHz or 500 MHz NMR spectrometer at room temperature. Chemical shifts (δ) are given in ppm relative to TMS. High-resolution mass spectra were obtained using the ESI-TOF mode. UV-visible absorption and fluorescence emission spectra were recorded on commercial spectrophotometers (190–800 nm scan range). Relative fluorescence quantum yields (Φ_f) were calculated using rhodamine 6G ($\Phi = 0.88$ in anhydrous ethanol) as the standard for compounds **1a,b**, **5a–f**, **8a,b** and methylene blue ($\Phi = 0.03$ in anhydrous methanol) as the standard for compounds **6a–f** and **9a,b**.³⁵ For compounds **1a,b**, **5a–f**, **8a,b** the slit width was set at 3.0 nm for excitation and 3.0 nm for emission. For compounds **6a–f** and **9a,b** the slit width was set at 5.0 nm for excitation and 5.0 nm for emission. Non-degassed, spectroscopic-grade solvents and a 10 mm quartz cuvette were used. Dilute solutions ($0.01 < A < 0.05$) were used to minimize the reabsorption effects. The quantum yields were calculated using the previously reported equation: $\Phi_X = \Phi_S(I_X/I_S)(A_S/A_X)(n_X/n_S)^2$, where Φ_S stands for the reported quantum yield of the standard, I stands for the area under the emission spectra, A stands for the absorbance at the excitation wavelength, and n stands for the refractive index of the solvent ($n = 1$ when the same solvent was used for both the test sample and the standard). X subscript stands for the sample, and S subscript stands for the standard.³⁶

All commercial available reagents were used without further purification. The starting ethyl-4,5,6,7-tetrahydroisindole ester **2**,¹² **3a**¹² and 4-(benzyloxycarbonyl)phenyl-boronic acid²⁸ were prepared following literature procedures. All Suzuki coupling reactions were performed under an argon atmosphere in deoxygenated solvents and all other reactions were performed under nitrogen in commercial available solvents.

Synthesis of 3,5-diiodo-8-aryl-BODIPYs **1a,b**

To a solution of tetrahydroisindole **2** (772 mg, 4.00 mmol) p-TsOH monohydrate (40.0 mg, 0.210 mmol) and $n\text{Bu}_4\text{NI}$ (20.0 mg, 0.0541 mmol) in dichloromethane (50 mL) was added 0.6 equiv. of arylaldehyde. The reaction was stirred for 12 h at room temperature under inert atmosphere. The mixture was washed with sat. NaHCO_3 (1×50 mL) and with sat. NaCl (1×50 mL) before being dried over anhydrous Na_2SO_4 . The solvent was removed under vacuum and the residue was purified by silica gel column chromatography (elution : hexanes/ethyl acetate 5 : 1). Dipyrromethanes **3a** (from benzaldehyde) and **3b** (from 3,5-dimethoxybenzaldehyde) were obtained in 95% and 86% yield, respectively, and **3a**'s NMR and MS are in agreement with those reported.¹² For **3b**: orange solid, mp ($^\circ\text{C}$) 89; ^1H NMR (CDCl_3 , 400 MHz) δ 9.39 (s, 2H), 6.33 (t, $J = 2.3$ Hz, 1H), 6.24 (d, $J = 2.3$ Hz, 2H), 5.40 (s, 1H), 4.19–4.09 (m, 4H), 3.67 (s, 6H), 2.76 (t, $J = 6.3$ Hz, 4H), 2.27 (t, $J = 6.3$ Hz, 4H), 1.73–1.64 (m, 8H), 1.24 (t, $J = 7.1$ Hz, 6H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 161.9, 161.0, 141.7, 130.8, 129.0, 119.7, 116.7, 106.5, 98.3, 59.7, 55.1, 40.3, 23.3, 23.2, 23.1, 21.3, 14.3; HRMS (ESI-TOF) m/z 535.2811 $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{31}\text{H}_{39}\text{N}_2\text{O}_6$ 535.2803. Dipyrromethane **3a** or **3b** (1.00 mmol) was dissolved in THF/methanol 1 : 1 (12 mL) and a solution of KOH (504 mg, 8.98 mmol) in water (10 mL) was added. The final mixture was refluxed for 4 h before being cooled to room temperature, poured into 2 M HCl (50 mL) and stirred at room

temperature for 15 min. The precipitate was collected under vacuum filtration and dissolved in 45 mL methanol. A solution of NaHCO₃ (0.54 g) and I₂ (0.50 g) in water (15 mL) was added, the mixture was sonicated for 5 min and then stirred for 24 h under Ar. The mixture was filtered and the precipitate washed with cold hexanes to remove excess iodine. The precipitate was dissolved in dichloromethane (50 mL) and cooled with an ice bath. Triethylamine (2.0 mL) and BF₃·OEt₂ (3.0 mL) were added. After 5 min the ice bath was removed and the solution was stirred at room temperature for 2 h. The solvents were removed under vacuum and the resulting residue was dissolved in ethyl acetate (100 mL) and washed with 1 M HCl (1 × 100 mL), sat. NaHCO₃ (1 × 50 mL) and sat. NaCl (1 × 50 mL). Ethyl acetate was removed and the oily residue was purified by silica gel column chromatography (elution : hexanes/dichloromethane 1 : 2). 3,5-Diiodo-BODIPYs **1a** and **1b** were obtained in 40% and 42% yields, respectively, as brown solids.

