Supporting information for:

Water-soluble BODIPY photocages with tunable cellular localization

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1. Supporting figures:

Table S1:

Compound	λ_{ex} nm	λ_{em} nm	ε	Φ_{fl}[a]	$\phi_{rel}\times10^{-4}$	$T_{1/2}$ (s)	$\varepsilon^*\phi_{rel}$	Yield[b] (%)
1	516	529	46500	0.97	0.6	229.2	3	49
5	543	564	48390	0.64	3.9	30.8	19	46
6	545	565	42612	0.61	NA	NA	NA	NA
7	545	559	43321	0.63	1.4	87.2	6	46
8	552	565	50500	0.65	3.7	36.7	19	70
9	560	574	45000	0.51	2.6	39.4	12	53
10	550	570	47073	0.44	5.1	42.1	24	59
11	560	577	48600	0.41	3.6	59.7	18	60
16	549	567	43589	0.49	4.76	128	20.77	-
18	558	578	57217	0.60	1.93	190	11.02	-
21	542	561	43835	0.68	1.22	208	5.35	-
22	558	574	46808	0.54	2.32	182	10.86	-

Photophysical properties and photoreaction quantum yields of BODIPY derivatives in CH_3CN/water (7/3).

[a]Chemical yield of photolysis as quantified by spectrophotometry, NA: Not applicable.

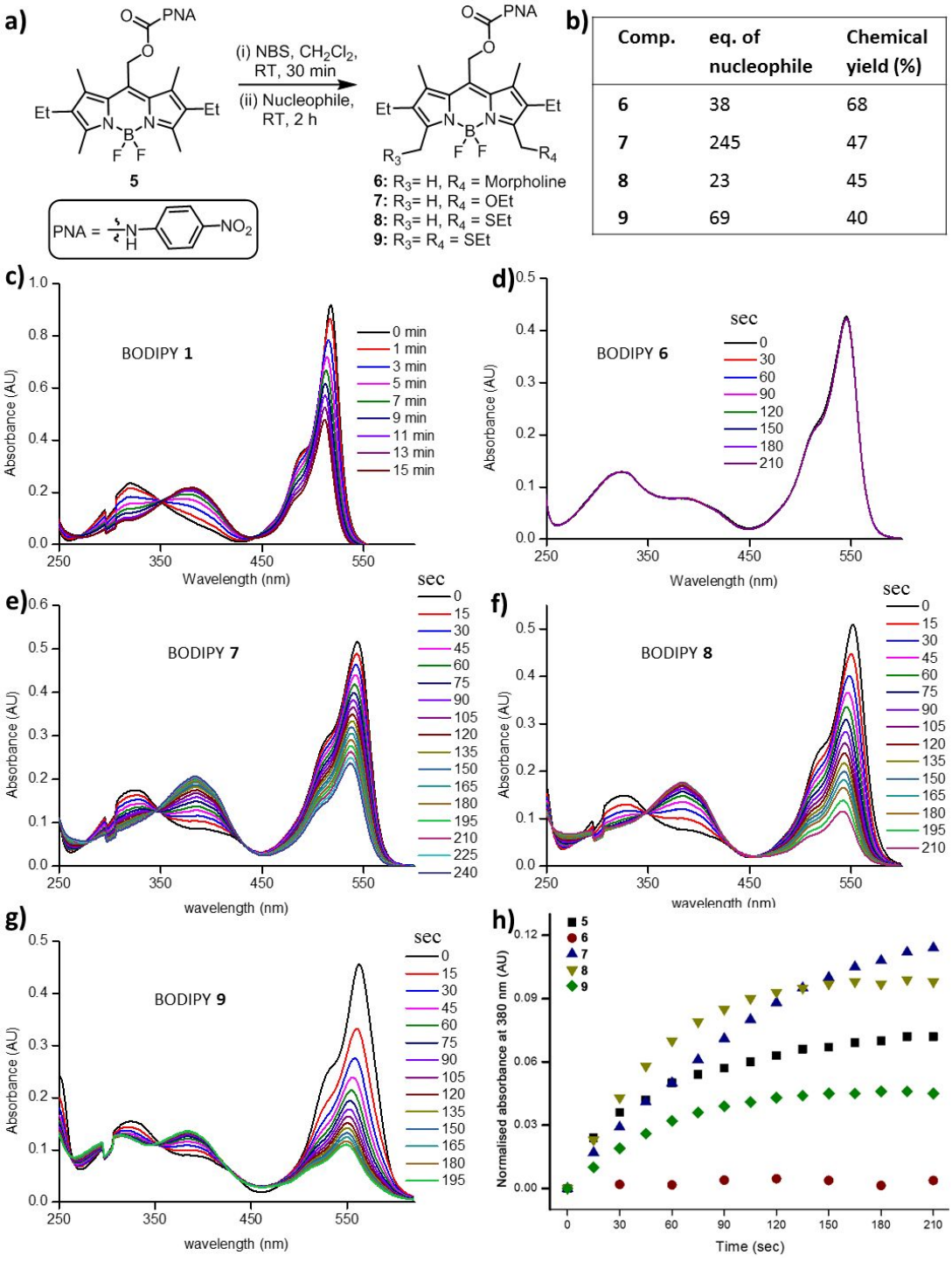
Table S2:

Photophysical properties and photoreaction quantum yields of BODIPYs **10** and **11** in PBS and HBSS containing 1% FBS.

Comp.	Solvent	λ_{ex} nm	ε	$\phi_{rel}\times10^{-4}$	$T_{1/2}$ (s)	$\varepsilon^*\phi_{rel}$	Yield[a] (%)

10	PBS	551	19012	2.5	60	4.68	46
11	PBS	560	24052	5.5	32	13.29	86
10	HBSS+ 1% FBS	557	21358	1.02	144	2.19	56
11	HBSS+ 1% FBS	564	24305	2.6	90	6.28	67

[a]Chemical yield of photolysis as quantified by spectrophotometry.



Comp.	eq. of nucleophile	Chemical yield (%)
6	38	68
7	245	47
8	23	45
9	69	40

Figure S1:

(**a**) Synthetic scheme for BODIPYs **6-9**, (**b**) Number of equivalents of nucleophiles and chemical yields of the optimized reactions, (**c-g**) UV-Vis spectra for light-induced release of PNA from BODIPYs **1** and **7-9**. 10 µM of each compound separately irradiated: compound **1** with 520/30 nm (49 mW/cm^2) and compounds **7-9** with 545/30 nm (49 mW/cm^2) light irradiation in CH_3CN/water (7/3) for the indicated times, (**h**) Light-induced release of PNA from **5-9**.

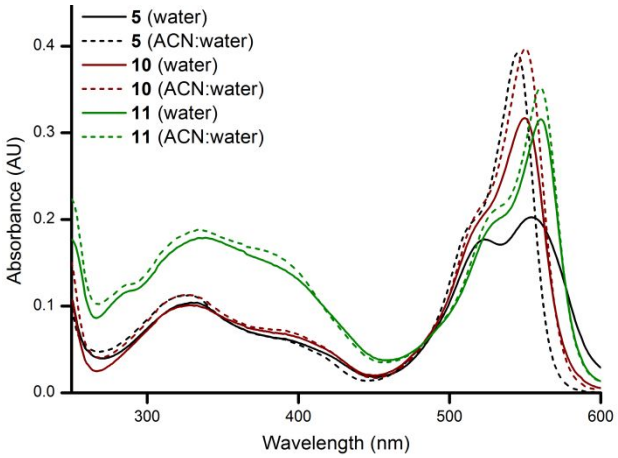


Figure S2:

Absorbance spectra of BODIPYs **5**, **10** and **11** (10 µM each) in CH_3CN/water (7/3) (dashed line) and in water (continuous line).

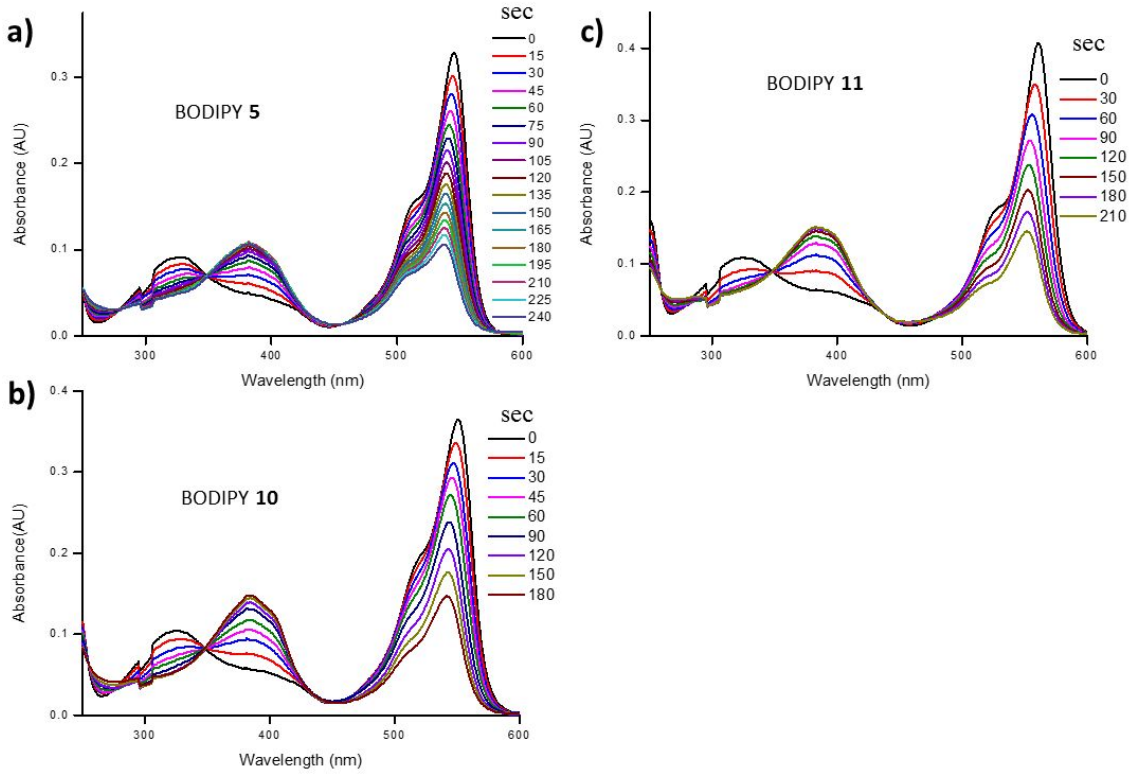


Figure S3:

(**a-c**) UV-Vis spectra for light-induced release of PNA from BODIPYs **5**, **10** and **11**. 10 µM of each compound separately irradiated with 545/30 nm (49 mW/cm^2) light in CH_3CN/water (7/3) for the indicated times.

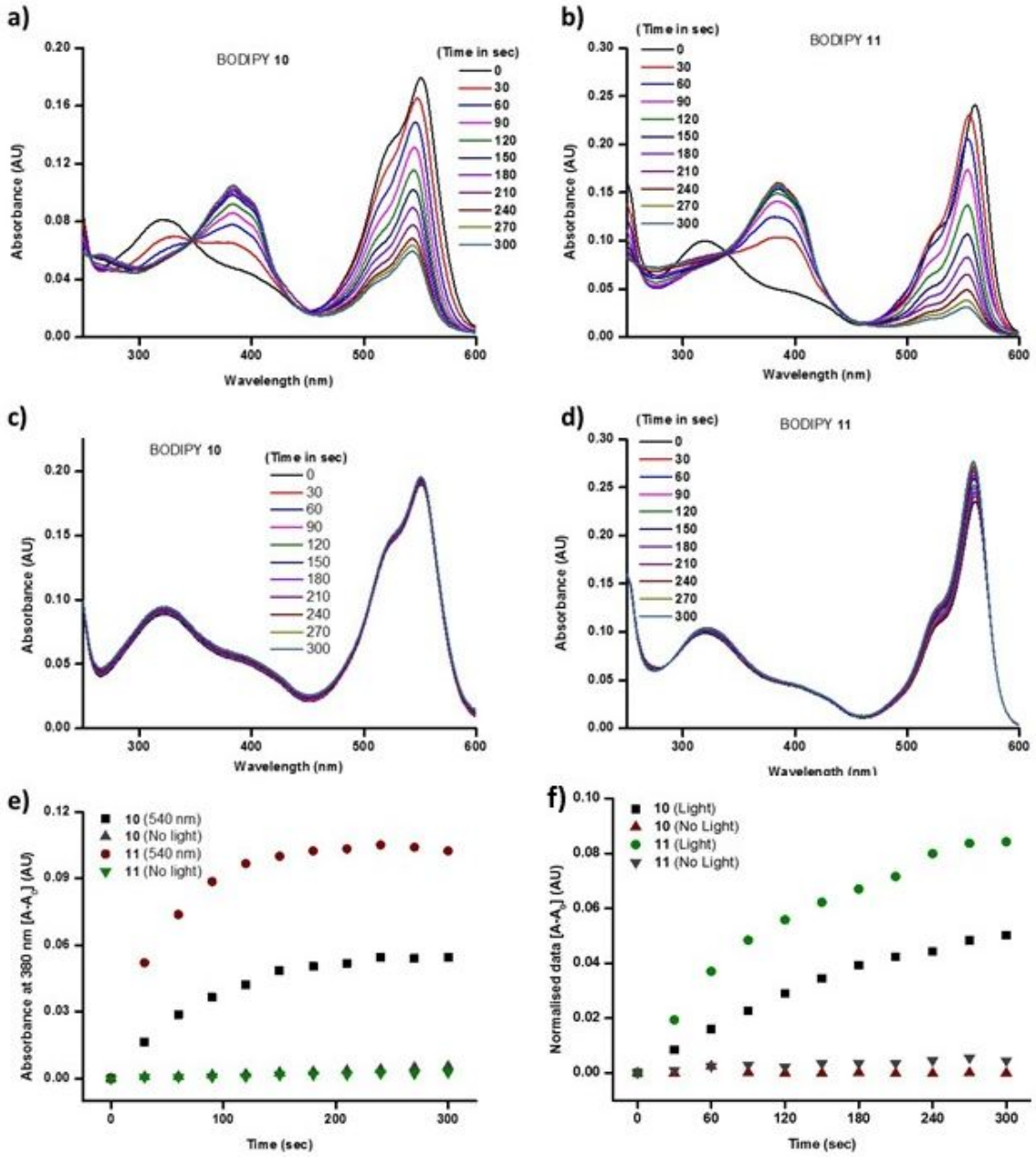


Figure S4:

(**a-b**) UV-Vis spectra for light-induced release of PNA from BODIPYs **10** and **11** with λ_{irr} = 545/50 nm. 10 µM of each compound separately irradiated with 545/30 nm (49 mW/cm^2) light in PBS for the indicated times; (**c-d**) UV-Vis spectra of BODIPYs **10** and **11** in the absence of light; (**e**) PNA release in PBS either in the presence of 545/30 nm (49 mW/cm^2) light or in absence of light from BODIPY photocages **10** and **11**; (**f**) PNA release in the presence and absence of light from BODIPY photocages **10** and **11**. 10 µM of each compound separately was either irradiated with 545/30 nm (49 mW/cm^2) light or kept in dark in HBSS buffer containing 1%FBS for the indicated times.

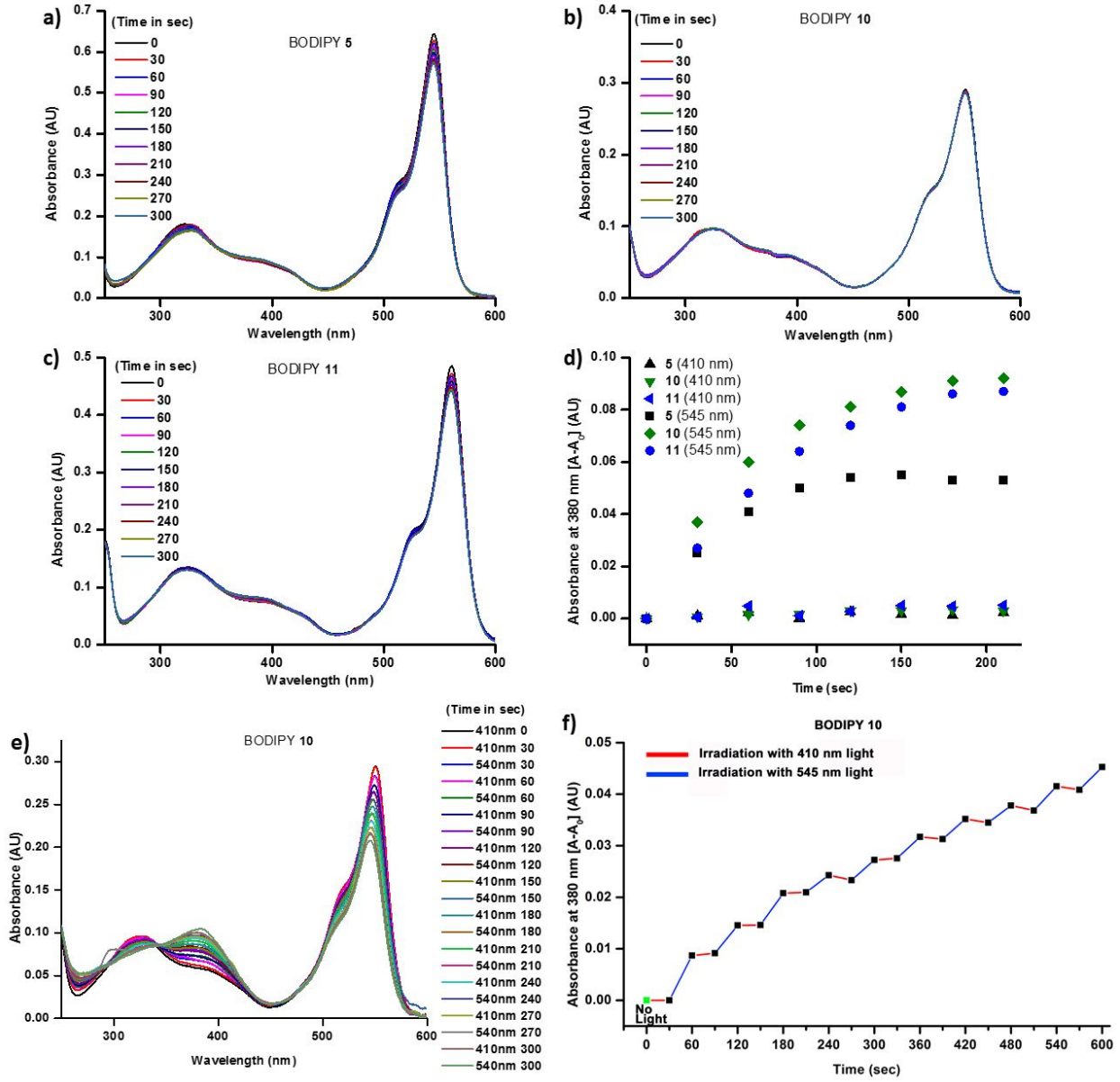


Figure S5:

(a-c) UV-Vis spectra for light-induced release of PNA from BODIPYs **5**, **10** and **11** with λ_{irr} = 410/16 nm. 10 µM of each compound separately irradiated with 410/16 nm (56.2 mW/cm^2) light in CH_3CN/water (7/3); (**d**) PNA release in the presence of either 545/30 nm (49 mW/cm^2) or 410/16 nm (56.2 mW/cm^2) light from BODIPYs **5**, **10** and **11**; (**e**) UV-Vis spectra for light-induced release of PNA from BODIPY **10** (10 µM) irradiated alternatively with 410/16 nm (56.2 mW/cm^2) light and 545/30 nm (49 mW/cm^2) in CH_3CN/water (7/3); (**f**) Normalised absorbance at 380 nm *Vs* time plotted from figure **e.**

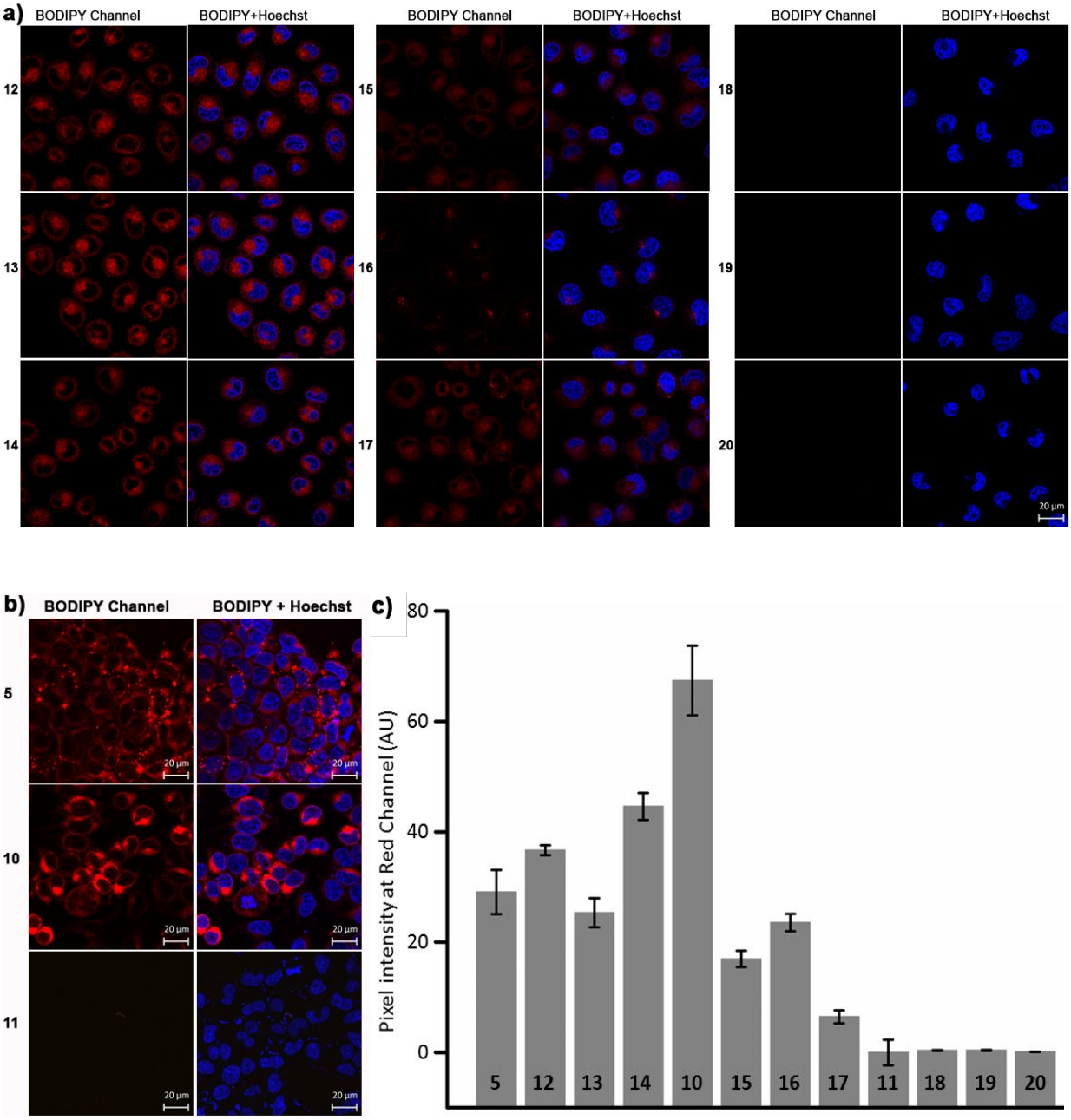


Figure S6:

Cellular permeability of BODIPYs **10**-**20** (**a**) and BODIPYs **5**, **10** and **11** (**b**). HeLa cells were treated with Hoechst dye and 10 µM of **5** and **10**-**20** for 30 min, washed thrice and imaged; (**c**) quantification of pixel intensity at red (BODIPY) channel for selected region of interest (*ROI*). Six cells were selected from each image. Error bars represent standard deviation. Scale bar is 20 µm.

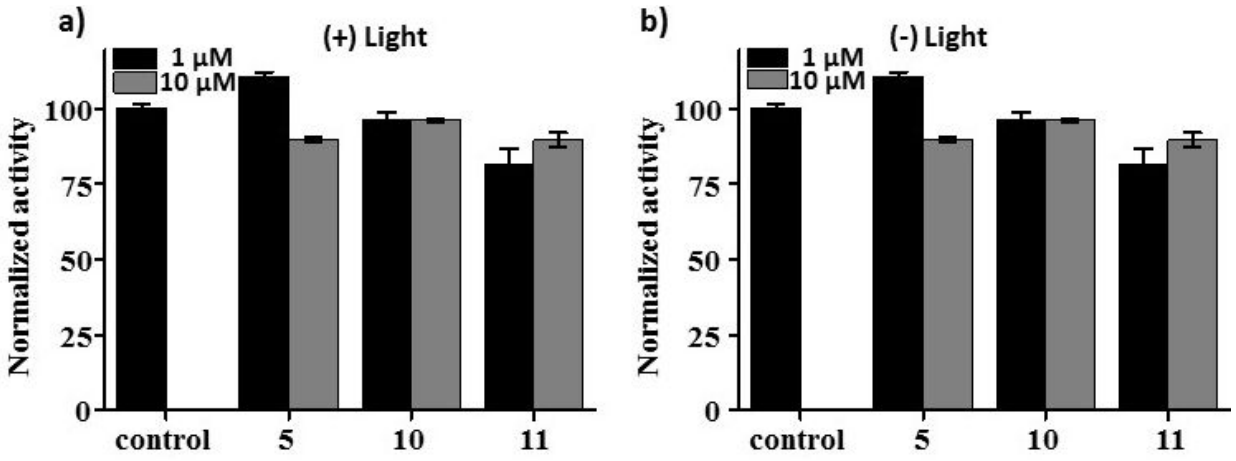


Figure S7:

WST-1 cell viability assay. HeLa cells treated with BODIPY **5**, **10** and **11** (1 and 10 µM) were either irradiated with 545/30 nm (49 mW/cm^2) light (**a**) or untreated (**b**) followed by incubation at 37 ˚C for 24 h. Control experiments contained 0.1% DMSO. Error bars represent standard error (SE).

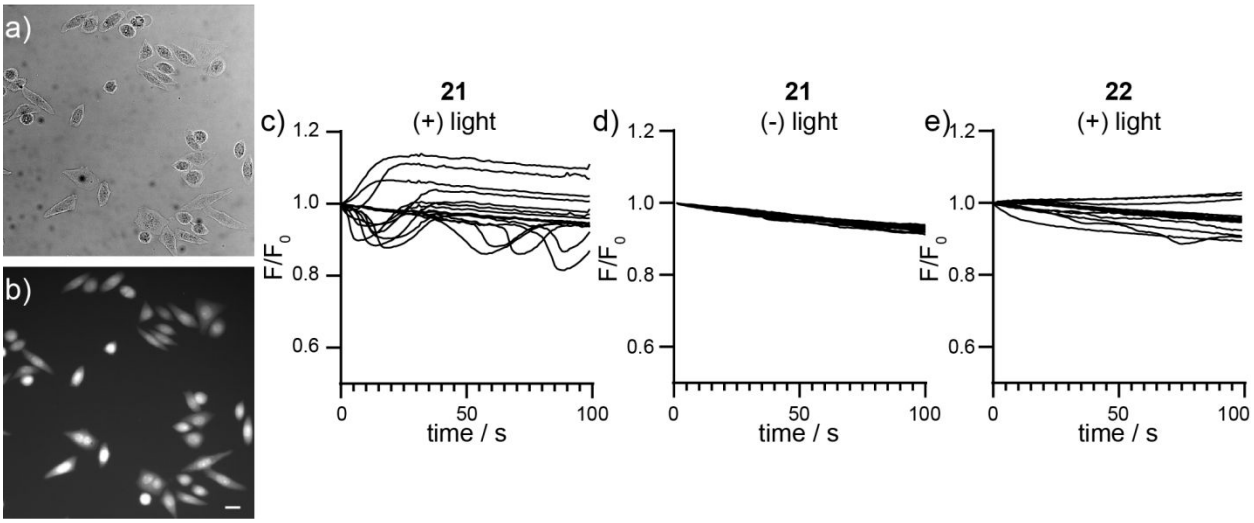


Figure S8:

Uncaging of sphingosine with BODIPY-based photocages. (**a)** Transmitted light and **(b)** widefield fluorescence image of fura-2 associated fluorescence in HeLa cells loaded with BODIPY sphingosine **21**. Scale bar is 20 µm. Plots of change in fura-2 fluorescence vs time for HeLa cells loaded with fura-2 (2 µM) and treated with (**c)** BODIPY sphingosine **21** + green light, (**d)** BODIPY sphingosine **21** without green light, and (**e)** di-MESNA-BODIPY sphingosine **22** + green light. Both BODIPY sphingosine **21** and **22** were used at 5 µM. Uncaging light was provided for 10 s at 90 mW/mm^2.

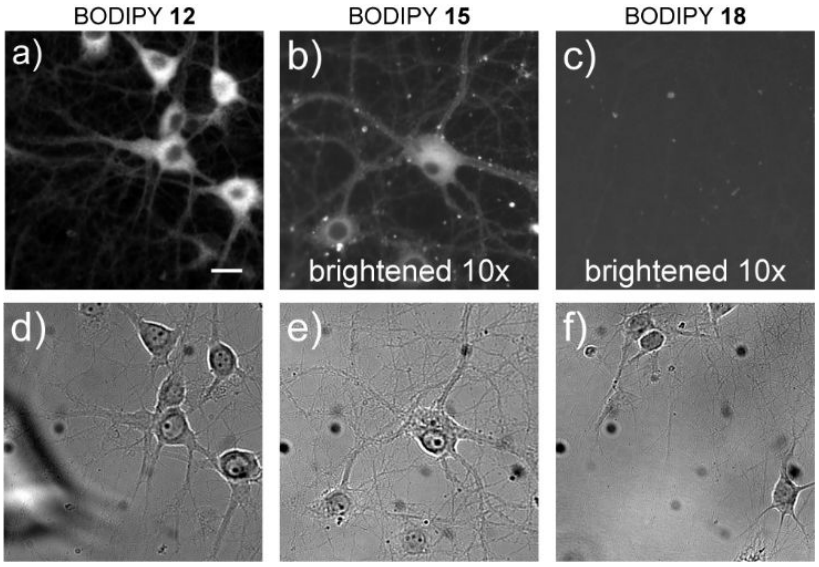


Figure S9:

MESNA-BODIPY dopamine staining in neurons. Wide-field epifluorescence microscopy (**a**-**c**) and DIC images (**d**-**f**) of cultured rat hippocampal neurons stained with **a**, **d**) BODIPY-dopamine **12**, **b**, **e**) mono-MESNA BODIPY-dopamine 15, or **c**, **f**) di-MESNA-BODIPY-dopamine **18**. Images b and c were brightened 10×. Scale bar is 20 μm.

