Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

BODIPY dyads from a,c-biladiene salts

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1. General information

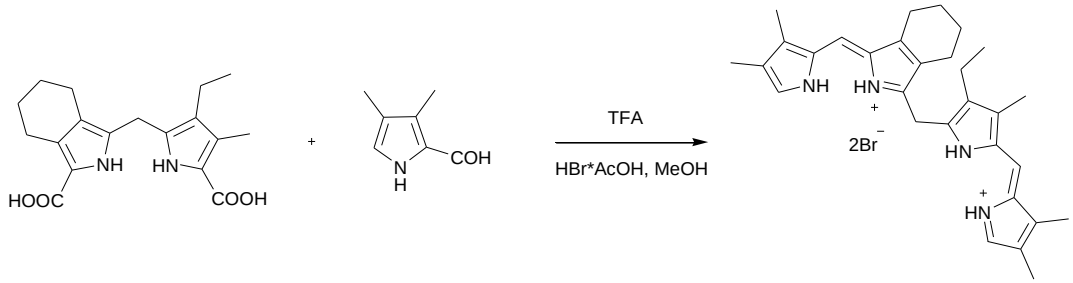
Silica gel 60 (70–230 mesh, Sigma Aldrich) or basic alumina (Type T, Merck) were used for column chromatography. Reagents and solvents (Sigma-Aldrich) were of the highest grade available and were used without further purification. UV-vis spectra were recorded in THF on a Cary 50 spectrophotometer. The reactions were monitored by TLC using silica gel plates with 254 indicator (0.2 mm, polyester backed, 60Å, precoated).

NMR spectroscopy, including ^{1}H-, ^{11}B-, ^{13}C- and ^{19}F-NMR were recorded using either a Bruker AV400 (400 MHz) or a Bruker AV500 (500 MHz) spectrometers. Experiments were performed in $CDCl_3$ at 300 K. Chemical shifts are given in ppm relative to TMS**.** High-resolution mass spectra were obtained using the ESI-TOF mode.

2. Synthesis

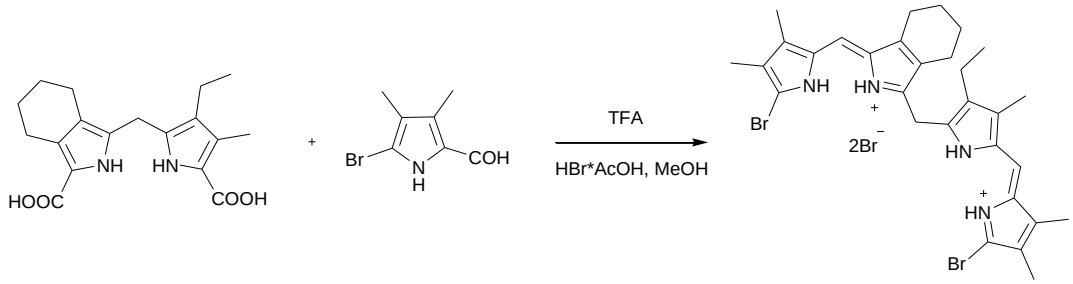
Starting pyrroles and dipyrromethane were prepeared following literature procedures [1,2] . The a,c-biladienes **1** and **2** were prepared as shown below, following literature procedures [3].

a,c-Biladiene 1



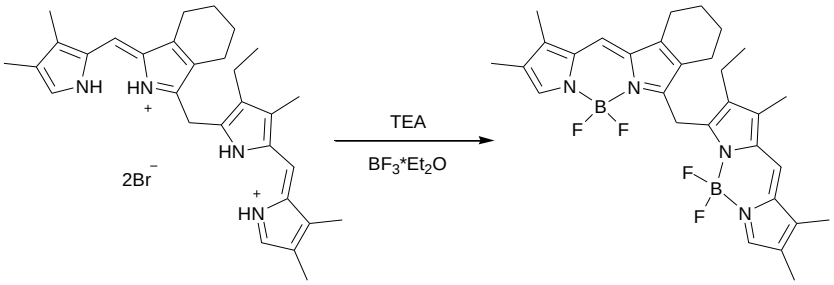
Yield = 88 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ, ppm 13.55 (s, 1 H, N-*H*), 13.46 (s, 1 H, N-*H*), 13.20 (s, 1 H, N-*H*), 13.12 (s, 1 H, N-*H*), 7.66 (s, 1 H, *Hα*), 7.63 (s, 1 H, *Hα*), 7.16 (s, 1 H, *Hmeso*), 5.22 (s, 2 H, C*H*$_2$), 2.72 (m, 2 H, cyclohexyl-C*H*$_2$), 2.52 (q, 2 H, *J* = 7.48 Hz, C*H*$_2$CH$_3$), 2.33 (s, 3 H, C*H*$_3$), 2.32 (s, 3 H, C*H*$_3$), 2.30 (s, 3 H, C*H*$_3$), 2.11 (s, 3 H, C*H*$_3$), 2.10 (s, 3 H, C*H*$_3$), 1.73 (m, 6 H, cyclohexyl-C*H*$_2$), 0.78 (t, 3 H, *J* = 7.48 Hz, CH$_2$C*H*$_3$). ESI-HRMS: *m/z* calcd for $C_{30}H_{38}Br_2N_4$ $[M]^{2+}$: 227.1543; found: 227.1557.

a,c-Biladiene 2



Yield = 76 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ, ppm 13.98 (s, 1 H, N-*H*), 13.90 (s, 1 H, N-*H*), 13.71 (s, 1 H, N-*H*), 13.64 (s, 1 H, N-*H*), 7.14 (s, 1 H, *Hmeso*), 7.02 (s, 1 H, *Hmeso*), 5.21 (s, 2 H, C*H*$_2$), 2.67 (m, 2 H, cyclohexyl-C*H*$_2$), 2.51 (q, 2 H, *J* = 7.52 Hz, C*H*$_2$CH$_3$), 2.34 (s, 3 H, C*H*$_3$), 2.31 (s, 3 H, C*H*$_3$), 2.29 (s, 3 H, C*H*$_3$), 2.06 (s, 3 H, C*H*$_3$), 2.05 (s, 3 H, C*H*$_3$), 1.70 (m, 6 H, cyclohexyl-C*H*$_2$), 0.73 (t, 3 H, *J* = 7.52 Hz, CH$_2$C*H*$_3$). ESI-HRMS: *m/z* calcd for $C_{30}H_{36}Br_2N_4$ $[M]^{2+}$: 305.0648; found: 305.0659.

BODIPY dyad 3



329 µL TEA (2,81 mmol) were added to a stirring solution of 86 mg a,c-biladiene **1** (0,140 mmol) in 23 mL DCE at 0°C under N_2. After 15 min stirring, 520 µL BF_3•Et_2O (4,2 mmol) was slowly added and the solution was stirred at 0°C for another 15 min. Then, the solution was warmed up to room temperature and stirred for 6 h until disappearance of the starting material by TLC. The solvent was removed under reduced pressure and the residue was chromatographed on a silica gel column using CH_2Cl_2/hexane 7/3 as eluent. The title product was recrystallized from CH_2Cl_2/hexane, obtaining 29 mg of pure compound. Yield = 38%. m.p.: decomposition over 250°C.

