Supporting Information

Controlled Knoevenagel Reactions of Methyl Groups of 1,3,5,7-Tetramethyl BODIPY Dyes for Unique BODIPY Dyes

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Experimental Section

Instrumentation and methods ^{1}H NMR and ^{13}C NMR spectra were taken on a 400 MHz Varian Unity Inova spectrophotometer instrument. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$, chemical shifts (δ) are given in ppm relative to solvent peaks (^{1}H: δ 7.26; ^{13}C: δ 77.3) as internal standard. Absorption spectra were taken on a Perkin Elmer Lambda 35 UV/VIS spectrometer. Fluorescence spectra were recorded on a Jobin Yvon Fluoromax-4 spectrofluorometer. The excitation and emission slit width were set to 1 nm for quantum yield calculations and all samples were scanned with increments of 1 nm. Fluorescence quantum yields of BODIPY dyes were measured in dichloromethane and aqueous solution by using standard 1cm path-length quartz fluorescence cell. And they were calculated by using fluorescein excited at 490 nm in 0.1 N NaOH aqueous solution as the reference quantum efficiency (ϕ_n = 85%).[1-4] Concentrations of BODIPY dyes ranging from 1.0 x 10^{-6} mol/L to 5.0 x 10^{-6} mol/L (in which the quantum yields do not change with varying concentration) were used to measure fluorescence quantum yields, absorption and fluorescent spectra.

All the spectra of BODIPY dye for fluorescence sensing of L-cysteine were measured in 0.01 M PBS buffer pH 7.4 at room temperature. The L-cysteine stock solution (1.0 M in 0.01 M PBS buffer pH 7.4) was prepared freshly for every single measurement. Small portion of L-cysteine stock solution (25 μL) was added to 2.5 mL PBS buffer solution of BODIPY dye $\mathbf{E_b}$ or $\mathbf{G_b}$ (20 μM) and then the solution was measured by UV-vis absorption spectroscopy and fluorescence spectroscopy every 60 minutes until near saturation. The excitation and emission slit width used was 3 nm for L-cysteine fluorescent sensing with excitation wavelength of 470 nm and 620 nm for BODIPY dyes $\mathbf{E_b}$ and $\mathbf{G_b}$, respectively. For measurement of selectivity to various amino acids, BODIPY dye $\mathbf{G_b}$ (10 μM) was treated with 500 equiv. series of amino acids including Alanine (Ala), Arginine (Arg), Asparagine (Asn), Aspartic acid (Asp), Ethionine (Eth), Glycine (Gly), Leucine (Leu), Lysine (Lys), Methionine (Met), Phenylalanine (Phe), Proline (Pro), Serine (Ser), Threonine (Thr) , Tyrosine (Tyr), Valine (Val) in 0.01M PBS buffer solution pH 7.4 for 10 hours at room temperature. And the 3 nm excitation and 4 nm emission slit width were used for all fluorescence spectra collection. L-cysteine and other amino acids were purchased from Sigma-Aldrich and other reagents are analytical grade and were used without further purification.

General remarks for the synthesis

Materials. Unless otherwise indicated, all reagents and solvents were obtained from commercial suppliers (Aldrich, Sigma, Fluka, Acros Organics, Fisher Scientific, Lancaster) and used without further purification. Air- and moisture-sensitive reactions were conducted in oven-dried glassware using a standard Schlenk line or drybox techniques under an inert atmosphere of dry nitrogen.

4,4-Difluoro-8-(4-methoxyphenyl)-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene (2).

The 4-methoxybenzaldehyde (3.26 g, 24 mmol) and 2,4-dimethylpyrrole (5.0 g, 52.6 mmol) were dissolved in dry CH_2Cl_2 (1000 mL). Eight drops of trifluoroacetic acid (TFA) were added to the reaction mixture, and the resulting mixture was stirred in the dark for 12 h under nitrogen atmosphere at room temperature. After the complete consumption of aldehyde, DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone) (6.54 g, 28.8 mmol) was added to the reaction mixture. When the mixture was stirred for 40 min, 25 mL of diisopropylethylamine (DIPEA) and 25 mL of $BF_3{\cdot}OEt_2$ were added to the mixture. After the mixture was further stirred for 40 min, it was concentrated, and then was washed twice with water, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by column chromatography to obtain orange-red crystal solid **2** (2.63 g, 31%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15 (d, J = 8.4 Hz, 2H), 6.99 (d, J = 8.4 Hz, 2H), 5.97 (s, 2H), 3.86 (s, 3H), 2.54 (s, 6H), 1.42 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.4, 155.4, 143.4, 142.1, 132.1, 129.4, 127.2, 121.3, 114.7, 55.5, 14.7.

4,4-Difluoro-8-(4-methoxyphenyl)-1,3,5,7-tetramethyl-2-formyl-4-bora-3a,4a-diaza-s-indacene (3). [5]

A mixture of DMF (6 mL) and $POCl_3$ (6 mL) was stirred in an ice bath for 5 min under argon. After the solution was warmed to room temperature, it was stirred for additional 30 min. To this reaction mixture was added compound **2** (149 mg, 0.42 mmol) in dichloroethane (50 mL), the temperature was raised to 50 ^{o}C, and the mixture was stirred for an additional 2 h. The reaction

mixture was cooled to room temperature and slowly poured into saturated aqueous $NaHCO_3$ (300 mL) under ice-cold conditions. After being warmed to room temperature, the reaction mixture was further stirred for 60 min and washed with water. The organic layers were combined, dried over anhydrous Na_2SO_4, and evaporated in vacuo. The crude product was further purified using column chromatography (silica gel, hexane/EtOAc/CH_2Cl_2, 4/0.5/2, v/v) to give BODIPY **3** (142 mg, 89%) as red crystal solid.^{1}H NMR (400 MHz, $CDCl_3$): δ 9.98 (s, 1H), 7.14 (d, J = 8.4 Hz, 2H), 7.02 (d, J = 8.4 Hz, 2H), 6.12 (s, 1H), 3.86 (s, 3H), 2.79 (s, 3H), 2.58 (s, 3H), 1.69 (s, 3H), 1.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.1, 161.6, 160.8, 156.6, 147.5, 144.0, 143.1, 134.7, 130.4, 129.2, 126.5, 126.3, 124.1, 115.1, 55.6, 15.3, 13.2, 12.0.

4,4-Difluoro-8-(4-methoxyphenyl)-1,3,5,7-tetramethyl-2-iodo-6-formyl-4-bora-3a,4a-diaza-s-indacene (4).

When iodic acid (597 mg, 3.39 mmol) in 5 mL of water was added dropwise to the ethanol (40 mL) and THF (10 mL) solution containing compound **3** (1.08 g, 2.83 mmol) and iodine (1.08 g, 4.24 mmol) in 30 minutes, the mixture was stirred for 5 h. The mixture was concentrated under reduced pressure, dissolved in CH_2Cl_2, and washed twice with water and saturated saline solution. The organic layer was collected, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by column chromatography to yield BODIPY dye **4** as red crystal solid (1.28 g, 89%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.01 (s, 1H), 7.14 (d, J = 6.4 Hz, 2H), 7.05 (d, J = 6.8 Hz, 2H), 3.89 (s, 3H), 2.81 (s, 3H), 2.68 (s, 3H), 1.70 (s, 3H), 1.48 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ185.9, 161.0, 160.6, 158.0, 148.0, 145.5, 144.2, 134.1, 130.6, 129.2, 127.1, 126.2, 115.3, 115.1, 55.6, 17.8, 16.6, 13.5, 12.2. IR (cm^{-1}): 2834, 1667, 1608, 1545, 1514, 1476, 1425, 1399, 1349, 1310, 1288, 1265, 1247, 1209, 1176, 1107, 1084, 1023, 994, 960, 890, 835, 815, 783, 766, 735, 707, 673. HRMS (FAB) calcd for $C_{21}H_{20}BF_2I_2N_2O_2I$ $[M]^+$, 508.0631; found, 508.0627.

4,4-Difluoro-8-(4-methoxyphenyl)-1,5,7-trimethyl-2-iodo-6-formyl-3-[(1E)-3,4,5-trimethoxyphenyl]-4-bora-3a,4a-diaza-s-indacene (A).

4,4-Difluoro-8-(4-methoxyphenyl)-1,5-dimethyl-2-iodo-6-formyl-3,7-bis-[(1E)-3,4,5-trimethoxyphenyl]-4-bora-3a,4a-diaza-s-indacene (B).

4,4-Difluoro-8-(4-methoxyphenyl)-1-methyl-2-iodo-6-formyl-3,5,7-tri-[(1E)-3,4,5-trimethoxyphenyl]-4-bora-3a,4a-diaza-s-indacene (C).

When BODIPY dye **4** (270 mg, 0.53 mmol), and compound **5a** (2.0 g, 10.2 mmol) were dissovled in a mixture of toluene (250 mL), piperidine (0.8 mL) and AcOH (0.6 mL), the mixture was stirred at 108 ^{o}C under reflux for 4 h. Any water formed during the reaction was removed azeotropically by using a Dean-Stark apparatus. After the reaction was quenched with water at room temperature, the mixture was diluted with EtOAc and washed with water and brine, respectively. The organic layer was collected, dried over Na_2SO_4 and concentrated in vacuo. The crude product was purified by silica gel column chromatography by using mobile phase (hexane/EtOAc/CH_2Cl_2, 4/0.5/2 to 3/1/2, v/v) to obtain monostyryl BODIPY dye **A** (36 mg, 10%) as purple crystal solid, distyryl BODIPY dye **B** (168 mg, 37%) as blue powder and tristyryl BODIPY dye **C** (23 mg, 5%) as green powder and recovered compound **5a** (1.5 g). Monostyryl BODIPY dye **A**, ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.02 (s, 1H), 8.10 (d, *J* = 16.8 Hz, 1H), 7.54 (d, *J* = 16.8 Hz, 1H), 7.18 (d, *J* = 6.8 Hz, 2H), 7.06 (d, *J* = 6.8 Hz, 2H), 6.85 (s, 2H), 3.94 (s, 6H), 3.90 (s, 3H), 3.89 (s, 3H), 2.85 (s, 3H), 1.72 (s, 3H), 1.54 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.0, 161.0, 158.4, 153.7, 153.0, 148.5, 145.6, 143.2, 141.3, 140.2, 134.9, 132.2, 131.3, 129.4, 127.4, 126.4, 118.0, 115.3, 105.2, 61.2, 56.5, 55.6, 18.2, 13.7, 12.3. IR (cm^{-1}): 2923, 2844, 1649, 1613, 1580, 1504, 1470, 1413, 1354, 1312, 1269, 1248, 1210, 1182, 1157, 1100, 1047, 1004, 993, 952, 900, 844, 817, 797, 771, 747, 712, 675, 662. HRMS (FAB) calcd for $C_{31}H_{30}BF_2N_2O_5I$ $[M]^+$, 686.1260; found, 686.1259. Distyryl BODIPY dye **B**, ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.85 (s, 1H), 8.12 (d, *J* = 16.8 Hz, 1H), 7.55 (d, *J* = 16.4 Hz, 1H), 7.21 (d, *J* = 7.6 Hz, 2H), 6.99 (d, *J* = 7.6 Hz, 2H), 6.84 (s, 2H), 6.40 (d, *J* = 16.0 Hz, 1 H), 6.24 (s, 2H), 5.75 (d, *J* = 16.0 Hz, 1H), 3.92-3.81 (s × 6 OCH_3, 18H), 3.71 (s, 3H), 2.90 (s, 3H), 1.53 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.3, 160.8, 158.0, 153.7, 153.5, 153.1, 148.3, 145.3, 141.6, 140.2, 139.2, 138.2, 135.1, 132.1, 132.0, 131.0, 130.5, 126.4, 126.3, 118.9, 118.0, 115.1, 105.3, 104.1, 94.6, 85.0, 61.2, 61.1, 56.5, 56.2, 55.4, 18.3, 14.7. IR (cm^{-1}): 2938, 2839, 1731, 1661, 1618, 1579, 1505,

1468, 1418, 1382, 1360, 1321, 1270, 1249, 1162, 1151, 1128, 1103, 1073, 1005, 956, 856, 839, 819, 798, 763, 753, 714, 699, 685. HRMS (FAB) calcd for $C_{41}H_{40}BF_2N_2O_8I$ $[M]^+$, 864.1890; found, 864.1883. Tristyryl BODIPY dye **C**, ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.85 (s, 1H), 8.15 (d, J = 16.8 Hz, 1H), 8.11 (d, *J* = 16.4 Hz, 1H), 7.73 (d, J = 16.0 Hz, 1H), 7.62 (d, *J* = 16.4 Hz, 1H), 7.25 (d, *J* = 7.2 Hz, 1H), 7.01 (d, *J* = 7.6 Hz, 1H), 6.90 (s, 2H), 6.86 (s, 2H), 6.49 (d, *J* = 16.0 Hz, 1 H), 6.28 (s, 2H), 5.83 (d, *J* = 16.0 Hz, 1H), 3.96-3.84 (s × 9 OCH_3, 27H), 3.71 (s, 3H), 1.57 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.9, 186.8, 160.8, 153.8, 153.7, 153.5, 153.1, 148.1, 147.5, 147.0, 142.8, 141.6, 140.4, 140.0, 139.2, 139.1, 135.6, 132.7, 132.2, 132.0, 130.7, 128.6, 126.9, 126.5, 119.0, 118.1, 117.1, 115.2, 106.9, 105.5, 105.4, 104.2, 61.3, 61.2, 61.1, 56.7, 56.5, 56.4, 56.2, 55.4, 18.3. IR (cm^{-1}): 2937, 2837, 1671, 1618, 1579, 1505, 1463, 1418, 1360, 1327, 1246, 1175, 1151, 1126, 1103, 1006, 959, 821, 762, 704. HRMS (FAB) calcd for $C_{51}H_{50}BF_2N_2O_{11}I$ $[M]^+$, 1042.2520; found, 1042.2523.

4,4-Difluoro-8-(4-methoxyphenyl)-1,3,5,7-tetramethyl-2,6-diformyl-4-bora-3a,4a-diaza-s-indacene (6).

A mixture of DMF (6 mL) and $POCl_3$ (6 mL) was stirred in an ice bath for 5 min under argon. After the solution was warmed to room temperature, it was stirred for additional 30 min. To this reaction mixture was added compound **3** (160 mg, 0.42 mmol) in dichloroethane (50 mL), the temperature was raised to 60 ^{o}C, and the mixture was stirred for an additional 5 h. The reaction mixture was cooled to room temperature and slowly poured into saturated aqueous $NaHCO_3$ (300 mL) under ice-cold conditions. After being warmed to room temperature, the reaction mixture was further stirred for 60 min and washed with water. The organic layers were combined, dried over anhydrous Na_2SO_4, and evaporated in vacuo. The crude product was further purified using column chromatography (silica gel, hexane/EtOAc/CH_2Cl_2, 4/0.5/2, v/v) to give BODIPY **6** (141 mg, 82%) as red crystal solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.01(s, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 7.06 (d, *J* = 8.4 Hz, 2H), 3.87 (s, 3H), 2.82 (s, 6H), 1.73 (s, 6H). ^{13}C NMR (100

MHz, $CDCl_3$): δ 185.9, 161.2, 160.7, 148.6, 147.8, 132.5, 190.0, 128.2, 125.6, 115.5, 55.7, 13.9, 12.6. IR (cm^{-1}): 2925, 2840, 1670, 1608, 1569, 1514, 1471, 1443, 1406, 1380, 1307, 1292, 1250, 1175, 1082, 1026, 1009, 964, 949, 900, 851, 838, 820, 803, 787, 768, 733, 720, 705. HRMS (FAB) calcd for $C_{22}H_{22}N_2F_2BO_3$ $[M+H]^+$, 411.1692; found, 411.1692.

4,4-Difluoro-8-(4-methoxyphenyl)-3,5,7-trimethyl-2,6-diformyl-1-[(1E)-3,4,5-trimethoxyphenyl]-4-bora-3a,4a-diaza-s-indacene (D_a).

4,4-Difluoro-8-(4-methoxyphenyl)-3,5-dimethyl-2,6-diformyl-1,7-bis-[(1E)-3,4,5-trimethoxyphenyl]-4-bora-3a,4a-diaza-s-indacene (E_a).

4,4-Difluoro-8-(4-methoxyphenyl)-5-methyl-2,6-diformyl-1,3,7-tri-[(1E)-3,4,5-trimethoxyphenyl]-4-bora-3a,4a-diaza-s-indacene (F_a).

4,4-Difluoro-8-(4-methoxyphenyl)-2,6-diformyl-1,3,5,7-tetra-[(1E)-3,4,5-trimethoxyphenyl]-4-bora-3a,4a-diaza-s-indacene (G_a).

When BODIPY dye **6** (200 mg, 0.5 mmol), and compound **5a** (2.0 g, 10.2 mmol) were dissovled in a mixture of toluene (350 mL), piperidine (1.0 mL) and AcOH (0.8 mL), the mixture was stirred at 112 ^oC for 3 h. Any water formed during the reaction was removed azeotropically by using a Dean-Stark apparatus. After the reaction was quenched with water at room temperature, the mixture was diluted with EtOAc and washed with water and brine, respectively. The organic layer was collected, dried over Na_2SO_4 and concentrated in vacuo. The crude product was

purified by silica gel column chromatography by using mobile phase (hexane/EtOAc/CH_2Cl_2, 4/0.5/2 to 3/1/2, v/v) to obtain monostyryl BODIPY dye **D_a** (40 mg, 14%) as red-purple powder, distyryl BODIPY dye **E_a** (105 mg, 29%) as blue-purple powder, tristyryl BODIPY dye **F_a** (48 mg, 11%) as blue powder and tetrastyryl BODIPY dye **G_a** (16 mg, 3%) as green powder and recovered compound **5a** (1.6 g). Monostyryl BODIPY dye **D_a**, ^{1}H NMR (400 MHz, $CDCl_3$): δ10.03 (s, 1H), 9.85 (s, 1H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.01 (d, *J* = 8.4 Hz, 2H), 6.44 (d, *J* = 16.0 Hz, 1H), 6.25 (s, 2H), 5.75 (d, *J* = 16.0 Hz, 1H), 3.83 (s, 3H), 3.81 (s, 6H), 3.72 (s, 3H), 2.90 (s, 3H), 2.85 (s, 3H), 1.77 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.1, 185.8, 161.0, 160.9, 160.6, 153.5, 148.1, 146.3, 139.5, 139.4, 132.7, 132.1, 131.6, 130.1, 128.3, 127.1, 125.5, 118.4, 115.3, 104.3, 61.2, 56.2, 55.5, 14.8, 14.0, 12.6. IR (cm^{-1}): 2936, 2839, 1670, 1609, 1579, 1507, 1419, 1380, 1317, 1292, 1249, 1165, 1150, 1127, 1085, 1019, 915, 837, 798, 728, 712, 692. HRMS (FAB) calcd for $C_{32}H_{32}BF_2N_2O_6$ $[M+H]^+$, 589.2321; found, 589.2325. Distyryl BODIPY dye **E_a**, ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.86 (s, 2H), 7.28 (d, *J* = 8.8 Hz, 2H), 6.97 (d, *J* = 8.4 Hz, 2H), 6.50 (d, *J* = 16.0 Hz, 2H), 6.24 (s, 4H), 5.80 (d, *J* = 16.0 Hz, 2H), 3.81 (s, 6H), 3.79 (s, 12H), 3.72 (s, 3H), 2.90 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.0, 160.8, 153.5, 147.6, 144.7, 139.6, 139.5, 132.3, 131.6, 131.2, 127.0, 125.6, 118.4, 115.2, 104.3, 61.2, 56.2, 55.2, 14.8. IR (cm^{-1}): 2939, 2838, 1669, 1610, 1578, 1502, 1465, 1427, 1378, 1321, 1272, 1246, 1142, 1128, 1025, 1005, 963, 925, 866, 837, 729, 706, 693. HRMS (FAB) calcd for $C_{42}H_{42}BF_2N_2O_9$ $[M+H]^+$, 767.2951; found, 767.2946. Tristyryl BODIPY dye **F_a**, ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.91 (s, 1H), 9.87 (s, 1H), 8.20 (d, *J* = 16.0 Hz, 1H), 7.76 (d, *J* = 16.0 Hz, 1H), 7.31 (d, *J* = 8.4 Hz, 2H), 6.97 (d, *J* = 8.4 Hz, 2H), 6.93 (s, 2H), 6.54 (d, *J* = 16.0 Hz, 1H), 6.50 (d, *J* = 15.6 Hz, 1H), 6.28 (s, 2H), 6.25 (s, 2H), 5.87 (d, *J* =15.6 Hz, 1H), 5.84 (d, *J* = 16.0 Hz, 1H), 3.95-3.81 (s × 9 OCH_3, 27H), 3.56 (s, 3H), 2.98 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.1, 186.6, 160.8, 155.9, 153.7, 153.6, 153.5, 149.4, 147.2, 144.6, 143.2, 140.4, 140.2, 139.6, 139.5, 133.4, 132.3, 131.6, 131.4, 127.8, 125.8, 118.5, 118.4, 116.7, 115.2, 105.7, 104.4, 104.3, 61.3, 61.2, 56.5, 56.2, 55.2, 15.0. IR (cm^{-1}): 2928, 2840, 1672, 1608, 1579, 1504, 1463, 1417, 1377, 1328, 1245, 1176, 1128, 1006, 836, 764, 709. HRMS (FAB) calcd for $C_{52}H_{51}BF_2N_2O_{12}$ $[M]^+$, 944.3503; found, 944.3499. Tetrastyryl BODIPY dye **G_a**, ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.88 (s, 2H), 8.20 (d, *J* = 16.0 Hz, 2H), 7.79 (d, *J* = 16.4 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 6.93 (s, 4H), 6.57 (d, *J* = 16.0 Hz, 2H), 6.28 (s, 4H), 5.90 (d, *J* = 16.0 Hz, 2H), 3.93-3.73 (s × 12 OCH_3, 36H), 3.55 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.6, 160.8, 155.7, 153.7, 153.5, 149.0, 144.5,

141.8, 140.5, 140.3, 139.6, 133.6, 132.4, 131.6, 131.5, 127.8, 126.0, 118.7, 116.8, 115.2, 105.8, 104.4, 61.3, 61.2, 56.5, 56.2, 55.2. IR (cm^{-1}): 2918, 2848, 1730, 1670, 1619, 1579, 1501, 1463, 1419, 1381, 1325, 1267, 1244, 1127, 1028, 1003, 964, 822, 735, 701. HRMS (FAB) calcd for $C_{62}H_{61}BF_2N_2O_{15}$ $[M]^+$, 1122.4133; found, 1122.4128.

4,4-Difluoro-8-(4-methoxyphenyl)-3,5-dimethyl-2,6-diformyl-1,7-di-[(1E)-3,4-bis(3-{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}-2-{2-[2-(2-methoxyethoxy)ethoxy]ethoxymethyl}-propoxy)phenyl]-4-bora-3a,4a-diaza-s-indacene (E_b).

When BODIPY dye **6** (100 mg, 0.244 mmol), and compound **5b** (876 mg, 0.976 mmol) were dissovled in a mixture of toluene (100 mL), piperidine (0.6 mL) and AcOH (0.5 mL), the mixture was stirred at 110 ^oC for 2 h. Any water formed during the reaction was removed azeotropically by using a Dean-Stark apparatus. After the reaction was quenched with water at room temperature, the mixture was diluted with EtOAc and then washed with water and brine, respectively. The organic layer was collected, dried over Na_2SO_4 and concentrated in vacuo. The crude product was purified by silica gel column chromatography by using mobile phase (MeOH/hexane/EtOAc/CH_2Cl_2, 0.5/5/1/3, v/v) to obtain distyryl BODIPY dye **E_b** (190 mg, 36%) as purple oil. ^1H NMR (400 MHz, $CDCl_3$): δ 9.83 (s, 2H), 7.23 (d, *J* = 7.6 Hz, 7.00 (d, *J* = 8.4 Hz, 2H), 6.69 (d, *J* = 8.0 Hz, 2H), 6.50-6.45 (m, 6H) 5.75 (d, *J* = 16.0 Hz, 2H), 3.98 (d, *J* = 5.6 Hz, 4H), 3.90 (d, *J* = 5.6 Hz, 4H), 3.68 (s, 3H), 3.58-3.44 (m, 112H), 3.31-3.28 (s× 8 OCH_3, 24H), 2.88 (s, 6H), 2.38-2.35 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.1, 161.1, 160.5, 155.1, 150.5, 149.2, 148.0, 144.6, 139.6, 132.2, 130.9, 130.1, 129.2, 126.8, 125.6, 120.3, 117.1, 115.5, 113.1, 112.1, 77.5, 72.1, 70.8, 70.7, 70.7, 70.6, 69.5, 69.4, 69.2, 67.1, 59.2, 55.8, 55.7,

40.2, 40.1, 14.8. HRMS (MAIDL) calcd for $C_{108}H_{173}BF_2N_2O_{39}Na$ $[M+Na]^+$, 2194.1572; found, 2194.1599.

