Supporting Information

Exploring the Relationship Between Structure and Activity in BODIPYs Designed for Antimicrobial Phototherapy

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1. X-ray crystallography

Table S1: Details of XRD data refinement for compound **11a** and **29**

Compound	**KJF202 (11a)**	**CJK009 (29)**
Empirical formula	$C_{18}H_{13}BF_2N_4O_2$	$C_{21}H_{20}BF_6N_3O$
Formula weight	366.13	455.21 g/mol
Temperature/K	100(2)	100(2)
Crystal system	Triclinic	orthorhombic
Space group	$P\bar{1}$	P *c a* 2_1
a/Å	7.6304(2)	27.747(3)
b/Å	9.5936(2)	9.3839(9)
c/Å	11.6142(3)	7.7982(8)
α/°	110.5569(10)	90
β/°	92.1349(11)	90
γ/°	98.3717(10)	90
Volume/Å^3	783.98(3)	2030.5(3)
Z	2	4
ρ_{calc}g/cm^3	1.551	1.489
μ/mm^{-1}	0.119	0.130
F(000)	376.0	936
Crystal size/mm^3	0.373×0.325×0.234	0.068×0.256×0.290
Radiation	MoK_α	MoK_α
Wavelength/Å	λ = 0.71073	λ = 0.71073
2ϑ/°	3.762–55.800	4.34–59.96
Reflections collected	98665	25995
Independent reflections	3744	5645
R_{int}	0.0214	0.0508
R_{sigma}	0.0062	0.0487
Restraints	1	1
Parameters	252	299
GooF	1.072	1.028
R_1 [I>=2σ (I)]	0.0310	0.0498
wR_2 [I>=2σ (I)]	0.0824	0.0861
R_1 [all data]	0.0328	0.0649
wR_2 [all data]	0.0845	0.0895
Largest peak/e Å^{-3}	0.367	0.286
Deepest hole/ e Å^{-3}	-0.212	-0.361

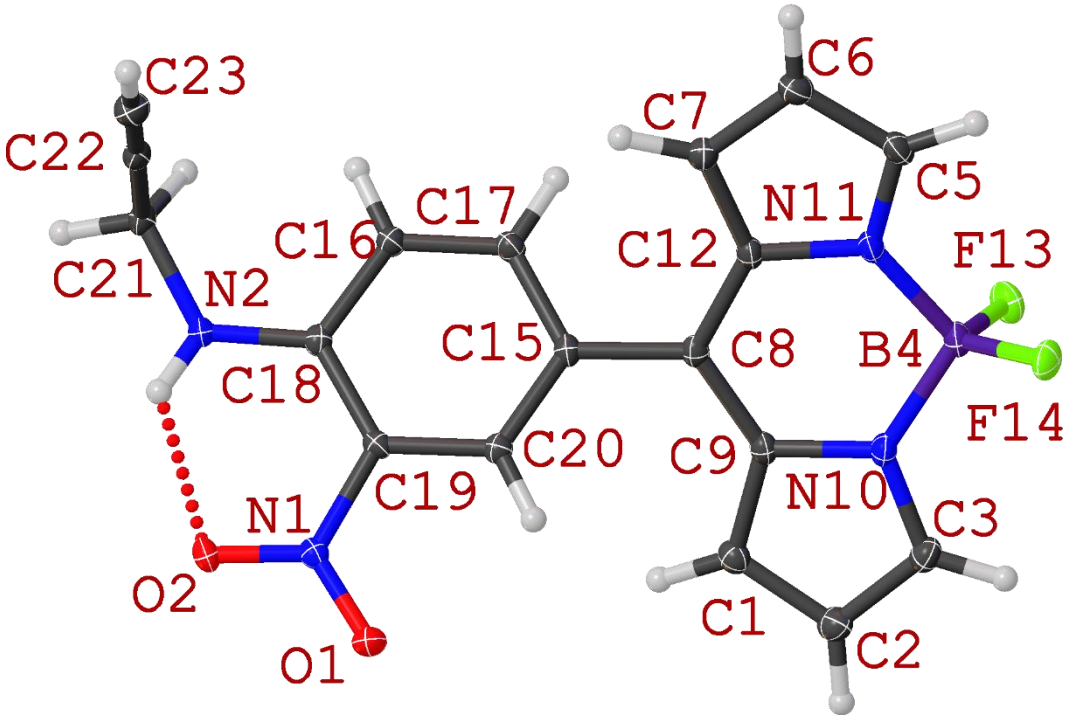

Figure S1: View of the molecular structure of **KJF202/11a** in the crystal (thermal displacement 50%).

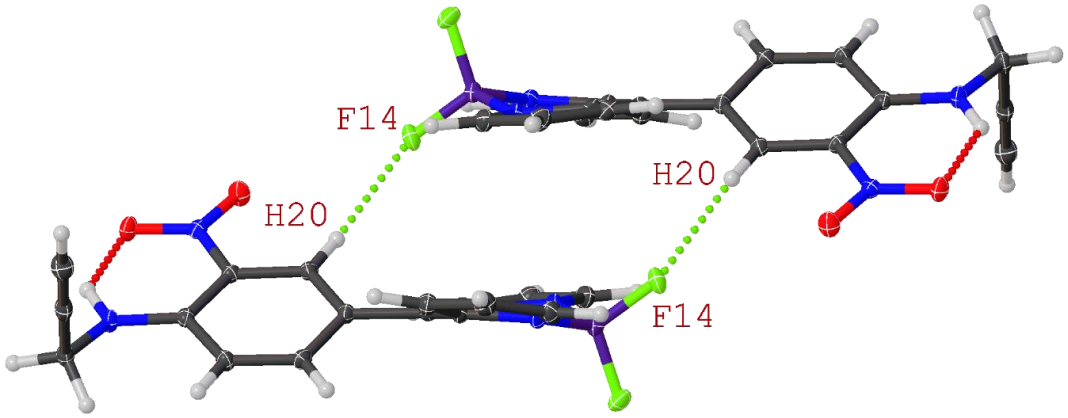

Figure S2: Expanded structure of **KJF202/11a** showing the interaction between C(20)–H(20)···F(14) [2.395(7) Å, 161.3(6)°] and the resultant stacking interaction between the BODIPY core [centroid to centroid distance of 4.332(7) Å and plane-to-plane shift of 2.514(9) Å] (thermal displacement 50%).

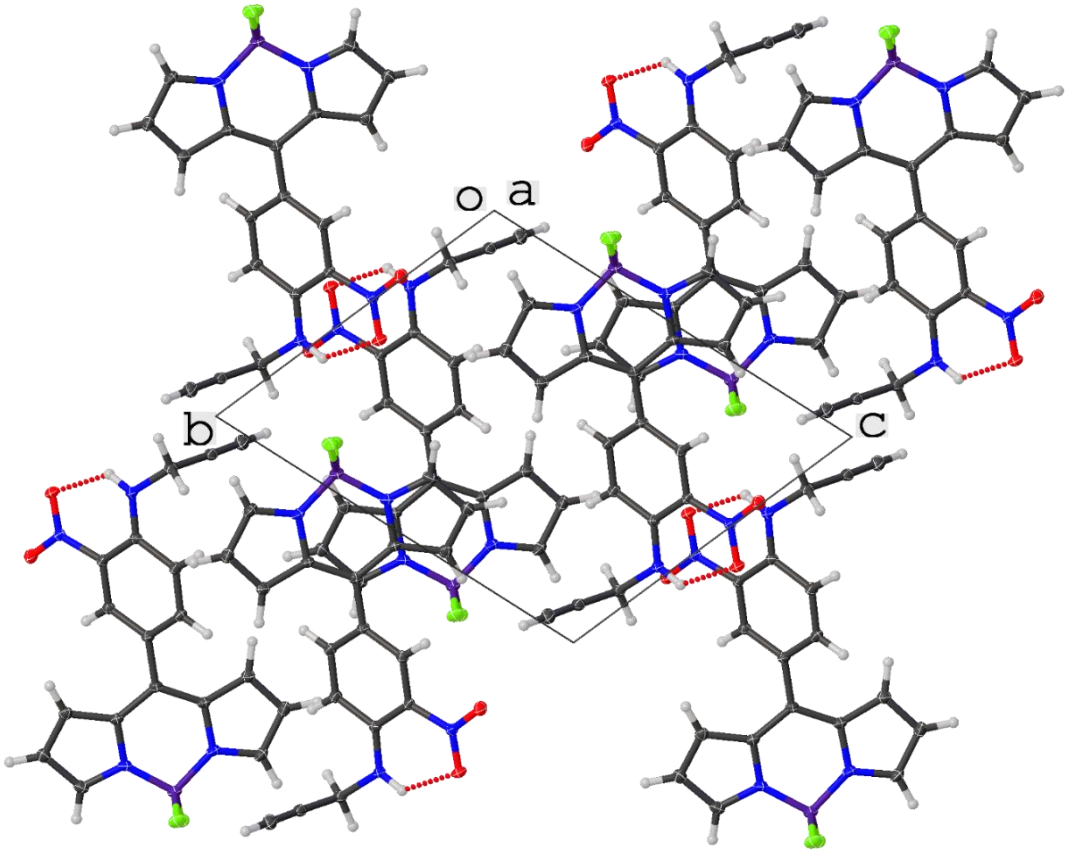

Figure S3: Moiety packing of **KJF202/11a** looking down the *a*-axis (thermal displacement 50%).

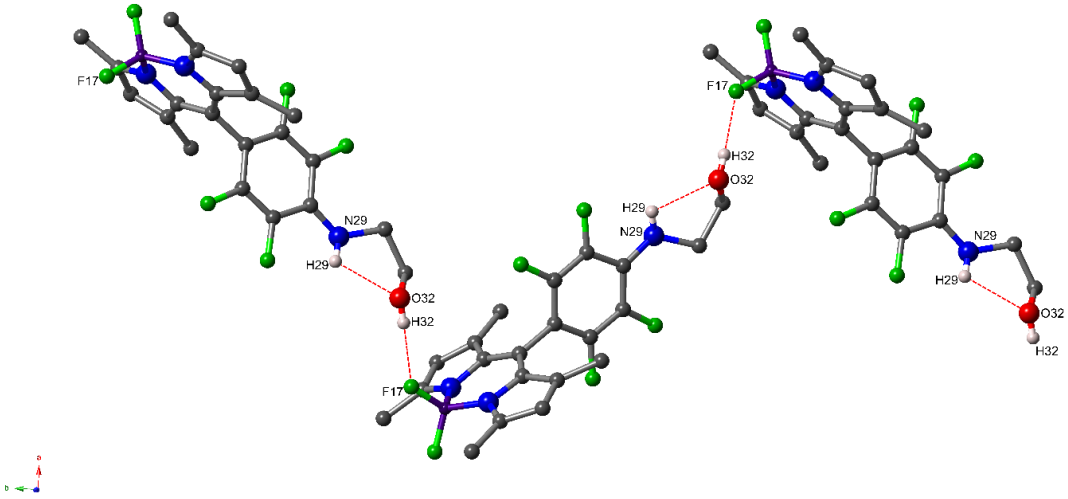

Figure S4: The intra- and inter-molecular hydrogen bonding in the crystal structure of **29**. Observed intramolecular O–H···F interactions (2.799(3) Å O···F, 171(4)°) form supramolecular chains in two directions, each parallel with the crystallographic *bc*- plane. H-atoms not involved in hydrogen-bonding are omitted for clarity; atoms are represented as spheres.

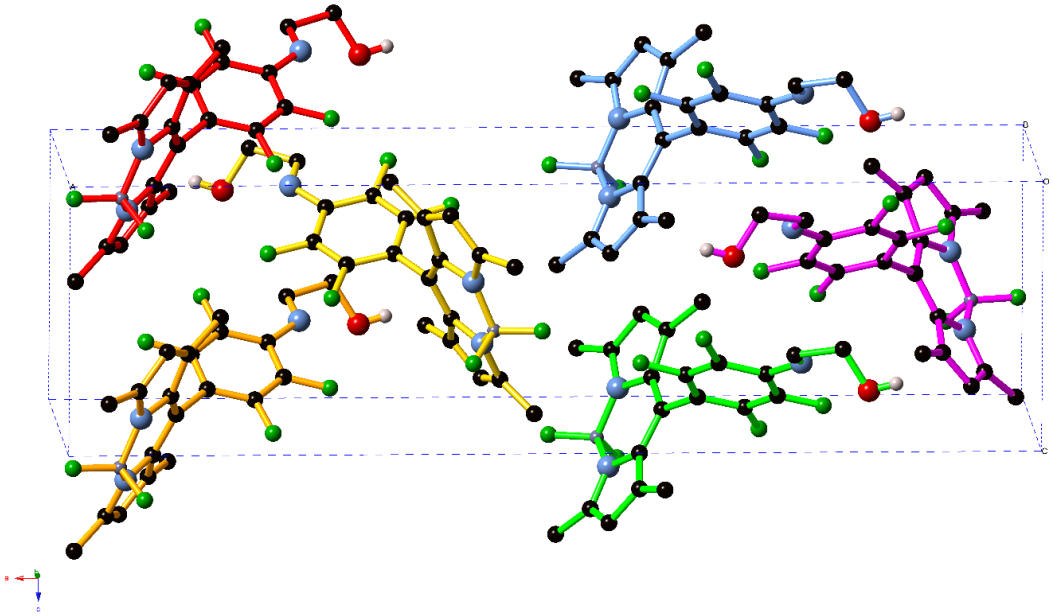

Figure S5: a packing diagram of molecules which are resident or partially resident in the unit cell of **29** (Z = 4). The unit cell is indicated in blue dashed lines; colours of bonds within each identical molecule are different as a visual aid.

Experimental

Crystals were grown following the protocol developed by Hope by dissolving the compound in CH_2Cl_2 and layering with MeOH for liquid-liquid diffusion.[1] Single crystal X-ray diffraction data for all compounds were collected on a Bruker APEX 2 DUO CCD diffractometer by using graphite-monochromated MoK_α (λ = 0.71073 Å) radiation. Crystals were mounted on a MiTeGen MicroMount and collected at 100(2) K by using an Oxford Cryosystems Cobra low-temperature device. Data were collected by using omega and phi scans and were corrected for Lorentz and polarization effects by using the APEX software suite.[2] The structure was solved with the XT structure solution program, using the intrinsic phasing solution method and refined against |F2| with XL using least-squares minimization, using the Olex2 and ShelXle graphical interfaces.[3] Hydrogen atoms were generally placed in geometrically calculated positions and refined using a riding model unless otherwise stated. All images were rendered using Olex2.[3a] Details of data refinements can found in tables S1 in the supporting information. **Refinement details for KJF202**: The hydrogen attached to N2 (H2) was allowed to freely refine. The distance of this bond was fixed using the DFIX restraint at 0.88 (0.01) Å. **Refinement details for CJK009**: N- and O-bound H atoms were allowed to freely refine, with riding isotropic thermal parameters.

CCDC 1975111 (for CJK009) and 1975112 (for KJF202) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

2. General remarks

All reactions were performed in standard round bottom flasks. DCM, *n*-pentane, and methanol were purchased and used as received. Other solvents were purchased and distilled at reduced pressure. Purchased chemicals were used as received without further purification. All liquid reagents were added through syringes. Reactions were monitored by thin-layer chromatography (Merck, TLC Silica gel 60 F_{254} and visualized under UV light (254 nm and 366 nm). Flash column chromatography was performed on silica gel (Fluka silica gel 60M, 40-63µm). NMR spectra were recorded with JEOL ECX400, JEOL ECP500, JEOL ECZ600, and Bruker Avance700 Instruments. Multiplicity of the signals was assigned as follows: s = singlet, br s = broad singlet, d = doublet, t = triplet, dd = doublet of doublets, dt = doublet of triplets, tt = triplet of triplets, ddd = doublet of doublets of doublets, ddt = doublet of doublets of triplets, m = multiplet, m_c = centered multiplet. Chemical shifts are reported relative to $CDCl_3$ (^{1}H: δ = 7.26 ppm, ^{13}C: δ = 77.2 ppm), THF-d_8 (^{1}H: δ = 3.58 ppm, ^{13}C: δ = 67.6 ppm), DMSO-d_6 (^{1}H: δ = 2.50 ppm, ^{13}C: δ = 39.5 ppm). All ^{13}C NMR spectra are proton-decoupled and coupling constants are given in hertz (Hz). For a detailed peak assignment 2D spectra were measured (COSY, HMBC, and HMQC). HRMS analyses were carried out on an Agilent Technologies 6210 ESI-TOF (electrospray ionization, time of flight) instrument. IR spectra were measured with a JASCO FT/IR 4100 spectrometer equipped with a PIKE MIRacle™ ATR instrument. UV/Vis spectra were recorded on a SPECORD S300 UV/Vis spectrometer (Analytic Jena) in quartz cuvettes (1 cm length). The fluorescence spectra of the BODIPYs were recorded with a JASCO FP 6500 spectrofluorometer in quartz cuvettes (1 cm length). Specified melting points were recorded on a Reichert Thermovar Apparatus and are not corrected.
Compounds **1, 3** – **12**, **1a, 3a**, **4a**, **6a** – **12a**, **25** and **27** were prepared according to the literature. [4,5]

3. Antibacterial testing

The bacterium *S. aureus* is a typical Gram-positive member of the microflora. Cultured bacterial cells of *S. aureus* ATCC25923 (WDCM 00034) are suspended in sterile phosphate-buffered saline (PBS) or sterile PBS supplemented with 10% sterile horse blood serum. The bacterial suspensions are placed into sterile black well plates with clear bottoms. Concentrations of the BODIPYs used in the study were as follows: 100 µM, 10 µM and 1 µM. After an incubation time period of 30 minutes, the samples are exposed to white light (KL 2500 LCD; Schott), with a power density and irradiation time resulting in an energy fluency of about 100 J/cm². After irradiation, the samples are removed and suspended again in the culture media. The numbers of colony-forming units (CFU/ml) are enumerated after an adequate incubation time period. Control plates contained no BODIPY and are not exposed to white light. The

control samples for dark toxicity are only exposed to BODIPY without any illumination. In an additional control experiment the bacterial suspension was subjected to white light illumination only (Figure S15). In the same way as described above the experiments with the Gram-negative bacterium P. aeruginosa ATCC 27853 (WDCM 00025) were performed.

The following figures show the antibacterial activity of the BODIPYs (**5a** – **7a**, **10a**, **52**, and **54**), the 1,3,5,7-tetramethyl substituted BODIPYs (**33**, **44**, and **48**), and the related monobrominated (**17**, **18**, **21**, and **22**) and dibrominated conjugates (**34**, **38**, **42**, **46**, and **50**), which are not shown in the main article.

3.1 Antibacterial activity in PBS

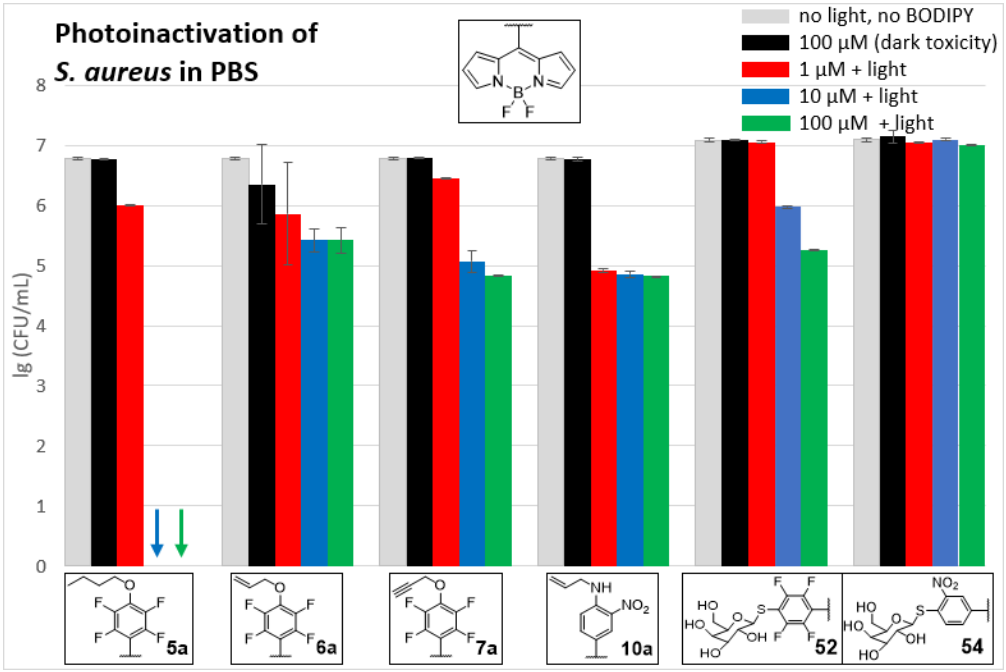

Figure S6: Photoinactivation of *S. aureus* by BODIPYs with a non-functionalized core structure (30 min incubation and radiation with white light) in phosphate-buffered saline (PBS). The antibacterial toxicity is expressed as logarithm of the number of colony-forming units, lg (CFU mL^{-1}). "↓" indicates suppression of bacterial growth below the detection limit.

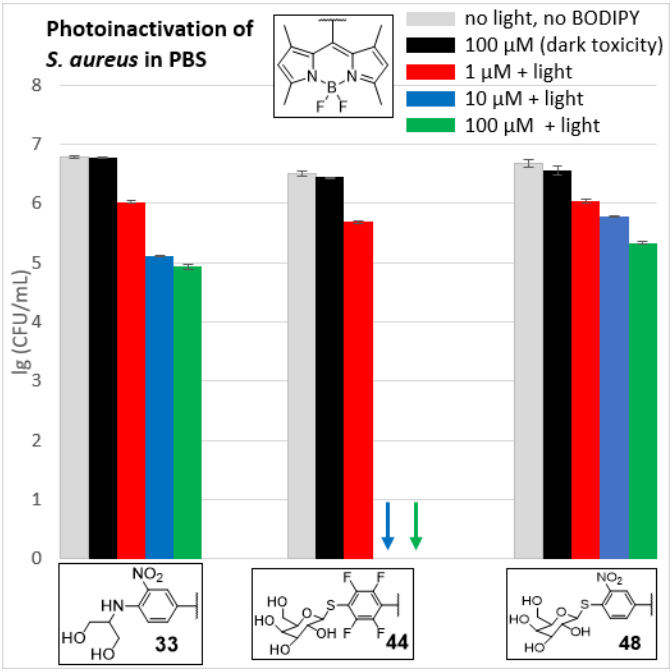

Figure S7: Photoinactivation of *S. aureus* by 1,3,5,7-tetramethyl substituted BODIPYs (30 min incubation and radiation with white light) in phosphate-buffered saline (PBS). The antibacterial toxicity is expressed as logarithm of the number of colony-forming units, lg (CFU mL^{-1}). "↓" indicates suppression of bacterial growth below the detection limit.

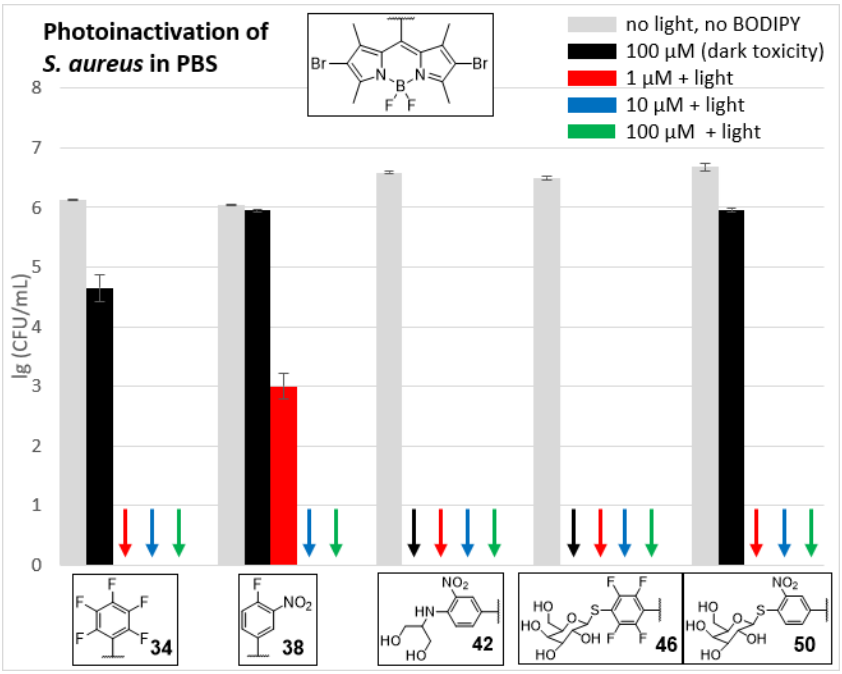

Figure S8: Photoinactivation of *S. aureus* by 2,6-dibromo-substituted BODIPYs (30 min incubation and radiation with white light) in phosphate-buffered saline (PBS). The antibacterial toxicity is expressed as logarithm of the number of colony-forming units, lg (CFU mL^{-1}). "↓" indicates suppression of bacterial growth below the detection limit.

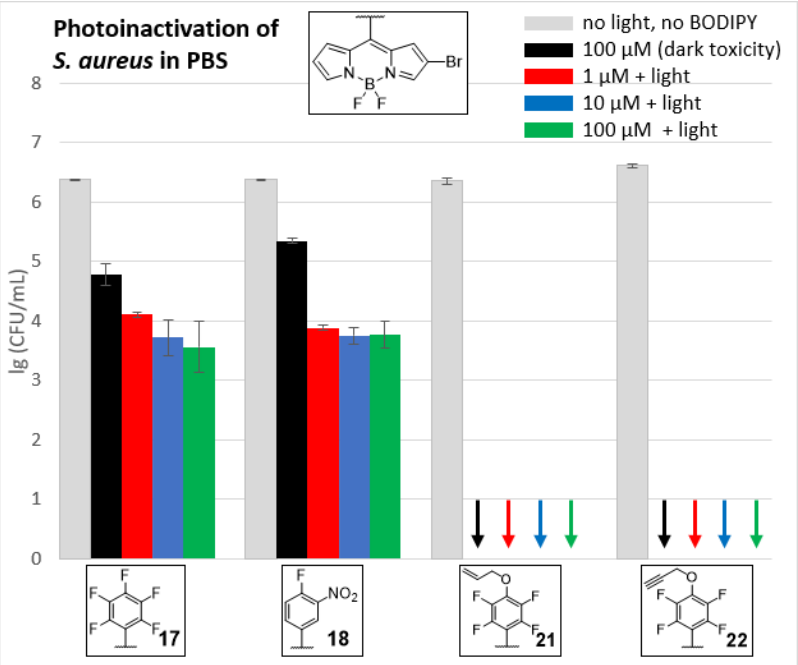

Figure S9: Photoinactivation of *S. aureus* by 2-bromo-substituted BODIPYs (30 min incubation and radiation with white light) in phosphate-buffered saline (PBS). The antibacterial toxicity is expressed as logarithm of the number of colony-forming units, lg (CFU mL^{-1}). "↓" indicates suppression of bacterial growth below the detection limit.

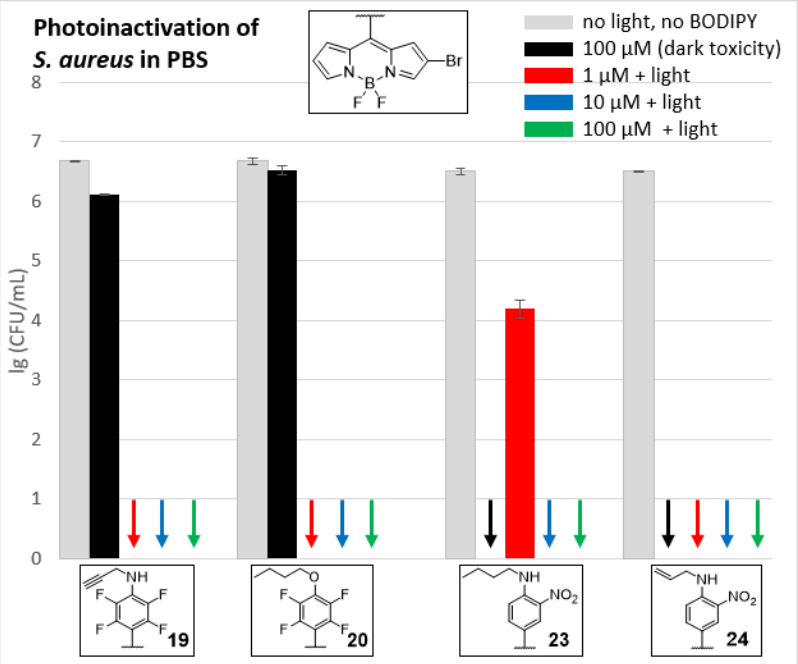

Figure S10: Photoinactivation of *S. aureus* by 2-bromo-substituted BODIPYs (30 min incubation and radiation with white light) in phosphate-buffered saline (PBS). The antibacterial toxicity is expressed as logarithm of the number of colony-forming units, lg (CFU mL^{-1}). "↓" indicates suppression of bacterial growth below the detection limit.

3.2 Antibacterial activity in PBS supplemented by 10% serum

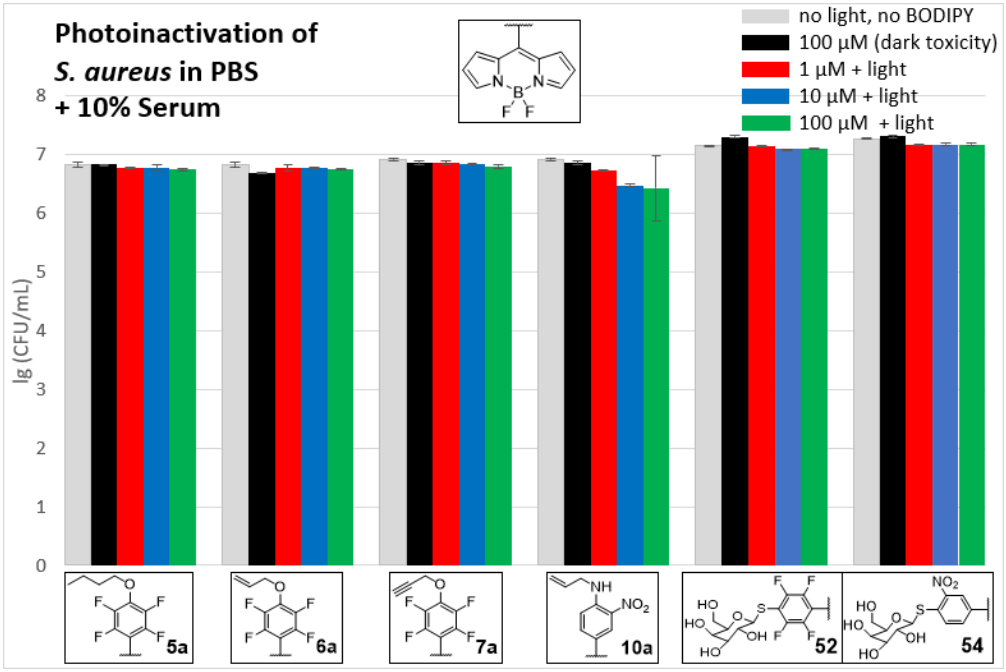

Figure S11: Photoinactivation of *S. aureus* by BODIPYs with a non-functionalized core structure (30 min incubation and radiation with white light) in phosphate-buffered saline (PBS) with 10% serum. The antibacterial toxicity is expressed as logarithm of the number of colony-forming units, lg (CFU mL^{-1}).

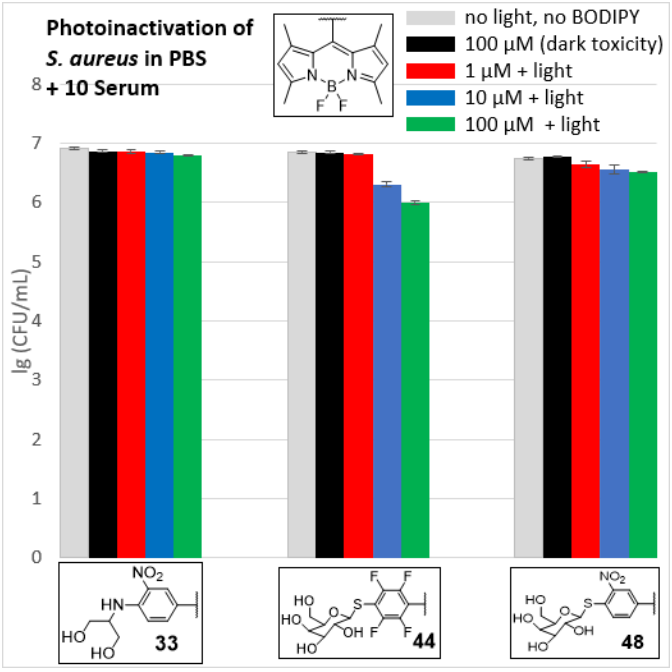

Figure S12: Photoinactivation of *S. aureus* by 1,3,5,7-tetramethyl substituted BODIPYs (30 min incubation and radiation with white light) in phosphate-buffered saline (PBS) with 10% serum. The antibacterial toxicity is expressed as logarithm of the number of colony-forming units, lg (CFU mL^{-1}).

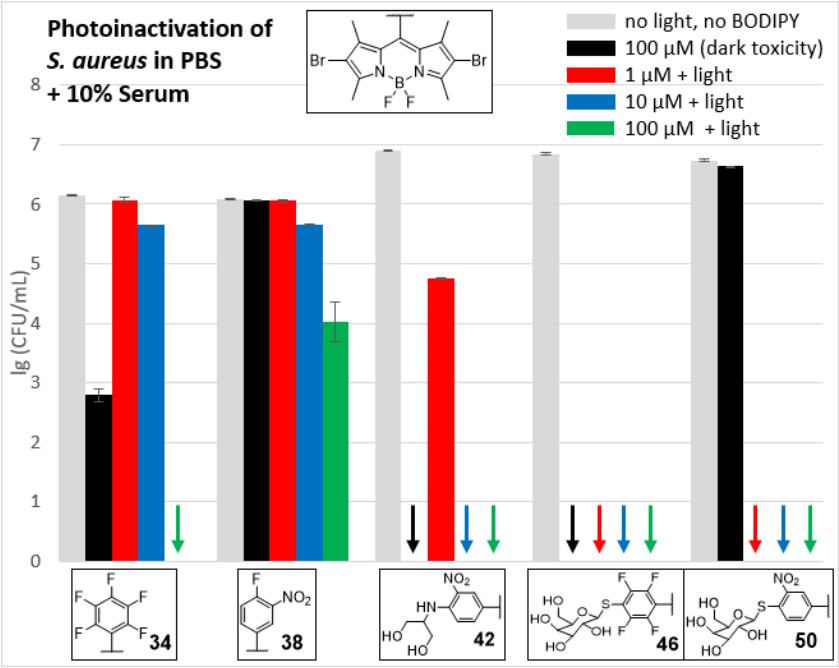

Figure S13: Photoinactivation of *S. aureus* by 2,6-dibromo-substituted BODIPYs (30 min incubation and radiation with white light) in phosphate-buffered saline (PBS) with 10% serum. The antibacterial toxicity is expressed as logarithm of the number of colony-forming units, lg (CFU mL^{-1}). "↓" indicates suppression of bacterial growth below the detection limit.

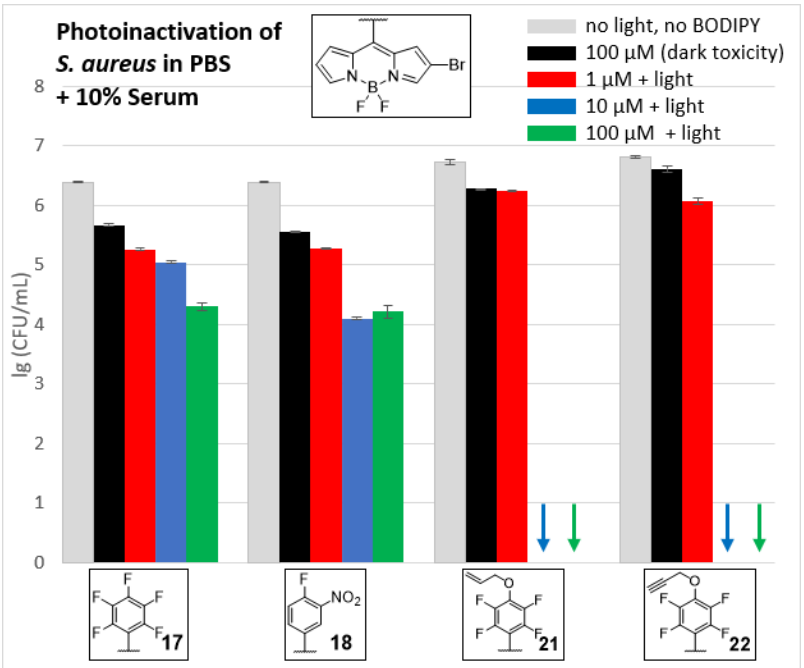

Figure S14: Photoinactivation of *S. aureus* by 2-bromo-substituted BODIPYs (30 min incubation and radiation with white light) in phosphate-buffered saline (PBS) with 10% serum. The antibacterial toxicity is expressed as logarithm of the number of colony-forming units, lg (CFU mL^{-1}). "↓" indicates suppression of bacterial growth below the detection limit.

3.3 Effect of light on *S. aureus* and *P. aeruginosa*

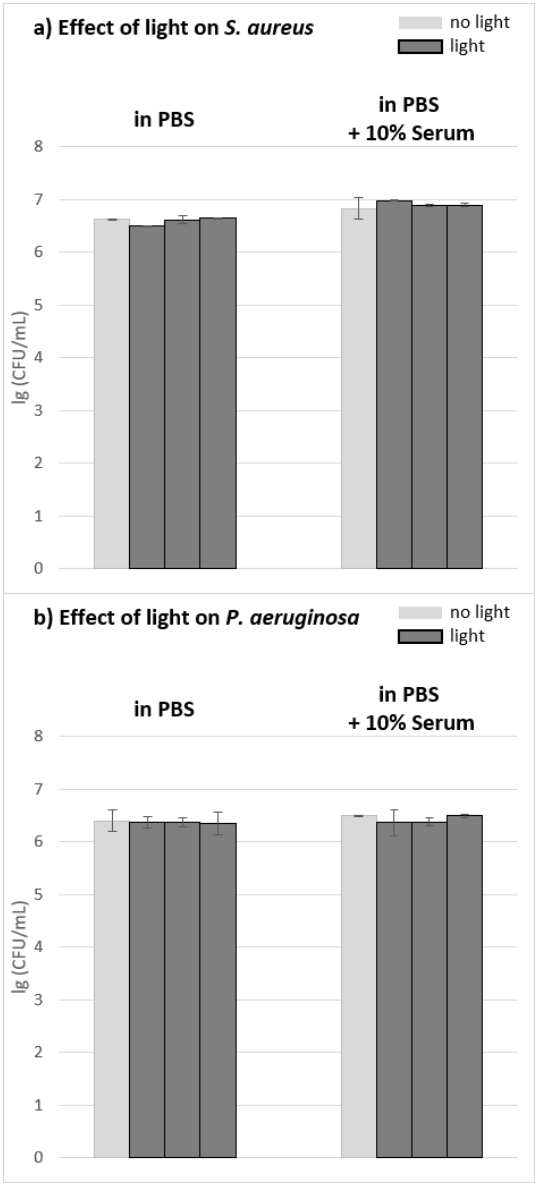

Figure S15: Control Experiment for the effect of light on the bacteria *S. aureus* (a) and *P. aeruginosa* (b). The experiments with light were performed in triplicate.

4. Preparation of 5-[4-(*N*-butylamino)-2,3,5,6-tetrafluorophenyl]-dipyrromethane (2)

5-Pentafluorophenyldipyrromethane (2.00 g, 6.40 mmol, 1 eq.) was dissolved in 10 mL of DMSO and *n*-butylamine (7.00 mL, 128.00 mmol, 20 eq.) was added. The mixture was stirred for 24 h at 80°C. Afterwards, the reaction mixture was diluted with EtOAc and washed with water several times. The

organic layer was dried with Na_2SO_4, filtrated, and evaporated to dryness. After column chromatography (silica gel, DCM) dipyrromethane **2** was obtained as a yellow oil (1.90 g, 5.19 mmol, 81 %).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 0.96 (t, J = 7.3 Hz, 3H, Me), 1.37–1.46 (m, 2H, CH_2), 1.54–1.62 (m, 2H, CH_2), 3.36–3.41 (m, 2H, CH_2), 3.74 (s, 1H, NH), 5.80 (s, 1H, CH), 6.04 (s, 2H, $H_{pyrrole}$), 6.15–6.17 (m, 2H, $H_{pyrrole}$), 6.69–6.71 (m, 2H, $H_{pyrrole}$), 8.11 (br s, 2H, NH).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 13.9 (Me), 19.9 (CH_2), 32.8 (CH), 32.95 (CH_2), 45.8 (CH_2), 107.3 ($C_{pyrrole}$), 108.5 ($C_{pyrrole}$), 117.8 ($C_{pyrrole}$), 127.3–127.5 (Ar-C_{para}), 129.8 ($C_{pyrrole}$), 137.7 (dd, J = 242.3, 20.3 Hz, Ar-C_{meta}), 145. (d, J = 241.4 Hz, Ar-C_{ortho}).

^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) = -144.60 (d, J = 19.8 Hz, CF_{meta}), -159.63 (d, J = 14.7 Hz, CF_{ortho}).

HRMS (ESI-TOF): *m/z* calcd. for $C_{19}H_{18}F_4N_3^+$ [dipyrrin+H]$^+$: 364.1431, found: 364.1424. Under the conditions of the ESI measurement, the dipyrromethane was oxidized to the corresponding dipyrromethene (dipyrrin).

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3384 [ν(NH)], 2958 and 2931 [ν(CH_2), ν(Me)], 2873 [ν(CH)], 1656 [ν(C=N)], 1499 [δ(CH_2), δ(Me)], 716 [δ(-HC= CH-)].

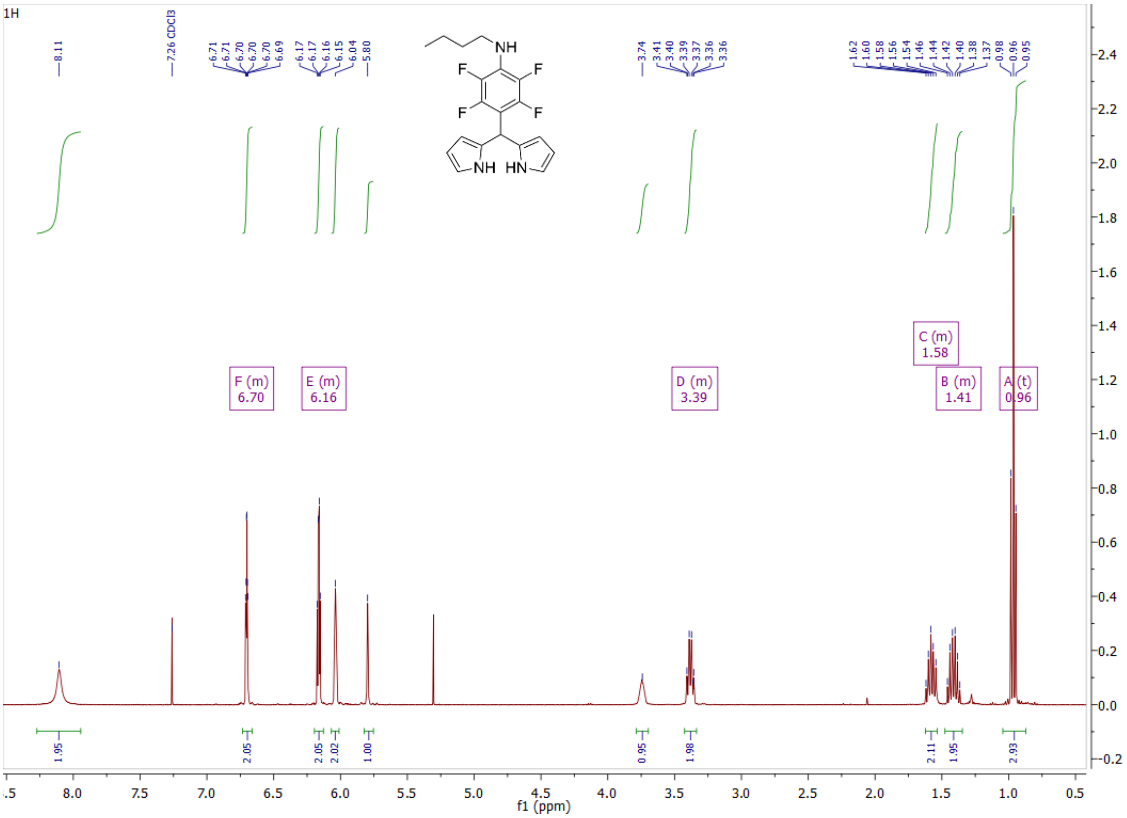

Figure S16: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of dipyrromethane **2**.

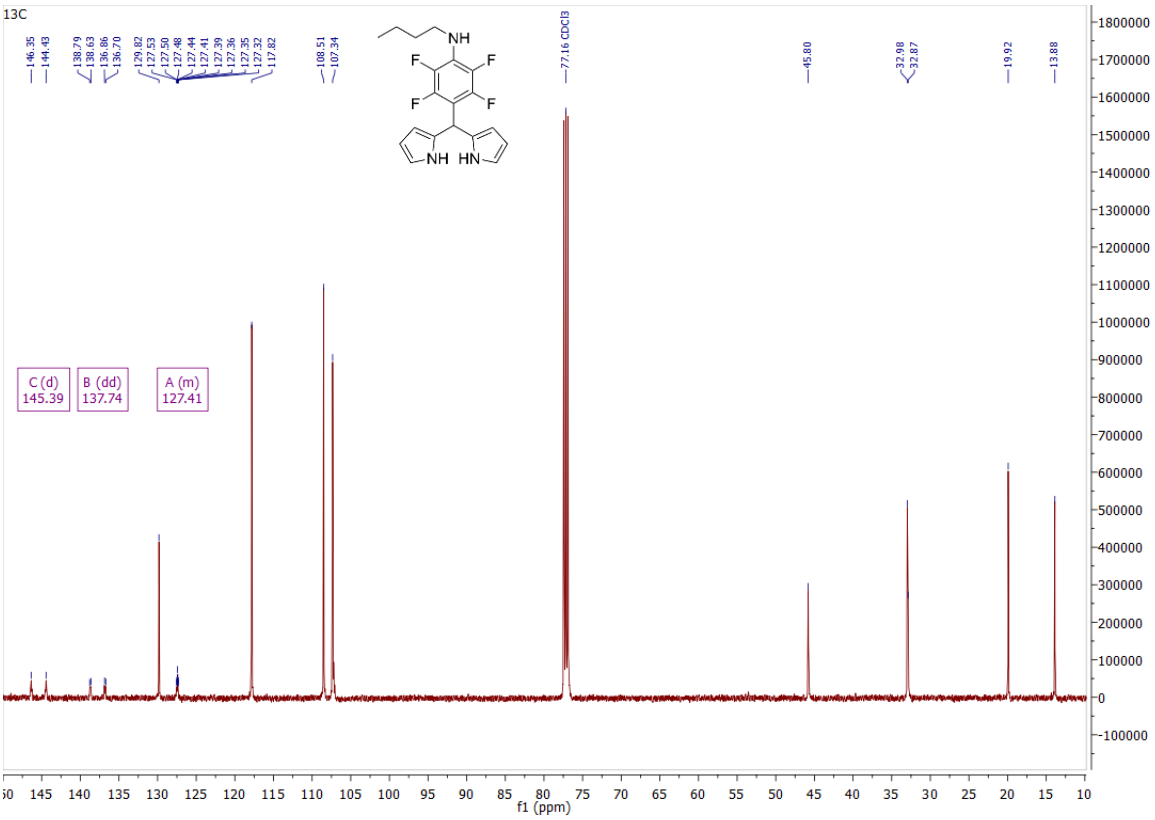

Figure S17: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of dipyrromethane **2**.

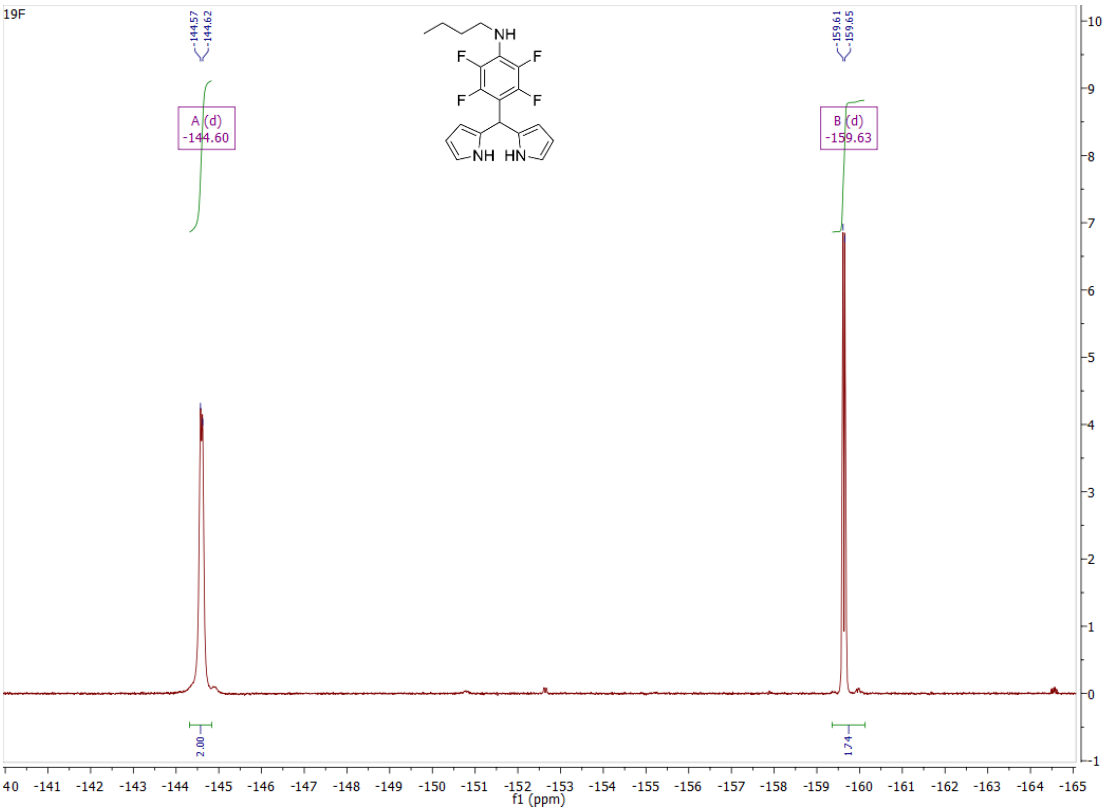

Figure S18: ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of dipyrromethane **2**.

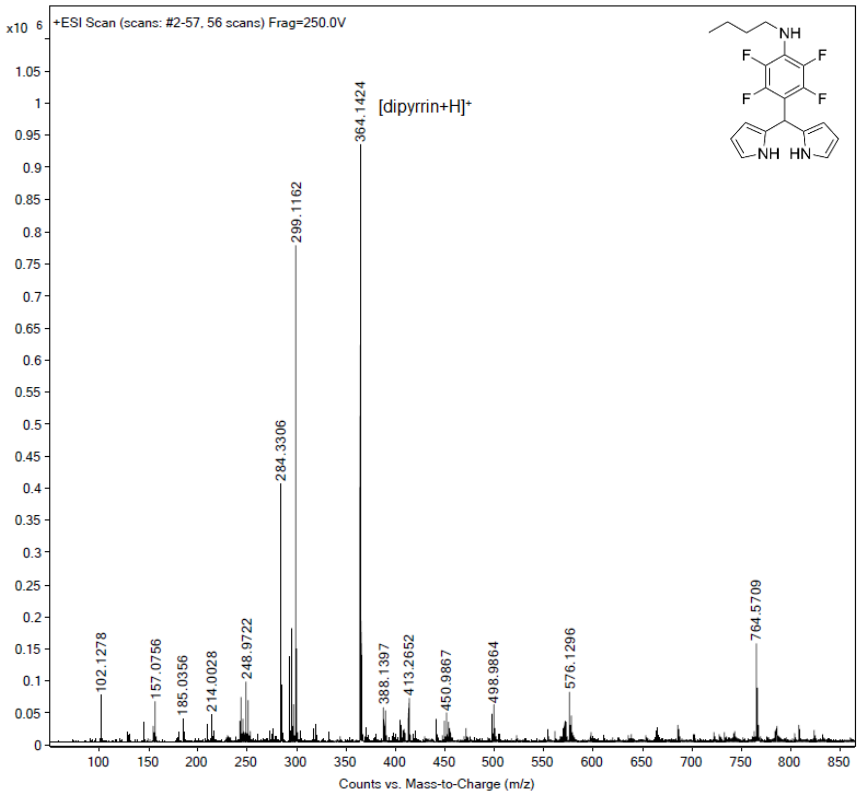

Figure S19: HRMS spectrum (ESI+) of dipyrromethane **2**.

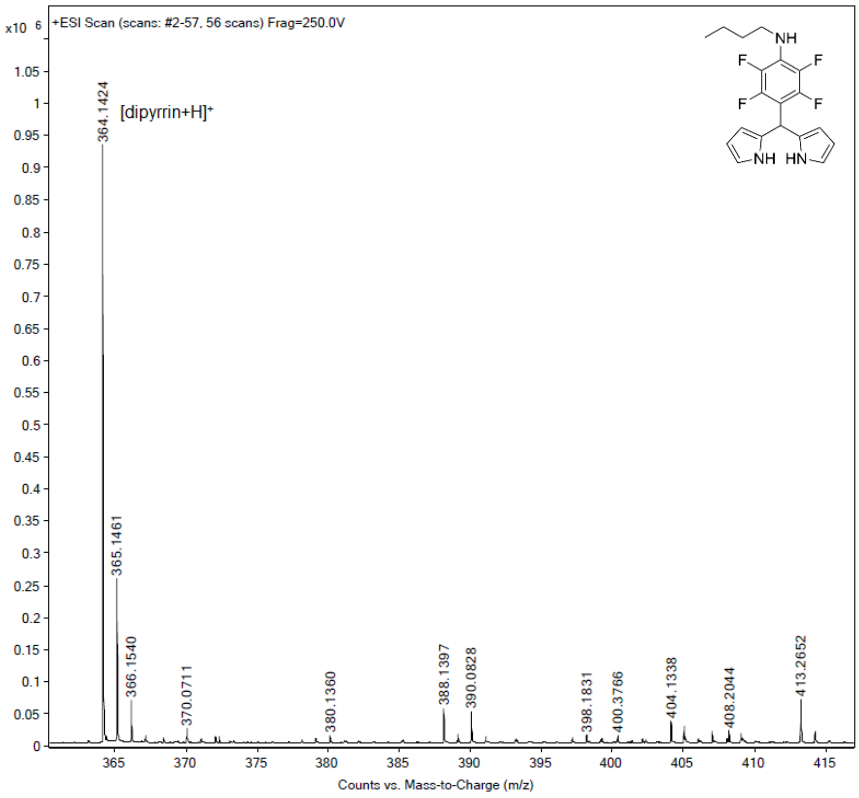

Figure S20: Zoom in from HRMS spectrum (ESI+) of dipyrromethane **2**.

5. Preparation of 8-[4-(*N*-butylamino)-2,3,5,6-tetrafluorophenyl]-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (2a)

Dipyrromethane **2** (1.13 g, 3.09 mmol) was dissolved in 30 mL of DCM, DDQ (716 mg, 3.09 mmol, 1 eq., suspended in 5 mL of DCM) was added and the reaction mixture was stirred for 5 min at rt. After the indicated time, DIPEA (3.70 ml, 21.76 mmol, 7 eq.) was added and stirred for 15 min. Afterwards, $BF_3{\cdot}OEt_2$ (2.75 ml, 21.76 mmol, 7 eq.) was added and the reaction mixture was stirred for additional 20 min at rt. Water was added to the mixture and extracted with DCM several times. The combined organic phases were washed again with water. The organic layer was dried with Na_2SO_4, filtrated, and evaporated to dryness. After column chromatography (silica gel, DCM/*n*-hexane = 9/1, v/v) BODIPY **2a** was obtained as a red solid (204 mg, 0.50 mmol, 16 %).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 0.99 (t, *J* = 7.4 Hz, 3H, Me), 1.42–1.49 (m, 2H, CH_2), 1.63–1.69 (m, 2H, CH_2), 3.52 (q, *J* = 7.0 Hz, 2H, CH_2), 4.15 (br s, 1H, NH), 6.53 (d, *J* = 4.0 Hz, 2H, $H_{pyrrole}$), 6.90 (d, *J* = 3.9 Hz, 2H, $H_{pyrrole}$), 7.92 (s, 2H, $H_{pyrrole}$).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 13.9 (Me), 19.95 (CH_2), 33.1 (CH_2), 45.5 (CH_2), 98.7 (Ar-C_{ipso}), 119.1 ($C_{pyrrole}$), 130.5 (t, *J* = 10.6 Hz, Ar-C_{para}), 130.9 ($C_{pyrrole}$), 135.6 ($C_{pyrrole}$), 136.9 (dd, *J* = 224.3, 6.6 Hz, Ar-C_{meta}), 144.9 (dd, *J* = 248.6, 23.3 Hz, Ar-C_{ortho}), 145.4 ($C_{pyrrole}$).

^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) = -139.75 (d, *J* = 16.8 Hz, 2F, CF_{meta}), -144.78 – -150.01 (m_C, 2F, BF_2), -159.83 (d, *J* = 16.5 Hz, 2F, CF_{ortho}).

HRMS (ESI-TOF): *m/z* calcd. for $C_{19}H_{16}BF_6N_3Na^+$ $[M+Na]^+$: 434.1234, found: 434.1227, *m/z* calcd. for $C_{19}H_{16}BF_6N_3K^+$ $[M+K]^+$: 450.0973, found: 450.0964, *m/z* calcd. for $C_{38}H_{32}B_2F_{12}N_6Na^+$ $[2M+Na]^+$: 845.2575, found: 845.2559.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3408 [ν(NH)], 2959 and 2933 [$\nu(CH_2)$, ν(Me)], 2873 [ν(CH)], 1652 [ν(C=N)], 1174 [ν(BF)], 753 [δ(-HC=CH-)].

UV/Vis (DCM): λ_{max} (nm) [log (ε/L mol^{-1} cm^{-1})] = 515 [4.50].

Fluorescence (DCM): λ_{max} (nm) = 531 at $\lambda_{Excitation}$ (nm) = 500.

M.P. (°C): 45 – 49.

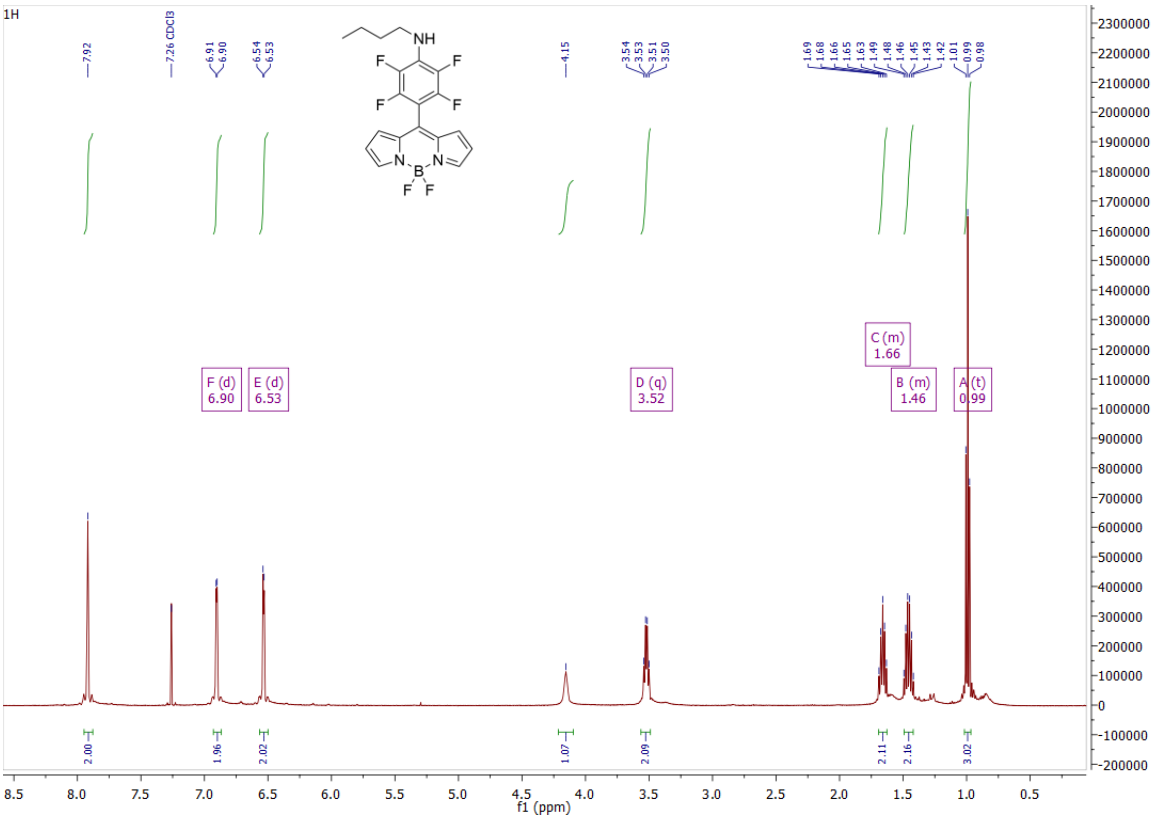

Figure S21: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of BODIPY **2a**.

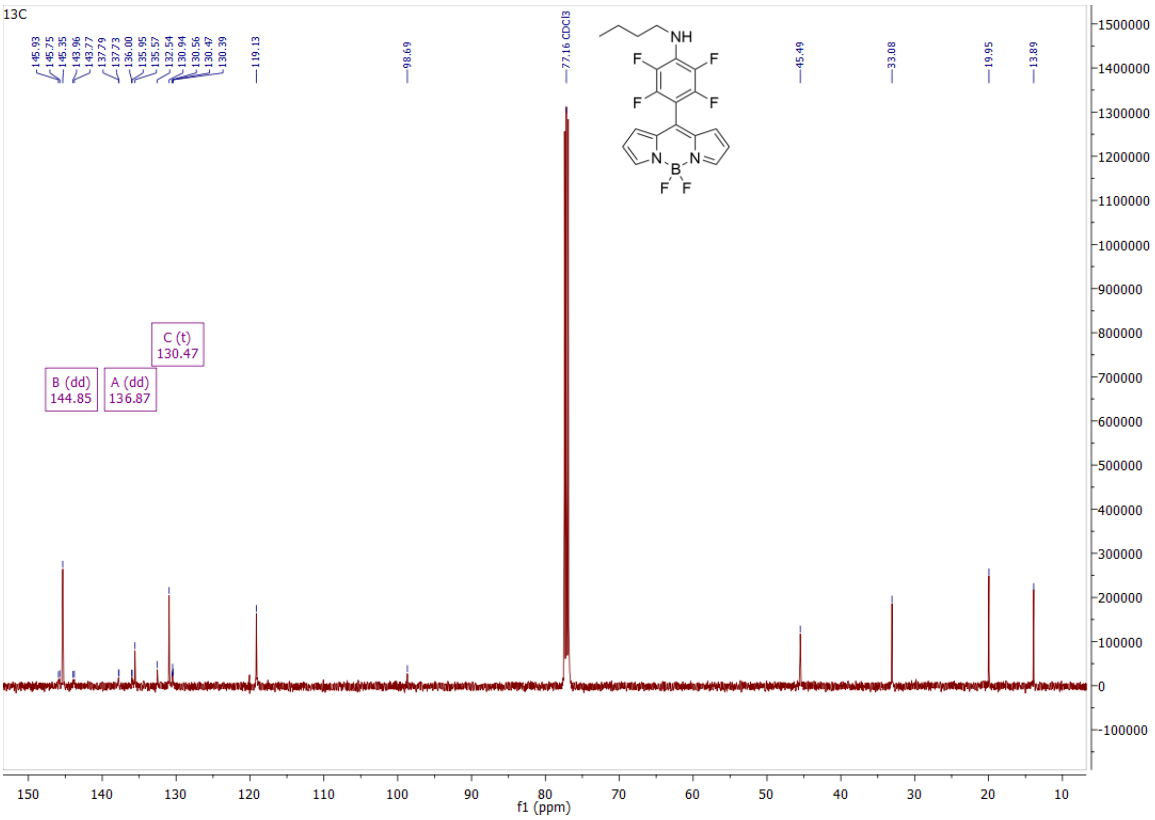

Figure S22: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of BODIPY **2a**.

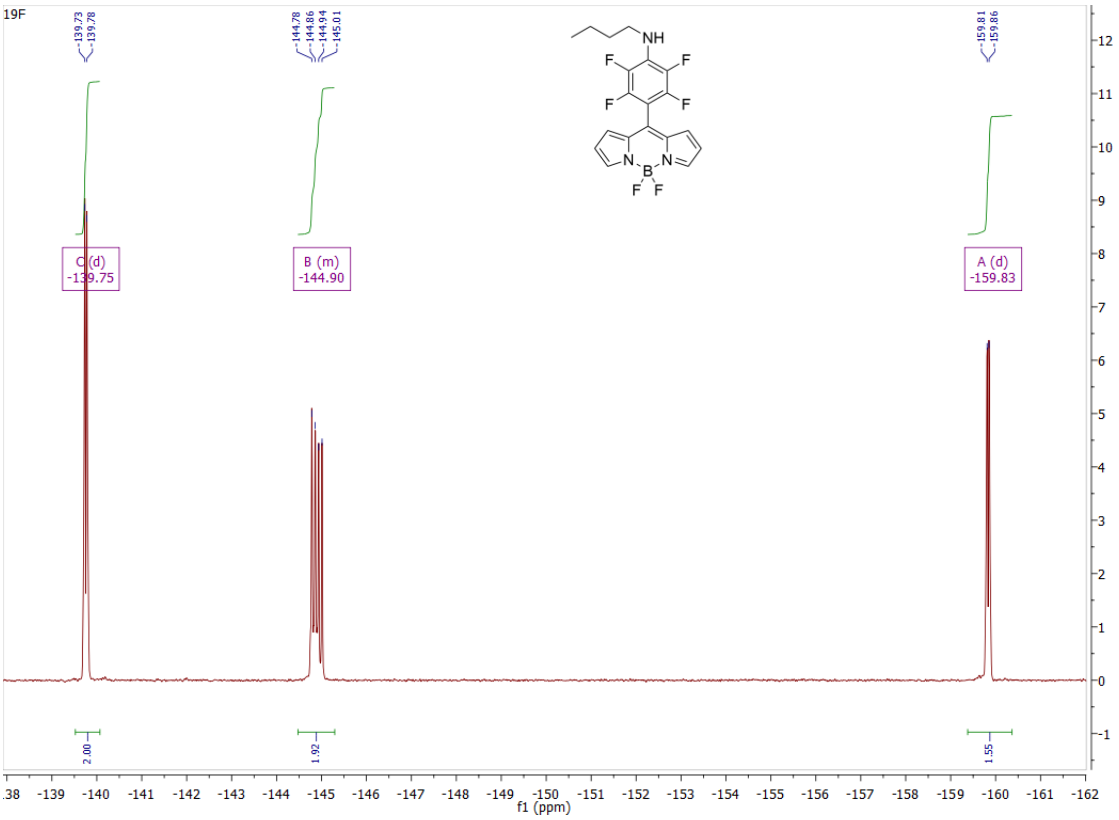

Figure S23: ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of BODIPY **2a**.

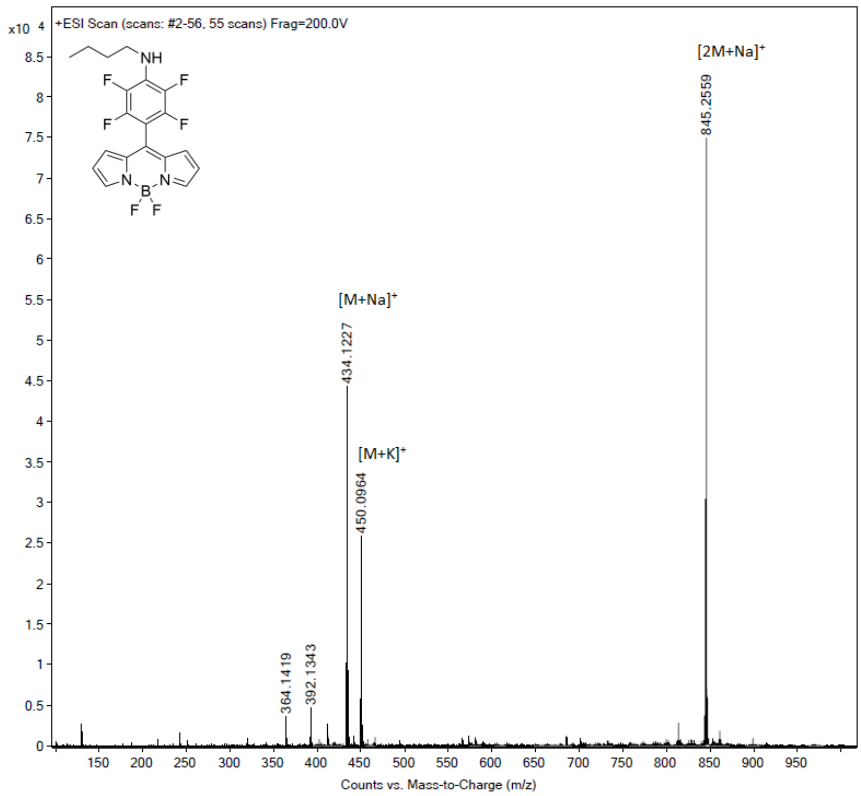

Figure S24: HRMS spectrum (ESI+) of BODIPY **2a**.

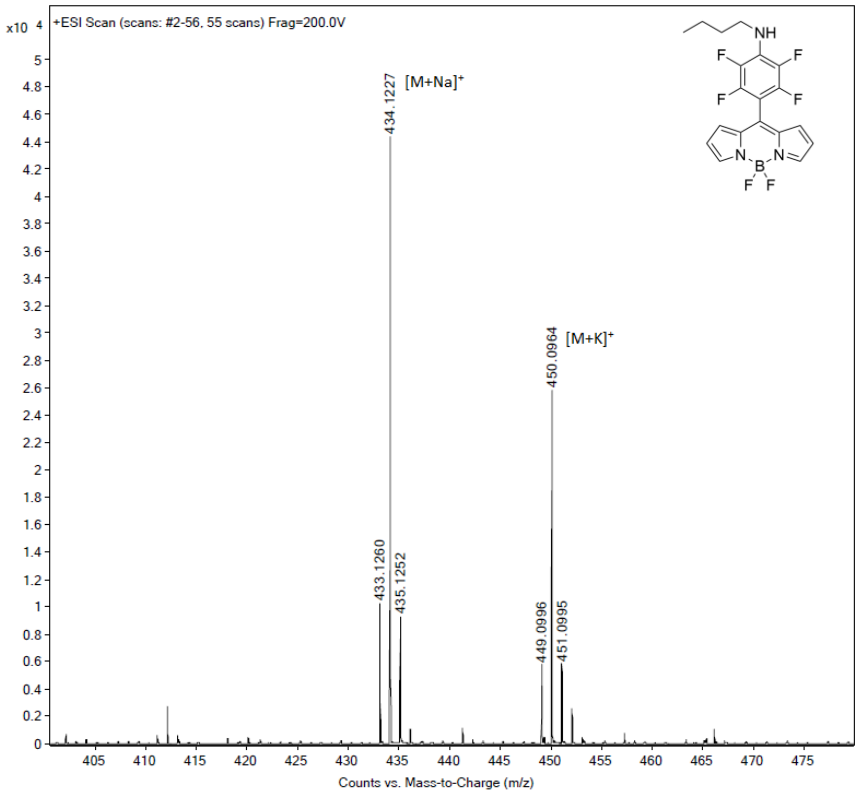

Figure S25: Zoom in from HRMS spectrum (ESI+) of BODIPY **2a**.

6. Preparation of 8-(4-butyloxy-2,3,5,6-tetrafluorophenyl)-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (5a)

Dipyrromethane **5** (843 mg, 2.33 mmol) was dissolved in 40 mL of DCM, DDQ (534 mg, 2.33 mmol, 1 eq., suspended in 5 mL of DCM) was added and the reaction mixture was stirred for 5 min at rt. After the indicated time, DIPEA (3.60 ml, 21.17 mmol, 7 eq.) was added and stirred for 15 min. Afterwards, $BF_3{\cdot}OEt_2$ (2.80 ml, 21.17 mmol, 7 eq.) was added and the reaction mixture was stirred for additional 20 min at rt. Water was added to the mixture and extracted with DCM several times. The combined organic phases were washed again with water. The organic layer was dried with Na_2SO_4, filtrated, and evaporated to dryness. After column chromatography (silica gel, DCM/*n*-hexane = 1/1, v/v) BODIPY **5a** was obtained as a dark reddish-green solid (203 mg, 0.49 mmol, 21 %).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 1.01 (t, J = 7.4 Hz, 3H, Me), 1.52–1.58 (m, 2H, CH_2), 1.80–1.86 (m, 2H, CH_2), 4.38 (t, J = 6.5 Hz, 2H, CH_2), 6.55 (d, J = 4.0 Hz, 2H, $H_{pyrrole}$), 6.85 (d, J = 4.0 Hz, 2H, $H_{pyrrole}$), 7.95 (s, 2H, $H_{pyrrole}$).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 13.8 (Me), 18.9 (CH_2), 32.1 (CH_2), 75.4 (CH_2), 105.6 (t, J = 18.1 Hz, Ar-C_{ipso}), 119.6 ($C_{pyrrole}$), 130.8 ($C_{pyrrole}$), 131.1 (Ar-C_{para}), 135.3 ($C_{pyrrole}$), 141.1 (dd, J = 249.4, 19.1 Hz, Ar-C_{meta}), 144.7 (dd, J = 251.2, 19.4 Hz, Ar-C_{ortho}), 146.2 ($C_{pyrrole}$).

^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) = -138.19 (d, J = 10.2 Hz, 2F, CF_{meta}), -144.67 – -144.89 (m_C, 2F, BF_2), -153.62 (d, J = 15.8 Hz, 2F, CF_{ortho}).

HRMS (ESI-TOF): *m/z* calcd. for $C_{19}H_{15}BF_6N_2ONa^+$ $[M+Na]^+$: 435.1074, found: 435.1107, *m/z* calcd. for $C_{38}H_{30}B_2F_{12}N_4O_2Na^+$ $[2M+Na]^+$: 847.2255, found: 847.2309.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2961 and 2936 [ν(Me), ν(CH_2)], 2875 [ν(CH)], 1651 [ν(C=N)], 1074 [ν(BF)], 759 [δ(-HC=CH-)].

UV/Vis (DCM): λ_{max} (nm) [log (ε/L mol^{-1} cm^{-1})] = 348 [4.03], 517 [4.73].

Fluorescence (DCM): λ_{max} (nm) = 534 at $\lambda_{Excitation}$ (nm) = 500.

M.P. (°C): 99 – 103.

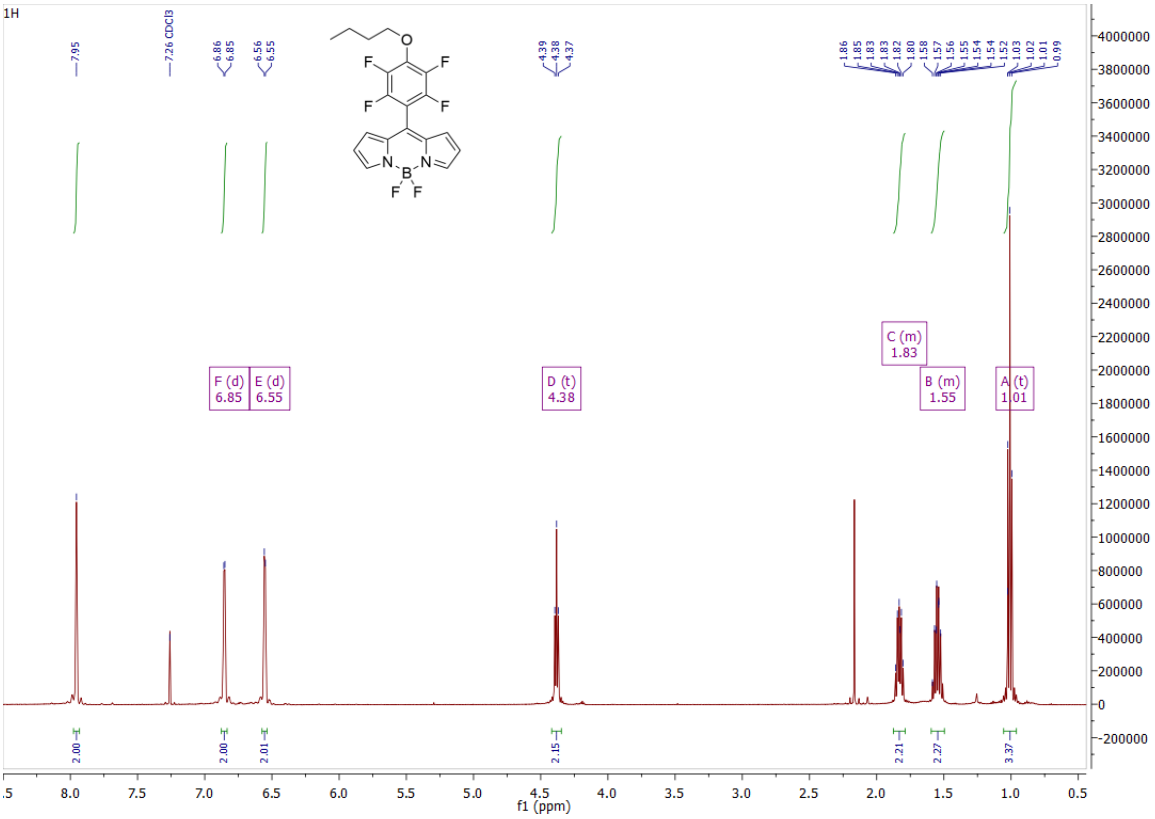

Figure S26: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of BODIPY **5a**.

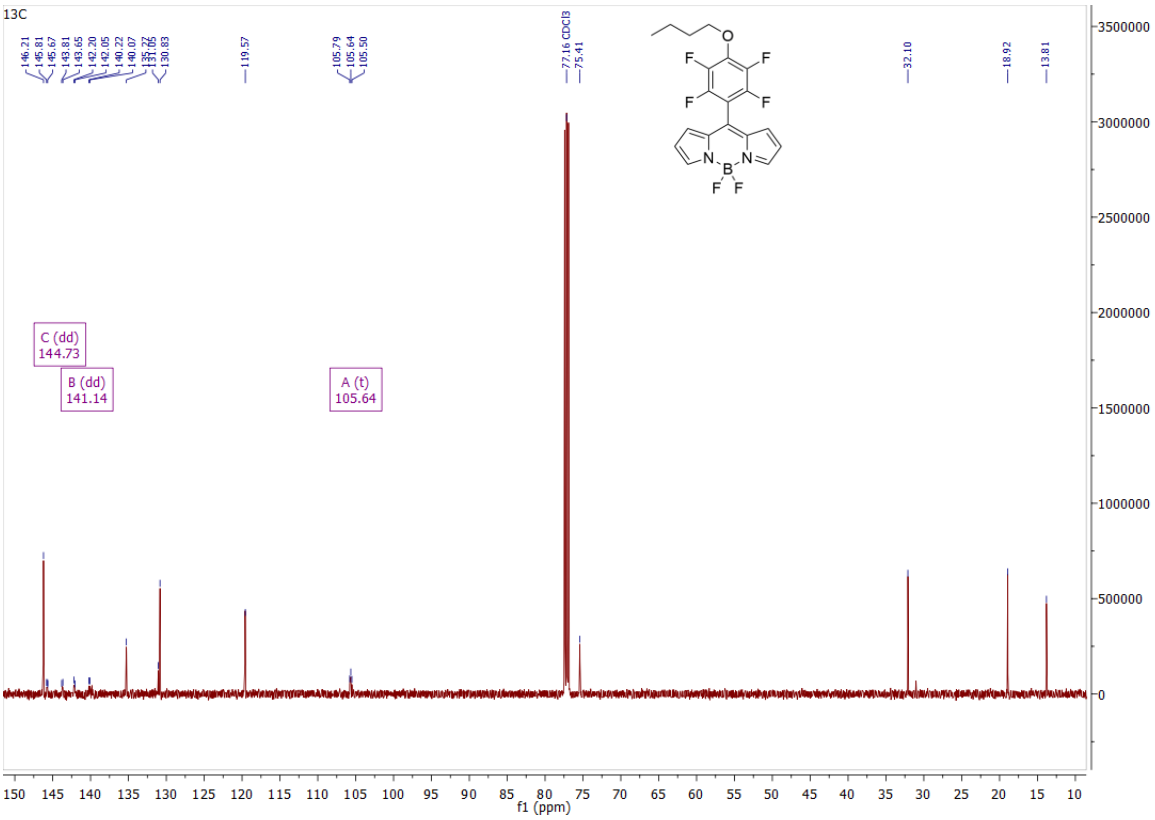

Figure S27: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of BODIPY **5a**.

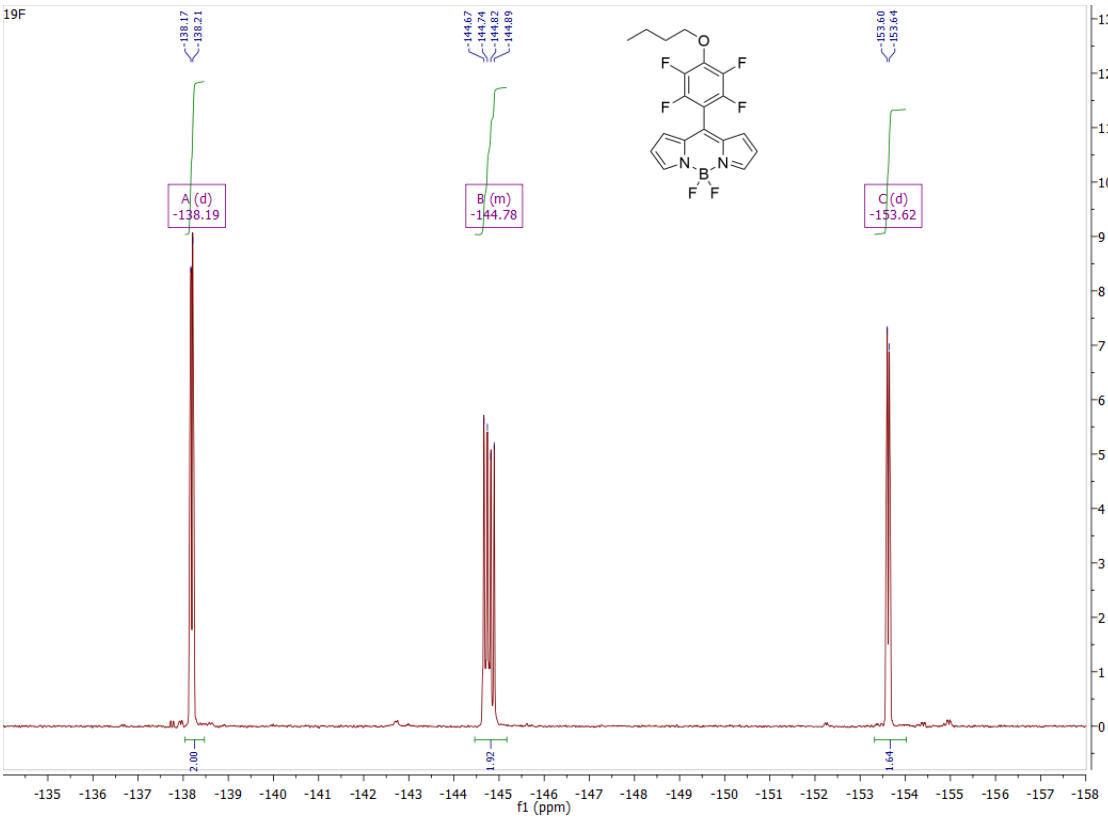

Figure S28: ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of BODIPY **5a**.

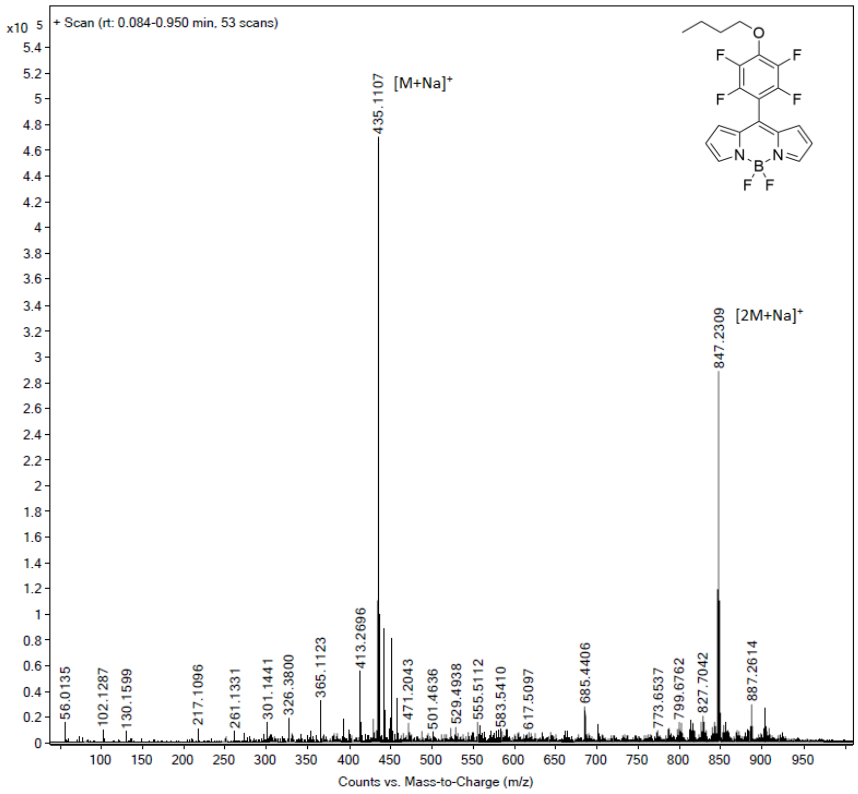

Figure S29: HRMS spectrum (ESI+) of BODIPY **5a**.