UV-vis (THF): λ_{max}, nm (log ε) 495 (4,40), 530 (sh, 4.61), 556 (5.20). ^{1}H NMR (400 MHz, $CDCl_3$): δ, ppm 7.48 (s, 1 H, *H*-5), 7.45 (s, 1 H, *H*-5), 7.14 (s, 1 H, *H*-8), 7.05 (s, 1 H, *H*-8), 4.70 (s, 2 H, C*H*$_2$), 2.61 (m, 2 H, C*H*$_2$CH$_3$), 2.20 (s, 6 H, 2C*H*$_3$), 2.18 (s, 3 H, C*H*$_3$), 2.02 (s, 6 H, 2C*H*$_3$), 1.54 (m, 8 H, cyclohexyl-C*H*$_2$), 0.81 (t, 3 H, *J* = 7.52 Hz, CH$_2$C*H*$_3$). ^{13}C NMR (500 MHz, $CDCl_3$): δ, ppm 201.80, 199.72, 190.08, 175.18, 165.18, 155.94, 154.17, 144.40, 142.77, 141.61, 140.69, 137.51, 135.47, 135.09, 134.28, 125.96, 121.56, 120.95, 119.35, 114.84, 114.07, 112.54, 77.41, 77.16, 76.91, 29.86, 27.58, 23.03, 22.20, 21.80, 20.42, 16.87, 13.51, 9.97, 9.74, 9.71, 9.68. ^{19}F NMR (400 MHz, $CDCl_3$): δ, ppm -140.33 (dq, 1 F, *J'* = 33.82 Hz, *J''* = 112.12 Hz), -142.21 (dq, 1 F, *J'* = 35.88 Hz, *J''* = 114.68 Hz), -143.10 (dq, 1 F, *J'* = 33.82 Hz, *J''* = 112.12 Hz), -145.11 (dq, 1 F, *J'* = 35.88 Hz, *J''* = 114.68 Hz). ^{11}B NMR (400 MHz, $CDCl_3$): δ, ppm 0.47 (t, 1 B, *J* = 97.44 Hz), 0.41 (t, 1 B, *J* = 98.62 Hz). ESI-HRMS: *m/z* calcd for $C_{30}H_{34}B_2F_4N_4$ $[M\text{-}HF]^+$: 527.2989; found: 527.2961.