4,4-Difluoro-8-(4-methoxyphenyl) -2,6-diformyl-1,3,5,7-tetra-[(1E)-3,4-bis(3-{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}-2-{2-[2-(2-methoxyethoxy)ethoxy]ethoxymethyl}-propoxy)phenyl]-4-bora-3a,4a-diaza-s-indacene (G_b).

When BODIPY dye **6** (100 mg, 0.244 mmol), and compound $\mathbf{5_b}$ (2.2 g, 2.44 mmol) were dissovled in a mixture of toluene (100 mL), piperidine (0.6 mL) and AcOH (0.5 mL), the mixture was stirred at 116 ^oC for 4 h. Any water formed during the reaction was removed azeotropically by using a Dean-Stark apparatus. The mixture was directly concentrated in vacuo, diluted with EtOAc and then washed with water and brine, respectively. The organic layer was collected, dried over Na_2SO_4 and concentrated in vacuo. The crude product was purified by silica gel column chromatography by using mobile phase (MeOH/hexane/EtOAc/CH_2Cl_2, 1/5/1/3, v/v) to obtain tetrastyryl BODIPY dye $\mathbf{G_b}$ (403 mg, 42%) as dark green oil. ^1H NMR (400 MHz, $CDCl_3$): δ 9.79 (s, 2H), 8.10 (d, *J* = 16.0 Hz, 2H), 7.68 (d, *J* = 16.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 5.6 Hz, 2H), 7.07 (s, 2H), 6.96-6.90 (m, 4H), 6.68 (d, *J* = 8.4 Hz, 2H), 6.57-6.50 (m, 6H), 5.82 (d, *J* = 16.0 Hz, 2H). 4.05 (br, 8H), 3.98 (d, *J* = 5.2 Hz, 4H), 3.90 (d, *J* = 5.2 Hz, 4H), 3.65-3.43 (m, 224H), 3.29-3.27 (s× 16 OCH_3, 48H), 2.41-2.33 (m, 8H).^{13}C NMR (100 MHz, $CDCl_3$): δ 186.5, 161.0, 155.9, 151.1, 150.4, 149.2, 149.1, 148.9, 144.4, 140.1, 133.7,

131.4, 130.0, 129.4, 127.4, 126.3, 121.2, 120.6, 117.6, 115.5, 114.5, 113.5, 113.0, 112.1, 77.5, 72.1, 72.0, 70.8, 70.8, 70.7, 70.6, 70.6, 69.5, 69.4, 67.3, 67.1, 59.1, 55.7, 40.3, 40.2. HRMS (MAIDL) calcd for $C_{194}H_{325}BF_2N_2O_{75}Na$ $[M+Na]^+$, 3955.1633; found, 3955.1687.

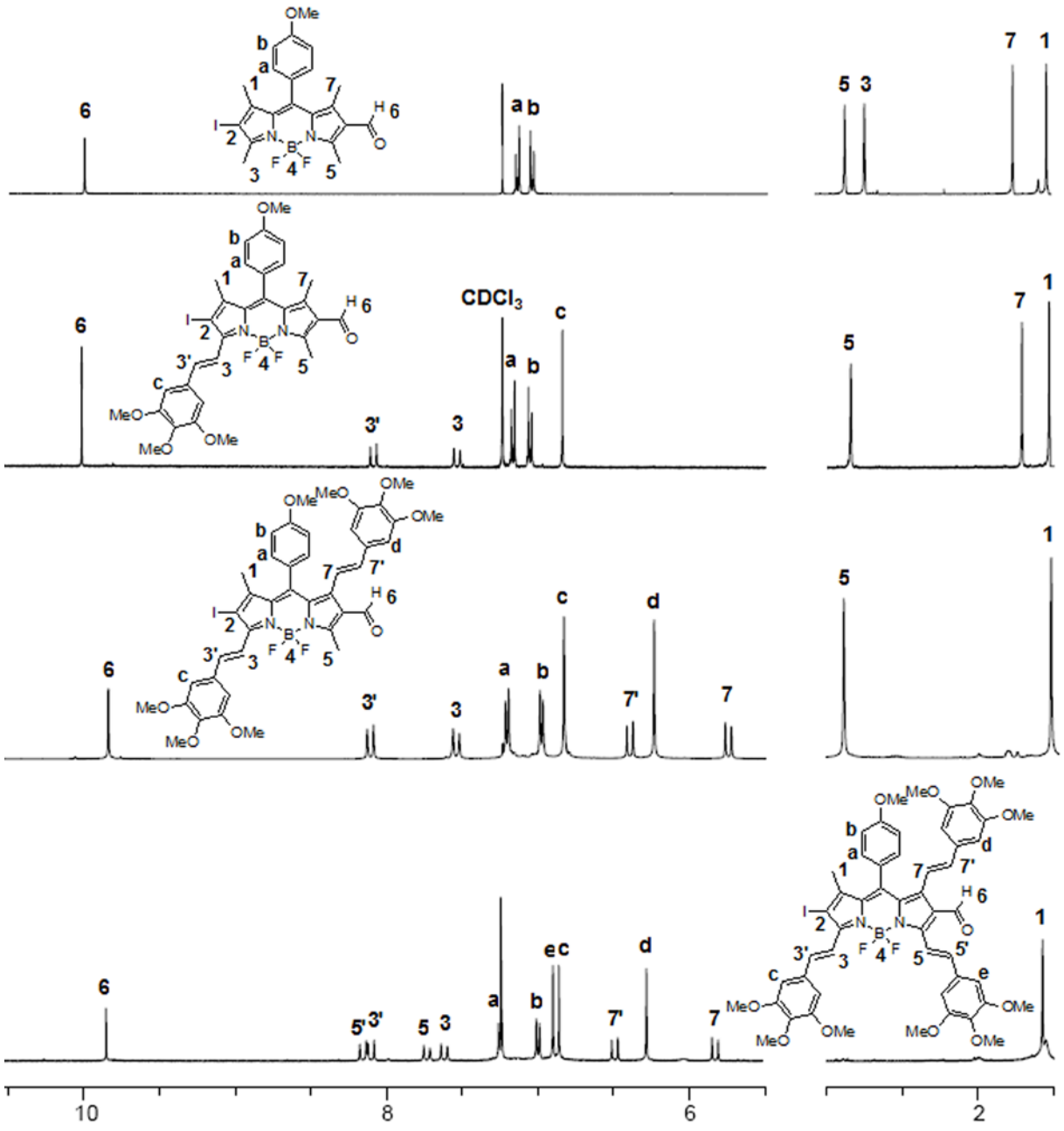

Figure S1. Comparison of ^{1}H spectra of BODIPY dye **4**, **A**, **B** and **C**

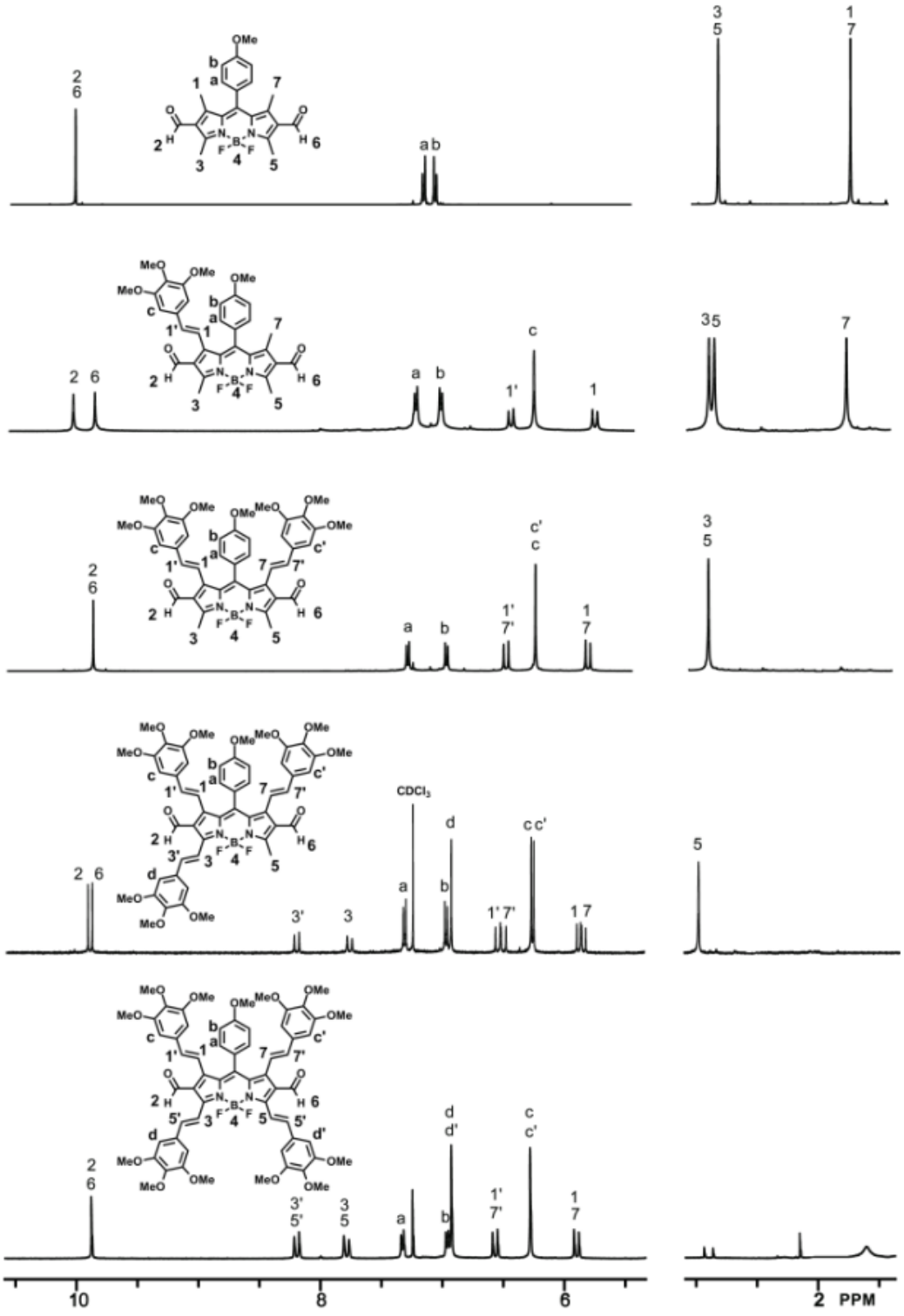

Figure S2. ^{1}H NMR spectra ($CDCl_3$, 400 MHz) of BODIPY dyes (**6**, $\mathbf{D_a}$, $\mathbf{E_a}$, $\mathbf{F_a}$ and $\mathbf{G_a}$ from the top to the bottom)

Formation of the first vinyl bond at the 1-position in BODIPY dye (**D_a**) results in the disappearance of the methyl proton peak at 1.73 ppm for this 1-position, and, shifts the aldehyde proton peak at the 2-position to higher field by 0.16 ppm. The methyl proton resonance for the 3-position is shifted to lower field by 0.08 ppm, and the proton resonances corresponding to the a,b-positions of the meso phenyl ring separates from 0.09 ppm to 0.21 ppm. Formation of the second vinyl bond at the 7-position in BODIPY dye (**E_a**) causes the disappearance of the corresponding methyl proton resonance at 1.73 ppm, and shifts the aldehyde proton resonance at the 6-position to higher field resulting in an overlap with that at the 2-position. Additionally, the methyl proton resonance at the 5-position shifts to lower field and overlaps with that from the 3-position. Formation of the third vinyl bond at the 3-position in BODIPY dye (**F_a**) results in the disappearance of the corresponding methyl proton resonance at 2.90 ppm, and shifts the proton resonances at the 2- and 5-positions to lower fields by 0.05 and 0.08 ppm respectively. Formation of the fourth vinyl bond at 5-position in BODIPY dye (**F_a**) causes the disappearance of the corresponding methyl proton resonance at 2.90 ppm, and results in an overlap in the aldehyde proton resonances at the 2,6-positions (Figure 2).

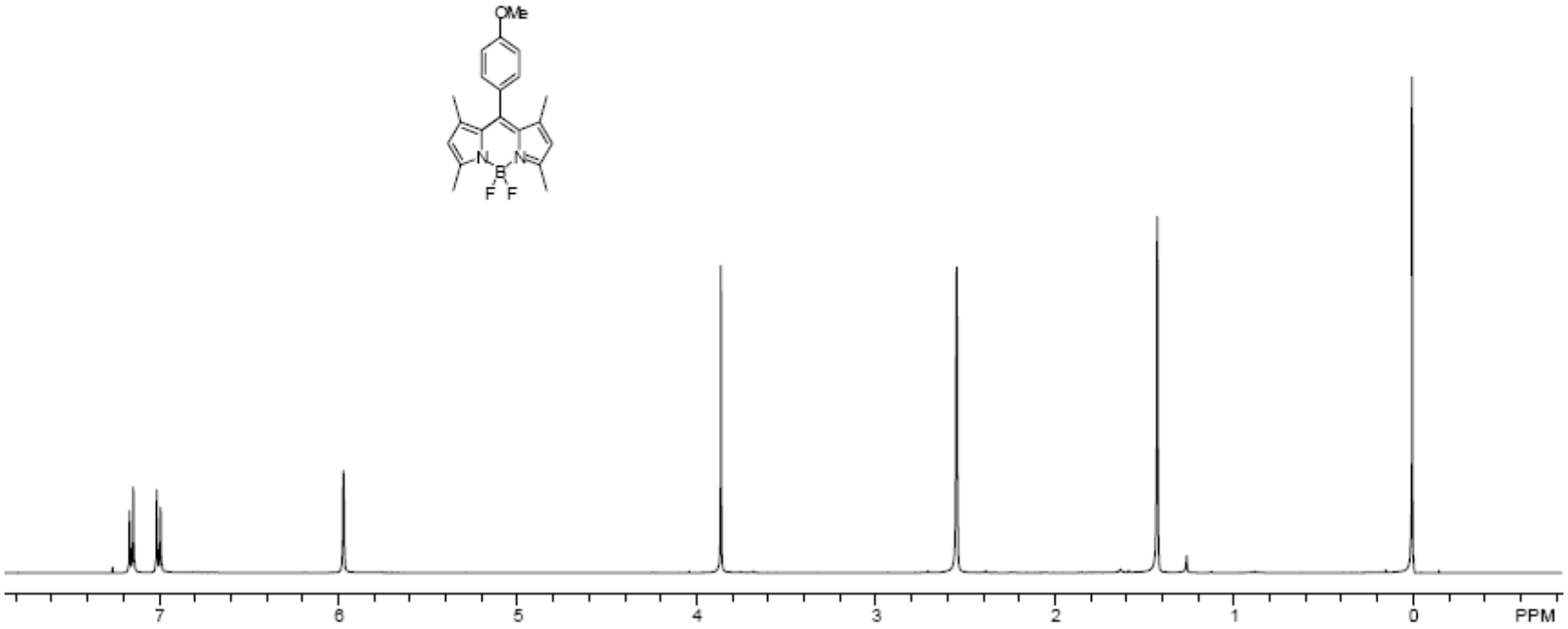

Figure S3. ^{1}H NMR spectrum of BODIPY dye **2** in $CDCl_3$ solution.

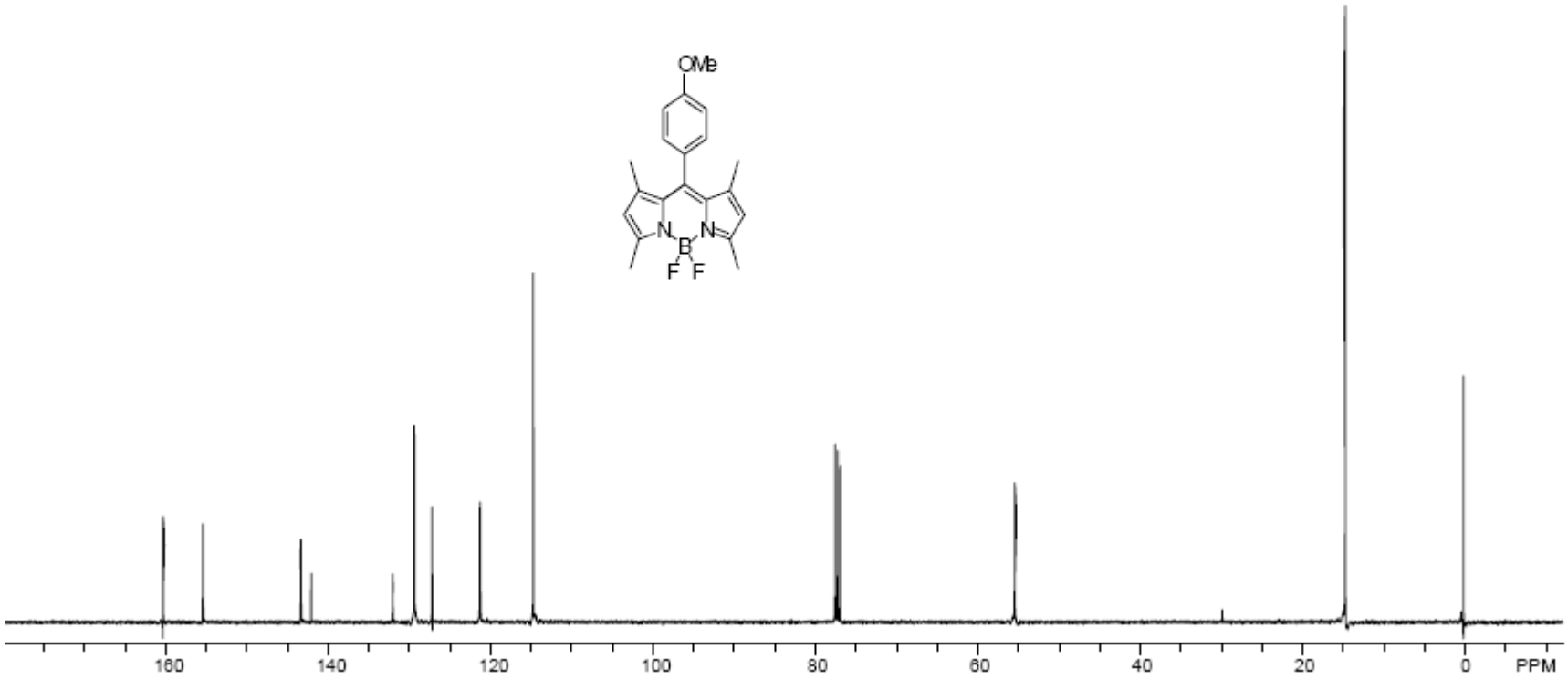

Figure S4. ^{13}C NMR spectrum of BODIPY dye **2** in $CDCl_3$ solution.

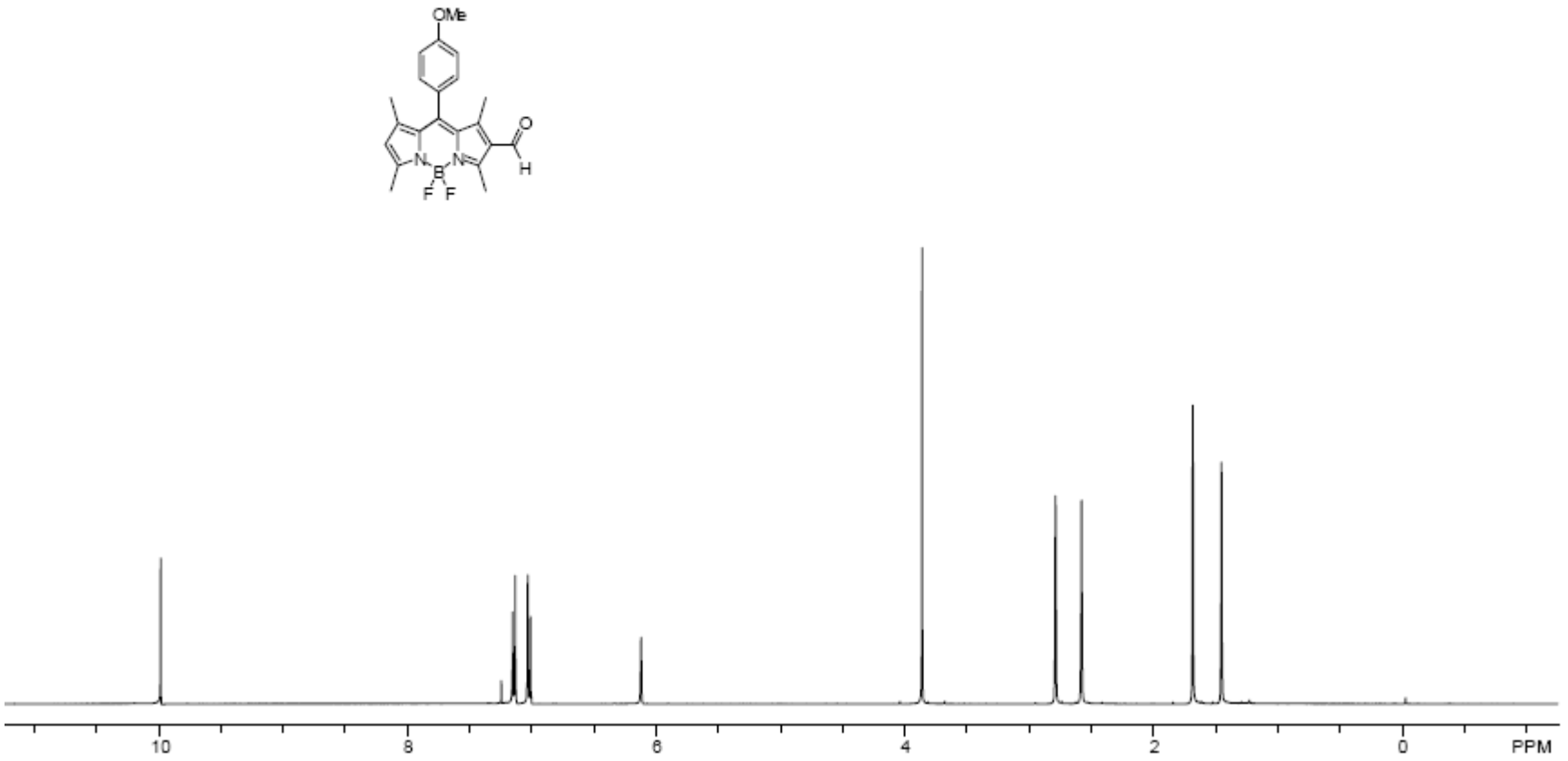

Figure S5. ^{1}H NMR spectrum of BODIPY dye **3** in $CDCl_3$ solution.