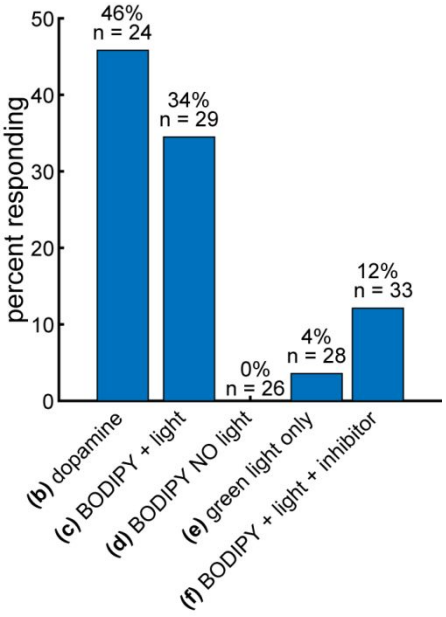


Figure S10:

Quantification of responding neurons from Figure 4. Plot depicts percentage of neurons that responded during the observation period. Neurons were treated with **b)** dopamine (5 μM), or **c) 18** (5 μM) and uncaging light, or **d**) **18** (5 μM) without light, or **e**) only with uncaging light and **f**) **18** (5 μM) and light in the presence of the dopamine receptor antagonist butaclamol (100 μM). Uncaging light was provided for 10 s at 90 mW/mm^2. Percentage values are included above the appropriate bars; numbers of neurons analyzed (n) are also displayed above the bars.

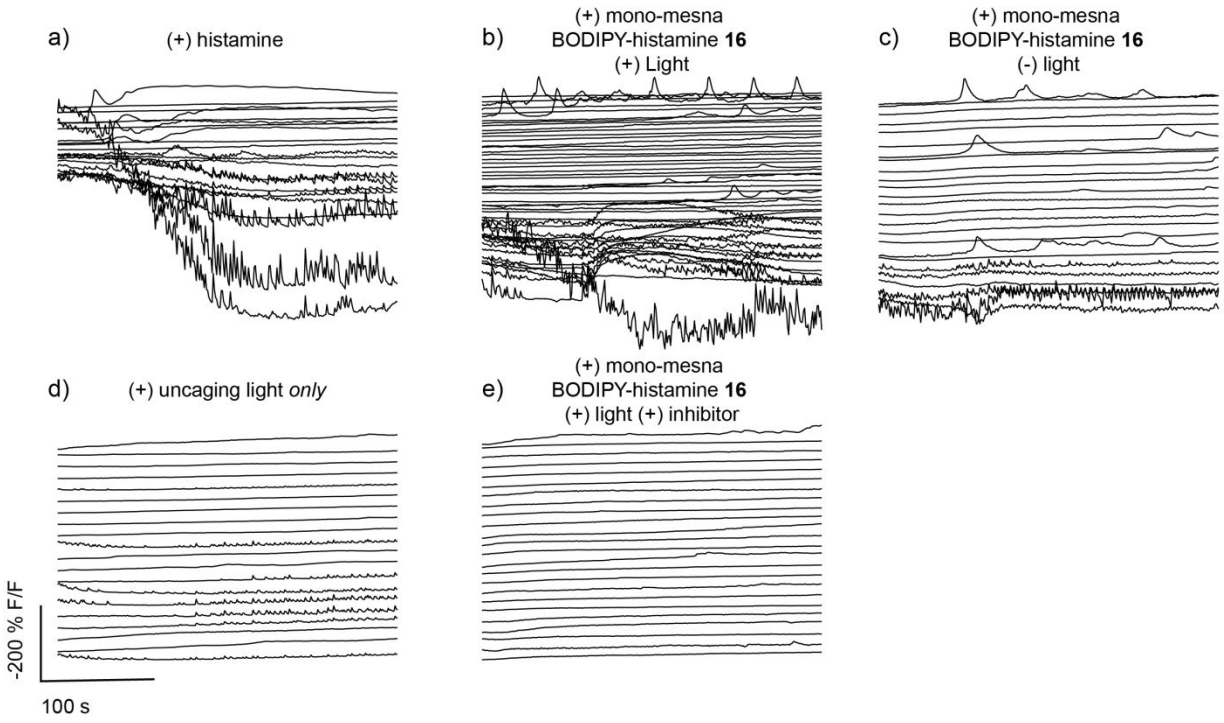


Figure S11:

Uncaging of histamine with mono-MESNA-BODIPY histamine **16** causes Ca^{2+} oscillations in cultured rat hippocampal neurons. Ca^{2+} imaging in neurons treated with (**a)** histamine (5 μM), or (**b)** mono-MESNA-BODIPY histamine **16** (5 μM) and uncaging light, or (**c) 16** (5 μM) without uncaging light, or (**d)** only with uncaging light, or (**e)** mono-MESNA-BODIPY histamine **16** (5 μM) and uncaging light in the presence of the histamine receptor antagonist pyrilamine (1 μM). Plots represent F/F_{max} for representative cells vs. time and are inverted. An increase in cellular Ca^{2+} concentration results in a decrease in fura-2 fluorescence (2 μM), under the illumination conditions used in this study. Uncaging light was provided for 10 s at 90 mW/mm^2.

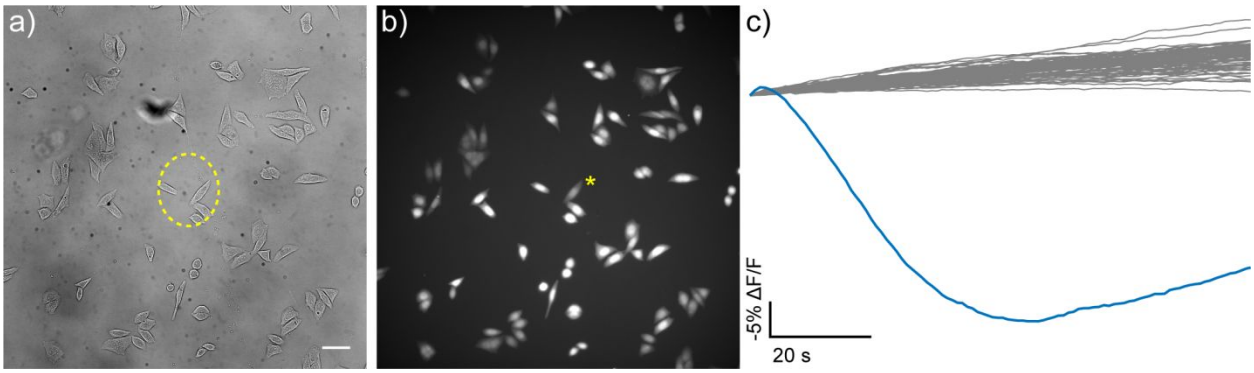


Figure S12:

Spatial control of histamine uncaging with mono-MESNA-BODIPY histamine **16** in HeLa cells. HeLa cells were loaded with fura-2 (2 μM) and incubated with mono-MESNA-BODIPY histamine **16** (5 μM). Uncaging light (542 nm, 90 mW/mm^2, 10 s) was provided over a small area **(a)** indicated by the yellow circle. Fluorescence from fura-2 was monitored **(b)**. **c)** Plot of % ΔF/F vs time for the cells in panel (b). Most cells show very little change in fura-2 associated fluorescence, while the cell with sustained change in Ca^{2+} concentration (indicated by yellow asterisk in panel (b)) was within the uncaging region. Scale bar is 50 μm.

2. General experimental methods:

Pyrromethene 605 was purchased from Exciton. All other chemicals were purchased from Sigma-Aldrich and used as received unless otherwise stated. Anhydrous solvents and reagents (DCM, THF, DMSO and DMF) were obtained as SureSeal bottles from Sigma-Aldrich. Thin-layer chromatography and flash chromatography were performed using EMD pre-coated silica gel 60 F-254 plates and silica gel 60 (230-400 mesh), respectively. UV absorbance spectra were recorded on Agilent Cary 60 UV-Vis Spectrophotometer. Low resolution ESI mass spectrometry was performed on LC/MS Acquity QDa detector coupled with Waters HPLC. High resolution ESI mass spectrometry was performed on a Waters SYNAPT system. ^{1}H- and ^{13}CNMR spectra were collected in $CDCl_3$, Acetone-d_6, DMSO-d_6 or CD_3OD (Cambridge Isotope Laboratories, Cambridge, MA) at 25 °C using a Bruker Advance III spectrometer at 400 MHz and 101 MHz respectively at the Department of Chemistry NMR Facility at Tel-Aviv University. All chemical shifts are reported in the standard δ notation of parts per million using the either TMS or residual solvent peak as an internal reference. Analytical HPLC was performed on Waters HPLC with XBridge C18 column using either Method A [water (solvent A) and acetonitrile (solvent B) with 0.1% TFA as an additive] or Method B [water (solvent A) and acetonitrile/ water: 9/1 (solvent B) with 10 mM NH_4HCO_3 as an additive]. Abbreviations: THF: tetrahydrofuran, DMF: dimethylformamide, DCM: dichloromethane, DIPEA: diisopropylethylamine, DMAP: dimethylaminopyridine, Et_3N: trimethylamine, PNA: *p*-nitroaniline, PNP: *p*-nitrophenol, EtOAc: ethyl acetate, Hex: hexane, RT: room temperature, CH_3CN: acetonitrile, TFA: trifluoroacetic acid, MESNA: 2-mercaptoethane sulfonate Na.

Preparative HPLC purification conditions.

Preparative HPLCs was performed on Waters HPLC with XBridge C18 column with flow rate of 15 mL/min. Method A: water containing 0.1% TFA (solvent A) and acetonitrile containing 0.1% TFA (solvent B) Method B: water containing 10 mM NH_4HCO_3 (solvent A) and acetonitrile/Water (9/1) containing 10 mM NH_4HCO_3

HPLC-MS Analysis conditions

HPLC-MS analysis was performed on Waters HPLC with XBridge C18 column (100 X 3 mm, 5 μm) using a water-acetonitrile gradient of 0% to 100% solvent B in 17 minutes then 3 minutes at 100% solvent B at flow rate of 1 mL/min. Mass spectrometry was performed on LC/MS Acquity QDa detector coupled with Waters HPLC. Method A: water containing 0.1% TFA (solvent A) and acetonitrile containing 0.1% TFA (solvent B) Method B: water containing 10 mM NH_4HCO_3 (solvent A) and acetonitrile/Water (9/1) containing 10 mM NH_4HCO_3

Molar absorption coefficient measurements

Molar absorption coefficients (ε) and maximum absorbance wavelengths (λ_{max}) were determined in 70% acetonitrile in water and/or 100% acetonitrile using Beer's law, from plots of absorbance vs. concentration. Recordings were performed in 10 mm path length quartz cuvettes at room temperature.

General photolysis, monitoring procedures and photolysis quantum yield calculations

Compound sample (2 mL of 10 μM in 70% acetonitrile in water) was placed in 10x10x30 mm quartz cuvette (10 mm path) equipped with an internal magnetic stirrer. The cuvette was placed in front of a light source (Prizmatix) with a 545/30 nm filter (Chroma) and irradiated for the indicated times while constantly stirred. Light intensity at the cuvette was measured by light meter to be 49 mW/cm^2 in all experiments. At each time point, samples were taken for analysis by UV-vis spectrophotometer and/or HPLC-MS. Calibration curves for all tested and reference compounds were generated in each detection method. Photolysis half-lives ($t_{1/2}$) of compounds were calculated by monoexponential fitting in Origin 8.0 software. Quantum yields of photorelease were measured[1] in an aerated mixture of CH_3CN/water

(7/3) with compounds concentration of 10 μM and λ_{irr} = 545/30 nm (49 mW cm^{-2}) (LED) at room temperature and under constant stirring. The optical output power of the LED at the specified peak value was measured using a calibrated optical thermal power meter (2A-BB-9, Ophir Photonics). The photoreaction was monitored to completion and the concentration of released leaving group at each time point was determined by spectrophotometry or by HPLC-MS (against a standardized calibration curve of the leaving group). Only data points from the linear portion of the photoreaction progress were used for quantum yield calculation. Quantum yields values were cross validated for previously reported BODIPY derivatives.[2,3]

General cell culture methods

In a glass-based dish, either 293T or HeLa cells were grown in DMEM (Biological Industries) supplemented with 10% fetal bovine serum (Biological Industries), 2 mM glutamine (Biological Industries), 1 mM Sodium Pyruvate (Biological Industries), 100 units/ml penicillin, and 0.1 mg/ml streptomycin. Cells were incubated in a humidified 37 ºC incubator with 5% CO_2 (LUMITRON).

Cell Viability Assay:

HeLa cells were seeded in 96-well plates at a density of 2×10^4 cells (100 μL of culture)$^{-1}$ well^{-1} except for the first and last columns to which only growth media was added. After a 24h adhering period, the cells were either left untreated or treated with different concentrations of BODIPY **5**, **10** and **11** (1 and 10 μM). After a 24 h incubation period, the WST-1 tetrazolium salt colorimetric 19 proliferation assay was performed by adding 10 μL of dissolved WST-1 solution into each well and incubating for 3 h at 37 °C in a 5% CO_2 incubator. The absorbance of samples was determined using a microtiter plate reader at a wavelength of 450 nm against a background control; the reference wavelength was 690 nm. Each data point represents an average of 6 replicate wells.

Cell imaging instrumentation

Assessment of compound uptake by cells were imaged with a laser scanning confocal microscope (Zeiss LSM 780 inverted microscope) equipped with a 63x 1.35 Oil objective lens. BODIPY compounds were excited with 561 nm laser and emitted light was collected between 580 and 615 nm. Hoechst dye was excited with 405 nm laser and emitted light was collected between 410 and 494 nm.

Ca^{2+} imaging

Fura-2 AM was from ThermoFisher (F-1201). Imaging was performed on an AxioExaminer Z-1 (Zeiss) equipped with a Spectra-X Light engine LED light (Lumencor), controlled with Slidebook (v6, Intelligent Imaging Innovations). Images were acquired with a W-Plan-Apo 20x/1.0 water objective (20x; Zeiss) and focused onto an OrcaFlash4.0 sCMOS camera (sCMOS; Hamamatsu). Excitation for fura-2 imaging was provided at 390/22, passed through a quadruple dichroic mirror (432/38, 509/22, 586/40, 654LP), and a quadruple emission filter (430/32, 508/14, 586/30, 708/98). In this configuration, increases in [Ca^{2+}] result in decreases in fura-2 fluorescence. Photo-uncaging of BODIPY compounds was conducted at 542/33 nm, passing through the same dichroic and emission filter. Samples were uncaged with 542 nm light for 10 s at maximum power (90 mW/mm^2), followed by Ca^{2+} imaging, 50-100 ms exposures every second for 3 to 5 minutes after uncaging.

HeLa cells were cultured in DMEM with 10% FBS and 5% GlutaMax and plated on 12 mm round coverslips in 24 well trays at a density of 7.5×10^5 cells/well 12-18 hours prior to imaging experiments. For Ca^{2+} imaging with caged sphingosines, BODIPY-caged sphingosine **21** or **22** was added first, at a concentration of 5 μM for 10 min at 37 °C. After removal of the BODIPY solution, cells were rinsed 2x with Dulbecco's phosphate buffered saline (dPBS), and

then fura-2 AM (2 μM, from a 2.5 mM stock in 1:1 DMSO:Pluronic F-127) was added. After 20 min at 37 °C, cells were washed 2x with dPBS and then placed into HBSS for imaging.

Neurons were harvested from rat embryonic hippocampus and cortex. All animal procedures were approved by the UC Berkeley Animal Care and Use Committees and conformed to the NIH Guide for the Care and Use and Laboratory Animals and the Public Health Policy. Hippocampi were dissected from embryonic day 19 Sprague Dawley rats (Charles River Laboratory) in cold sterile HBSS (zero Ca^{2+}, zero Mg^{2+}). All dissection products were supplied by Invitrogen, unless otherwise stated. Hippocampal tissue was treated with trypsin (2.5%) for 15 min at 37 °C. The tissue was triturated using fire polished Pasteur pipettes, in minimum essential media (MEM) supplemented with 5% fetal bovine serum (FBS; Thermo Scientific), 2% B-27, 2% 1M D-glucose (Fisher Scientific) and 1% Glutamax. The dissociated cells were plated onto 12 mm diameter coverslips (Fisher Scientific) pre-treated with PDL at a density of 30-35,000 cells per coverslip in MEM supplemented media (as above). Neurons were maintained at 37 °C in a humidified incubator with 5% CO_2. At 1 day in vitro (DIV) half of the MEM supplemented media was removed and replaced with Neurobasal media containing 2% B-27 supplement and 1% GlutaMax. Imaging was performed on mature neurons 14-18 DIV. Prior to imaging, cells were incubated with 2 μM fura-2 AM at 37 °C for ~30 min, washed once, and transferred to a 35 mm imaging dish containing 2 mL HBSS. BODIPY cages (for histamine and dopamine) were diluted from stocks in DMSO (1000x) to 3x concentration in 1 mL HBSS. This was added to the imaging dish and then the experiment began. Pyrilamine maleate (1 μM, Sigma) or (+)-butaclamol (100 μM, Sigma) was added prior to treatment with histamine, dopamine, or BODIPY compounds. Neurons were treated with a 3x stock of KCl (150 mM stock, 50 mM final) to prime the response to dopamine. After initial Ca^{2+} transients, as measured by fura-2 reached baseline levels, dopamine or BODIPY was added and the photolysis began.

For Ca^{2+} imaging in hippocampal neurons, a 25-pixel Gaussian filter was applied to each time point using ImageJ. This background was subtracted from each image in the time series before plotting. For Ca^{2+} imaging in HeLa cells, the cellular fluorescence intensity was divided by the initial intensity and plotted vs. time.

Data Analysis

Image analysis and signal quantification were done with the measurement function of ZEN lite 2012 software.

Rate constant, k and Half-life of the reaction ($t_{1/2}$)

Rate constant, k and reaction time for 50% completion ($t_{1/2}$) for each BODIPY photocage were determined according to the Equation .(S1).

$$A = a \times [1 - e^{-(kt)}] \qquad \text{Eq. S1}$$

Where, A = absorbance at 380 nm, a = arbitrary constant, k = pseudo first order rate constant, t = time.

Half-life of the reaction ($t_{1/2}$) was calculated using Equation (S2)

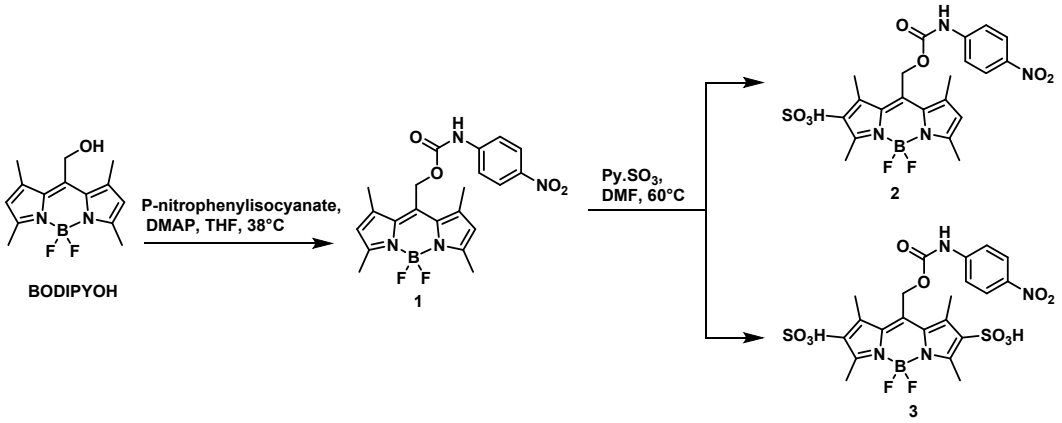
$$t_{1/2} = 0.693/k \qquad \text{Eq. S2}$$

Where k = pseudo first order rate constant.

3. Synthetic procedures

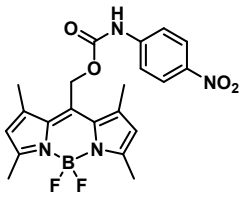
Scheme S2:

Synthetic scheme for **2** and **3**:



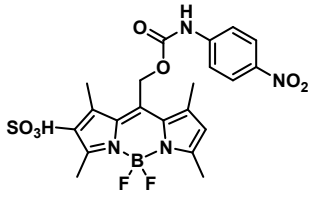
*a) Synthesis of **1**:*

To a stirred solution of BODIPYOH (100 mg, 0.36 mmol) in toluene (5.0 mL) at room temperature under argon atmosphere, *p*-nitrophenylisocyanate (236 mg, 1.44 mmol) and Et_3N (150 µL, 1.08 mmol) were added. The reaction mixture was stirred for 5 h at that temperature. After full conversion of starting material (TLC, mobile phase 20 % EtOAc in n-Hexanes), the reaction was diluted with EtOAc (20.0 mL) and washed with saturated NH_4Cl solution (10.0 mL) and brine (10.0 mL). The water fractions were extracted with EtOAc (10.0 mL X 2). The combined organic phase was dried with $MgSO_4$, filtered and solvents were removed under reduced pressure. The crude mixture was purified by silica gel chromatography (0 – 12 % EtOAc in n-Hexane gradient) to yield **1** (65 mg, 41 %) as an orange solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.22 (d, J = 9.0 Hz, 2H), 7.57 (d, J = 9.0 Hz, 2H), 7.14 (br S, 1H), 6.10 (s, 2H), 5.46 (s, 2H), 2.54 (s, 6H), 2.42 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 157.0, 152.1, 143.4, 143.2, 125.3, 122.5, 117.9, 58.8, 29.7, 15.7, 14.7; LC/MS (Method B): Retention time 13.45 min, 441.24 $[M-H]^+$; HR-MS(ESI) calcd. for formula $C_{21}H_{21}BF_2N_4O_4Na[M+Na]^+$: 465.1522; Found: 465.1555.


1

*b) Synthesis of **2**:*

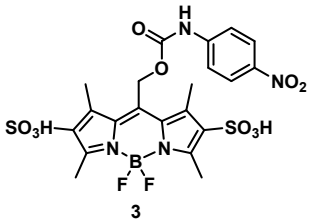
To a stirred solution of **1** (25 mg, 0.056 mmol) in dry DMF (5.0 mL) at room temperature under argon atmosphere was added sulfur trioxide-pyridine (90 mg, 0.56 mmol). The reaction mixture was stirred for 24 h at 60 °C. Upon complete consumption of starting material the reaction was stopped and cooled to room temperature. The reaction was diluted with EtOAc (15.0 mL) and washed with saturated NH_4Cl solution (10.0 mL) and brine (10.0 mL). The water fractions were extracted with EtOAc (10.0 mL X 2). The combined organic phase was dried with $MgSO_4$, filtered and solvents were removed under reduced pressure. The crude was purified by silica gel chromatography (0 – 5 % methanol in DCM gradient) to yield **2** (15 mg, 50 %) as an orange solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 10.65 (S, 1H), 8.21 (d, J = 9.0 Hz, 2H), 7.70 (d, J = 9.0 Hz, 2H), 6.32 (S, 1H), 5.46 (s, 2H), 2.63 (s, 6H), 2.43 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 157.0, 155.1, 153.1, 145.6, 142.7, 142.4, 138.9, 138.5, 135.3, 132.9, 131.0, 125.6, 123.2,


2

118.3, 58.5, 15.9, 14.8, 14.4, 13.3; LC/MS (Method A): Retention time 9.20 min, 521.26 $[M-H]^+$; HR-MS(ESI) calcd. for formula $C_{21}H_{20}BF_2N_4O_7S[M-H]^+$: 521.1114; Found: 521.1122.

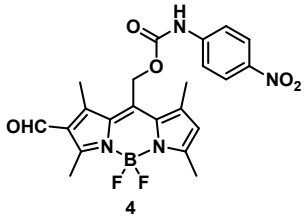
*c) Synthesis of **3**:*

To a stirred solution of **1** (25 mg, 0.056 mmol) in DMF (5.0 mL) at room temperature under argon atmosphere was added sulfur trioxide-pyridine (107 mg, 0.67 mmol). The reaction mixture was stirred for 48 h at 60 °C. The reaction was stopped and cooled to room temperature. Following the removal of the solvent under reduced pressure, the crude product was purified by silica gel chromatography (0 – 20 % methanol in DCM gradient) to yield **3** (9 mg, 26 %) as an orange solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 10.71 (S, 1H), 8.22 (d, *J* = 9.0 Hz, 2H), 7.72 (d, *J* = 9.0 Hz, 2H), 5.51 (s, 2H), 2.63 (s, 12H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 155.7, 153.1, 145.7, 142.4, 139.0, 138.7, 136.2, 131.6, 125.5, 118.4, 58.5, 13.5, 10.0; LC/MS (Method A): Retention time 6.32 min, 601.01 $[M-H]^+$; HR-MS(ESI) calcd. for formula $C_{21}H_{21}BF_2N_4O_{10}S_2Na[M+Na]^+$: 625.0658; Found: 625.0653.



3

*d) Synthesis of **4**:*

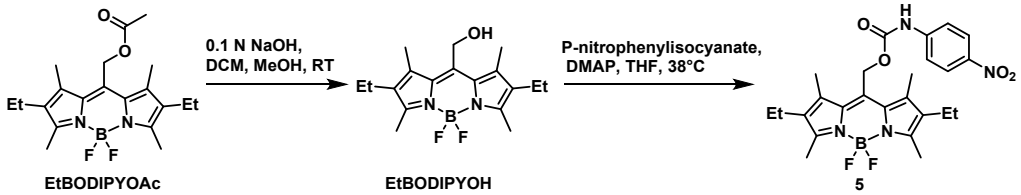


4

Dry DMF (1.25 mL) was added to dry DCM (4 mL) at room temperature under argon atmosphere, and then cooled in an ice bath to 0 °C. $POCl_3$ (1.5 mL) was added dropwise and the reaction mixture was warmed to room temperature and stirring was continued for 30 min at that temperature. **1** (25 mg, 0.057 mmol) was added in one portion and the mixture was stirred for 3 h. After that time, reaction mixture was cooled to 0 °C before the addition of saturated aq. $NaHCO_3$ (4 mL). The mixture was stirred 30 min at room temperature and the organic layer was separated. The aqueous layer was extracted with DCM (3 × 10 mL) and the combined organic layers were dried over Na_2SO_4, filtered, and volatiles were removed *in vacuo*. The crude mixture was purified by column chromatography (0 – 50 % EtOAc in n-Hexane gradient) to afford compound **4** as an orange powder (14 mg, 53%). ^{1}H NMR (400 MHz, DMSO d_6) δ (ppm): 10.71 (s, 1H), 10.13 (s, 1H), 8.29 (d, J = 9.1 Hz, 2H), 7.76 (d, J = 9.1 Hz, 2H), 6.67 (s, 1H), 5.60 (s, 2H), 2.78 (d, J = 11.2 Hz, 6H), 2.65 – 2.33 (m, 6H, merged with residual DMSO); ^{13}C NMR (100 MHz, DMSO d_6) δ (ppm): 187.3, 155.8, 152.8, 147.1, 145.4, 142.3, 140.8, 136.5, 130.0, 126.1, 125.5, 118.2, 58.2, 16.3, 15.3, 13.0, 12.1; LC/MS (Method A): Retention time 10.90 min, 471.17 $[M+H]^+$; HR-MS(ESI) calcd. for formula $C_{22}H_{21}BF_2N_4O_5Na[M+Na]^+$: 493.1471; Found: 493.1464.