Figure S1: ^{1}H NMR spectrum of BODIPY dyad **3**

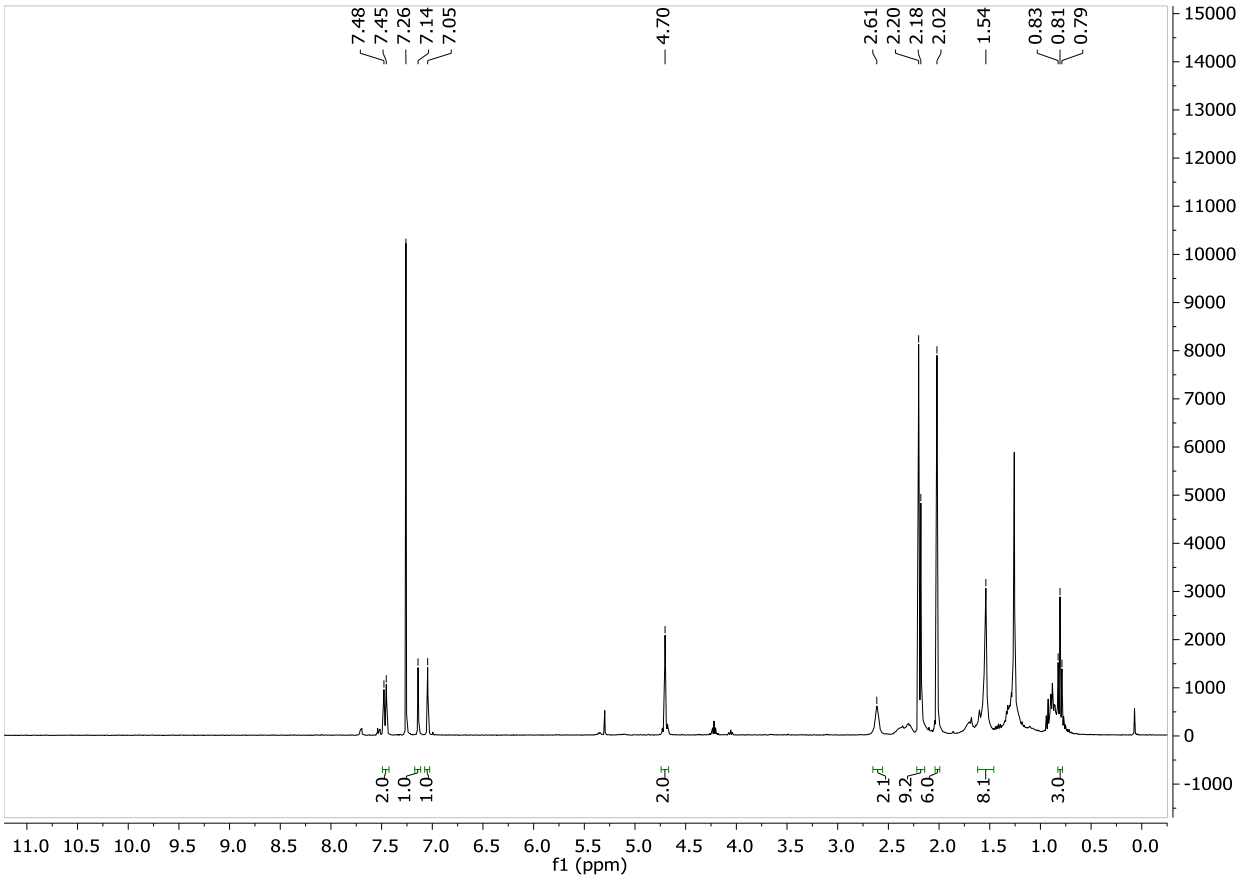


Figure S2: ^{13}C NMR spectrum of BODIPY dyad **3**

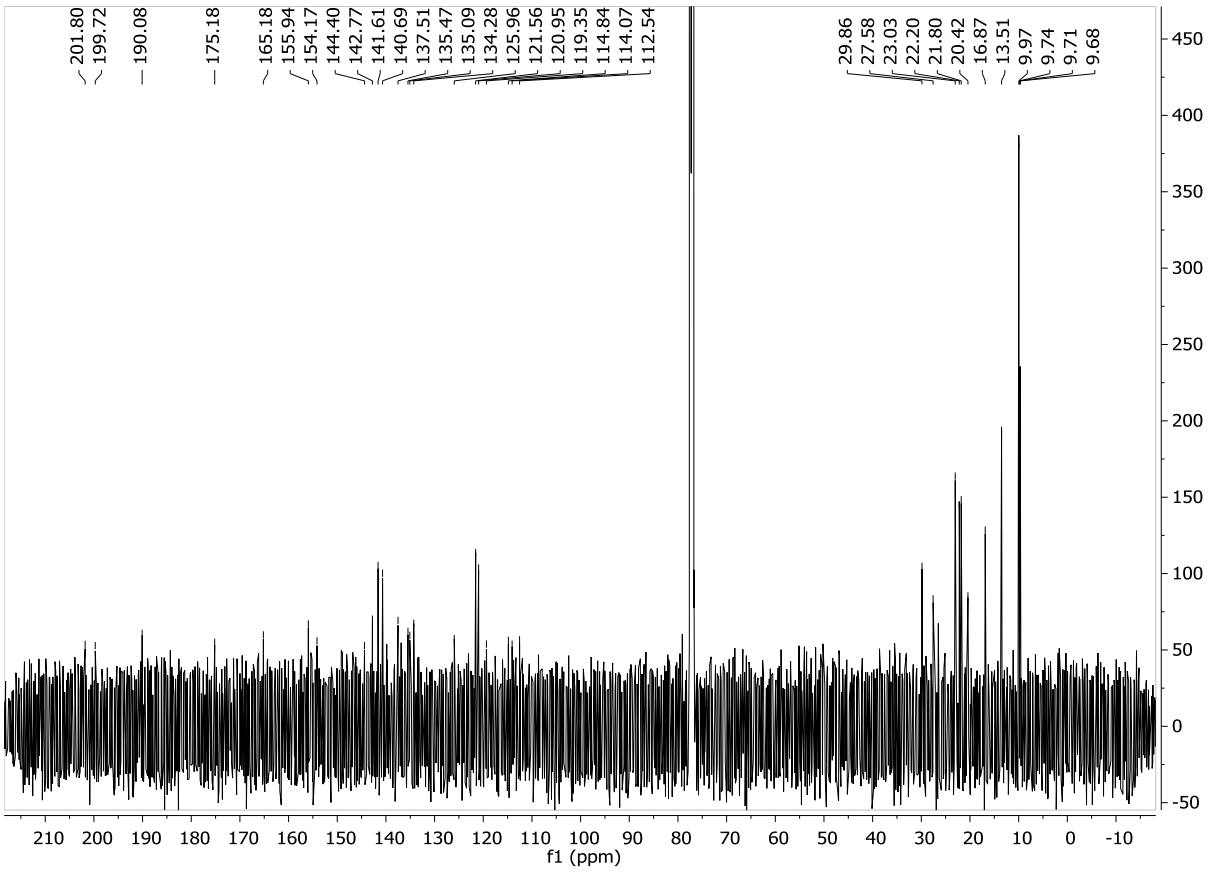


Figure S3: ^{19}F NMR spectrum of BODIPY dyad **3**

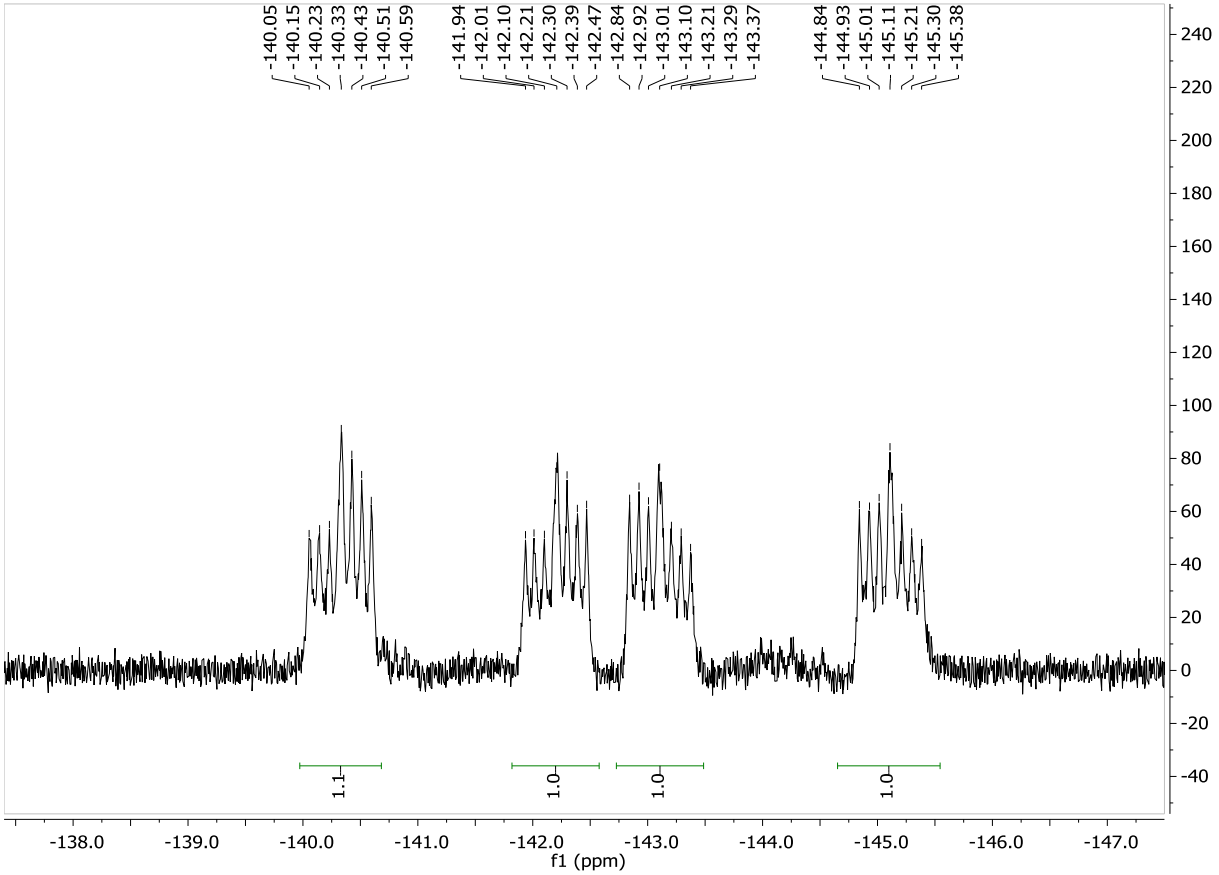
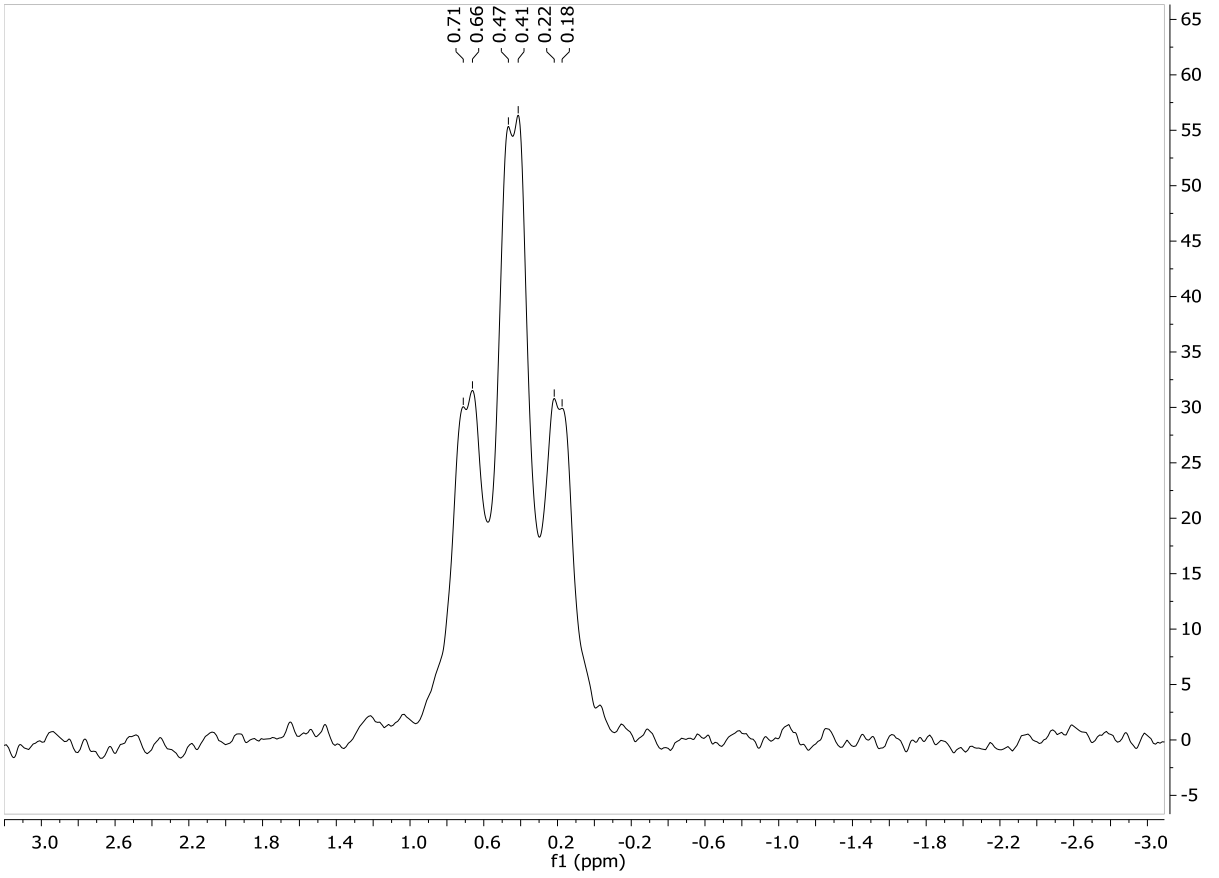
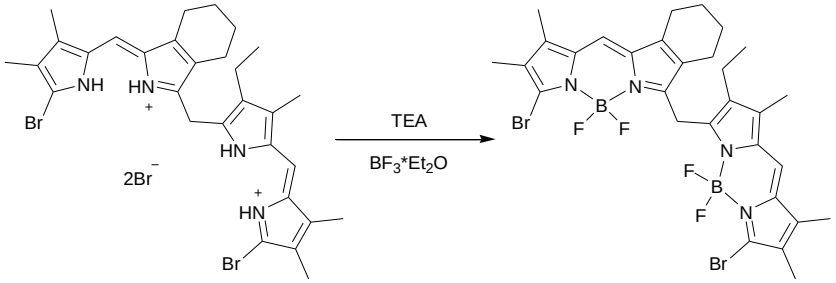


