Supplementary Information

Mitochondria-targeting biocompatible fluorescent BODIPY probes

Edward R. H. Walter,[‡ab] Lawrence Cho-Cheung Lee,[‡bc] Peter Kam-Keung Leung,[cd] Kenneth Kam-Wing Lo*[cd] and Nicholas J. Long*[a]

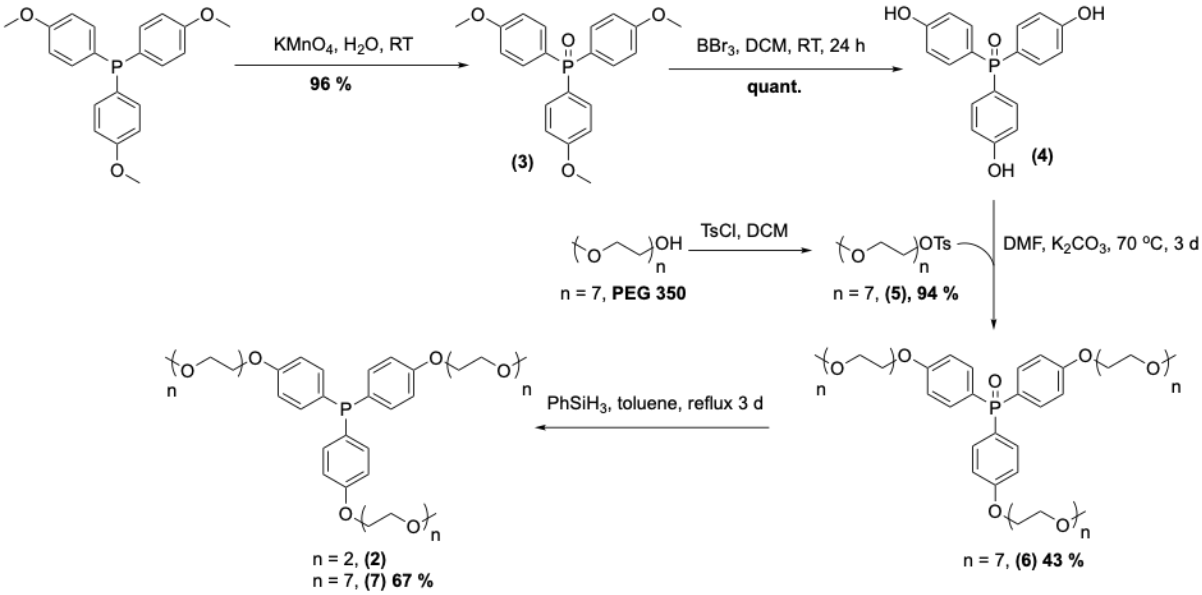
[a] *Department of Chemistry, Imperial College London, Molecular Sciences Research Hub (MSRH), London, W12 0BZ, UK.*

[b] *Laboratory for Synthetic Chemistry and Chemical Biology Limited, Units 1503-1511, 15/F, Building 17 W, Hong Kong Science Park, New Territories, Hong Kong, P. R. China.*

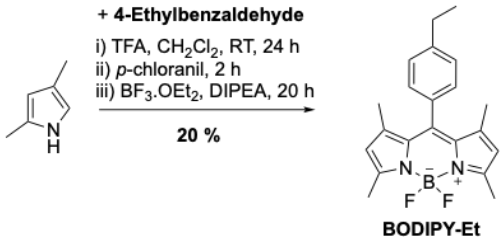
[c] *Department of Chemistry, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong, P. R. China.*

[d] *State Key Laboratory of Terahertz and Millimeter Waves, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong, P. R. China.*

1. Figures and Schemes



Scheme S1. Synthesis of compound (**7**)**.** The synthetic procedures for the synthesis of compounds (**2**), (**3**) and (**4**) were first reported by Wang and co-workers.[1]



Scheme S2. Synthesis of **BODIPY-Et**.

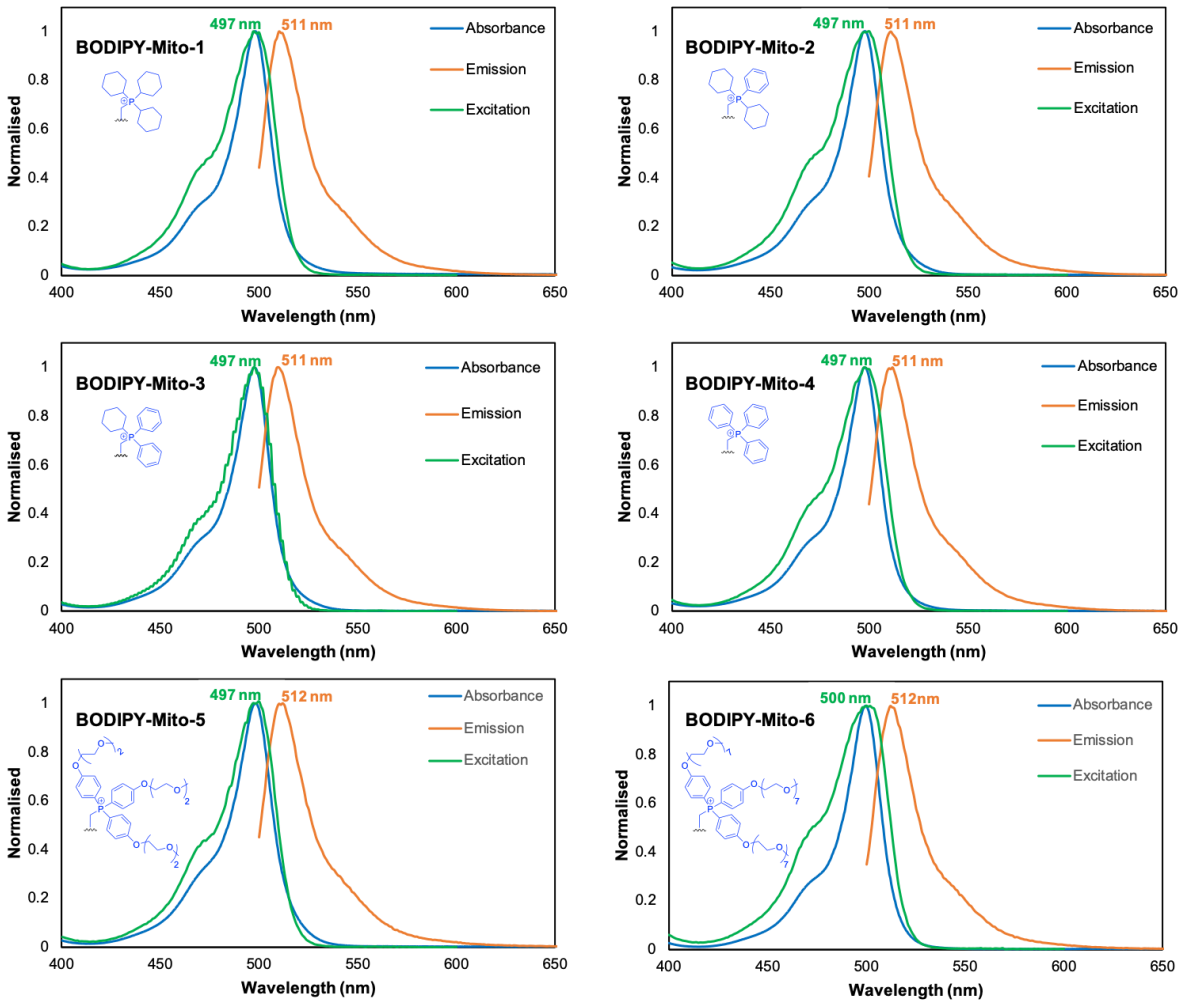


Fig. S1. Absorbance (*blue*), emission (*orange*) and excitation (*green*) spectra of analogues **BODIPY-Mito-1** to **BODIPY-Mito-6**. **[BODIPY]** = 10 μM, PBS (pH = 7.4), 298 K. λ_{ex}= 497 nm, λ_{em}= 511 nm.

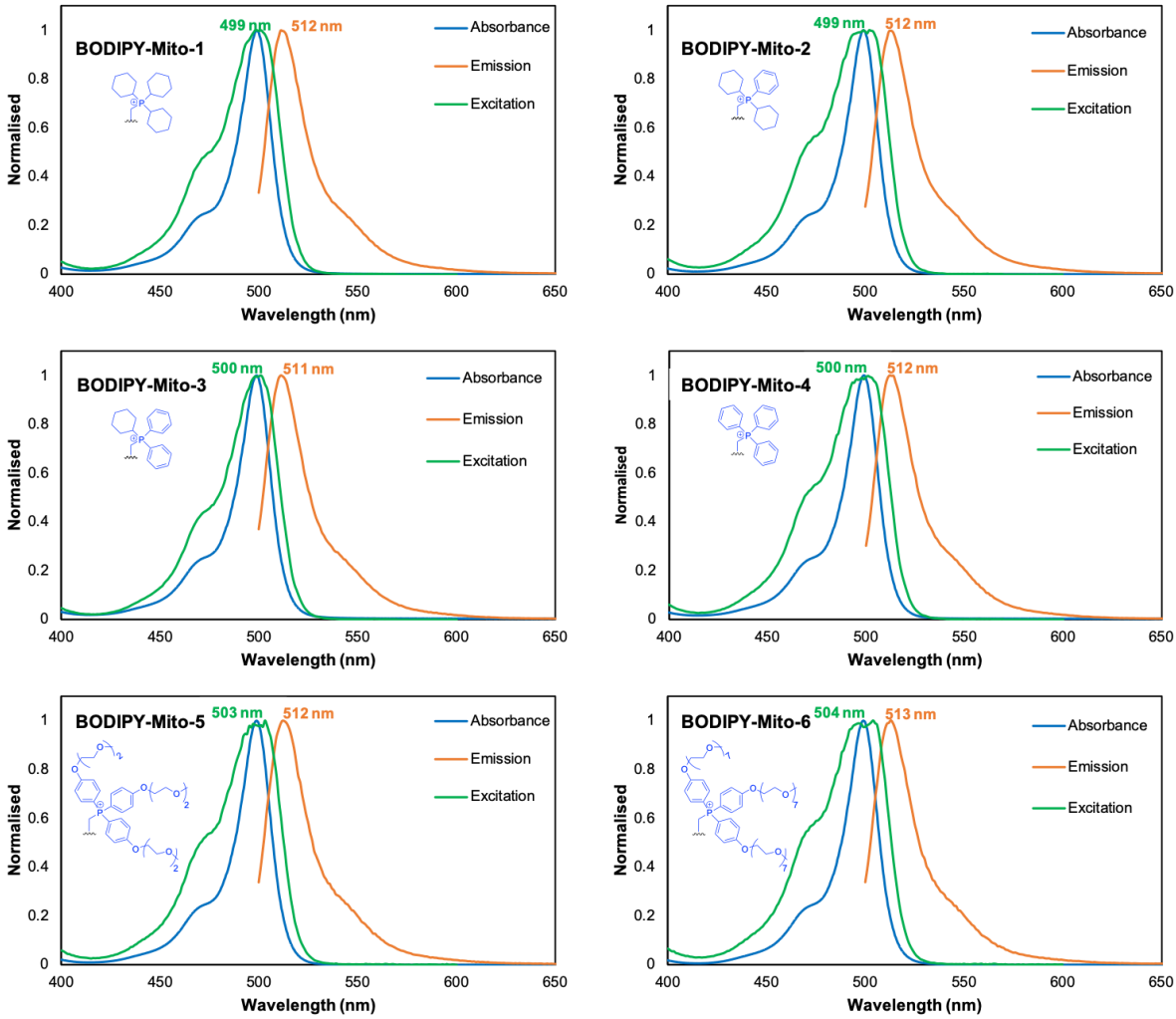


Fig. S2. Absorbance (*blue*), emission (*orange*) and excitation (*green*) spectra of analogues **BODIPY-Mito-1** to **BODIPY-Mito-6**. **[BODIPY]** = 10 μM, CH_3CN, 298 K. λ_{ex}= 499 nm, λ_{em}= 512 nm.

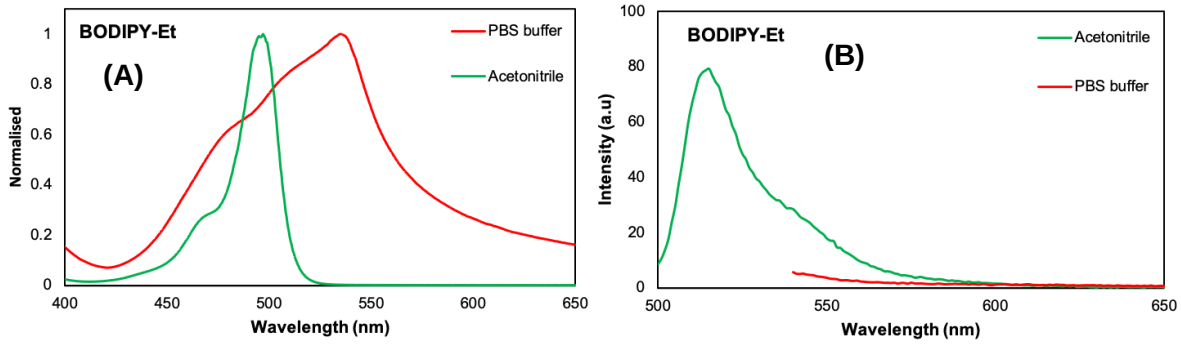


Fig. S3. Comparison of **(A)** absorbance and **(B)** emission spectra of **BODIPY-Et**. **[BODIPY-Et]** = 10 μM. λ_{ex} = 535 nm in PBS (pH = 7.4) and λ_{ex}= 497 nm in acetonitrile, 298 K.

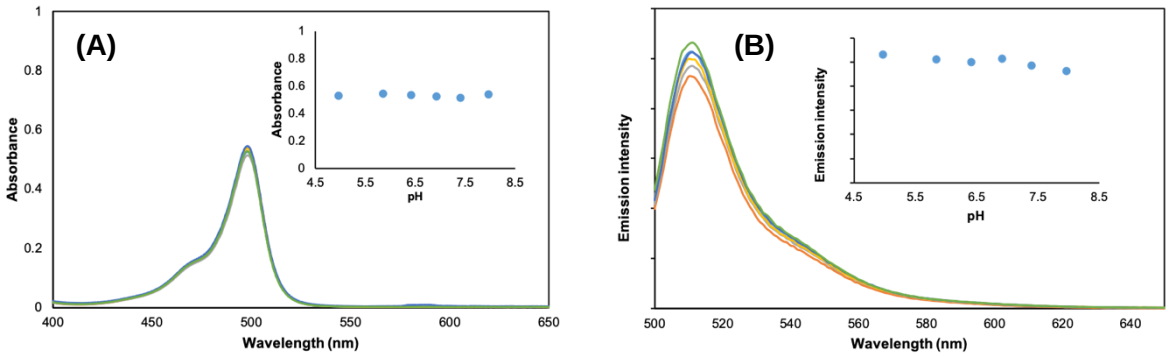


Fig. S4. Variation of the **(A)** absorbance and **(B)** emission spectra of **BODIPY-Mito-1** with pH. Inset shows the plot of absorbance/emission intensity vs. pH. **[BODIPY-Mito-1]** = 10 μM, 298 K.

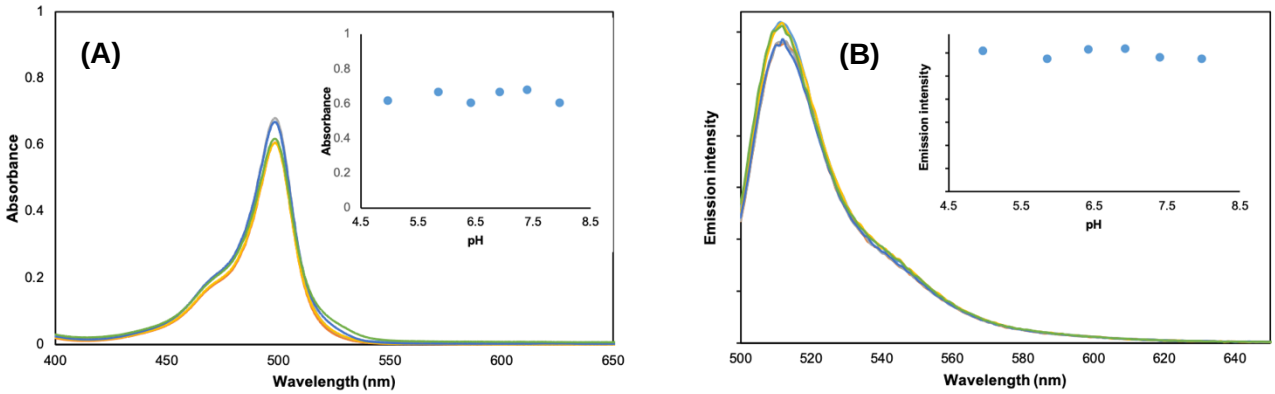


Fig. S5. Variation of the **(A)** absorbance and **(B)** emission spectra of **BODIPY-Mito-2** with pH. Inset shows the plot of absorbance/emission intensity vs. pH. **[BODIPY-Mito-2]** = 10 μM, 298 K.

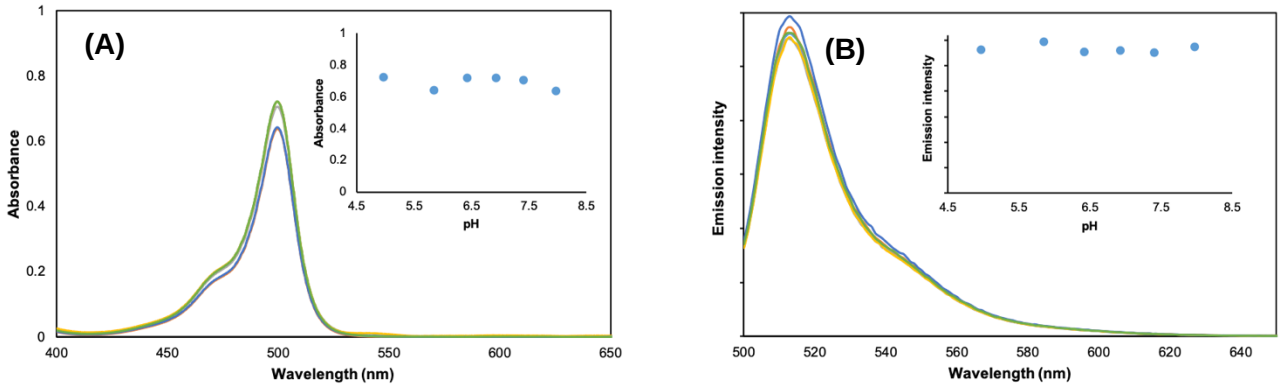


Fig. S6. Variation of the **(A)** absorbance and **(B)** emission spectra of **BODIPY-Mito-6** with pH. Inset shows the plot of absorbance/emission intensity vs. pH. **[BODIPY-Mito-6]** = 10 μM, 298 K.

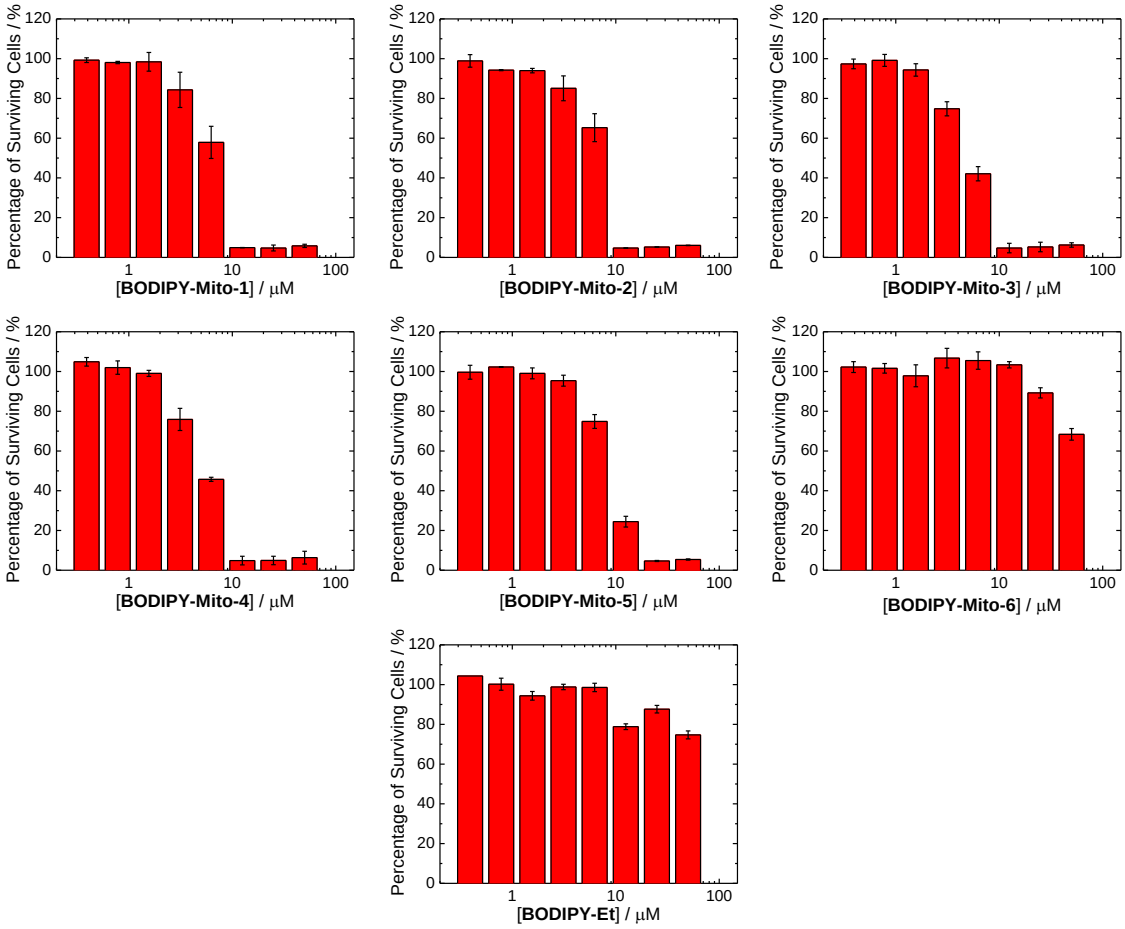


Fig. S7. Percentage of surviving HeLa cells after exposure to the **BODIPY** compounds for 24 h.