Scheme S3:

Synthetic scheme for **5**:



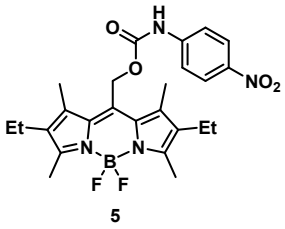
*a) Synthesis of **EtBODIPYOH**:*

To a mixture of EtBODIPYOAc (250 mg, 0.66 mmol) in CH_2Cl_2 (7.5 mL) and methanol (15 mL) at room temperature under argon atmosphere was added 0.1 M NaOH solution (4.0 mL). Stirring was continued for 6 h at room temperature under argon atmosphere in the dark. Progress of the reaction was monitored by TLC (mobile phase 20 % EtOAc in n-Hexanes). Upon complete consumption of starting material, the reaction mixture was evaporated under reduced pressure. The residue was dissolved in DCM (30 mL) and washed with saturated NH_4Cl solution (20 mL), followed by brine solution (20 mL). The organic layer was dried with $MgSO_4$ and filtered. Solvent was removed under reduced pressure to obtain a dark brown residue, which was purified by silica gel column chromatography (Eluent: 0 - 12 % EtOAc in n-Hexane gradient) to furnish **EtBODIPYOH** as dark orange/brown solid (150 mg, 68 %). LC/MS (Method A): Retention time 10.73 min, 335.14 $[M+H]^+$. Analytical data for EtBODIPYOH matched those previously reported.[3]


EtBODIPYOH

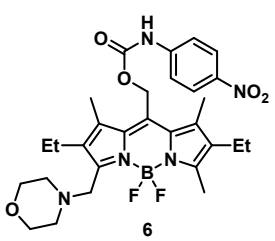
*b) Synthesis of **5**:*

To a stirred solution of EtBODIPYOH (70 mg, 0.21 mmol) in dry THF (4.0 mL), *p*-nitrophenylisocyanate (138 mg, 0.84 mmol) and DMAP (34 mg, 0.27 mmol) were added under argon atmosphere, at room temperature. The reaction mixture was warmed to 38°C (oil bath temperature) and stirred for 2 h. Progress of the reaction was monitored by TLC (mobile phase 0 - 20 % EtOAc in n-Hexanes). Upon complete consumption of starting material, the reaction was diluted with EtOAc (20.0 mL) and washed with saturated NH_4Cl solution (10.0 mL) and brine (10.0 mL). The water fractions were extracted with EtOAc (10 mL X 2). The combined organic phase was dried with $MgSO_4$, filtered and solvents were removed under reduced pressure. The crude mixture was purified by silica gel chromatography (0 – 12 % EtOAc in n-Hexane gradient) to yield **5** (90 mg, 87 %) as a dark orange solid. (110 mg, 0.38 mmol). LC/MS (Method A): Retention time 13.61 min, 499.45 $[M+H]^+$. Analytical data for EtBODIPYPNA matched those previously reported.[3]


5

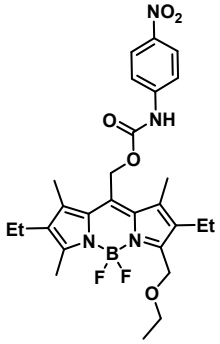
*c) Synthesis of **6**:*

To a stirred solution of **5** (15 mg, 0.03 mmol) in dry CH_2Cl_2 (2 mL) at room temperature under argon atmosphere was added *N*-bromosuccinimide (6 mg, 0.03 mmol). The reaction mixture was stirred for 30 min at that temperature. Morpholine (100 µL, 1.14 mmol) was added to the reaction mixture and stirring was continued for 2h at room temperature. The reaction mixture was evaporated under reduced pressure to obtain a dark brown residue, which was purified by silica gel column chromatography (Eluent: 0 - 12 % EtOAc in n-Hexane gradient) to furnish **6** as a dark orange/brown solid (12 mg, 68 %). ^{1}H NMR (400


6

MHz, $CDCl_3$) δ (ppm): 8.23 (d, *J* = 9.1 Hz, 2H), 7.58 (d, *J* = 9.1 Hz, 2H), 7.18 (s, 1H), 5.49 (s, 2H), 3.80 (s, 2H), 3.67 (s, 4H), 2.43 – 2.58 (m, 9H), 2.34 – 2.41 (m, 8H), 1.12 (t, *J* = 7.5 Hz, 3H), 1.02 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 157.4, 153.6, 152.1, 143.3, 143.2, 137.4, 136.6, 135.0, 134.7, 132.8, 131.6, 131.2, 125.3, 117.9, 67.2, 59.2, 54.3, 53.7, 29.7, 17.4, 17.1, 14.6 (2), 12.9, 12.6; LC/MS (Method A): Retention time 10.59 min, 584.41 $[M+H]^+$; HR-MS(ESI) calcd. for formula $C_{29}H_{35}BF_2N_5O_5[M-H]^+$: 582.2699; Found: 582.2704.

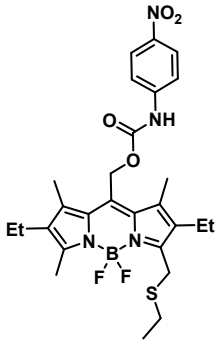
*d) Synthesis of **7**:*



7

To a stirred solution of **5** (70 mg, 0.14 mmol) in dry DCM (2.0 mL) at room temperature under argon atmosphere was added N-bromosuccinimide (25 mg, 0.14 mmol). After stirring for 1.5 h at room temperature ethanol (2 mL) was added to the reaction mixture and stirring was continued for 2 h. The reaction mixture was evaporated under reduced pressure. The crude was purified by silica gel chromatography (0 – 15 % EtOAc in n-Hexane gradient) to yield **7** (36 mg, 47 %) as an orange solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.15 (d, *J* = 9.0 Hz, 2H), 7.60 (s, 1H), 7.55 (d, *J* = 9.0 Hz, 2H), 5.46 (s, 2H), 4.75 (s, 2H), 3.57 (q, *J* = 7.0 Hz, 2H), 2.55 (s, 3H), 2.49 (q, *J* = 7.5 Hz, 2H), 2.41 (q, *J* = 7.5 Hz, 2H), 2.35 (s, 3H), 2.30 (s, 3H), 1.19 (t, *J* = 7.0 Hz, 3H), 1.05 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 159.0, 152.2, 150.9, 143.6, 143.1, 138.4, 136.0, 135.2, 134.3, 133.7, 132.0, 131.5, 125.1, 117.9, 66.3, 63.7, 59.1, 17.2, 17.1, 15.2, 14.9, 14.5, 13.1, 12.8, 12.4; LC/MS (Method A): Retention time 13.81 min, 565.36 $[M+Na]^+$; HR-MS(ESI) calcd. for formula $C_{27}H_{33}BF_2N_4O_5Na[M+Na]^+$: 565.2410; Found: 565.2413.

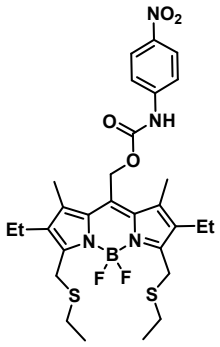
*e) Synthesis of **8**:*



8

To a stirred solution of **5** (30 mg, 0.06 mmol) in dry DCM (2.0 mL) at room temperature under argon atmosphere was added N-bromosuccinimide (11 mg, 0.06 mmol). After stirring for 2 h at room temperature Ethanethiol (100 µL) was added to the reaction mixture and stirring was continued for 2 h. The reaction mixture was evaporated under reduced pressure. The crude mixture was purified by silica gel chromatography (0 – 10 % EtOAc in n-Hexane gradient) to yield **8** (15 mg, 45 %) as orange solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.18 (d, *J* = 9.1 Hz, 2H), 7.56 (d, *J* = 9.1 Hz, 2H), 7.44 (S, 1H), 5.48 (s, 2H), 4.00 (s, 2H), 2.66 (q, *J* = 7.4 Hz, 2H), 2.49-2.55 (m, 5H), 2.45 (q, *J* = 7.5 Hz, 2H), 2.34 (s, 6H), 1.26 (t, *J* = 7.0 Hz, 3H), 1.14 (t, *J* = 7.4 Hz, 3H), 1.06 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 157.62, 152.6, 152.2, 143.5, 143.2, 137.7, 136.7, 134.8, 133.8, 131.2, 125.2, 117.9, 59.1, 29.7, 27.2, 27.0, 17.2, 17.1, 14.8, 14.6, 12.8, 12.7; LC/MS (Method A): Retention time 14.13 min, 557.12 $[M-H]^+$; HR-MS(ESI) calcd. for formula $C_{27}H_{33}BF_2N_4O_4SNa[M+Na]^+$: 581.2181; Found: 581.2186.

*f) Synthesis of **9**:*



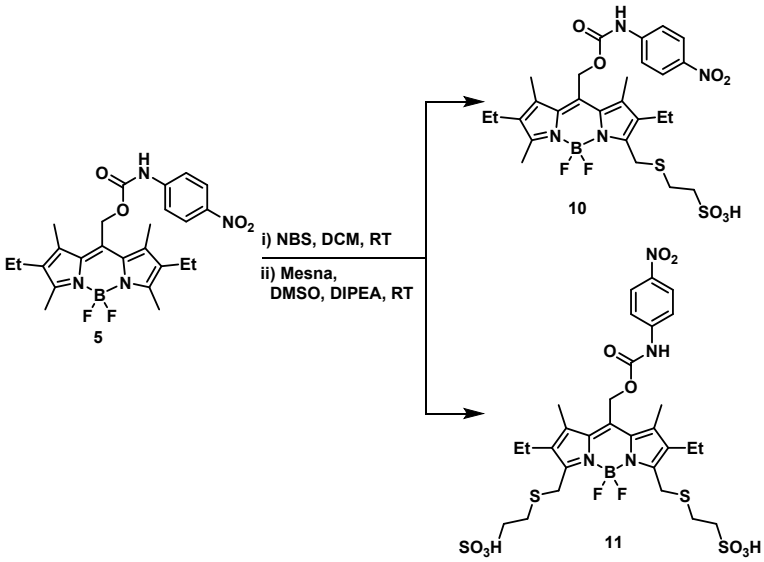
9

To a stirred solution of **5** (20 mg, 0.04 mmol) in dry DCM (2.0 mL) at room temperature under argon atmosphere was added N-bromosuccinimide (14 mg, 0.08 mmol). After stirring for 2 h at room temperature ethanethiol (200 µL) was added to the reaction mixture and stirring was continued for 2 h. The reaction mixture was evaporated under reduced pressure. The crude mixture was purified by reverse phase prep-HPLC [Method A]. Fractions containing desired compound were evaporated under reduced pressure to remove acetonitrile. Residue was extracted from aqueous phase in DCM (20 mL) and washed with brine solution (15 mL). The organic layer was dried with $MgSO_4$, filtered and solvent was removed under reduced pressure to yield **9** (10 mg, 40 %) as an orange solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.18 (d, *J* = 9.1 Hz, 2H), 7.57 (d, *J* = 9.1 Hz, 2H), 7.44 (s, 1H), 5.49 (s, 2H), 4.01 (s, 4H), 2.65 (q, *J* = 7.3

Hz, 4H), 2.49 (q, J = 7.5 Hz, 4H), 2.35 (s, 6H), 1.13-1.27 (m, 6H), 1.12 (t, J = 7.5 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 155.0, 152.1, 143.4, 143.2, 138.0, 134.7, 132.6, 131.9, 125.2, 117.9, 59.1, 29.7, 27.1, 26.9, 17.2, 14.7, 12.8; LC/MS (Method A): Retention time 14.65 min, 617.45 $[M-H]^+$; HR-MS(ESI) calcd. for formula $C_{29}H_{37}BF_2N_4O_4S_2Na[M+Na]^+$: 641.2215; Found: 641.2184.

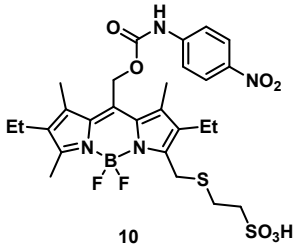
Scheme S4:

Synthetic scheme for **10** and **11**:



*a) Synthesis of **10**:*

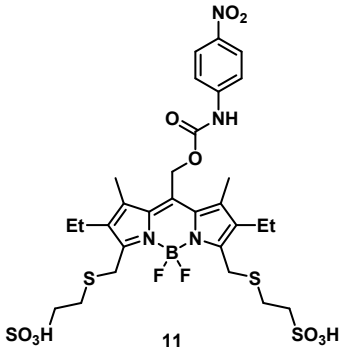
To a stirred solution of **5** (20 mg, 0.04 mmol) in dry DCM (2.0 mL) at room temperature under argon atmosphere was



added *N*-bromosuccinimide (7 mg, 0.04 mmol). The reaction mixture was stirred at that temperature for 1.5 h. Progress of the reaction was monitored by TLC (mobile phase 20 % EtOAc in n-Hexanes). Upon complete consumption of starting material, a solution of MESNA (66 mg, 0.4 mmol) in dry DMSO (0.5 mL) was added to the reaction mixture. Resulting solution was stirred at RT under argon atmosphere for 2 h. The reaction mixture was diluted with DCM (10.0 mL) followed by addition of water (5.0 mL). The water fractions were extracted with DCM (5.0 mL X 2). The combined organic phase was dried with $MgSO_4$, filtered and solvents were removed under reduced pressure. The crude was purified by silica gel chromatography (0 – 10 % methanol in DCM) to yield **10** (13 mg, 50 %) as a dark orange solid. ^{1}H NMR (400 MHz, CD_3OD) δ (ppm): 8.11 (d, J = 9.2 Hz, 2H), 7.61 (d, J = 9.2 Hz, 2H), 5.42 (s, 2H) 3.98 (s, 2H), 2.91-2.99 (m, 4H), 2.46 (q, J = 7.3 Hz, 2H), 2.38-2.41 (m, 5H), 2.31 (s, 3H), 2.30 (s, 3H), 1.06 (t, J = 6.3 Hz, 3H), 0.98 (t, J = 6.3 Hz, 3H); ^{13}C NMR (100 MHz, CD_3OD) δ (ppm): 155.8, 151.5, 149.6, 143.5, 141.1, 136.8, 135.5, 133.0, 131.8, 131.6, 131.3, 130.1, 122.9, 116.0, 56.8, 50.1, 37.4, 25.3, 25.1, 15.2, 14.9, 12.3, 12.0, 10.1, 9.8; LC/MS (Method B): Retention time 10.89 min, 637.78 $[M-H]^+$; HR-MS(ESI) calcd. for formula $C_{27}H_{32}BF_2N_4O_7S_2[M-H]^+$: 637.1774; Found: 637.1773.

*b) Synthesis of **11**:*

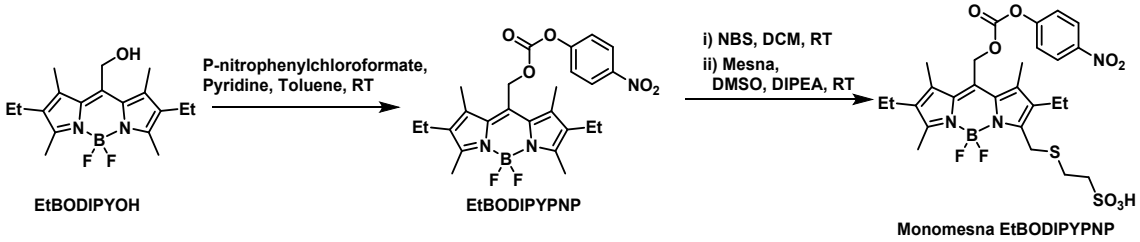
To a stirred solution of **5** (15 mg, 0.03 mmol) in dry DCM (2.0 mL) at room temperature under argon atmosphere was added *N*-bromosuccinimide (11 mg, 0.06 mmol). The reaction mixture was stirred at that temperature for 2 h. Progress of the reaction was monitored by TLC (mobile phase 40 % EtOAc in n-Hexanes). Upon complete consumption of starting material, a solution of Mesna (50 mg, 0.3 mmol) in dry DMSO (0.5 mL) was added to the reaction mixture. Resulting solution was stirred at RT under argon atmosphere for 2 h. The reaction mixture was evaporated under reduced pressure. The crude was purified by reverse phase prep-HPLC [Method A]. Fractions containing desired compound were immediately frozen and lyophilized to afford **11** (8 mg, 33 %) as a dark orange solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 10.76 (s, 1H), 8.22 (d, J = 9.2 Hz, 2H), 7.71 (d, J = 9.2 Hz, 2H), 5.45 (s, 2H) 4.01 (s, 4H), 2.75-2.79 (m, 4H), 2.56-2.61 (m, 4H), 2.33 (s, 6H), 1.07 (t, J = 7.3 Hz, 6H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 154.5, 153.1, 145.7, 142.3, 138.9, 134.5, 134.1, 132.4, 126.9, 125.6, 118.2, 112.9, 58.9, 51.9, 28.2, 27.2, 17.1, 15.1, 12.8; LC/MS (Method B): Retention time 9.13 min, 777.21 $[M-H]^+$; HR-MS(ESI) calcd. for formula $C_{29}H_{36}BF_2N_4O_{10}S_4[M-H]^+$: 777.1375; Found: 777.1375.



11

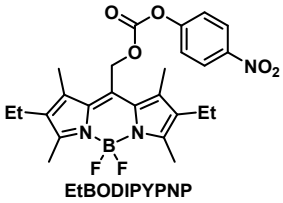
Scheme S5:

Synthetic scheme for monomesna EtBODIPYPNP:



*a) Synthesis of **EtBODIPYPNP**:*

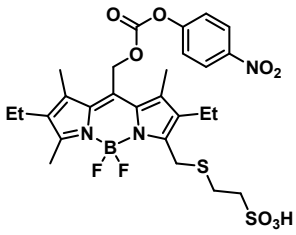
To a stirred solution of EtBODIPYOH (100 mg, 0.30 mmol) in toluene (10 mL) at room temperature under argon atmosphere, *p*-nitrophenylchloroformate (241 mg, 1.20 mmol) and pyridine (197 µL, 1.5 mmol) were added. The reaction mixture was stirred at room temperature for 3 h. Upon completion, the reaction was diluted with EtOAc (10 mL) and washed with saturated NH_4Cl solution (10 mL) and brine (10 mL), dried with MgSO4, filtered and solvents were removed under reduced pressure. The crude product was purified by reverse phase prep-HPLC [Method A]. Fractions containing desired compound were evaporated under reduced pressure to remove acetonitrile. Residue was extracted from aqueous phase in DCM (20 mL) and washed with brine solution (15 mL). The organic layer was dried with $MgSO_4$, filtered and solvent was removed under reduced pressure to yield **EtBODIPYPNP** (110 mg, 74 %) as orange solid. LC/MS (Method A): Retention time 12.72 min, 500.18 $[M+H]^+$. Analytical data for EtBODIPYPNP matched those previously reported.[3]



EtBODIPYPNP

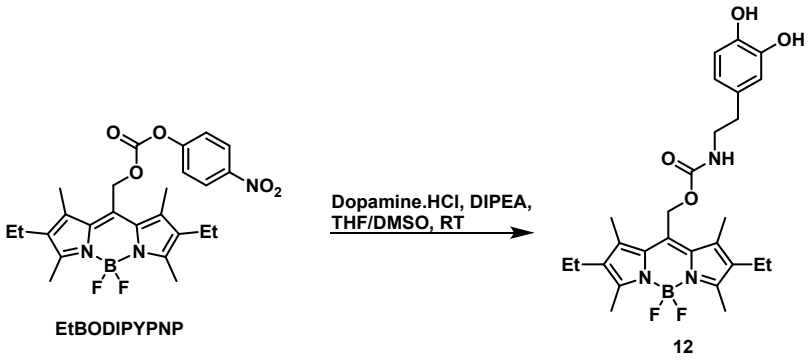
*b) Synthesis of **MonomesnaEtBODIPYPNP**:*

To a stirred solution of EtBODIPYPNP (70 mg, 0.14 mmol) in dry DCM (2.0 mL) at room temperature under argon atmosphere was added *N*-bromosuccinimide (25 mg, 0.14 mmol). The reaction mixture was stirred at that temperature for 2 h. Progress of the reaction was monitored by TLC (mobile phase 20 % EtOAc in n-Hexanes). Upon complete consumption of starting material, solution of MESNA (50 mg, 0.3 mmol) in dry DMSO (0.5 mL) was added to the reaction mixture. Resulting reaction mixture was stirred at RT under argon atmosphere for 2 h. The reaction mixture was evaporated under reduced pressure. The crude was purified by silica gel chromatography (0 – 10 % methanol in DCM) to yield **MonomesnaEtBODIPYPNP** (60 mg, 67 %) as an orange solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 8.33 (d, *J* = 9.2 Hz, 2H), 7.64 (d, *J* = 9.2 Hz, 2H), 5.62 (s, 2H), 3.98 (s, 2H), 2.76-2.84 (m, 2H), 2.60-2.72 (m, 4H), 2.47 (s, 3H), 2.42 (d, *J* = 7.2 Hz, 2H), 2.38 (s, 3H), 2.36 (s, 3H) 1.66 (t, *J* = 6.6 Hz, 3H), 1.60 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ (ppm): 157.7, 155.6, 152.4, 152.1, 145.8, 137.7, 135.0, 133.7, 132.8, 131.9, 126.6, 125.9, 123.2, 116.2, 62.2, 51.9, 28.4, 27.1, 17.1, 16.9, 15.2, 14.9, 13.2, 13.0, 12.8; LC/MS (Method B): Retention time 10.51 min, 638.38 $[M-H]^+$; HR-MS(ESI) calcd. for formula $C_{27}H_{31}BF_2N_3O_8S_2[M-H]^+$: 638.1614; Found: 638.1625.



Monomesna EtBODIPYPNP

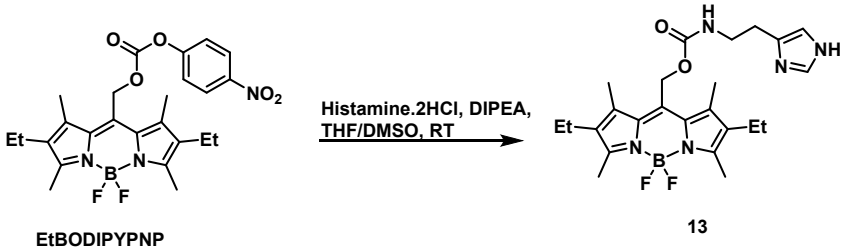
*c) Synthesis of **12**:*



EtBODIPYPNP **12**

To a stirred solution of EtBODIPYPNP (25 mg, 0.05 mmol) in dry THF (3.0 mL) at room temperature under argon atmosphere was added a solution of dopamine·HCl (14 mg, 0.075 mmol) and DIPEA (26 µL, 0.15 mmol) in dry DMSO (1.0 mL). The reaction mixture was stirred at that temperature for 2 h. Upon completion, the reaction was evaporated under reduced pressure. The crude mixture was purified by silica gel chromatography (0 – 10 % methanol in DCM) to yield **12** (15 mg, 58 %) as an orange solid. LC/MS (Method A): Retention time 10.82 min, 536.31 $[M+Na]^+$. Analytical data complies with previously reported analytical data.[3]

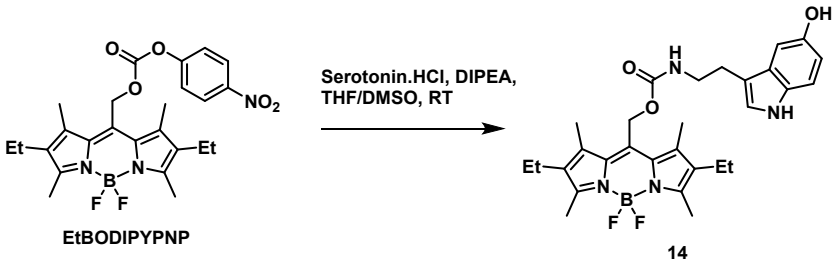
*d) Synthesis of **13**:*



EtBODIPYPNP **13**

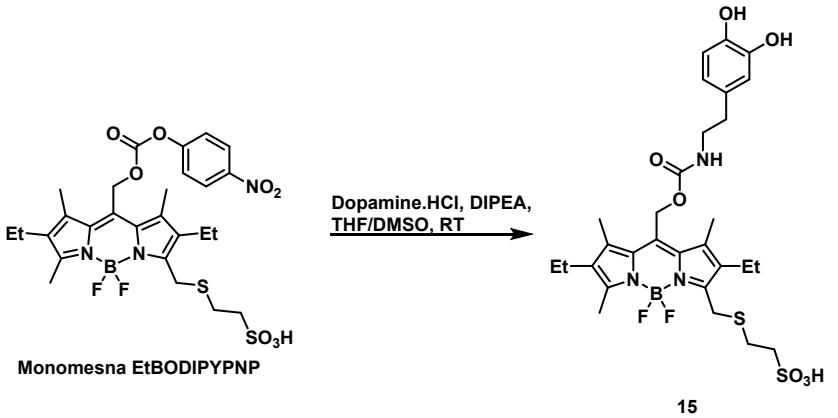
To a stirred solution of EtBODIPYPNP (30 mg, 0.06 mmol) in dry THF (2 mL) at room temperature under argon atmosphere was added a solution of histamine dihydrochloride (16 mg, 0.09 mmol) and DIPEA (52 µL, 0.3 mmol) in DMSO (1 mL). The reaction mixture was stirred for 1.5 h at room temperature and evaporated under reduced pressure. The crude product was purified by silica gel chromatography (0 – 10 % methanol in DCM) to yield **13** (20 mg, 71 %) as an orange solid. 1H NMR (400 MHz, $CDCl_3$+ 1 drop CD_3OD) δ 7.49 (s, 1H), 6.73 (s, 1H), 5.25 (s, 2H), 3.41 (s, 2H), 2.75 (t, J = 6.3 Hz, 2H), 2.45 (s, 6H), 2.34 (dd, J = 14.8, 7.3 Hz, 4H), 2.24 (s, 6H), 1.00 (t, J = 7.5 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$+ 1 drop CD_3OD) δ (ppm): 156.3, 154.9, 136.9, 134.9, 133.6, 132.3, 132.1, 116.5, 58.4, 40.7, 40.6, 27.3, 17.2, 14.7, 12.7, 12.6; LC/MS (Method A): Retention time 9.54 min, 472.19 $[M+H]^+$; HR-MS(ESI) calcd. for formula $C_{24}H_{33}BF_2N_5O_2[M+H]^+$: 472.2695; Found: 472.2694.

*e) Synthesis of **14**:*



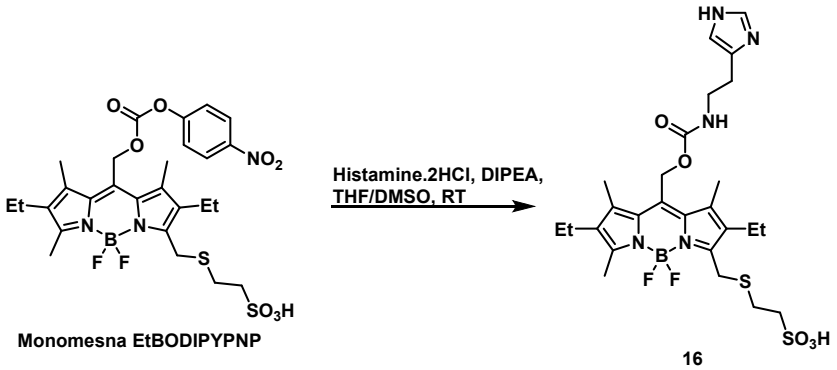
To a stirred solution of EtBODIPYPNP (20 mg, 0.04 mmol) in dry THF (1.0 mL) at room temperature under argon atmosphere was added a solution of serotonin·HCl (17 mg, 0.08 mmol) and DIPEA (21 µL, 0.12 mmol) in dry DMSO (1.5 mL). The reaction mixture was stirred at that temperature for 4 h. Upon completion, the reaction mixture was diluted with EtOAc (8.0 mL) and washed with saturated NH_4Cl solution (6.0 mL) and brine (6.0 mL), dried with $MgSO_4$, filtered and solvents were removed under reduced pressure. The crude product was purified by silica gel chromatography (0 - 1% methanol in DCM) to yield **14** (15 mg, 71 %) as an orange solid.^1H NMR (400 MHz, CD_3OD) δ (ppm): 7.07 (d, *J* = 8.6 Hz, 1H), 6.90 (s, 1H), 6.85 (d, *J* = 2.0 Hz, 1H), 6.58 (dd, *J* = 8.6 and 2.0 Hz, 1H), 5.19 (s, 2H), 3.33 (t, *J* = 7.2 Hz, 2H), 2.79 (t, *J* = 7.2 Hz, 2H), 2.33 (m, 10H), 2.19 (s, 6H), 0.96 (t, *J* = 7.3 Hz, 6H); ^{13}C NMR (100 MHz, CD_3OD) δ (ppm): 155.3, 152.6, 148.1, 135.4, 131.6, 131.3, 130.5, 130.1, 126.5, 121.3, 109.6, 109.3, 100.5, 56.3, 39.7, 23.7, 14.9, 12.1, 9.7; LC/MS (Method A): Retention time 11.74 min, 559.47 $[M+Na]^+$; HR-MS(ESI) calcd. for formula $C_{29}H_{34}BF_2N_4O_3[M-H]^+$: 535.2692; Found: 535.2688.