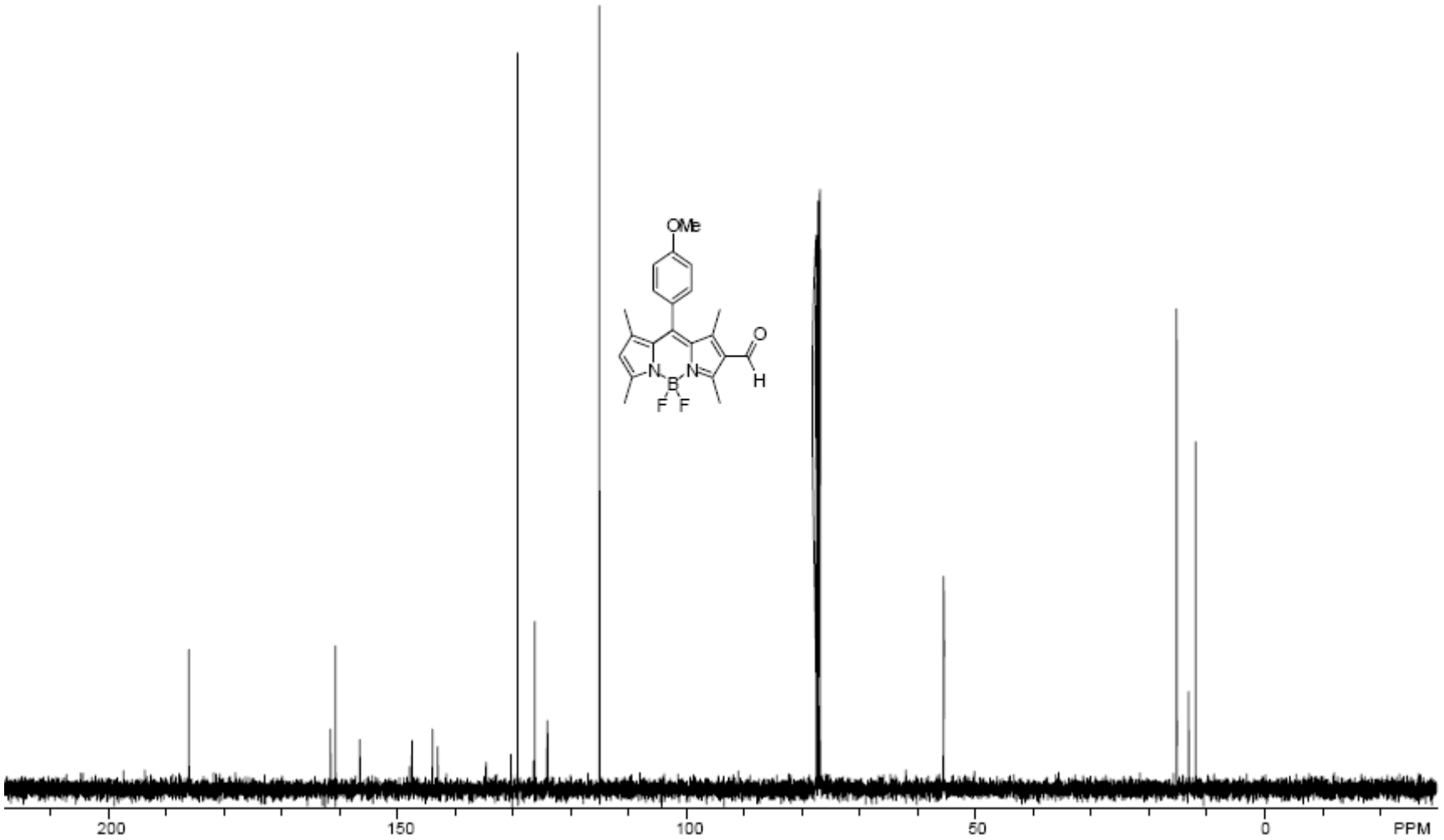

Figure S6. ^{13}C NMR spectrum of BODIPY dye **3** in $CDCl_3$ solution.

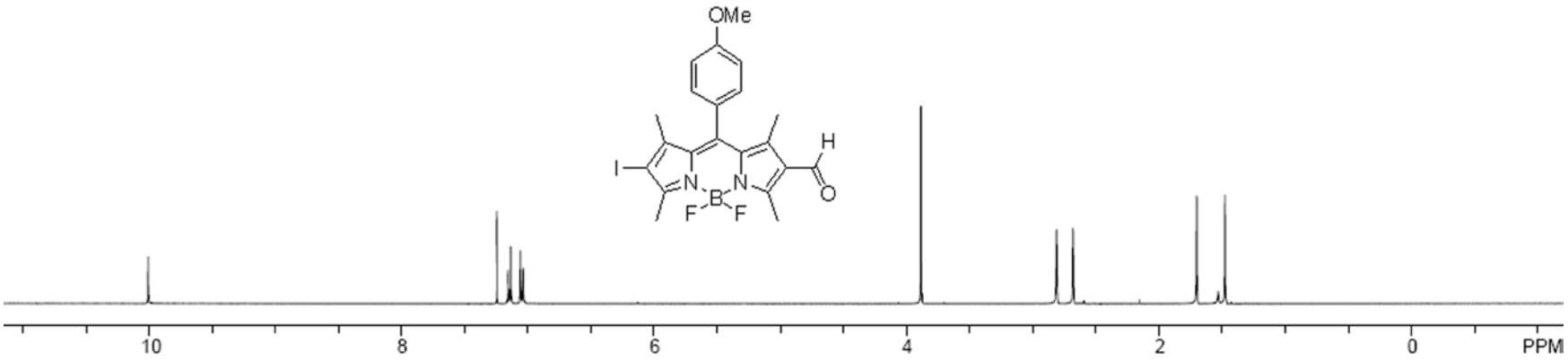

Figure S7. ^{1}H NMR spectrum of BODIPY dye **4** in $CDCl_3$ solution.

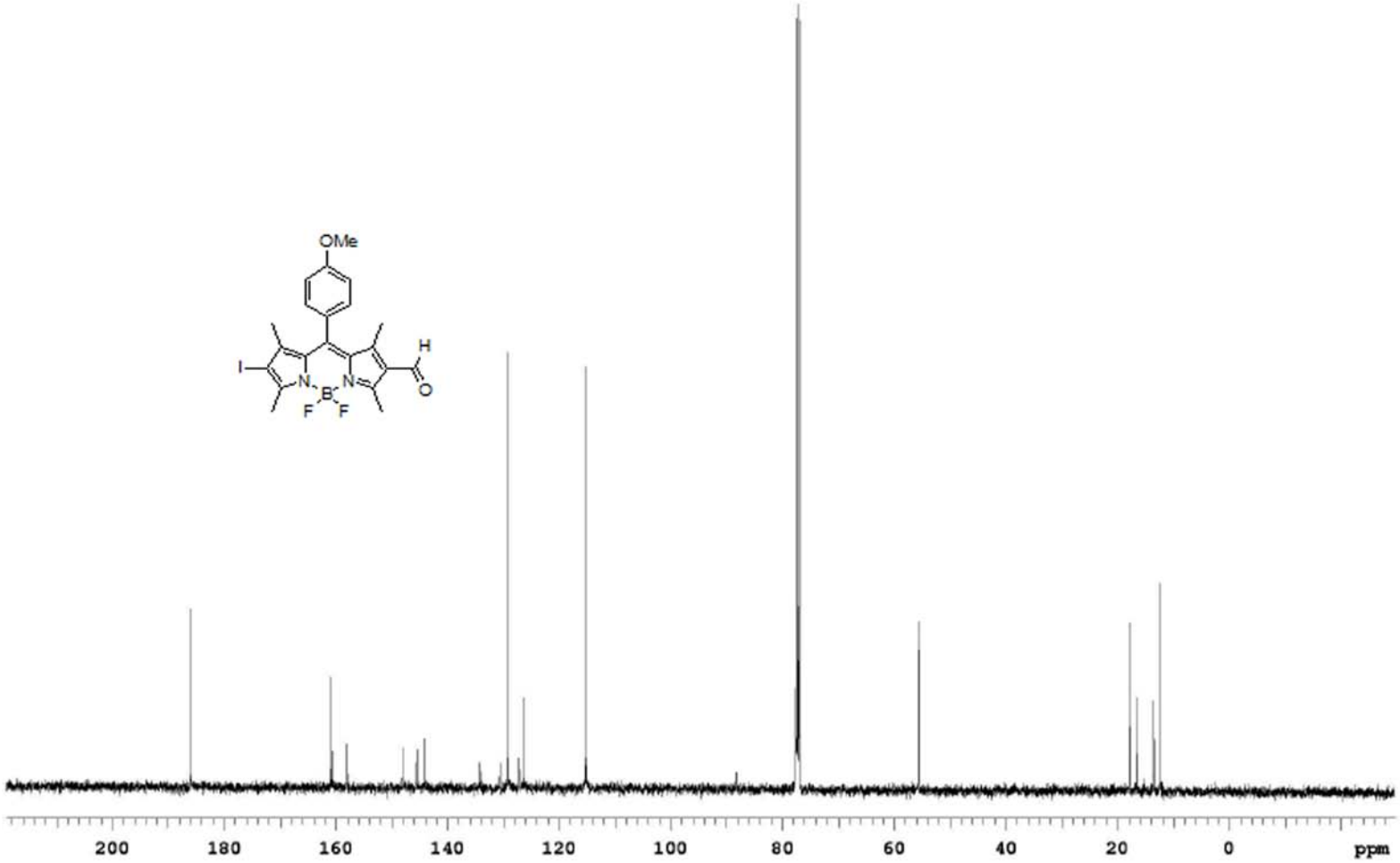

Figure S8. ^{13}C NMR spectrum of BODIPY dye **4** in $CDCl_3$ solution.

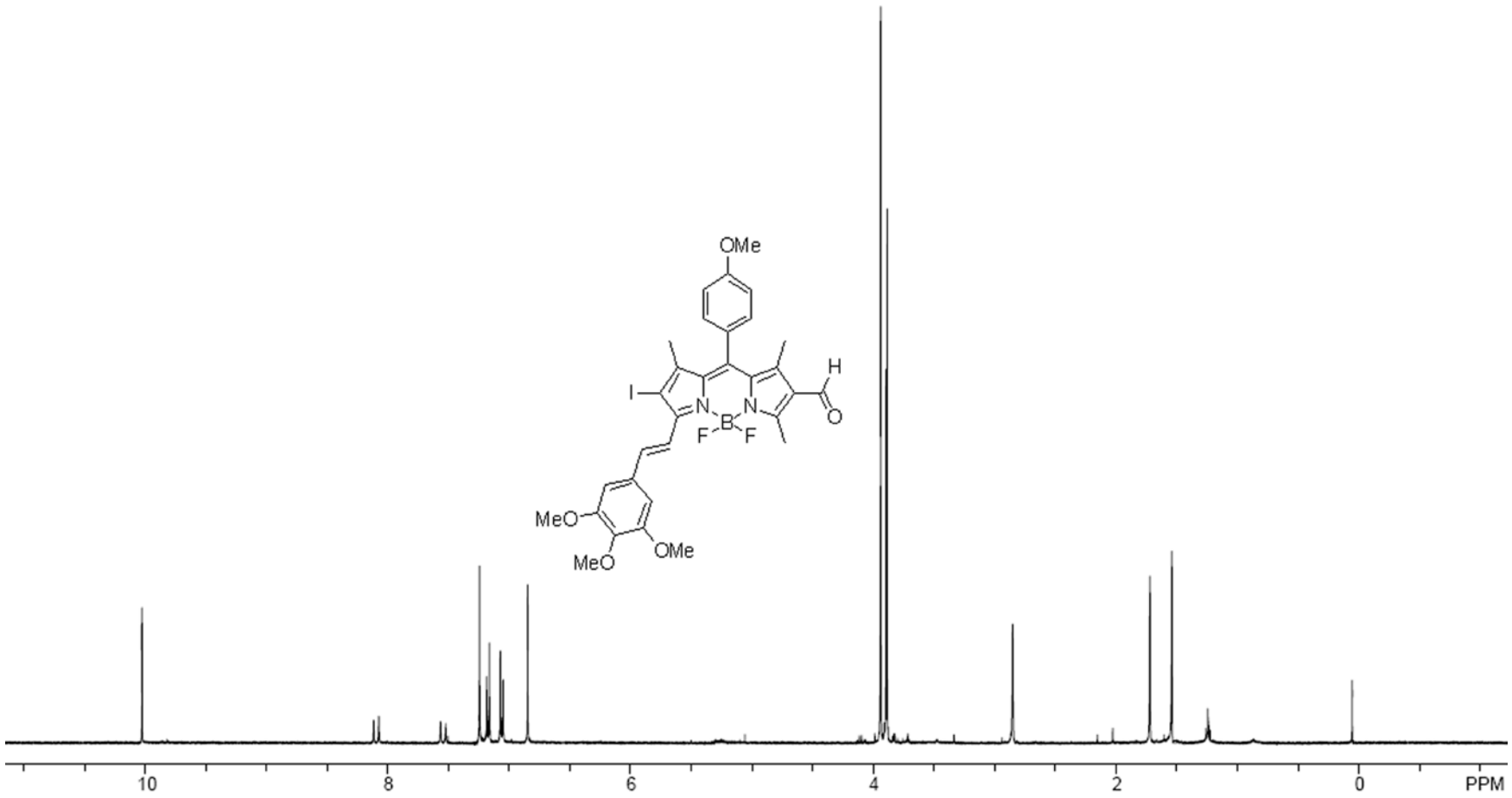

Figure S9. ^{1}H NMR spectrum of BODIPY dye **A** in $CDCl_3$ solution.

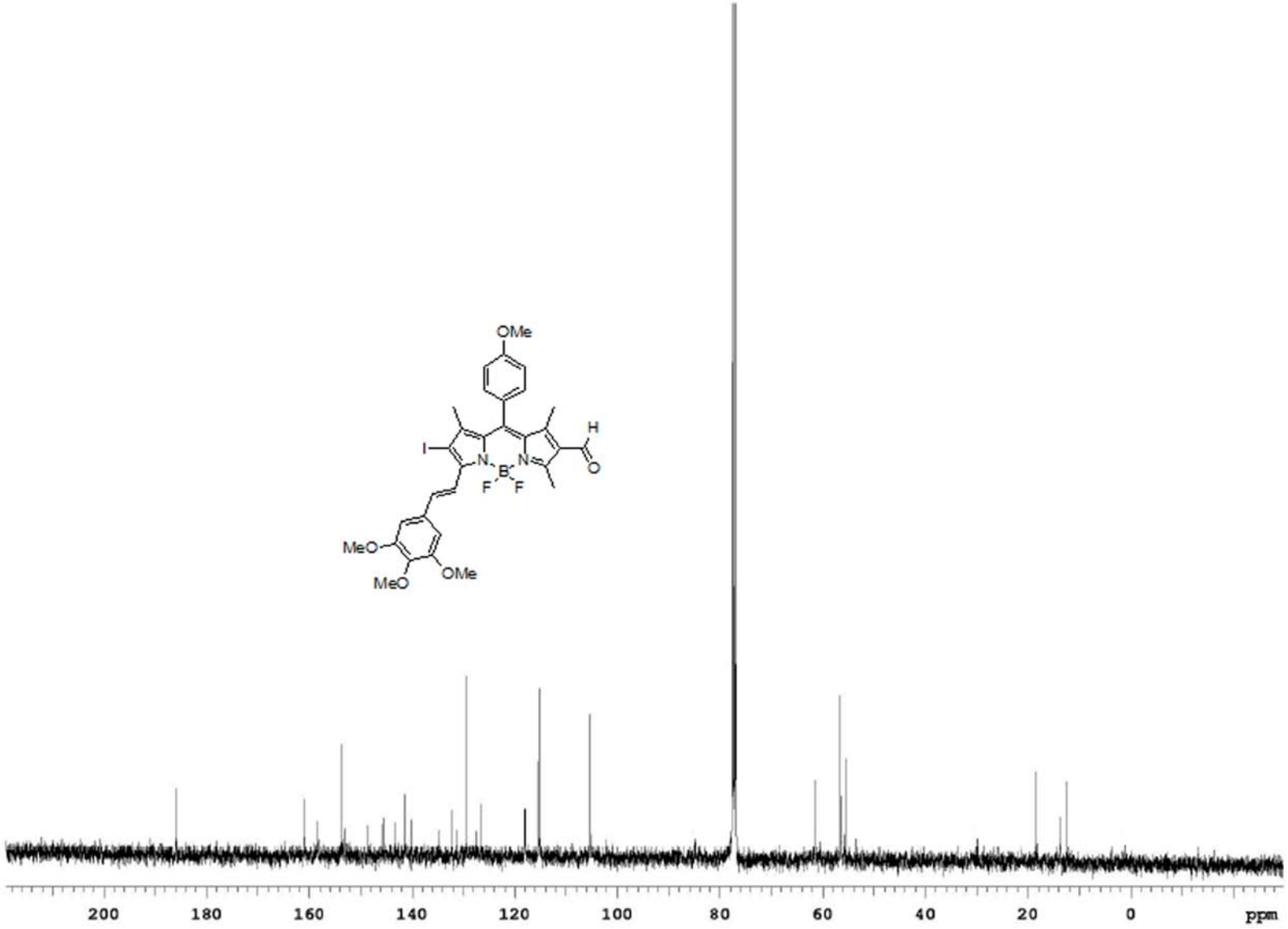

Figure S10. ^{13}C NMR spectrum of BODIPY dye **A** in $CDCl_3$ solution.

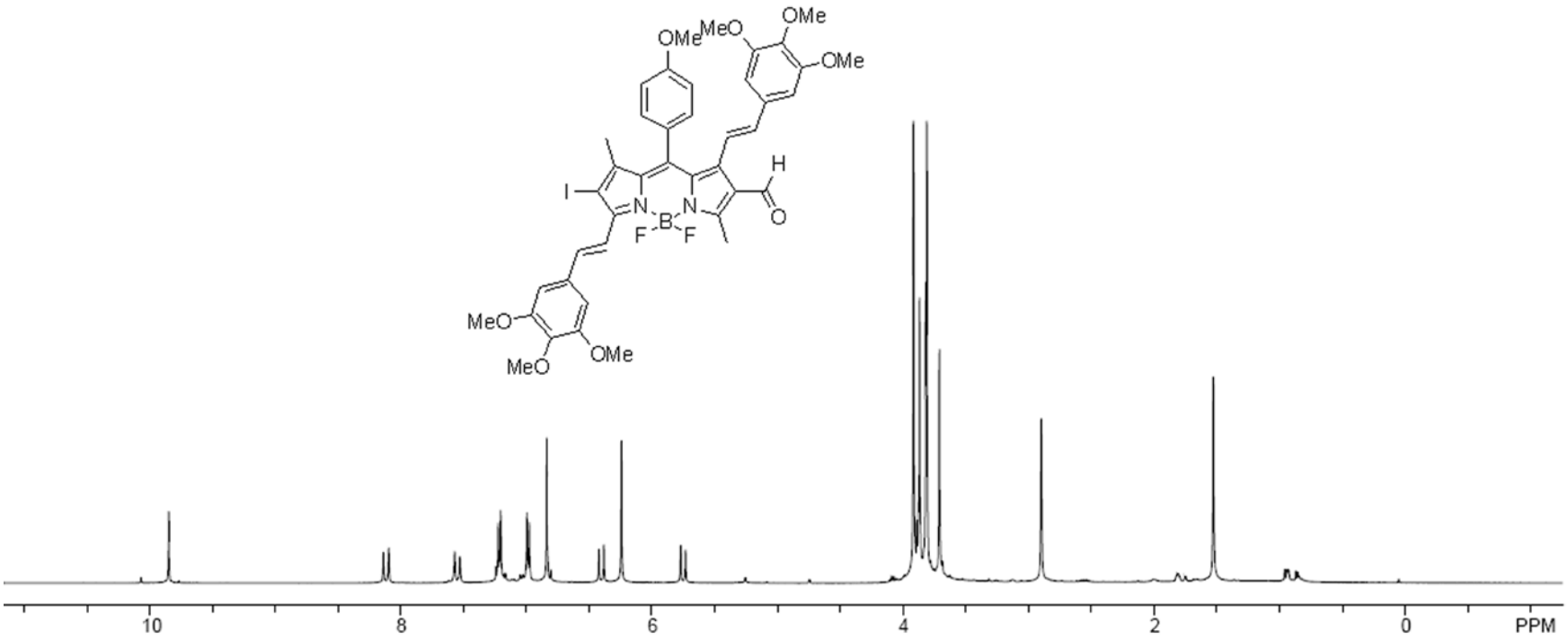

Figure S11. ^{1}H NMR spectrum of BODIPY dye **B** in $CDCl_3$ solution.

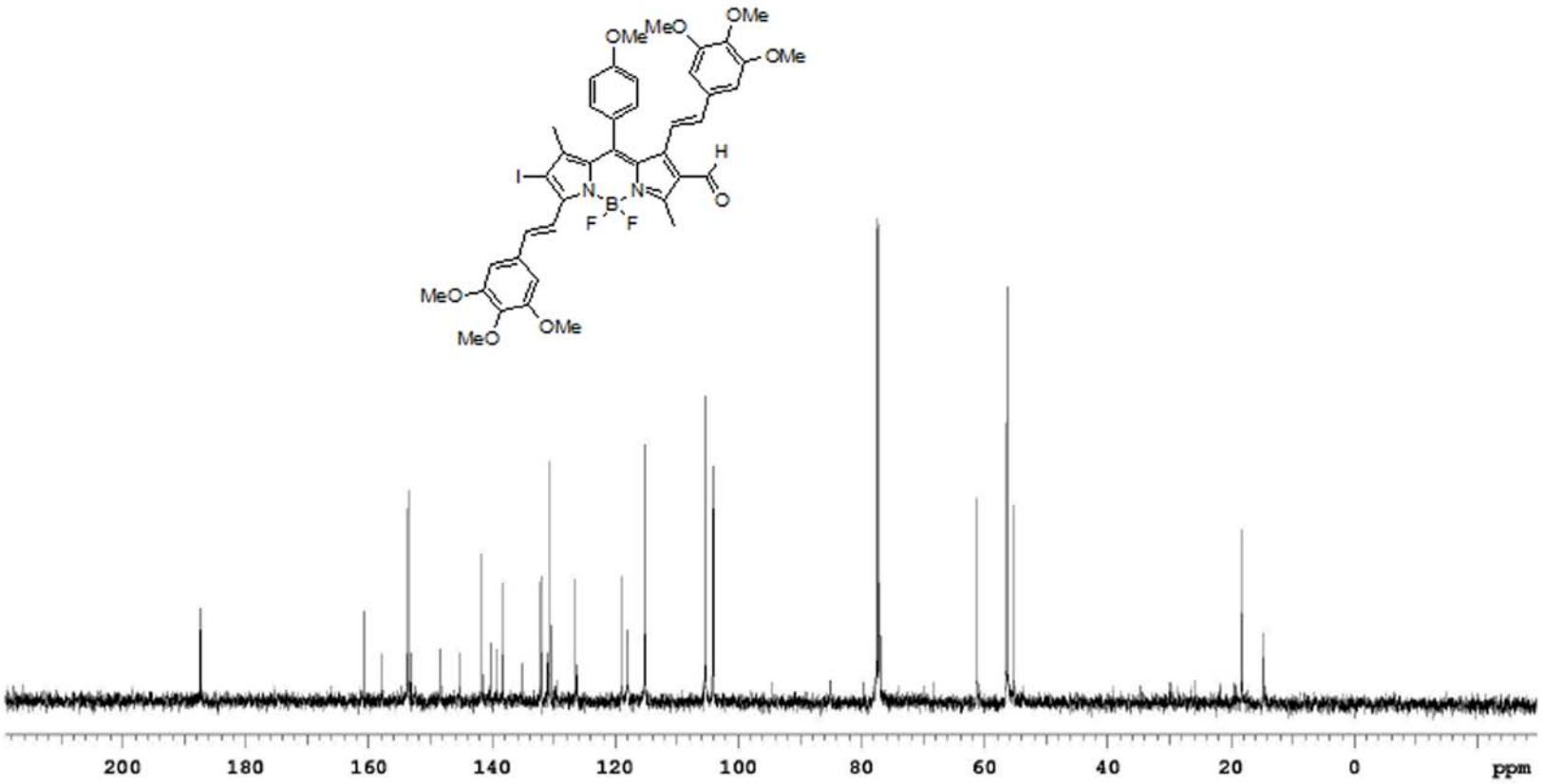

Figure S12. ^{13}C NMR spectrum of BODIPY dye **B** in $CDCl_3$ solution.