Figure S4: ^{11}B NMR spectrum of BODIPY dyad **3**



BODIPY dyad 4



91 µL TEA (0,653 mmol) was added to a stirring solution of 25 mg a,c-biladiene **2** (0,033 mmol) in 6 mL DCE at 0°C under N_2. After 15 min stirring, 121 µL $BF_3 \bullet Et_2O$ (0,979 mmol) was slowly added and the solution was stirred at 0°C for another 15 min. Then, the solution was warmed up to room temperature and stirred for 6 h until complete disappearance of the starting material by TLC. The solvent was removed under reduced pressure and the residue was chromatographed on a silica gel column using CH_2Cl_2/hexane 7/3 as eluent. The title product was recrystallized from CH_2Cl_2/hexane, obtaining 13 mg of pure compound. Yield = 54%. m.p.: decomposition over 210°C.

UV-vis (THF): λ_{max}, nm (log ε) 499 (4,38), 538 (sh, 4.44), 566 (5.03). ^{1}H NMR (400 MHz, $CDCl_3$): δ, ppm 7.07 (s, 1 H, *H*-8), 6.97 (s, 1 H, *H*-8), 4.76 (s, 2 H, C*H*$_2$), 2.62 (m, 2 H, C*H*$_2$CH$_3$), 2.25 (s, 3 H, C*H*$_3$), 2.22 (s, 3 H, C*H*$_3$), 2.21 (s, 3 H, C*H*$_3$), 2.02 (s, 3 H, C*H*$_3$), 2.01 (s, 3 H, C*H*$_3$), 1.57 (m, 8 H, cyclohexyl-C*H*$_2$), 0.83 (t, 3 H, *J* = 7.56 Hz, CH$_2$C*H*$_3$). ^{13}C NMR (500 MHz, $CDCl_3$): δ, ppm 188.09, 169.38, 159.73, 156.03, 155.89, 145.59, 142.66, 139.71, 134.86, 133.72, 132.82, 128.80, 126.73, 126.38, 124.34, 119.65, 119.62, 119.06, 118.08, 111.79, 38.74, 31.93, 23.75, 22.83, 21.96, 21.62, 16.72, 13.29, 10.07, 10.03, 9.92, 9.60. ^{19}F NMR (400 MHz, $CDCl_3$): δ, ppm -141.51 (dq, 1 F, *J'* = 33.84 Hz, *J''* = 107.44 Hz), -142.80 (dq, 1 F, *J'* = 34.36 Hz, *J''* = 105.92 Hz), -142.82 (dq, 1 F, *J'* = 33.84 Hz, *J''* = 107.44 Hz), -145.11 (dq, 1 F, *J'* = 34.36 Hz, *J''* = 105.92 Hz). ^{11}B NMR (400 MHz, $CDCl_3$): δ, ppm 0.66 (t, 1 B, *J* = 100.04 Hz), 0.58 (t, 1 B, *J* = 99.40 Hz). ESI-HRMS: *m/z* calcd for $C_{30}H_{32}B_2Br_2F_4N_4$ $[M]^-$: 704.1121; found: 704.1144.

