Electronic Supplementary Information

For

Meso-Substitution Controlled Synthesis of BODIPY–DPM Conjugates: A Pathway to Tailored Photophysical Properties

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1. Experimental Section

1.1 General Information and Instrumentation

All chemicals and reagents were obtained from commercial suppliers (Merck, TCI Chemicals (India), and BLD Pharma) and used as received unless otherwise stated. Literature procedures were followed for the preparation of precursors.[1,2] Reactions were carried out under an inert atmosphere in dry DMF unless otherwise noted. Reaction progress was monitored by thin-layer chromatography (TLC) using silica gel 60 F254 aluminum-backed plates (Merck). Microwave-assisted reactions were performed in a Monowave 300 microwave synthesis reactor (Anton Paar). Column chromatography was performed using silica gel (100–200 mesh). NMR spectra were recorded at 298 K on a Bruker AVANCE II spectrometer (^{1}H NMR: 400 MHz; ^{13}C NMR: 100 MHz; ^{19}F NMR: 370 MHz) using $CDCl_3$ or DMSO-d_6 as solvents. Chemical shifts (δ) are reported in ppm relative to residual solvent signals (^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26; ^{13}C NMR (100 MHz, $CDCl_3$): δ 77.0; ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.50; ^{13}C NMR (100 MHz, DMSO-d_6): δ 39.5). Multiplicities are designated as s, d, t, q, or m; coupling constants (*J*) are given in Hz. High-resolution mass spectra (HRMS) were recorded using electrospray ionization (ESI). UV/Vis absorption spectra were recorded on a Jasco V-650 spectrophotometer. Steady-state fluorescence spectra were obtained using a FluoroMax Plus spectrofluorometer with a 10 mm path-length quartz cuvette. Fluorescence lifetime measurements were performed on a Fluorolog-3 spectrofluorometer (HORIBA) equipped with a single-photon counting module, a NanoLED excitation source (λ = 525 nm), and an R928 photomultiplier tube detector. Single-crystal X-ray diffraction data were collected on a Rigaku Oxford Diffraction XtaLAB instrument equipped with a CCD detector. Structures were solved and refined using Olex2 and SHELXL by full-matrix least-squares refinement.[3,4]
The ground-state (S0) geometries were optimized using density functional theory (DFT) with the Gaussian 16 program at the B3LYP-D3BJ/6-31G(d) level of theory. The first excited singlet state (S1) geometries were optimized at the same level using time-dependent DFT (TD-DFT). Spin-orbit coupling matrix elements (SOCMEs) between the five lowest singlet and triplet states were calculated at the B3LYP-D3BJ/6-31G(d) level using the Orca 5.0.3 software package.[5]

1. Synthetic Procedures

General Procedure 1: Synthetic procedure for the compounds 2, 7, and 9
In a microwave reaction vial, meso-aryl-1,3,5,7-tetramethyl BODIPY (1.0 equiv.) and pyrrole-2-aldehyde (1.2 to 4.0 equiv.) were dissolved in dry DMF. Acetic acid (12 equiv.) and piperidine (20 equiv.) were added, and the reaction mixture was purged with nitrogen. The sealed tube was subjected to microwave irradiation at 150 °C for 5–10 min. Reaction progress was monitored by thin-layer chromatography (TLC). After completion, the reaction mixture was diluted with dichloromethane (DCM) and washed successively with aqueous $NaHCO_3$ solution and brine. The organic layer was extracted using DCM, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (100–200 mesh) to afford the desired BODIPY derivative.

General Procedure 2: Synthetic procedure for the compounds 3,6, and 8
In a microwave reaction vial, meso-aryl-1,3,5,7-tetramethyl BODIPY (1.0 equiv.) and pyrrole-2-aldehyde (2.2 to 10.0 equiv.) were dissolved in dry DMF. Acetic acid (12 equiv.) and piperidine (20 equiv.) were added, and the reaction mixture was purged with nitrogen. The sealed tube was subjected to microwave irradiation at 150 °C for 5–10 min. Reaction progress was monitored by thin-layer chromatography (TLC). After completion, the reaction mixture was diluted with dichloromethane (DCM) and washed successively with aqueous $NaHCO_3$ solution and brine. The organic layer was extracted using DCM, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced

pressure. The crude product was purified by column chromatography on silica gel (100–200 mesh) to afford the desired BODIPY derivative.

General Procedure 3: Synthetic procedure for the compounds 10-13

In a microwave reaction vial, meso-tolyl-1,3,5,7-tetramethyl BODIPY (1.0 equiv.) and meso-aryl-1,9-diformyl dipyrromethane (1.5 equiv.) were dissolved in dry DMF. Acetic acid (12 equiv.) and piperidine (20 equiv.) were added, and the reaction mixture was purged with nitrogen. The sealed tube was subjected to microwave irradiation at 150 °C for 10 minutes. Reaction progress was monitored by thin-layer chromatography (TLC). After completion, the reaction mixture was diluted with dichloromethane (DCM) and washed successively with aqueous $NaHCO_3$ solution and brine. The organic layer was extracted using DCM, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (100–200 mesh) to afford the desired BODIPY derivative.

General Procedure 4: Synthetic procedure for the compounds 14-17

In a microwave reaction vial, meso-pentafluorophenyl-1,3,5,7-tetramethyl BODIPY (1.0 equiv.) and meso-aryl-1,9-diformyl dipyrromethane (1.5 equiv.) were dissolved in dry DMF. Acetic acid (12 equiv.) and piperidine (20 equiv.) were added, and the reaction mixture was purged with nitrogen. The sealed tube was subjected to microwave irradiation at 150 °C for 10 minutes. Reaction progress was monitored by thin-layer chromatography (TLC). After completion, the reaction mixture was diluted with dichloromethane (DCM) and washed successively with aqueous $NaHCO_3$ solution and brine. The organic layer was extracted using DCM, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (100–200 mesh) to afford the desired BODIPY derivative.

1-(2-Vinylpyrrole)-3,5,7-trimethyl-meso-tolyl BODIPY (2)

This compound was synthesized using the general procedure 1. A reaction of meso-tolyl-1,3,5,7-tetramethyl BODIPY (**1**) (40 mg, 0.118 mmol, 1.0 equiv.) with pyrrole-2-aldehyde (45 mg, 0.473 mmol, 4.0 equiv.), in dry DMF (1 mL), with acetic acid (12 equiv.) and piperidine (20 equiv.) was performed at 150 ^{o}C under microwave irradiation for 10 min. After completion, the reaction mixture was diluted with dichloromethane (DCM) and washed successively with aqueous $NaHCO_3$ solution and brine. The organic layer was extracted using DCM, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude reaction mixture was subjected to column chromatography and desired compound was eluted as blue band using 1:1 to 3:2 DCM/hexane. Yield: 61%, 30 mg. M.p. = 223 °C (dec.). R_f = 0.75 (DCM: Hexane, 9:1).^{1}H NMR: (400 MHz, $CDCl_3$): δ 9.04 (s, 1H), 7.28 (d, *J* = 7.8 Hz, 2H), 7.16 (d, *J* = 8.1 Hz, 2H), 7.13 (d, J = 8.9 Hz, 2H), 6.93 (q, *J* = 6.72, 1.9 Hz, 1H), 6.53 (s, 1H), 6.44 (m, 1H), 6.28 – 6.23 (m, 1H), 5.97 (s, 1H), 2.56 (s, 3H), 2.44 (s, 3H), 1.44 (s, 3H), 1.40 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 142.5, 139.0, 135.5, 134.7, 131.9, 129.8, 128.8, 128.1, 122.8, 119.8, 117.8, 21.4, 14.7 ppm. HRMS (ESI) m/z calcd. for $C_{25}H_{24}BF_2N_3$ $(M)^+$ 415.2031 found: 415.2063. UV-Vis. (DCM), λ_{max} (log ε): 345 (4.10), 545 (sh) (4.22), 584 (4.65).

1,7-Bis(2-vinylpyrrole)-3,5-dimethyl-meso-tolyl BODIPY (3)

This compound was synthesized by using the general procedure 2. A reaction of meso-tolyl-1,3,5,7-tetramethyl BODIPY (**1**) (40 mg, 0.118 mmol, 1.0 equiv.) with pyrrole-2-aldehyde (112 mg, 1.18 mmol, 10.0 equiv.), in dry DMF (1 mL), with acetic acid (12 equiv.) and piperidine (20 equiv.)was performed at 150 ^{o}C under microwave irradiation for 10 min. After completion, the reaction mixture was diluted with dichloromethane (DCM) and washed successively with aqueous $NaHCO_3$ solution and brine. The organic layer was extracted using DCM, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude reaction mixture was subjected to column chromatography and desired compound was eluted as green band using 1:1 to 4:1 DCM/hexane. Yield: 72%,42 mg. M.p = 300 °C (dec). R_f = 0.71(DCM: Hexane, 9:1). ^{1}H NMR: (400 MHz, $CDCl_3$): δ 9.60 (s, 2H), 7.44 (d, *J* = 16.3 Hz, 2H), 7.31 (d, *J* = 7.8 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.01 (s, 2H), 6.59 (s, 2H), 6.52 (s,

2H), 6.28 (s, 2H), 6.14 (s, 2H), 2.46 (s, 3H), 1.48 (s, 6H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.4, 141.3, 138.7, 133.0, 132.2, 130.8, 129.6, 128.6, 126.1, 122.1, 117.0, 113.9, 112.3, 110.1, 21.5, 14.7 ppm. HRMS (ESI) m/z calcd. for $C_{30}H_{28}BF_2N_4$ $[M+H]^+$ 493.2370 found: 493.2376. UV-Vis. (DCM), λ_{max} (log ε): 384 (4.41), 618 (sh) (4.23), 670 (4.65).

1,7-Bis(2-vinylpyrrole)-3,5-dimethyl-meso-(4-nitrophenyl) BODIPY (6)

This compound was synthesized by using the general procedure 2. A reaction of meso-(4-nitrophenyl)-1,3,5,7-tetramethyl BODIPY (**4**) (40 mg, 0.108 mmol, 1.0 equiv.) with pyrrole-2-aldehyde (22.52 mg, 0.237 mmol, 2.2 equiv.), in dry DMF (1 mL), with acetic acid (12 equiv.) and piperidine (20 equiv.) was performed at 150 °C under microwave irradiation for 5 min. After completion, the reaction mixture was diluted with dichloromethane (DCM) and washed successively with aqueous $NaHCO_3$ solution and brine. The organic layer was extracted using DCM, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude reaction mixture was subjected to column chromatography and desired compound was eluted as green band using 1:1 DCM/hexane to DCM. Yield: 67%, 38 mg. M.p = 303 °C (dec). R_f = 0.85 (DCM). ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.57 (s, 2H), 8.39 (d, J = 8.3 Hz, 2H), 7.78 (d, J = 8.3 Hz, 2H), 7.32 (d, J = 16.2 Hz, 2H), 7.18 (d, J = 16.2 Hz, 2H), 7.02 – 7.00 (m, 2H), 6.82 (s, 2H), 6.49 (m, 2H), 6.21 (m, 2H), 1.38 (s, 6H) ppm. ^{13}C NMR (101 MHz, DMSO): δ 153.1, 148.3, 142.1, 140.4, 133.3, 132.0, 131.3, 130.9, 128.1, 124.5, 123.5, 118.3, 112.8, 112.7, 110.9, 79.7, 79.4, 79.1, 31.1, 14.9 ppm. HRMS (ESI) m/z calcd. for $C_{29}H_{24}BF_2N_5O_2$ $[M+H]^+$ 523.1991 found: 523.2005. UV-Vis. (DCM), λ_{max} (log ε): 351 (3.45), 555 (sh) (2.98), 595 (3.40).

1-(2-Vinylpyrrole)-3,5,7-trimethyl-meso-(4-nitrophenyl) BODIPY (7)

This compound was synthesized by using the general procedure 1. A reaction of meso-(4-nitrophenyl)-1,3,5,7-tetramethyl BODIPY (**4**) (40 mg, 0.108 mmol, 1.0 equiv.) with pyrrole-2-aldehyde (12.35 mg, 0.130 mmol, 1.2 equiv.) in dry DMF (1 mL) with 12 equiv. of acetic acid and 20 equiv. of piperidine was performed at 150 °C under microwave irradiation for 5 min. After completion, the reaction mixture was diluted with dichloromethane (DCM) and washed successively with aqueous $NaHCO_3$ solution and brine. The organic layer was extracted using DCM, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude reaction mixture was subjected to column chromatography, and the desired compound was eluted as a blue band using 1:1 to 3:2 DCM/hexane. Yield: 61%, 32 mg. M.p. = 225 °C (dec). R_f = 0.80 (DCM: Hexane, 4:1). ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.75 (s, 1H), 8.39 (d, J = 8.7 Hz, 2H), 7.76 (d, J = 8.7 Hz, 2H), 7.43 (d, J = 16.1 Hz, 1H), 7.14 (d, J = 16.2 Hz, 1H), 7.04 (q, J = 1.3 Hz, 1H), 6.92 (s, 1H), 6.52 (m, 1H), 6.25 – 6.19 (m, 1H), 6.14 (s, 1H), 2.47 (s, 3H), 1.39 (s, 3H), 1.33 (s, 3H) ppm. ^{13}C NMR: (101 MHz, DMSO-d_6): δ 148.4, 142.9, 141.8, 139.5, 136.0, 130.9, 130.6, 130.3, 124.6, 121.0, 119.3, 115.0, 111.8, 111.0, 15.1, 14.6, 14.6 ppm. HRMS (ESI) m/z calcd. for $C_{24}H_{21}BF_2N_4O_2$ $[M^+]$ 446.1726 found: 446.1735. UV-Vis. (DCM), λ_{max} (log ε): 391 (2.71), 630 (sh) (2.82), 684 (1.90).

1,7-Bis(2-vinylpyrrole)-3,5-dimethyl-meso-(tetrafluoro-4-piperidin-1-yl)phenyl BODIPY (8)

This compound was synthesized by using the general procedure 2. A reaction of meso-pentafluorophenyl-1,3,5,7-tetramethyl BODIPY (**5**) (40 mg, 0.096 mmol, 1.0 equiv.) with pyrrole-2-aldehyde (20 mg, 0.211 mmol, 2.2 equiv.), in dry DMF (1 mL) with acetic acid (12 equiv.) and piperidine (20 equiv.) was performed at 150 °C under microwave irradiation for 7 min. After completion, the reaction mixture was diluted with dichloromethane (DCM) and washed successively with aqueous $NaHCO_3$ solution and brine. The organic layer was extracted using DCM, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude reaction mixture was subjected to column chromatography, and the desired compound was eluted as a green band using 1:1 to 3:2 DCM/hexane. Yield: 74%, 45 mg. M.p = 300 °C (dec). R_f = 0.6 (DCM: Hexane, 4:1).^{1}H NMR (400 MHz, $CDCl_3$): 9.80 (s, 2H), 7.54 (d, J = 16.2 Hz, 2H), 6.96 (d, J = 16.2 Hz, 2H), 6.57 (s, 2H), 6.50 (s, 2H), 6.25 (s, 2H), 6.09 (m, 2H), 3.35 – 3.28 (m, 4H), 1.74 (s, 9H), 1.68 (s, 3H) ppm. ^{13}C NMR: (101 MHz, $CDCl_3$) δ 153.5, 139.6, 132.9, 130.7, 127.3, 122.8, 117.7, 114.9, 111.7,

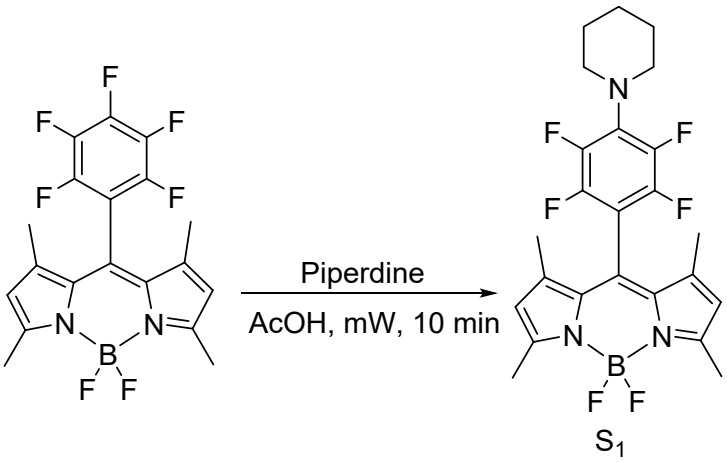
110.2, 52.4, 29.7, 26.4, 24.0, 13.7 ppm. HRMS (ESI) m/z calcd. for $C_{34}H_{30}BF_6N_5$ $[M+H]^+$ 634.2577 found: 634.2586. UV-Vis. (DCM), λ_{max} (log ε): 353 (3.87), 564 (sh) (3.30), 606 (3.78).

1-(2-Vinylpyrrole)-3,5,7-trimethyl-meso-(tetrafluoro-4-piperidin-1-yl)phenyl BODIPY (9)

This compound was synthesized by using a general procedure 1. A reaction of meso-pentafluorophenyl-1,3,5,7-tetramethyl BODIPY (**5**) (40 mg, 0.096 mmol, 1.0 equiv.) with pyrrole-2-aldehyde (11 mg, 0.115 mmol, 1.2 equiv.), in dry DMF (1 mL), with acetic acid (12 equiv.) and piperidine (20 equiv.) was performed at 150 °C under microwave irradiation for 7 min. After completion, the reaction mixture was diluted with dichloromethane (DCM) and washed successively with aqueous $NaHCO_3$ solution and brine. The organic layer was extracted using DCM, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude reaction mixture was subjected to column chromatography, and the desired compound was eluted as a blue band using 1:1 to 3:2 DCM/hexane. Yield: 65%, 35 mg. M.p. = 222 °C. R_f = 0.62 (DCM: Hexane, 4:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.97 (s, 1H), 7.16 (s, 2H), 6.95 (s, 1H), 6.60 (s, 1H), 6.49 (m, 1H), 6.29 (s, 1H), 6.03 (s, 1H), 3.30 (s, 3H), 3.07 (s, 3H), 2.58 (s, 3H), 1.71 (s, 2H), 1.69 (d, *J* = 3.6 Hz, 3H), 1.66 (d, *J* = 3.5 Hz, 6H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 155.0, 154.2, 130.5, 127.5, 122.6, 121.0, 118.1, 114.6, 112.5, 111.0, 52.4, 43.2, 26.4, 24.0, 14.6, 13.8, 13.4 ppm. HRMS (ESI) m/z calcd. for $C_{29}H_{27}BF_6N_4$ $[M+H]^+$ 557.2311 found: 557.2320. UV-Vis. (DCM), λ_{max} (log ε): 394 (2.88), 642 (sh) (2.95), 699 (2.31).

Meso-(tetrafluoro-4-piperidin-1-yl)phenyl-1,3,5,7-tetramethyl BODIPY (S1)

meso-Pentafluorophenyl-1,3,5,7-tetramethyl BODIPY **(5)** (50 mg, 0.120 mmol) was dissolved in dry DMF (1 mL), and acetic acid (12 equiv.) followed by piperidine (20 equiv.) were added to the reaction mixture under an inert atmosphere. The reaction mixture was subjected to microwave irradiation at 150 °C for 10 min. After completion, the reaction mixture was diluted with DCM, washed with $NaHCO_3$, and the organic layer was extracted with DCM (2 × 100 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by column chromatography on silica gel using 50% DCM/hexane as the eluent to afford the desired product. Yield: 52%, 30 mg. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.03 (s, 2H), 3.30 – 3.27 (m, 4H), 2.56 (d, *J* = 1.3 Hz, 6H), 1.74 – 1.69 (m, 4H) 1.65 (s, 8H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 156.9, 141.9, 131.5, 125.1, 121.8, 52.4, 26.4, 24.0, 14.7, 13.5 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ -142.62 – -142.79 (m), -146.20 (q, *J* = 65.0, 32.4 Hz), -150.05 – -150.23 (m). HRMS (ESI) m/z calcd. for $C_{24}H_{24}BF_6N_3$ $[M+H]^+$ 480.2045 found: 480.2013.



Scheme S1. Synthesis of Meso-(tetrafluoro-4-piperidin-1-yl)phenyl-1,3,5,7-tetramethyl BODIPY (**S1**).

1-(1-Vinyl-5-phenyl-9-formyldipyrromethane)-3,5,7-trimethyl-meso-tolyl BODIPY (10)

Compound **10** was synthesized according to General Procedure 3. Meso-tolyl-1,3,5,7-tetramethyl BODIPY (**1**) (40 mg, 0.118 mmol, 1.0 equiv.) and 1,9-diformyl-5-phenyl-dipyrromethane (47.0 mg, 0.177 mmol, 1.5 equiv.) were dissolved in dry DMF (1 mL) under an inert atmosphere. After that, acetic acid (12 equiv.) and piperidine (20 equiv.) were added to the reaction mixture and heated at 150 °C under microwave irradiation for 10 min. After completion, the reaction mixture was diluted with dichloromethane (DCM) and washed successively with aqueous $NaHCO_3$ solution and brine. The organic layer was extracted using DCM, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude reaction mixture was subjected to column chromatography, and the desired compound was eluted as a green band using a 1:1 to 4:1 DCM/hexane gradient. Yield: 64%, 45 mg. M.p. = 280 °C, R_f = 0.45 (DCM: Hexane, 9:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.40 (s, 1H), 9.31 (s, 1H), 9.20 (s, 1H), 7.38 – 7.27 (m, 5H), 7.21 (d, *J* = 6.9 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 9.6 Hz, 2H), 6.92 (dd, J= 2.1 Hz, 1H), 6.51 (s, 1H), 6.37 – 6.35 (m, 1H), 6.13 (dd, *J* = 2.1 Hz, 1H), 5.95 (d, *J* = 6.2 Hz, 2H), 5.50 (s, 1H), 2.52 (s, 3H), 2.43 (s, 3H), 1.42 (s, 3H), 1.39 (s, 3H).^{13}C NMR:(101 MHz, $CDCl_3$): δ 178.8, 141.5, 139.8, 139.4, 138.7, 136.0, 132.5, 132.1, 131.1, 129.7, 129.0, 128.3, 128.1, 127.6, 126.4, 122.1, 120.5, 117.3, 114.4, 112.6, 111.0, 110.5, 44.4, 29.7, 29.6, 22.7, 21.4, 14.7, 14.5, 14.3, 14.1 ppm. HRMS (ESI) m/z calcd. for $C_{37}H_{33}BF_2N_4O$[M-H]$^-$ 597.2649 found: 597.2649. UV-Vis. (DCM), λ_{max} (log ε). 353 (4.37), 405 (sh) (3.97), 556 (sh) (4.50), 593 (4.87).