*f) Synthesis of **15**:*



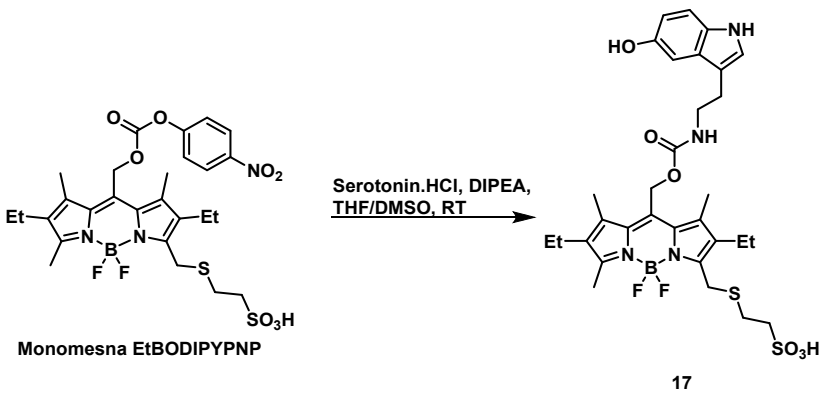
To a stirred solution of MonomesnaEtBODIPYPNP (28 mg, 0.044 mmol) in dry THF. (3.0 mL) at room temperature under argon atmosphere was added a solution of dopamine·HCl (10 mg, 0.053 mmol) and DIPEA (23 µL, 0.13 mmol) in dry DMSO (1.0 mL). The reaction mixture was stirred at that temperature for 2 h. Upon completion, the reaction was evaporated under reduced pressure. The crude mixture was purified by reverse phase prep-HPLC [Method B]. Fractions containing desired compound were immediately frozen and lyophilized to afford **15** (14.0 mg, 48 %) as an orange solid. ^{1}H NMR (400 MHz, MeOD) δ (ppm): 6.74 (dd, *J* = 11.0, 4.8 Hz, 2H), 6.60 (dd, *J* = 8.0, 1.6 Hz, 1H), 5.36 (s, 2H), 4.71 (s, 2H), 4.12 (s, 2H), 3.14 – 3.03 (m, 4H), 2.72 (t, *J* = 7.1 Hz, 2H), 2.64 (dd, *J* = 14.8, 7.4 Hz, 2H), 2.57 – 2.50 (m, 5H), 2.38 (d, *J* = 4.3 Hz, 6H), 1.22 (t, *J* = 7.5 Hz, 3H), 1.14 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (101 MHz, MeOD) δ (ppm): 156.9, 156.7, 150.8, 144.7, 143.2, 138.3, 136.9, 134.3, 133.5, 133.1, 131.5, 130.3, 119.6, 115.4, 114.8, 57.7, 51.6, 42.0, 34.8, 26.8, 26.5, 16.6, 16.3, 13.7, 13.4, 11.4, 11.3, 11.1; LC/MS (Method B): Retention time 9.37 min, 652.29 $[M-H]^{+}$; HR-MS(ESI) calcd. for formula $C_{29}H_{37}BF_2N_3O_7S_2[M-H]^{+}$: 652.2134; Found: 652.2117**.**

*g) Synthesis of **16**:*



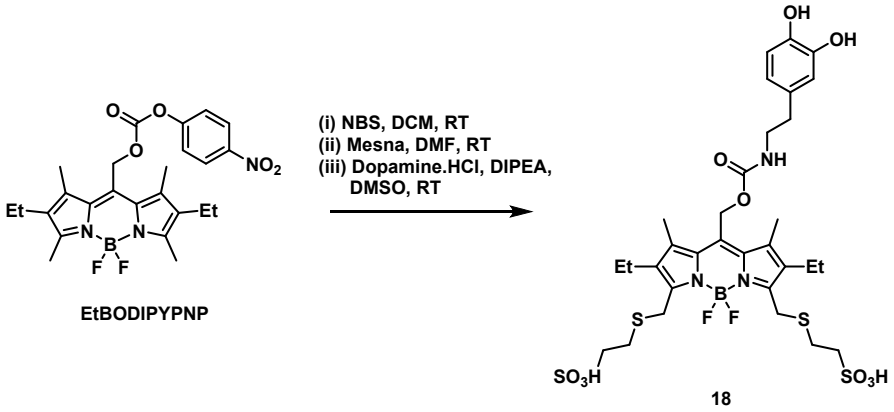
To a stirred solution of MonomesnaEtBODIPYPNP (30 mg, 0.047 mmol) in dry THF. (3.0 mL). at room temperature under argon atmosphere was added a solution of histamine·2HCl (11 mg, 0.056 mmol) and DIPEA (29 µL, 0.16 mmol) in dry DMSO (1.0 mL). The reaction mixture was stirred at that temperature for 2 h and evaporated under reduced pressure. The crude mixture was purified by reverse phase prep-HPLC [Method B]. Fractions containing desired compound were immediately frozen and lyophilized to afford **16** (12.0 mg, 41 %) as an orange solid. ^{1}H NMR (400 MHz, CD_3OD) δ (ppm): 8.75 (s, 1H), 7.34 (s, 1H), 5.40 (s, 2H), 4.13 (s, 2H), 3.53 (t, J = 6.5 Hz, 2H), 3.43 (s, 1H), 3.05 (s, 4H), 2.97 (t, J = 6.4 Hz, 2H), 2.64 (dd, J = 15.0, 7.5 Hz, 2H), 2.59 – 2.48 (m, 5H), 2.41 (s, 3H), 2.38 (s, 3H), 1.22 (t, J = 7.5 Hz, 3H), 1.14 (t, J = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, CD_3OD) δ (ppm) 157.0, 156.5, 151.0, 138.2, 136.8, 134.3, 133.6, 133.4, 133.1, 132.9, 131.5, 131.4, 116.3, 57.7, 51.6, 39.0, 29.2, 26.5, 24.8, 16.6, 16.3, 13.7, 13.4, 11.5, 11.2; LC/MS (Method B): Retention time 8.70 min, 610.28 $[M-H]^{+}$; HR-MS(ESI) calcd. for formula $C_{26}H_{35}BF_2N_5O_5S_2[M-H]^{+}$: 610.2141; Found: 610.2158**.**

*h) Synthesis of **17**:*



To a stirred solution of MonomesnaEtBODIPYPNP (15 mg, 0.02 mmol) in dry THF (1.0 mL) at room temperature under argon atmosphere was added a solution of serotonin·HCl (15 mg, 0.07 mmol) and DIPEA (24 µL, 0.14 mmol) in dry DMSO (1.0 mL). The reaction mixture was stirred at that temperature for 2 h. Upon completion, the reaction was evaporated under reduced pressure. The crude was purified by reverse phase prep-HPLC [Method B]. Fractions containing desired compound were immediately frozen and lyophilized to afford **17** (7.0 mg, 45 %) as an orange solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 10.48 (s, 1H), 8.57 (s, 1H), 7.60 (t, *J* = 5.6 Hz, 1H), 7.11 (d, *J* = 8.6 Hz, 1H), 7.00 (s, 1H), 6.80 (d, *J* = 2.0 Hz, 1H), 6.57 (dd, *J* = 8.6 and 2.0 Hz, 1H), 5.22 (s, 2H), 3.96 (s, 2H), 3.26 (q, *J* = 6.5 Hz, 2H), 2.70-2.77 (m, 4H), 2.56-2.60 (m, 2H), 2.44 (s, 3H), 2.37 (q, *J* = 7.9 Hz, 4H), 2.28 (s, 3H), 2.26 (s, 3H), 1.06 (t, *J* = 7.4 Hz, 3H), 0.99 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 156.8, 156.1, 151.7, 150.6, 138.8, 137.6, 134.6, 134.5, 133.1, 132.8, 131.5, 131.2, 128.3, 123.6, 112.1, 111.6, 110.8, 102.5, 57.8, 51.9, 41.5, 28.2, 27.1, 25.8, 17.1, 16.9, 15.2, 15.0, 13.1, 12.8, 12.5; LC/MS (Method B): Retention time 9.74 min, 675.29 $[M-H]^+$; HR-MS(ESI) calcd. for formula $C_{31}H_{38}BF_2N_4O_6S_2[M-H]^+$: 675.2294; Found: 675.2277**.**

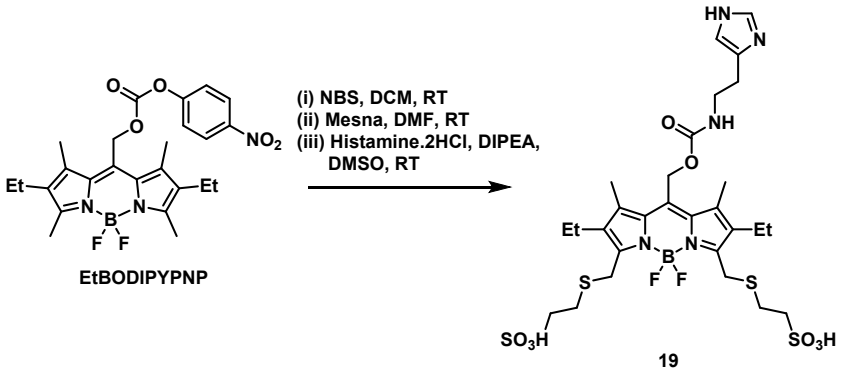
*i) Synthesis of **18**:*



To a stirred solution of EtBODIPYPNP (20 mg, 0.04 mmol) in dry DCM. (3.0 mL) at room temperature under argon atmosphere was added *N*-bromosuccinimide (16 mg, 0.088 mmol). After 2 h, solution of MESNA (15 mg, 0.088 mmol) in dry DMF (1.0 mL) was added to the reaction mixture. Resulting reaction mixture was stirred at RT under argon atmosphere for 12 h. Then a solution of dopamine·HCl (9 mg, 0.048 mmol) and DIPEA (11 µL, 0.064 mmol) in dry DMSO (1.0 mL) was added to the reaction mixture. The reaction mixture was stirred at room temperature for 2 h. The crude was purified by reverse phase prep-HPLC [Method B]. Fractions containing desired compound were

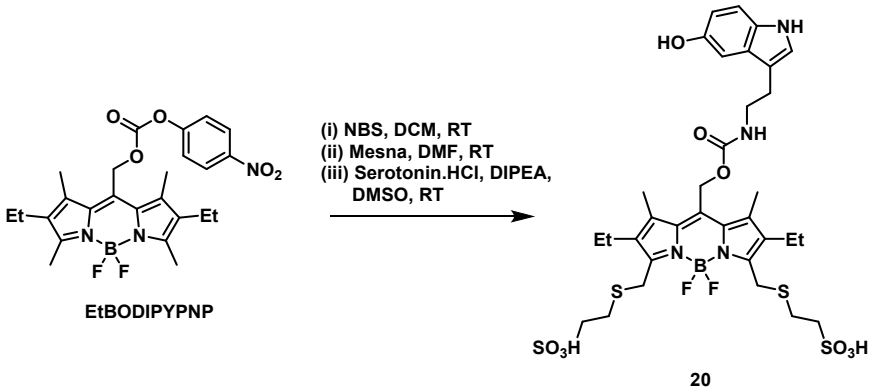
immediately frozen and lyophilized to afford **18** (17.0 mg, 54 %) as an orange solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 8.80 (s, 1H), 8.71 (s, 1H), 7.64 (d, J = 5.2 Hz, 1H), 6.74 – 6.56 (m, 1H), 6.48 (d, J = 8.0 Hz, 1H), 5.34 (m, 2H), 4.06 (s, 4H), 3.21 (d, J = 6.3 Hz, 2H), 2.96 – 2.79 (m, 6H), 2.77 – 2.62 (m, 4H), 2.55 (d, J = 10.7 Hz, 4H), 2.44 – 2.21 (m, 6H), 1.15 (t, J = 7.4 Hz, 6H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 13C NMR (101 MHz, DMSO) δ 153.9, 145.3, 143.8, 138.9, 134.1, 132.3, 130.3, 119.6, 116.3, 115.7, 55.6, 51.8, 28.6, 28.3, 27.1, 20.2, 17.0, 15.0, 12.6; LC/MS (Method B): Retention time 7.91 min, 792.31 $[M-H]^+$; HR-MS(ESI) calcd. for formula $C_{31}H_{41}BF_2N_3O_{10}S_4[M-H]^+$: 792.1736; Found: 792.1747.

*j) Synthesis of **19**:*



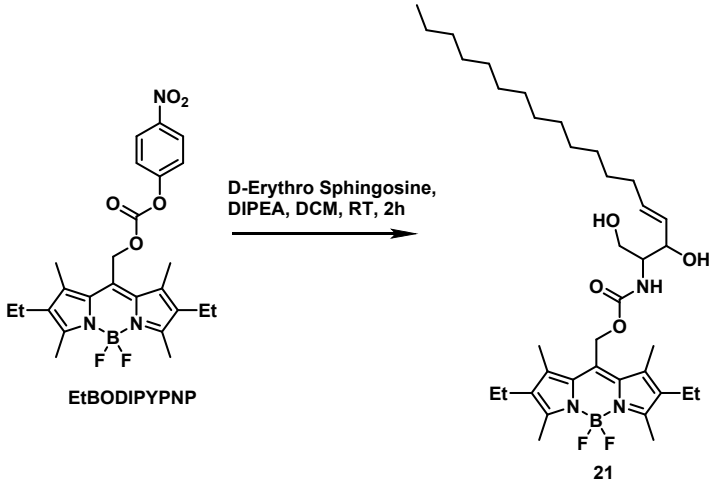
To a stirred solution of EtBODIPYPNP (20 mg, 0.04 mmol) in dry DCM (2.0 mL) at room temperature under argon atmosphere was added *N*-bromosuccinimide (16 mg, 0.088 mmol). After 2 h, solution of MESNA (15 mg, 0.088 mmol) in dry DMF (1.0 mL) was added to the reaction mixture. Resulting reaction mixture was stirred at RT under argon atmosphere for 12 h. Then a solution of histamine·2HCl (10 mg, 0.052 mmol) and DIPEA (23 µL, 0.13 mmol) in dry DMSO (1.0 mL) was added to the reaction mixture. The reaction mixture was stirred at room temperature for 2 h. The crude was purified by reverse phase prep-HPLC [Method B]. Fractions containing desired compound were immediately frozen and lyophilized to afford **19** (11.0 mg, 37 %) as an orange solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 9.05 (s, 1H), 7.74 (t, *J* = 5.7 Hz 1H), 7.48 (s, 1H), 5.23 (s, 2H), 4.06 (s, 4H), 2.81-2.89 (m, 8H), 2.64-2.69 (m, 6H), 2.4 (t, *J* = 6.1 Hz 2H), 2.32 (s, 6H), 1.15 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 155.9, 154.0, 138.8, 135.1, 134.2, 132.2, 131.0, 117.3, 116.80, 51.70, 34.1, 29.0, 28.1, 27.0, 25.0, 17.0, 15.0, 12.6; LC/MS (Method B): Retention time 7.10 min, 750.46 $[M-H]^+$; HR-MS(ESI) calcd. for formula $C_{28}H_{39}BF_2N_5O_8S_4[M-H]^+$: 750.1743; Found: 750.1761.

*k) Synthesis of **20**:*



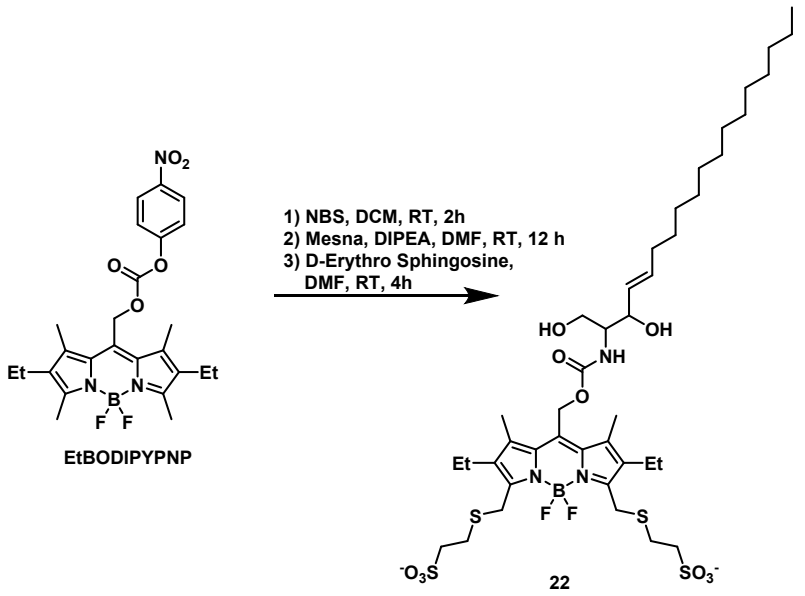
To a stirred solution of EtBODIPYPNP (25 mg, 0.05 mmol) in dry DCM (2.0 mL) at room temperature under argon atmosphere was added *N*-bromosuccinimide (20 mg, 0.11 mmol). After 2 h, solution of MESNA (17 mg, 0.11 mmol) in dry DMF (1.0 mL) was added to the reaction mixture. Resulting reaction mixture was stirred at RT under argon atmosphere for 12 h. Then a solution of serotonin·HCl (12 mg, 0.055 mmol) and DIPEA (16 µL, 0.10 mmol) in dry DMSO (1.0 mL) was added to the reaction mixture. The reaction mixture was stirred at room temperature for 2 h. The crude was purified by Reverse phase Prep-HPLC [Method B]. Fractions containing desired compound were immediately frozen and lyophilized to afford **20** (21.0 mg, 51 %) as an orange solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 10.49 (s, 1H), 8.59 (s, 1H), 7.66 (t, *J* = 5.6 Hz, 1H), 7.16 (s, 1H), 7.02 (s, 1H), 6.82 (s, 1H), 6.59 (dd, *J* = 8.6 and 2.0 Hz, 1H), 5.25 (s, 2H), 4.00 (s, 4H), 3.24 (q, *J* = 6.7 Hz, 2H), 2.77-2.81 (m, 5H), 2.69-2.75 (m, 4H), 2.60-2.64 (m, 5H), 2.29 (s, 6H), 1.08 (t, *J* = 7.4 Hz, 6H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 156.0, 154.0, 150.6, 139.0, 135.5, 134.2, 131.2, 128.3, 123.6, 112.0, 111.6, 110.8, 102.5, 57.8, 51.9, 41.5, 28.4, 27.2, 25.8, 17.1, 15.1, 12.7; LC/MS (Method B): Retention time 8.14 min, 815.22 $[M-H]^+$; HR-MS(ESI) calcd. for formula $C_{33}H_{42}BF_2N_4O_9S_4[M-H]^+$: 815.1896; Found: 815.1844**.**

*l) Synthesis of **21**:*



To a stirred solution of EtBODIPYPNP (9 mg, 0.017 mmol) in dry THF (3.0 mL) at room temperature under argon atmosphere was added a solution of D-erythro-sphingosine (5 mg, 0.017 mmol) and DIPEA (3 µL, 0.17 mmol) in dry THF (0.5 mL). The reaction mixture was stirred at that temperature for 2 h. Upon completion, the reaction was evaporated under reduced pressure. The crude mixture was purified by silica gel column chromatography (Eluent: 0 – 30 % EtOAc in DCM gradient) to furnish **21** as a dark orange solid (9 mg, 76 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.87 – 5.71 (m, 1H), 5.66 – 5.47 (m, 2H), 5.35 (s, 2H), 4.35 (s, 1H), 3.99 (d, *J* = 11.3 Hz, 1H), 3.81 – 3.63 (m, 2H), 2.51 (s, 6H), 2.39 (q, *J* = 7.6 Hz, 4H), 2.31 (s, 6H), 2.26 (d, *J* = 4.8 Hz, 1H), 2.12 – 1.98 (m, 2H), 1.27 (d, *J* = 16.8 Hz, 21H), 1.05 (t, *J* = 7.6 Hz, 6H), 0.88 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): δ 155.96, 154.8, 136.5, 134.5, 133.4, 132.1, 131.6, 128.5, 74.6, 62.2, 58.4, 55.5, 32.1, 31.8, 29.6, 29.4, 29.2, 29.1, 28.9, 22.6, 17.0, 14.6, 14.0, 12.5. LC/MS (Method A): Retention time 14.98 min, 682.52 $[M+Na]^+$, HR-MS(ESI) calcd. for formula $C_{37}H_{59}BF_2N_3O_4[M-H]^+$: 658.4561; Found: 658.4561**.**

*m) Synthesis of **22**:*



To a stirred solution of EtBODIPYPNP (20 mg, 0.04 mmol) in dry DCM (2.0 mL) at room temperature under argon atmosphere was added *N*-bromosuccinimide (16 mg, 0.088 mmol). After 2 h, solution of MESNA (15 mg, 0.088 mmol) and DIPEA (15 µL, 0.088 mmol) in dry DMF (1.0 mL) was added to the reaction mixture. Resulting reaction mixture was stirred at RT under argon atmosphere for 12 h. Then a solution of D-erythro-sphingosine (12 mg, 0.04 mmol)) in dry DMF (1.0 mL) was added to the reaction mixture. The reaction mixture was stirred at room temperature for 4 h. The crude was purified by reverse phase prep-HPLC [Method B]. Fractions containing desired compound were immediately frozen and lyophilized to afford **22** (1.5 mg, 4 %) as an orange solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 5.60-5.67 (m, 1H), 5.43 (dd, J = 6.6 and 15.4 Hz 1H), 4.76 (s, 2H), 4.0-4.03 (m, 5H), 3.51-3.55 (m, 5H), 3.35-3.40 (m, 9H), 2.79-2.88 (m, 5H), 2.63-2.67 (m, 5H), 2.46-2.52 (m, 5H), 2.44 (s, 6H), 1.99 (q, J = 6.8 Hz, 1H), 1.12-1.34 (m, 11H), 1.10 (t, J = 7.4 Hz, 6H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 152.8, 141.2, 139.2, 133.4, 132.8, 132.2, 129.5, 70.4, 59.9, 57.3, 54.8, 51.9, 32.0, 31.6, 29.4, 29.3, 29.0, 28.9, 28.4, 27.1, 22.4, 17.0, 15.0, 14.3, 12.6; LC/MS (Method B): Retention time 10.14 min, 938.56 $[M-H]^+$; HR-MS(ESI) calcd. for formula $C_{41}H_{67}BF_2N_3O_{10}S_4$ $[M-H]^+$: 938.3770; Found: 938.3721.

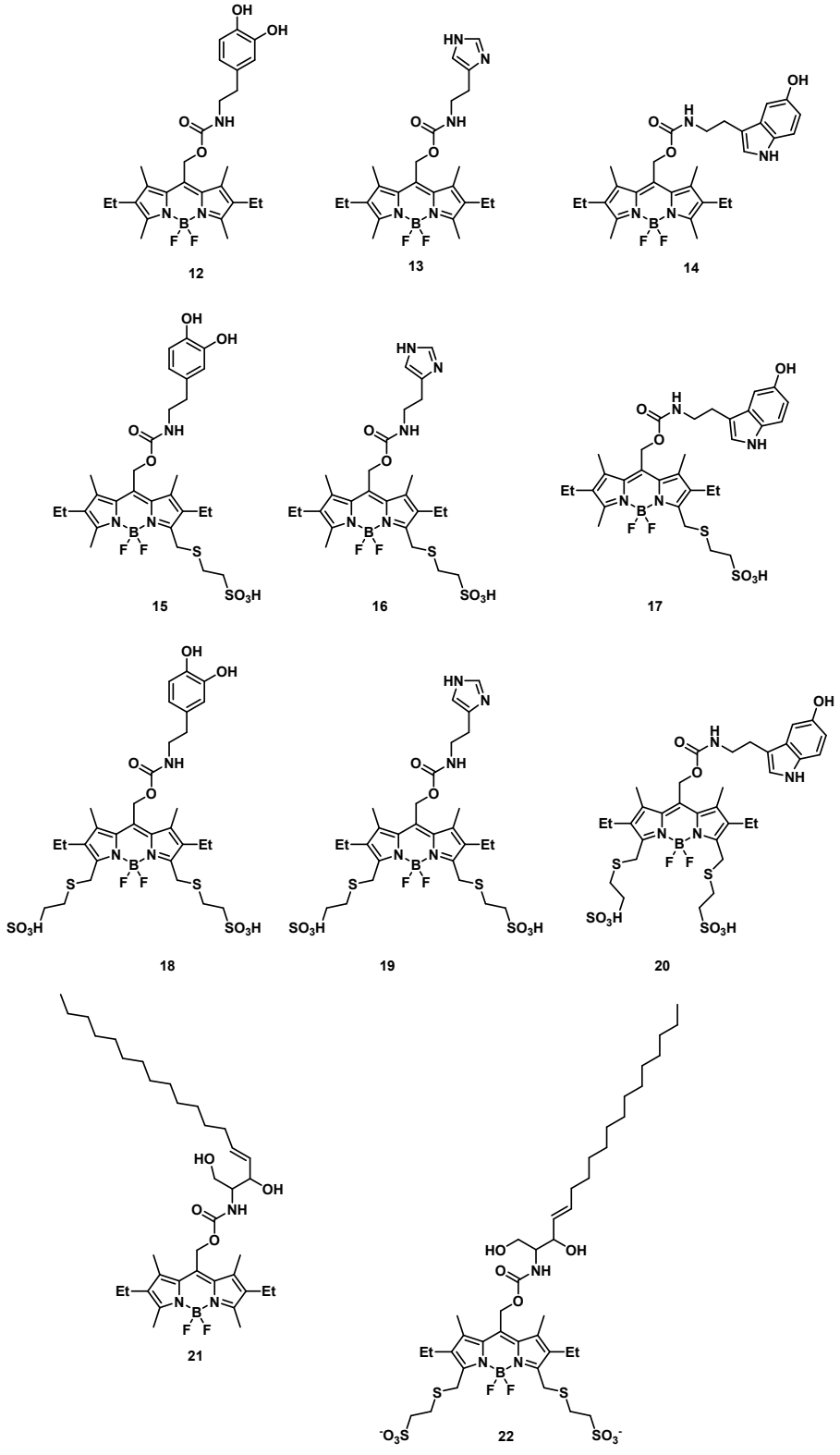


Figure S13:

Structures of BODIPY-photocaged bio-active molecules **12-22**.

4. Photophysical and spectroscopic data

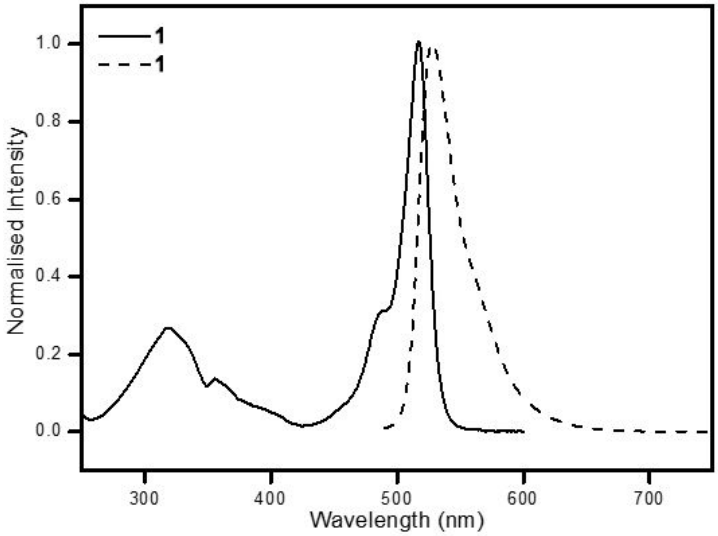


Figure S14:

Absorption (solid line) and normalized emission spectrum of BODIPY **1** (dashed line; excitation wavelength: 480 nm) in (7/3) CH_3CN/water. ($c \sim 1 \times 10^{-5}$ M).

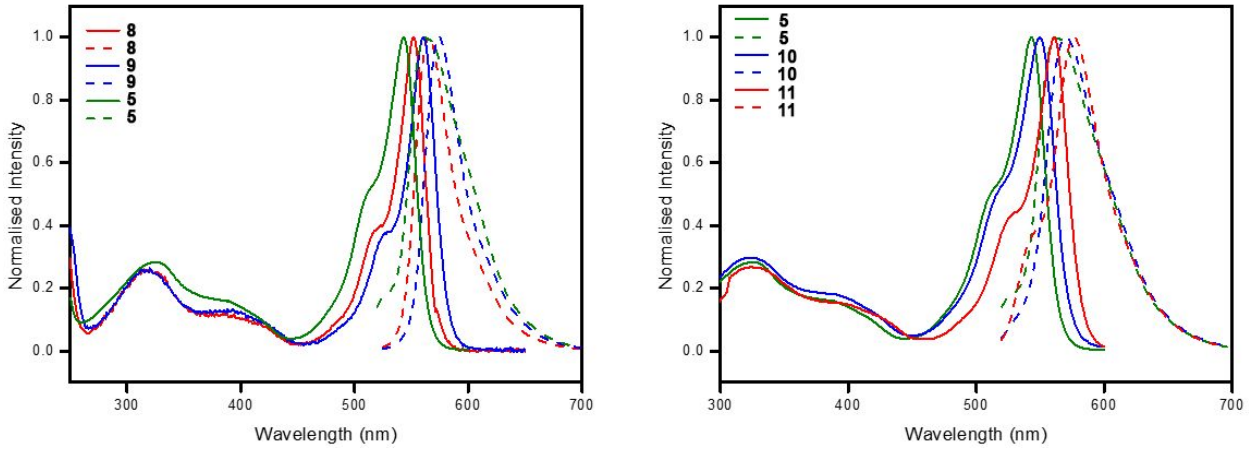


Figure S15:

Absorption (solid line) and normalized emission spectrum of BODIPYs **5** and **8-11** (dashed line; excitation wavelength: 480 nm) in (7/3) CH_3CN/water. ($c \sim 1 \times 10^{-5}$ M).

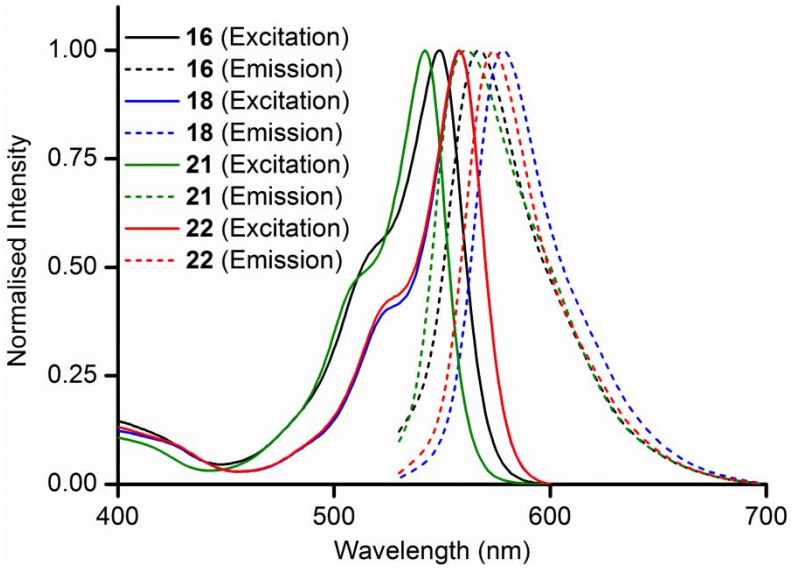


Figure S16:

Absorption (solid line) and normalized emission spectrum of BODIPYs **16**, **18**, **21** and **22** (dashed line; excitation wavelength: 480 nm) in (7/3) CH_3CN/water. ($c \sim 1 \times 10^{-5}$ M).