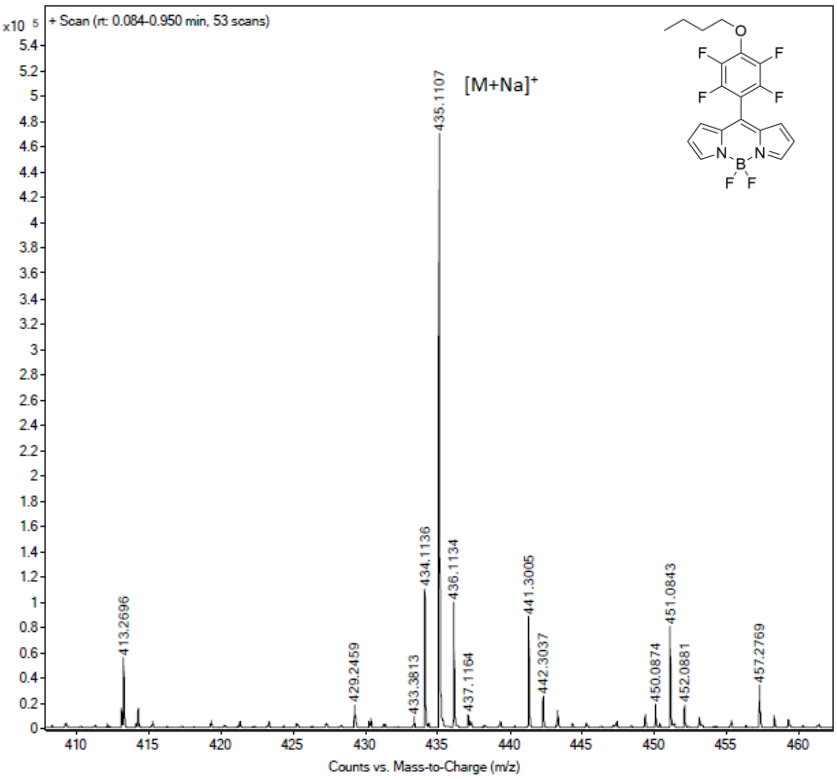

Figure S30: Zoom in from HRMS spectrum (ESI+) of BODIPY **5a**.

7. Dihalogenation of BODIPYs (13 – 16)

General synthetic procedure

The corresponding BODIPY (1 equiv.) was dissolved in 2 mL of HFIP. NBS (2.5 equiv.) was added and the mixture was stirred for the indicated time at rt. Afterwards, the reaction mixture was diluted with DCM and washed with water several times. The organic layer was dried with Na_2SO_4, filtrated and evaporated to dryness. The crude product was purified by column chromatography.

2,6-Dibromo-8-pentafluorophenyl-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (**13**):
BODIPY **13** was prepared according to the general synthetic procedure. BODIPY **1a** (100 mg, 0.24 mmol), NBS (103 mg, 0.58 mmol, 2.5 equiv.) were dissolved in HFIP stirred for 2 min at rt. After purification by column chromatography (silica gel, *n*-hexane/EtOAc = 9/1, v/v) BODIPY **13** could not be isolated in pure form. The product still contained other BODIPYs.

2,6-Dibromo-8-[(4-prop-2-ynyloxy)-2,3,5,6-tetrafluorophenyl]-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (**14**):
BODIPY **14** was prepared according to the general synthetic procedure. BODIPY **7a** (60 mg, 0,15 mmol), NBS (65 mg, 0,37 mmol) were dissolved in HFIP and stirred for 2 min at rt. After purification by column chromatography (silica gel, DCM/n-hexane = 1/1, v/v) BODIPY **14** could not be isolated in pure form. The product still contained other BODIPYs.

2,6-Dibromo-8-(4-fluoro-3-nitrophenyl)-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (**15**):
BODIPY **15** was prepared according to the general synthetic procedure. BODIPY **8a** (150 mg, 0.45 mmol), NBS (193 mg, 1.08 mmol) were dissolved in HFIP and stirred for 5 min at rt. After purification by column chromatography (silica gel, DCM/*n*-hexane = 4/1, v/v) BODIPY **15** could not be isolated in pure form. The product still contained other BODIPYs.

2,6-Dibromo-8-[(4-*N*-butylamino)-3-nitrophenyl]-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (**16**):
BODIPY **16** was prepared according to the general synthetic procedure. BODIPY **9a** (86 mg, 0.22 mmol), NBS (96 mg, 0.54 mmol) were dissolved in HFIP and stirred for 5 min at rt. After purification by column chromatography (silica gel, DCM/*n*-hexane = 4/1, v/v) BODIPY **16** could not be isolated in pure form. The product still contained other BODIPYs.

8. Targeted dihalogenation of BODIPYs under modified conditions (13 and 15)

General synthetic procedure

The corresponding BODIPY (1 equiv.) was dissolved in DCM. NBS (2.5 equiv., dissolved in DCM) was added and the mixture was stirred for the indicated time at rt. Afterwards, the reaction mixture was diluted with DCM and washed with water several times. The organic layer was dried with Na_2SO_4, filtrated and evaporated to dryness. The crude product was purified by column chromatography.

2,6-Dibromo-8-pentafluorophenyl-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (**13**):
BODIPY **13** was prepared according to the general synthetic procedure. BODIPY **1a** (256 mg, 0.72 mmol) was dissolved in 5 mL of DCM. NBS (318 mg, 1.79 mmol, 2.5 eq.) was added and the mixture was stirred for 4 d at rt. After purification by column chromatography (silica gel, DCM/*n*-hexane = 1/1, v/v) two fractions could be isolated. The first fraction referred to BODIPY **13** (2,6-dibromo substituted) and was obtained as a reddish–green solid (31 mg, 60 µmol, 8 %). The second fraction could be identified as the corresponding BODIPY **17** (2-bromo substituted) and was obtained as a red solid (148 mg, 0.34 mmol, 47 %).

13: 2,6-Dibromo-8-pentafluorophenyl-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 6.84 (s, 2H, $H_{pyrrole}$), 7.89 (s, 2H, $H_{pyrrole}$).
^{13}C NMR (176 MHz, $CDCl_3$): δ (ppm) = 107.1 (t, *J* = 17.6 Hz, Ar-C_{ipso}), 108.95–109.0 (C_{Br}), 128.9 (Ar-C_{para}), 130.6 ($C_{pyrrole}$), 134.9 ($C_{pyrrole}$), 138.1 (dd, *J* = 254.9, 6.2 Hz, Ar-C_{meta}), 144.53 (dd, *J* = 253.2, 8.4 Hz, Ar-C_{ortho}), 147.0 ($C_{pyrrole}$).
^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) = -136.30 (d, *J* = 19.3 Hz, 2F, CF_{meta}), -144.63 – -144.85 (m_C, 2F, BF_2), -148.23 (t, *J* = 20.8 Hz, CF_{para}), -158.58 (t, *J* = 19.0 Hz, CF_{ortho}).
IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3135 [ν(CH_{aromat})], 1655 [ν(C=C)], 1078 and 1092 [ν(BF), ν(CBr)], 758 [δ(-HC=CH-)].
UV/Vis (DCM): λ_{max} (nm) [log (ε/L mol^{-1} cm^{-1})] = 384 [4.06], 565 [4.69].
Fluorescence (DCM): λ_{max} (nm) = 591 at $\lambda_{Excitation}$ (nm) = 370, 550.
M.P. (°C): 161 – 168.

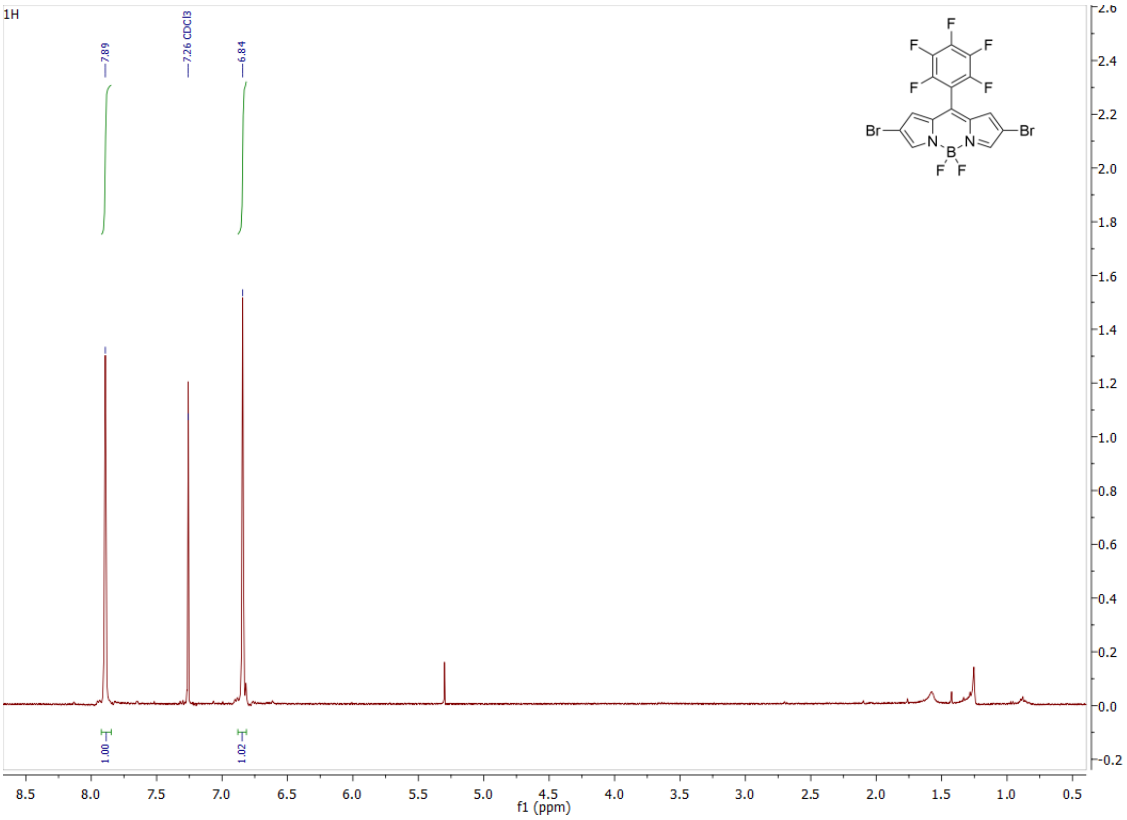

Figure S31: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of BODIPY **13**.

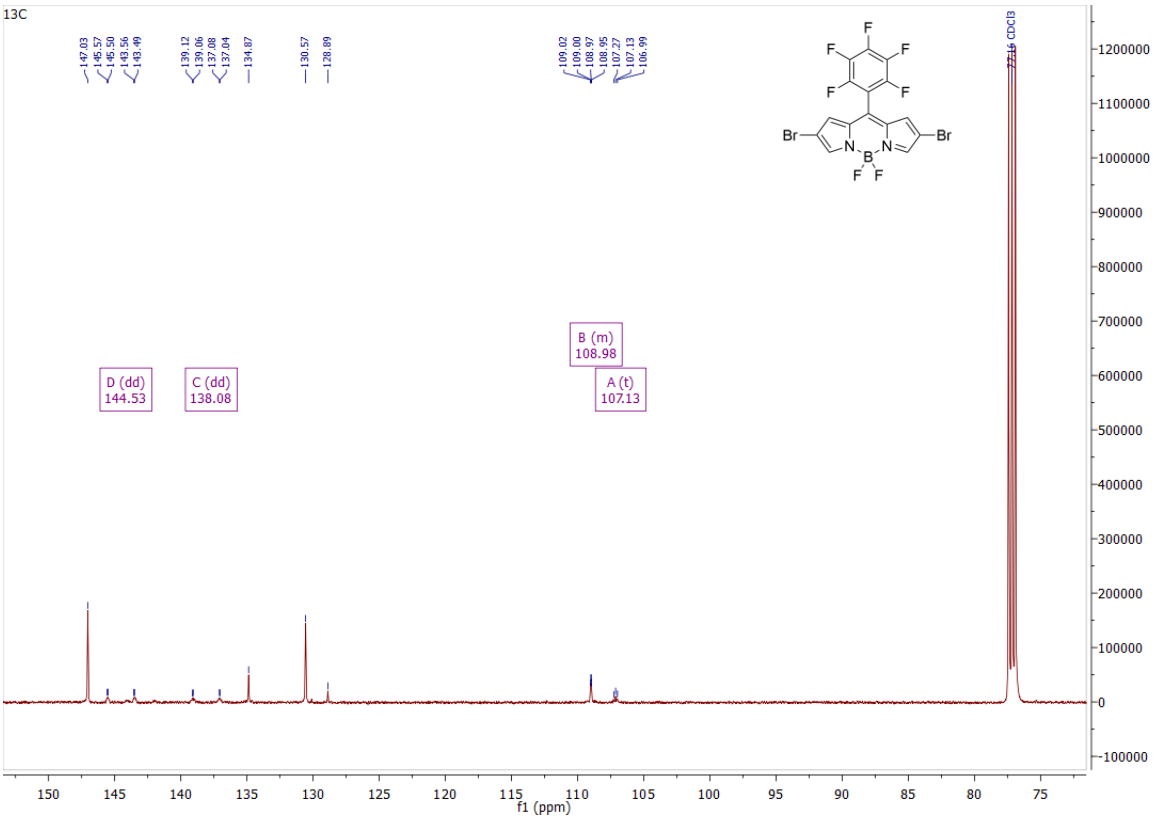

Figure S32: ^{13}C NMR (176 MHz, $CDCl_3$) spectrum of BODIPY **13**.

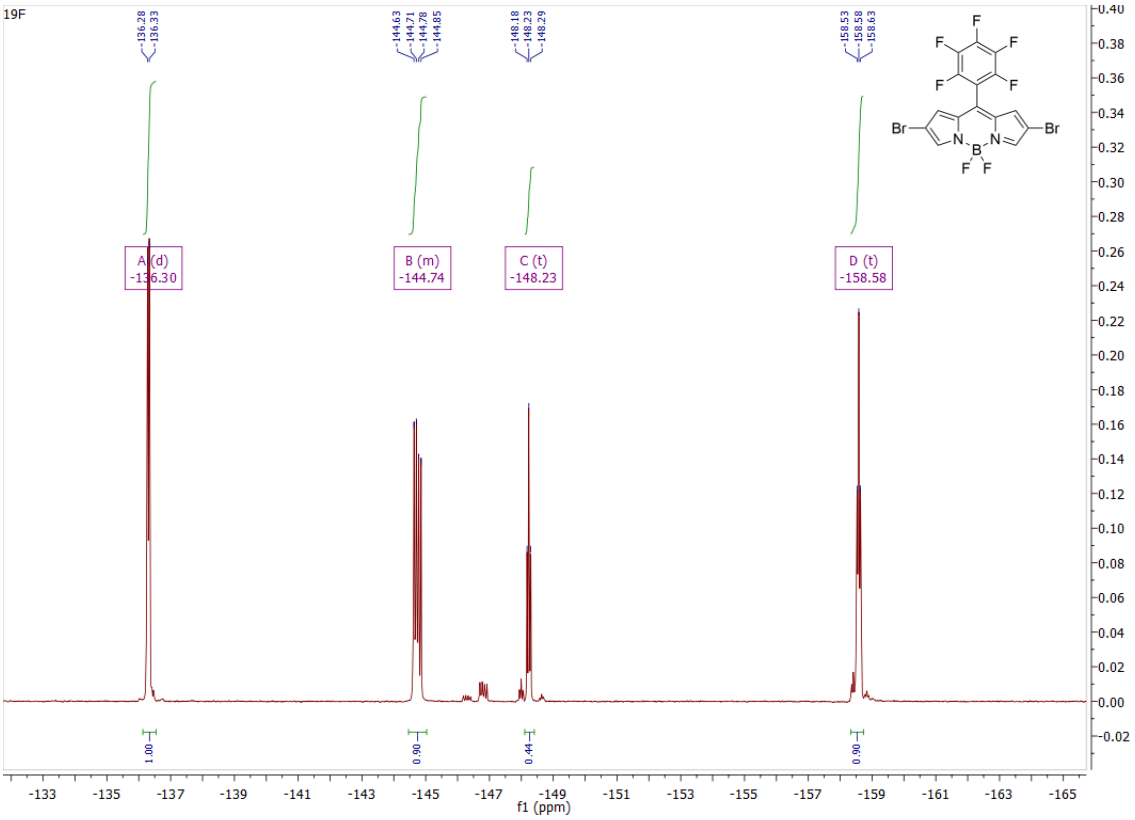

Figure S33: ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of BODIPY **13**.

17: 2-Bromo-8-pentafluorophenyl-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 6.64 (d, J = 4.4 Hz, 1H, $H_{pyrrole}$), 6.77 (s, 1H, $H_{pyrrole}$), 6.88 (d, J = 4.3 Hz, 1H, $H_{pyrrole}$), 7.83 (s, 1H, $H_{pyrrole}$), 8.06 (s, 1H, $H_{pyrrole}$).

^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) = -136.10 (d, J = 18.0 Hz, 2F, CF_{meta}), -144.54 – -144.75 (m_C, 2F, BF_2), -147.50 (t, J = 20.9 Hz, 1F, CF_{para}), -158.11 (t, J = 19.1 Hz, 2F, CF_{ortho}).

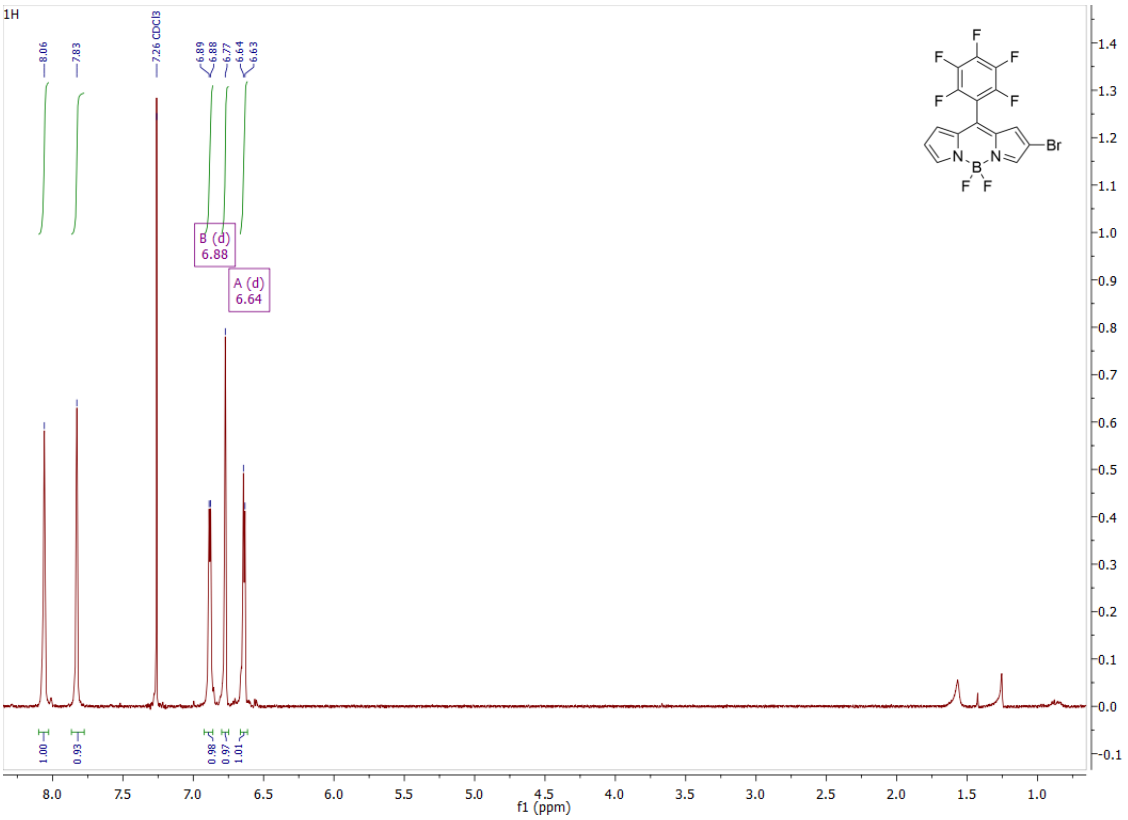

Figure S34: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of BODIPY **17** (received from the dibromination).

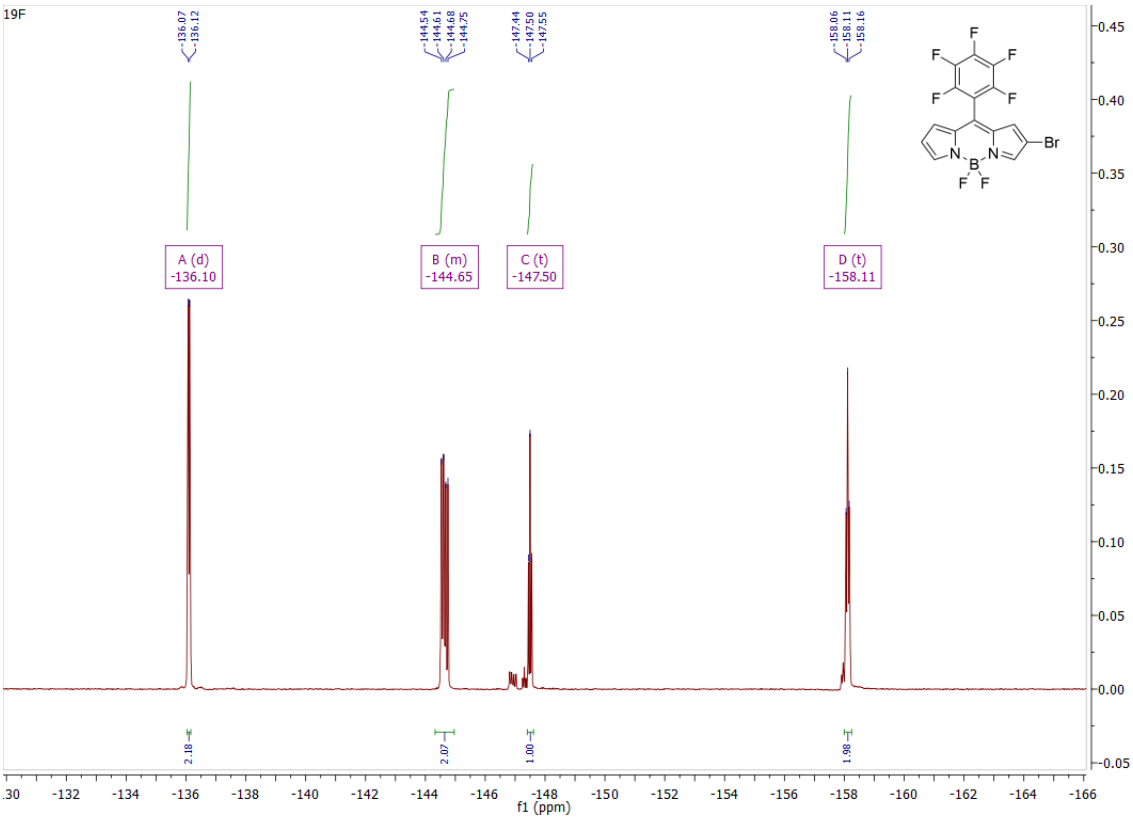

Figure S35: ^{19}F NMR (400 MHz, $CDCl_3$) spectrum of BODIPY **17** (received from the dibromination).

2,6-Dibromo-8-(4-fluoro-3-nitrophenyl)-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (**15**):

BODIPY **15** was prepared according to the general synthetic procedure. BODIPY **8a** (50 mg, 0.15 mmol) was dissolved in 5 mL of DCM. NBS (67 mg, 0.38 mmol, 2.5 eq.) was added and the mixture was stirred for 4 d at rt. After purification by column chromatography (silica gel, DCM/*n*-hexane = 1/1, v/v) two fractions could be isolated. The first fraction referred to BODIPY **15** (2,6-dibromo-substituted) and was obtained as a dark yellow solid (15 mg, 31 µmol, 20 %). The second fraction could be identified as the corresponding BODIPY **18** (2-bromo-substituted) and was obtained as a reddish–green solid (25 mg, 61 µmol, 41 %).

15: 2,6-Dibromo-8-(4-fluoro-3-nitrophenyl)-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene

^{1}H NMR (700 MHz, $CDCl_3$): δ (ppm) = 6.88 (s, 2H, $H_{pyrrole}$), 7.54 (dd, *J* = 10.0, 8.6 Hz, 1H, Ar-H_{meta}), 7.82 (ddd, *J* = 8.6, 4.1, 2.3 Hz, 1H, Ar-H_{ortho}), 7.91 (s, 2H, $H_{pyrrole}$), 8.26 (dd, *J* = 6.8, 2.3 Hz, 1H, Ar-H_{ortho}).

^{13}C NMR (176 MHz, $CDCl_3$): δ (ppm) = 108.5–108.6 (m, C-Br), 119.7 (d, J_{C-F} = 21.2 Hz, Ar-C_{meta}), 127.8 (Ar-C_{ortho}), 130.7 ($C_{pyrrole}$), 131.1*, 134.5 ($C_{pyrrole}$), 136.8 (d, J_{C-F} = 9.3 Hz, Ar-C_{ortho}), 137.8 (d, J_{C-F} = 6.6 Hz)*,141.7 (C_{meso}), 146.1 ($C_{pyrrole}$), 157.1 (d, *J* = 271.7 Hz, Ar-C_{para}). *These signals could not be assigned exactly to corresponding carbon atoms. They belong to the Ar-C_{ipso} and the Ar-C_{nitro} of the aryl residue.

^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) = -111.98 (s, 1F, CF), -144.33 – -145.04 (m, 2F, BF_2).

HRMS (ESI-TOF): *m/z* calcd. for $C_{15}H_7BBr_2F_3N_3O_2^-$ $[M]^-$: 488.8935, found: 488.8920.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3120 [ν(CH_{aromat})], 1618 [ν(C=C)], 1586 [$\nu_{asym}(NO_2)$], 1348 [$\nu_{sym}(NO_2)$], 1253 [C=CF], 1085 [ν(BF), ν(CBr)].

UV/Vis (DCM): λ_{max} (nm) [log (ε/L mol^{-1} cm^{-1})] = 554 [4.78].

Fluorescence (DCM): λ_{max} (nm) = 580 at $\lambda_{Excitation}$ (nm) = 540.

M.P. (°C): 170–179.

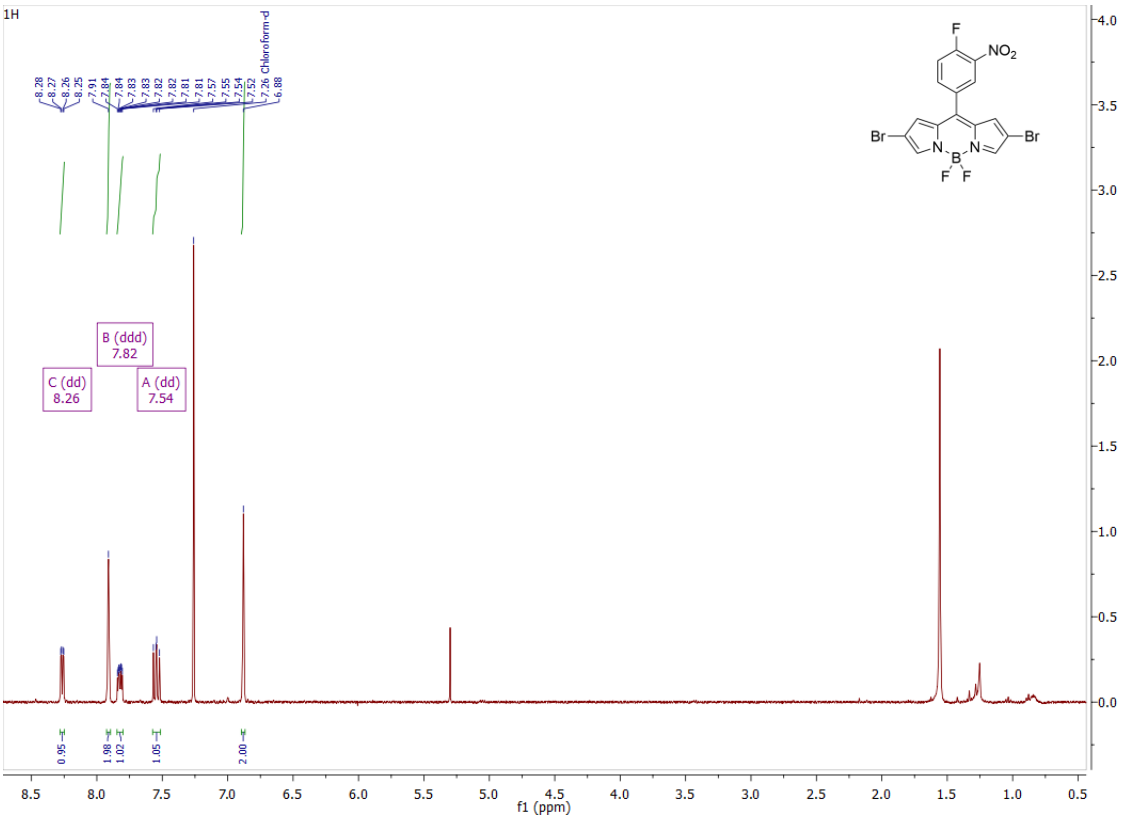

Figure S36: ^{1}H NMR (700 MHz, $CDCl_3$) spectrum of BODIPY **15**.

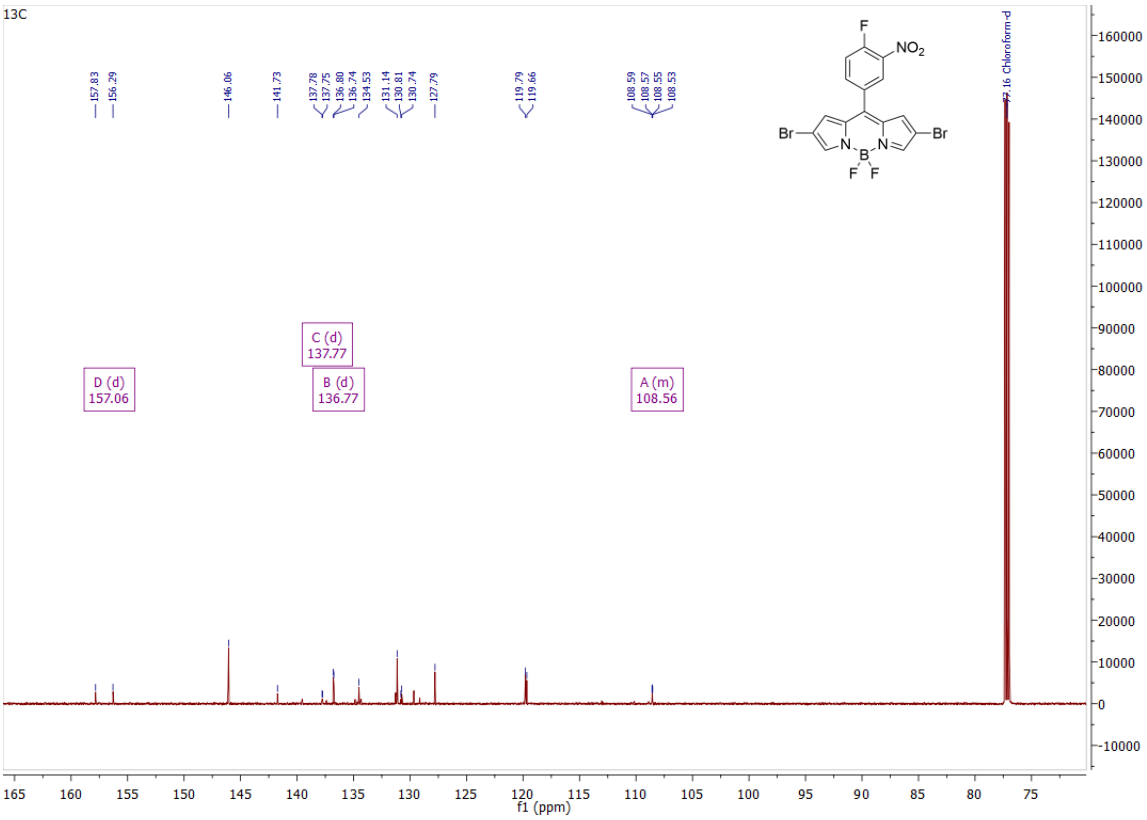

Figure S37: ^{13}C NMR (176 MHz, $CDCl_3$) spectrum of BODIPY **15**.

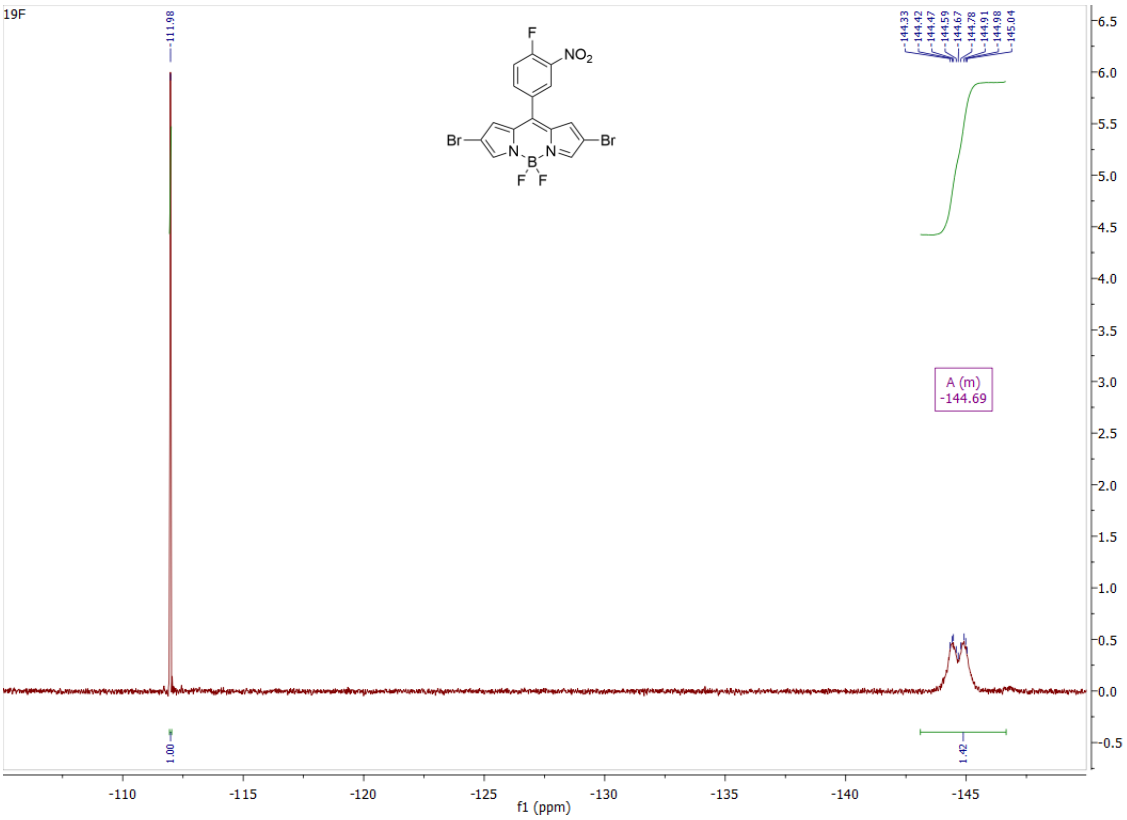

Figure S38: ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of BODIPY **15**.

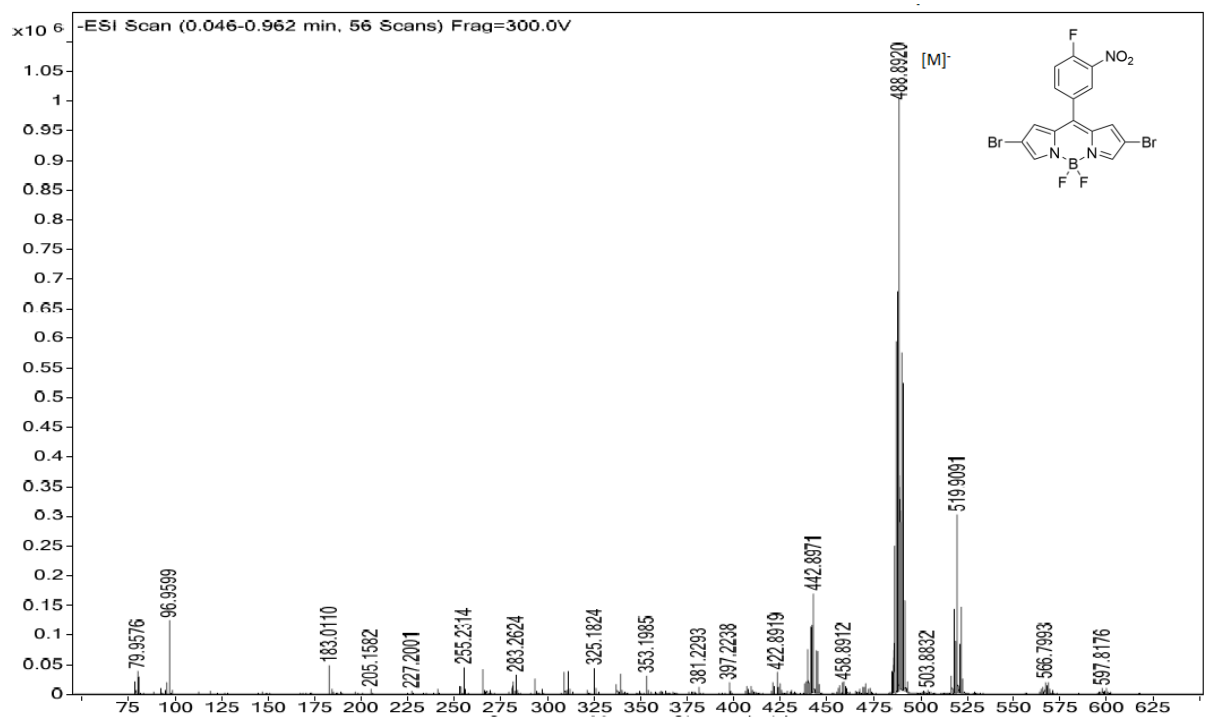

Figure S39: HRMS spectrum (ESI-, in MeOH) of BODIPY **15**.

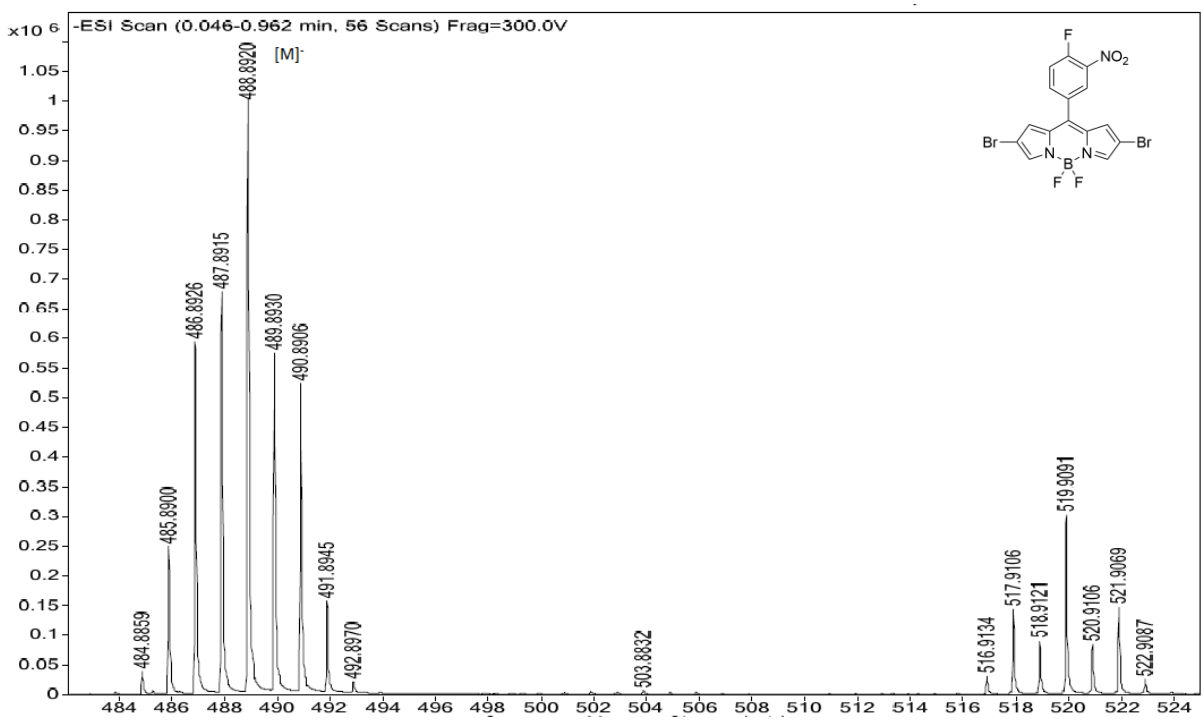

Figure S40: Zoom in from HRMS spectrum (ESI-, in MeOH) of BODIPY **15**.

18: 2-Bromo-8-(4-fluoro-3-nitrophenyl)-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (received from the dibromination)

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 6.67 (d, J = 4.4 Hz, 1H, $H_{pyrrole}$), 6.81 (s, 1H, $H_{pyrrole}$), 6.93 (d, J = 4.7 Hz, 1H, $H_{pyrrole}$), 7.53 (dd, J = 10.1, 8.6 Hz, 1H, Ar-H_{meta}), 7.82–7.86 (m, 2H, $H_{pyrrole}$, Ar-H_{ortho}), 8.07 (s, 1H, $H_{pyrrole}$), 8.27 (dd, J = 6.9, 2.3 Hz, 1H, Ar-H_{ortho}).

^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) = -112.67 – -112.72 (s, 1F, CF), -144.32 – -145.10 (m, 2F, BF_2).

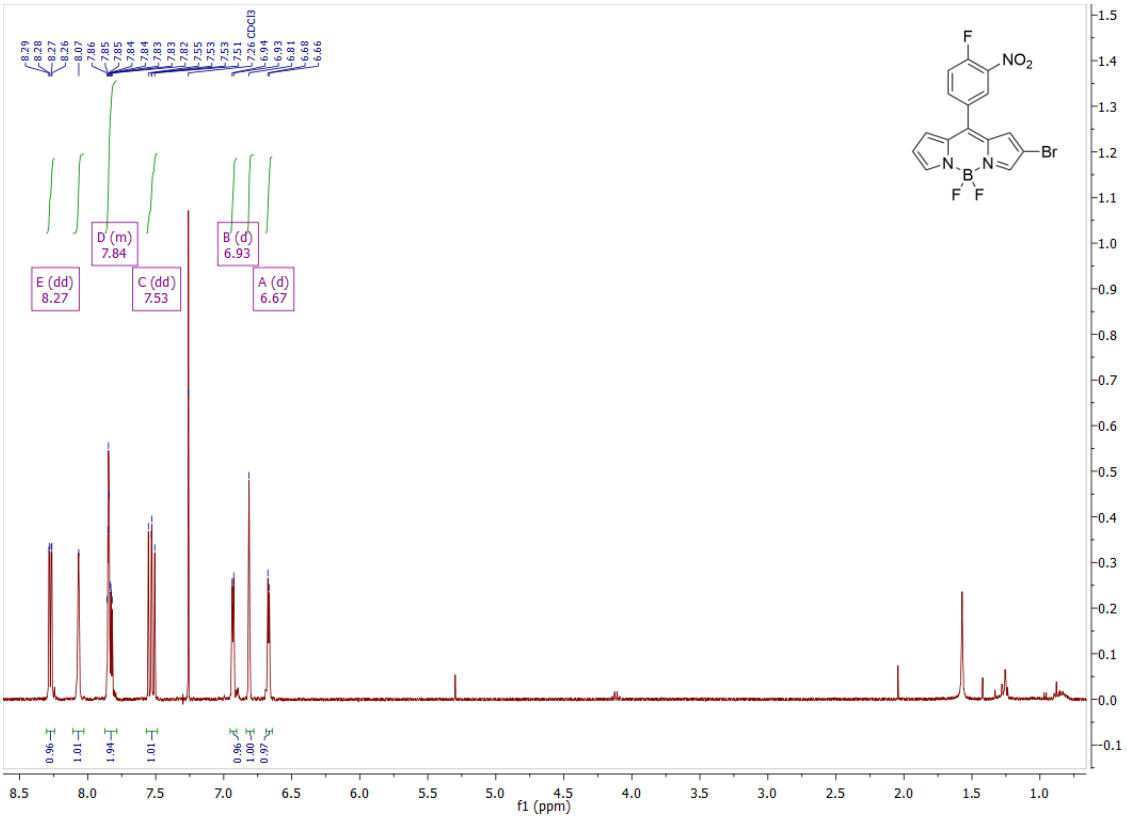

Figure S41: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of BODIPY **18** (received form the dibromination).

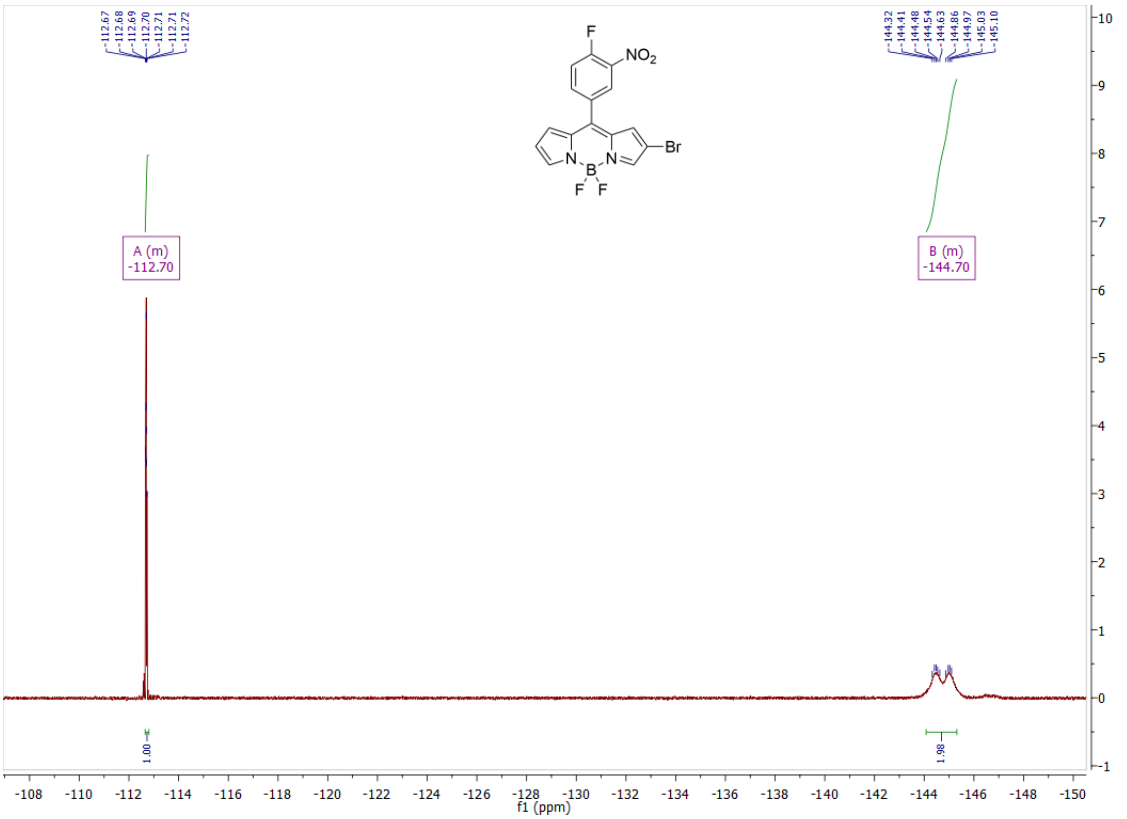

Figure S42: ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of BODIPY **18** (received form the dibromination).

9. Targeted monohalogenation of BODIPYs (17 – 24)

General synthetic procedure

The corresponding BODIPY (1 equiv.) was dissolved in DCM. NBS (2.5 equiv., dissolved in DCM) was added and the mixture was stirred for the indicated time at rt. Afterwards, the reaction mixture was diluted with DCM and washed with water several times. The organic layer was dried with Na_2SO_4, filtrated and evaporated to dryness. The crude product was purified by column chromatography.

2-Bromo-8-pentafluorophenyl-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (**17**):
BODIPY **17** was prepared according to the general synthetic procedure. BODIPY **1a** (100 mg, 0.28 mmol) and NBS (119 mg, 0.67 mmol) were dissolved in 10 mL of DCM. The mixture was stirred for 2.5 h. After column chromatography (silica gel, DCM/*n*-hexane = 2/1, v/v) BODIPY **17** was obtained as a purple solid (102 mg, 0.23 mmol, 84 %).

^{1}H NMR (700 MHz, $CDCl_3$): δ (ppm) = 6.63–6.64 (m, 1H, $H_{pyrrole}$), 6.77 (s, 1H, $H_{pyrrole}$), 6.88 (d, J = 4.5 Hz, 1H, $H_{pyrrole}$), 7.82 (s, 1H, $H_{pyrrole}$), 8.05 (s, 1H, $H_{pyrrole}$).
^{13}C NMR (176 MHz, $CDCl_3$): δ (ppm) = 107.5–107.7 (m, Ar-C_{ipso} + C_{Br}), 121.1 ($C_{pyrrole}$), 129.2 ($C_{pyrrole}$), 129.2 (Ar-C_{para}), 132.1 ($C_{pyrrole}$), 134.2 ($C_{pyrrole}$), 135.7 ($C_{pyrrole}$), 138.0 (ddd, J = 255.2, 28.7, 5.2 Hz, Ar-C_{meta}), 144.6 (dd, J = 253.0, 10.9 Hz, Ar-C_{ortho}) 144.8 ($C_{pyrrole}$), 149.1 ($C_{pyrrole}$).
^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) = -140.15 (dt, J = 21.0, 5.5 Hz, 2F, CF_{meta}), -144.51 – -144.73 (m_C, 2F, BF_2), -153.67 (tt, J = 20.7, 2.9 Hz, 1F, CF_{para}), -162.35 – -162.50 (m, 2F, CF_{ortho}).
HRMS (ESI-TOF): *m/z* calcd. for $C_{15}H_5BBrF_6N_2^+$ $[M\text{-}F]^+$: 416.9628, found: 416.9636, *m/z* calcd. for $C_{15}H_5BBrF_7N_2Na^+$ $[M+Na]^+$: 458.9510, found: 458.9516.
IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 1654 [ν(C=C)], 1075 [ν(BF), ν(CBr)] 768 [δ(-HC=CH-)].
UV/Vis (DCM): λ_{max} (nm) [log (ε/L mol^{-1} cm^{-1})] = 536 [4.75].
Fluorescence (DCM): λ_{max} (nm) = 564 at $\lambda_{Excitation}$ (nm) = 520.
M.P. (°C): 141–146.

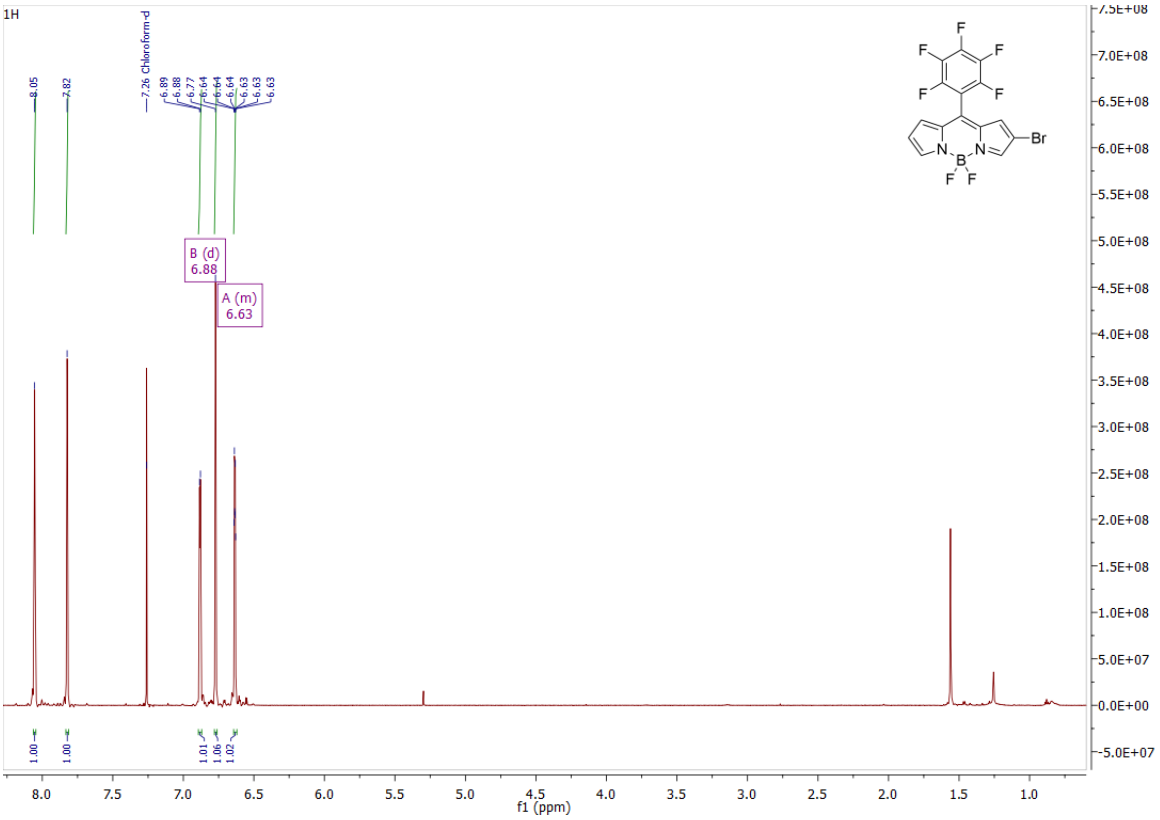

Figure S43: ^{1}H NMR (700 MHz, $CDCl_3$) spectrum of BODIPY **17**.

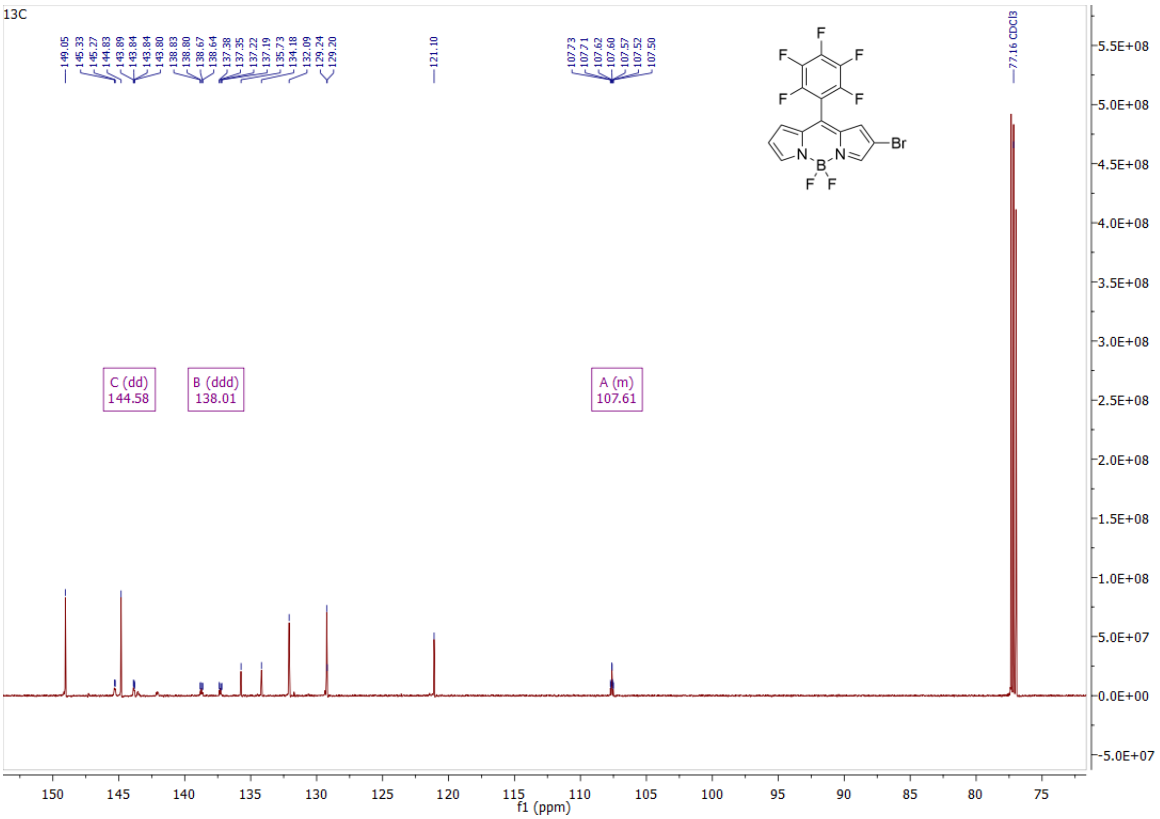

Figure S44: ^{13}C NMR (176 MHz, $CDCl_3$) spectrum of BODIPY **17**.

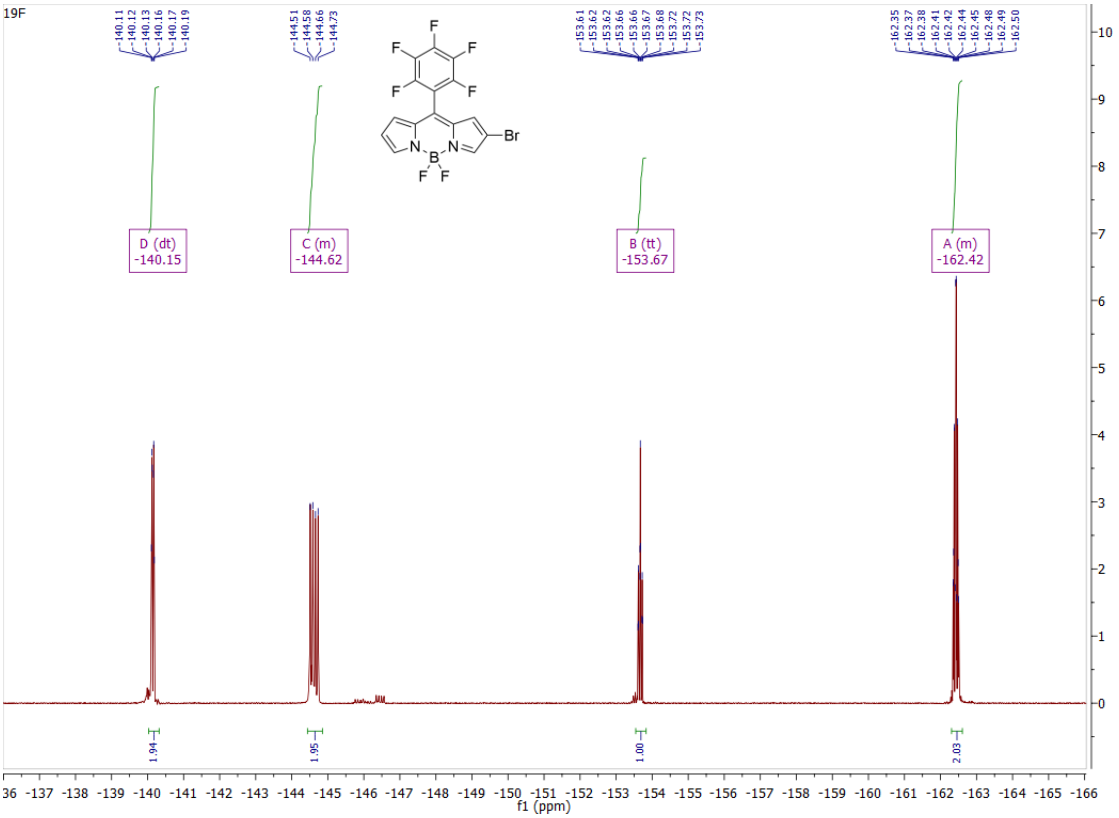

Figure S45: ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of BODIPY **17**.

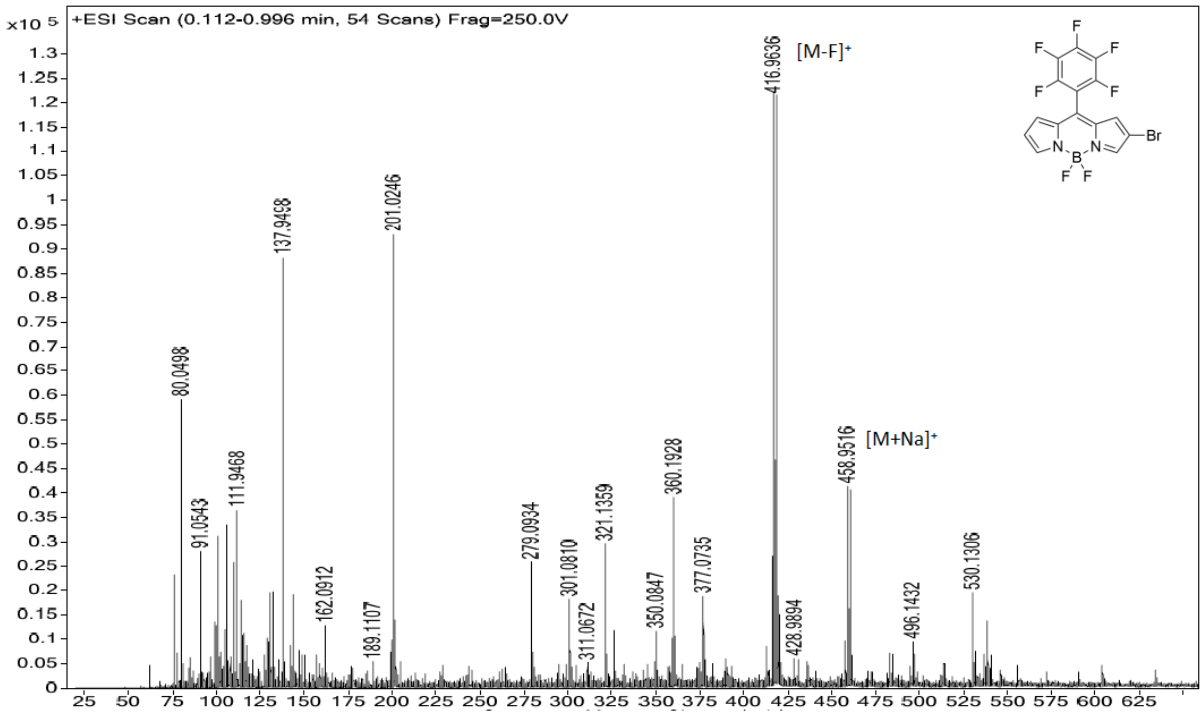

Figure S46: HRMS spectrum (ESI+) of BODIPY **17**.

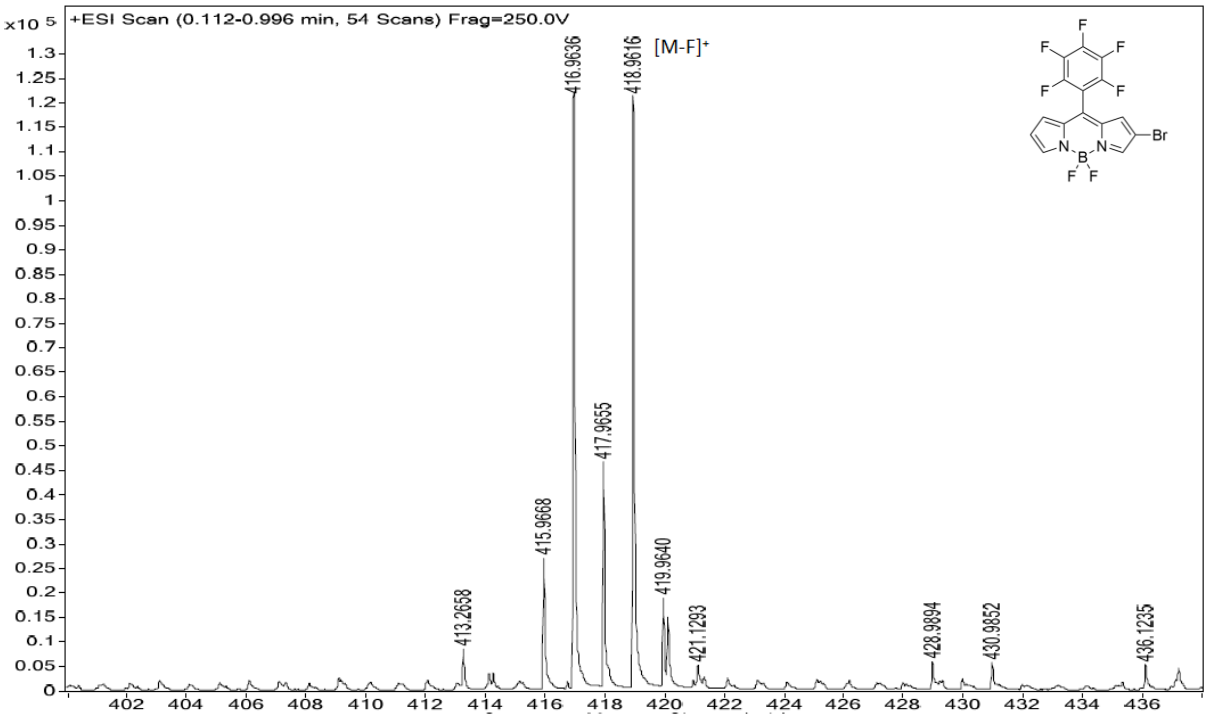

Figure S47: Zoom in from HRMS spectrum (ESI+) of BODIPY **17**.

2-Bromo-8-[4-(*N*-prop-2-ynylamino)-2,3,5,6-tetrafluorophenyl]-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (**19**):

BODIPY **19** was prepared according to the general synthetic procedure. BODIPY **3a** (100 mg, 0.25 mmol) and NBS (113 mg, 0.64 mmol) were dissolved in 10 mL of DCM. The mixture was stirred for 1.5 h. After column chromatography (silica gel, DCM/*n*-hexane = 1/1, v/v) BODIPY **19** obtained as a green solid (75 mg, 0.16 mmol, 63 %).

^{1}H NMR (500 MHz, THF-d$_8$): δ (ppm) = 2.74 (t, *J* = 2.4 Hz, 1H, CH), 4.22–4.24 (m, 2H, CH_2), 6.36 (s, 1H, NH), 6.67 (d, *J* = 4.3 Hz, 1H, $H_{pyrrole}$), 7.07 (s, 1H, $H_{pyrrole}$), 7.15 (d, *J* = 4.2 Hz, 1H, $H_{pyrrole}$), 7.94 (s, 1H, $H_{pyrrole}$), 8.13 (s, 1H, $H_{pyrrole}$).

^{13}C NMR (126 MHz, THF-d$_8$): δ (ppm) = 35.3 (CH_2), 73.3 (CH), 81.6 (C), 99.97 (t, *J* = 18.3 Hz, Ar-C_{ipso}), 107.1–107.2 (m, C_{Br}), 121.5 ($C_{pyrrole}$), 130.4 ($C_{pyrrole}$), 130.9–131.1 (m, Ar-C_{para}), 132.7 (C_{meso}), 133.6 ($C_{pyrrole}$), 135.6 ($C_{pyrrole}$), 137.4 ($C_{pyrrole}$), 138.63 (dd, *J* = 235.0, 22.2 Hz, Ar-C_{meta}), 144.5 ($C_{pyrrole}$), 138.63 (dd, *J* = 235.0, 22.2 Hz), 145.91 (dd, *J* = 246.2, 12.2 Hz, Ar-C_{ortho}), 149.6 ($C_{pyrrole}$).

^{19}F NMR (376 MHz, THF-d$_8$): δ (ppm) = -142.07 (d, *J* = 17.7 Hz, 2F, CF_{meta}), -145.46 – -145.68 (m_C, 2F, BF_2), -159.92 (d, *J* = 17.9 Hz, 2F, CF_{ortho}).

HRMS (ESI-TOF): *m/z* calcd. for $C_{18}H_9BBrF_6N_3Na^+$ $[M+Na]^+$: 493.9869, found: 493.9886.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3400 [ν(NH)], 3297 [ν(C≡CH)], 2948 [$\nu(CH_2)$], 1652 [ν(C=C)], 1087 [ν(BF), ν(CBr)], 761 [δ(-HC=CH-)].

UV/Vis (DCM): λ_{max} (nm) [log (ε/L mol^{-1} cm^{-1})] = 389 [4.05], 536 [4.63].

Fluorescence (DCM): λ_{max} (nm) = 562 at $\lambda_{Excitation}$ (nm) = 380, 520.

M.P. (°C): 80–82.

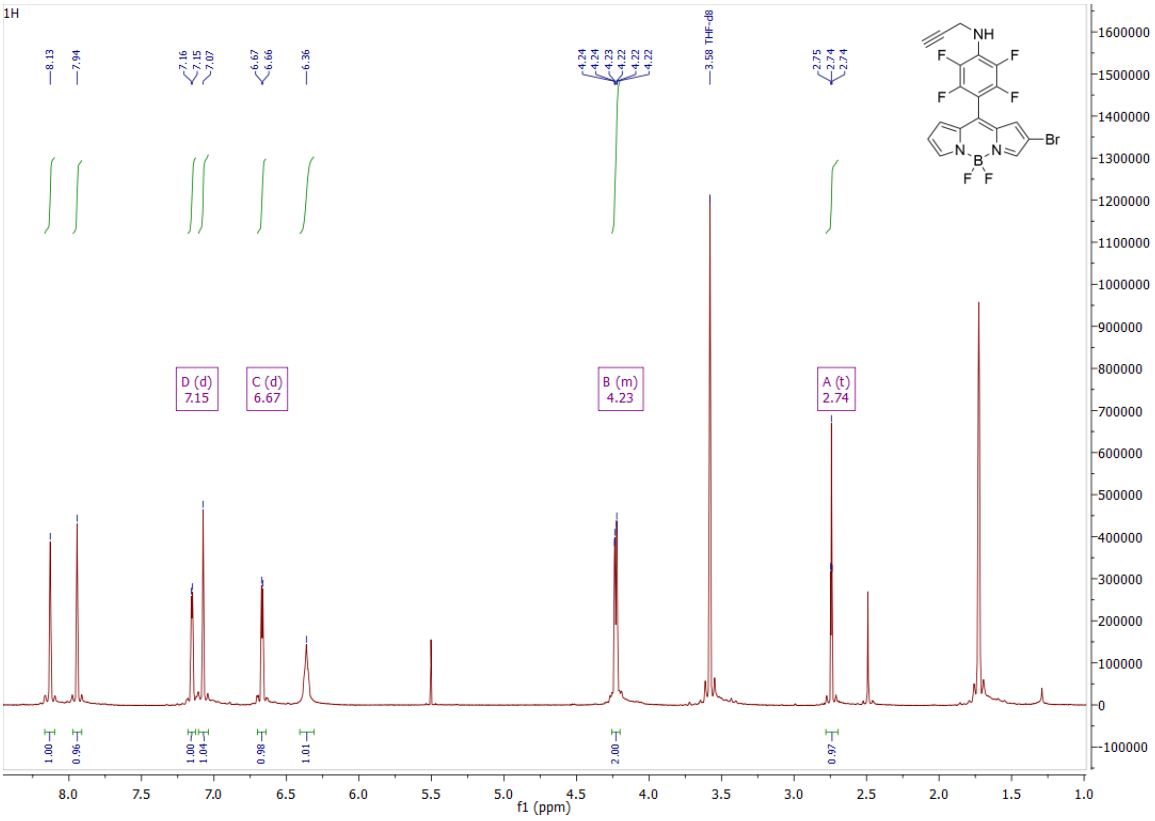

Figure S48: ^{1}H NMR (500 MHz, THF-d_8) spectrum of BODIPY **19**.

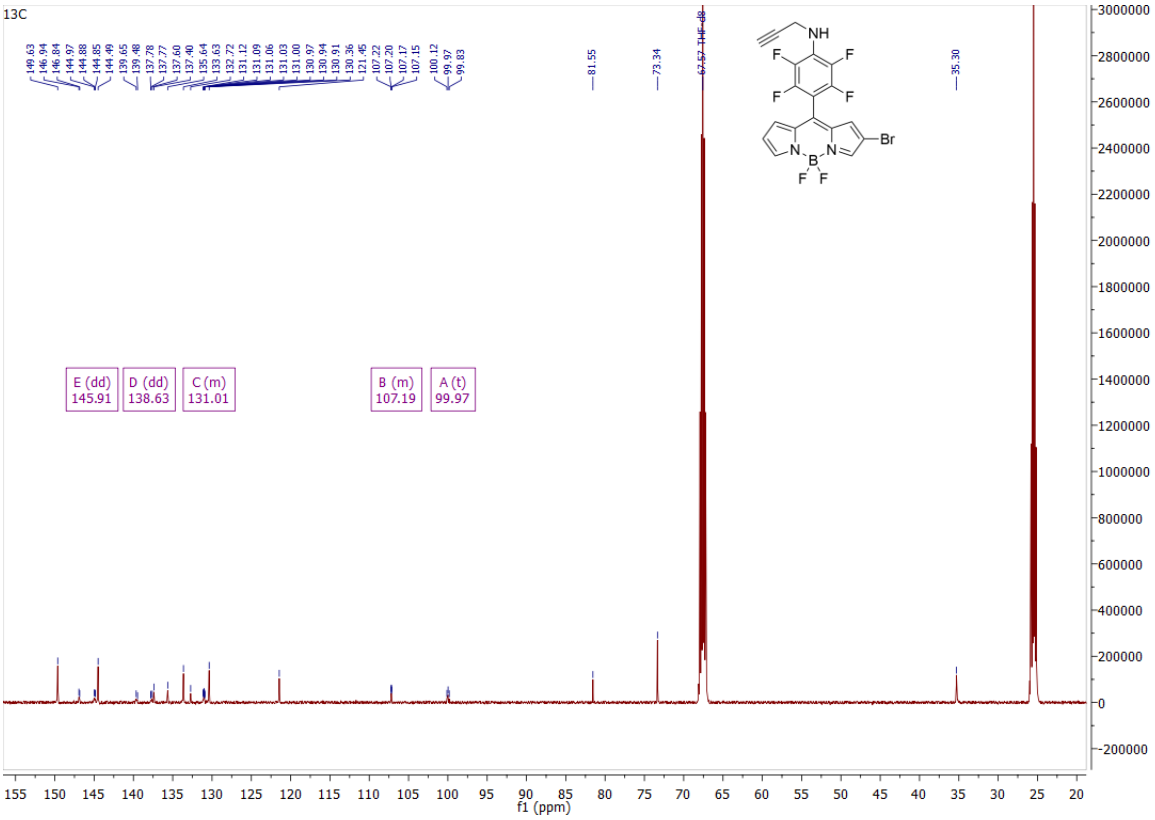

Figure S49: ^{13}C NMR (126 MHz, THF-d_8) spectrum of BODIPY **19**.

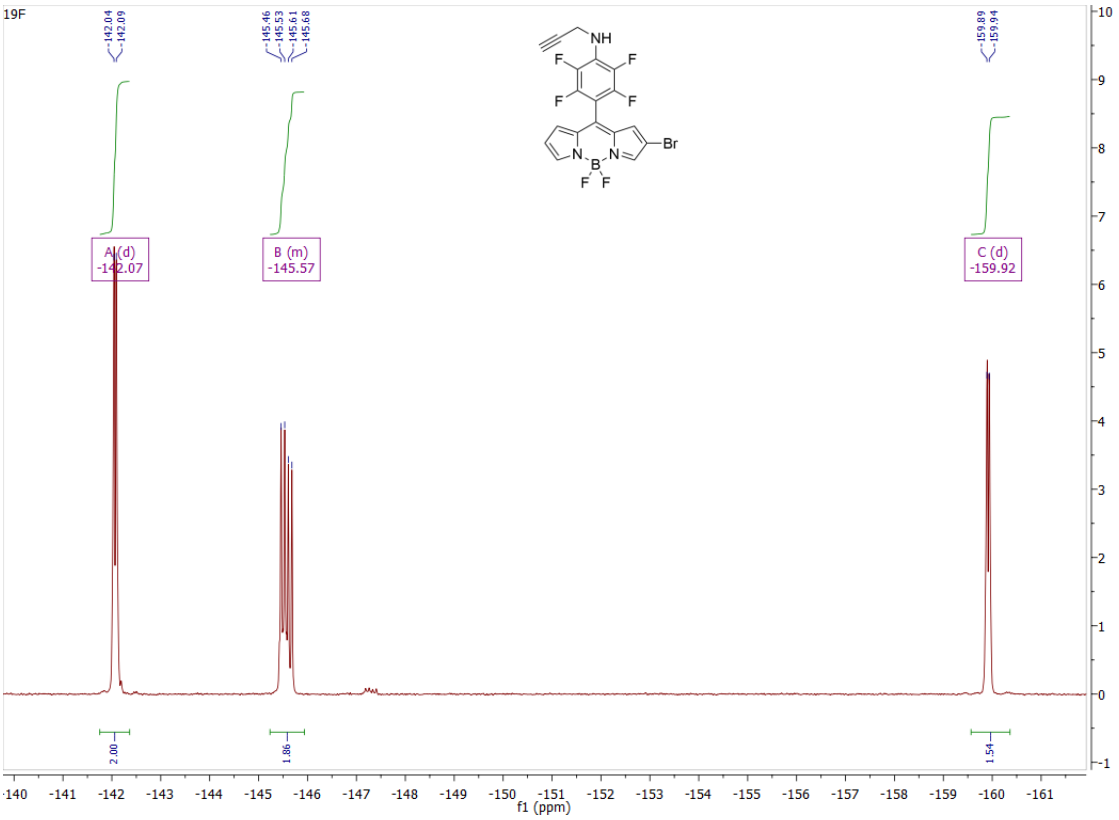

Figure S50: ^{19}F NMR (376 MHz, THF-d_8) spectrum of BODIPY **19**.

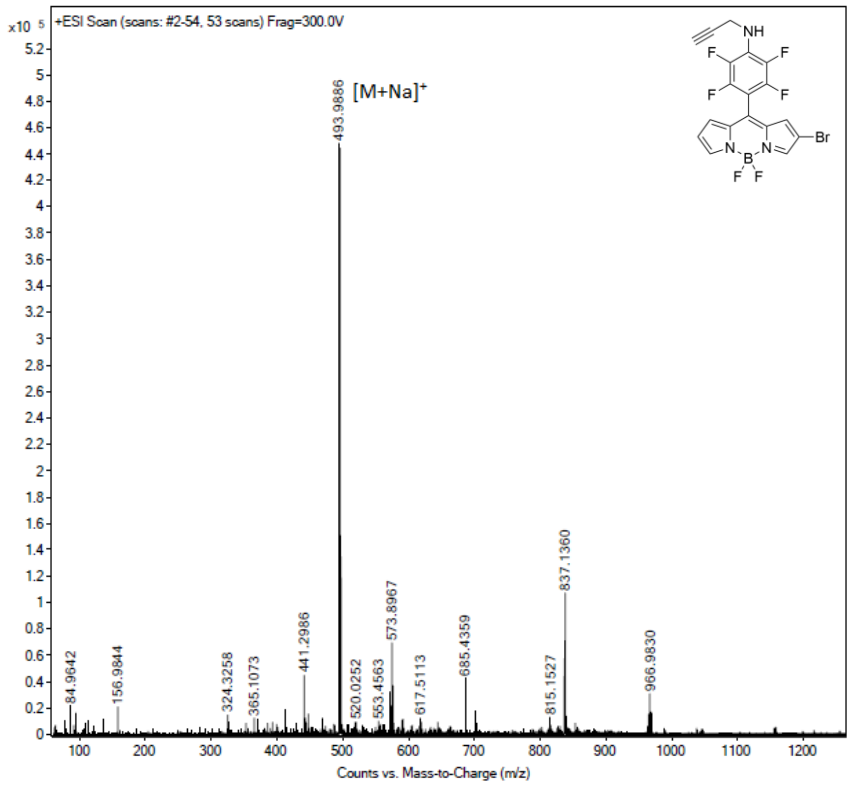

Figure S51: HRMS spectrum (ESI+) of BODIPY **19**.

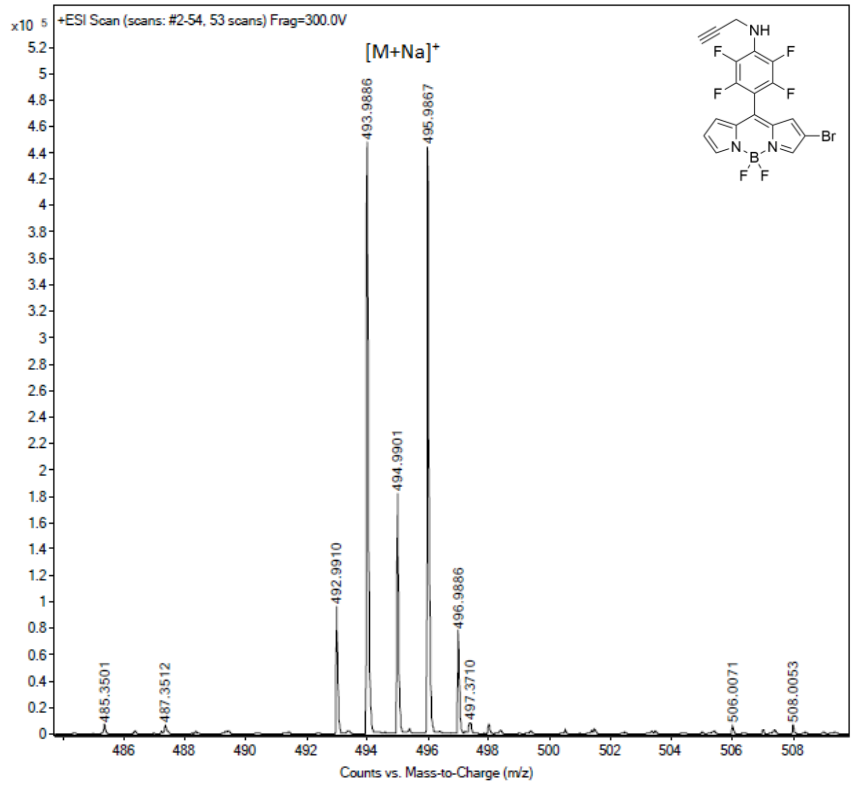

Figure S52: Zoom in from HRMS spectrum (ESI+) of BODIPY **19**.

2-Bromo-8-(4-butyloxy-2,3,5,6-tetrafluorophenyl)]-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (**20**): BODIPY **20** was prepared according to the general synthetic procedure. BODIPY **5a** (100 mg, 0.24 mmol) and NBS (108 mg, 0.61 mmol) were dissolved in 10 mL of DCM. The mixture was stirred for 1 h. After column chromatography (silica gel, DCM/ *n*-hexane = 1/2, v/v) BODIPY **20** was obtained as a reddish-green solid (63 mg, 0.13 mmol, 53 %).

^{1}H NMR (500 MHz, THF-d_8): δ (ppm) = 1.01 (t, *J* = 7.4 Hz, 1H, Me), 1.52–1.59 (m, 2H, CH_2), 1.80–1.85 (m, 2H, CH_2), 4.40 (t, *J* = 6.4 Hz, 2H, CH_2), 6.69 (d, *J* = 4.4 Hz, 1H, $H_{pyrrole}$), 7.07 (s, 1H, $H_{pyrrole}$), 7.15 (d, *J* = 4.4 Hz, 1H, $H_{pyrrole}$), 8.01 (s, 1H, $H_{pyrrole}$), 8.19 (s, 1H, $H_{pyrrole}$).

^{13}C NMR (126 MHz, THF-d_8): δ (ppm) = 14.2 (Me), 19.9 (CH_2), 33.0 (CH_2), 76.4 (CH_2), 106.2–106.5 (m, Ar-C_{ipso}), 107.6–107.7 (m, C_{Br}), 121.9 ($C_{pyrrole}$), 128.9 (Ar-C_{para}), 130.3 ($C_{pyrrole}$), 131.3 (C_{meso}), 133.6 ($C_{pyrrole}$), 135.4 ($C_{pyrrole}$), 137.2 ($C_{pyrrole}$), 141.26 (dd, *J* = 70.4, 13.8 Hz, Ar-C_{meta}), 144.3 ($C_{pyrrole}$), 138.63 (dd, *J* = 235.0, 22.2 Hz), 145.91 (dd, *J* = 253.0, 10.5 Hz, Ar-C_{ortho}), 150.5 ($C_{pyrrole}$).

^{19}F NMR (376 MHz, THF-d_8): δ (ppm) = -141.26 (d, *J* = 19.1 Hz, 2F, CF_{meta}), -145.42 – -145.64 (m_C, 2F, BF_2), -157.18 (d, *J* = 17.3 Hz, 2F, CF_{ortho}).

HRMS (ESI-TOF): *m/z* calcd. for $C_{19}H_{14}BBrF_6N_2ONa^+$ $[M+Na]^+$: 513.0179, found: 513.0196, *m/z* calcd. for $C_{19}H_{14}BBrF_6N_2OK^+$ $[M+K]^+$: 530.9898, found: 530.9988.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2962 and 2933 [*ν*(Me), *ν*(CH_2)], 2874 [*ν*(CH)], 1651 [*ν*(C=N)], 1083 [*ν*(BF), *ν*(CBr)], 765 [*δ*(-HC=CH-)].

UV/Vis (DCM): λ_{max} (nm) [log (ε/L mol^{-1} cm^{-1})] = 368 [4.11], 536 [4.71].

Fluorescence (DCM): λ_{max} (nm) = 562 at $\lambda_{Excitation}$ (nm) = 350, 520.

M.P. (°C): 114–116.