Table S1. Photophysical data for **BODIPY-Mito-*n*** compounds in this study and **BODIPY-Et** in acetonitrile.[a]

BODIPY	λ_{abs} / nm	λ_{ex} / nm	λ_{em} / nm	QY (ϕ)
BODIPY-Mito-1	499	499	512	0.60
BODIPY-Mito-2	499	499	512	0.60
BODIPY-Mito-3	499	500	511	0.55
BODIPY-Mito-4	499	500	512	0.57
BODIPY-Mito-5	499	503	512	0.62
BODIPY-Mito-6	499	504	513	0.60
BODIPY-Et [b]	497	497	514	0.57

[a] **[BODIPY]** = 10 μM in acetonitrile, λ_{ex}= 499 nm, 298 K. [b] λ_{ex}= 497 nm, 298 K. Quantum yields (ϕ) were measured using fluorescein in 0.1 M NaOH ($\phi_{496\ nm}$= 0.95)[2] as the standard. Estimated error = ± 20 %.

Table S2. Flow cytometric results of HeLa cells incubated with **BODIPY-Mito-1**–**6** (1 h) without or with the posttreatment with CCCP (10 μM, 30 min).

	Relative intensity / A.U.		Percentage decrease / %
BODIPY	**– CCCP**	**+ CCCP**	
BODIPY-Mito-1 [a]	42.1	29.7	29.5
BODIPY-Mito-2 [a]	32.5	12.3	62.1
BODIPY-Mito-3 [a]	43.2	30.8	28.6
BODIPY-Mito-4 [a]	47.1	28.2	40.1
BODIPY-Mito-5 [b]	2696.3	1728.6	35.9
BODIPY-Mito-6 [c]	736.4	183.1	75.1

[a] **[BODIPY]** = 500 nM. [b] **[BODIPY]** = 5 μM. [c] **[BODIPY]** = 25 μM.

Table S3. Cytotoxicity of the **BODIPY** compounds towards HeLa cells upon incubation at 37 °C for 24 h, as determined by the MTT assay.

BODIPY	IC_{50} / μM
BODIPY-Mito-1	6.51 ± 0.58
BODIPY-Mito-2	6.61 ± 0.70
BODIPY-Mito-3	4.95 ± 0.43
BODIPY-Mito-4	5.74 ± 0.24
BODIPY-Mito-5	8.00 ± 0.70
BODIPY-Mito-6	> 50
BODIPY-Et	> 50

2. Experimental Details

General Procedures: All commercially available reagents were used as received from suppliers without further purification. Solvents used were laboratory grade. Anhydrous solvents were obtained from departmental solvent towers and stored over 3 Å molecular sieves. Moisture-sensitive reactions were carried out by Schlenk-line techniques, under an inert atmosphere of nitrogen. Thin-layer chromatography was performed on silica (Merk Art 5554) and visualised under UV radiation. Automated flash column chromatography was executed using a Biotage Isolera Four unit and KP-SIL silica cartridges (10 g or 25 g). ^{1}H (400 MHz), ^{31}P NMR {^{1}H} (162 MHz) and ^{13}C {^{1}H} (101 MHz) NMR spectra were recorded on a Bruker AV-400 spectrometer, Imperial College London at 298 K. Chemical shifts are reported in parts per million (ppm) and coupling constants in Hertz (Hz). Peak multiplicities are abbreviated as; s = singlet, m = multiple, d = doublet, t = triplet, q = quartet, dd = doublet of doublet and br = broad. Mass spectrometry analysis (ESI, accurate

mass) was conducted by the Mass Spectrometry Service, Imperial College London, unless stated otherwise.

2.1 Photophysical Characterisation

Sample Preparation: Stock solutions of **BODIPY** analogues were prepared in DMSO (1 mL) with a concentration range of 1 – 3 mM, and stored at -20 °C in the dark. Samples were thawed to room temperature directly before use. All samples were diluted to 10 μM in PBS (pH = 7.4) for the photophysical measurements.

UV-Vis Spectroscopy: UV-Visible absorption spectra were measured using an Agilent Technologies Cary 60 Spectrophotometer operating with WinUV software. The sample was held in a quartz cuvette with a path length of 1 cm. Absorption spectra were recorded against a baseline of pure solvent in an optically matched cuvette with a scan rate of 600 nm / min and a data interval of 1.0 nm. Extinction coefficients were calculated from the Beer Lambert Law (**Equation 1**):

$$A = \varepsilon c l \qquad \textbf{Equation 1.}$$

where *A* = the absorbance at a particular wavelength, ε is the extinction coefficient, *c* is the concentration and *l* is the path length (width of the quartz cuvette, 1 cm).

Fluorescence Spectroscopy: Emission and excitation spectra were acquired on an Agilent Technologies Carry Eclipse Fluorescence Spectrophotometer, in quartz cuvettes with a path length of 1 cm. Emission and excitation spectra were collected with a scan rate of 120.0 nm / min, a delay interval of 1.0 nm and band-passes of 5 nm unless stated otherwise.

Quantum Yields: The fluorescence quantum yields of **BODIPY** analogues were determined relative to fluorescein ($\phi_{496\ \mathrm{nm}}$ = 0.95) in 0.1 M NaOH.[2] Solutions of the reference and the sample were prepared so that the absorbance at 496 nm was ≤ 0.1. All measurements were recorded under aerated conditions at room temperature in PBS (pH = 7.4). Absorbance and emission spectra were run consecutively with identical instrumentation parameters. The quantum yield for the **BODIPY** analogues were calculated from **Equation 2**:

$$\phi_{\mathrm{a}} = \left(\frac{I_{\mathrm{a}}}{I_{\mathrm{b}}}\right) \mathrm{x} \left(\frac{A_{\mathrm{b}}}{A_{\mathrm{a}}}\right) \mathrm{x} \left(\frac{n_{\mathrm{a}}}{n_{\mathrm{b}}}\right)^2 \mathrm{x}\, \phi_{\mathrm{b}} \qquad \textbf{Equation 2.}$$

where ϕ is the quantum yield, *I* is the integrated intensity of the emission spectrum, *A* is the absorbance at the excitation wavelength and *n* is the refractive index of the solvent. '*a*' refers to the sample, and '*b*' refers to the standard. Based on our experience in photophysical

measurements, an error of ± 20 % in the determination of fluorescence quantum yields is estimated.

pH Measurements: Measurements were recorded using a Jenway 3510 pH meter in combination with a Jenway 924 005 pH electrode. Before the independent titration, the pH probe was calibrated using pH 4, 7 and 10 buffer solutions. Aqueous solutions of KCl (100 mM) / MES (50 mM) and KCl (100 mM) / HEPES (50 mM) were made up and used for pH ranges 4.97 – 6.42 and 6.92 – 7.97 respectively. The pH of each solution was confirmed following addition of **BODIPY-Mito-1**, **BODIPY-Mito-2** or **BODIPY-Mito-6** ([**BODIPY**] = 10 μM, 298 K).

2.2 Biological Characterisation

Cell Cultures: HeLa cells were grown in Dulbecco's Modified Eagle Medium (DMEM) supplemented with 10 % fetal bovine serum (FBS) and 1 % penicillin/streptomycin at 37 °C under a 5 % CO_2 atmosphere. They were subcultured every 2 to 3 days.

Live-cell Confocal Imaging: HeLa cells in growth medium were seeded on a sterilised coverslip in a 35-mm tissue culture dish and grown at 37 °C under a 5 % CO_2 atmosphere for 48 h. The growth medium was removed and replaced with the **BODIPY** compounds (0.5, 5 or 25 μM) in growth medium/DMSO (99:1, *v* / *v*) at 37 °C under a 5 % CO_2 atmosphere for 1 h. The medium was removed, and the cell layer was gently washed with PBS (1 mL × 3). The coverslip was mounted onto a sterilised glass slide and then imaging was performed using a Leica TCS SPE confocal microscope with an oil immersion 63× objective and an excitation wavelength at 488 nm. For the co-staining experiments, after treatment with the **BODIPY** compounds, the medium was removed, and the cell layer was gently washed with PBS (1 mL × 3). The cells were then incubated with MitoTracker Deep Red FM (100 nM) or Lipi-Blue (500 nM) in growth medium at 37 °C under a 5 % CO_2 atmosphere for 30 min. The medium was then removed, and the cell layer was gently washed with PBS (1 mL × 3) prior to imaging. The excitation wavelength of MitoTracker Deep Red FM was 635 nm and that of Lipi-Blue was 405 nm. The Pearson's correlation coefficients were determined using the program ImageJ (Version 1.4.3.67). For the mitochondrial-membrane potential (MMP) experiments, after treatment with the **BODIPY** compounds, the medium was removed, and the cell layer was gently washed with PBS (1 mL × 3). The cells were then incubated with carbonyl cyanide *m*-chlorophenylhydrazone (CCCP) (10 μM) at 37°C under a 5 % CO_2 atmosphere for 30 min. The medium was removed, and the cell layer was gently washed with PBS (1 mL × 3) prior to imaging.

Flow Cytometry: HeLa cells in growth medium were seeded on a 35-mm tissue culture dish and grown at 37 °C under a 5 % CO_2 atmosphere for 48 h. The growth medium was removed and

replaced with the **BODIPY** compounds (0.5, 5 or 25 μM) in growth medium/DMSO (99:1, *v* / *v*) at 37 °C under a 5 % CO_2 atmosphere for 1 h. The medium was removed, and the cell layer was gently washed with PBS (1 mL × 3). The cells were trypsinised and harvested with PBS. The resultant solution (2 mL) was analysed by a FACSCalibur flow cytometer (Becton, Dickinson and Co., Franklin Lakes, NJ, USA) with an excitation wavelength at 488 nm. The number of cells analysed for each sample was between 9,000 and 10,000. For the MMP experiments, after treatment with the **BODIPY** compounds, the medium was removed, and the cell layer was gently washed with PBS (1 mL × 3). The cells were then incubated with CCCP (10 μM) at 37 °C under a 5 % CO_2 atmosphere for 30 min. The medium was removed, and the cell layer was gently washed with PBS (1 mL × 3) prior to analysis.

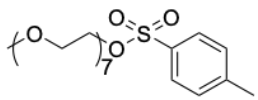
MTT Assays: HeLa cells were seeded in a 96-well flat-bottomed microplate (*ca.* 10,000 cells per well) in growth medium (100 μL) and incubated at 37 °C under a 5 % CO_2 atmosphere for 24 h. The growth medium was removed and replaced with the **BODIPY** compounds at concentrations ranging from 10^{-8} to 10^{-5} M in growth medium/DMSO (99:1, *v* / *v*). Wells containing untreated cells were used as blank controls. The microplate was incubated at 37°C under a 5% CO_2 atmosphere for 24 h. Then, MTT in PBS (10 μL, 5 mg mL^{-1}) was added to each well. The microplate was incubated at 37 °C under a 5 % CO_2 atmosphere for 4 h. The growth medium was then removed, and DMSO (200 μL) was added to each well. The microplate was further incubated at 37 °C for 15 min. The absorbance of the solutions at 570 nm was measured with an Epoch 2 microplate spectrophotometer (BioTek., Santa Clara, CA). The IC_{50} values of the **BODIPY** compounds were determined from dose dependence of surviving cells after exposure to the compounds.

2.3 Compound Synthesis

Compounds (**1**) (WO2012/95628, 2012, A1), (**2**)[1], (**3**)[1] and (**4**)[1] were prepared in accordance with previous literature reports.

PEG350-Tosylate, (5)

Procedure was adapted from Wang and co-workers.[1]

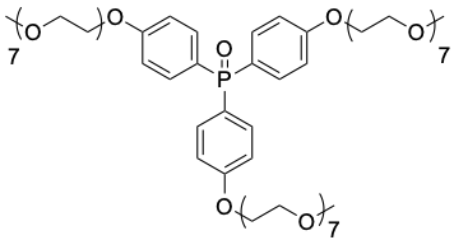


A solution of tosyl chloride (2.1 g, 11.01 mmol) in THF (5 mL) was added to an ice cold (0 – 5 °C) solution of **PEG350** (2.04 g, 5.83 mmol) and sodium hydroxide (682.0 mg, 17.05 mmol) in water (5 mL). The colourless solution was stirred in ice for 4 h and gradually warmed to room temperature over 1 h. The reaction was diluted with water (10 mL) and washed with CH_2Cl_2 (3 x 20 mL). Organic extracts were combined and washed with brine (20 mL) and water (20 mL) and dried over Na_2SO_4 and filtered. The solvent was removed under reduced pressure to form the title compound as a colourless oil that was used in subsequent

steps without additional purification (2.8 g, 94 %). ^{1}H NMR (400 MHz, $CDCl_3$) 7.80 – 7.77 (2 H, br m), 7.35 – 7.32 (2 H, br m), 4.16 – 4.13 (2 H, m), 3.68 – 3.52 (28 H, m), 3.37 3 H, br s), 2.44 (3 H, br s); ^{13}C NMR {^{1}H} (101 MHz, $CDCl_3$) 144.9, 133.1, 129.4, 128.1, 72.0, 70.7 (br m*), 69.4, 68.8, 59.2, 21.8; ESI-LRMS $[C_{22}H_{39}O_{10}S]^+$, (+) m/z 495.2, ESI-HRMS calculated for $[C_{22}H_{39}O_{10}S]^+$, 495.2264 found, 495.2267.

*multiple carbon environments present.

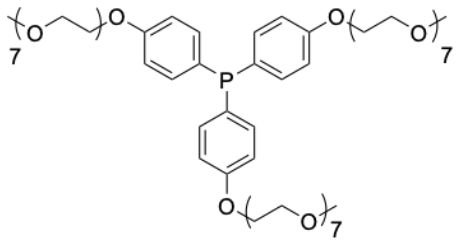
Tris(4-(2-methoxyethoxy)phenyl)phosphine oxide, (6)



PEG-350 tosylate (1.65 g, 3.33 mmol) in anhydrous DMF (14 mL) was added to a stirring suspension of (**4**) (353.3 mg, 1.08 mmol) and potassium carbonate (1.48 g, 10.71 mmol) in anhydrous DMF (12 mL) at room temperature. The suspension was heated to 70 °C and stirred under an inert atmosphere of nitrogen for 3 d. After 3 d, the reaction was cooled to room temperature, diluted with CH_2Cl_2 (50 mL) and filtered under reduced pressure to remove inorganic impurities. The solvent was removed under reduced pressure to form an off-white residue. Purification by silica gel column chromatography (99 % CH_2Cl_2 / 1 % NEt_3 to 94 % CH_2Cl_2, 5 % MeOH / 1 % NEt_3) formed the title compound as colourless oil (595.4 mg, 43 %). ^{1}H NMR (400 MHz, $CDCl_3$) 7.54 – 7.49 (6 H, m), 6.94 (6 H, d, $^{3}J_{H\text{-}H}$ 8.1), 4.15 – 4.13 (6 H, m), 3.86 – 3.84 (6 H, m), 3.72 – 3.70 (6 H, m), 3.67 – 3.63 (62 H, m), 3.54 – 3.51 (6 H, m), 3.36 (9 H, br s); ^{31}P NMR {^{1}H} (162 MHz, $CDCl_3$) 28.6; ^{13}C NMR {^{1}H} (101 MHz, $CDCl_3$) 161.6, 133.9 (d, $^{3}J_{C\text{-}P}$ 11.1), 124.8 (d, $^{1}J_{C\text{-}P}$ 110.3), 114.6 (d, $^{2}J_{C\text{-}P}$ 13.2), 72.1, 71.0, 70.7 – 70.6 (br m*), 69.6, 67.6, 59.2; ESI-LRMS $[C_{63}H_{106}O_{25}P]^+$, (+) m/z 1293.7, ESI-HRMS calculated for $[C_{63}H_{106}O_{25}P]^+$, 1293.6761 found, 1293.6758.

*multiple carbon environments present.

Tris(4-(2-methoxyethoxy)phenyl)phosphine, (7)



Phenyl silane (1.5 mL, 12.17 mmol) was added to a solution of tris(4-(2-methoxyethoxy)phenyl)phosphine oxide, (**6**), in toluene (6 mL). The solution was heated to 110 °C, and heated at 110 °C under an inert atmosphere of nitrogen for 3 d. The reaction was then cooled to room temperature and the solvent was removed under reduced pressure to form a light yellow residue. Purification by silica gel column chromatography (99 % CH_2Cl_2 / 1 % NEt_3 to 94 % CH_2Cl_2, 5 % MeOH / 1 % NEt_3) formed the title compound as colourless oil (384.5 mg, 67 %). ^{1}H NMR (400 MHz, $CDCl_3$) 7.19 – 7.15 (6 H, m), 6.88 – 6.85 (6 H, d, $^{3}J_{H\text{-}H}$ 8.2), 4.12 (6 H, $^{3}J_{H\text{-}H}$ 4.9), 3.84 (6 H, $^{3}J_{H\text{-}H}$ 4.9), 3.73 – 3.70 (6 H, m), 3.68 – 3.62 (60 H, m), 3.55 – 3.53 (4 H m), 3.37 (9 H, br s); ^{31}P NMR {^{1}H} (162 MHz, $CDCl_3$) – 10.2; ^{13}C NMR {^{1}H} (101 MHz, $CDCl_3$) 159.4, 135.0 (d, $^{2}J_{C\text{-}P}$ 20.6),

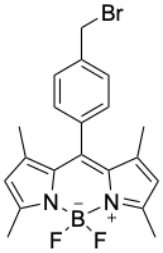
129.2 (br s), 114.9 (d, $^{3}J_{C\text{-}P}$ 7.8), 72.1, 71.0, 70.8 – 70.6 (br m*), 69.8, 67.4, 59.2; ESI-LRMS $[C_{63}H_{106}O_{24}P]^{+}$, (+) m/z 1277.7, ESI-HRMS calculated for $[C_{63}H_{106}O_{24}P]^{+}$, 1277.6812 found, 1277.6838.

*multiple carbon environments present.

Note: It was discovered that extending the PEG chain length from *n* = 2 to *n* = 7 increased the likelihood of oxidation back to the phosphine oxide. Therefore, compound (**7**) was stored at –20 °C and thawed immediately before use.

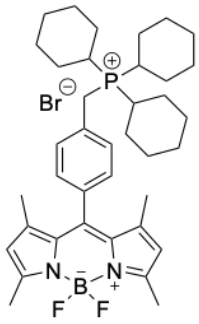
BODIPY-Br

Procedure adapted from Zhang and co-workers.[3]



Trifluoroacetic acid (30 μL, 0.41 mmol) was added to a solution of (**1**) (538.0 mg, 2.7 mmol) and 2,4-dimethylpyrrole (0.68 mL, 6.48 mmol) in anhydrous CH_2Cl_2 (150 mL) and the solution was stirred at room temperature overnight with protection from light under an inert atmosphere of nitrogen. After 20 h, *p*-chloranil (702.2 mg, 2.86 mmol) was added and the reaction was stirred for an additional 3 h. Diisopropylethylamine (DIPEA, 8 mL, 45.9 mmol) and $BF_3.OEt_2$ (6 mL, 48.6 mmol) were then added, and the reaction was stirred at room temperature under an inert atmosphere of nitrogen for a further 18 h. The suspension was diluted with CH_2Cl_2 (100 mL) and washed with H_2O (1 x 100 mL) and brine (1 x 100 mL) and dried over Na_2SO_4. The solvent was removed under reduced pressure to form a dark red viscous oil. Purification by silica gel column chromatography (gradient 100 % hexane to 80 % hexane / 20 % CH_2Cl_2) formed the title compound as a fine orange powder (408.5 mg, 36 %). ^{1}H NMR (400 MHz, $CDCl_3$) 7.53 (2 H, d, $^{3}J_{H\text{-}H}$ 8.1), 7.29 (2 H, d, $^{3}J_{H\text{-}H}$ 8.1), 5.98 (2 H, s), 4.66 (2 H, s), 2.55 (6 H, s), 1.38 (6 H, s); ^{13}C NMR {^{1}H} (101 MHz, $CDCl_3$) 155.8, 143.2, 141.1, 138.7, 135.2, 131.5, 129.4, 128.6, 121.5, 45.8, 14.7, 14.6; ESI-LRMS $[C_{20}H_{21}BN_2FBr]^{+}$, (+) m/z 417.1, ESI-HRMS calculated for $[C_{20}H_{21}BN_2FBr]^{+}$, 417.0949 found, 417.0950.

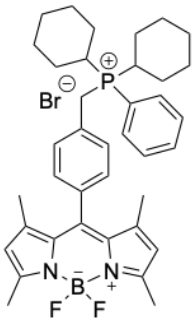
BODIPY-Mito-1



Tricylohexylphosphine (119.4 mg, 0.43 mmol) was added to a solution of **BODIPY-Br** (106.9 mg, 0.26 mmol) in toluene (12 mL). The reaction was heated to 110 °C and stirred under an inert atmosphere of nitrogen for 3 d. The reaction was cooled to room temperature, and the crude product was isolated by filtration and washed with toluene (2 x 10 mL) and diethyl ether (10 mL). Recrystalisation from CH_2Cl_2 / hexane formed the title compound as a fine orange powder (103.4 mg, 60 %). ^{1}H NMR (400 MHz, $CDCl_3$) 7.63 (2 H, d, $^{3}J_{H\text{-}H}$ 7.8), 7.31 (2 H, d, $^{3}J_{H\text{-}H}$ 7.8), 5.95 (2 H, s), 4.56 (2 H, d, $^{2}J_{H\text{-}P}$ 14.7), 2.78 (3 H, m), 2.52 (6 H, s), 2.08 – 2.04 (6 H, m), 1.92 – 1.86 (6 H, m), 1.81 – 1.75 (3 H, m), 1.59 – 1.48 (6 H, m), 1.46 – 1.37

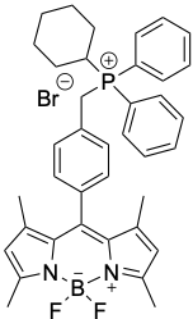
(6 H, m), 1.33 (6 H, s), 1.28 – 1.20 (3 H, m); ^{31}P NMR {^{1}H} (162 MHz, $CDCl_3$) 29.3; ^{13}C NMR {^{1}H} (101 MHz, $CDCl_3$) 156.0, 142.6, 140.4, 135.3, 131.7, 131.6, 131.5, 131.3, 129.4, 31.2 (d, $^{1}J_{C\text{-}P}$ 39.0), 27.4 (d, $^{3}J_{C\text{-}P}$ 4.1), 26.7 (d, $^{2}J_{C\text{-}P}$ 11.9), 25.6, 22.8 (d, $^{1}J_{C\text{-}P}$ 40.9), 14.8, 14.7; ESI-LRMS $[C_{38}H_{53}{}^{11}BN_2F_2P]^+$, (+) m/z 617.4, ESI-HRMS calculated for $[C_{38}H_{53}{}^{11}BN_2F_2P]^+$, 617.4008 found, 617.3995.