1-(1-Vinyl-5-tolyl-9-formyldipyrromethane)-3,5,7-trimethyl-meso-tolyl BODIPY (11)

Compound **11** was synthesized according to General Procedure 3. Meso-tolyl-1,3,5,7-tetramethyl BODIPY (**1**) (40 mg, 0.118 mmol, 1.0 equiv.) and 1,9-diformyl-5-tolyl-dipyrromethane (52 mg, 0.177 mmol), were dissolved in dry DMF (1 mL) under an inert atmosphere. After that acetic acid (12 equiv.) and piperidine (20 equiv.) were added to the reaction mixture and heated at 150 °C under microwave irradiation for 10 min. After completion, the reaction mixture was diluted with dichloromethane (DCM) and washed successively with aqueous $NaHCO_3$ solution and brine. The organic layer was extracted using DCM, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude reaction mixture was subjected to column chromatography, and the desired compound was eluted as a green band using a 1:1 to 4:1 DCM/hexane gradient. Yield: 65%, 47 mg. M.p.= 280 °C. R_f = 0.82 (DCM: Hexane, 9:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.38 (s, 1H), 9.29 (s, 1H), 9.02 (s, 1H), 7.14 (q, *J* = 3.5 Hz, 5H), 7.10 – 6.98 (m, 5H), 6.91 (m, 1H), 6.50 (s, 1H), 6.36 (t, *J* = 3.0 Hz, 1H), 6.13 – 6.09 (m, 1H), 5.97 – 5.91 (m, 2H), 5.45 (s, 1H), 2.52 (s, 3H), 2.43 (s, 3H), 2.34 (s, 3H), 1.41 (s, 3H), 1.38 (s, 3H) ppm.^{13}C NMR(101 MHz, $CDCl_3$): δ 178.7, 141.7, 139.4, 138.7, 137.4, 136.6, 136.1, 132.4, 132.1, 131.0, 129.7, 129.7, 128.2, 128.1, 126.3, 120.5, 117.3, 114.3, 112.6, 110.9, 110.4, 46.8, 44.0, 40.6, 31.6, 29.7, 26.9, 26.6, 25.1, 24.7, 22.6, 22.6, 21.4, 21.0, 14.7, 14.5, 14.3, 14.1, 11.4 ppm. HRMS (ESI) m/z calcd. for $C_{38}H_{35}BF_2N_4O$ [M-H]$^-$ 611.2806 found: 611.2794. UV-Vis. (DCM) λ_{max} (log ε): 354 (4.28), 406 (sh) (3.86), 557 (sh) (4.42), 594 (4.80) ppm.

1-(1-Vinyl-5-(4-bromophenyl)-9-formyldipyrromethane)-3,5,7-trimethyl-meso-tolyl BODIPY (12)

Compound **12** was synthesized according to General Procedure 3. Meso-tolyl-1,3,5,7-tetramethyl BODIPY (**1**) (40 mg, 0.118 mmol, 1.0 equiv.) and 1,9-diformyl-5-(4-bromophenyl)-dipyrromethane (63.37 mg, 0.177 mmol), were dissolved in dry DMF (1 mL) under an inert atmosphere. After that, acetic acid (12 equiv.) and piperidine (20 equiv.) were added to the reaction mixture and heated at 150 °C under microwave irradiation for 10 min. After completion, the reaction mixture was diluted with dichloromethane (DCM) and washed successively with aqueous $NaHCO_3$ solution and brine. The organic layer was extracted using DCM, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude reaction mixture was subjected to column chromatography, and the desired compound was eluted as a green band using 1:1 to 4:1 DCM/hexane. Yield 62%. M.p. = 282 °C. R_f = 0.75 (DCM: Hexane, 9:1).^{1}H NMR (400 MHz, $CDCl_3$): δ 9.60 (s, 1H), 9.45 (s, 1H), 9.37 (s, 1H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.19 – 6.99 (m, 8H), 6.93 – 6.91 (m, 1H), 6.51 (s, 1H), 6.36 – 6.33 (m, 1H), 6.10 – 6.05 (m, 1H), 5.97 (s, 1H), 5.92 – 5.89 (m, 1H), 5.44 (s, 1H), 2.51 (s, 3H), 2.43 (s,

3H), 1.42 (s, 3H), 1.39 (s, 3H) ppm.^{13}C NMR (101 MHz, $CDCl_3$): δ 132.6, 132.0, 131.3, 130.0, 129.7, 128.1, 121.5, 111.1, 110.5, 43.8, 31.6, 31.6, 29.7, 29.6, 29.0, 26.9, 22.6, 22.6, 21.4, 14.7 ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 132.6, 132.0, 131.3, 130.0, 129.7, 128.1, 121.5, 111.1, 110.5, 43.8, 31.6, 31.6, 29.7, 29.6, 29.0, 26.9, 22.6, 22.6, 21.4, 14.7 ppm. HRMS (ESI) m/z calcd. for $C_{37}H_{32}BBrF_2N_4O$ $[M-H]^-$ 677.1740 found: 677.1756. UV-Vis. (DCM) λ_{max} (log ε): 353 (4.36), 402 (sh) (3.93), 554 (sh) (4.48), 592 (4.87).

1-(1-Vinyl-5-pentafluorophenyl-9-formyldipyrromethane)-3,5,7-trimethyl-meso-tolyl BODIPY (13)

Compound **13** was synthesized according to General Procedure 3. Meso-tolyl-1,3,5,7-tetramethyl BODIPY (**1**) (40 mg, 0.118 mmol, 1.0 equiv.) and 1,9-diformyl-5-pentafluorophenyl-dipyrromethane (63.37 mg, 0.177 mmol were dissolved in dry DMF (1 mL) under an inert atmosphere. After that, acetic acid (12 equiv.) and piperidine (20 equiv.) were added to the reaction mixture and heated at 150 °C under microwave irradiation for 10 min. After completion, the reaction mixture was diluted with dichloromethane (DCM) and washed successively with aqueous $NaHCO_3$ solution and brine. The organic layer was extracted using DCM, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude reaction mixture was subjected to column chromatography, and the desired compound was eluted as a green band using a 1:1 to 4:1 DCM/hexane gradient. Yield: 59%, 48 mg. M.p. = 283 °C. R_f = 0.56 (DCM: Hexane, 9:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.63 (s, 1H), 9.42 (s, 1H), 9.38 (s, 1H), 7.18 – 7.12 (m, 5H), 7.02 (d, *J* = 16.5 Hz, 2H), 6.93 (d, *J* = 3.9 Hz, 1H), 6.51 (s, 1H), 6.37 (m, 1H), 6.17 (d, *J* = 3.9 Hz, 1H), 6.10 (s, 1H), 5.96 (s, 1H), 5.92 (s, 1H), 2.51 (d, *J* = 8.8 Hz, 3H), 2.43 (s, 3H), 1.43 (s, 3H), 1.40 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.0, 129.7, 128.0, 125.7, 117.3, 114.0, 110.7, 31.9, 30.3, 29.7, 29.6, 29.3, 29.3, 27.2, 22.7, 21.4, 14.7, 14.5, 14.4, 14.1 ppm. HRMS (ESI) m/z calcd. for $C_{37}H_{28}BF_7N_4O$ $[M]^+$ 687.2178 found: 687.2167. UV-Vis. (DCM) λ_{max} (log ε): 349 (4.01), 549 (sh) (4.05), 587 (4.47).

Cyclic BODIPY-DPM conjugate 14

This compound was synthesized using a general procedure 4. A reaction of meso-pentafluorophenyl-1,3,5,7-tetramethyl BODIPY (**5**) (50 mg, 0.120 mmol) with 1,9-diformyl-5-phenyldipyrromethane (50.4 mg, 0.181 mmol), in dry DMF (1 mL), with 12 equiv. of acetic acid and 20 equiv. of piperidine under inert atmosphere was performed at 150 °C under microwave irradiation for 7 min. After completion, the reaction mixture was diluted with dichloromethane (DCM) and washed successively with aqueous $NaHCO_3$ solution and brine. The organic layer was extracted using DCM, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude reaction mixture was subjected to column chromatography, and the desired compound was eluted as a green band using 1:1 to 3:2 DCM/hexane. Yield: 54%, 47 mg. M.p. > 300 °C. R_f = 0.5 (DCM: Hexane, 4:1). ^{1}H NMR:(400 MHz, $CDCl_3$): δ 9.59 (s, 2H), 7.37 – 7.27 (m, 5H), 7.11 (d, *J* = 16.5 Hz, 2H), 7.04 (d, *J* = 16.1 Hz, 2H), 6.53 (s, 2H), 6.33 (t, *J* = 3.1 Hz, 2H), 5.91 (s, 2H), 5.63 (s, 1H), 3.28 (s, 3H), 3.05 (t, *J* = 2.1 Hz, 2H), 1.71 (d, *J* = 5.8 Hz, 4H), 1.67 (d, *J* = 3.5 Hz, 7H) ppm.^{13}C NMR: (101 MHz, $CDCl_3$): δ 152.7, 139.7, 138.1, 133.3, 130.6, 128.6, 128.2, 127.1, 126.3, 117.6, 115.4, 112.2, 110.5, 52.4, 43.3, 29.7, 26.4, 24.0, 13.7 ppm. HRMS (ESI) m/z calcd. for $C_{41}H_{34}BF_6N_5$ $[M]^+$ 721.2813 found: 721.2766. UV-Vis. (DCM) λ_{max} (log ε): 349 (4.01), 549 (sh) (4.05), 587 (4.47).

Cyclic BODIPY-DPM conjugate 15

This compound was synthesized by using a general procedure 4. A reaction of meso-pentafluorophenyl-1,3,5,7-tetramethyl BODIPY (**5**) (50 mg, 0.120 mmol), 1,9-diformyl-5-tolyldipyrromethane (52.9 mg, 0.181 mmol), in dry DMF (1 mL), with 12 equiv. of acetic acid and 20 equiv. of piperidine under an inert atmosphere was performed at 150 °C under microwave irradiation for 7 min. After completion, the reaction mixture was diluted with dichloromethane (DCM) and washed successively with aqueous $NaHCO_3$ solution and brine. The organic layer was extracted using DCM, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude reaction mixture was subjected to column chromatography, and the desired compound was eluted as a green

band using 1:1 to 3:2 DCM/hexane. . Yield: 48%, 42 mg. M.p >300°C, R_f = 0.78 (DCM: Hexane, 4:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.06 (s, 2H), 7.16 (s, 4H), 7.11 (d, *J* = 16.6 Hz, 2H), 7.04 (d, *J* = 16.2 Hz, 2H), 6.53 (s, 2H), 6.33 – 6.30 (m, 2H), 5.88 (s, 2H), 5.55 (s, 1H), 3.28 (d, *J* = 6.1 Hz, 4H), 2.34 (s, 3H), 1.78 (s, 8H), 1.71 (m, 4H) ppm. ^{13}C NMR: (101 MHz, $CDCl_3$) δ 152.7, 139.7, 138.0, 133.3, 130.7, 129.3, 128.1, 126.1, 117.6, 115.1, 112.4, 110.6, 52.4, 44.4, 26.4, 24.0, 21.0, 13.6 ppm. HRMS (ESI) m/z calcd. for $C_{42}H_{36}BF_6N_5$ $[M+H]^+$ 735.3077 found: 735.2999. UV-Vis. (DCM) λ_{max} (log ε): 420 (4.48), 492 (4.04), 665 (4.68), 705 (sh) (4.46).

Cyclic BODIPY-DPM conjugate 16

This compound was synthesized by using a general procedure 4. A reaction of meso-pentafluorophenyl-1,3,5,7-tetramethyl BODIPY (**5**) (50 mg, 0.120 mmol) with 1,9-diformyl-5-(4-formylphenyl)dipyrromethane (64.61 mg, 0.181 mmol), in dry DMF (1 mL) with 12 equiv. of acetic acid and 20 equiv. of piperidine under an inert atmosphere was performed at 150 °C under microwave irradiation for 7 min. After completion, the reaction mixture was diluted with dichloromethane (DCM) and washed successively with aqueous $NaHCO_3$ solution and brine. The organic layer was extracted using DCM, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude reaction mixture was subjected to column chromatography, and the desired compound was eluted as a green band using 1:1 to 3:2 DCM/hexane. . Yield: 57%, 55 mg. M.p. > 300°C. R_f = 0.6 (DCM:Hexane, 4:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.07 (s, 2H), 7.46 (d, *J* = 8.1 Hz, 2H), 7.11 (d, *J* = 11.6 Hz, 4H), 7.06 (s, 2H), 6.54 (s, 2H), 6.31 (s, 2H), 5.83 (s, 2H), 5.51 (s, 1H), 3.29 (s, 5H), 1.71 (s, 4H), 1.67 (s, 7H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.6, 139.9, 137.1, 133.3, 131.7, 130.8, 129.9, 126.1, 121.1, 117.7, 115.2, 112.5, 110.7, 52.4, 44.0, 30.3, 29.7, 27.7, 26.4, 24.0, 19.1, 13.7 ppm. HRMS (ESI) m/z calcd. for $C_{41}H_{33}BF_6BrN_5$ $[M]^+$ 800.1940 found: 800.1849. UV-Vis. (DCM) λ_{max} (log ε): 416 (4.54), 488 (4.08), 661 (4.76), 702 (sh) (4.53).

Cyclic BODIPY-DPM conjugate 17

This compound was synthesized by using a general procedure 4. A reaction of meso-pentafluorophenyl-1,3,5,7-tetramethyl BODIPY (**5**) (50 mg, 0.120 mmol), 1,9-diformyl-5-pentafluorophenyl dipyrromethane (53.35 mg, 0.181 mmol), in dry DMF (1 mL), with 12 equiv. of acetic acid and 20 equiv. of piperidine under inert atmosphere was performed at 150 °C under microwave irradiation for 7 min. After completion, the reaction mixture was diluted with dichloromethane (DCM) and washed successively with aqueous $NaHCO_3$ solution and brine. The organic layer was extracted using DCM, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude reaction mixture was subjected to column chromatography, and the desired compound was eluted as a green band using 1:1 to 3:2 DCM/hexane. Yield: 49%, 48 mg. M.p. > 300 °C. R_f = 0.65 (DCM: Hexane, 4:1).^{1}H NMR (400 MHz, CDCl 3): δ 9.59 (s, 2H), 7.16 (d, J = 16.2 Hz, 2H), 7.04 (d, J = 16.4 Hz, 2H), 6.55 (s, 2H), 6.40 – 6.34 (m, 2H), 6.30 (s, 2H), 6.01 (s, 1H), 3.29 (s, 5H), 1.72 (s, 4H), 1.68 (s, 7H) ppm.·. HRMS (ESI) m/z calcd. for $C_{41}H_{29}BF_{11}N_5$ $[M]^+$ 811.2342 found: 811.2324. UV-Vis. (DCM) λ_{max} (log ε): 412 (4.332), 486 (3.875), 656 (3.878), 698 (sh) (4.339).

2. NMR Spectra

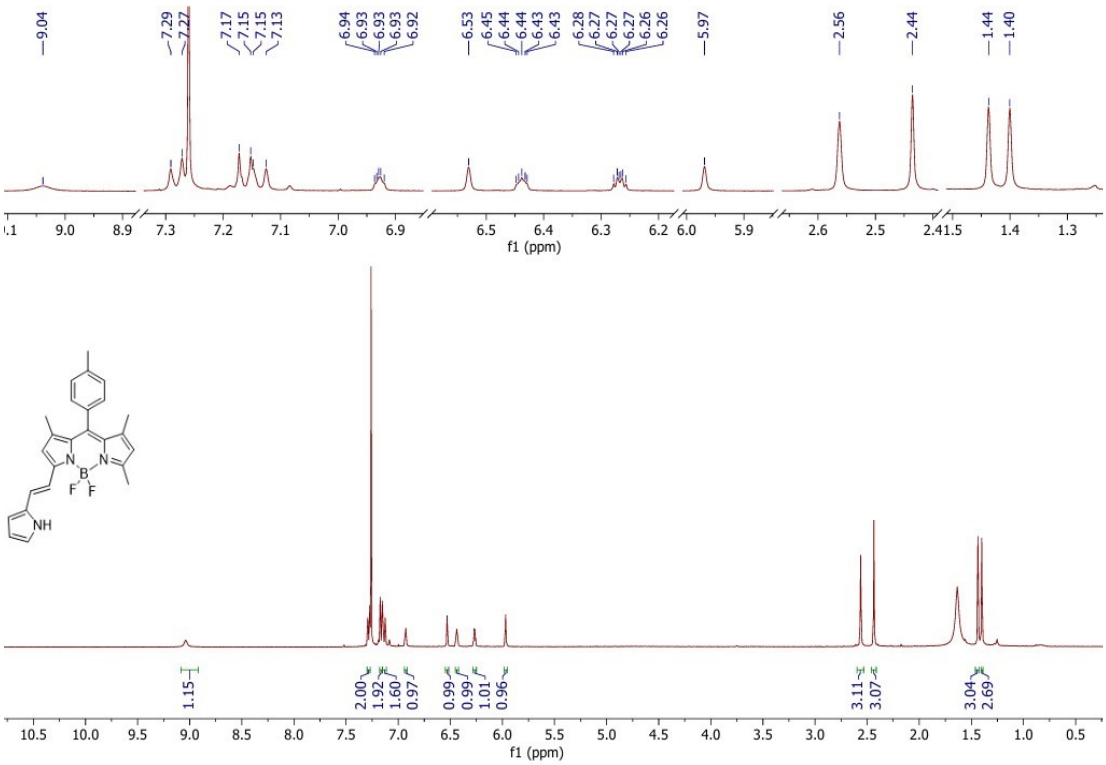


Fig S1. ^{1}H NMR spectrum of compound **2** in $CDCl_3$ at 298K.