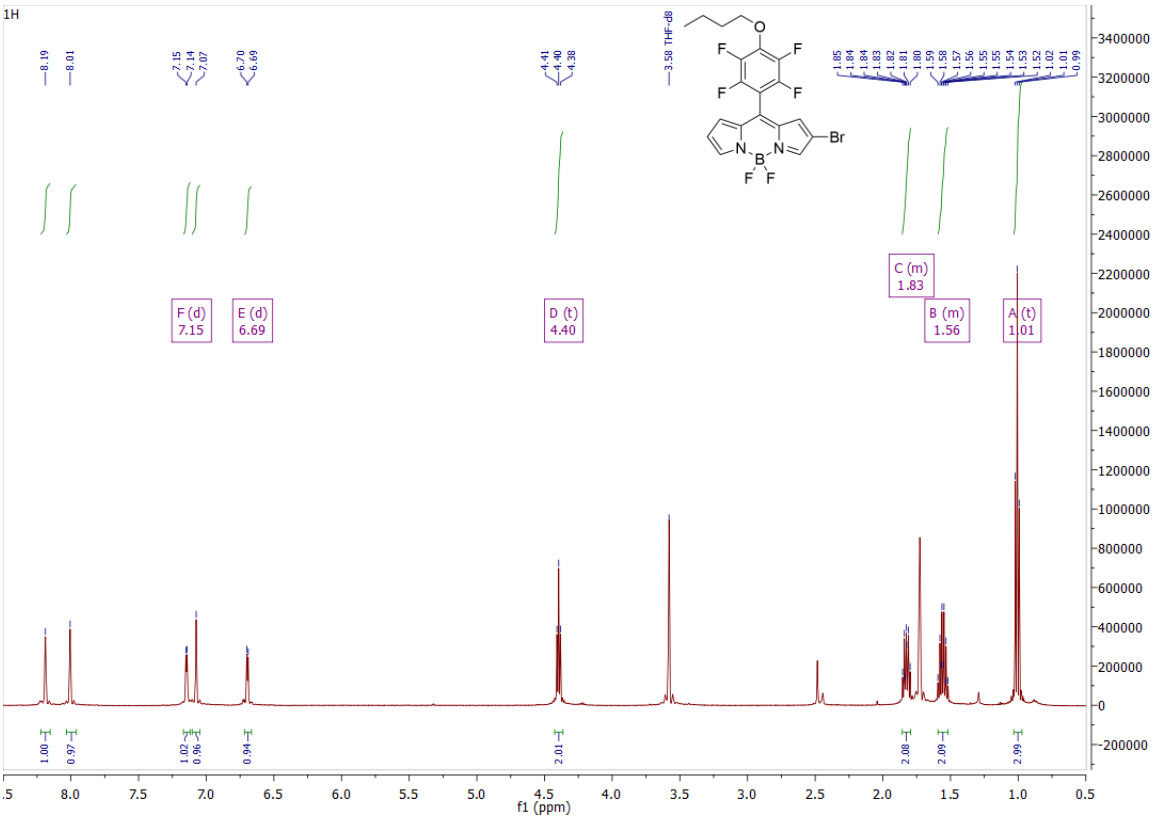

Figure S53: ^{1}H NMR (500 MHz, THF-d_8) spectrum of BODIPY **20**.

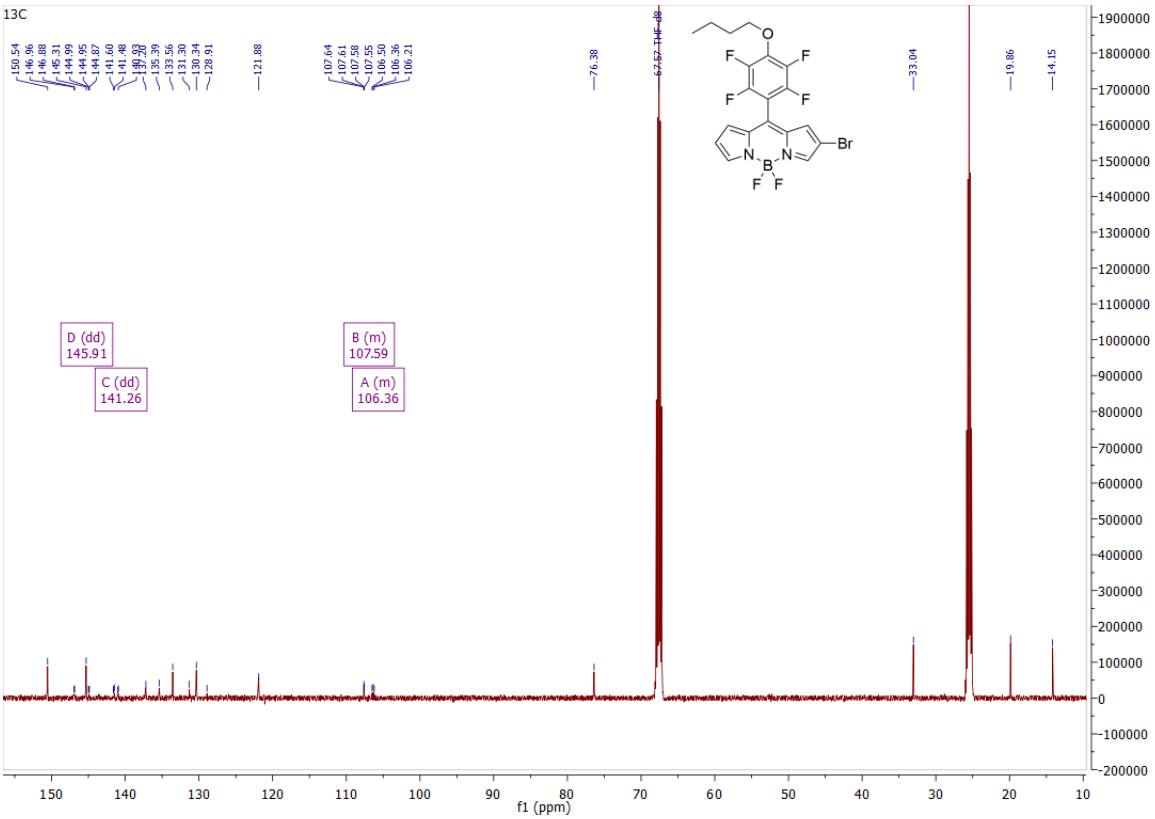

Figure S54: ^{13}C NMR (126 MHz, THF-d_8) spectrum of BODIPY **20**.

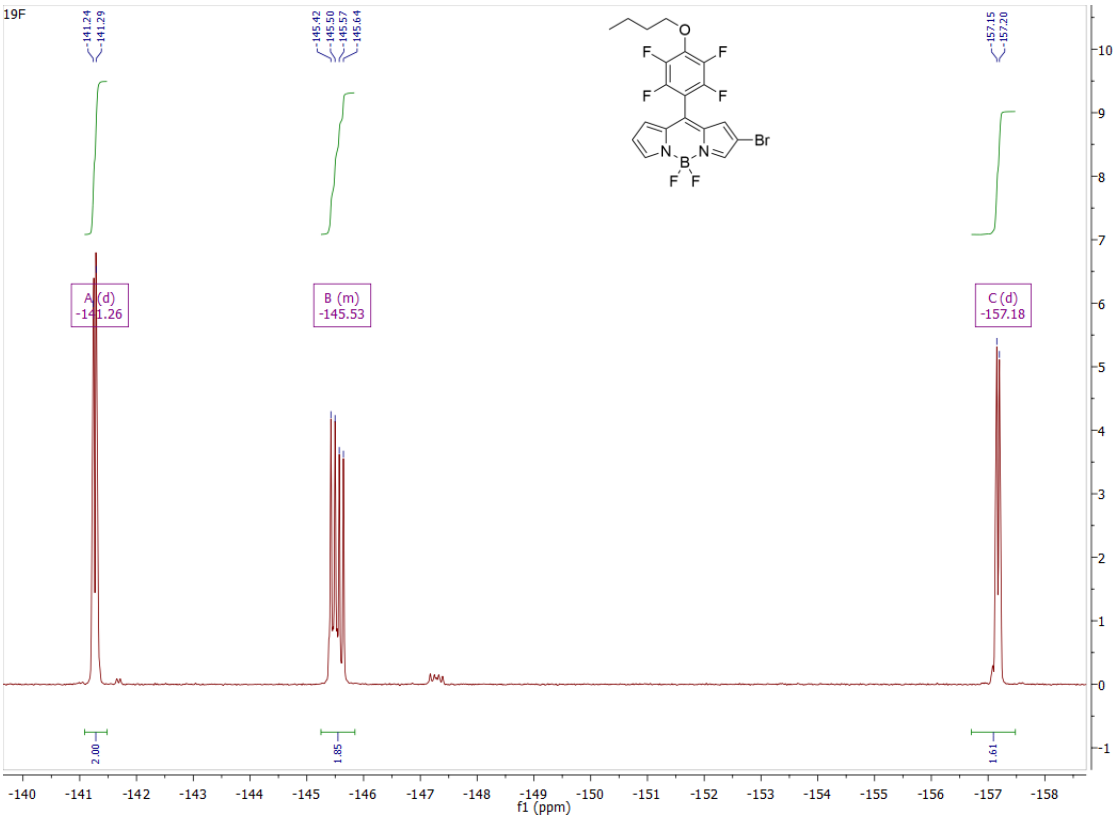

Figure S55: ^{19}F NMR (376 MHz, THF-d_8) spectrum of BODIPY **20**.

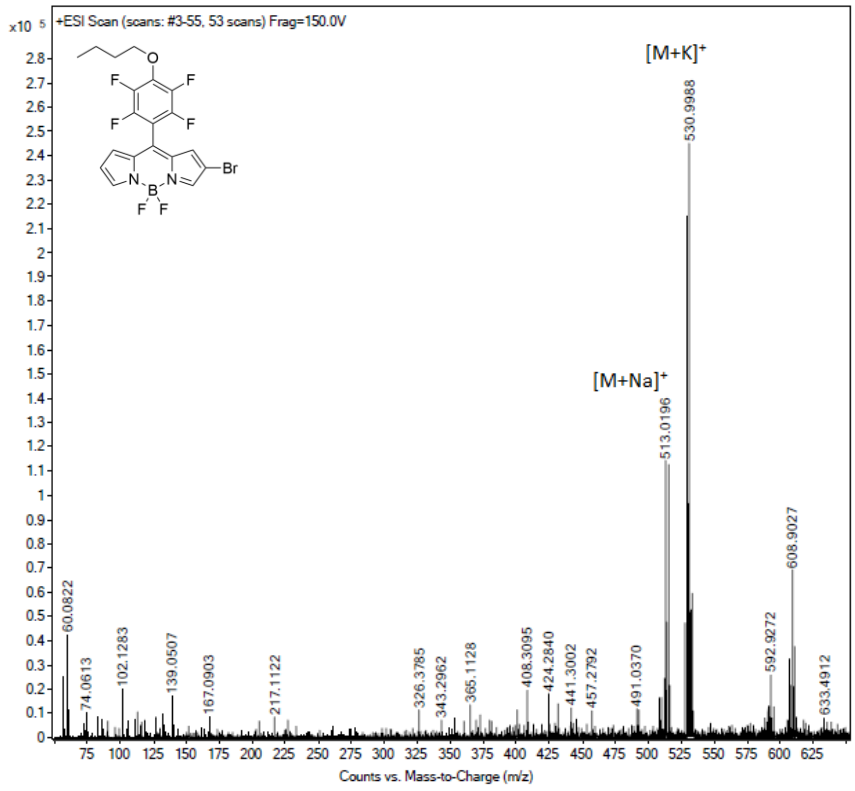

Figure S56: HRMS spectrum (ESI+) of BODIPY **20**.

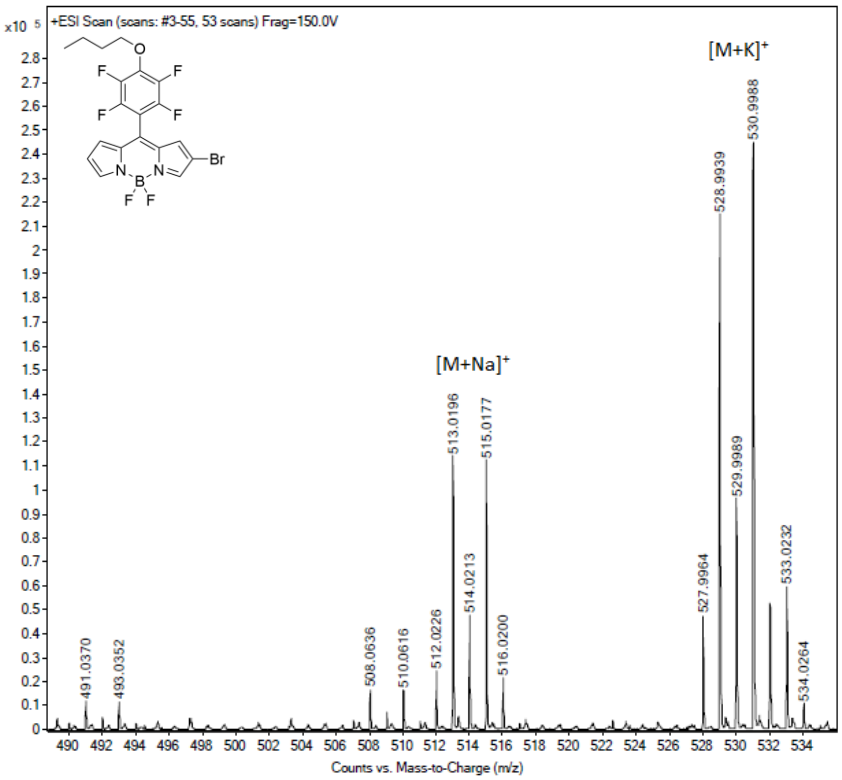

Figure S57: Zoom in from HRMS spectrum (ESI+) of BODIPY **20**.

2-Bromo-8-[4-(prop-2-enyloxy)-2,3,5,6-tetrafluorophenyl]-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (**21**):

BODIPY **21** was prepared according to the general synthetic procedure. BODIPY **6a** (100 mg, 0.25 mmol) and NBS (112 mg, 0.63 mmol) were dissolved in 10 mL of DCM. The mixture was stirred for 1 h. After column chromatography (silica gel, DCM/*n*-hexane = 1/1, v/v) BODIPY **21** was obtained as a reddish-green solid (37 mg, 78 µmol, 31 %).

^{1}H NMR (500 MHz, THF-d$_8$): δ (ppm) = 4.89 (d, *J* = 5.9 Hz, 2H, CH_2), 5.34 (dd, *J* = 10.4, 1.1 Hz, 1H, -HC=**CH$_2$**), 5.48 (dd, *J* = 17.1, 1.5 Hz, 1H, -HC=**CH$_2$**), 6.11 (ddt, *J* = 16.6, 10.9, 5.9 Hz, 1H, -**HC**=CH_2), 6.70 (d, *J* = 4.3 Hz, 1H, $H_{pyrrole}$), 7.06 (s, 1H, $H_{pyrrole}$), 7.13 (d, *J* = 4.3 Hz, 1H, $H_{pyrrole}$), 8.01 (s, 1H, $H_{pyrrole}$), 8.19 (s, 1H, $H_{pyrrole}$).

^{13}C NMR (126 MHz, THF-d$_8$): δ (ppm) = 76.7 (CH_2), 106.74 (t, *J* = 18.5 Hz, Ar-C_{ipso}), 107.6–107.7 (m, C_{Br}), 119.98 (-HC=**CH$_2$**), 121.9 ($C_{pyrrole}$), 130.3 ($C_{pyrrole}$), 131.2 (C_{meso}), 133.5 ($C_{pyrrole}$), 133.7 (-**HC**=CH_2), 135.4 ($C_{pyrrole}$), 137.2 ($C_{pyrrole}$), 140.36 (dd, *J* = 8.1, 3.4 Hz, Ar-C_{para}), 142.60 (dd, *J* = 242.4, 13.7 Hz, Ar-C_{meta}), 145.4 ($C_{pyrrole}$), 145.82 (dd, *J* = 248.9, 19.3 Hz, Ar-C_{ortho}), 150.6 ($C_{pyrrole}$).

^{19}F NMR (376 MHz, THF-d$_8$): δ (ppm) = -141.18 (d, *J* = 18.1 Hz, 2F, CF_{meta}), -145.45 – -145.67 (m_C, 2F, BF_2), -156.46 (d, *J* = 18.3 Hz, 2F, CF_{ortho}).

HRMS (ESI-TOF): *m/z* calcd. for $C_{18}H_{10}BBrF_6N_2ONa^+$ $[M+Na]^+$: 498.9845, found: 498.9851.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3121 [ν(Ar-H)], 1651 [ν(C=C)], 1488 [$\delta(CH_2)$], 1084 [ν(BF) ν(CBr)], 764 [δ(-HC=CH-)].

UV/Vis (DCM): λ_{max} (nm) [log (ε/L mol^{-1} cm^{-1})] = 366 [4.05], 537 [4.66].

Fluorescence (DCM): λ_{max} (nm) = 562 at $\lambda_{Excitation}$ (nm) = 340, 520.

M.P. (°C): 101–103.

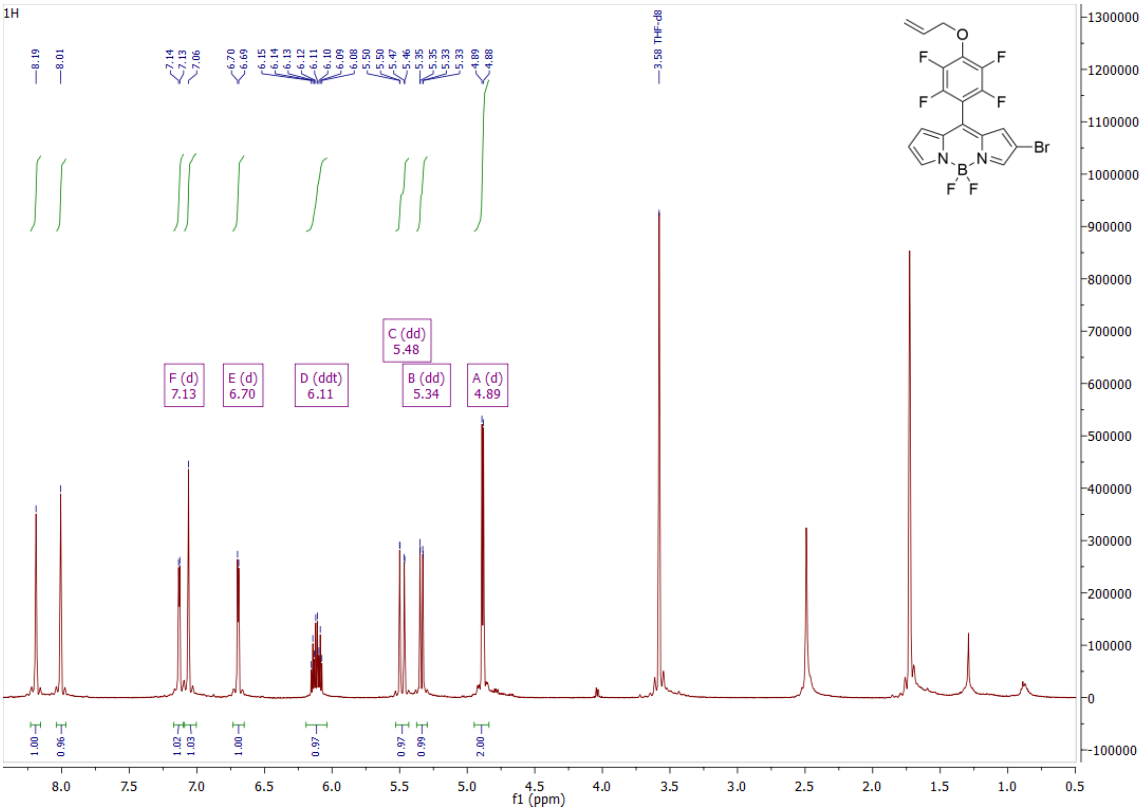

Figure S58: ^{1}H NMR (500 MHz, THF-d_8) spectrum of BODIPY **21**.

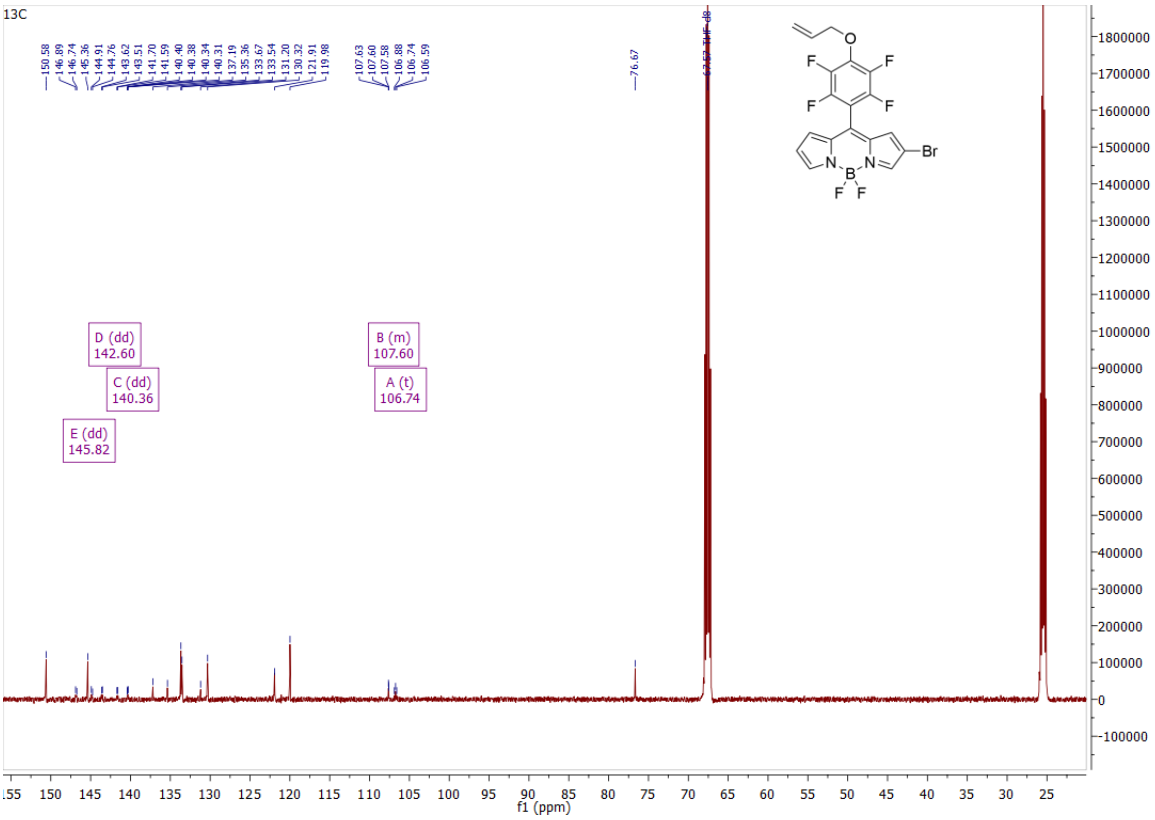

Figure S59: ^{13}C NMR (126 MHz, THF-d_8) spectrum of BODIPY **21**.

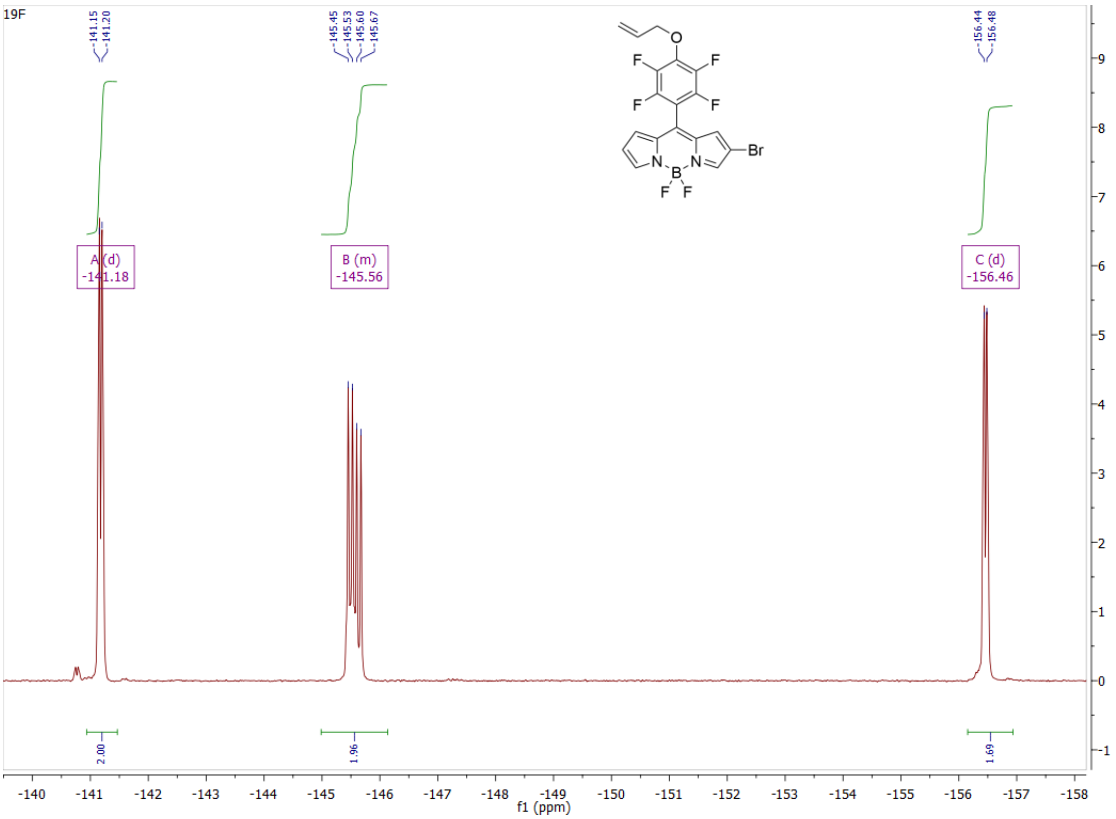

Figure S60: ^{19}F NMR (376 MHz, THF-d_8) spectrum of BODIPY **21**.

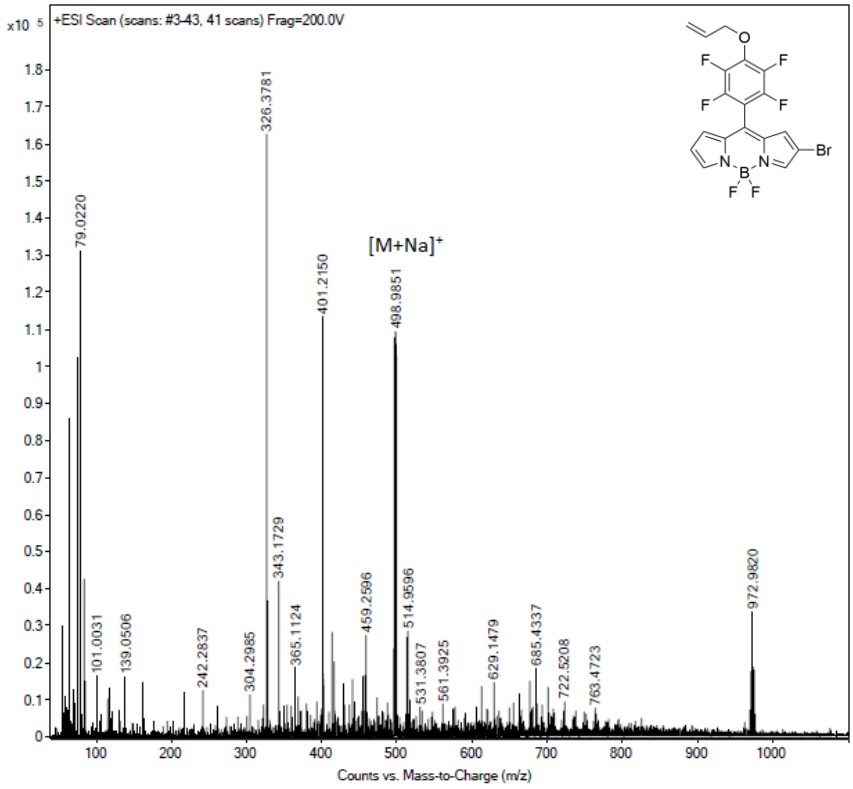

Figure S61: HRMS spectrum (ESI+) of BODIPY **21**.

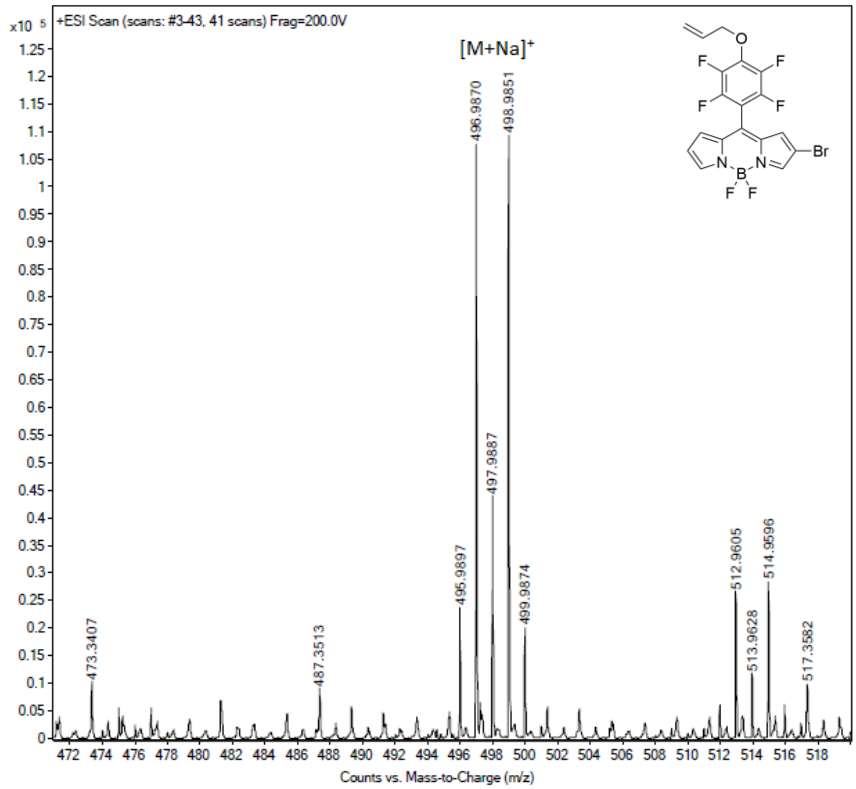

Figure S62: Zoom in from HRMS spectrum (ESI+) of BODIPY **21**.

2-Bromo-8-[4-(prop-2-ynyloxy)-2,3,5,6-tetrafluoro-phenyl]-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (**22**):

BODIPY **22** was prepared according to the general synthetic procedure. BODIPY **7a** (100 mg, 0.25 mmol) and NBS (113 mg, 0.64 mmol) were dissolved in 10 mL of DCM. The mixture was stirred for 1 h. After column chromatography (silica gel, DCM/*n*-hexane = 1/1, v/v) BODIPY **22** was obtained as a reddish-green solid (41 mg, 87 µmol, 34 %).

^{1}H NMR (500 MHz, THF-d_8): δ (ppm) = 3.25 (t, *J* = 2.4 Hz, 1H, CH), 5.06 (d, *J* = 2.4 Hz, 2H, CH_2), 6.70 (d, *J* = 4.3 Hz, 1H, $H_{pyrrole}$), 7.07 (s, 1H, $H_{pyrrole}$), 7.14 (d, *J* = 4.2 Hz, 1H, $H_{pyrrole}$), 8.02 (s, 1H, $H_{pyrrole}$), 8.20 (s, 1H, $H_{pyrrole}$).

^{13}C NMR (126 MHz, THF-d_8): δ (ppm) = 63.1 (CH_2), 78.2 (CH), 79.4 (C), 107.5 – 107.8 (m, C_{Br} + Ar-C_{ipso}), 121.97 ($C_{pyrrole}$), 130.3 ($C_{pyrrole}$), 131.0 (C_{meso}), 133.5 ($C_{pyrrole}$), 135.3 ($C_{pyrrole}$), 137.1 ($C_{pyrrole}$), 139.1–139.3 (m, Ar-C_{para}), 142.92 (dd, *J* = 248.7, 10.8 Hz, Ar-C_{meta}), 145.5 ($C_{pyrrole}$), 145.76 (dd, *J* = 248.0, 13.2 Hz, Ar-C_{ortho}), 150.7 ($C_{pyrrole}$).

^{19}F NMR (376 MHz, THF-d_8): δ (ppm) = -140.98 (d, *J* = 19.7 Hz, 2F, CF_{meta}), -145.43 – -145.65 (m_C, 2F, BF_2), -155.64 (d, *J* = 17.3 Hz, 2F, CF_{ortho}).

HRMS (ESI-TOF): *m/z* calcd. for $C_{18}H_8BBrF_6N_2ONa^+$ $[M+Na]^+$: 496.9689, found: 496.9686, *m/z* calcd. for $C_{18}H_8BBrF_6N_2OK^+$ $[M+K]^+$: 512.9428, found: 512.9428, *m/z* calcd. for $C_{36}H_{16}B_2Br_2F_{12}N_4O_2Na^+$ $[2M+Na]^+$: 968.9506, found: 968.9496.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3295 [ν(C≡CH)], 2948 [$\nu(CH_2)$], 1651 [ν(C=C)], 1488 [$\delta(CH_2)$], 1081 [ν(BF), ν(CBr)], 763 [δ(-HC=CH-)].

UV/Vis (DCM): λ_{max} (nm) [log (ε/L mol^{-1} cm^{-1})] = 367 [4.09], 537 [4.73].

Fluorescence (DCM): λ_{max} (nm) = 562 at $\lambda_{Excitation}$ (nm) = 340, 520.

M.P. (°C): 139–141.

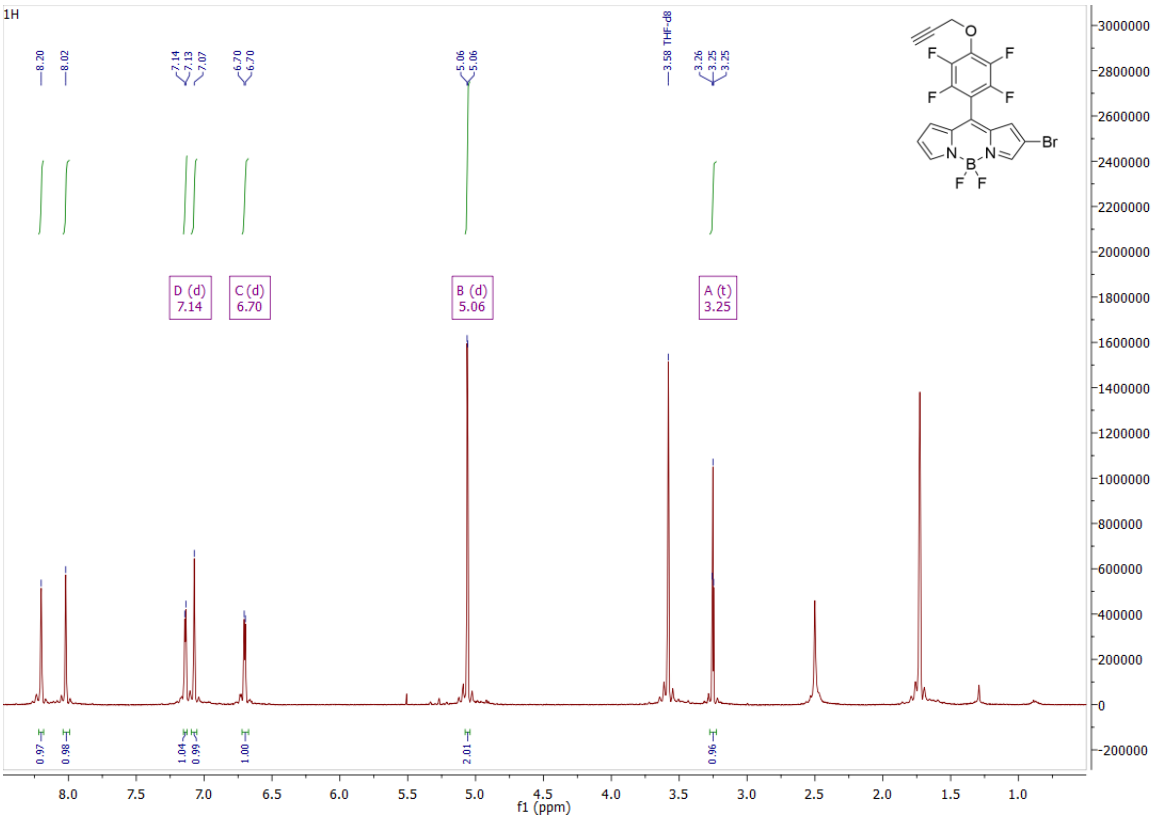

Figure S63: ^{1}H NMR (500 MHz, THF-d_8) spectrum of BODIPY **22**.

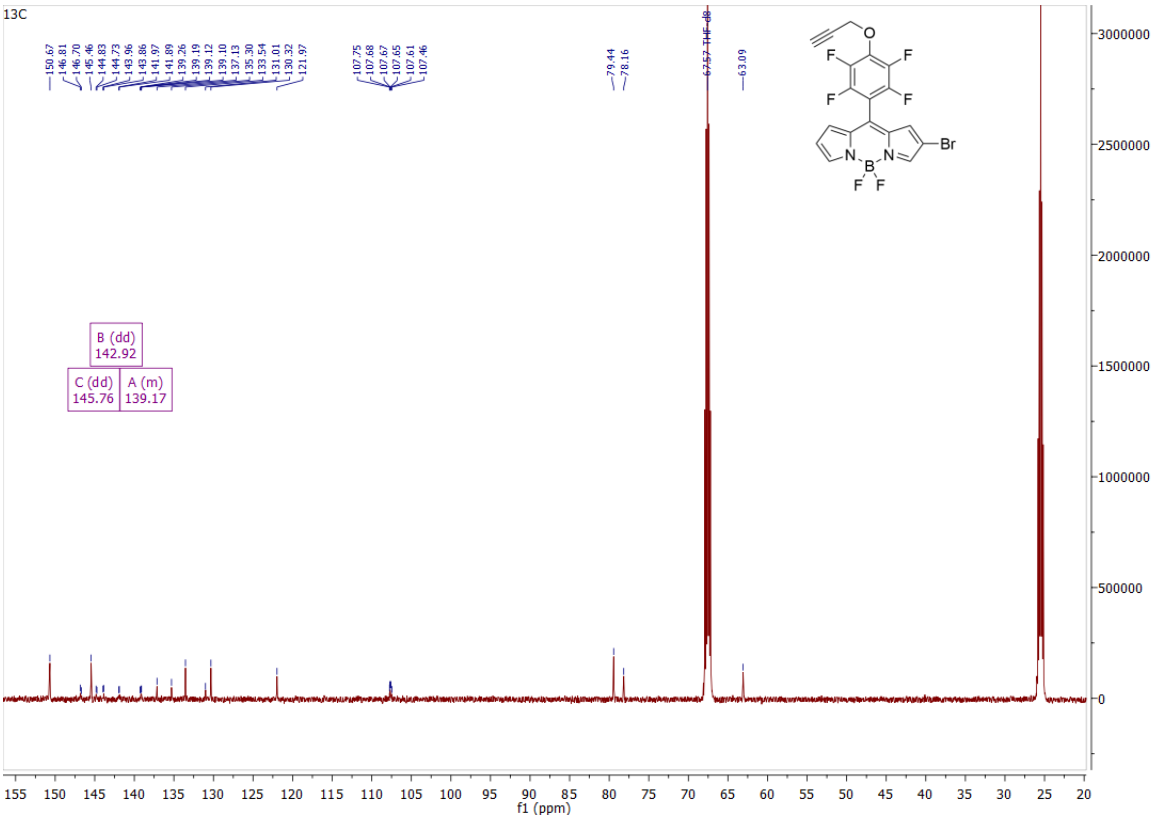

Figure S64: ^{13}C NMR (126 MHz, THF-d_8) spectrum of BODIPY **22**.

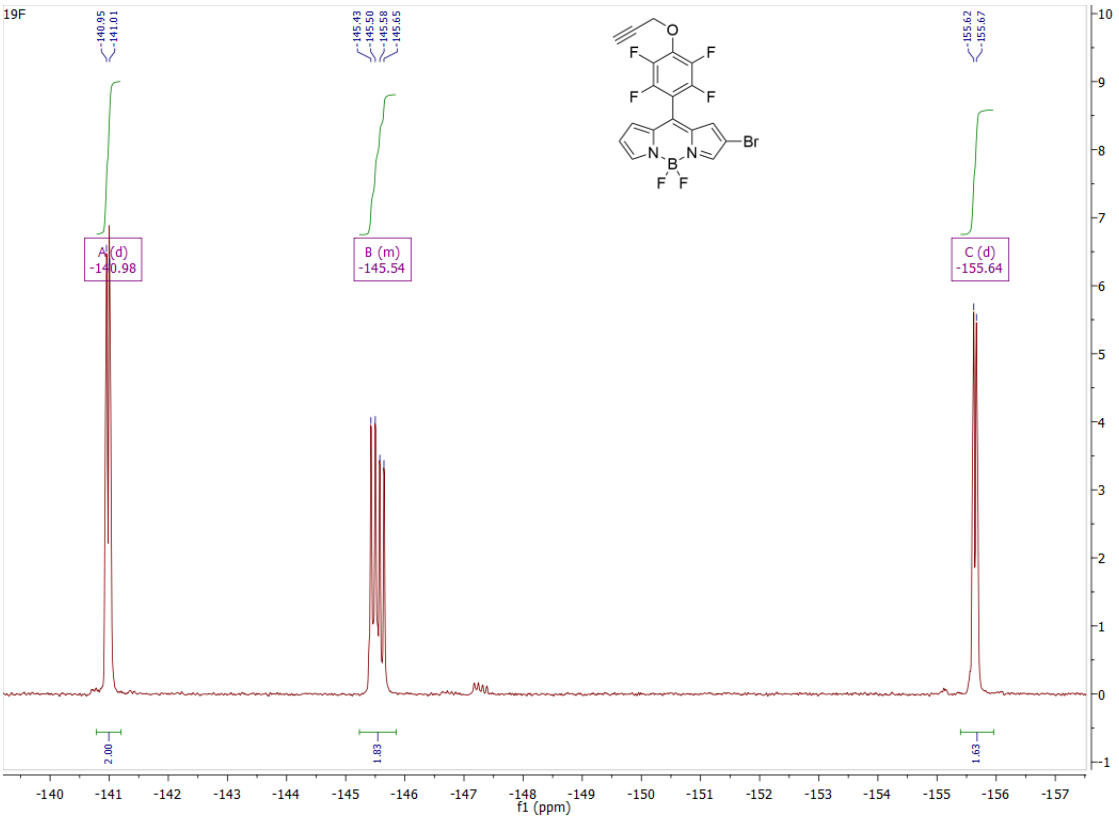

Figure S65: ^{19}F NMR (376 MHz, THF-d_8) spectrum of BODIPY **22**.

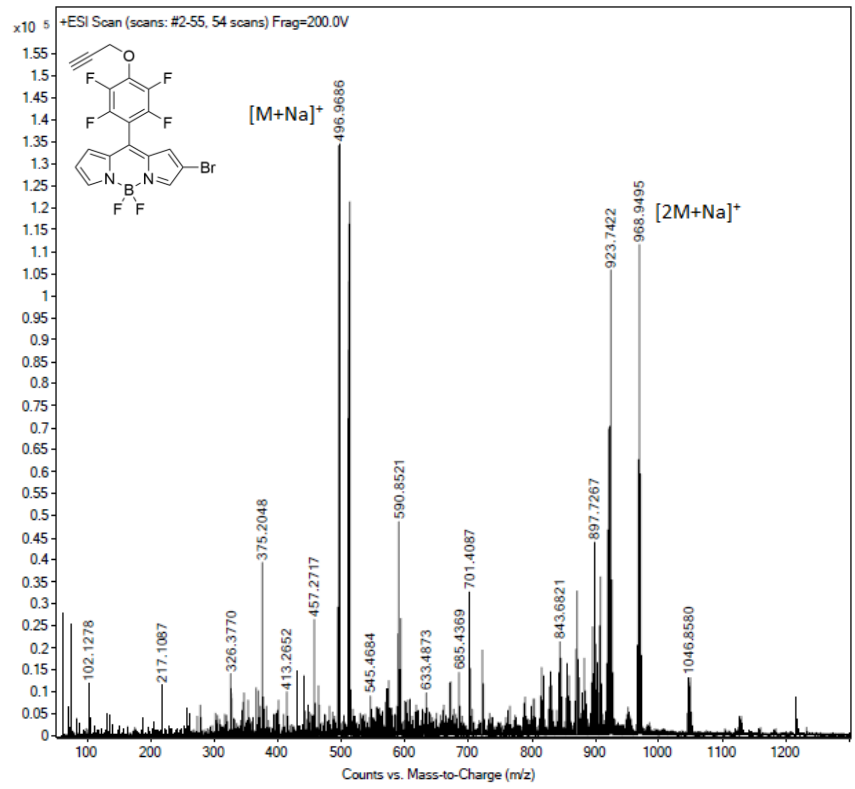

Figure S66: Zoom in from HRMS spectrum (ESI+) of BODIPY **22**.

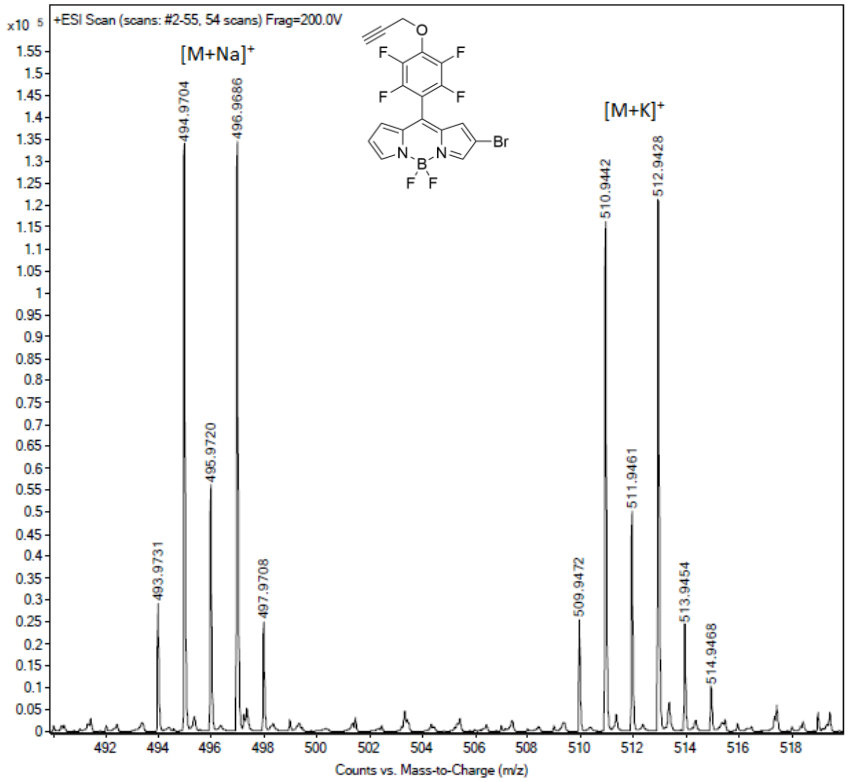

Figure S67: HRMS spectrum (ESI+) of BODIPY **22**.

2-Bromo-8-(4-fluoro-3-nitrophenyl)-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (**18**):

BODIPY **18** was prepared according to the general synthetic procedure. BODIPY **8a** (100 mg, 0.30 mmol) and NBS (129 mg, 0.75 mmol) were dissolved in 5 mL of DCM. The mixture was stirred for 3 h. After column chromatography (silica gel, DCM/*n*-hexane = 1/1, v/v) BODIPY **18** was obtained as a reddish–green solid (79 mg, 0.19 mmol, 64 %).

^{1}H NMR (700 MHz, $CDCl_3$): δ (ppm) = 6.66–6.67 (m, 1H, $H_{pyrrole}$), 6.81 (s, 1H, $H_{pyrrole}$), 6.93 (d, J = 4.4 Hz, 1H, $H_{pyrrole}$), 7.53 (dd, J = 10.1, 8.5 Hz, 1H, Ar-H_{meta}), 7.83–7.85 (m, 2H, $H_{pyrrole}$, Ar-H_{ortho}), 8.06 (s, 1H, $H_{pyrrole}$), 8.27 (dd, J = 6.8, 2.3 Hz, 1H, Ar-H_{ortho}).

^{13}C NMR (176 MHz, $CDCl_3$): δ (ppm) = 107.2 (C-Br), 119.5 (d, $J_{C\text{-}F}$ = 21.4 Hz, Ar-C_{meta}), 120.8 ($C_{pyrrole}$), 127.8 (Ar-C_{ortho}), 129.8 ($C_{pyrrole}$), 130.1* , 132.6 ($C_{pyrrole}$), 134.0 ($C_{pyrrole}$), 135.3 ($C_{pyrrole}$), 136.9 (d, $J_{C\text{-}F}$ = 9.1 Hz, Ar-C_{ortho}), 137.7 (d, $J_{C\text{-}F}$ = 8.2 Hz)*, 142.0 (C_{meso}), 143.96 ($C_{pyrrole}$), 147.98 ($C_{pyrrole}$), 156.89 (d, $J_{C,F}$ = 271.0 Hz, Ar-C_{para}). *These signals could not be assigned exactly to corresponding carbon atoms. They belong to the Ar-C_{ipso} and the Ar-C_{nitro} of the aryl residue.

^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) = -116.84 (s, 1F, CF), -144.18 – -144.63 (m, 2F, BF_2).

HRMS (ESI-TOF): *m/z* calcd. for $C_{15}H_8BBrF_3N_3NaO_2^+$ $[M+Na]^+$: 431.9737, found 431.9743.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3120 [$\nu(CH_{aromat})$], 1618 [$\nu(C{=}C)$], 1586 [$\nu_{asym}(NO_2)$], 1358 [$\nu_{sym}(NO_2)$], 1255 [C=CF], 1087 [ν(BF), ν(CBr)].

UV/Vis (DCM): λ_{max} (nm) [log (ε/L mol^{-1} cm^{-1})] = 527 [4.69].

Fluorescence (DCM): λ_{max} (nm) = 550 at $\lambda_{Excitation}$ (nm) = 510.

M.P. (°C): 165–167.

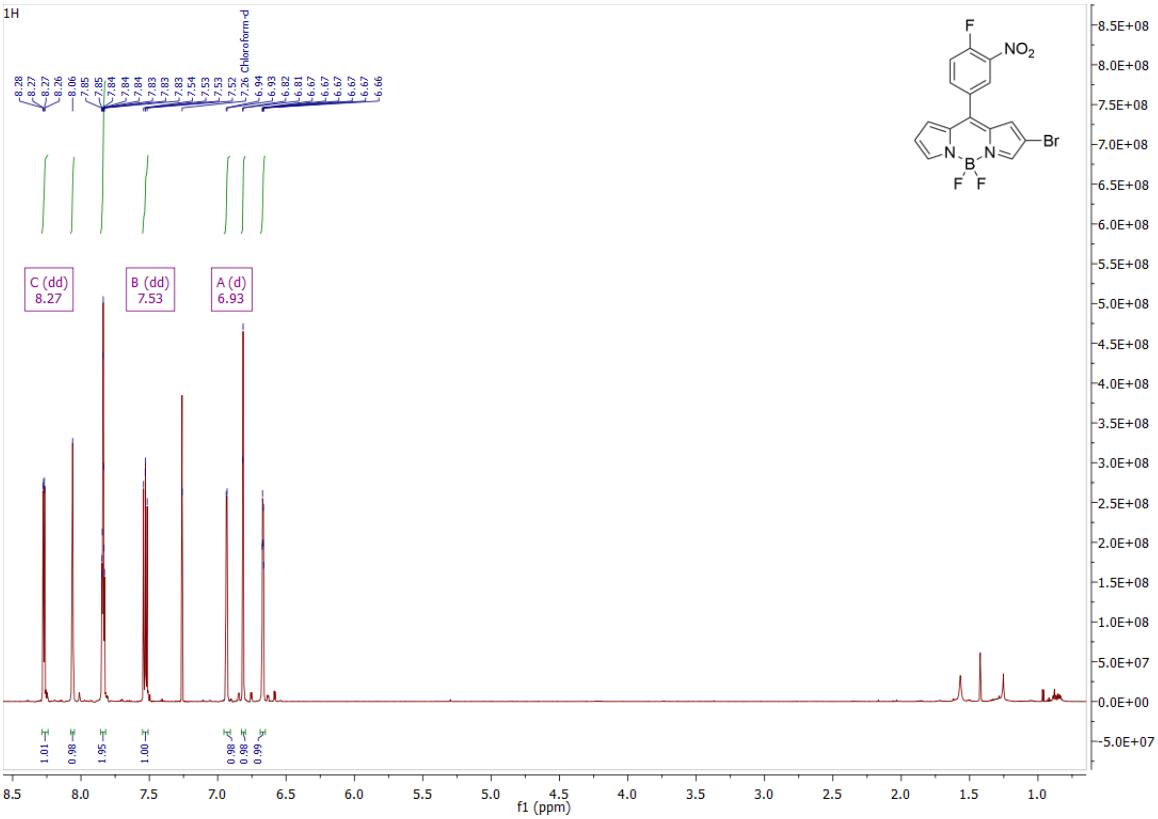

Figure S68: ^{1}H NMR (700 MHz, $CDCl_3$) spectrum of BODIPY **18**.

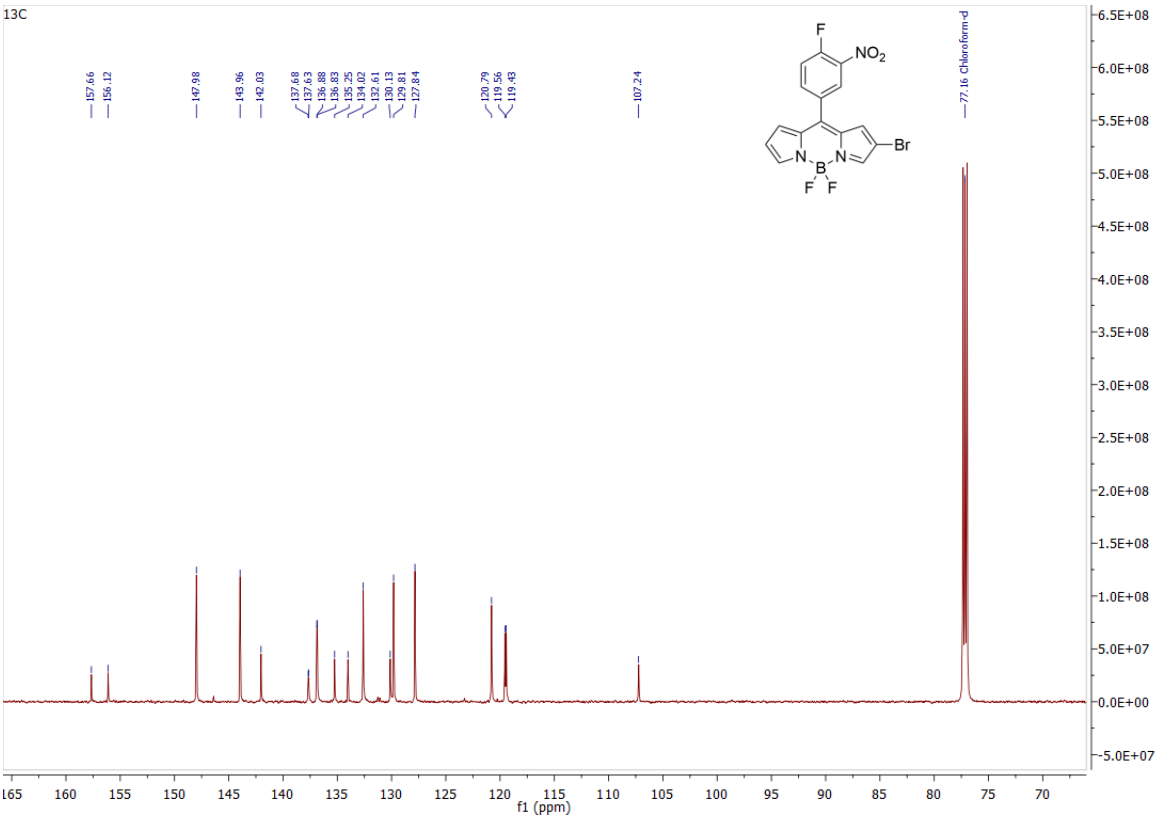

Figure S69: ^{13}C NMR (176 MHz, $CDCl_3$) spectrum of BODIPY **18**.

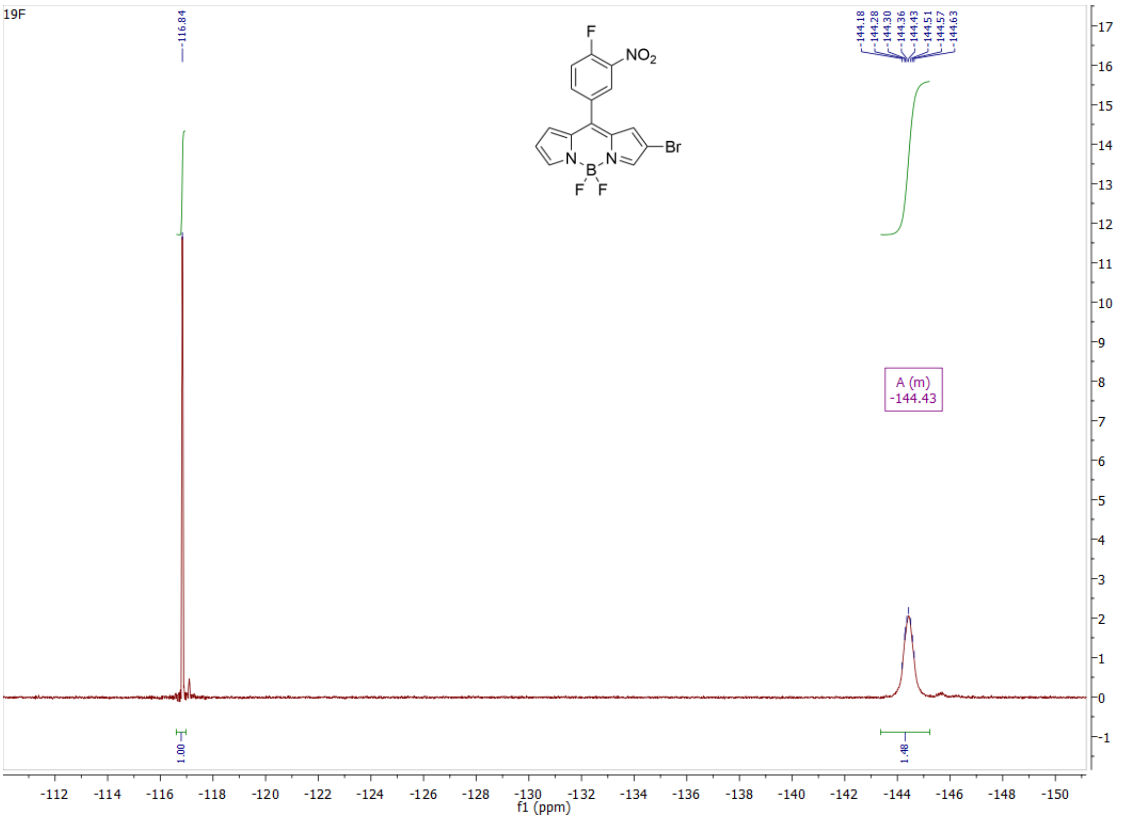

Figure S70: ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of BODIPY **18**.

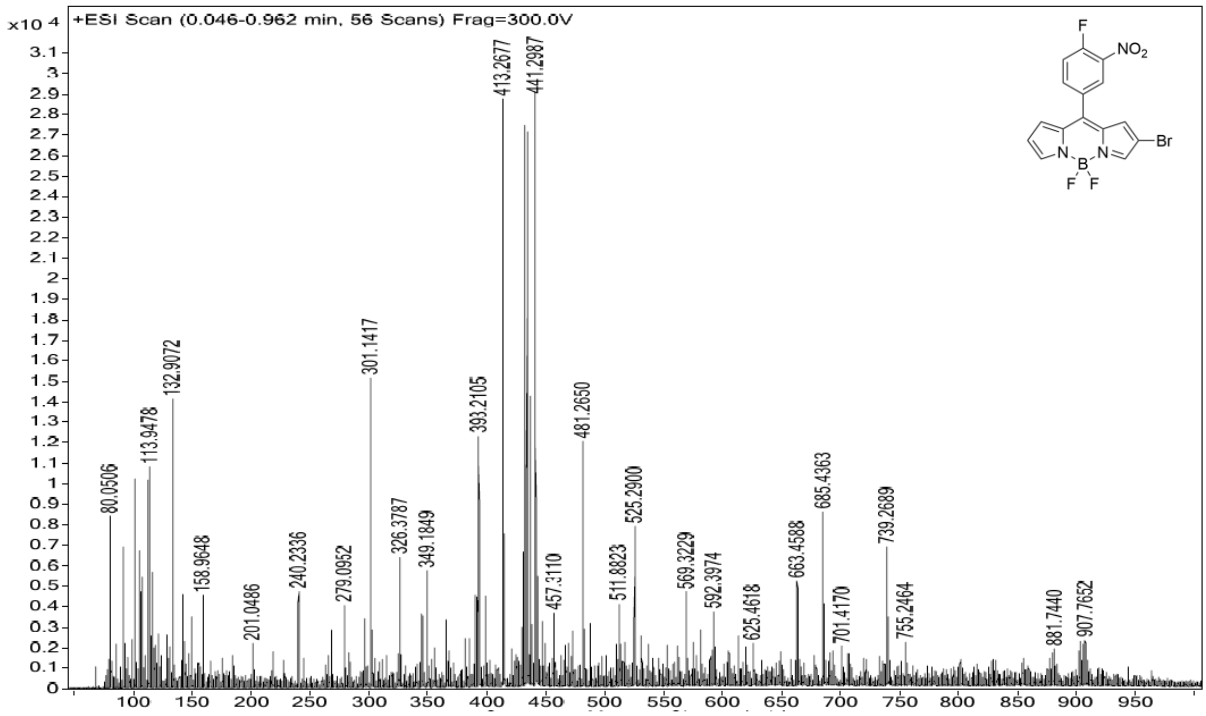

Figure S71: HRMS spectrum (ESI+) of BODIPY **18**.

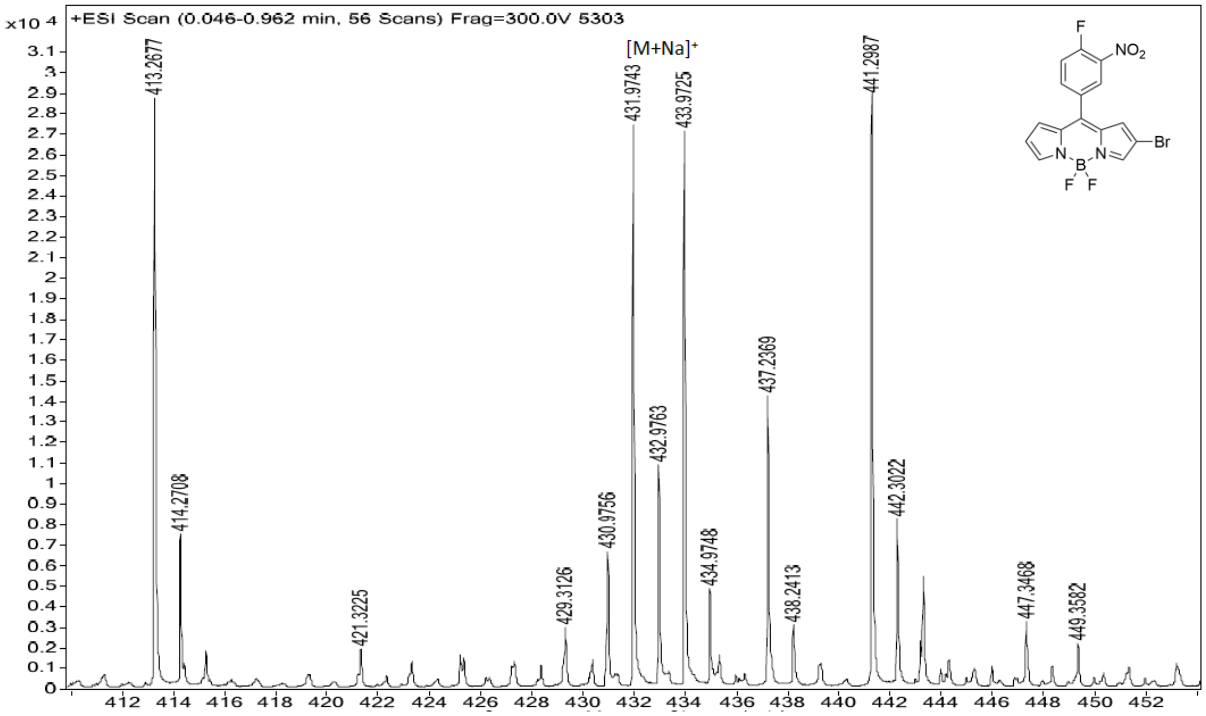

Figure S72: Zoom in from HRMS spectrum (ESI+) of BODIPY **18**.

2-Bromo-8-[4-(*N*-butylamino)-3-nitrophenyl]-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (**23**):
BODIPY **23** was prepared according to the general synthetic procedure. BODIPY **9a** (100 mg, 0.26 mmol) and NBS (116 mg, 0.65 mmol) were dissolved in 10 mL of DCM. The mixture was stirred for 3 h. After column chromatography (silica gel, DCM/*n*-hexane = 4/1, v/v) BODIPY **23** was obtained as a red solid (58 mg, 0.13 mmol, 48 %).

^{1}H NMR (500 MHz, THF-d_8): δ (ppm) = 1.02 (t, J = 7.4 Hz, 3H, Me), 1.48–1.55 (m, 2H, CH_2), 1.75–1.80 (m, 2H, CH_2), 3.48–3.52 (m, 2H, CH_2), 6.68 (d, J = 4.3 Hz, 1H, $H_{pyrrole}$), 7.07 (s, 1H, $H_{pyrrole}$), 7.18 (d, J = 4.1 Hz, 1H, $H_{pyrrole}$), 7.23 (d, J = 9.0 Hz, 1H, Ar-H_{meta}), 7.80 (dd, J = 8.9, 2.2 Hz, 1H, Ar-H_{ortho}), 7.89 (s, 1H, $H_{pyrrole}$), 8.06 (s, 1H, $H_{pyrrole}$), 8.46–8.48 (m, 1H, NH), 8.49 (d, J = 2.2 Hz, 1H, Ar-H_{ortho}).
^{13}C NMR (126 MHz, THF-d_8): δ (ppm) = 14.3 (Me), 21.2 (CH_2), 32.0 (CH_2), 43.8 (CH_2), 106.3 (C_{Br}), 115.7 (Ar-C_{meta}), 120.5*, 121.1 ($C_{pyrrole}$), 130.1 ($C_{pyrrole}$), 131.1 (Ar-C_{ortho}), 133.1 ($C_{pyrrole}$), 133.2*, 135.0 ($C_{pyrrole}$), 136.2 ($C_{pyrrole}$), 138.7 (Ar-C_{ortho}), 142.5 ($C_{pyrrole}$), 146.5 (Ar-C_{para}), 147.0 ($C_{pyrrole}$), 148.0 (C_{meso}). *These signals could not be assigned exactly to corresponding carbon atoms. They belong to the Ar-C_{ipso} and the Ar-C_{nitro} of the aryl residue.
^{19}F NMR (376 MHz, THF-d_8): δ (ppm) = -145.66 – -145.44 (m_c, 2F, BF_2).
HRMS (ESI-TOF): *m/z* calcd. for $C_{19}H_{18}BBrF_2N_4O_2Na^+$ $[M+Na]^+$: 485.0566, found: 485.0548.
IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3370 [ν(NH)], 3118 [ν(Ar-H)], 2957 and 2929 [$\nu(CH_2)$, ν(Me)], 2871 [ν(CH)], 1619 [ν(C=N)], 1546 [$\nu_{as}(NO_2)$], 1478 [$\delta(CH_2)$, δ(Me)], 1356 [$\nu_{sym}(NO_2)$], 1114 and 1078 [ν(BF), ν(CBr)], 738 [δ(HC=CH)].
UV/Vis (DCM): λ_{max} (nm) [log (ε/L mol^{-1} cm^{-1})] = 518 [4.73].
Fluorescence (DCM): λ_{max} (nm) = 544 at $\lambda_{Excitation}$ (nm) = 500.
M.P.(°C): 129–132.

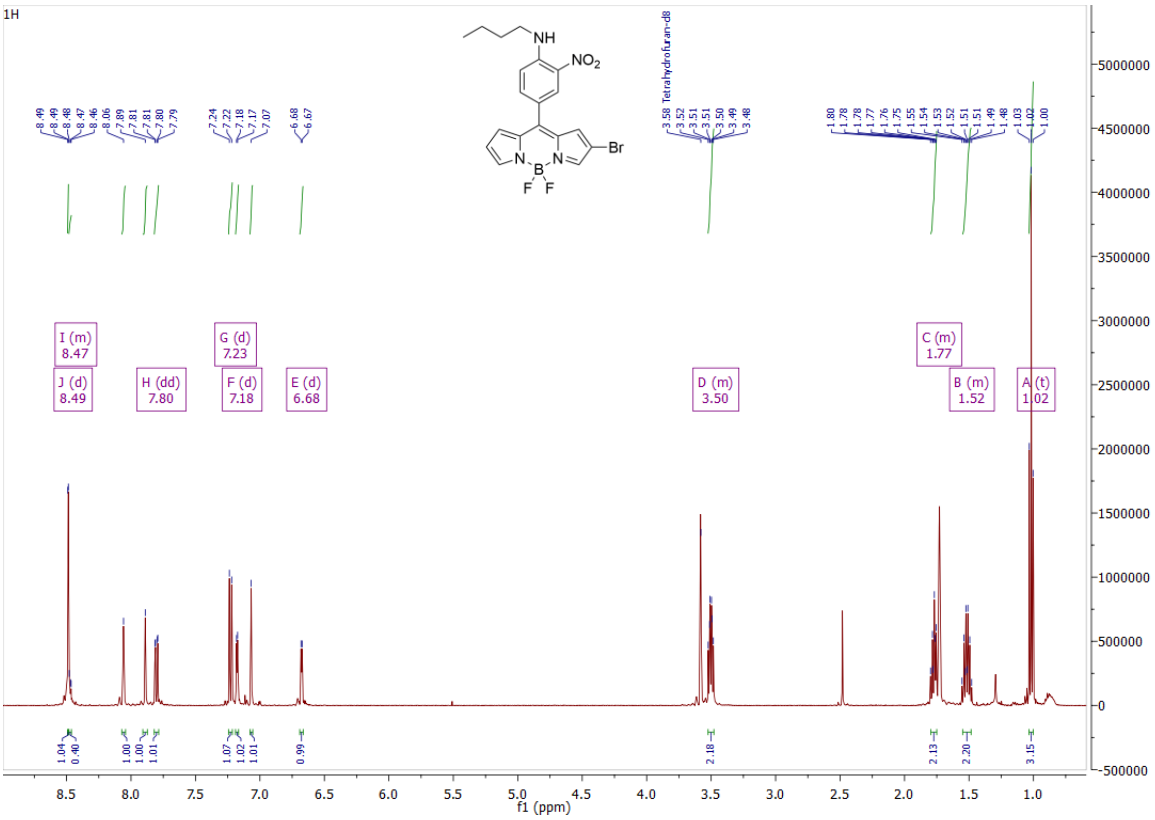

Figure S73: ^{1}H NMR (500 MHz, THF-d_8) spectrum of BODIPY **23**.

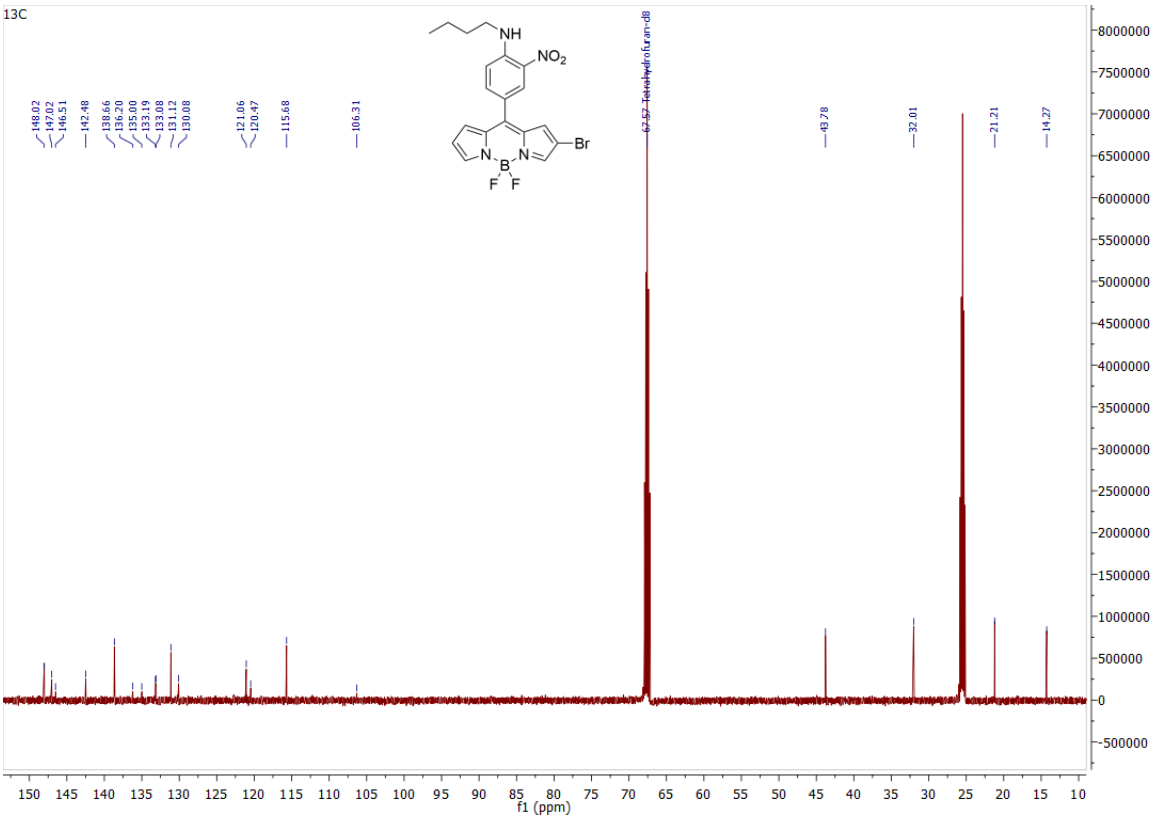

Figure S74: ^{13}C NMR (126 MHz, THF-d_8) spectrum of BODIPY **23**.

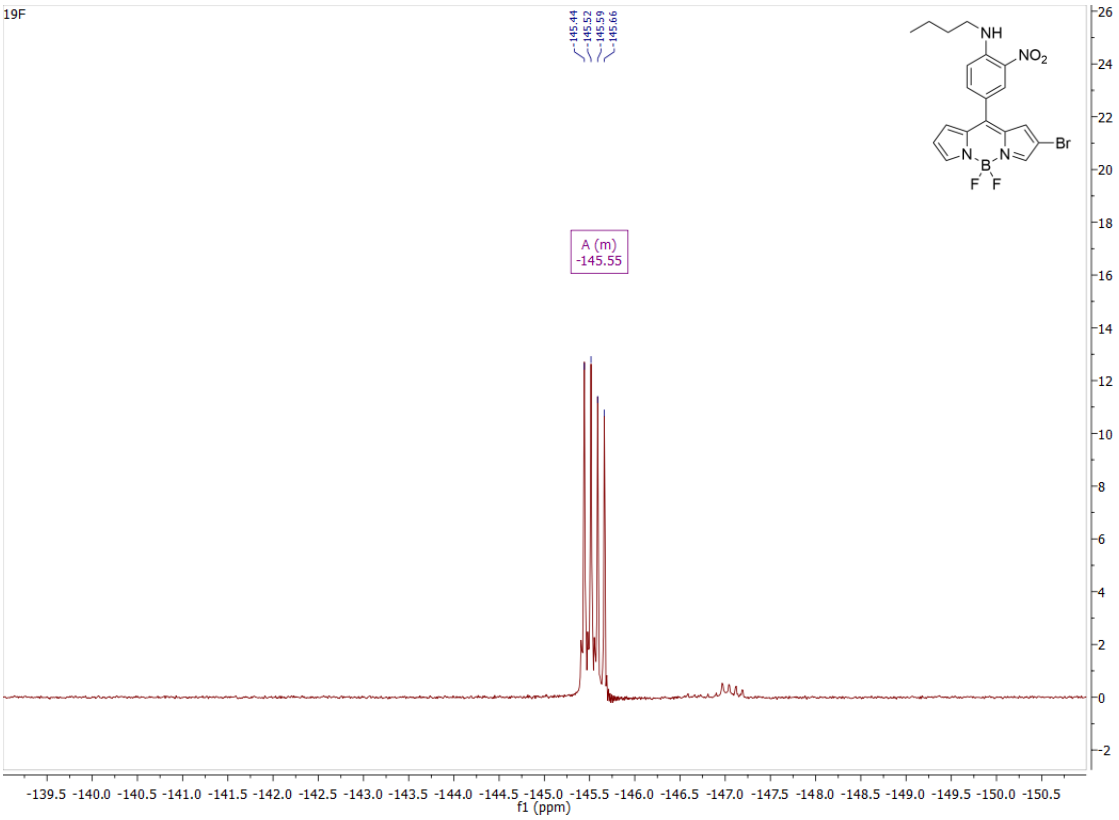

Figure S75: ^{19}F NMR (376 MHz, THF-d_8) spectrum of BODIPY **23**.

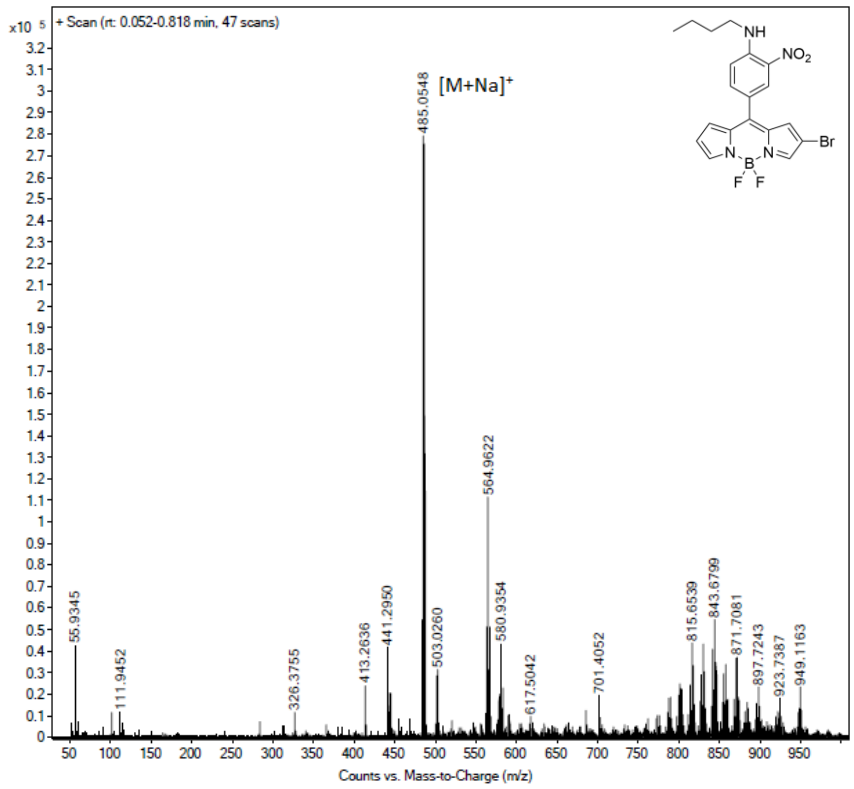

Figure S76: HRMS spectrum (ESI+) of BODIPY **23**.

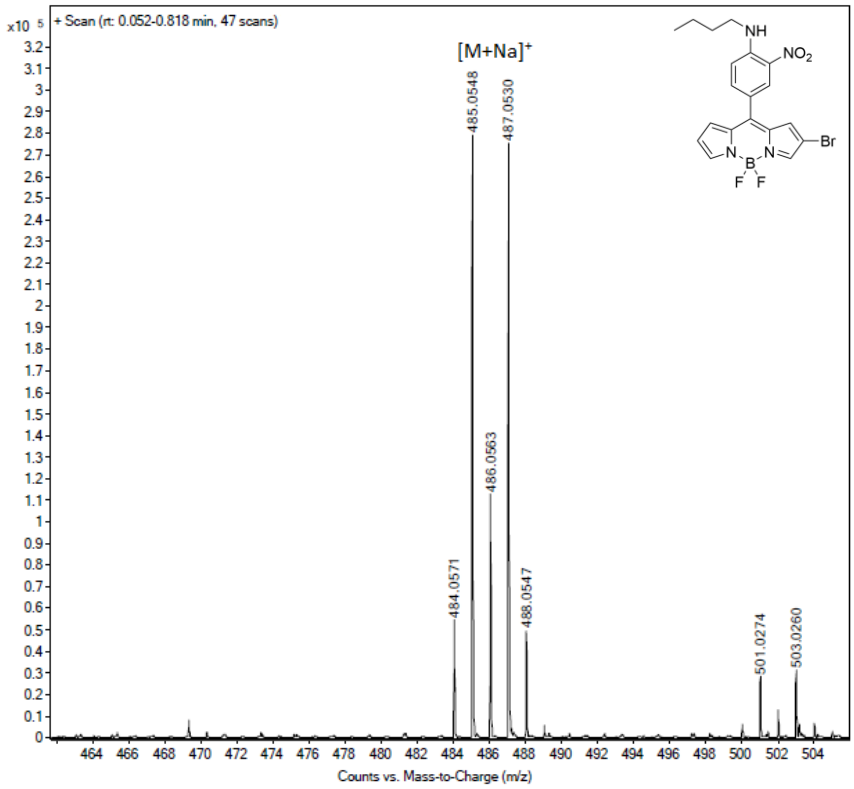

Figure S77: Zoom in from HRMS spectrum (ESI, in MeOH of BODIPY **23**.

2-Bromo-8-[3-nitro-4-(*N*-prop-2-enylamino)phenyl]-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (**24**): BODIPY **24** was prepared according to the general synthetic procedure. BODIPY **10a** (95 mg, 0.26 mmol) and NBS (115 mg, 0.65 mmol) were dissolved in 10 mL of DCM. The mixture was stirred for 3 h. After column chromatography (silica gel, DCM/*n*-hexane = 4/1, v/v) BODIPY **24** was obtained as a red solid (35 mg, 78 µmol, 30 %).

^{1}H NMR (500 MHz, THF-d$_8$): δ (ppm) = 4.16–4.18 (m, 2H, CH_2), 5.23–5.26 (m, 1H, **H_2C**=CH-), 5.32–5.37 (m, 1H, **H_2C**=CH-), 6.01 (ddt, *J* = 17.2, 10.1, 4.9 Hz, 1H, H_2C=**CH**-), 6.67 (d, *J* = 4.5 Hz, 1H, $H_{pyrrole}$), 7.06 (s, 1H, $H_{pyrrole}$), 7.16–7.18 (m, 2H, $H_{pyrrole}$ + Ar-H_{meta}), 7.79 (dd, *J* = 9.0, 2.2 Hz, 1H, Ar-H_{ortho}), 7.89 (s, 1H, $H_{pyrrole}$), 8.06 (s, 1H, $H_{pyrrole}$), 8.50 (d, *J* = 2.2 Hz, 1H, Ar-H_{ortho}), 8.66 (t, *J* = 6.2 Hz, 1H, NH).

^{13}C NMR (126 MHz, THF-d$_8$): δ (ppm) = 46.7 (CH_2), 106.4 (C_{Br}), 116.1 (Ar-C_{meta}), 117.1 (**H_2C**=CH-), 120.5 ($C_{pyrrole}$), 121.4*, 130.1 ($C_{pyrrole}$), 130.97 (Ar-C_{ortho}), 133.25 ($C_{pyrrole}$), 133.33*, 134.8 (H_2C=**CH**-), 135.0 ($C_{pyrrole}$), 136.2 ($C_{pyrrole}$), 138.5 (Ar-C_{ortho}), 142.6 ($C_{pyrrole}$), 146.4 (Ar-C_{para}), 147.1 ($C_{pyrrole}$), 147.9 (C_{meso}). *These signals could not be assigned exactly to corresponding carbon atoms. They belong to the Ar-C_{ipso} and the Ar-C_{nitro} of the aryl residue.

^{19}F NMR (376 MHz, THF-d$_8$): δ (ppm) = -145.66 – -145.43 (m_c, 2F, BF_2).

HRMS (ESI-TOF): *m/z* calcd. for $C_{18}H_{14}BBrF_2N_4O_2Na^+$ $[M+Na]^+$: 469.0253, found: 469.0262.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3374 ν(NH)], 3117 [ν(Ar-H)], 2925 [$\nu(CH_2)$], 2854 [ν(CH)], 1617 [ν(C=C)], 1545 [$\nu_{as}(NO_2)$], 1522 [δ(Ar-C)], 1468 [$\delta(CH_2)$, δ(Me)], 1358 [$\nu_{sym}(NO_2)$], 1115 and 1078 [ν(BF) ν(CBr)], 738 [δ(HC=CH)].

UV/Vis (DCM): λ_{max} (nm) [log (ε/L mol^{-1} cm^{-1})] = 519 [4.64].

Fluorescence (DCM): λ_{max} (nm) = 543 at $\lambda_{Excitation}$ (nm) = 500.

M.P.(°C): 160–162.

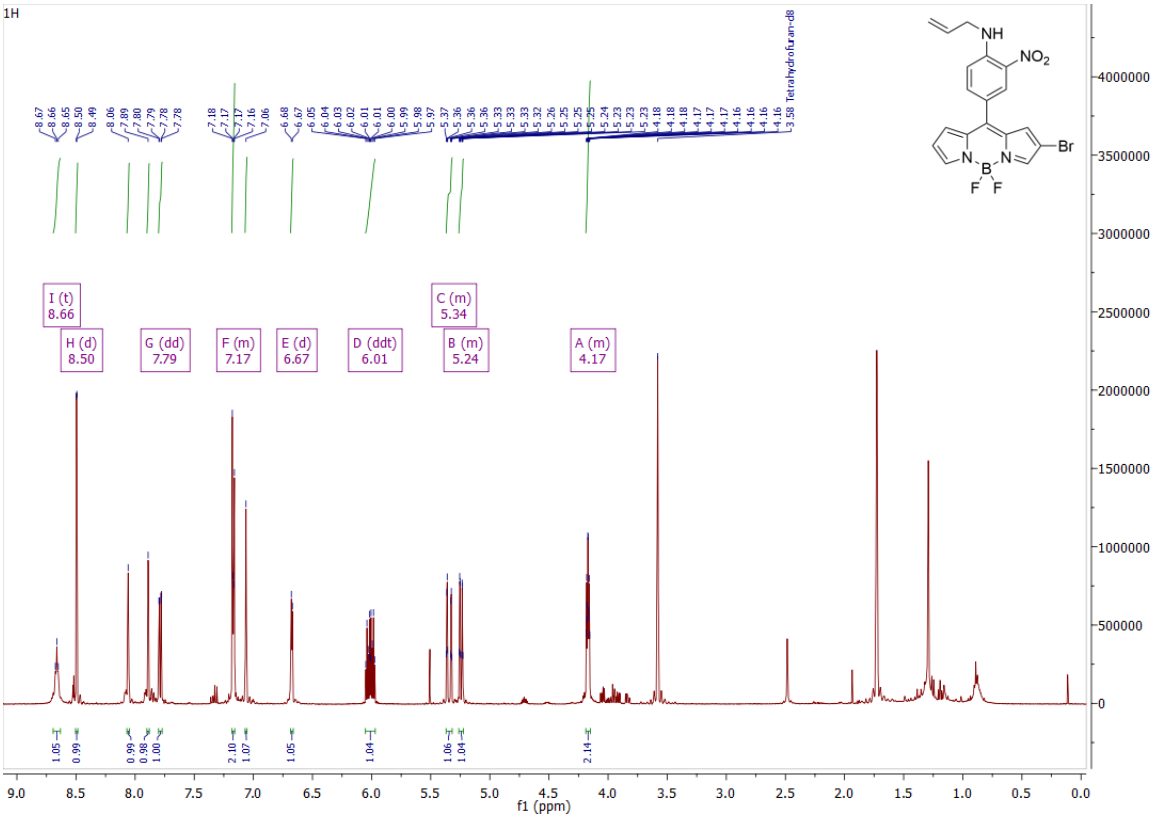

Figure S78: ^{1}H NMR (500 MHz, THF-d_8) spectrum of BODIPY **24**.

