Supporting Information

Access to 2,6-Dipropargylated BODIPYs as “Clickable” Congeners of Pyrromethene-567 dye: Photostability and Synthetic Versatility

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1. General Information

All solvents and reagents were commercial grade and used as received unless stated otherwise. All anhydrous reactions were run under a positive pressure of argon. Reactions were monitored by TLC analysis on Kieselgel 60 F254 (Merk) with UV detection were applicable. Flash column chromatography was carried out using 230–400 mesh silica gel. Melting points were determined with a Stuart SMP20 instrument. 1H, 13C, 11B and 19F NMR spectra were recorded on a BRUKER AVANCE III HD-400 or a JEOL JNM-EZC400R. Chemical shifts were recorded in parts per million (ppm, δ) relative to the residual solvent peak as internal standard. Coupling constants (J) are given in Hz. 13C NMR spectra were proton-decoupled. Optical rotations were measured on a Jasco P2000 polarimeter with [α]D values reported in degrees with concentrations expressed in grams per 100 mL. The HRMS experiments were carried out on an Agilent 6500 Accurate Mass Q-TOF LC-MS mass spectrometer and the HRMS data accurate within 5 ppm.

1,3,5,7,8-pentamethyl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene 4, 8-phenyl-1,3,5,7-tetramethyl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene 7b, 1,3,5,7-tetramethyl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene 7c, 2-azidoethyl 2,3,4,6-tetra-O-acetyl-α-D-mannopyranoside 16 and 8-(2-azidomethylphenyl)-1,3,5,7-tetramethyl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene 20 were prepared according to previously reported methods.

2. General Procedures

**General procedure A. Nicholas reaction of BODIPYs with dicobalt hexacarbonyl propargyl alcohol complex 5**

A solution of the corresponding BODIPY (4, 7a-c) and dicobalt hexacarbonyl propargyl alcohol complex 5 (1.1 or 2.2 equiv.) in dry CH2Cl2 was cooled at –15 °C, then BF3·OEt2 (0.5 equiv.) was added. After stirring at –15 °C (1–3 h) the solution was diluted with CH2Cl2, washed twice with NaHCO3, dried over MgSO4 and concentrated. The resulting crude was purified by flash chromatography.

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**General procedure B. Oxidative iodine-mediated decobaltation**

A solution of the corresponding propargylcobalt-BODIPY (1 equiv.) in THF or CH$_2$Cl$_2$ was cooled to 0 °C, then solid iodine (3 equiv.) was added. The mixture was stirred under these conditions for 30-90 min, then poured into saturated aqueous NaHCO$_3$ + 10% Na$_2$S$_2$O$_3$ solution and partitioned twice with ether or CH$_2$Cl$_2$. The combined organic layers were washed once with brine, dried over MgSO$_4$, and filtered, and the solvent was removed in vacuo. The crude material was purified through silicagel column chromatography.

**General procedure C. Non-oxidative 1,2-ethylenediamine mediated decobaltation**

A solution of the corresponding propargylcobalt-BODIPY (1 equiv.) in THF was treated with 1,2-ethylenediamine (3 equiv.). The reaction mixture was stirred at room temperature until TLC showed complete disparition of the complex, then it was diluted with Et$_2$O and washed with a 3% HCl solution and brine. The organic layer was dried over MgSO$_4$ and concentrated. The residue was purified by silica column chromatography.

**General procedure D. Copper(I)-catalyzed azide-alkyne cycloaddition reaction (CuAAC)**

The corresponding azide (14-16, 20-21, 0.9–1.5 equiv./alkyne) and the appropriate alkyne-BODIPY (10a-b, 19, 1 equiv.) in CH$_2$Cl$_2$ were added to a solution of sodium ascorbate (3 equiv.) and CuSO$_4$ (1.5 equiv.) in H$_2$O (CH$_2$Cl$_2$/H$_2$O, 3:1, v/v). The solution was placed in a glass seal tube (65 °C) until no starting materials were left. The reaction mixture was then diluted with CH$_2$Cl$_2$ and washed with brine. The organic layer was dried over MgSO$_4$ and concentrated. The residue was purified by silica column chromatography.

**General procedure E. Attempted direct propargylation with propargyl trichloroacetimidate.**

In a flame dried flask BODIPY 7b$^6$ (1.0 equiv.) was dissolved in anhydrous CH$_2$Cl$_2$ (0.2 M) followed by the addition of the propargyl trichloroacetimidate $^6$ (2.0 equiv.). To this solution the corresponding Lewis acid (BF$_3$OEt$_2$, Yb(OTf)$_3$, TMSOTf; acid-washed molecular sieves) was added. The resulting mixture was stirred and the reaction was followed by t.l.c.. The reaction mixture was then quenched with the addition of 1M NaOH. The combined organic extracts were dried over MgSO$_4$, filtered and concentrated. The residue was then purified, if necessary, by silical gel chromatography. In most instances the starting BODIPY was recovered unchanged. In one of the ocassions (using BF$_3$.OEt$_2$ as Lewis acid) the dipropargyl derivative 10b could be isolated (37% yield).

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3. Compound Characterization

1,3,5,7,8-pentamethyl-2,6-di[prop-2-in-1-yl]-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (3).

This compound was prepared following the general procedure B starting from 2,6-dipropargylcobalt-BODIPY 6 (100 mg, 0.11 mmol) in THF (5 mL) and I2 (42 mg, 0.33 mmol) for 1 h. After work-up, the residue was purified on a silica gel column chromatography (hexane/ethyl acetate, 95:5 to 9:1) to afford 3 as an orange solid (12.3 mg, 33%). Mp >300 °C; 1H NMR (CDCl3, 400 MHz): δ 3.30 (s, 4H), 2.62 (s, 3H), 2.56 (s, 6H), 2.41 (s, 6H), 2.01 (s, 2H). NMR 13C {1H} (CDCl3, 125 MHz): δ 152.3, 141.5, 137.5, 131.9, 125.2, 81.4, 68.6, 17.2, 14.8, 13.8, 12.7; HRMS (ESI/Q-TOF) m/z: [M+H]+ Calcd for C20H22BF2N2 339.1842; Found: 339.1833.

Dicobalt hexacarbonyl propargyl alcohol complex (5)

To a solution of propargylic alcohol (0.2 mL, 3.6 mmol, 1 equiv.) in dry CH2Cl2 (25 mL) was added dicobalt octacarbonyl (1.47 g, 4.32 mmol, 1.2 equiv.). After stirring 1 h, the crude was concentrated on a rotary evaporator and the residue was purified by flash chromatography (hexane/ethyl acetate, 9:1) to give 57 as a brown solid (1.17 g, 95%); Mp 50-52 °C. 1H NMR (CDCl3, 300 MHz): δ 6.07 (s, 1H), 4.80 (d, J = 6.0 Hz, 2H), 1.79 (t, J = 6.0 Hz, 1H).

Bis Co2(CO)6 1,3,5,7,8-pentamethyl-2,6-di[prop-2-in-1-yl]-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (6). BODIPY 4 (200 mg, 0.76 mmol) was reacted with dicobalt hexacarbonyl propargyl alcohol complex 5 (571 mg, 1.67 mmol) and BF3OEt2 (47 µL, 0.38 mmol) following the general

7 Wells, S. M.; Widen, J. C.; Harki, D. A.; Brummond, K. M. Org. Lett. 2016, 18, 4566–4569.
procedure A (30 min). The residue was purified by flash silicagel chromatography (toluene) to give derivative 6 as a brown solid (692 mg, 73%). Mp >300 °C; 1H NMR (CDCl₃, 400 MHz): δ 5.99 (s, 2H), 3.94 (s, 4H), 2.63 (s, 3H), 2.57 (s, 6H), 2.43 (s, 6H). 13C {1H} NMR (CDCl₃, 125 MHz): δ 199.6, 152.4, 141.5, 137.1, 132.0, 129.9, 95.7, 73.3, 28.9, 17.2, 15.3, 12.8. HRMS (ESI/Q-TOF) m/z: [M+H]+ Calcd for C₃₂H₂₂BCo₄F₂N₂O₁₂ 910.8562; Found 910.8591.