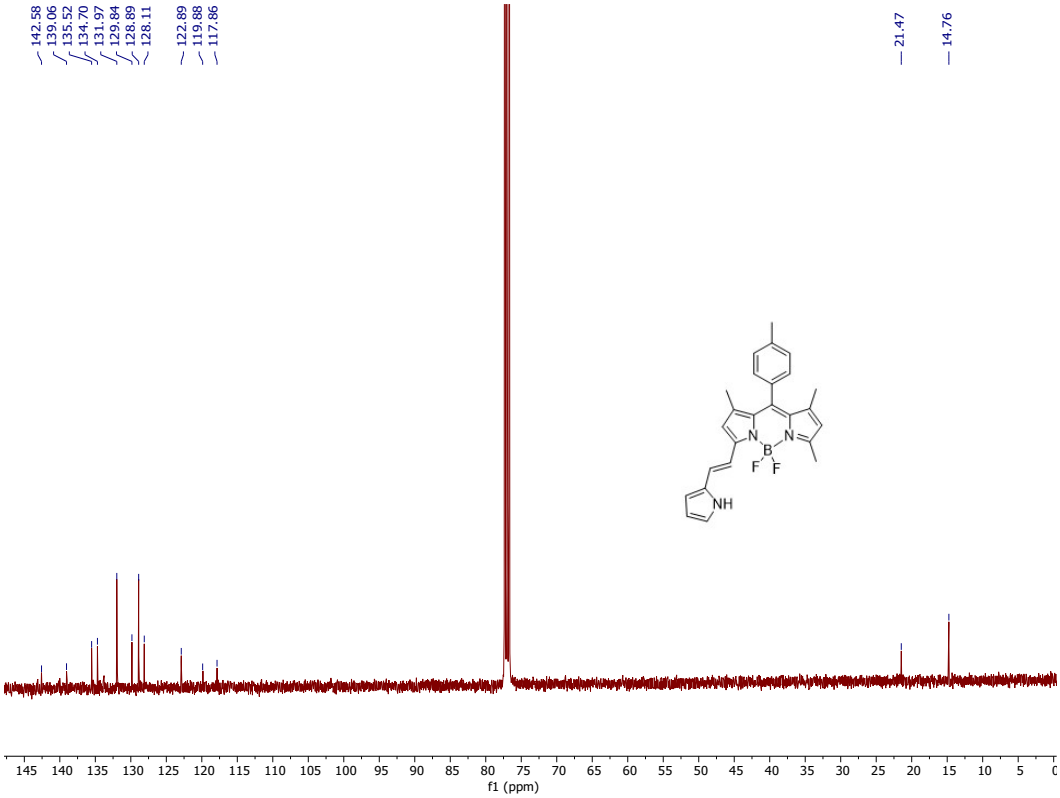


Fig S2.^{13}C NMR spectrum of compound **2** in $CDCl_3$ at 298

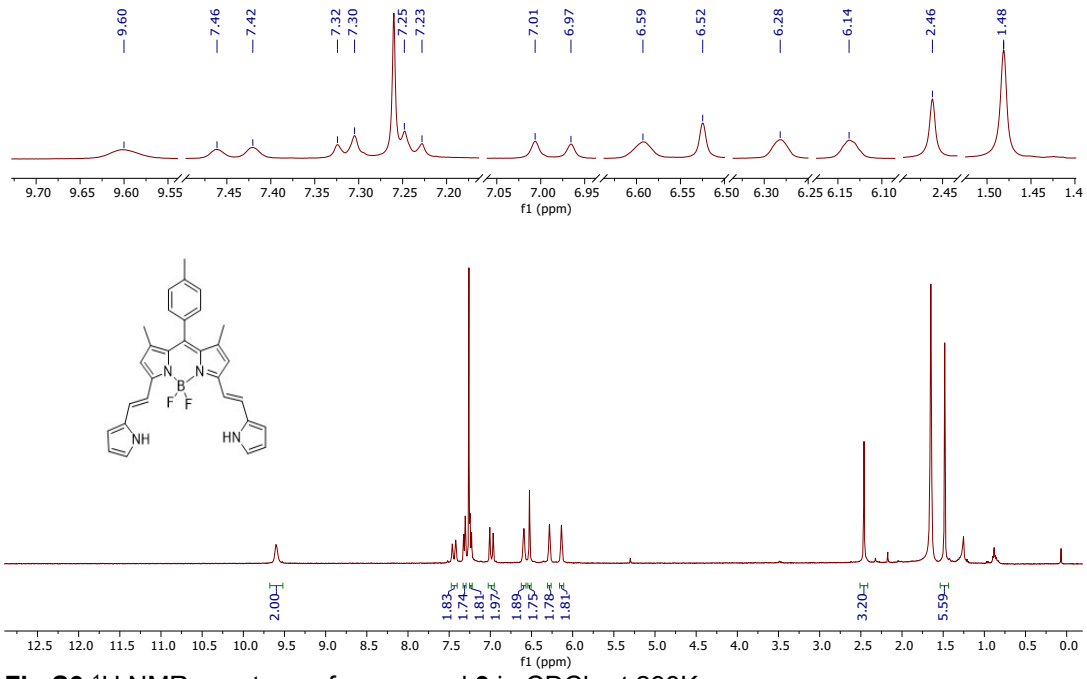


Fig S3.^{1}H NMR spectrum of compound **3** in $CDCl_3$ at 298K.

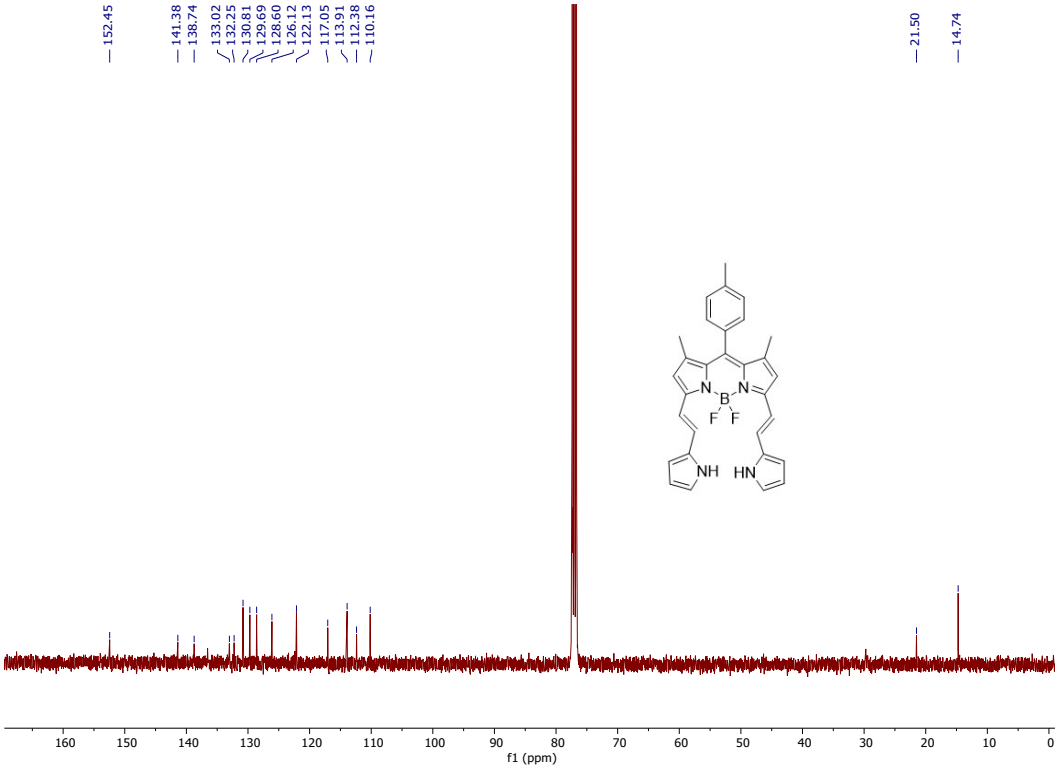


Fig S4. ^{13}C NMR spectrum of compound **3** in $CDCl_3$ at 298K.

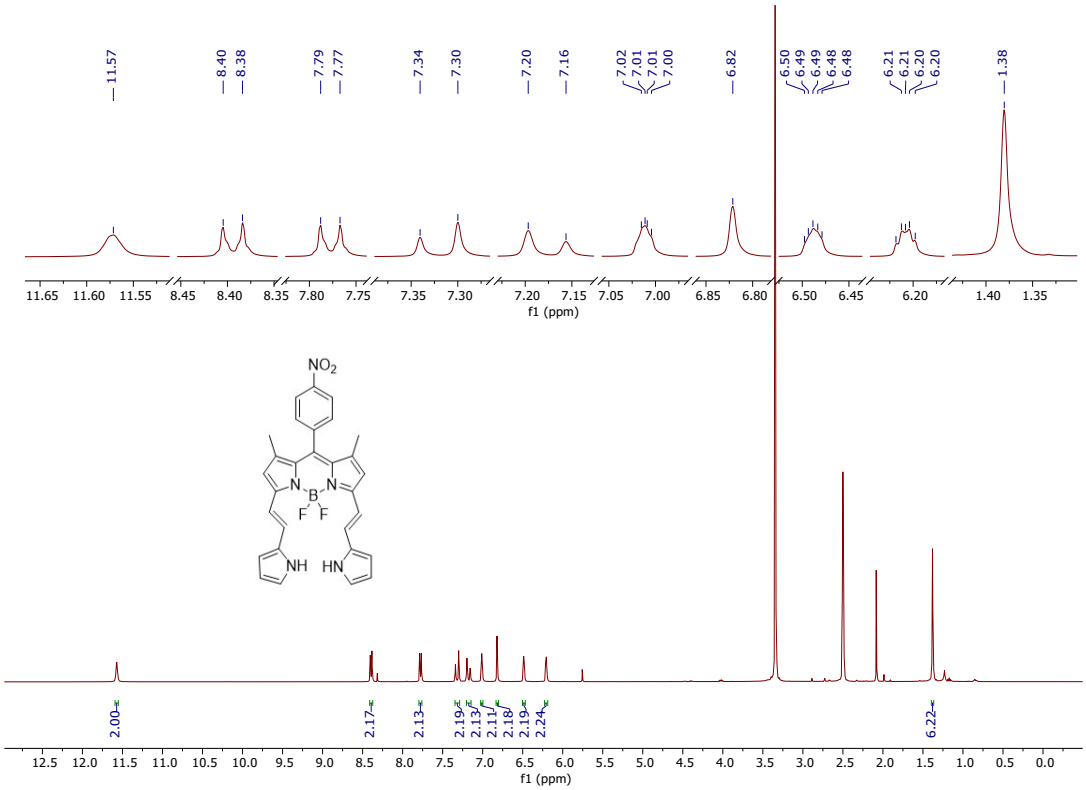


Fig S5.^{1}H NMR spectrum of compound **6** in DMSO-d_6 at 298K.

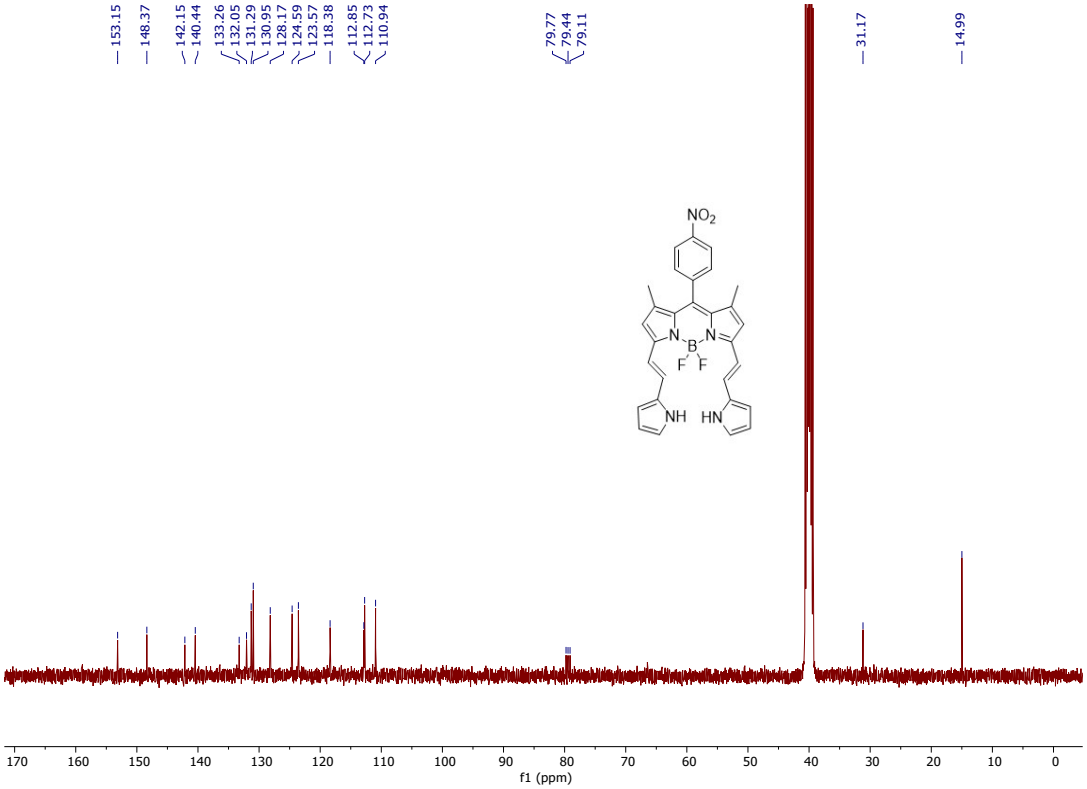


Fig S6. ^{13}C NMR spectrum of compound **6** in DMSO-d_6 at 298K.

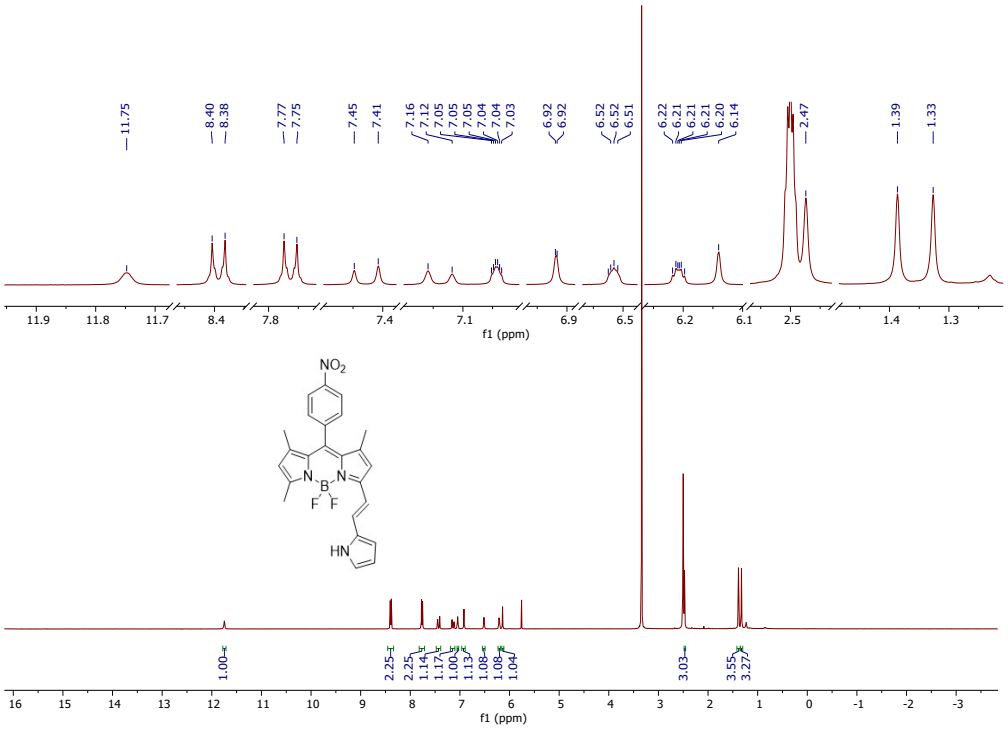


Fig S7. ^{1}H NMR spectrum of compound **7** in DMSO -d_6 at 298K.

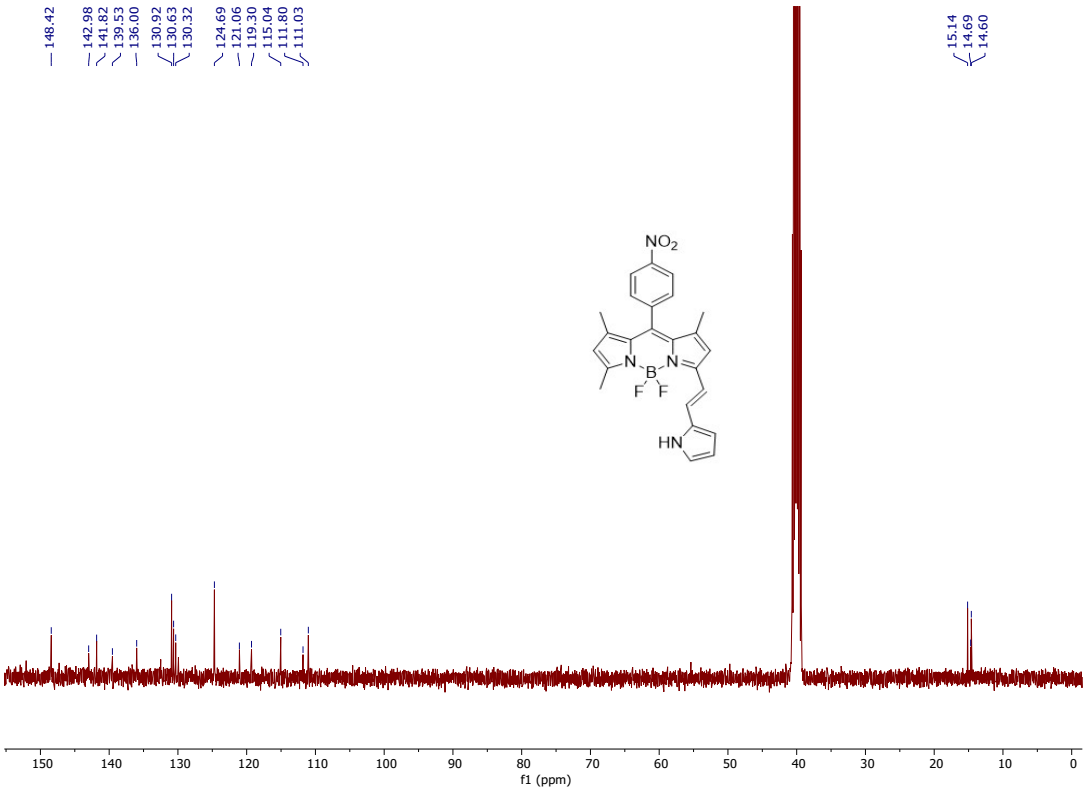


Fig S8. ^{13}C NMR spectrum of compound **7** in DMSO-d_6 at 298K.

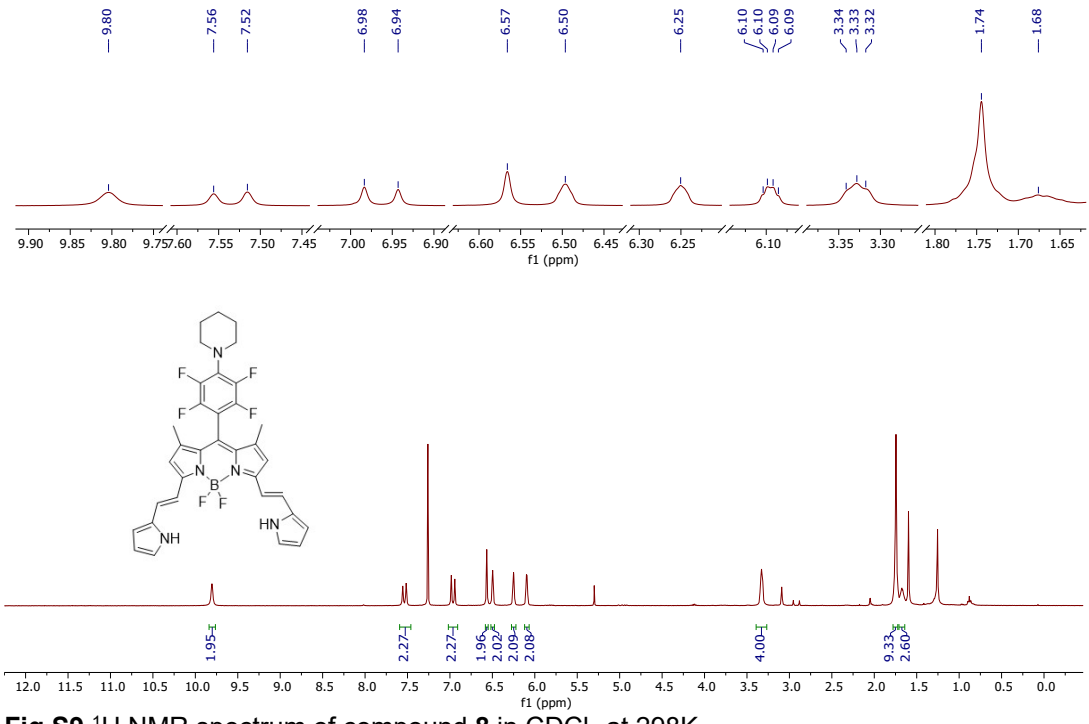


Fig S9.^{1}H NMR spectrum of compound **8** in $CDCl_3$ at 298K.

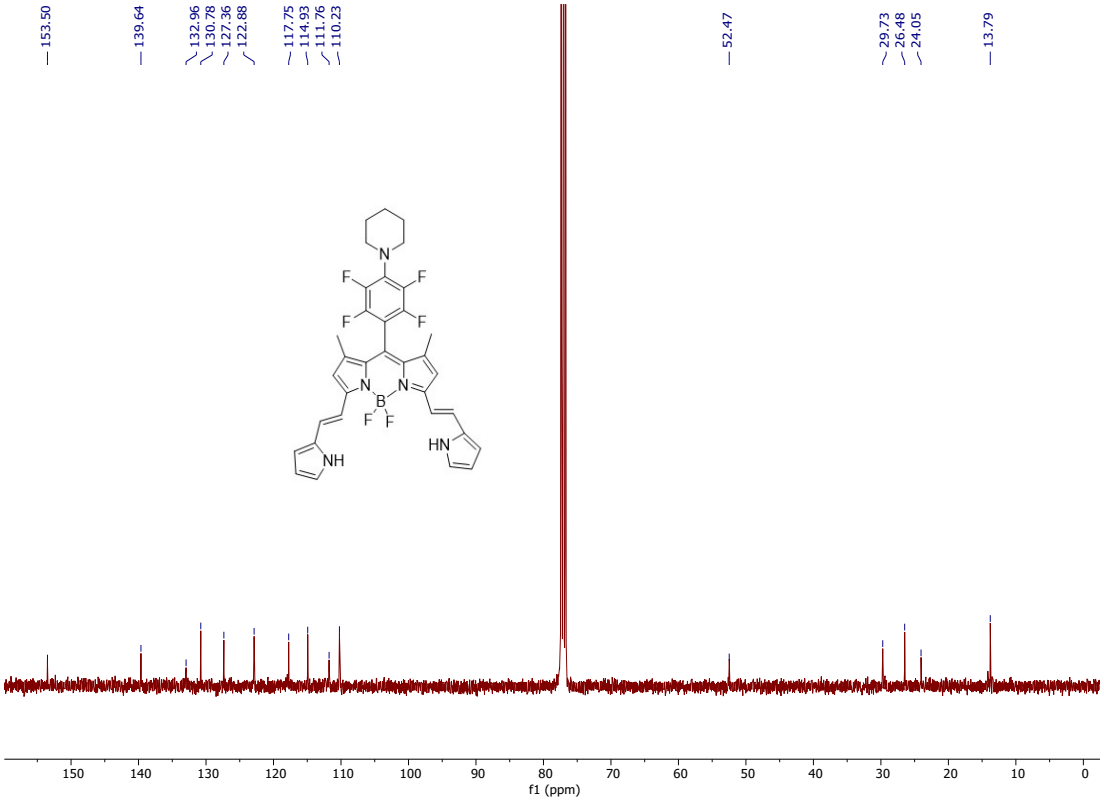


Fig S10. ^{13}C NMR spectrum of compound **8** in $CDCl_3$ at 298K.