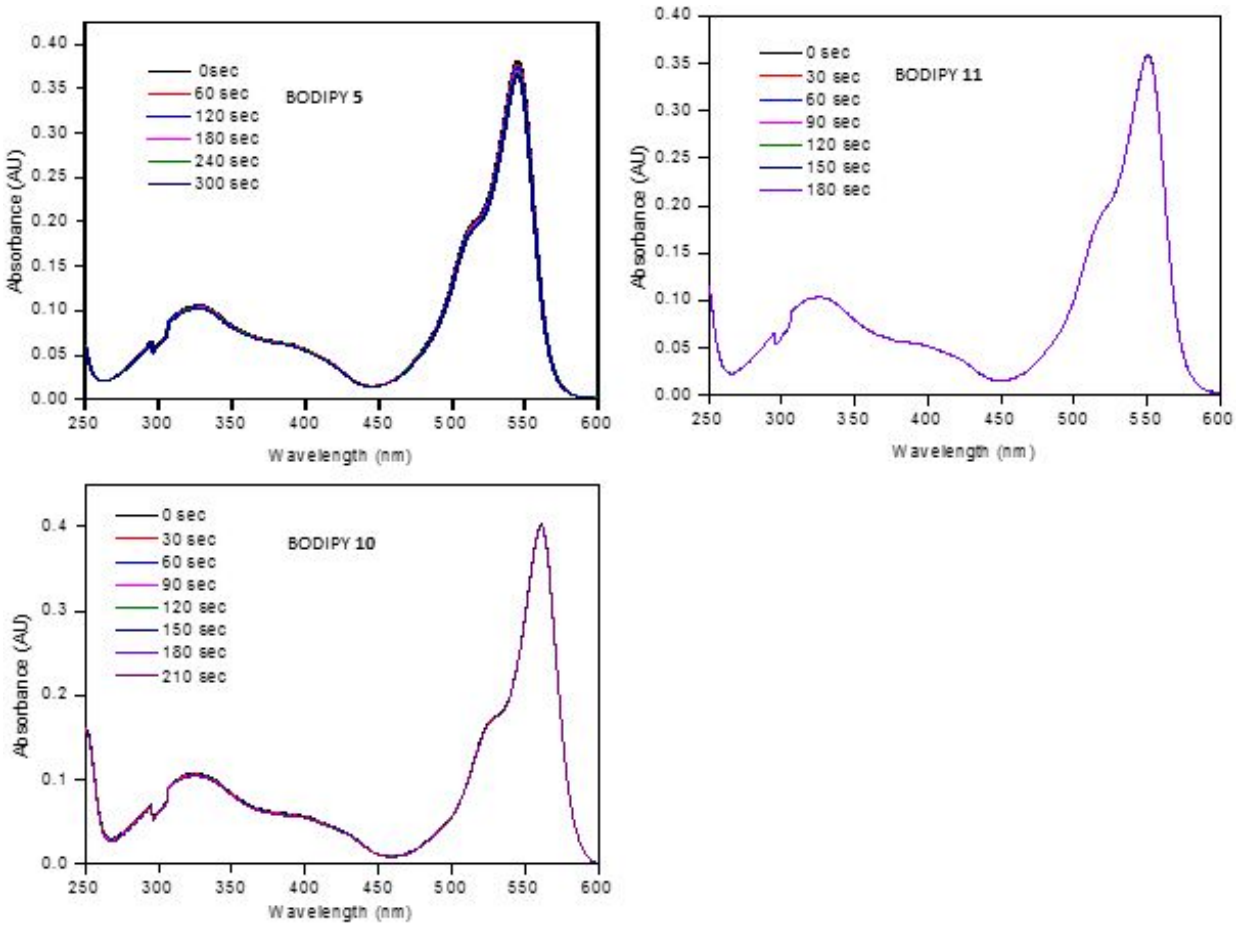


Figure S17:

UV-Vis spectra for stability in dark of BODIPYs **5**, **10** and **11**. 10 μM of each compound was separately kept in dark in CH_3CN/water (7/3) for the indicated times and spectra were acquired.

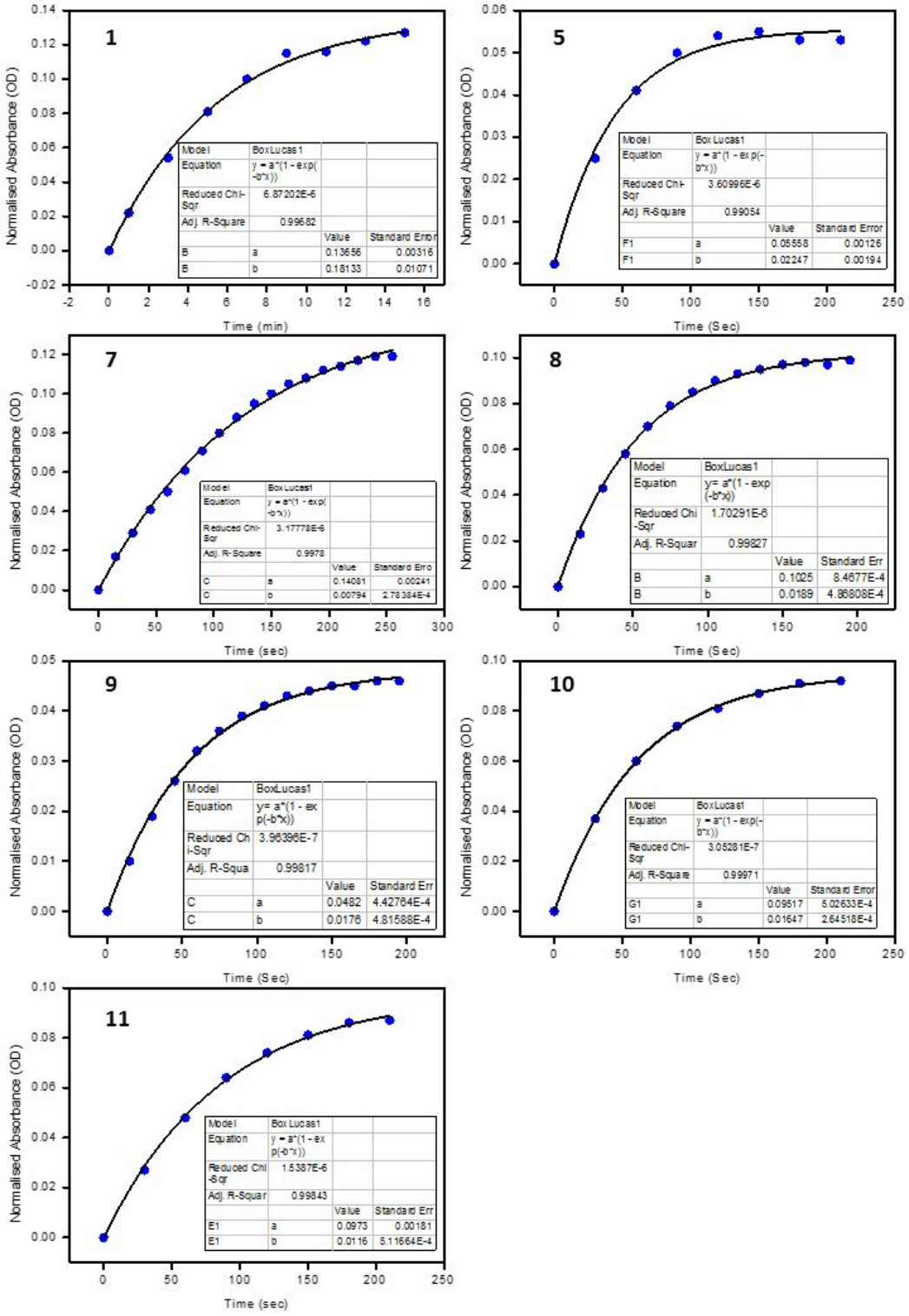


Figure S18:

Kinetics graphs for rate constant, (*k*) of BODIPYs **1**, **5**, and **7-11**. 10 μM of each compound was separately irradiated with 545/30 nm (49 mW/cm^2) (except **1**: 520/30 nm; 49 mW/cm^2) light in CH_3CN/water (7/3) for the indicated times. Normalised absorbance ($A-A_0$) at 380 nm *Vs* time were plotted.

5. Computation methods and data

All calculations were performed using the Gaussian 09 software package[4] utilizing the B3LYP functional[5-7] and 6-31+G(d,p) polarized double-ζ basis set. In all cases, optimized geometries were found to have zero imaginary frequencies and corrections for the zero-point vibrational energy and thermal energy were added unscaled. When multiple rotamers were possible, the lowest energy rotamer was used. When not denoted, calculations were performed in the gas-phase at the default temperature (298.15 K). Where noted, the SMD solvent model[8] was used with water as the solvent.

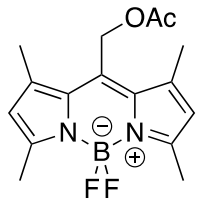
For computing the energy of singlet state structures, an unrestricted broken-symmetry approach to computing the singlet states was used for B3LYP calculations. Unfortunately, this approach using DFT very frequently suffers from considerable spin contamination when there is also a low-energy triplet state, which is indicated by $\langle S^2 \rangle$ values greater than zero. In these cases, the following equation was used to titrate out contamination from a low-energy-triplet state and determine a spin-purified energy of the singlet state.[9-12]

$$E_{singlet} = \frac{2\,E_{\langle S_Z \rangle = 0} - \langle S^2 \rangle\, E_{\langle S_Z \rangle = 1}}{2 - \langle S^2 \rangle}$$

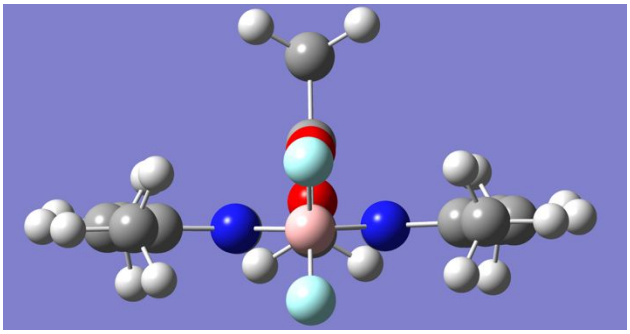
where $E_{singlet}$ is the corrected singlet energy, $E_{\langle S_Z \rangle = 0}$ is the broken-symmetry energy, $\langle S^2 \rangle$ is the expectation value of the total-spin operator for the broken-symmetry calculation (anywhere from about zero to one), and $E_{\langle S_Z \rangle = 1}$ is the energy of the triplet state at the singlet geometry.

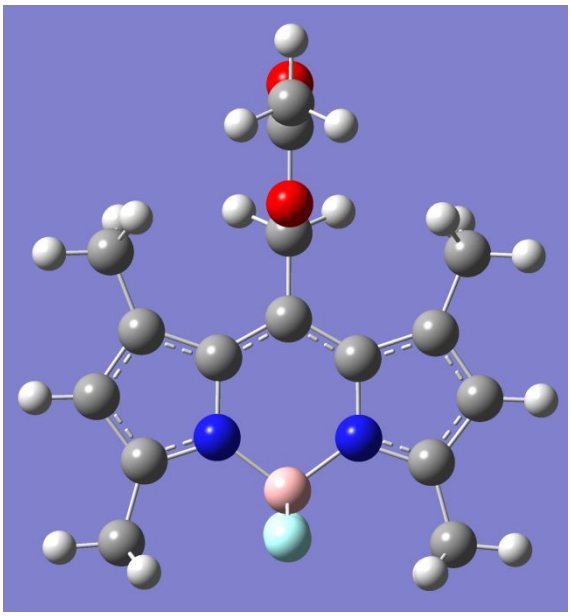
Calculation of the C-O bond breaking energy was accomplished by performing a relaxed potential energy scan on the triplet state by increasing the C-O bond length by 0.1 Å. The bond breaking energy was then computed by calculating the difference between the SCF Energy of the structure with the intact C-O bond (reactant) and the highest energy structure in the scan (transition). The B3LYP functional, 6-31+G(d,p) polarized double-ζ basis set, and SMD solvent model with water as the solvent were utilized for these calculations.

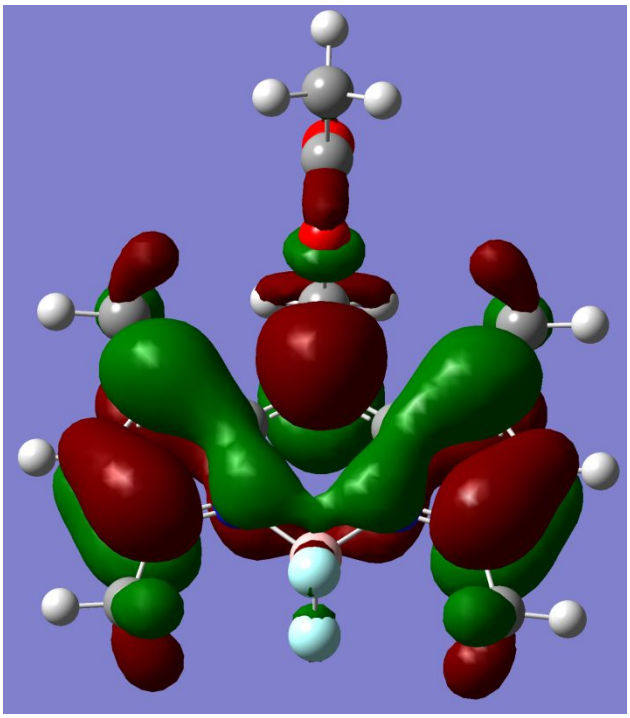
The σ_p Hammett parameters were used directly from the work of H. Hansch, A. Leo and D. Hoekman.[13]



1

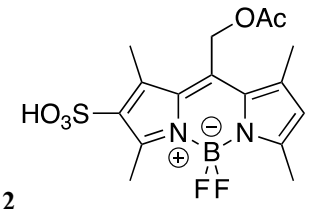




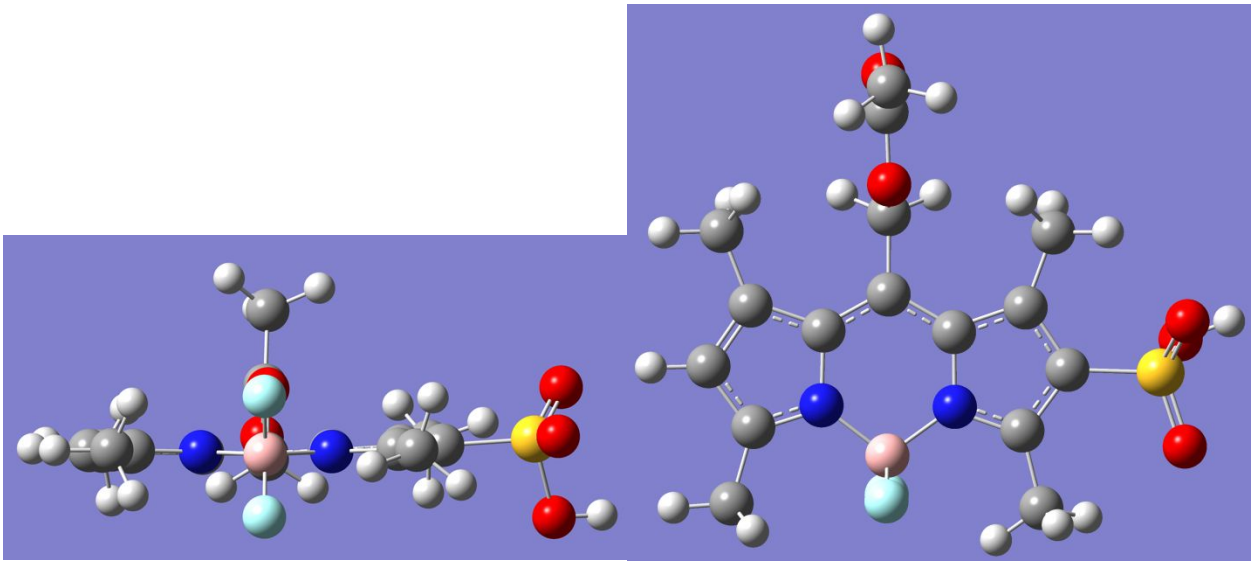


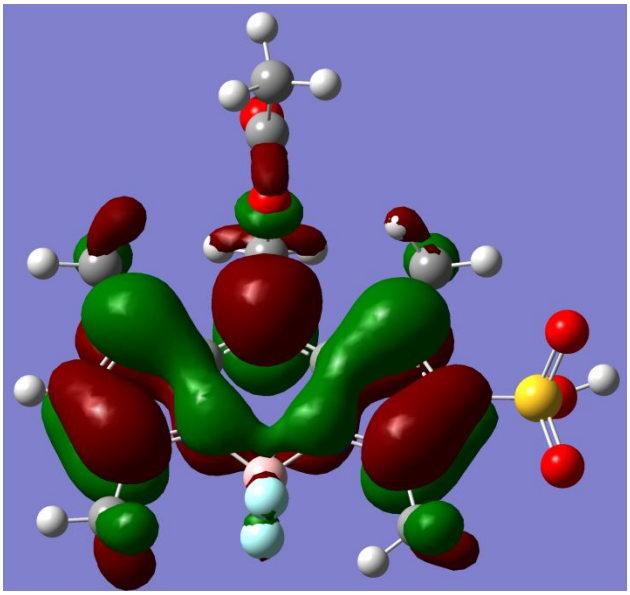
Computation S1:

Side view and top view of singlet state, gas-phase optimized structure **1**, as well as the LUMO for **1**.



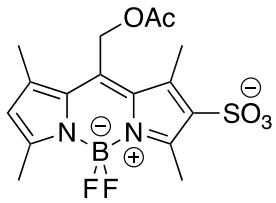
2



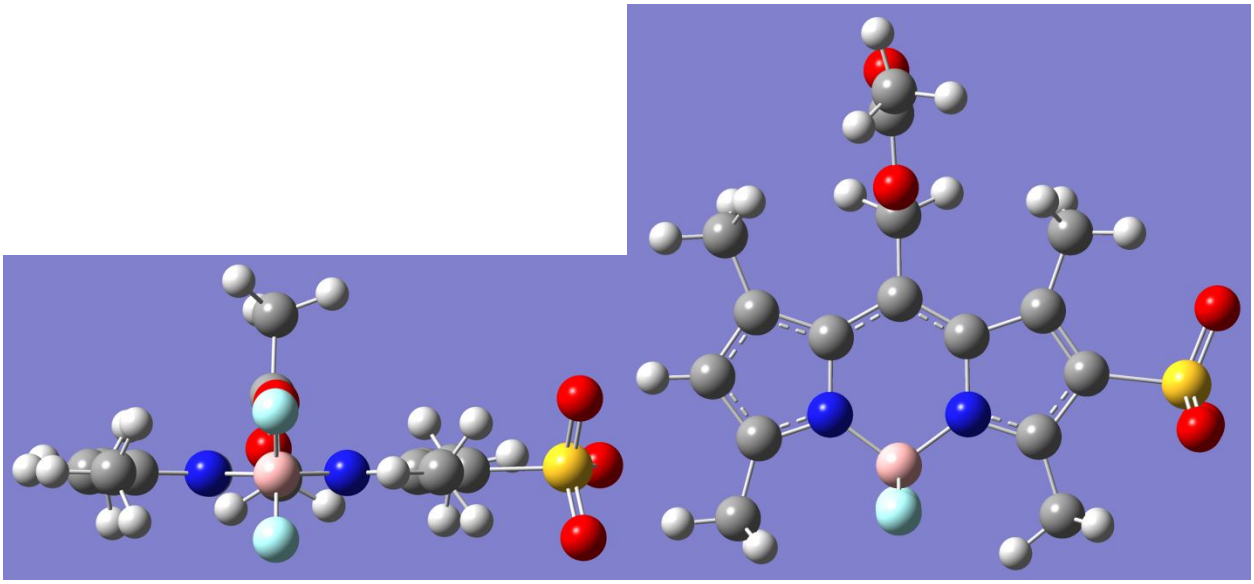


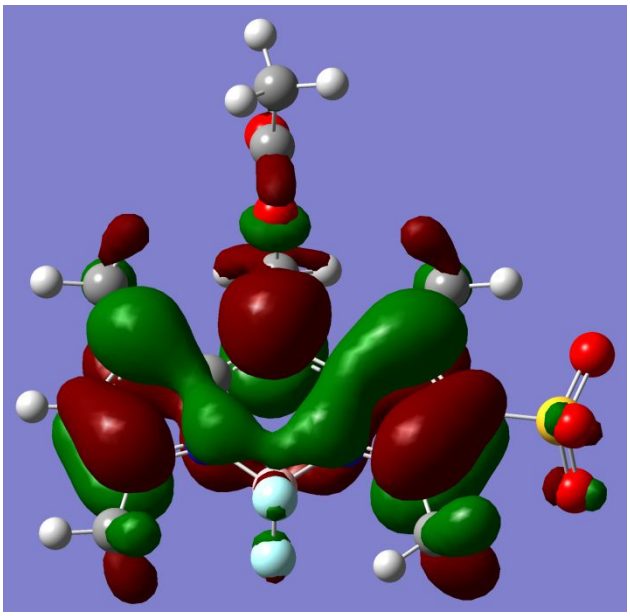
Computation S2:

Side view and top view of singlet state, gas-phase optimized structure **2**, as well as the LUMO for **2**



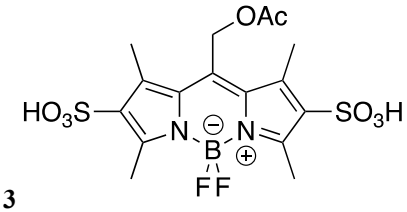
2 anion



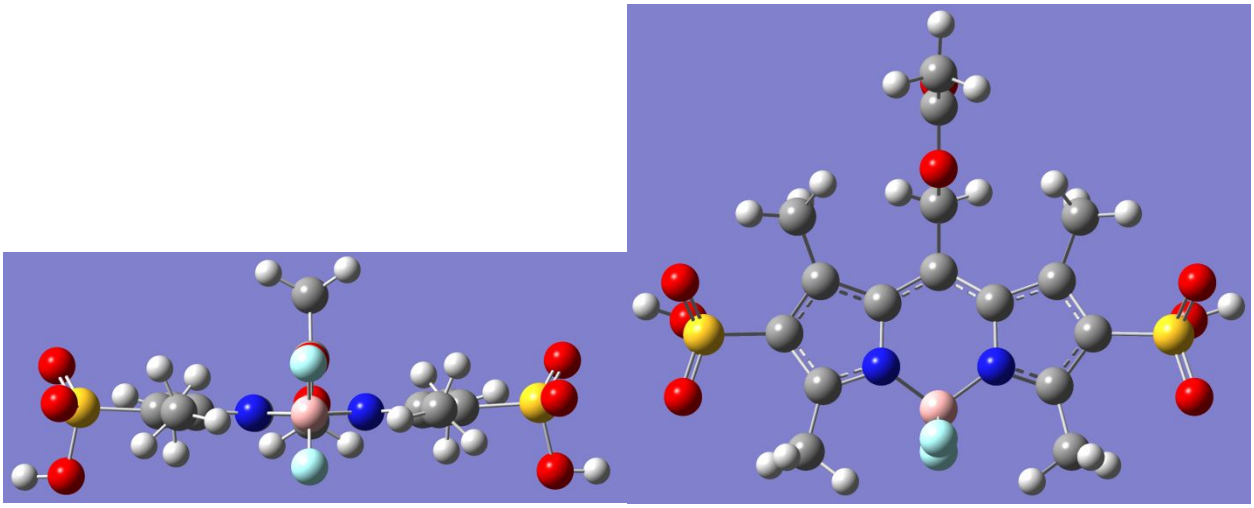


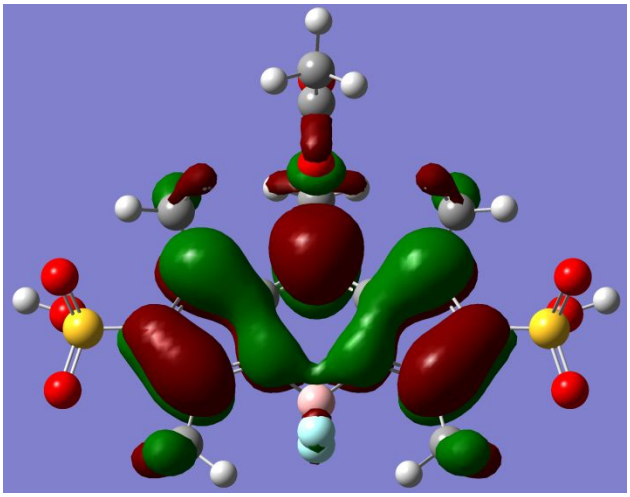
Computation S3:

Side view and top view of singlet state, gas-phase optimized structure **2** in its anion form, as well as the LUMO for **2** in its anion form.



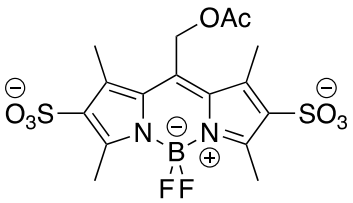
3



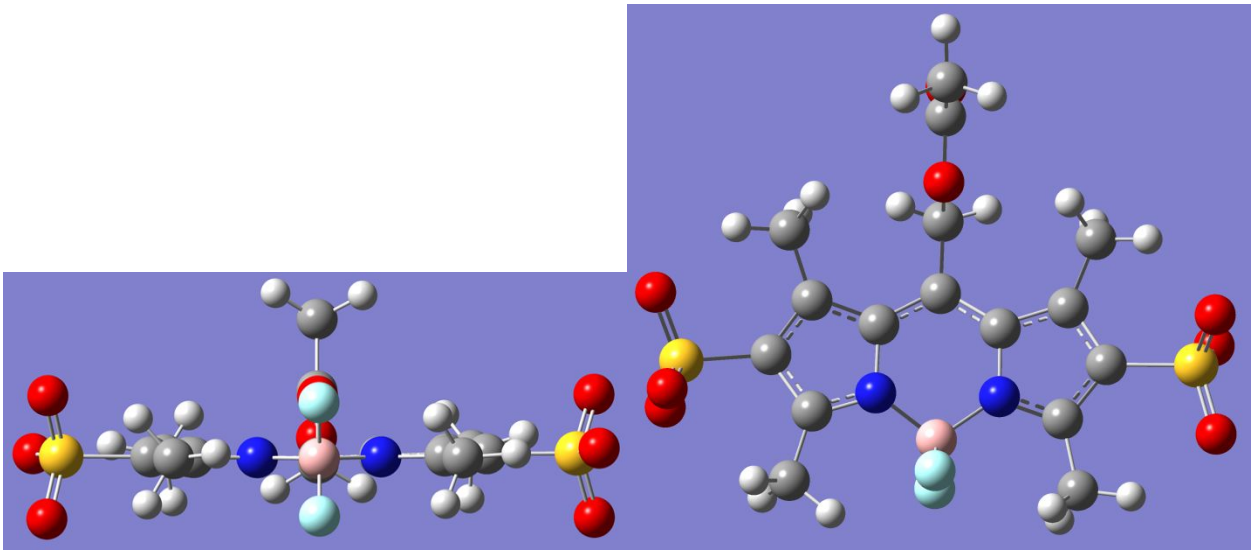


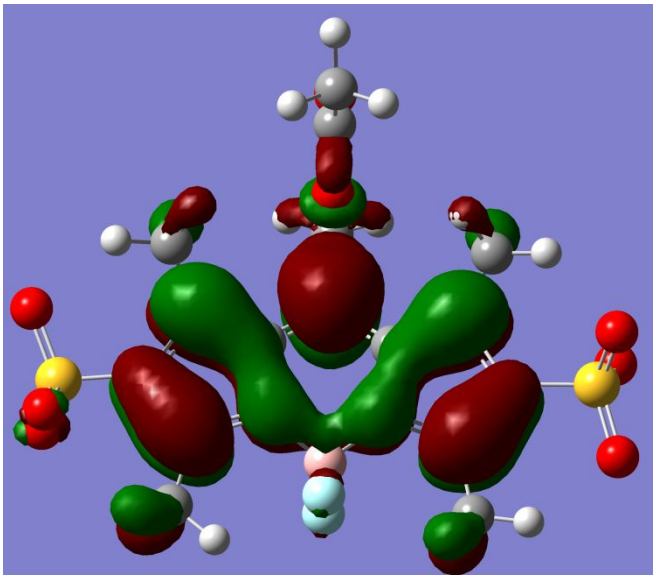
Computation S4:

Side view and top view of singlet state, gas-phase optimized structure **3**, as well as the LUMO for **3**.



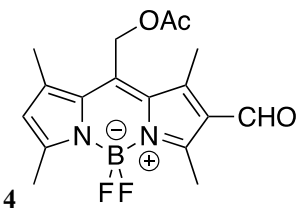
3 anion



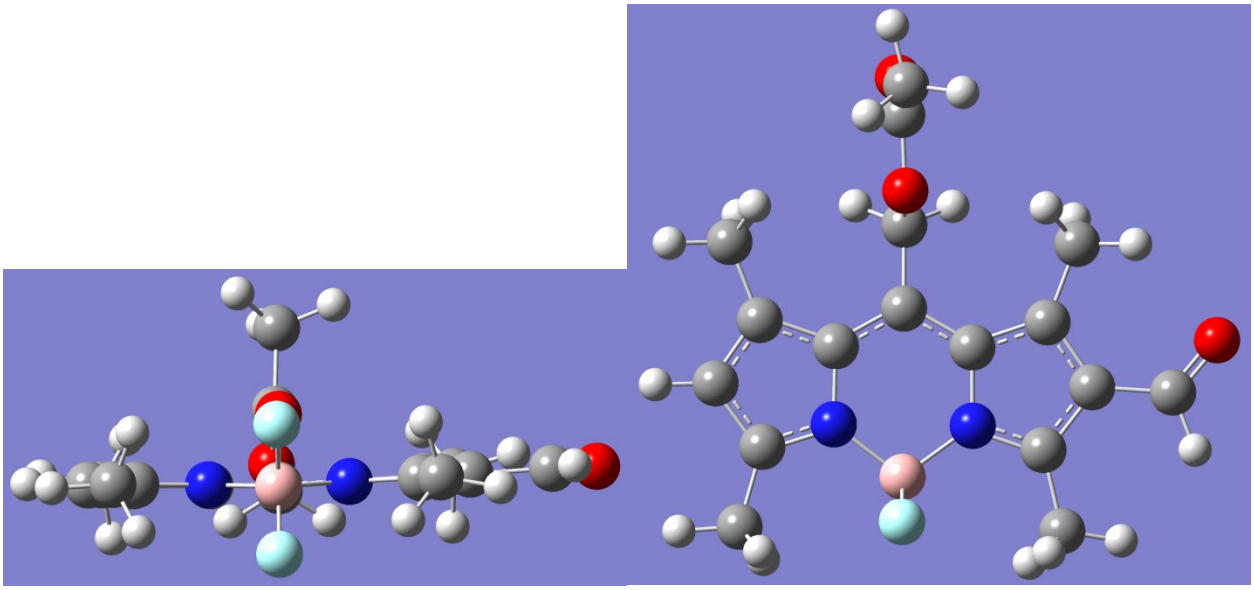


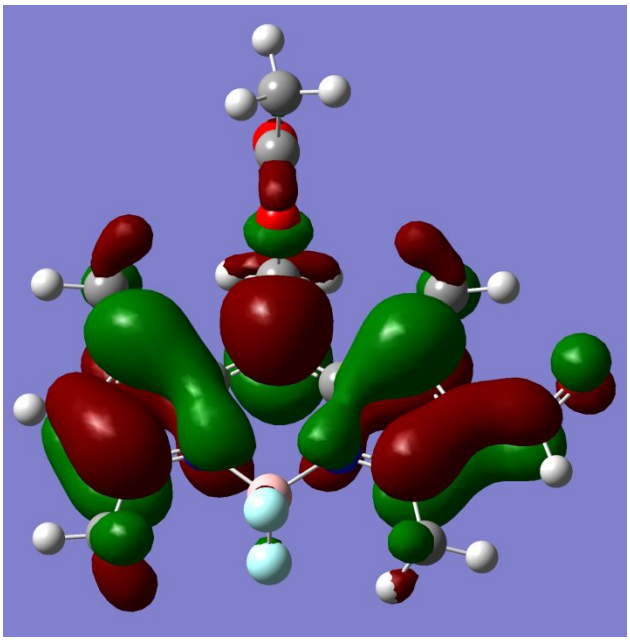
Computation S5:

Side view and top view of singlet state, gas-phase optimized structure **3** in its anion form, as well as the LUMO for **3** in its anion form.