8-(2-acetoxymethyl-phenyl)-1,3,5,7-tetramethyl-4,4-difluoro-4-bora- 3a,4a-diaza-s-indacene (7a). To a stirred solution of 8-(2-hydroxymethyl-phenyl)-1,3,5,7-tetramethyl-4,4-difluoro-4-bora- 3a,4a-diaza-s-indacene⁵ (200 mg, 0.56 mmol) in pyridine (8 mL) was added acetic anhydride (2 mL). After stirring 1 h, the crude was concentrated and the residue was purified by flash chromatography (hexane/ethyl acetate, 9:1) to give 7a (219 mg, 98%). 1H NMR (CDCl₃, 400 MHz): δ 7.50-7.40 (m, 3H), 7.23-7.20 (m, 4H), 5.96 (s, 2H), 5.00 (s, 2H), 2.53 (s, 6H), 1.91 (s, 3H), 1.34 (s, 6H). 13C {1H} NMR (CDCl₃, 125MHz): δ 170.4, 155.8, 142.8, 139.1, 134.1, 133.7, 131.0, 129.5, 129.2, 129.1, 128.5, 121.3, 63.7, 20.4, 14.6, 13.8. HRMS (ESI/Q-TOF) m/z: [M+H]+ Calcd for C₂₂H₂₄BF₂N₂O₂ 397.1898; Found 397.1873.

Bis-Co₂(CO)₆ 8-(2-acetoxymethyl-phenyl)-1,3,5,7-tetramethyl-2,6-di(prop-2-in-1-yl)-4,4-difluoro-4-bora- 3a,4a-diaza-s-indacene (8a). Following the general procedure A, BODIPY 7a (100 mg, 0.25 mmol) was reacted with dicobalt hexacarbonyl propargyl alcohol complex 5 (190 mg, 0.55 mmol) and BF₃OEt₂ (15.4 µL, 0.125 mmol) (1 h). The residue was purified by flash silicagel chromatography (hexane/ethyl acetate, 98 :2 to 95 :5) to give derivative 8a as brown solid (256 mg, 98%). Mp 136-140 °C; 1H NMR (CDCl₃, 400 MHz): δ 7.51-7.46 (m, 3H), 7.12-7.10 (m, 1H), 5.96 (s, 2H), 4.96 (s, 2H), 3.84 (s, 4H), 2.62 (s, 6H), 2.03 (s, 3H), 1.37 (s, 6H). 13C {1H} NMR
(CDCl$_3$, 125MHz): $\delta$ 199.6, 170.5, 154.7, 139.3, 139.0, 134.2, 133.9, 131.1, 130.7, 130.4, 129.8, 129.2, 129.0, 128.5, 95.3, 73.3, 63.2, 28.8, 20.8, 13.0, 11.9; HRMS (ESI/Q-TOF) m/z: [M+NH$_4$]$^+$
Calcd for C$_{40}$H$_{31}$BCo$_4$F$_2$N$_3$O$_{14}$ 1061.9197; Found: 1061.9191.

Bis-C$_2$(CO)$_6$ 8-phenyl-1,3,5,7-tetramethyl-2,6-di(prop-2-in-1-yl)-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (8b) BODIPY 7b$^2$ (250 mg, 0.77 mmol) was reacted with dicobalt hexacarbonyl propargyl alcohol complex 5 (579 mg, 1.70 mmol) and BF$_3$OEt$_2$ (47 $\mu$L, 0.38 mmol) following the general procedure A (90 min). The residue was purified by flash chromatography (hexane/ethyl acetate 95:5) to give derivative 8b as a brown solid (726 mg, 97%). Mp >300 °C; $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.51-7.50 (m, 3H), 7.19-7.17 (m, 2H), 5.95 (s, 2H), 3.83 (s, 4H), 2.62 (s, 6H), 1.37 (s, 6H). $^{13}$C ($^1$H) NMR (CDCl$_3$, 125 MHz): $\delta$ 199.6, 154.2, 142.0, 139.3, 135.4, 131.1, 130.2, 129.5, 129.2, 128.0, 95.5, 73.3, 28.8, 13.0, 12.4. HRMS (ESI/Q-TOF) m/z: [M+H]$^+$
Calcd for C$_{37}$H$_{23}$BCo$_4$FN$_2$O$_{12}$ 952.8657; Found 952.8682.

Bis-C$_2$(CO)$_6$ 1,3,5,7-tetramethyl-2-(prop-2,6-in-1-yl)-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (8c). Following the general procedure A, BODIPY 7c$^3$ (50 mg, 0.2 mmol) was reacted with dicobalt hexacarbonyl propargyl alcohol complex 5 (152 mg, 0.44 mmol) and BF$_3$OEt$_2$ (12.3 $\mu$L, 0.1 mmol) (45 min). The residue was purified by flash silicagel chromatography (hexane/ethyl acetate 95:5) to give derivative 8c as a brown solid (147 mg, 82%). Mp >300°C; $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.03 (s, 1H), 6.01 (s, 2H), 3.92 (s, 4H), 2.58 (s, 6H), 2.27 (s, 6H). $^{13}$C ($^1$H) NMR (CDCl$_3$, 125 MHz): $\delta$ 199.6, 155.3, 137.5, 132.5, 129.1, 120.2, 95.3, 73.3, 29.1, 13.0, 9.9. HRMS (ESI/Q-TOF) m/z: [M+H]$^+$
Calcd for C$_{31}$H$_{22}$BCo$_4$F$_2$N$_2$O$_{12}$ 896.8405; Found 896.8424.
**Co₂(CO)₆ 8-(2-acetoxymethyl-phenyl)-1,3,5,7-tetramethyl-2-(prop-2-in-1-yl)-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (9a).** This compound was prepared following the general procedure A starting from BODIPY 7a (198 mg, 0.55 mmol), dicobalt hexacarbonyl propargyl alcohol complex 5 (188 mg, 0.55 mmol) and BF₃OEt₂ (31 µL, 0.25 mmol) (1 h). After work-up, the residue was purified on a silica gel column chromatography (hexane/ethyl acetate, 98:2 to 95:5) to afford BODIPY 9a (101 mg, 28%) along with BODIPY 8a (100 mg, 19%). Compound 9a: ¹H NMR (CDCl₃, 400 MHz): δ 7.52-7.44 (m, 3H), 7.19-7.18 (m, 1H), 5.98 (s, 1H), 5.97 (s, 1H), 5.01 (d, J = 13.4 Hz, 1H), 4.97 (d, J = 13.3 Hz, 1H), 3.85 (s, 2H), 2.62 (s, 3H), 2.56 (s, 3H), 1.98 (s, 3H), 1.38 (s, 3H), 1.35 (s, 3H). ¹³C {¹H} NMR (CDCl₃, 125 MHz): δ 199.6, 170.6, 156.7, 154.0, 143.5, 139.2, 138.6, 134.1, 134.04, 131.5, 130.3, 130.1, 129.7, 129.3, 129.0, 128.6, 121.7, 95.5, 73.4, 63.5, 28.8, 20.7, 14.8, 14.0, 13.0, 11.9. HRMS (ESI/Q-TOF) m/z: [M+H]⁺ Calcd for C₃₁H₂₆BCo₂F₂N₂O₈ 721.0414; Found 721.0403; [M+Na]⁺ Calcd for C₃₁H₂₅BCo₂F₂N₂NaO₈ 743.0234; Found 743.0219.

**Co₂(CO)₆ 8-phenyl-1,3,5,7-tetramethyl-2-prop-2-in-1-yl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (9b).** Following the general procedure A, BODIPY 7b² (250 mg, 0.77 mmol) was reacted with dicobalt hexacarbonyl propargyl alcohol complex 5 (289 mg, 0.85 mmol) and BF₃OEt₂ (47 µL, 0.38 mmol) (1 h). The residue was purified by flash silicagel chromatography (toluene) to give BODIPY 9b as orange solid (140 mg, 28%) along with BODIPY 8b (150 mg, 20%). Compound 9b: Mp 151-154 °C; ¹H NMR (CDCl₃, 400 MHz): δ 7.50-7.49 (m, 3H), 7.24-7.22 (m, 2H), 5.98 (s, 1H), 5.96 (s, 1H), 3.84 (s, 2H), 2.62 (s, 3H), 2.55 (s, 3H), 1.38 (s, 3H), 1.36 (s, 3H). ¹³C {¹H} NMR (CDCl₃, 125 MHz): δ 199.6, 156.2, 153.6, 143.7, 141.9, 139.0, 135.3, 131.8, 130.9, 129.9, 129.4,
129.2, 128.0, 121.6, 95.6, 73.4, 28.8, 14.7, 14.5, 13.0, 12.4. HRMS (ESI/Q-TOF) m/z: [M+H]+ Calcd for C_{28}H_{22}BCO_{2}F_{2}N_{2}O_{6} 649.0202; Found 649.0216.