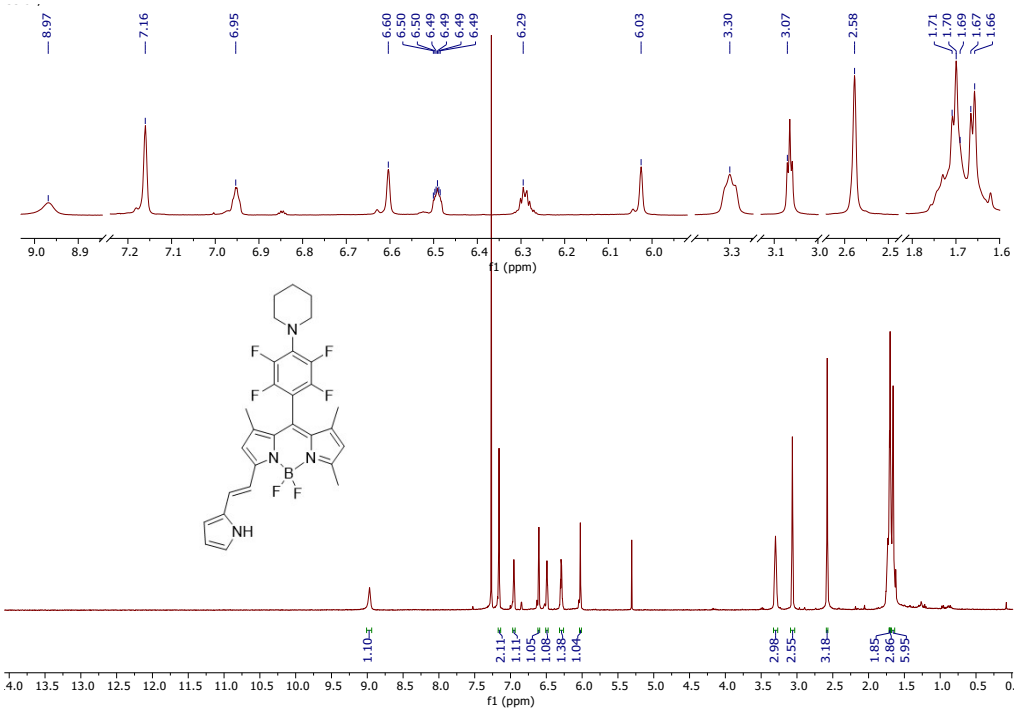


Fig S11. ^{1}H NMR spectrum of compound **9** in $CDCl_3$ at 298K.

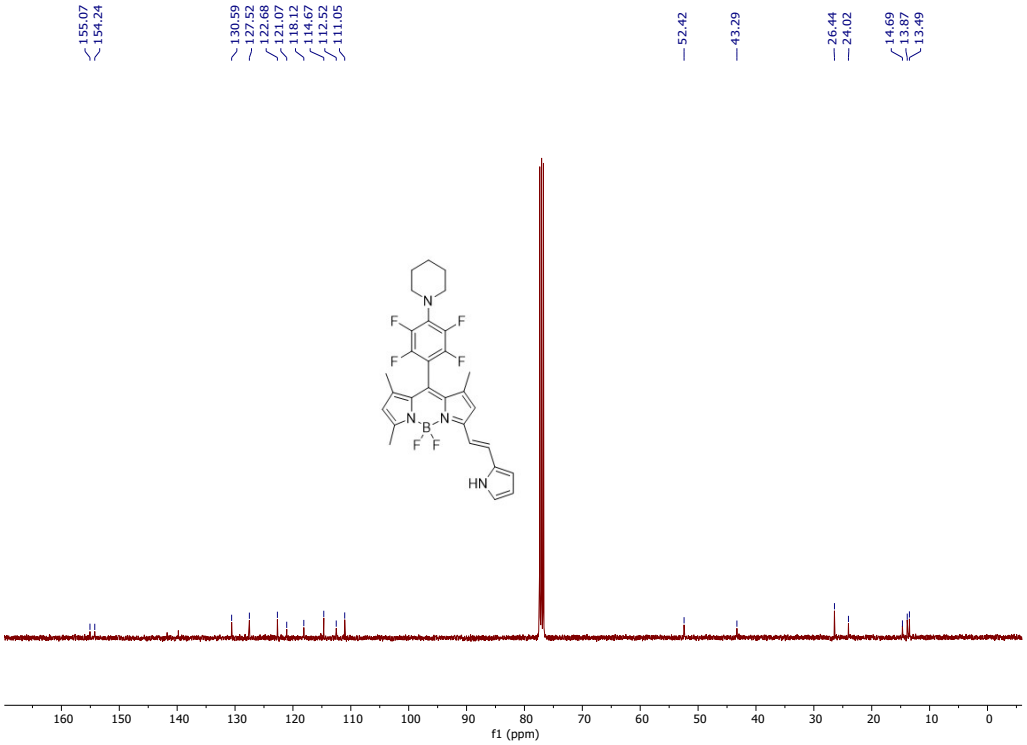


Fig S12. ^{13}C NMR spectrum of compound **9** in $CDCl_3$ at 298K.

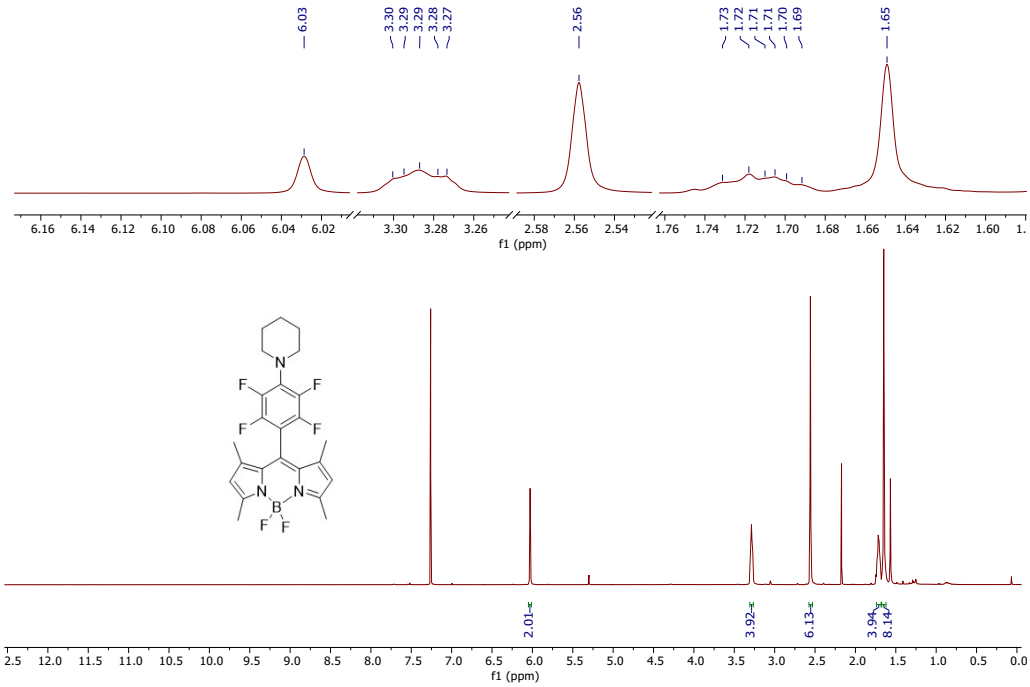


Fig S13. ^{1}H NMR spectrum of compound **S1** in $CDCl_3$ at 298K.

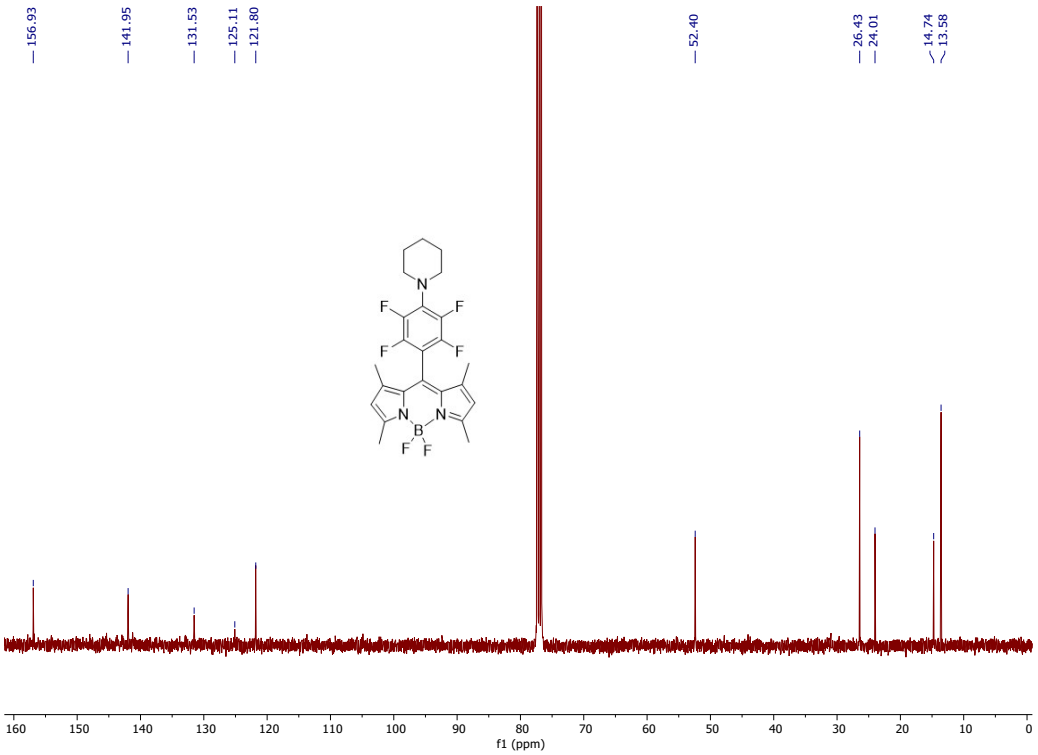


Fig S14. ^{13}C NMR spectrum of compound **S1** in $CDCl_3$ at 298K.

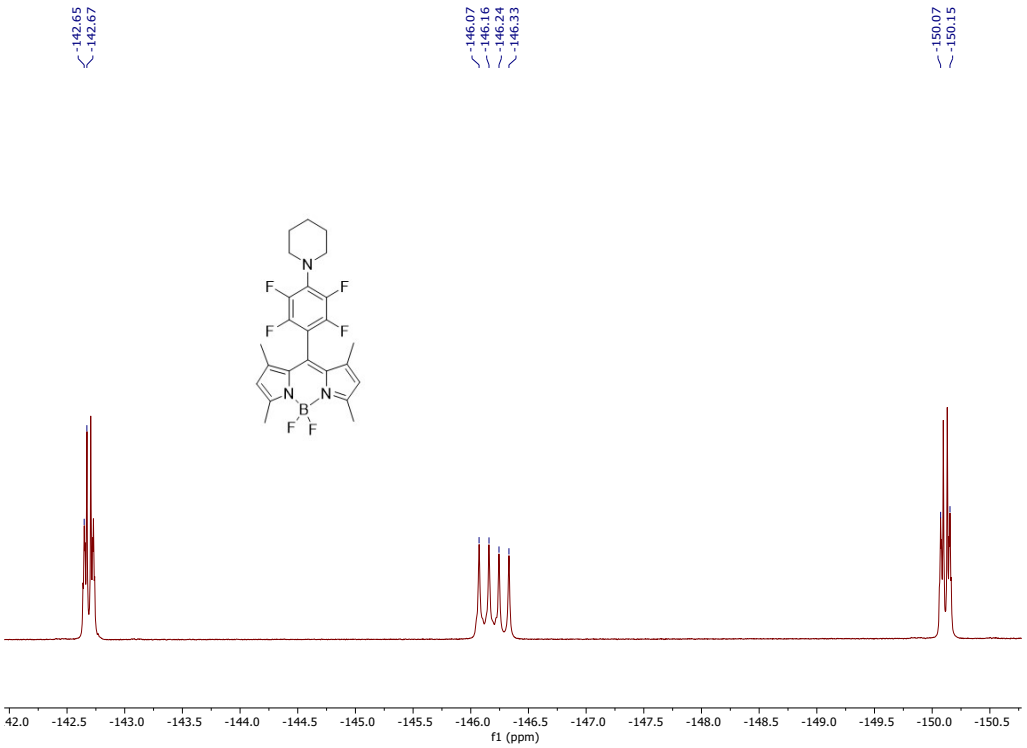


Fig S15. ^{19}F NMR spectrum of compound **S1** in $CDCl_3$ at 298K.

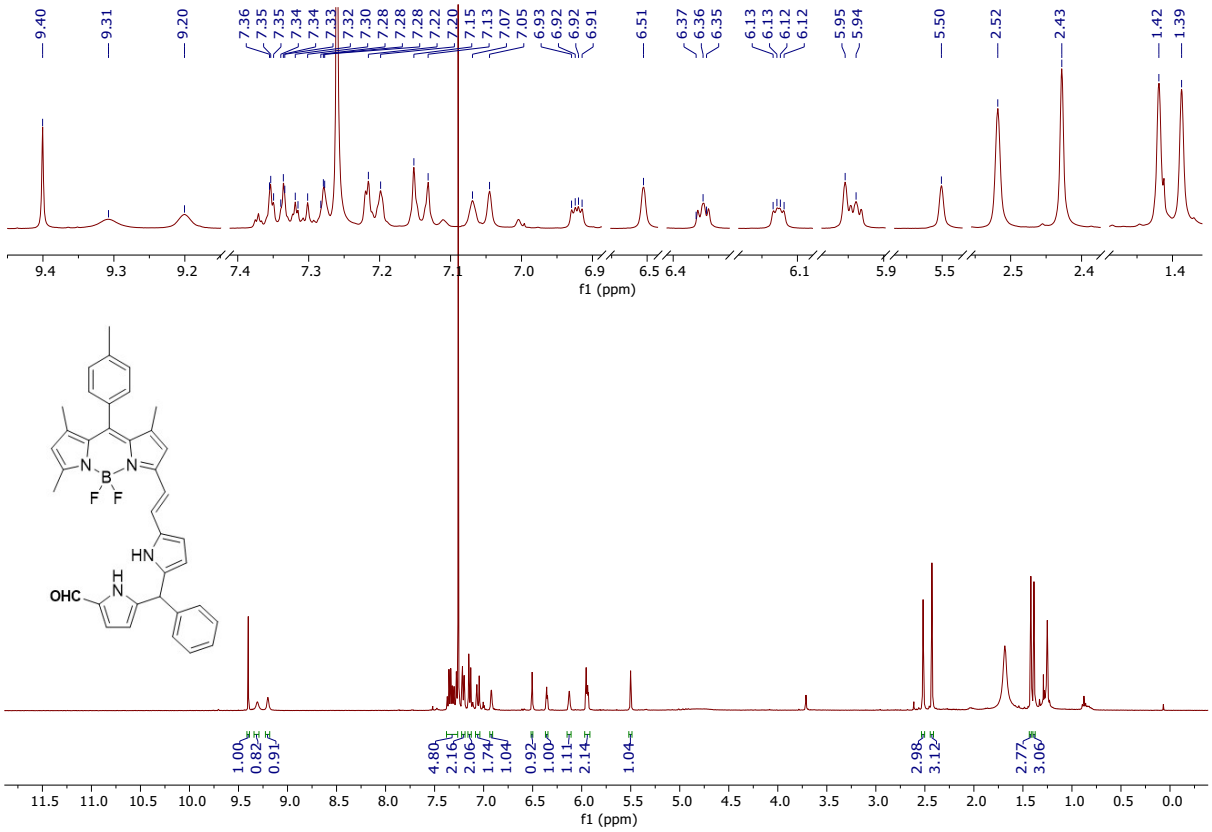


Fig S16. ^{1}H NMR spectrum of compound **10** in $CDCl_3$ at 298K.

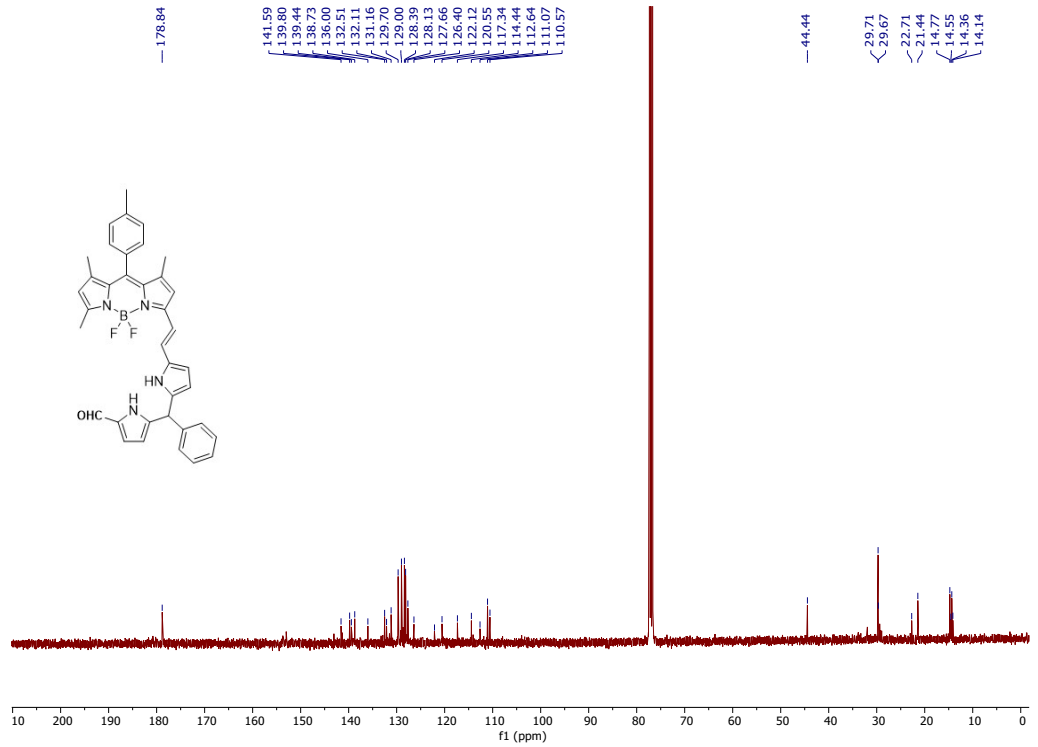


Fig S17. ^{13}C NMR spectrum of compound **10** in $CDCl_3$ at 298K.

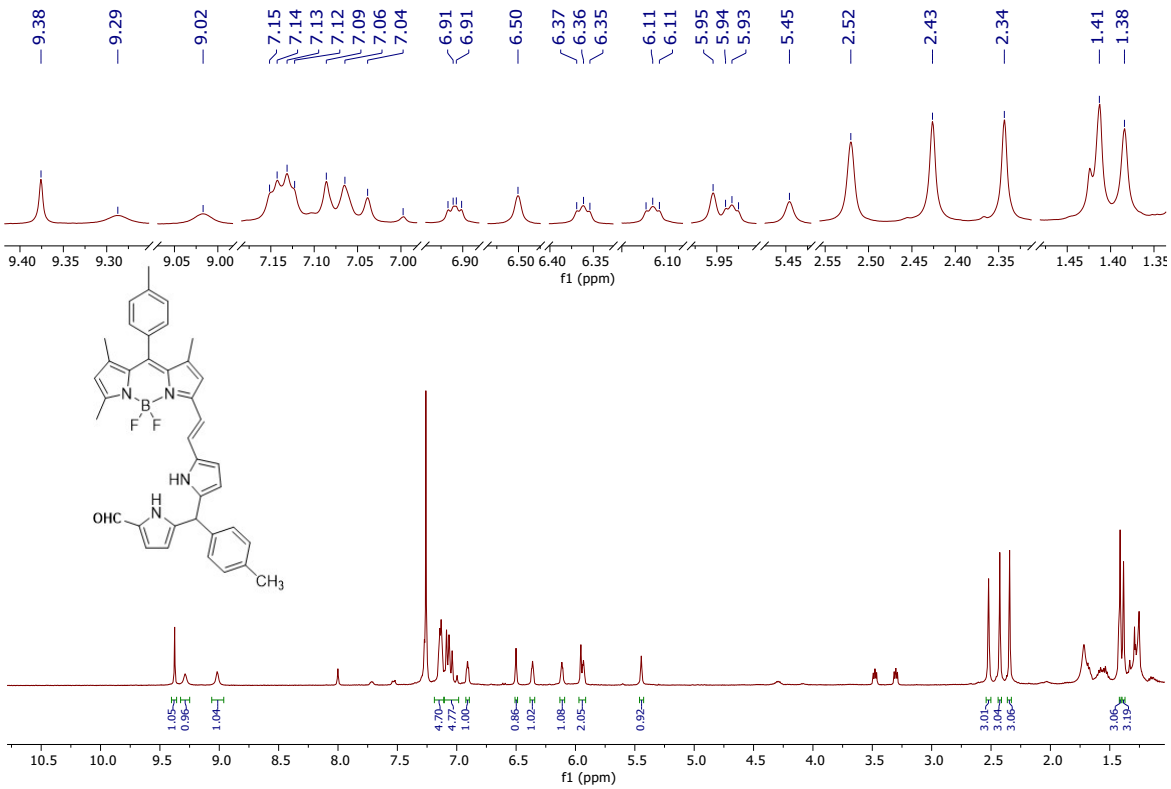


Fig S18. ^{1}H NMR spectrum of compound **11** in $CDCl_3$ at 298K.