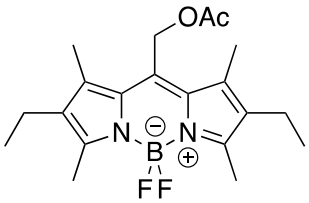
4



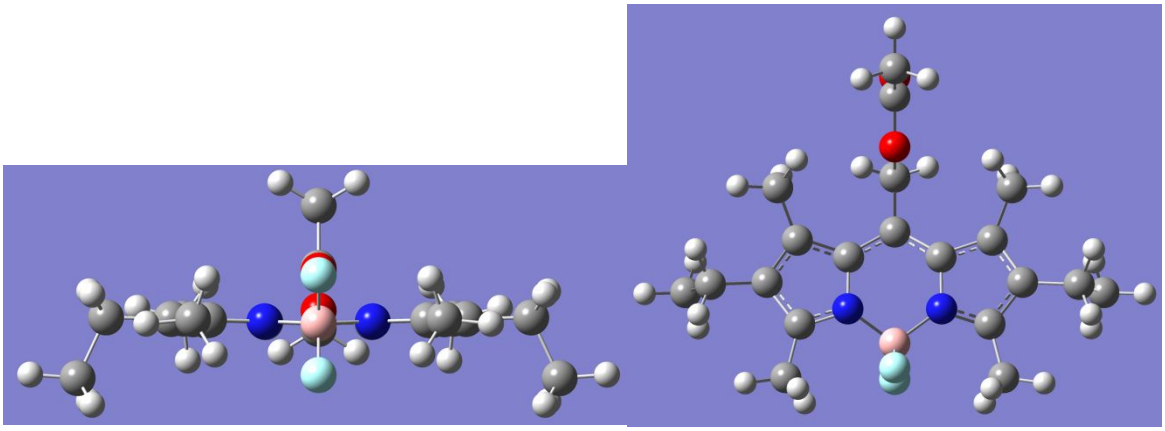


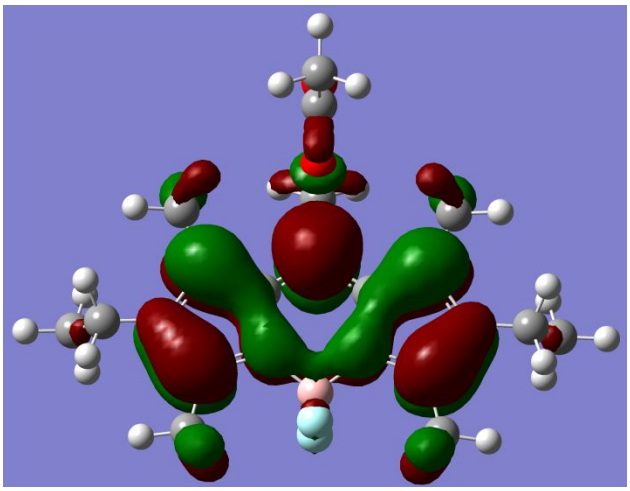
Computation S6:

Side view and top view of singlet state, gas-phase optimized structure **4**, as well as the LUMO for **4**.



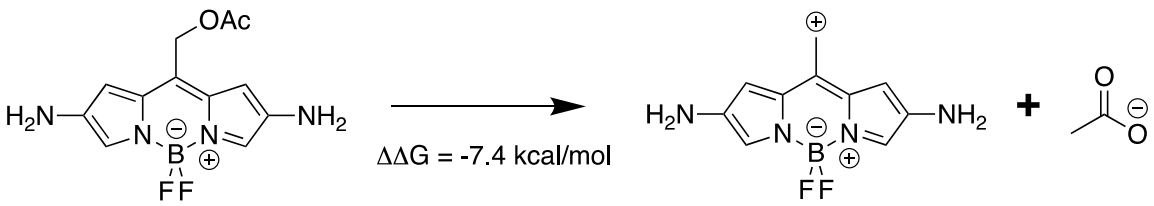
5





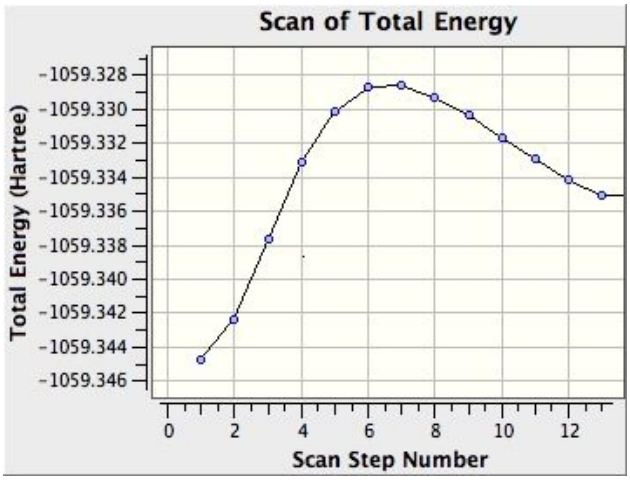
Computation S7:

Side view and top view of singlet state, gas-phase optimized structure **5**, as well as the LUMO for **5**.



Computation S8a:

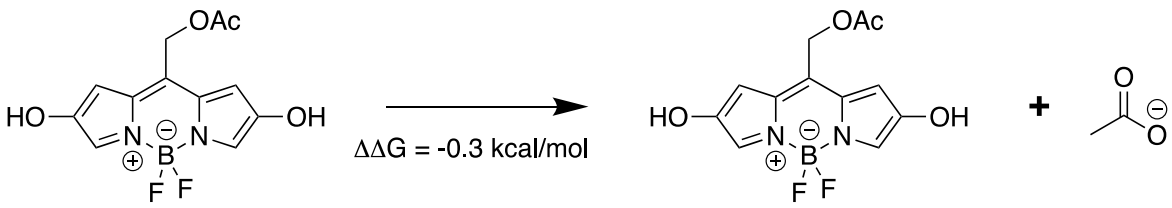
Reaction modeled using B3LYP/6-31+G(d,p) and SMD = water. ΔΔG determined from the optimized energies of the BODIPY structure triplet states and the optimized energy of the acetate structure singlet state.



$\Delta E^{\pm}$ (From Scan): 10.1 $^{kcal}/_{mol}$

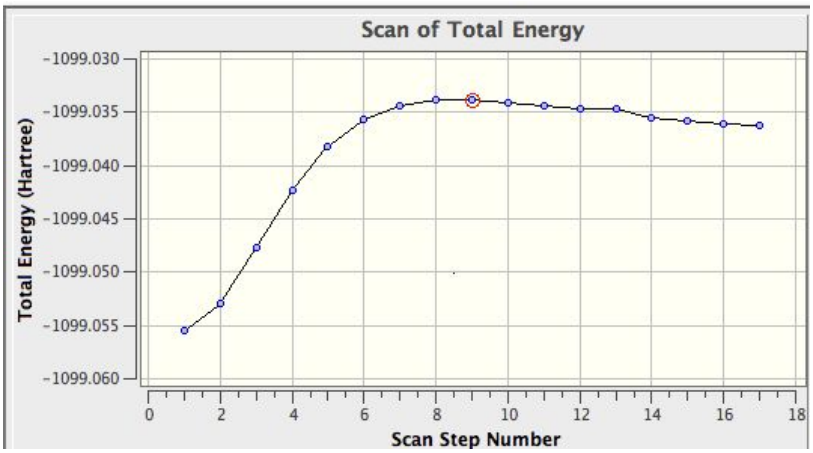
Computation S8b:

Graph generated by the relaxed potential energy scan of the C-O bond breaking on the triplet state modeled using B3LYP/6-31+G(d,p) and SMD = water for the reaction in **Computation S8a**.



Computation S9a:

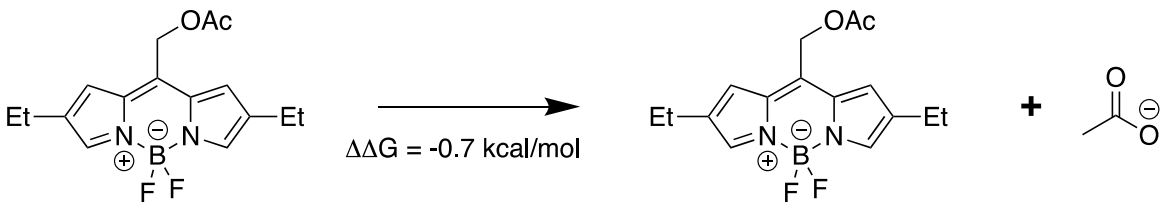
Reaction modeled using B3LYP/6-31+G(d,p) and SMD = water. ΔΔG determined from the optimized energies of the BODIPY structure triplet states and the optimized energy of the acetate structure singlet state.



$\Delta E^{\pm}$ (From Scan): 13.6 $^{kcal}/_{mol}$

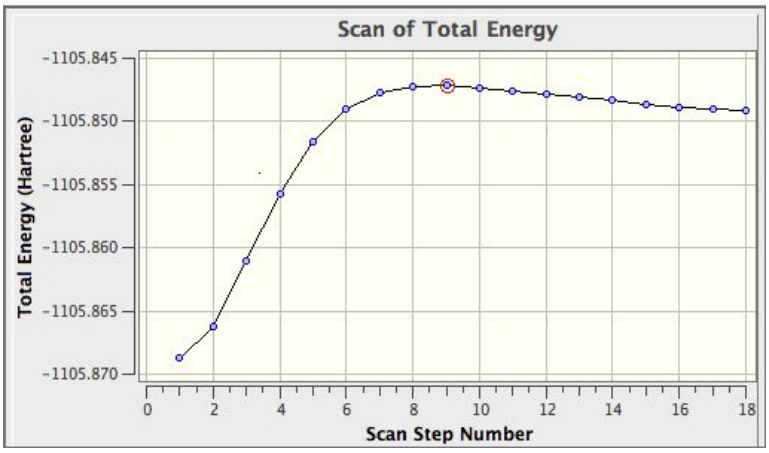
Computation S9b:

Graph generated by the relaxed potential energy scan of the C-O bond breaking on the triplet state modeled using B3LYP/6-31+G(d,p) and SMD = water for the reaction in **Computation S9a**.



Computation S10a:

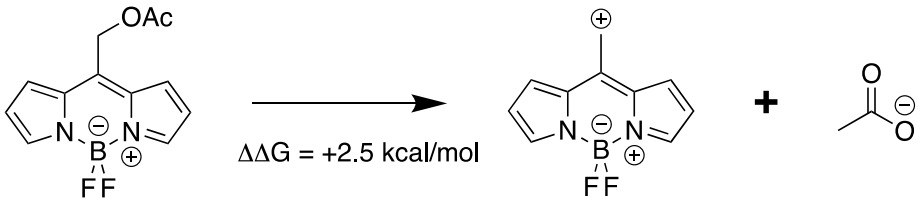
Reaction modeled using B3LYP/6-31+G(d,p) and SMD = water. ΔΔG determined from the optimized energies of the BODIPY structure triplet states and the optimized energy of the acetate structure singlet state.



$\Delta E^{\pm}$ (From Scan): 13.5 $^{kcal}/_{mol}$

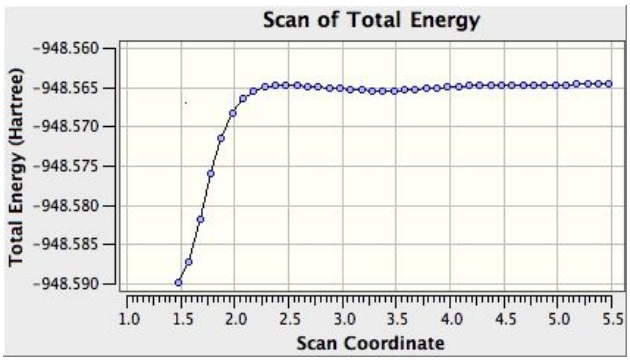
Computation S10b:

Graph generated by the relaxed potential energy scan of the C-O bond breaking on the triplet state modeled using B3LYP/6-31+G(d,p) and SMD = water for the reaction in **Computation 10a**.



Computation S11a:

Reaction modeled using B3LYP/6-31+G(d,p) and SMD = water. ΔΔG determined from the optimized energies of the BODIPY structure triplet states and the optimized energy of the acetate structure singlet state.



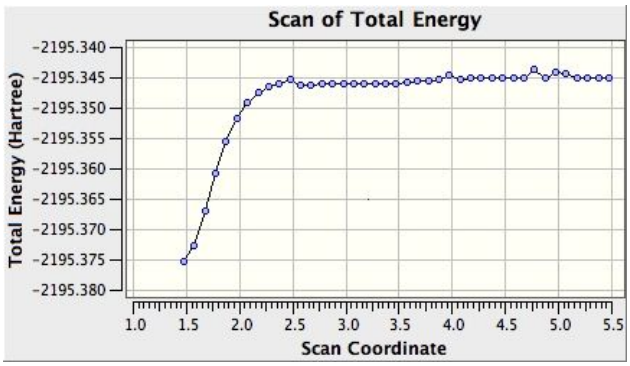
$\Delta E^{\pm}$ (From Scan): 15.7 $^{kcal}/_{mol}$

Computation S11b:

Graph generated by the relaxed potential energy scan of the C-O bond breaking on the triplet state modeled using B3LYP/6-31+G(d,p) and SMD = water for the reaction in **Computation S11a**.

Computation S12a:

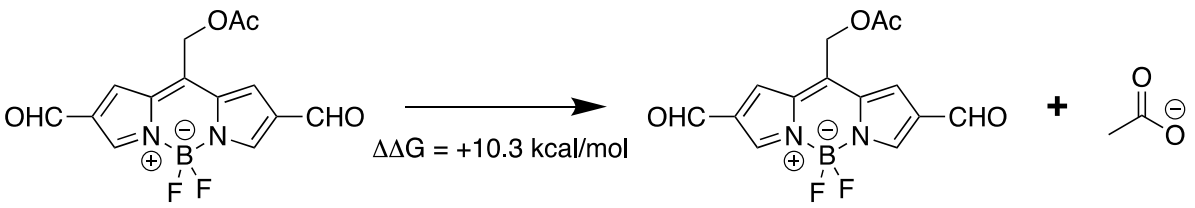
Reaction modeled using B3LYP/6-31+G(d,p) and SMD = water. ΔΔG determined from the optimized energies of the BODIPY structure triplet states and the optimized energy of the acetate structure singlet state.



$\Delta E^{\pm}$ (From Scan): 18.9 $^{kcal}/_{mol}$

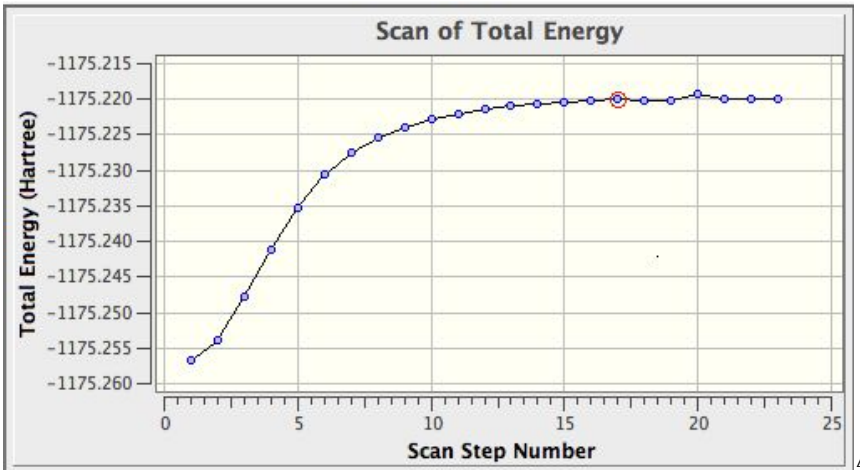
Computation S12b:

Graph generated by the relaxed potential energy scan of the C-O bond breaking on the triplet state modeled using B3LYP/6-31+G(d,p) and SMD = water for the reaction in **Computation S12a**.



Computation S13a:

Reaction modeled using B3LYP/6-31+G(d,p) and SMD = water. ΔΔG determined from the optimized energies of the BODIPY structure triplet states and the optimized energy of the acetate structure singlet state.

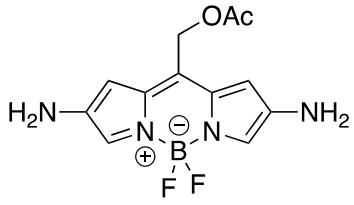


$\Delta E^{\pm}$ (From Scan): 23.0 $^{kcal}/_{mol}$

Computation S13b:

Graph generated by the relaxed potential energy scan of the C-O bond breaking on the triplet state modeled using B3LYP/6-31+G(d,p) and SMD = water for the reaction in **Computation S13a**.

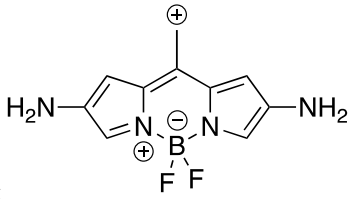
6. Cartesian Coordinates



Triplet uB3LYP/6-31+G(d,p) smd=water

C	0.88796700	3.37327600	-0.13038800
C	1.98604600	2.50793400	0.15410600
C	0.20755900	1.22108400	-0.31694800
C	-0.49033500	0.00729900	-0.51697400
C	0.18574800	-1.22403800	-0.32154300
C	-0.22155300	2.55850400	-0.42073600
C	-1.93060400	0.01983400	-0.88723800
C	1.94605100	-2.53837800	0.15114400
C	-0.26784100	-2.54724400	-0.42793800
C	0.83032600	-3.38477400	-0.13555900
B	2.44083800	-0.01908600	0.27269100
F	2.97068800	-0.02613800	1.59532000
F	3.55760200	-0.02881500	-0.61218400
N	1.55101400	-1.24576700	0.03879800
N	1.57065100	1.21932600	0.04114600
H	3.00010600	2.76905800	0.42265300
H	-1.21650400	2.89422800	-0.67513400
H	2.95493800	-2.81898900	0.41901500
H	-1.26788100	-2.86683800	-0.68235700
N	0.86717200	-4.73419900	-0.10791900
H	1.73048300	-5.22413200	0.08207900
H	0.05263400	-5.27800200	-0.35699400
N	0.94238200	4.73197100	-0.06973600
H	0.18318000	5.26830600	-0.46816500
H	1.84752000	5.18314200	-0.04793100
H	-2.20412200	0.91356600	-1.45000300
H	-2.21619200	-0.86149200	-1.46365100
O	-2.74504600	0.01543600	0.35330600
C	-4.08009000	0.02787700	0.21079300
O	-4.63512700	0.04095100	-0.88507400
C	-4.79145200	0.02571000	1.53329900
H	-5.86995100	0.02142400	1.37504900
H	-4.49663300	-0.85522400	2.11185100
H	-4.50447100	0.91203000	2.10793400

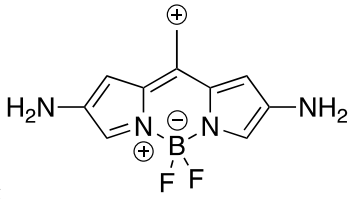
Sum of Electronic and Thermal Free Energies = -1059.146365



Triplet uB3LYP/6-31+G(d,p) smd=water

C	3.38547100	0.19211600	0.00008800
C	2.51054300	-0.95018700	0.00012600
C	1.25061500	0.88943000	0.00000500
C	0.00000000	1.63271200	-0.00006700
C	-1.25061500	0.88943000	0.00000400
C	2.56024200	1.34110500	0.00002600
C	0.00000000	2.99701300	-0.00015400
C	-2.51054300	-0.95018700	0.00012500
C	-2.56024200	1.34110500	0.00002500
C	-3.38547100	0.19211600	0.00008800
B	0.00000000	-1.44509200	-0.00007200
F	0.00000000	-2.26330800	1.14421700
F	0.00000000	-2.26287600	-1.14472700
N	-1.24398900	-0.52172300	0.00006700
N	1.24398900	-0.52172300	0.00006800
H	2.77677500	-1.99867600	0.00019400
H	2.89474600	2.36775200	0.00000400
H	-2.77677500	-1.99867600	0.00019300
H	-2.89474600	2.36775200	0.00000300
N	-4.72210500	0.11550900	0.00016900
H	-5.18903500	-0.78327500	0.00002500
H	-5.29023100	0.95377700	-0.00002300
N	4.72210500	0.11550900	0.00016800
H	5.29023100	0.95377700	-0.00002400
H	5.18903500	-0.78327500	0.00002400
H	0.92581200	3.56052500	-0.00016800
H	-0.92581200	3.56052500	-0.00016800

Sum of Electronic and Thermal Free Energies = -830.520936

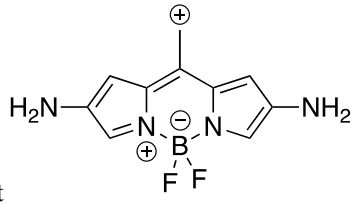


Singlet uB3LYP/6-31+G(d,p)

C	3.35561900	0.17861300	-0.31053300
C	2.48114700	-0.96674600	-0.21262800
C	1.25228400	0.87209600	0.04907400
C	-0.00000200	1.60699900	0.24428200
C	-1.25228800	0.87209600	0.04908500
C	2.54516000	1.32909300	-0.14033700
C	-0.00000300	2.91930900	0.57758900
C	-2.48113400	-0.96674600	-0.21269300
C	-2.54517600	1.32909000	-0.14025900
C	-3.35561600	0.17861200	-0.31053900
B	0.00000000	-1.44564500	0.31493000
F	0.00000800	-1.76952500	1.65797900
F	-0.00000800	-2.54993300	-0.51113800
N	-1.24040200	-0.53451200	-0.00376800
N	1.24040200	-0.53451700	-0.00377900
H	2.72120100	-2.01973000	-0.27824100
H	2.87238200	2.35695000	-0.18937700
H	-2.72117500	-2.01973000	-0.27835700
H	-2.87240800	2.35694700	-0.18924100
N	-4.67825000	0.10925900	-0.53326700
H	-5.15046300	-0.77729500	-0.64491300
H	-5.24578200	0.94386000	-0.58481100
N	4.67825500	0.10926600	-0.53326000
H	5.24577300	0.94387300	-0.58487000
H	5.15048200	-0.77728800	-0.64484600
H	0.92230000	3.46739600	0.72937200
H	-0.92230700	3.46739800	0.72935000

Uncorrected Sum of Electronic and Thermal Free Energies = -830.422984

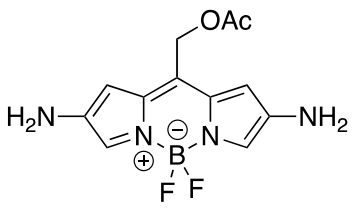
Corrected Sum of Electronic and Thermal Free Energies = -830.419121



Triplet uB3LYP/6-31+G(d,p)

C	3.37472400	0.18786700	-0.20854700
C	2.49353600	-0.95700600	-0.16412700
C	1.25075300	0.87573300	0.03689000
C	-0.00001100	1.61034900	0.16015300
C	-1.25074700	0.87569300	0.03688100
C	2.55926000	1.33227700	-0.07643400
C	-0.00001200	2.96106000	0.36743100
C	-2.49356000	-0.95702800	-0.16409200
C	-2.55926100	1.33224900	-0.07638800
C	-3.37474000	0.18784900	-0.20854300
B	0.00000700	-1.46239800	0.21492100
F	0.00001900	-1.90734400	1.52304000
F	0.00004600	-2.49195500	-0.70276500
N	-1.24290100	-0.53023400	-0.02183500
N	1.24288400	-0.53018800	-0.02184200
H	2.73809200	-2.00976400	-0.22127200
H	2.89088200	2.35960600	-0.09305200
H	-2.73813400	-2.00978200	-0.22125100
H	-2.89088000	2.35957800	-0.09293700
N	-4.70909000	0.11143600	-0.35825200
H	-5.18129200	-0.77696200	-0.44929400
H	-5.28293100	0.94263500	-0.37661800
N	4.70908000	0.11142900	-0.35821900
H	5.28294300	0.94261400	-0.37655000
H	5.18126300	-0.77697900	-0.44925800
H	0.92181500	3.52168800	0.46244400
H	-0.92185000	3.52168300	0.46239400

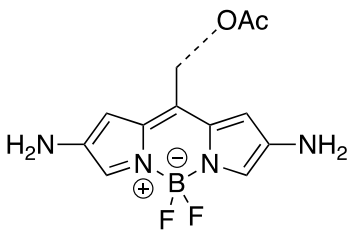
Sum of Electronic and Thermal Free Energies = -830.427342



Triplet Scan uB3LYP/6-31+G(d,p) smd=water (Reactant)

C	-0.88286300	-3.37226700	-0.08284300
C	-1.98584800	-2.50642800	0.18082700
C	-0.20872500	-1.22105300	-0.29936600
C	0.48823500	-0.00789800	-0.50666500
C	-0.18515300	1.22377000	-0.30451900
C	0.22522800	-2.55822900	-0.38114300
C	1.92554900	-0.02149300	-0.88808400
C	-1.94222900	2.53913000	0.17696700
C	0.27521000	2.54615400	-0.38855800
C	-0.82031000	3.38435900	-0.08817300
B	-2.45799700	0.02077400	0.21816800
F	-3.08427300	0.02976700	1.49600500
F	-3.50656900	0.03017000	-0.74866500
N	-1.55242200	1.24645600	0.04799400
N	-1.57373700	-1.21825700	0.05167400
H	-3.00113900	-2.76710200	0.44512000
H	1.22393600	-2.89369900	-0.62074400
H	-2.95209800	2.82062900	0.44013500
H	1.27953800	2.86424800	-0.62755300
N	-0.84991700	4.73323900	-0.03569900
H	-1.71063600	5.22451600	0.16234700
H	-0.03055900	5.27696600	-0.26849400
N	-0.93209900	-4.72964600	0.00239400
H	-0.16829700	-5.27053000	-0.38067600
H	-1.83512100	-5.18458700	0.03099400
H	2.19291700	-0.91585700	-1.45287200
H	2.20568400	0.85925700	-1.46810900
O	2.75371600	-0.01643600	0.34333700
C	4.08686600	-0.02981900	0.18364400
O	4.62758000	-0.04388200	-0.91940200
C	4.81597400	-0.02798200	1.49627500
H	5.89214600	-0.01770200	1.32311200
H	4.52463100	0.84916900	2.08221300
H	4.54181600	-0.91807600	2.07143600

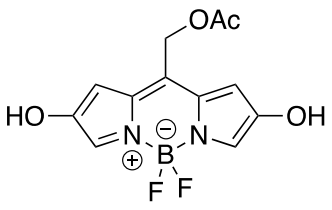
SCF Energy = -1059.34470949



Triplet Scan uB3LYP/6-31+G(d,p) smd=water (Transition)

C	-0.88171100	-3.38556800	-0.11557000
C	-1.97316700	-2.52362100	0.23587200
C	-0.26541100	-1.23861700	-0.41506100
C	0.40191800	0.00333300	-0.69981400
C	-0.27758900	1.23863900	-0.41507600
C	0.18354500	-2.55551000	-0.52165000
C	1.70875000	0.00985100	-1.18495000
C	-1.99788700	2.50679400	0.23583700
C	0.15856600	2.55985900	-0.52117600
C	-0.91472000	3.37939700	-0.11487500
B	-2.48004300	-0.01081900	0.30965500
F	-2.96042700	-0.01280800	1.63835800
F	-3.59836500	-0.01664600	-0.55769600
N	-1.60402600	1.23214900	0.05518900
N	-1.59173700	-1.24515500	0.05558500
H	-2.95768400	-2.79503100	0.59155900
H	1.16121600	-2.88083900	-0.84524800
H	-2.98507300	2.76841900	0.59147700
H	1.13314600	2.89477500	-0.84431000
N	-0.97054600	4.72264200	-0.04677000
H	-1.80658700	5.19129900	0.27561500
H	-0.17205000	5.28677800	-0.30452500
N	-0.92475600	-4.72935900	-0.04845000
H	-0.12119600	-5.28584300	-0.30712700
H	-1.75648000	-5.20615900	0.27314300
H	2.15366700	-0.90473700	-1.55180300
H	2.14440300	0.92896800	-1.55164700
O	2.95123400	0.01639300	0.48815700
C	4.22337200	0.01656700	0.27610900
O	4.75935100	0.01562600	-0.86150800
C	5.08781800	0.01570000	1.52920200
H	6.14888500	0.03490800	1.27296700
H	4.84559100	0.88637500	2.14715200
H	4.87338400	-0.87877900	2.12333800