**Co_{2}(CO)_{6} 1,3,5,7-tetramethyl-2-(prop-2-in-1-yl)-4,4-difluoro-4-bora-3a,4a-diazo-s-indaceno (9c).** BODIPY 7c\(^1\) (50 mg, 0.2 mmol) was reacted with dicobalt hexacarbonyl propargyl alcohol complex 5 (74 mg, 0.22 mmol) and BF_{3}OEt_{2} (12.3 µL, 0.1 mmol) following the general procedure A (45 min). The residue was purified by flash chromatography (toluene) to give derivative 9c as a brown solid (57.2 mg, 50%). Mp >300 °C; \(^1\)H NMR (CDCl_{3}, 400 MHz): δ 7.04 (s, 1H), 6.05 (s, 1H), 6.02 (s, 1H), 3.93 (s, 2H), 2.58 (s, 3H), 2.53 (s, 3H), 2.27 (s, 3H), 2.24 (s, 3H). \(^{13}\)C \(^1\)H NMR (CDCl_{3}, 125 MHz): δ 199.6, 157.7, 154.5, 141.5, 137.2, 133.9, 132.4, 128.8, 120.2, 119.4, 95.5, 73.3, 29.2, 14.8, 13.0, 11.4, 9.9. HRMS (ESI/Q-TOF) m/z: [M+H]+ Calcd for C_{22}H_{18}BCO_{2}F_{2}N_{2}O_{6} 572.9888; Found 572.9891.

**8-(2-acetoxymethyl-phenyl)-1,3,5,7-tetramethyl-2,6-di(prop-2-in-1-yl)-4,4-difluoro-4-bora-3a,4a-diazo-s-indacene (10a).** This compound was prepared following the general procedure B starting from cobalt-complex 8a (115 mg, 0.11 mmol) in THF (5 mL) and I_{2} (42 mg, 0.33 mmol) (90 min). After work-up, the residue was purified on a silica gel column chromatography (hexane/ethyl acetate, 9:1) to afford 10a as an orange solid (48.8 mg, 94%). Mp 135-138 °C; \(^1\)H NMR (CDCl_{3}, 400 MHz): δ 7.52-7.47 (m, 3H), 7.26-7.24 (m, 1H), 5.00 (s, 2H), 3.20 (d, J = 2.8 Hz, 4H), 2.60 (s, 6H), 1.95 (t, J = 2.7 Hz, 2H), 1.91 (s, 3H), 1.33 (s, 6H). \(^{13}\)C \(^1\)H NMR (CDCl_{3}, 125MHz): δ 170.7, 154.6, 139.3, 139.1, 134.6, 133.9, 130.6, 129.8, 129.6, 129.4, 128.9, 125.7, 81.1, 68.6, 64.0, 20.7, 13.7, 12.9, 11.6. HRMS (ESI/Q-TOF) m/z: [M+H]+ Calcd for C_{28}H_{28}BF_{2}N_{2}O_{2} 473.22111; Found 473.2235; [M+NH_{4}]^{+} Calcd for C_{28}H_{31}BF_{2}N_{3}O_{2} 491.2506; Found: 491.2527.
8-phenyl-1,3,5,7-tetramethyl-2,6-di(prop-2-in-1-yl)-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (10b). This compound was prepared following the general procedure B starting from cobalt-complex 8b (150 mg, 0.15 mmol) in CH₂Cl₂ (5 mL) and I₂ (57 mg, 0.45 mmol) (1 h). After work-up, the residue was purified on a silica gel column chromatography (hexane/ethyl acetate, 95:5) to afford 10b as an orange solid (56 mg, 94%). Mp 178-181 °C; ¹H NMR (CDCl₃, 400 MHz): δ 7.50-7.48 (m, 3H), 7.29-7.26 (m, 2H), 3.20 (d, J = 2.8 Hz, 4H), 2.60 (s, 6H), 1.96 (t, J = 2.7 Hz, 2H), 1.35 (s, 6H).¹³C {¹H} NMR (CDCl₃, 125MHz): δ 154.1, 141.7, 139.6, 135.3, 130.9, 129.3, 129.2, 128.2, 125.5, 81.1, 77.4, 68.5, 13.7, 12.8, 12.0. HRMS (ESI/Q-TOF) m/z: [M+H]⁺ Calcd for C₂₅H₂₄BF₂N₂ 401.2000; Found 401.2008.

1,3,5,7-tetramethyl-2,6-di(prop-2-in-1-yl)-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (10c). BODIPY 8c (100 mg, 0.11 mmol) was reacted with 1,2-ethylenediamine (22 µL, 0.33 mmol) in THF (5 mL) following the general procedure C (45 min). The residue was purified by flash silicagel chromatography (hexane-ethyl acetate 9:1) to give derivative 10c (26 mg, 73%). Mp 205-208 °C; ¹H NMR (CDCl₃, 400 MHz): δ 7.03 (s, 1H), 3.29 (d, J = 2.8 Hz, 4H), 2.56 (s, 6H), 2.24 (s, 6H), 2.02 (t, J = 2.7 Hz, 2H).¹³C {¹H} NMR (CDCl₃, 125 MHz): δ 155.2, 141.7, 139.6, 135.3, 130.9, 129.3, 129.2, 139.9, 81.1, 77.4, 68.5, 13.7, 12.9, 9.8. HRMS (ESI/Q-TOF) m/z: [M+H]⁺ Calcd for C₁₉H₂₀BF₂N₂ 325.1686; Found 325.1693.
8-(2-acetoxymethyl-phenyl)-1,3,5,7-tetramethyl-2-(prop-2-in-1-yl)-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (11a). This compound was prepared according to the general procedure B from BODIPY 9a (100 mg, 0.14 mmol) and I$_2$ (53 mg, 0.42 mmol) in THF (4 mL). The residue was purified by flash silicagel chromatography (hexane-ethyl acetate 9:1) to give derivative 11a (57.1 mg, 94%). Mp 134-137 °C; $^1$H NMR (CDCl$_3$, 400 MHz): δ 7.51-7.44 (m, 3H), 7.26-7.24 (m, 1H), 5.98 (s, 1H), 5.01 (s, 2H), 3.20 (d, $J = 2.8$ Hz, 2H), 2.60 (s, 3H), 2.55 (s, 3H), 1.95 (t, $J = 2.8$ Hz, 1H), 1.92 (s, 3H), 1.34 (s, 6H). $^{13}$C ($^1$H) NMR (CDCl$_3$, 125 MHz): δ 170.6, 156.2, 154.4, 143.1, 139.2, 134.5, 133.9, 131.2, 130.5, 129.7, 129.4, 129.3, 128.8, 125.6, 121.6, 81.1, 68.6, 63.9, 20.6, 14.8, 14.0, 13.7, 12.9, 11.5. HRMS (ESI/Q-TOF) m/z: [M+H]$^+$ Calcd for C$_{25}$H$_{26}$BF$_2$N$_2$O$_2$ 435.2054; Found 435.2054.

8-phenyl-1,3,5,7-tetramethyl-2-(prop-2-in-1-yl)-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (11b). BODIPY 9b (100 mg, 0.15 mmol) was reacted with I$_2$ (57 mg, 0.45 mmol) in CH$_2$Cl$_2$ (5 mL) following the general procedure B (30 min). The residue was purified by flash silicagel chromatography (hexane-ethyl acetate 95:5) to give derivative 11b as an orange solid (39 mg, 72%). Mp 175-180 °C; $^1$H NMR (CDCl$_3$, 400 MHz): δ 7.50-7.48 (m, 3H), 7.27-7.18 (m, 2H), 5.96 (s, 1H), 3.18 (d, $J = 2.7$ Hz, 1H), 2.58 (s, 3H), 2.54 (s, 3H), 1.94 (t, $J = 2.8$ Hz, 1H), 1.34 (s, 6H). $^{13}$C ($^1$H) NMR (CDCl$_3$, 125MHz): δ 155.8, 154.0, 143.4, 141.8, 139.5, 135.2, 131.6, 130.9, 129.3, 129.1, 128.2, 125.4, 121.4, 81.2, 68.5, 14.7, 14.5, 13.7, 12.8, 12.0. HRMS (ESI/Q-TOF) m/z: [M+H]$^+$ Calcd for C$_{22}$H$_{22}$BF$_2$N$_2$ 363.1843; Found 363.1852. [M+Na]$^+$ Calcd for C$_{22}$H$_{21}$BF$_2$N$_2$Na 385.1662; Found 385.1667.