Figure S5: ^{1}H NMR spectrum of BODIPY dyad **4**

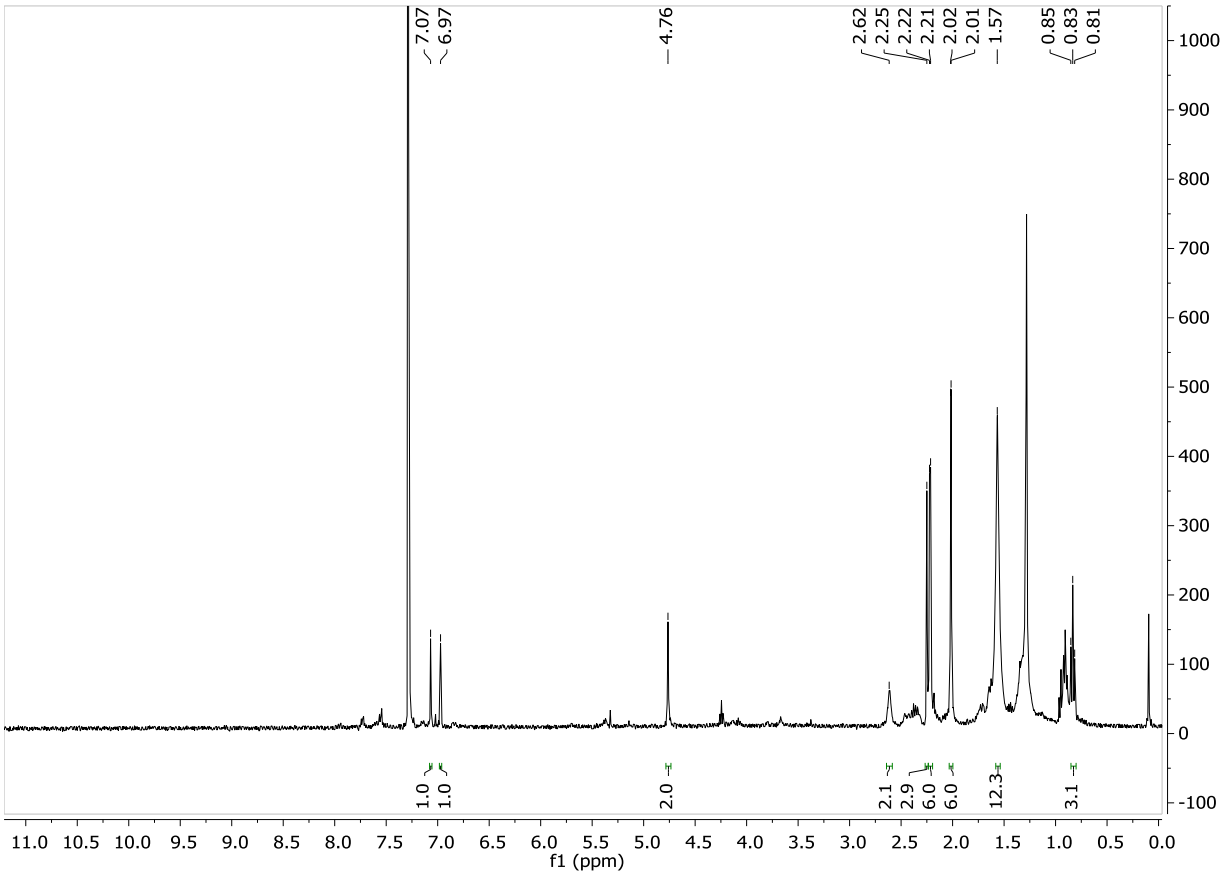


Figure S6: ^{13}C NMR spectrum of BODIPY dyad **4**

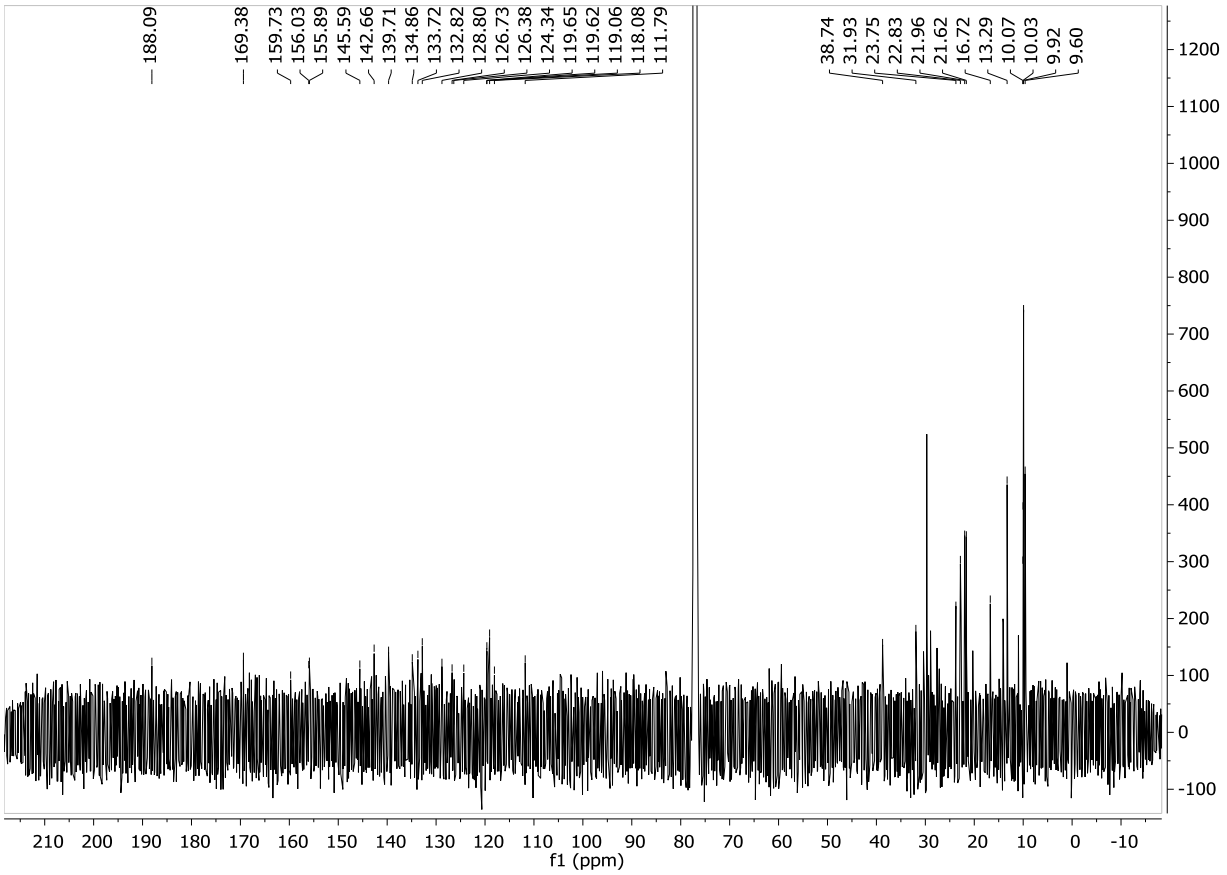


Figure S7: ^{19}F NMR spectrum of BODIPY dyad **4**

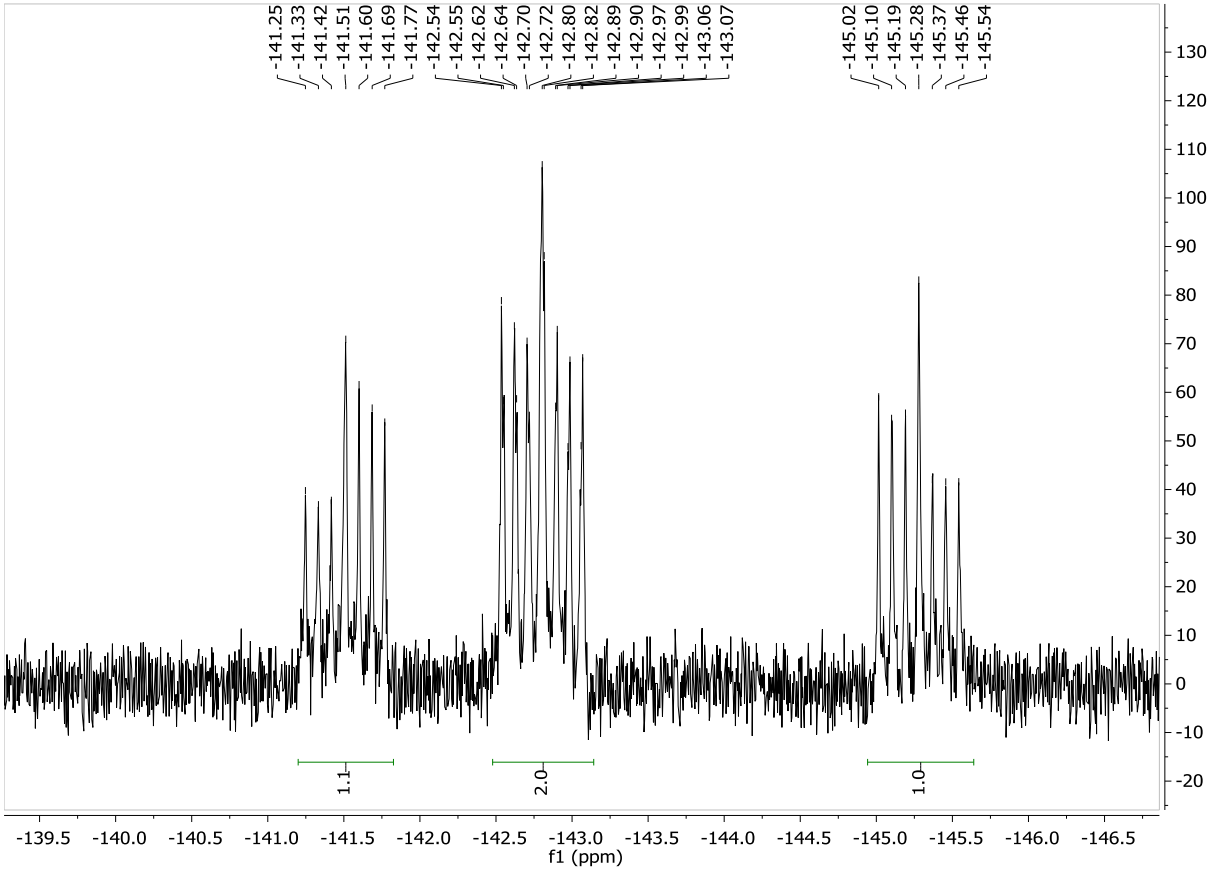
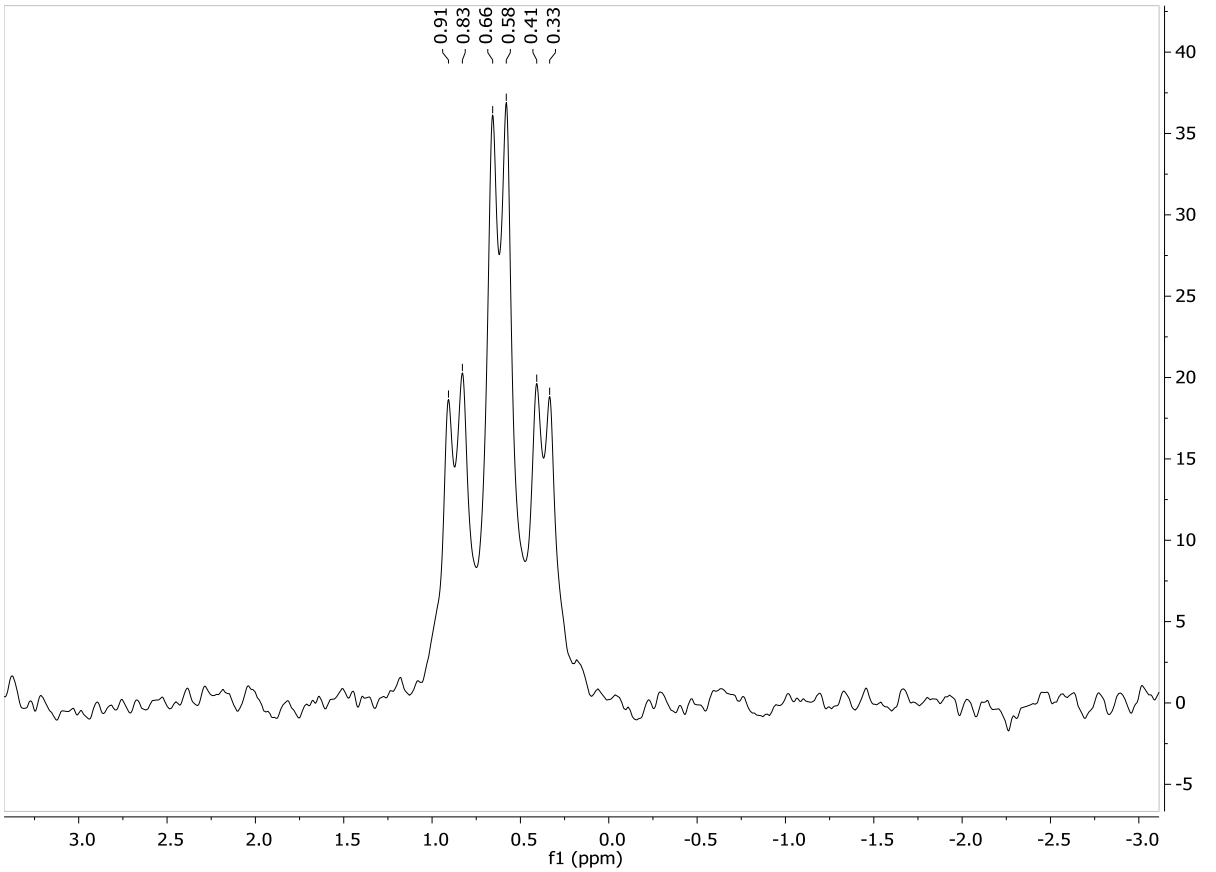
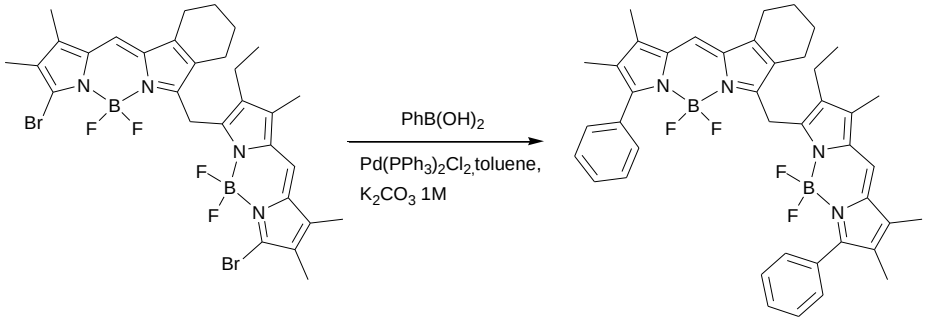