BODIPY-Mito-2



Dicyclohexylphenylphosphine (95.2 mg, 0.35 mmol) was added to a solution of **BODIPY-Br** (70.0 mg, 0.168 mmol) in toluene (10 mL). The reaction was heated to 110 °C and stirred under an inert atmosphere of nitrogen for 3 d. The reaction was cooled to room temperature, and the crude product was isolated by filtration and washed with toluene (2 x 10 mL) and diethyl ether (10 mL). Recrystalisation from CH_2Cl_2 / hexane formed the title compound as a fine orange powder (106.5 mg, 92 %). ^{1}H NMR (400 MHz, $CDCl_3$) 8.01 – 7.96 (2 H, m), 7.83 – 7.70 (3 H, m), 7.44 (2 H, d, $^{3}J_{H\text{-}H}$ 8.0), 7.17 (2 H, d, $^{3}J_{H\text{-}H}$ 8.0), 5.93 (2 H, s), 4.88 (2 H, d, $^{2}J_{H\text{-}P}$ 14.3), 3.25 (2 H, m), 2.50 (6 H, s), 2.16 – 2.12 (4 H, m), 2.03 – 1.99 (2 H, m), 1.86 – 1.75 (6 H, m), 1.53 – 1.37 (6 H, m), 1.28 (6 H, s), 1.13 – 1.03 (2 H, m); ^{31}P NMR {^{1}H} (162 MHz, $CDCl_3$) 29.5; ^{13}C NMR {^{1}H} (101 MHz, $CDCl_3$) 155.9, 142.5, 140.3, 135.2, 134.6, 133.4 (d, $^{3}J_{C\text{-}P}$ 7.6), 131.4, (d, $^{3}J_{C\text{-}P}$ 5.4), 131.2, 130.7 (d, $^{2}J_{C\text{-}P}$ 8.2), 130.4 (d, $^{2}J_{C\text{-}P}$ 11.1), 129.1, 121.5, 115.2 (d, $^{1}J_{C\text{-}P}$ 73.5), 31.1 (d, $^{1}J_{C\text{-}P}$ 41.9), 26.5 (d, $^{3}J_{C\text{-}P}$ 10.9), 26.3 (d, $^{2}J_{C\text{-}P}$ 12.8), 25.5, 24.2 (d, $^{1}J_{C\text{-}P}$ 42.7), 14.8, 14.7; ESI-LRMS $[C_{38}H_{47}{}^{11}BN_2F_2P]^+$, (+) m/z 611.4, ESI-HRMS calculated for $[C_{38}H_{47}{}^{11}BN_2F_2P]^+$, 611.3538 found, 611.3546.

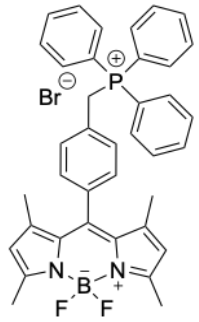
BODIPY-Mito-3



Cyclohexyldiphenylphosphine (107.1 mg, 0.40 mmol) was added to a solution of **BODIPY-Br** (110.1 mg, 0.264 mmol) in toluene (12 mL). The reaction was heated to 110 °C and stirred under an inert atmosphere of nitrogen for 3 d. The reaction was cooled to room temperature, and the crude product was isolated by filtration and washed with toluene (2 x 10 mL) and diethyl ether (10 mL). Recrystalisation from CH_2Cl_2 / hexane formed the title compound as a fine orange powder (141.9 mg, 79 %). ^{1}H NMR (400 MHz, $CDCl_3$) 7.93 – 7.88 (4 H, m), 7.78 – 7.74 (2 H, m), 7.67 – 7.63 (4 H, m), 7.16 (2 H, d, $^{3}J_{H\text{-}H}$ 8.2), 6.97 (2 H, d, $^{3}J_{H\text{-}H}$ 8.2), 5.90 (2 H, s), 5.28 (2 H, d, $^{2}J_{H\text{-}P}$ 14.5), 4.09 – 4.00 (1 H, m), 2.48 (6 H, s), 2.26 – 2.19 (4 H, m), 1.77 – 1.74 (2 H, m), 1.66 – 1.54 (2 H, m), 1.15 (6 H, s), 1.05 – 0.93 (2 H, m); ^{31}P NMR {^{1}H} (162 MHz, $CDCl_3$) 32.0; ^{13}C NMR {^{1}H} (101 MHz, $CDCl_3$) 155.8, 142.6, 140.1, 134.8, 134.8, 134.7 (d, $^{2}J_{C\text{-}P}$ 8.5), 131.7 ($^{3}J_{C\text{-}P}$ 5.3), 131.2, 130.1 (d, $^{2}J_{C\text{-}P}$ 11.8), 129.9, 128.5, 121.3, 115.1 (d, $^{1}J_{C\text{-}P}$ 79.7), 32.0 (d, $^{1}J_{C\text{-}P}$ 45.0), 27.2 (d,

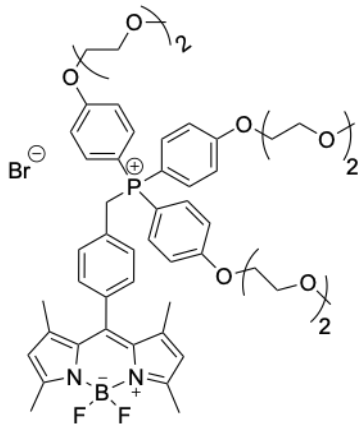
$^{1}J_{C\text{-}P}$ 44.1), 25.8 (br s), 25.6, 25.4, 14.8, 14.7; ESI-LRMS $[C_{38}H_{41}{}^{11}BN_2F_2P]^+$, (+) m/z 605.3, ESI-HRMS calculated for $[C_{38}H_{41}{}^{11}BN_2F_2P]^+$, 605.3068 found, 605.3062.

BODIPY-Mito-4



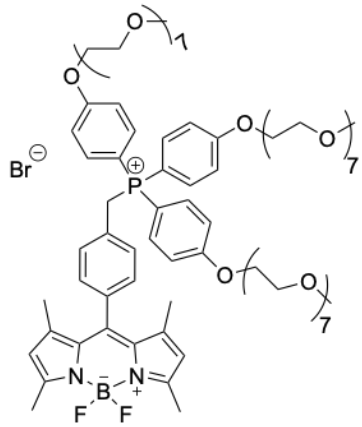
Triphenylphosphine (137.1 mg, 0.52 mmol) was added to a solution of **BODIPY-Br** (97.1 mg, 0.23 mmol) in acetonitrile (10 mL). The reaction was heated to 85 °C and stirred under an inert atmosphere of nitrogen for 3 d. The reaction was cooled to room temperature, and the solvent was removed under reduced pressure to form a dark orange residue. Purification by silica gel column chromatography (gradient 100 % CH_2Cl_2 to 95 % CH_2Cl_2/ 5 % methanol) formed the title compound as a fine orange powder (106.5 mg, 68 %). ^{1}H NMR (400 MHz, $CDCl_3$) 7.86 – 7.72 (9 H, m), 7.66 – 7.61 (6 H, m), 7.34 – 7.31 (2 H, m), 7.07 (2 H, d, $^{3}J_{H\text{-}H}$ 7.7), 5.92 (2 H, s), 5.62 (2 H, d, $^{2}J_{H\text{-}P}$ 15.1), 2.49 (6 H, s), 1.26 (6 H, s); ^{31}P NMR {^{1}H} (162 MHz, $CDCl_3$) 22.8; ^{13}C NMR {^{1}H} (101 MHz, $CDCl_3$) 155.8, 142.6, 140.5, 135.2, 134.4 (d, $^{3}J_{C\text{-}P}$ 9.8), 132.5 (d, $^{3}J_{C\text{-}P}$ 5.5), 131.2, 130.3 (d, $^{2}J_{C\text{-}P}$ 12.5), 129.1, 129.0, 128.7, 121.4, 117.9 (d, $^{1}J_{H\text{-}P}$ 85.8), 30.4 ($^{1}J_{C\text{-}P}$ 47.4), 14.8, 14.7; ESI-LRMS $[C_{38}H_{35}{}^{11}BN_2F_2P]^+$, (+) m/z 599.3, ESI-HRMS calculated for $[C_{38}H_{35}{}^{11}BN_2F_2P]^+$, 559.2599 found, 559.2603.

BODIPY-Mito-5



Compound (**2**) (342.0 mg, 0.55 mmol) was added to a solution of **BODIPY-Br** (140.2 mg, 0.34 mmol) in acetonitrile (15 mL). The reaction was heated to 85 °C and stirred under an inert atmosphere of nitrogen for 3 d. The reaction was cooled to room temperature, and the solvent was removed under reduced pressure to form a dark orange residue. Purification by silica gel column chromatography (gradient 100 % CH_2Cl_2 to 95 % CH_2Cl_2 / 5 % methanol) formed the title compound as an orange oil (228.2 mg, 65 %). ^{1}H NMR (400 MHz, $CDCl_3$) 7.65 – 7.60 (6 H, m), 7.30 (2 H, d, $^{3}J_{H\text{-}H}$ 7.7), 7.11 – 7.08 (8 H, m), 5.94 (2 H, s), 5.23 (2 H, d, $^{2}J_{H\text{-}P}$ 15.1), 4.22 – 4.19 (6 H, m), 3.88 – 3.85 (6 H, m), 3.70 – 3.67 (6 H, m), 3.56 – 3.53 (6 H, m), 3.35 (9 H, s), 2.50 (6 H, s), 1.29 (6 H, s); ^{31}P NMR {^{1}H} (162 MHz, $CDCl_3$) 20.4; ^{13}C NMR {^{1}H} (101 MHz, $CDCl_3$) 164.0, 155.8, 142.6, 140.6, 136.2 (d, $^{2}J_{C\text{-}P}$ 11.5), 135.1, 132.4 (d, $^{3}J_{C\text{-}P}$ 5.9), 131.2, 129.5 (d, $^{3}J_{C\text{-}P}$ 8.2), 128.6, 121.4, 116,4 (d, $^{2}J_{C\text{-}P}$ 13.6), 108.5 (d, $^{1}J_{C\text{-}P}$ 93.7), 71.9, 70.8, 69.3, 68.1, 59.2, 31.7 (d, $^{1}J_{C\text{-}P}$ 50.1), 14.8, 14.7; ESI-LRMS $[C_{53}H_{65}{}^{11}BN_2O_9F_2P]^+$, (+) m/z 953.4, ESI-HRMS calculated for $[C_{53}H_{65}{}^{11}BN_2O_9F_2P]^+$, 953.4489 found, 953.4485.

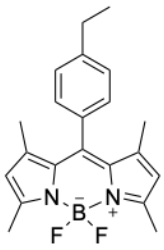
BODIPY-Mito-6



BODIPY-Br (48.2 mg, 0.12 mmol) was added to a solution of compound (**6**) (122.0 mg, 0.096 mmol) in acetonitrile (5 mL). The reaction was heated to 85 °C and stirred under an inert atmosphere of nitrogen for 3 d. The reaction was cooled to room temperature, and the solvent was removed under reduced pressure to form a dark orange residue. Purification by silica gel column chromatography (gradient 99 % CH_2Cl_2 / 1 % NEt_3 to 94 % CH_2Cl_2 / 5 % methanol / 1 % NEt_3) formed the title compound as an orange oil (80.6 mg, 50 %). ^{1}H NMR (400 MHz, $CDCl_3$) 7.66 – 7.60 (6 H, m), 7.29 – 7.27 (2 H, m), 7.11 – 7.08 (8 H, m), 5.93 (2 H, s), 5.26 (2 H, d, $^2J_{H\text{-}P}$ 14.5), 4.20 – 4.17 (6 H, br m), 3.87 – 3.84 (6 H, br m), 3.70 – 3.68 (6 H, br m), 3.65 – 3.59 (60 H, br m), 3.52 – 3.49 (6 H, br m), 3.34 (9 H, s), 2.50 (6 H, s), 1.29 (6 H, s); ^{31}P NMR {^{1}H} (162 MHz, $CDCl_3$) 20.5; ^{13}C NMR {^{1}H} (101 MHz, $CDCl_3$) 163.9 (d, $^3J_{C\text{-}P}$ 3.0), 155.7, 142.6, 140.6, 136.1 (d, $^2J_{C\text{-}P}$ 11.4), 135.0, 132.4 (d, $^3J_{C\text{-}P}$ 5.3), 131.2, 129.6, 128.6, 121.4, 116.4 ($^2J_{C\text{-}P}$ 13.7), 108.6 (d, $^1J_{C\text{-}P}$ 93.6), 71.9, 70.8, 70.6 – 70.5 (br m*), 69.3, 68.0, 59.0, 31.4 (d, $^1J_{C\text{-}P}$ 48.8), 14.8, 14.6; ESI-LRMS $[C_{83}H_{125}{}^{11}BN_2O_{24}F_2P]^+$, (+) m/z 1613.8, ESI-HRMS calculated for $[C_{83}H_{125}{}^{11}BN_2O_{24}F_2P]^+$, 1613.8416 found, 1613.8425.

*multiple carbon environments present.

BODIPY-Et



Trifluoroacetic acid (0.1 mL, 1.30 mmol) was added to a solution of 4-ethylbenzaldehyde (0.52 mL, 3.80 mmol) and 2,4-dimethylpyrrole (0.90 mL, 8.70 mmol) in anhydrous CH_2Cl_2 and the solution was stirred at room temperature overnight with protection from light under an inert atmosphere of nitrogen. After 20 h the solvent was removed under reduced pressure to form a dark red / brown residue and purified by silica gel column chromatography (gradient 100 % hexane to 50 % hexane / 50 % CH_2Cl_2) to form the dipyrromethane intermediate (742.0 mg, 2.42 mmol) which was subsequently dissolved in CH_2Cl_2 (100 mL). *p*-Chloranil (829.0 mg, 3.37 mmol) was added and stirred for 3 h at room temperature, before the addition of diisopropylethylamine (DIPEA, 7.0 mL, 40.8 mmol) and $BF_3.OEt_2$ (4.8 mL, 38.7 mmol). The reaction was stirred at room temperature under an inert atmosphere of nitrogen for a further 18 h. The suspension was diluted with CH_2Cl_2 (80 mL) and washed with H_2O (1 x 80 mL) and brine (1 x 100 mL) and dried over Na_2SO_4. The solvent was removed under reduced pressure to form a dark red viscous oil. Purification by silica gel column chromatography (gradient 100 % hexane to 25 % hexane / 75 % CH_2Cl_2) formed the title compound as a crystalline orange powder (265.3 mg, 20 %). ^{1}H NMR (400 MHz, $CDCl_3$) 7.30 (2 H, d, $^3J_{H\text{-}H}$ 7.8), 7.16 (2 H, d, $^3J_{H\text{-}H}$ 7.8), 5.97 (2 H, s), 2,73 (2 H, q, $^3J_{H\text{-}H}$ 7.6), 2.55 (6 H, s), 1.39 (6 H, s), 1.28

(3 H, t, $^{3}J_{H\text{-}H}$ 7.6); ^{13}C {^{1}H} NMR (400 MHz, $CDCl_3$) 155.3, 145.4, 143.3, 142.4, 132.3, 131.8, 128.7, 127.9, 121.2, 28.8, 15.7, 14.7, 14.5; ESI-LRMS $[C_{21}H_{24}N_2F_2B]^+$, (+) m/z 353.2, ESI-HRMS calculated for $[C_{21}H_{24}N_2F_2B]^+$, 353.2001 found, 353.2018.

2.3.1 NMR Spectra

PEG350-Tosylate, (5)

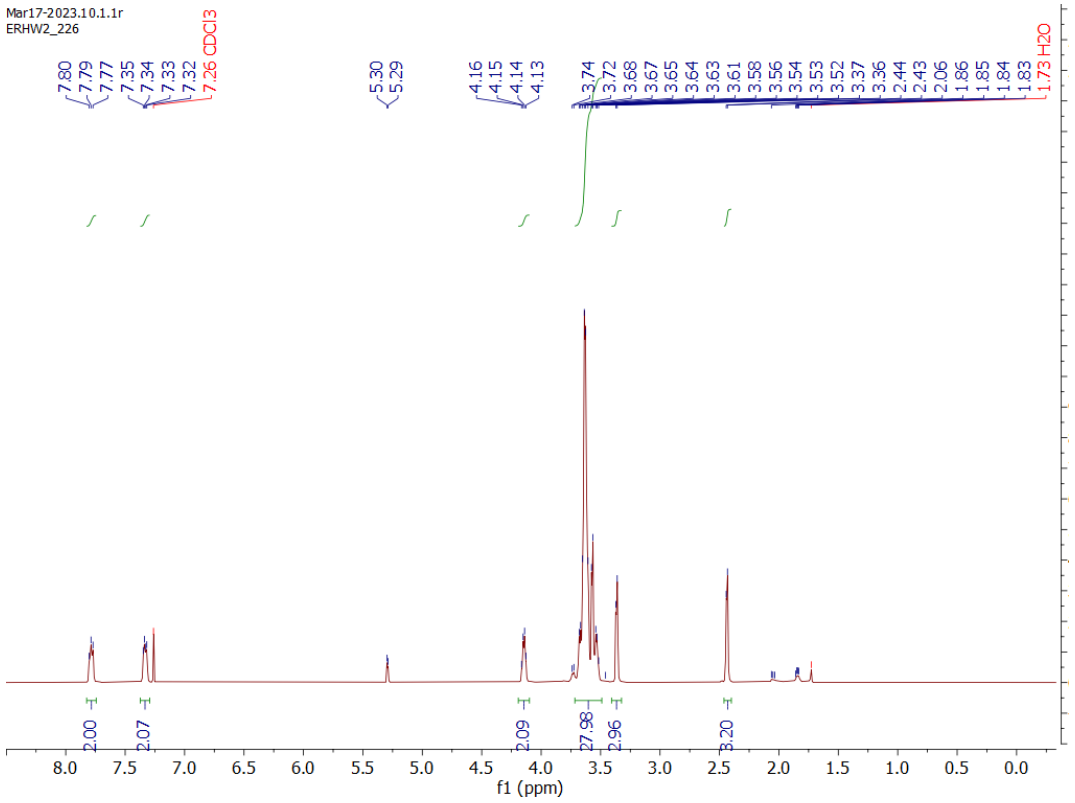


Fig. S8. The ^{1}H NMR spectra of PEG350-Tosylate, (**5**) in $CDCl_3$, 298 K.

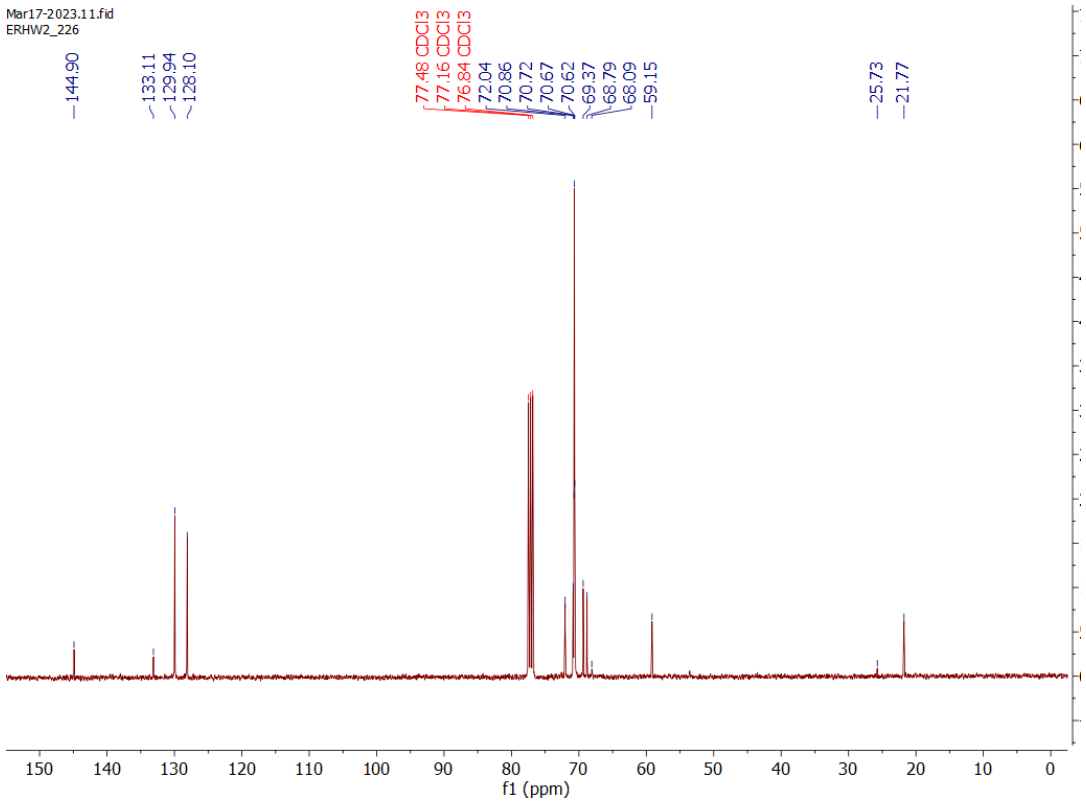


Fig. S9. The ^{13}C {^{1}H} NMR spectra of PEG350-Tosylate, (**5**), in $CDCl_3$, 298 K.