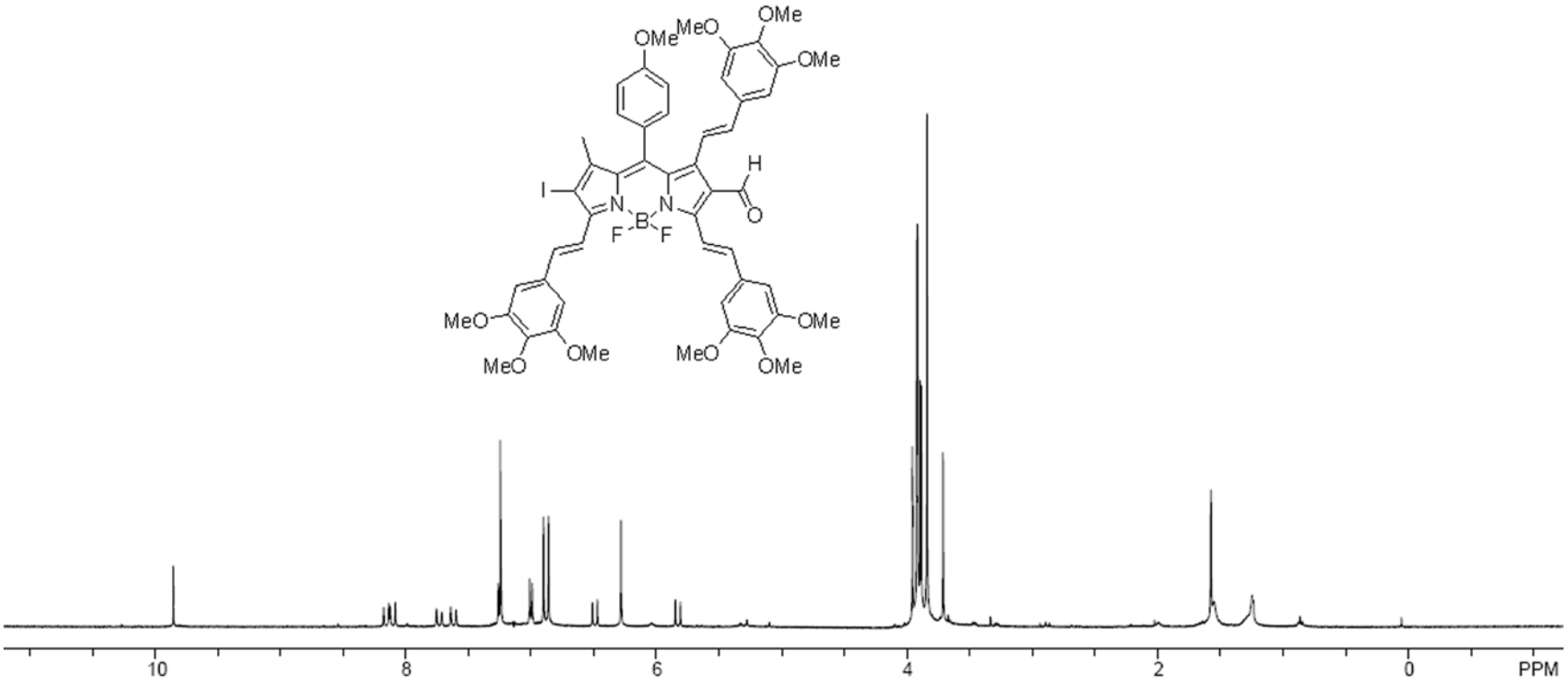

Figure S13. ^{1}H NMR spectrum of BODIPY dye **C** in $CDCl_3$ solution.

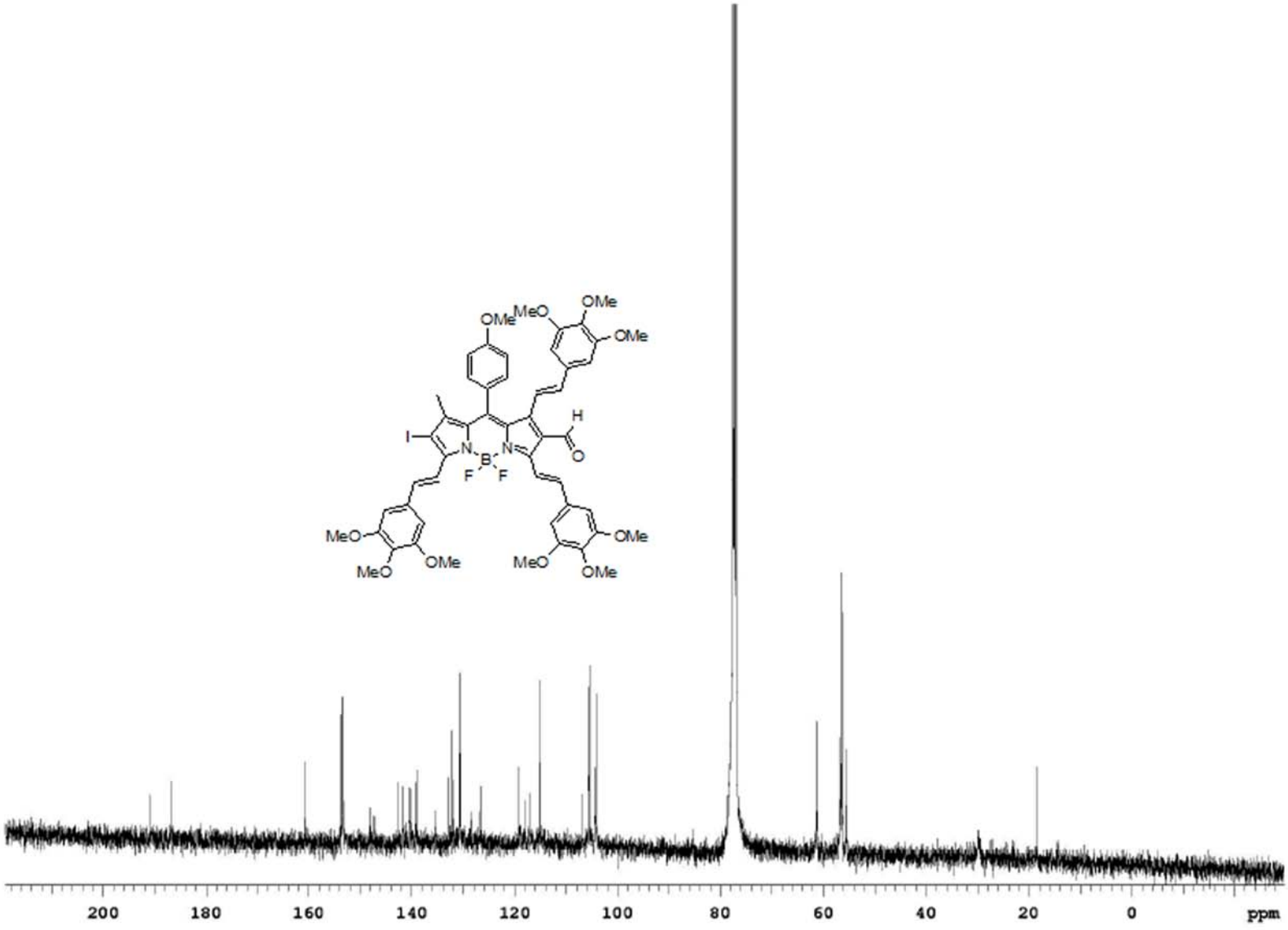

Figure S14. ^{13}C NMR spectrum of BODIPY dye **C** in $CDCl_3$ solution.

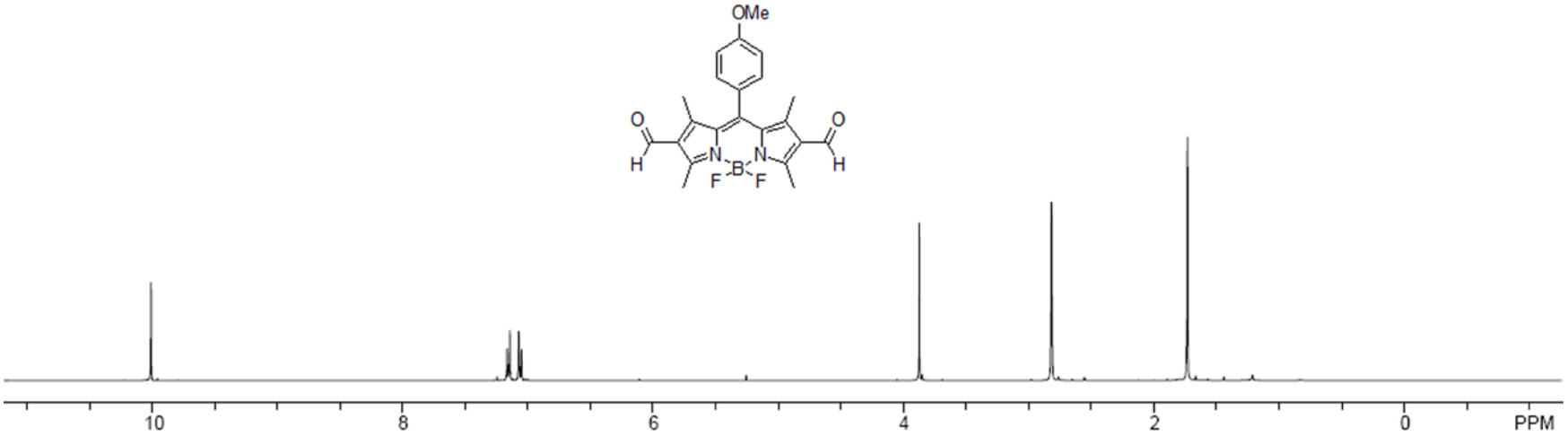

Figure S15. ^{1}H NMR spectrum of BODIPY dye **6** in $CDCl_3$ solution.

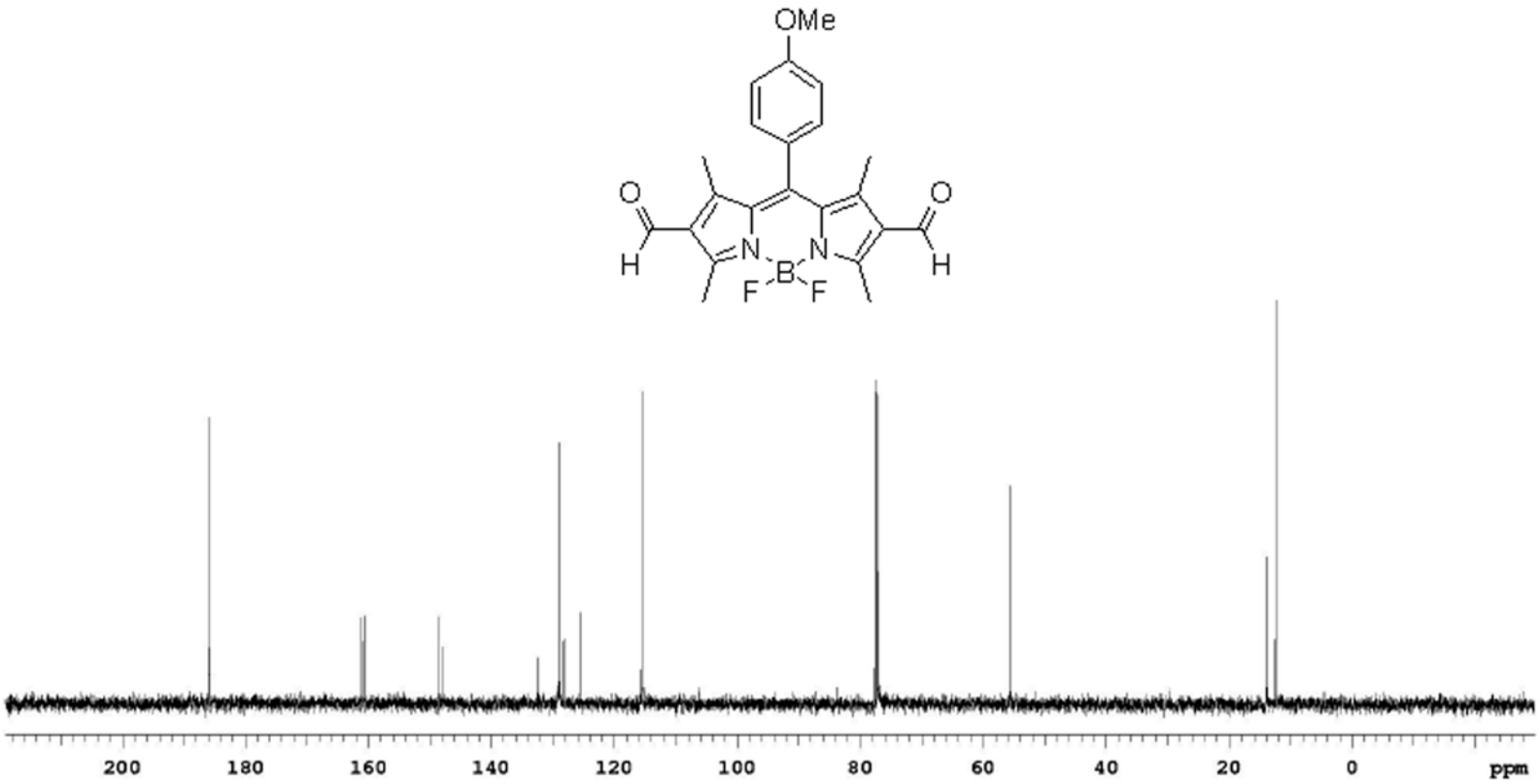

Figure S16. ^{13}C NMR spectrum of BODIPY dye **6** in $CDCl_3$ solution.

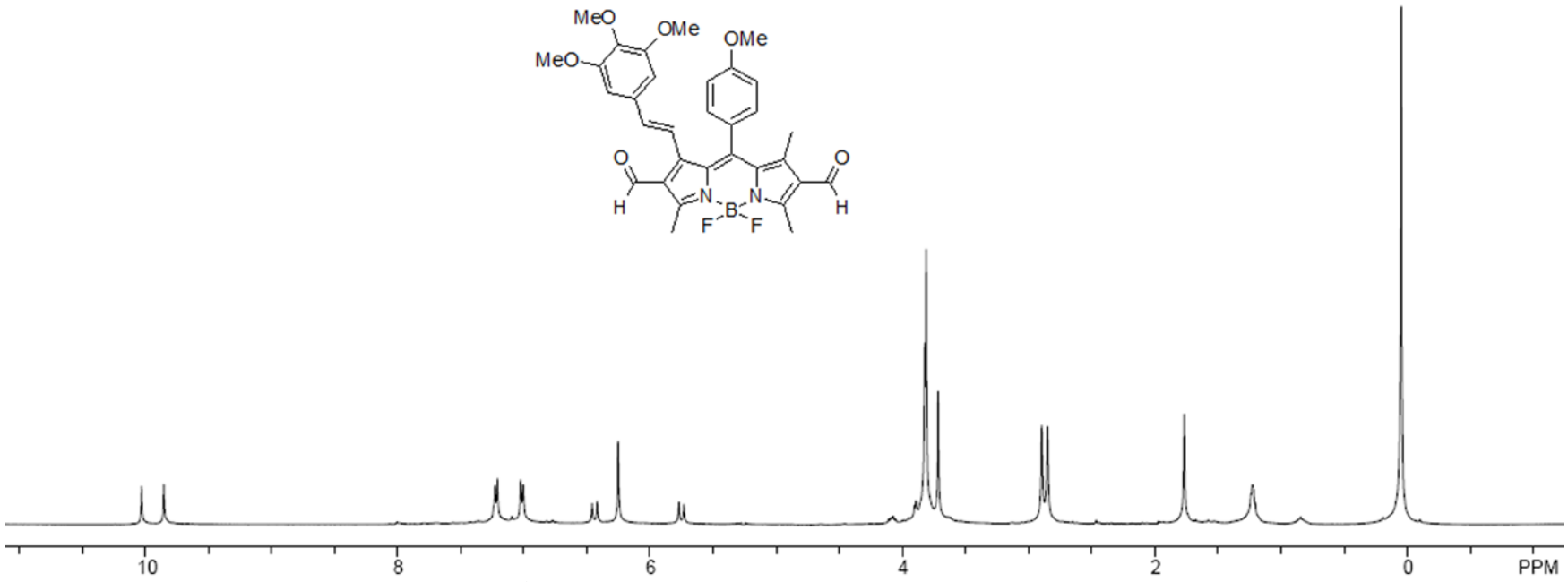

Figure S17. ^{1}H NMR spectrum of BODIPY dye $\mathbf{D_a}$ in $CDCl_3$ solution.

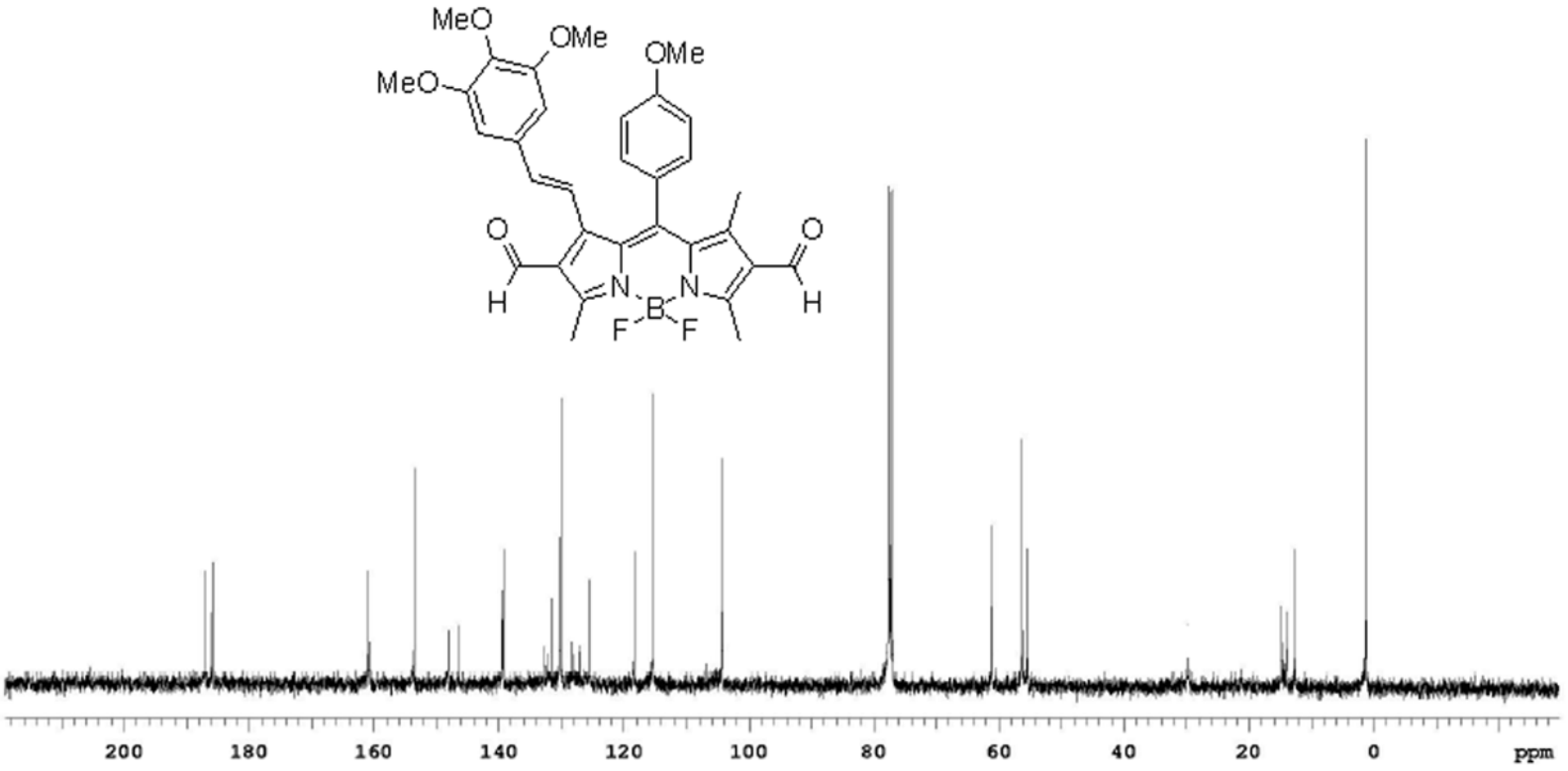

Figure S18. ^{13}C NMR spectrum of BODIPY dye $\mathbf{D_a}$ in $CDCl_3$ solution.

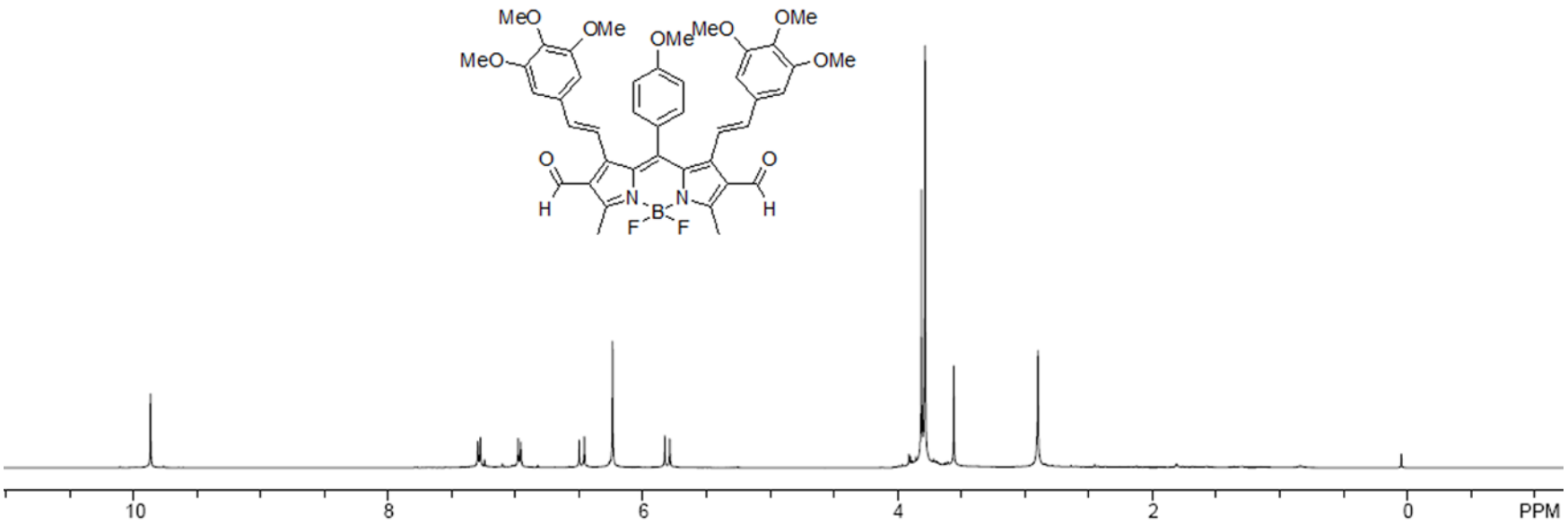

Figure S19. ^{1}H NMR spectrum of BODIPY dye $\mathbf{E_a}$ in $CDCl_3$ solution.

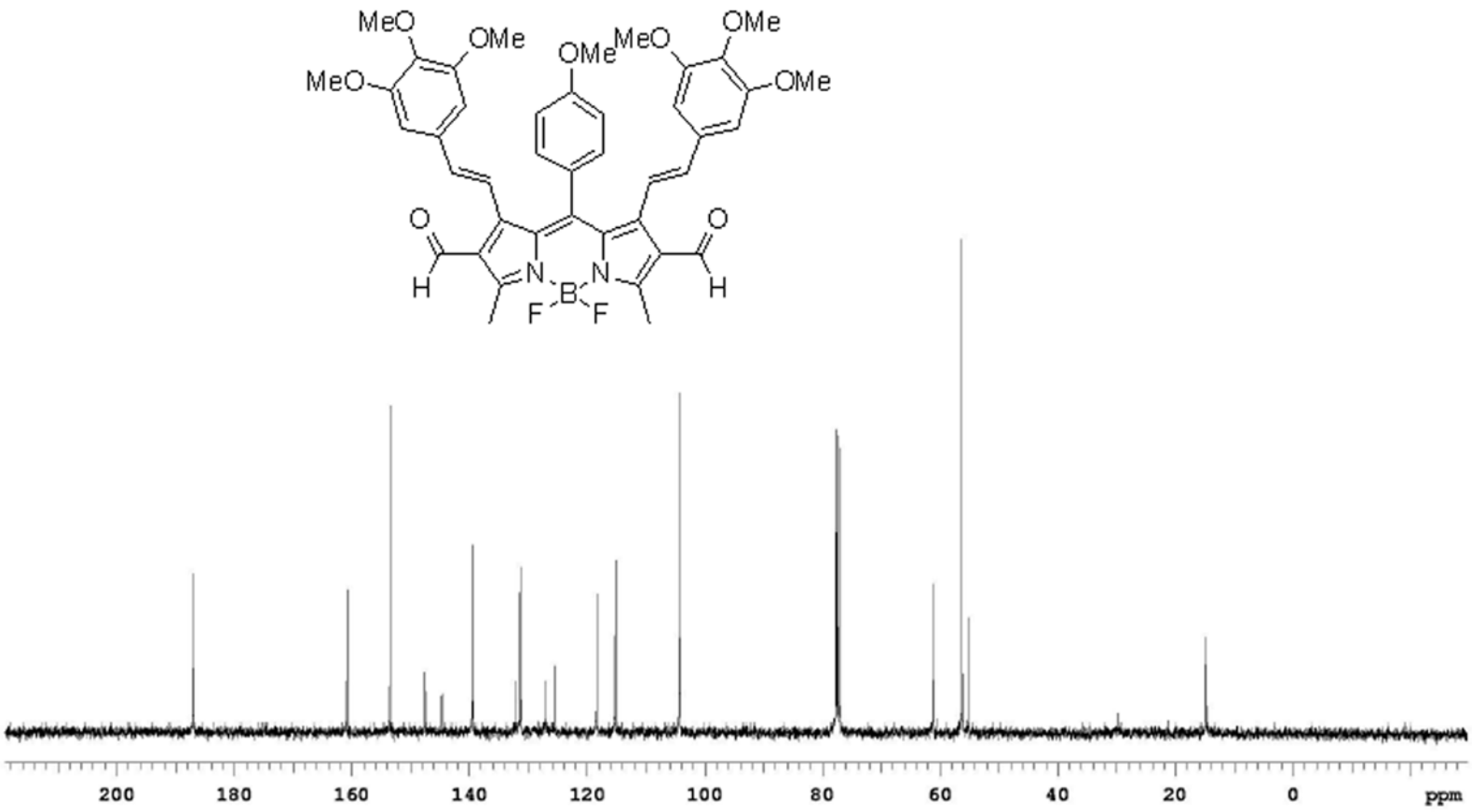

Figure S20. ^{13}C NMR spectrum of BODIPY dye $\mathbf{E_a}$ in $CDCl_3$ solution.