3,5-Diiodo-8-phenyl-BODIPY 1a—Mp (°C) 220; ¹H NMR (CDCl₃, 400 MHz) δ 7.49 (dd, *J* = 5.1, 1.9 Hz, 3H), 7.26–7.20 (m, 2H), 2.30 (tt, *J* = 6.3, 1.3 Hz, 4H), 1.62–1.56 (m, 4H), 1.53 (t, *J* = 6.3 Hz, 4H), 1.42–1.36 (m, 4H); ¹³C NMR (CDCl₃, 125 MHz) δ 142.2, 139.1, 136.3, 134.6, 134.3, 129.5, 129.4, 127.7, 106.2, 24.4, 24.2, 23.1, 22.4; ¹¹B NMR (CDCl₃, 128 MHz) δ 0.47 (t, *J*_{BF} = 30.7 Hz); ¹⁹F NMR (CDCl₃, 376 MHz) δ –143.71 (septet, ¹*J*_{10BF} = 10.3 Hz), –143.76 (quartet, ¹*J*_{11BF} = 30.7 Hz); HRMS (ESI-TOF) *m/z* 649.9796 [M + Na]⁺ calcd for C₂₃H₂₁BF₂I₂N₂Na 649.9784.

3,5-Diiodo-8-(3,5-dimethoxyphenyl)-BODIPY 1b—Mp (°C) 226; ¹H NMR (CDCl₃, 400 MHz) δ 6.55 (t, *J* = 2.3 Hz, 1H), 6.39 (d, *J* = 2.3 Hz, 2H), 3.80 (s, 6H), 2.31 (t, *J* = 6.2 Hz, 4H), 1.74 (t, *J* = 6.2 Hz, 4H), 1.65–1.59 (m, 4H), 1.48–1.40 (m, 4H); ¹³C NMR (CDCl₃, 125 MHz) δ 161.7, 142.1, 138.6, 136.09, 136.06, 135.7, 134.2, 106.1, 105.4, 101.1, 55.6, 24.2, 23.8, 23.1, 22.3; ¹¹B NMR (CDCl₃, 128 MHz) δ 0.44 (t, *J*_{BF} = 30.6 Hz); ¹⁹F NMR (CDCl₃, 376 MHz) δ –143.71 (septet, ¹*J*_{10BF} = 10.2 Hz), –143.79 (quartet, ¹*J*_{11BF} = 30.6 Hz); HRMS (ESI-TOF) *m/z* 668.0104 [M – F]⁺ calcd for C₂₅H₂₄BF₂I₂N₂O₂ 668.0113.

General Suzuki cross-coupling conditions

For symmetric BODIPYs, 62.8 mg (0.100 mmol) **1a** or 68.8 mg (0.100 mmol) **1b**, 5.00 mg Pd(dppf)Cl₂ and 5 equiv. (0.500 mmol) of aryl boronic acid were mixed under inert atmosphere. Toluene (2 mL) and THF (2 mL) were added *via* syringe and the solution was heated at 70 °C in an oil bath for 3 min. K₂CO₃ (1 M, 0.5 mL) solution was added *via* syringe and the reaction was monitored by TLC until complete consumption of 3,5-diiodo-BODIPY. The cooled solution was filtered through celite to remove excess palladium and boronic acid, and the solvent was concentrated under vacuum. The residue was purified by silica gel column chromatography to afford the corresponding 3,5-diaryl-BODIPYs as red solids, which were recrystallized using 1 : 1 dichloromethane/hexane. For the unsymmetric BODIPYs, 62.8 mg (0.100 mmol) BODIPY **1a** or 68.8 mg (0.100 mmol) BODIPY **1b**, 5.00 mg Pd(dppf)Cl₂ and 3 equiv. (0.300 mmol) of (4-(benzyloxy carbonyl)phenyl)boronic acid were mixed under inert atmosphere. Toluene (2 mL) and THF (2 mL) were added *via* syringe and the solution was heated at 70 °C for 3 minutes. K₂CO₃ (1 M, 0.5 mL) solution was added *via* syringe and the reaction was heated at 70 °C for 30 min. The cooled solution was filtered through celite and the solvent removed under vacuum. The residue was purified

by silica gel column chromatography. The second band corresponding to the 3-aryl-5-iodo-BODIPY was collected, and immediately reacted with 5.00 mg Pd(dppf)Cl₂ and 5 equiv. of 4-(trifluoromethyl)phenylboronic acid under inert atmosphere. Toluene (2 mL) and THF (2 mL) were added *via* syringe and the solution was heated at 70 °C for 3 minutes. K₂CO₃ (1 M, 0.5 mL) solution was added *via* syringe and the reaction was heated at 70 °C for 30 min. The cooled solution was filtered through celite and the solvent removed under vacuum. The residue was purified by silica gel column chromatography and recrystallized using 1 : 1 dichloromethane/hexane.

BODIPY 5a—Yield 85%. Mp (°C) > 300; ¹H NMR (CD₂Cl₂, 400 MHz) δ 7.55 (dd, *J* = 5.0, 1.9 Hz, 3H), 7.50 (dd, *J* = 7.4, 2.3 Hz, 4H), 7.43–7.36 (m, 8H), 2.28 (s, 4H), 1.72 (t, *J* = 6.1 Hz, 4H), 1.57–1.52 (m, 4H), 1.48–1.43 (m, 4H); ¹³C NMR (CDCl₃, 125 MHz) δ 154.5, 141.6, 141.6, 135.7, 132.2, 131.3, 129.7, 129.62, 129.59, 129.57, 129.1, 129.0, 128.5, 128.1, 127.7, 24.3, 23.1, 22.7, 22.6; ¹¹B NMR (CDCl₃, 128 MHz) δ 0.87 (t, *J*_{BF} = 32.0 Hz); ¹⁹F NMR (CD₂Cl₂, 376 MHz) δ –131.45 (septet, ¹*J*_{10BF} = 10.4 Hz), –131.53 (quartet, ¹*J*_{11BF} = 32.0 Hz); HRMS (ESI-TOF) *m/z* 508.2638 [M – F]⁺ calcd for C₃₅H₃₁BFN₂ 508.2595.