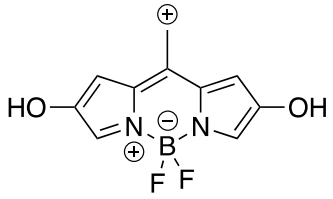
SCF Energy = -1059.32863872



Triplet uB3LYP/6-31+G(d,p) smd=water

C	0.14800400	1.21297500	-0.29849500
C	-0.47807700	-0.03942200	-0.50222200
C	0.27485900	-1.21819100	-0.28938600
B	2.47888800	0.11868600	0.19969200
F	3.12191300	0.15714700	1.46174600
F	3.49475100	0.16947200	-0.79189700
N	1.63847600	-1.15945800	0.05308000
N	1.50911400	1.30072700	0.04645600
C	-0.38567000	2.52320600	-0.37323900
C	1.83247000	2.60993900	0.18254200
C	0.66225500	3.38675600	-0.07272500
C	2.09940400	-2.42671800	0.19151000
C	-0.11701600	-2.57826000	-0.35733600
C	1.01833300	-3.32413800	-0.05957400
C	-1.91383500	-0.11251900	-0.88948000
H	-2.21737400	0.74725800	-1.48877500
H	-2.14188400	-1.02499500	-1.44233400
O	-2.74037200	-0.11474000	0.33604900
C	-4.07403700	-0.16672600	0.17117500
O	-4.60699600	-0.21107200	-0.93380800
C	-4.80688000	-0.16871400	1.48100000
H	-4.51729300	0.70485700	2.07272000
H	-5.88236700	-0.15899900	1.30387100
H	-4.53470200	-1.06246000	2.05176300
O	1.18485900	-4.66120500	0.01351200
H	0.34828100	-5.11717600	-0.17879000
O	0.68345600	4.73373000	0.00178600
H	-0.19768600	5.09736400	-0.18874200
H	-1.40665200	2.79079700	-0.60275300
H	2.82600000	2.94641900	0.44209700
H	3.12344700	-2.65482600	0.45044500
H	-1.10375800	-2.95294300	-0.58627200

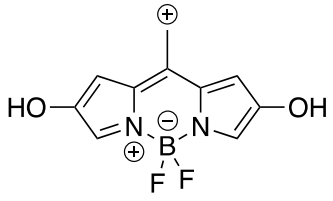
Sum of Electronic and Thermal Free Energies = -1098.878798



Triplet uB3LYP/6-31+G(d,p) smd=water

C	-1.24084400	0.86973100	-0.00007200
C	0.00000000	1.60665200	-0.00040200
C	1.24084400	0.86973100	-0.00007200
B	0.00000000	-1.47287300	-0.00068300
F	0.00000200	-2.27807700	-1.14624100
F	-0.00000100	-2.28021300	1.14337500
N	1.24313300	-0.53842000	0.00022900
N	-1.24313300	-0.53842000	0.00022600
C	-2.56505200	1.33861000	0.00036100
C	-2.51018100	-0.95208800	0.00080700
C	-3.37075600	0.20666500	0.00061800
C	2.51018100	-0.95208700	0.00081200
C	2.56505200	1.33861000	0.00036000
C	3.37075600	0.20666600	0.00061800
C	-0.00000100	2.98338900	-0.00119100
H	-0.92650700	3.54503100	-0.00161600
H	0.92650400	3.54503200	-0.00158600
O	4.69675100	0.07026600	0.00095600
H	5.14124800	0.93669000	0.00007200
O	-4.69675000	0.07026500	0.00095700
H	-5.14124800	0.93669000	0.00007600
H	-2.88934300	2.36837900	0.00039000
H	-2.79301600	-1.99643400	0.00098300
H	2.79301600	-1.99643300	0.00099000
H	2.88934300	2.36837900	0.00038800

Sum of Electronic and Thermal Free Energies = -870.242083

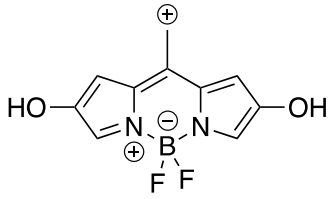


Singlet uB3LYP/6-31+G(d,p)

C	-1.25290500	0.85769100	0.04652900
C	0.00000000	1.59075800	0.20692000
C	1.25290400	0.85769100	0.04652700
B	0.00000000	-1.46889400	0.27290200
F	0.00000000	-2.54480100	-0.57904300
F	0.00000200	-1.80893300	1.60762500
N	1.24420100	-0.54351300	-0.02382500
N	-1.24420200	-0.54351300	-0.02382300
C	-2.56428300	1.32943800	-0.10387500
C	-2.49115200	-0.96588000	-0.20850200
C	-3.35940500	0.19352600	-0.26959900
C	2.49115200	-0.96588000	-0.20850100
C	2.56428200	1.32943900	-0.10388000
C	3.35940500	0.19352700	-0.26959900
C	0.00000000	2.92069700	0.48520200
H	-0.92157700	3.47600600	0.61353100
H	0.92157700	3.47600700	0.61352400
O	4.66036900	0.04191000	-0.46624800
H	5.13829600	0.88666600	-0.48114800
O	-4.66036800	0.04191000	-0.46625000
H	-5.13829500	0.88666600	-0.48115000
H	-2.88694100	2.35987300	-0.12649300
H	-2.75681000	-2.01222200	-0.28365800
H	2.75681000	-2.01222200	-0.28365400
H	2.88694000	2.35987400	-0.12650200

Uncorrected Sum of Electronic and Thermal Free Energies = -870.136901

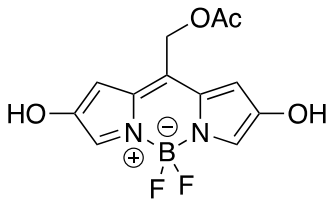
Corrected Sum of Electronic and Thermal Free Energies = -870.130539



Triplet uB3LYP/6-31+G(d,p)

C	-1.24489900	0.86152400	0.03916800
C	0.00000000	1.59279300	0.14514800
C	1.24489900	0.86152400	0.03916800
B	0.00000000	-1.48684400	0.19306200
F	0.00000100	-2.49203000	-0.74162400
F	-0.00000100	-1.93674000	1.49416100
N	1.24478600	-0.54205600	-0.03026900
N	-1.24478600	-0.54205600	-0.03027100
C	-2.56763100	1.33340300	-0.05641300
C	-2.49764000	-0.95724200	-0.16331200
C	-3.36792900	0.20220900	-0.18886900
C	2.49764100	-0.95724200	-0.16331000
C	2.56763100	1.33340300	-0.05641500
C	3.36792900	0.20220900	-0.18886900
C	0.00000000	2.95835100	0.31958500
H	-0.92167700	3.52122100	0.39974700
H	0.92167700	3.52122100	0.39974800
O	4.67714900	0.04696500	-0.32814600
H	5.15695600	0.89049800	-0.32458100
O	-4.67714900	0.04696500	-0.32814700
H	-5.15695600	0.89049800	-0.32458000
H	-2.89103700	2.36373000	-0.05665300
H	-2.76944500	-2.00300100	-0.22816400
H	2.76944600	-2.00300200	-0.22816000
H	2.89103600	2.36373000	-0.05665700

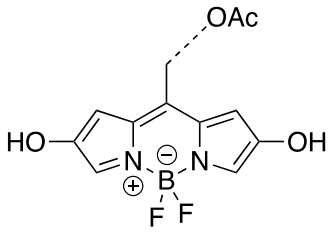
Sum of Electronic and Thermal Free Energies = -870.143268



Triplet Scan uB3LYP/6-31+G(d,p) smd=water (Reactant)

C	0.14800400	1.21297500	-0.29849500
C	-0.47807700	-0.03942200	-0.50222200
C	0.27485900	-1.21819100	-0.28938600
B	2.47888800	0.11868600	0.19969200
F	3.12191300	0.15714700	1.46174600
F	3.49475100	0.16947200	-0.79189700
N	1.63847600	-1.15945800	0.05308000
N	1.50911400	1.30072700	0.04645600
C	-0.38567000	2.52320600	-0.37323900
C	1.83247000	2.60993900	0.18254200
C	0.66225500	3.38675600	-0.07272500
C	2.09940400	-2.42671800	0.19151000
C	-0.11701600	-2.57826000	-0.35733600
C	1.01833300	-3.32413800	-0.05957400
C	-1.91383500	-0.11251900	-0.88948000
H	-2.21737400	0.74725800	-1.48877500
H	-2.14188400	-1.02499500	-1.44233400
O	-2.74037200	-0.11474000	0.33604900
C	-4.07403700	-0.16672600	0.17117500
O	-4.60699600	-0.21107200	-0.93380800
C	-4.80688000	-0.16871400	1.48100000
H	-4.51729300	0.70485700	2.07272000
H	-5.88236700	-0.15899900	1.30387100
H	-4.53470200	-1.06246000	2.05176300
O	1.18485900	-4.66120500	0.01351200
H	0.34828100	-5.11717600	-0.17879000
O	0.68345600	4.73373000	0.00178600
H	-0.19768600	5.09736400	-0.18874200
H	-1.40665200	2.79079700	-0.60275300
H	2.82600000	2.94641900	0.44209700
H	3.12344700	-2.65482600	0.45044500
H	-1.10375800	-2.95294300	-0.58627200

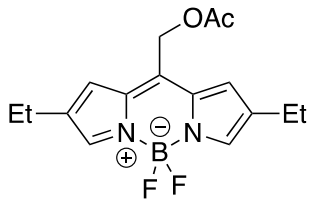
SCF Energy = -1099.05553104



Triplet Scan uB3LYP/6-31+G(d,p) smd=water (Transition)

C	0.42188300	1.23044700	-0.43696500
C	-0.34910100	0.05801800	-0.74687500
C	0.21527200	-1.22881900	-0.44465500
B	2.50822200	-0.18604200	0.34225100
F	2.95704600	-0.22461600	1.67198900
F	3.61710500	-0.28163100	-0.51806400
N	1.51567100	-1.34500800	0.07296700
N	1.72546800	1.12435600	0.07492700
C	0.08027800	2.59117300	-0.55237800
C	2.19996400	2.36156100	0.27613000
C	1.18618700	3.30483700	-0.10789600
C	1.77634700	-2.64542600	0.26612500
C	-0.34749400	-2.51264100	-0.57302200
C	0.62161800	-3.40354300	-0.12940900
C	-1.62529900	0.16677000	-1.28175900
H	-2.00699400	1.12383900	-1.60747600
H	-2.16325200	-0.71127000	-1.60980000
O	-3.00586600	0.28770800	0.52645100
C	-4.26839400	0.27525000	0.30504100
O	-4.79937100	0.26637800	-0.84146700
C	-5.17760700	0.24235600	1.52853200
H	-4.64421200	0.51828000	2.44046100
H	-6.03164200	0.90940700	1.38070700
H	-5.56605300	-0.77621800	1.64544500
O	0.60419800	-4.73962500	-0.03565600
H	-0.24791100	-5.09506100	-0.34301800
O	1.39284700	4.62413900	-0.00328500
H	0.61157800	5.11993800	-0.30455600
H	-0.85611100	2.99678800	-0.90558500
H	3.19019000	2.55794300	0.66429900
H	2.71792700	-3.00741800	0.65568800
H	-1.33635900	-2.75395000	-0.93355600

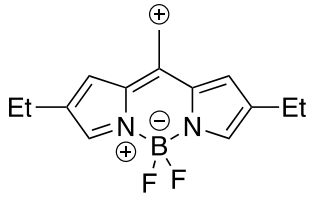
SCF Energy = -1099.03380297



Triplet uB3LYP/6-31+G(d,p) smd=water

C	-3.39851500	-0.66441900	0.02452300
C	-2.53532800	-1.75409700	0.35401100
C	-1.21352100	-0.04188400	-0.18144800
C	0.00000200	0.65004200	-0.41078800
C	1.21351500	-0.04190000	-0.18145000
C	-2.57424800	0.39906700	-0.30573100
C	0.00001100	2.07401100	-0.84371400
H	-0.88701800	2.32525700	-1.42696300
O	0.00002300	2.93411500	0.35911700
H	0.88703900	2.32524300	-1.42697100
C	2.53530000	-1.75413200	0.35400300
C	2.57424800	0.39903400	-0.30573000
C	3.39850100	-0.66446300	0.02452200
B	-0.00001700	-2.24745200	0.50456900
F	-0.00002500	-3.39374400	-0.33272600
F	-0.00001900	-2.70845300	1.84734000
N	1.23146000	-1.37043400	0.22961900
N	-1.23148300	-1.37041800	0.22962000
C	0.00003700	4.26402000	0.15879100
O	0.00003800	4.76893500	-0.96015000
C	0.00005300	5.03042200	1.44931100
H	0.00005200	6.10106600	1.24484600
H	-0.88364300	4.76427100	2.03765300
H	0.88376300	4.76426900	2.03763000
C	-4.89708700	-0.71256800	0.03595800
H	-5.23723600	-1.04730400	1.02450300
H	-5.28443500	0.30087900	-0.10941000
C	4.89707300	-0.71263200	0.03595900
H	5.23721600	-1.04737800	1.02450200
H	5.28443300	0.30081200	-0.10940200
C	-5.48055300	-1.65247700	-1.03462600
H	-5.19298200	-1.32833400	-2.04056200
H	-5.12815100	-2.68005600	-0.89515700
H	-6.57419800	-1.65907400	-0.97726700
C	5.48052900	-1.65254000	-1.03463000
H	6.57417400	-1.65915100	-0.97726900
H	5.12811300	-2.68011600	-0.89516800
H	5.19296300	-1.32838700	-2.04056500
H	-2.79603600	-2.75509500	0.67059400
H	-2.88177700	1.39198100	-0.60305800
H	2.88178900	1.39194500	-0.60305200
H	2.79599500	-2.75513400	0.67058200

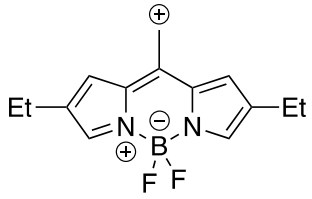
Sum of Electronic and Thermal Free Energies = -1105.595260



Triplet uB3LYP/6-31+G(d,p) smd=water

C	3.40408800	0.28941300	-0.14230300
C	2.52211000	-0.85630100	-0.20486100
C	1.23291300	0.93217900	-0.13694000
C	0.00000000	1.67331300	-0.11542300
C	-1.23291300	0.93217900	-0.13694000
C	2.58220900	1.39433600	-0.10006300
C	0.00000000	3.05386000	-0.07190700
H	0.92732100	3.61369300	-0.05552200
H	-0.92732100	3.61369300	-0.05552300
C	-2.52211000	-0.85630100	-0.20486100
C	-2.58220900	1.39433600	-0.10006300
C	-3.40408800	0.28941300	-0.14230300
B	0.00000000	-1.39499600	-0.26928100
F	0.00000000	-2.28114000	0.81435700
F	0.00000000	-2.11711400	-1.46948800
N	-1.24185600	-0.45989900	-0.20147800
N	1.24185600	-0.45989900	-0.20147800
C	4.89575700	0.21574200	-0.11917300
H	5.23060400	-0.36116800	-0.99103000
H	5.30128700	1.22633400	-0.22149800
C	-4.89575700	0.21574200	-0.11917300
H	-5.23060400	-0.36116800	-0.99103000
H	-5.30128700	1.22633400	-0.22149800
C	5.44212300	-0.44896300	1.15895400
H	5.16165300	0.12378800	2.04876200
H	5.05892500	-1.46853000	1.27291000
H	6.53444100	-0.50009700	1.11249700
C	-5.44212300	-0.44896300	1.15895400
H	-6.53444100	-0.50009700	1.11249700
H	-5.05892600	-1.46853000	1.27291000
H	-5.16165300	0.12378800	2.04876200
H	2.78883200	-1.90453300	-0.25708600
H	2.88821300	2.42947400	-0.04909900
H	-2.88821300	2.42947400	-0.04909900
H	-2.78883200	-1.90453300	-0.25708600

Sum of Electronic and Thermal Free Energies = -876.959214

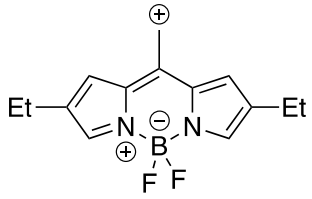


Singlet uB3LYP/6-31+G(d,p)

C	3.41881400	0.28822200	-0.23948200
C	2.52525900	-0.85591000	-0.26976900
C	1.24978600	0.92661300	-0.08110100
C	0.00000000	1.66403200	0.00611800
C	-1.24978600	0.92661300	-0.08110200
C	2.59954900	1.39163000	-0.11731600
C	0.00000000	3.01914900	0.15796700
H	0.92204200	3.58448000	0.22544000
H	-0.92204300	3.58447600	0.22546300
C	-2.52525900	-0.85591000	-0.26977000
C	-2.59954800	1.39163000	-0.11731800
C	-3.41881300	0.28822300	-0.23948200
B	0.00000000	-1.41533200	-0.09607200
F	0.00000000	-2.06449000	1.12009500
F	0.00000000	-2.27553500	-1.17007100
N	-1.24826900	-0.45359000	-0.17814100
N	1.24826900	-0.45359000	-0.17814100
C	4.90973800	0.21571100	-0.31649200
H	5.19068100	-0.35242400	-1.21336300
H	5.31034600	1.22562400	-0.44406500
C	-4.90973800	0.21571200	-0.31649100
H	-5.19068100	-0.35242200	-1.21336400
H	-5.31034500	1.22562500	-0.44406200
C	5.54619300	-0.45297100	0.92252500
H	5.31944900	0.10876100	1.83326000
H	5.19231200	-1.48000700	1.05722000
H	6.63226500	-0.48826800	0.80314400
C	-5.54619300	-0.45297200	0.92252500
H	-6.63226500	-0.48826800	0.80314500
H	-5.19231200	-1.48000900	1.05721800
H	-5.31944800	0.10875800	1.83326100
H	2.77199500	-1.90704100	-0.35715600
H	2.91918600	2.42313100	-0.07486700
H	-2.91918500	2.42313100	-0.07486800
H	-2.77199500	-1.90704100	-0.35715600

Uncorrected Sum of Electronic and Thermal Free Energies = -876.873056

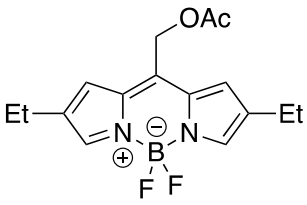
Corrected Sum of Electronic and Thermal Free Energies = -876.869261



Triplet uB3LYP/6-31+G(d,p)

C	3.40947900	0.29255100	-0.23836200
C	2.51598000	-0.85574300	-0.26910000
C	1.23824600	0.92800500	-0.07894400
C	0.00000000	1.66286600	0.00668500
C	-1.23824600	0.92800500	-0.07894300
C	2.58811100	1.39310400	-0.11507600
C	0.00000000	3.03786100	0.15163400
H	0.92270200	3.60105000	0.21490100
H	-0.92270100	3.60105100	0.21489400
C	-2.51598000	-0.85574300	-0.26910000
C	-2.58811100	1.39310400	-0.11507500
C	-3.40947900	0.29255200	-0.23836100
B	0.00000000	-1.42635000	-0.09719000
F	0.00000000	-2.07637700	1.11791400
F	0.00000000	-2.28408300	-1.17269300
N	-1.24519800	-0.46172300	-0.17808800
N	1.24519800	-0.46172400	-0.17808900
C	4.89982300	0.22088000	-0.31529900
H	5.18072000	-0.34566600	-1.21328600
H	5.30030600	1.23107600	-0.44047400
C	-4.89982300	0.22088100	-0.31529900
H	-5.18072000	-0.34566500	-1.21328700
H	-5.30030600	1.23107600	-0.44047300
C	5.53572500	-0.45092900	0.92264500
H	5.30931600	0.10912400	1.83444300
H	5.18172400	-1.47821400	1.05516100
H	6.62170900	-0.48622900	0.80292900
C	-5.53572500	-0.45092900	0.92264400
H	-6.62171000	-0.48622900	0.80292800
H	-5.18172400	-1.47821400	1.05515900
H	-5.30931700	0.10912300	1.83444300
H	2.76859600	-1.90575500	-0.35632500
H	2.90521900	2.42523100	-0.07139900
H	-2.90521900	2.42523100	-0.07139700
H	-2.76859600	-1.90575500	-0.35632600

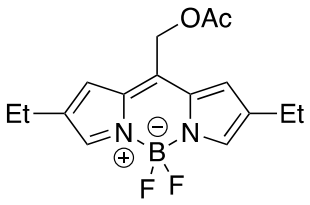
Sum of Electronic and Thermal Free Energies = -876.879649



Triplet Scan uB3LYP/6-31+G(d,p) smd=water (Reactant)

C	-3.39851500	-0.66441900	0.02452300
C	-2.53532800	-1.75409700	0.35401100
C	-1.21352100	-0.04188400	-0.18144800
C	0.00000200	0.65004200	-0.41078800
C	1.21351500	-0.04190000	-0.18145000
C	-2.57424800	0.39906700	-0.30573100
C	0.00001100	2.07401100	-0.84371400
H	-0.88701800	2.32525700	-1.42696300
O	0.00002300	2.93411500	0.35911700
H	0.88703900	2.32524300	-1.42697100
C	2.53530000	-1.75413200	0.35400300
C	2.57424800	0.39903400	-0.30573000
C	3.39850100	-0.66446300	0.02452200
B	-0.00001700	-2.24745200	0.50456900
F	-0.00002500	-3.39374400	-0.33272600
F	-0.00001900	-2.70845300	1.84734000
N	1.23146000	-1.37043400	0.22961900
N	-1.23148300	-1.37041800	0.22962000
C	0.00003700	4.26402000	0.15879100
O	0.00003800	4.76893500	-0.96015000
C	0.00005300	5.03042200	1.44931100
H	0.00005200	6.10106600	1.24484600
H	-0.88364300	4.76427100	2.03765300
H	0.88376300	4.76426900	2.03763000
C	-4.89708700	-0.71256800	0.03595800
H	-5.23723600	-1.04730400	1.02450300
H	-5.28443500	0.30087900	-0.10941000
C	4.89707300	-0.71263200	0.03595900
H	5.23721600	-1.04737800	1.02450200
H	5.28443300	0.30081200	-0.10940200
C	-5.48055300	-1.65247700	-1.03462600
H	-5.19298200	-1.32833400	-2.04056200
H	-5.12815100	-2.68005600	-0.89515700
H	-6.57419800	-1.65907400	-0.97726700
C	5.48052900	-1.65254000	-1.03463000
H	6.57417400	-1.65915100	-0.97726900
H	5.12811300	-2.68011600	-0.89516800
H	5.19296300	-1.32838700	-2.04056500
H	-2.79603600	-2.75509500	0.67059400
H	-2.88177700	1.39198100	-0.60305800
H	2.88178900	1.39194500	-0.60305200
H	2.79599500	-2.75513400	0.67058200

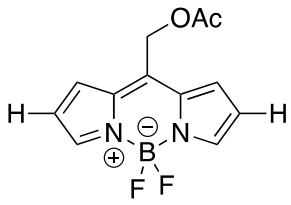
SCF Energy = -1105.86871525



Triplet Scan uB3LYP/6-31+G(d,p) smd=water (Transition)

C	-3.40135300	-0.70595100	-0.01188600
C	-2.52414800	-1.75736500	0.43360400
C	-1.22896700	-0.13712200	-0.33410900
C	0.00000200	0.52692300	-0.66730500
C	1.22897800	-0.13711100	-0.33412300
C	-2.57980900	0.29665800	-0.48770500
C	0.00000000	1.78776900	-1.25105300
H	-0.92103100	2.23656400	-1.59449900
O	0.00005700	3.22783500	0.51493800
H	0.92103700	2.23655700	-1.59449600
C	2.52419100	-1.75734000	0.43357100
C	2.57981000	0.29669500	-0.48771500
C	3.40137400	-0.70590200	-0.01190500
B	0.00002500	-2.26429400	0.59501600
F	0.00002500	-3.45790200	-0.14829100
F	0.00004100	-2.57838600	1.96464800
N	1.23863600	-1.40422000	0.23878600
N	-1.23859900	-1.40422700	0.23880900
C	-0.00019000	4.48570600	0.26141800
O	-0.00047400	4.98692500	-0.89722500
C	0.00018300	5.40406400	1.47884000
H	-0.00252100	6.45478500	1.18186400
H	-0.88065700	5.19826600	2.09590200
H	0.88452800	5.20196000	2.09214500
C	-4.89540000	-0.75367900	0.04057200
H	-5.20590000	-0.99881200	1.06427300
H	-5.28942500	0.24075000	-0.18927700
C	4.89542100	-0.75360300	0.04055000
H	5.20592800	-0.99880200	1.06423200
H	5.28942400	0.24085200	-0.18923000
C	-5.49467900	-1.79314400	-0.92545100
H	-5.23781900	-1.55696600	-1.96330800
H	-5.12681200	-2.80048900	-0.70346900
H	-6.58565800	-1.80245000	-0.83511800
C	5.49472000	-1.79298500	-0.92555100
H	6.58569900	-1.80227000	-0.83522600
H	5.12687800	-2.80035400	-0.70363700
H	5.23784700	-1.55673900	-1.96339000
H	-2.78510600	-2.71002300	0.87642800
H	-2.88888300	1.24727400	-0.89862500
H	2.88886400	1.24732300	-0.89862600
H	2.78517000	-2.70999900	0.87637800

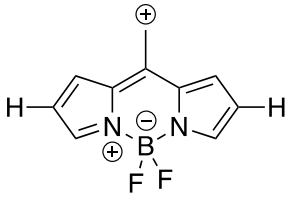
SCF Energy = -1105.84718062



Triplet uB3LYP/6-31+G(d,p) smd=water

C	-0.95518800	3.39126100	-0.13317200
C	-2.05395300	2.54283200	0.13723400
C	-0.32426900	1.21131300	-0.31752400
C	0.38049400	-0.00002000	-0.51710800
C	-0.32430700	-1.21132900	-0.31751700
C	0.12895800	2.58153900	-0.41616000
C	1.82136300	-0.00004400	-0.89348600
H	2.09309700	0.88670700	-1.46795800
O	2.63113200	-0.00005300	0.34097400
H	2.09306900	-0.88680700	-1.46795300
C	-2.05403300	-2.54279200	0.13724800
C	0.12887700	-2.58157000	-0.41614300
C	-0.95529400	-3.39125700	-0.13315200
B	-2.55760000	0.00002800	0.24722200
F	-3.64759100	0.00004300	-0.65907500
F	-3.09459600	0.00004100	1.55872300
N	-1.66278900	-1.23194800	0.02510300
N	-1.66275000	1.23197500	0.02509500
C	3.96879000	-0.00007200	0.19221800
O	4.51533900	-0.00000400	-0.90648300
C	4.68391700	0.00002500	1.51160000
H	5.76167300	0.00009400	1.34883000
H	4.39488000	0.88377400	2.08894800
H	4.39500000	-0.88372400	2.08900600
H	-0.98295400	-4.47196000	-0.11328400
H	-0.98281300	4.47196500	-0.11331000
H	-3.07064700	2.80049200	0.40056700
H	1.13604700	2.88412300	-0.66497000
H	-3.07073500	-2.80041900	0.40058200
H	1.13595700	-2.88418800	-0.66495100

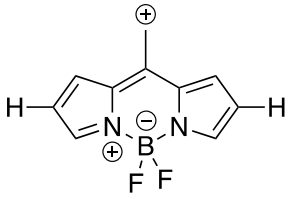
Sum of Electronic and Thermal Free Energies = -948.419188



Triplet uB3LYP/6-31+G(d,p) smd=water

C	3.39640800	0.23686400	-0.00078000
C	2.53112500	-0.90465900	-0.00094200
C	1.23016600	0.87661900	0.00006700
C	0.00000600	1.62217100	0.00034100
C	-1.23016200	0.87662700	0.00005800
C	2.59251000	1.34634300	-0.00026900
C	0.00001700	3.00295800	0.00063400
C	-2.53113200	-0.90464700	-0.00093000
C	-2.59250500	1.34635500	-0.00025900
C	-3.39640900	0.23688100	-0.00080400
B	-0.00000500	-1.44618700	0.00046100
F	-0.00001300	-2.24724400	1.14679900
F	-0.00000200	-2.24980700	-1.14400100
N	-1.24241900	-0.50600200	-0.00049400
N	1.24241400	-0.50600900	-0.00048300
H	-4.47623500	0.19535300	-0.00119500
H	4.47623300	0.19533100	-0.00115400
H	2.79553300	-1.95431100	-0.00135500
H	2.89361000	2.38373300	-0.00007100
H	-2.79554600	-1.95429700	-0.00134300
H	-2.89360300	2.38374500	-0.00005300
H	-0.92735100	3.56294000	0.00106000
H	0.92739800	3.56292000	0.00076800

Sum of Electronic and Thermal Free Energies = -719.778030

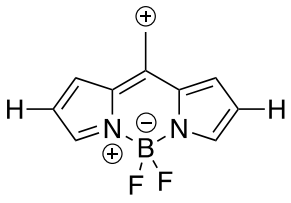


Singlet uB3LYP/6-31+G(d,p)

C	-0.00000200	-0.22908700	3.41474300
C	-0.00000500	0.90787500	2.54201200
C	0.00000300	-0.87085200	1.24641400
C	0.00000700	-1.61352400	0.00000000
C	0.00000300	-0.87085200	-1.24641400
C	0.00000300	-1.34183100	2.61394400
C	0.00001500	-2.97911000	0.00000000
H	0.00002000	-3.54963800	0.92161400
H	0.00002000	-3.54963800	-0.92161400
C	-0.00000500	0.90787500	-2.54201200
C	0.00000300	-1.34183100	-2.61394400
C	-0.00000200	-0.22908700	-3.41474300
B	-0.00000400	1.46755700	0.00000000
F	1.14991400	2.21966800	0.00000000
F	-1.14992400	2.21966400	0.00000000
N	-0.00000200	0.49794400	-1.25086400
N	-0.00000200	0.49794400	1.25086400
H	-0.00000400	-0.18850300	-4.49474400
H	-0.00000400	-0.18850300	4.49474400
H	-0.00000900	1.96200300	2.78981100
H	0.00000600	-2.37408100	2.93303400
H	-0.00000900	1.96200300	-2.78981100
H	0.00000600	-2.37408100	-2.93303400