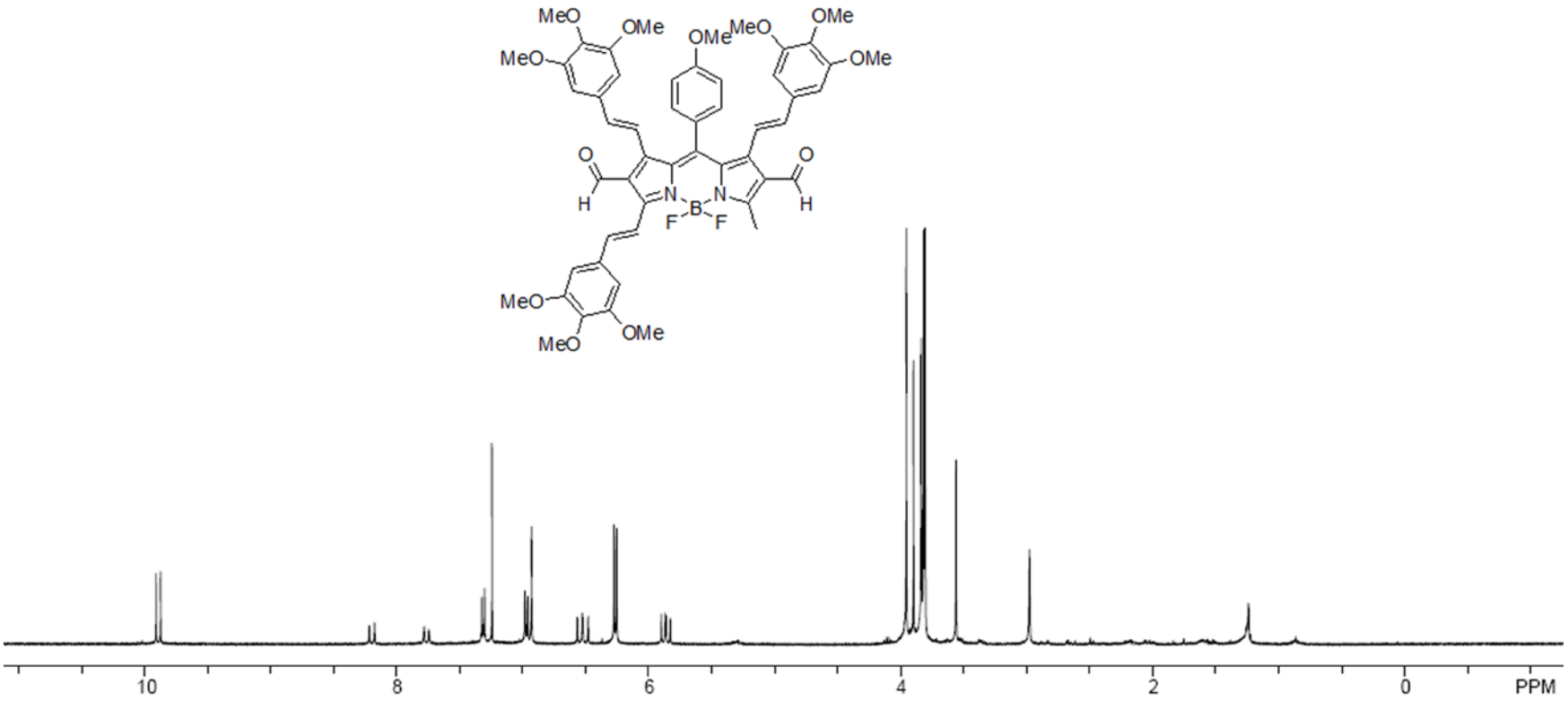

Figure S21. ^{1}H NMR spectrum of BODIPY dye $\mathbf{F_a}$ in $CDCl_3$ solution.

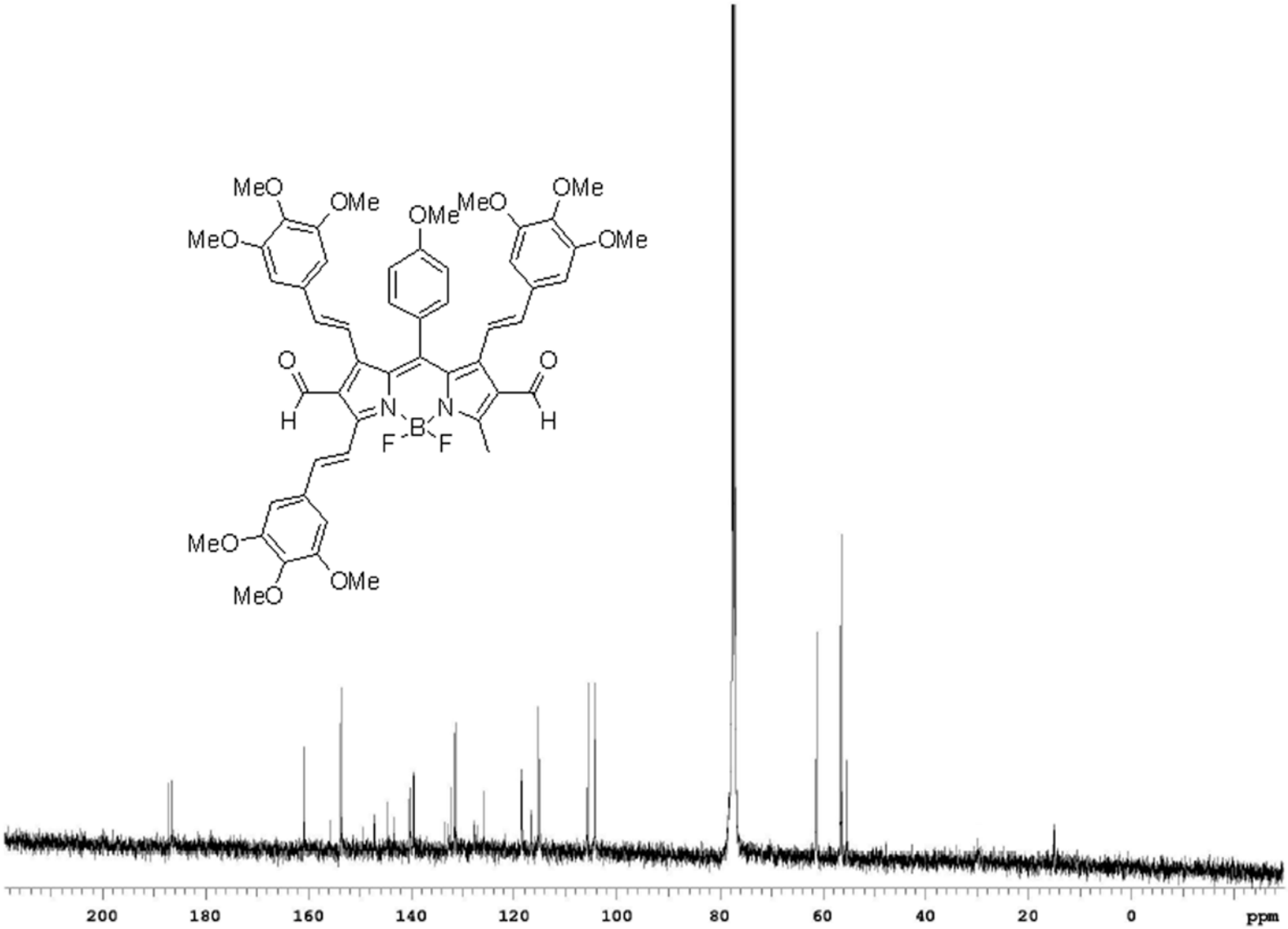

Figure S22. ^{13}C NMR spectrum of BODIPY dye $\mathbf{F_a}$ in $CDCl_3$ solution.

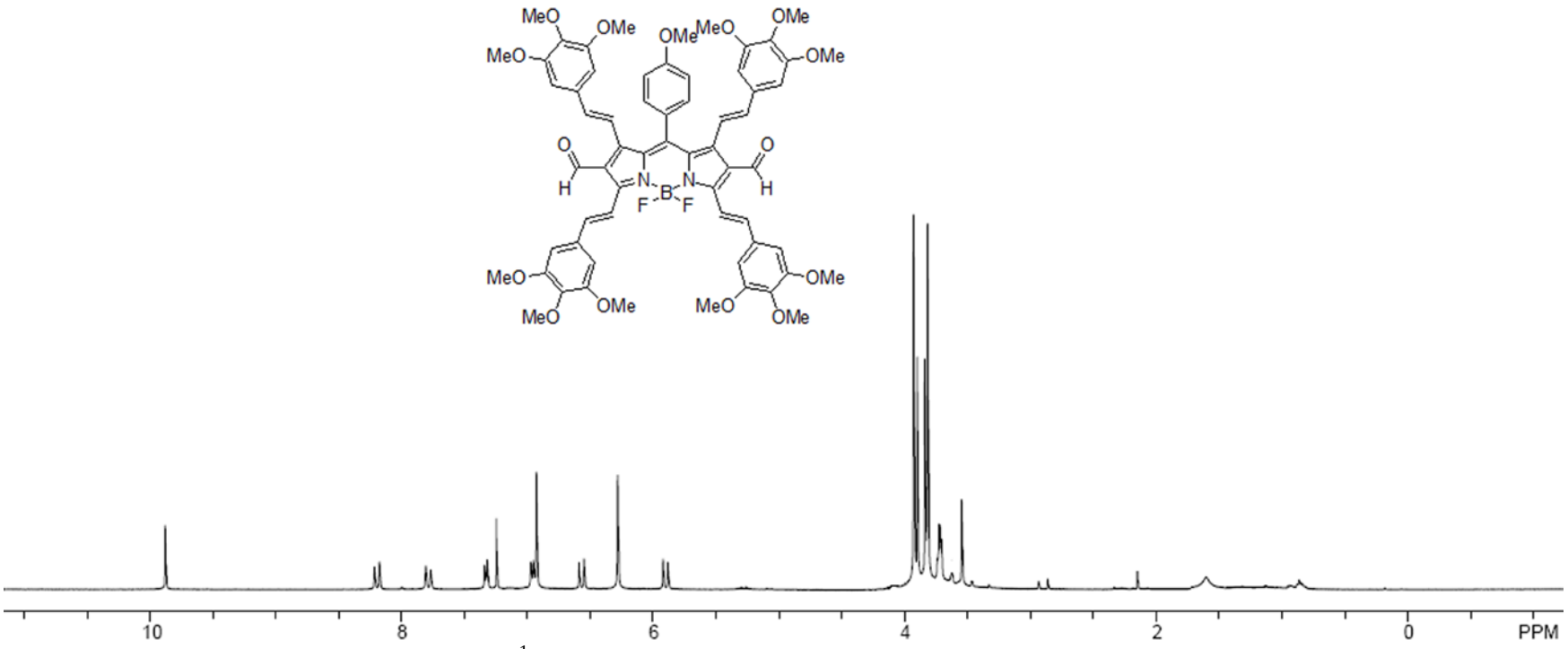

Figure S23. ^{1}H NMR spectrum of BODIPY dye $\mathbf{G_a}$ in $CDCl_3$ solution.

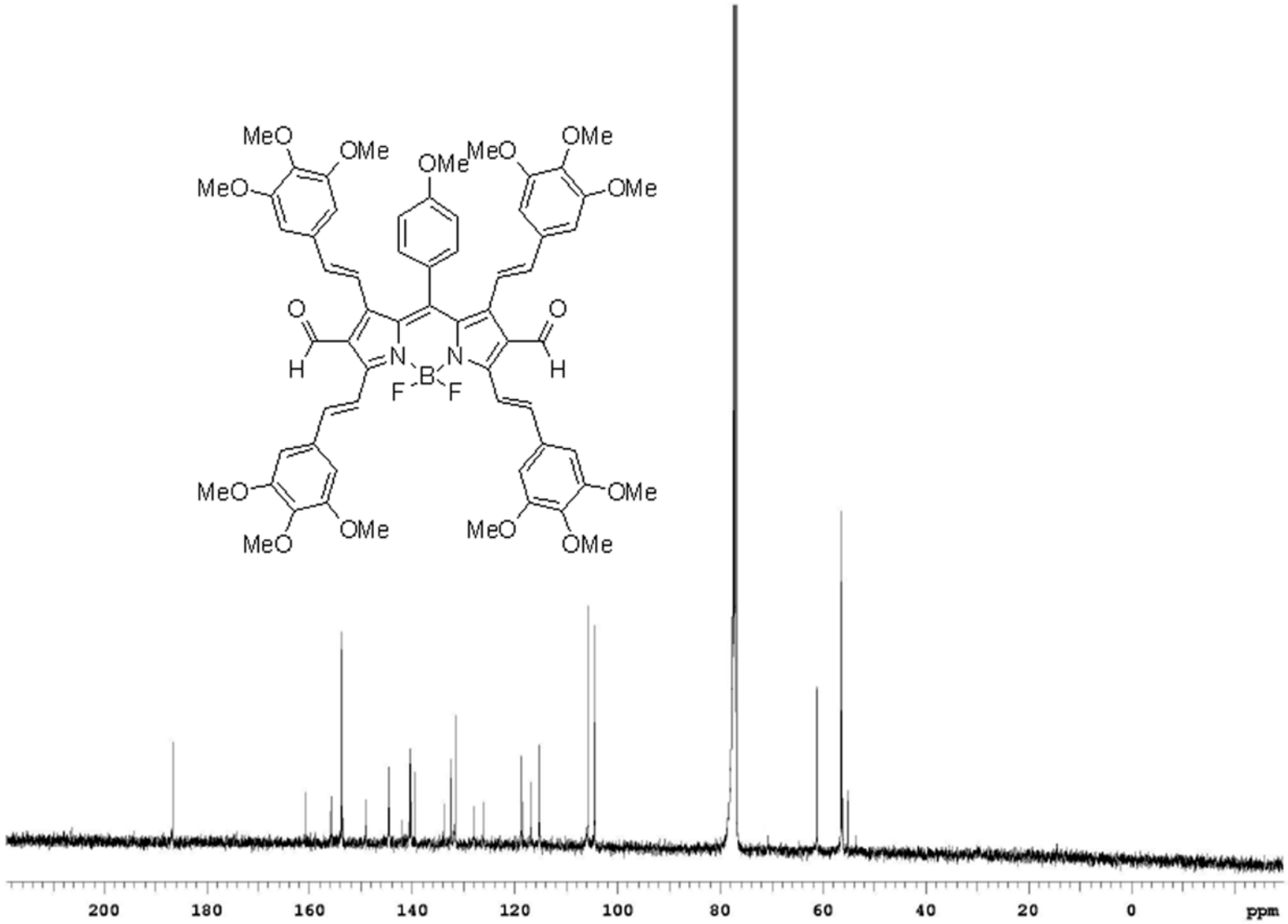

Figure S24. ^{13}C NMR spectrum of BODIPY dye $\mathbf{G_a}$ in $CDCl_3$ solution.

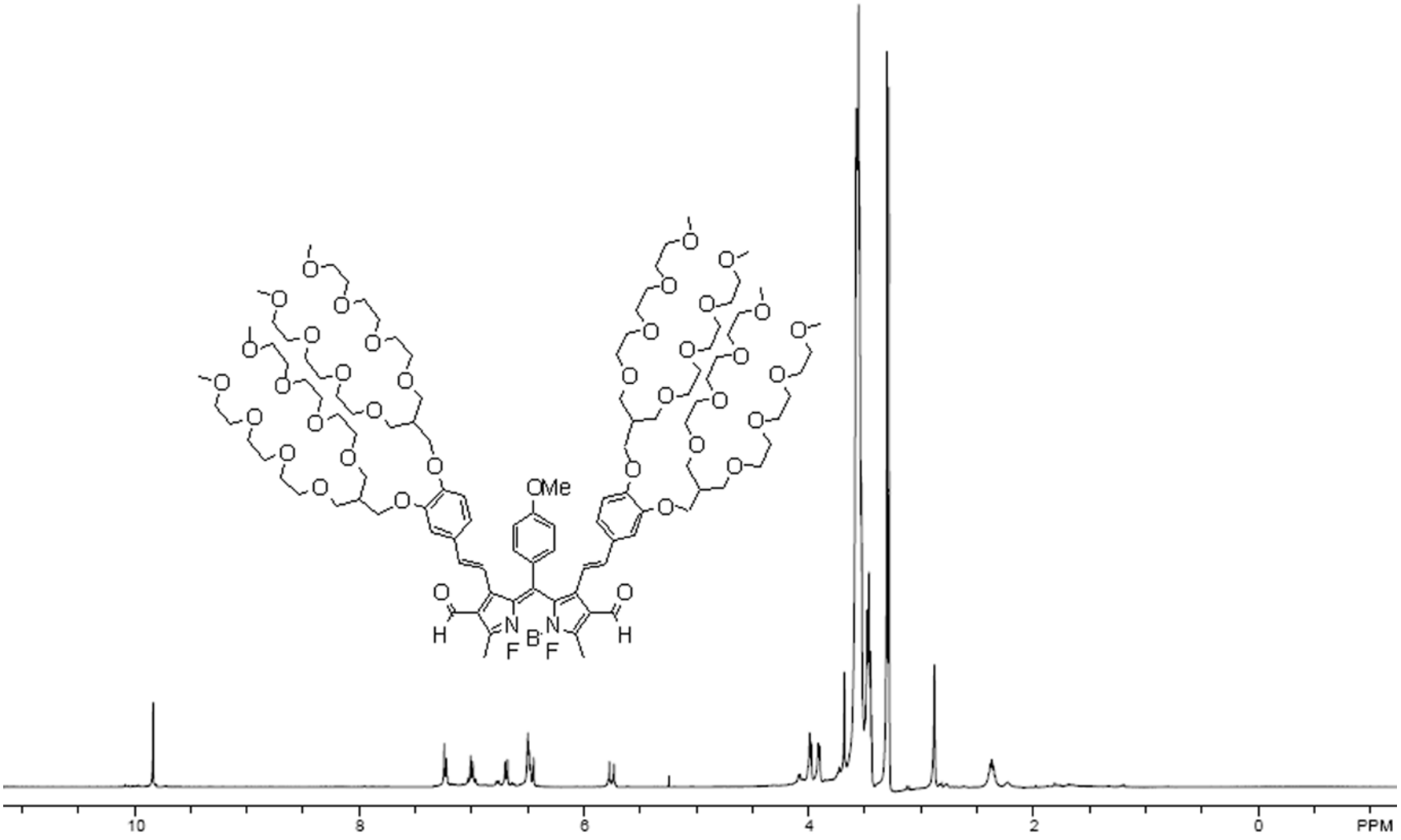

Figure S25. ^{1}H NMR spectrum of BODIPY dye $\mathbf{D_b}$ in $CDCl_3$ solution.

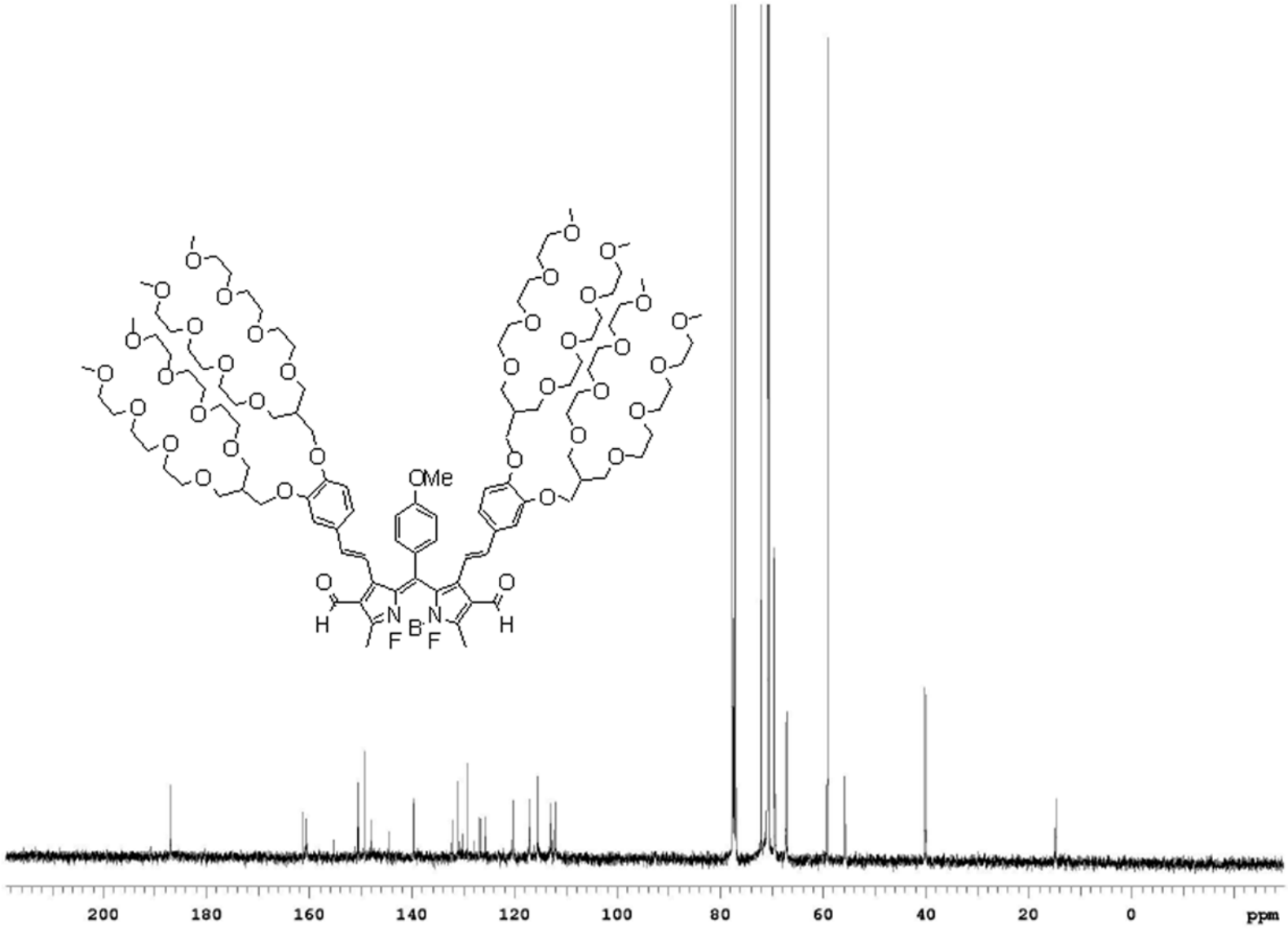

Figure S26. ^{13}C NMR spectrum of BODIPY dye $\mathbf{D_b}$ in $CDCl_3$ solution.