BODIPY 5b—Yield 83%. Mp (°C) > 300; ¹H NMR (CD₂Cl₂, 400 MHz) δ 8.25–8.18 (m, 4H), 7.75–7.65 (m, 4H), 7.61–7.54 (m, 3H), 7.44–7.35 (m, 2H), 2.27 (t, *J* = 6.1 Hz, 4H), 1.74 (t, *J* = 6.1 Hz, 4H), 1.59–1.52 (m, 4H), 1.50–1.42 (m, 4H); ¹³C NMR (CD₂Cl₂, 100 MHz) δ 152.0, 147.8, 144.0, 143.4, 138.7, 134.8, 132.3, 130.79, 130.75, 130.7, 130.4, 129.52, 129.46, 127.9, 122.9, 24.4, 23.0, 22.5, 22.4; ¹¹B NMR (CD₂Cl₂, 128 MHz) δ 0.67 (t, *J*_{BF} = 32.3 Hz); ¹⁹F NMR (CD₂Cl₂, 376 MHz) δ –130.81 (septet, ¹*J*_{10BF} = 10.7 Hz), –130.89 (quartet, ¹*J*_{11BF} = 32.3 Hz); HRMS (ESI-TOF) *m/z* 617.2240 [M]⁺ calcd for C₃₅H₂₉BF₂N₂O₄ 617.2281.

BODIPY 5c—Yield 85%. Mp (°C) > 300; ¹H NMR (CD₂Cl₂, 400 MHz) δ 7.72–7.60 (m, 8H), 7.60–7.53 (m, 3H), 7.42–7.35 (m, 2H), 2.25 (t, *J* = 6.1 Hz, 4H), 1.72 (t, *J* = 6.1 Hz, 4H), 1.57–1.52 (m, 4H), 1.46 (q, *J* = 5.6 Hz, 4H); ¹³C NMR (CD₂Cl₂, 100 MHz) δ 152.3, 143.8, 143.2, 136.7, 134.9, 132.1, 131.6, 130.4, 130.40, 130.37, 130.3, 129.5, 129.4, 127.9, 118.6, 112.4, 24.4, 23.0, 22.5, 22.4; ¹¹B NMR (CDCl₃, 128 MHz) δ 0.70 (t, *J*_{BF} = 32.3 Hz); ¹⁹F NMR (CDCl₃, 376 MHz) δ –131.06 (septet, ¹*J*_{10BF} = 10.7 Hz), –131.13 (quartet, ¹*J*_{11BF} = 32.3 Hz); HRMS (ESI-TOF) *m/z* 600.2407 [M + Na]⁺ calcd for C₃₇H₂₉BF₂N₄Na 600.2382.

BODIPY 5d—Yield 82%. Mp (°C) > 300; ¹H NMR (CDCl₃, 400 MHz) δ 7.65 (q, *J* = 8.4 Hz, 8H), 7.55 (dd, *J* = 4.9, 1.9 Hz, 3H), 7.42–7.33 (m, 2H), 2.26 (t, *J* = 6.0 Hz, 4H), 1.70 (t, *J* = 6.0 Hz, 4H), 1.57–1.52 (m, 4H), 1.49–1.42 (m, 4H); ¹³C NMR (CDCl₃, 125 MHz) δ 154.6, 141.72, 135.8, 132.3, 131.4, 129.9, 129.8, 129.2, 129.1, 128.7, 128.3, 127.9, 24.4, 23.3, 22.84, 22.77; ¹¹B NMR (CDCl₃, 128 MHz) δ 0.78 (t, *J*_{BF} = 32.1 Hz); ¹⁹F NMR (CDCl₃, 376 MHz) δ –62.70 (s), δ –131.48 (septet, ¹*J*_{10BF} = 10.7 Hz), –131.55 (quartet, ¹*J*_{11BF} = 32.1 Hz); HRMS (ESI-TOF) *m/z* 644.2352 [M – F]⁺ calcd for C₃₇H₂₉BF₇N₂ 644.2343.

BODIPY 5e—Yield 86%. Mp (°C) > 300; ¹H NMR (CD₂Cl₂, 400 MHz) δ 8.22 (s, 2H), 8.11 (dt, *J* = 8.0, 1.5 Hz, 2H), 7.81 (dt, *J* = 7.9, 1.4 Hz, 2H), 7.58 (dd, *J* = 5.2, 1.9 Hz, 3H),

7.53–7.45 (m, 6H), 7.45–7.34 (m, 8H), 5.37 (s, 4H), 2.29 (t, $J = 6.0$ Hz, 4H), 1.76 (t, $J = 6.1$ Hz, 4H), 1.61–1.53 (m, 4H), 1.50–1.44 (m, 4H); ^{13}C NMR (CD_2Cl_2 , 100 MHz) δ 165.9, 153.3, 143.1, 142.7, 137.0, 136.4, 135.2, 131.9, 130.3, 130.2, 129.80, 129.77, 129.3, 129.0, 128.6, 128.2, 128.09, 128.06, 66.7, 24.5, 23.1, 22.6, 22.5; ^{11}B NMR (CD_2Cl_2 , 128 MHz) δ 0.77 (t, $J_{\text{BF}} = 32.3$ Hz); ^{19}F NMR (CDCl_3 , 376 MHz) δ –131.40 (septet, $^1J_{10\text{BF}} = 10.8$ Hz), –131.47 (quartet, $^1J_{11\text{BF}} = 32.3$ Hz); HRMS (ESI-TOF) m/z 818.3172 $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{51}\text{H}_{43}\text{BF}_2\text{N}_2\text{O}_4\text{Na}$ 818.3212.