Figure S8: ^{11}B NMR spectrum of BODIPY dyad **4**



BODIPY dyad 5



17 mg of bis-BODIPY **4** (0,024 mmol) were added to a stirring solution of 29,5 mg $PhB(OH)_2$ (0,242 mmol) and 3,4 mg $Pd(PPh_3)_2Cl_2$ (0,005 mmol) in 3 mL of dry toluene under N_2. 484 µL aq. K_2CO_3 1M were added and the reaction was stirred at 75°C for 2 h, until complete disappearance of the starting material by TLC. The solvent was removed under reduced pressure and the residue was chromatographed on a silica gel column using CH_2Cl_2/hexane 7/3 as eluent. The title product was recrystallized from CH_2Cl_2/hexane, obtaining 12 mg of pure compound. Yield = 74%. m.p.: > 300°C. UV-vis (THF): λ_{max}, nm (log ε) 507 (4,59), 544 (sh, 4.52), 577 (5.14). ^{1}H NMR (400 MHz, $CDCl_3$): δ, ppm 7.60-7.56 (m, 4 H, *Ph*), 7.46-7.37 (m, 6 H, *Ph*), 7.14 (s, 1 H, *H*-8), 7.03 (s, 1 H, *H*-8), 4.56 (s, 2 H, C*H*$_2$), 2.63-2.57 (m, 2 H, C*H*$_2$CH$_3$), 2.25 (s, 3 H, C*H*$_3$), 2.22 (s, 3 H, C*H*$_3$), 2.18 (s, 3 H, C*H*$_3$), 1.92 (s, 3 H, C*H*$_3$), 1.91 (s, 3 H, C*H*$_3$), 1.53 (m, 8 H, cyclohexyl-C*H*$_2$), 0.75 (t, 3 H, *J* = 7.52 Hz, CH_2C*H*$_3$). ^{13}C NMR (500 MHz, $CDCl_3$): δ, ppm 155.48, 155.41, 154.56, 154.26, 141.24, 138.69, 138.25, 137.60, 136.92, 133.87, 133.16, 133.06, 132.97, 132.51, 132.42, 132.25, 132.19, 130.15, 129.91, 129.84, 128.78, 128.73, 128.62, 127.72, 127.68, 125.90, 125.44, 120.20, 120.08, 119.65, 27.46, 22.94, 22.12, 21.61, 20.34, 16.83, 13.43, 13.22, 9.89, 9.85, 9.56, 9.46. ^{19}F NMR (400 MHz, $CDCl_3$): δ, ppm -131.87 (dq, 1 F, *J'* = 36.32 Hz, *J''* = 110.08 Hz), -134.28 (dq, 1 F, *J'* = 35.52 Hz, *J''* = 108.84 Hz), -138.10 (dq, 1 F, *J'* = 35.52 Hz, *J''* = 108.84 Hz), -139.92 (dq, 1 F, *J'* = 36.32 Hz, *J''* = 110.08 Hz). ^{11}B NMR (400 MHz, $CDCl_3$): δ, ppm 0.82 (t, 1 B, *J* = 103.80 Hz), 0.76 (t, 1 B, *J* = 102.80 Hz). ESI-HRMS: *m/z* calcd for $C_{42}H_{42}B_2F_4N_4$ $[M\text{-}F]^+$: 681.3548; found: 681.3549.