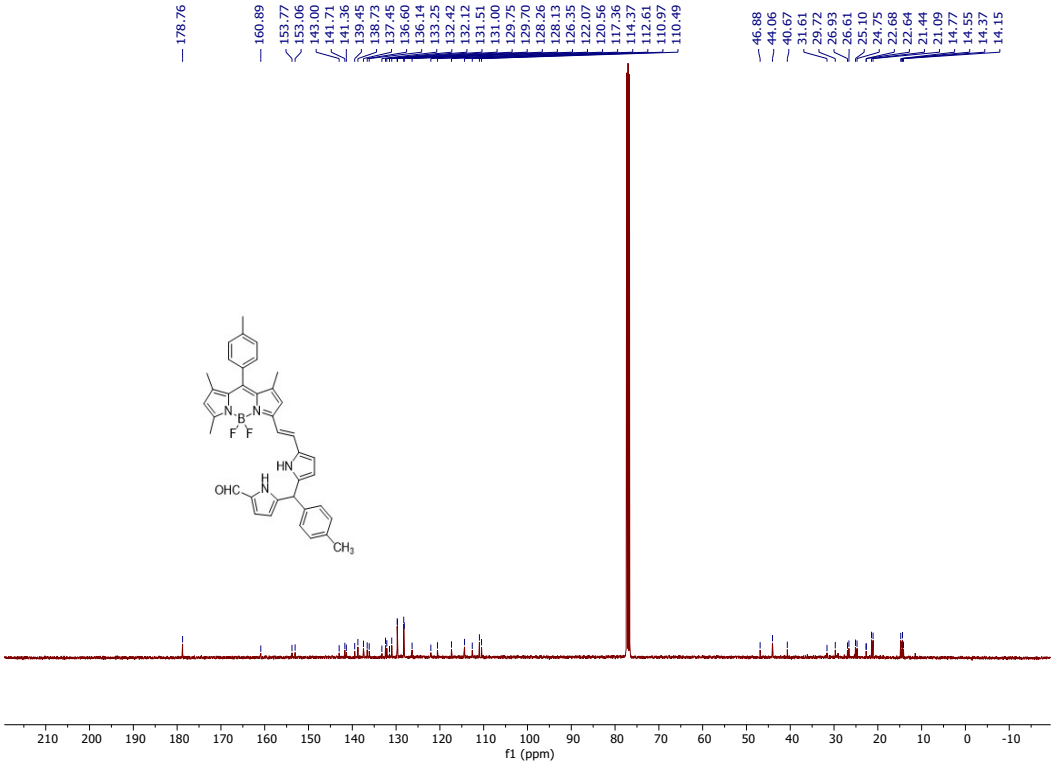


Fig S19. ^{13}C NMR spectrum of compound **11** in $CDCl_3$ at 298K.

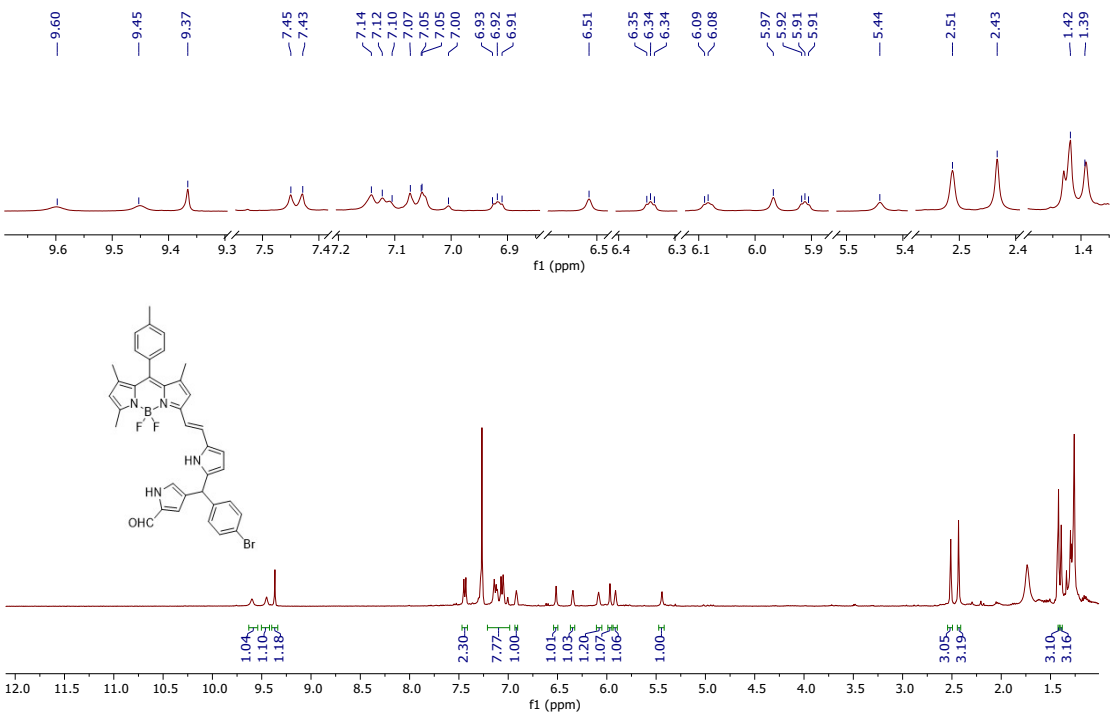


Fig S20. ^{1}H NMR spectrum of compound **12** in $CDCl_3$ at 298K.

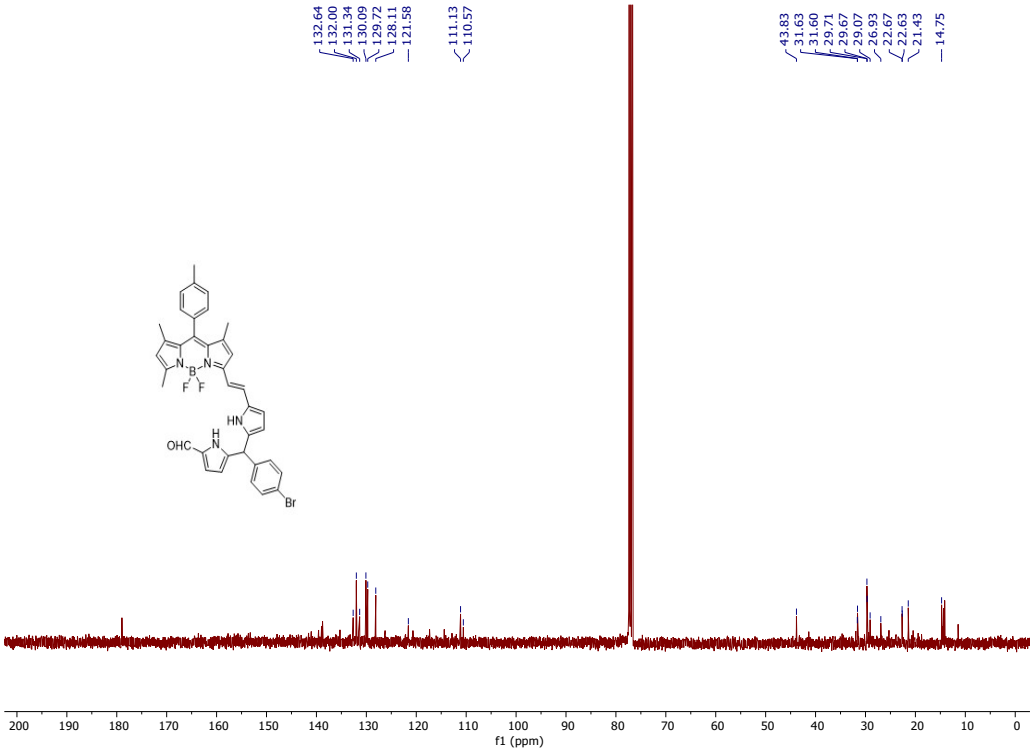


Fig S21. ^{13}C NMR spectrum of compound **12** in $CDCl_3$ at 298K.

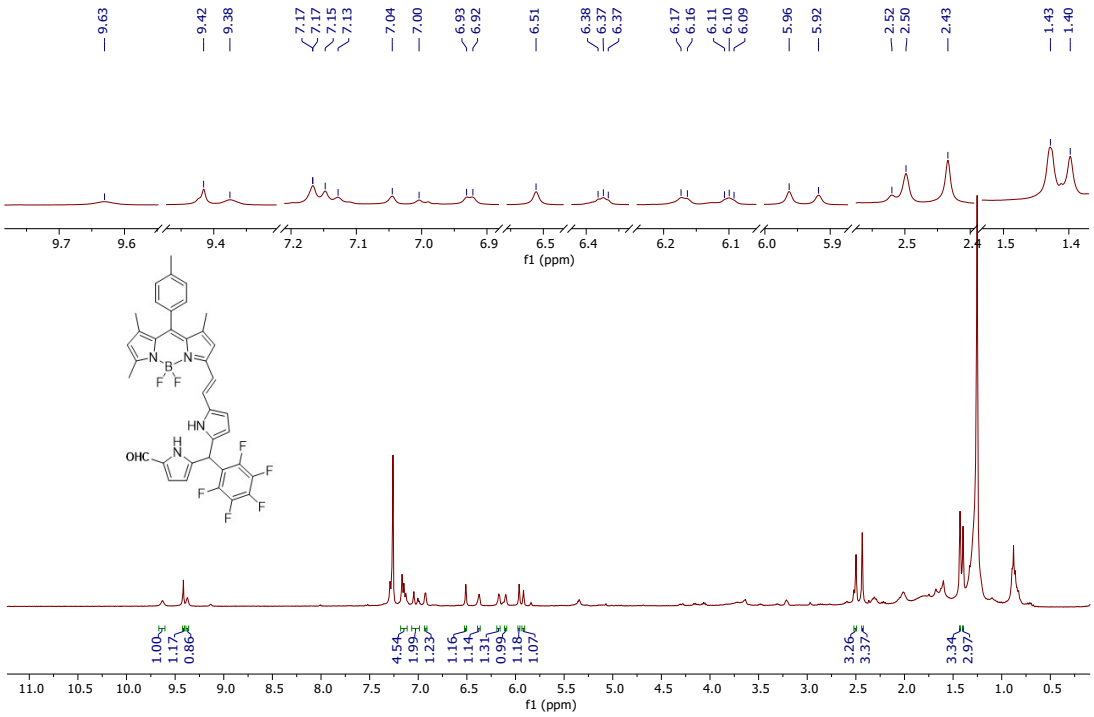


Fig S22. ^{1}H NMR spectrum of compound **13** in $CDCl_3$ at 298K.

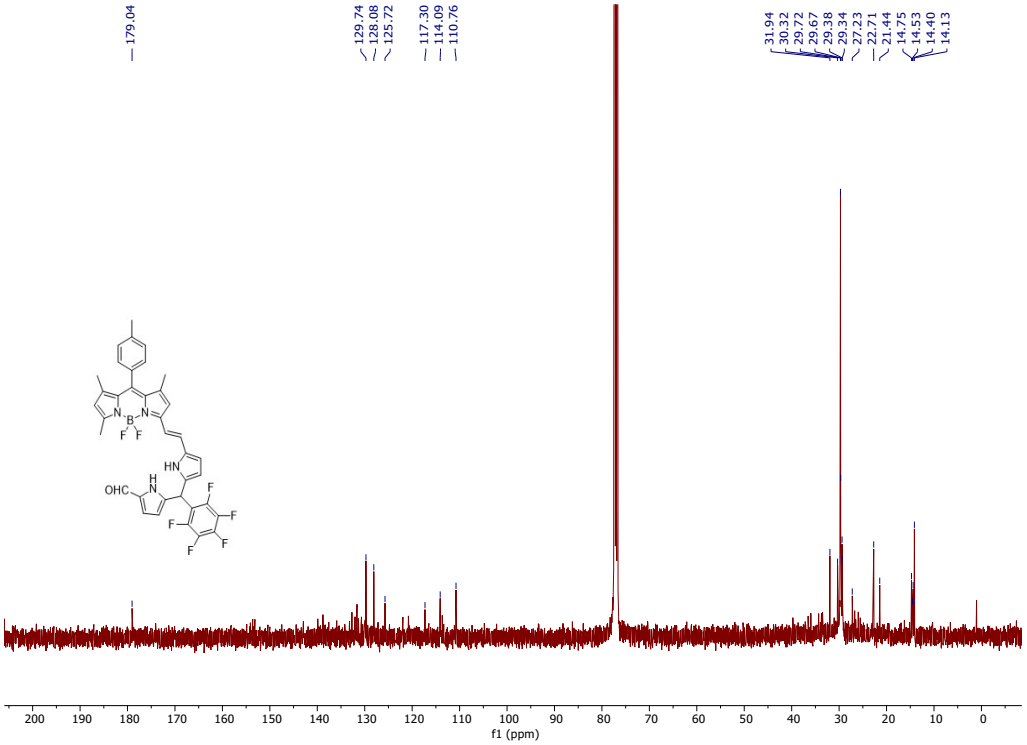


Fig S23. ^{13}C NMR spectrum of compound **13** in $CDCl_3$ at 298K.

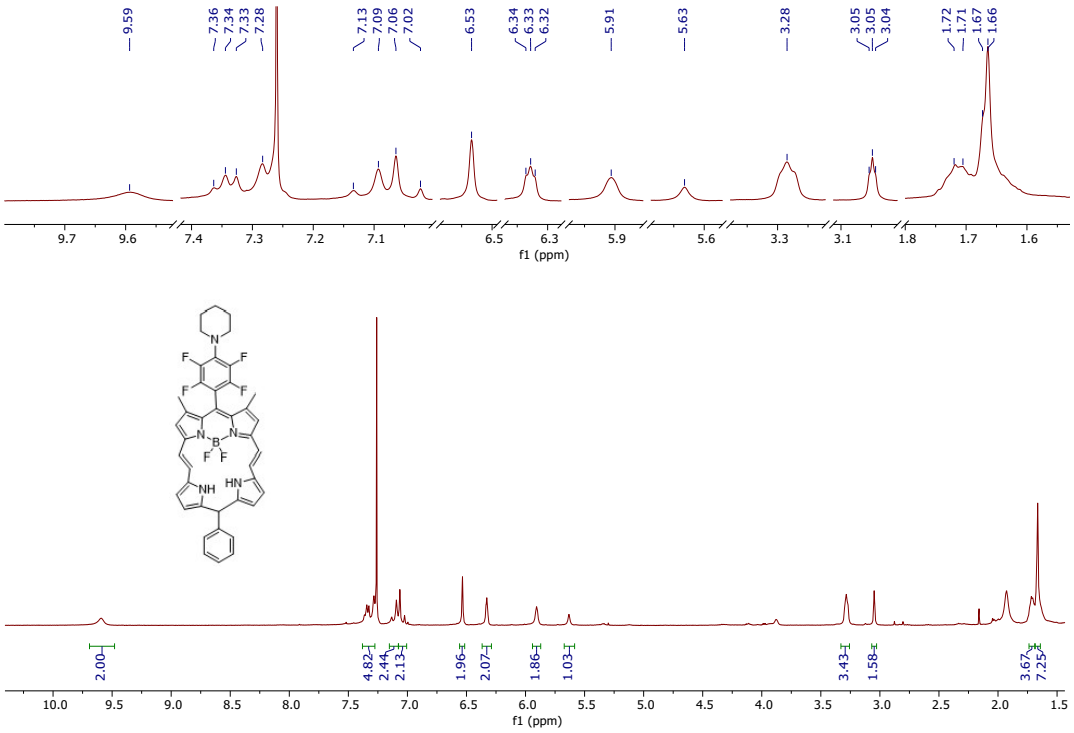


Fig S24.[1]H NMR spectrum of compound **14** in $CDCl_3$ at 298K

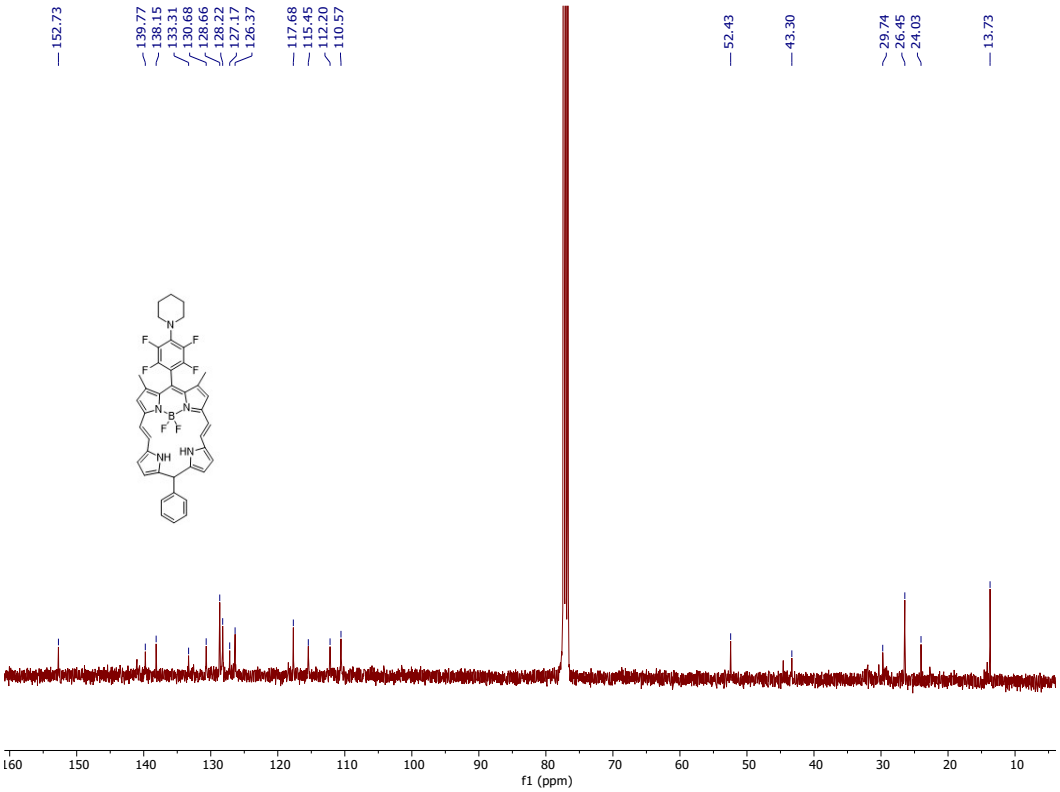


Fig S25. [13]C NMR spectrum of compound **14** in $CDCl_3$ at 298K.

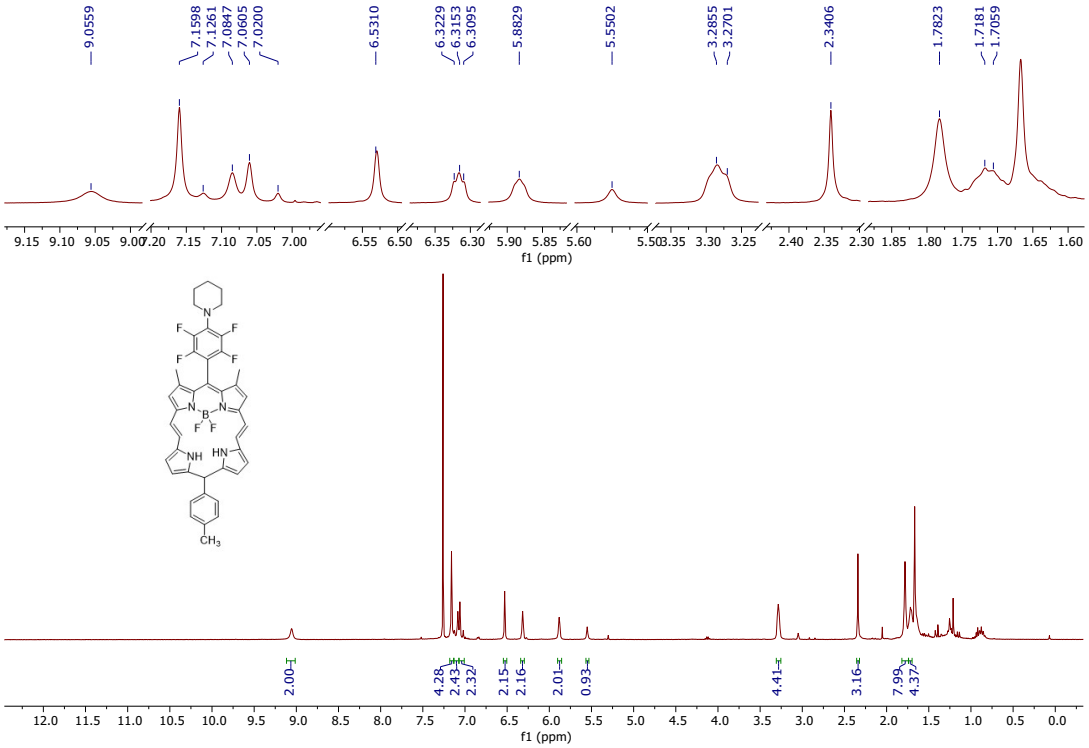


Fig S26.[1]H NMR spectrum of compound **15** in $CDCl_3$ at 298K.