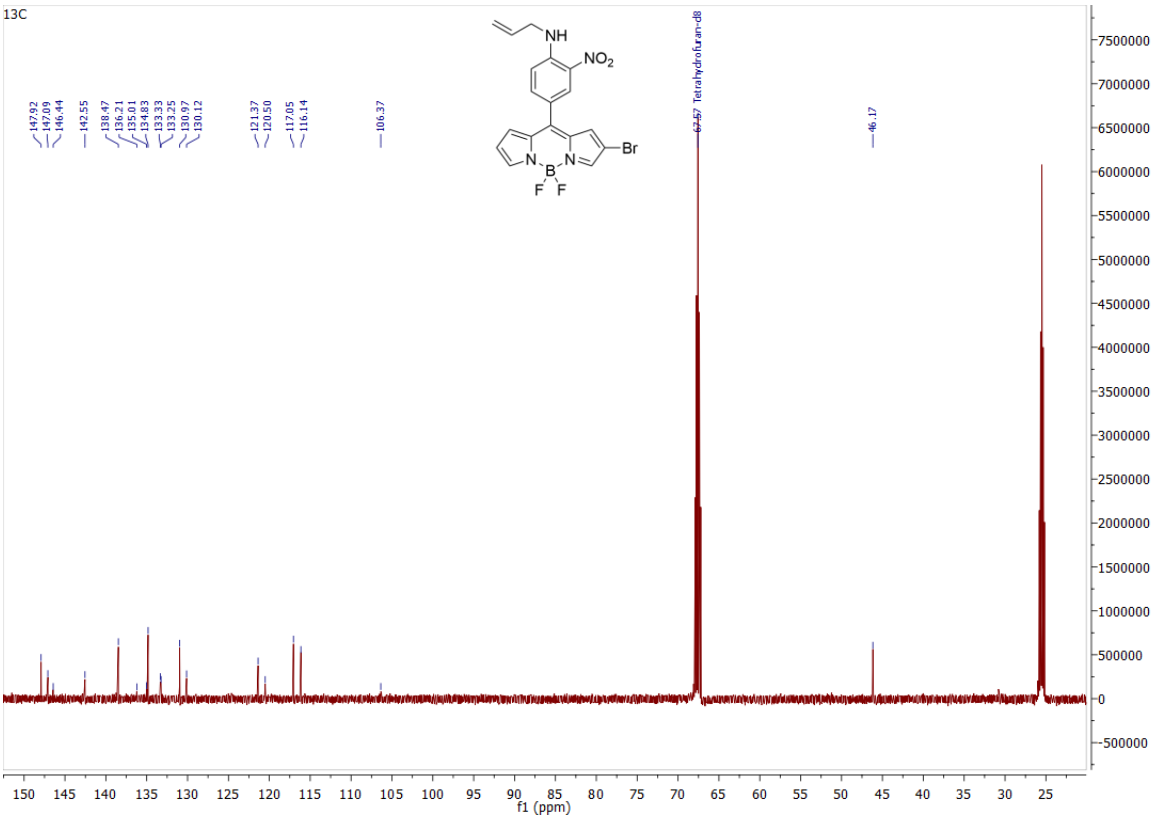

Figure S79: ^{13}C NMR (126 MHz, THF-d_8) spectrum of BODIPY **24**.

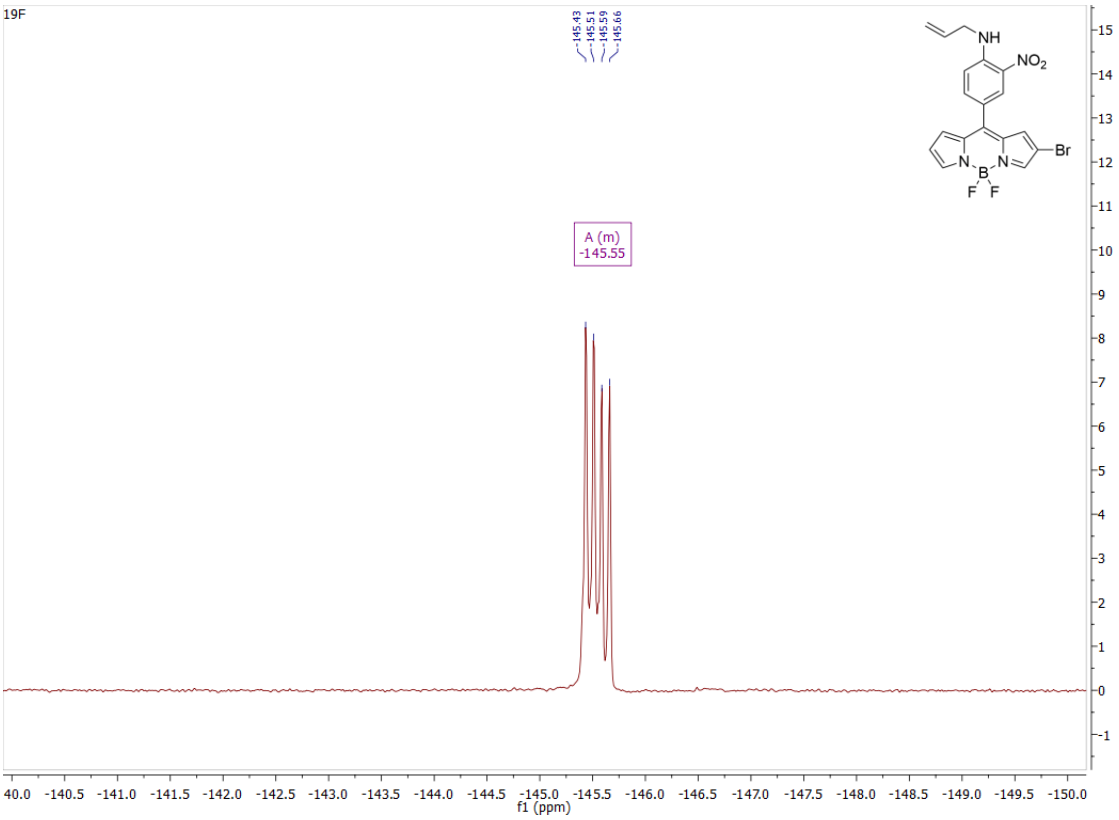

Figure S80: ^{19}F NMR (376 MHz, THF-d_8) spectrum of BODIPY **24**.

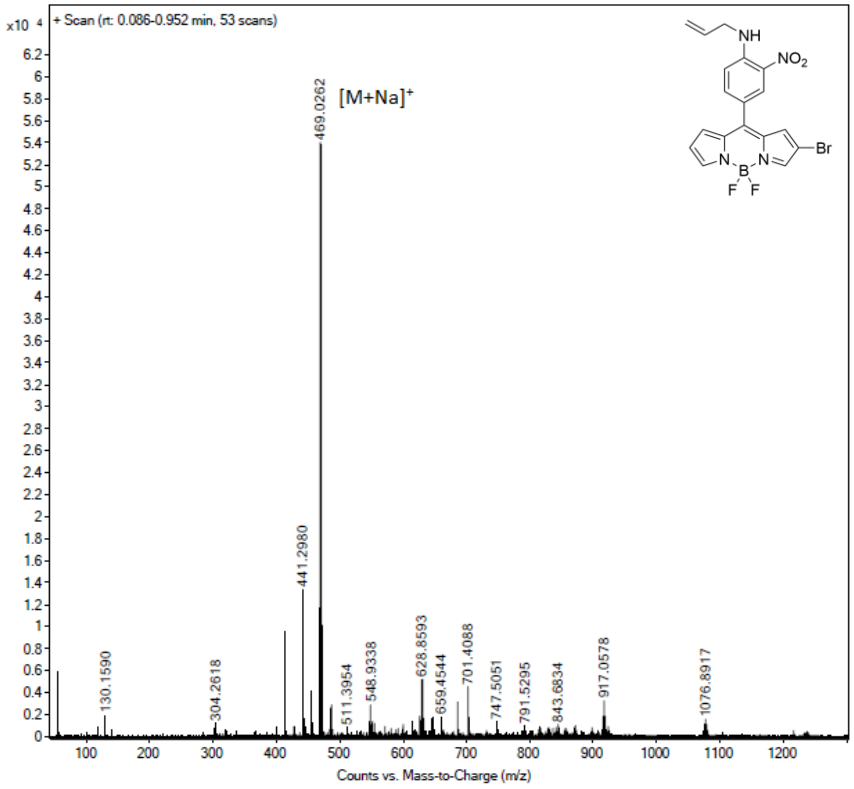

Figure S81: HRMS spectrum (ESI+, in MeOH) of BODIPY **24**.

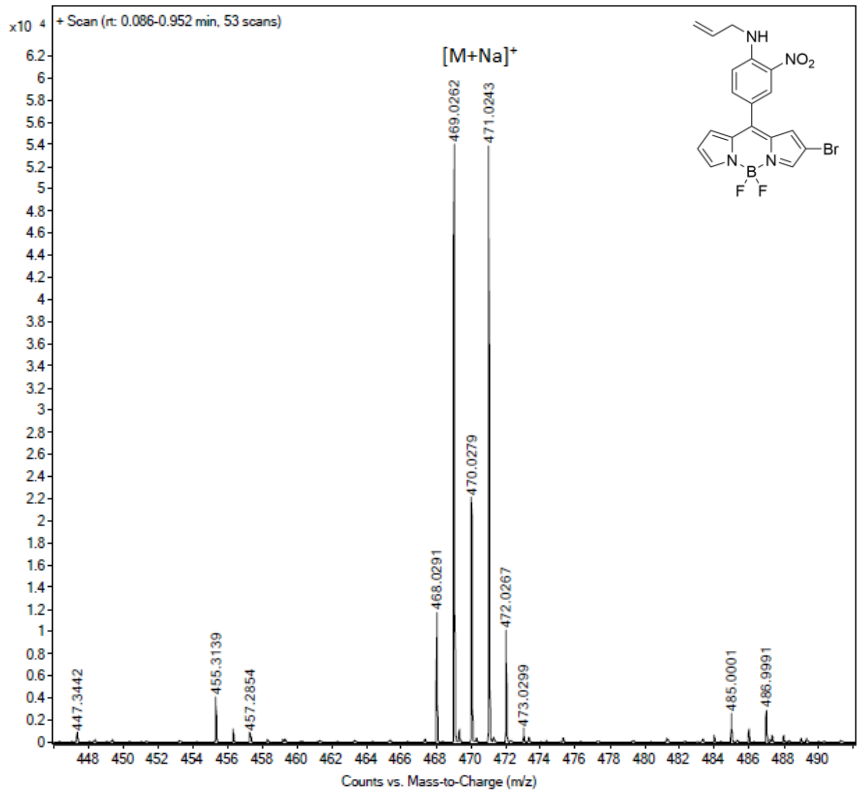

Figure S82: Zoom in from HRMS spectrum (ESI+) of BODIPY **24**.

10. Preparation of 8-(4-fluoro-3-nitrophenyl)-1,3,5,7-tetramethyl-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (26)

4-Fluoro-3-nitrobenzaldehyde (500 mg, 2.96 mmol) was dissolved in 35 mL of DCM. 2,4-Dimethylpyrrole (900 µL, 8.87 mmol, 3 eq.) and trifluoroacetic acid (37 µL, 0.48 mmol, 15 mol%) were added and the mixture was stirred for 2.5 h at rt. After the indicated time, DDQ (671 mg, 2.96 mmol, 1 eq.) was added and stirred for additional 1h at rt. Afterwards, DIPEA (5.8 mL, 34.10 mmol, 11 eq.) and $BF_3{\cdot}OEt_2$ (5.8 mL, 45.70 mmol, 15 eq.) were added and stirred for 1.5 h at rt. Water was added and the mixture was extracted with DCM several times. The combined organic phases were concentrated and filtered over a silica gel filled glass frit (DCM). The filtrate was dried with Na_2SO_4, filtrated, and evaporated to dryness. After purification by column chromatography (silica gel, *n*-hexane/EtOAc = 9/1, v/v) BODIPY **26** was obtained as an orange-green solid (536 mg, 1.38 mmol, 47 %).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 1.43 (s, 6H, Me), 2.56 (s, 6H, Me), 6.03 (s, 2H, $H_{pyrrole}$), 7.47 (dd, *J* = 10.3, 8.5 Hz, 1H, Ar-H_{meta}), 7.60 (ddd, *J* = 8.5, 4.1, 2.2 Hz, 1H, Ar-H_{ortho}), 8.05 (dd, *J* = 6.9, 2.3 Hz, 1H, Ar-H_{ortho}).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 14.8 (Me), 15.2 (Me), 119.7 (d, J_{C-F} = 21.1 Hz, Ar-C_{meta}), 122.2 ($C_{pyrrole}$), 126.5 (d, J_{C-F} = 2.4 Hz, Ar-C_{ortho}), 131.1 ($C_{pyrrole}$), 132.1* , 135.7 (d, J_{C-F} = 8.5 Hz, Ar-C_{ortho}), 136.7 (C_{meso}), 138.1 (d, J_{C-F} = 8.0 Hz)*, 142.4 ($C_{pyrrole}$), 155.79 (d, $J_{C,F}$ = 268.0 Hz, Ar-C_{para}), 157.1 ($C_{pyrrole}$). *These signals could not be assigned exactly to corresponding carbon atoms. They belong to the Ar-C_{ipso} and the Ar-C_{nitro} of the aryl residue.

^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) = -111.85 (s, 1F, CF), -145.85 – -146.23 (m_c, 2F, BF_2).

HRMS (ESI-TOF): *m/z* calcd. for $C_{19}H_{18}BF_3N_3O_2^+$ $[M+H]^+$: 388.1439, found: 388.1438.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3061 [ν(CH_{aromat})], 2961 and 2926 [ν(Me)], 1619 [ν(C=C)], 1545 [$\nu_{asym}(NO_2)$], 1347 [$\nu_{sym}(NO_2)$], 1261 [C=CF], 1082 [ν(BF)].

UV/Vis (DCM): λ_{max} (nm) [log (ε/L mol^{-1} cm^{-1})] = 507 [4.77].

Fluorescence (DCM): λ_{max} (nm) = 526 at $\lambda_{Excitation}$ (nm) 490.

M.P. (°C): 171–175.

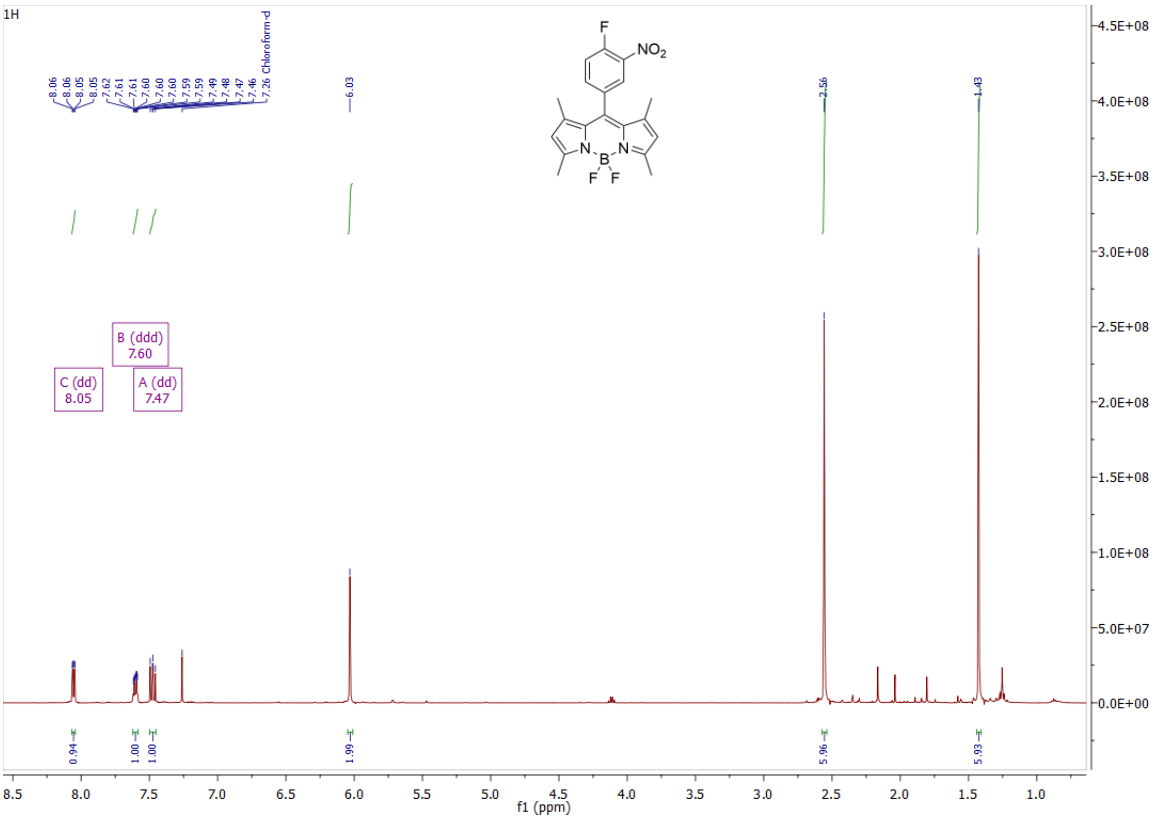

Figure S83: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of BODIPY **26**.

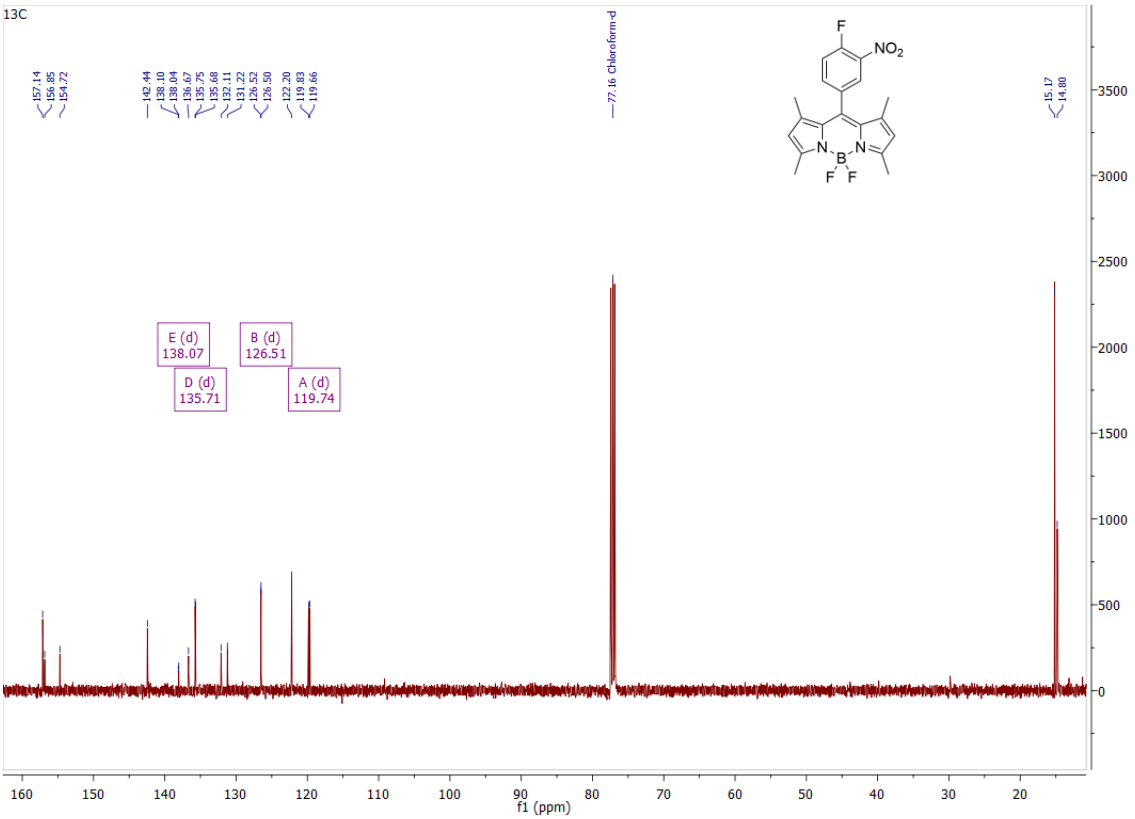

Figure S84: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of BODIPY **26**.

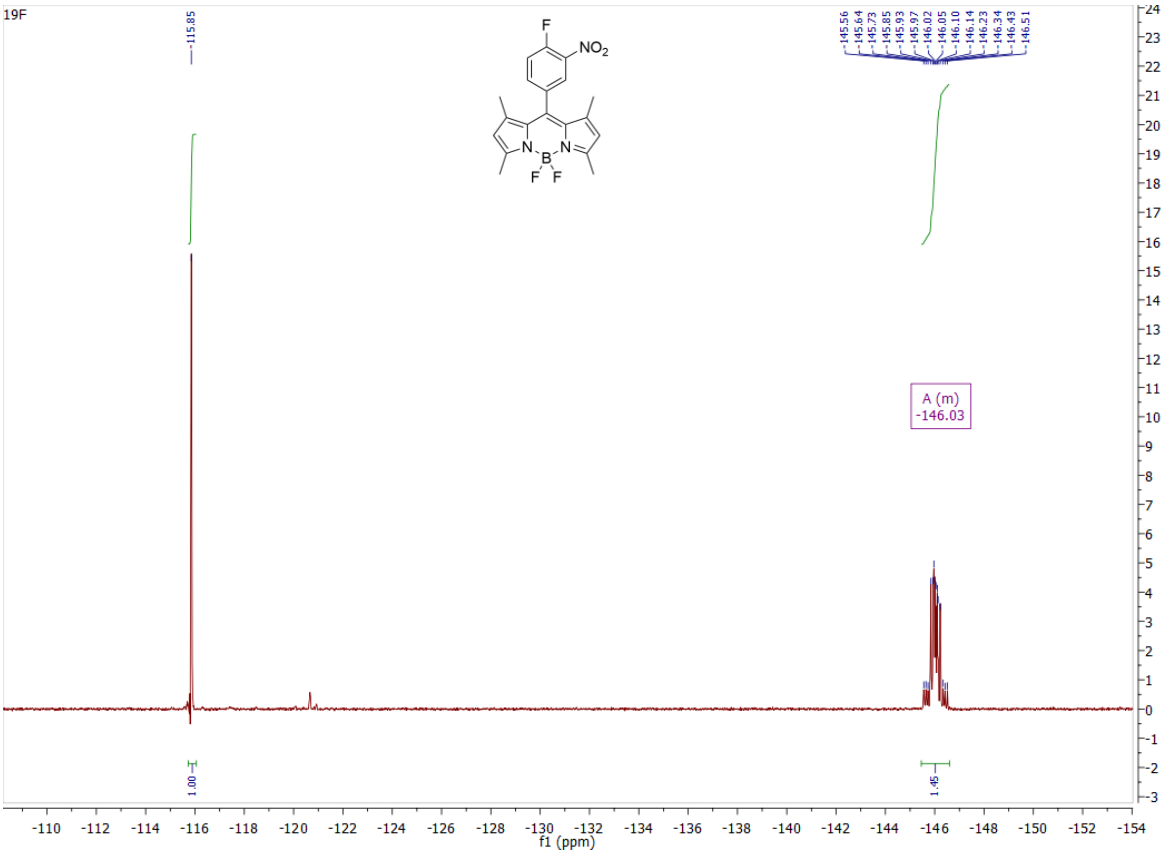

Figure S85: ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of BODIPY **26**.

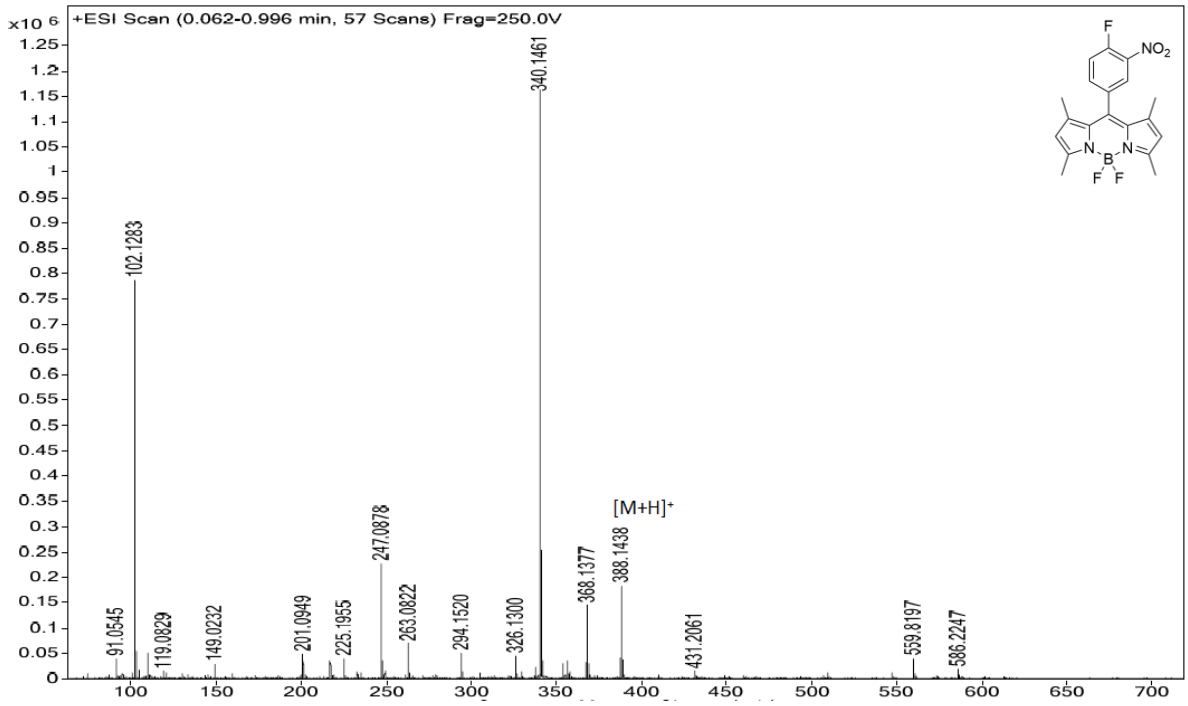

Figure S86: HRMS spectrum (ESI+) of BODIPY **26**.

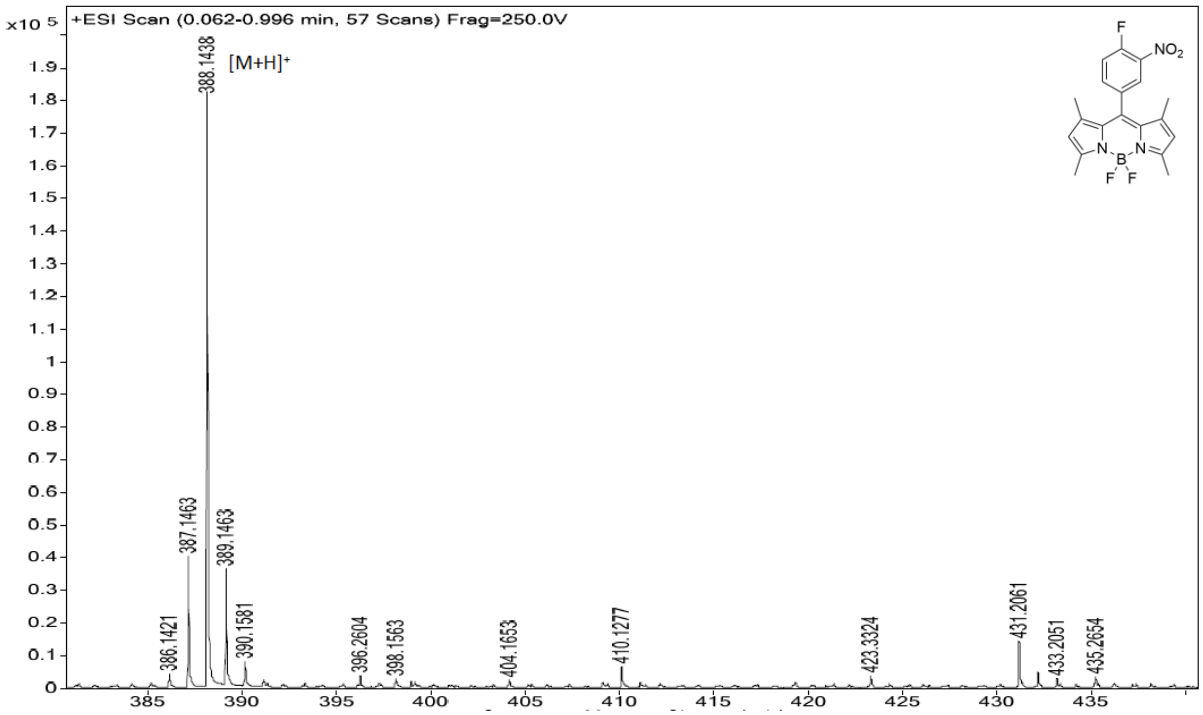

Figure S87: Zoom in from HRMS spectrum (ESI+) of BODIPY **26**.

11. Nucleophilic aromatic substitution of BODIPY 25 and 26 with amines (28 – 33)

General synthetic procedure

The BODIPY (1 equiv.) was dissolved in DMF, DCM, or DMSO and the corresponding amine (10 – 20 equiv.) was added. The mixture was stirred for the indicated time. Afterwards, the mixture was diluted with EtOAc and washed with water several times. The organic layer was dried with Na_2SO_4, filtered, and evaporated to dryness. The crude product was purified by column chromatography.

8-[4-(*N*-Prop-2-ynylamino)-2,3,5,6-tetrafluorophenyl]-1,3,5,7-tetramethyl-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (**28**):

BODIPY **28** was prepared according to the general synthetic procedure. BODIPY **25** (200 mg, 0.48 mmol) and propargylamine (0.31 mL, 4.83 mmol) were dissolved in 5 mL DMF. After column chromatography (silica gel, EtOAc/*n*-hexane = 1/9, v/v) BODIPY **28** was obtained as an orange solid (53 mg, 0.12 mmol, 23 %).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 1.66 (s, 6H, Me), 2.27–2.28 (m, 1H, CH), 2.56 (s, 6H, Me), 4.22 (br s, 2H, CH_2), 6.02 (s, 2H, $H_{pyrrole}$).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 13.6 (Me), 14.9 (Me), 35.8 (CH_2), 72.9 (C), 121.95 ($CH_{pyrrole}$), 131.8 ($C_{pyrrole}$), 133.8 (Ar-C_{para}), 142.1 ($C_{pyrrole}$), 157.1 ($C_{pyrrole}$).

^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) = -142.41 (d, J = 18.8 Hz, 2F, CF_{meta}), -145.89 – -146.15 (m_C, 2F, BF_2), -157.16 (d, J = 18.0 Hz, 2F, CF_{ortho}).

HRMS (ESI-TOF): *m/z* calcd. for $C_{22}H_{18}BF_6N_3Na^+$ $[M+Na]^+$: 472.1390, found: 472.1407, *m/z* calcd. for $C_{22}H_{18}BF_6N_3K^+$ $[M+K]^+$: 488.1130, found: 488.1130, *m/z* calcd. for $C_{44}H_{36}B_2F_{12}N_6Na^+$ $[2M+Na]^+$: 921.2888, found: 921.2910.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3392 [ν(NH)], 3310 [ν(C≡CH)], 2957 and 2925 [$\nu(CH_2)$, ν(Me)], 2862 [ν(CH)], 1657 [ν(C=C)], 1496 [$\delta(CH_2)$, δ(Me)], 1153 [ν(BF)], 763 [δ(-HC=CH-)].

UV/Vis (DCM): λ_{max} (nm) [log (ε/L mol^{-1} cm^{-1})] = 515 [4.72].

Fluorescence (DCM): λ_{max} (nm) = 528 at $\lambda_{Excitation}$ (nm) = 500.

M.P. (°C): 215–221.

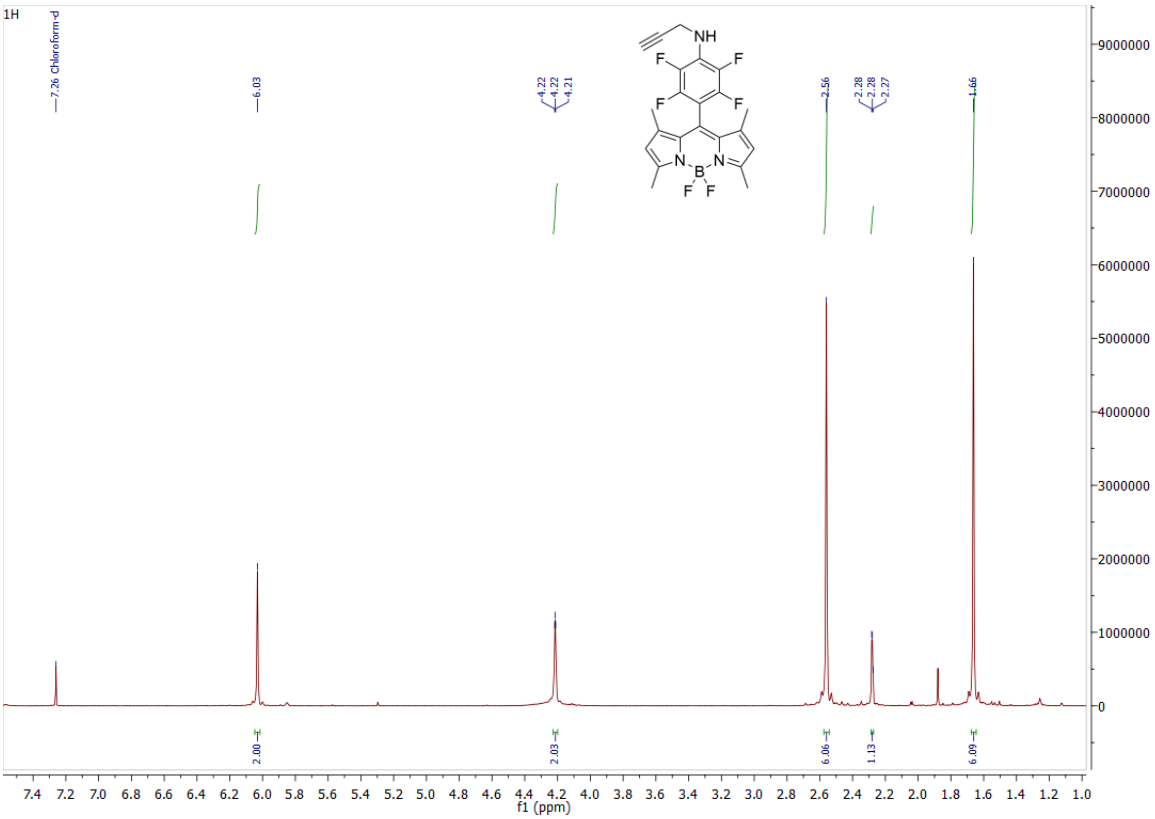

Figure S88: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of BODIPY **28**.

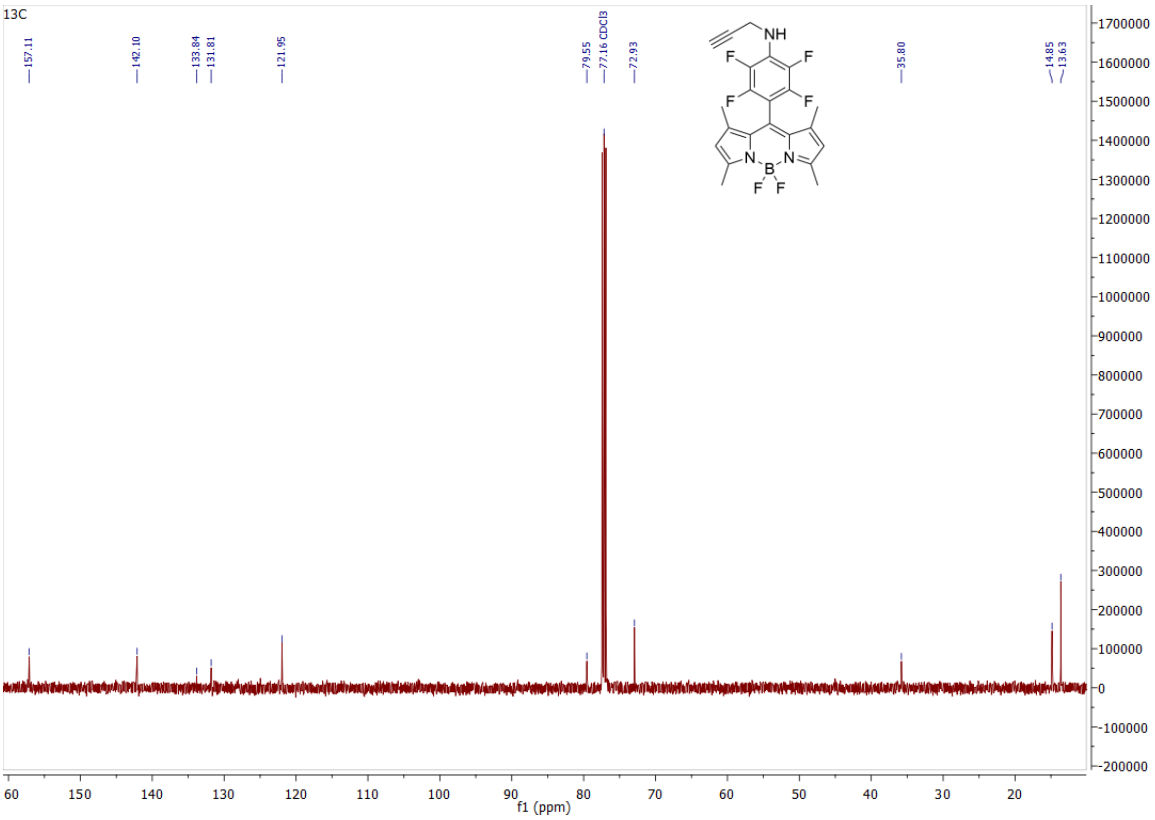

Figure S89: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of BODIPY **28**.

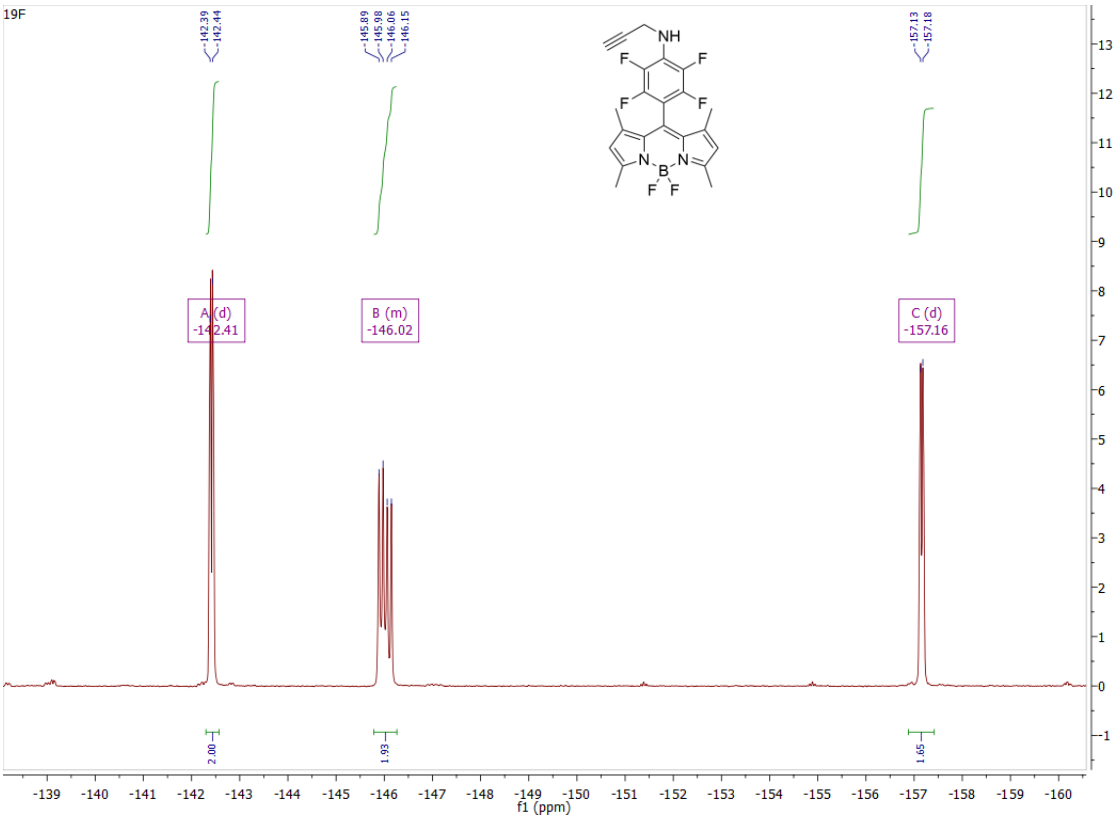

Figure 90: ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of BODIPY **28**.

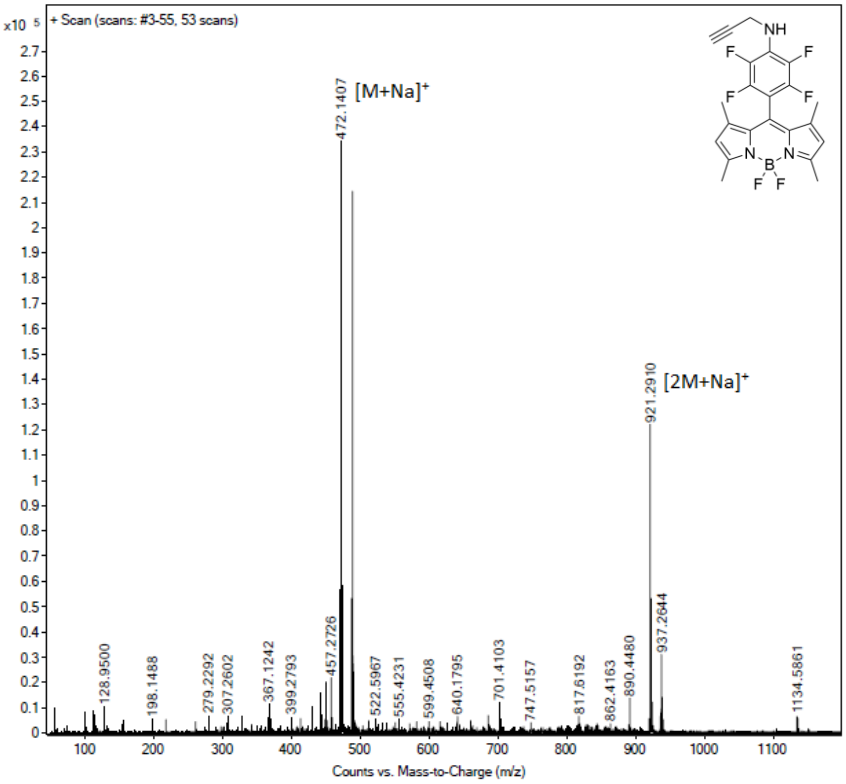

Figure 91: HRMS spectrum (ESI+) of BODIPY **28**.

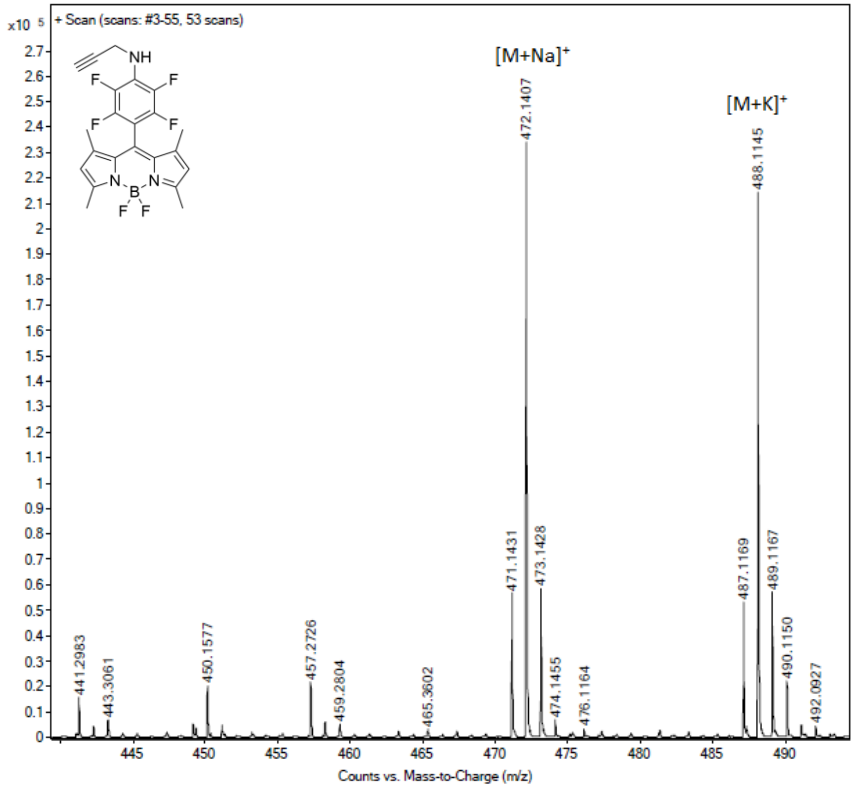

Figure S92: Zoom in from HRMS spectrum (ESI+) of BODIPY **28**.

8-[4-(*N*-2-Hydroxyethylamino)-2,3,5,6-tetrafluorophenyl]-1,3,5,7-tetramethyl-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (**29**):

BODIPY **29** was prepared according to the general synthetic procedure. BODIPY **25** (200 mg, 0.48 mmol) and ethanolamine (0.50 mL, 8.93 mmol) were dissolved in 5 mL of DMF. After column chromatography (silica gel, EtOAc/*n*-hexane = 1/1, v/v) BODIPY **29** was obtained as an orange-green solid (91 mg, 0.20 mmol, 41 %).

^{1}H NMR (500 MHz, THF-d$_8$): δ (ppm) = 1.70 (s, 6H, Me), 2.49 (s, 6H, Me), 3.52 -3.56 (m, 2H, CH_2), 3.69 (t, J = 5.5 Hz, 2H, CH_2), 4.06 (br s, 1H, OH), 5.57 (s, 1H, NH), 6.09 (s, 2H, $H_{pyrrole}$).

^{13}C NMR (126 MHz, THF-d$_8$): δ (ppm) = 13.8 (Me), 14.8 (Me), 48.7 (CH_2), 62.2 (CH_2), 100.03 (t, J = 19.8 Hz, Ar-C_{ipso}), 122.5 ($CH_{pyrrole}$), 126.5 (C_{meso}), 131.4–131.6 (m, Ar-C_{para}), 132.95 ($C_{pyrrole}$), 139.03 (dd, J = 242.1, 25.0 Hz, Ar-C_{meta}), 142.9 ($C_{pyrrole}$), 145.27 (ddt, J = 242.3, 8.6, 4.1 Hz, Ar-C_{ortho}), 157.8 ($C_{pyrrole}$).

^{19}F NMR (376 MHz, THF-d$_8$): δ (ppm) = -145.87 (d, J = 17.7 Hz, 2F, CF_{meta}), -146.58 – -146.84 (m_C, 2F, BF_2), -161.12 (d, J = 18.3 Hz, 2F, CF_{ortho}).

HRMS (ESI-TOF): *m/z* calcd. for $C_{21}H_{20}BF_6N_3ONa^+$ $[M+Na]^+$: 478.1496, found: 478.1524, *m/z* calcd. for $C_{21}H_{20}BF_6N_3OK^+$ $[M+K]^+$: 494.1235, found: 494.1267, *m/z* calcd. for $C_{42}H_{40}B_2F_{12}N_6O_2Na^+$ $[2M+Na]^+$: 933.3099, found: 933.3149.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3396 [ν(OH), ν(NH)], 2958 and 2928 [$\nu(CH_2)$, ν(Me)], 2862 [ν(CH)], 1657 [ν(C=C)], 1497 [$\delta(CH_2)$, δ(Me)], 1190 [ν(BF)], 768 [δ(-HC=CH-)].

UV/Vis (DCM): λ_{max} (nm) [log (ε/L mol^{-1} cm^{-1})] = 515 [4.89].

Fluorescence (DCM): λ_{max} (nm) = 528 at $\lambda_{Excitation}$ (nm) = 500.

M.P. (°C): 154–157.

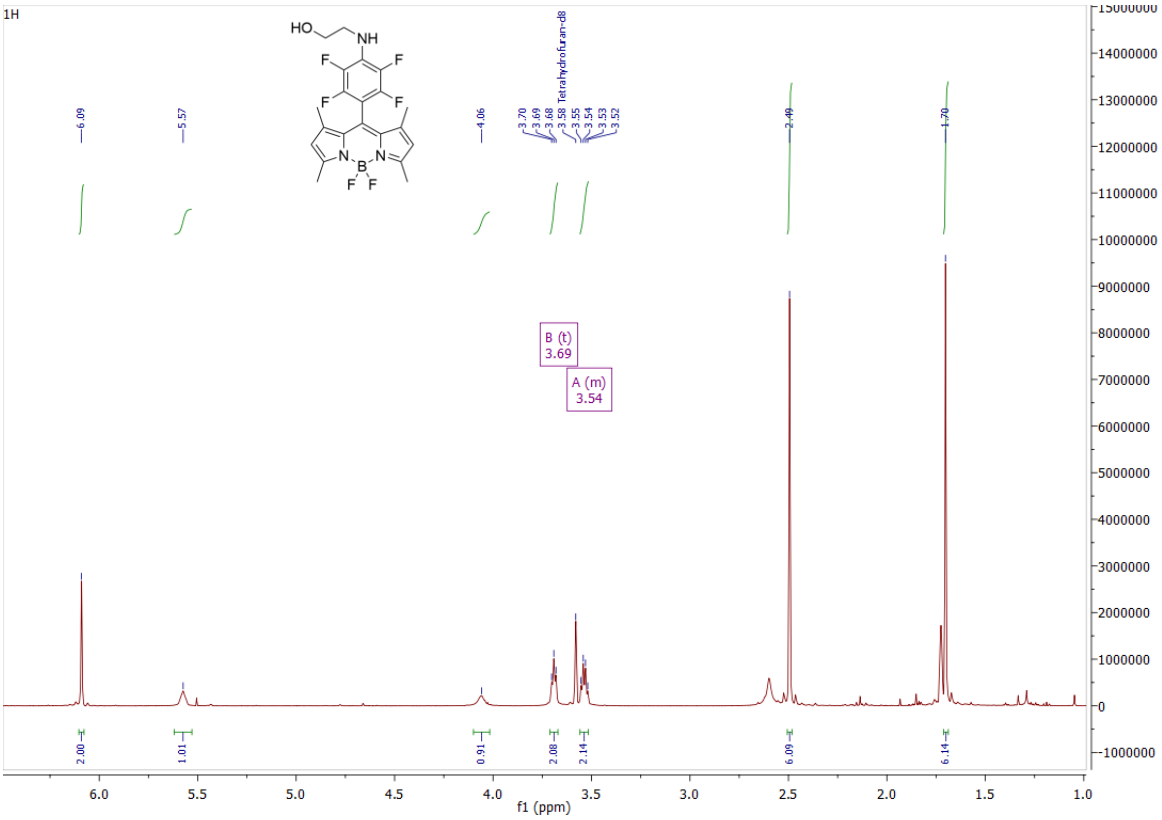

Figure S93: ^{1}H NMR (500 MHz, THF-d_8) spectrum of BODIPY **29**.

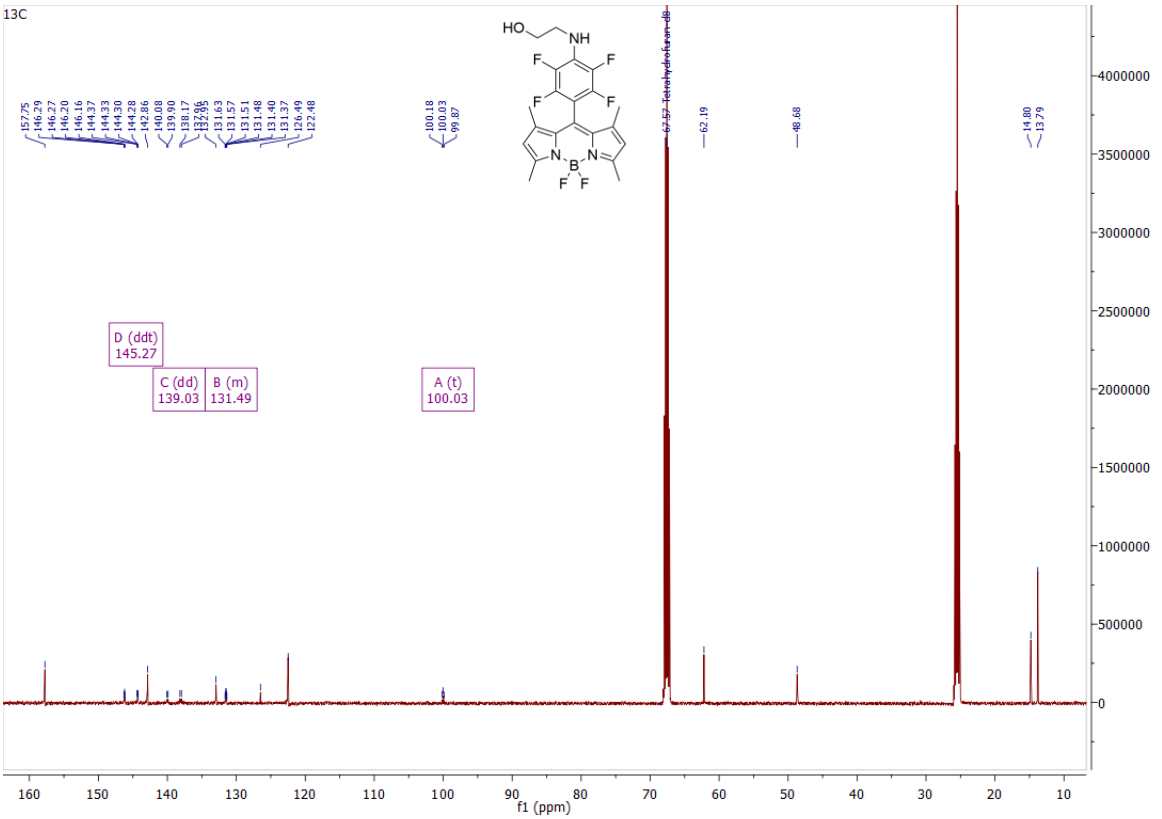

Figure S94: ^{13}C NMR (126 MHz, THF-d_8) spectrum of BODIPY **29**.

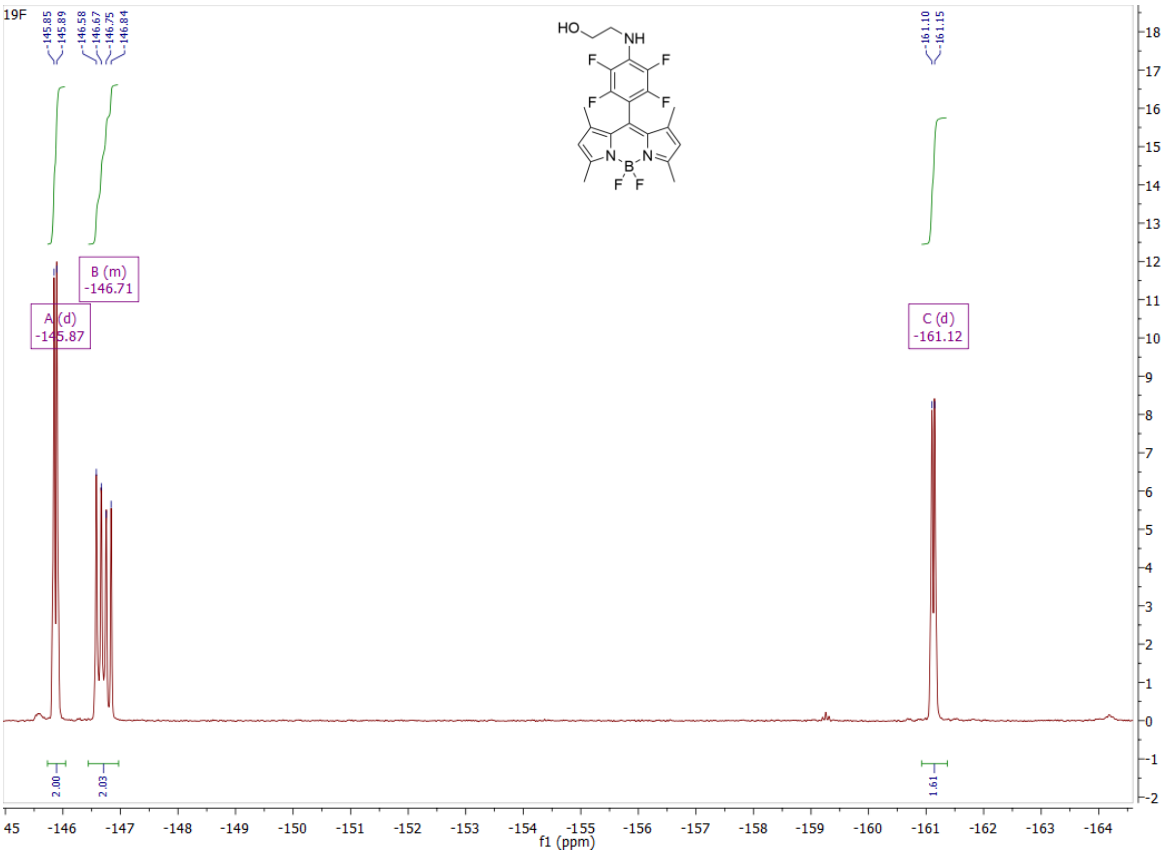

Figure S95: ^{19}F NMR (376 MHz, THF-d_8) spectrum of BODIPY **29**.

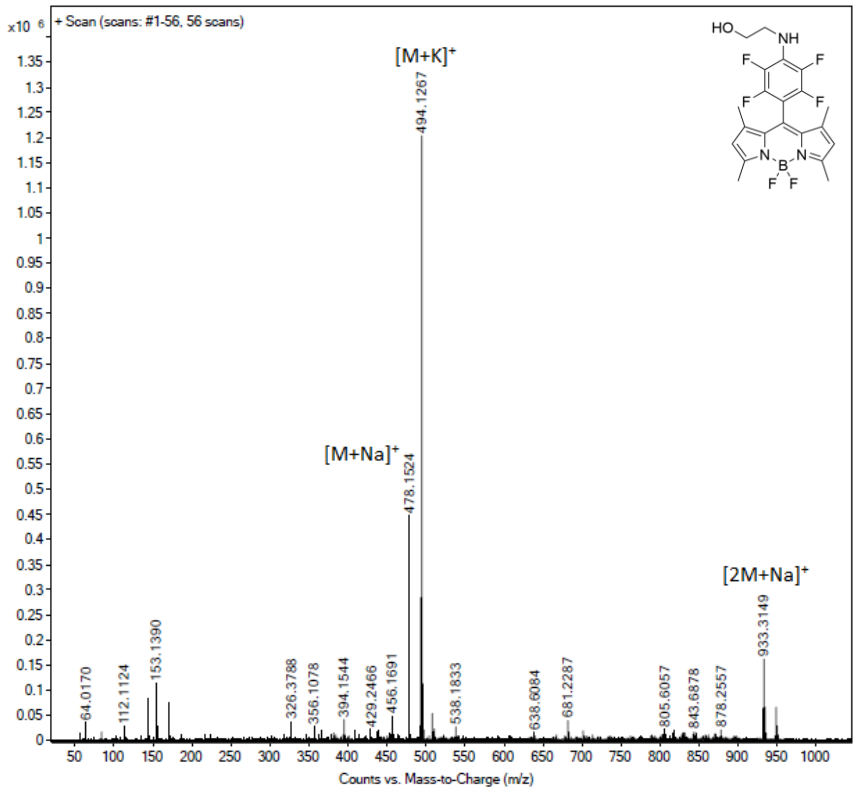

Figure S96: HRMS spectrum (ESI+) of BODIPY **29**.

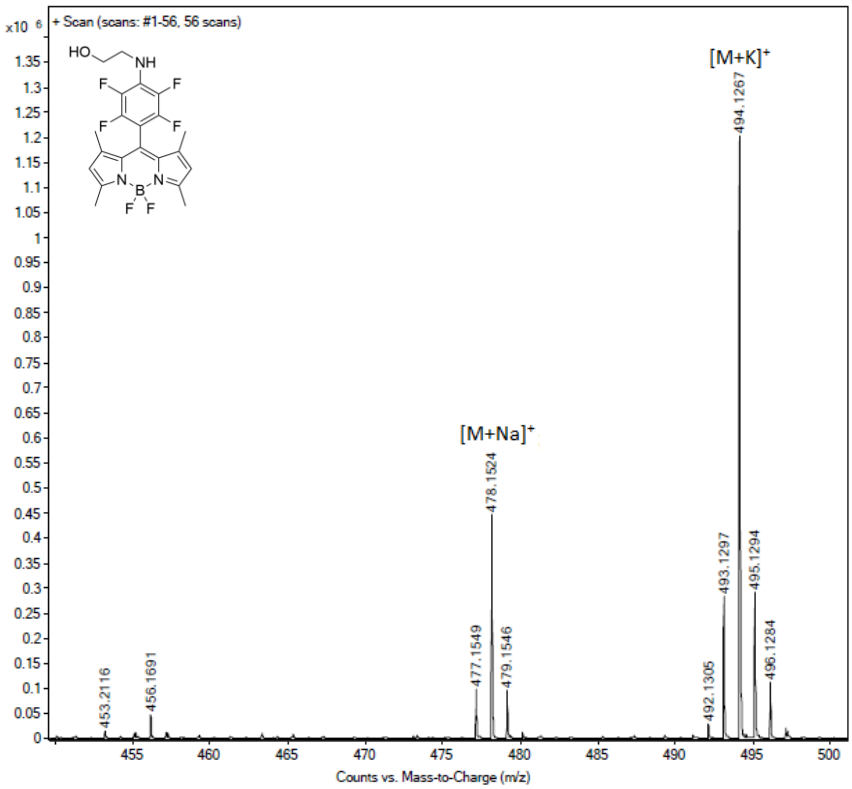

Figure S97: Zoom in from HRMS spectrum (ESI+) of BODIPY **29**.

8-[4-(*N*-1-Hydroxymethyl-2-hydroxyethylamino)-2,3,5,6-tetrafluorophenyl]-1,3,5,7-tetramethyl-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene

The nucleophilic substitution was prepared according to the general synthetic procedure. BODIPY **26** (200 mg, 0.48 mmol) and 2-amino-1,3-dihydroxypropane (660 mg, 7.24 mmol, 15 equiv.) were dissolved in 5 mL of DMSO. The mixture was stirred for 24 h at rt. The crude product was purified by column chromatography (silica gel, EtOAc). After purification no product could be observed.

8-[4-(*N*-Butylamino)-3-nitrophenyl]-1,3,5,7-tetramethyl-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (**30**):

BODIPY **30** was prepared according to the general synthetic procedure. BODIPY **26** (116 mg, 0.30 mmol) and *n*-butylamine (0.6 mL, 5.99 mmol, 20 equiv.) were dissolved in 10 mL of DCM. The mixture was stirred for 90 min at rt. After column chromatography (silica gel, EtOAc/*n*-hexane = 1/2, v/v) BODIPY **30** was obtained as an orange solid (116 mg, 0.26 mmol, 88 %).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 1.02 (t, J = 7.4 Hz, 3H, Me_{butyl}), 1.49–1.58 (m, 8H, CH_2 + Me), 1.75–1.81 (m, 2H, CH_2), 2.55 (s, 3H, Me), 3.36 (td, J = 7.2, 4.7 Hz, 2H, CH_2), 6.00 (s, 2H, $H_{pyrrole}$), 7.00 (d, J = 8.8 Hz, 1H, Ar-H_{meta}), 7.31 (dd, J = 8.8, 2.1 Hz, 1H, Ar-H_{ortho}), 8.13 (d, J = 2.1 Hz, 1H, Ar-H_{ortho}), 8.14–8.16 (m, 1H, NH).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 13.9 (Me_{butyl}), 14.8 (Me), 15.4 (Me), 20.4 (CH_2), 31.1 (CH_2), 43.1 (CH_2), 114.9 (Ar-C_{meta}), 120.1 (C_{meso}), 121.4*, 121.6 ($CH_{pyrrole}$), 126.9 (Ar-C_{ortho}), 131.9 ($C_{pyrrole}$), 136.1 (Ar-C_{ortho}), 139.4*, 142.8 ($C_{pyrrole}$), 145.6 (Ar-C_{para}), 156.1 ($C_{pyrrole}$). *These signals could not be assigned exactly to corresponding carbon atoms. They belong to the Ar-C_{ipso} and the Ar-C_{nitro} of the aryl residue.

^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) = -145.60 – -146.69 (m_c, 2F, BF_2).

HRMS (ESI-TOF): *m/z* calcd. for $C_{23}H_{27}BF_2N_4O_2Na^+$ $[M+Na]^+$: 463.2087, found: 463.2120, *m/z* calcd. for $C_{23}H_{27}BF_2N_4O_2K^+$ $[M+K]^+$: 479.1827, found: 479.1856, *m/z* calcd. for $C_{46}H_{54}B_2F_4N_8O_4Na^+$ $[2M+Na]^+$: 903.4282, found: 903.4319.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3381 [ν(NH)], 2957 and 2926 [$\nu(CH_2)$, ν(Me)], 2862 [ν(CH)], 1628 [ν(C=N)], 1542 [$\nu_{as}(NO_2)$], 1508 [δ(Ar-C)], 1488 [$\delta(CH_2)$, δ(Me)], 1353 [$\nu_{sym}(NO_2)$], 1082 [ν(BF)], 758 [δ(HC=CH)].

UV/Vis (DCM): λ_{max} (nm) [log (ε/L mol^{-1} cm^{-1})] = 505 [4.75].

Fluorescence (DCM): λ_{max} (nm) = 526 at $\lambda_{Excitation}$ (nm) 490.

M.P. (°C): 133–139.

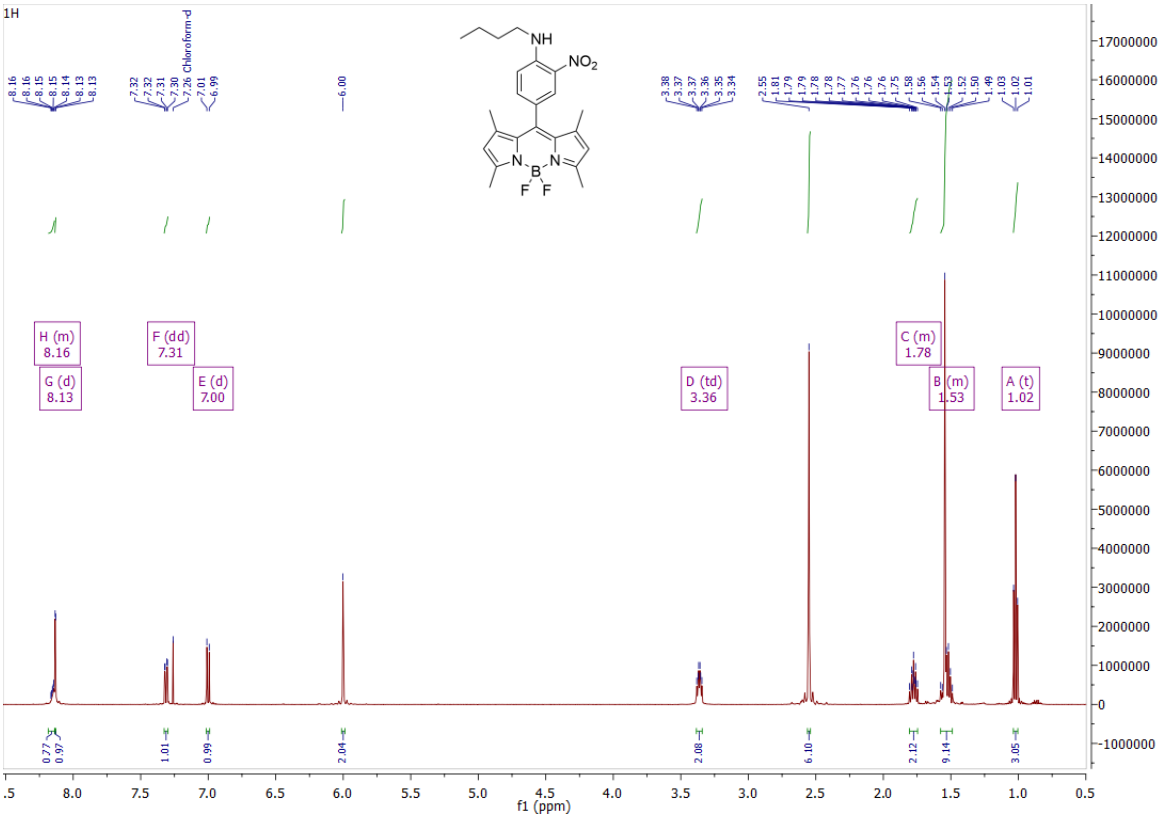

Figure S98: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of BODIPY **30**.

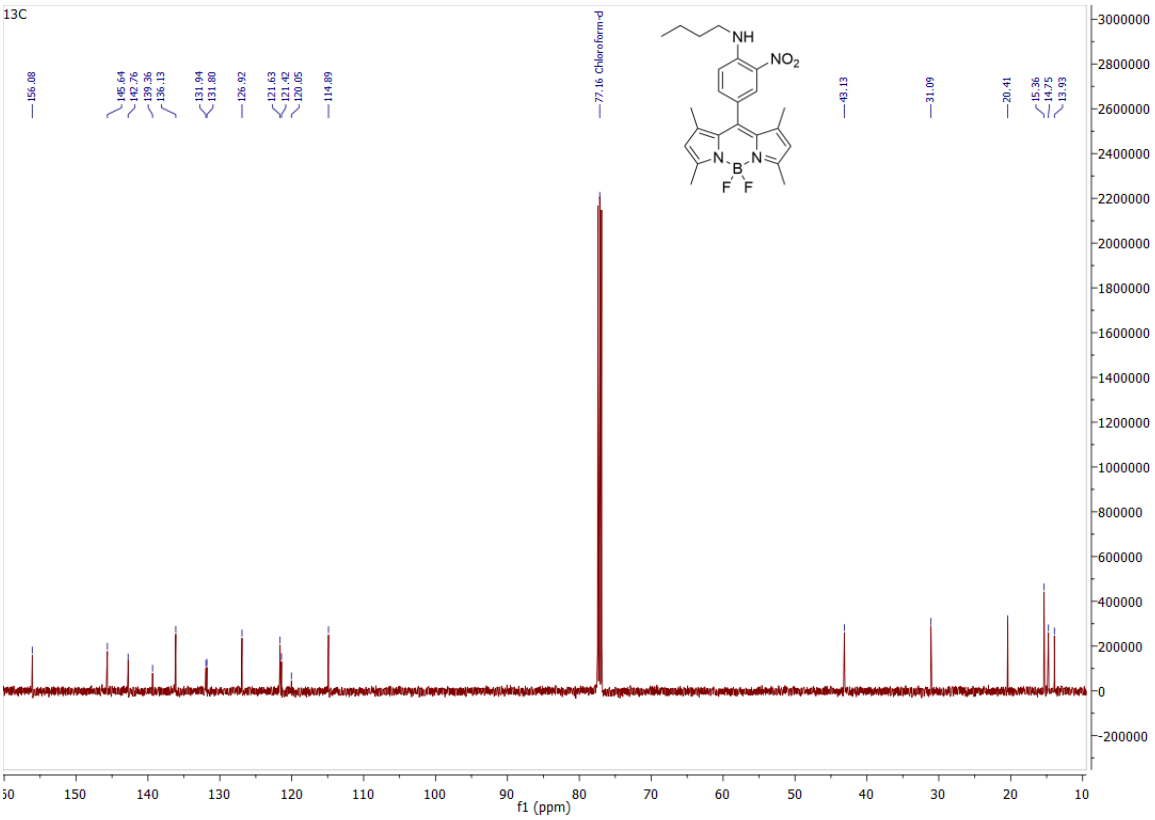

Figure S99: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of BODIPY **30**.

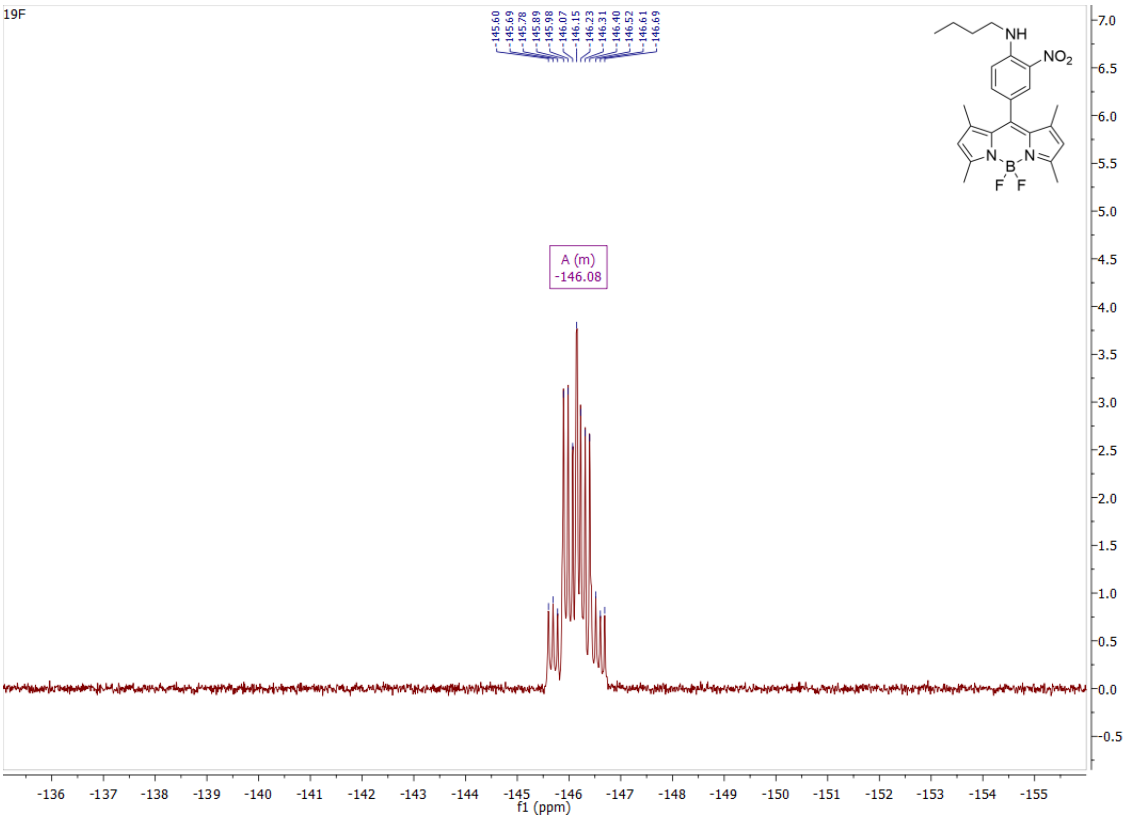

Figure S100: ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of BODIPY **30**.

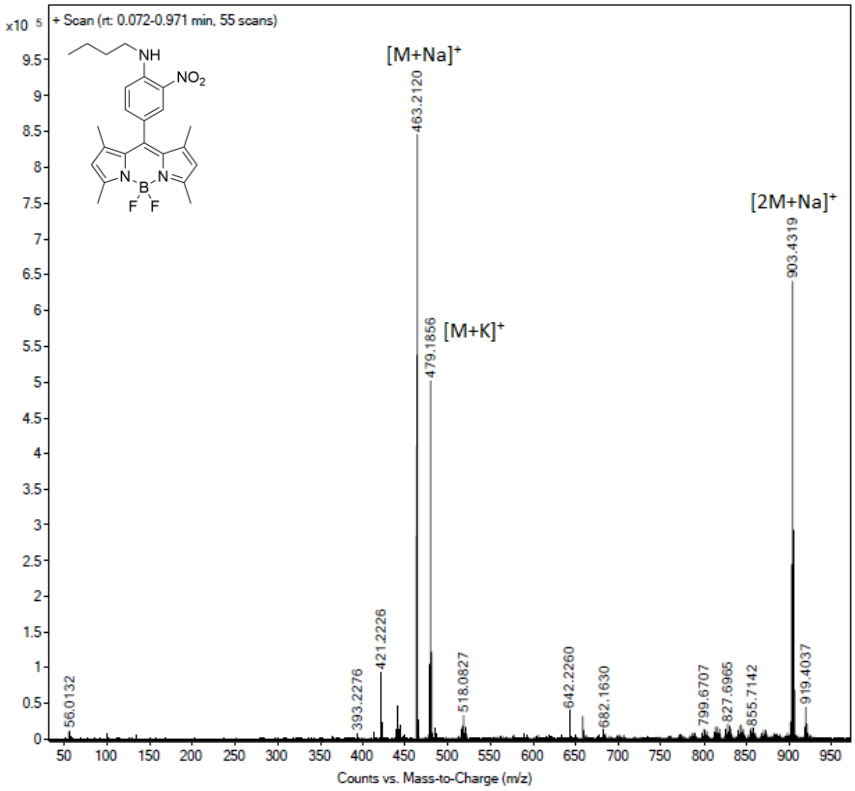

Figure S101: Zoom in from HRMS spectrum (ESI+) of BODIPY **30**.

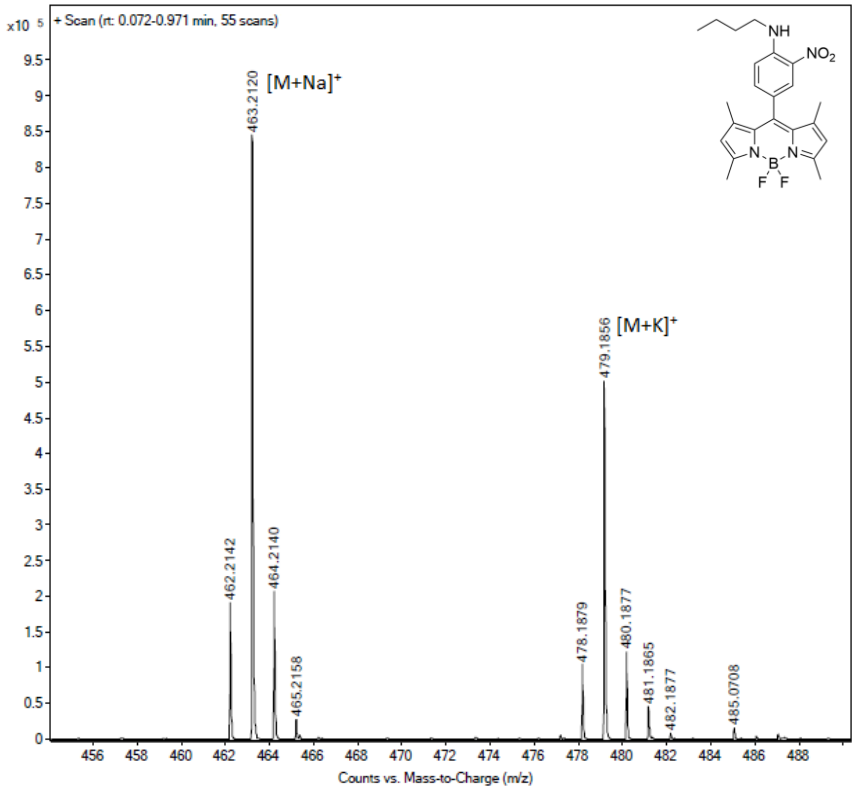

Figure S102: HRMS spectrum (ESI+) of BODIPY **30**.

8-[3-Nitro-4-(*N*-2-prop-2-ynylamino)phenyl]-1,3,5,7-tetramethyl-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (**31**):

BODIPY **31** was prepared according to the general synthetic procedure. BODIPY **26** (116 mg, 0.30 mmol) and propargylamine (0.4 mL, 5.99 mmol, 20 eqiuv.) were dissolved in 10 mL of DCM. The mixture was stirred for 24 h at rt. After column chromatography (silica gel, *n*-hexane/EtOAc = 9/1, v/v) BODIPY **31** was obtained as an orange solid (56 mg, 0.13 mmol, 44 %).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 1.51 (s, 6H, Me), 2.34 (t, *J* = 2.5 Hz, 1H, CH), 2.55 (s, 6H, Me), 4.20 (dd, *J* = 5.7, 2.5 Hz, 2H, CH_2), 6.00 (s, 2H, $H_{pyrrole}$), 7.12 (d, *J* = 8.7 Hz, 1H, Ar-H_{meta}), 7.40 (dd, *J* = 8.7, 2.1 Hz, 1H, Ar-H_{ortho}), 8.17 (d, *J* = 2.1 Hz, 1H, Ar-H_{ortho}), 8.23 (t, *J* = 5.6 Hz, 1H, NH).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 14.8 (Me), 15.3 (Me), 32.97 (CH_2), 72.99 (CH), 78.4 (C), 115.1 (Ar-C_{meta}), 121.7*, 122.9 ($CH_{pyrrole}$), 126.9 (Ar-C_{ortho}), 131.8 (C_{meso}), 132.9 ($C_{pyrrole}$), 136.1 (Ar-C_{ortho}), 138.9*, 142.8 ($C_{pyrrole}$), 144.3 (Ar-C_{para}), 156.3 ($C_{pyrrole}$). *These signals could not be assigned exactly to corresponding carbon atoms. They belong to the Ar-C_{ipso} and the Ar-C_{nitro} of the aryl residue.

^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) = -145.56 – -146.60 (m_c, 2F, BF_2).

HRMS (ESI-TOF): *m/z* calcd. for $C_{22}H_{21}BF_2N_4O_2Na^+$ $[M+Na]^+$: 445.1618, found: 445.1634, *m/z* calcd. for $C_{22}H_{21}BF_2N_4O_2Na^+$ $[M+K]^+$: 461.1357, found: 461.1492, *m/z* calcd. for $C_{44}H_{42}B_2F_4N_8O_4Na^+$ $[2M+Na]^+$: 867.3343, found: 867.3348.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3385 [ν(NH)], 3289 [ν(C≡CH)], 2958 and 2922 [$\nu(CH_2)$], 2858 [ν(CH)], 1627 [ν(C=C)], 1528 [$\nu_{as}(NO_2)$], 1509 [δ(Ar-C)], 1469 [$\delta(CH_2)$, δ(Me)], 1343 [$\nu_{sym}(NO_2)$], 1083 [ν(BF)], 735 [δ(HC=CH)].

UV/Vis (DCM): λ_{max} (nm) [log (ε/L mol^{-1} cm^{-1})] = 505 [4.47].

Fluorescence (DCM): λ_{max} (nm) = 528 at $\lambda_{Excitation}$ (nm) 490.

M.P. (°C): 130–135.

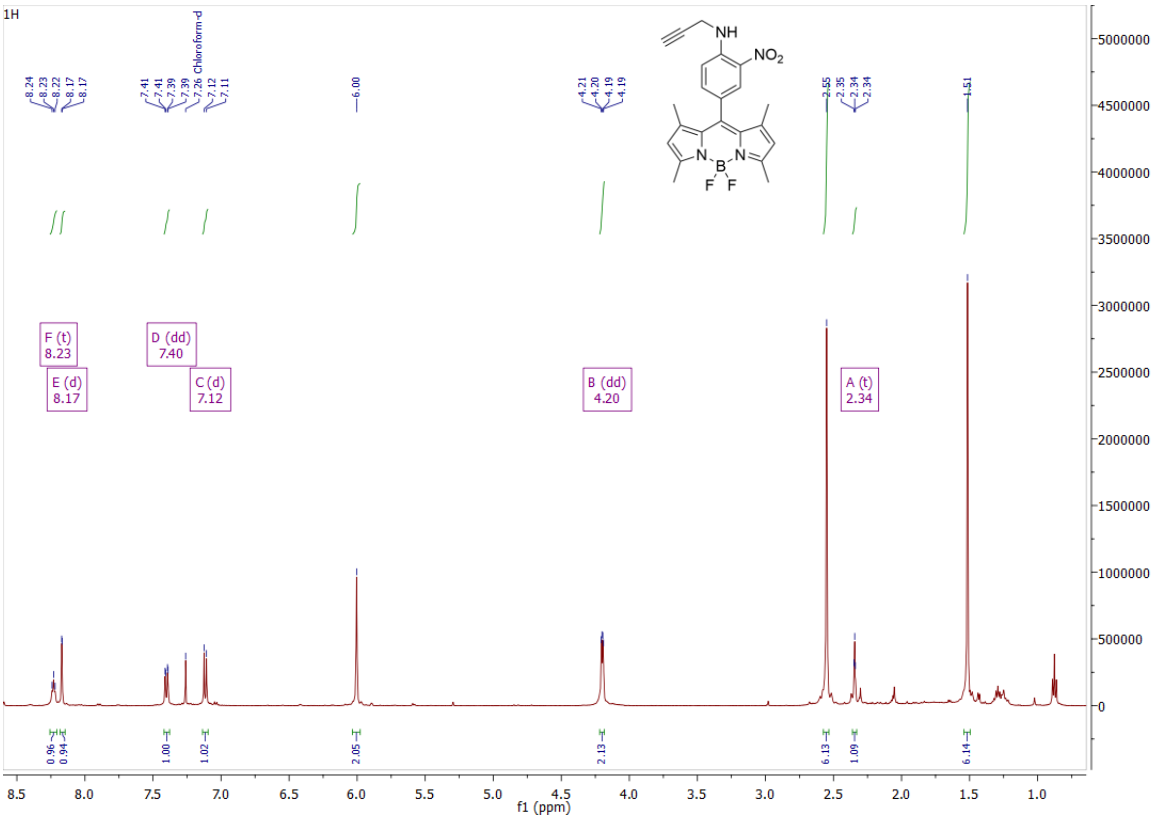

Figure S103: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of BODIPY **31**.