1,3,5,7-tetramethyl-2-(prop-2-in-1-yl)-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (11c). BODIPY 9c (100 mg, 0.175 mmol) was reacted with 1,2-ethylenediamine (35 µL, 0.52 mmol) in THF (5 mL) following the general procedure C (30 min). The residue was purified by flash silicagel chromatography (hexane-ethyl acetate 95:5) to give derivative 9c as an orange solid (30.5 mg, 61%). Mp 163-166°C; $^1$H NMR (CDCl$_3$, 400 MHz): δ 7.02 (s, 1H), 6.03 (s, 1H), 3.27 (d, $J = 2.7$ Hz,
2H), 2.55 (s, 3H), 2.52 (s, 3H), 2.22 (s, 3H), 2.21 (s, 3H), 2.02 (t, \( J = 2.7 \) Hz, 1H). \(^{13}\)C \(^{1}\)H NMR (CDCl\(_3\), 125MHz): \( \delta = \) 156.9, 154.9, 141.4, 137.8, 133.6, 132.4, 124.1, 120.1, 119.1, 81.0, 68.8, 14.8, 13.9, 12.8, 11.3, 9.7. HRMS (ESI/Q-TOF) m/z: [M+H]\(^{+}\) Calcd for C\(_{16}\)H\(_{18}\)BF\(_2\)N\(_2\) 287.1529; Found 287.1520.

1,3,5,7,8-pentamethyl-2,6-di[prop-2-in-1-yl]-4,4-dicyan-4-bora-3a,4a-diaza-s-indacene (12). To a stirred solution of 3 (100 mg, 0.296 mmol) in CH\(_2\)Cl\(_2\) (5 mL) at 0 °C was added BF\(_3\)OEt\(_2\) (8 \( \mu \)L, 0.06 mmol) and trimethylsilyl cyanide TMSCN (91 \( \mu \)L, 0.89 mmol). The mixture was stirred for 1 h, then poured into saturated aqueous NaHCO\(_3\) solution and extracted twice with CH\(_2\)Cl\(_2\). The combined organic layers were dried over MgSO\(_4\), and filtered, and the solvent was removed in vacuo. The crude material was purified through silicagel column chromatography (hexane-ethyl acetate 9:1 to 8:2) to give derivative 12 as orange solid (104 mg, quant.); \(^1\)H NMR (CDCl\(_3\), 400 MHz): 3.36 (d, \( J = 2.7 \) Hz, 4H), 2.73 (s, 6H), 2.69 (s, 3H), 2.47 (s, 6H), 2.04 (t, \( J = 2.7 \) Hz, 2H). \(^{13}\)C \(^{1}\)H NMR (CDCl\(_3\)) \( \delta \) 152.8, 142.6, 138.9, 130.4, 126.9, 126.6 (q, \( J = 74.0 \) Hz), 80.5, 69.3, 17.5, 15.1, 14.0, 13.8, 13.7. HRMS (ESI/Q-TOF) m/z: [M+H]\(^{+}\) Calcd for C\(_{22}\)H\(_{21}\)BN\(_4\) 353.1936; Found 353.1925.

8-phenyl-1,3,5,7-tetramethyl-2,6-di[prop-2-in-1-yl]-4,4-dicyan-4-bora-3a,4a-diaza-s-indacene (13). To a stirred solution of 10b (55 mg, 0.137 mmol) in CH\(_2\)Cl\(_2\) (5 mL) at 0 °C was added BF\(_3\)OEt\(_2\) (4 \( \mu \)L, 0.03 mmol) and trimethylsilyl cyanide TMSCN (42 \( \mu \)L, 0.41 mmol). The mixture was stirred for 90 min, then poured into saturated aqueous NaHCO\(_3\) solution and extracted twice with CH\(_2\)Cl\(_2\). The combined organic layers were dried over MgSO\(_4\), and filtered, and the solvent was removed in vacuo. The crude material was purified through silicagel column chromatography (hexane-ethyl acetate 9:1) to give derivative 13 as an orange solid (48.2 mg, 85%). Mp 175-180 °C; \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(^1\)H NMR (CDCl\(_3\), 400 MHz): 7.55-7.52 (m, 3H), 7.29-7.27 (m, 2H), 3.25 (d, \( J = 2.7 \) Hz, 4H), 2.77 (s, 6H), 2.00 (t, \( J = 2.7 \) Hz, 2H), 1.39 (s, 6H). \(^{13}\)C \(^{1}\)H NMR (CDCl\(_3\),
125MHz): 154.6, 142.6, 141.0, 129.4, 127.9, 127.7, 127.2, 127.1, 127.0, 126.3, 125.5, 80.4, 69.2, 13.9, 13.8, 12.3. 11B NMR (128 MHz, CDCl3) δ 16.80. HRMS (ESI/Q-TOF) m/z: [M+H]+ Calcd for C27H24BN4 415.2093; Found 415.2104; [M+Na]+ Calcd for C27H23BN4Na 437.1913; Found 437.1915.

**Cholesterol-3β-yl 2-Azidoacetate (15).** To a stirred solution of Cholesterol (300 mg, 0.78 mmol), 2-azidoacetic acid (63 µL, 0.85 mmol) and N- (3-dimethylaminopropyl)-N’-ethylcarbodiimide EDC (301 mg, 1.01 mmol) in dry CH2Cl2 (5 mL) was added 4-dimethylaminopyridine (9.5 mg, 0.078 mmol). The mixture was stirred at room temperature for 1 h, then diluted with CH2Cl2 (25 mL) and poured into brine (15 mL). The organic layer was dried over MgSO4, filtered and the solvent was removed in vacuo. The crude material was purified through silicagel column chromatography (hexane-ethyl acetate 9:1) to give derivative 15 (335 mg, 91%), the data are in agreement with literature values.8 Mp = 122-125 °C; 1H NMR (CDCl3, 300 MHz): δ 5.38 (d, J = 6.7 Hz, 2H), 4.74-4.65 (m, 1H), 3.82 (s, 2H), 2.35 (m, 2H), 2.02-1.07 (m, 25H), 1.01 (s, 3H), 0.90 (d, J = 6.7 Hz, 2H), 0.85 (d, J = 6.7 Hz, 2H), 0.67 (s, 3H); 13C {1H} NMR (CDCl3, 125MHz): 167.7, 139.2, 123.2, 75.9, 56.7, 56.2, 50.5, 50.1, 42.4, 39.8, 39.6, 38.1, 37.0, 36.6, 36.3, 35.9, 32.0, 31.9, 28.3, 28.1, 27.8, 24.4, 24.0, 22.9, 22.7, 21.1, 19.3, 18.8, 11.9.