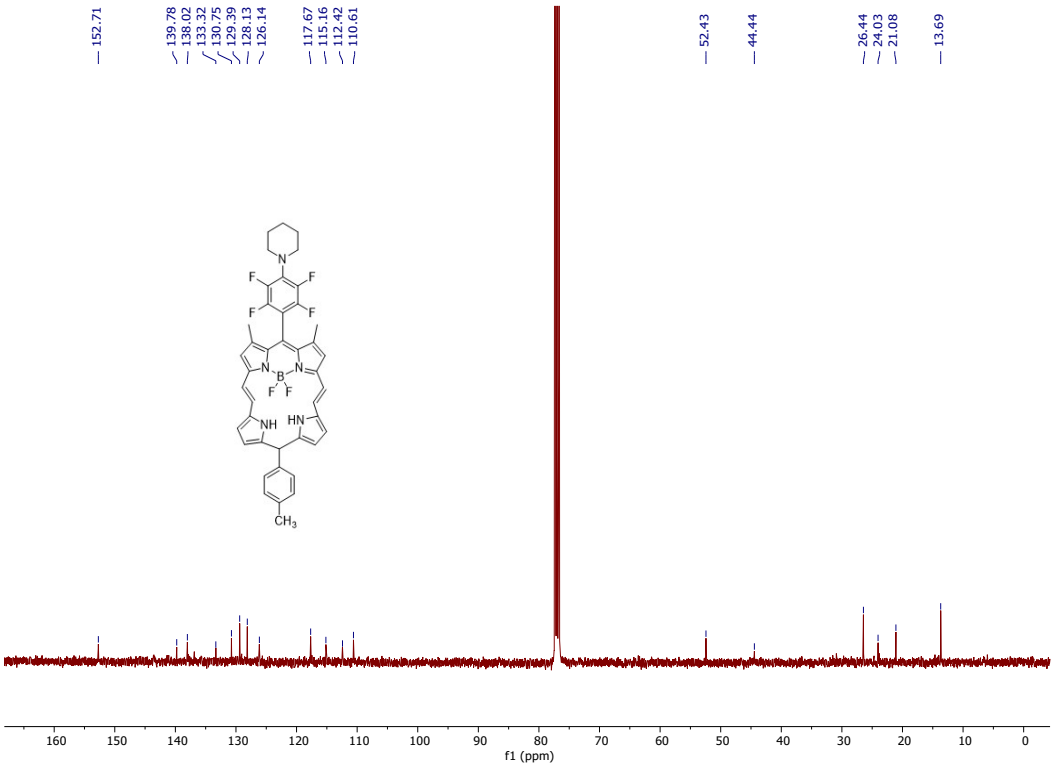


Fig S27.[13]C NMR spectrum of compound **15** in $CDCl_3$ at 298K.

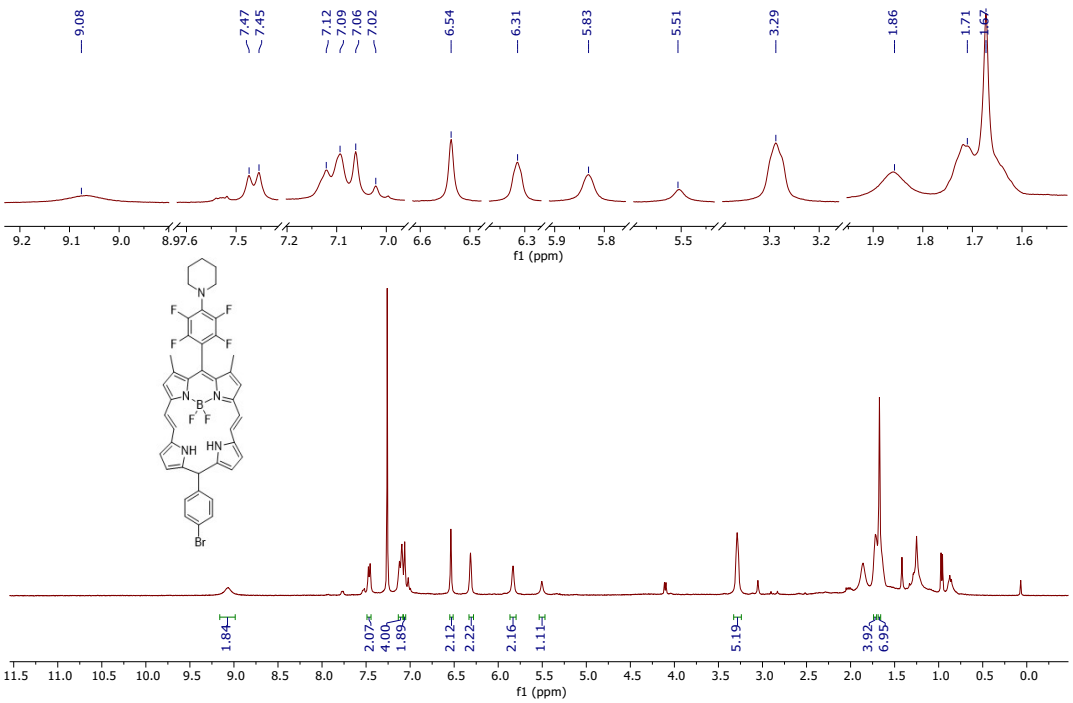


Fig S28.[1]H NMR spectrum of compound **16** in $CDCl_3$ at 298K.

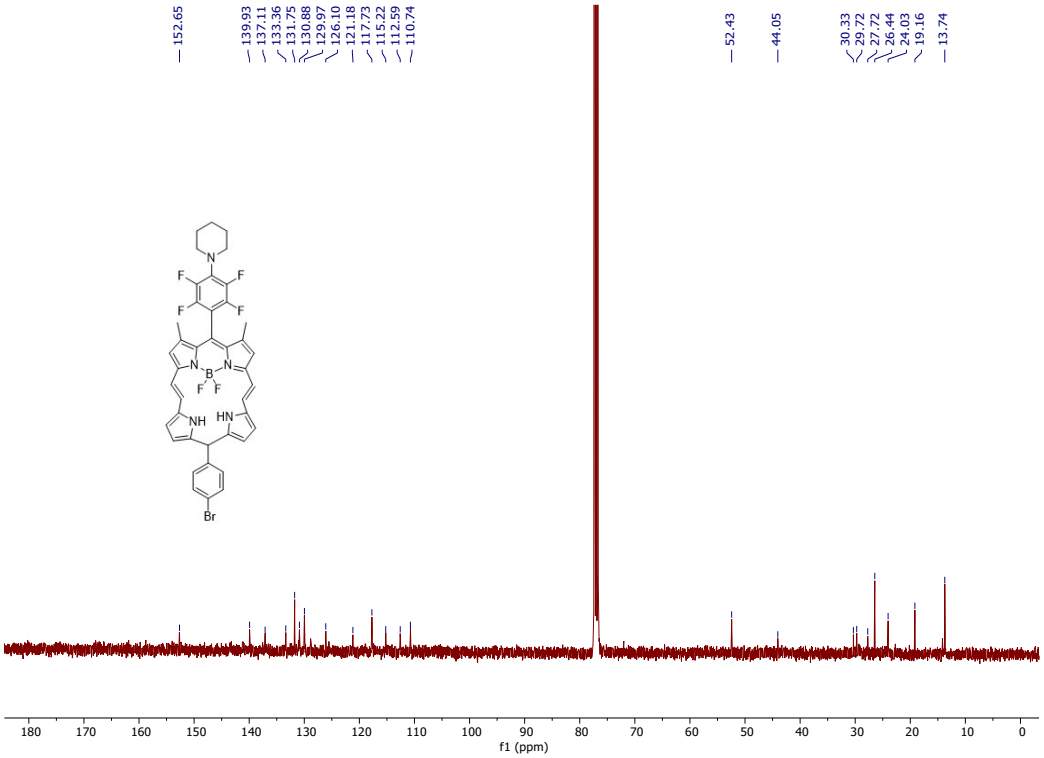


Fig S29.[13]C NMR spectrum of compound **16** in $CDCl_3$ at 298K.

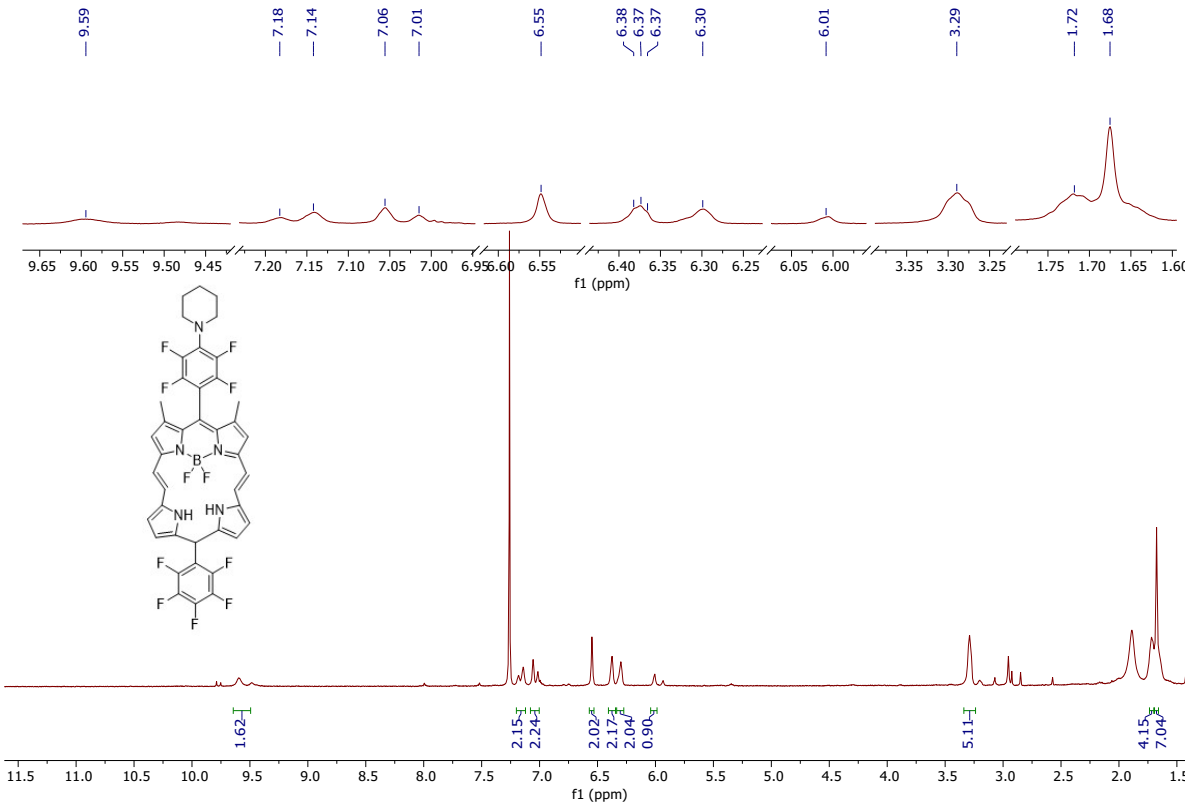


Fig S30.[1]H NMR spectrum of compound **17** in $CDCl_3$ at 298K.

3. Single Crystal X-Ray Analysis

Table S1. Crystal data and structure refinement for compound S1.	
Internal Code	**ss-41_auto_re_1**
Empirical Formula	$C_{24}H_{24}BF_6N_3$
Formula weight (g/mol)	479.27
Temperature(K)	293
Crystal System	Monoclinic
Space group	P 21/c
a(Å)	14.2658 (5)
b (Å)	9.9649 (4)
c (Å)	17.1301 (6)
α (°)	90
β (°)	110.444 (4)
γ (°)	90
Volume ($Å^3$)	2281.79 (16)
Z	4
ρ calc (g/cm^3)	1.395
μ (mm^{-1})	0.117

F(000)	992.0
Crystal size (mm^3)	0.11 X 0.12 X 0.13
Radiation	Mo Kα
2θ(°)	3.046 to 48.922
Reflections collected	16003
Independent reflections	3723
R_{int}	0.0227
R_{sigma}	0.0212
Restraints	18
Parameters	311
GooF (S)	1.097
R_1[I>2 σ (I)]	0.0429
wR_2[I>2 σ (I)]	0.1247
R_1 [all data]	0.0600
wR_2 [all data]	0.1356
Largest peak (e $Å^{-3}$)	0.19
Deepest hole (e $Å^{-3}$)	-0.23
Flack parameter	-
CCDC no.	**2518156**

Nucleophilic aromatic substitution at the *ipso*-fluorine atom of the pentafluorophenyl group was unambiguously confirmed by single-crystal X-ray diffraction of compound **S1** (Figure S31). The molecule crystallizes in the monoclinic space group **$P2_1/c$** with unit cell parameters a = 14.2658 Å, b = 9.9649 Å, c = 17.1301 Å, and β = 110.44°. The structure clearly shows replacement of the *ipso*-F atom by the piperidine nitrogen, forming a C–N bond (1.41 Å), with the remaining fluorine atoms intact, confirming the SNAr process. The BODIPY core adopts a nearly planar geometry. The meso-aryl ring is almost orthogonal to the BODIPY core (dihedral angle = **87.32°**), consistent with minimal π-electronic communication between the two units. The piperidine ring is twisted relative to the meso-aryl ring, with a dihedral angle of 41.56°, thereby minimizing steric strain and improving molecular packing efficiency.

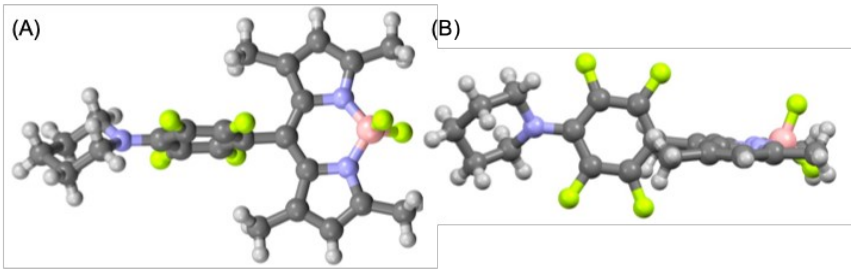


Fig S31. Single-crystal X-ray of compound S1: (A) Top view; (B) Side view.

4. Photophysical Studies

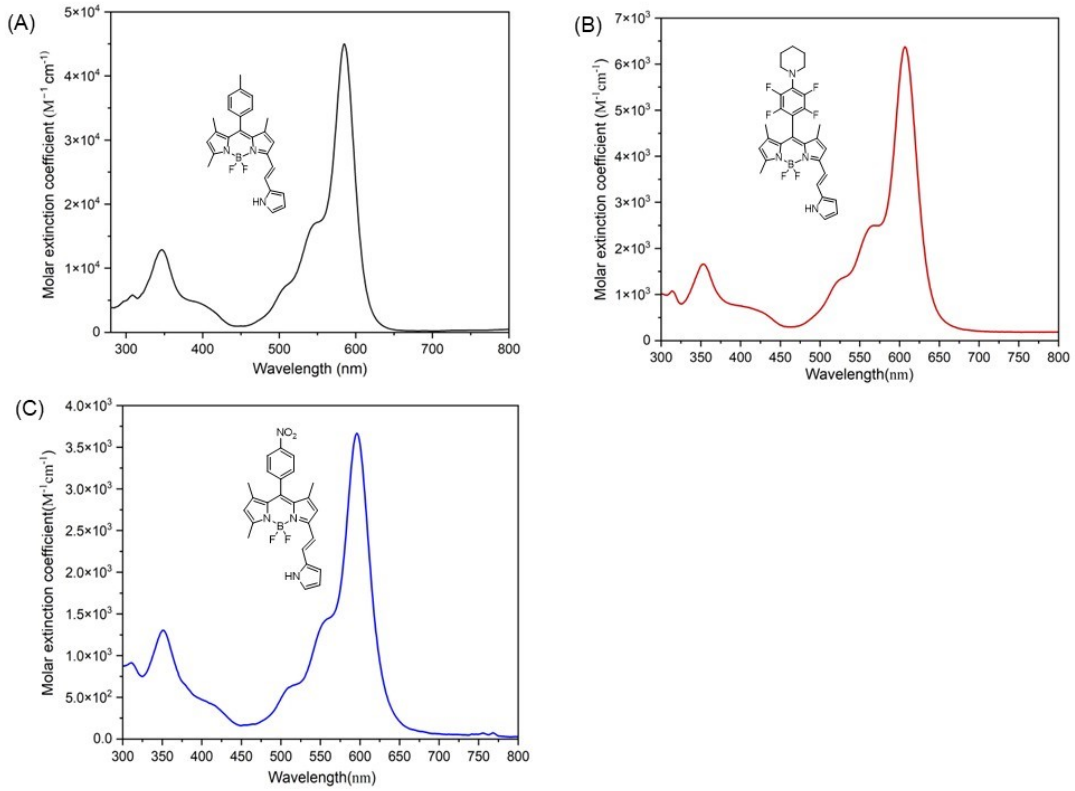


Fig S32. UV-Vis spectra of (A) **2**, (B) **9**, and (C) **7** in CH_2Cl_2 at 298K.

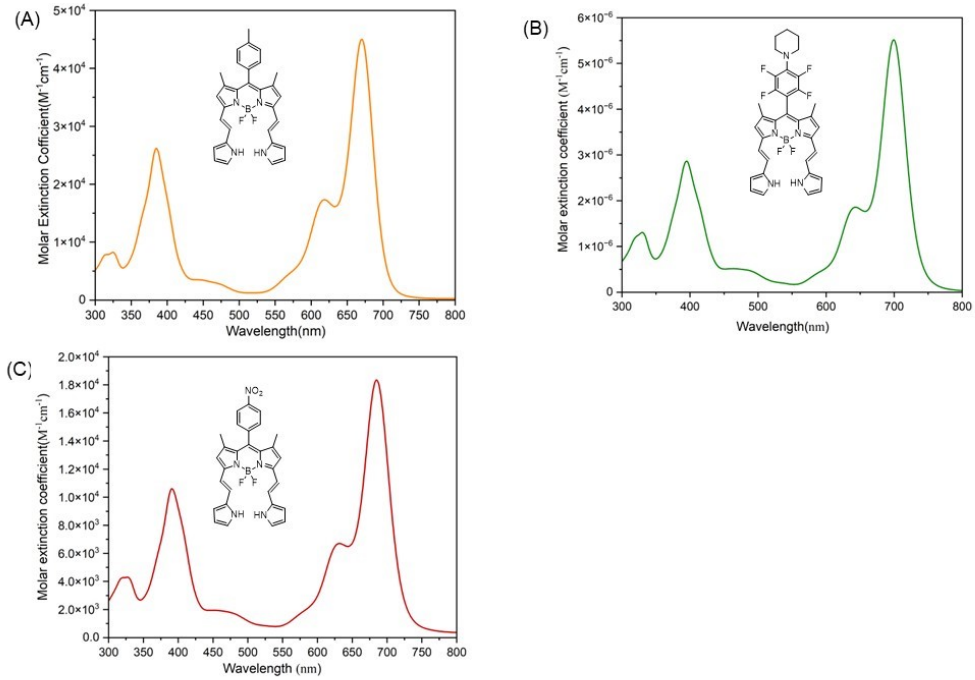


Fig S33. UV-Vis spectra of (A) **3**, (B) **6**, and (C) **8** in CH_2Cl_2 at 298K.

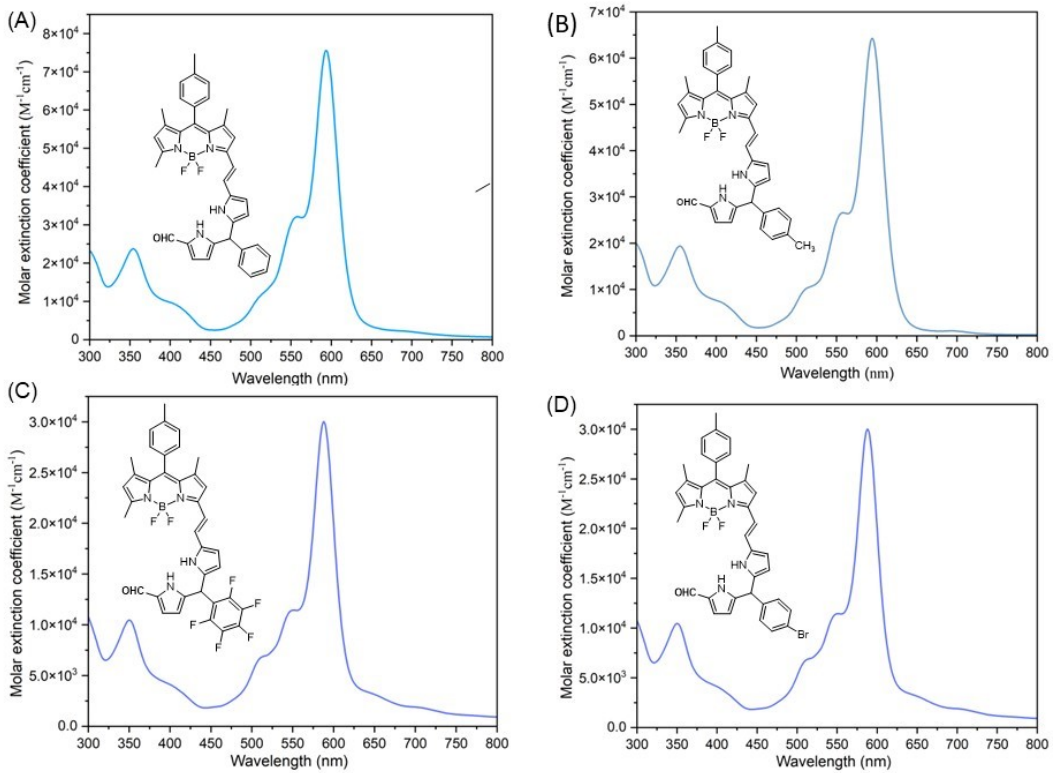


Fig S34. UV-Vis spectra of (A) **10**, (B) **11**, (C) **13**, and (D) **12** in CH_2Cl_2 at 298K.