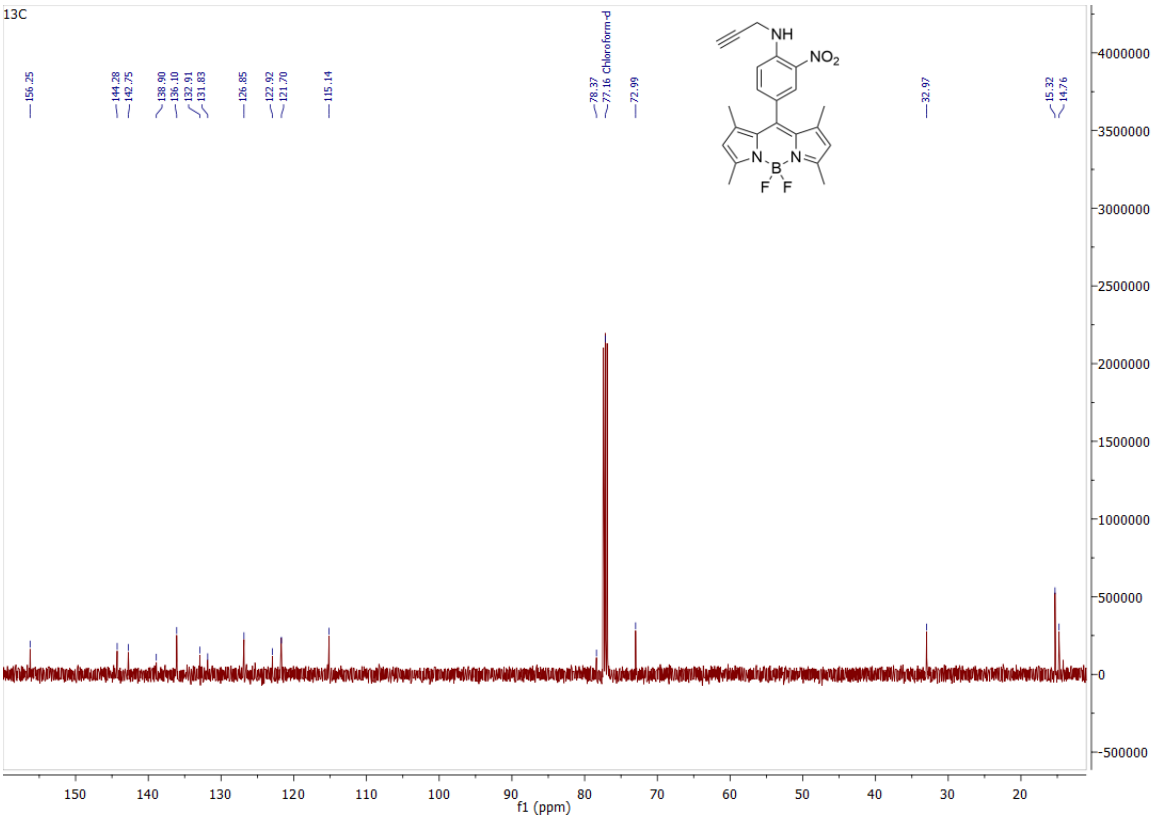

Figure S104: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of BODIPY **31**.

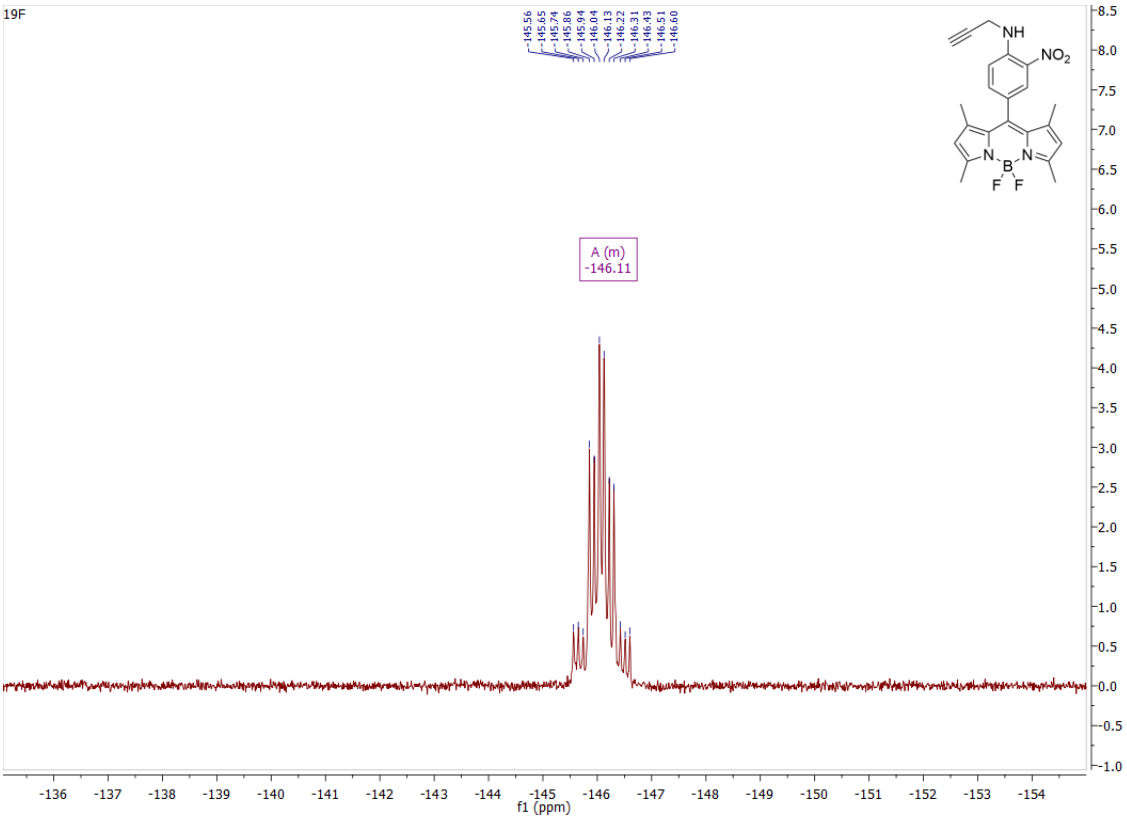

Figure S105: ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of BODIPY **31**.

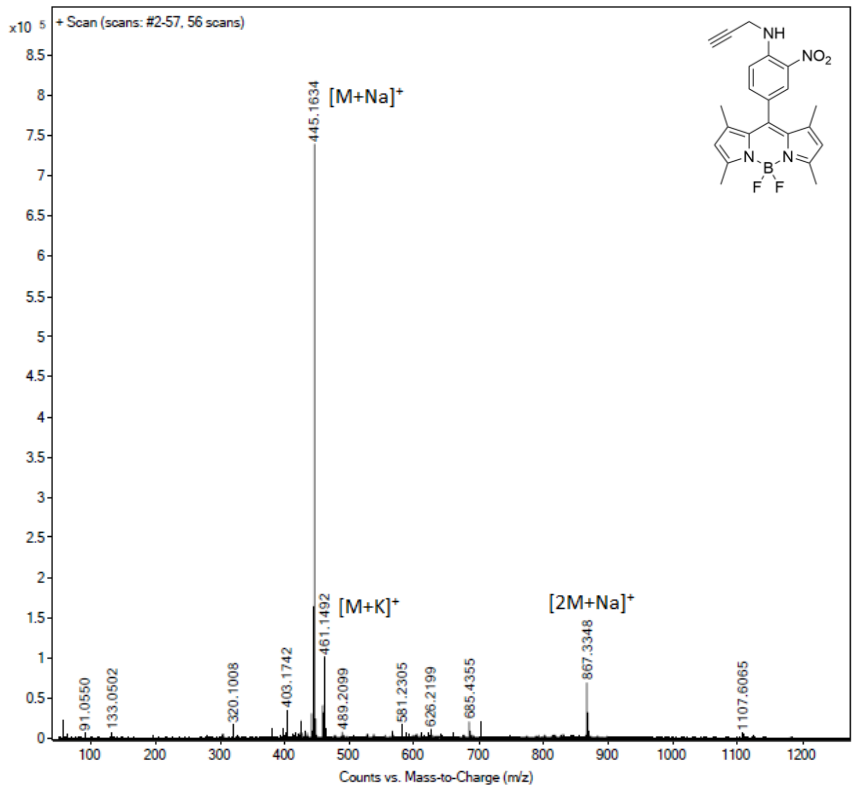

Figure S106: HRMS spectrum (ESI+) of BODIPY **31**.

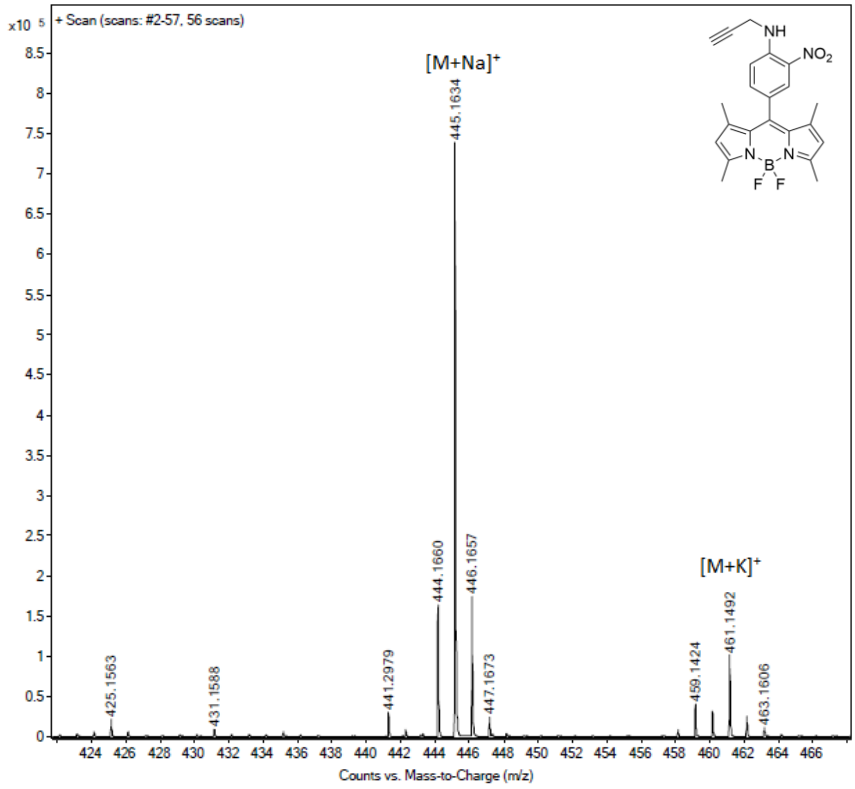

Figure S107: Zoom in from HRMS spectrum (ESI+) of BODIPY **31**.

8-[4-(*N*-2-Hydroxyethylamino)-3-nitrophenyl]-1,3,5,7-tetramethyl-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (**32**):

BODIPY **32** was prepared according to the general synthetic procedure. BODIPY **26** (100 mg, 0.26 mmol) and ethanolamine (0.3 mL, 5.17 mmol, 20 equiv.) were dissolved in 10 mL of DCM. The mixture was stirred for 24 h at rt. After column chromatography (silica gel, EtOAc) BODIPY **32** was obtained as an orange solid (96 mg, 0.22 mmol, 87 %).

^{1}H NMR (500 MHz, THF-d$_8$): δ (ppm) = 1.57 (s, 6H, Me), 2.49 (s, 6H, Me), 3.48–3.51 (m, 2H, CH_2), 3.80–3.83 (m, 2H, CH_2), 4.23 (t, *J* = 4.9 Hz, 1H, OH), 6.04 (s, 2H, $H_{pyrrole}$), 7.24 (d, *J* = 8.8 Hz, 1H, Ar-H_{meta}), 7.42 (dd, *J* = 8.7, 2.2 Hz, 1H, Ar-H_{ortho}), 8.15 (d, *J* = 2.2 Hz, 1H, Ar-H_{ortho}), 8.41 (t, *J* = 5.3 Hz, 1H, NH).

^{13}C NMR (126 MHz, THF-d$_8$): δ (ppm) = 14.7 (Me), 15.5 (Me), 46.4 (CH_2), 60.9 (CH_2), 116.4 (Ar-C_{meta}), 121.1*, 122.0 ($CH_{pyrrole}$), 127.7 (Ar-C_{ortho}), 132.9 ($C_{pyrrole}$), 133.2*, 136.8 (Ar-C_{ortho}), 141.2(C_{meso}), 143.5 ($C_{pyrrole}$), 146.8 (Ar-C_{para}), 156.5 ($C_{pyrrole}$). *These signals could not be assigned exactly to corresponding carbon atoms. They belong to the Ar-C_{ipso} and the Ar-C_{nitro} of the aryl residue.

^{19}F NMR (376 MHz, THF-d$_8$): δ (ppm) = -146.42 – -147.30 (m_c, 2F, BF_2).

HRMS (ESI-TOF): *m/z* calcd. for $C_{21}H_{23}BF_2N_4O_3Na^+$ $[M+Na]^+$: 451.1723, found: 451.1789, , *m/z* calcd. for $C_{42}H_{46}B_2F_4N_8O_6Na^+$ $[2M+Na]^+$: 879.3555, found: 879.3647.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3575 [ν(OH), ν(NH)], 2955 and 2925 [$\nu(CH_2)$, ν(Me)], 1627 [ν(C=C)], 1541 [$\nu_{as}(NO_2)$], 1525 [δ(Ar-C)], 1468 [$\delta(CH_2)$, δ(Me)], 1349 [$\nu_{sym}(NO_2)$], 1069 [ν(BF)], 734 [δ(HC=CH)].

UV/Vis (DCM): λ_{max} (nm) [log (ε/L mol^{-1} cm^{-1})] = 505 [4.54].

Fluorescence (DCM): λ_{max} (nm) = 515 at $\lambda_{Excitation}$ (nm) 490.

M.P. (°C): 170–175.

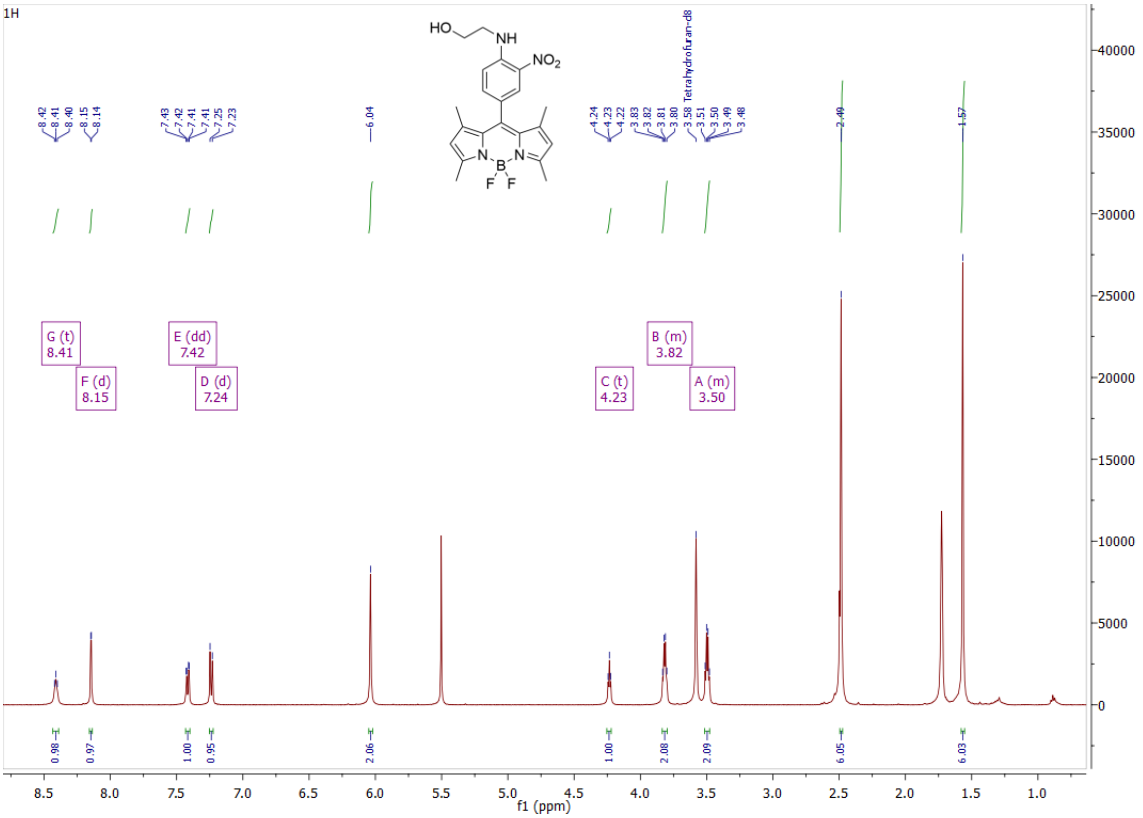

Figure S108: ^{1}H NMR (500 MHz, THF-d_8) spectrum of BODIPY **32**.

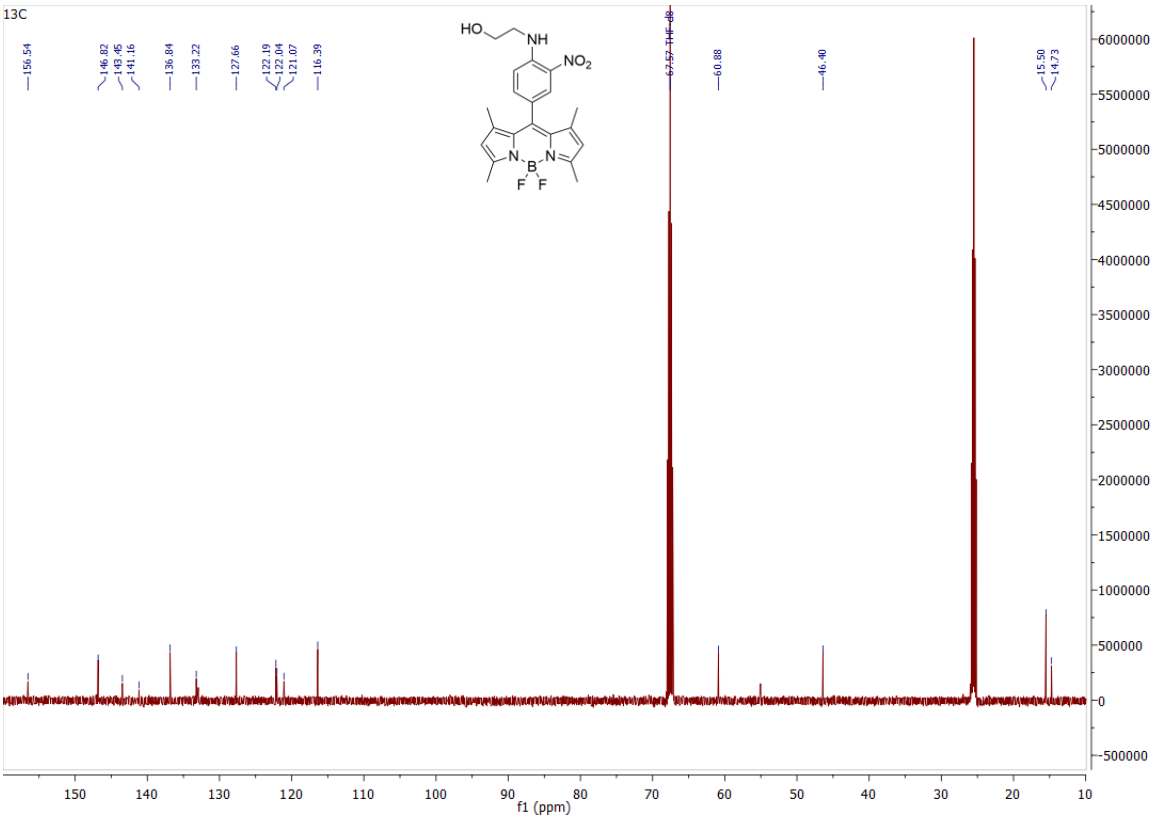

Figure S109: ^{13}C NMR (126 MHz, THF-d_8) spectrum of BODIPY **32**.

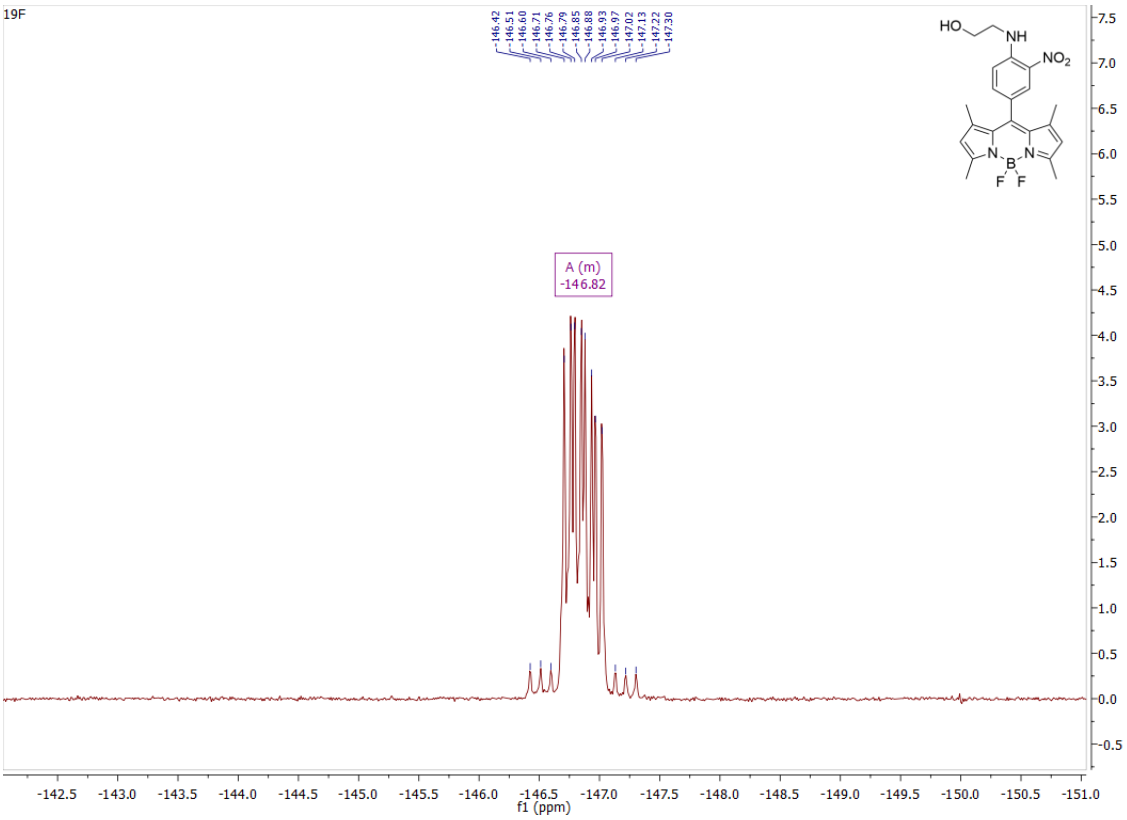

Figure S110: ^{19}F NMR (376 MHz, THF-d_8) spectrum of BODIPY **32**.

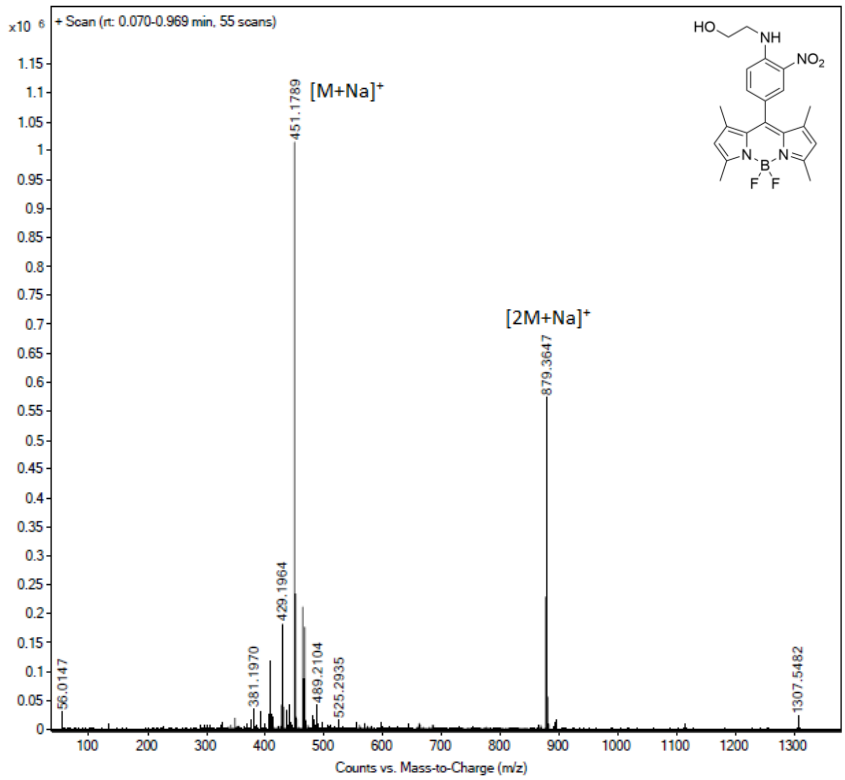

Figure S111: HRMS spectrum (ESI+) of BODIPY **32**.

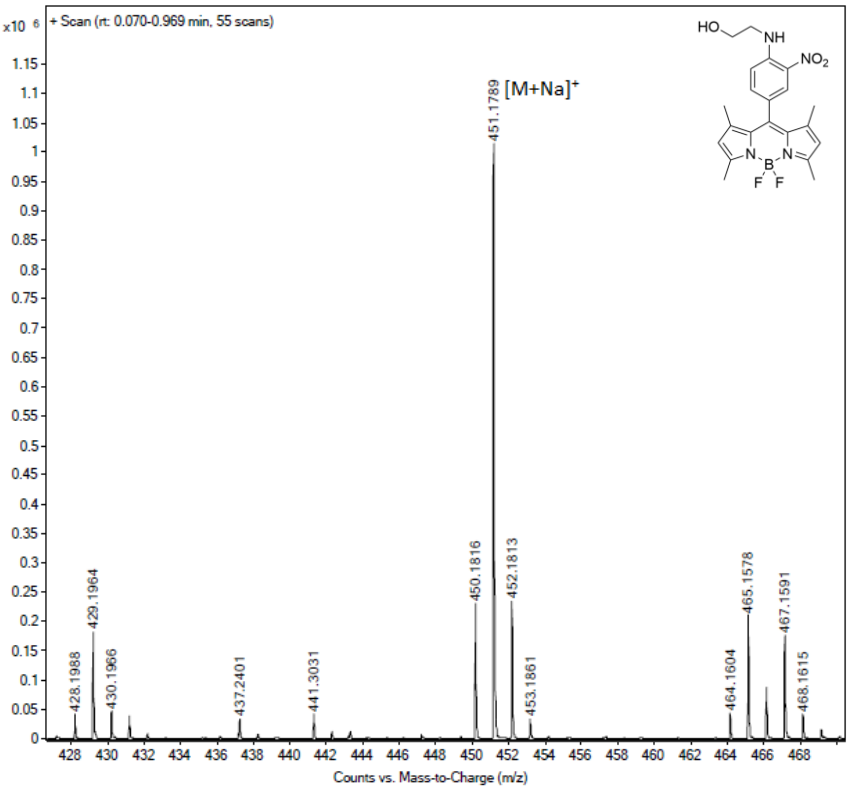

Figure S112: Zoom in from HRMS spectrum (ESI+) of BODIPY **32**.

8-[4-(*N*-1-Hydroxymethyl-2-hydroxyethylamino)-3-nitrophenyl]-1,3,5,7-tetramethyl-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (**33**):

BODIPY **33** was prepared according to the general synthetic procedure. BODIPY **26** (200 mg, 0.52 mmol, 1 equiv.) and 2-amino-1,3-dihydroxypropane (706 mg, 7.75 mmol, 15 equiv.) were dissolved in 20 mL of DMSO. The mixture was stirred for 24 h at rt. After column chromatography (silica gel, EtOAc) BODIPY **33** was obtained as an orange-green solid (54 mg, 0.12 mmol, 23 %).

^{1}H NMR (500 MHz, THF-d_8): δ (ppm) = 1.58 (s, 6H, Me), 2.48 (s, 6H, Me), 3.72–3.76 (m, 2H, CH_2), 3.80–3.82 (m, 3H, CH_2 + CH), 4.25 (br s, 2H, OH), 6.04 (s, 2H, $H_{pyrrole}$), 7.33 (d, *J* = 8.9 Hz, 1H, Ar-H_{meta}), 7.39 (dd, *J* = 8.8, 2.1 Hz, 1H, Ar-H_{ortho}), 8.14 (d, *J* = 2.0 Hz, 1H, Ar-H_{ortho}), 8.59 (d, *J* = bb7.3 Hz, 1H, NH).

^{13}C NMR (126 MHz, THF-d_8): δ (ppm) = 14.7 (Me), 15.5 (Me), 56.9 (CH), 61.5 (CH_2), 116.9 (Ar-C_{meta}), 122.0 ($CH_{pyrrole}$), 122.1*, 127.8 (Ar-C_{ortho}), 132.9 ($C_{pyrrole}$), 133.2*, 136.7 (Ar-C_{ortho}), 141.2 (C_{meso}), 143.5 ($C_{pyrrole}$), 146.5 (Ar-C_{para}), 156.5 ($C_{pyrrole}$). *These signals could not be assigned exactly to corresponding carbon atoms. They belong to the Ar-C_{ipso} and the Ar-C_{nitro} of the aryl residue.

^{19}F NMR (376 MHz, THF-d_8): δ (ppm) = -146.71 – -147.02 (m_c, 2F, BF_2).

HRMS (ESI-TOF): *m/z* calcd. for $C_{22}H_{25}BFN_4O_4^+$ $[M-F]^+$: 439.1947, found: 439.1957, *m/z* calcd. for $C_{22}H_{26}BF_2N_4O_4^+$ $[M+H]^+$: 459.2010, found: 459.2016, *m/z* calcd. for $C_{22}H_{25}BF_2N_4O_4Na^+$ $[M+Na]^+$: 481.1829, found: 481.1837, *m/z* calcd. for $C_{22}H_{25}BF_2N_4O_4K^+$ $[M+K]^+$: 497.1569, found: 497.1575.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3356 [ν(OH), ν(NH)], 2927 [ν(CH_2), ν(Me)], 1627 [ν(C=C)], 1543 [ν_{as}(NO_2)], 1525 [δ(Ar-C)], 1469 [δ(CH_2), δ(Me)], 1351 [ν_{sym}(NO_2)], 1053 [ν(BF)], 758 [δ(HC=CH)].

UV/Vis (MeOH): λ_{max} (nm) [log (ε/L mol^{-1} cm^{-1})] = 501 [4.80].

Fluorescence (DCM): λ_{max} (nm) = 519 at $\lambda_{Excitation}$ (nm) 490.

M.P. (°C): 110–116.

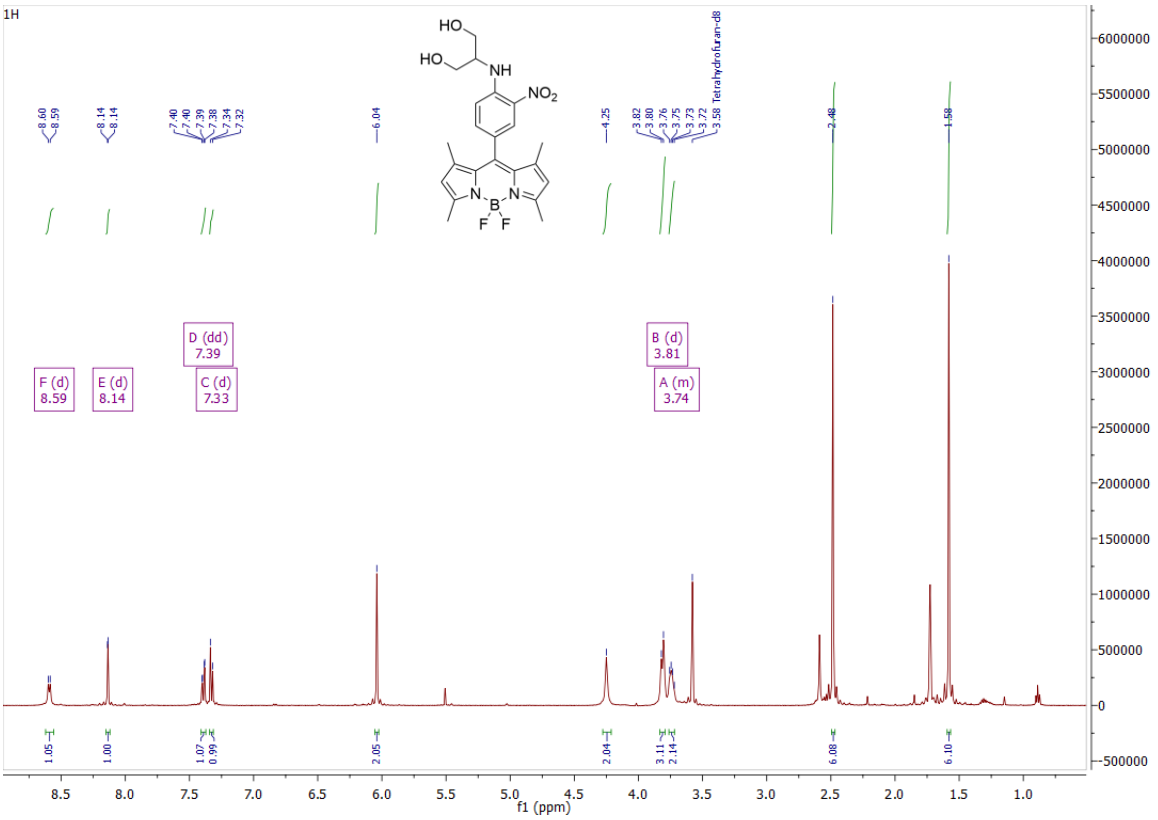

Figure S113: ^{1}H NMR (500 MHz, THF-d_8) spectrum of BODIPY **33**.

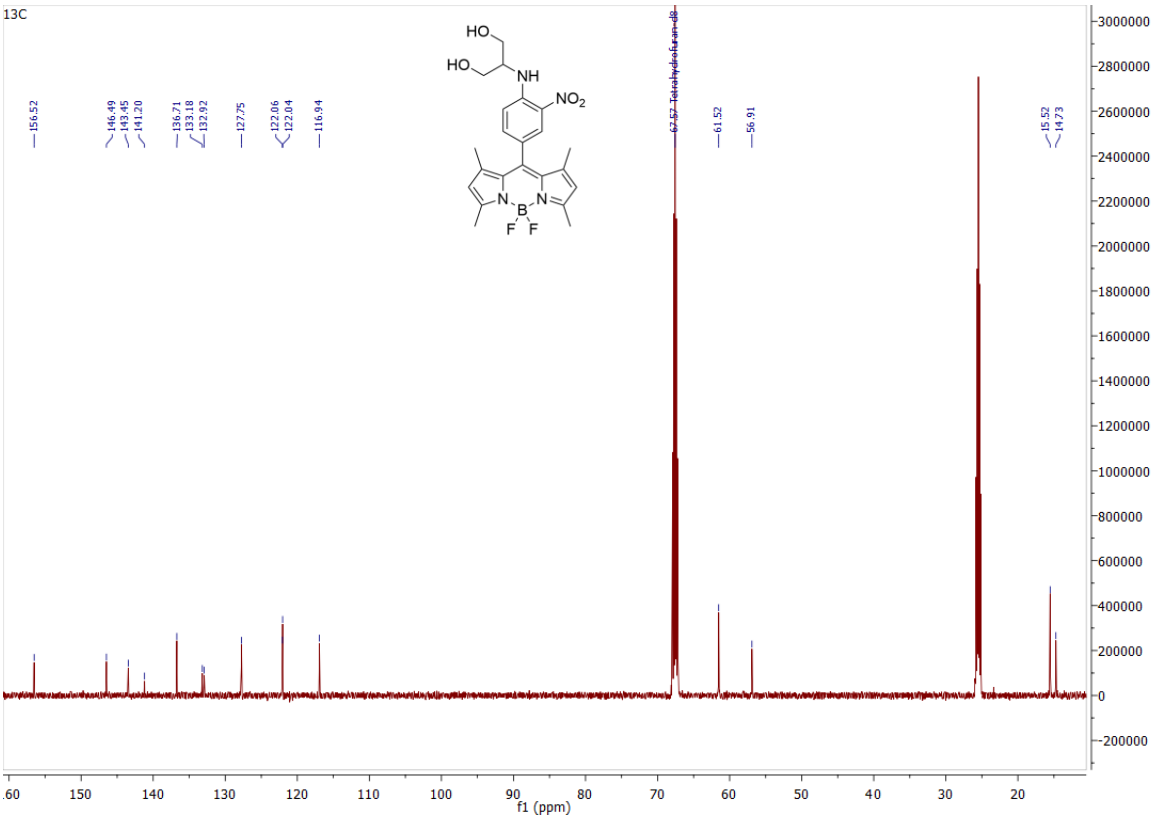

Figure S114: ^{13}C NMR (126 MHz, THF-d_8) spectrum of BODIPY **33**.

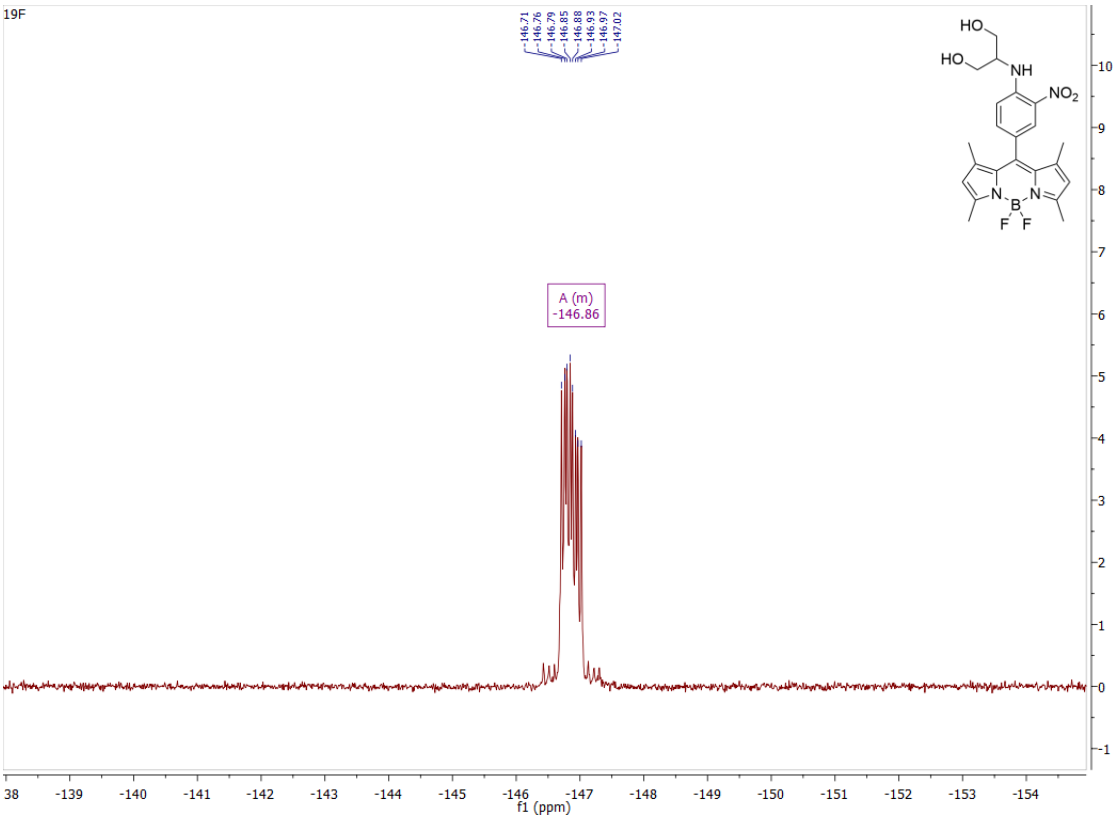

Figure S115: ^{19}F NMR (376 MHz, THF-d_8) spectrum of BODIPY **33**.

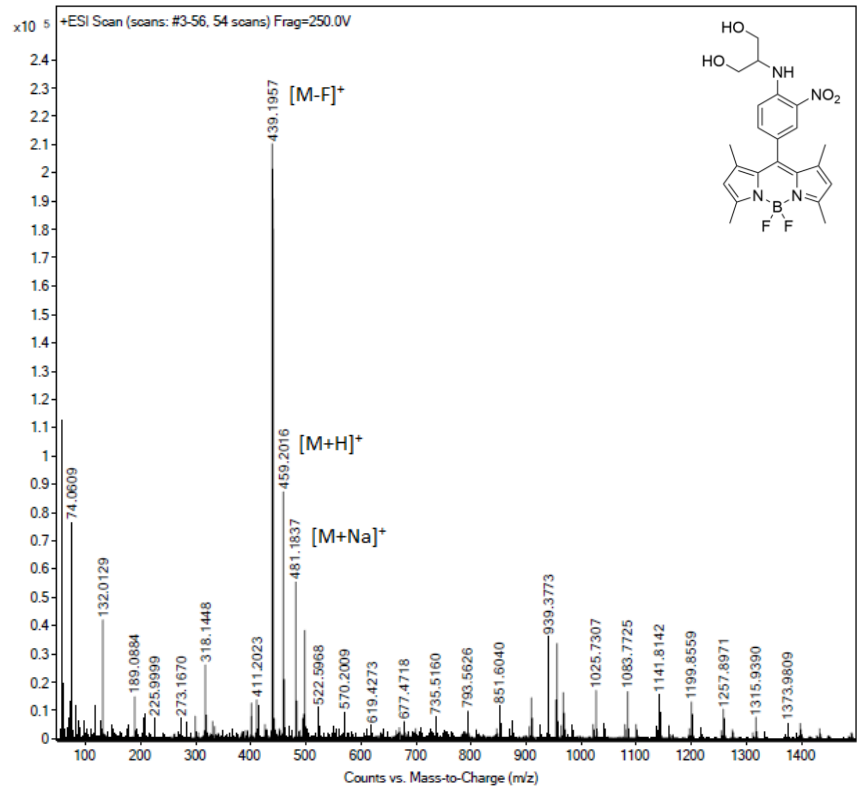

Figure S116: HRMS spectrum (ESI+) of BODIPY **33**.

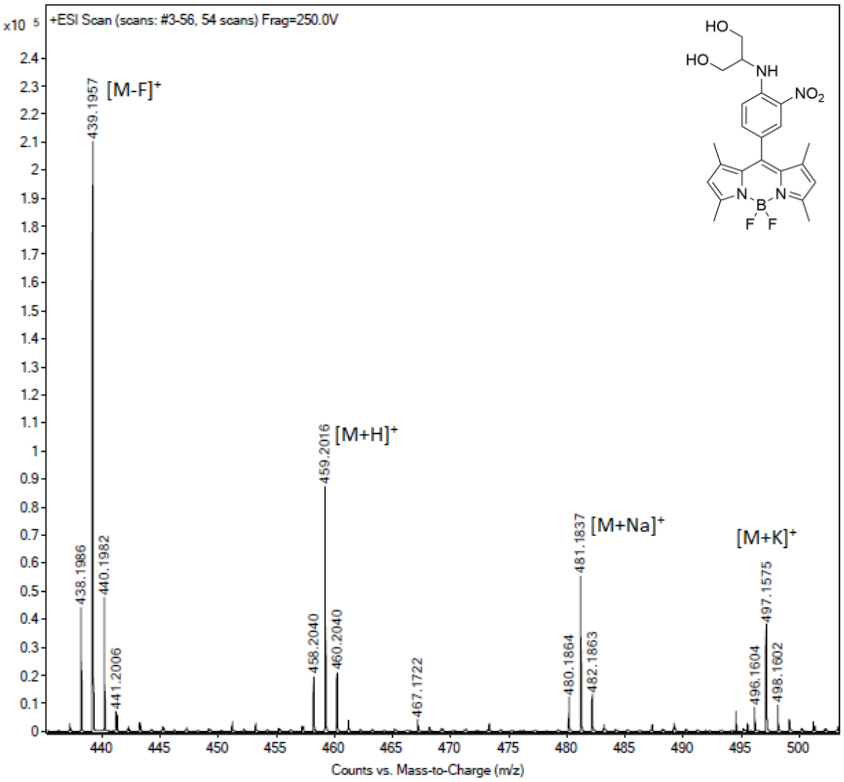

Figure S117: Zoom in from HRMS spectrum (ESI+) of BODIPY **33**.

12. Glycosylation of BODIPY 1a, 8a, 25, and 26

General synthetic procedure

The BODIPY (1 equiv.) was dissolved in DMF and the corresponding 1'-thio-carbohydrate sodium salt (1.2 equiv.) was added. The mixture was stirred for the indicated time. Afterwards, 5 ml water was added and stirred for additional 5 min at rt. Due to the high polarity of the product, the mixture was directly evaporated to dryness with a rotary evaporator. The crude product was purified by column chromatography and recrystallized.

8-[2,3,5,6-Tetrafluoro-4-(1'-thio-β-D-glucosyl)phenyl]-1,3,5,7-tetramethyl-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (**43**):

BODIPY **43** was prepared according to the general synthetic procedure. BODIPY **25** (100 mg, 0.24 mmol) and 1'-thio-β-D-glucose sodium salt (63 mg, 0.29 mmol) were dissolved in 5 mL of DMF. The mixture was stirred for 30 min at rt. After column chromatography (silica gel, DCM/MeOH = 6/1, v/v) and recrystallization (DCM + MeOH/*n*-hexane) BODIPY **43** was obtained as an orange solid (98 mg, 0.17 mol, 69 %).

^{1}H NMR (500 MHz, THF-d_8): δ (ppm) = 1.66 (s, 6H, Me), 2.51 (s, 6H, Me), 3.16–3.20 (m, 1H, 3´-H), 3.25–3.29 (m, 2H, 2´-H + 5´-H), 3.43 (dd, J = 7.2, 4.9 Hz, 1H, 4´-H), 3.50 (ddd, J = 11.7, 7.1, 5.1 Hz, 1H, 6´-H), 3.63 (ddd, J = 11.5, 4.8, 2.7 Hz, 1H, 6´-H), 4.50 (s, 1H, OH), 4.77 (s, 1H, OH), 4.88 (d, J = 8.6 Hz, 1H, 1´-H), 4.97 (s, 1H, OH), 6.12 (s, 2H, $H_{pyrrole}$).

^{13}C NMR (126 MHz, THF-d_8): δ (ppm) = 13.9 (Me), 14.8 (Me), 62.9 (6´-C), 71.5 (2´-C), 76.2 (4´-C), 79.98 (3´-C), 82.7 (5´-C), 85.8 (1´-C), 119.4 (Ar-C_{ipso}), 122.9 ($CH_{pyrrole}$), 125.0 (Ar-C_{para}), 131.8 ($C_{pyrrole}$), 142.95 ($C_{pyrrole}$), 158.5 ($C_{pyrrole}$).

^{19}F NMR (376 MHz, THF-d_8): δ (ppm) = -132.29 – -132.39 (m, 2F, CF_{ortho}), -142.89 (dd, J = 24.8, 11.1 Hz, 2F, CF_{meta}), -146.50 – -146.75 (m_C, 2F, BF_2).

HRMS (ESI-TOF): *m/z* calcd. for $C_{25}H_{26}BF_6N_2O_5S^+$ $[M+H]^+$: 591.1554, found: 591.1565, *m/z* calcd. for $C_{25}H_{25}BF_6N_2O_5SNa^+$ $[M+Na]^+$: 613.1374, found: 613.1390, *m/z* calcd. for $C_{25}H_{25}BF_6N_2O_5SK^+$ $[M+K]^+$: 629.1113, found: 629.1137, *m/z* calcd. for $C_{50}H_{50}B_2F_{12}N_6$ $O_{10}S_2Na^+$ $[2M+Na]^+$: 1203.2855, found: 1203.2887.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3374 [ν(OH), 2962 and 2923 [ν(Me)], 2866 [ν(CH)], 1644 [ν(C=C)], 1469 [δ(Me)], 1151 [ν(BF)], 773 [δ(-HC=CH-)].

UV/Vis (MeOH): λ_{max} (nm) [log (ε/L mol^{-1} cm^{-1})] = 513 [4.72].

Fluorescence (MeOH): λ_{max} (nm) = 523 at $\lambda_{Excitation}$ (nm) = 500.

M.P. (°C): 180–183.

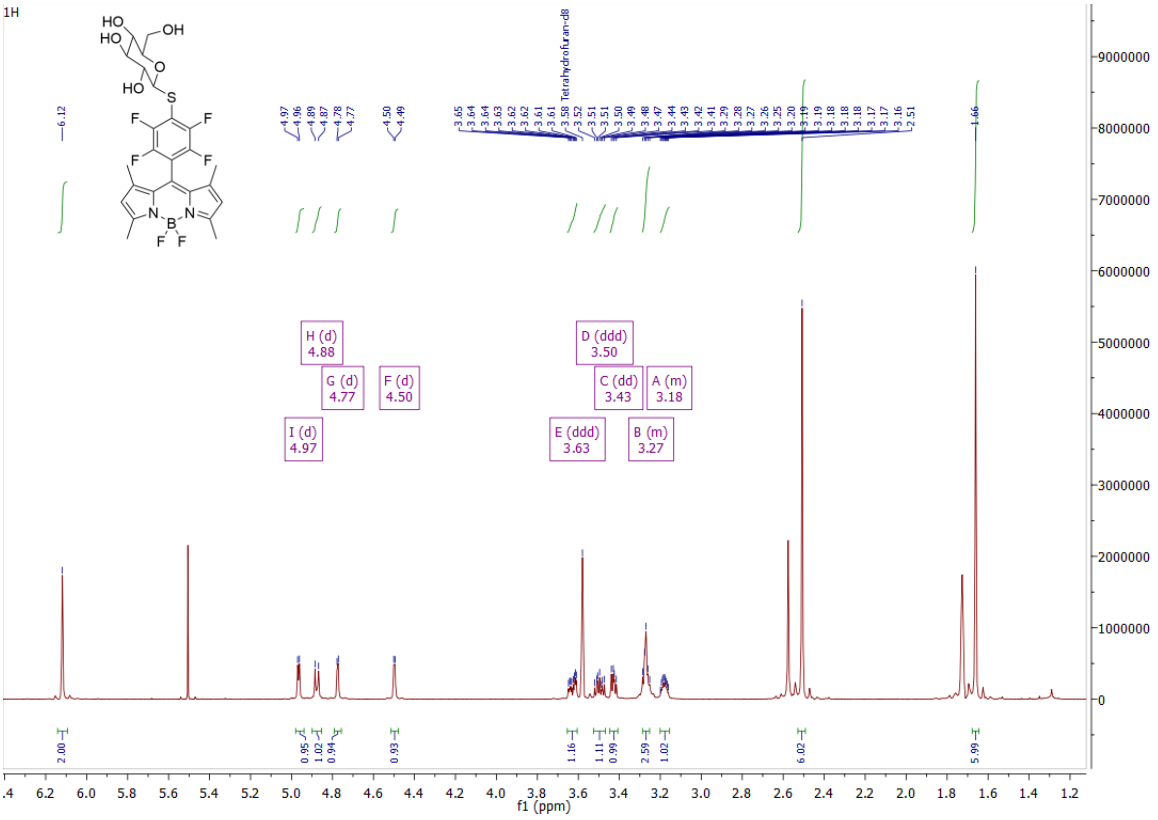

Figure S118: ^{1}H NMR (500 MHz, THF-d_8) spectrum of BODIPY **43**.

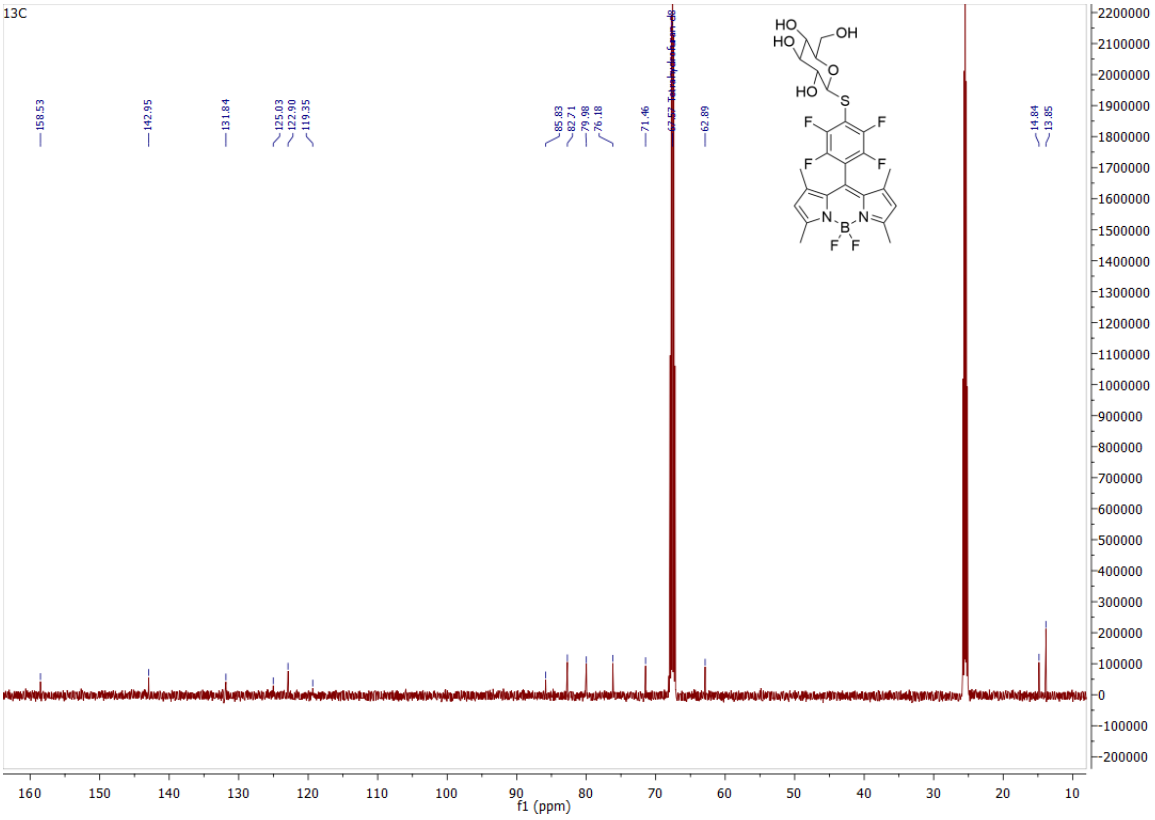

Figure S119: ^{13}C NMR (126 MHz, THF-d_8) spectrum of BODIPY **43**.

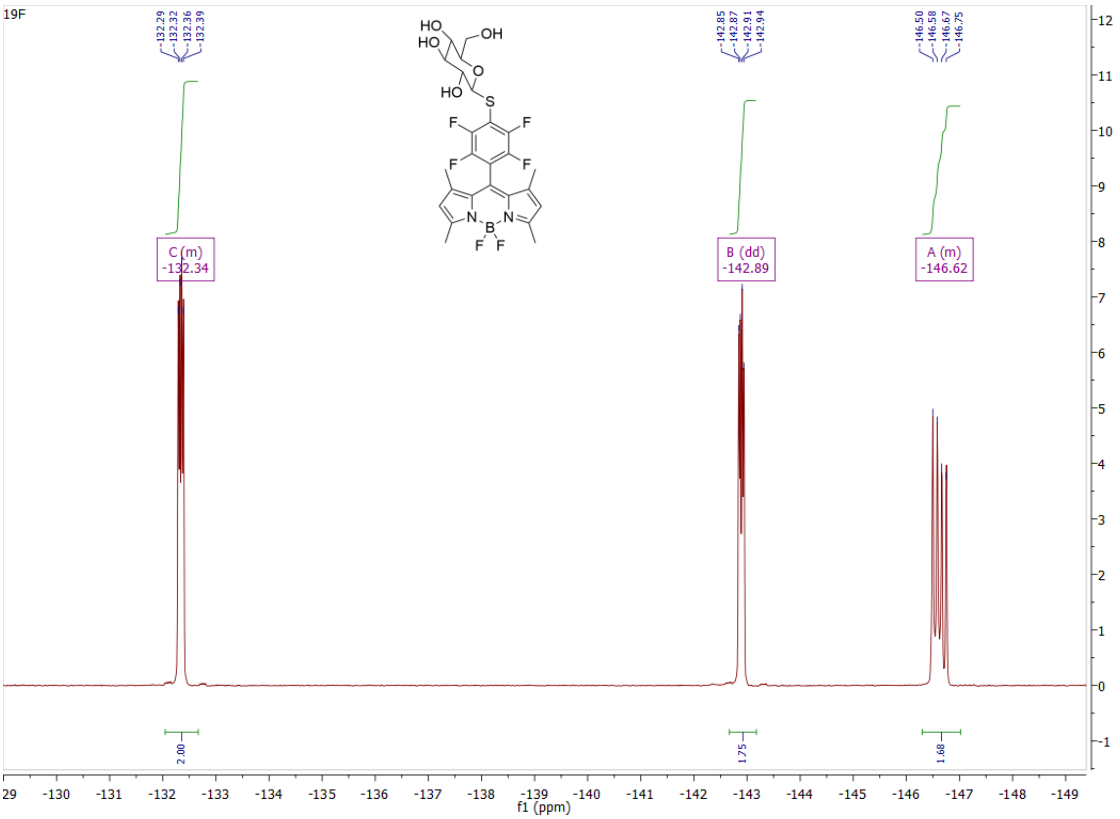

Figure S120: ^{19}F NMR (376 MHz, THF-d_8) spectrum of BODIPY **43**.

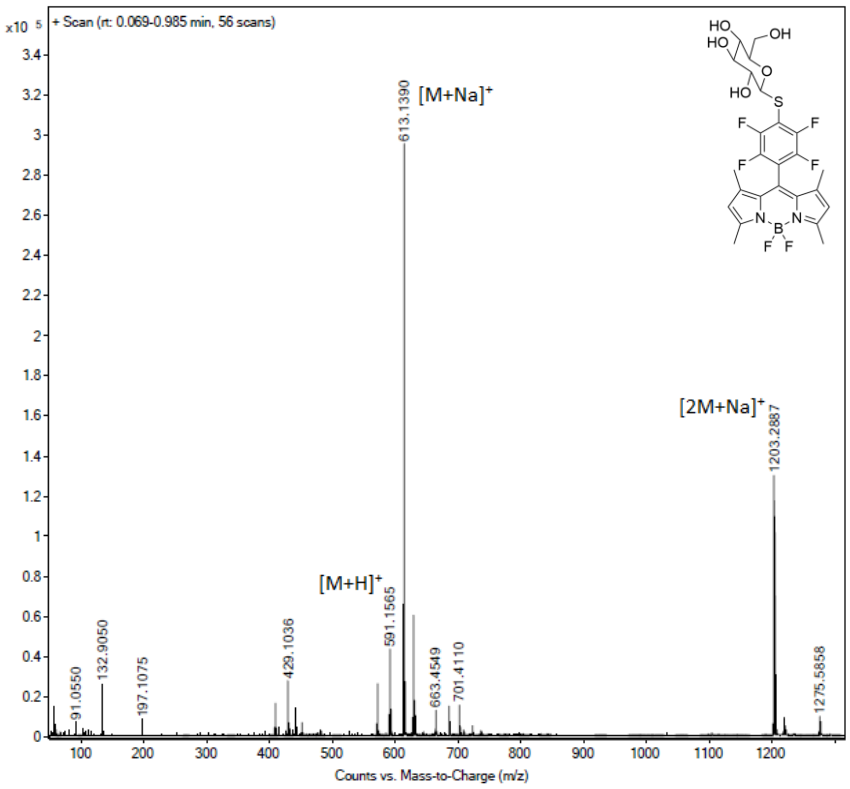

Figure S121: HRMS spectrum (ESI+) of BODIPY **43**.

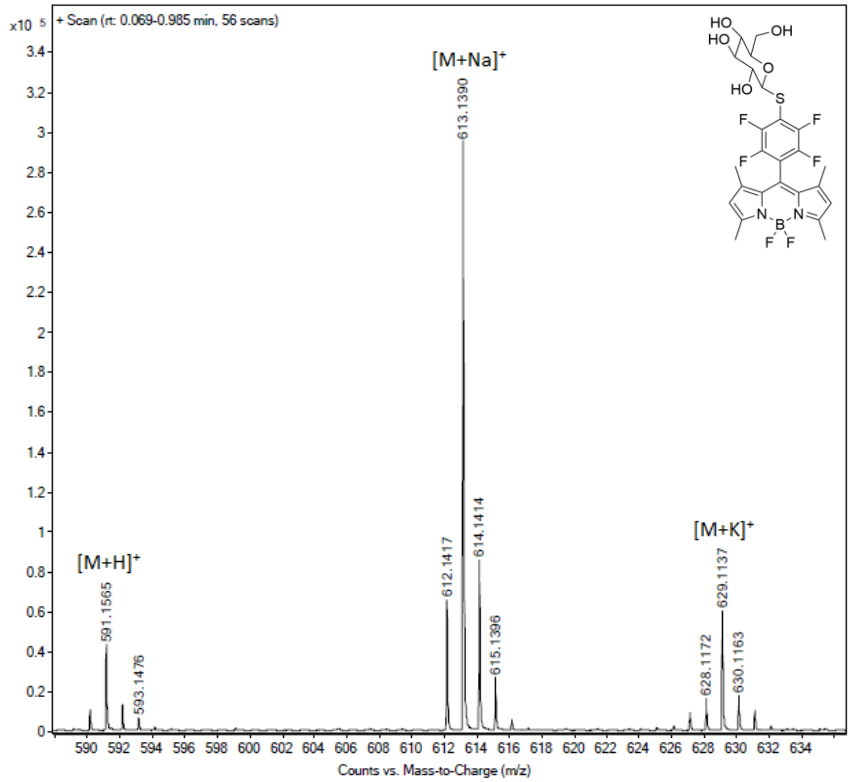

Figure S122: Zoom in from HRMS spectrum (ESI+) of BODIPY **43**.

8-[2,3,5,6-Tetrafluoro-4-(1'-thio-β-D-galactosyl)phenyl]-1,3,5,7-tetramethyl-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (**44**):

BODIPY **44** was prepared according to the general synthetic procedure. BODIPY **25** (200 mg, 0.48 mmol) and 1'-thio-β-D-galactose sodium salt (126 mg, 0.58 mmol,) were dissolved in 5 mL of DMF. The mixture was stirred for 20 min at rt. After column chromatography (silica gel, DCM/MeOH = 9/1, v/v) and recrystallization (DCM + MeOH/*n*-hexane) BODIPY **44** was obtained as an orange solid (130 mg, 0.22 mmol, 46 %).

^{1}H NMR (500 MHz, THF-d_8): δ (ppm) = 1.66 (s, 6H, Me), 2.51 (s, 6H, Me), 3.37 (ddd, *J* = 9.2, 6.3, 3.3 Hz, 1H, 3´-H), 3.43 (dd, *J* = 6.6, 6.0 Hz, 1H, 5´-H), 3.47 (dd, *J* = 10.6, 5.6 Hz, 1H, 6´-H), 3.56–3.61 (m, 2H, 4´-H + 6´-H), 3.66 (t, *J* = 5.5 Hz, 1H, OH), 3.82 (t, *J* = 3.3 Hz, 1H, 2´-H), 3.95 (d, *J* = 4.1 Hz, 1H, OH), 4.39 (d, *J* = 6.3 Hz, 1H, OH), 4.76–4.77 (m, 1H, 1´-H), 4.79 (d, 1H, OH), 6.12 (s, 2H, $H_{pyrrole}$).

^{13}C NMR (126 MHz, THF-d_8): δ (ppm) = 13.9 (Me), 14.8 (Me), 62.0 (6´-C), 70.0 (2´-C), 73.3 (4´-C), 76.5 (3´-C), 81.3 (5´-C), 86.3 (1´-C), 115.0 (Ar-C_{ipso}), 122.9 ($CH_{pyrrole}$), 125.1 (C_{meso}), 131.8 ($C_{pyrrole}$), 131.9 (Ar-C_{para}), 142.97 ($C_{pyrrole}$), 158.5 ($C_{pyrrole}$).

^{19}F NMR (376 MHz, THF-d_8): δ (ppm) = -131.26 (dd, *J* = 25.4, 11.7 Hz, 2F, CF_{ortho}), -142.24 (dd, *J* = 25.5, 11.7 Hz 2F, CF_{meta}), -145.71 – -145.96 (m_C, 2F, BF_2).

HRMS (ESI-TOF): *m/z* calcd. for $C_{25}H_{25}BF_6N_2O_5SNa^+$ $[M+Na]^+$: 613.1374, found: 613.1402.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3362 [ν(OH), 2957 and 2925 [ν(Me)], 2871 [ν(CH)], 1608 [ν(C=C)], 1469 [δ(Me)], 1157 [ν(BF)], 753 [δ(-HC=CH-)].

UV/Vis (MeOH): λ_{max} (nm) [log (ε/L mol^{-1} cm^{-1})] = 513 [4.54].

Fluorescence (MeOH): λ_{max} (nm) = 526 at $\lambda_{Excitation}$ (nm) = 500.

M.P. (°C): 213–216.

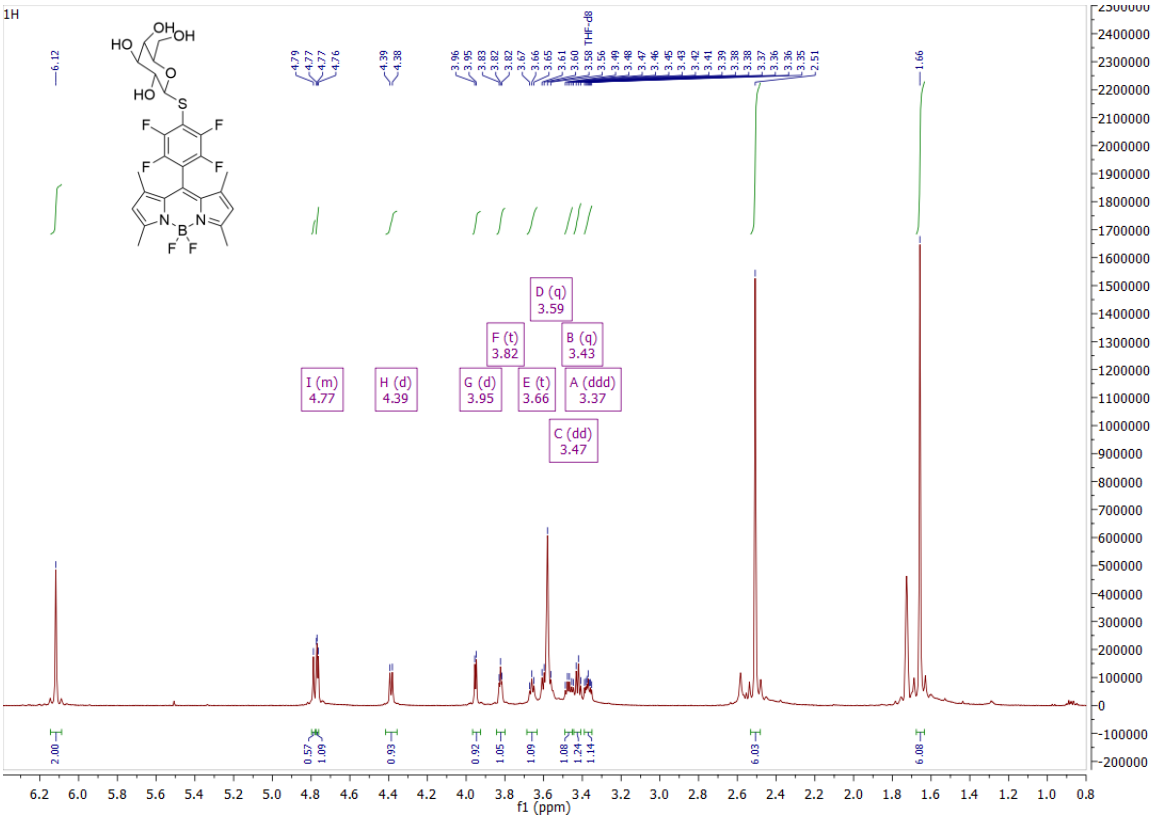

Figure S123: ^{1}H NMR (500 MHz, THF-d_8) spectrum of BODIPY **44**.

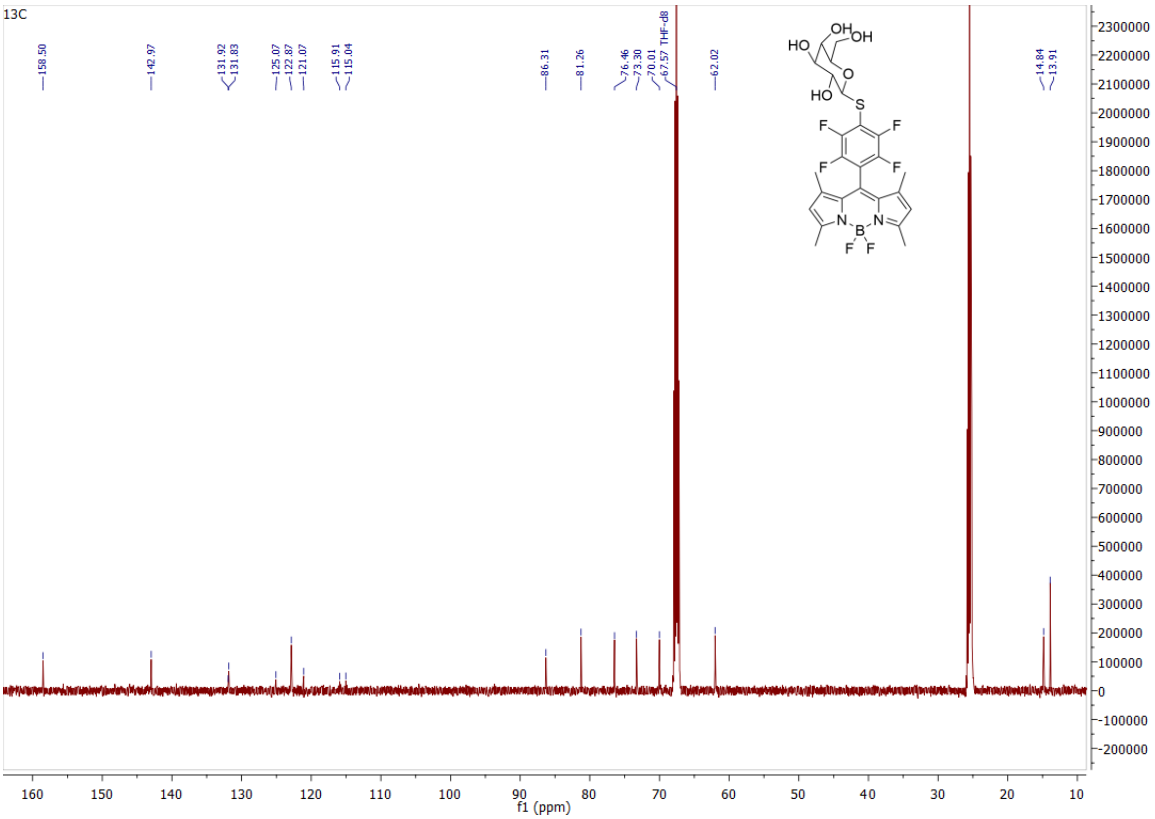

Figure S124: ^{13}C NMR (126 MHz, THF-d_8) spectrum of BODIPY **44**.

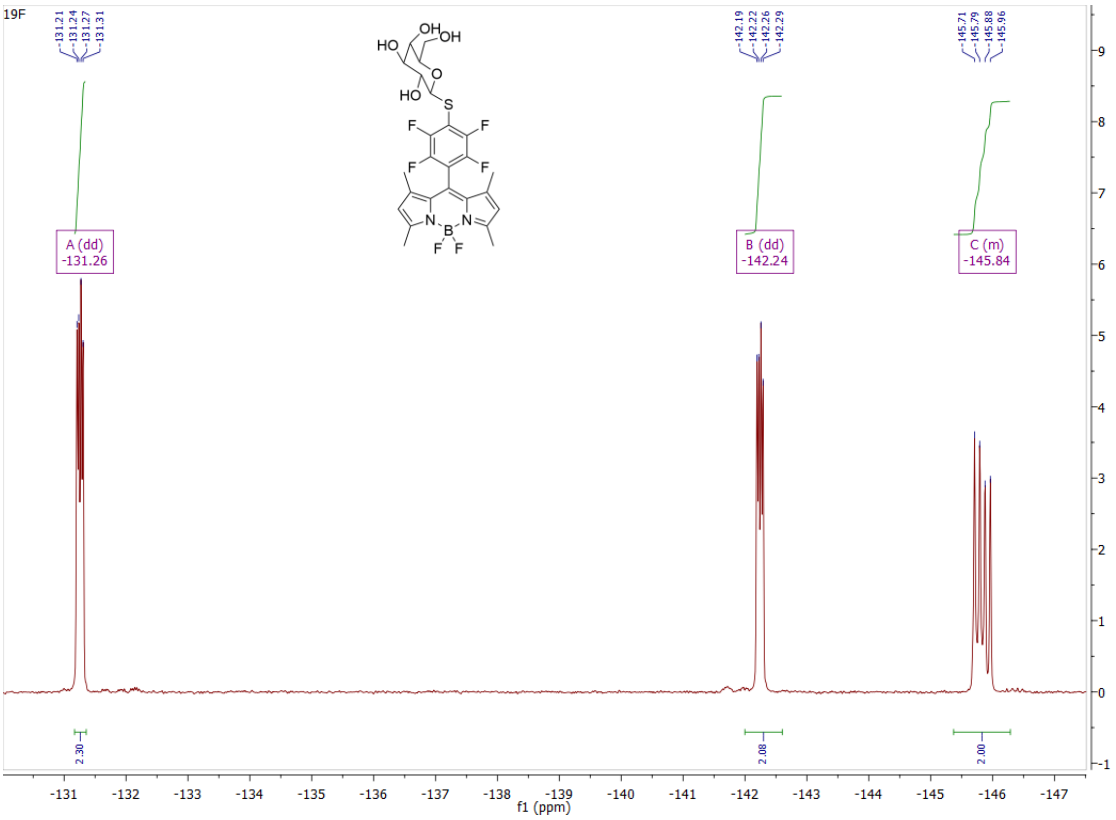

Figure S125: ^{19}F NMR (376 MHz, THF-d_8) spectrum of BODIPY **44**.

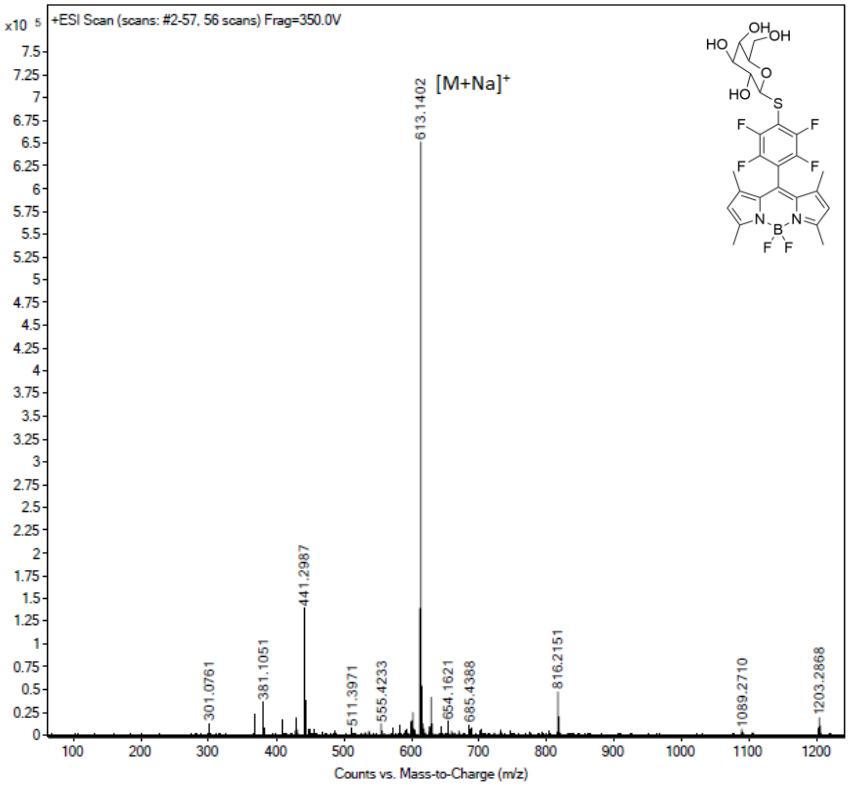

Figure S126: HRMS spectrum (ESI+) of BODIPY **44**.

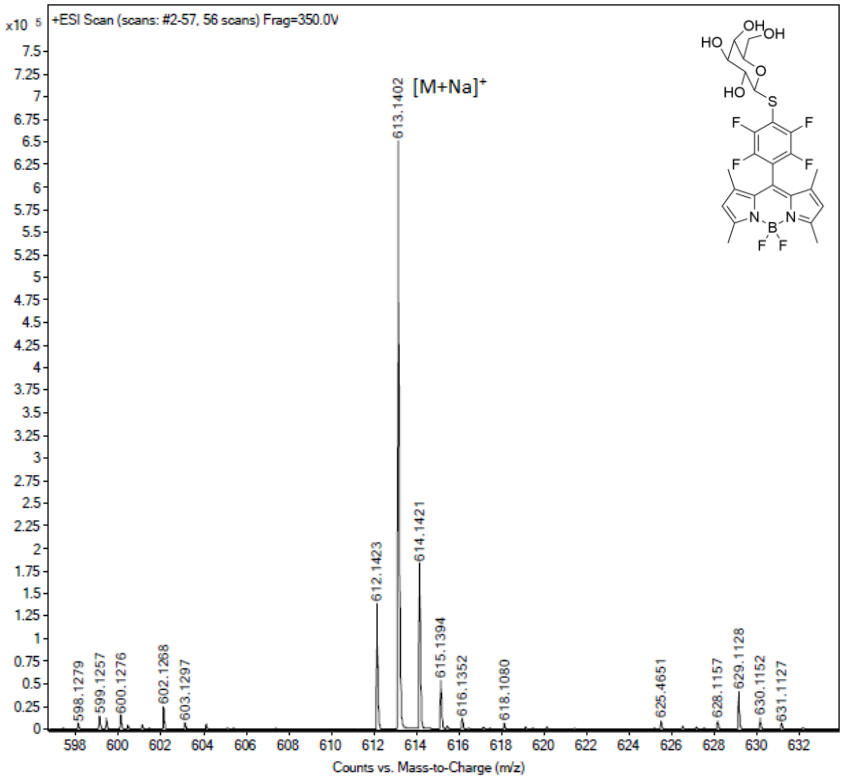

Figure S127: Zoom in from HRMS spectrum (ESI+) of BODIPY **44**.

8-[2,3,5,6-Tetrafluoro-4-(1'-thio-β-D-glucosyl)phenyl]-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (**51**):

BODIPY **51** was prepared according to the general synthetic procedure. BODIPY **1a** (100 mg, 0.28 mmol) and 1'-thio-β-D-glucose sodium salt (73 mg, 0.34 mmol) were dissolved in 5 mL of DMF. The mixture was stirred for 15 min at rt. After column chromatography (silica gel, DCM/MeOH = 8/1, v/v) and recrystallization (DCM + MeOH/*n*-hexane) BODIPY **51** was obtained as a dark yellow solid (130 mg, 0.24 mmol, 88 %).

The synthesis of this BODIPY has previously been described in the literature.[6] However, this BODIPY has not been characterized at that time by NMR or mass spectrometry. Therefore, the full characterization of BODIPY **51** is given here.

^{1}H NMR (500 MHz, THF-d$_8$): δ (ppm) = 3.21–3.26 (m, 2H, 2´-H + 5´-H), 3.27–3.30 (m, 2H, 3´-H + 4´-H), 3.46–3.51 (m, 1H, 6´-H), 3.72–3.75 (m, 1H, 6´-H), 4.43 (s, 1H, OH), 4.82 (s, 1H, OH), 4.93 (d, *J* = 9.0 Hz, 1H, 1´-H), 6.60–6.61 (m, 2H, $H_{pyrrole}$), 7.05 (s, 2H, $H_{pyrrole}$), 8.04 (s, 2H, $H_{pyrrole}$).

^{13}C NMR (126 MHz, THF-d$_8$): δ (ppm) = 63.2 (6´-C), 71.8 (2´-C), 76.1 (4´-C), 80.1 (3´-C), 82.8 (5´-C), 85.8 (1´-C), 120.5 ($C_{pyrrole}$), 131.8 ($C_{pyrrole}$), 136.0 ($C_{pyrrole}$), 147.8 ($C_{pyrrole}$).

^{19}F NMR (376 MHz, THF-d$_8$): δ (ppm) = -133.29 (dd, *J* = 23.5, 10.6 Hz, 2F, CF_{ortho}), -140.54 – -140.63 (m, 2F, CF_{meta}), -145.33 – -145.56 (m_C, 2F, BF_2).

HRMS (ESI-TOF): *m/z* calcd. for $C_{21}H_{17}BF_5N_2O_5S^+$ [M-F]$^+$: 515.0866, found: 515.0844, *m/z* calcd. for $C_{21}H_{17}BF_6N_2O_5SNa^+$ [M+Na]$^+$: 557.0748, found: 557.0729.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3365 [ν(OH), 2897 [ν(CH)], 1644 [ν(C=C)], 1440 [δ(Me)], 1078 [ν(BF)], 754 [δ(-HC=CH-)].

UV/Vis (MeOH): λ_{max} (nm) [log (ϵ/L mol^{-1} cm^{-1})] = 356 [3.84], 513 [4.58].

Fluorescence (MeOH): λ_{max} (nm) = 534 at $\lambda_{Excitation}$ (nm) = 340, 500.

M.P. (°C): 100–109.

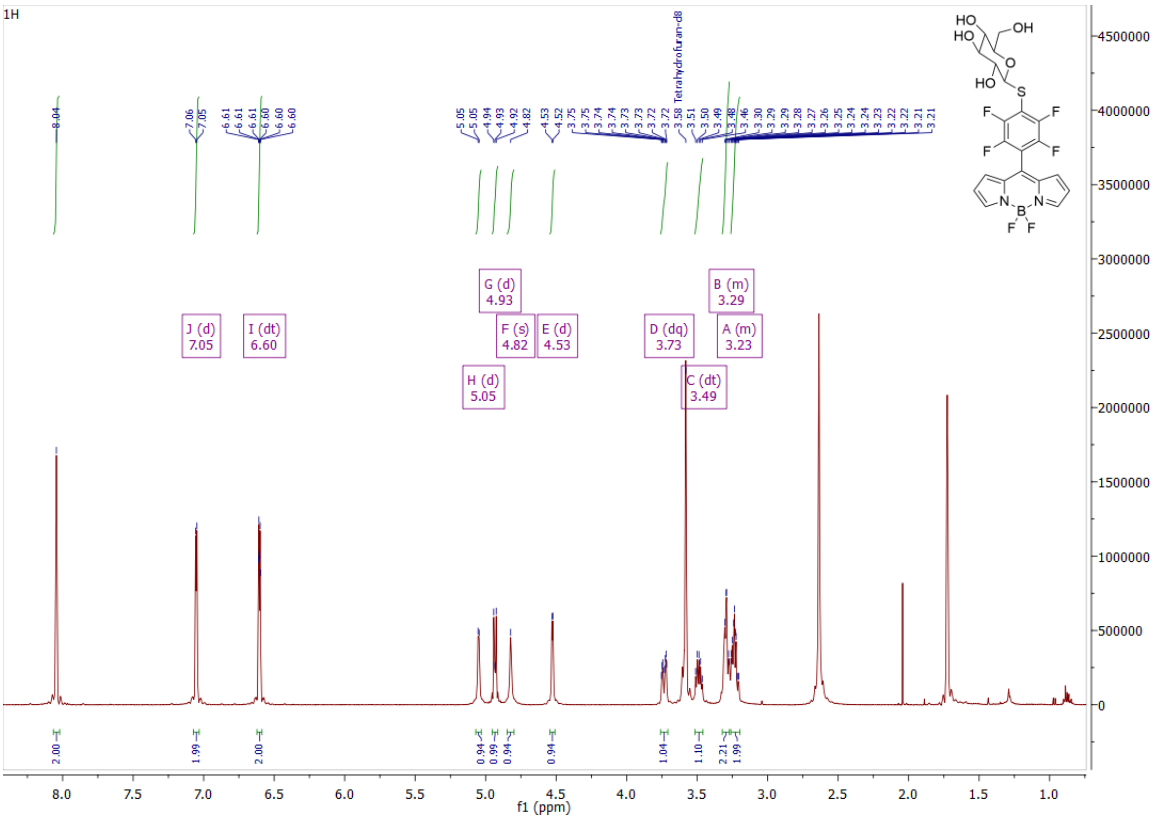

Figure S128: ^{1}H NMR (500 MHz, THF-d$_8$) spectrum of BODIPY **51**.