BODIPY 5f—Yield 92%. Mp ($^\circ\text{C}$) > 300; ^1H NMR (CDCl_3 , 400 MHz) δ 8.06 (d, $J = 8.0$ Hz, 4H), 7.59 (d, $J = 8.1$ Hz, 4H), 7.45 (d, $J = 7.2$ Hz, 4H), 7.42–7.31 (m, 6H), 6.61 (t, $J = 2.2$ Hz, 1H), 6.54 (d, $J = 2.2$ Hz, 2H), 5.35 (s, 4H), 3.84 (s, 6H), 2.27 (t, $J = 6.0$ Hz, 4H), 1.93 (t, $J = 6.0$ Hz, 4H), 1.67–1.37 (m, 8H); ^{13}C NMR (CD_2Cl_2 , 125 MHz) δ 165.9, 161.9, 153.3, 142.7, 136.9, 136.7, 136.3, 131.5, 130.3, 130.1, 129.77, 129.75, 129.7, 128.9, 128.6, 128.2, 128.1, 124.9, 105.8, 101.2, 66.7, 55.7, 24.1, 23.1, 22.6, 22.5; ^{11}B NMR (CDCl_3 , 128 MHz) δ 0.73 (t, $J_{\text{BF}} = 32.0$ Hz); ^{19}F NMR (CD_2Cl_2 , 376 MHz) δ –131.25 (septet, $^1J_{10\text{BF}} = 10.7$ Hz), –131.32 (quartet, $^1J_{11\text{BF}} = 32.0$ Hz); HRMS (ESI-TOF) m/z 836.3535 $[\text{M} - \text{F}]^+$ calcd for $\text{C}_{53}\text{H}_{47}\text{BFN}_2\text{O}_6$ 836.3542.

BODIPY 8a—Yield 40%. Mp ($^\circ\text{C}$) > 300; ^1H NMR (CDCl_3 , 400 MHz) δ 8.17–8.11 (m, 2H), 7.75–7.64 (m, 6H), 7.58 (dd, $J = 5.0$ Hz, 1.9 Hz, 3H), 7.51–7.46 (m, 2H), 7.45–7.36 (m, 5H), 5.40 (s, 2H), 2.31 (dt, $J = 6.5$, 3.2 Hz, 4H), 1.75 (t, $J = 6.0$ Hz, 4H), 1.63–1.54 (m, 4H), 1.52–1.47 (m, 4H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 166.0, 153.5, 152.7, 142.7, 142.4, 142.2, 136.6, 135.9, 135.6, 135.1, 131.8, 131.6, 130.4, 130.0, 129.9, 129.6, 129.2, 129.1, 128.5, 128.2, 128.1, 127.8, 124.7, 124.7, 66.7, 24.3, 22.9, 22.5, 22.4; ^{11}B NMR (CDCl_3 , 128 MHz) δ 0.82 (t, $J_{\text{BF}} = 32.1$ Hz); ^{19}F NMR (CDCl_3 , 376 MHz) δ –62.61 (s), –131.28 (septet, $^1J_{10\text{BF}} = 10.3$ Hz), –131.35 (quartet, $^1J_{11\text{BF}} = 32.1$ Hz); HRMS (ESI-TOF) m/z 729.2839 $[\text{M}]^+$ calcd for $\text{C}_{44}\text{H}_{36}\text{BF}_5\text{N}_2\text{O}_2$ 729.2821.

BODIPY 8b—Yield 40%. Mp ($^\circ\text{C}$) > 300; ^1H NMR (CD_2Cl_2 , 400 MHz) δ 8.12–8.05 (m, 2H), 7.65 (s, 4H), 7.63–7.57 (m, 2H), 7.48–7.43 (m, 2H), 7.42–7.33 (m, 3H), 6.62 (t, $J = 2.3$ Hz, 1H), 6.55 (d, $J = 2.3$ Hz, 2H), 5.36 (s, 2H), 3.84 (s, 6H), 2.27 (t, $J = 6.0$ Hz, 4H), 1.95 (t, $J = 6.0$ Hz, 4H), 1.61–1.49 (m, 8H); ^{13}C NMR (CD_2Cl_2 , 100 MHz) δ 165.9, 161.9, 153.6, 152.6, 143.0, 142.9, 142.7, 136.9, 136.7, 136.3, 136.1, 131.6, 131.4, 130.4, 130.33, 130.25, 130.14, 130.07, 129.8, 129.0, 128.62, 128.58, 128.2, 128.1, 127.3, 125.6, 124.69, 124.66, 122.9, 105.8, 101.2, 66.8, 55.7, 24.2, 23.1, 22.6, 22.5, 22.4; ^{11}B NMR (CD_2Cl_2 , 128 MHz) δ 0.70 (t, $J_{\text{BF}} = 32.3$ Hz); ^{19}F NMR (CD_2Cl_2 , 376 MHz) δ –62.96 (s), –131.25 (septet, $^1J_{10\text{BF}} = 10.4$ Hz), –131.32 (quartet, $^1J_{11\text{BF}} = 32.3$ Hz); HRMS (ESI-TOF) m/z 812.2922 $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{46}\text{H}_{40}\text{BF}_5\text{N}_2\text{O}_4\text{Na}$ 812.2930.

General procedure for DDQ aromatization

β,β' -Bicyclo-3,5,8-triaryl-BODIPYs (0.100 mmol) and 204 mg (0.900 mmol) of DDQ were dissolved in 4 mL toluene. The solution was then refluxed under inert atmosphere for 30 min. The reaction was monitored by TLC and UV-Vis spectroscopy. The solvent was removed under vacuum and the residue was dissolved in 100 mL dichloromethane and washed with sat. NaHCO_3 (1 $\times$ 100 mL). The aqueous solution was extracted with

dichloromethane (2×50 mL) and the organic solvent was removed under vacuum. The residue was purified by silica gel column chromatography and the product was recrystallized using 1 : 1 dichloromethane/hexane.