Tris(4-(2-methoxyethoxy)phenyl)phosphine, (6)

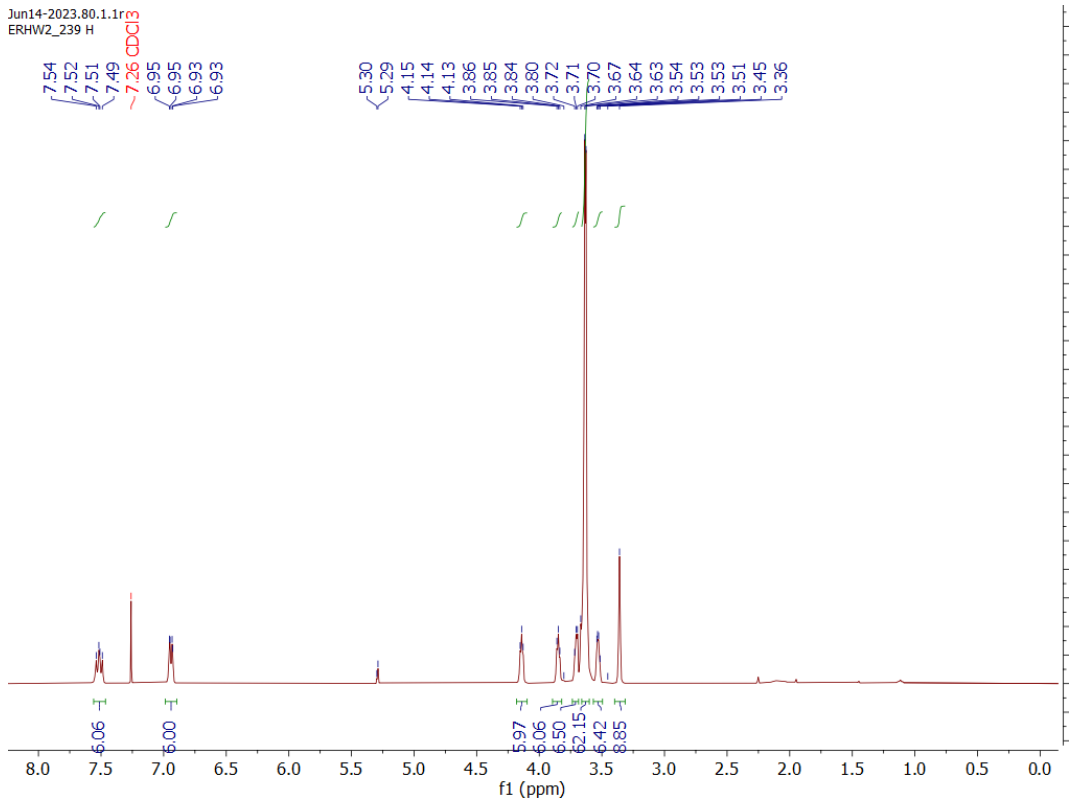


Fig. S10. The ^{1}H NMR spectra of tris(4-(2-methoxyethoxy)phenyl)phosphine oxide, (**6**), in $CDCl_3$, 298 K.

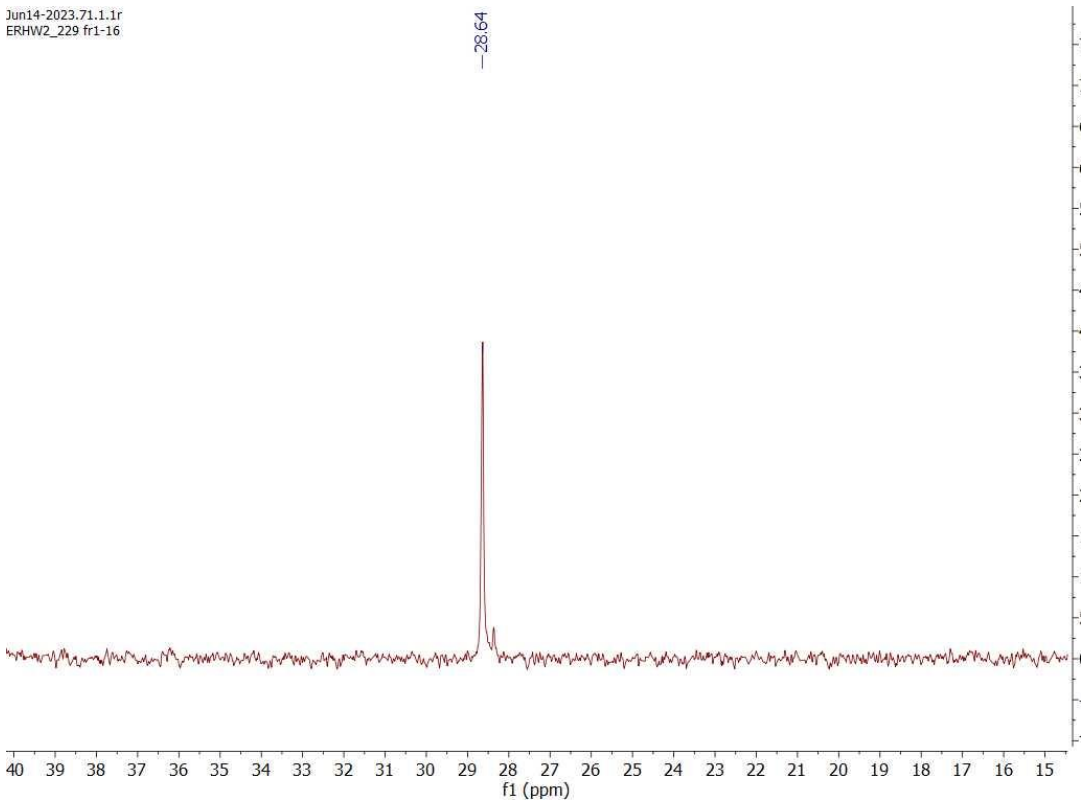


Fig. S11. The ^{31}P $\{^{1}H\}$ NMR spectra of tris(4-(2-methoxyethoxy)phenyl)phosphine oxide, (**6**), in $CDCl_3$, 298 K.

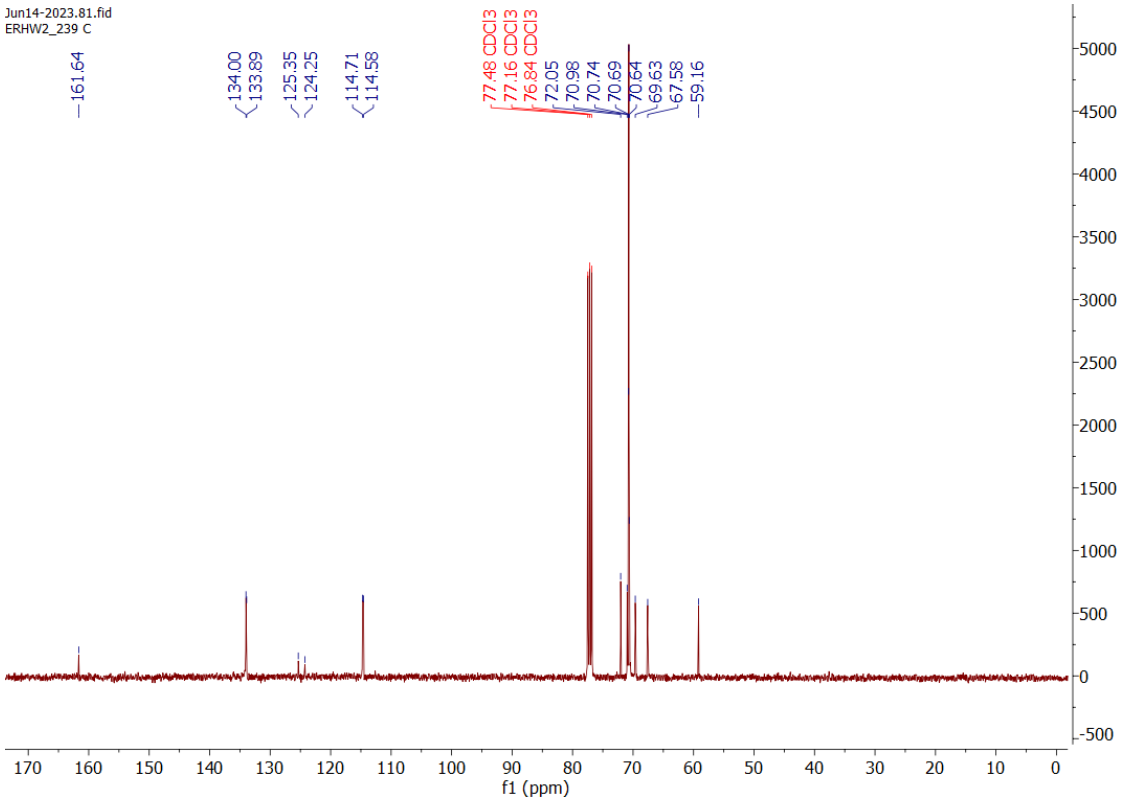


Fig. S12. The ^{13}C {^{1}H} NMR spectra of tris(4-(2-methoxyethoxy)phenyl)phosphine oxide, (**6**), in $CDCl_3$, 298 K.

Tris(4-(2-methoxyethoxy)phenyl)phosphine, (7)

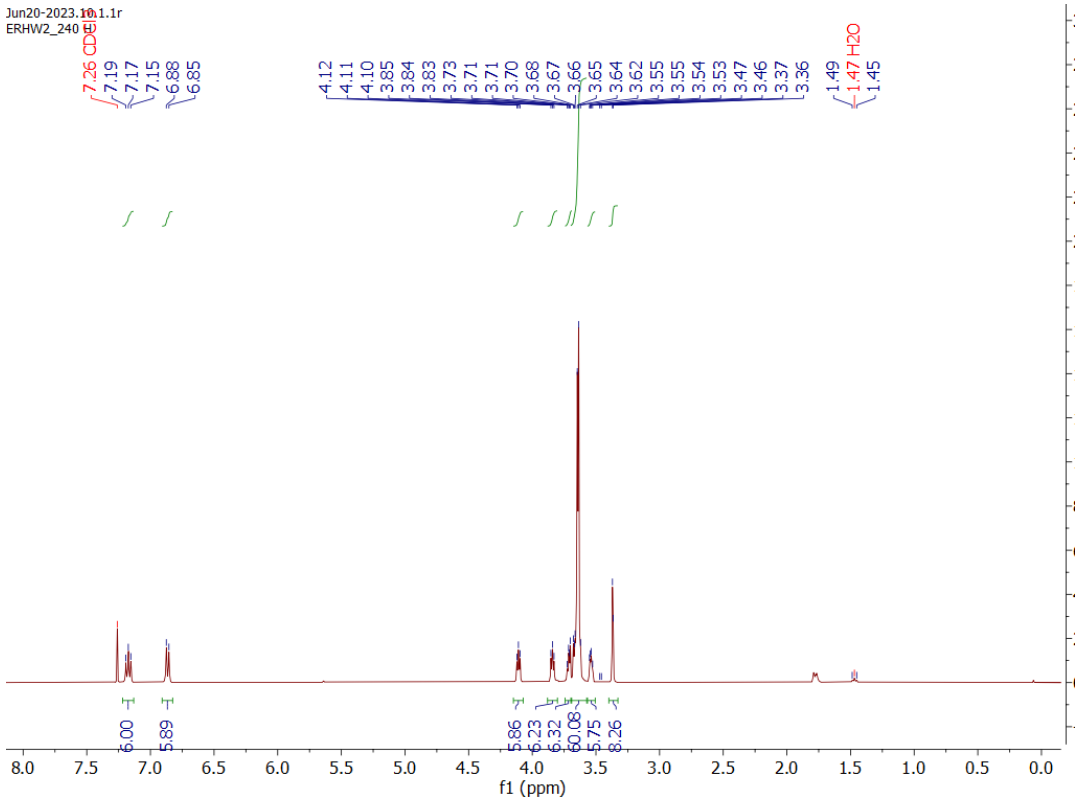


Fig. S13. The ^{1}H NMR spectra of tris(4-(2-methoxyethoxy)phenyl)phosphine, (**7**), in $CDCl_3$, 298 K.

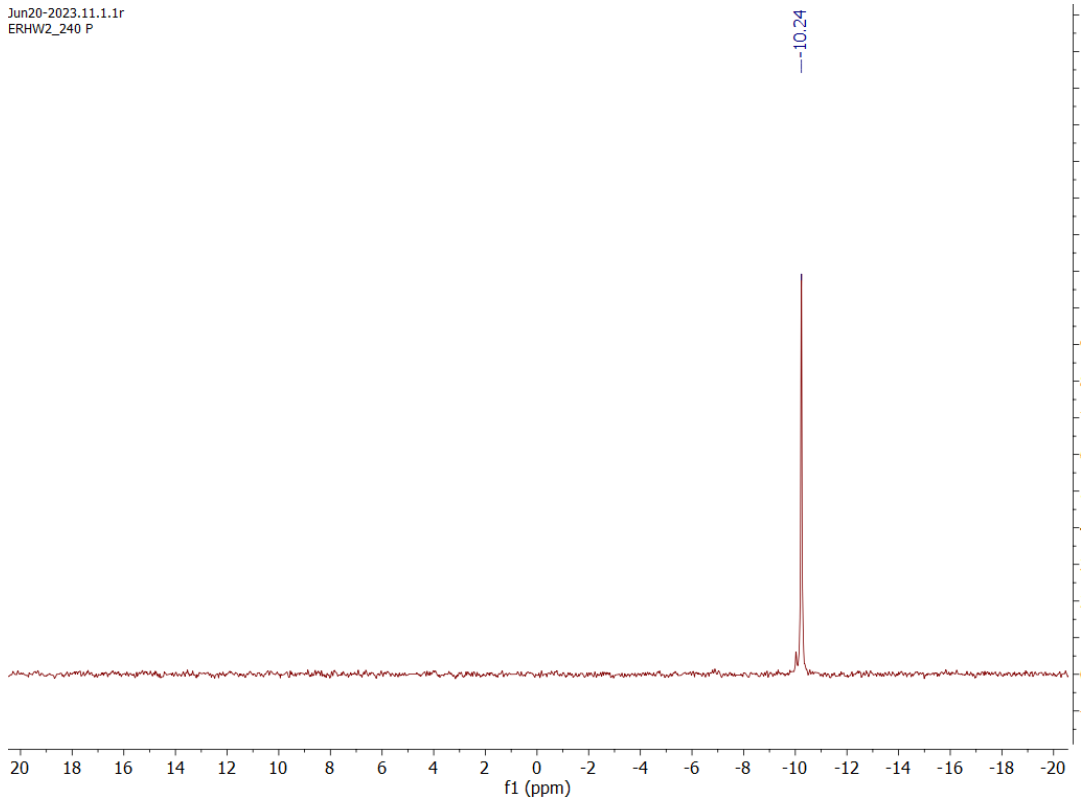


Fig. S14. The ^{31}P {^{1}H} NMR spectra of tris(4-(2-methoxyethoxy)phenyl)phosphine, (**7**), in $CDCl_3$, 298 K.

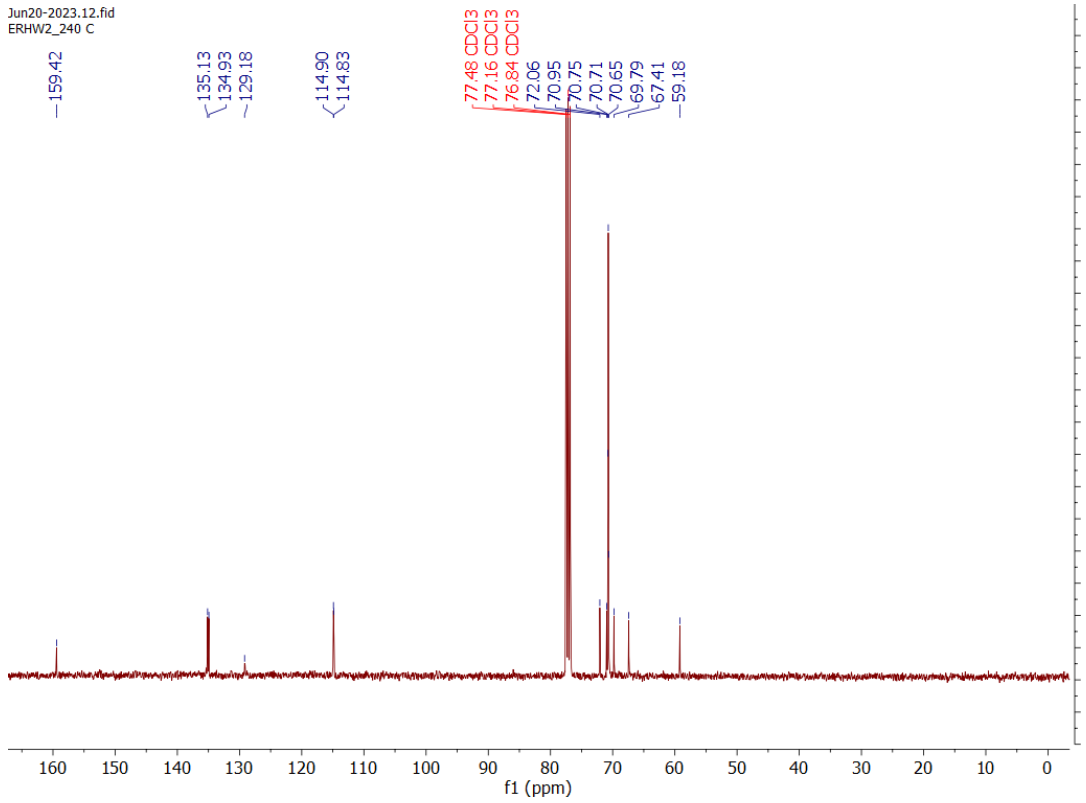


Fig. S15. The ^{13}C {^{1}H} NMR spectra of tris(4-(2-methoxyethoxy)phenyl)phosphine, (**7**), in $CDCl_3$, 298 K.

BODIPY-Mito-1

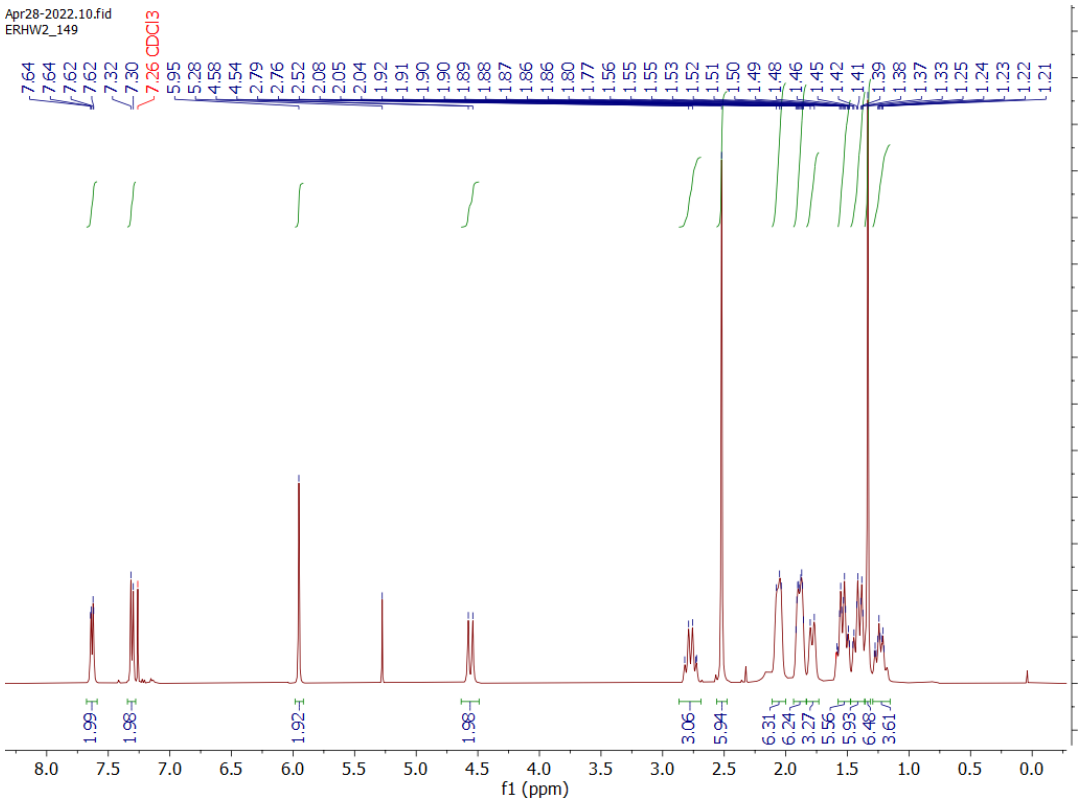


Fig. S16. The ^{1}H NMR spectra of **BODIPY-Mito-1** in $CDCl_3$, 298 K.

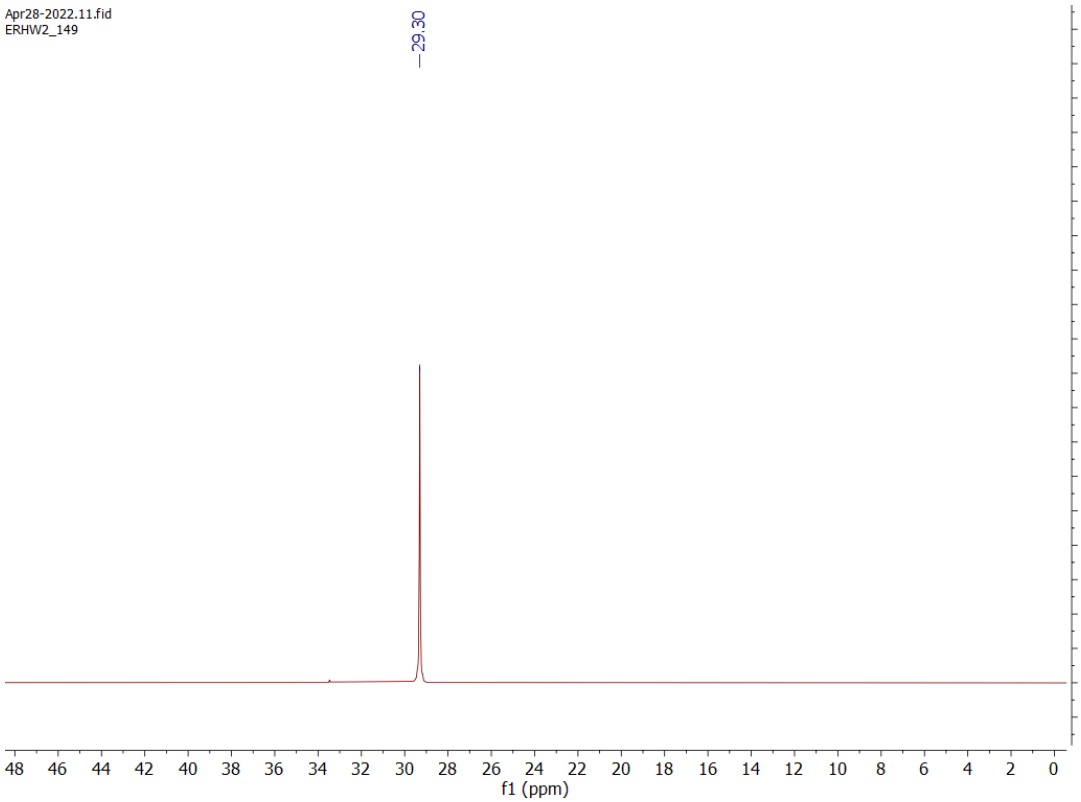


Fig. S17. The ^{31}P $\{^{1}H\}$ NMR spectra of **BODIPY-Mito-1** in $CDCl_3$, 298 K.