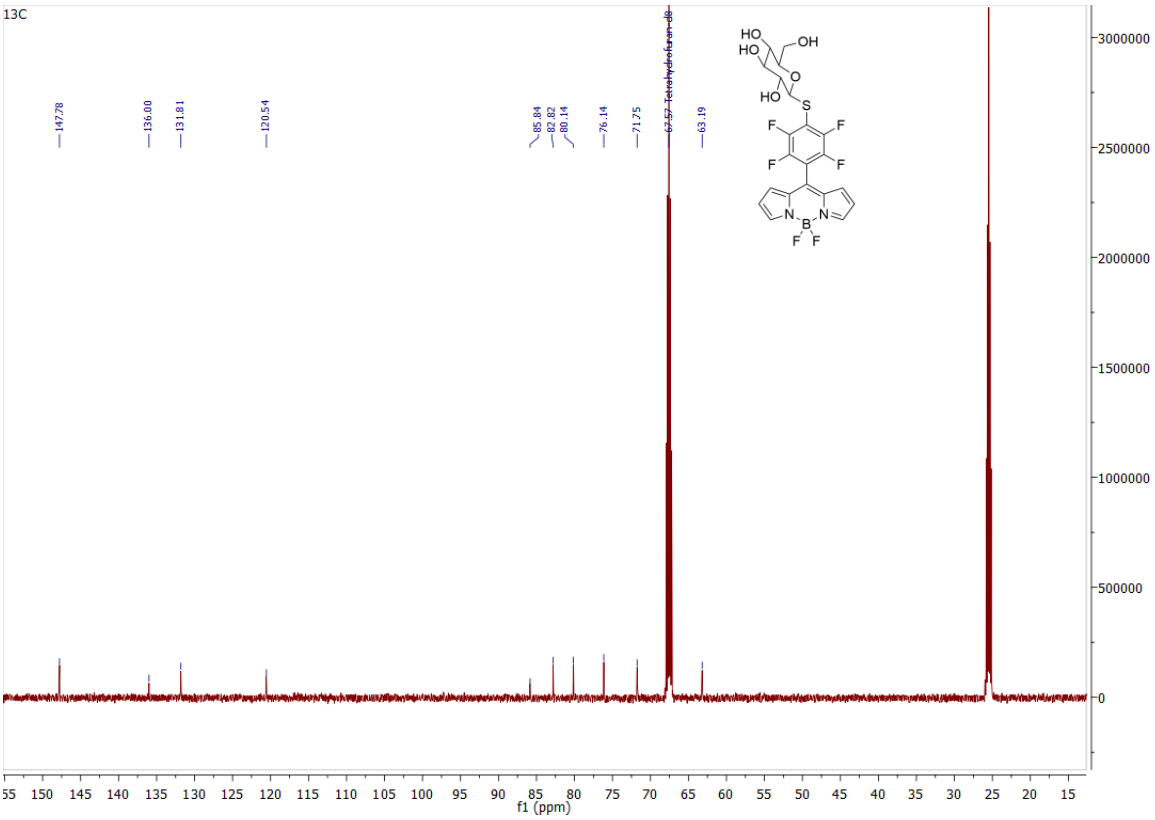

Figure S129: ^{13}C NMR (126 MHz, THF-d_8) spectrum of BODIPY **51**.

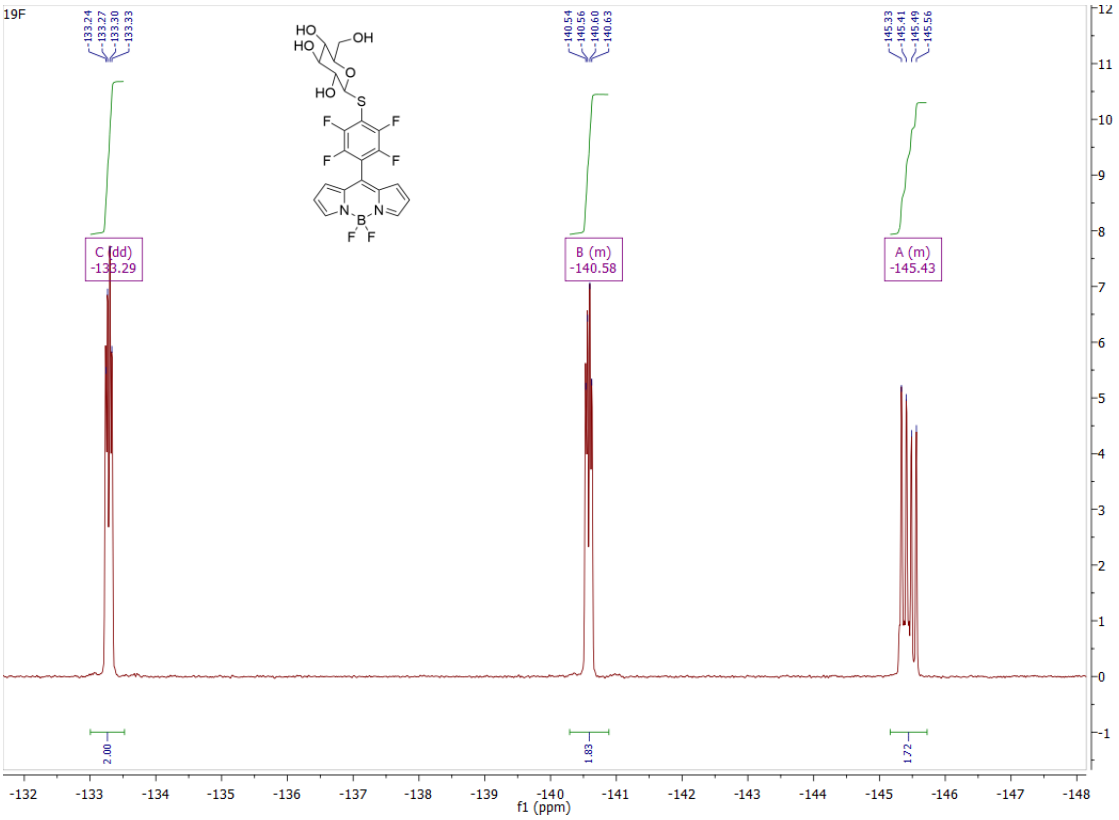

Figure S130: ^{19}F NMR (376 MHz, THF-d_8) spectrum of BODIPY **51**.

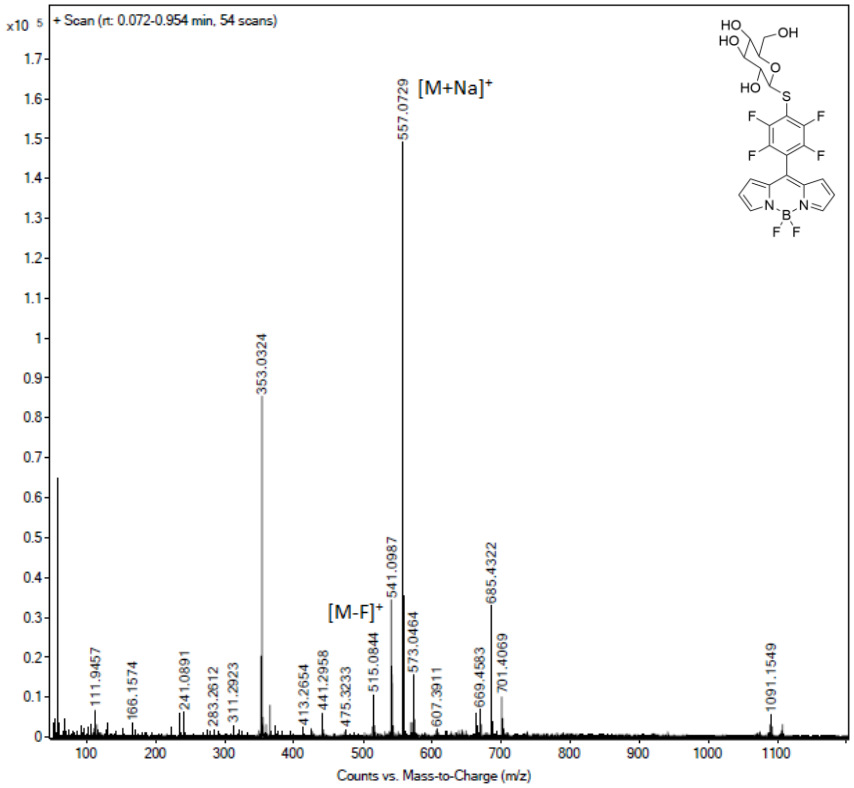

Figure S131: HRMS spectrum (ESI+) of BODIPY **51**.

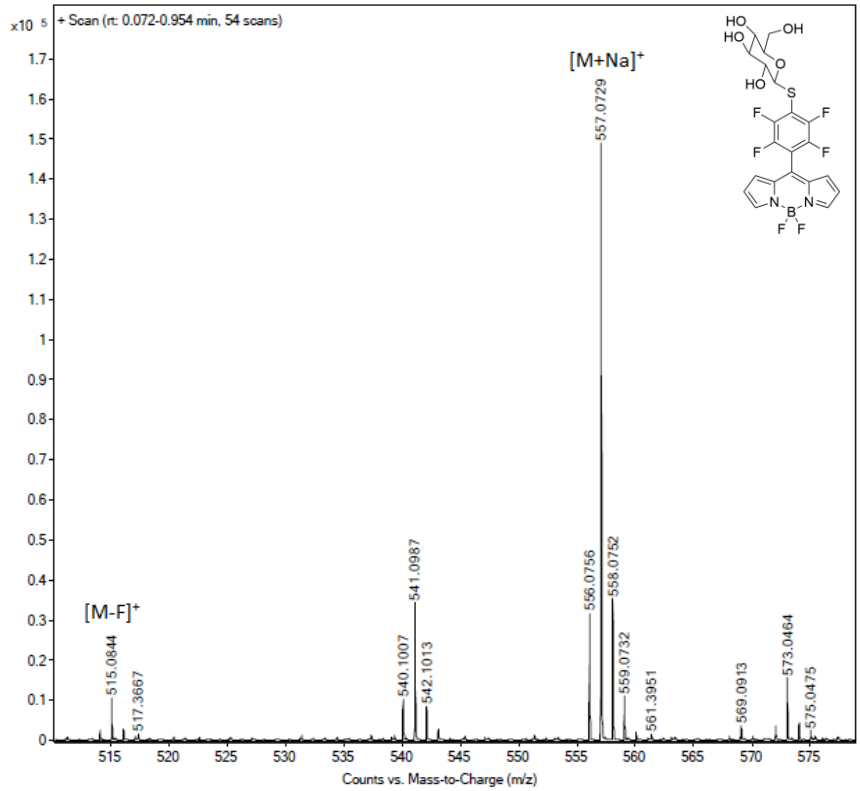

Figure S132: Zoom in from HRMS spectrum (ESI+) of BODIPY **51**.

8-[2,3,5,6-Tetrafluoro-4-(1'-thio-β-D-galactosyl)phenyl]-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (**52**):

BODIPY **52** was prepared according to the general synthetic procedure. BODIPY **1a** (100 mg, 0.28 mmol) and 1'-thio-β-D-glucose sodium salt (73 mg, 0.34 mmol) were dissolved in 5 mL of DMF. The mixture was stirred for 15 min at rt. After column chromatography (silica gel, DCM/MeOH = 8/1, v/v) and recrystallization (DCM + MeOH/*n*-hexane) BODIPY **52** was obtained as an orange-red solid (91 mg, 0.17 mmol, 61 %).

The synthesis of this BODIPY has previously been described in the literature.[6] However, this BODIPY has not been characterized at that time by NMR or mass spectrometry. Therefore, the full characterization of BODIPY **52** is given here.

^{1}H NMR (600 MHz, THF-d_8): δ (ppm) = 3.39 (dd, *J* = 8.7, 4.1 Hz, 1H, 3´-H), 3.45 (dd, *J* = 5.9, 5.6 Hz, 1H, 5´-H), 3.60 – 3.63 (m, 3H, 4´-H + 6´-H), 3.73 (br s, 1H, OH), 3.82 (br s, 1H, 2´-H), 3.99 (br s, 1H, OH), 4.43 (br s, 1H, OH), 4.86 (dd, *J* = 9.5, 4.8 Hz, 2H, 1´-H + OH), 6.60 (s, 2H, $H_{pyrrole}$), 7.04 (s, 2H, $H_{pyrrole}$), 8.04 (s, 2H, $H_{pyrrole}$).

^{13}C NMR (151 MHz, THF-d_8): δ (ppm) = 62.0 (6´-C), 69.9 (2´-C), 72.9 (4´-C), 76.2 (3´-C), 81.1 (5´-C), 86.1 (1´-C), 112.86 (t, *J* = 18.7 Hz, Ar-C_{ipso}), 116.61 (t, *J* = 20.3 Hz, Ar-C_{para}), 120.2 ($C_{pyrrole}$), 131.0 (C_{meso}), 131.4 ($C_{pyrrole}$), 135.6 ($C_{pyrrole}$), 144.73 (ddt, *J* = 250.2, 15.8, 4.5 Hz, Ar-C_{meta}), 147.4 ($C_{pyrrole}$), 147.95 (ddt, *J* = 245.5, 13.1, 4.5 Hz, Ar-C_{ortho}).

^{19}F NMR (376 MHz, THF-d_8): δ (ppm) = -133.09 (dd, *J* = 24.7, 10.6 Hz, 2F, CF_{ortho}), -140.54 – -140.74 (m, 2F, CF_{meta}), -145.40 – -145.62 (m_C, 2F, BF_2).

HRMS (ESI-TOF): *m/z* calcd. for $C_{21}H_{17}BF_5N_2O_5S^+$ $[M-F]^+$: 515.0866, found: 515.0856, *m/z* calcd. for $C_{21}H_{17}BF_6N_2O_5SNa^+$ $[M+Na]^+$: 557.0748, found: 557.0749, *m/z* calcd. for $C_{42}H_{34}B_2F_{12}N_4O_{10}S_2Na^+$ $[2M+Na]^+$: 1091.1603, found: 1091.1615.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3365 [ν(OH), 2897 [ν(CH)], 1644 [ν(C=C)], 1440 [δ(Me)], 1078 [ν(BF)], 754 [δ(-HC=CH-)].

UV/Vis (MeOH): λ_{max} (nm) [log (ε/L mol^{-1} cm^{-1})] = 352 [3.69], 513 [4.45].

Fluorescence (MeOH): λ_{max} (nm) = 534 at $\lambda_{Excitation}$ (nm) = 370, 500.

M.P. (°C): 110–115.

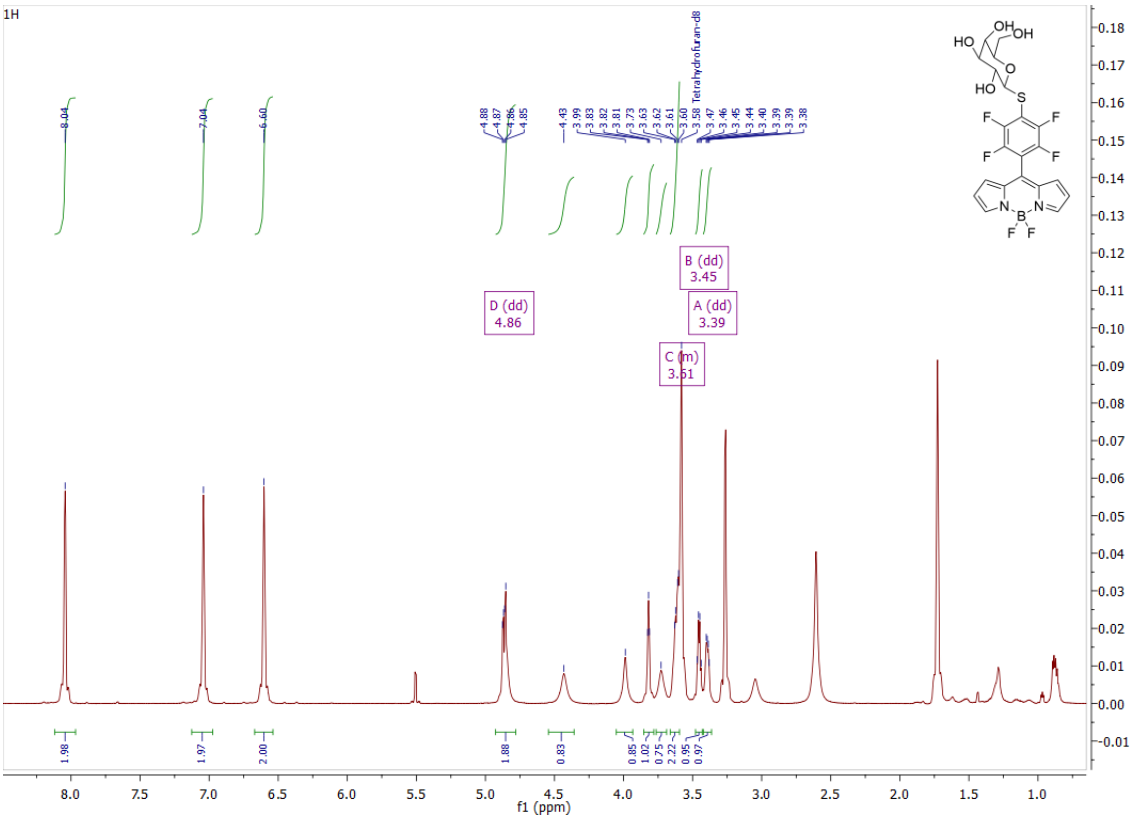

Figure S133: ^{1}H NMR (600 MHz, THF-d_8) spectrum of BODIPY **52**.

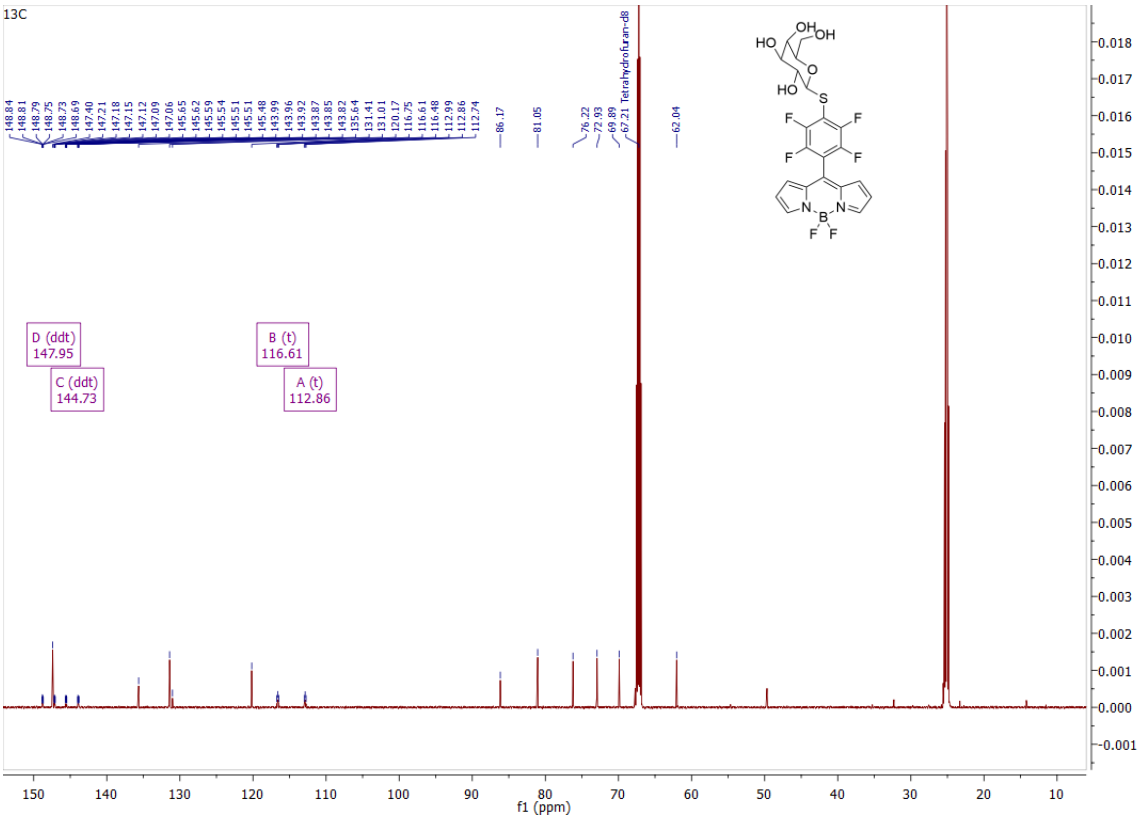

Figure S134: ^{13}C NMR (151 MHz, THF-d_8) spectrum of BODIPY **52**.

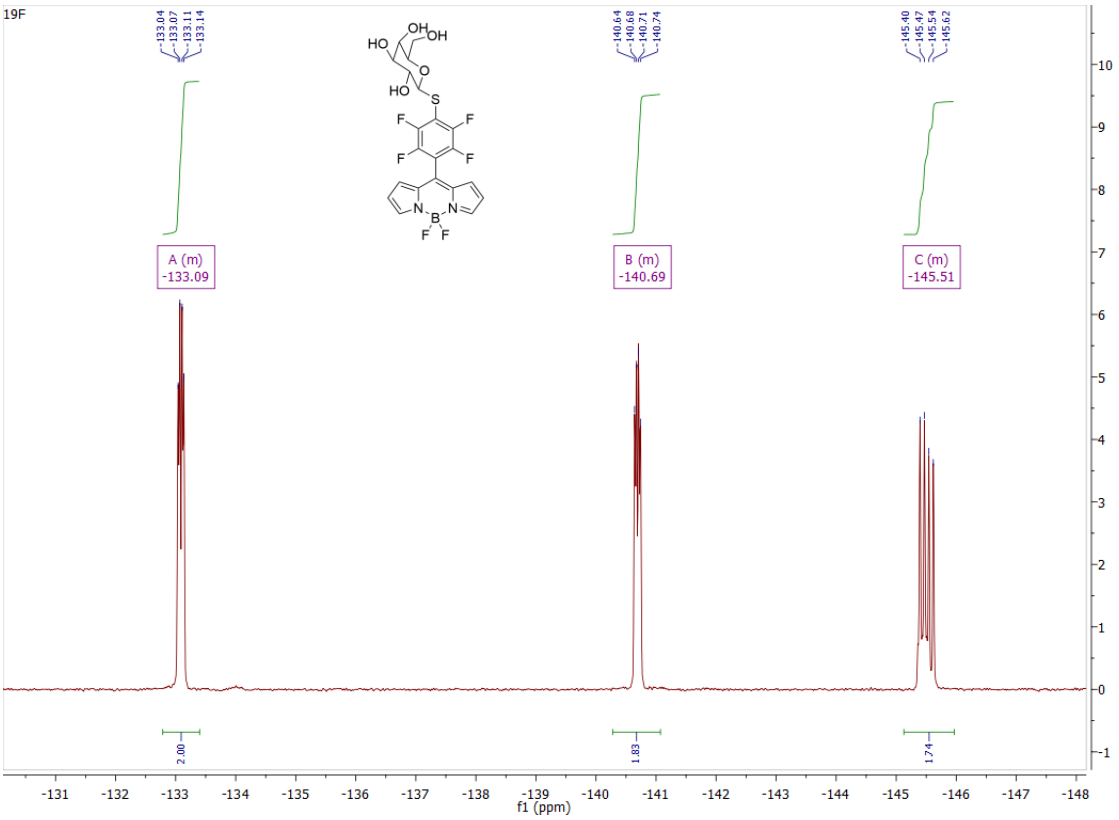

Figure S135: ^{19}F NMR (376 MHz, THF-d_8) spectrum of BODIPY **52**.

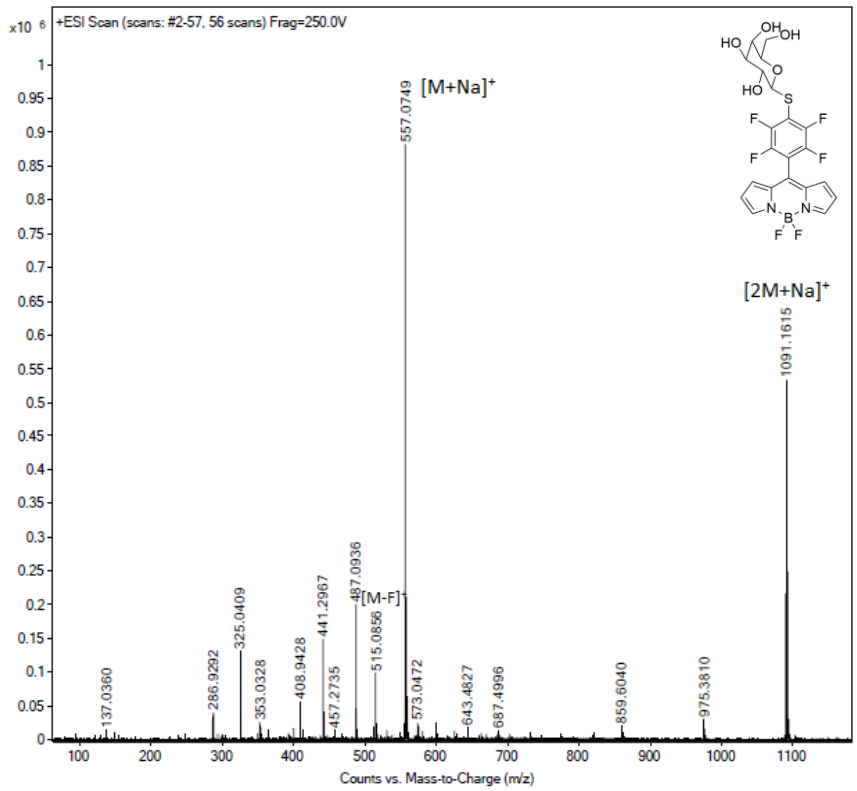

Figure S136: HRMS spectrum (ESI+) of BODIPY **52**.

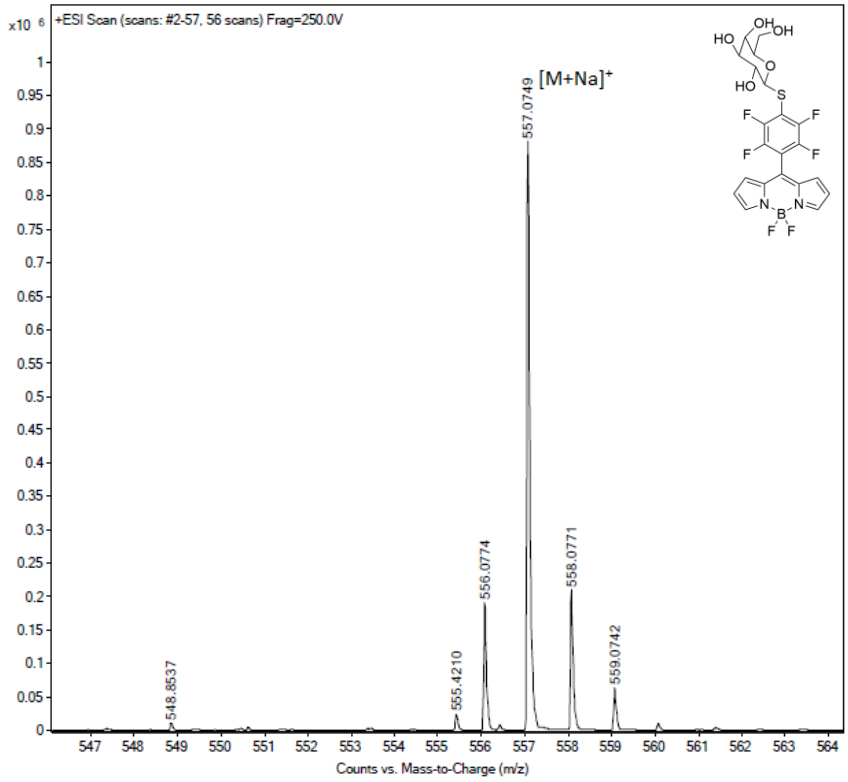

Figure S137: Zoom in from HRMS spectrum (ESI+) of BODIPY **52**.

8-[3-Nitro-4-(1'-thio-β-D-glucosyl)phenyl]-1,3,5,7-tetramethyl-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (**47**):

BODIPY **47** was prepared according to the general synthetic procedure. BODIPY **26** (100 mg, 0.26 mmol, 1 equiv.) and 1'-Thio-β-D-glucose sodium salt (67 mg, 0.31 mmol, 1.2 equiv.) were dissolved in 5 mL of DMF. The mixture was stirred for 15 min at rt. After column chromatography (silica gel, DCM/MeOH = 6/1, v/v) and recrystallization (DCM + MeOH/*n*-hexane) BODIPY **47** was obtained as an orange solid (67 mg, 0.12 mmol, 46 %).

^{1}H NMR (600 MHz, THF-d$_8$): δ (ppm) = 1.48 (d, *J* = 6.6 Hz, 6H, Me), 2.50 (s, 6H, Me), 3.31–3.37 (m, 3H, 2´-H + 3'-H + 4´-H), 3.42 (ddd, *J* = 8.9, 5.9, 2.5 Hz, 1H, 5´-H), 3.57–3.60 (m,4H, 6´-H + THF), 3.81 (dd, *J* = 12.0, 2.5 Hz, 1H, 6´-H), 3.88 (br s, 1H, OH), 4.61 (br s, 1H, OH), 4.84 br s, 1H, OH), 4.88–4.89 (m, 1H, 1´-H), 5.07 (br s, 1H, OH), 6.07 (d, *J* = 3.6 Hz, 2H, H$_{pyrrole}$), 7.65 (dd, *J* = 8.3, 2.0 Hz, 1H, Ar-H$_{ortho}$), 8.12 (d, *J* = 8.3 Hz, 1H, Ar-H$_{meta}$), 8.23 (d, *J* = 1.9 Hz, 1H, Ar-H$_{ortho}$).

^{13}C NMR (151 MHz, THF-d$_8$): δ (ppm) = 14.4 (Me), 15.1 (Me), 62.7 (6´-C), 70.9 (4´-C), 73.6 (2´-C), 79.9 (3´-C), 81.9 (5´-C), 86.4 (1´-C), 121.99 (CH$_{pyrrole}$), 126.3 (Ar-C$_{ortho}$), 130.7 (Ar-C$_{meta}$), 131.9 (C$_{pyrrole}$), 132.9 (Ar-C$_{para}$), 134.3 (Ar-C$_{ortho}$), 138.1*, 139.3*, 143.2 (C$_{pyrrole}$), 148.0 (C$_{meso}$), 156.7 (C$_{pyrrole}$). *These signals could not be assigned exactly to corresponding carbon atoms. They belong to the Ar-C$_{ipso}$ and the Ar-C$_{nitro}$ of the aryl residue.

^{19}F NMR (376 MHz, THF-d_8): δ (ppm) = -146.71 – -146.89 (m_c, 2F, BF_2).

HRMS (ESI-TOF): *m/z* calcd. for $C_{25}H_{30}N_3O_7S^+$ [dipyrrin+H]$^+$: 516.1799, found: 516.1802, *m/z* calcd. for $C_{25}H_{28}BF_2N_3O_7SNa^+$ [M+Na]$^+$: 586.1601, found: 586.1614.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3388 [ν(OH), 2923 [ν(Me)], 1608 [ν(C=C)], 1549 [ν_{as}(NO_2)], 1512 [δ(Ar-C)], 1469 [δ(Me)], 1308 [ν_{sym}(NO_2)], 1055 [ν(BF)], 753 [δ(HC=CH)].

UV/Vis (MeOH): λ_{max} (nm) [log (ε/L mol^{-1} cm^{-1})] = 382 [3.58], 503 [4.52].

Fluorescence (DCM): λ_{max} (nm) = 520 at $\lambda_{Excitation}$ (nm) 370, 490.

M.P. (°C): 158–163.

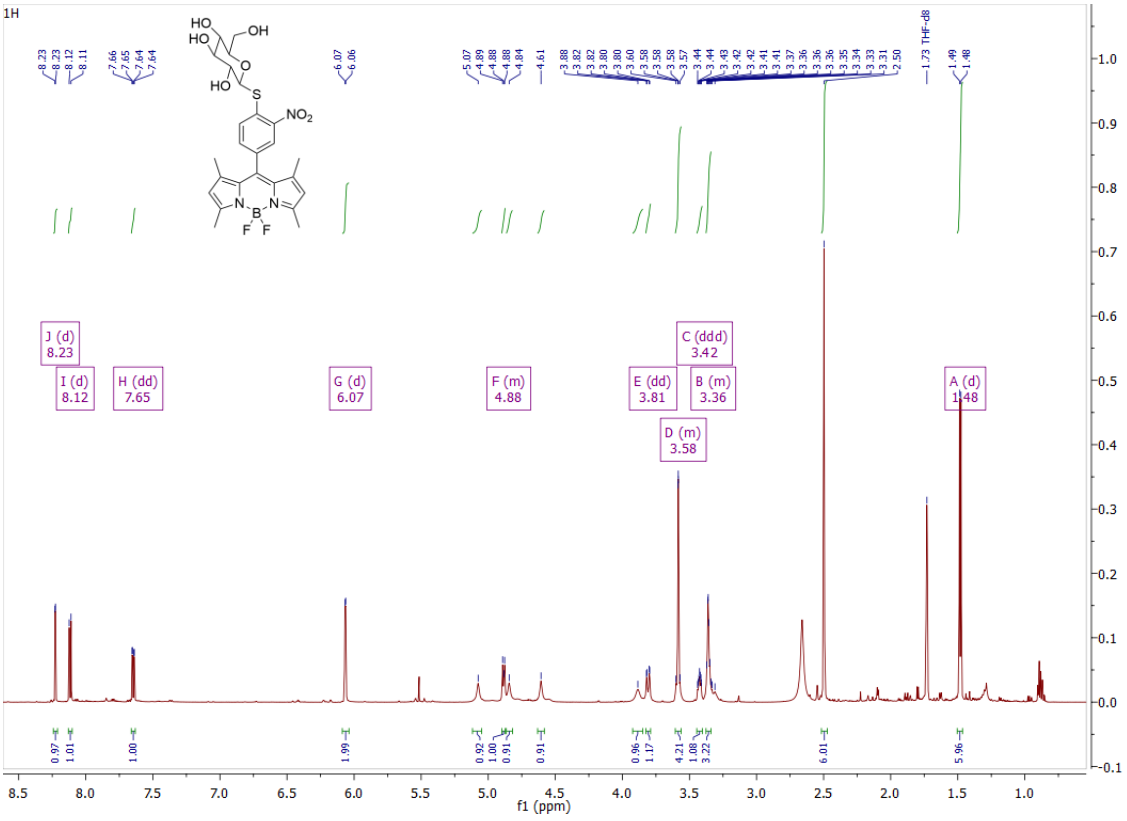

Figure S138: ^{1}H NMR (600 MHz, THF-d_8) spectrum of BODIPY **47**.

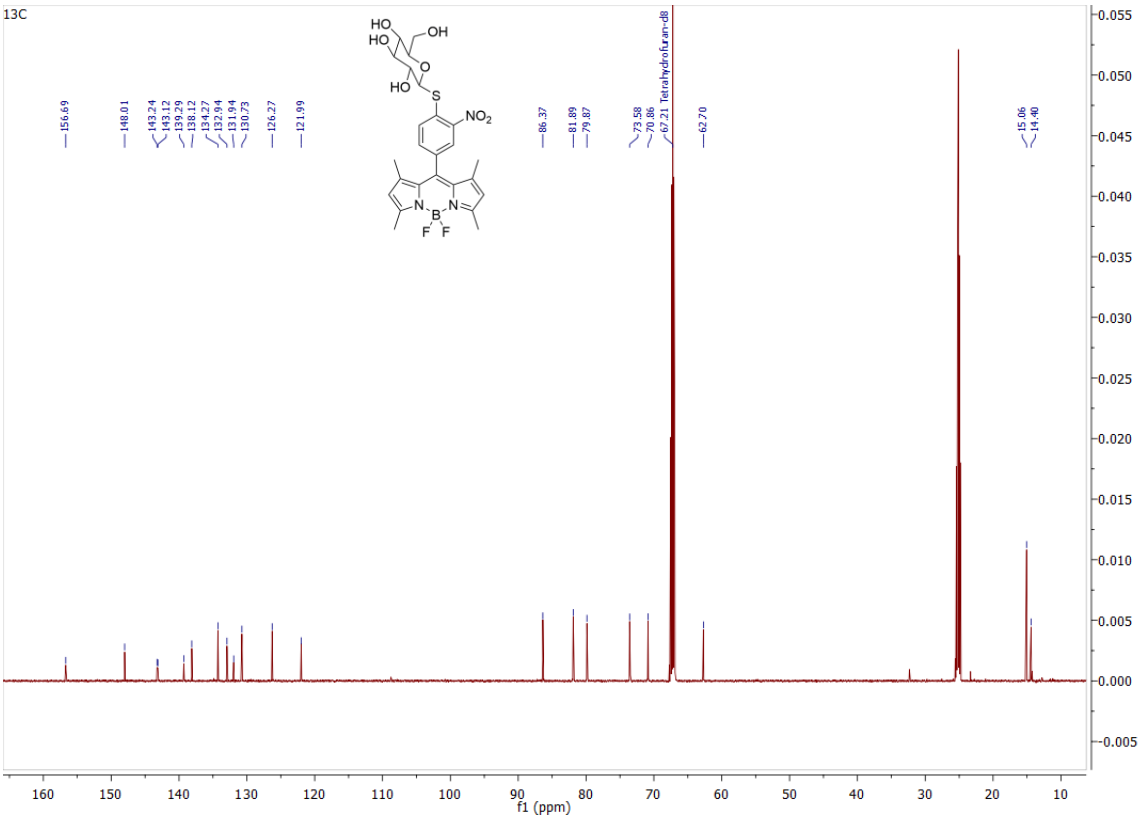

Figure S139: ^{13}C NMR (151 MHz, THF-d_8) spectrum of BODIPY **47**.

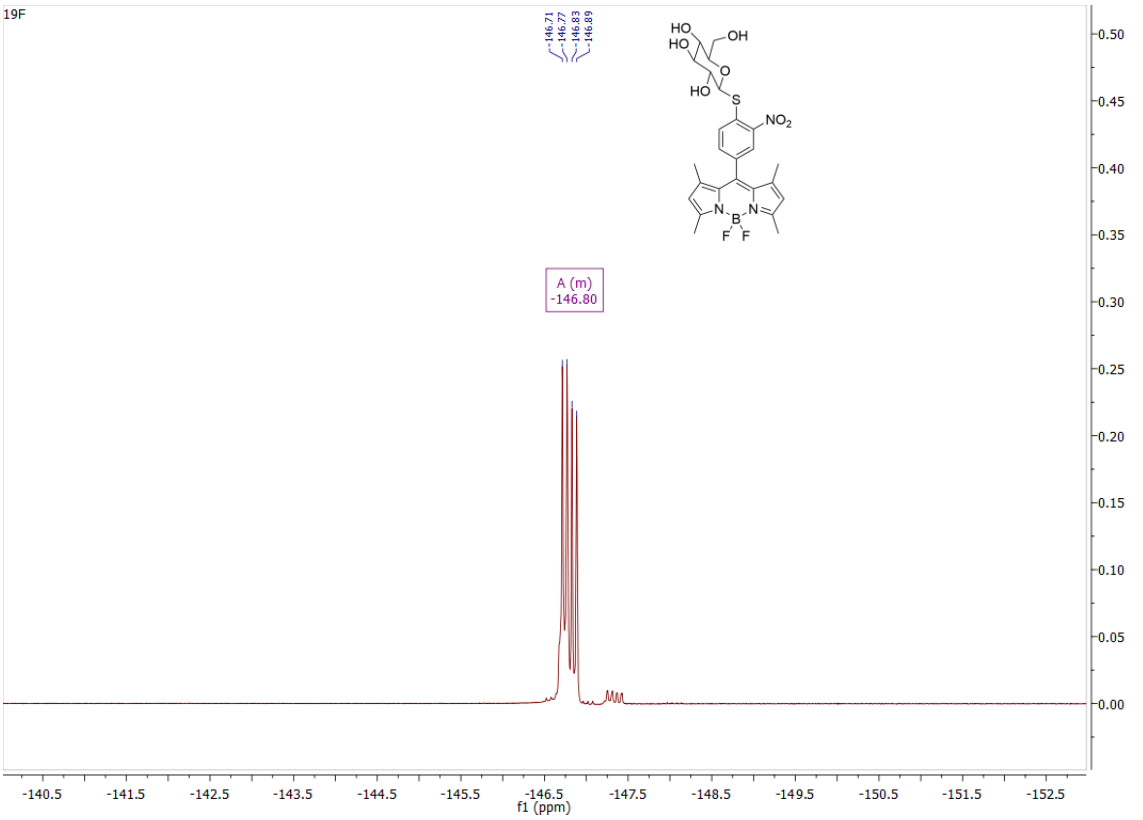

Figure S140: ^{19}F NMR (376 MHz, THF-d_8) spectrum of BODIPY **47**.

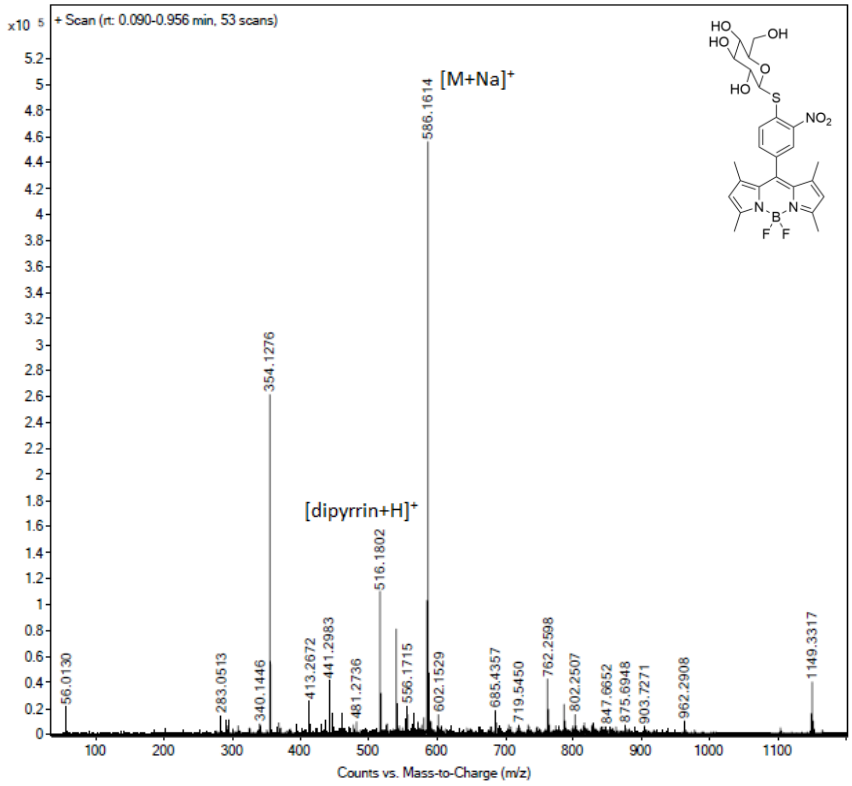

Figure S141: HRMS spectrum (ESI+) of BODIPY **47**.

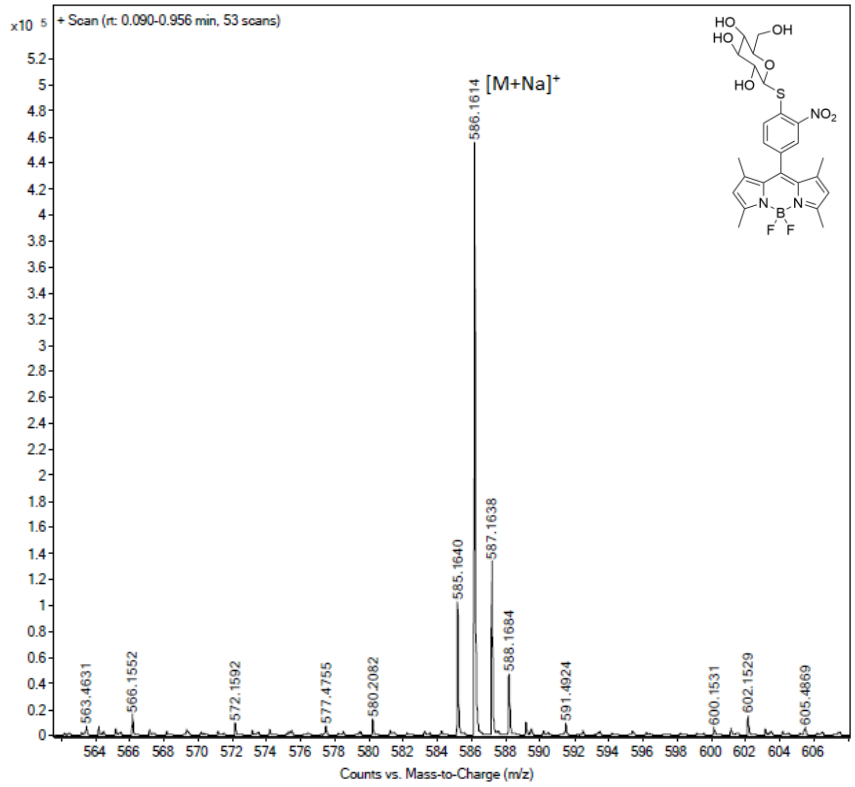

Figure S142: Zoom in from HRMS spectrum (ESI+) of BODIPY **47**.

8-[3-Nitro-(1'-thio-β-D-galactosyl)phenyl]-1,3,5,7-tetramethyl-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (**48**):

BODIPY **48** was prepared according to the general synthetic procedure. BODIPY **26** (100 mg, 0.26 mmol, 1 equiv.) and 1'-Thio-β-D-glucose sodium salt (68 mg, 0.31 mmol, 1.2 equiv.) were dissolved in 5 mL of DMF. The mixture was stirred for 15 min at rt. After column chromatography (silica gel, DCM/MeOH = 9/1, v/v) and recrystallization (DCM + MeOH/*n*-hexane) BODIPY **48** was obtained as an orange-red solid (116 mg, 0.21 mmol, 80 %).

^{1}H NMR (500 MHz, THF-d_8): δ (ppm) = 1.48 (d, *J* = 5.3 Hz, 6H, Me), 2.50 (s, 6H, Me), 3.46 (d, *J* = 8.4 Hz, 1H, 3'-H), 3.64–3.67 (m, 2H, 5´-H + 6´-H), 3.70–3.74 (m, 2H, 2´-H + 6´-H), 3.89 (br s, 1H, 4´-H), 4.00 (br s, 1H, OH), 4.53 (br s, 1H, OH), 4.79 (d, *J* = 9.7 Hz, 1H, 1´-H), 4.89 (br s, 1H, OH), 6.06 (s, 2H, $H_{pyrrole}$), 7.62 (dd, *J* = 8.3, 1.9 Hz, 1H, Ar-H_{ortho}), 8.19 (d, *J* = 8.4 Hz, 1H, Ar-H_{meta}), 8.21 (d, *J* = 1.9 Hz, 1H, Ar-H_{ortho}).

^{13}C NMR (126 MHz, THF-d_8): δ (ppm) = 14.8 (Me), 15.4 (Me), 62.7 (6´-C), 70.1 (4´-C), 70.9 (2´-C), 79.6 (3´-C), 80.95 (5´-C), 87.3 (1´-C), 122.6 ($CH_{pyrrole}$), 126.3 (Ar-C_{ortho}), 131.5 (Ar-C_{meta}), 133.2 ($C_{pyrrole}$), 134.4 (Ar-C_{ortho}), 138.5*, 139.7 (Ar-C_{para}), 143.5*, 143.6 ($C_{pyrrole}$), 148.5 (C_{meso}), 157.1 ($C_{pyrrole}$). *These signals could not be assigned exactly to corresponding carbon atoms. They belong to the Ar-C_{ipso} and the Ar-C_{nitro} of the aryl residue.

^{19}F NMR (376 MHz, THF-d_8): δ (ppm) = -146.68 – -146.94 (m_c, 2F, BF_2).

HRMS (ESI-TOF): *m/z* calcd. for $C_{25}H_{30}N_3O_7S^+$ [dipyrrin+H]$^+$: 516.1799, found: 516.1836, *m/z* calcd. for $C_{25}H_{28}BF_2N_3O_7SNa^+$ [M+Na]$^+$: 586.1601, found: 586.1642, *m/z* calcd. for $C_{25}H_{28}BF_2N_3O_7SK^+$ [M+K]$^+$: 602.1341, found: 602.1380.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3384 [ν(OH), 2925 [ν(Me)], 1609 [ν(C=C)], 1547 [$\nu_{as}(NO_2)$], 1510 [δ(Ar-C)], 1469 [δ(Me)], 1308 [$\nu_{sym}(NO_2)$], 1056 [ν(BF)], 753 [δ(HC=CH)].

UV/Vis (MeOH): λ_{max} (nm) [log (ε/L mol^{-1} cm^{-1})] = 359 [3.89], 502 [4.77].

Fluorescence (DCM): λ_{max} (nm) = 520 at $\lambda_{Excitation}$ (nm) 370, 490.

M.P. (°C): 151–158.

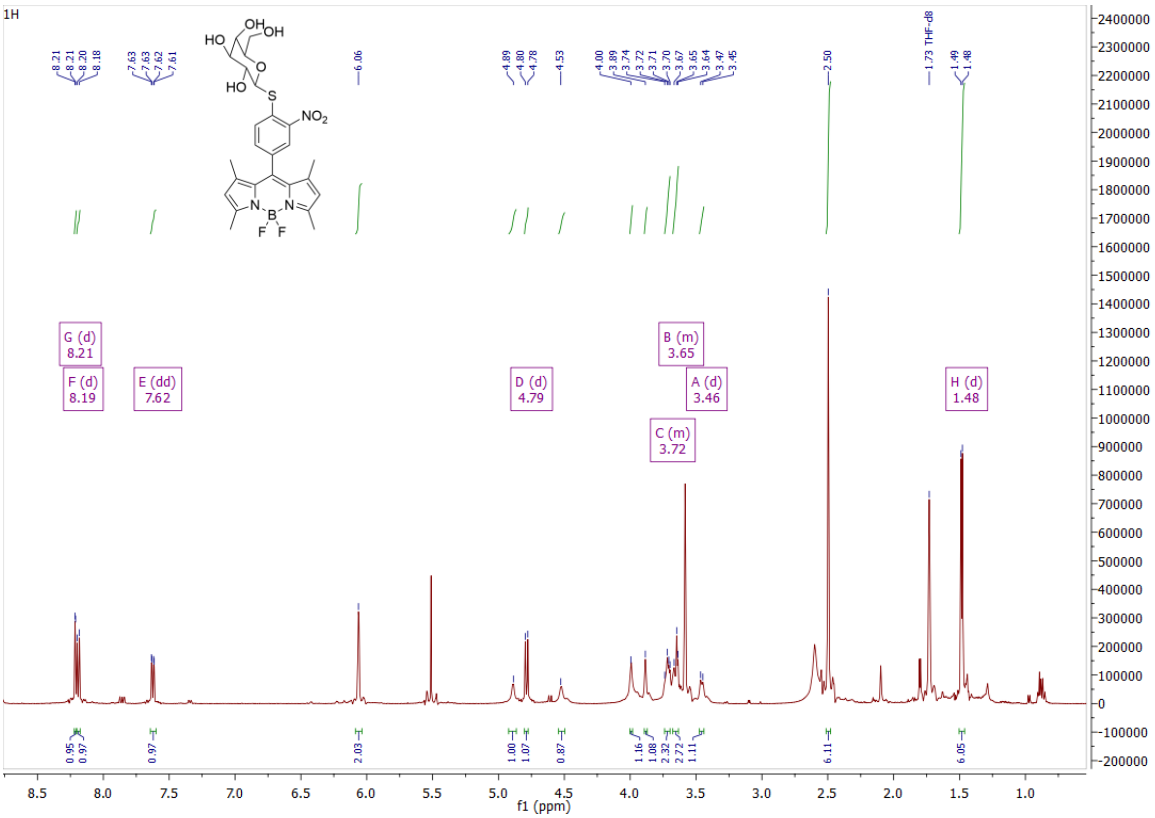

Figure S143: ^{1}H NMR (500 MHz, THF-d_8) spectrum of BODIPY **48**.

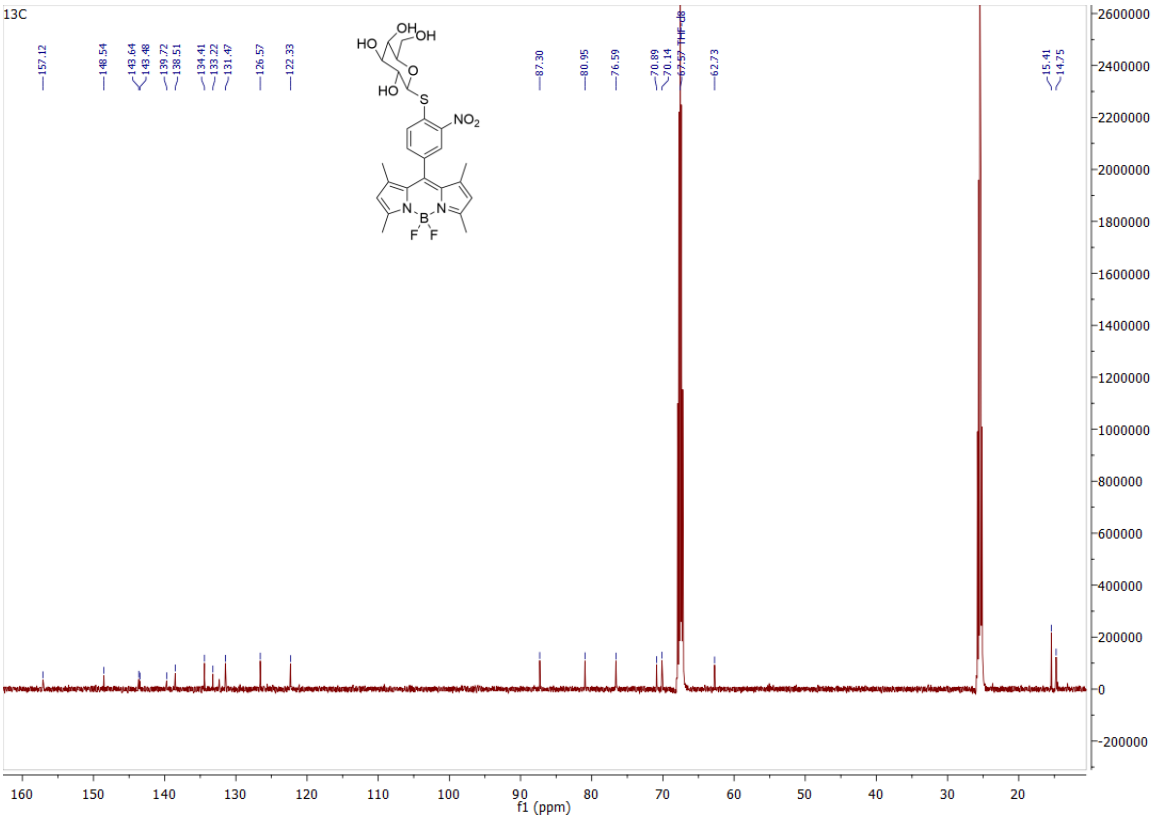

Figure S144: ^{13}C NMR (126 MHz, THF-d_8) spectrum of BODIPY **48**.

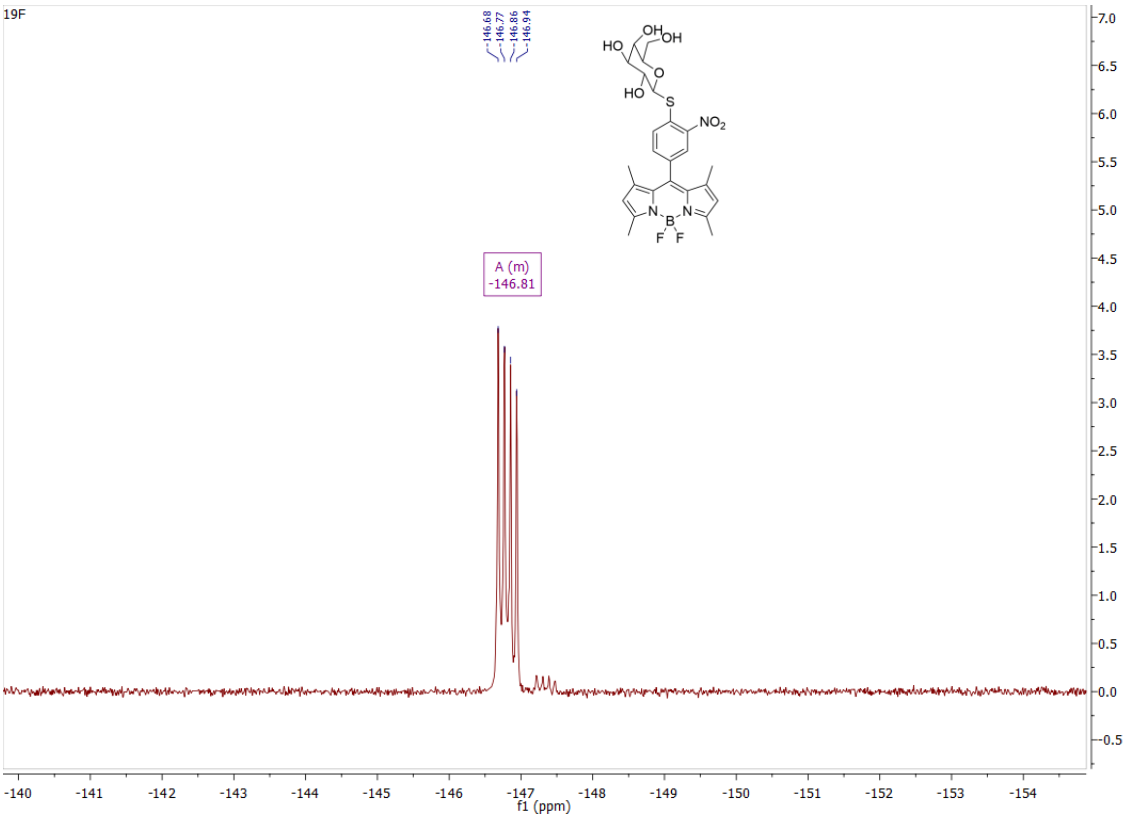

Figure S145: ^{19}F NMR (376 MHz, THF-d_8) spectrum of BODIPY **48**.

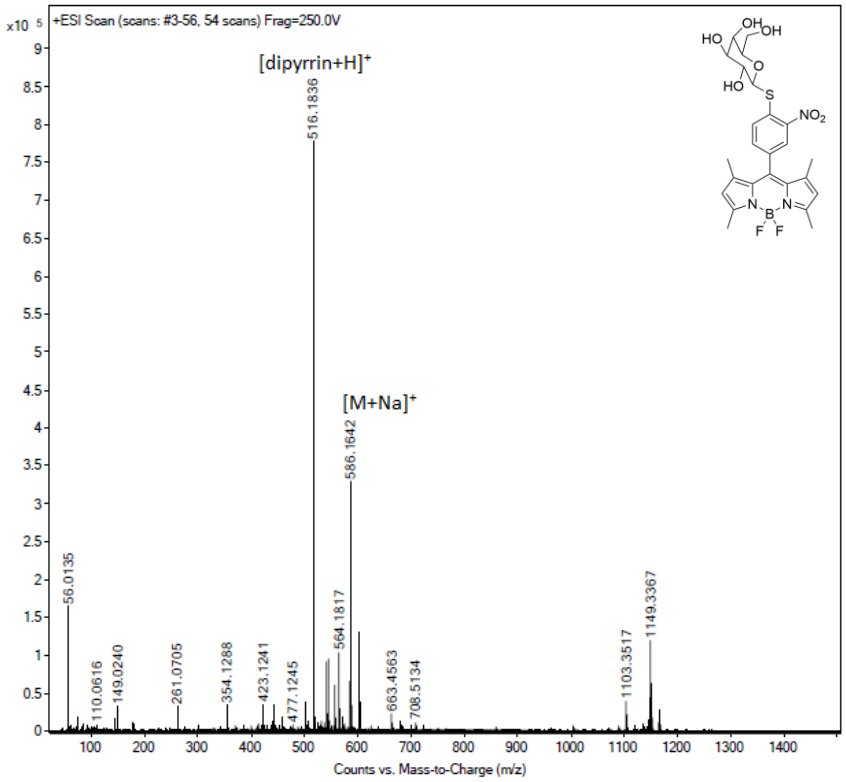

Figure S146: HRMS spectrum (ESI+) of BODIPY **48**.

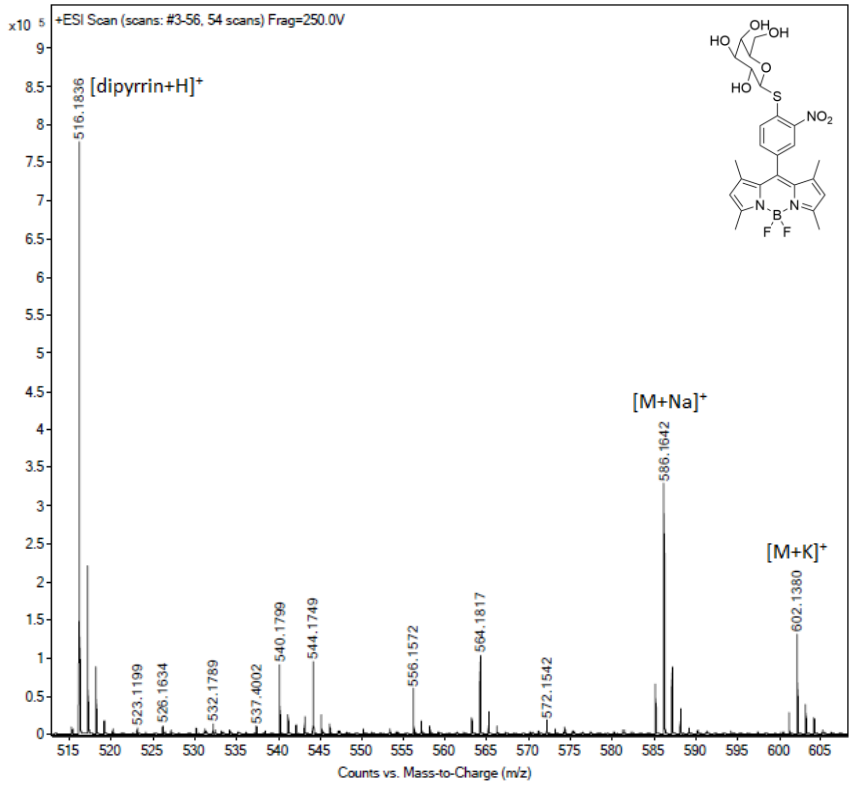

Figure S147: Zoom in from HRMS spectrum (ESI+) of BODIPY **48**.

8-[3-Nitro-4-(1'-thio-β-D-glucosyl)phenyl]-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacen (**53**):

BODIPY **53** was prepared according to the general synthetic procedure. BODIPY **8a** (100 mg, 0.30 mmol) and 1'-thio-β-D-glucose sodium salt (79 mg, 0.36 mmol) were dissolved in 5 mL of DMF. The mixture was stirred for 15 min at rt. After column chromatography (silica gel, DCM/MeOH = 6/1, v/v) and recrystallization (DCM + MeOH/*n*-hexane) BODIPY **53** was obtained as an orange-red solid (140 mg, 0.28 mmol, 91 %).

^{1}H NMR (500 MHz, DMSO-d$_6$): δ (ppm) = 3.19–3.21 (m, 1H, 4´-H), 3.27–3.33 (m, 2H, 2´-H + 3´-H), 3.42–3.48 (m, 2H, 5´-H + 6´-H), 3.73 (d, *J* = 10.4 Hz, 1H, 6´-H), 4.63 (br s, 1H, OH), 4.98 (d, *J* = 9.3 Hz, 1H, 1´-H), 5.13 (br s, 1H, OH), 5.26 (br s, 1H, OH), 5.67 (br s, 1H, OH), 6.72 (dd, *J* = 4.3, 1.9 Hz, 2H, H$_{pyrrole}$), 7.18 (d, *J* = 4.2 Hz, , H$_{pyrrole}$), 7.92 (dd, *J* = 8.5, 2.0 Hz, 1H, Ar-H$_{ortho}$), 8.01 (d, *J* = 8.5 Hz, 1H, Ar-H$_{meta}$), 8.19 (s, 2H, H$_{pyrrole}$), 8.39 (d, *J* = 2.0 Hz, 1H, Ar-H$_{ortho}$).

^{13}C NMR (126 MHz, DMSO-d$_6$): δ (ppm) = 60.9 (6´-C), 69.7 (4´-C), 72.4 (2´-C), 78.2 (3´-C), 81.1 (5´-C), 84.4 (1´-C), 119.7 (C$_{pyrrole}$), 127.5 (Ar-C$_{ortho}$), 129.8 (Ar-C$_{para}$), 128.95 (Ar-C$_{meta}$), 131.8 (C$_{pyrrole}$), 134.1 (C$_{pyrrole}$), 135.3 (Ar-C$_{ortho}$), 138.8*, 143.6*, 145.0 (C$_{pyrrole}$), 145.7 (C$_{meso}$). * These signals could not be assigned exactly to corresponding carbon atoms. They belong to the Ar-C$_{ipso}$ and the Ar-C$_{nitro}$ of the aryl residue.

^{19}F NMR (376 MHz, DMSO-d$_6$): δ (ppm) = -141.29 – -141.06 (m$_c$, 2F, BF$_2$).

HRMS (ESI-TOF): *m/z* calcd. for $C_{21}H_{20}BF_2N_3O_7SNa^+$ $[M+Na]^+$: 530.0975, found: 530.0988.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3386 [ν(OH)], 1604 [ν(C=C)], 1561 [$\nu_{as}(NO_2)$], 1533 [δ(Ar-C)], 1385 [$\nu_{sym}(NO_2)$], 1079 [ν(BF)], 737 [δ(HC=CH)].

UV/Vis (MeOH): λ_{max} (nm) [log (ϵ/L mol^{-1} cm^{-1})] = 373 [4.24], 504 [4.68].

Fluorescence (MeOH): λ_{max} (nm) = 529 at $\lambda_{Excitation}$ (nm) = 360, 490.

M.P. (°C): >250.

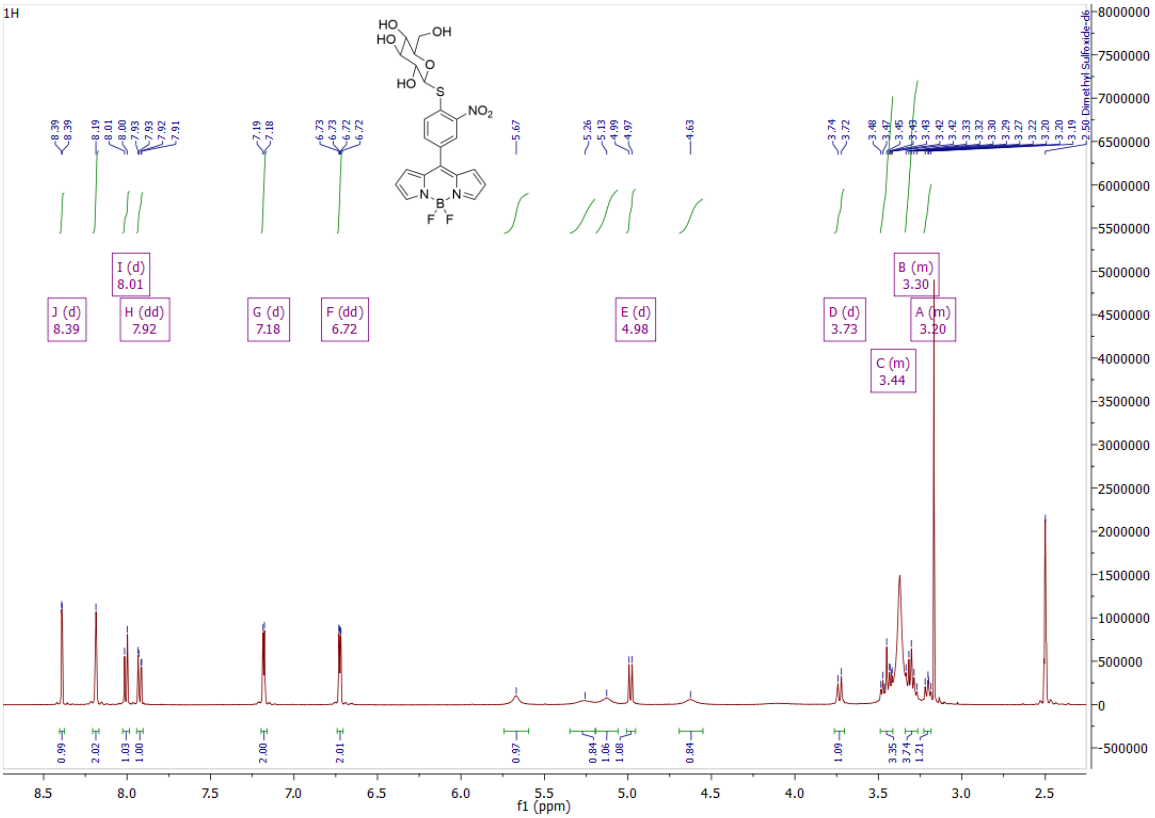

Figure S148: ^{1}H NMR (500 MHz, DMSO-d_6) spectrum of BODIPY **53**.

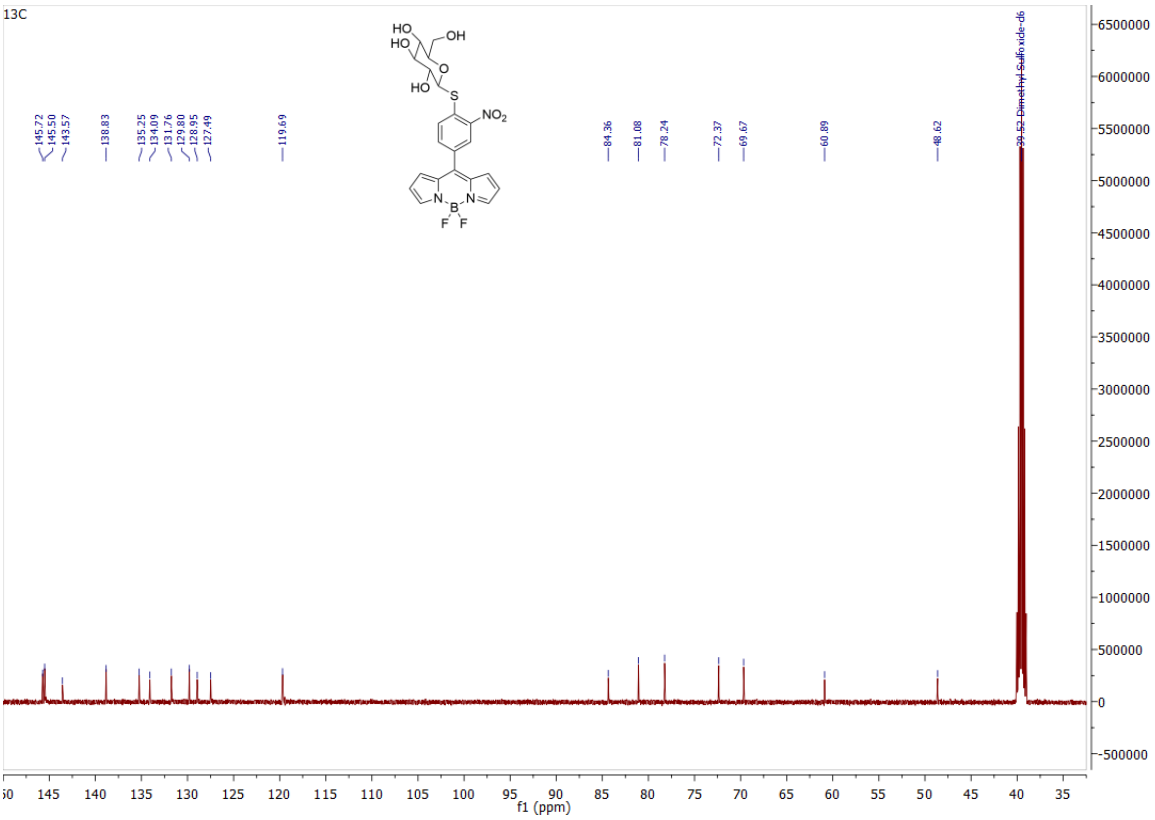

Figure S149: ^{13}C NMR (126 MHz, DMSO-d_6) spectrum of BODIPY **53**.

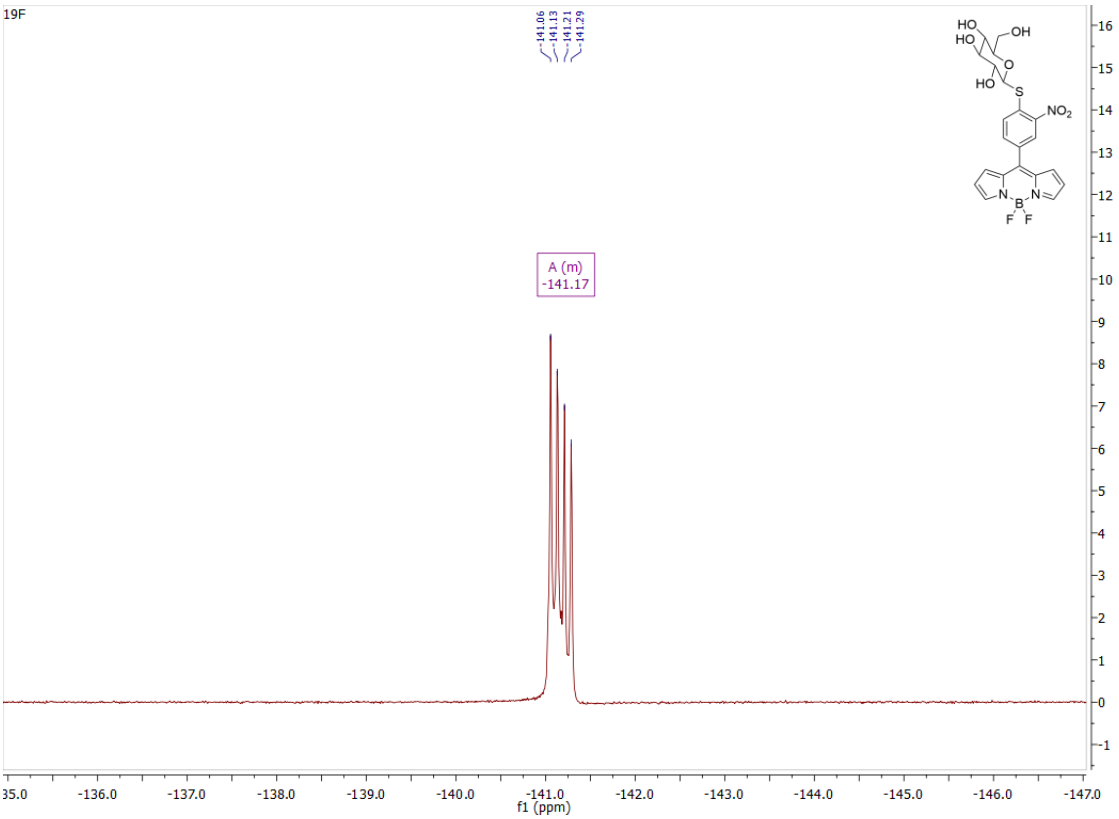

Figure S150: ^{19}F NMR (376 MHz, DMSO-d_6) spectrum of BODIPY **53**.

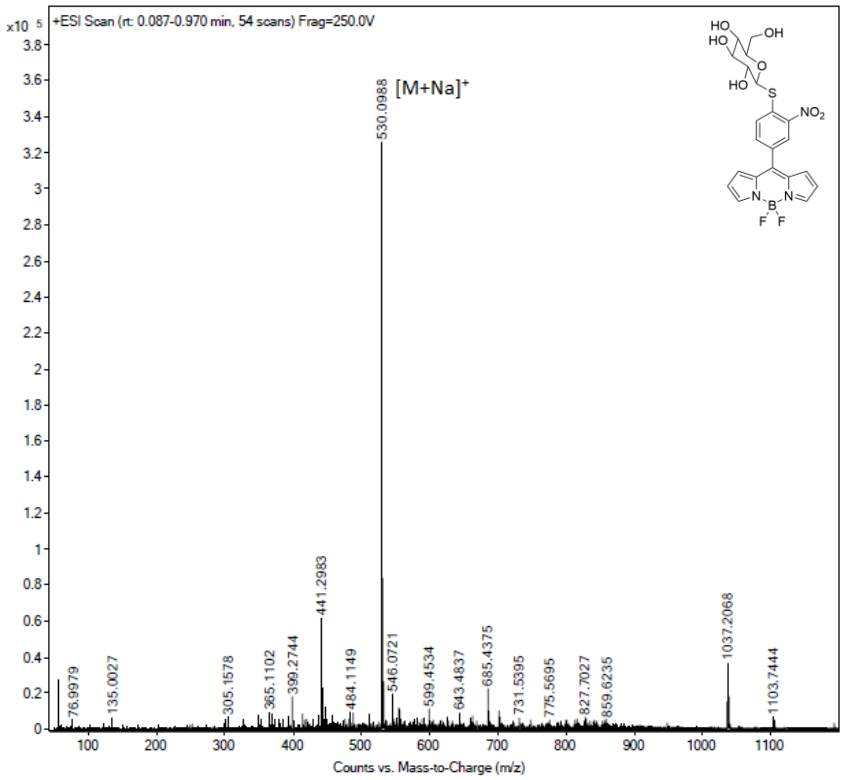

Figure S151: HRMS spectrum (ESI+) of BODIPY **53**.

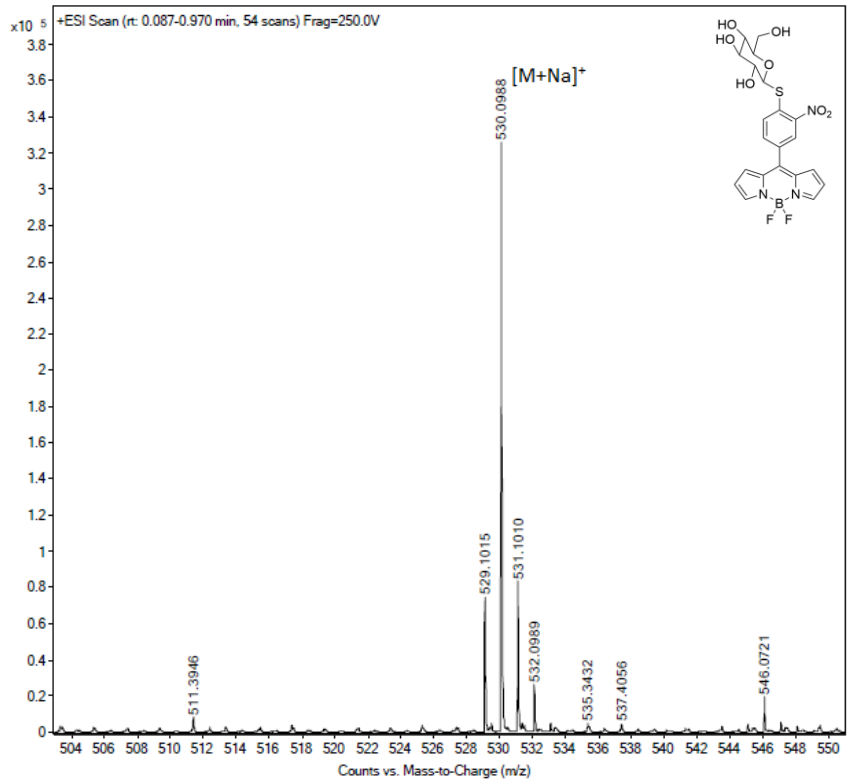

Figure S152: Zoom in from HRMS spectrum (ESI+) of BODIPY **53**.

8-[3-Nitro-4-(1′-thio-β-D-galactosyl)phenyl]-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacen (**54**):

BODIPY **54** was prepared according to the general synthetic procedure. BODIPY **8a** (100 mg, 0.30 mmol) and 1′-thio-β-D-glucose sodium salt (79 mg, 0.36 mmol) were dissolved in 5 mL of DMF. The mixture was stirred for 15 min at rt. After column chromatography (silica gel, DCM/MeOH = 6/1, v/v) and recrystallization (DCM + MeOH/*n*-hexane) BODIPY **54** was obtained as an orange-red solid (125 mg, 0.25 mmol, 82 %).

^{1}H NMR (600 MHz, DMSO-d$_6$): δ (ppm) = 3.44–3.46 (m, 1H, 3′-H), 3.54 (d, *J* = 5.9 Hz, 2H, 6′-H), 3.63 (t, *J* = 9.1 Hz, 1H, 2′-H), 3.68 (t, *J* = 6.0 Hz, 1H, 5′-H), 3.78–3.79 (m, 1H, 4′-H), 4.64 (br s, 1H, OH), 4.73 (br s, 1H, OH), 4.92 (d, *J* = 9.7 Hz, 1′-H), 5.04 (br s, 1H, OH), 5.50 (br s, 1H, OH), 6.71–6.72 (m, 2H, $H_{pyrrole}$), 7.17 (d, *J* = 4.2 Hz, 2H, $H_{pyrrole}$), 7.92 (dd, *J* = 8.4, 2.1 Hz, 1H, Ar-H_{ortho}), 8.05 (d, *J* = 8.5 Hz, 1H, Ar-H_{meta}), 8.17 (s, 2H, $H_{pyrrole}$), 8.38 (d, *J* = 2.1 Hz, 1H, Ar-H_{ortho}).

^{13}C NMR (151 MHz, DMSO-d$_6$): δ (ppm) = 60.6 (6′-C), 68.4 (4′-C), 69.0 (2′-C), 74.7 (3′-C), 79.4 (5′-C), 85.0 (1′-C), 119.8 ($C_{pyrrole}$), 127.5 (Ar-C_{ortho}), 128.8 (Ar-C_{para}), 128.99 (Ar-C_{meta}), 131.8 ($C_{pyrrole}$), 134.1 ($C_{pyrrole}$), 135.2 (Ar-C_{ortho}), 139.1*, 143.6*, 145.5 ($C_{pyrrole}$), 145.8 (C_{meso}). * These signals could not be assigned exactly to corresponding carbon atoms. They belong to the Ar-C_{ipso} and the Ar-C_{nitro} of the aryl residue.

^{19}F NMR (376 MHz, DMSO-d$_6$): δ (ppm) = -141.35 – -141.12 (m_c, 2F, BF_2).

HRMS (ESI-TOF): *m/z* calcd. for $C_{21}H_{20}BF_2N_3O_7SNa^+$ $[M+Na]^+$: 530.0975, found: 530.0985, *m/z* calcd. for $C_{21}H_{20}BF_2N_3O_7SK^+$ $[M+K]^+$: 546.0715, found: 546.0712.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3459 [ν(OH)], 1608 [ν(C=C)], 1556 [$\nu_{as}(NO_2)$], 1518 [δ(Ar-C)], 1382 [$\nu_{sym}(NO_2)$], 1070 [ν(BF)], 742 [δ(HC=CH)].

UV/Vis (MeOH): λ_{max} (nm) [log (ε/L mol^{-1} cm^{-1})] = 371 [4.14], 503 [4.57].

Fluorescence (MeOH): λ_{max} (nm) = 528 at $\lambda_{Excitation}$ (nm) = 385, 490.

M.P. (°C): 221–225.

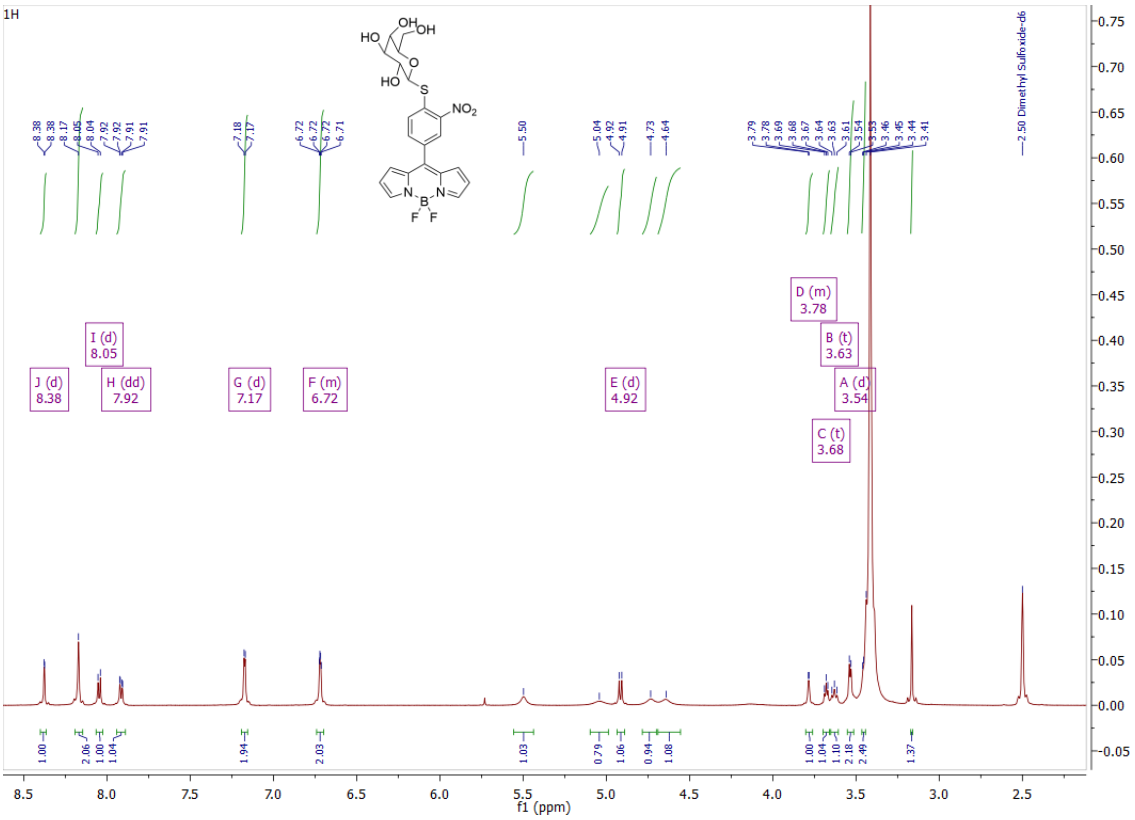

Figure S153: ^{1}H NMR (600 MHz, DMSO-d_6) spectrum of BODIPY **54**.