BODIPY 6a—Yield 50%. Mp ($^{\circ}\text{C}$) > 300 ; ^1H NMR (CD_2Cl_2 , 400 MHz) δ 7.80 (d, $J = 7.0$ Hz, 4H), 7.72 (d, $J = 6.8$ Hz, 3H), 7.64 (d, $J = 6.9$ Hz, 2H), 7.51 (dd, $J = 14.3, 7.7$ Hz, 8H), 7.07 (dt, $J = 23.6, 7.3$ Hz, 4H), 6.24 (d, $J = 8.3$ Hz, 2H); ^{13}C NMR (CD_2Cl_2 , 100 MHz) δ 151.7, 135.3, 134.3, 131.2, 131.0, 130.3, 129.6, 129.5, 129.4, 129.1, 128.8, 128.2, 126.4, 124.7, 123.6, 121.4; ^{11}B NMR (CDCl_3 , 128 MHz) δ 1.81 (t, $J_{\text{BF}} = 31.2$ Hz); ^{19}F NMR (CDCl_3 , 376 MHz) δ -129.13 (septet, $^1J_{10\text{BF}} = 10.5$ Hz), -129.20 (quartet, $^1J_{11\text{BF}} = 31.2$ Hz); HRMS (ESI-TOF) m/z 519.1960 $[\text{M}]^+$ calcd for $\text{C}_{35}\text{H}_{23}\text{BF}_2\text{N}_2$ 519.1953.

BODIPY 6b—Yield 32%. Mp ($^{\circ}\text{C}$) > 300 ; ^1H NMR (CD_2Cl_2 , 400 MHz) δ 8.39–8.28 (m, 4H), 7.99–7.91 (m, 4H), 7.80–7.74 (m, 3H), 7.66 (dq, $J = 6.5, 2.2$ Hz, 2H), 7.52 (dt, $J = 8.2, 1.1$ Hz, 2H), 7.20 (ddd, $J = 8.1, 6.9, 1.1$ Hz, 2H), 7.13 (ddd, $J = 8.1, 6.9, 1.1$ Hz, 2H), 6.32 (dd, $J = 8.2, 1.1$ Hz, 2H); ^{13}C NMR (CD_2Cl_2 , 125 MHz) δ 149.2, 148.3, 138.1, 137.4, 134.62, 134.55, 131.5, 131.42, 131.39, 131.0, 130.9, 130.0, 129.9, 129.6, 128.9, 128.8, 127.7, 125.8, 124.9, 123.4, 122.8, 121.9; ^{11}B NMR (CDCl_3 , 128 MHz) δ 1.67 (t, $J_{\text{BF}} = 31.8$ Hz); ^{19}F NMR (CD_2Cl_2 , 376 MHz) δ -128.20 (septet, $^1J_{10\text{BF}} = 10.6$ Hz), -128.28 (quartet, $^1J_{11\text{BF}} = 31.8$ Hz); HRMS (ESI-TOF) m/z 610.1739 $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{35}\text{H}_{22}\text{BF}_2\text{N}_2\text{O}_4$ 611.1739.

BODIPY 6c—Yield 52%. Mp ($^{\circ}\text{C}$) > 300 ; ^1H NMR (CD_2Cl_2 , 400 MHz) δ 7.89 (d, $J = 8.0$ Hz, 4H), 7.84–7.74 (m, 7H), 7.64 (d, $J = 6.4$ Hz, 2H), 7.49 (d, $J = 8.1$ Hz, 2H), 7.18 (t, $J = 7.5$ Hz, 2H), 7.11 (t, $J = 7.6$ Hz, 2H), 6.31 (d, $J = 8.3$ Hz, 2H); ^{13}C NMR (CD_2Cl_2 , 100 MHz) δ 149.4, 135.5, 134.6, 132.0, 131.04, 131.01, 130.97, 129.92, 129.86, 129.5, 128.9, 125.7, 122.8, 121.8, 118.5, 113.2; ^{11}B NMR (CDCl_3 , 128 MHz) δ 1.68 (t, $J = 31.7$ Hz); ^{19}F NMR (CDCl_3 , 376 MHz) δ -128.19 (septet, $^1J_{10\text{BF}} = 10.6$ Hz), -128.26 (quartet, $^1J_{11\text{BF}} = 31.7$ Hz); HRMS (ESI-TOF) m/z 550.1918 $[\text{M} - \text{F}]^+$ calcd for $\text{C}_{37}\text{H}_{20}\text{BFN}_4$ 550.1874.

BODIPY 6d—Yield 48%. Mp ($^{\circ}\text{C}$) > 300 ; ^1H NMR (CD_2Cl_2 , 400 MHz) δ 7.91 (d, $J = 8.1$ Hz, 4H), 7.82–7.74 (m, 7H), 7.67–7.62 (m, 2H), 7.51–7.46 (m, 2H), 7.17 (m, 2H), 7.10 (ddd, $J = 8.1, 6.8, 1.2$ Hz, 2H), 6.34–6.27 (m, 2H); ^{13}C NMR (CD_2Cl_2 , 100 MHz) δ 150.0, 134.8, 134.5, 131.1, 130.8, 129.8, 129.4, 128.9, 127.1, 125.4, 125.2, 125.1, 123.0, 121.7; ^{11}B NMR (CDCl_3 , 128 MHz) δ 1.74 (t, $J = 31.6$ Hz); ^{19}F NMR (CD_2Cl_2 , 376 MHz) δ -63.02 (s), -128.56 (septet, $^1J_{10\text{BF}} = 10.5$ Hz), -128.64 (quartet, $^1J_{11\text{BF}} = 31.6$ Hz); HRMS (ESI-TOF) m/z 636.1695 $[\text{M} - \text{F}]^+$ calcd for $\text{C}_{37}\text{H}_{21}\text{BF}_7\text{N}_2$ 636.1717.