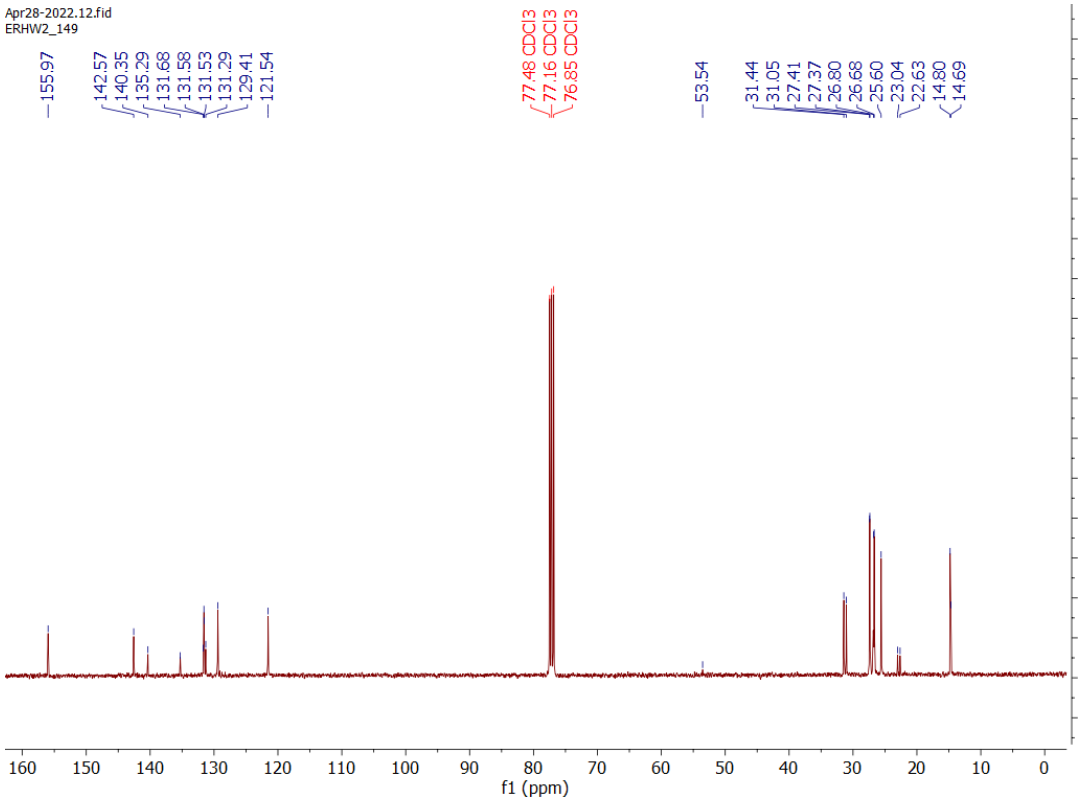


Fig. S18. The ^{13}C {^{1}H} NMR spectra of **BODIPY-Mito-1** in $CDCl_3$, 298 K.

BODIPY-Mito-2

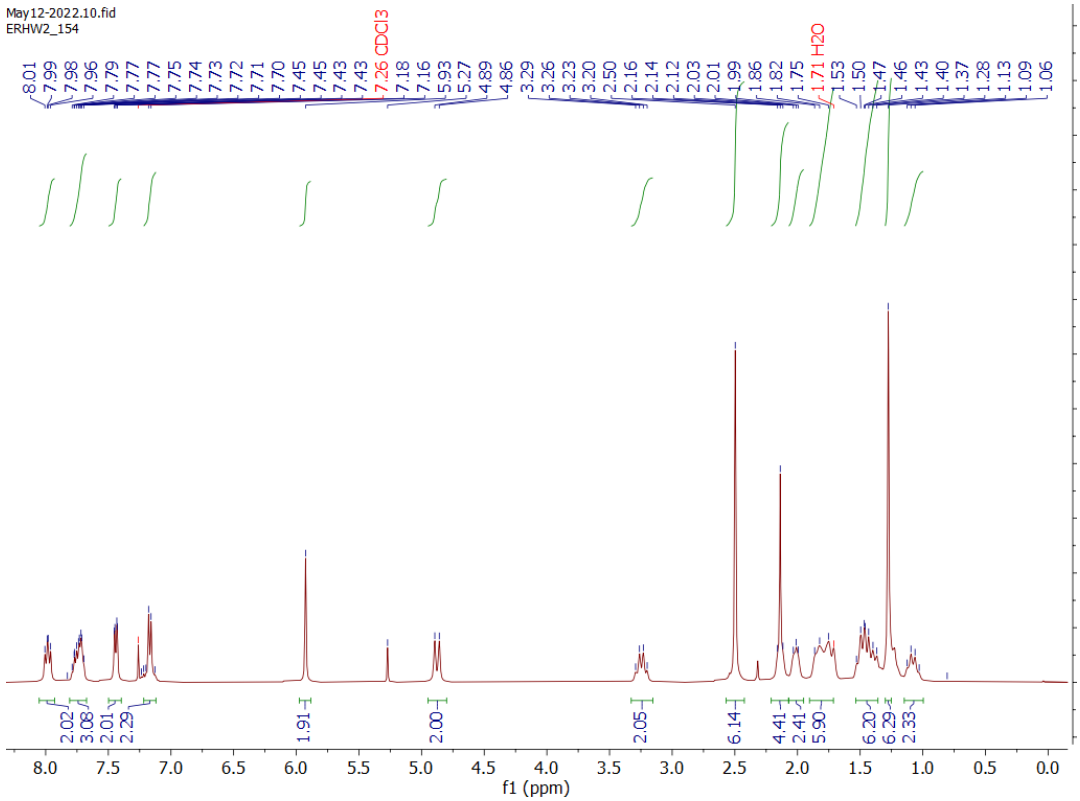


Fig. S19. The ^{1}H NMR spectra of **BODIPY-Mito-2** in $CDCl_3$, 298 K.

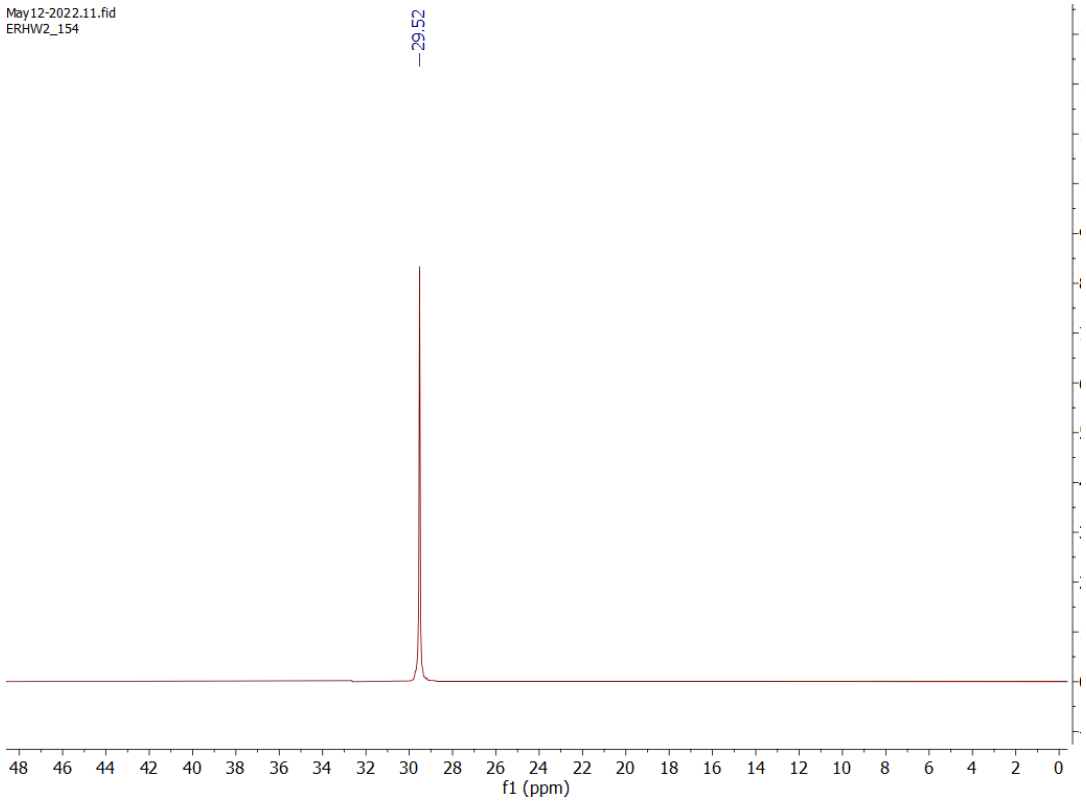


Fig. S20. The ^{31}P $\{^{1}H\}$ NMR spectra of **BODIPY-Mito-2** in $CDCl_3$, 298 K.

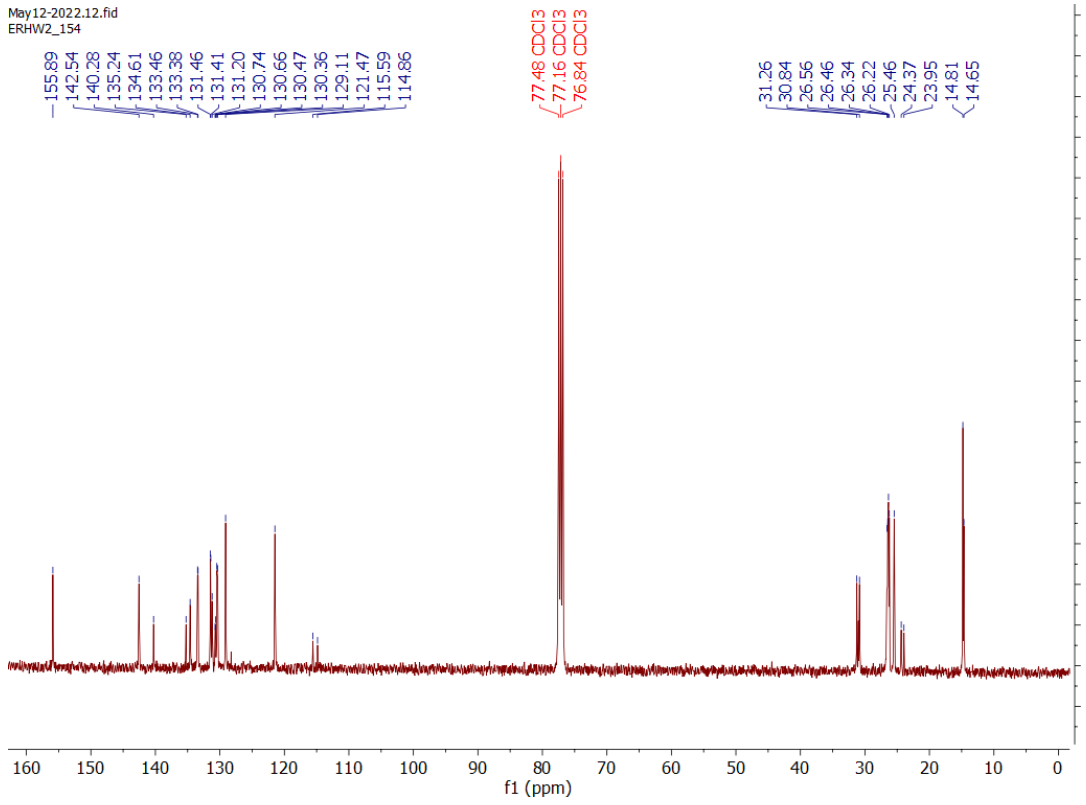


Fig. S21. The ^{13}C $\{^{1}H\}$ NMR spectra of **BODIPY-Mito-2** in $CDCl_3$, 298 K.

BODIPY-Mito-3

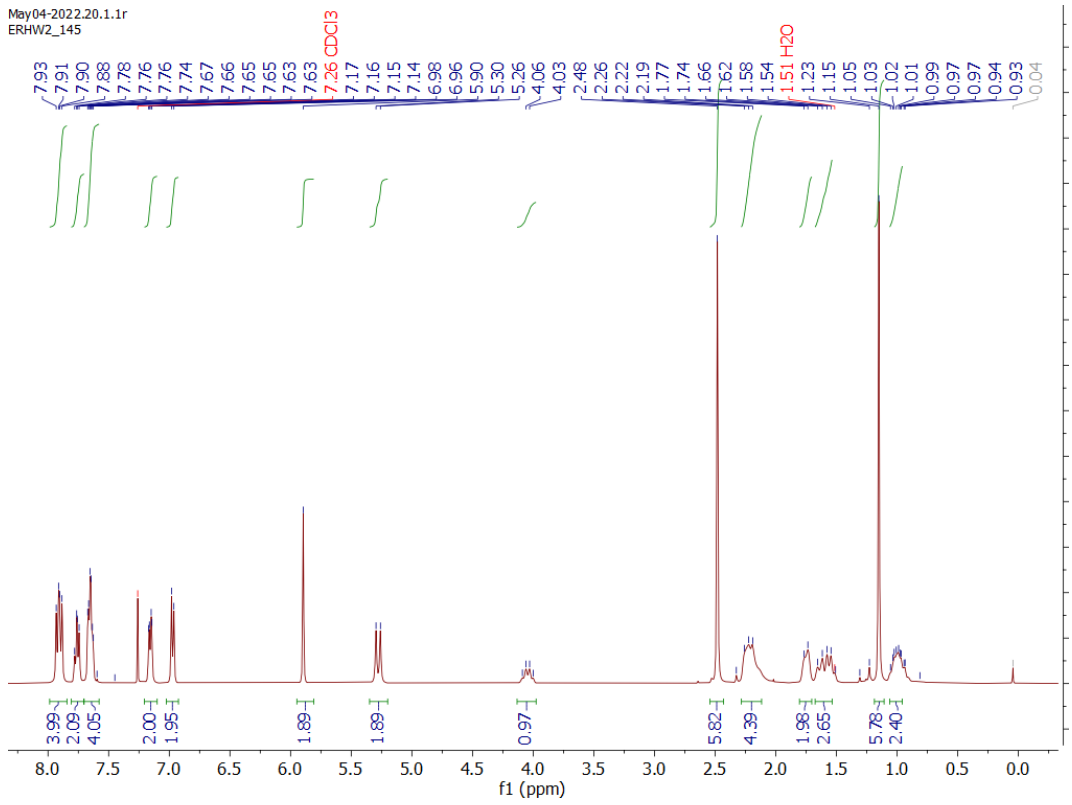


Fig. S22. The ^{1}H NMR spectra of **BODIPY-Mito-3** in $CDCl_3$, 298 K.

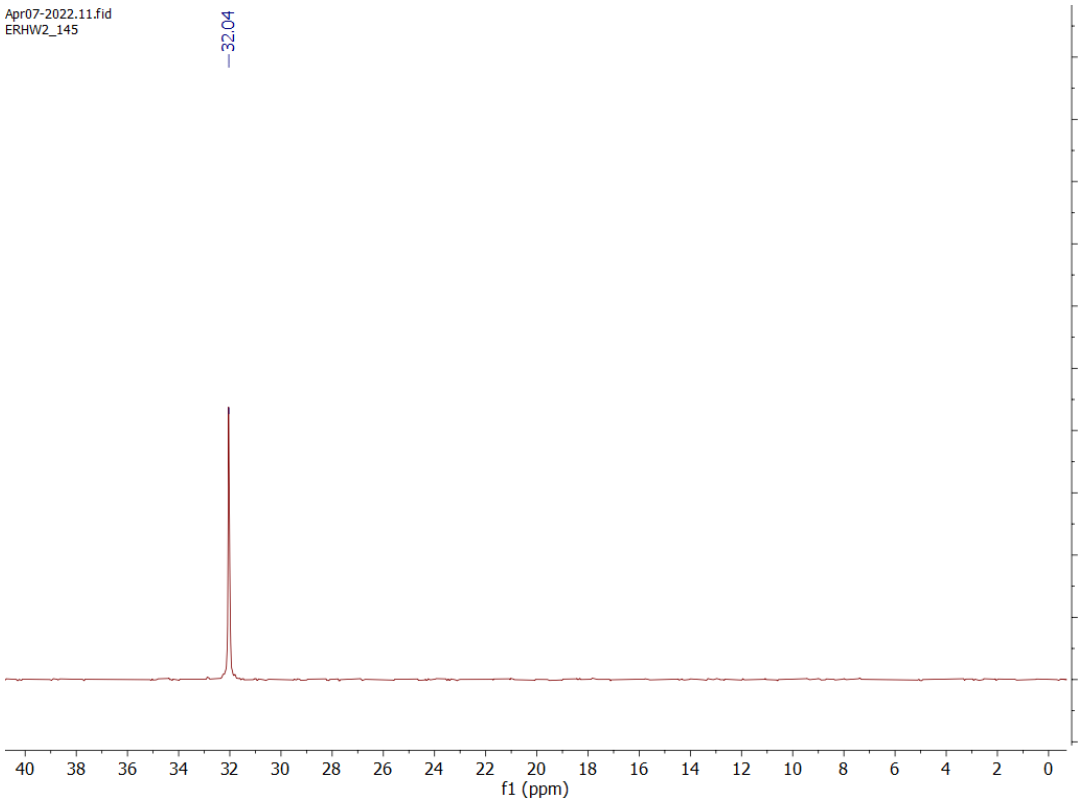


Fig. S23. The ^{31}P $\{^{1}H\}$ NMR spectra of **BODIPY-Mito-3** in $CDCl_3$, 298 K.

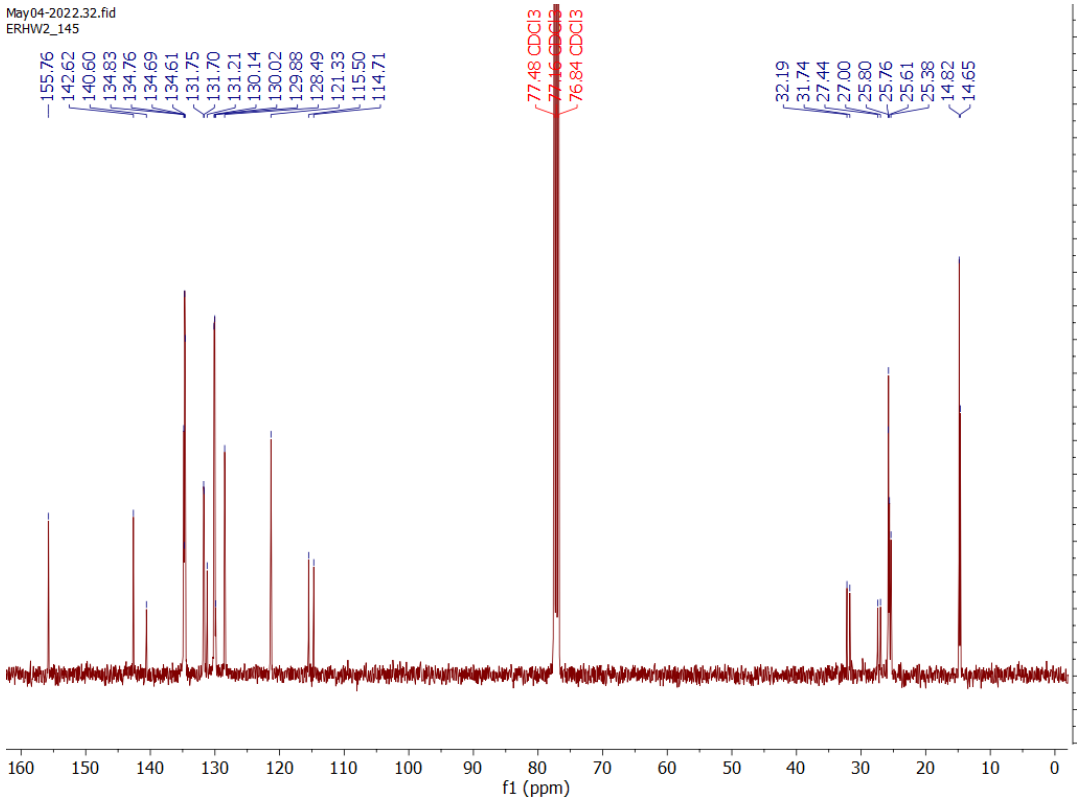


Fig. S24. The ^{13}C {^{1}H} NMR spectra of **BODIPY-Mito-3** in $CDCl_3$, 298 K.

BODIPY-Mito-4

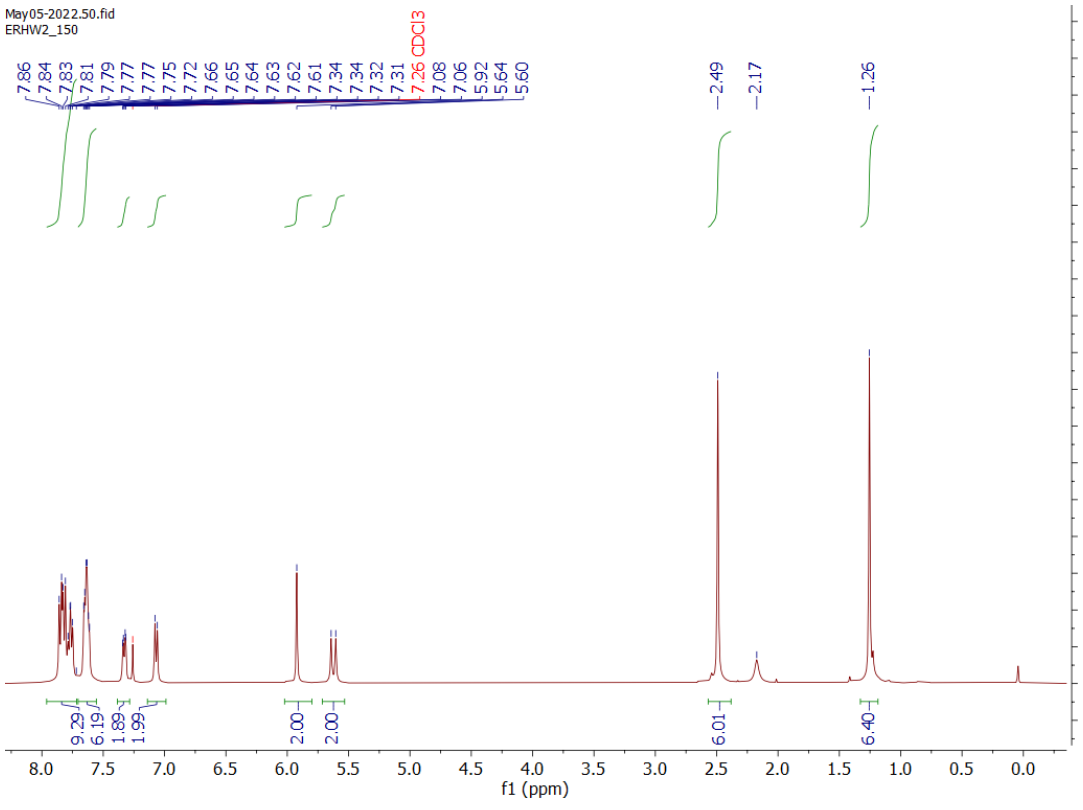


Fig. S25. The ^{1}H NMR spectra of **BODIPY-Mito-4** in $CDCl_3$, 298 K.