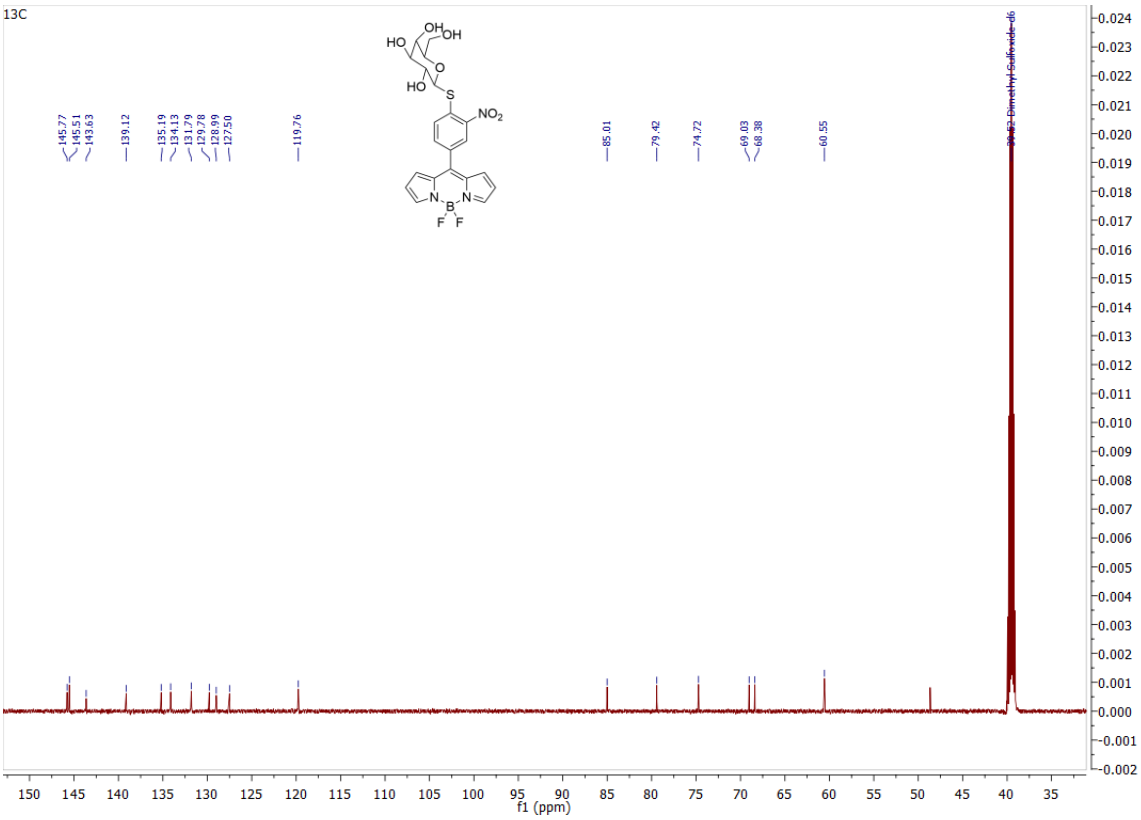

Figure S154: ^{13}C NMR (151 MHz, DMSO-d_6) spectrum of BODIPY **54**.

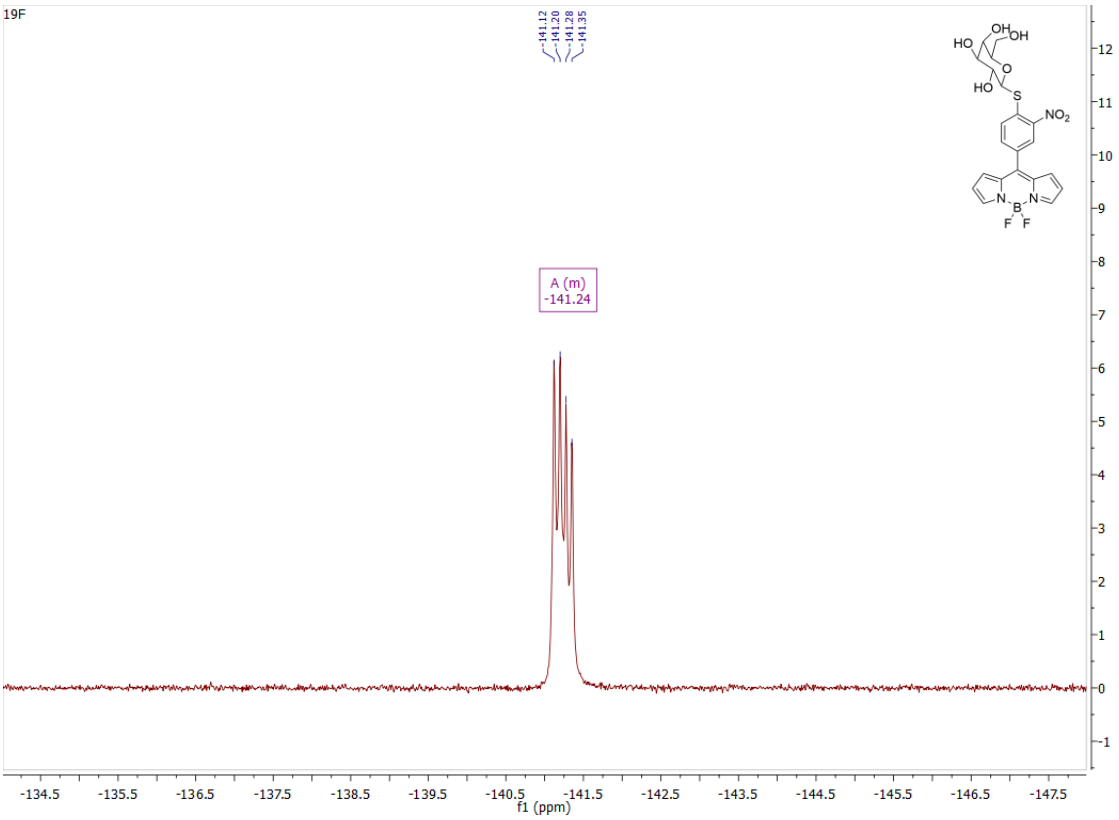

Figure S155: ^{19}F NMR (376 MHz, DMSO-d_6) spectrum of BODIPY **54**.

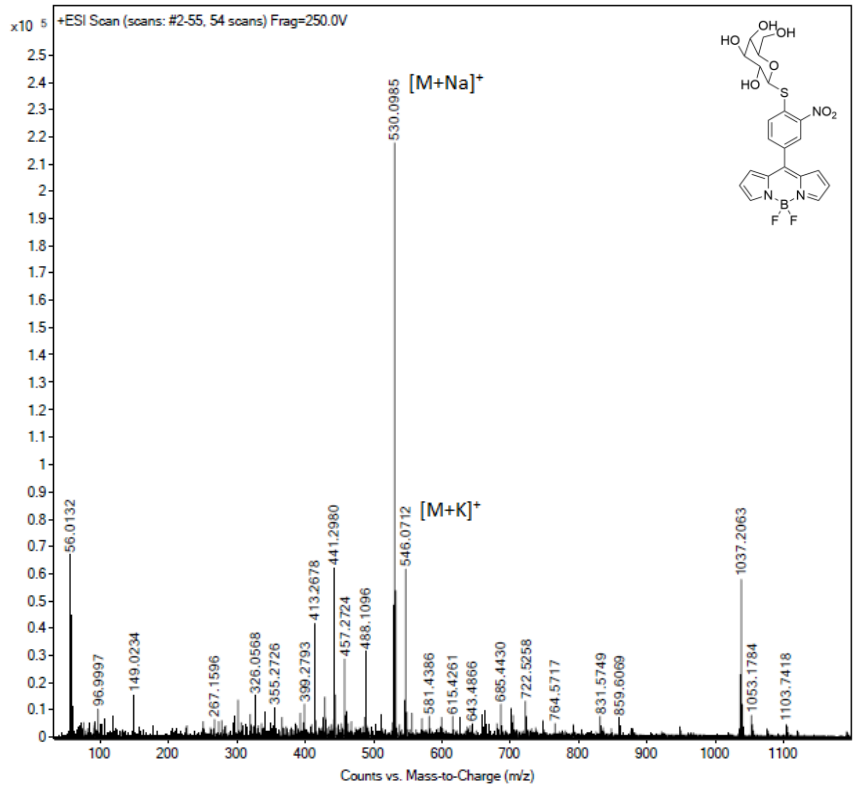

Figure S156: HRMS spectrum (ESI+) of BODIPY **54**.

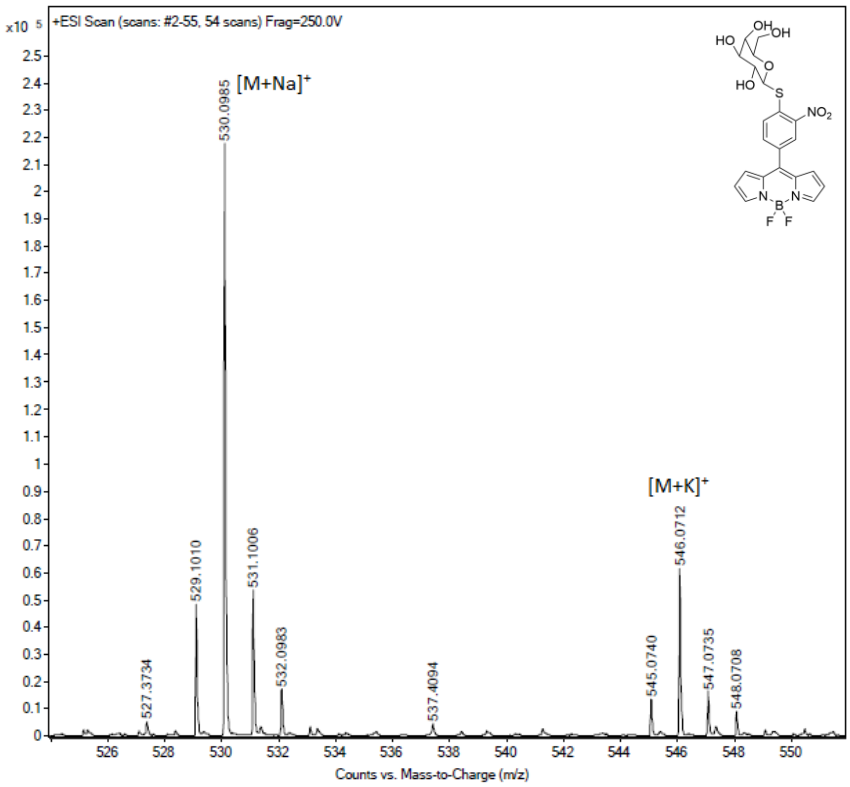

Figure S157: Zoom in from HRMS spectrum (ESI+) of BODIPY **54**.

13. Targeted dihalogenation of the tetramethyl BODIPYs (34 – 42, 45, 46, 49, and 50)

General synthetic procedure

The corresponding 1,3,5,7-tetramethyl substituted BODIPY (1 equiv.) was dissolved in 2 mL of HFIP, NBS (2.5 equiv.) was added and the mixture was stirred for 1 min at rt. Afterwards, the reaction mixture was diluted with EtOAc and washed with water several times. The organic layer was dried with Na_2SO_4, filtered, and evaporated to dryness. The crude product was purified by column chromatography.

2,6-Dibromo-8-pentafluorophenyl-1,3,5,7-tetramethyl-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (**34**):

BODIPY **34** was prepared according to the general synthetic procedure. BODIPY **25** (100 mg, 0.24 mmol) and NBS (107 mg, 0.60 mmol) were dissolved in HFIP. After column chromatography (silica gel, EtOAc/*n*-hexane = 1/9, v/v) BODIPY **34** was obtained as an orange-red solid (85 mg, 0.15 mmol, 62 %).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 1.62 (s, 6H, Me), 2.63 (s, 6H, Me).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 13.1 (Me), 14.1 (Me), 113.2 ($C_{pyrrole}$), 114.0 (Ar-C_{ipso}), 121.2 (C_{meso}), 130.2 ($C_{pyrrole}$), 139.1 ($C_{pyrrole}$), 156.6 ($C_{pyrrole}$).

^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) = -138.79 – -138.87 (m, 2F, CF_{meta}), -145.62 – -145.87 (m_C, 2F, BF_2), -148.83 (t, J = 20.8 Hz, 1F, CF_{para}), -158.36 – -158.49 (m, 2F, CF_{meta}).

HRMS (ESI-TOF): *m/z* calcd. for $C_{19}H_{11}BBr_2F_7N_2^-$ $[M-H]^-$: 570.9255, found: 570.9248.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2924 and 2854 [ν(Me)], 1624 [ν(C=C)], 1496 [δ(Me)], 1116 and 1100 [ν(BF), ν(CBr)].

UV/Vis (DCM): λ_{max} (nm) [log (ε/L mol^{-1} cm^{-1})] = 551 [4.79].

Fluorescence (DCM): λ_{max} (nm) = 568 at $\lambda_{Excitation}$ (nm) = 535.

M.P. (°C): >250°C.

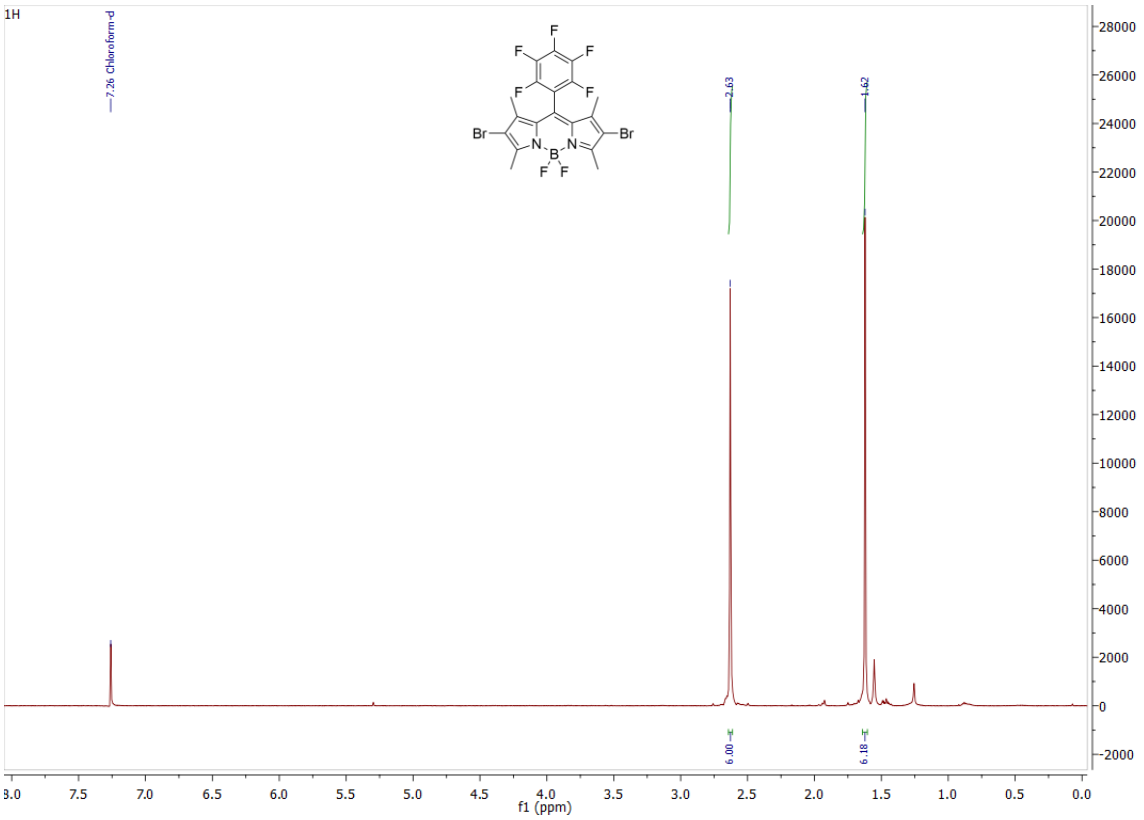

Figure S158: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of BODIPY **34**.

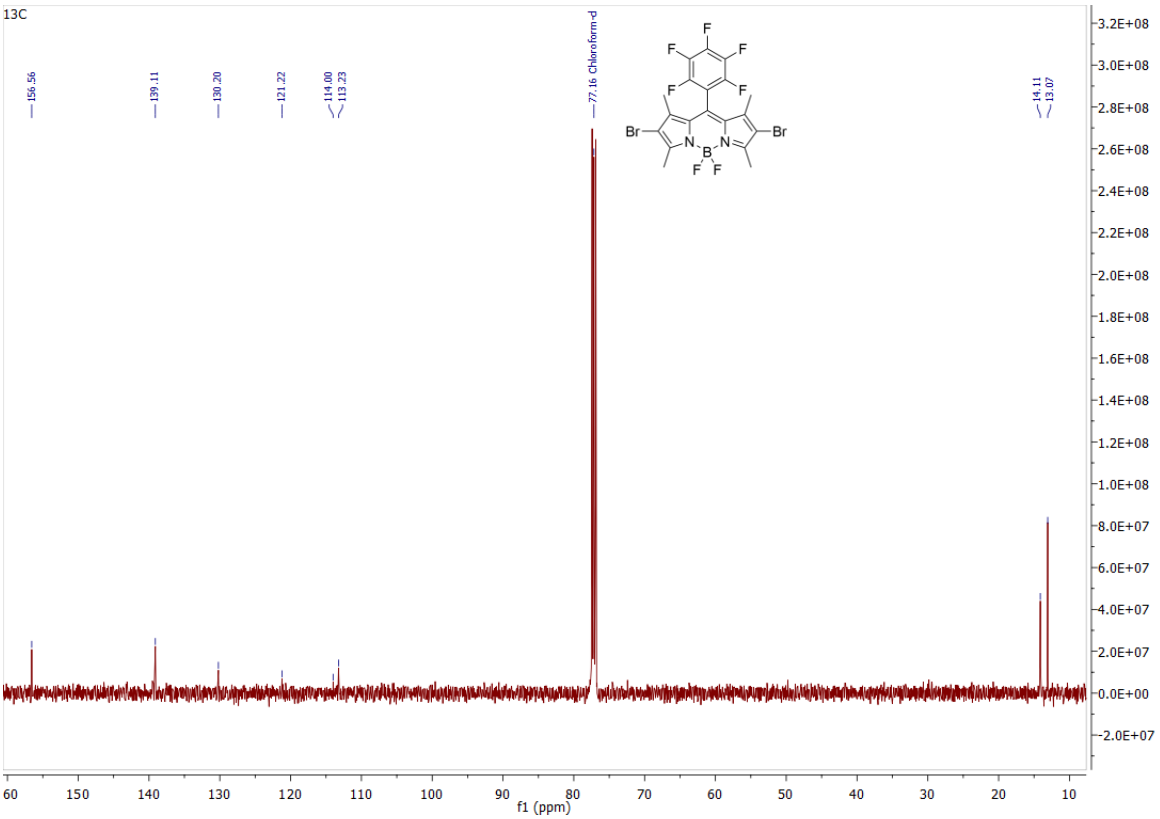

Figure S159: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of BODIPY **34**.

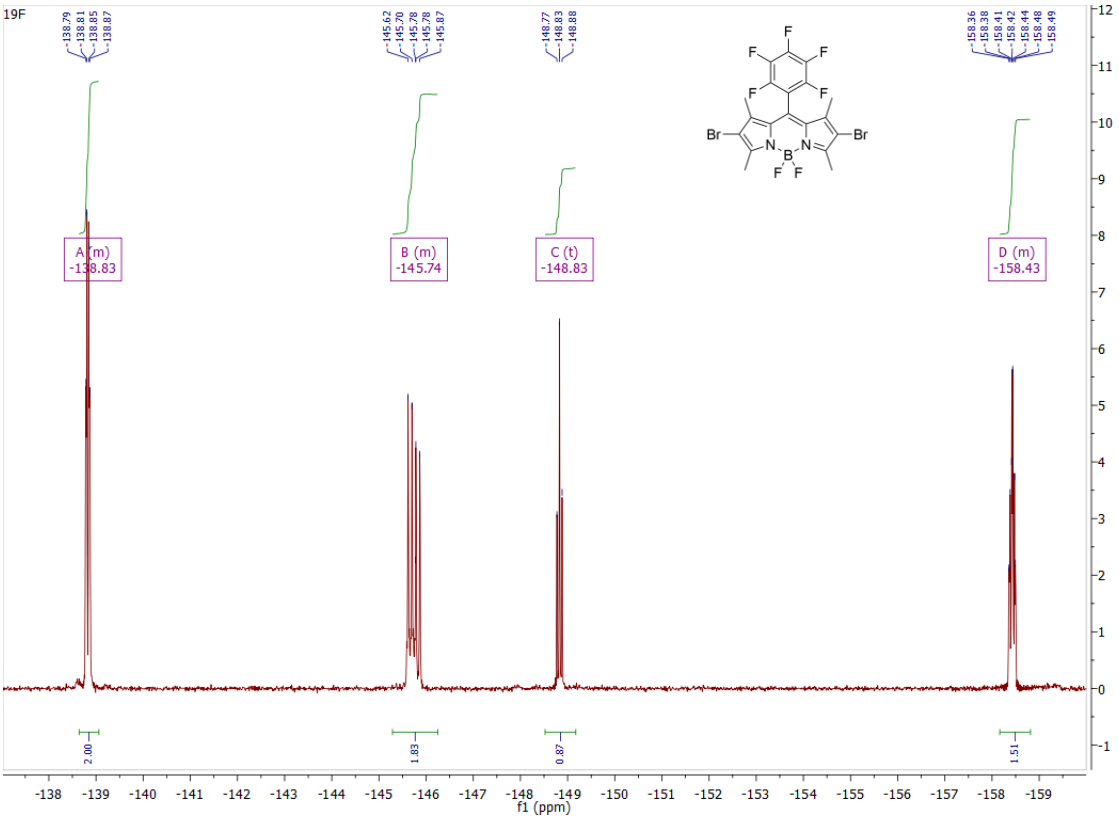

Figure S160: ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of BODIPY **34**.

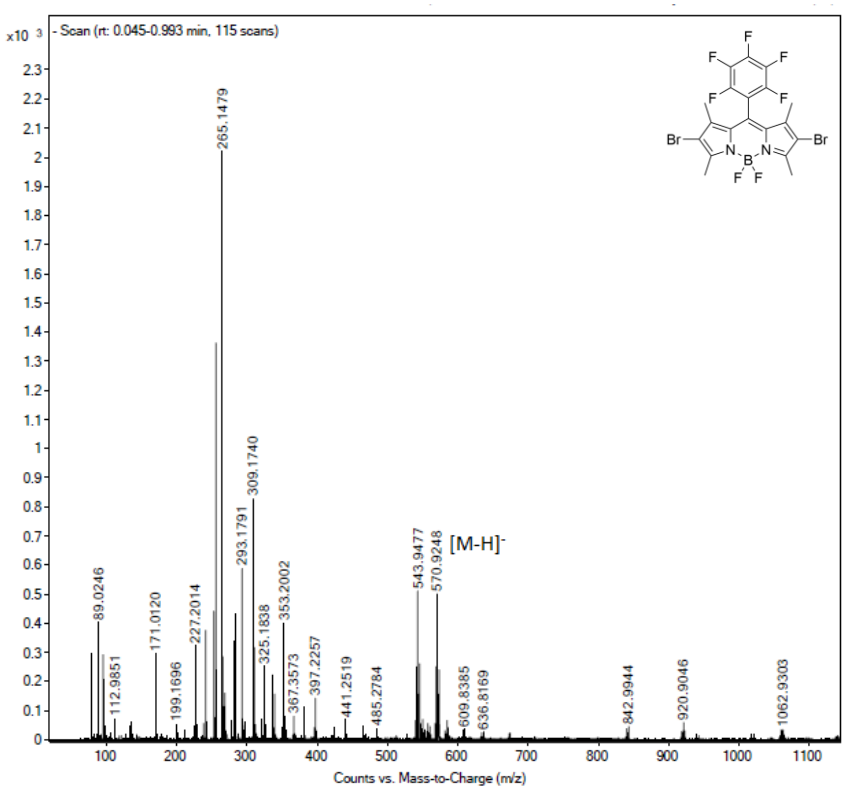

Figure S161: HRMS spectrum (ESI-, in DCM/MeOH) of BODIPY **34**.

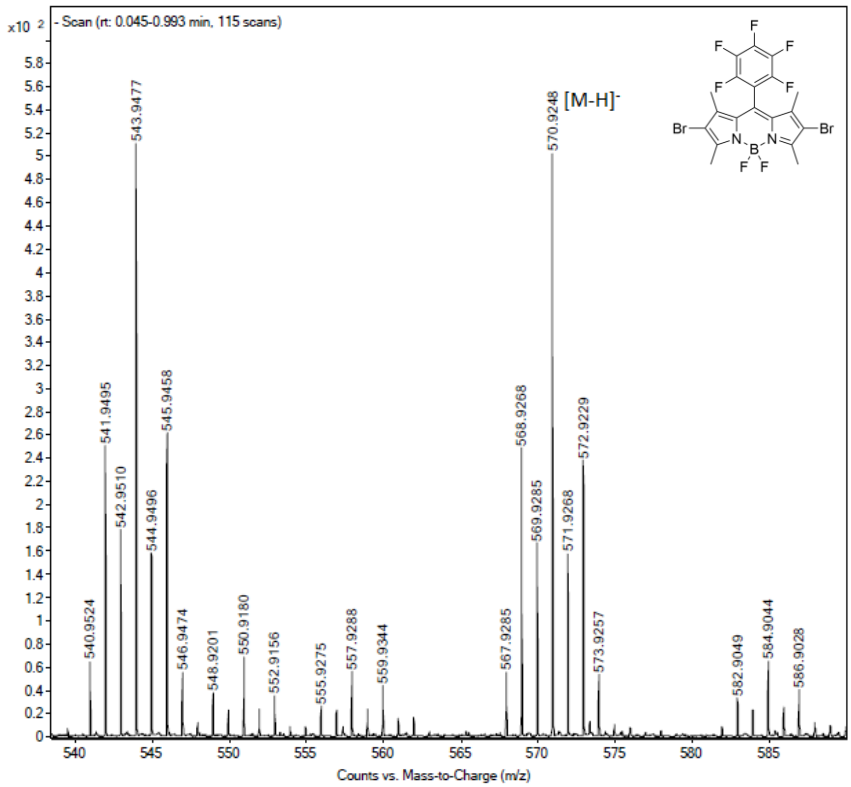

Figure S162: Zoom in from HRMS spectrum (ESI-, in DCM/MeOH) of BODIPY **34**.

8-[4-(*N*-Butylamino)-2,3,5,6-tetrafluorophenyl]-2,6-dibromo-1,3,5,7-tetramethyl-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (**35**):

BODIPY **35** was prepared according to the general synthetic procedure. BODIPY **27** (95 mg, 0.20 mmol) and NBS (90 mg, 0.51 mmol) were dissolved in HFIP. After column chromatography (silica gel, EtOAc/*n*-hexane = 1/9, v/v) BODIPY **35** was obtained as a red solid (68 mg, 0.11 mmol, 54 %).

^{1}H NMR (500 MHz, THF-d_8): δ (ppm) = 0.96 (t, J = 7.4 Hz, 3H, Me), 1.39–1.46 (m, 2H, CH_2), 1.61–1.67 (m, 2H, CH_2), 1.73 (s, 6H, Me), 2.57 (s, 6H, Me), 3.45–3.50 (m, 2H, CH_2), 5.83 (s, 1H, NH).

^{13}C NMR (126 MHz, THF-d_8): δ (ppm) = 13.1 (Me), 14.0 (Me),14.3 (Me_{Butyl}), 20.9 (CH_2), 33.9 (CH_2), 45.96 (CH_2), 98.61 (t, J = 19.9 Hz, Ar-C_{ipso}), 112.9 – 112.99 (m, C_{Br}), 127.5 (C_{meso}), 131.9 (Ar-C_{para}), 132.0 ($C_{pyrrole}$), 138.82 (dd, J = 241.3, 26.0 Hz, Ar-C_{meta}), 140.5 ($C_{pyrrole}$), 145.26 (dd, J = 242.0, 11.9 Hz, Ar-C_{ortho}), 156.2 ($C_{pyrrole}$).

^{19}F NMR (376 MHz, THF-d_8): δ (ppm) = -145.65 (d, J = 17.6 Hz, 2F, CF_{meta}), -146.17 – -146.42 (m_C, 2F, BF_2), -161.13 (d, J = 17.6 Hz, 2F, CF_{meta}).

HRMS (ESI-TOF): *m/z* calcd. for $C_{23}H_{22}BBr_2F_6N_3Na^+$ $[M+Na]^+$: 648.0049, found: 648.0058, *m/z* calcd. for $C_{46}H_{44}B_2Br_4F_{12}N_6Na^+$ $[2M+Na]^+$: 1237.0207, found: 1237.0221.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3415 [ν(NH)], 2959 and 2930 [$\nu(CH_2)$, ν(Me)], 2873 [ν(CH)], 1655 [ν(C=N)], 1171 and 1118 [ν(BF), ν(CBr)], 767 [δ(-HC=CH-)].

UV/Vis (DCM): λ_{max} (nm) [log (ε/L mol^{-1} cm^{-1})] = 391 [4.12], 545 [4.93].

Fluorescence (DCM): λ_{max} (nm) = 562 at $\lambda_{Excitation}$ (nm) = 380, 530.

M.P. (°C): 133–135.

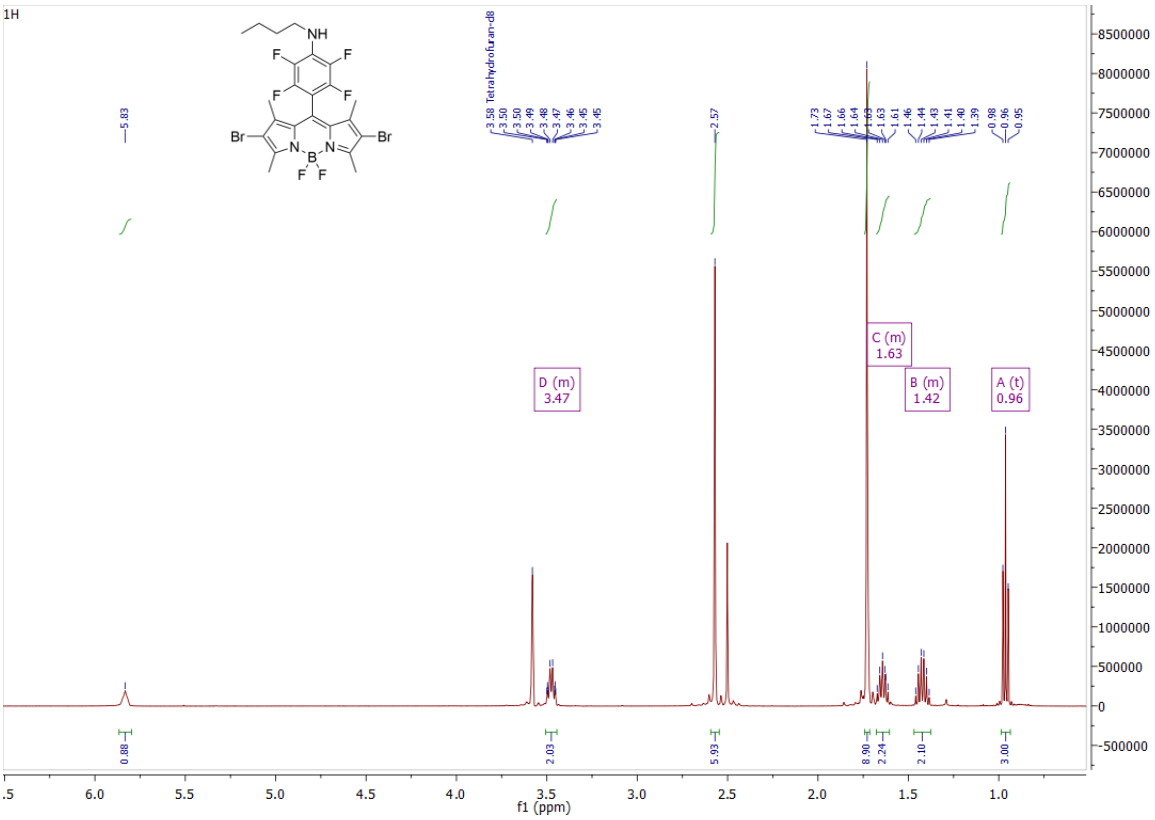

Figure S163: ^{1}H NMR (500 MHz, THF-d_8) spectrum of BODIPY **35**.

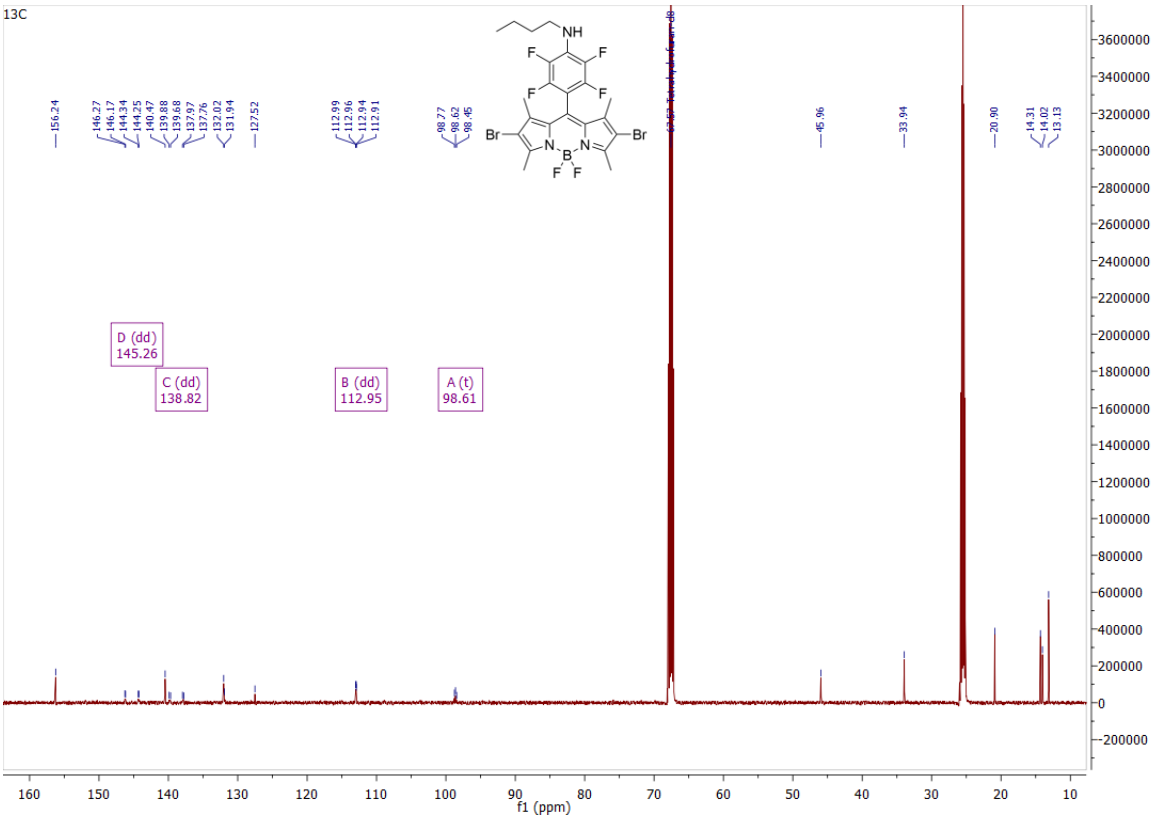

Figure S164: ^{13}C NMR (126 MHz, THF-d_8) spectrum of BODIPY **35**.

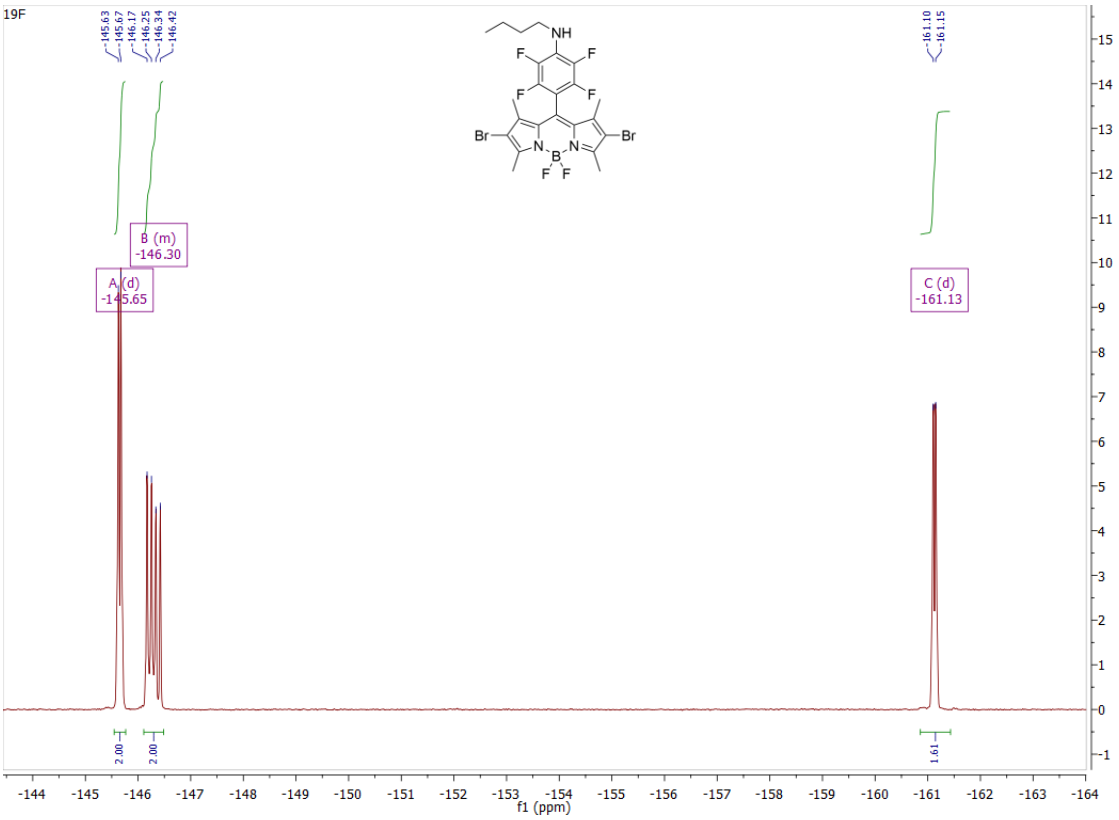

Figure S165: ^{19}F NMR (376 MHz, THF-d_8) spectrum of BODIPY **35**.

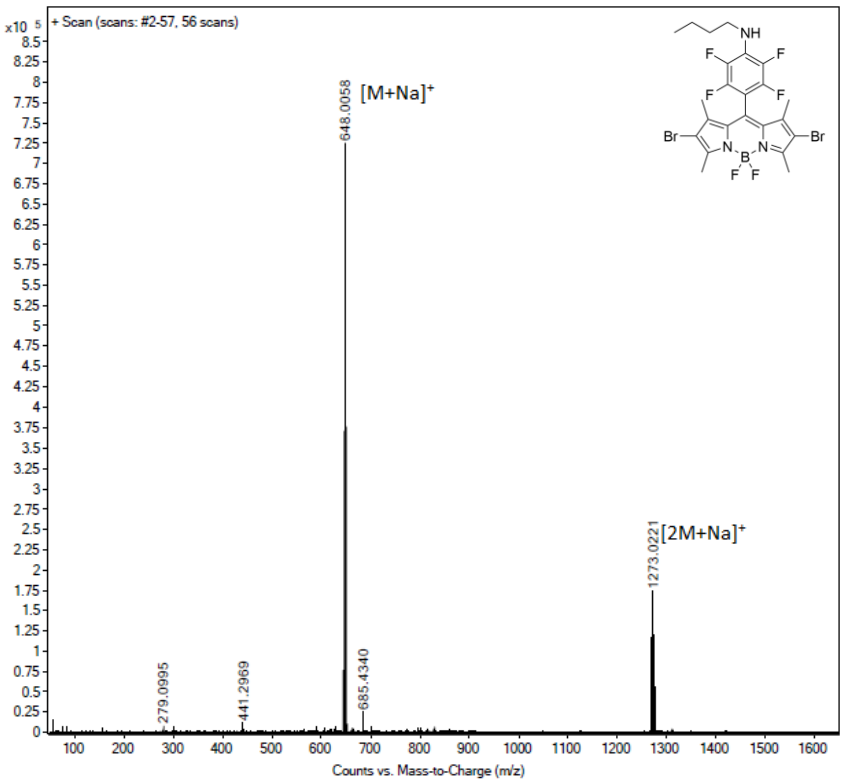

Figure S166: HRMS spectrum (ESI+) of BODIPY **35**.

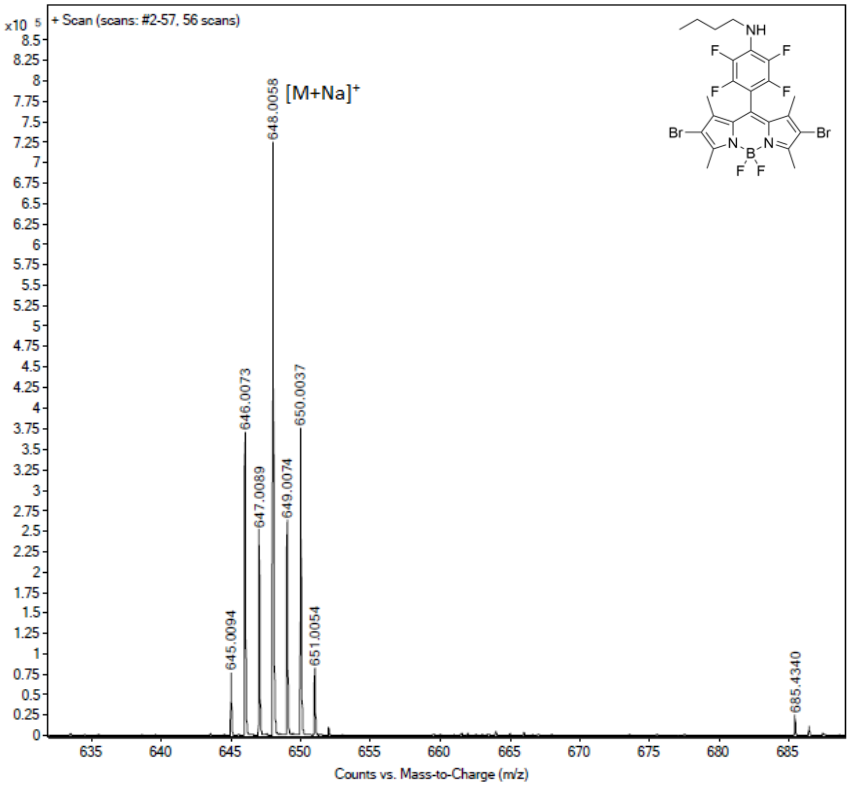

Figure S167: Zoom in from HRMS spectrum (ESI+) of BODIPY **35**.

2,6-Dibromo-8-[4-(*N*-prop-2-ynylamino)-2,3,5,6-tetrafluorophenyl]-1,3,5,7-tetramethyl-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (**36**):

BODIPY **36** was prepared according to the general synthetic procedure. BODIPY **28** (87 mg, 0.19 mmol) and NBS (86 mg, 0.48 mmol) were dissolved in HFIP. After column chromatography (silica gel, EtOAc/*n*-hexane = 1/9, v/v) BODIPY **36** was obtained as a green solid (54 mg, 89 µmol, 44 %).

^{1}H NMR (500 MHz, THF-d$_8$): δ (ppm) = 1.72 (s, 6H, Me), 2.58 (s, 6H, Me), 2.72 (t, J = 2.4 Hz, 1H, CH), 4.19–4.21 (m, 2H, CH_2), 6.20–6.23 (s, 1H, NH).

^{13}C NMR (126 MHz, THF-d$_8$): δ (ppm) = 13.1 (Me), 14.1 (Me), 35.6 (CH_2), 73.5 (C), 81.0 (CH), 101.20 (t, J = 18.7 Hz, Ar-C_{ipso}), 113.0–113.1 (m, C_{Br}), 127.1 (C_{meso}), 130.8–131.0 (Ar-C_{para}), 131.8 ($C_{pyrrole}$), 139.85 (ddd, J = 242.5, 15.8, 10.5 Hz, Ar-C_{meta}), 140.5 ($C_{pyrrole}$), 145.03 (dd, J = 244.1, 16.7 Hz, Ar-C_{ortho}), 156.4 ($C_{pyrrole}$).

^{19}F NMR (376 MHz, THF-d$_8$): δ (ppm) = -145.33 (d, J = 14.5 Hz, 2F, CF_{meta}), -146.14 – -146.29 (m_C, 2F, BF_2), -158.57 (d, J = 15.4 Hz, 2F, CF_{meta}).

HRMS (ESI-TOF): *m/z* calcd. for $C_{22}H_{15}BBr_2F_6N_3^-$ $[M-H]^-$: 605.9615, found: 605.9587.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3384 [ν(NH)], 3302 [ν(C≡CH)], 2962 and 2923 [$\nu(CH_2)$, ν(Me)], 2843 [ν(CH)], 1653 [ν(C=C)], 1485 [$\delta(CH_2)$, δ(Me)], 1161 and 1120 [ν(BF), ν(CBr)], 768 [δ(-HC=CH-)].

UV/Vis (DCM): λ_{max} (nm) [log (ε/L mol^{-1} cm^{-1})] = 391 [3.97], 546 [4.76].

Fluorescence (DCM): λ_{max} (nm) = 564 at $\lambda_{Excitation}$ (nm) = 380, 530.

M.P. (°C): 184–188.

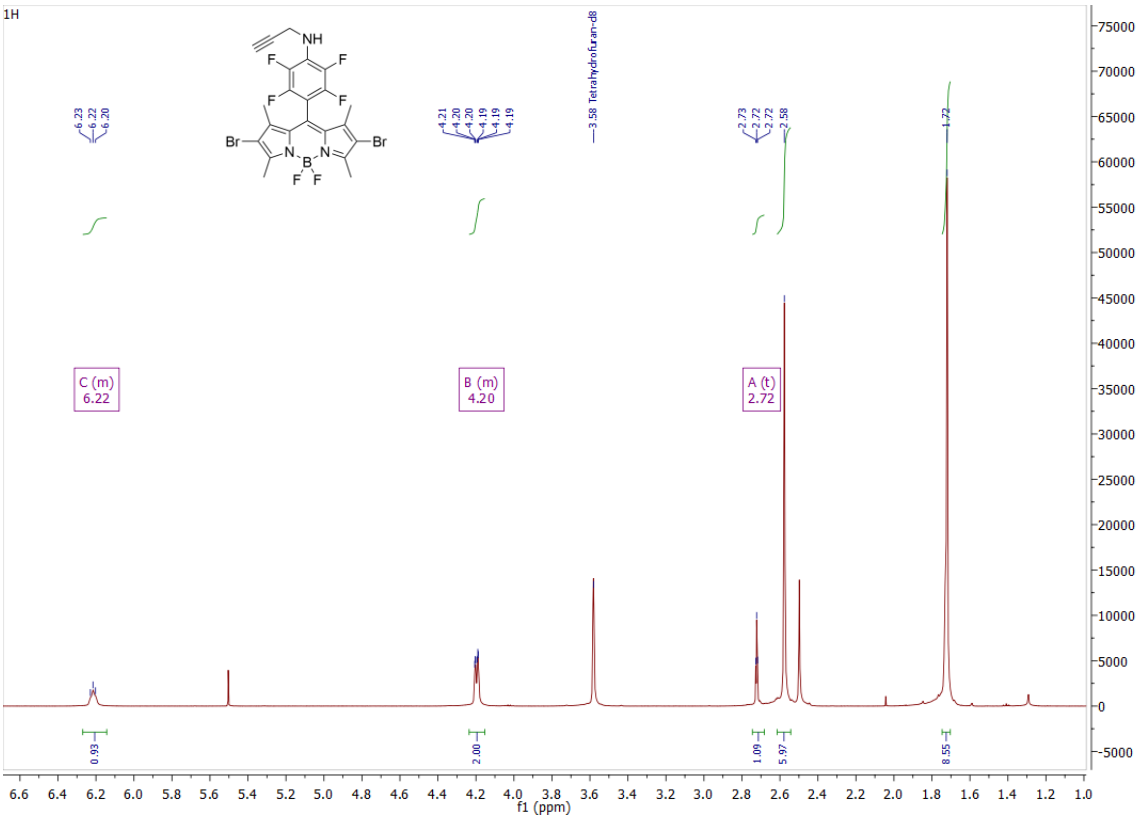

Figure S168: ^{1}H NMR (500 MHz, THF-d_8) spectrum of BODIPY **36**.

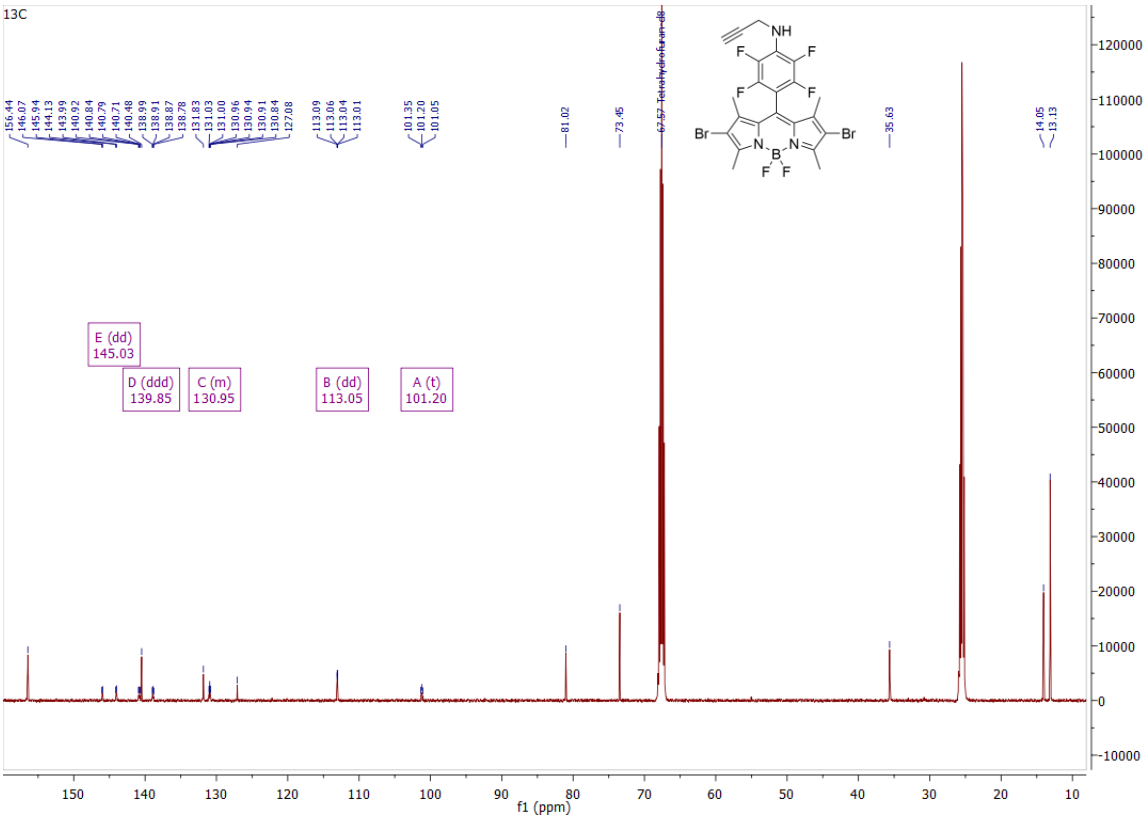

Figure S169: ^{13}C NMR (126 MHz, THF-d_8) spectrum of BODIPY **36**.

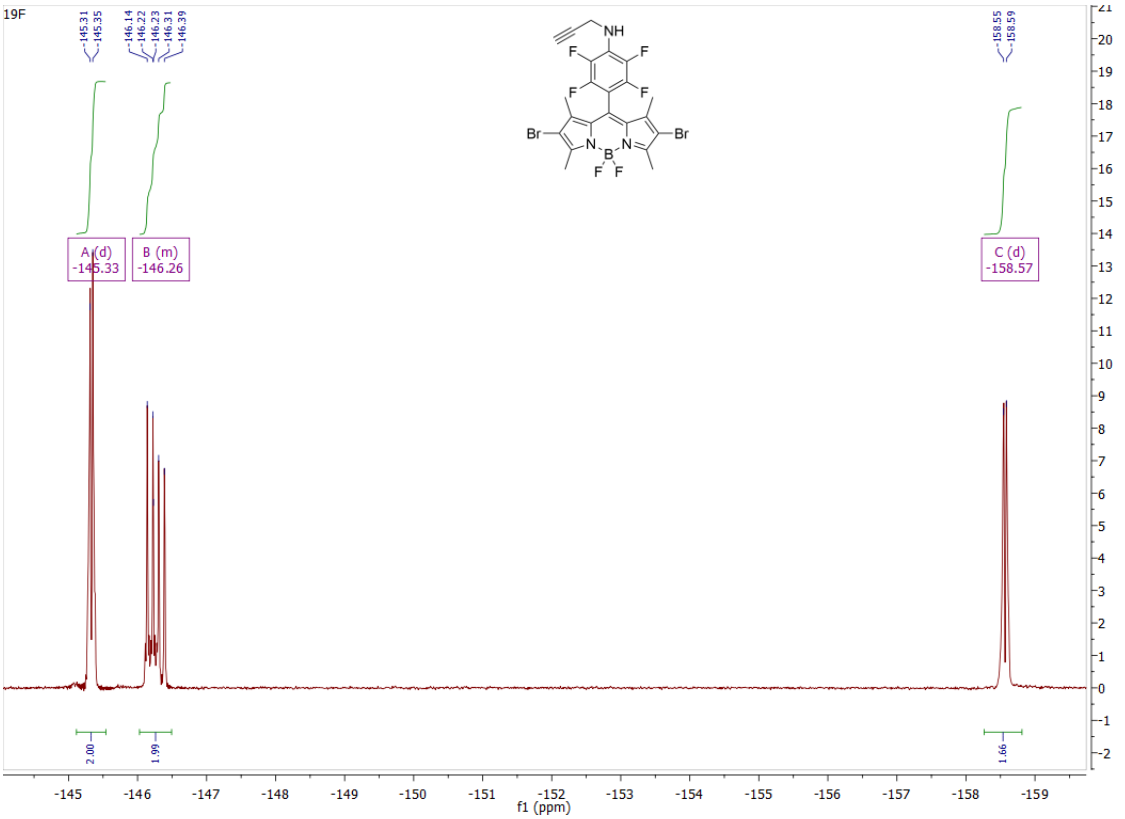

Figure S170: ^{19}F NMR (376 MHz, THF-d_8) spectrum of BODIPY **36**.

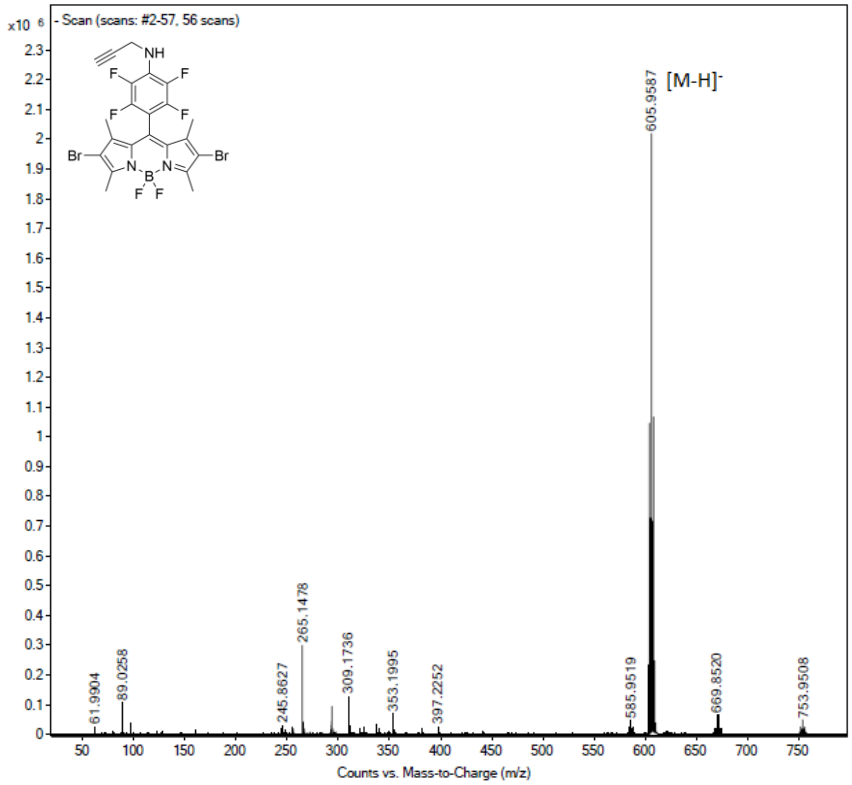

Figure S171: HRMS spectrum (ESI+) of BODIPY **36**.

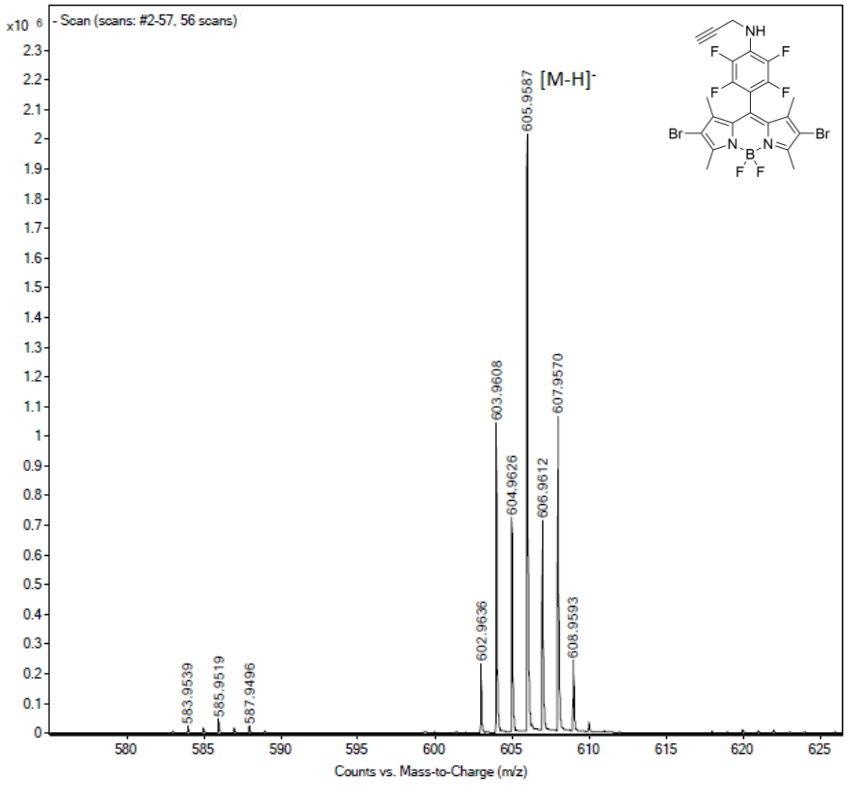

Figure S172: Zoom in from HRMS spectrum (ESI+) of BODIPY **36**.

2,6-Dibromo-8-[4-(*N*-2-hydroxyethylamino)-2,3,5,6-tetrafluorophenyl]-1,3,5,7-tetramethyl-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (**37**):

BODIPY **37** was prepared according to the general synthetic procedure. BODIPY **29** (94 mg, 0.21 mmol) and NBS (92 mg, 0.52 mmol) were dissolved in HFIP. After column chromatography (silica gel, EtOAc/*n*-hexane = 1/9, v/v) BODIPY **37** was obtained as a red solid (56 mg, 91 µmol, 44 %).

^{1}H NMR (500 MHz, THF-d_8): δ (ppm) = 1.73 (s, 6H, Me), 2.57 (s, 6H, Me), 3.54–3.58 (m, 2H, CH_2), 3.69–3.72 (m, 2H, CH_2), 4.05 (t, J = 5.2 Hz, 1H, OH), 5.71–5.74 (NH).

^{13}C NMR (126 MHz, THF-d_8): δ (ppm) = 13.2 (Me), 14.0 (Me), 48.7 (CH_2), 62.3 (CH_2), 112.9–113.0 (m, C_{Br}), 124.7 (C_{meso}), 132.0 (Ar-C_{para}), 132.0 ($C_{pyrrole}$), 140.5 ($C_{pyrrole}$), 156.2 ($C_{pyrrole}$).

^{19}F NMR (376 MHz, THF-d_8): δ (ppm) = -145.76 (d, J = 15.7 Hz, 2F, CF_{meta}), -146.21 – -146.38 (m_C, 2F, BF_2), -160.61 (d, J = 15.4 Hz, 2F, CF_{meta}).

HRMS (ESI-TOF): *m/z* calcd. for $C_{21}H_{18}BBr_2F_6N_3ONa^+$ $[M+Na]^+$: 635.9686, found: 635.9687, *m/z* calcd. for $C_{21}H_{18}BBr_2F_6N_3OK^+$ $[M+K]^+$: 651.9425, found: 651.9436, *m/z* calcd. for $C_{42}H_{36}B_2Br_4F_{12}N_6O_2Na^+$ $[2M+Na]^+$: 1248.9479, found: 1248.9480.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3404 [ν(OH), ν(NH)], 2926 [ν(CH_2), ν(Me)], 1656 [ν(C=C)], 1496 [δ(CH_2), δ(Me)], 1180 and 1119 [ν(BF), ν(CBr)], 767 [δ(-HC=CH-)].

UV/Vis (DCM): λ_{max} (nm) [log (ε/L mol^{-1} cm^{-1})] = 391 [4.03], 546 [4.83].

Fluorescence (DCM): λ_{max} (nm) = 562 at $\lambda_{Excitation}$ (nm) = 380, 530.

M.P. (°C): 103–108.

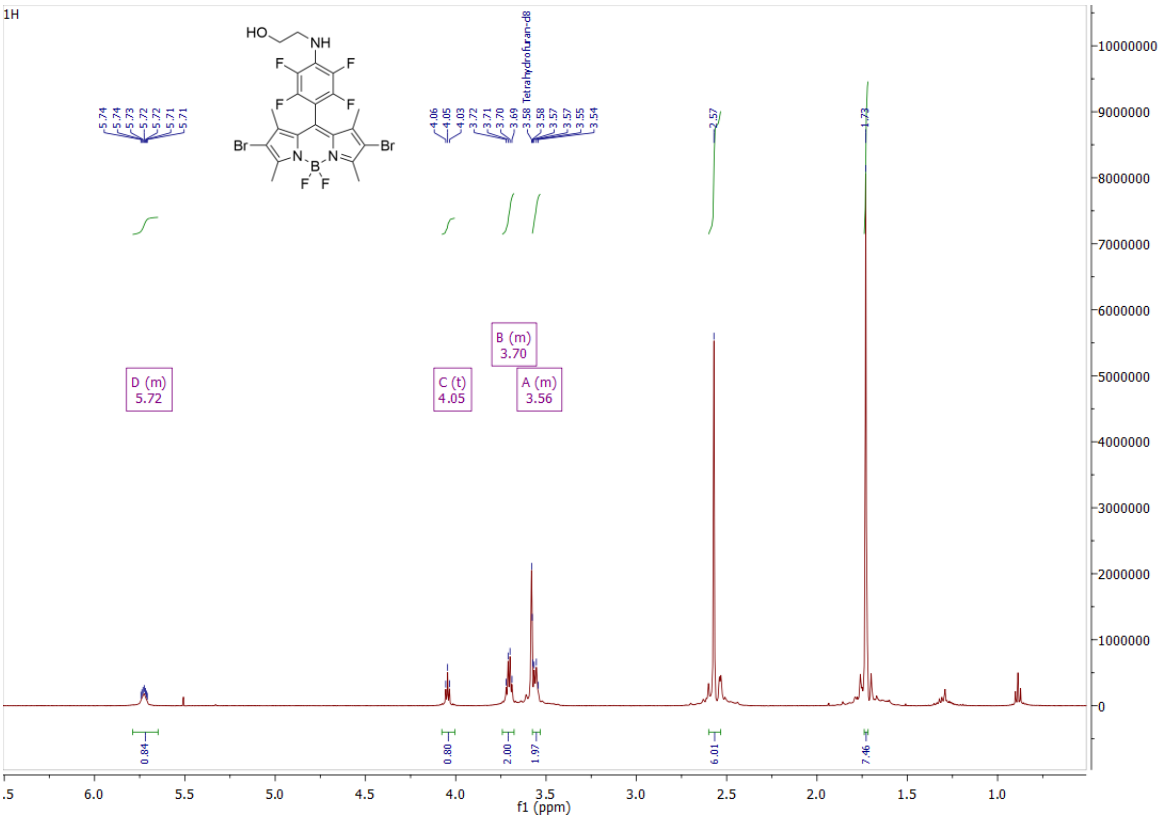

Figure S173: ^{1}H NMR (500 MHz, THF-d_8) spectrum of BODIPY **37**.

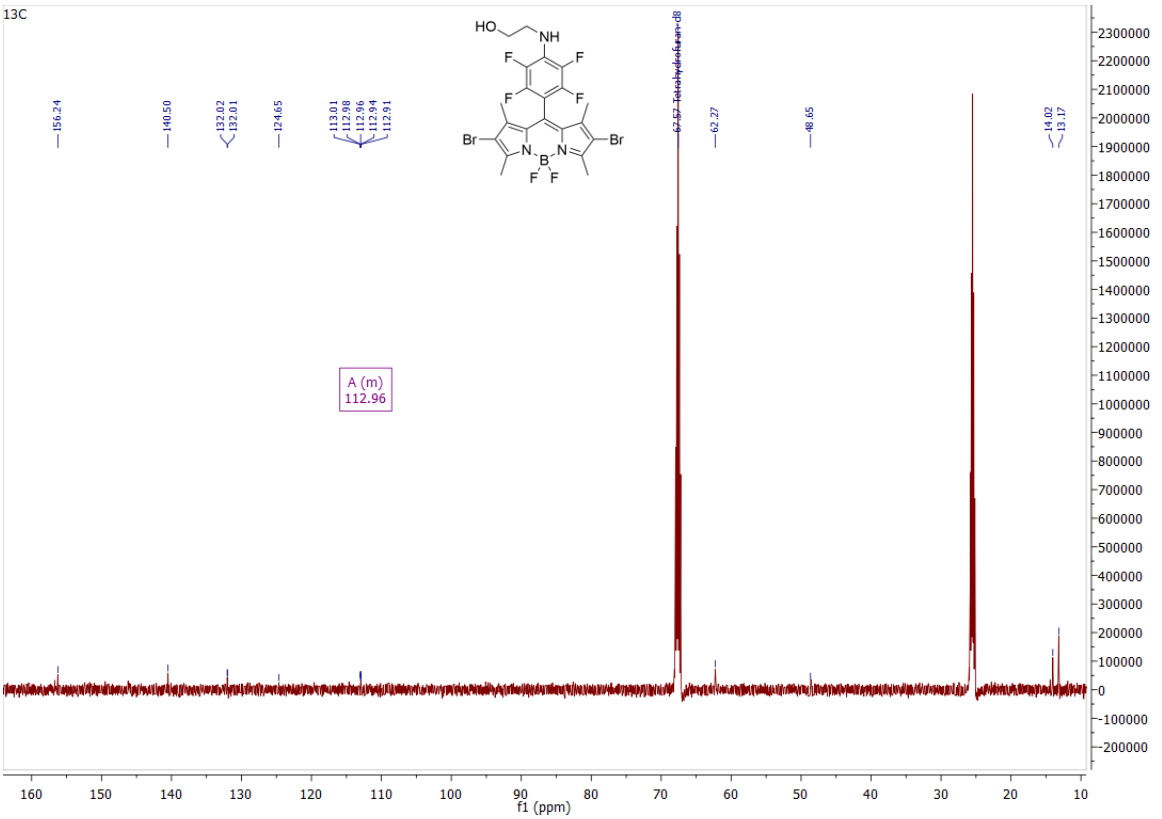

Figure S174: ^{13}C NMR (126 MHz, THF-d_8) spectrum of BODIPY **37**.

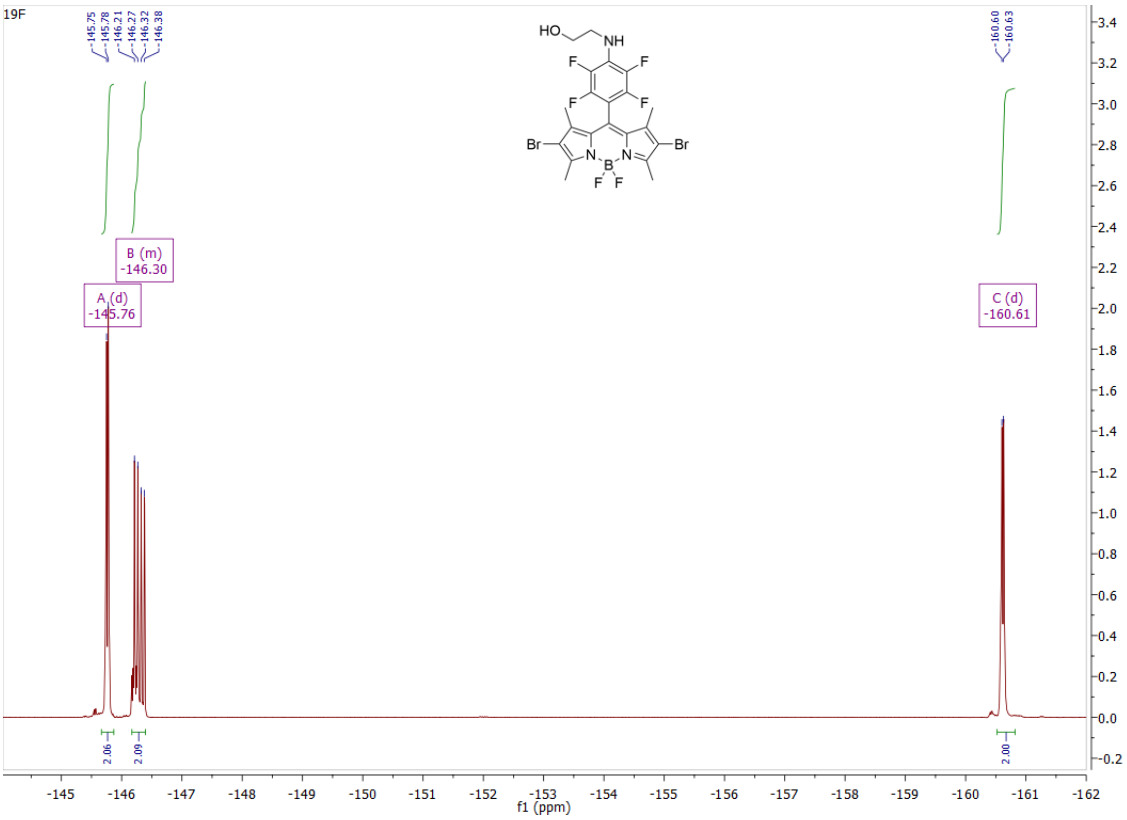

Figure S175: ^{19}F NMR (376 MHz, THF-d_8) spectrum of BODIPY **37**.

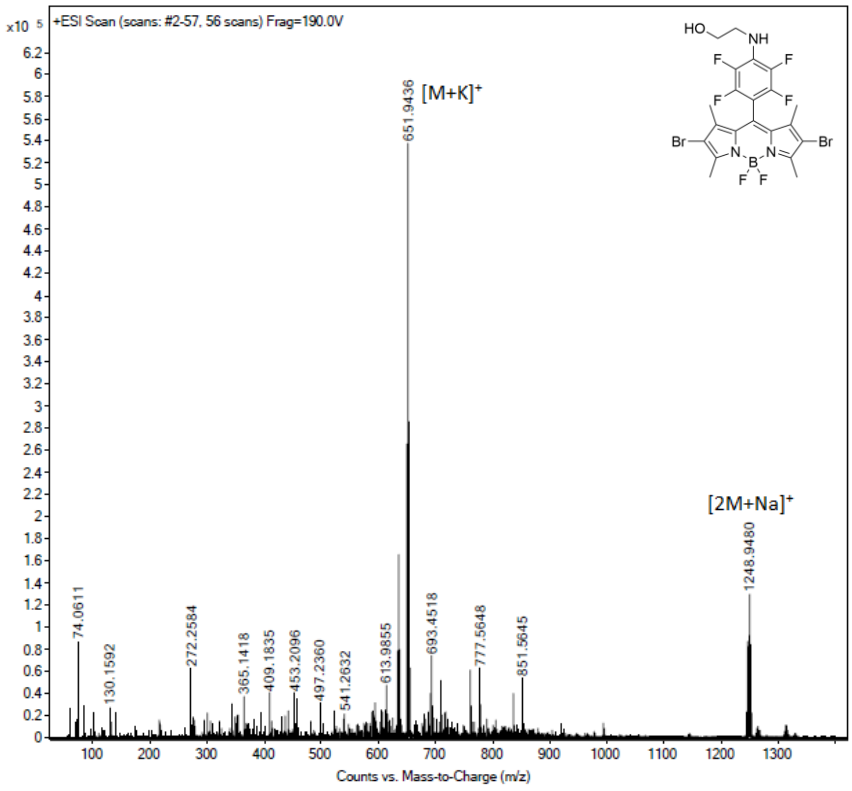

Figure S176: HRMS spectrum (ESI+) of BODIPY **37**.

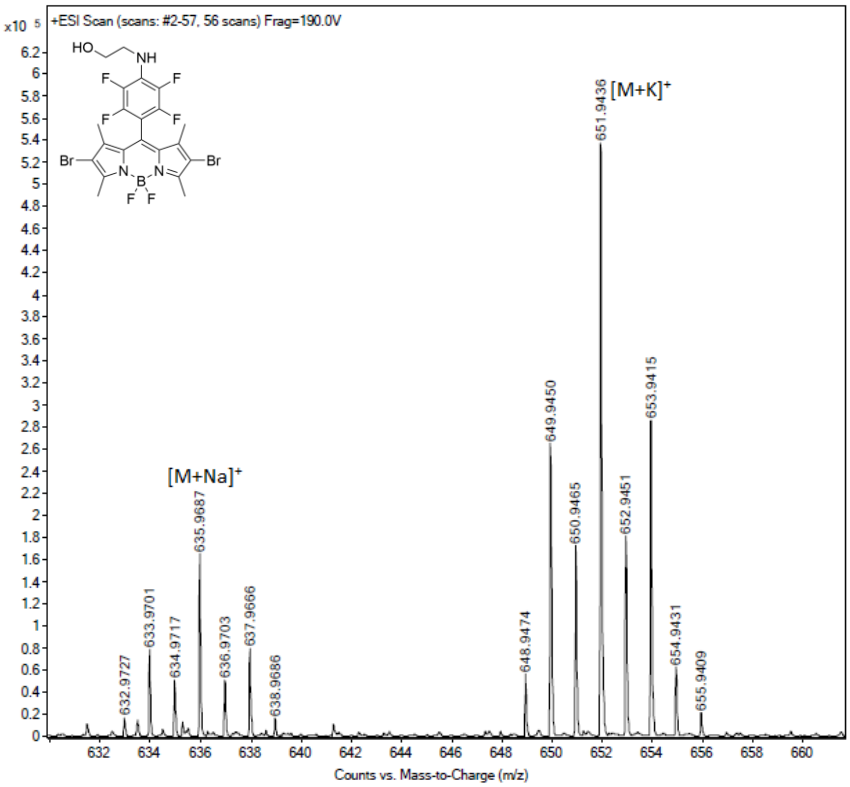

Figure S177: Zoom in from HRMS spectrum (ESI+) of BODIPY **37**.

2,6-Dibromo-8-(4-fluoro-3-nitrophenyl)-1,3,5,7-tetramethyl-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (**38**):

BODIPY **38** was prepared according to the general synthetic procedure. BODIPY **26** (60 mg, 0.16 mmol) and NBS (66 mg, 0.37 mmol) were dissolved in HFIP. After column chromatography (silica gel, EtOAc/*n*-hexane = 1/4, v/v) BODIPY **38** was obtained as a reddish-green solid (48 mg, 88 µmol, 57 %).

^{1}H NMR (500 MHz, THF-d$_8$): δ (ppm) = 1.48 (s, 6H, Me), 2.58 (s, 6H, Me), 7.71 (dd, *J* = 10.8, 8.5 Hz, 1H, Ar-H$_{meta}$), 7.81 (ddd, *J* = 8.5, 4.2, 2.2 Hz, 1H, Ar-H$_{ortho}$), 8.30 (dd, *J* = 7.0, 2.3 Hz, 1H, Ar-H$_{ortho}$).

^{13}C NMR (126 MHz, THF-d$_8$): δ (ppm) = 13.96 (Me), 14.7 (Me), 112.6–112.7 (m, C-Br), 120.99 (d, *J* = 20.9 Hz, Ar-C$_{meta}$), 127.9 (d, *J* = 2.1 Hz, Ar-C$_{ortho}$), 131.4 (C$_{pyrrole}$), 132.2*, 136.9 (d, *J* = 9.3 Hz, Ar-C$_{ortho}$), 139.9*, 141.2 (C$_{pyrrole}$), 155.7 (C$_{pyrrole}$), 156.9 (d, *J* = 329.8 Hz, Ar-C$_{para}$). * These signals could not be assigned exactly to corresponding carbon atoms. They belong to the Ar-C$_{ipso}$ and the Ar-C$_{nitro}$ of the aryl residue.

^{19}F NMR (376 MHz, THF-d$_8$): δ (ppm) = -117.54 (s, 1F, CF), -146.26 – -146.51 (m$_c$, 2F, BF$_2$).

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2922 and 2851 [ν(Me)], 1622 [ν(C=C)], 1536 [ν$_{asym}$(NO$_2$)], 1344 [ν$_{sym}$(NO$_2$)], 1260 [C=CF], 1090 [ν(BF), ν(CBr)], 750 [δ(HC=CH)].

UV/Vis (DCM): λ_{max} (nm) [log (ε/L mol^{-1} cm^{-1})] = 538 [4.66].

Fluorescence (DCM): λ_{max} (nm) = 554 at $\lambda_{Excitation}$ (nm) = 520.

M.P. (°C): > 250.

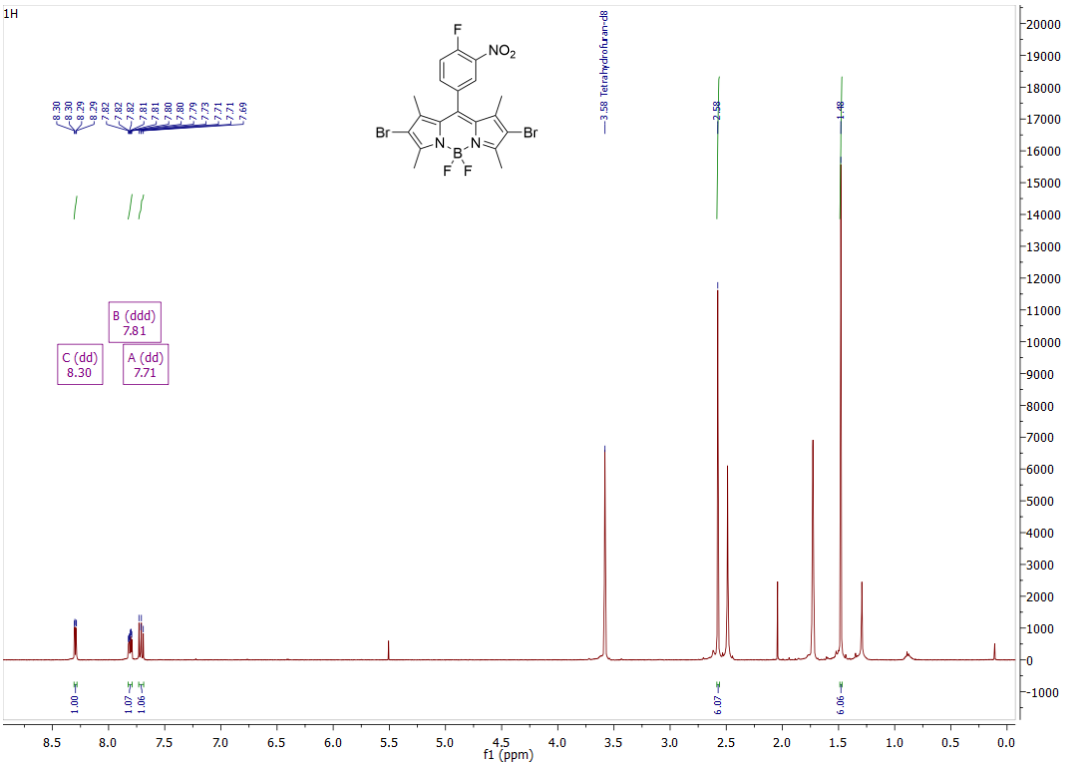

Figure S178: ^{1}H NMR (500 MHz, THF-d_8) spectrum of BODIPY **38**.

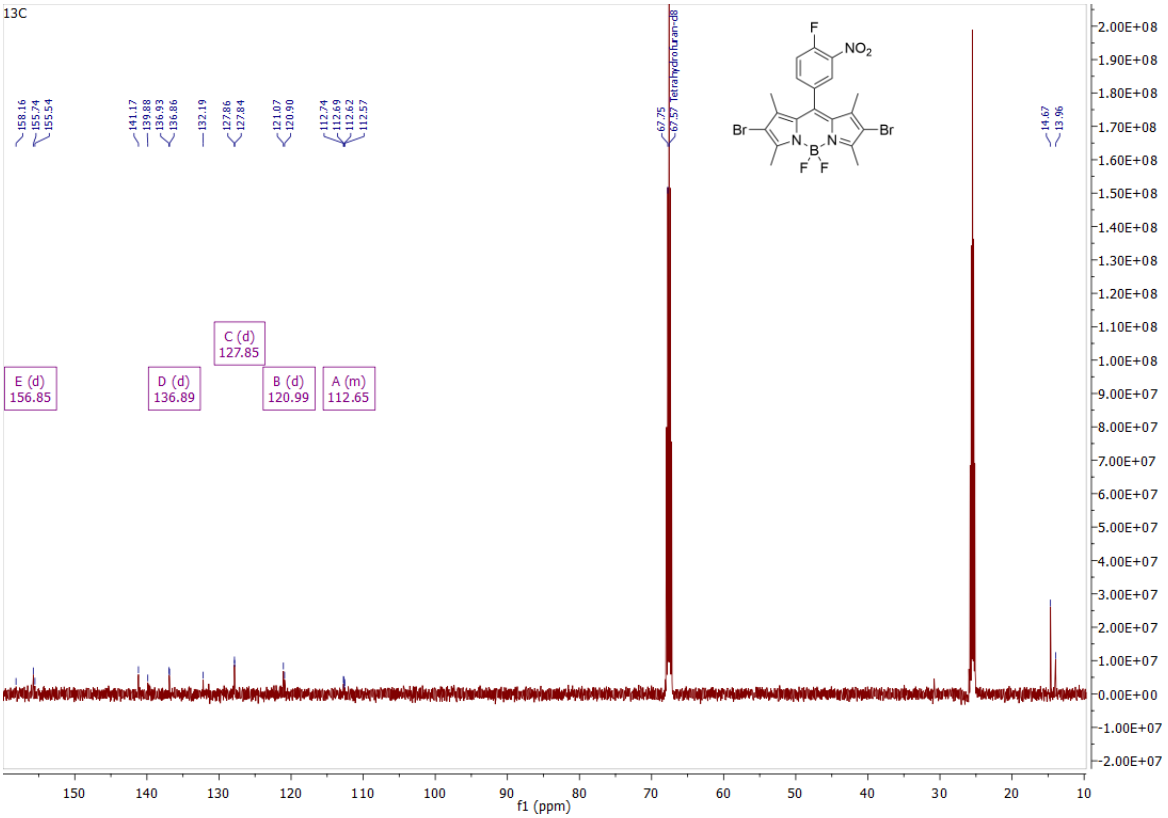

Figure S179: ^{13}C NMR (126 MHz, THF-d_8) spectrum of BODIPY **38**.

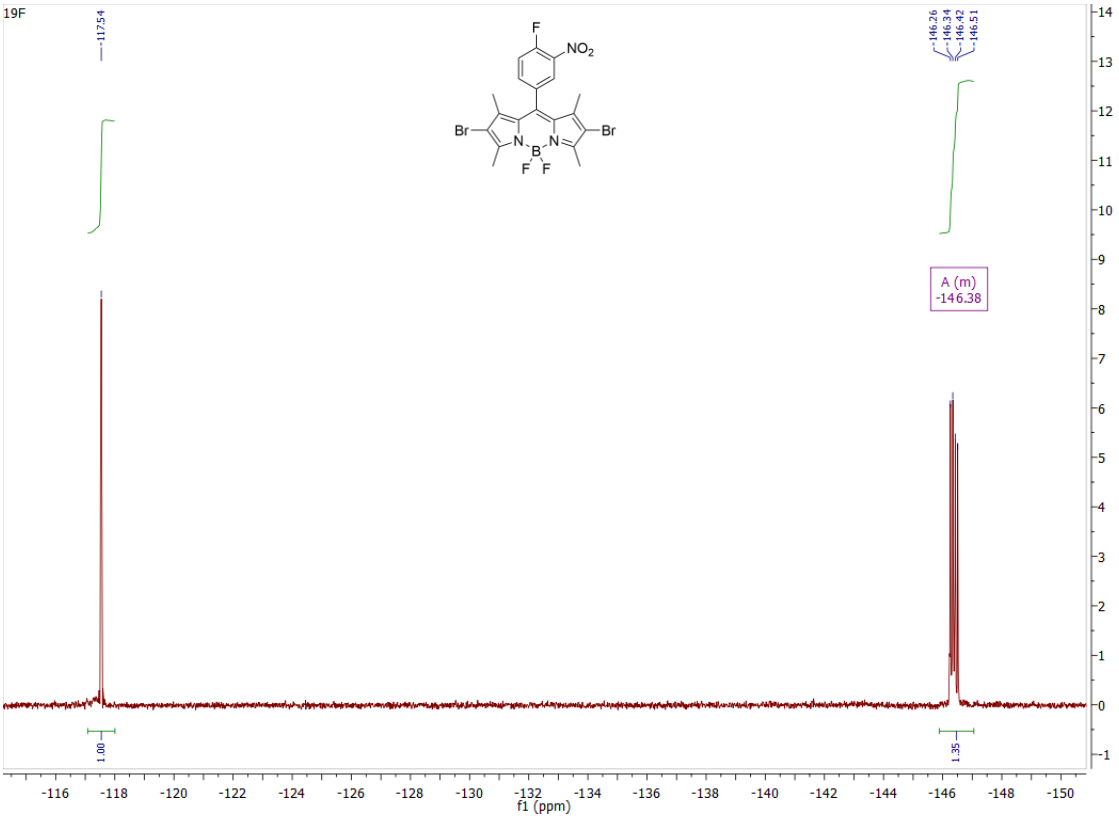

Figure S180: ^{19}F NMR (376 MHz, THF-d_8) spectrum of BODIPY **38**.

2,6-Dibromo-8-[4-(*N*-butylamino)-3-nitrophenyl]-1,3,5,7-tetramethyl-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (**39**):

BODIPY **39** was prepared according to the general synthetic procedure. BODIPY **30** (95 mg, 0.22 mmol) and NBS (96 mg, 0.54 mmol) were dissolved in HFIP. After column chromatography (silica gel, EtOAc/*n*-hexane = 1/9, v/v) BODIPY **39** was obtained as a red solid (81 mg, 0.16 mmol, 63 %).

^{1}H NMR (500 MHz, THF-d_8): δ (ppm) = 1.02 (t, J = 7.4 Hz, 3H, Me_{Butyl}), 1.49–1.55 (m, 2H, CH_2), 1.59 (s, 6H, Me), 1.75–1.79 (m, 2H, CH_2), 2.56 (s, 6H, Me), 3.45 (td, J = 7.3, 5.4 Hz, 2H, CH_2), 7.27 (d, J = 8.8 Hz, 1H, Ar-H_{meta}), 7.43 (dd, J = 8.7, 2.1 Hz, 1H, Ar-H_{ortho}), 8.18 (d, J = 2.2 Hz, 1H, Ar-H_{ortho}), 8.26 (t, J = 5.5 Hz, 1H, NH).