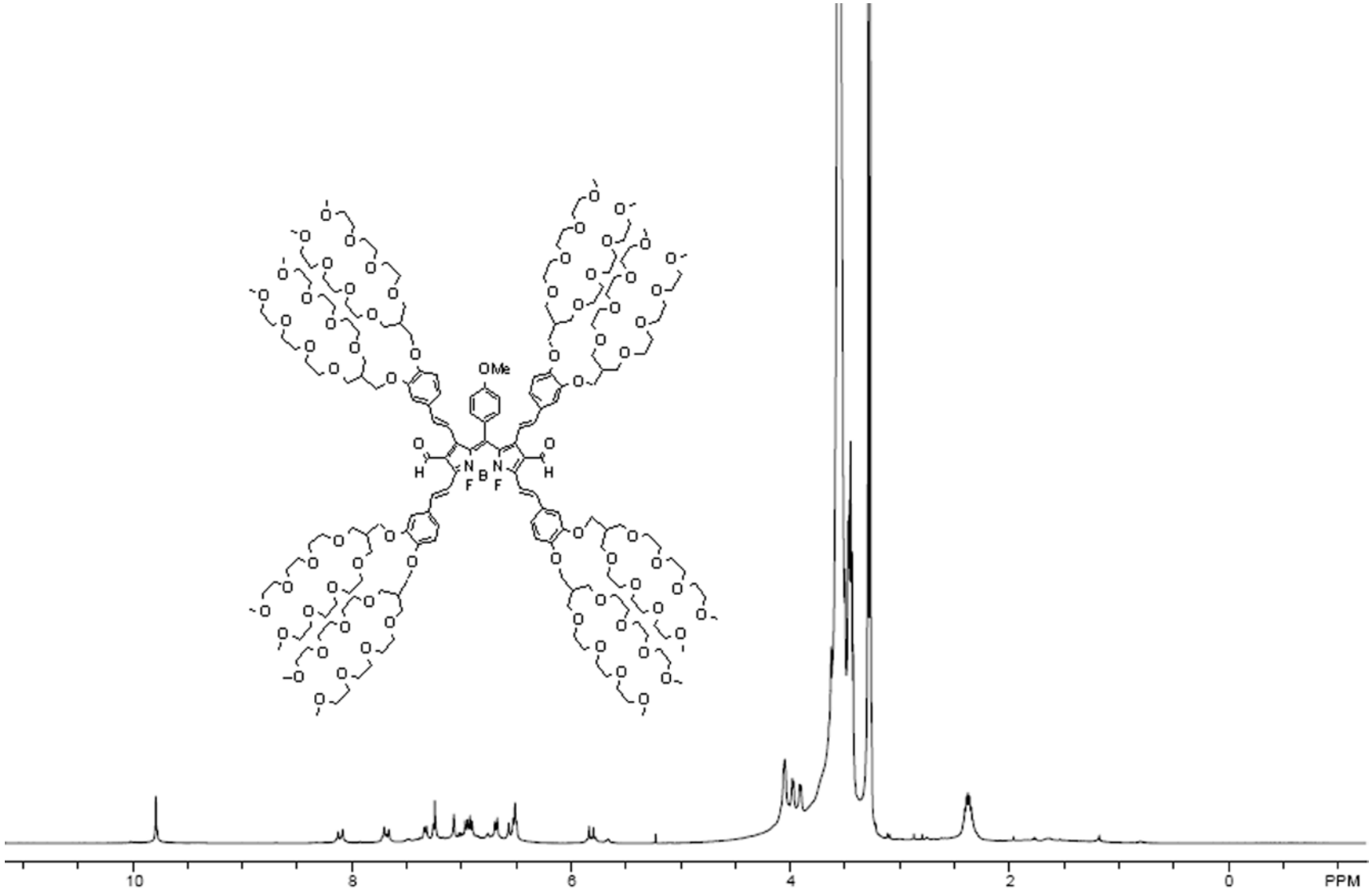

Figure S27. ^{1}H NMR spectrum of BODIPY dye $\mathbf{E_b}$ in $CDCl_3$ solution.

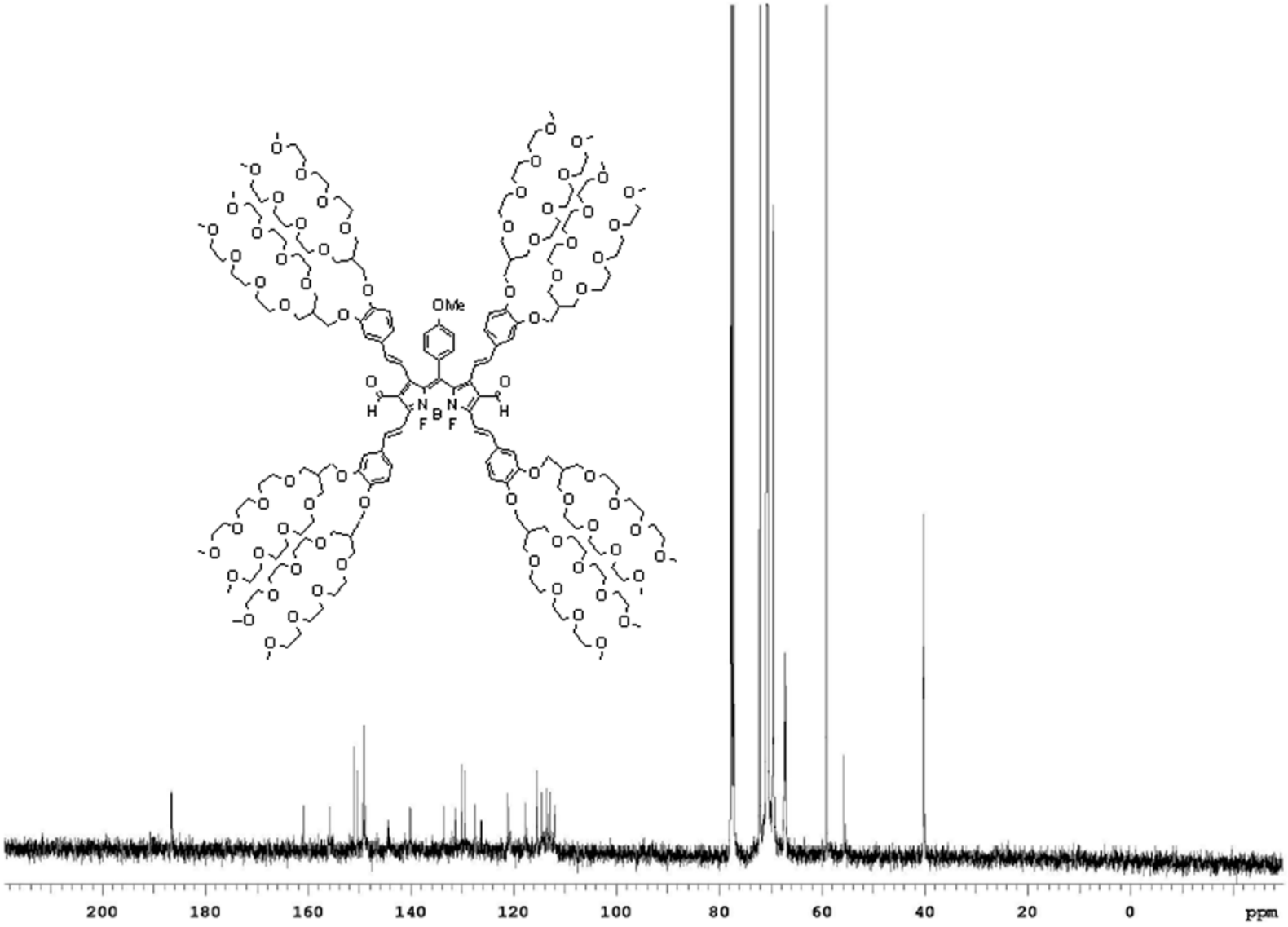

Figure S28. ^{13}C NMR spectrum of BODIPY dye $\mathbf{E_b}$ in $CDCl_3$ solution.

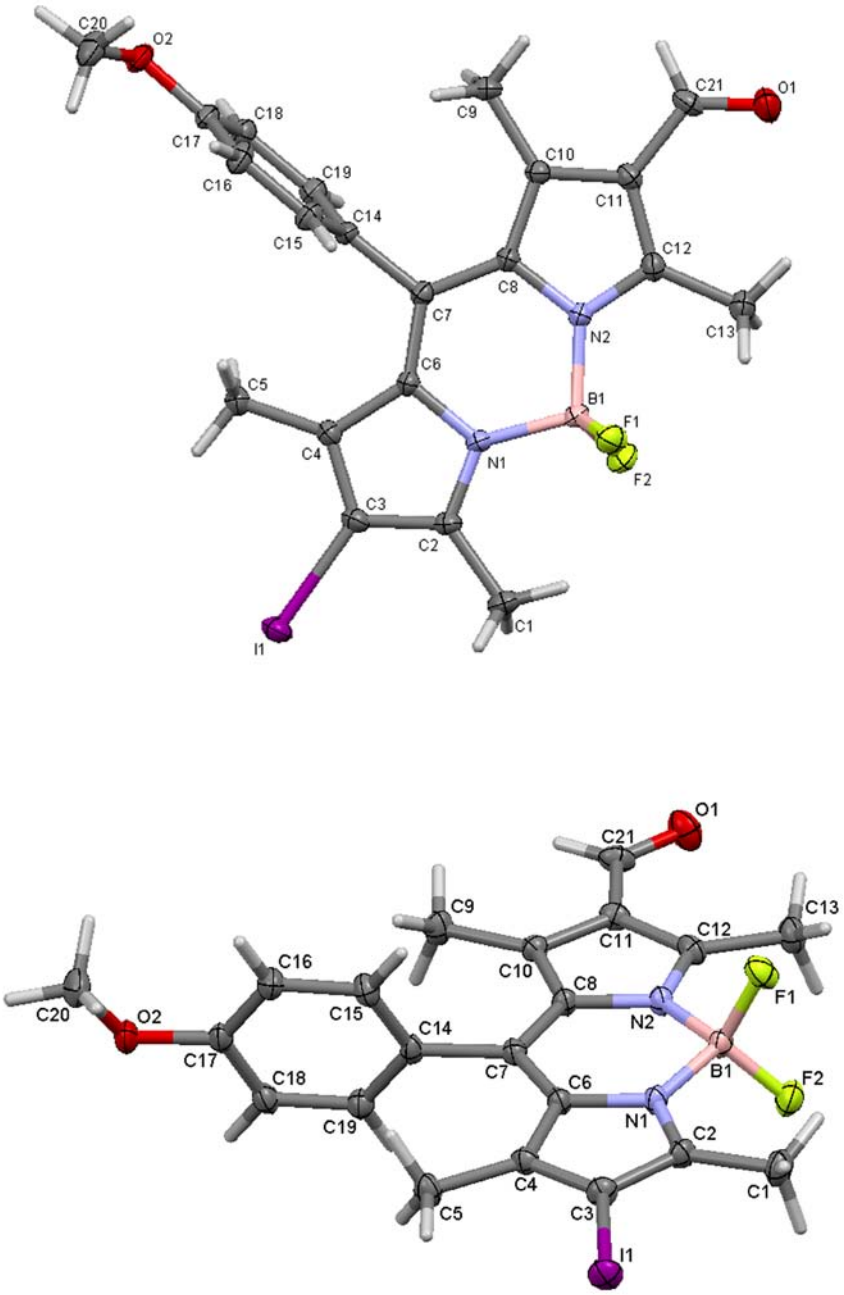

Figure S29. X-ray structure of BODIPY dye **4**

Table S1. Experimental details for BODIPY dye 4

	11mz066_0m
Crystal data	

Chemical formula	$C_{21}H_{20}BF_2IN_2O_2$
M_r	508.10
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	100
a, *b*, *c* (Å)	9.4100 (18), 10.603 (2), 11.494 (2)
α, β, γ (°)	66.655 (2), 83.633 (3), 69.026 (2)
V (Å^3)	982.5 (3)
Z	2
F(000)	504
D_x (Mg m^{-3})	1.717
Radiation type	Mo *K*α
μ (mm^{-1})	1.67
Crystal shape	Plate
Colour	Red
Crystal size (mm)	0.44 × 0.39 × 0.14
Data collection	
Diffractometer	Bruker AXS *SMART APEX* CCD diffractometer
Radiation source	fine-focus sealed tube
Monochromator	graphite
Scan method	ω scans
Absorption correction	Multi-scan Apex2 v2009.7-0 (Bruker, 2009)
T_{min}, T_{max}	0.641, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	17619, 5863, 5590
R_{int}	0.023
θ values (°)	θ_{max} = 31.5, θ_{min} = 1.9
Range of *h*, *k*, *l*	*h* = -13→13, *k* = -15→15, *l* = -16→16
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.041, 0.097, 1.30
No. of reflections	5863
No. of parameters	277
No. of restraints	3
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.84, -1.33

Computer programs: Apex2 v2011.2-0 (Bruker, 2009), Apex2 v2011.2-0, *SHELXTL* 6.14 (Bruker, 2000-2003; Sheldrick, 2008), *SHELXTL* 6.14.

Comments:

The iodine and aldehyde substituents are disordered over two chemically equivalent positions with a refined occupancy ratio of 0.8967(8) to 0.1033(8). Atoms of the minor moiety were constrained to have ADPs identical to their equivalents in the major moiety, and equivalent bond lengths were restrained to be the same in both moieties.

Table S2. Selected geometric parameters (Å, º) for BODIPY dye 4

B1-F2	1.382 (4)	C10-C11	1.403 (4)
B1-F1	1.406 (4)	C11-C12	1.415 (4)
B1-N2	1.545 (4)	C11-C21	1.455 (5)
B1-N1	1.547 (4)	C11-I1B	1.996 (4)
C1-C2	1.486 (4)	C12-N2	1.347 (4)
C1-H1A	0.9800	C12-C13	1.496 (4)
C1-H1B	0.9800	C13-H13A	0.9800
C1-H1C	0.9800	C13-H13B	0.9800
C2-N1	1.341 (4)	C13-H13C	0.9800
C2-C3	1.416 (4)	C14-C15	1.385 (4)
C3-C4	1.389 (4)	C14-C19	1.395 (4)
C3-C21B	1.485 (17)	C15-C16	1.396 (4)
C3-I1	2.061 (3)	C15-H15	0.9500
C4-C6	1.432 (4)	C16-C17	1.383 (5)
C4-C5	1.495 (4)	C16-H16	0.9500
C5-H5A	0.9800	C17-O2	1.371 (3)
C5-H5B	0.9800	C17-C18	1.391 (5)
C5-H5C	0.9800	C18-C19	1.386 (4)
C6-C7	1.387 (4)	C18-H18	0.9500
C6-N1	1.405 (4)	C19-H19	0.9500
C7-C8	1.410 (4)	C20-O2	1.427 (4)
C7-C14	1.490 (4)	C20-H20A	0.9800
C8-N2	1.402 (4)	C20-H20B	0.9800
C8-C10	1.411 (4)	C20-H20C	0.9800
C9-C10	1.498 (4)	C21-O1	1.212 (5)
C9-H9A	0.9800	C21-H21	0.9500
C9-H9B	0.9800	C21B-O1B	1.238 (19)
C9-H9C	0.9800	C21B-H21B	0.9500
F2-B1-F1	109.1 (2)	C12-C11-C21	126.9 (3)
F2-B1-N2	111.3 (3)	C10-C11-I1B	130.7 (2)

F1-B1-N2	109.9 (3)	C12-C11-I1B	121.3 (2)
F2-B1-N1	110.5 (3)	N2-C12-C11	108.7 (3)
F1-B1-N1	109.2 (3)	N2-C12-C13	122.6 (3)
N2-B1-N1	106.8 (2)	C11-C12-C13	128.7 (3)
C2-C1-H1A	109.5	C12-C13-H13A	109.5
C2-C1-H1B	109.5	C12-C13-H13B	109.5
H1A-C1-H1B	109.5	H13A-C13-H13B	109.5
C2-C1-H1C	109.5	C12-C13-H13C	109.5
H1A-C1-H1C	109.5	H13A-C13-H13C	109.5
H1B-C1-H1C	109.5	H13B-C13-H13C	109.5
N1-C2-C3	108.8 (3)	C15-C14-C19	119.3 (3)
N1-C2-C1	123.7 (3)	C15-C14-C7	119.0 (3)
C3-C2-C1	127.5 (3)	C19-C14-C7	121.7 (3)
C4-C3-C2	108.8 (3)	C14-C15-C16	120.5 (3)
C4-C3-C21B	118.5 (10)	C14-C15-H15	119.7
C2-C3-C21B	130.7 (10)	C16-C15-H15	119.7
C4-C3-I1	127.6 (2)	C17-C16-C15	119.6 (3)
C2-C3-I1	123.5 (2)	C17-C16-H16	120.2
C3-C4-C6	105.6 (3)	C15-C16-H16	120.2
C3-C4-C5	126.0 (3)	O2-C17-C16	124.5 (3)
C6-C4-C5	128.3 (3)	O2-C17-C18	115.0 (3)
C4-C5-H5A	109.5	C16-C17-C18	120.5 (3)
C4-C5-H5B	109.5	C19-C18-C17	119.6 (3)
H5A-C5-H5B	109.5	C19-C18-H18	120.2
C4-C5-H5C	109.5	C17-C18-H18	120.2
H5A-C5-H5C	109.5	C18-C19-C14	120.5 (3)
H5B-C5-H5C	109.5	C18-C19-H19	119.7
C7-C6-N1	120.6 (3)	C14-C19-H19	119.7
C7-C6-C4	131.3 (3)	O2-C20-H20A	109.5
N1-C6-C4	108.1 (2)	O2-C20-H20B	109.5
C6-C7-C8	120.9 (3)	H20A-C20-H20B	109.5
C6-C7-C14	119.4 (3)	O2-C20-H20C	109.5
C8-C7-C14	119.6 (3)	H20A-C20-H20C	109.5
N2-C8-C7	120.4 (3)	H20B-C20-H20C	109.5
N2-C8-C10	108.3 (2)	O1-C21-C11	126.3 (4)
C7-C8-C10	131.3 (3)	O1-C21-H21	116.8
C10-C9-H9A	109.5	C11-C21-H21	116.8
C10-C9-H9B	109.5	O1B-C21B-C3	118.7 (19)
H9A-C9-H9B	109.5	O1B-C21B-H21B	120.6
C10-C9-H9C	109.5	C3-C21B-H21B	120.6
H9A-C9-H9C	109.5	C2-N1-C6	108.7 (2)

H9B-C9-H9C	109.5	C2-N1-B1	125.9 (2)
C11-C10-C8	106.2 (3)	C6-N1-B1	125.4 (2)
C11-C10-C9	124.8 (3)	C12-N2-C8	108.8 (2)
C8-C10-C9	128.9 (3)	C12-N2-B1	125.8 (2)
C10-C11-C12	108.0 (3)	C8-N2-B1	125.2 (2)
C10-C11-C21	125.1 (3)	C17-O2-C20	117.2 (3)
N1-C2-C3-C4	0.4 (4)	C7-C14-C15-C16	177.8 (3)
C1-C2-C3-C4	-179.5 (3)	C14-C15-C16-C17	0.9 (5)
N1-C2-C3-C21B	163.8 (17)	C15-C16-C17-O2	-179.6 (3)
C1-C2-C3-C21B	-16.1 (18)	C15-C16-C17-C18	-0.4 (5)
N1-C2-C3-I1	-177.0 (2)	O2-C17-C18-C19	179.2 (3)
C1-C2-C3-I1	3.1 (5)	C16-C17-C18-C19	0.0 (5)
C2-C3-C4-C6	-1.2 (4)	C17-C18-C19-C14	0.0 (5)
C21B-C3-C4-C6	-167.0 (15)	C15-C14-C19-C18	0.5 (5)
I1-C3-C4-C6	176.0 (2)	C7-C14-C19-C18	-178.2 (3)
C2-C3-C4-C5	175.7 (3)	C10-C11-C21-O1	179.6 (4)
C21B-C3-C4-C5	10.0 (16)	C12-C11-C21-O1	-0.7 (6)
I1-C3-C4-C5	-7.0 (5)	I1B-C11-C21-O1	24.9 (15)
C3-C4-C6-C7	179.1 (3)	C4-C3-C21B-O1B	-179 (2)
C5-C4-C6-C7	2.2 (6)	C2-C3-C21B-O1B	19 (4)
C3-C4-C6-N1	1.6 (3)	I1-C3-C21B-O1B	-52 (3)
C5-C4-C6-N1	-175.2 (3)	C3-C2-N1-C6	0.7 (4)
N1-C6-C7-C8	1.9 (5)	C1-C2-N1-C6	-179.4 (3)
C4-C6-C7-C8	-175.3 (3)	C3-C2-N1-B1	178.3 (3)
N1-C6-C7-C14	-176.0 (3)	C1-C2-N1-B1	-1.7 (5)
C4-C6-C7-C14	6.8 (5)	C7-C6-N1-C2	-179.2 (3)
C6-C7-C8-N2	-0.2 (5)	C4-C6-N1-C2	-1.4 (3)
C14-C7-C8-N2	177.7 (3)	C7-C6-N1-B1	3.1 (5)
C6-C7-C8-C10	179.1 (3)	C4-C6-N1-B1	-179.1 (3)
C14-C7-C8-C10	-3.0 (5)	F2-B1-N1-C2	53.3 (4)
N2-C8-C10-C11	0.6 (3)	F1-B1-N1-C2	-66.7 (4)
C7-C8-C10-C11	-178.8 (3)	N2-B1-N1-C2	174.5 (3)
N2-C8-C10-C9	-179.6 (3)	F2-B1-N1-C6	-129.4 (3)
C7-C8-C10-C9	1.0 (6)	F1-B1-N1-C6	110.6 (3)
C8-C10-C11-C12	-0.5 (3)	N2-B1-N1-C6	-8.2 (4)
C9-C10-C11-C12	179.6 (3)	C11-C12-N2-C8	0.1 (3)
C8-C10-C11-C21	179.2 (3)	C13-C12-N2-C8	-179.4 (3)
C9-C10-C11-C21	-0.7 (5)	C11-C12-N2-B1	-174.2 (3)
C8-C10-C11-I1B	-177.3 (3)	C13-C12-N2-B1	6.3 (5)
C9-C10-C11-I1B	2.8 (5)	C7-C8-N2-C12	179.1 (3)

C10-C11-C12-N2	0.3 (4)	C10-C8-N2-C12	-0.4 (3)
C21-C11-C12-N2	-179.4 (3)	C7-C8-N2-B1	-6.6 (5)
I1B-C11-C12-N2	177.4 (2)	C10-C8-N2-B1	173.9 (3)
C10-C11-C12-C13	179.7 (3)	F2-B1-N2-C12	-56.0 (4)
C21-C11-C12-C13	0.0 (6)	F1-B1-N2-C12	65.0 (4)
I1B-C11-C12-C13	-3.1 (5)	N1-B1-N2-C12	-176.7 (3)
C6-C7-C14-C15	79.3 (4)	F2-B1-N2-C8	130.6 (3)
C8-C7-C14-C15	-98.6 (4)	F1-B1-N2-C8	-108.4 (3)
C6-C7-C14-C19	-102.0 (4)	N1-B1-N2-C8	9.9 (4)
C8-C7-C14-C19	80.1 (4)	C16-C17-O2-C20	-10.5 (5)
C19-C14-C15-C16	-1.0 (5)	C18-C17-O2-C20	170.3 (3)