Figure S9: ^{1}H NMR spectrum of BODIPY dyad **5**

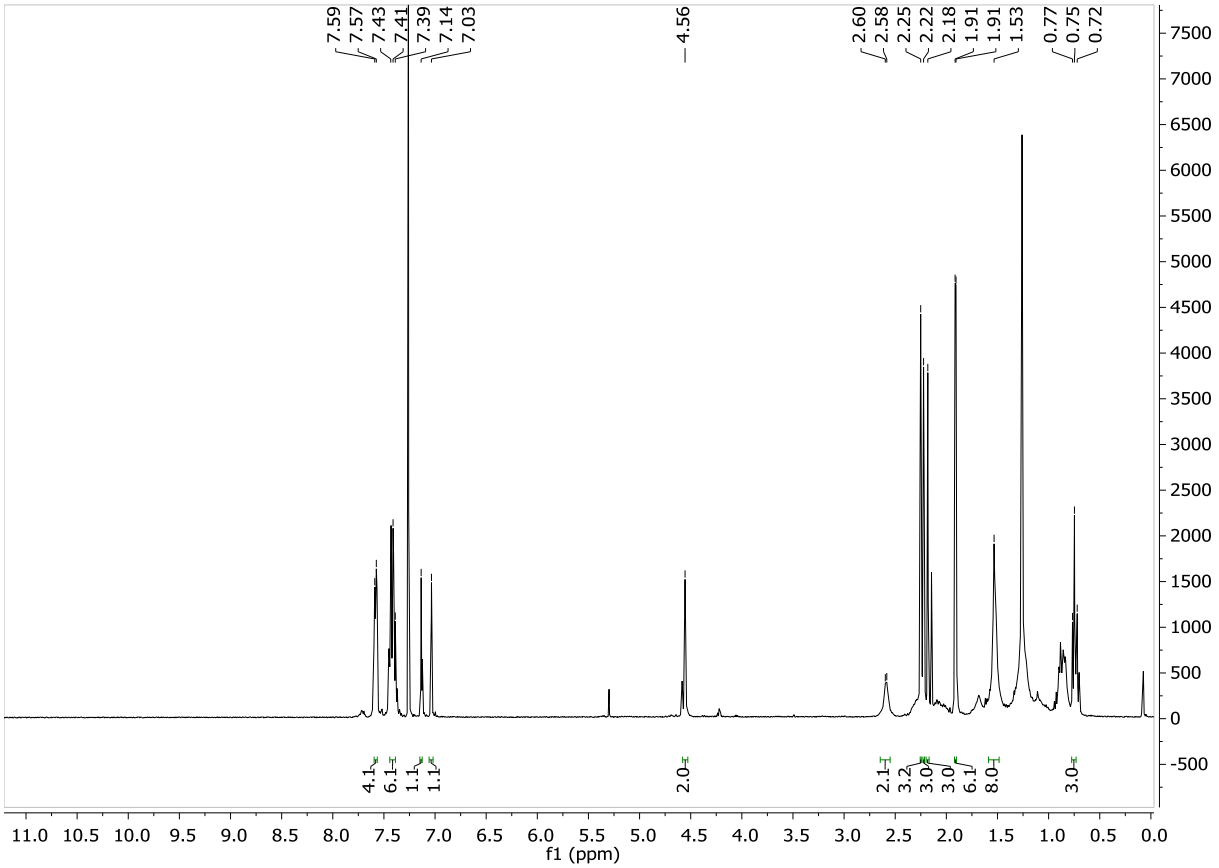


Figure S10: ^{13}C NMR spectrum of BODIPY dyad **5**

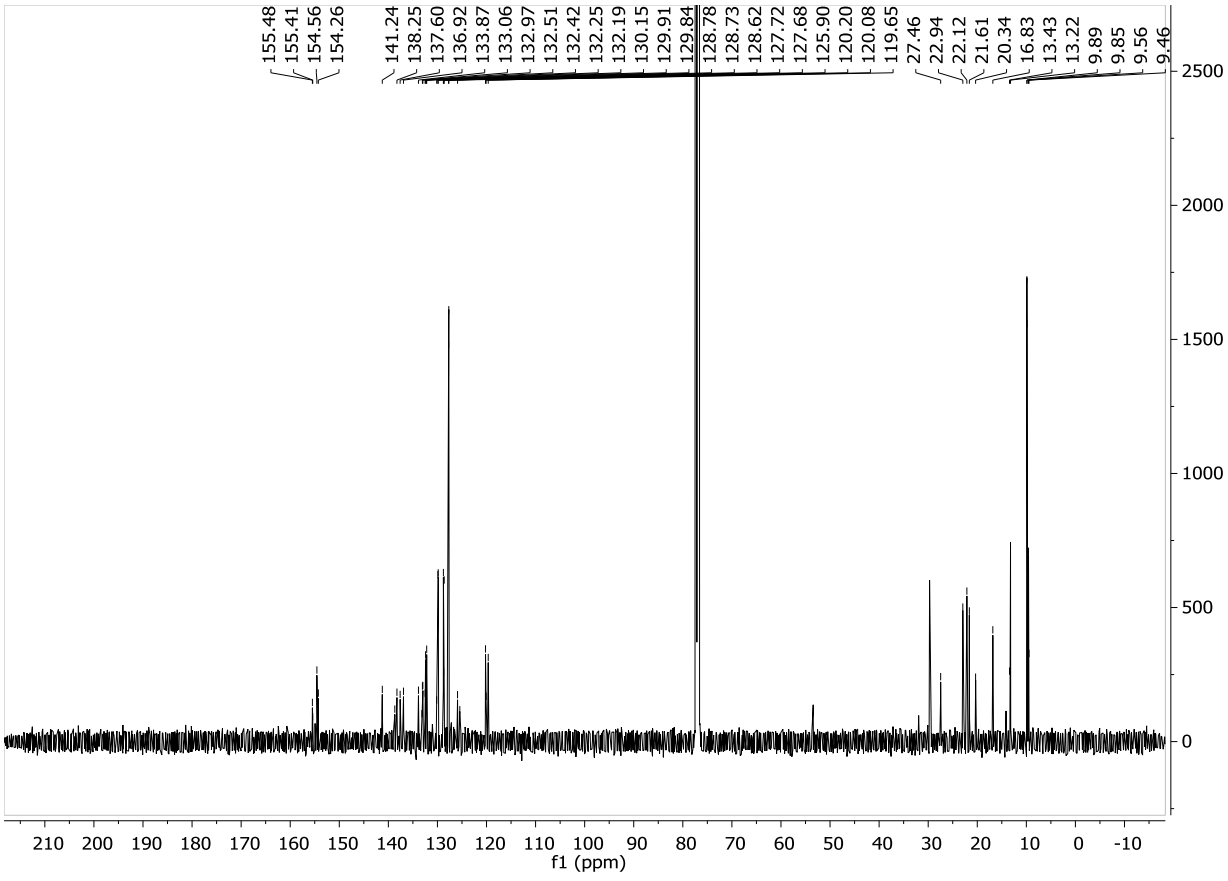


Figure S11: ^{19}F NMR spectrum of BODIPY dyad **5**

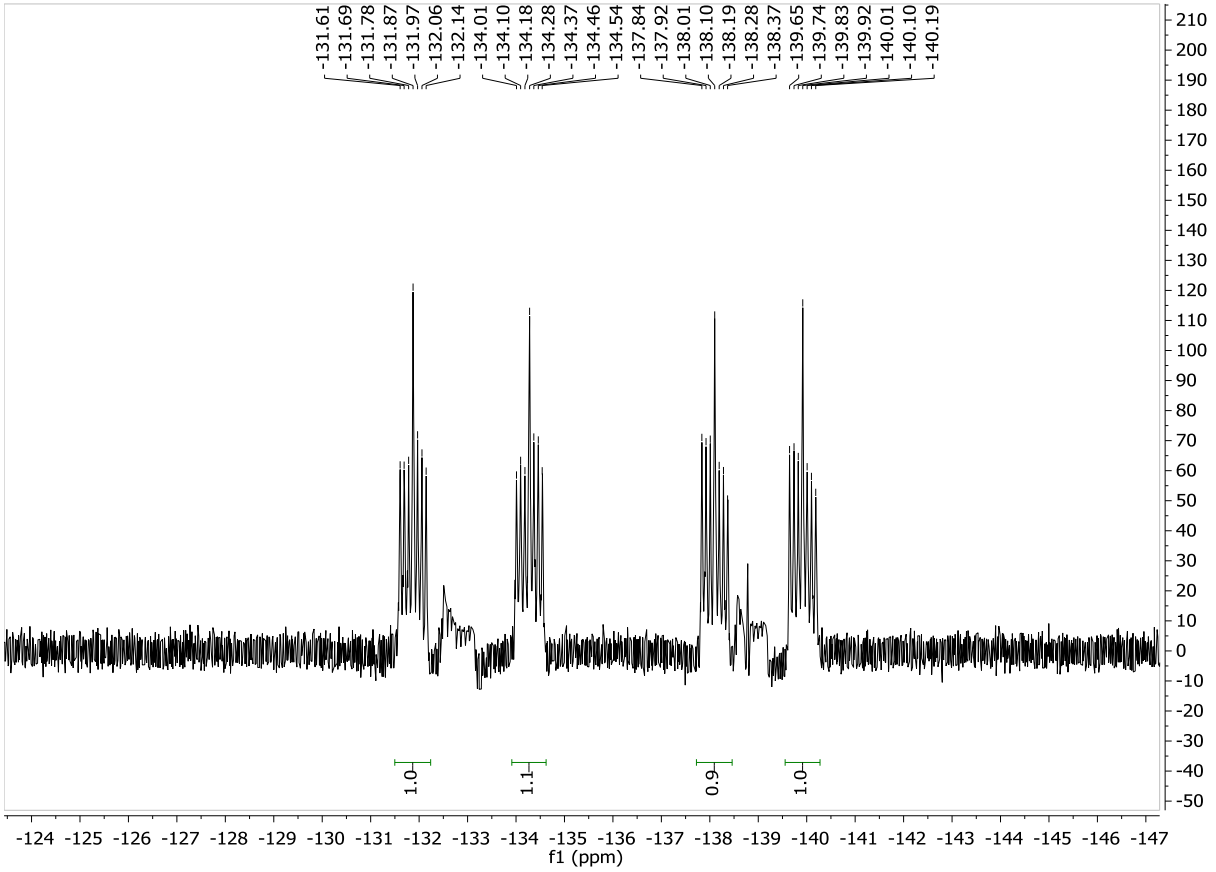
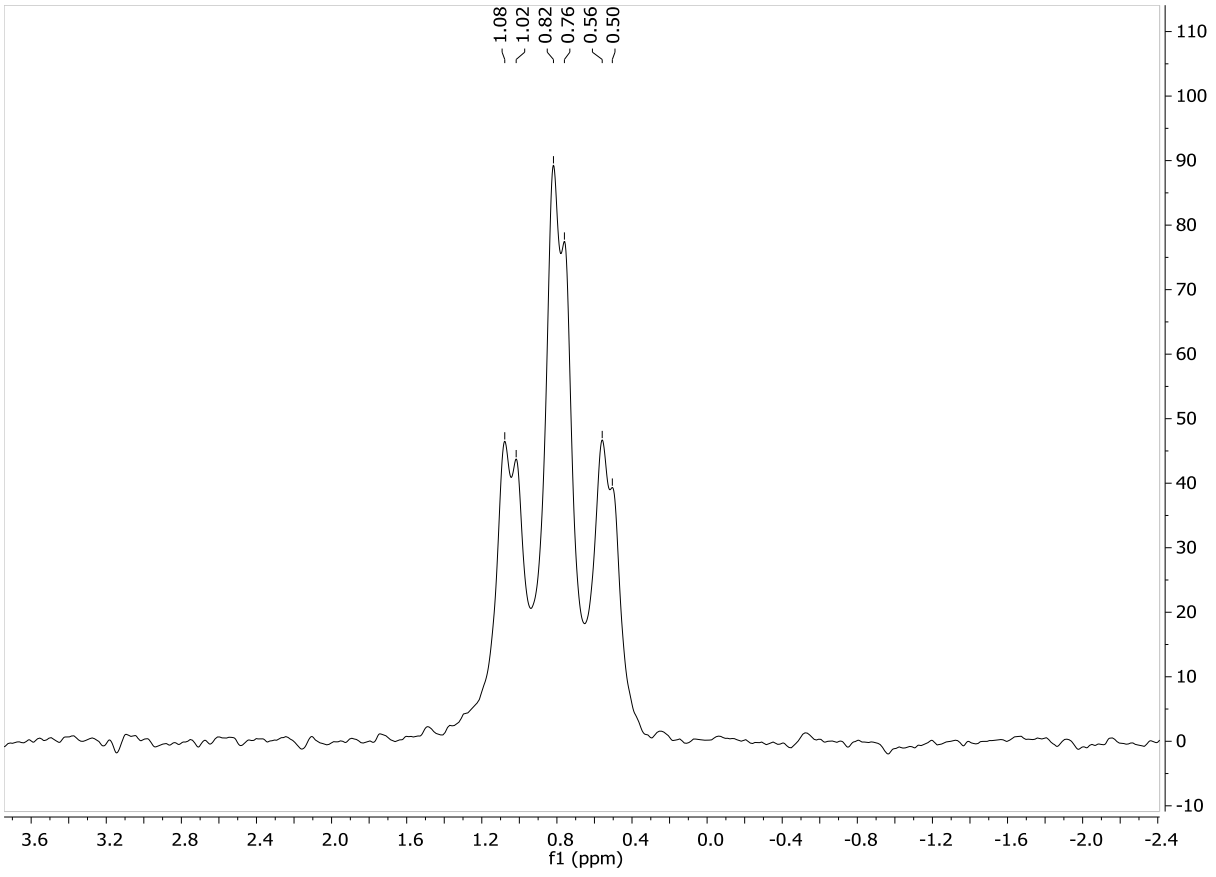


Figure S12: ^{11}B NMR spectrum of BODIPY dyad **5**



3. Fluorescence excitation spectra

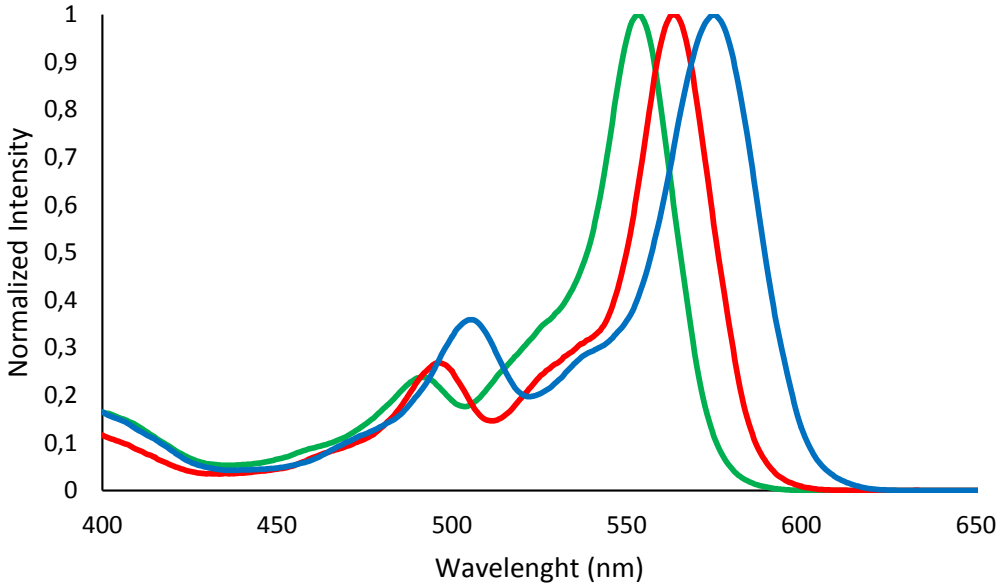