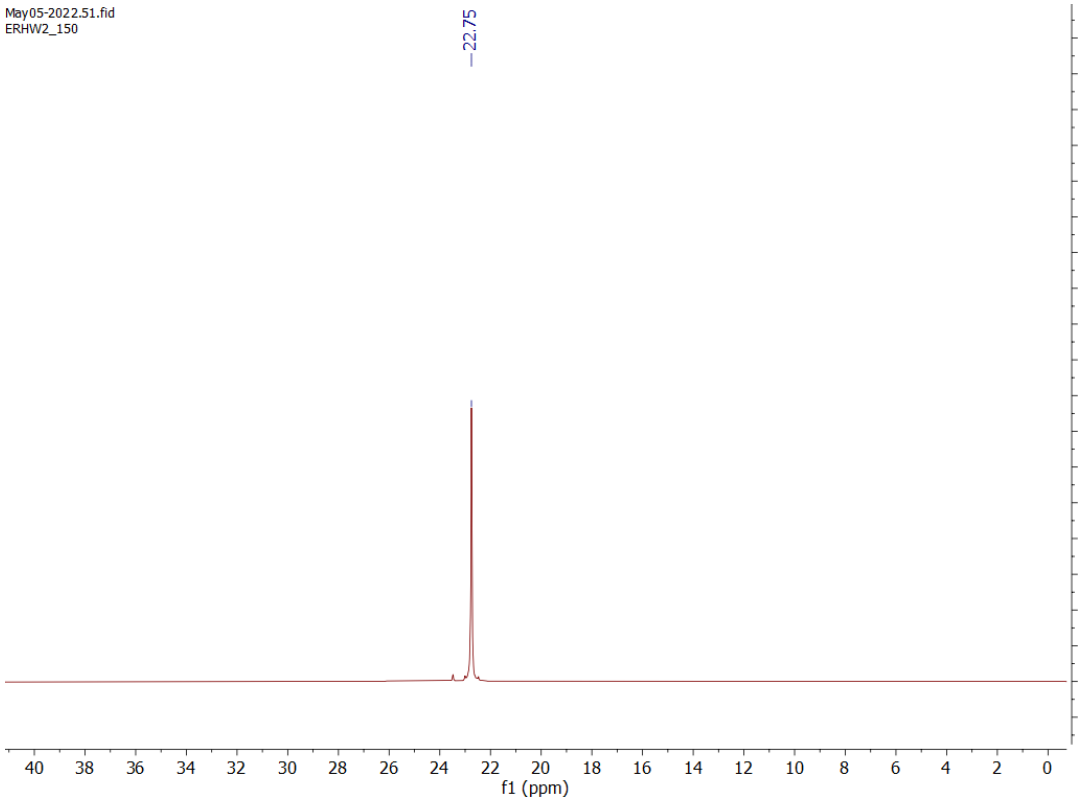


Fig. S26. The ^{31}P {^{1}H} NMR spectra of **BODIPY-Mito-4** in $CDCl_3$, 298 K.

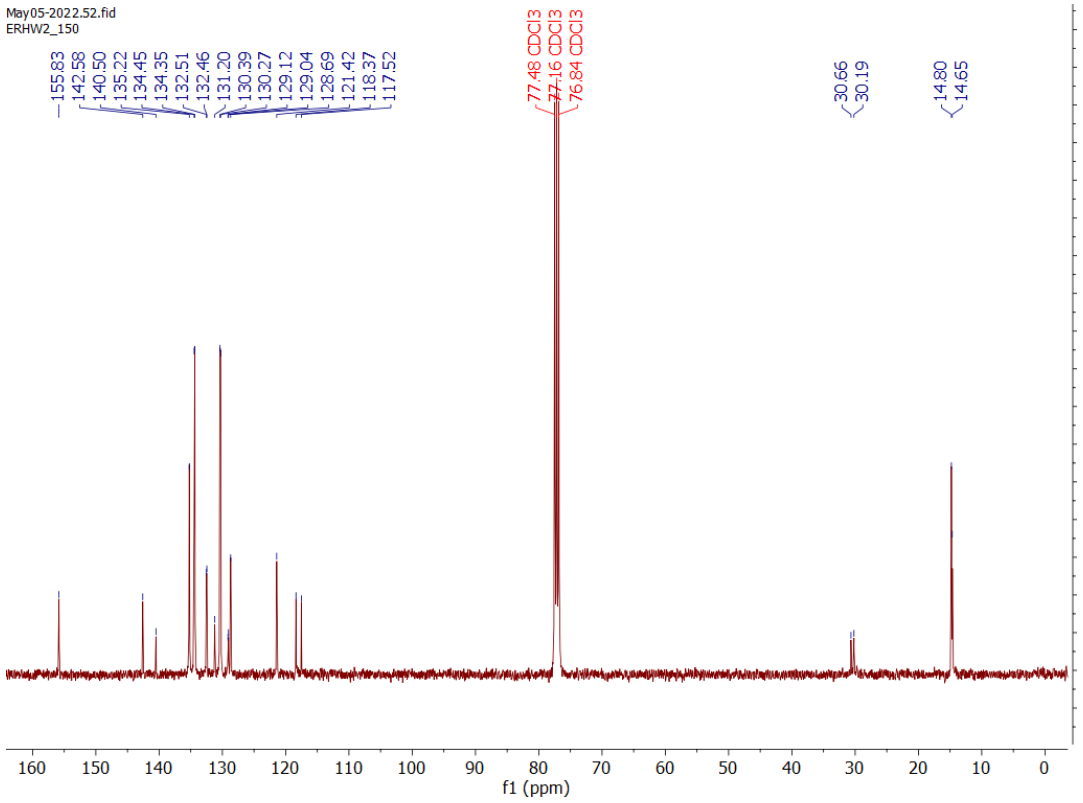


Fig. S27. The ^{13}C {^{1}H} NMR spectra of **BODIPY-Mito-4** in $CDCl_3$, 298 K.

BODIPY-Mito-5

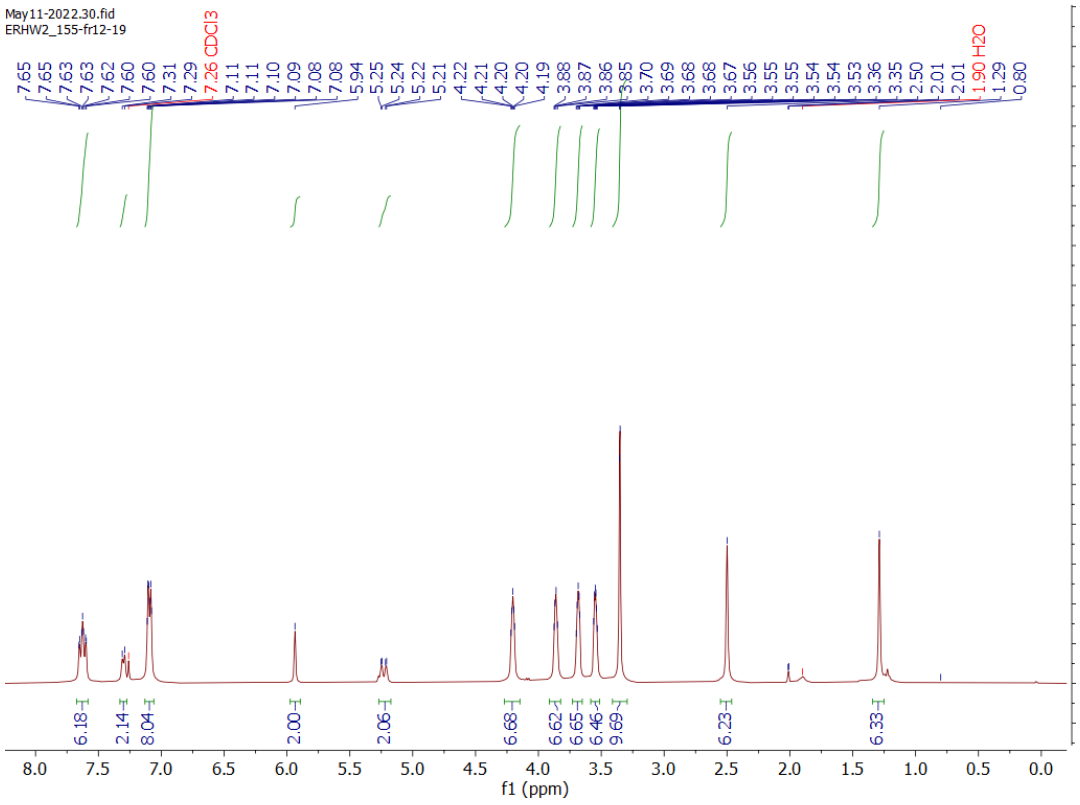


Fig. S28. The ^{1}H NMR spectra of **BODIPY-Mito-5** in $CDCl_3$, 298 K.

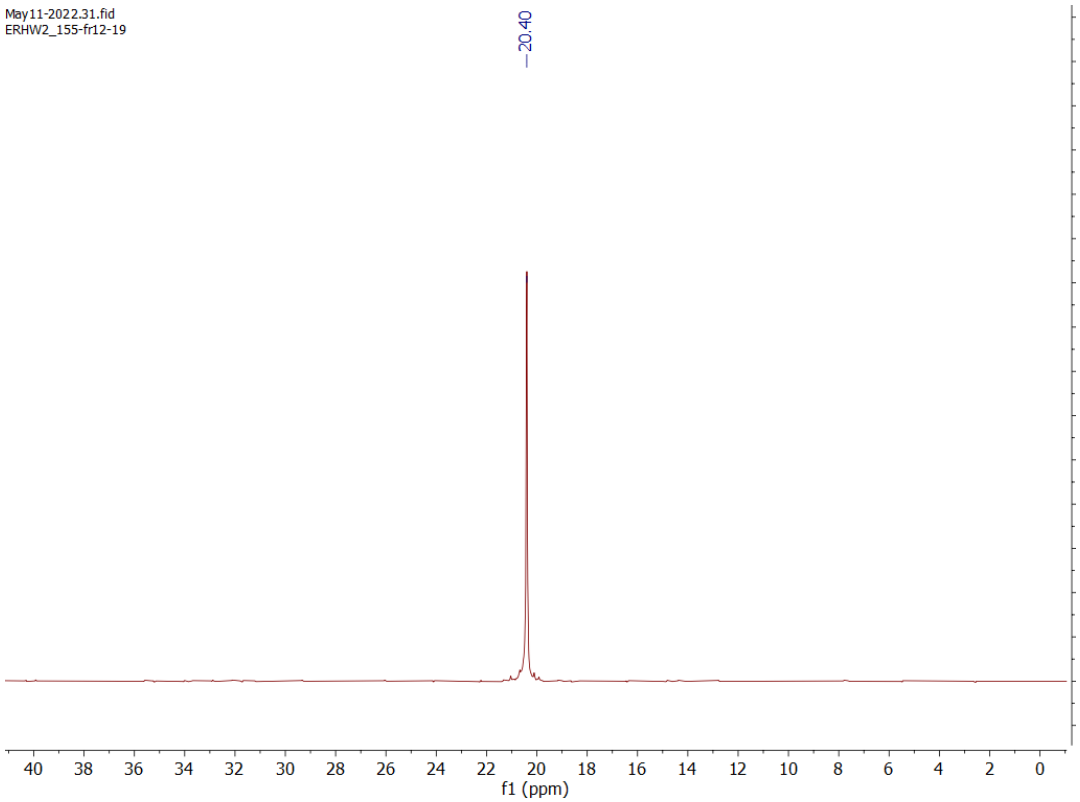


Fig. S29. The ^{31}P $\{^{1}H\}$ NMR spectra of **BODIPY-Mito-5** in $CDCl_3$, 298 K.

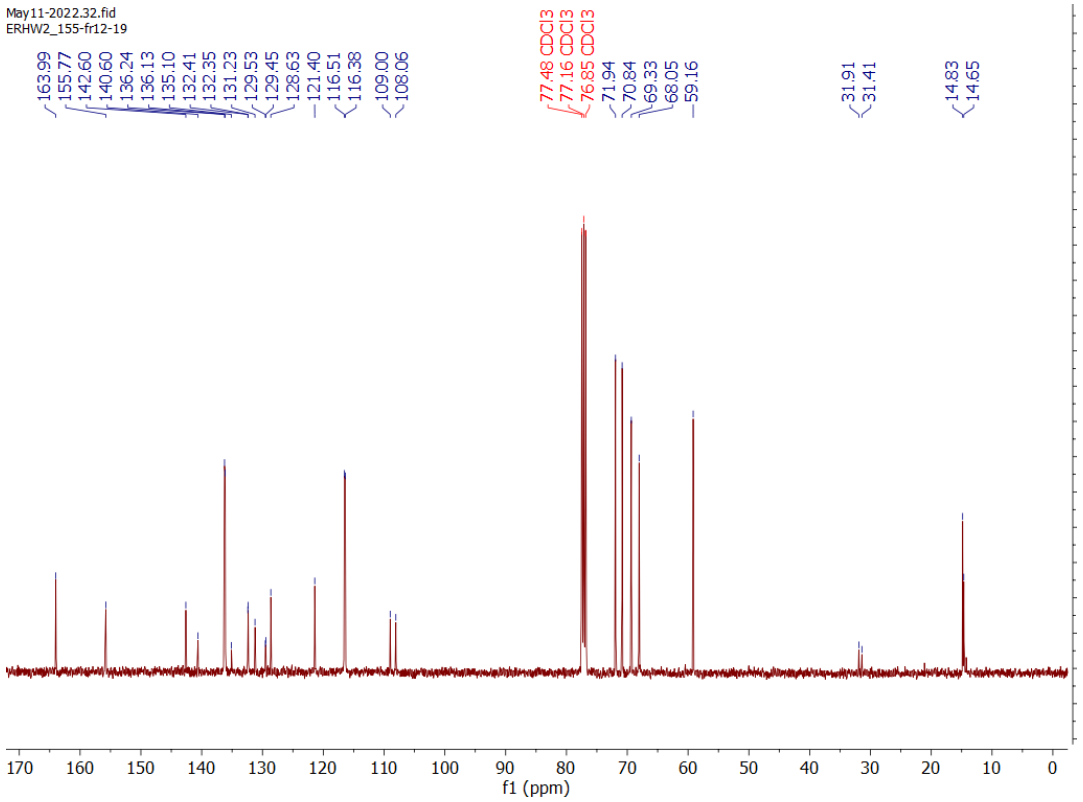


Fig. S30. The ^{13}C {^{1}H} NMR spectra of **BODIPY-Mito-5** in $CDCl_3$, 298 K.

BODIPY-Mito-6

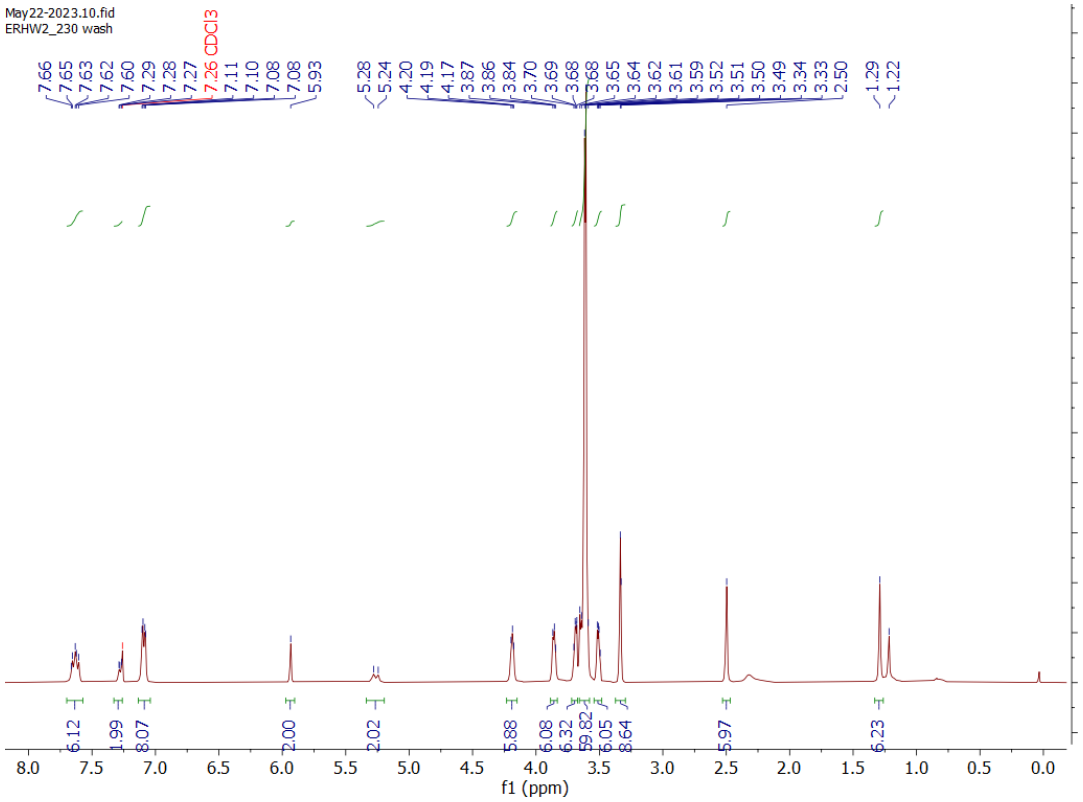


Fig. S31. The ^{1}H NMR spectra of **BODIPY-Mito-6** in $CDCl_3$, 298 K.

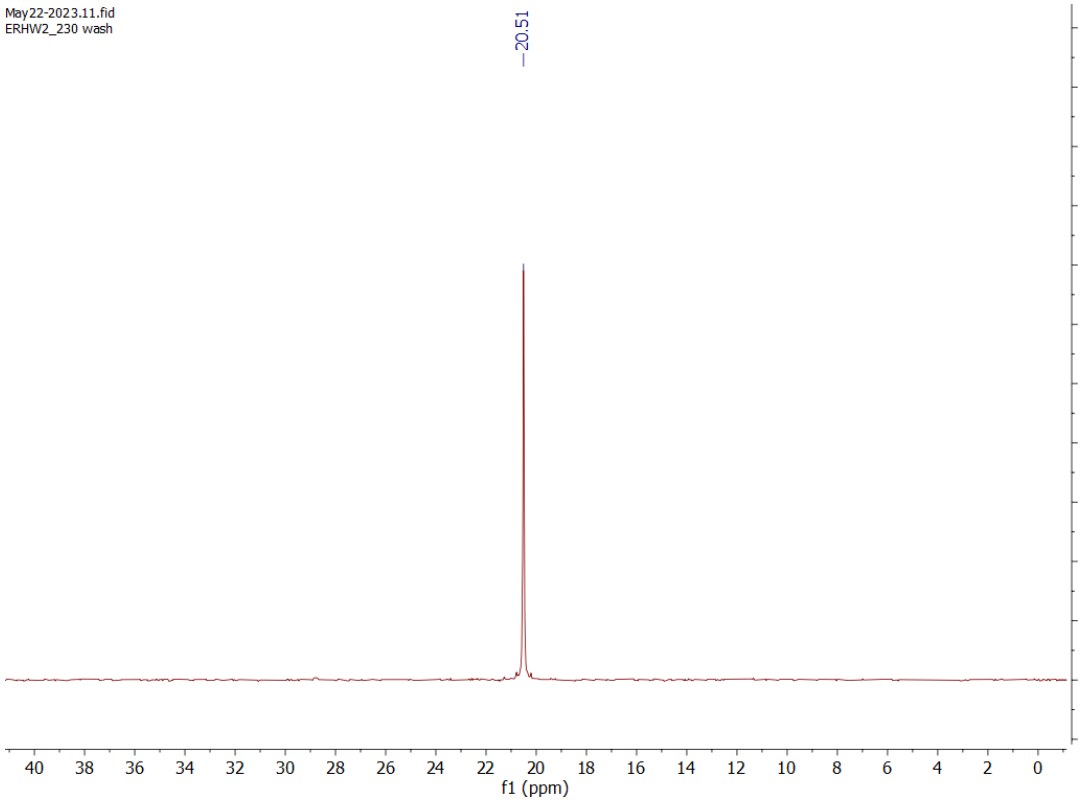


Fig. S32. The ^{31}P $\{^{1}H\}$ NMR spectra of **BODIPY-Mito-6** in $CDCl_3$, 298 K.