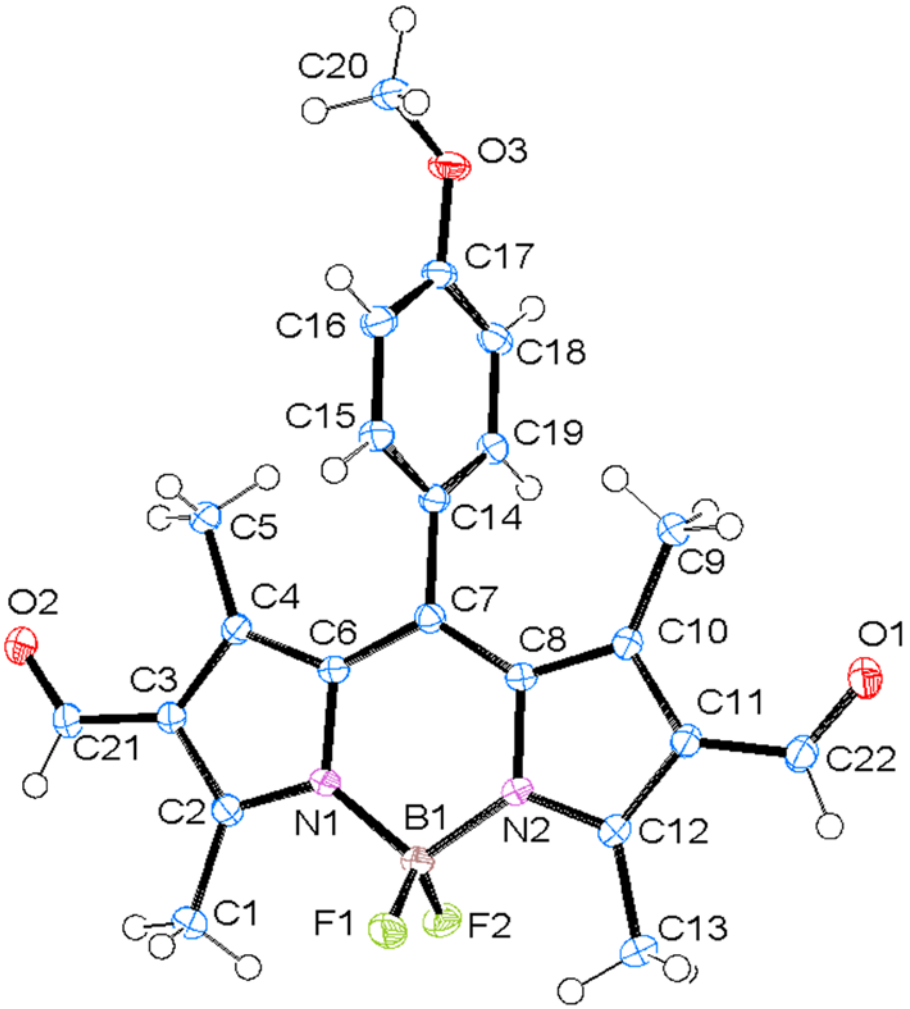

Figure S30. X-ray structure of BODIPY dye **6**

Table S3. Crystal data and structure refinement for 11rlr004_0m.
For BODIPY dye 6

Identification code	11rlr004_0m
Empirical formula	C22 H21 B F2 N2 O3
Formula weight	410.22
Temperature	447(2) K
Wavelength	0.71073 A

Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 6.5685(5) A alpha = 81.7570(10) deg.
	b = 8.8104(6) A beta = 84.9650(10) deg.
	c = 16.4780(10) A gamma = 85.8970(10) deg.
Volume	938.42(11) A^3
Z, Calculated density	2, 1.452 Mg/m^3
Absorption coefficient	0.109 mm^-1
F(000)	428
Crystal size	0.55 x 0.17 x 0.06 mm
Theta range for data collection	1.25 to 30.25 deg.
Limiting indices	-9<=h<=9, -12<=k<=12, -22<=l<=22
Reflections collected / unique	10755 / 5282 [R(int) = 0.0222]
Completeness to theta = 28.00	98.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.746 and 0.677
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5282 / 0 / 276
Goodness-of-fit on F^2	1.029
Final R indices [I>2sigma(I)]	R1 = 0.0477, wR2 = 0.1132
R indices (all data)	R1 = 0.0640, wR2 = 0.1258
Largest diff. peak and hole	0.371 and -0.373 e.A^-3

Table S4. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for 11rlr004_0m. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor. For BODIPY dye 6

	x	y	z	U(eq)
B(1)	7496(3)	3068(2)	6190(1)	18(1)
F(1)	8582(2)	3217(1)	5428(1)	25(1)
F(2)	6347(2)	4426(1)	6295(1)	24(1)
N(1)	6064(2)	1722(1)	6273(1)	16(1)
N(2)	8983(2)	2675(1)	6881(1)	16(1)
C(1)	4168(3)	2747(2)	5047(1)	22(1)
C(2)	4545(2)	1621(2)	5793(1)	17(1)
C(3)	3454(2)	305(2)	6108(1)	17(1)
C(4)	4382(2)	-432(2)	6806(1)	16(1)
C(5)	3699(2)	-1886(2)	7309(1)	20(1)
C(6)	6040(2)	463(2)	6904(1)	15(1)
C(7)	7478(2)	293(2)	7496(1)	15(1)
C(8)	8950(2)	1377(2)	7484(1)	15(1)
C(9)	11247(2)	308(2)	8697(1)	20(1)
C(10)	10607(2)	1419(2)	7979(1)	16(1)
C(11)	11599(2)	2768(2)	7659(1)	16(1)
C(12)	10551(2)	3510(2)	6983(1)	17(1)
C(13)	11016(3)	4973(2)	6446(1)	22(1)

C(14)	7471(2)	-1086(2)	8127(1)	16(1)
C(15)	8091(2)	-2514(2)	7896(1)	18(1)
C(16)	8114(2)	-3835(2)	8469(1)	20(1)
C(17)	7487(2)	-3725(2)	9289(1)	19(1)
C(18)	6833(2)	-2292(2)	9527(1)	19(1)
C(19)	6836(2)	-987(2)	8951(1)	17(1)
O(3)	7473(2)	-4927(1)	9906(1)	25(1)
C(20)	8110(3)	-6405(2)	9681(1)	28(1)
C(21)	1641(2)	-95(2)	5756(1)	20(1)
O(1)	14470(2)	2683(1)	8458(1)	24(1)
C(22)	13424(2)	3341(2)	7927(1)	20(1)
O(2)	569(2)	-1153(1)	6035(1)	25(1)

Table S5. Bond lengths [A] and angles [deg] for 11rlr004_0m. For BODIPY dye 6

B(1)-F(1)	1.3825(19)
B(1)-F(2)	1.3920(19)
B(1)-N(1)	1.549(2)
B(1)-N(2)	1.551(2)
N(1)-C(2)	1.3423(18)
N(1)-C(6)	1.4067(17)
N(2)-C(12)	1.3427(18)
N(2)-C(8)	1.4027(17)
C(1)-C(2)	1.491(2)
C(1)-H(1A)	0.9600
C(1)-H(1B)	0.9600
C(1)-H(1C)	0.9600
C(2)-C(3)	1.418(2)
C(3)-C(4)	1.402(2)
C(3)-C(21)	1.456(2)
C(4)-C(6)	1.423(2)
C(4)-C(5)	1.4970(19)
C(5)-H(5A)	0.9600
C(5)-H(5B)	0.9600
C(5)-H(5C)	0.9600
C(6)-C(7)	1.4029(19)
C(7)-C(8)	1.4040(19)
C(7)-C(14)	1.4811(19)
C(8)-C(10)	1.422(2)
C(9)-C(10)	1.4936(19)
C(9)-H(9A)	0.9600
C(9)-H(9B)	0.9600
C(9)-H(9C)	0.9600
C(10)-C(11)	1.4097(19)

C(11)-C(12)	1.415(2)
C(11)-C(22)	1.459(2)
C(12)-C(13)	1.4905(19)
C(13)-H(13A)	0.9600
C(13)-H(13B)	0.9600
C(13)-H(13C)	0.9600
C(14)-C(15)	1.389(2)
C(14)-C(19)	1.398(2)
C(15)-C(16)	1.390(2)
C(15)-H(15)	0.9300
C(16)-C(17)	1.392(2)
C(16)-H(16)	0.9300
C(17)-O(3)	1.3588(17)
C(17)-C(18)	1.402(2)
C(18)-C(19)	1.382(2)
C(18)-H(18)	0.9300
C(19)-H(19)	0.9300
O(3)-C(20)	1.429(2)
C(20)-H(20A)	0.9600
C(20)-H(20B)	0.9600
C(20)-H(20C)	0.9600
C(21)-O(2)	1.2211(18)
C(21)-H(21)	0.9300
O(1)-C(22)	1.2154(19)
C(22)-H(22)	0.9300

F(1)-B(1)-F(2)	110.14(12)
F(1)-B(1)-N(1)	110.23(13)
F(2)-B(1)-N(1)	109.78(13)
F(1)-B(1)-N(2)	110.21(13)
F(2)-B(1)-N(2)	109.63(13)
N(1)-B(1)-N(2)	106.79(11)
C(2)-N(1)-C(6)	108.73(12)
C(2)-N(1)-B(1)	125.65(12)
C(6)-N(1)-B(1)	125.46(12)
C(12)-N(2)-C(8)	109.07(12)
C(12)-N(2)-B(1)	125.10(12)
C(8)-N(2)-B(1)	125.80(12)
C(2)-C(1)-H(1A)	109.5
C(2)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1B)	109.5
C(2)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5
N(1)-C(2)-C(3)	109.11(12)
N(1)-C(2)-C(1)	123.02(13)
C(3)-C(2)-C(1)	127.87(13)
C(4)-C(3)-C(2)	107.94(13)
C(4)-C(3)-C(21)	128.84(14)
C(2)-C(3)-C(21)	123.16(13)
C(3)-C(4)-C(6)	106.14(12)
C(3)-C(4)-C(5)	124.41(13)
C(6)-C(4)-C(5)	129.44(13)
C(4)-C(5)-H(5A)	109.5

C(4)-C(5)-H(5B)	109.5
H(5A)-C(5)-H(5B)	109.5
C(4)-C(5)-H(5C)	109.5
H(5A)-C(5)-H(5C)	109.5
H(5B)-C(5)-H(5C)	109.5
C(7)-C(6)-N(1)	120.39(12)
C(7)-C(6)-C(4)	131.53(13)
N(1)-C(6)-C(4)	108.06(12)
C(6)-C(7)-C(8)	121.16(13)
C(6)-C(7)-C(14)	118.88(12)
C(8)-C(7)-C(14)	119.93(13)
N(2)-C(8)-C(7)	120.22(13)
N(2)-C(8)-C(10)	108.11(12)
C(7)-C(8)-C(10)	131.62(13)
C(10)-C(9)-H(9A)	109.5
C(10)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(10)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(11)-C(10)-C(8)	105.91(12)
C(11)-C(10)-C(9)	124.71(13)
C(8)-C(10)-C(9)	129.38(13)
C(10)-C(11)-C(12)	107.97(13)
C(10)-C(11)-C(22)	128.50(13)
C(12)-C(11)-C(22)	123.49(13)
N(2)-C(12)-C(11)	108.93(12)
N(2)-C(12)-C(13)	122.91(13)
C(11)-C(12)-C(13)	128.16(13)
C(12)-C(13)-H(13A)	109.5
C(12)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(12)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(15)-C(14)-C(19)	119.11(13)
C(15)-C(14)-C(7)	119.44(13)
C(19)-C(14)-C(7)	121.45(13)
C(14)-C(15)-C(16)	121.20(14)
C(14)-C(15)-H(15)	119.4
C(16)-C(15)-H(15)	119.4
C(15)-C(16)-C(17)	119.32(14)
C(15)-C(16)-H(16)	120.3
C(17)-C(16)-H(16)	120.3
O(3)-C(17)-C(16)	124.67(14)
O(3)-C(17)-C(18)	115.43(14)
C(16)-C(17)-C(18)	119.90(13)
C(19)-C(18)-C(17)	120.14(14)
C(19)-C(18)-H(18)	119.9
C(17)-C(18)-H(18)	119.9
C(18)-C(19)-C(14)	120.32(14)
C(18)-C(19)-H(19)	119.8
C(14)-C(19)-H(19)	119.8
C(17)-O(3)-C(20)	116.71(13)

O(3)-C(20)-H(20A)	109.5
O(3)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
O(3)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
O(2)-C(21)-C(3)	125.77(14)
O(2)-C(21)-H(21)	117.1
C(3)-C(21)-H(21)	117.1
O(1)-C(22)-C(11)	125.83(14)
O(1)-C(22)-H(22)	117.1
C(11)-C(22)-H(22)	117.1

Symmetry transformations used to generate equivalent atoms:

Table S6. Anisotropic displacement parameters (A^2 x 10^3) for 11rlr004_0m.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12] For BODIPY dye 6

	U11	U22	U33	U23	U13	U12
B(1)	19(1)	16(1)	17(1)	2(1)	-4(1)	-3(1)
F(1)	28(1)	31(1)	17(1)	3(1)	-2(1)	-11(1)
F(2)	27(1)	14(1)	32(1)	2(1)	-9(1)	0(1)
N(1)	18(1)	15(1)	15(1)	1(1)	-5(1)	-2(1)
N(2)	18(1)	13(1)	16(1)	0(1)	-2(1)	-3(1)
C(1)	26(1)	19(1)	20(1)	1(1)	-7(1)	-1(1)
C(2)	19(1)	16(1)	16(1)	-2(1)	-3(1)	-1(1)
C(3)	19(1)	15(1)	18(1)	-2(1)	-6(1)	-1(1)
C(4)	16(1)	14(1)	17(1)	-2(1)	-2(1)	-2(1)
C(5)	21(1)	18(1)	22(1)	2(1)	-6(1)	-6(1)
C(6)	17(1)	14(1)	15(1)	0(1)	-2(1)	-2(1)
C(7)	16(1)	14(1)	15(1)	-2(1)	-1(1)	0(1)
C(8)	17(1)	13(1)	15(1)	0(1)	-2(1)	-1(1)
C(9)	20(1)	19(1)	21(1)	1(1)	-7(1)	-4(1)
C(10)	17(1)	15(1)	16(1)	-3(1)	-2(1)	-2(1)
C(11)	18(1)	16(1)	16(1)	-3(1)	-2(1)	-3(1)
C(12)	18(1)	14(1)	19(1)	-2(1)	-2(1)	-3(1)
C(13)	27(1)	15(1)	24(1)	2(1)	-3(1)	-6(1)
C(14)	14(1)	15(1)	18(1)	1(1)	-4(1)	-3(1)
C(15)	20(1)	18(1)	18(1)	0(1)	-1(1)	-3(1)
C(16)	21(1)	16(1)	23(1)	0(1)	-2(1)	-2(1)
C(17)	16(1)	19(1)	20(1)	6(1)	-5(1)	-4(1)
C(18)	18(1)	23(1)	16(1)	2(1)	-2(1)	-3(1)
C(19)	17(1)	17(1)	18(1)	-1(1)	-3(1)	-2(1)

O(3)	27(1)	21(1)	23(1)	9(1)	-5(1)	-5(1)
C(20)	31(1)	18(1)	34(1)	7(1)	-13(1)	-7(1)
C(21)	22(1)	20(1)	20(1)	-3(1)	-8(1)	-3(1)
O(1)	23(1)	27(1)	22(1)	-3(1)	-6(1)	-6(1)
C(22)	21(1)	20(1)	20(1)	-3(1)	-2(1)	-7(1)
O(2)	26(1)	25(1)	25(1)	-2(1)	-8(1)	-9(1)

Table S7. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for 11rlr004_0m. For BODIPY dye 6

	x	y	z	U(eq)
H(1A)	4442	3757	5146	33
H(1B)	2767	2737	4925	33
H(1C)	5053	2471	4589	33
H(5A)	2242	-1919	7305	30
H(5B)	4054	-1918	7864	30
H(5C)	4363	-2752	7080	30
H(9A)	12703	304	8720	30
H(9B)	10877	-703	8638	30
H(9C)	10573	610	9195	30
H(13A)	10272	5067	5963	33
H(13B)	12458	4971	6287	33
H(13C)	10618	5825	6741	33
H(15)	8499	-2587	7347	22
H(16)	8544	-4782	8307	24
H(18)	6397	-2220	10073	23
H(19)	6413	-38	9112	21
H(20A)	7243	-6647	9283	42
H(20B)	8012	-7165	10160	42
H(20C)	9501	-6397	9448	42
H(21)	1266	510	5275	24
H(22)	13821	4294	7668	24

Absorption and Emission spectra of BODIPY dyes

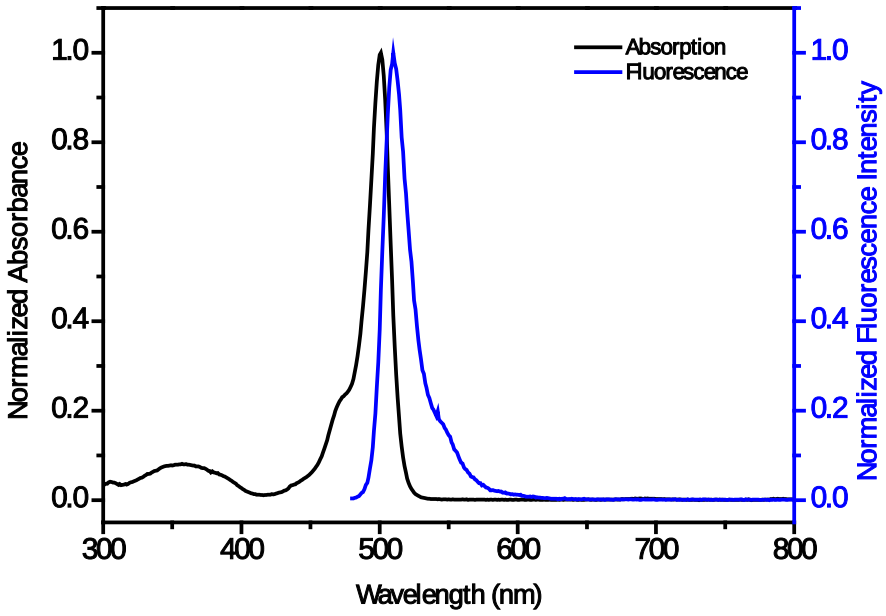

Figure S31. Normalized absorption and emission spectra of BODIPY dye **2** in methylene chloride solution (excitation wavelength was at 470 nm).

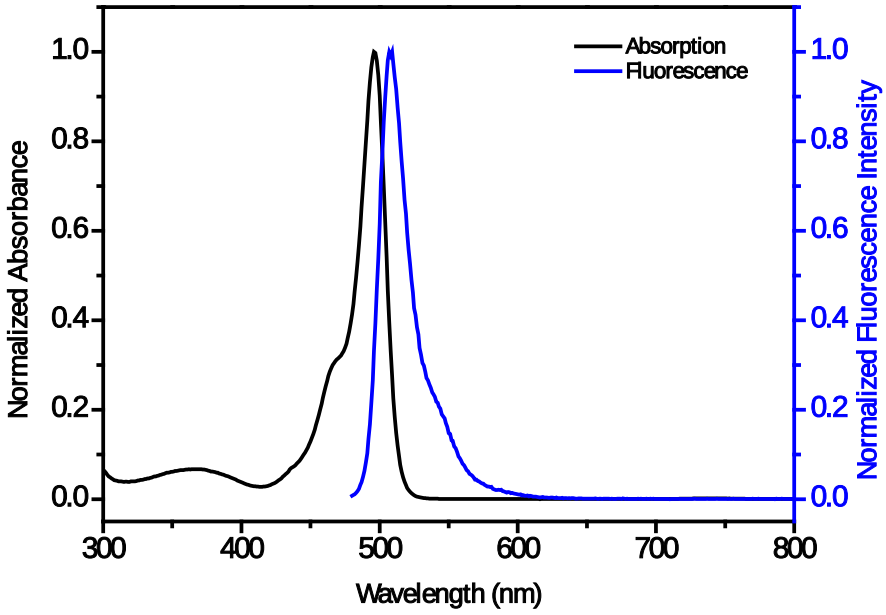

Figure S32. Normalized absorption and emission spectra of BODIPY dye **3** in methylene chloride solution (excitation wavelength was at 470 nm).

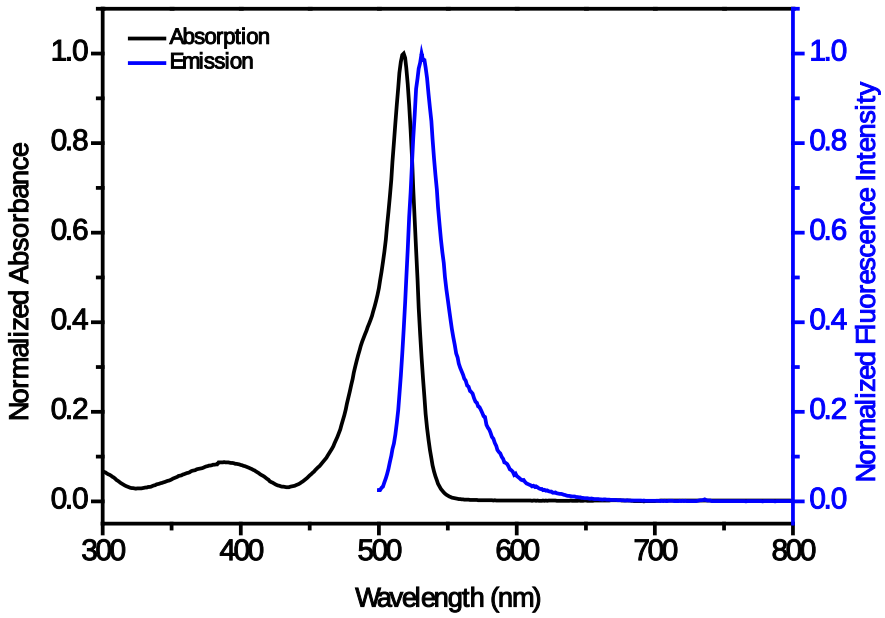

Figure S33. Normalized absorption and emission spectra of BODIPY dye **4** in methylene chloride solution (excitation wavelength was at 490 nm)

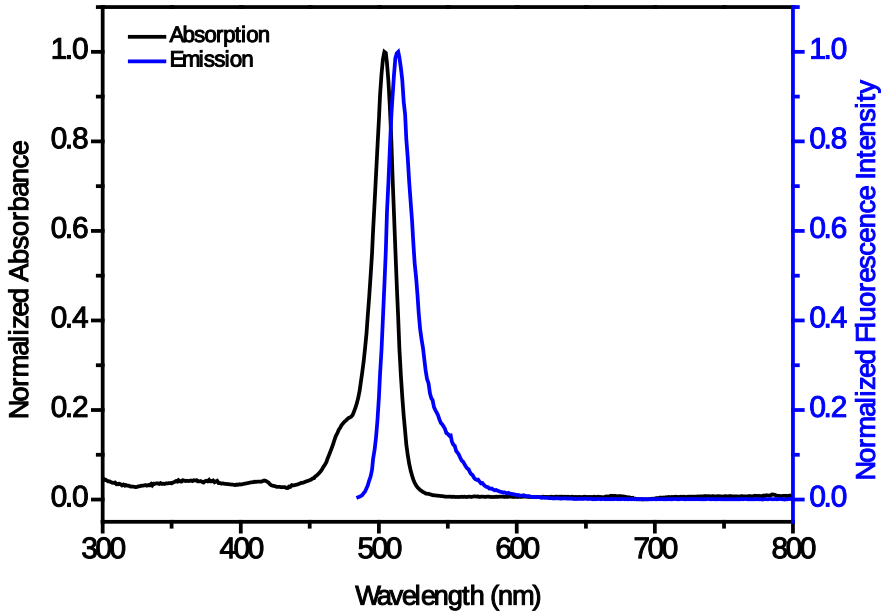

Figure S34. Normalized absorption and emission spectra of BODIPY dye **6** in methylene chloride solution (excitation wavelength was at 475 nm)

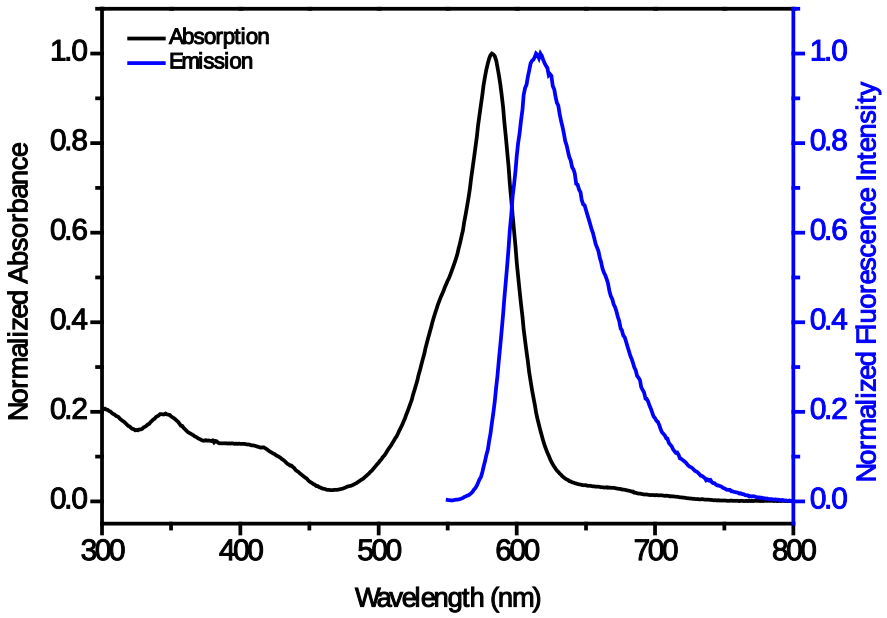

Figure S35. Normalized absorption and emission spectra of BODIPY dye **A** in methylene chloride solution (excitation wavelength was at 540 nm)