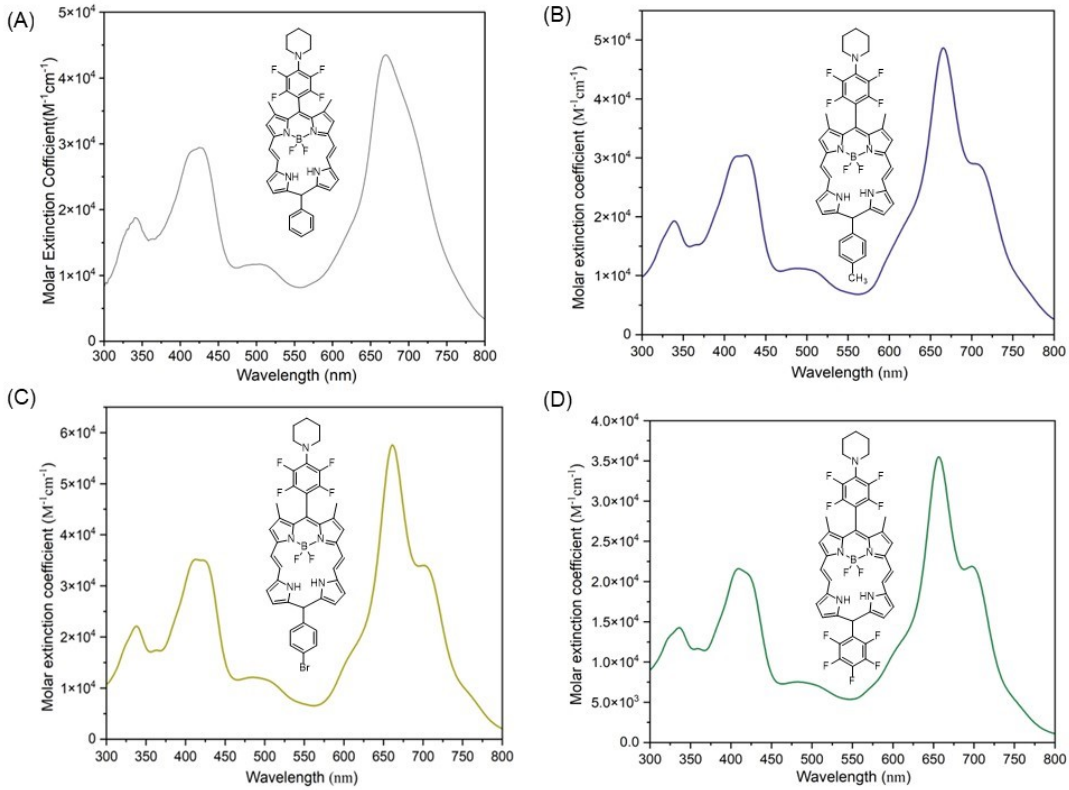


Fig S35. UV-Vis spectra of (A) **14**, (B) **15**, (C) **16**, and (D) **17** in CH_2Cl_2 at 298K.

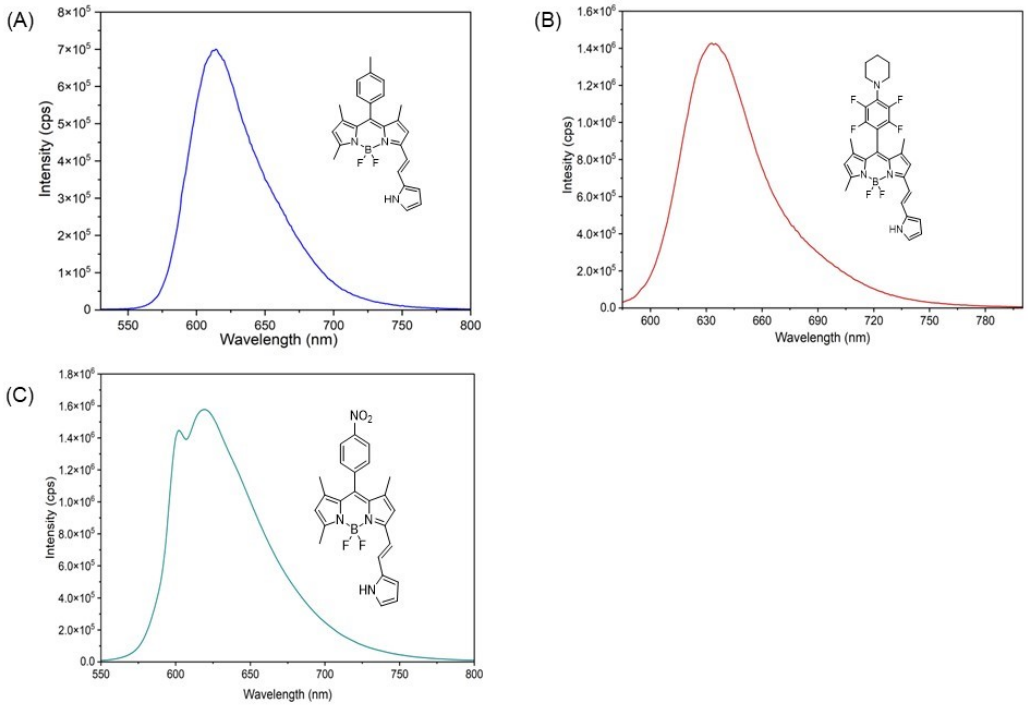


Fig S36. Fluorescence spectra of (A) **2**, (B) **9**, and (C) **7** in CH_2Cl_2 at 298K.

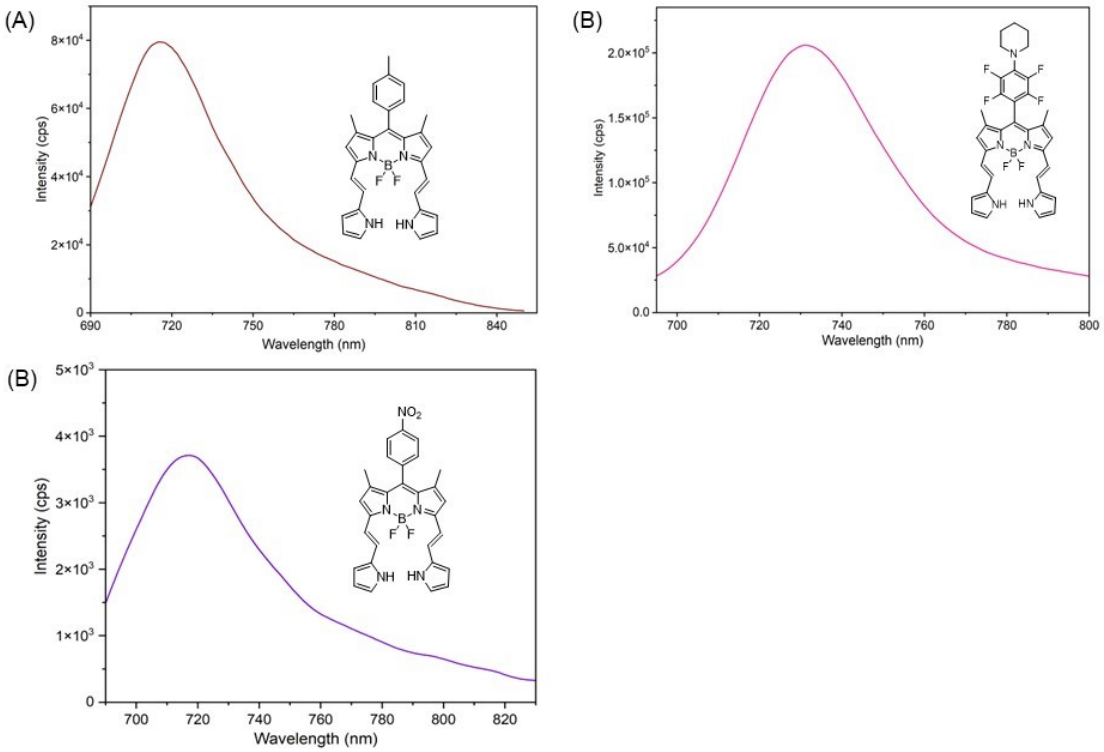


Fig S37. Fluorescence spectra of (A) **3**, (B) **6**, and (C) **8** in CH_2Cl_2 at 298K.

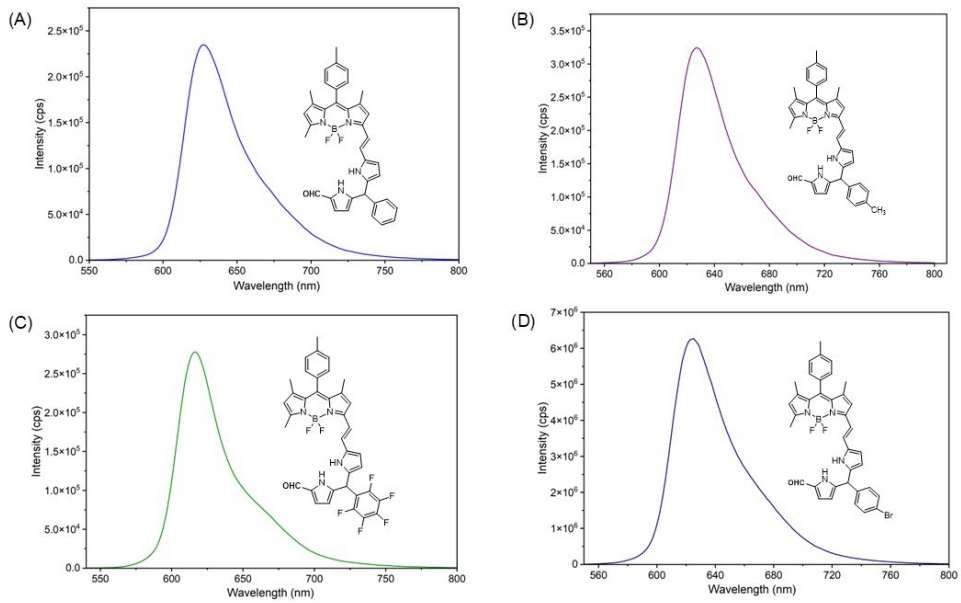


Fig S38. Fluorescence spectra of (A) **10**, (B) **11**, (C) **13**, and (D) **12** in CH_2Cl_2 at 298K.

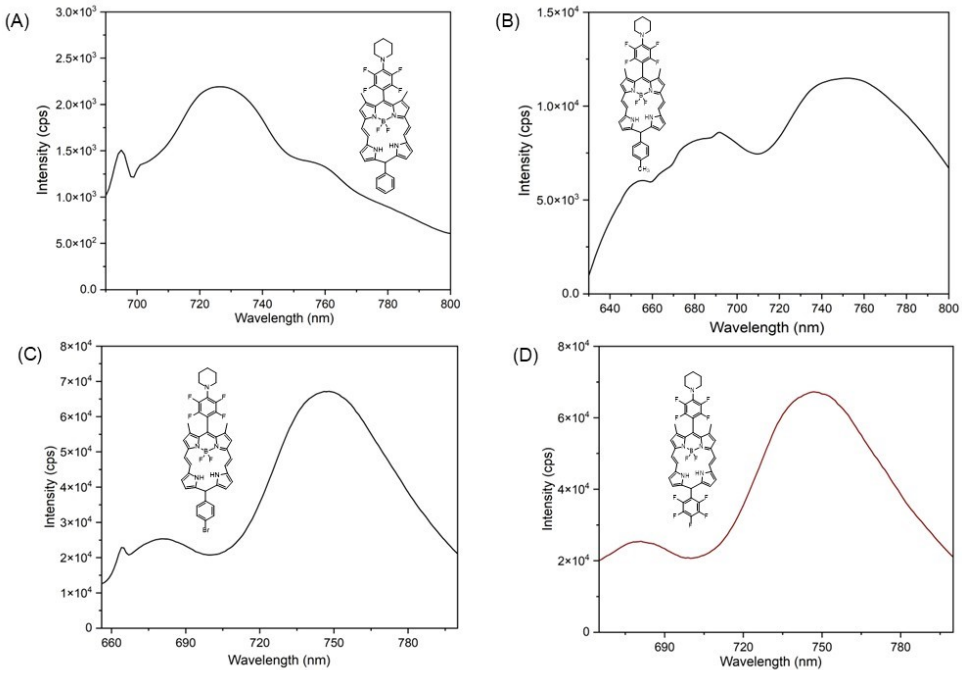


Fig S39. Fluorescence spectra of (A) **14**, (B) **15**, (C) **16**, and (D) **17** in CH_2Cl_2 at 298K.

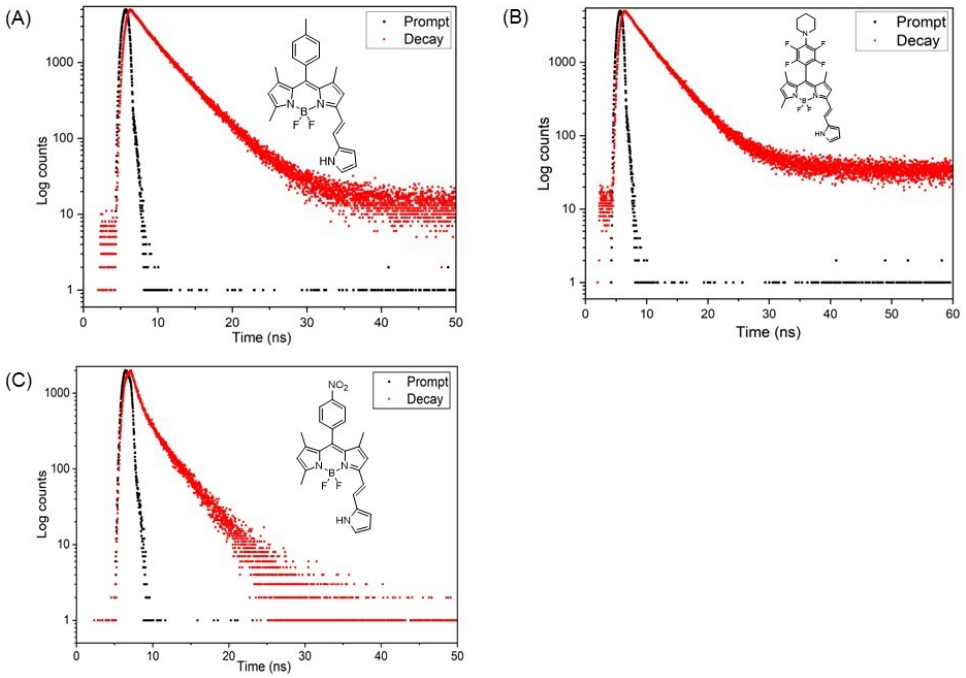


Fig S40. Fluorescence lifetime decay profile of (A) **2**, (B) **9**, and (C) **7** in CH_2Cl_2 at 298K.

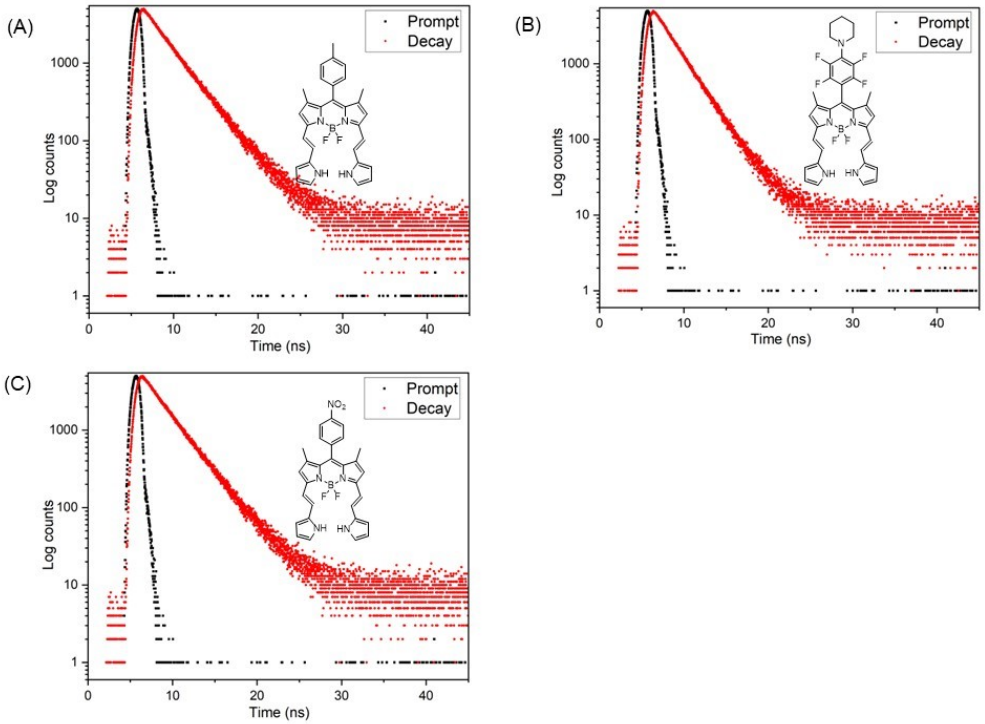


Fig S41. Fluorescence lifetime decay profile of (A) **3**, (B) **6**, and (C) **8** in CH_2Cl_2 at 298K.

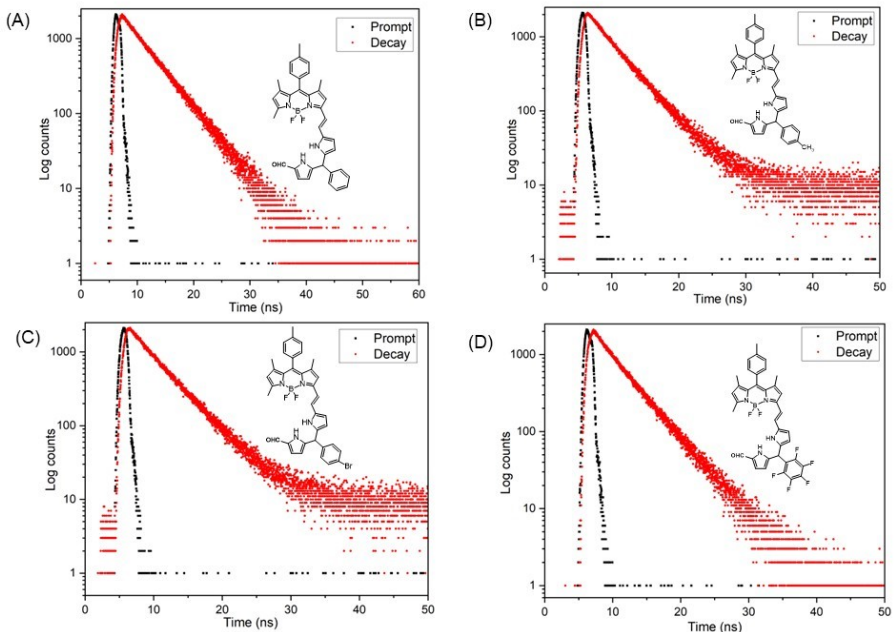


Fig S42. Fluorescence lifetime decay profile of (A) **10**, (B) **11**, (C) **13**, and (D) **12** in CH_2Cl_2 at 298K.