**Compound 17a.** Following the general procedure D, BODIPY 10b (52 mg, 0.13 mmol) and benzyl azide (38 µL, 0.31 mmol) in CH2Cl2 (6 mL) were added to a solution of sodium ascorbate (78 mg, 0.39 mmol) and CuSO4 (48 mg, 0.19 mmol) in H2O (2 mL). The solution was placed in a glass seal tube (65 °C) for 1 h. The residue was purified by silica column chromatography (hexane/ethyl acetate: 6:4) to afford BODIPY 17a (82 mg, 95%). Mp 118-121 °C; 1H NMR (CDCl3, 400 MHz): δ

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Compound 17b. Following the general procedure D, BODIPY 10b (30 mg, 0.075 mmol) and azidocholesteryl derivative 15 (105 mg, 0.22 mmol) in CH$_2$Cl$_2$ (6 mL) were added to a solution of sodium ascorbate (45 mg, 0.22 mmol) and CuSO$_4$ (28 mg, 0.11 mmol) in H$_2$O (2 mL). The solution was placed in a glass seal tube (65 °C) for 6 h. The residue was purified by silica column chromatography (hexane/ethyl acetate: 7 :3) to afford BODIPY 17b (42 mg, 42%). Mp 206-209 °C; [α]$_D^{21} = -108.6$ (c 0.05, CHCl$_3$); $^1$H NMR (CDCl$_3$, 400 MHz): δ 7.47-7.45 (m, 3H), 7.27-7.25 (m, 2H), 7.20 (m, 2H), 5.37-5.36 (m, 2H), 5.04 (s, 4H), 4.71-4.64 (m, 2H), 3.79 (s, 4H), 2.53 (s, 6H), 2.31-2.30 (m, 4H), 2.03-1.94 (m, 4H), 1.88-1.80 (m, 6H), 1.59-1.43 (m, 14H), 1.36-1.29 (m, 12H), 1.24-1.06 (m, 16H), 1.02-0.95 (m, 12H), 0.91 (d, J = 6.7 Hz, 1H), 0.86 (d, J = 6.7 Hz, 1H) 0.67 (s, 6H). $^{13}$C ($^1$H) NMR (CDCl$_3$, 125MHz): 165.8, 154.5, 147.2, 141.5, 140.0, 139.3, 135.3, 131.1, 129.3, 129.2, 128.2, 127.8, 123.4, 122.5, 76.5, 56.8, 56.3, 51.2, 50.1, 42.4, 39.8, 39.6, 38.0, 36.9, 36.6, 36.3, 35.9, 32.0, 31.9, 28.3, 28.1, 27.7, 24.4, 24.0, 23.0, 22.7, 21.1, 20.9, 19.4, 18.8, 12.9, 12.2, 12.0. HRMS (ESI/Q-TOF) m/z: [M+Na]$^+$ Calcd for C$_{83}$H$_{117}$BF$_2$NaO$_4$ 1361.9157; Found 1361.9172.

Compound 17c. Following the general procedure D, BODIPY 10b (30 mg, 0.075 mmol) and 1-ethylene-2-azido-α-D-mannopyranosyl glycoside (94 mg, 0.22 mmol) in CH$_2$Cl$_2$ (6 mL) were added to a solution of sodium ascorbate (45 mg, 0.22 mmol) and CuSO$_4$ (28 mg, 0.11 mmol) in H$_2$O (2 mL). The solution was placed in a glass seal tube (65 °C) for 24 h. The residue was purified.
by silica column chromatography (hexane/ethyl acetate: 1/1 to ethyl acetate) to afford BODIPY 17c (85 mg, 92%). [α]D21 = −66.2 (c 0.08, CHCl3); 1H NMR (CDCl3, 400 MHz): δ 7.44-7.42 (m, 3H), 7.28-7.26 (m, 4H), 5.21 (t, J = 9.6 Hz, 2H), 5.14-5.10 (m, 4H), 4.75 (bs, 2H), 4.49 (bs, 4H), 4.17 (dd, J = 12.4, 5.0 Hz, 2H), 4.09-4.04 (m, 2H), 4.01-3.98 (m, 2H), 3.84-3.79 (m, 2H), 3.74 (m, 2H), 3.57-3.51 (m, 2H), 2.49 (s, 6H), 2.08 (s, 6H), 2.04 (s, 6H), 2.00 (s, 6H), 1.91 (s, 6H), 1.31 (s, 6H). 13C (1H) NMR (CDCl3, 125 MHz): 170.6, 170.1, 169.8, 169.7, 154.2, 141.4, 139.8, 135.4, 131.0, 129.2, 129.0, 128.2, 127.8, 97.5, 69.2, 69.1, 68.8, 66.3, 65.6, 62.2, 49.7, 20.8, 20.7, 20.6, 12.8, 12.1.

HRMS (ESI/Q-TOF) m/z: [M+H]+ Calcd for C57H70BF2N8O12 1235.4771; Found 1235.4791; [M+Na]+ Calcd for C57H69BF2N8NaO12 1257.4591; Found 1257.4621.

**Compound 17d.** Following the general procedure D, compound 18 (35 mg, 0.04 mmol) and 1-ethylene-2-azido α-D-mannopyranosyl glycoside (33.5 mg, 0.08 mmol) in CH2Cl2 (6 mL) were added to a solution of sodium ascorbate (24 mg, 0.12 mmol) and CuSO4 (15 mg, 0.06 mmol) in H2O (2 mL). The solution was placed in a glass seal tube (65 °C) for 12 h. The residue was purified by silica column chromatography (hexane/ethyl acetate: 4/6 to ethyl acetate) to afford BODIPY 17d (40 mg, 78%). [α]D21 = −205.5 (c 0.03, CHCl3); 1H NMR (CDCl3, 400 MHz): δ 7.47-7.45 (m, 3H), 7.28-7.26 (m, 4H), 5.36-5.35 (m, 1H), 5.23 (t, J = 9.7 Hz, 1H), 5.17-5.12 (m, 2H), 5.04 (m, 2H), 4.78 (s, 1H), 4.70-4.62 (m, 1H), 4.51 (m, 2H), 4.20 (dd, J = 12.3, 5.1 Hz, 1H), 4.12-4.06 (m, 1H), 4.03-4.01 (m, 1H), 3.85-3.77 (m, 5H), 3.59 (m, 1H), 2.53 (s, 3H), 2.50 (s, 3H), 2.31-2.29 (m, 2H), 2.11 (s, 3H), 2.07 (s, 3H), 2.02 (s, 3H), 1.98 (m, 2H), 1.94 (s, 3H), 1.89-1.77 (m, 3H), 1.58-1.41 (m, 8H), 1.36-1.24 (m, 10H), 1.17-1.06 (m, 6H), 0.99 (s, 3H), 0.91 (d, J = 6.5 Hz, 3H), 0.85 (d, J = 6.6 Hz, 6H), 0.67 (s, 3H), 13C (1H) NMR (125 MHz, CDCl3) δ 170.7, 170.1, 169.9, 169.7, 165.8, 154.7, 154.1, 141.5, 140.1, 139.8, 139.1, 135.4, 131.2, 131.0, 129.3, 129.1, 128.2, 128.0, 127.6, 123.4, 97.6, 77.5, 77.4, 77.2, 76.8, 76.5, 69.3, 69.2, 68.9, 66.4, 65.7, 62.3, 56.8, 56.2, 51.2, 50.1, 42.4, 39.8, 39.6, 38.0, 36.9, 36.6, 36.3, 35.9, 32.0, 31.9, 28.3, 28.1, 27.7, 24.4, 23.9, 22.9, 22.7, 21.1, 20.9, 20.8, 20.8, 20.7, 19.4, 18.8, 12.9, 12.2, 12.1, 12.0. HRMS (ESI/Q-TOF) m/z: [M+H]+ Calcd for C70H89BF2NaO12 1287.7058; Found 1287.7065.
**Compound 18.** Following the general procedure D, BODIPY 10b (40 mg, 0.1 mmol) and azido-cholesteryl derivative 15 (42.2 mg, 0.09 mmol) in CH₂Cl₂ (6 mL) were added to a solution of sodium ascorbate (30 mg, 0.15 mmol) and CuSO₄ (75 mg, 0.3 mmol) in H₂O (2 mL). The solution was placed in a glass seal tube (65 °C) for 12 h. The residue was purified by silica column chromatography (hexane/ethyl acetate: 7:3) to afford derivative 18 (35 mg, 40%) along with 17b (37 mg, 28%).