BODIPY 6e—Yield 54%. Mp ($^{\circ}\text{C}$) > 300 ; ^1H NMR (CD_2Cl_2 , 400 MHz) δ 8.22 (d, $J = 8.0$ Hz, 4H), 7.87 (d, $J = 8.0$ Hz, 4H), 7.80–7.72 (m, 3H), 7.64 (d, $J = 6.7$ Hz, 2H), 7.52 (dd, $J = 8.0, 3.2$ Hz, 6H), 7.46–7.39 (m, 6H), 7.12 (dt, $J = 25.4, 7.2$ Hz, 4H), 6.32 (d, $J = 8.3$ Hz, 2H), 5.43 (s, 4H); ^{13}C NMR (CD_2Cl_2 , 100 MHz) δ 165.8, 136.3, 135.6, 134.9, 134.5, 131.0, 130.4, 129.80, 129.78, 129.3, 129.2, 129.0, 128.6, 128.3, 128.2, 125.3, 123.1, 121.7, 66.9; ^{11}B NMR (CD_2Cl_2 , 128 MHz) δ 1.76 (t, $J_{\text{BF}} = 31.5$ Hz); ^{19}F NMR (CD_2Cl_2 , 376 MHz) δ -128.56 (septet, $^1J_{10\text{BF}} = 10.5$ Hz), -128.63 (quartet, $^1J_{11\text{BF}} = 31.5$ Hz); HRMS (ESI-TOF) m/z 787.2701 $[\text{M}]^+$ calcd for $\text{C}_{51}\text{H}_{35}\text{BF}_2\text{N}_2\text{O}_4$ 787.2689.

BODIPY 6f—Yield 52%. Mp (°C) > 300; ^1H NMR (CD_2Cl_2 , 400 MHz) δ 8.19 (d, J = 8.0 Hz, 4H), 7.84 (d, J = 8.0 Hz, 4H), 7.50–7.46 (m, 4H), 7.44–7.33 (m, 6H), 7.20–7.14 (m, 3H), 6.83 (t, J = 2.3 Hz, 1H), 6.79 (d, J = 2.3 Hz, 2H), 5.40 (s, 4H), 3.86 (s, 6H); ^{13}C NMR (CD_2Cl_2 , 125 MHz) δ 165.8, 162.1, 136.3, 131.0, 130.4, 129.4, 129.3, 128.6, 128.24, 128.15, 125.4, 123.0, 122.0, 106.6, 101.8, 66.9, 55.8; ^{11}B NMR (CDCl_3 , 128 MHz) δ 1.70 (t, J_{BF} = 31.5 Hz); ^{19}F NMR (CDCl_3 , 376 MHz) δ -129.34 (septet, $^1J_{10\text{BF}}$ = 10.7 Hz), -129.41 (quartet, $^1J_{11\text{BF}}$ = 32.5 Hz); HRMS (ESI-TOF) m/z 848.2931 $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{53}\text{H}_{40}\text{BF}_2\text{N}_2\text{O}_6$ 848.2978.

BODIPY 9a—Yield 54%. Mp (°C) > 300; ^1H NMR (CD_2Cl_2 , 400 MHz) δ 8.25–8.17 (m, 2H), 7.94–7.83 (m, 4H), 7.81–7.71 (m, 5H), 7.67–7.60 (m, 2H), 7.55–7.46 (m, 4H), 7.45–7.33 (m, 3H), 7.19–7.06 (m, 4H), 6.30 (d, J = 8.3 Hz, 2H), 5.41 (s, 2H); ^{13}C NMR (CD_2Cl_2 , 125 MHz) δ 166.3, 151.3, 150.2, 138.0, 136.8, 136.0, 135.3, 135.1, 134.9, 131.6, 131.5, 131.34, 131.31, 131.0, 130.3, 129.9, 129.7, 129.4, 129.1, 128.8, 128.7, 125.91, 125.85, 125.64, 125.61, 123.6, 123.4, 122.17; ^{11}B NMR (CDCl_3 , 128 MHz) δ 1.72 (t, J_{BF} = 31.5 Hz); ^{19}F NMR (CD_2Cl_2 , 376 MHz) δ -62.98 (s), -128.52 (septet, $^1J_{10\text{BF}}$ = 10.6 Hz), -128.60 (quartet, $^1J_{11\text{BF}}$ = 31.5 Hz); HRMS (ESI-TOF) m/z 702.2183 $[\text{M} - \text{F}]^+$ calcd for $\text{C}_{44}\text{H}_{28}\text{BF}_4\text{N}_2\text{O}_2$ 702.2211.

BODIPY 9b—Yield 51%. Mp (°C) > 300; ^1H NMR (CD_2Cl_2 , 400 MHz) δ 8.25–8.16 (m, 2H), 7.92–7.82 (m, 4H), 7.82–7.75 (m, 2H), 7.55–7.46 (m, 4H), 7.45–7.34 (m, 3H), 7.21–7.15 (m, 4H), 6.84 (t, J = 2.3 Hz, 1H), 6.61–6.52 (m, 2H), 5.40 (s, 2H), 3.87 (s, 6H); ^{13}C NMR (CD_2Cl_2 , 100 MHz) δ 165.8, 162.2, 136.4, 136.3, 135.5, 131.1, 131.0, 130.8, 130.4, 129.5, 129.42, 129.35, 128.6, 128.3, 128.2, 125.5, 125.4, 125.2, 125.14, 125.10, 125.06, 123.1, 122.9, 122.0, 106.7, 101.8, 66.9, 55.8; ^{11}B NMR (CD_2Cl_2 , 128 MHz) δ 1.68 (t, J_{BF} = 31.5 Hz); ^{19}F NMR (CD_2Cl_2 , 376 MHz) δ -63.0 (s), -128.59 (septet, $^1J_{10\text{BF}}$ = 10.5 Hz), -128.67 (quartet, $^1J_{11\text{BF}}$ = 31.5 Hz); HRMS (ESI-TOF) m/z 820.2039 $[\text{M} + \text{K}]^+$ calcd for $\text{C}_{46}\text{H}_{32}\text{BF}_5\text{N}_2\text{O}_4\text{K}$ 820.2043.