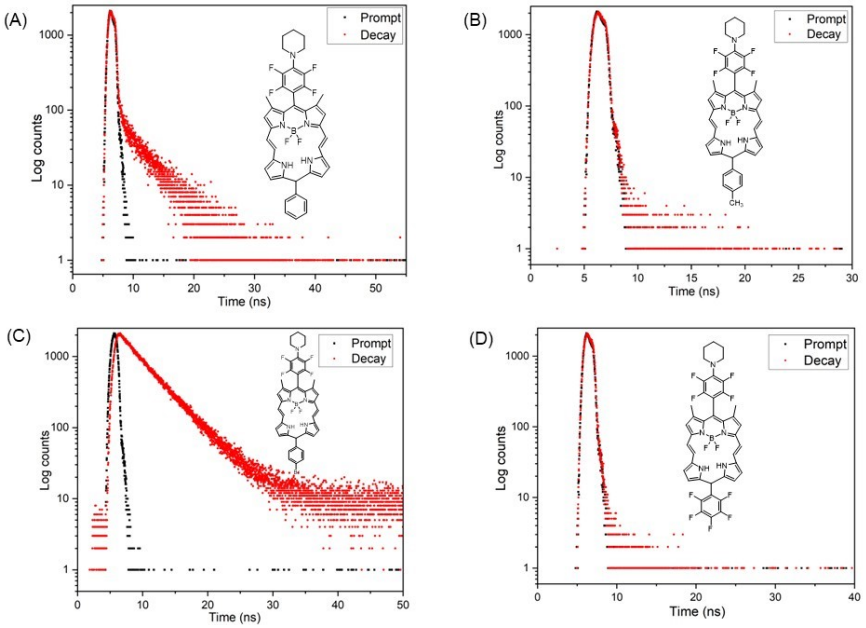


Fig S43. Fluorescence lifetime decay profile of (A) **14**, (B) **15**, (C) **16**, and (D) **17** in CH_2Cl_2 at 298K

Table S2. Photophysical data of synthesized compounds[a]						
BODIPY	**λ_{abs} (nm)**	**λ_{em} (nm)**	**Φ_f**	**τ_f (ns)**	**K_r (s^{-1})**	**K_{nr} (s^{-1})**
1	499	514	0.76	4.45	1.71×10^8	5.39×10^7
2	345, 545(sh), 584	613	0.22	3.74	5.88×10^7	2.09×10^8
3	384, 618(sh), 670	715	0.22	3.01	7.31×10^7	2.59×10^8
4	505	519	0.045	2.17	2.07×10^7	4.40×10^8
5	517	533	0.97	7.95	1.22×10^8	3.77×10^6
6	391, 630(sh), 684	717	0.014	0.62	2.25×10^7	1.59×10^9
7	351, 555(sh), 595	618	0.051	2.17	2.35×10^7	4.37×10^8
8	394, 642(sh), 699	731	0.55	2.57	2.14×10^8	1.75×10^8
9	353, 564(sh), 606	633	0.48	4.28	1.12×10^8	1.21×10^8
10	353, 405 (sh), 556(sh), 593	628	0.72	5.03	1.43×10^8	5.57×10^7
11	354, 406(sh), 557(sh), 594	626	0.65	5.50	1.18×10^8	6.36×10^7
12	353, 402(sh), 554(sh), 592	624	0.73	4.47	1.63×10^8	6.04×10^7
13	349, 549(sh), 587	616	0.88	4.46	1.97×10^8	2.69×10^7
14	422, 499, 670	725	0.011	0.91	1.21×10^7	1.09×10^9
15	420, 492, 665, 705 (sh)	683, 750	0.013	0.41	3.15×10^7	2.39×10^9
16	416, 488, 661, 702 (sh)	680, 747	0.014	0.03	4.67×10^8	3.29×10^{10}
17	412, 486, 656, 698 (sh)	679, 746	0.013	0.53	2.43×10^7	1.85×10^9
[a] values were recorded in CH_2Cl_2 at 298 K, sh = shoulder						

Table S3. Absorption and Emission of Synthesized Compounds in Toluene and DMF			
BODIPY	**Solvent**	**λ_{abs} (nm)**	**λ_{em} (nm)**
1	Toluene	499	514
	DMF	502	518
2	Toluene	350, 550,590	612
	DMF	350, 552(sh), 592	628
3	Toluene	388, 620, 678	702
	DMF	389, 624(sh), 682	714
4	Toluene	503	529
	DMF	507	530
5	Toluene	516	530
	DMF	520	540
6	Toluene	395, 634, 693	723
	DMF	396, 636(sh), 694	-
7	Toluene	357, 569, 613	640
	DMF	358, 571(sh), 617	-
8	Toluene	398, 645, 708	734
	DMF	402, 655, 715	756
9	Toluene	353, 564(sh), 606	640
	DMF	402, 655, 715	663
10	Toluene	356, 421, 558(sh), 600	624
	DMF	359, 512(sh), 562(sh), 607	647
11	Toluene	358, 418(sh), 557(sh), 601	624
	DMF	359, 418(sh), 564, 607	649
12	Toluene	357, 419, 555, 598	624
	DMF	359, 418(sh), 561(sh), 605	645
13	Toluene	353, 417(sh), 552(sh), 593	618
	DMF	355, 510, 557(sh), 601	636
14	Toluene	425, 507, 672, 721(sh)	785
	DMF	436, 516, 682, 731(sh)	-
15	Toluene	426, 513, 675, 719 (sh)	786
	DMF	426, 518, 682, 733(sh)	-
16	Toluene	426, 507, 670, 712(sh)	784
	DMF	424, 510, 680, 728(sh)	-
17	Toluene	421, 507, 671, 715(sh)	785
	DMF	425, 504, 677, 725(sh)	-

5. Singlet Oxygen Generation

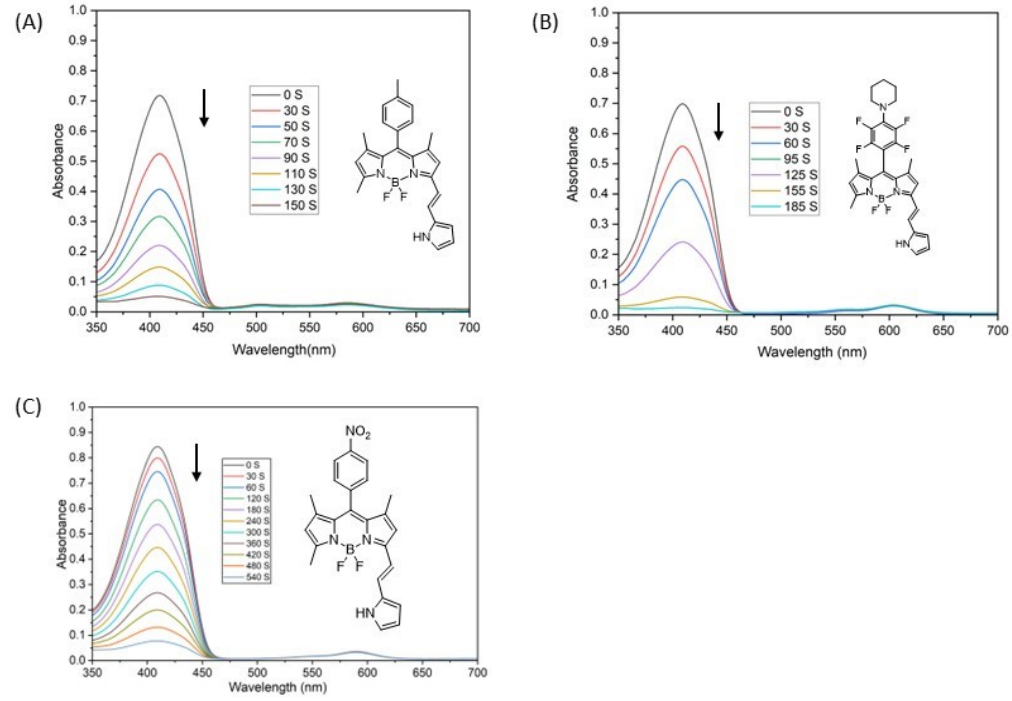


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Fig S44. Change in the absorption spectra of DPBF at 410 nm upon irradiation with green light (525 nm) in the presence of compounds (A) **2**, (B) **9**, and (C) **7** in ACN at 298K.

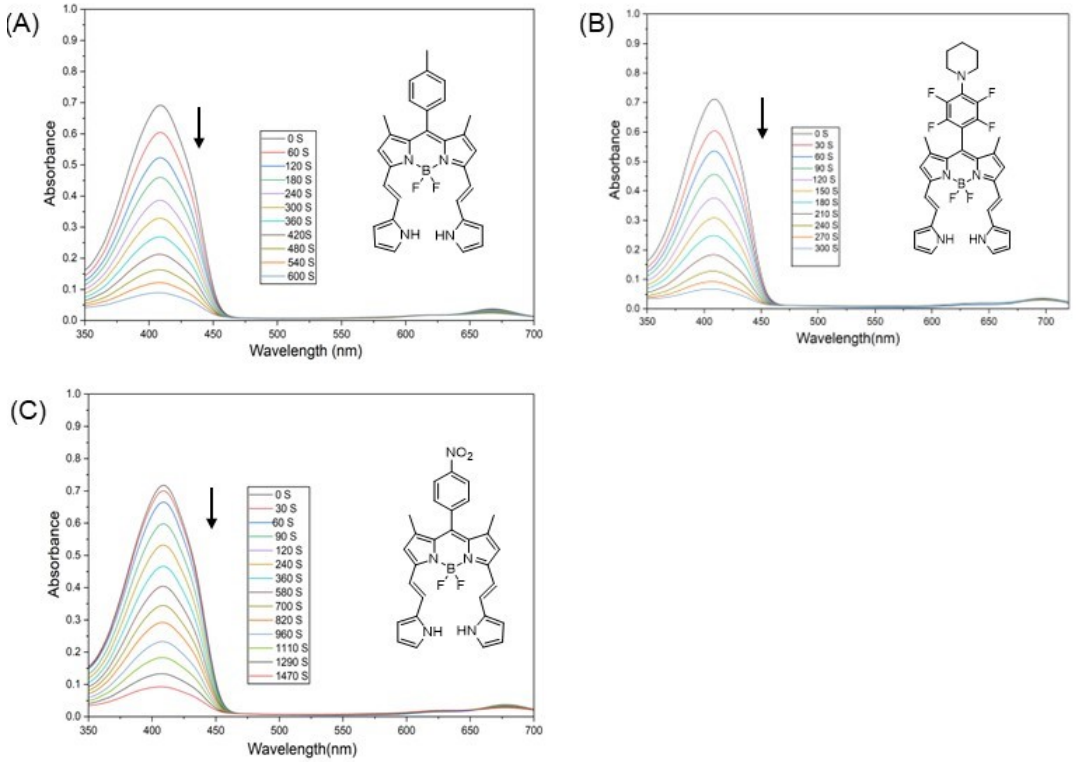

Fig S45. Change in the absorption spectra of DPBF at 410 nm upon irradiation with green light (525 nm) in the presence of compounds (A) **3**, (B) **6**, and (C) **8** in ACN at 298 K.

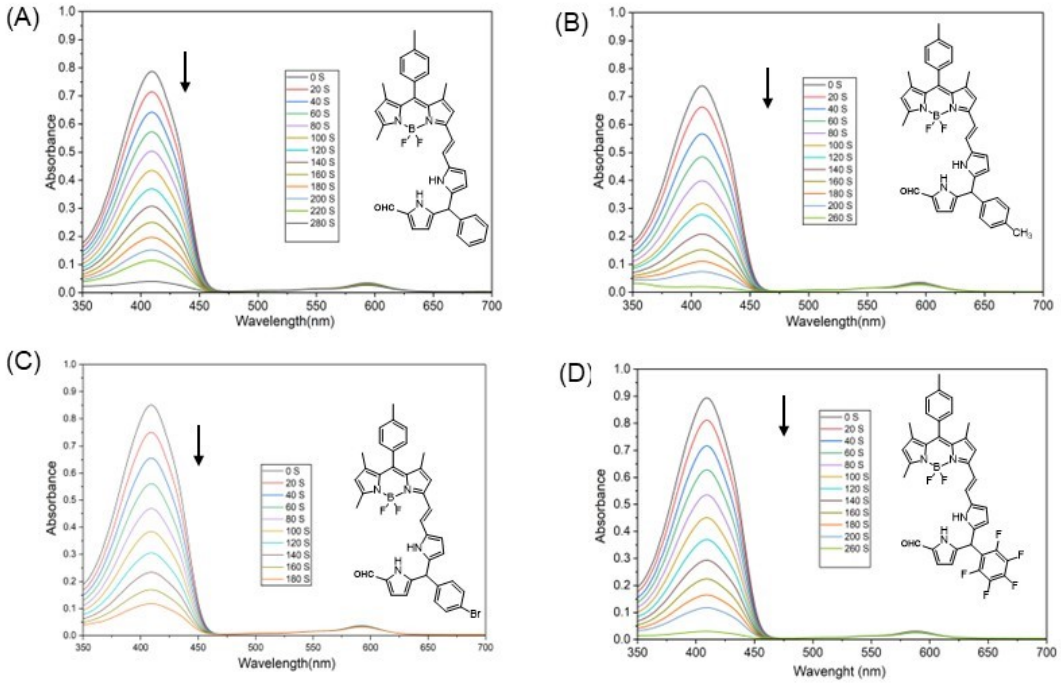

Fig S46. Change in the absorption spectra of DPBF at 410 nm upon irradiation with green light (525 nm) in the presence of compounds (A) **10**, (B) **11**, (C) **12**, and (D) **13** in ACN at 298 K.

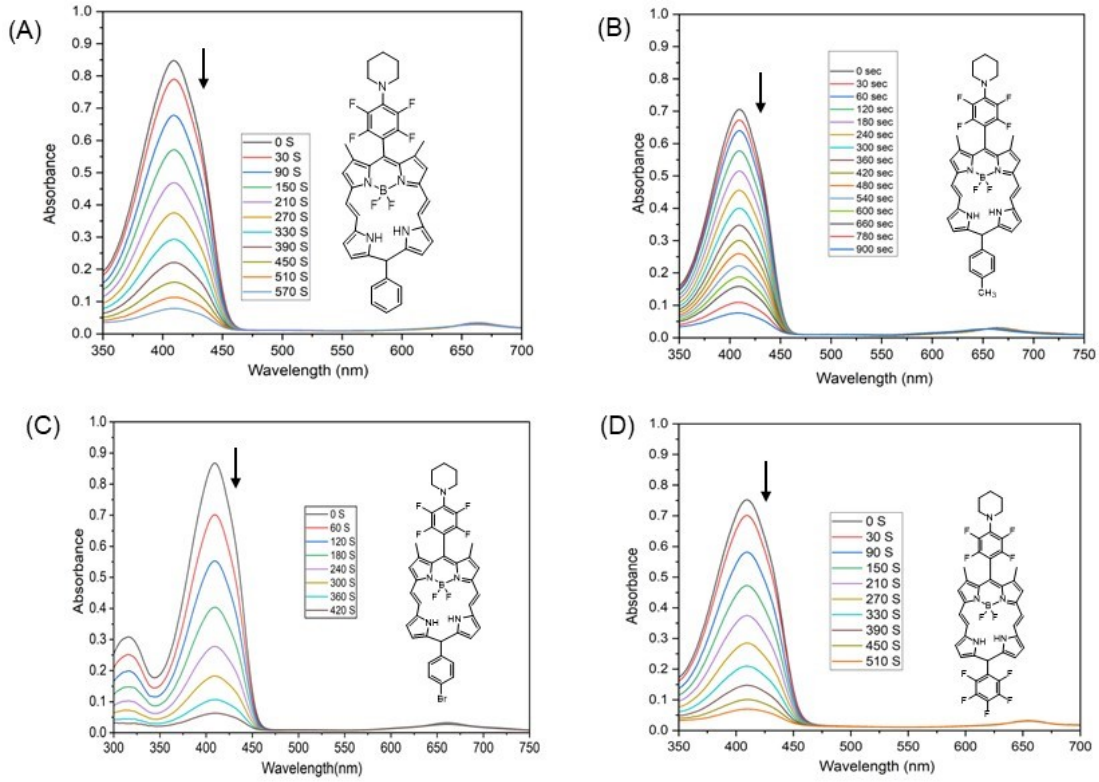

Fig S47. Change in the absorption spectra of DPBF at 410 nm upon irradiation with green light (525 nm) with compounds (A) **14**, (B) **15**, (C) **16**, and (D) **17** in ACN at 298 K.

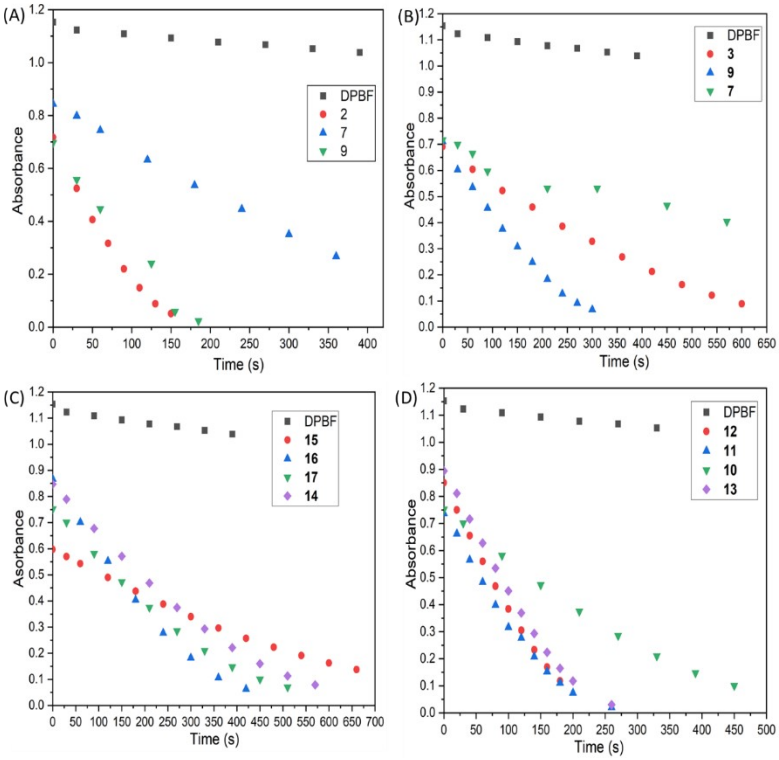

Fig S48. DPBF degradation over time in the combined presence of synthesized BODIPYs and light.

Table S4. Singlet oxygen quantum yield (ϕ_Δ) values.	
Compound	ϕ_Δ[a]
meso-Phenyl BODIPY	0.014
H_2TPP	0.6
2	0.47
3	0.08
5	0.37
7	0.13
8	0.20
9	0.36
10	0.25
11	0.26
12	0.45
13	0.35
14	0.13
15	0.06
16	0.19
17	0.28
[a] values were recorded in ACN at room temperature.	

6. Invitro Studies

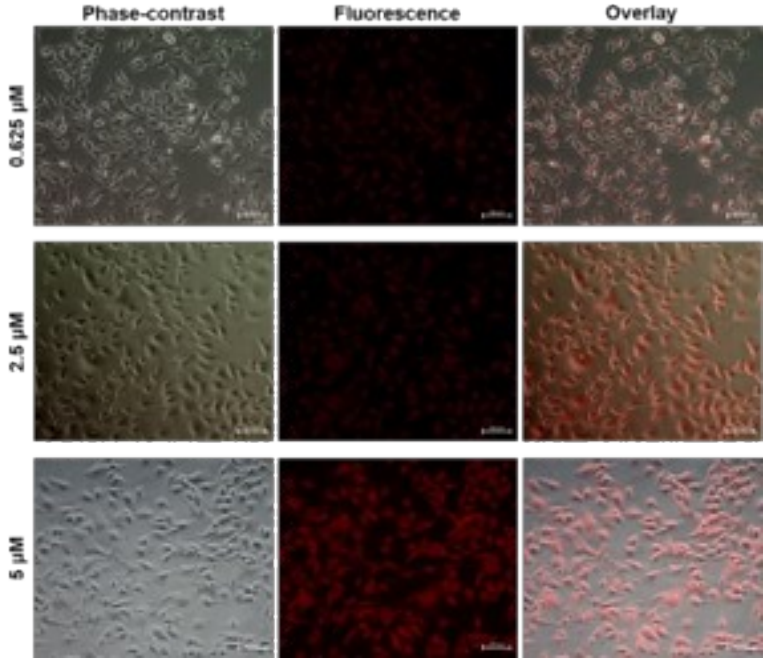

Fig 49. Dose-dependent increase of cellular internalization of the compound **10**.

7. DFT Analysis

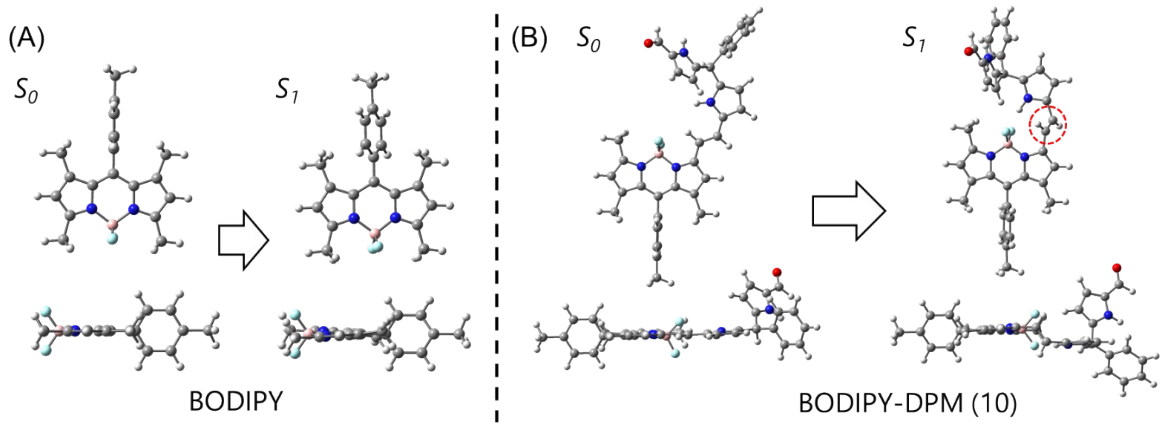

Fig S50. Ground state and excited state optimized state for (A) BODIPY **1** (B) BODIPY-DPM (**10**).

Table S5. Spin-Orbit Coupling Matrix Element (SOCME) values for **1** and **10**.

State	SOCME /cm^{-1}

T	S	**1**	**10**
1	0	0.23	0.35
1	1	0.12	0.04
2	1	0.01	0.09
3	1	2.01	1.78
4	1	0.14	0.54
5	1	0.42	0.62

8. References

1. M. E. El-Khouly, A. N. Amin, M. E. Zandler, S. Fukuzumi, and F. D'Souza *Chem. Eur. J.* 2012**,** **18**, 5239 – 5247.

2. G. Vives, C. Giansante, R. Bofinger, G. Raffy, A. Del Guerzo, B. Kauffmann, P. Batat, G. Jonusauskas, and N. D. McClenaghan *Chem. Commun.*, 2011, **47**, 10425–10427.

3. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339–341.

4. G. Sheldrick, *Acta Cryst. Sect. A*, **2015,** *71*, 3–8.

5. F. Neese WIREs Comput Mol Sci. **2022**;*12*, e1606.