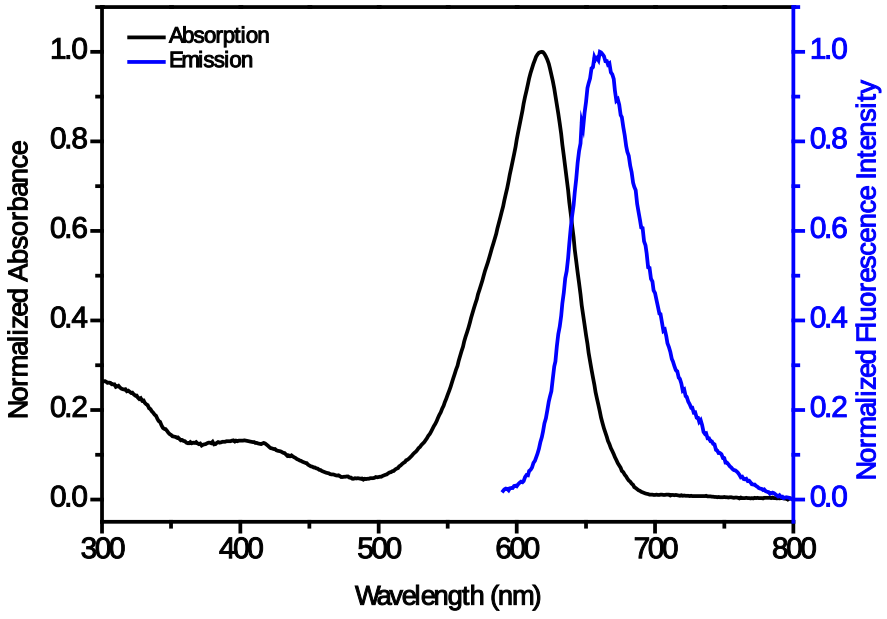

Figure S36. Normalized absorption and emission spectra of BODIPY dye **B** in methylene chloride solution (excitation wavelength was at 580 nm)

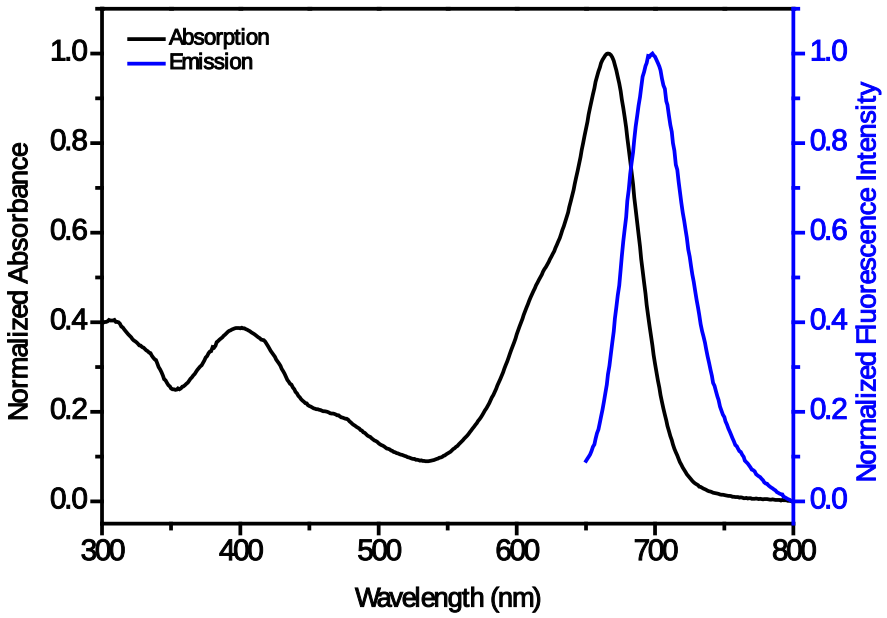

Figure S37. Normalized absorption and emission spectra of BODIPY dye **C** in methylene chloride solution (excitation wavelength was at 640 nm)

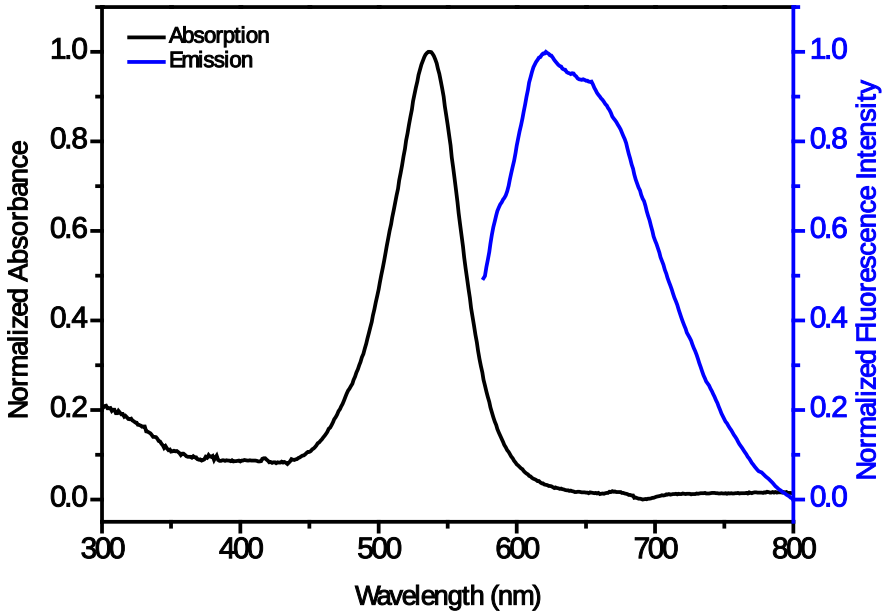

Figure S38. Normalized absorption and emission spectra of BODIPY dye $\mathbf{D_a}$ in methylene chloride solution (excitation wavelength was at 550 nm)

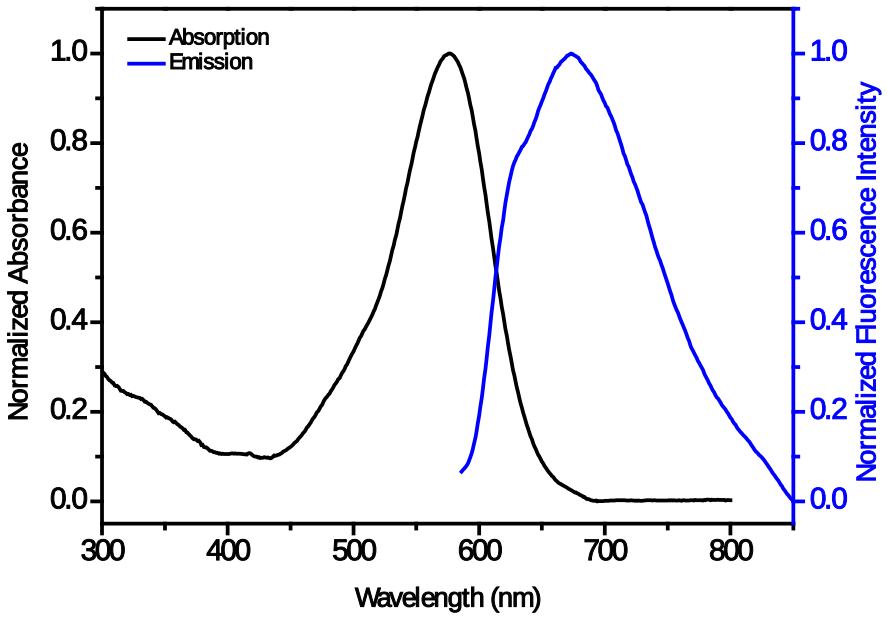

Figure S39. Normalized absorption and emission spectra of BODIPY dye $\mathbf{E_a}$ in methylene chloride solution (excitation wavelength was at 560 nm)

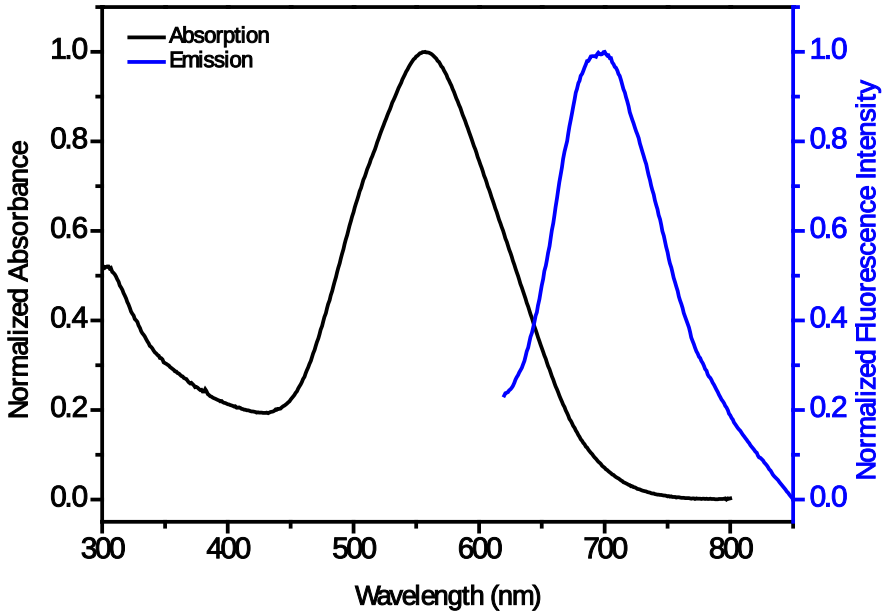

Figure S40. Normalized absorption and emission spectra of BODIPY dye $\mathbf{E_b}$ (4 μM) in aqueous solution (excitation wavelength was at 550 nm).

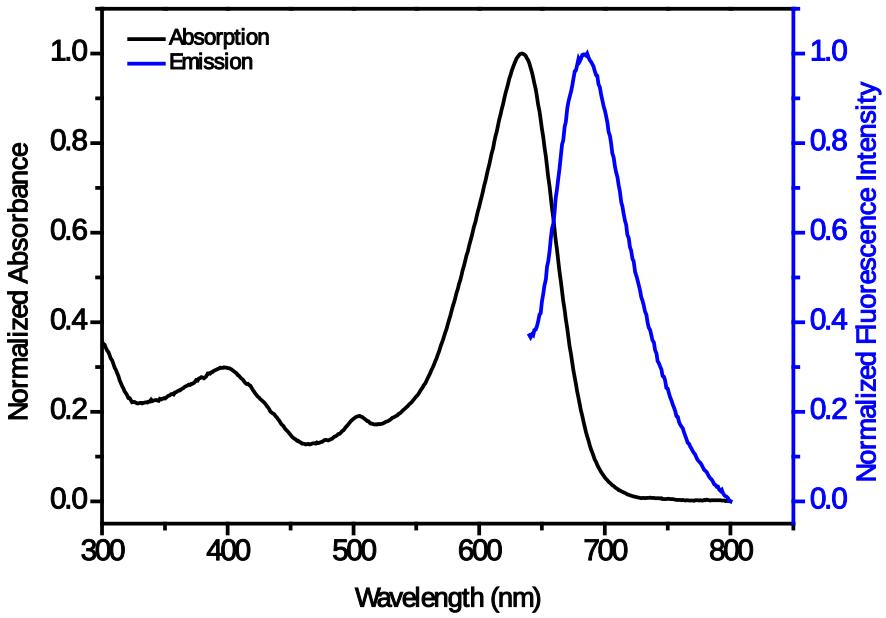

Figure S41. Normalized absorption and emission spectra of BODIPY dye $\mathbf{F_a}$ in methylene chloride solution (excitation wavelength was at 630 nm).

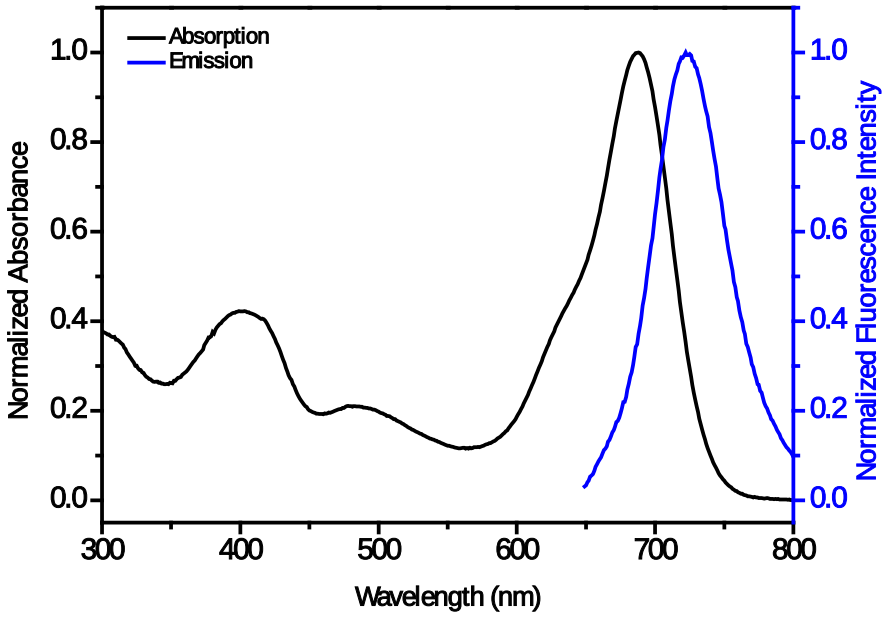

Figure S42. Normalized absorption and emission spectra of BODIPY dye $\mathbf{G_a}$ in methylene chloride solution (excitation wavelength was at 630 nm).

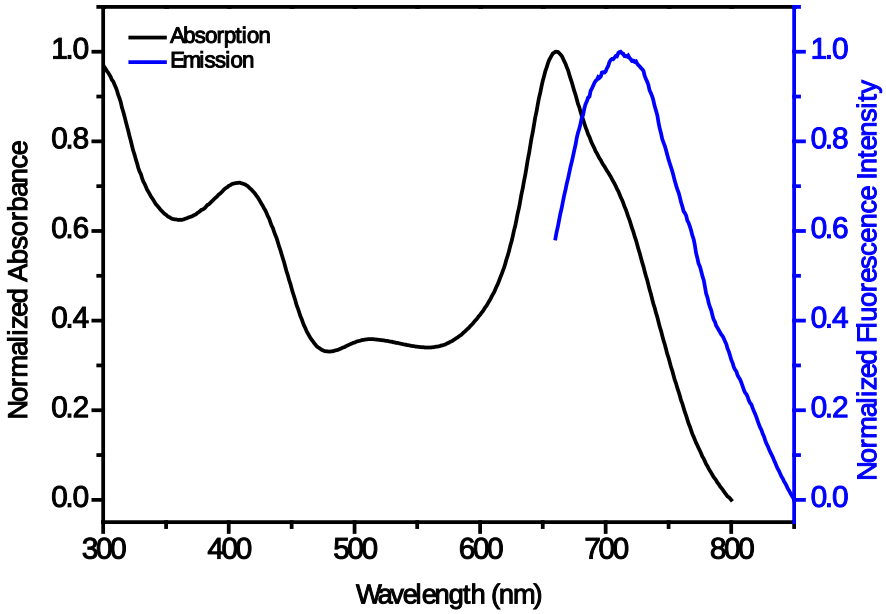

Figure S43. Normalized absorption and emission spectra of BODIPY dye $\mathbf{G_b}$ (4 μM) in aqueous solution (excitation wavelength was at 650 nm).

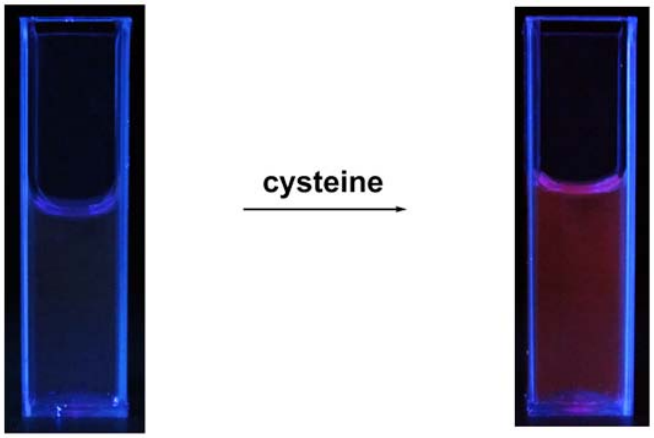

Figure S44. Visualized Images of BODIPY dye $\mathbf{E_b}$ (20 μM) in 0.01M PBS buffer pH 7.4 in the absence and presence of L-cysteine (10 mM). Images were taken under a transilluminator. Excitation wavelength was at 470 nm.

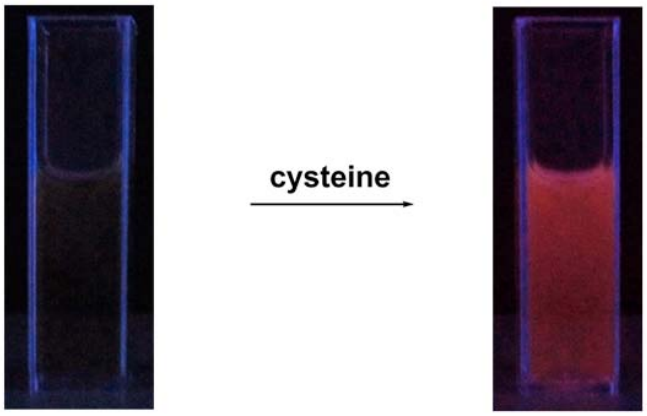

Figure S45. Visualized images of BODIPY dye $\mathbf{G_b}$ (20 μM) in 0.01M PBS buffer pH 7.4 in the absence and presence of L-cysteine (10 mM). Images were taken under a transilluminator. Excitation wavelength was at 470 nm.

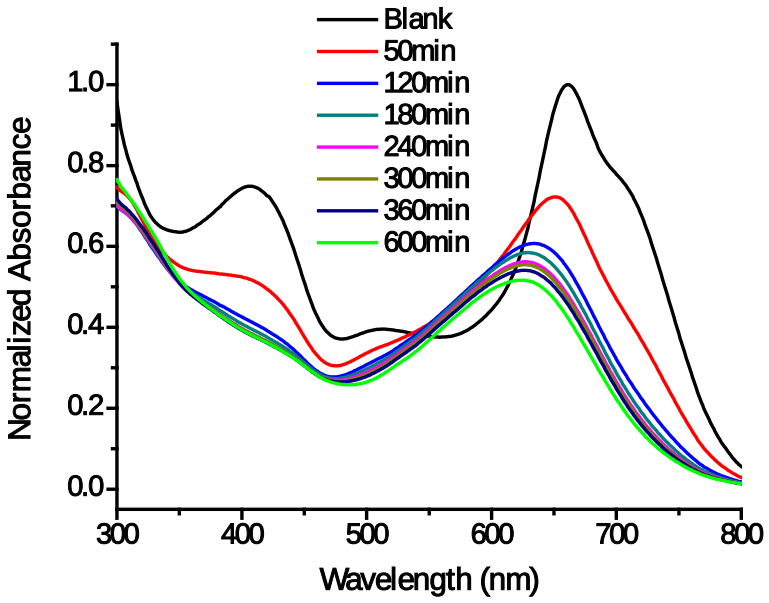

Figure S46. Normalized absorption spectra of BODIPY dye **G$_b$** (20 μM) in 0.01 M PBS buffer pH 7.4 in the absence and presence of L-cysteine (10 mM) at different times.

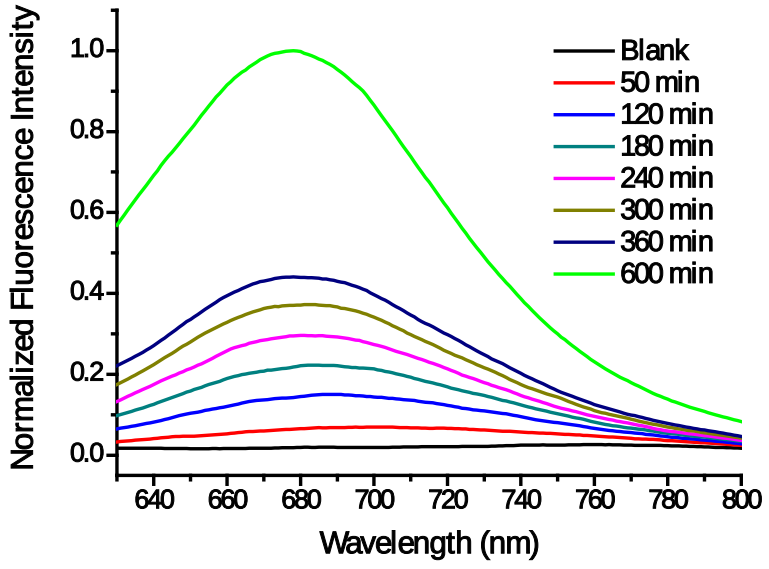

Figure S47. Normalized fluorescence spectra of BODIPY dye **G$_b$** (20 μM) in 0.01 M PBS buffer pH 7.4 in the absence and presence of L-cysteine (10 mM) at different times. Excitation wavelength was at 620 nm.

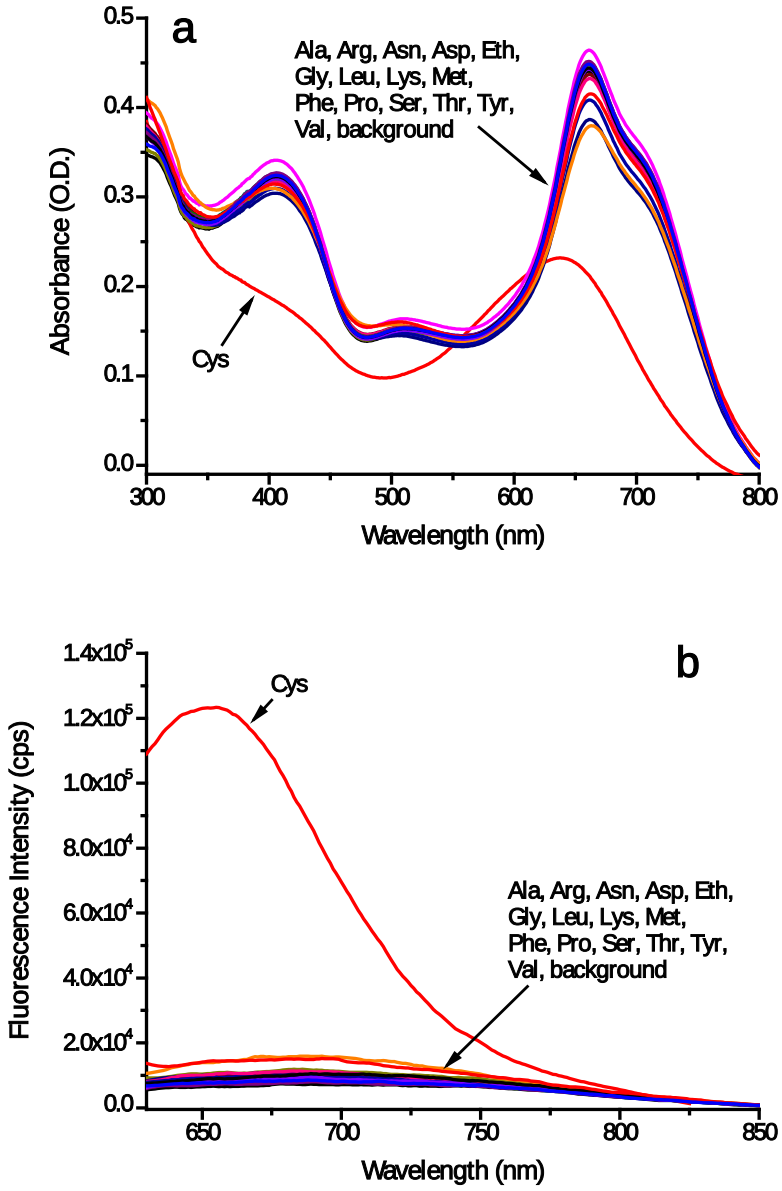

Figure S48. Absorption (a) and Emission (b) spectra of BODIPY dye $\mathbf{G_b}$ (10 μM) in the absence and presence of various amino acids (5 mM). (λ_{ex}=620 nm)

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