Figure S13. Normalized fluorescence excitation spectra of BODIPY dyads **3** (green), **4** (red), **5** (blue) in THF at 25°C.

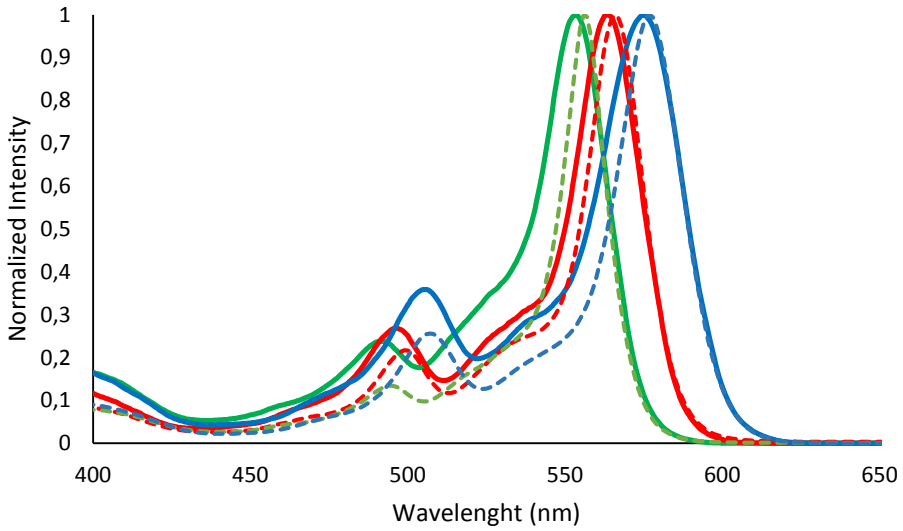


Figure S14. Overlaid spectra of normalized UV−vis spectra (dotted line) and normailzed excited spectra (solid line) of bis-BODIPY **3** (green), **4** (red), **5** (blue) in THF at 25°C.

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2. D.A. May, T.D. Lash, *J. Org. Chem.*, 1992, **57**, 4820.

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