X-ray structural determination

Crystal data—X-ray data were collected at low temperature with MoK α radiation on Bruker Kappa Apex-II DUO or Nonius KappaCCD (for **5c** and **6a**) diffractometers. **1a**, **5c** and **5e** were DCM solvates. **1a** and **6c** have two independent molecules, while **5b** has the molecule on a twofold axis. **5d** has conformational disorder of one 6-ring and **6c** has slight (5%) substitutional disorder by a monochloro derivative. **6b** was a nonmerohedral twin with 85:15 components. Crystal data: **1a**, $\text{C}_{23}\text{H}_{21}\text{BF}_2\text{I}_2\text{N}_2 \cdot \text{CH}_2\text{Cl}_2$, M = 712.95, orthorhombic, a = 8.2966(4) Å, b = 23.4782(12) Å, c = 25.1750(11) Å, T = 100 K, space group $\text{P}2_12_12_1$, Z = 8, 64679 reflections measured, 10489 unique (R_{int} = 0.046), θ_{max} = 26.8°, final R = 0.053, CCDC 1435988; **5a**, $\text{C}_{35}\text{H}_{31}\text{BF}_2\text{N}_2$, M = 528.43, orthorhombic, a = 11.0477(15) Å, b = 14.069(2) Å, c = 17.029(3) Å, T = 100 K, space group $\text{P}2_12_12_1$, Z = 4, 79 037 reflections measured, 5446 unique (R_{int} = 0.055), θ_{max} = 25.4°, final R = 0.033, CCDC 1435989; **5b**, $\text{C}_{35}\text{H}_{29}\text{BF}_2\text{N}_2\text{O}_4$, M = 618.43, monoclinic, a = 15.7880(6) Å, b = 12.5007(6) Å, c = 15.9397(7) Å, β = 116.931(4)°, T = 90 K, space group $\text{C}2/c$, Z = 4, 31 542 reflections measured, 5374 unique (R_{int} = 0.042), θ_{max} = 33.2°, final R = 0.047, CCDC 1435990; **5c**, $\text{C}_{37}\text{H}_{29}\text{BF}_2\text{N}_4 \cdot \text{CH}_2\text{Cl}_2$, M = 663.38, triclinic, a = 9.7694(8) Å, b = 13.1321(10) Å, c =

13.2027(8) Å, $\alpha = 93.757(5)^\circ$, $\beta = 104.793(4)^\circ$, $\gamma = 102.323(4)^\circ$, $T = 90$ K, space group $P\bar{1}$, $Z = 2$, 24 995 reflections measured, 8128 unique ($R_{\text{int}} = 0.062$), $\theta_{\text{max}} = 28.8^\circ$, final $R = 0.058$, CCDC 1435991; **5d**, $\text{C}_{37}\text{H}_{29}\text{BF}_8\text{N}_2$, $M = 664.43$, triclinic, $a = 8.1559(9)$ Å, $b = 13.0389(14)$ Å, $c = 15.7981(18)$ Å, $\alpha = 114.011(4)^\circ$, $\beta = 91.649(5)^\circ$, $\gamma = 102.179(5)^\circ$, $T = 90$ K, space group $P\bar{1}$, $Z = 2$, 35 888 reflections measured, 11 819 unique ($R_{\text{int}} = 0.028$), $\theta_{\text{max}} = 33.7^\circ$, final $R = 0.041$, CCDC 1435992; **5e**, $\text{C}_{51}\text{H}_{43}\text{BF}_2\text{N}_2\text{O}_4 \cdot \text{CH}_2\text{Cl}_2$, $M = 881.61$, monoclinic, $a = 9.5919(2)$ Å, $b = 34.4320(6)$ Å, $c = 13.4607(2)$ Å, $\beta = 107.8990(10)^\circ$, $T = 90$ K, space group $P2_1/n$, $Z = 4$, 50 441 reflections measured, 20 106 unique ($R_{\text{int}} = 0.037$), $\theta_{\text{max}} = 36.4^\circ$, final $R = 0.054$, CCDC 1435993; **6a**, $\text{C}_{35}\text{H}_{23}\text{BF}_2\text{N}_2$, $M = 520.36$, triclinic, $a = 8.9607(14)$ Å, $b = 10.4013(15)$ Å, $c = 14.964(3)$ Å, $\alpha = 98.262(9)^\circ$, $\beta = 106.170(6)^\circ$, $\gamma = 107.413(9)^\circ$, $T = 90$ K, space group $P\bar{1}$, $Z = 2$, 22 864 reflections measured, 5881 unique ($R_{\text{int}} = 0.034$), $\theta_{\text{max}} = 27.9^\circ$, final $R = 0.044$, CCDC 1435994; **6b**, $\text{C}_{35}\text{H}_{21}\text{BF}_2\text{N}_2\text{O}_4$, $M = 610.37$, monoclinic, $a = 12.2985(6)$ Å, $b = 12.9578(6)$ Å, $c = 18.4622(9)$ Å, $\beta = 108.407(2)^\circ$, $T = 90$ K, space group $P2_1/c$, $Z = 4$, 27 177 reflections measured, 26 528 unique ($R_{\text{int}} = 0.048$), $\theta_{\text{max}} = 27.3^\circ$, final $R = 0.053$, CCDC 1435995; **6c**, $\text{C}_{37}\text{H}_{20.95}\text{BCl}_{0.05}\text{F}_2\text{N}_2\text{O}_4$, $M = 572.02$, monoclinic, $a = 13.2913(16)$ Å, $b = 16.431(2)$ Å, $c = 13.4762(16)$ Å, $\beta = 107.238(2)^\circ$, $T = 90$ K, space group $P2_1$, $Z = 4$, 21 435 reflections measured, 12 492 unique ($R_{\text{int}} = 0.023$), $\theta_{\text{max}} = 29.2^\circ$, final $R = 0.040$, CCDC 1435996.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Fig. 1.
Current synthetic strategies to β,β' -benzo-fused BODIPYs.