**Compound 18**: [α]_D²¹ = −67.3 (c 0.04, CHCl₃); ¹H NMR (CDCl₃, 400 MHz): δ 7.49-7.47 (m, 3H), 7.28-7.25 (m, 2H), 7.21 (s, 1H), 5.38-5.37 (m, 1H), 5.05 (s, 2H), 4.72-4.64 (m, 1H), 3.81 (m, 2H), 3.20 (d, J = 2.8 Hz, 2H), 2.60 (s, 3H), 2.53 (s, 3H), 2.32-2.30 (m, 2H), 2.03-1.93 (m, 3H), 1.89-1.78 (m, 6H), 1.60-1.46 (m, 6H), 1.38-1.29 (m, 9H), 1.16-1.09 (m, 6H), 0.91 (d, J = 6.5 Hz, 3H), 0.86 (d, J = 6.6 Hz, 6H), 0.67 (s, 3H). ¹³C {¹H} NMR (CDCl₃, 125 MHz) δ 165.7, 154.6, 154.1, 147.1, 141.7, 140.1, 139.6, 139.1, 135.3, 131.1, 131.0, 129.5, 129.3, 129.2, 128.2, 127.9, 127.7, 125.5, 123.5, 122.7, 81.2, 68.5, 56.8, 56.2, 51.2, 50.1, 42.4, 39.8, 39.6, 38.0, 36.9, 36.6, 36.1, 35.9, 32.0, 31.9, 28.4, 28.2, 27.7, 24.4, 24.0, 23.0, 22.7, 21.1, 20.8, 19.4, 18.8, 13.7, 13.0, 12.9, 12.2, 12.1, 12.0. HRMS (ESI/Q-TOF) m/z: [M-F]⁺ Calcd for C₅₄H₇₀BF₅N₅O₂: 850.5607; Found 850.5603.

**8-phenyl-1,7-distyryl-3,5-dimethyl-2,6-di(prop-2-in-1-yl)-4,4-difluor-4-bora-3a,4a-diaza-s-indacene (19).** To a solution of BODIPY 10b (111 mg, 0.28 mmol) and benzaldehyde (141 µL, 1.39 mmol) in dry DMF (10 mL) were added piperidine (164 µL, 1.66 mmol) and acetic acid (95 µL, 1.66 mmol). The condensation reaction was performed under MW irradiation for 1 h at 80 °C. The resulting crude mixture was then partitioned between a éter/toluene (9/1) solution and water, the aqueous layer was re-extracted twice. The organic phase was dried over MgSO₄,
concentrated. The residue was purified by silica column chromatography (hexane/ethyl acetate: 9:1) to afford derivative 19 (126 mg, 79%). Mp 279-281 °C; \(^1\text{H} \text{NMR (CDCl}_3\text{, 400 MHz):} \) 7.79-7.75 (m, 2H), 7.68-7.66 (m, 4H), 7.53-7.32 (m, 13H), 3.44 (s, 4H), 2.09 (t, \(J = 2.7 \) Hz, 2H), 1.42 (s, 6H). \(^{13}\text{C} \{^{1}\text{H}\} \text{NMR (CDCl}_3\text{, 125 MHz):} \) δ 151.3, 140.5, 140.4, 138.1, 137.1, 135.47, 132.9, 129.4, 129.3, 129.0, 128.9, 128.5, 127.7, 126.2, 119.2, 81.3, 69.3, 15.6, 12.0. HRMS (ESI/Q-TOF) m/z: [M+H]\(^+\) Calcd for C\(_{39}\)H\(_{31}\)BF\(_2\)N\(_2\) 576.2548; Found 576.2552.

8-(2-azidomethylphenyl)-1,7-distyryl-3,5-dimethyl-4,4-difluor-4-bora-3a,4a-diaza-s-indacene (21). To a solution of azido-BODIPY 20 (300 mg, 0.79 mmol) and benzaldehyde (404 µL, 3.9 mmol) in dry DMF (10 mL) were added piperidine (468 µL, 4.7 mmol) and acetic acid (267 µL, 4.7 mmol). The condensation reaction was performed under MW irradiation for 1 h at 80 °C. The resulting crude mixture was then partitioned between a ether/toluene (9/1) solution and water, the aqueous layer was re-extracted twice. The organic phase was dried over MgSO\(_4\), concentrated. The residue was purified by silica column chromatography (hexane/ethyl acetate: 9:1) to afford derivative 21 (400 mg, 91%). Mp 212-215 °C; \(^1\text{H} \text{NMR (CDCl}_3\text{, 400 MHz):} \) δ 7.79-7.75 (m, 2H), 7.65-7.64 (m, 4H), 7.60-7.25 (m, 12H), 6.66 (s, 2H), 4.37 (s, 2H), 1.39 (s, 6H). \(^{13}\text{C} \{^{1}\text{H}\} \text{NMR (CDCl}_3\text{, 125 MHz):} \) δ 153.1, 141.9, 136.8, 136.6, 136.1, 134.3, 133.1, 132.9, 130.0, 129.2, 129.1, 128.9, 127.7, 119.2, 118.5, 52.2, 14.3. HRMS (ESI/Q-TOF) m/z: [M+H]\(^+\) Calcd for C\(_{34}\)H\(_{28}\)BF\(_2\)N\(_2\) 556.2485; Found 556.2474.
**Compound 22a.** Following the general procedure D, compound 10a (35 mg, 0.075 mmol) and azido-BODIPY 21 (108 mg, 0.19 mmol) in CH₂Cl₂ (6 mL) were added to a solution of sodium ascorbate (45 mg, 0.22 mmol) and CuSO₄ (28 mg, 0.11 mmol) in H₂O (2 mL). The solution was placed in a glass seal tube (65 °C) for 4 h. The residue was purified by silica column chromatography (hexane/ethyl acetate: 9/1 to 2/8) to afford BODIPY triad 22a (105 mg, 89%). Mp 230-235 °C; ¹H NMR (CDCl₃, 400 MHz): δ 7.72-7.67 (m, 4H), 7.59-7.23 (m, 36H), 7.05-7.03 (m, 2H), 6.76 (m, 2H), 6.65-6.64 (m, 4H), 5.34-5.25 (m, 4H), 4.82 (m, 2H), 3.49 (m, 4H), 2.46 (s, 6H), 1.70 (s, 3H), 1.26-1.24 (m, 12H), 1.04 (s, 6H). ¹³C {¹H} NMR (CDCl₃, 125 MHz) δ 170.3, 154.4, 153.3, 146.3, 141.9, 139.7, 138.6, 137.2, 137.2, 136.5, 136.4, 135.4, 133.9, 133.8, 133.55, 133.1, 132.8, 130.4, 130.2, 129.5, 129.2, 129.1, 129.0, 128.9, 128.8, 128.5, 128.3, 127.9, 127.6, 122.1, 119.1, 119.0, 118.3, 118.3, 62.8, 51.1, 20.6, 20.5, 14.2, 12.8, 11.5. ¹⁹F NMR (CDCl₃, 376 MHz) δ −137.07 (dq, J = 103.0, 28.3 Hz, 2F), −137.88 (dq, J = 103.0, 28.3 Hz, 2F), −143.52 −144.36 (m, 2F). HRMS (ESI/Q-TOF) m/z: [M+H]⁺ Calcd for C₉₆H₈₃B₃F₆N₁₂O₂ 1583.7055; Found 1583.7082.