Uncorrected Sum of Electronic and Thermal Free Energies = -719.684139

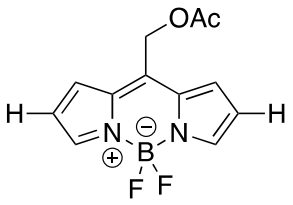
Corrected Sum of Electronic and Thermal Free Energies = -719.681787



Triplet uB3LYP/6-31+G(d,p)

C	-0.00000300	0.23583200	3.40439800
C	-0.00000100	-0.90815200	2.52933400
C	-0.00000100	0.87390600	1.23553800
C	-0.00000100	1.61797000	0.00000000
C	-0.00000100	0.87390600	-1.23553800
C	-0.00000300	1.34458800	2.60236500
C	-0.00000100	3.00081600	0.00000000
H	-0.00000100	3.56879200	0.92207100
H	-0.00000100	3.56879200	-0.92207100
C	-0.00000100	-0.90815200	-2.52933400
C	-0.00000300	1.34458800	-2.60236500
C	-0.00000300	0.23583200	-3.40439800
B	0.00000300	-1.47864300	0.00000000
F	-1.14996900	-2.23013100	0.00000000
F	1.14997900	-2.23012400	0.00000000
N	0.00000000	-0.50665000	-1.24747000
N	0.00000000	-0.50665000	1.24747000
H	-0.00000400	0.19549200	-4.48456200
H	-0.00000400	0.19549200	4.48456200
H	0.00000000	-1.96098400	2.78401400
H	-0.00000400	2.37759500	2.91848900
H	0.00000000	-1.96098400	-2.78401400
H	-0.00000400	2.37759500	-2.91848900

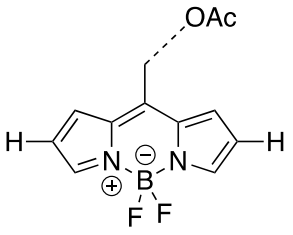
Sum of Electronic and Thermal Free Energies = -719.690160



Triplet Scan uB3LYP/6-31+G(d,p) smd=water (Reactant)

C	-0.95518800	3.39126100	-0.13317200
C	-2.05395300	2.54283200	0.13723400
C	-0.32426900	1.21131300	-0.31752400
C	0.38049400	-0.00002000	-0.51710800
C	-0.32430700	-1.21132900	-0.31751700
C	0.12895800	2.58153900	-0.41616000
C	1.82136300	-0.00004400	-0.89348600
H	2.09309700	0.88670700	-1.46795800
O	2.63113200	-0.00005300	0.34097400
H	2.09306900	-0.88680700	-1.46795300
C	-2.05403300	-2.54279200	0.13724800
C	0.12887700	-2.58157000	-0.41614300
C	-0.95529400	-3.39125700	-0.13315200
B	-2.55760000	0.00002800	0.24722200
F	-3.64759100	0.00004300	-0.65907500
F	-3.09459600	0.00004100	1.55872300
N	-1.66278900	-1.23194800	0.02510300
N	-1.66275000	1.23197500	0.02509500
C	3.96879000	-0.00007200	0.19221800
O	4.51533900	-0.00000400	-0.90648300
C	4.68391700	0.00002500	1.51160000
H	5.76167300	0.00009400	1.34883000
H	4.39488000	0.88377400	2.08894800
H	4.39500000	-0.88372400	2.08900600
H	-0.98295400	-4.47196000	-0.11328400
H	-0.98281300	4.47196500	-0.11331000
H	-3.07064700	2.80049200	0.40056700
H	1.13604700	2.88412300	-0.66497000
H	-3.07073500	-2.80041900	0.40058200
H	1.13595700	-2.88418800	-0.66495100

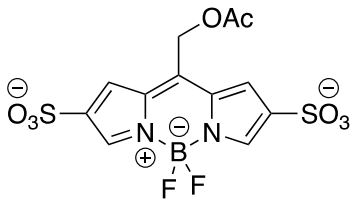
SCF Energy = -948.58973686



Triplet Scan uB3LYP/6-31+G(d,p) smd=water (Transition)

C	-1.04403100	3.39407400	-0.18997500
C	-2.09109700	2.53047300	0.25305700
C	-0.47320400	1.22775400	-0.50246800
C	0.19781800	0.00000200	-0.83091000
C	-0.47317600	-1.22776000	-0.50244600
C	-0.03471100	2.59031000	-0.66023600
C	1.45519600	0.00001100	-1.41119900
H	1.93049100	0.92281400	-1.71280400
O	2.96577400	0.00022300	0.55106400
H	1.93052100	-0.92279100	-1.71276200
C	-2.09104500	-2.53050200	0.25309300
C	-0.03465600	-2.59030900	-0.66019600
C	-1.04395900	-3.39408800	-0.18992300
B	-2.59972900	-0.00001900	0.41666100
F	-3.78540500	-0.00003700	-0.33247600
F	-2.91105400	-0.00001300	1.78342500
N	-1.73432300	-1.23951400	0.06121700
N	-1.73434900	1.23949000	0.06120000
C	4.22667700	0.00002100	0.33949400
O	4.76360900	-0.00020600	-0.80744700
C	5.11878200	0.00006900	1.57767000
H	6.17700600	-0.00015000	1.30829200
H	4.90040700	0.88253200	2.18839000
H	4.90011200	-0.88212100	2.18867700
H	-1.06954300	-4.47364700	-0.14751500
H	-1.06963800	4.47363400	-0.14758400
H	-3.04818900	2.78941800	0.68668700
H	0.91687700	2.89518000	-1.07081100
H	-3.04813300	-2.78946100	0.68672300
H	0.91693900	-2.89516500	-1.07076600

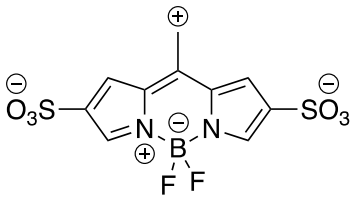
SCF Energy = -948.56471317



Triplet uB3LYP/6-31+G(d,p) smd=water

C	-3.38441500	-0.57062200	-0.09469400
C	-2.54684400	-1.68023200	0.18456900
C	-1.21548100	0.04760800	-0.28037400
C	-0.00055100	0.74661000	-0.48486300
C	1.20539500	0.03728900	-0.28250500
C	-2.57781600	0.51240400	-0.38284600
C	0.00567000	2.18657100	-0.86936700
H	-0.88151100	2.45767400	-1.44351800
O	0.01575500	2.99699900	0.35997000
H	0.89075700	2.44785000	-1.45119300
C	2.52585000	-1.70053200	0.18101600
C	2.57162800	0.49033500	-0.38392900
C	3.37113800	-0.60252000	-0.09523400
B	-0.01222800	-2.19677700	0.29857900
F	-0.02028600	-3.28318900	-0.60249700
F	-0.01411300	-2.71410200	1.61167200
N	1.22363400	-1.30210000	0.06668500
N	-1.24335000	-1.29085200	0.07009800
C	0.03494200	4.33505900	0.20588900
O	0.03755800	4.87585200	-0.89505700
C	0.05811900	5.05375600	1.52265100
H	0.02781500	6.13066300	1.35728900
H	-0.79647300	4.74434800	2.13182300
H	0.96934300	4.78870700	2.06854300
S	5.15595400	-0.64808700	-0.06564900
O	5.57534800	0.37291000	0.94542100
O	5.50667600	-2.04689300	0.33022900
O	5.59897300	-0.29896900	-1.45226200
S	-5.16732100	-0.61617400	-0.06462200
O	-5.53739400	-1.01097600	1.33144600
O	-5.60930800	0.76375500	-0.42682700
O	-5.55958300	-1.64878200	-1.07566000
H	-2.88334600	1.51642100	-0.63600800
H	-2.81483400	-2.69288000	0.45211000
H	2.78773500	-2.71419500	0.44795700
H	2.88111300	1.49424100	-0.63558400

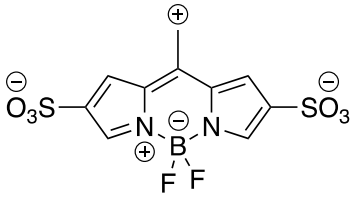
Sum of Electronic and Thermal Free Energies = -2195.213403



Triplet uB3LYP/6-31+G(d,p) smd=water

C	-3.38440700	0.17914900	-0.00234000
C	-2.52452000	-0.97238200	0.00514300
C	-1.23029600	0.81727500	-0.00092400
C	0.00001700	1.56228800	0.00022300
C	1.23030600	0.81722800	0.00122400
C	-2.58543800	1.29187200	-0.00598400
C	0.00005900	2.94339100	0.00036200
C	2.52448300	-0.97245700	-0.00517000
C	2.58547400	1.29178900	0.00630600
C	3.38439900	0.17903200	0.00251400
B	-0.00002100	-1.51561700	0.00025300
F	-0.00493800	-2.31000000	-1.14515100
F	0.00489200	-2.30937900	1.14611500
N	1.24454300	-0.56940300	-0.00480300
N	-1.24458700	-0.56939600	0.00481500
S	5.17114000	0.09906600	0.00009400
O	5.62947100	1.51155900	0.11881900
O	5.50983100	-0.75037500	1.18098900
O	5.52114000	-0.54166700	-1.30317700
S	-5.17114700	0.09905500	-0.00047900
O	-5.52168700	-0.54265800	1.30218200
O	-5.62948000	1.51164700	-0.11835400
O	-5.50922800	-0.74952300	-1.18213700
H	-2.89376400	2.32664700	-0.01295600
H	-2.79482700	-2.02061400	0.00873000
H	2.79468100	-2.02071800	-0.00881100
H	2.89385700	2.32654500	0.01329500
H	0.92726900	3.50363200	0.00180000
H	-0.92711200	3.50370000	-0.00062900

Sum of Electronic and Thermal Free Energies = -1966.568086

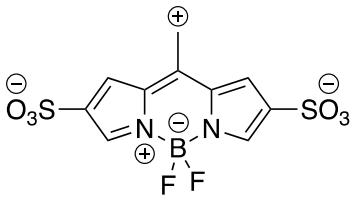


Singlet uB3LYP/6-31+G(d,p)

C	3.38466000	0.19179300	0.04455500
C	2.51536000	-0.95777800	0.01520800
C	1.25022600	0.84452100	-0.18170900
C	0.00000000	1.58272700	-0.28892000
C	-1.25022600	0.84452100	-0.18170900
C	2.57707700	1.30926600	-0.08433700
C	0.00000000	2.93153200	-0.46813500
C	-2.51536000	-0.95777800	0.01520800
C	-2.57707700	1.30926600	-0.08433700
C	-3.38466000	0.19179300	0.04455500
B	0.00000000	-1.48880300	-0.30452500
F	0.00000000	-2.48367800	0.65780300
F	0.00000000	-2.01128700	-1.59162500
N	-1.24694800	-0.55324100	-0.11642300
N	1.24694800	-0.55324100	-0.11642300
S	-5.15610500	0.08277700	0.22588000
O	-5.63400800	1.48129900	0.20281900
O	-5.52968700	-0.75080900	-0.95391500
O	-5.29199800	-0.62946800	1.52873700
S	5.15610500	0.08277700	0.22588000
O	5.52968700	-0.75080900	-0.95391600
O	5.63400800	1.48129900	0.20281900
O	5.29199800	-0.62946800	1.52873800
H	2.92147500	2.33233000	-0.08157200
H	2.78557100	-2.00250000	0.08116900
H	-2.78557100	-2.00250000	0.08116900
H	-2.92147500	2.33233000	-0.08157200
H	-0.92486500	3.48999300	-0.54748700
H	0.92486500	3.48999300	-0.54748700

Uncorrected Sum of Electronic and Thermal Free Energies = -1966.437785

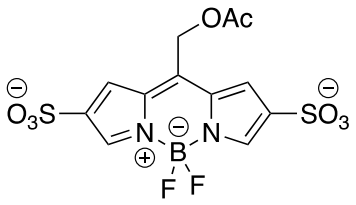
Corrected Sum of Electronic and Thermal Free Energies = -1966.437785



Triplet uB3LYP/6-31+G(d,p)

C	3.38786400	0.19487100	0.02345600
C	2.51837300	-0.95593200	0.01602600
C	1.24023900	0.84310800	-0.10954600
C	0.00000000	1.57585700	-0.16675000
C	-1.24023900	0.84310800	-0.10954600
C	2.57525100	1.30862400	-0.05920300
C	0.00000000	2.95392500	-0.25802200
C	-2.51837300	-0.95593200	0.01602600
C	-2.57525100	1.30862400	-0.05920300
C	-3.38786400	0.19487000	0.02345700
B	0.00000000	-1.50738000	-0.17435200
F	0.00000000	-2.42047200	0.86641300
F	0.00000000	-2.13461700	-1.41220200
N	-1.24705600	-0.55927600	-0.06113300
N	1.24705600	-0.55927600	-0.06113300
S	-5.16930900	0.08773400	0.12974800
O	-5.63663800	1.49013200	0.10141900
O	-5.49702500	-0.73121500	-1.07184300
O	-5.35662600	-0.63419200	1.42005300
S	5.16930900	0.08773400	0.12974800
O	5.49702600	-0.73121500	-1.07184300
O	5.63663800	1.49013200	0.10142000
O	5.35662500	-0.63419200	1.42005300
H	2.91835100	2.33212500	-0.06647400
H	2.79587800	-2.00024000	0.06085800
H	-2.79587800	-2.00024100	0.06085800
H	-2.91835100	2.33212500	-0.06647300
H	-0.92550000	3.51447900	-0.29760900
H	0.92550000	3.51447900	-0.29761000

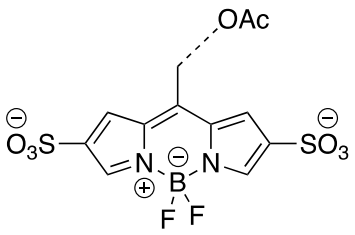
Sum of Electronic and Thermal Free Energies = -1966.444439



Triplet Scan uB3LYP/6-31+G(d,p) smd=water (Reactant)

C	-3.38441500	-0.57062200	-0.09469400
C	-2.54684400	-1.68023200	0.18456900
C	-1.21548100	0.04760800	-0.28037400
C	-0.00055100	0.74661000	-0.48486300
C	1.20539500	0.03728900	-0.28250500
C	-2.57781600	0.51240400	-0.38284600
C	0.00567000	2.18657100	-0.86936700
H	-0.88151100	2.45767400	-1.44351800
O	0.01575500	2.99699900	0.35997000
H	0.89075700	2.44785000	-1.45119300
C	2.52585000	-1.70053200	0.18101600
C	2.57162800	0.49033500	-0.38392900
C	3.37113800	-0.60252000	-0.09523400
B	-0.01222800	-2.19677700	0.29857900
F	-0.02028600	-3.28318900	-0.60249700
F	-0.01411300	-2.71410200	1.61167200
N	1.22363400	-1.30210000	0.06668500
N	-1.24335000	-1.29085200	0.07009800
C	0.03494200	4.33505900	0.20588900
O	0.03755800	4.87585200	-0.89505700
C	0.05811900	5.05375600	1.52265100
H	0.02781500	6.13066300	1.35728900
H	-0.79647300	4.74434800	2.13182300
H	0.96934300	4.78870700	2.06854300
S	5.15595400	-0.64808700	-0.06564900
O	5.57534800	0.37291000	0.94542100
O	5.50667600	-2.04689300	0.33022900
O	5.59897300	-0.29896900	-1.45226200
S	-5.16732100	-0.61617400	-0.06462200
O	-5.53739400	-1.01097600	1.33144600
O	-5.60930800	0.76375500	-0.42682700
O	-5.55958300	-1.64878200	-1.07566000
H	-2.88334600	1.51642100	-0.63600800
H	-2.81483400	-2.69288000	0.45211000
H	2.78773500	-2.71419500	0.44795700
H	2.88111300	1.49424100	-0.63558400

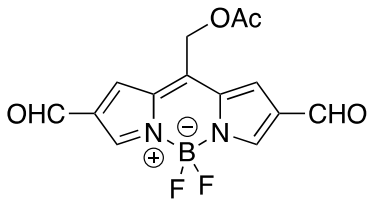
SCF Energy = -2195.37531762



Singlet Scan uB3LYP/6-31+G(d,p) smd=water (Transition)

C	-3.41723600	-0.56338100	-0.10558800
C	-2.57981300	-1.64557400	0.31606000
C	-1.25519100	-0.04998700	-0.45598400
C	-0.01598900	0.59008600	-0.80340700
C	1.19855500	-0.10863100	-0.48593300
C	-2.60097600	0.43080800	-0.58621200
C	0.00831400	1.84606100	-1.38784800
H	-0.90674100	2.34708600	-1.67173300
O	0.13047600	3.34992300	0.57087000
H	0.93730700	2.28994700	-1.71657500
C	2.46597200	-1.75505200	0.27572100
C	2.56208200	0.31301600	-0.63765100
C	3.34247100	-0.71424100	-0.16468400
B	-0.06799200	-2.23777600	0.39178800
F	-0.10610800	-3.36472100	-0.43622700
F	-0.06094400	-2.62885200	1.73213800
N	1.18925500	-1.37472200	0.07401300
N	-1.29175600	-1.31698000	0.10172600
C	0.22142300	4.61886500	0.33405100
O	0.25523600	5.15054500	-0.83476300
C	0.32618600	5.53939400	1.54960400
H	-0.23354200	6.46291600	1.37733600
H	-0.03071700	5.05225500	2.45972900
H	1.37980900	5.80822100	1.69140600
S	5.12644300	-0.76375600	-0.03649400
O	5.43945100	-0.23128500	1.32527000
O	5.47962800	-2.20616700	-0.19511700
O	5.62581100	0.10665100	-1.13996000
S	-5.20275900	-0.57949000	-0.02862000
O	-5.52561500	-0.94029200	1.38502400
O	-5.62815700	0.79643400	-0.41260100
O	-5.62006400	-1.63073100	-1.00665400
H	-2.89407000	1.39195000	-0.98147100
H	-2.86116500	-2.59831100	0.74528300
H	2.71389300	-2.71641600	0.70554500
H	2.88830200	1.25841900	-1.04533800

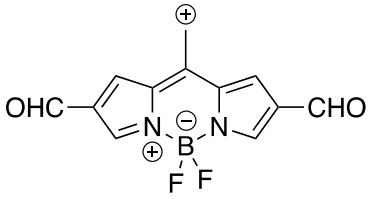
SCF Energy = -2195.34524488



Triplet uB3LYP/6-31+G(d,p) smd=water

C	-3.39041200	-0.86652600	-0.09040000
C	-2.53204600	-1.96055200	0.17348200
C	-1.21103400	-0.22469300	-0.28151700
C	-0.00004800	0.47853600	-0.48075600
C	1.21197800	-0.22283400	-0.28132300
C	-2.57535500	0.23214100	-0.37572700
C	-0.00116600	1.92130600	-0.86080800
H	-0.88735900	2.18619800	-1.43935300
O	-0.00274600	2.72262200	0.37086600
H	0.88524600	2.18784200	-1.43825200
C	2.53555500	-1.95672900	0.17378400
C	2.57562600	0.23601900	-0.37544800
C	3.39230300	-0.86143800	-0.09007600
B	0.00214200	-2.47360900	0.27723300
F	0.00307800	-3.53889300	-0.64237500
F	0.00238000	-3.00094800	1.58146900
N	1.23771300	-1.56588500	0.05910100
N	-1.23477800	-1.56778500	0.05885700
C	-0.00416500	4.06275800	0.22220400
O	-0.00375000	4.60633300	-0.87677100
C	-0.00622000	4.77544800	1.54200000
H	0.87679000	4.48567000	2.12006300
H	-0.00626500	5.85326900	1.38016700
H	-0.89090100	4.48527800	2.11733000
C	4.84468300	-0.93546300	-0.04884500
O	5.59161100	0.01952200	-0.27885100
H	5.26578400	-1.92218700	0.20728200
C	-4.84268300	-0.94270300	-0.04920300
O	-5.59103300	0.01117000	-0.27919000
H	-5.26230200	-1.93008100	0.20685800
H	-2.88501600	1.23787500	-0.61958100
H	-2.79183500	-2.97838300	0.43406300
H	2.88386200	1.24219300	-0.61929500
H	2.79685700	-2.97417400	0.43435600

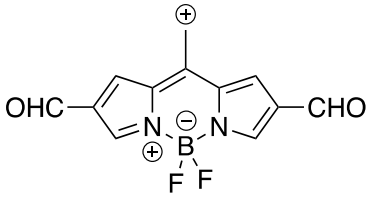
Sum of Electronic and Thermal Free Energies = -1175.073622



Triplet uB3LYP/6-31+G(d,p) smd=water

C	3.39648400	0.09480700	0.00008100
C	2.52778600	-1.04708900	-0.00001300
C	1.22972500	0.73772000	-0.00035900
C	0.00000000	1.48509800	-0.00036900
C	-1.22972500	0.73772000	-0.00035800
C	2.58799200	1.21159400	-0.00019100
C	0.00000000	2.86543600	-0.00025800
H	0.92747500	3.42543500	-0.00024500
H	-0.92747400	3.42543500	-0.00024500
C	-2.52778600	-1.04708900	-0.00001200
C	-2.58799200	1.21159400	-0.00019000
C	-3.39648400	0.09480700	0.00008300
B	0.00000000	-1.59232700	-0.00017200
F	0.00000000	-2.38340200	1.14598600
F	0.00000000	-2.38367100	-1.14611000
N	-1.24489600	-0.64467400	-0.00026100
N	1.24489600	-0.64467400	-0.00026200
C	-4.86303400	0.02569200	0.00047800
O	-5.58049000	1.02104100	0.00055600
H	-5.29658400	-0.98720200	0.00073100
C	4.86303400	0.02569200	0.00047600
O	5.58049000	1.02104100	0.00055900
H	5.29658400	-0.98720200	0.00073300
H	2.89529500	2.24738800	-0.00032800
H	2.79592500	-2.09652200	0.00009700
H	-2.89529500	2.24738800	-0.00032600
H	-2.79592500	-2.09652200	0.00009800

Sum of Electronic and Thermal Free Energies = -946.419947

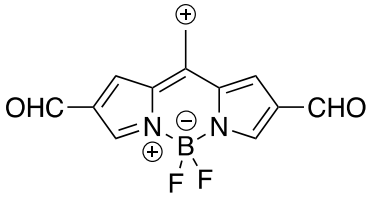


Singlet uB3LYP/6-31+G(d,p)

C	3.41387700	0.07567200	-0.05295400
C	2.53784800	-1.06501100	-0.05460900
C	1.24664700	0.71651700	0.03353600
C	0.00000000	1.45481300	0.07225600
C	-1.24664700	0.71651700	0.03354700
C	2.60503900	1.19015100	0.00457000
C	0.00000000	2.82131000	0.13812700
H	0.92225000	3.39080400	0.16811700
H	-0.92225100	3.39082100	0.16776700
C	-2.53784800	-1.06501200	-0.05460400
C	-2.60504000	1.19015100	0.00457900
C	-3.41387700	0.07567200	-0.05294100
B	0.00000000	-1.62815300	0.06655200
F	0.00000200	-2.28505200	1.27186000
F	-0.00000100	-2.46193700	-1.02217400
N	-1.25214700	-0.65766700	-0.00356200
N	1.25214700	-0.65766700	-0.00356500
C	-4.90012400	0.06442800	-0.10505200
O	-5.53965700	1.09454300	-0.09956900
H	-5.38664400	-0.92736100	-0.14854900
C	4.90012400	0.06442900	-0.10507300
O	5.53965800	1.09454300	-0.09955100
H	5.38664400	-0.92736100	-0.14853000
H	2.94530000	2.21623100	0.01717700
H	2.78641100	-2.11943100	-0.08926700
H	-2.94530000	2.21623100	0.01718400
H	-2.78641100	-2.11943100	-0.08926200

Uncorrected Sum of Electronic and Thermal Free Energies = -946.306880

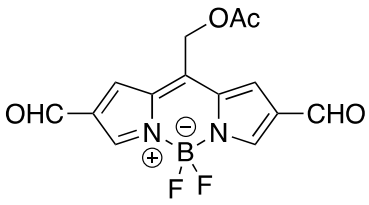
Corrected Sum of Electronic and Thermal Free Energies = -946.305635



Triplet uB3LYP/6-31+G(d,p)

C	3.40200100	0.08048700	-0.07973900
C	2.52326400	-1.06787700	-0.07912200
C	1.23637300	0.71686900	0.05205100
C	0.00000000	1.45833200	0.11364000
C	-1.23637300	0.71686900	0.05205500
C	2.59317000	1.19015500	0.00523500
C	0.00000000	2.83767100	0.21380300
H	0.92256200	3.40371900	0.25844900
H	-0.92256200	3.40371900	0.25845200
C	-2.52326400	-1.06787700	-0.07911500
C	-2.59317000	1.19015500	0.00524300
C	-3.40200200	0.08048700	-0.07972900
B	0.00000000	-1.63878200	0.10024100
F	0.00000200	-2.25235100	1.32812500
F	-0.00000100	-2.50899000	-0.95900600
N	-1.24778900	-0.66835400	-0.00258800
N	1.24778900	-0.66835400	-0.00259100
C	-4.88752600	0.06939100	-0.16005000
O	-5.52605000	1.10005800	-0.15403800
H	-5.37349300	-0.92139300	-0.22486300
C	4.88752500	0.06939100	-0.16006500
O	5.52605100	1.10005700	-0.15401900
H	5.37349400	-0.92139400	-0.22484800
H	2.92976700	2.21724600	0.02133300
H	2.77704400	-2.12073000	-0.12884100
H	-2.92976800	2.21724600	0.02134200
H	-2.77704500	-2.12073000	-0.12883300

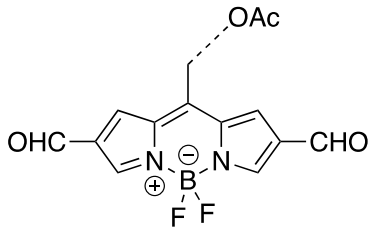
Sum of Electronic and Thermal Free Energies = -946.311270



Triplet Scan uB3LYP/6-31+G(d,p) smd=water (Reactant)

C	-3.39041200	-0.86652600	-0.09040000
C	-2.53204600	-1.96055200	0.17348200
C	-1.21103400	-0.22469300	-0.28151700
C	-0.00004800	0.47853600	-0.48075600
C	1.21197800	-0.22283400	-0.28132300
C	-2.57535500	0.23214100	-0.37572700
C	-0.00116600	1.92130600	-0.86080800
H	-0.88735900	2.18619800	-1.43935300
O	-0.00274600	2.72262200	0.37086600
H	0.88524600	2.18784200	-1.43825200
C	2.53555500	-1.95672900	0.17378400
C	2.57562600	0.23601900	-0.37544800
C	3.39230300	-0.86143800	-0.09007600
B	0.00214200	-2.47360900	0.27723300
F	0.00307800	-3.53889300	-0.64237500
F	0.00238000	-3.00094800	1.58146900
N	1.23771300	-1.56588500	0.05910100
N	-1.23477800	-1.56778500	0.05885700
C	-0.00416500	4.06275800	0.22220400
O	-0.00375000	4.60633300	-0.87677100
C	-0.00622000	4.77544800	1.54200000
H	0.87679000	4.48567000	2.12006300
H	-0.00626500	5.85326900	1.38016700
H	-0.89090100	4.48527800	2.11733000
C	4.84468300	-0.93546300	-0.04884500
O	5.59161100	0.01952200	-0.27885100
H	5.26578400	-1.92218700	0.20728200
C	-4.84268300	-0.94270300	-0.04920300
O	-5.59103300	0.01117000	-0.27919000
H	-5.26230200	-1.93008100	0.20685800
H	-2.88501600	1.23787500	-0.61958100
H	-2.79183500	-2.97838300	0.43406300
H	2.88386200	1.24219300	-0.61929500
H	2.79685700	-2.97417400	0.43435600

SCF Energy = -1175.25673511



Triplet Scan uB3LYP/6-31+G(d,p) smd=water (Transition)

C	-3.50358100	-0.61026300	-0.15429200
C	-2.75144300	-1.69583100	0.40299800
C	-1.29008600	-0.31675300	-0.51278100
C	0.00262000	0.18003300	-0.90131400
C	1.15220600	-0.59939600	-0.52589300
C	-2.59294900	0.25410600	-0.72669100
C	0.13613300	1.36637200	-1.59550900
H	-0.72873400	1.94650600	-1.89097400
O	0.34416200	3.34214300	0.74420400
H	1.10978200	1.73735300	-1.88921300
C	2.26962700	-2.27681000	0.37586100
C	2.54898400	-0.33865700	-0.75092400
C	3.24405100	-1.38776500	-0.18500900
B	-0.29675300	-2.47226500	0.62832200
F	-0.44516000	-3.71060600	0.00667200
F	-0.30524800	-2.61495700	2.01401300
N	1.03255900	-1.79173000	0.16338600
N	-1.43868000	-1.50352200	0.18027700
C	0.55860300	4.56607700	0.46373900
O	0.57394100	5.03995500	-0.71647800
C	0.85100600	5.51554900	1.62242600
H	1.93069900	5.50453800	1.81611500
H	0.56301100	6.54061900	1.37606500
H	0.34323500	5.19542100	2.53579300
C	4.69463900	-1.60172100	-0.13017300
O	5.50798800	-0.82548500	-0.62258200
H	5.02548300	-2.51593200	0.38885400
C	-4.96544200	-0.49629700	-0.10085300
O	-5.58507400	0.44147600	-0.59400900
H	-5.49177200	-1.31536800	0.41516500
H	-2.80038400	1.18221700	-1.23993100
H	-3.11707000	-2.56673500	0.93314800
H	2.95883100	0.52094100	-1.26158000
H	2.43285500	-3.20797200	0.90454400

SCF Energy = -1175.22001504

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