Fig. 2.
X-ray crystal structure of β,β' -bicyclo-3,5-diiodo-BODIPY **1a**, with 50% ellipsoids.

Fig. 3.
X-ray crystal structures of β,β' -bicyclo-3,5,8-triaryl-BODIPYs **5a**, **5b**, **5c**, **5d** and **5e**, with 50% ellipsoids.

Fig. 4.
X-ray crystal structure of β,β' -dibenzo-3,5,8-triaryl-BODIPYs **6a**, **6b** and **6c**, with 50% ellipsoids.

Fig. 5. Normalized UV-Vis spectra of selected BODIPYs **5b** (black), **5c** (blue), **5d** (purple), **6b** (red), **6c** (cyan) and **6d** (dark yellow) in THF at room temperature.

Fig. 6. Normalized fluorescence spectra of BODIPYs **5b** (black), **5c** (blue), **5d** (purple), **6b** (red), **6c** (cyan) and **6d** (dark yellow) in THF at room temperature.

Scheme 1.

Reaction conditions: (a) PhCHO or 3,5-(OMe)₂PhCHO, p-TsOH, *n*Bu₄NI, DCM, 12 h, 86–95%; (b) KOH, THF, methanol, water, reflux, 4 h; (c) 2 M HCl (aq), 30 min; (d) I₂, MeOH, water, NaHCO₃, rt, 24 h; (e) Et₃N, BF₃·OEt₂, DCM, 2 h, 40–42% for 4 steps.

Scheme 2.

Reaction conditions: (a) Pd(dppf)Cl₂, K₂CO₃, boronic acid, THF/toluene 1 : 1, reflux, 2 h (82–92%); (b) DDQ, toluene, reflux, 10–30 min (32–54%).

Scheme 3.

Reaction conditions: (a) Pd(dppf)Cl₂, K₂CO₃, (4-(benzyloxycarbonyl)phenyl)-boronic acid, THF/toluene 1 : 1, reflux, 30 min (42%); (b) Pd(dppf)Cl₂, K₂CO₃, (4-(trifluoromethyl)phenyl)-boronic acid, THF/toluene 1 : 1, reflux, 15 min (95%); (c) DDQ, toluene, reflux, 10–30 min (51–54%).

Table 1

Products and yields obtained in the Suzuki cross-couplings (**5a–f**) and DDQ aromatizations (**6a–f**) of BODIPYs **1a** and **1b** using the conditions shown in Scheme 2

BODIPY	Ar group	R group	Yield of 5 (%)	Yield of 6 (%)
5a/6a	Ph	H	85	50
5b/6b	Ph	NO ₂	83	32
5c/6c	Ph	CN	85	52
5d/6d	Ph	CF ₃	82	48
5e/6e	Ph	CO ₂ Bn	86	54
5f/6f	3,5-(OMe) ₂ Ph	CO ₂ Bn	92	52

Table 2

^{11}B - and ^{19}F -NMR chemical shifts of BF_2 group. In ^{11}B -NMR the signal is a triplet and in ^{19}F -NMR the signals are a quartet and septet ($J_{11\text{BF}} = 32 \text{ Hz}$, $J_{10\text{BF}} = 10 \text{ Hz}$)

BODIPY	^{11}B NMR δ (ppm)	^{19}F NMR δ (ppm)
1a	0.47	-143.71, -143.76
1b	0.44	-143.71, -143.79
5a	0.87	-131.45, -131.53
5b	0.67	-131.81, -131.89
5c	0.70	-131.06, -131.13
5d	0.78	-131.48, -131.55
5e	0.77	-131.40, -131.47
5f	0.73	-131.25, -131.32
6a	1.81	-129.13, -129.20
6b	1.67	-128.20, -128.28
6c	1.68	-128.19, -128.26
6d	1.74	-128.56, -128.64
6e	1.76	-128.56, -128.64
6f	1.70	-129.34, -129.41
8a	0.82	-131.28, -131.35
8b	0.70	-131.25, -131.32
9a	1.73	-128.52, -128.60
9b	1.68	-128.59, -128.67

Table 3

Spectroscopic properties of BODIPYs in THF

BODIPY	Abs λ_{max} (nm)	log ϵ ($\text{M}^{-1} \text{cm}^{-1}$)	Emi λ_{max} (nm)	Φ_{f}	Stokes shift (cm^{-1})
1a	550	5.00	560	0.14	325
1b	550	5.00	559	0.14	293
5a	548	4.74	574	0.42	827
5b	558	4.66	597	0.35	1171
5c	554	4.63	585	0.43	957
5d	548	4.75	575	0.52	857
5e	554	4.74	586	0.42	986
5f	555	4.76	585	0.40	924
6a	631	4.78	651	0.64	487
6b	651	4.72	683	0.23	720
6c	643	4.77	670	0.48	627
6d	635	4.79	656	0.67	504
6e	641	4.94	667	0.48	608
6f	642	4.99	667	0.46	584
9a	638	4.94	664	0.55	614
9b	638	4.89	663	0.55	591
8a	551	4.79	579	0.45	878
8b	551	4.75	580	0.46	907