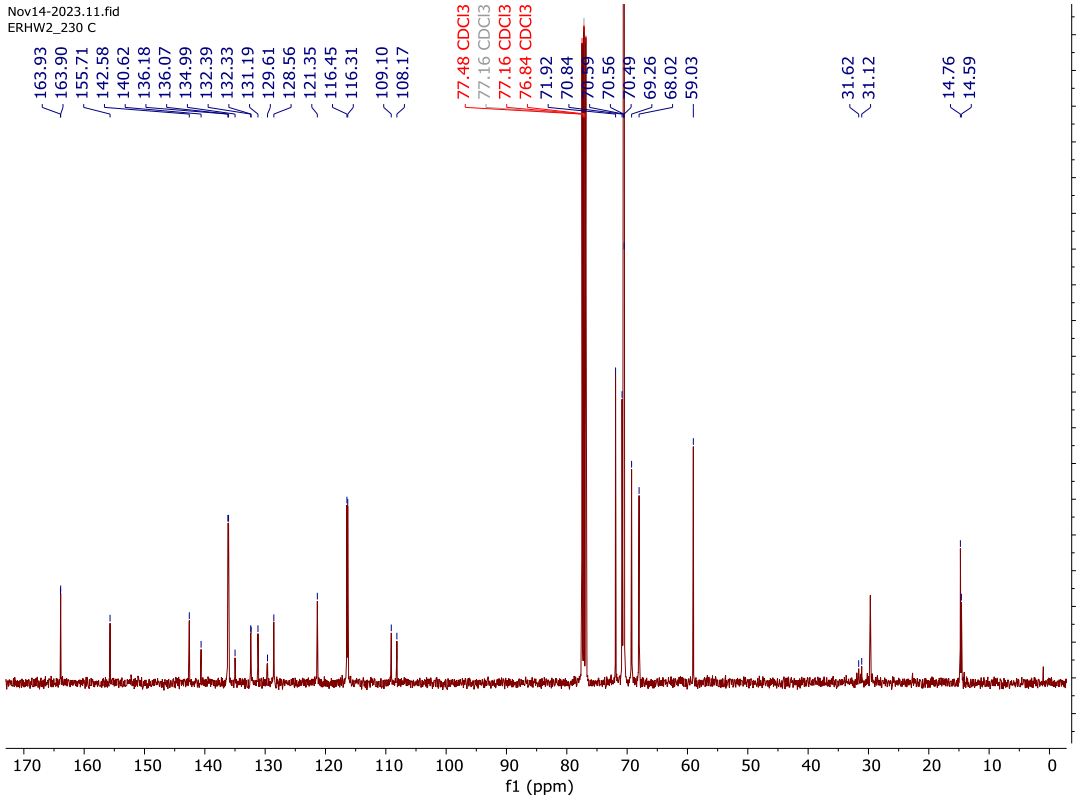


Fig. S33. The ^{13}C $\{^{1}H\}$ NMR spectra of **BODIPY-Mito-6** in $CDCl_3$, 298 K.

BODIPY-Et

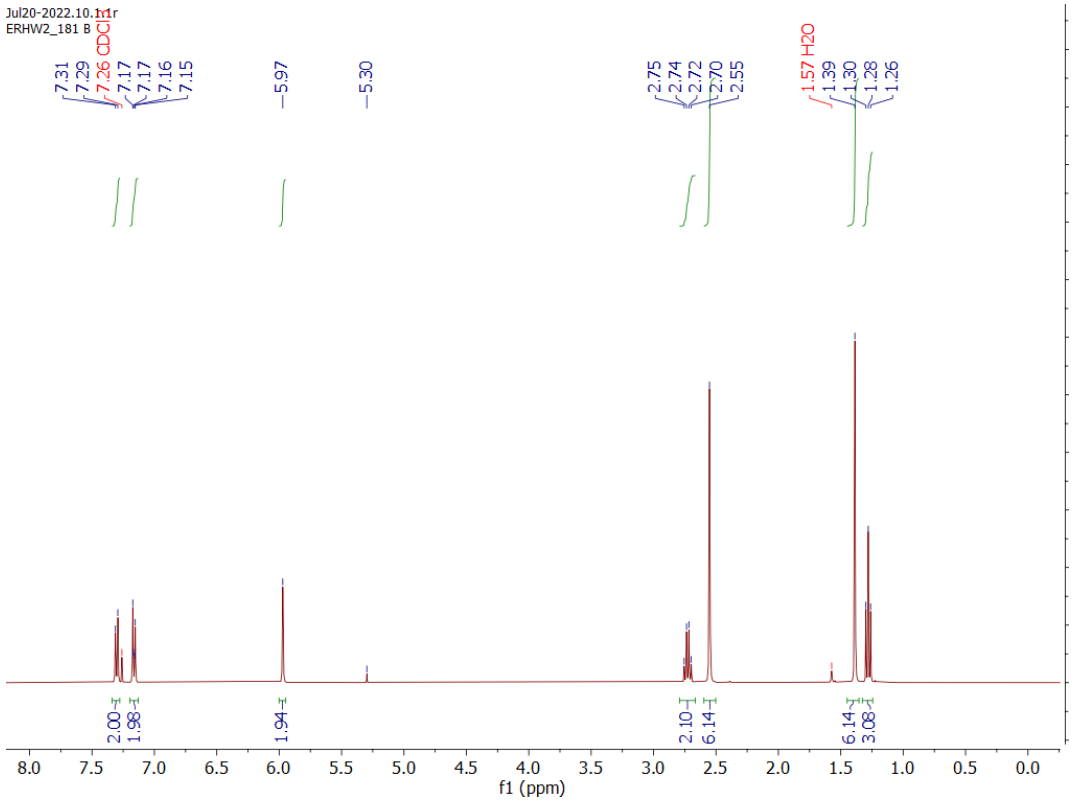


Fig. S34. The ^{1}H NMR spectra of **BODIPY-Et** in $CDCl_3$, 298 K.

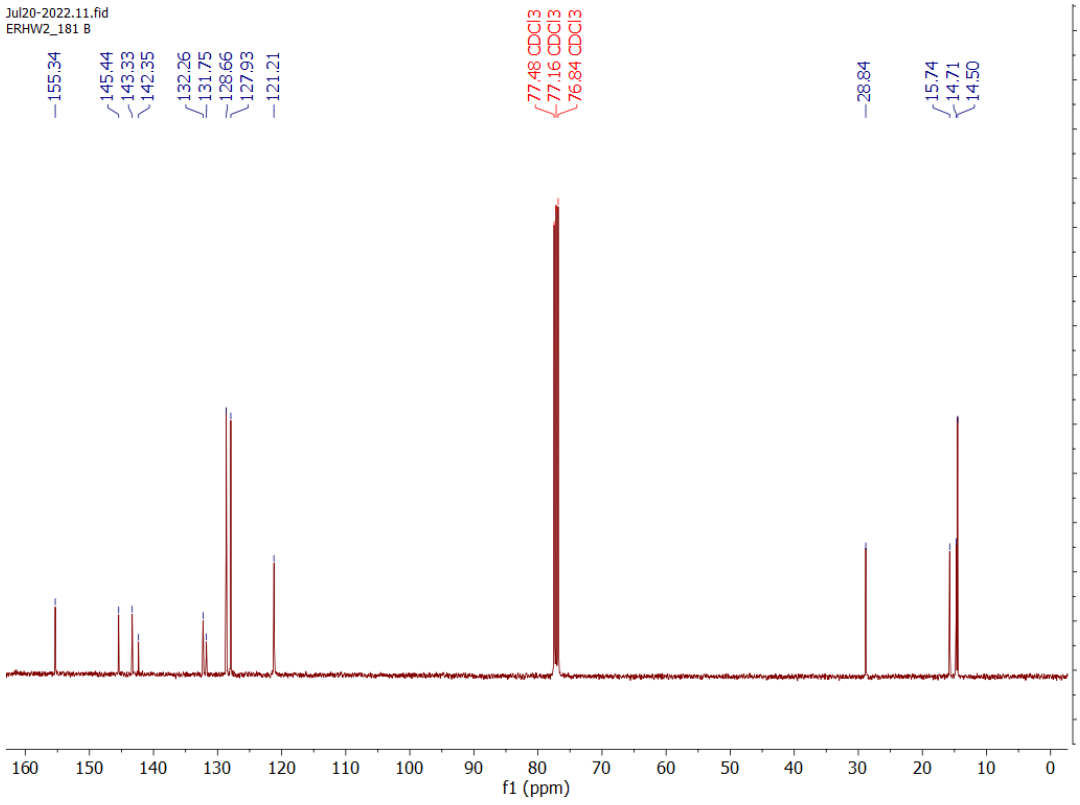
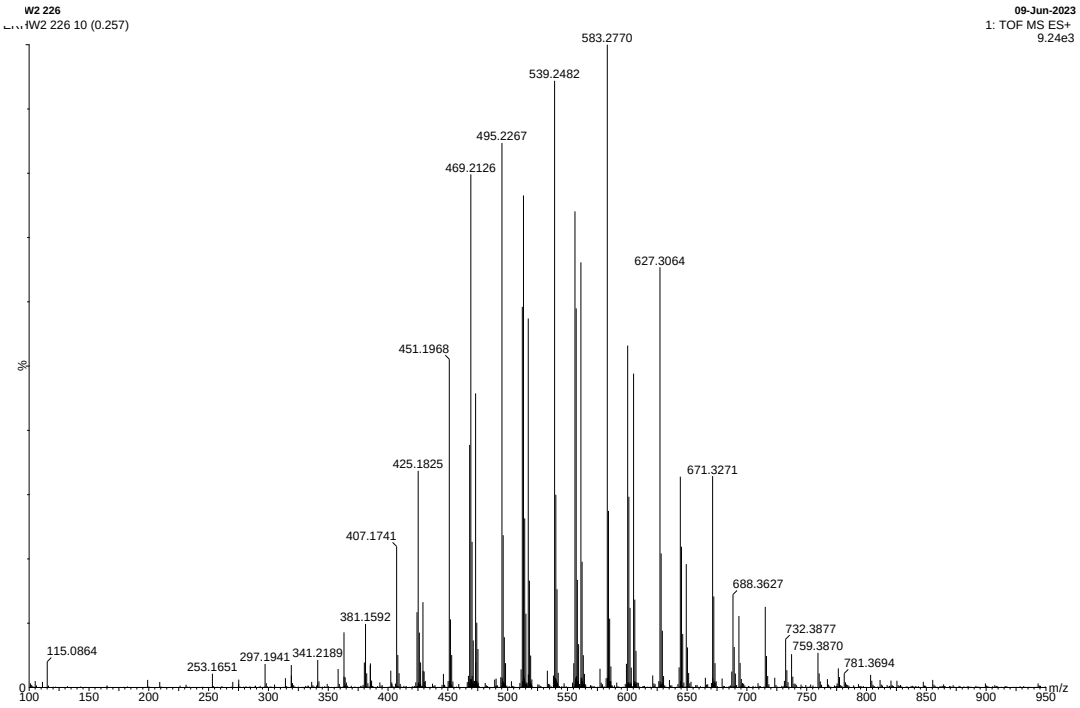


Fig. S35. The ^{13}C {^{1}H} NMR spectra of **BODIPY-Et** in $CDCl_3$, 298 K.

2.3.2 Mass Spectrometry Data

PEG350-Tosylate, (5)

(A)



(B)

Elements Used:

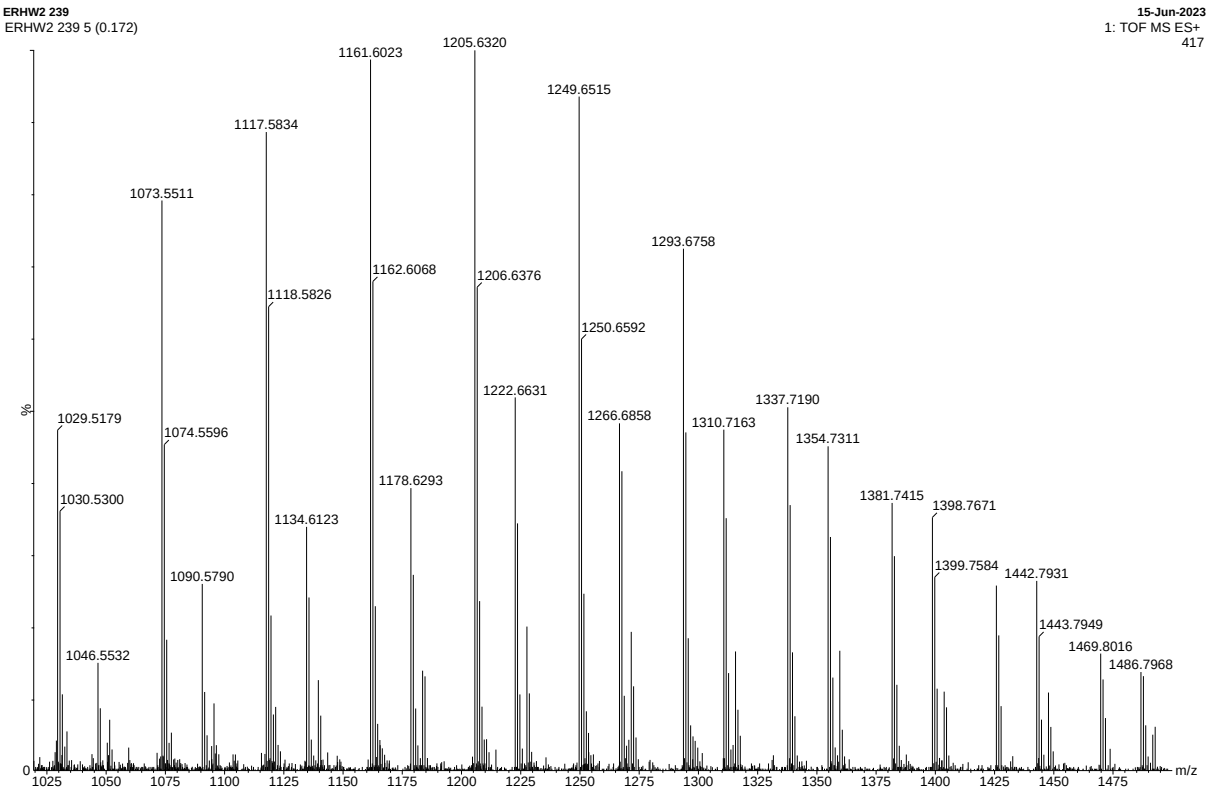
C: 10-25 H: 0-200 O: 0-10 S: 1-2

Minimum:				-1.5			
Maximum:		5.0	5.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
495.2267	495.2264	0.3	0.6	3.5	153.1	0.0	C22 H39 O10 S

Fig. S36. (A) The ESI-MS of PEG350-Tosylate, (**5**), and **(B)** the calculated and found HRMS data.

Tris(4-(2-methoxyethoxy)phenyl)phosphine oxide, (6)

(A)



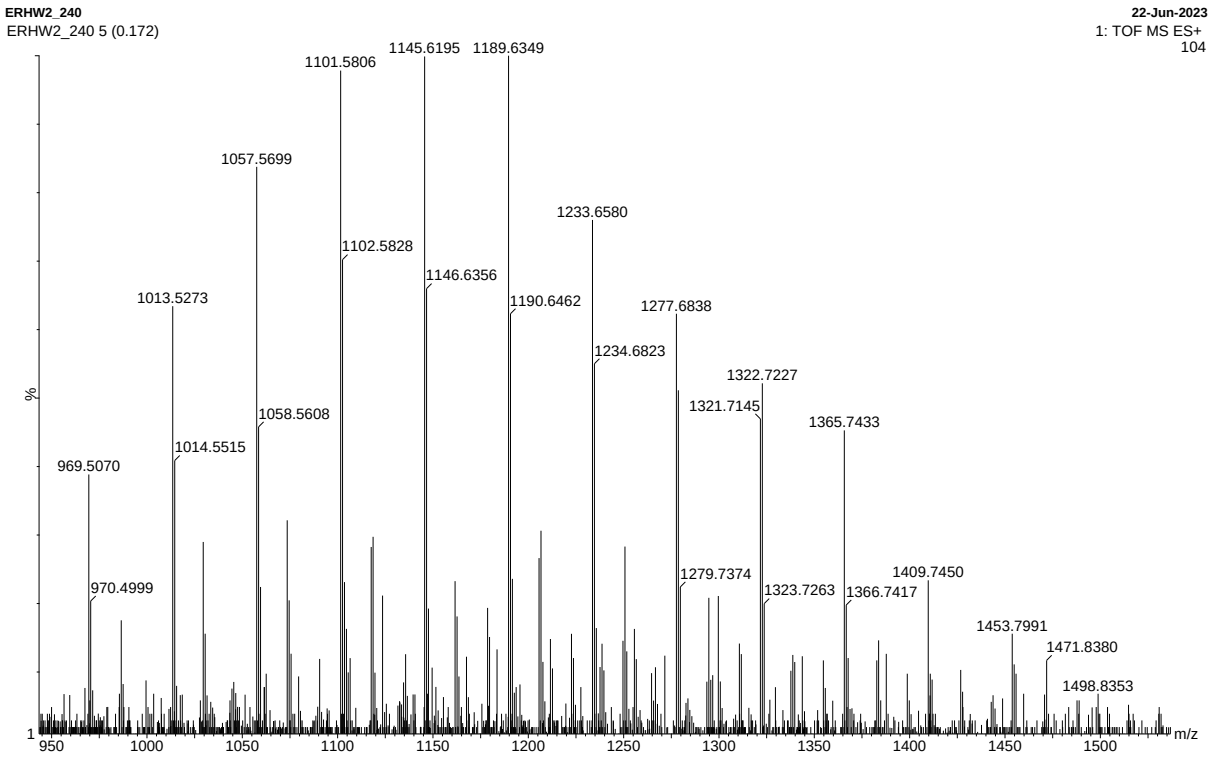
(B)

Minimum:				-1.5			
Maximum:		5.0	5.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
1293.6758	1293.6761	-0.3	-0.2	11.5	25.5	0.0	C63 H106 O25 P

Fig. S37 (A) The ESI-MS of tris(4-(2-methoxyethoxy)phenyl)phosphine oxide, (**6**) and **(B)** the calculated and found HRMS data.

Tris(4-(2-methoxyethoxy)phenyl)phosphine, (7)

(A)



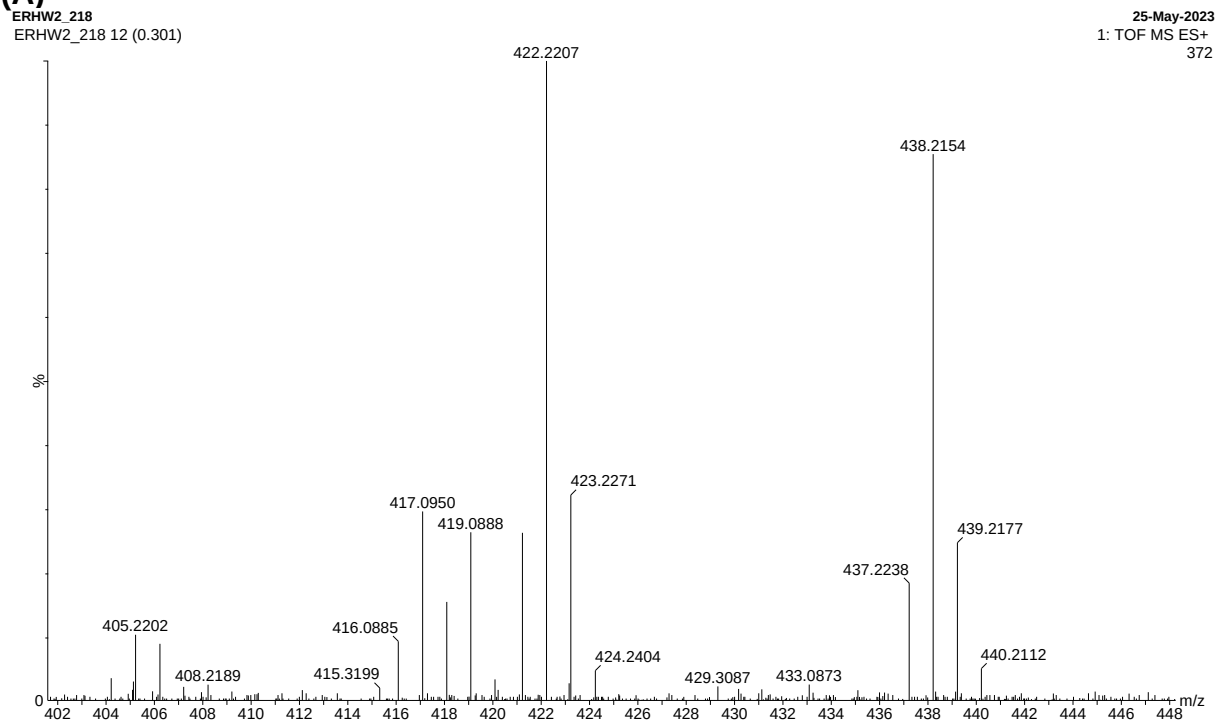
(B)

Minimum:			-1.5				
Maximum:	5.0	5.0	100.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	For-mula
1277.6838	1277.6812	2.6	2.0	11.5	24.0	0.0	C63 H106 O24 P

Fig. S38 (A) The ESI-MS of tris(4-(2-methoxyethoxy)phenyl)phosphine, (**7**) and **(B)** the calculated and found HRMS data.