**Compound 22b.** Following the general procedure D, compound 10b (40 mg, 0.1 mmol) and azido-BODIPY 21 (144 mg, 0.26 mmol) in CH₂Cl₂ (6 mL) were added to a solution of sodium ascorbate (60 mg, 0.3 mmol) and CuSO₄ (37 mg, 0.15 mmol) in H₂O (2 mL). The solution was placed in a glass seal tube (65 °C) for 24 h. The residue was purified by silica column chromatography (hexane/ethyl acetate: 9/1 to 1/1) to afford BODIPY triad 22b (90 mg, 60%). Mp 208-211 °C; ¹H NMR (CDCl₃, 400 MHz): δ 7.74-7.70 (m, 2H), 7.59-7.57 (m, 4H), 7.52-7.21 (m, 25H), 7.12-7.09 (m, 2H), 6.68-6.65 (m, 4H), 5.30 (s, 4H), 3.54 (s, 4H), 2.46 (s, 6H), 1.27 (s, 12H), 1.06 (s, 6H). ¹³C {¹H} NMR (CDCl₃, 125 MHz) δ 154.1, 153.5, 146.7, 141.9, 141.4, 140.1, 137.3, 136.6, 135.4, 135.1, 134.0, 133.1, 132.9, 131.0, 130.5, 130., 129.6, 129.3, 129.2, 129.0, 128.9, 128.1, 127.7, 121.9, 119.2, 118.4, 51.2, 20.7, 14.3, 12.9, 12.1. ¹⁹F NMR (CDCl₃, 376 MHz) δ −137.07 (dq, J = 103.0, 28.3 Hz, 2F), −139.31 (dq, J = 101.4, 31.5 Hz, 2F), −143.52 −144.36 (m, 2F). HRMS (ESI/Q-TOF) m/z: [M+H]⁺ Calcd for C₉₃H₇₉B₃F₆N₁₂O₂ 1511.6843; Found 1511.6893.
Compound 23. Following the general procedure D, compound 19 (41 mg, 0.071 mmol) and azido-BODIPY 20 (70 mg, 0.18 mmol) in CH$_2$Cl$_2$ (8 mL) were added to a solution of sodium ascorbate (42 mg, 0.21 mmol) and CuSO$_4$ (26 mg, 0.11 mmol) in H$_2$O (2 mL). The solution was placed in a glass seal tube (65 °C) for 12 h. The residue was purified by silica column chromatography (hexane/ethyl acetate: 6/4) to afford BODIPY triad 23 (54 mg, 56%). Mp 210-213 °C; $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.78-7.72 (m, 2H), 7.54-7.29 (m, 21H), 7.12-7.06 (m, 2H), 6.74 (s, 2H), 5.95 (s, 4H), 5.34 (s, 4H), 4.00 (s, 4H), 2.48 (s, 12H), 1.33 (s, 6H), 1.16 (s, 12H).$^{13}$C $^1$H NMR (CDCl$_3$, 125 MHz) $\delta$ 156.7, 151.3, 142.9, 140.8, 140.0, 138.1, 137.8, 136.9, 135.3, 133.8, 133.0, 132.7, 131.0, 130.2, 129.6, 129.6, 129.4, 129.1, 128.9, 128.6, 128.2, 127.6, 121.9, 119.1, 51.1, 22.6, 14.7, 14.0, 12.2. $^{19}$F NMR (CDCl$_3$, 376 MHz) $\delta$ −139.04 (q, $J = 30.1$ Hz, 2F), −146.16 (dq, $J = 108.1, 30.4$ Hz, 2F), −147.69 (dq, $J = 108.1, 30.4$ Hz, 2F). HRMS (ESI/Q-TOF) m/z: [M+H]$^+$ Calcd for C$_{79}$H$_{72}$B$_3$F$_6$N$_{12}$ 1335.6286; Found 1335.6269.

4. Photophysical properties

Spectroscopic signatures were recorded using diluted dye solutions (ca. 2 $\times$ 10$^{-6}$ M) prepared from a concentrated stock solution in acetone (ca. 10$^{-3}$ M), after solvent evaporation under reduced pressure, and subsequent dilution with the desired solvent of spectroscopic grade. UV-vis absorption and fluorescence spectra were recorded on a Varian (model CARY 4E) spectrophotometer and an Edinburgh Instrument spectrofluorometer (model FLSP 920), respectively. Fluorescence quantum yields ($\phi$) were determined from corrected spectra (detector sensibility to the wavelength) by the optically dilute relative method. PM567 ($\phi = 0.84$ in ethanol) for simple yellow-emitting BODIPYs and cresyl violet ($\phi = 0.54$ in methanol) for the red-emitting cassettes were used as references. The aforementioned spectrofluorometer is also equipped with a wavelength-tunable pulsed Fianium laser. Thus, the Time Correlated Single-Photon Counting (TCSPC) technique was used to record the fluorescence decay curves. Fluorescence emission was monitored at the maximum emission wavelength after excitation by
the said Fianium at the maximum absorption wavelengths. The fluorescence lifetime (τ) was obtained from the slope of the exponential fit of the decay curve, after the deconvolution of the instrumental response signal (recorded by means of a ludox scattering suspension) by means of an iterative method. The goodness of the exponential fit was controlled by statistical parameters (chi-square and the analysis of the residuals). The radiative (k_r) and non-radiative (k_{nr}) rate constants were calculated from the fluorescence quantum yield and lifetime; k_r = \phi/τ and k_{nr} = (1-\phi)/τ.

5. Lasing properties
Laser efficiency was evaluated from concentrated solutions (millimolar) of dyes in ethyl acetate contained in 1-cm optical-path rectangular quartz cells carefully sealed to avoid solvent evaporation during experiments. The liquid solutions were transversely pumped with 5 mJ, 8 ns FWHM pulses from the second (532 nm) and third (355 nm) harmonic of a Q-switched Nd:YAG laser (Lotis TII 2134) at a repetition rate of 1 Hz. The exciting pulses were line-focused onto the cell using a combination of positive and negative cylindrical lenses (f = 15 cm and f = -15 cm, respectively) perpendicularly arranged. The plane parallel oscillation cavity (2 cm length) consisted of a 90% reflectivity aluminium mirror acting as back reflector, and the lateral face of the cell acting as output coupler (4% reflectivity). The pump and output energies were detected by a GenTec powermeter. The photostability of the dyes in ethyl acetate solution was evaluated by using a pumping energy and geometry equal to the laser experimental set-up. We used spectroscopic quartz cuvettes with 0.1 cm optical to allow for the minimum solution volume (40 μL) to be excited. The lateral faces were grounded, whereupon no laser oscillation was obtained. Information about photostability was obtained by monitoring the decrease in laser-induced fluorescence (LIF) intensity after 130 000 pump pulses and 10 Hz repetition rate to speed up the experimental running. Laser emission emissions was monitored perpendicular to the exciting beam, collected by an optical fiber, and imaged onto a spectrometer (Acton Research corporation) and detected with a charge-coupled device (CCD) (SpectruMM:GS128B). Laser-induced emission was monitored in front-face configuration and recorded by feeding the signal to the boxcar (Stanford Research, model 250) to be integrated before being digitized and processed by a computer. The estimated error in the energy and photostability measurements was 10%.
6. **Computational chemistry**

Ground state geometries were optimized with the b3lyp hybrid functional, within the Density Functional Theory (DFT), using the double valence basis set with a polarization function (6-31G*). The geometries were considered as energy minimum when the corresponding frequency analysis did not give any negative value. The absorption spectra was simulated as a Franck-Condon vertical transition from the optimized ground state geometries using the time dependent method with the aforementioned functional and basis set (td b3lyp/6-31g*). All the theoretical calculations were carried out using the GAUSSIAN 16 program suite, implemented in the computational cluster provided by the SGiker resources of UPV-EHU.
7. Table S1. Photophysical\textsuperscript{a)} and lasing\textsuperscript{b)} properties of representative propargylated BODIPYs at positions 2 and/or 6.

The corresponding data of the commercially available BODIPYs 2 (PM567) in ethyl acetate are also added for comparison (in italics).

|    | $\lambda_{ab}$ (nm) | $\varepsilon_{\text{max}} \cdot 10^{-4}$ (M$^{-1}$ cm$^{-1}$) | $\lambda_{\text{fl}}$ (nm) | $\phi$ | $\tau$ (ns) | $k_{\text{fl}}$ (10$^8$ s$^{-1}$) | $k_{\text{nr}}$ (10$^8$ s$^{-1}$) | $\lambda_{\text{la}}$ (nm) | Eff(%) |
|----|---------------------|-------------------------------------------------|-----------------|------|----------|----------------|----------------|----------------|-------|
| 3  | EtOAc               | 509.0                                           | 8.4             | 527.0| 0.97     | 5.79           | 1.67           | 0.05           | 546   | 59    |
|    | ACN                 | 506.0                                           | 9.2             | 525.5| 0.97     | 5.99           | 1.62           | 0.05           |       |       |
| 10b| EtOAc               | 514.0                                           | 7.4             | 526.0| 0.77     | 4.78           | 1.61           | 0.48           | 546   | 54    |
|    | ACN                 | 512.0                                           | 6.2             | 524.5| 0.69     | 4.73           | 1.46           | 0.65           |       |       |
| 11b| EtOAc               | 506.5                                           | 6.9             | 518.0| 0.68     | 4.19           | 1.62           | 0.76           | 541   | 46    |
|    | ACN                 | 504.5                                           | 6.5             | 516.5| 0.60     | 4.12           | 1.45           | 0.97           |       |       |
| 12 | EtOAc               | 508.0                                           | 6.4             | 524.5| 1.00     | 5.91           | 1.69           | 0.00           | 546   | 61    |
|    | ACN                 | 506.0                                           | 6.0             | 521.5| 1.00     | 6.22           | 1.61           | 0.00           |       |       |
| 13 | EtOAc               | 513.5                                           | 9.3             | 525.0| 0.92     | 5.73           | 1.61           | 0.14           | 543   | 56    |
|    | ACN                 | 512.0                                           | 8.2             | 522.5| 0.90     | 5.80           | 1.55           | 0.17           |       |       |
| 2  |                     | 517.0                                           | 7.6             | 533.0| 0.84     | 5.78           | 1.45           | 0.28           | 568   | 48    |

\textsuperscript{a)} Dye concentration: 2 µM. Absorption ($\lambda_{ab}$) and fluorescence ($\lambda_{\text{fl}}$) wavelength, molar absorption ($\varepsilon_{\text{max}}$), fluorescence quantum yield ($\phi$) and lifetime ($\tau$), radiative ($k_{\text{fl}}$) and non-radiative ($k_{\text{nr}}$) rate constants.

\textsuperscript{b)} Dye concentrations in ethyl acetate ranging from 1 $\times$ 10$^{-3}$ M to 7 $\times$ 10$^{-3}$ M to match the optical density at the irradiation wavelength (532 nm). Laser wavelength ($\lambda_{\text{la}}$) and efficiency (%Eff).

EtOAc: ethyl acetate; ACN: acetonitrile
8. Table S2. Photophysical \(^a\) and lasing\(^b\) properties of BODIPYs after click conjugation with biomolecules.

|     | \(\lambda_{ab}\) (nm) | \(\varepsilon_{\text{max}} \times 10^4\) (M\(^{-1}\) cm\(^{-1}\)) | \(\lambda_{fl}\) (nm) | \(\phi\) | \(\tau\) (ns) | \(k_{fl}\) (10\(^8\) s\(^{-1}\)) | \(k_{nr}\) (10\(^8\) s\(^{-1}\)) | \(\lambda_{la}\) (nm) | Eff(%) |
|-----|----------------|-----------------|-----------------|-----|-----|-------------|-----------------|-----------------|----------------|-----|
| 17a | EtOAc         | 519.0           | 6.5             | 532.0 | 0.79 | 4.74        | 1.66            | 0.44            | 549            | 52  |
|     | ACN           | 517.0           | 4.6             | 530.0 | 0.67 | 4.64        | 1.44            | 0.71            |                |
| 17b | EtOAc         | 518.5           | 5.8             | 532.0 | 0.75 | 4.88        | 1.54            | 0.51            | 550            | 47  |
|     | ACN           | 517.0           | 5.1             | 530.5 | 0.74 | 4.90        | 1.51            | 0.53            |                |
| 17c | EtOAc         | 519.0           | 9.3             | 532.5 | 0.81 | 5.03        | 1.61            | 0.38            | 549            | 55  |
|     | ACN           | 517.5           | 8.8             | 531.0 | 0.76 | 5.04        | 1.51            | 0.47            |                |
| 17d | EtOAc         | 518.5           | 7.4             | 532.0 | 0.78 | 4.89        | 1.59            | 0.45            | 547            | 51  |
|     | ACN           | 517.0           | 7.0             | 530.5 | 0.78 | 4.98        | 1.57            | 0.44            |                |

\(^a\) Dye concentration: 2 µM. Absorption (\(\lambda_{ab}\)) and fluorescence (\(\lambda_{fl}\)) wavelength, molar absorption (\(\varepsilon_{\text{max}}\)), fluorescence quantum yield (\(\phi\)) and lifetime (\(\tau\)), radiative (\(k_{fl}\)) and non-radiative (\(k_{nr}\)) rate constants.

\(^b\) Dye concentrations in ethyl acetate ranging from 6\(\times\)10\(^{-4}\) M to 9 \(\times\) 10\(^{-4}\) M to match the optical density at the irradiation wavelength (532 nm). Laser wavelength (\(\lambda_{la}\)) and efficiency (%Eff). EtOAc: ethyl acetate; ACN: acetonitrile.
9. Table S3. Photophysical\textsuperscript{a)} and lasing\textsuperscript{b)} properties of the all-BODIPYs based cassettes.

The corresponding data of the isolated red-emitting fragment 19 are also added for comparison.

|     | \(\lambda_{ab}\) (nm) | \(\varepsilon_{\text{max}} \times 10^{-4}\) (M\(^{-1}\) cm\(^{-1}\)) | \(\lambda_{\text{fl}}\) (nm) | \(\phi^*\) | \(\tau^*\) (ns) | \(\lambda_{la}^*\) (nm) | Eff(\%)* |
|-----|------------------------|---------------------------------|-----------------|--------|----------------|-----------------|--------|
| 22a | EtOAc                  | 624.5                           | 17.7            | 640.5  | 0.61           | 1.86(9%)-4.67(81%) |        |
|     |                        | 523.5                           | 8.7             |        |                |                  |        |
|     |                        | 346.0                           | 14.6            |        |                |                  |        |
|     | ACN                    | 623.0                           | 14.9            | 639.5  | 0.19           | 1.16(70%)-2.86(30%) |        |
|     |                        | 522.5                           | 8.4             |        |                |                  |        |
|     |                        | 345.5                           | 12.5            |        |                |                  |        |
| 22b | EtOAc                  | 625.0                           | 15.3            | 637.0  | 0.46           | 2.17(17%)-4.37(83%) | 708    | 12    |
|     |                        | 521.0                           | 7.8             |        |                |                  |        |
|     |                        | 346.0                           | 13.0            |        |                |                  |        |
|     | ACN                    | 623.0                           | 12.1            | 635.0  | 0.11           | 0.47(21%)-1.14(79%) |        |
|     |                        | 519.0                           | 6.9             |        |                |                  |        |
|     |                        | 345.0                           | 10.4            |        |                |                  |        |
| 23  | EtOAc                  | 628.0                           | 6.5             | 644.0  | 0.64           | 4.81            | 712    | 25    |
|     |                        | 502.0                           | 13.2            |        |                |                  |        |
|     |                        | 344.0                           | 6.6             |        |                |                  |        |
|     | ACN                    | 625.0                           | 8.0             | 644.5  | 0.38           | 2.67            |        |
|     |                        | 502.0                           | 12.7            |        |                |                  |        |
|     |                        | 345.0                           | 6.6             |        |                |                  |        |
| 19  | EtOAc                  | 617.0                           | 7.0             | 636.5  | 0.73           | 4.86            | 701    | 31    |
|     |                        | 344.0                           | 6.2             |        |                |                  |        |
|     | ACN                    | 617.0                           | 6.8             | 636.5  | 0.81           | 5.10            |        |
|     |                        | 343.0                           | 5.8             |        |                |                  |        |

\textsuperscript{a)} Dye concentration: 2 \(\mu\)M. Absorption \((\lambda_{ab})\) and fluorescence \((\lambda_{fl})\) wavelength, molar absorption \((\varepsilon_{\text{max}})\), fluorescence quantum yield \((\phi^*)\) and lifetime \((\tau^*)\).

\textsuperscript{b)} Dye concentrations in ethyl acetate ranging from \(1 \times 10^{-4}\) M to \(1 \times 10^{-3}\) M to match the optical density at the irradiation wavelengths (532 nm and 355 nm). Laser wavelength \((\lambda_{la})\) and efficiency (Eff(\%)\).

EtOAc: ethyl acetate; ACN: acetonitrile

*these fluorescence and laser parameters remain the same regardless of the excited fragment
10. Figure S1. Absorption and fluorescence spectra of the propargylated BODIPYs in diluted solutions (2 µM) of ethyl acetate.

11. Figure S2. Absorption and fluorescence spectra of clickable BODIPYs at 2 and 6 positions in diluted solutions (2 µM) of ethyl acetate.
12. Figure S3. Theoretically predicted absorption spectra (td b3lyp/6-31g*) of triads 22b and 23.
The corresponding absorption spectrum of the isolated red-emitting fragment 19 is added for comparison.
13. Figure S4. Theoretically calculated (b3lyp/6-31g*) molecular orbitals involved in the main visible electronic transitions from ground state optimized geometries of the all-BODIPY based cassettes.
\[
\text{Co}_2(\text{CO})_6 \quad 6
\]

1H-NMR (400 MHz, CDCl3)
$^{13}$C ($^1$H) NMR (125 MHz, CDCl$_3$)