BODIPY-Br

(A)

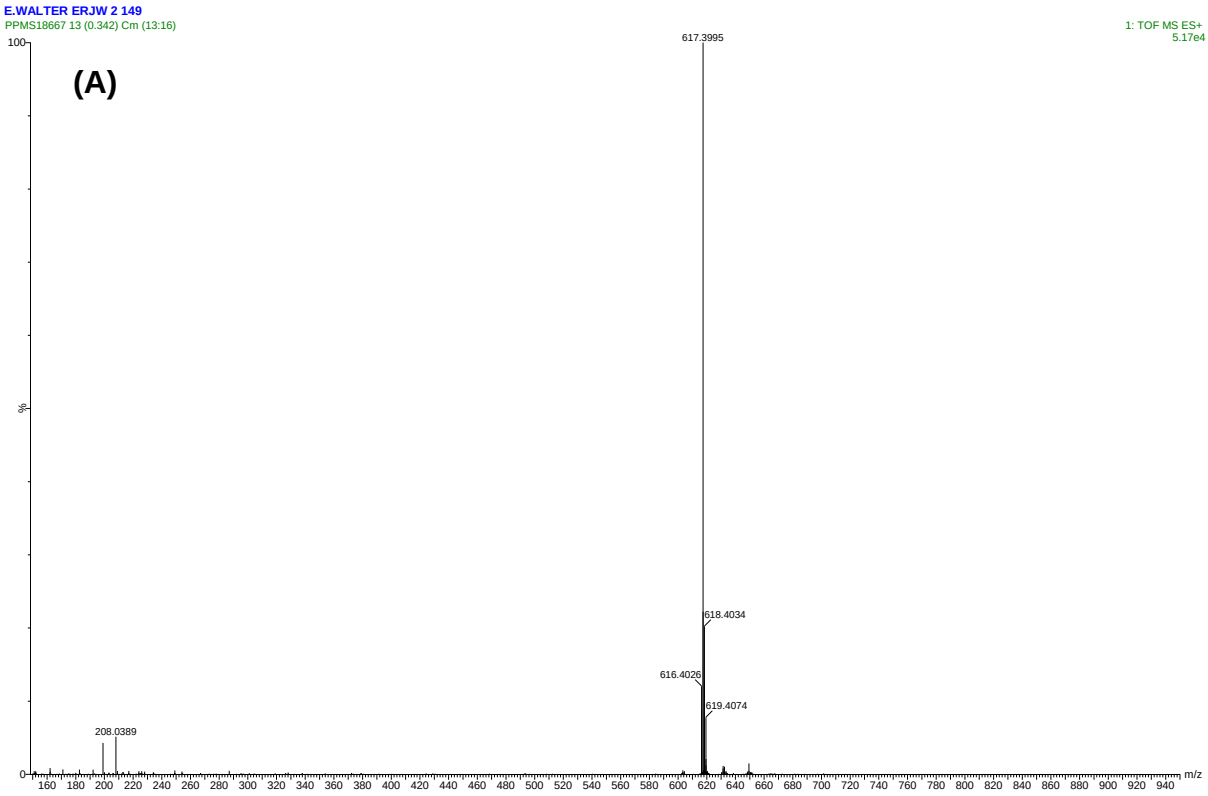


(B)

Minimum:				-1.5			
Maximum:		5.0	5.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
417.0950	417.0949	0.1	0.2	10.5	80.5	0.0	C20 H21 B N2 F2 Br

Fig. S39. (A) The ESI-MS of **BODIPY-Br** and **(B)** the calculated and found HRMS data.

BOPIPY-Mito-1



(B)

Elements Used:

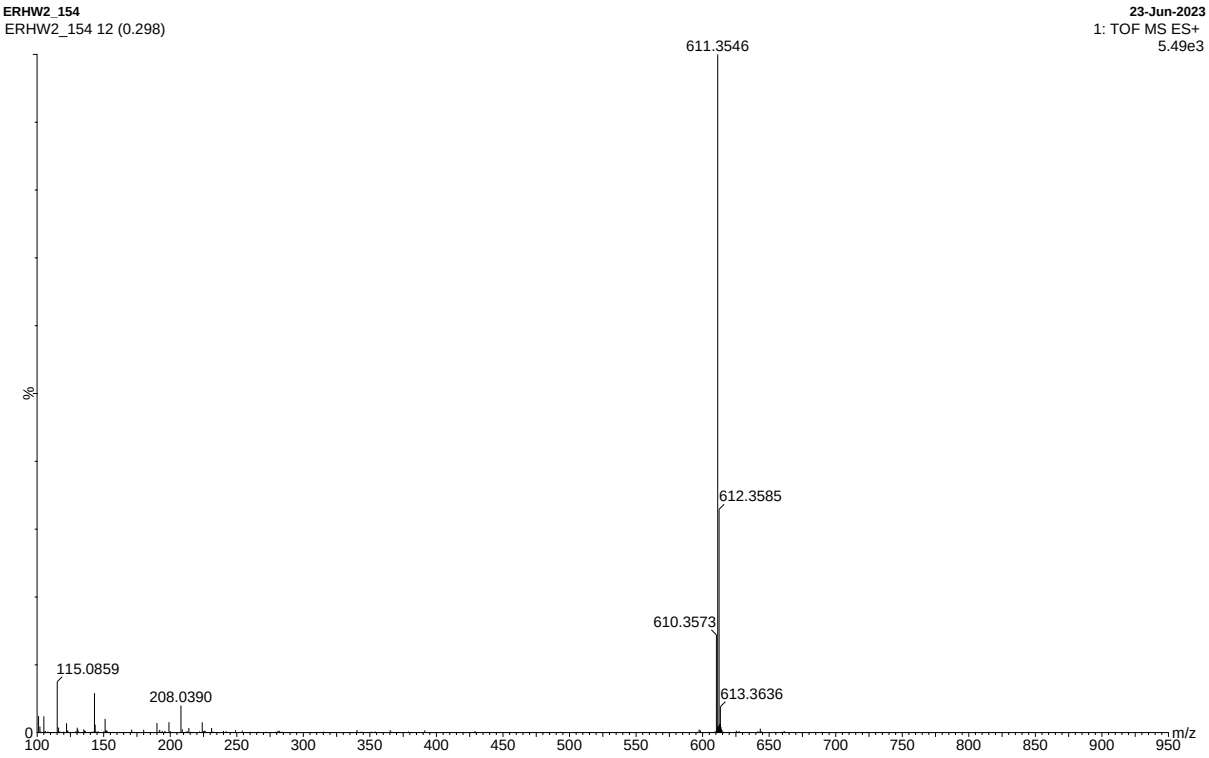
C: 38-38 H: 0-100 11B: 0-1 N: 0-10 O: 0-10 F: 2-2 P: 1-1 I: 0-2

Minimum:				-15.0		
Maximum:		5.0	10.0	100.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
617.3995	617.4008	-1.3	-2.1	13.5	3187.1	C38 H53 11B N2 F2 P

Fig. S40. (A) The ESI-MS of **BODIPY-Mito-1** and **(B)** the calculated and found HRMS data.

BOPIPY-Mito-2

(A)



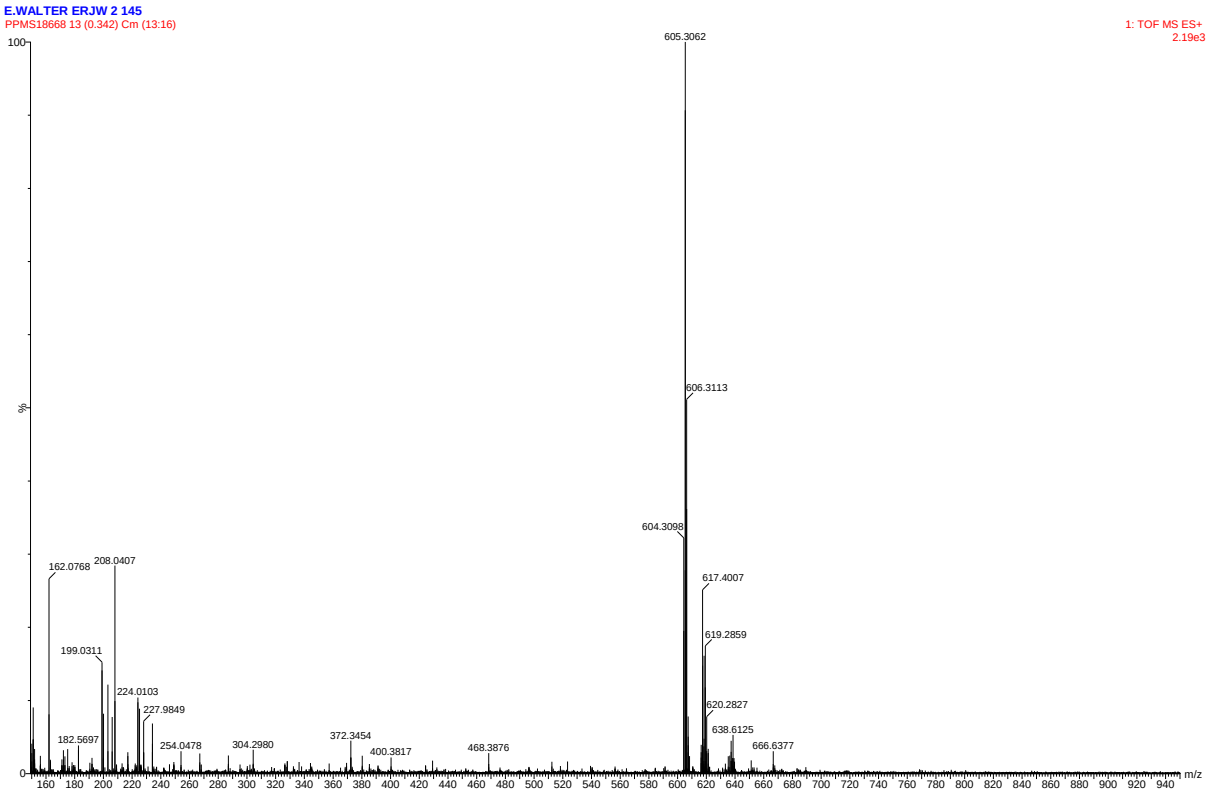
(B)

Minimum:				-1.5			
Maximum:		5.0	5.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
611.3546	611.3538	0.8	1.3	16.5	139.9	0.0	C38 H47 N2 P F2 B

Fig. S41. (A) The ESI-MS of **BODIPY-Mito-2** and **(B)** the calculated and found HRMS data.

BODIPY-Mito-3

(A)



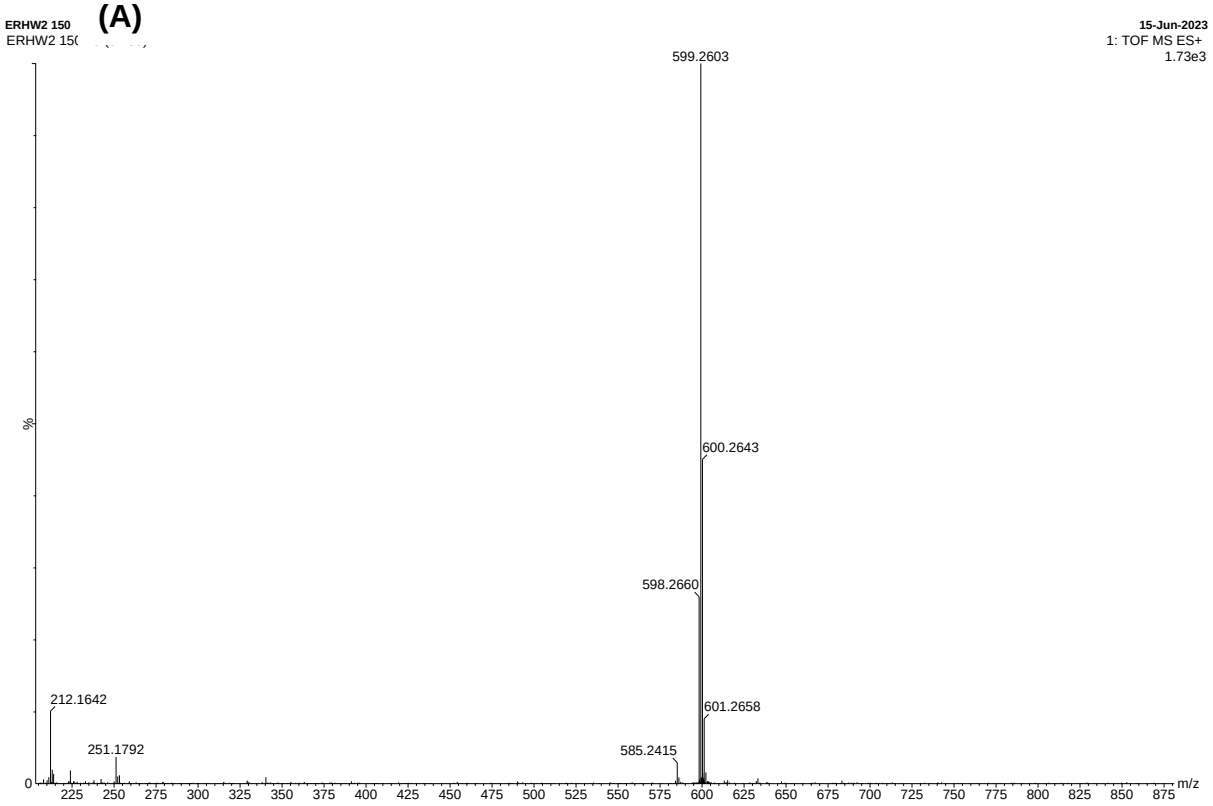
(B)

Minimum:				-15.0		
Maximum:		5.0	10.0	100.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
605.3062	605.3068	-0.6	-1.0	19.5	17.6	C38 H41 11B N2 F2 P

Fig. S42. (A) The ESI-MS of **BODIPY-Mito-3** and **(B)** the calculated and found HRMS data.

BODIPY-Mito-4

(A)



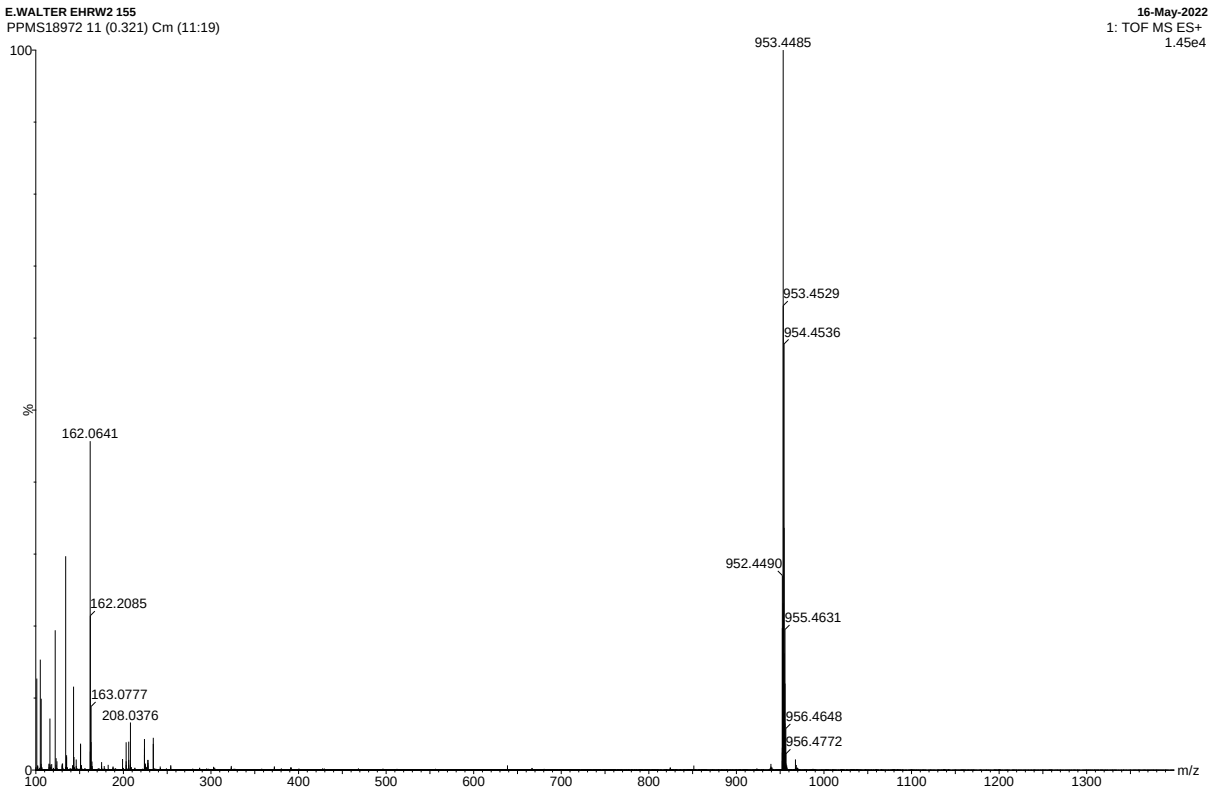
(B)

Minimum:				-1.5			
Maximum:		5.0	5.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
599.2603	599.2599	0.4	0.7	22.5	95.9	0.0	C38 H35 B N2 F2 P

Fig. S43. (A) The ESI-MS of **BODIPY-Mito-4** and **(B)** the calculated and found HRMS data.

BODIPY-Mito-5

(A)



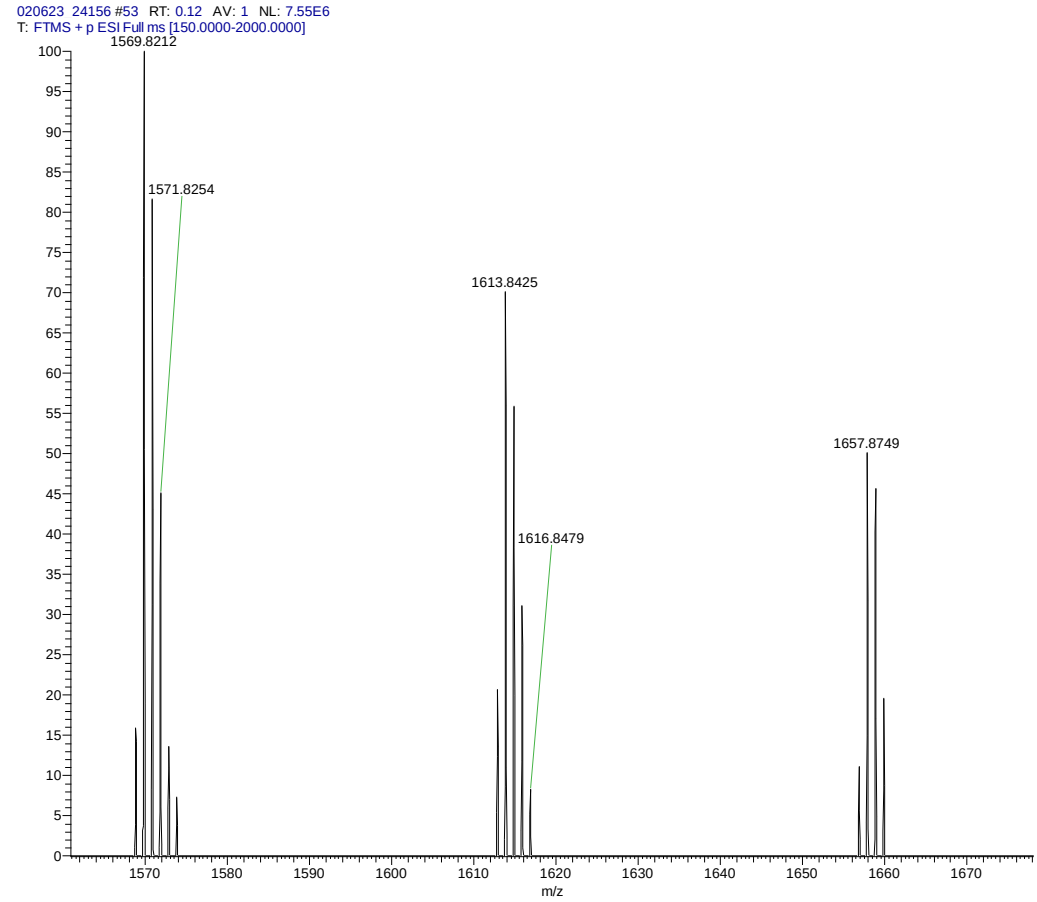
(B)

Minimum:				-1.5			
Maximum:		5.0	7.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
953.4485	953.4489	-0.4	-0.4	22.5	589.1	0.0	C53 H65 N2 O9 F2 11B P

Fig. S44. (A) The ESI-MS of **BODIPY-Mito-5** and **(B)** the calculated and found HRMS data.

BODIPY-Mito-6

(A)



(B) THEORETICAL MASS FOR C83H125BF2N2O24P= 1613.8416

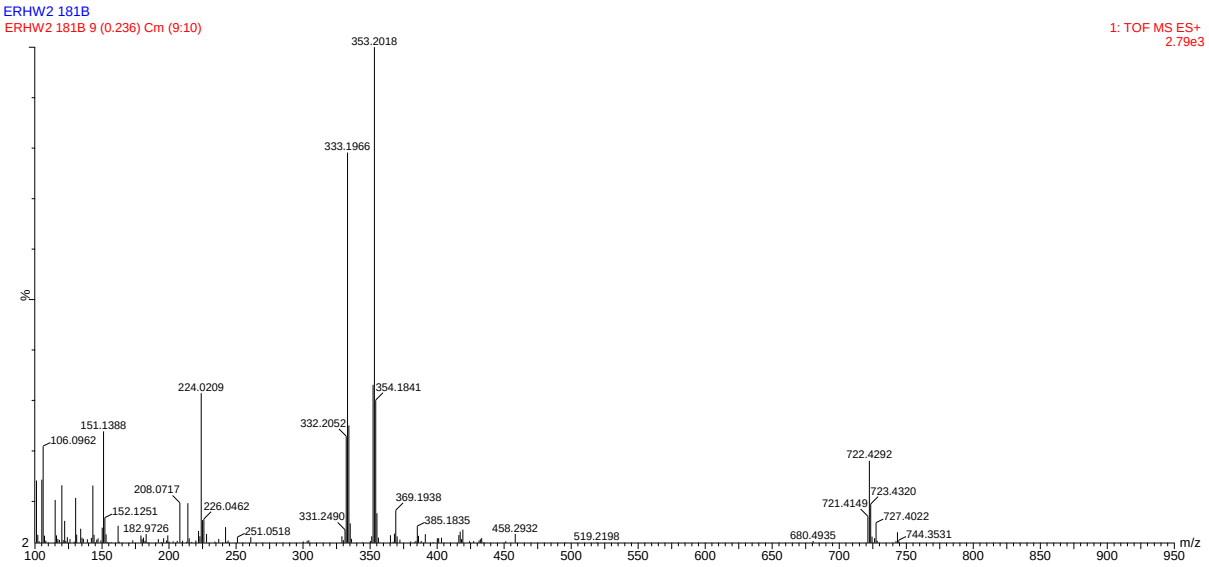
FOUND MASS: 1613.8425

ERROR (ppm): 0.58

Fig. S45. (A) The ESI-MS of **BODIPY-Mito-6** and **(B)** the calculated and found HRMS data.

BODIPY-Et

(A)



(B)

Minimum:				-1.5		
Maximum:		5.0	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
353.2018	353.2001	1.7	4.8	10.5	5546253.5	C21 H24 N2 F2 B

Fig. S46. (A) The ESI-MS of **BODIPY-Et** and **(B)** the calculated and found HRMS data.

References:

1 M. Jiang, J. Wu, W. Liu, H. Ren, W. Zhang, C. S. Lee and P. Wang, *Chem. Eur. J.*, 2021, **27**, 11195–11204.

2 J. H. Brannon and D. Magde, *J. Phys. Chem.*, 1978, **82**, 705–709.

3 B. Yuan, H. Wu, H. Wang, B. Tang, J. F. Xu and X. Zhang, *Angew. Chem., Int. Ed.*, 2021, **60**, 706–710.