^{13}C NMR (126 MHz, THF-d_8): δ (ppm) = 13.9 (Me), 14.3 (Me), 14.9 (Me_{Butyl}), 21.3 (CH_2), 32.1 (CH_2), 43.8 (CH_2), 112.3 (C_{Br}), 116.5 (Ar-C_{meta}), 121.1 (C_{meso}), 127.9 (Ar-C_{ortho}), 132.0 ($C_{pyrrole}$), 133.2*, 136.6 (Ar-C_{ortho}), 141.1 ($C_{pyrrole}$), 146.9 (Ar-C_{para}), 154.9 ($C_{pyrrole}$). *These signals could not be assigned exactly to corresponding carbon atoms. They belong to the Ar-C_{ipso} and the Ar-C_{nitro} of the aryl residue.

^{19}F NMR (376 MHz, THF-d_8): δ (ppm) = -146.84 – -145.98 (m_c, 2F, BF_2).

HRMS (ESI-TOF): *m/z* calcd. for $C_{23}H_{25}BBr_2F_2N_4O_2Na^+$ $[M+Na]^+$: 621.0277, found: 621.0314, *m/z* calcd. for $C_{46}H_{50}B_2Br_4F_4N_8O_4Na^+$ $[2M+Na]^+$: 1219.0662, found: 1219.0712.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3384 [ν(NH)], 2958 and 2928 [$\nu(CH_2)$, ν(Me)], 2866 [ν(CH)], 1631 [ν(C=N)], 1533 [$\nu_{as}(NO_2)$], 1497 [$\delta(CH_2)$, δ(Me)], 1346 [$\nu_{sym}(NO_2)$], 1167 and 1119 [ν(BF), ν(CBr)], 755 [δ(HC=CH)].

UV/Vis (DCM): λ_{max} (nm) [log (ε/L mol^{-1} cm^{-1})] = 397 [4.19], 533 [4.87].

Fluorescence (DCM): λ_{max} (nm) = 548 at $\lambda_{Excitation}$ (nm) = 380, 520.

M.P.(°C): 191–194.

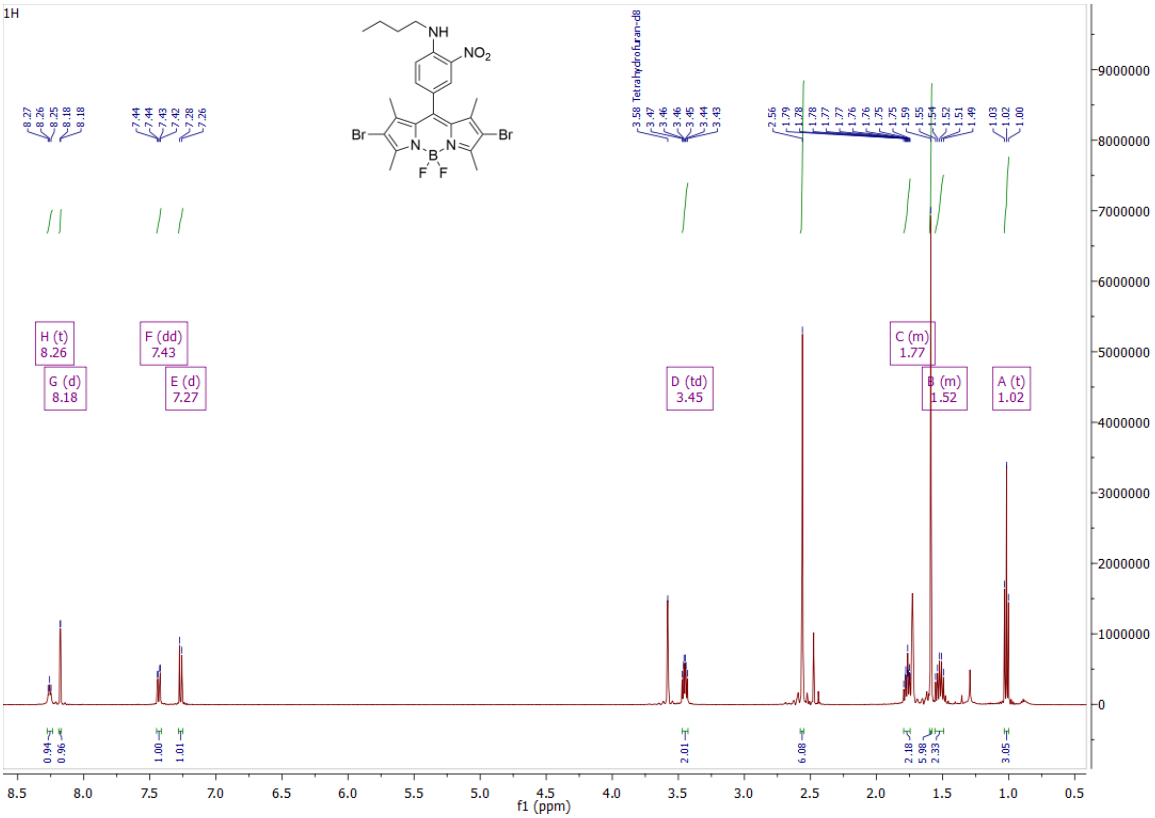

Figure S181: ^{1}H NMR (500 MHz, THF-d_8) spectrum of BODIPY **39**.

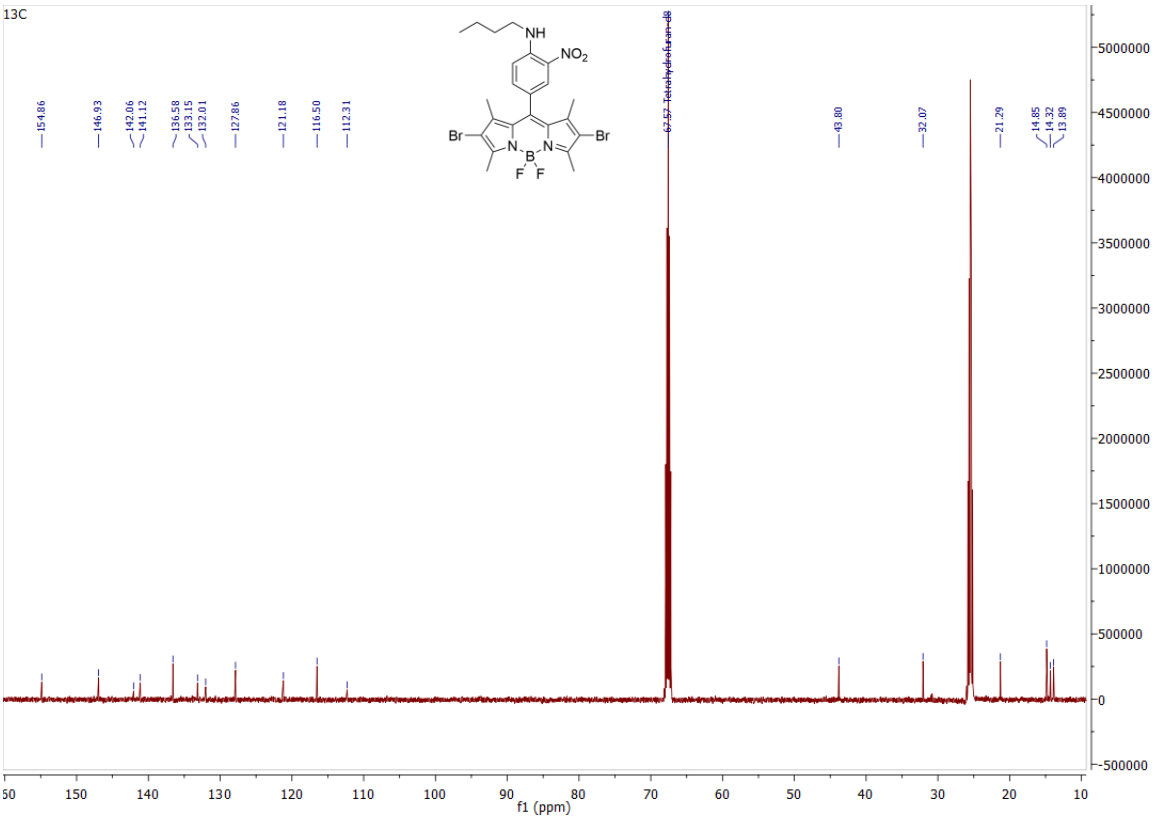

Figure S182: ^{13}C NMR (126 MHz, THF-d_8) spectrum of BODIPY **39**.

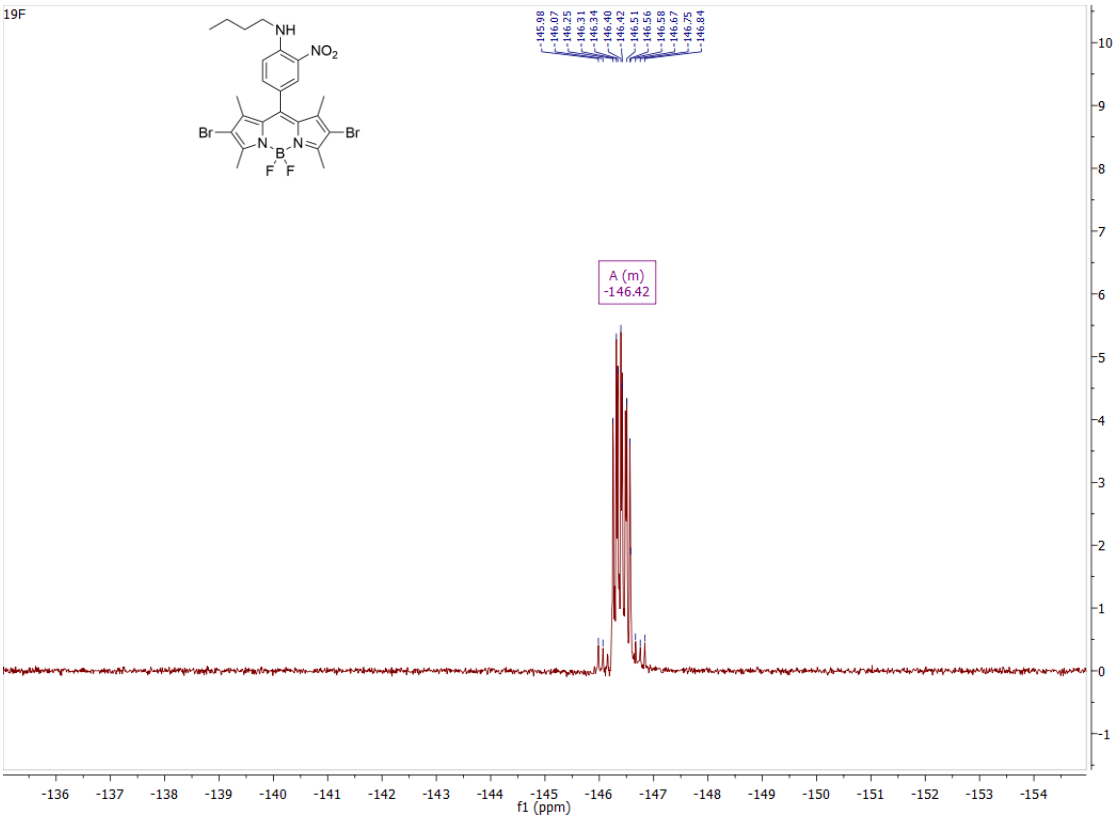

Figure S183: ^{19}F NMR (376 MHz, THF-d_8) spectrum of BODIPY **39**.

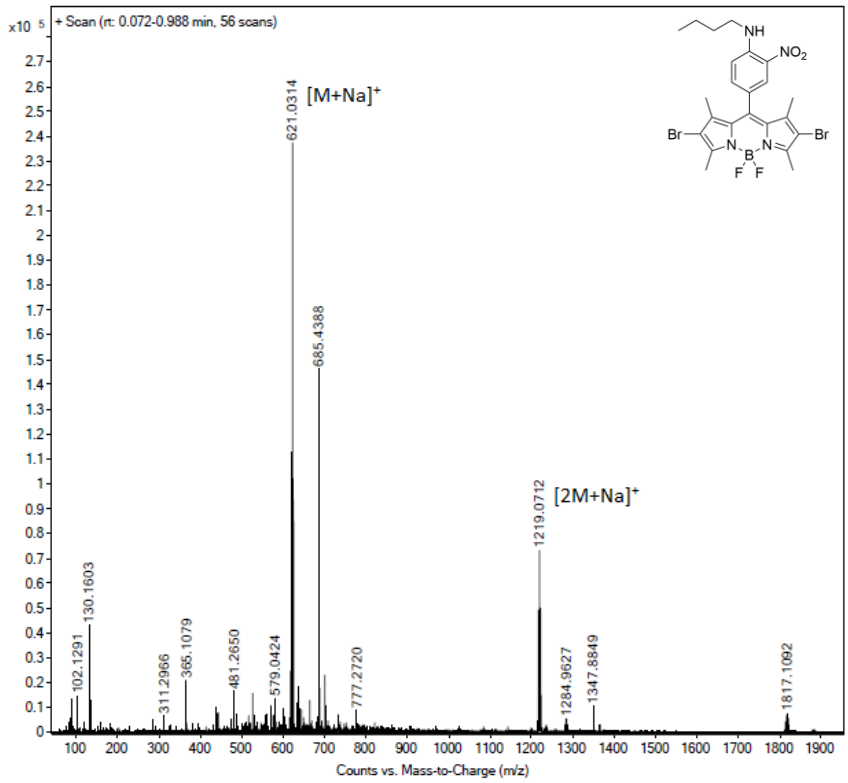

Figure S184: HRMS spectrum (ESI+) of BODIPY **39**.

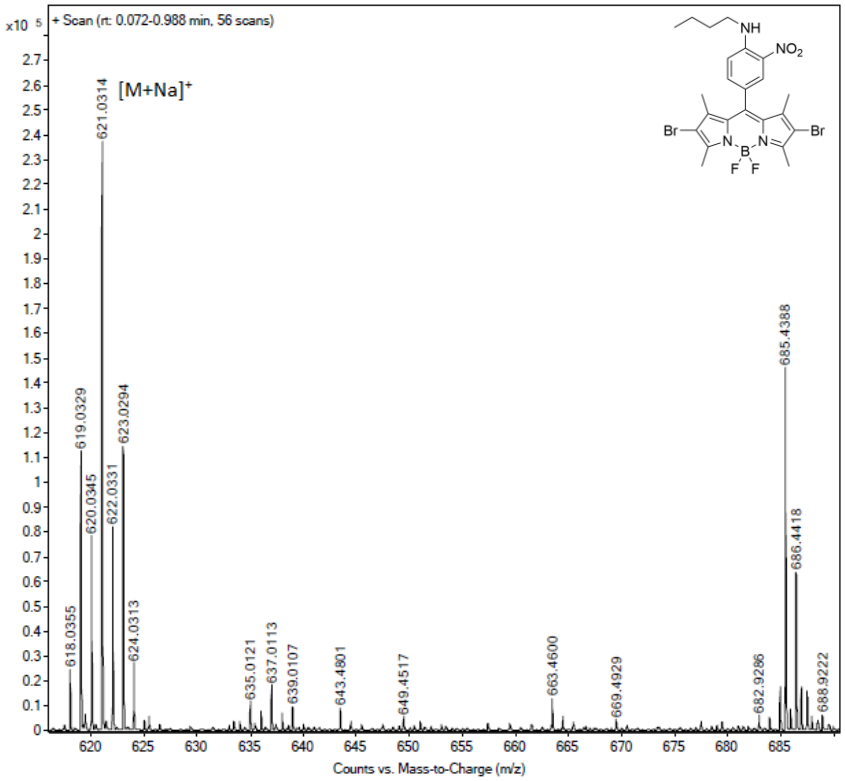

Figure S185: Zoom in from HRMS spectrum (ESI+) of BODIPY **39**.

2,6-Dibromo-8-[3-nitro-4-(*N*-2-prop-2-ynylamino)phenyl]-1,3,5,7-tetramethyl-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (**40**):

BODIPY **40** was prepared according to the general synthetic procedure. BODIPY **31** (90 mg, 0.21 mmol) and NBS (95 mg, 0.53 mmol) were dissolved in HFIP. After column chromatography (silica gel, EtOAc/*n*-hexane = 1/9, v/v) BODIPY **40** was obtained as a red solid (35 mg, 60 µmol, 28 %).

^{1}H NMR (500 MHz, THF-d_8): δ (ppm) = 1.57 (m, 6H, Me), 2.56 (s, 6H, Me), 2.76 (t, *J* = 2.4 Hz, 1H, CH), 4.30 (dd, *J* = 5.9, 2.5 Hz, 2H, CH_2), 7.36 (d, *J* = 8.8 Hz, 1H, Ar-H_{meta}), 7.50 (dd, *J* = 8.8, 2.1 Hz, 1H, Ar-H_{ortho}), 8.21 (d, *J* = 2.2 Hz, 1H, Ar-H_{ortho}), 8.43 (t, *J* = 5.9 Hz, 1H, NH).

^{13}C NMR (126 MHz, THF-d_8): δ (ppm) = 13.99 (Me), 14.8 (Me), 33.2 (CH_2), 73.5 (CH), 80.2 (C), 112.4 (C_{Br}), 117.1 (Ar-C_{meta}), 122.5*, 127.7 (Ar-C_{ortho}), 131.98 ($C_{pyrrole}$), 134.1*, 136.4 (Ar-C_{ortho}), 141.2 ($C_{pyrrole}$), 141.9 (C_{meso}), 145.9 (Ar-C_{para}), 154.95 ($C_{pyrrole}$). *These signals could not be assigned exactly to corresponding carbon atoms. They belong to the Ar-C_{ipso} and the Ar-C_{nitro} of the aryl residue.

^{19}F NMR (376 MHz, THF-d_8): δ (ppm) = -146.56 – -146.27 (m_c, 2F, BF_2).

HRMS (ESI-TOF): *m/z* calcd. for $C_{22}H_{19}BBr_2FN_4O_2^+$ $[M-F]^+$: 560.9926, found: 560.9975, *m/z* calcd. for $C_{22}H_{19}BBr_2F_2N_4O_2Na^+$ $[M+Na]^+$: 602.9808, found: 602.9862, *m/z* calcd. for $C_{22}H_{19}BBr_2F_2N_4O_2K^+$ $[M+K]^+$: 618.9547, found: 618.9608, *m/z* calcd. for $C_{44}H_{38}B_2Br_4F_4N_8O_4Na^+$ $[2M+Na]^+$: 1182.9723, found: 1182.9824.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3389 [ν(NH)], 3297 [ν(C≡CH)], 2924 [$\nu(CH_2)$], 2847 [ν(CH)], 1632 [ν(C=C)], 1531 [$\nu_{as}(NO_2)$], 1464 [$\delta(CH_2)$, δ(Me)], 1348 [$\nu_{sym}(NO_2)$], 1166 and 1119 [ν(BF), ν(CBr)], 755 [δ(HC=CH)].

UV/Vis (DCM): λ_{max} (nm) [log (ε/L mol^{-1} cm^{-1})] = 397 [4.25], 533 [4.87].

Fluorescence (DCM): λ_{max} (nm) = 550 at $\lambda_{Excitation}$ (nm) = 380, 520.

M.P.(°C): 229–235.

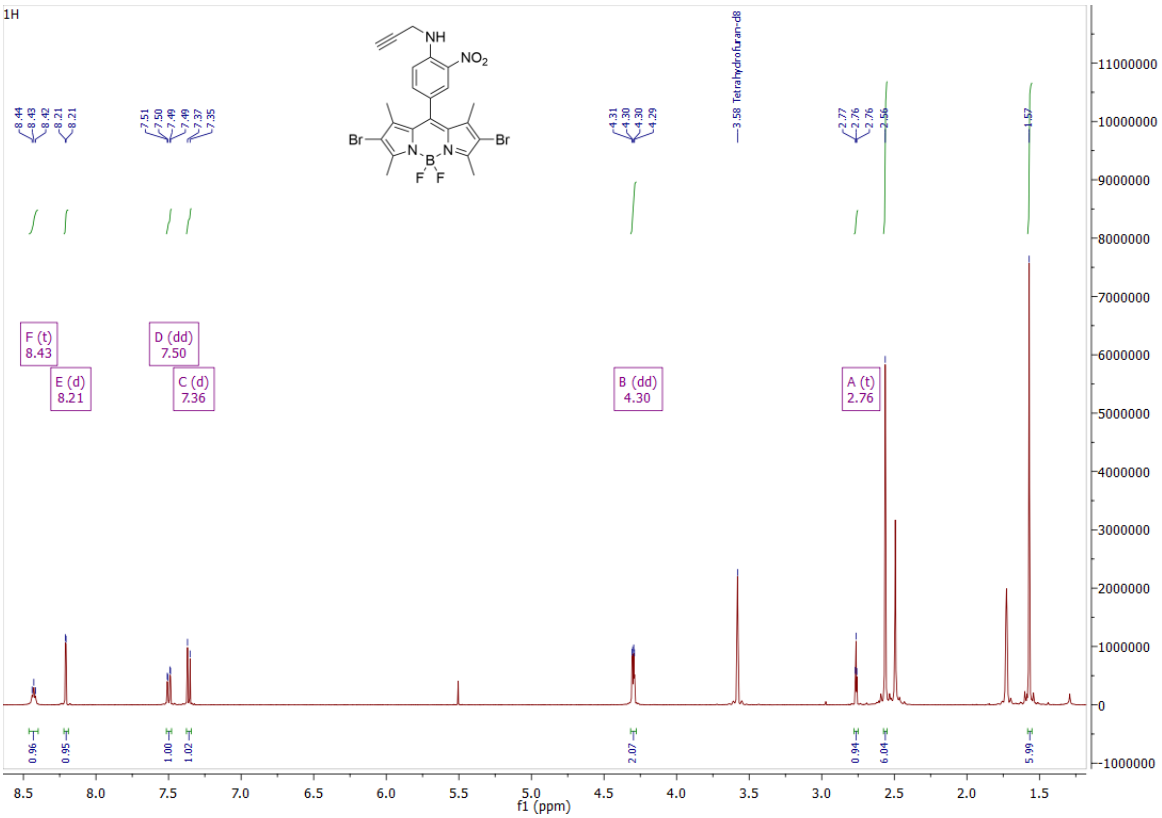

Figure S186: ^{1}H NMR (500 MHz, THF-d_8) spectrum of BODIPY **40**.

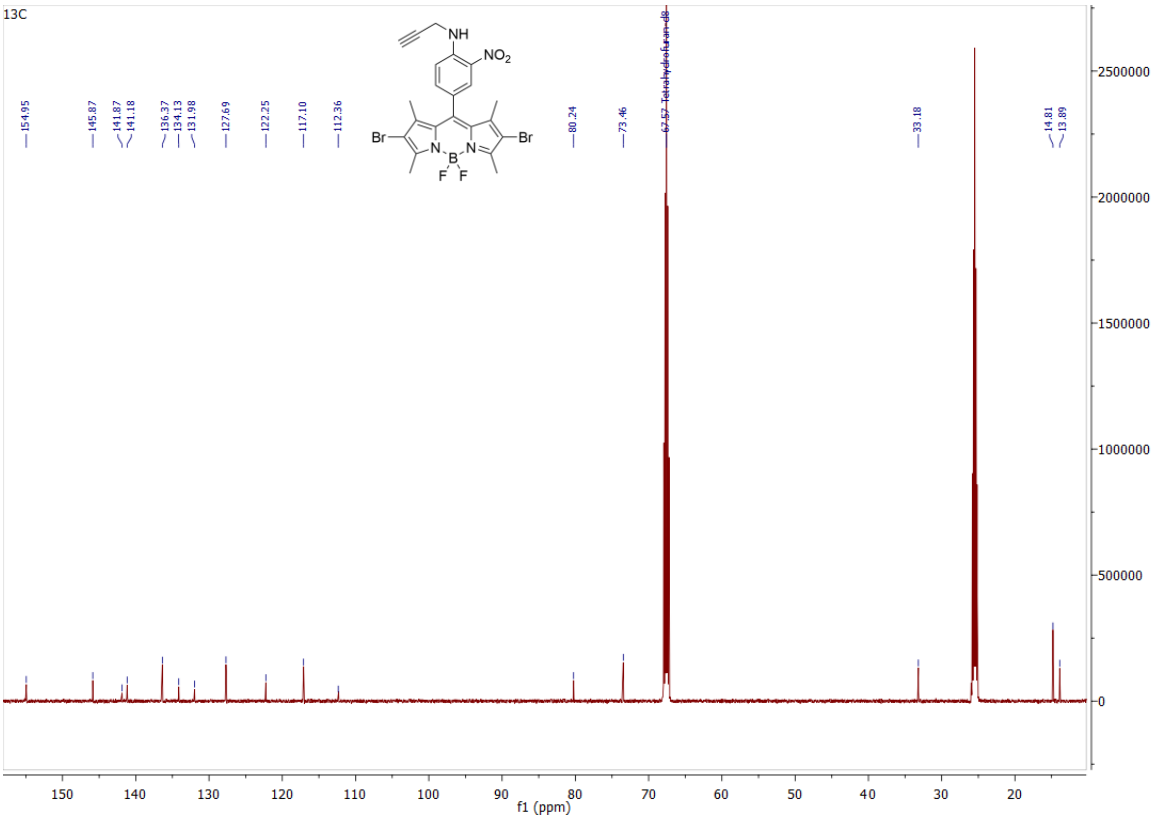

Figure S187: ^{1}H NMR (500 MHz, THF-d_8) spectrum of BODIPY **40**.

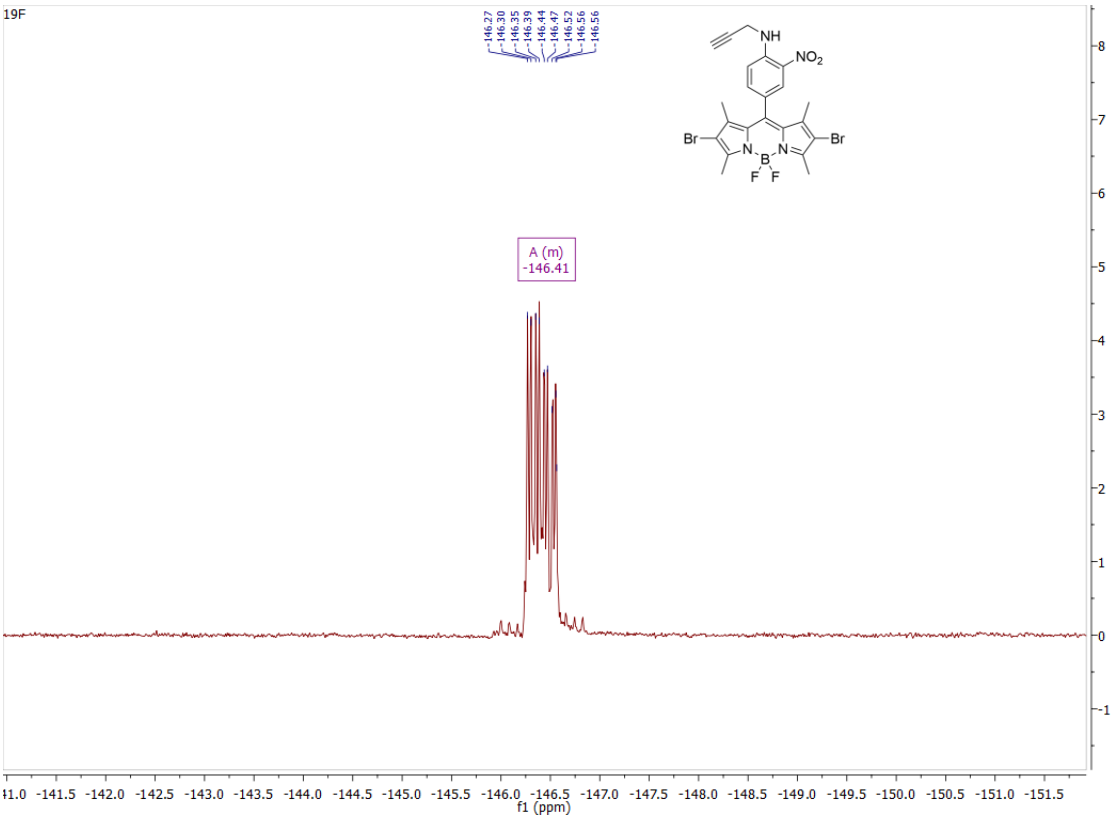

Figure S188: ^{19}F NMR (376 MHz, THF-d_8) spectrum of BODIPY **40**.

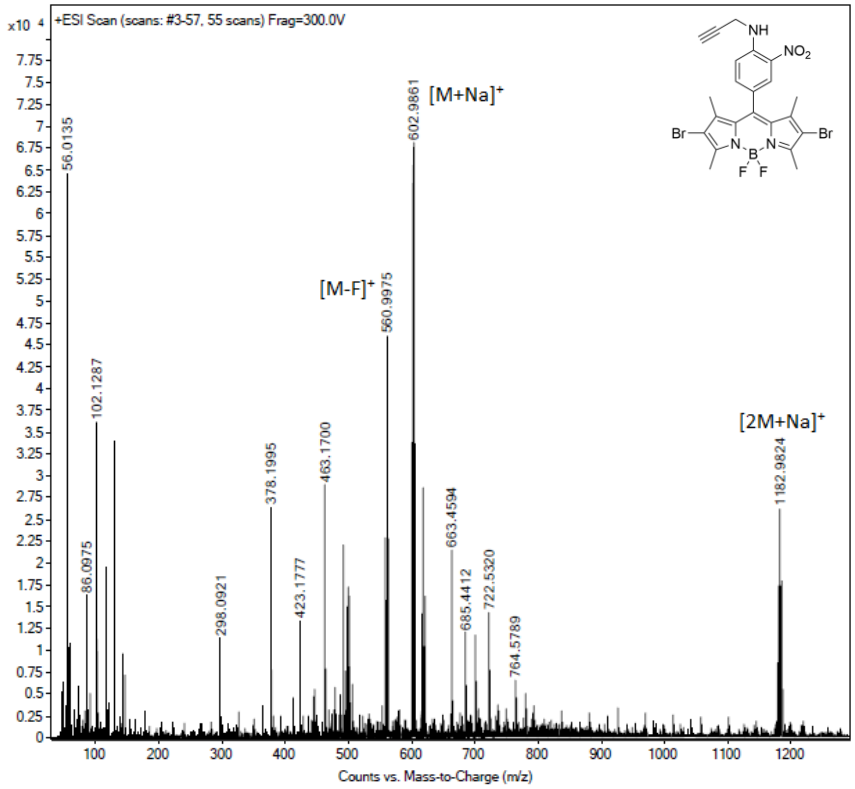

Figure S189: HRMS spectrum (ESI+) of BODIPY **40**.

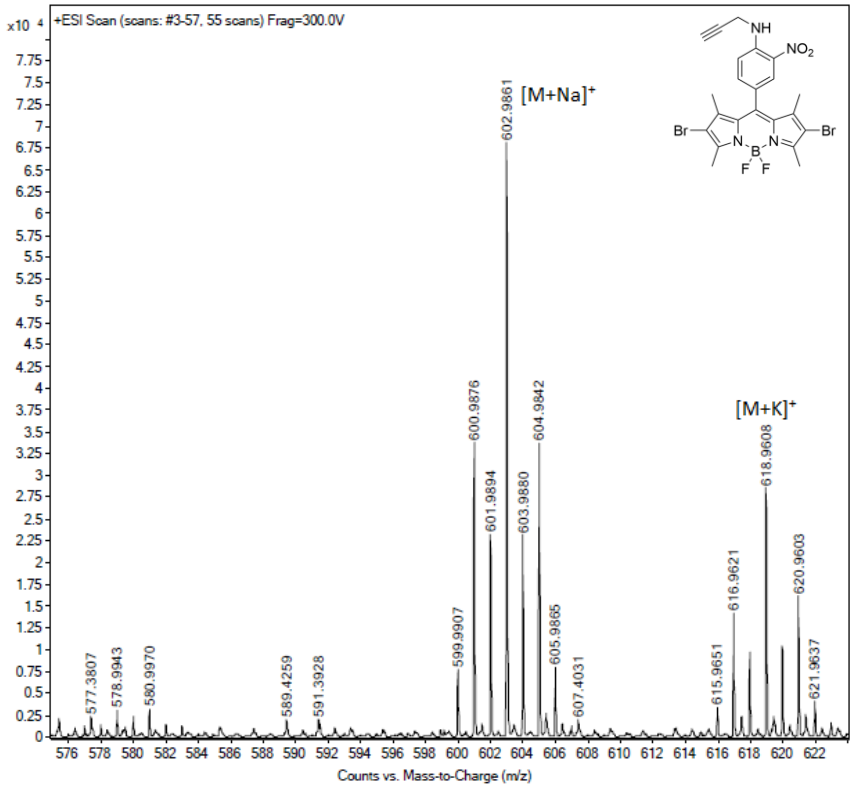

Figure S190: Zoom in from HRMS spectrum (ESI+) of BODIPY **40**.

2,6-Dibromo-8-[4-(*N*-2-hydroxyethylamino)-3-nitrophenyl]-1,3,5,7-tetramethyl-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (**41**):

BODIPY **41** was prepared according to the general synthetic procedure. BODIPY **32** (90 mg, 0.21 mmol) and NBS (94 mg, 0.53 mmol) were dissolved in HFIP. After column chromatography (silica gel, EtOAc/*n*-hexane = 4/1, v/v) BODIPY **41** was obtained as a red solid (39 mg, 67 µmol, 32 %).

^{1}H NMR (500 MHz, THF-d$_8$): δ (ppm) = 1.59 (s, 6H, Me), 2.56 (s, 6H, Me), 3.52 (t, J = 5.4 Hz, 2H, CH_2), 3.82 (t, J = 5.4 Hz, 2H, CH_2), 7.30 (d, J = 8.8 Hz, 1H, Ar-H_{meta}), 7.42 (dd, J = 8.8, 2.2 Hz, 1H, Ar-H_{ortho}), 8.17 (d, J = 2.1 Hz, 1H, Ar-H_{ortho}).

^{13}C NMR (126 MHz, THF-d$_8$): δ (ppm) = 13.9 (Me), 14.9 (Me), 46.2 (CH_2), 60.7 (CH_2), 112.2 (C_{Br}), 116.7 (Ar-C_{meta}), 121.2*, 127.8 (Ar-C_{ortho}), 132.0 ($C_{pyrrole}$), 133.3*, 136.5 (Ar-C_{ortho}), 141.1 ($C_{pyrrole}$), 142.1 (Ar-C_{para}), 154.8 ($C_{pyrrole}$). *These signals could not be assigned exactly to corresponding carbon atoms. They belong to the Ar-C_{ipso} and the Ar-C_{nitro} of the aryl residue.

^{19}F NMR (376 MHz, THF-d$_8$): δ (ppm) = -146.57 – -146.26 (m_c, 2F, BF_2).

HRMS (ESI-TOF): *m/z* calcd. for $C_{21}H_{21}BBr_2F_2N_4O_3Na^+$ $[M+Na]^+$: 608.9913, found: 608.9924, *m/z* calcd. for $C_{21}H_{21}BBr_2F_2N_4O_3K^+$ $[M+K]^+$: 624.9653, found: 624.9670, *m/z* calcd. for $C_{42}H_{42}B_2Br_4F_4N_8O_6K^+$ $[2M+K]^+$: 1210.9674, found: 1210.9682.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3370 [ν(OH), ν(NH)], 2926 [$\nu(CH_2)$, ν(Me)], 1632 [ν(C=C)], 1534 [$\nu_{as}(NO_2)$], 1460 [$\delta(CH_2)$, δ(Me)], 1348 [$\nu_{sym}(NO_2)$], 1167 and 1119 [ν(BF), ν(CBr)], 755 [δ(HC=CH)].

UV/Vis (MeOH): λ_{max} (nm) [log (ε/L mol^{-1} cm^{-1})] = 401 [3.76], 528 [4.36].

Fluorescence (DCM): λ_{max} (nm) = 547 at $\lambda_{Excitation}$ (nm) = 390, 510.

M.P.(°C): >250.

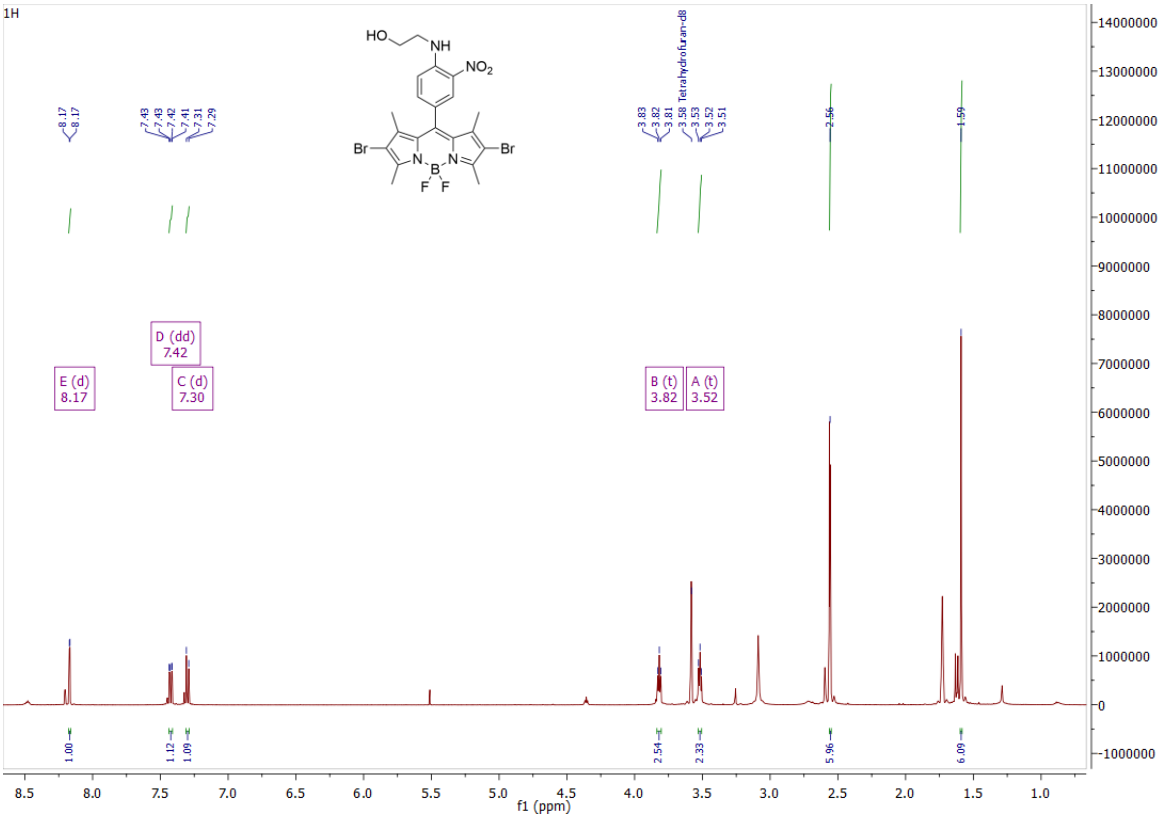

Figure S191: ^{1}H NMR (500 MHz, THF-d_8) spectrum of BODIPY **41**.

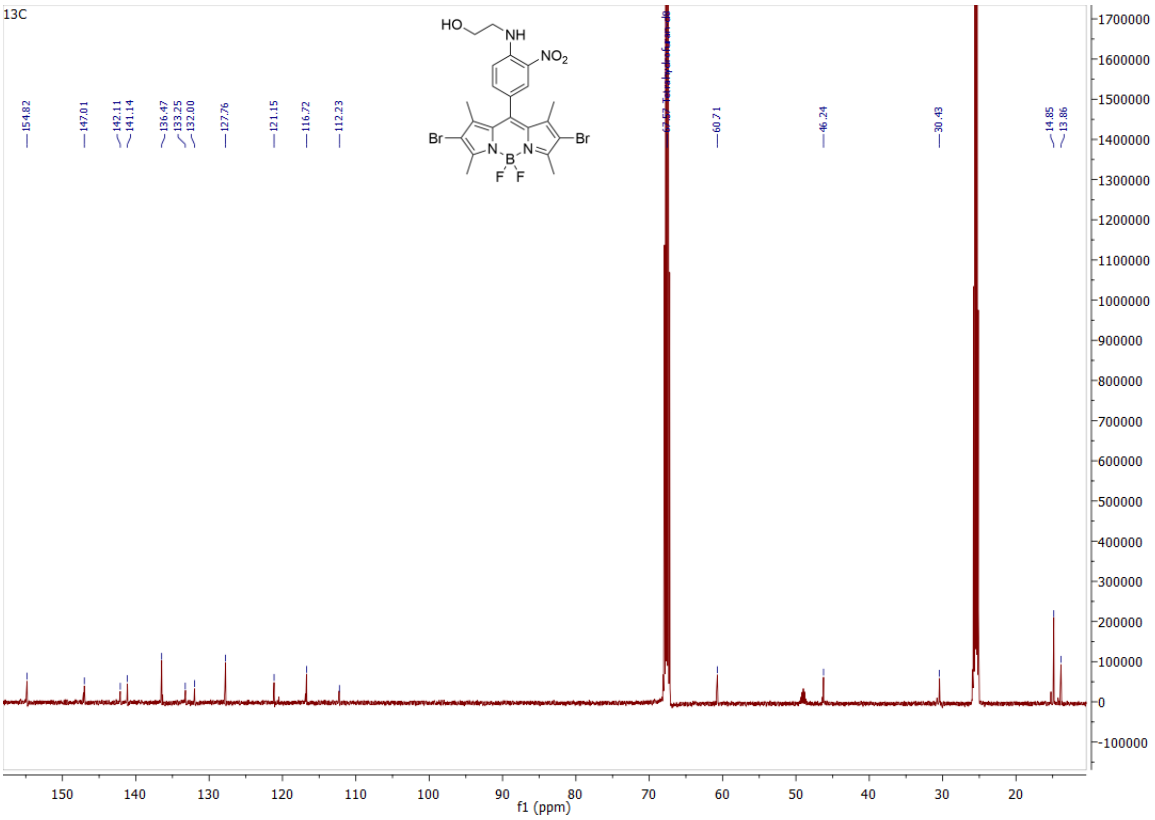

Figure S192: ^{13}C NMR (126 MHz, THF-d_8) spectrum of BODIPY **41**.

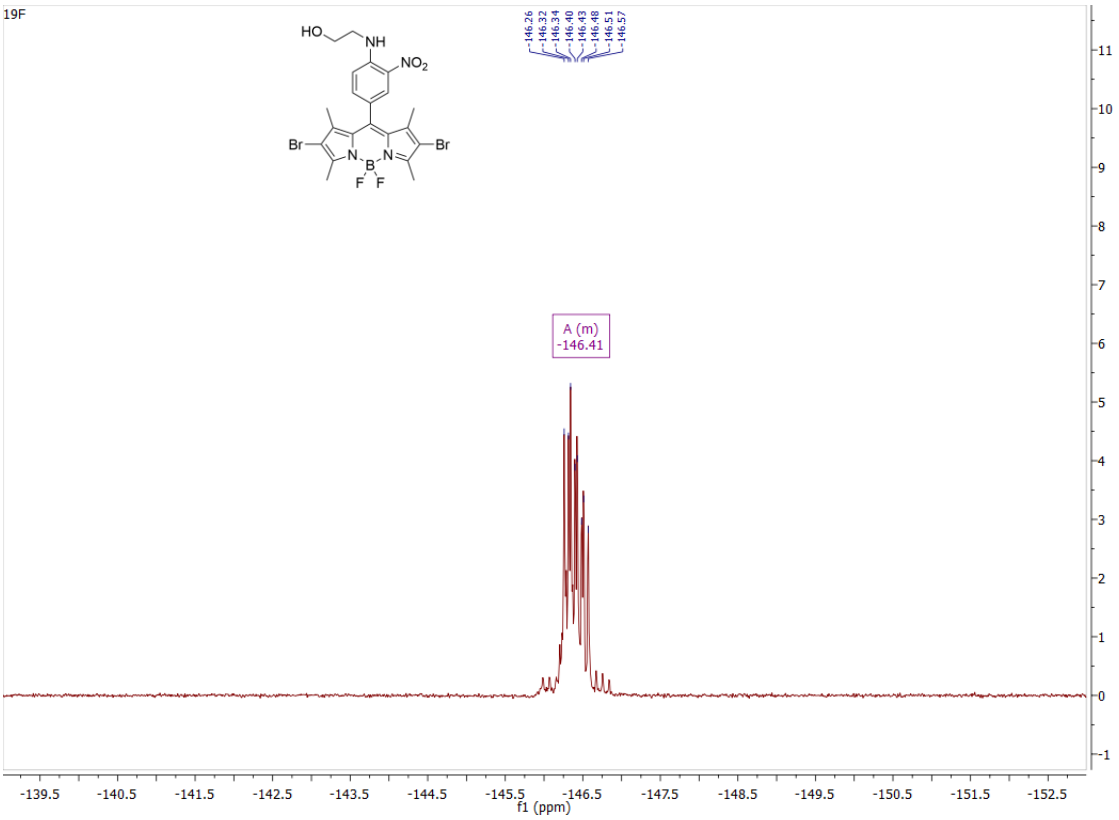

Figure S193: ^{19}F NMR (376 MHz, THF-d_8) spectrum of BODIPY **41**.

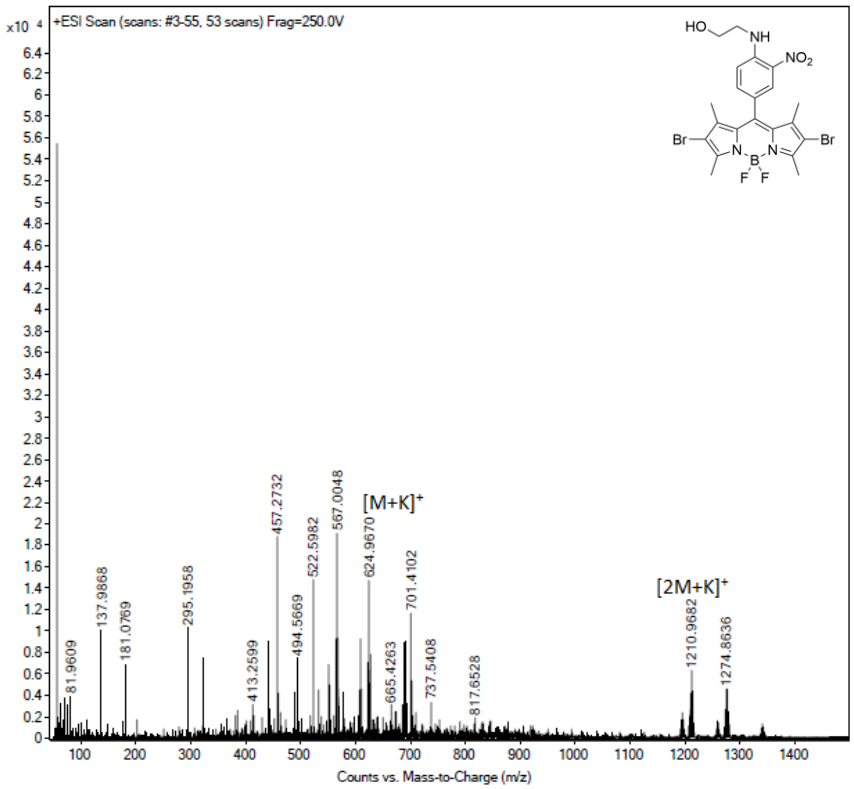

Figure S194: HRMS spectrum (ESI+) of BODIPY **41**.

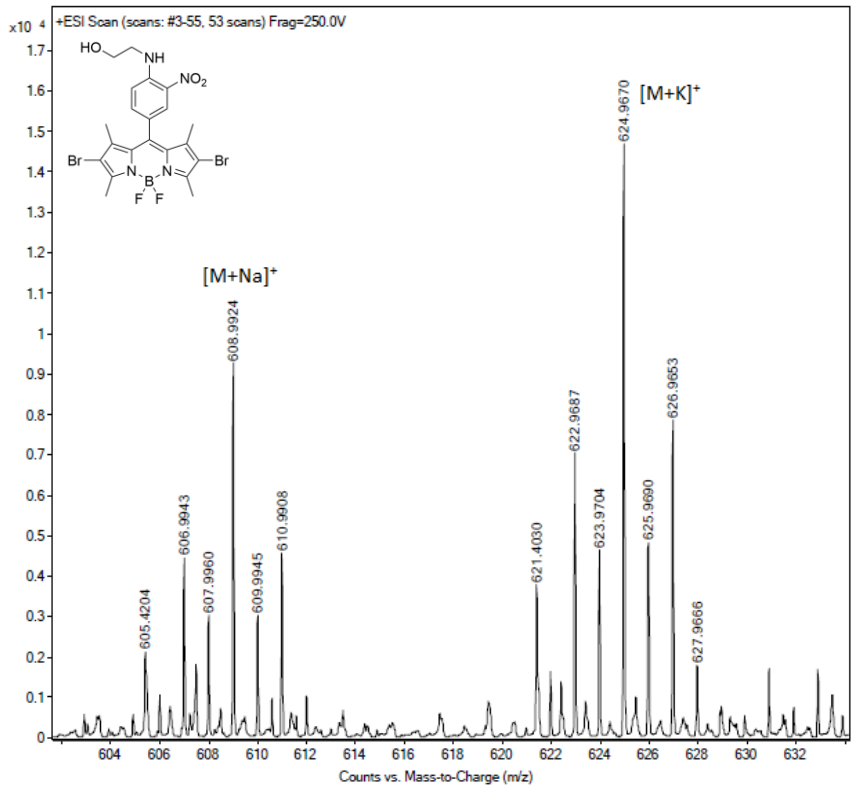

Figure S195: Zoom in from HRMS spectrum (ESI+) of BODIPY **41**.

2,6-Dibromo-8-[4-(*N*-1-hydroxymethyl-2-hydroxyethylamino)-3-nitrophenyl]-1,3,5,7-tetramethyl-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (**42**):

BODIPY **42** was prepared according to the general synthetic procedure. BODIPY **33** (94 mg, 0.21 mmol) and NBS (91 mg, 0.51 mmol) were dissolved in 2 mL of HFIP. After column chromatography (silica gel, EtOAc/*n*-hexane = 9/1, v/v) BODIPY **42** was obtained as red solid (61 mg, 99 µmol, 48 %).

^{1}H NMR (500 MHz, THF-d_8): δ (ppm) = 1.61 (s, 6H, Me), 2.56 (s, 6H, Me + H_2O), 3.73–3.78 (m, 2H, CH_2), 3.81–3.84 (m, 3H, CH_2 + CH), 4.28 (t, J = 5.1 Hz, 2H, OH), 7.39 –7.40 (m, 2H, Ar-H_{meta} + Ar-H_{ortho}), 8.17 (dd, J = 1.5, 1.0 Hz, 1H, Ar-H_{ortho}), 8.65 (d, J = 7.8 Hz, 1H, NH).

^{13}C NMR (126 MHz, THF-d_8): δ (ppm) = 13.9 (Me), 14.9 (Me), 56.96 (CH), 61.6 (CH_2), 112.28 (dd, J = 6.1, 2.9 Hz, C_{Br}), 117.3 (Ar-C_{meta}), 121.0*, 127.9 (Ar-C_{ortho}), 132.0 ($C_{pyrrole}$), 133.2*, 136.3 (Ar-C_{ortho}), 141.1 ($C_{pyrrole}$), 142.2 (C_{meso}), 146.8 (Ar-C_{para}), 154.8 ($C_{pyrrole}$). *These signals could not be assigned exactly to corresponding carbon atoms. They belong to the Ar-C_{ipso} and the Ar-C_{nitro} of the aryl residue.

^{19}F NMR (376 MHz, THF-d_8): δ (ppm) = -146.72 – -146.12 (m_c, 2F, BF_2).

HRMS (ESI-TOF): *m/z* calcd. for $C_{22}H_{23}BBr_2FN_4O_4^+$ $[M-F]^+$: 597.0137, found: 597.0165, *m/z* calcd. for $C_{22}H_{23}BBr_2F_2N_4O_4Na^+$ $[M+Na]^+$: 639.0019, found: 639.0050.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3360 [ν(OH), ν(NH)], 2927 [ν(CH_2), ν(Me)], 1630 [ν(C=C)], 1535 [ν_{as}(NO_2)], 1465 [δ(CH_2), δ(Me)], 1348 [ν_{sym}(NO_2)], 1171 and 1119 [ν(BF), ν(CBr)], 756 [δ(HC=CH)].

UV/Vis (MeOH): λ_{max} (nm) [log (ε/L mol^{-1} cm^{-1})] = 402 [4.03], 528 [4.72].

Fluorescence (DCM): λ_{max} (nm) = 546 at $\lambda_{Excitation}$ (nm) = 390, 510.

M.P.(°C): >250.

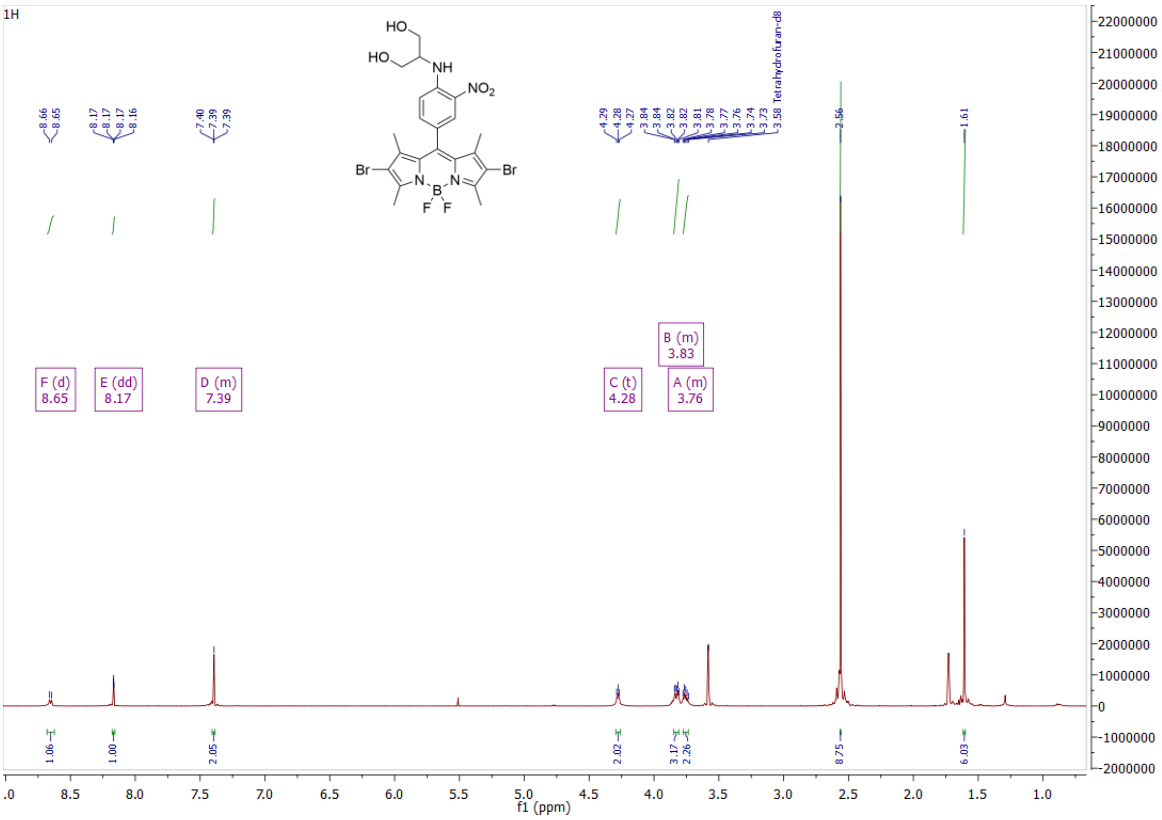

Figure S196: ^{1}H NMR (500 MHz, THF-d_8) spectrum of BODIPY **42**.

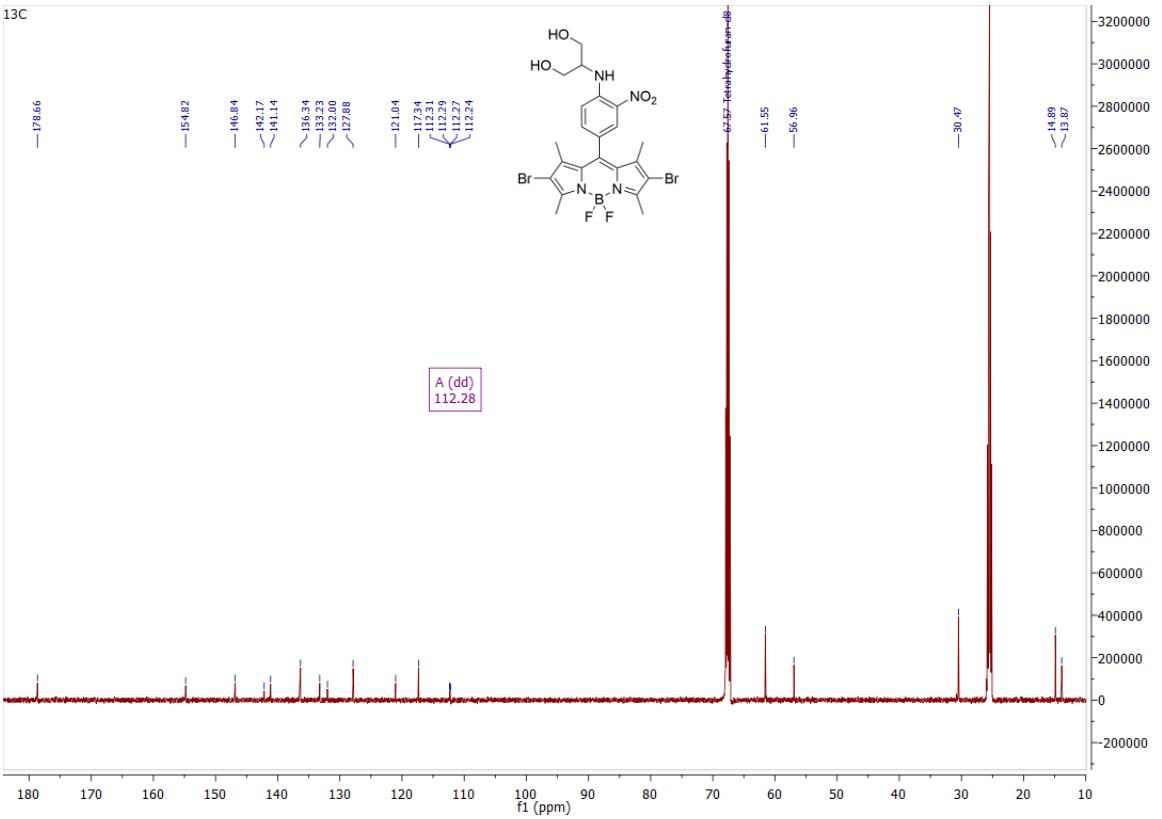

Figure S197: ^{13}C NMR (126 MHz, THF-d_8) spectrum of BODIPY **42**.

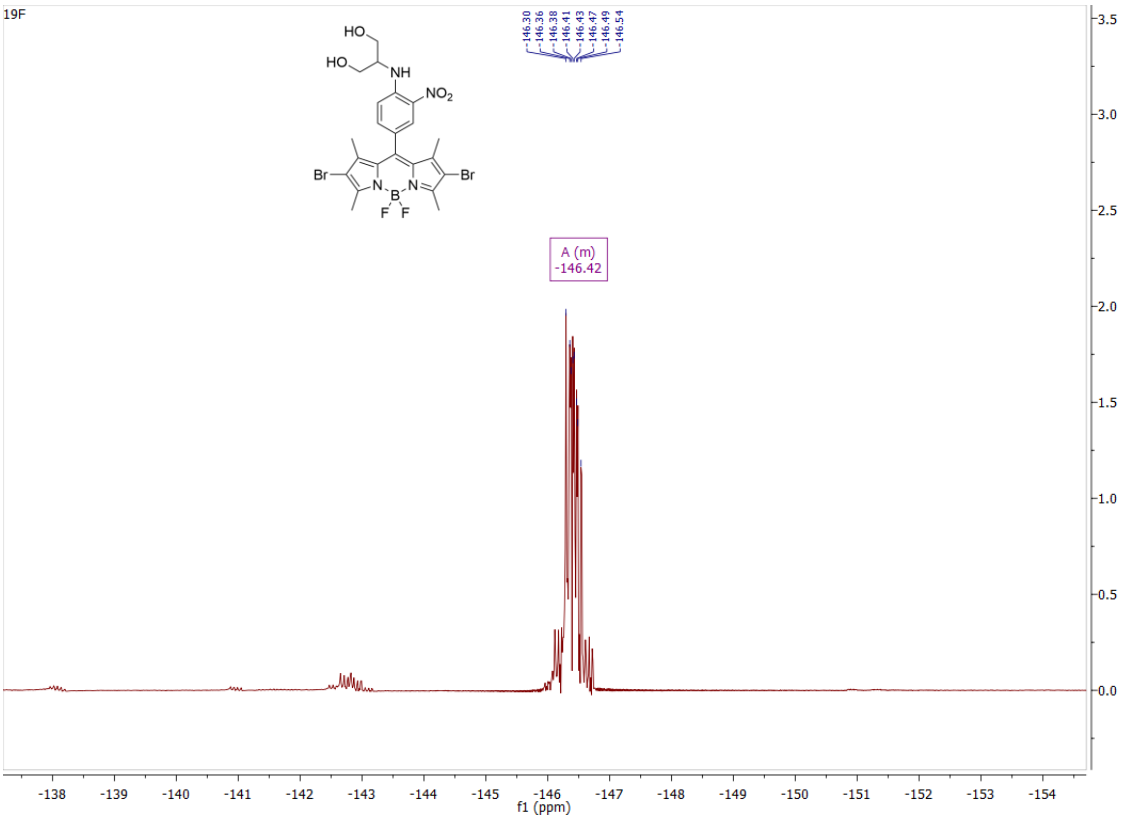

Figure S198: ^{19}H NMR (376 MHz, THF-d_8) spectrum of BODIPY **42**.

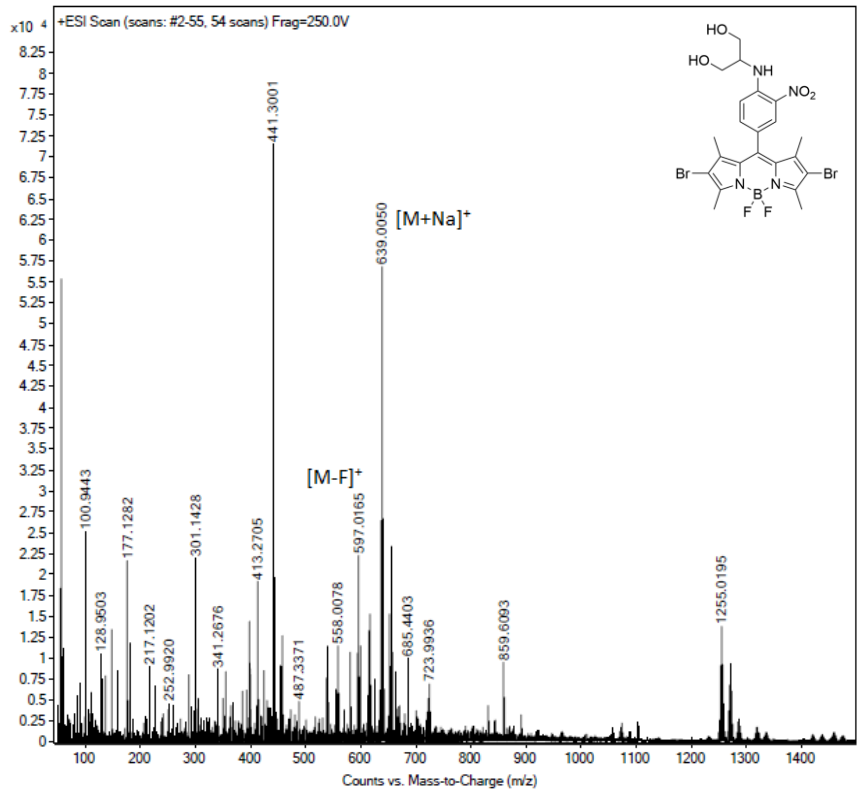

Figure S199: HRMS spectrum (ESI+) of BODIPY **42**.

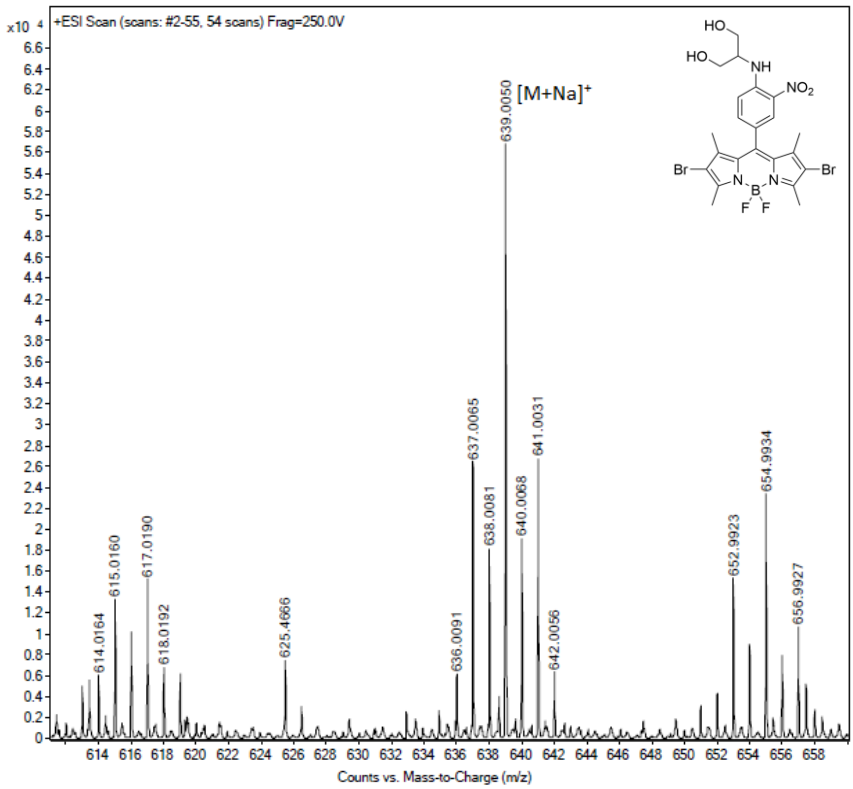

Figure S200: Zoom in from HRMS spectrum (ESI+) of BODIPY **42**.

2,6-Dibromo-8-[2,3,5,6-tetrafluoro-4-(1'-thio-β-D-glucosyl)phenyl]-1,3,5,7-tetramethyl-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (**45**):

BODIPY **45** was prepared according to the general synthetic procedure. BODIPY **43** (100 mg, 0.17 mmol) and NBS (75 mg, 0.42 mmol) were dissolved in HFIP. After column chromatography (silica gel, DCM/MeOH = 9/1, v/v) and recrystallization (MeOH/*n*-hexane) BODIPY **45** was obtained as a dark yellow solid (79 mg, 0.11 mmol, 62 %).

^{1}H NMR (500 MHz, THF-d$_8$): δ (ppm) = 1.69 (s, 6H, Me), 2.58 (s, 6H, Me), 3.21 (dd, *J* = 5.4, 2.6 Hz, 1H, 5´-H), 3.26–3.29 (m, 2H, 2´-H + 3´-H + 4´-H), 3.50 (dd, *J* = 11.7, 5.3 Hz, 1H, 6´-H), 3.67 (dd, *J* = 11.7, 2.6 Hz, 1H, 6´-H), 4.89–4.90 (m, 1H, 1´-H), 4.91 (s, 1H, OH).

^{13}C NMR (126 MHz, THF-d$_8$): δ (ppm) = 13.3 (Me), 14.1 (Me), 62.9 (6´-C), 71.5 (2´-C), 76.3 (4´-C), 79.97 (3´-C), 82.9 (5´-C), 85.7 (1´-C), 113.4 (C_{Br}), 117.1 (Ar-C_{ipso}), 130.9 ($C_{pyrrole}$), 140.6 ($C_{pyrrole}$), 157.0 ($C_{pyrrole}$).

^{19}F NMR (376 MHz, THF-d$_8$): δ (ppm) = -131.51 (dd, *J* = 24.2, 10.3 Hz, 2F, CF_{ortho}), -142.80 (dd, *J* = 24.1, 10.7 Hz, 2F, CF_{meta}), -146.07 – -146.32 (m_C, 2F, BF_2).

HRMS (ESI-TOF): *m/z* calcd. for $C_{25}H_{23}BBr_2F_6N_2O_5SNa^+$ $[M+Na]^+$: 770.9563, found: 770.9560, *m/z* calcd. for $C_{50}H_{46}B_2Br_4F_{12}N_4O_{10}S_2Na^+$ $[2M+Na]^+$: 1518.9235, found: 1518.9218.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3349 [ν(OH), 2924 [ν(Me)], 1634 [ν(C=C)], 1468 [δ(Me)], 1176 and 1117 [ν(BF), ν(CBr)], 773 [δ(-HC=CH-)].

UV/Vis (DCM): λ_{max} (nm) [log (ε/L mol^{-1} cm^{-1})] = 544 [4.63].

Fluorescence (DCM): λ_{max} (nm) = 564 at $\lambda_{Excitation}$ (nm) = 530.

M.P. (°C): 162–169.

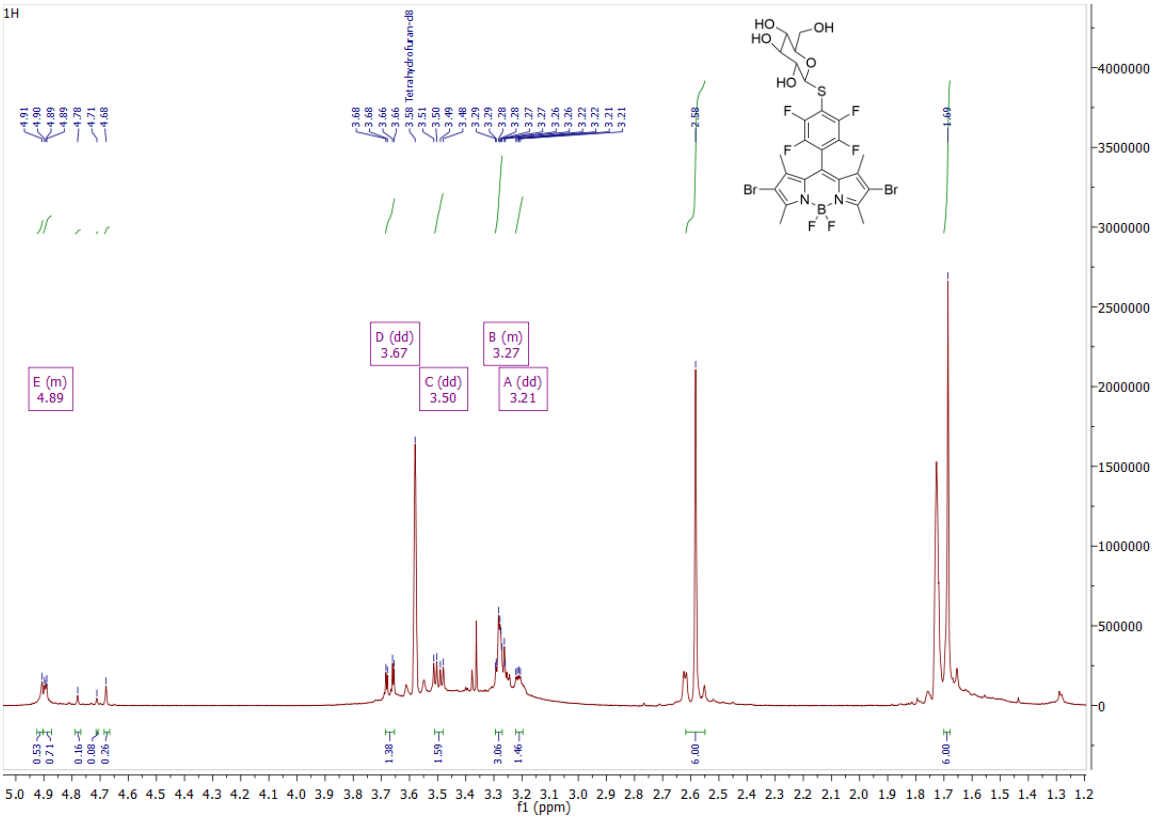

Figure S201: ^{1}H NMR (500 MHz, THF-d$_8$) spectrum of BODIPY **45**.

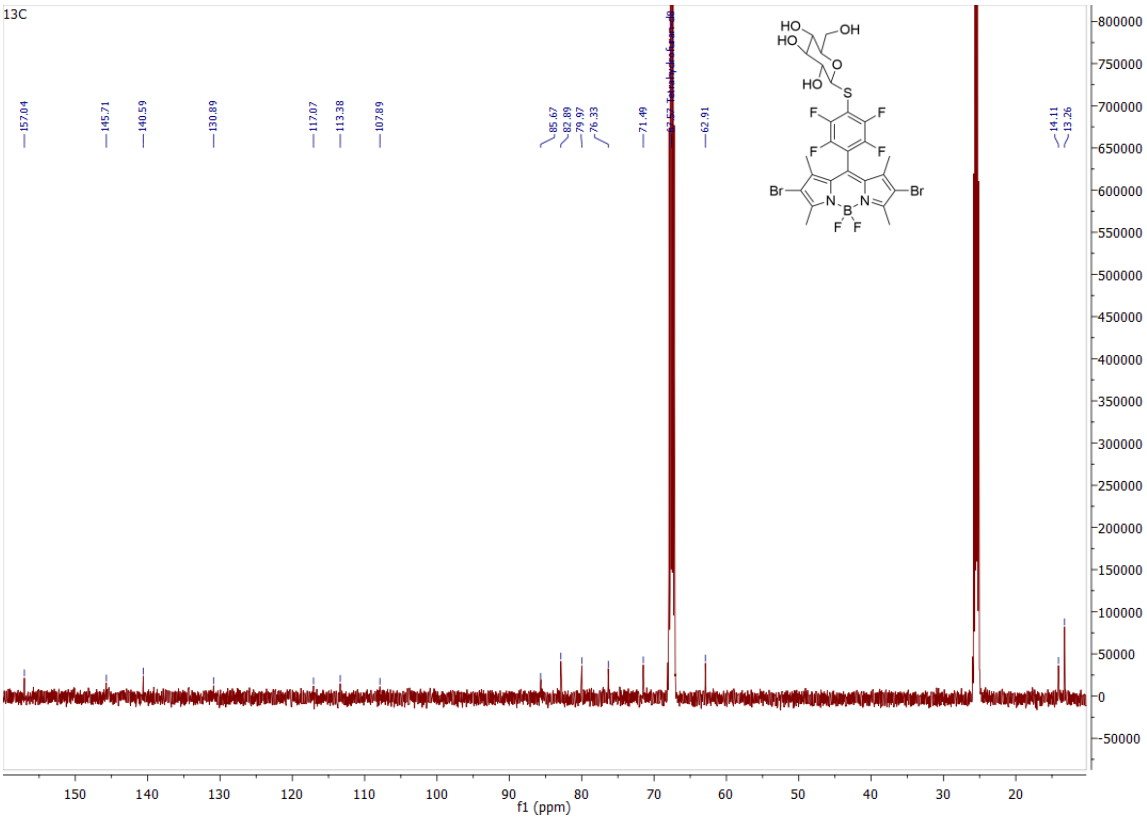

Figure S202: ^{13}C NMR (126 MHz, THF-d_8) spectrum of BODIPY **45**.

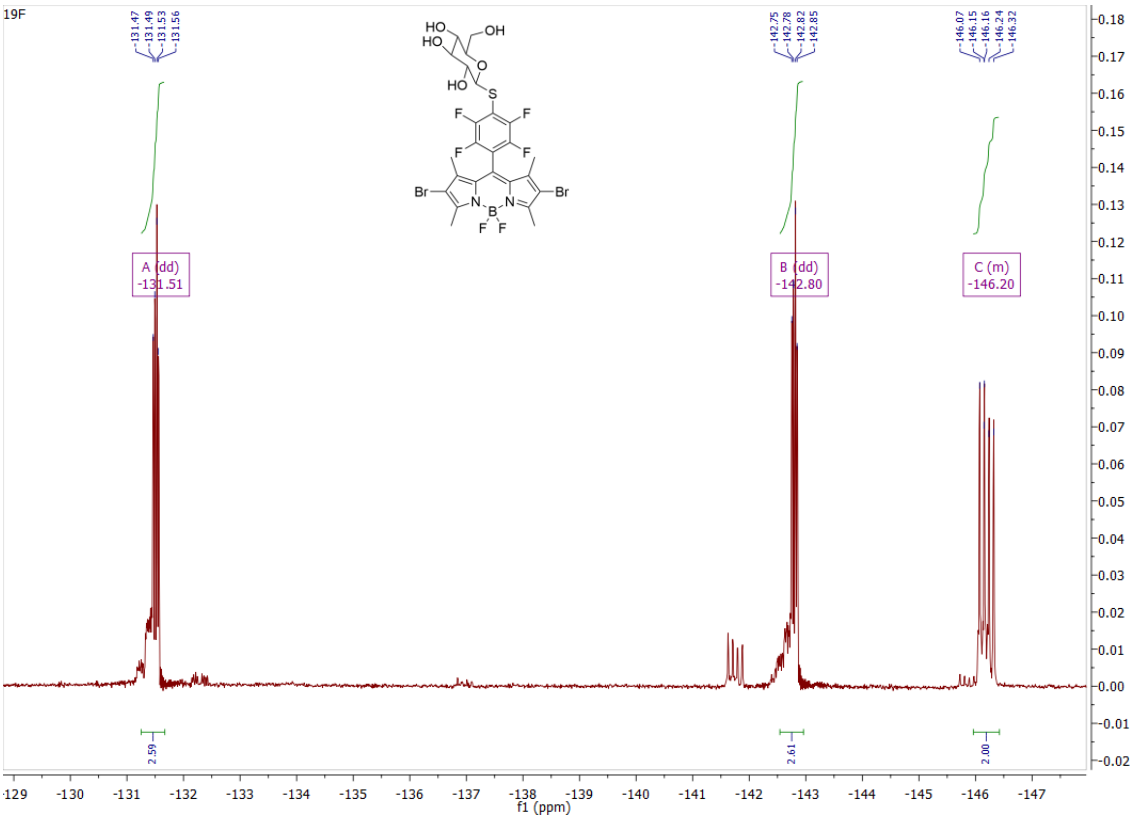

Figure S203: ^{19}F NMR (376 MHz, THF-d_8) spectrum of BODIPY **45**.

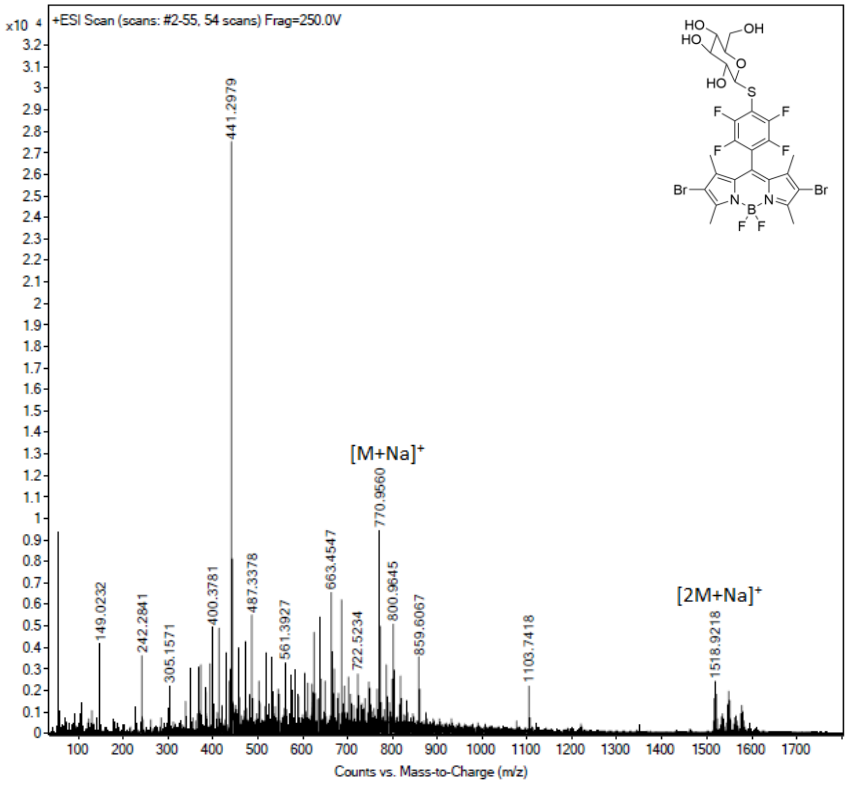

Figure S204: HRMS spectrum (ESI+) of BODIPY **45**.

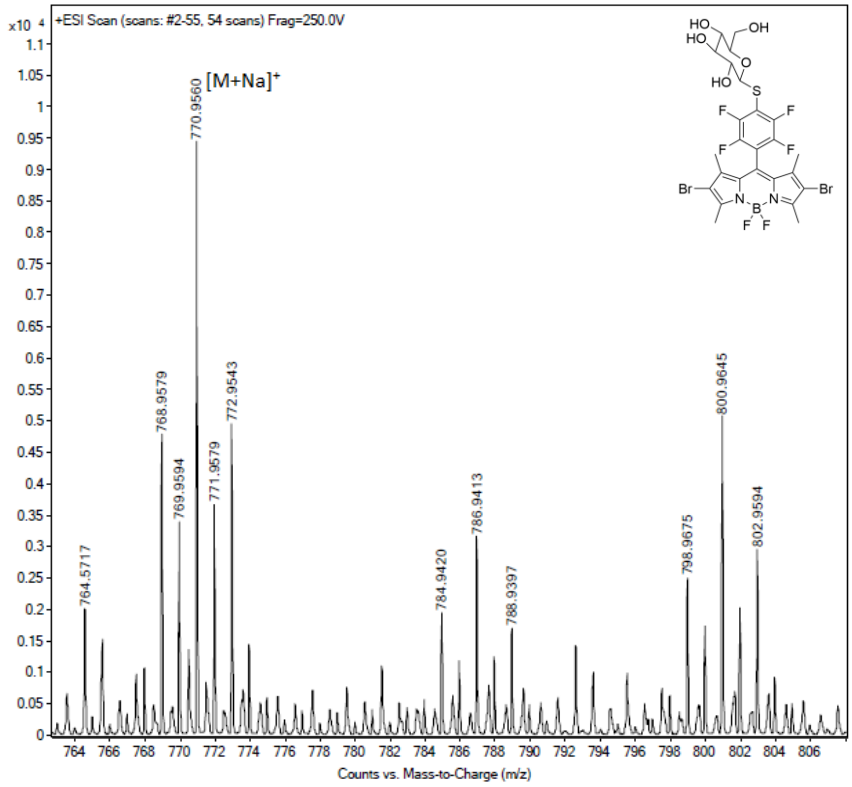

Figure S205: Zoom in from HRMS spectrum (ESI+) of BODIPY **45**.

2,6-Dibromo-8-[2,3,5,6-tetrafluoro-4-(1'-thio-β-D-galactosyl)phenyl]-1,3,5,7-tetramethyl-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (**46**):

BODIPY **46** was prepared according to the general synthetic procedure. BODIPY **44** (100 mg, 0.17 mmol) and NBS (75 mg, 0.42 mmol) were dissolved in HFIP. After column chromatography (silica gel, DCM/MeOH = 9/1, v/v) and recrystallization (MeOH/*n*-hexane) BODIPY **46** was obtained as a dark yellow solid (73 mg, 98 µmol, 58 %).

^{1}H NMR (500 MHz, THF-d_8): δ (ppm) = 1.68 (s, 6H, Me), 2.58 (s, 6H, Me), 3.38 (dd, *J* = 8.5, 3.7 Hz, 1H, 3´-H), 3.45 (t, *J* = 6.0 Hz, 1H, 5´-H), 3.47 (dd, *J* = 10.6, 5.6 Hz, 1H, 6´-H), 3.50 (dd, *J* = 10.6, 6.0 Hz, 1H, 6´-H), 3.59–3.61 (m, 2H, 4´-H, 6´-H), 3.83 (d, *J* = 2.7 Hz, 1H, 2´-H), 4.79 (d, *J* = 9.3 Hz, 1H, 1´-H).

^{13}C NMR (126 MHz, THF-d_8): δ (ppm) = 13.3 (Me), 14.1 (Me), 62.1 (6´-C), 70.0 (2´-C), 73.4 (4´-C), 76.5 (3´-C), 81.4 (5´-C), 86.2 (1´-C), 113.3–113.4 (m, C_{Br}), 114.00 (t, *J* = 18.3 Hz, Ar-C_{ipso}), 116.90 (t, *J* = 20.6 Hz, Ar-C_{para}), 125.9 (C_{meso}), 130.9 ($C_{pyrrole}$), 140.6 ($C_{pyrrole}$), 144.33 (dd, *J* = 247.6, 18.1 Hz, Ar-C_{meta}), 149.27 (dd, *J* = 246.0, 14.9 Hz, Ar-C_{ortho}), 157.0 ($C_{pyrrole}$).

^{19}F NMR (376 MHz, THF-d_8): δ (ppm) = -131.09 (dd, *J* = 25.2, 11.9 Hz, 2F, CF_{ortho}), -142.89 (dd, *J* = 24.3, 10.8 Hz, 2F, CF_{meta}), -146.07 – -146.32 (m_C, 2F, BF_2).

HRMS (ESI-TOF): *m/z* calcd. for $C_{25}H_{23}BBr_2F_6N_2O_5SNa^+$ $[M+Na]^+$: 770.9563, found: 770.9550, *m/z* calcd. for $C_{50}H_{46}B_2Br_4F_{12}N_4O_{10}S_2Na^+$ $[2M+Na]^+$: 1518.9235, found: 1518.9208.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3386 [ν(OH), 2924 [ν(Me)], 1634 [ν(C=C)], 1489 [δ(Me)], 1173 and 1119 [ν(BF), ν(CBr)], 773 [δ(-HC=CH-)].

UV/Vis (DCM): λ_{max} (nm) [log (ε/L mol^{-1} cm^{-1})] = 393 [3.96], 544 [4.83].

Fluorescence (DCM): λ_{max} (nm) = 564 at $\lambda_{Excitation}$ (nm) = 380, 530.

M.P. (°C): 173–180.

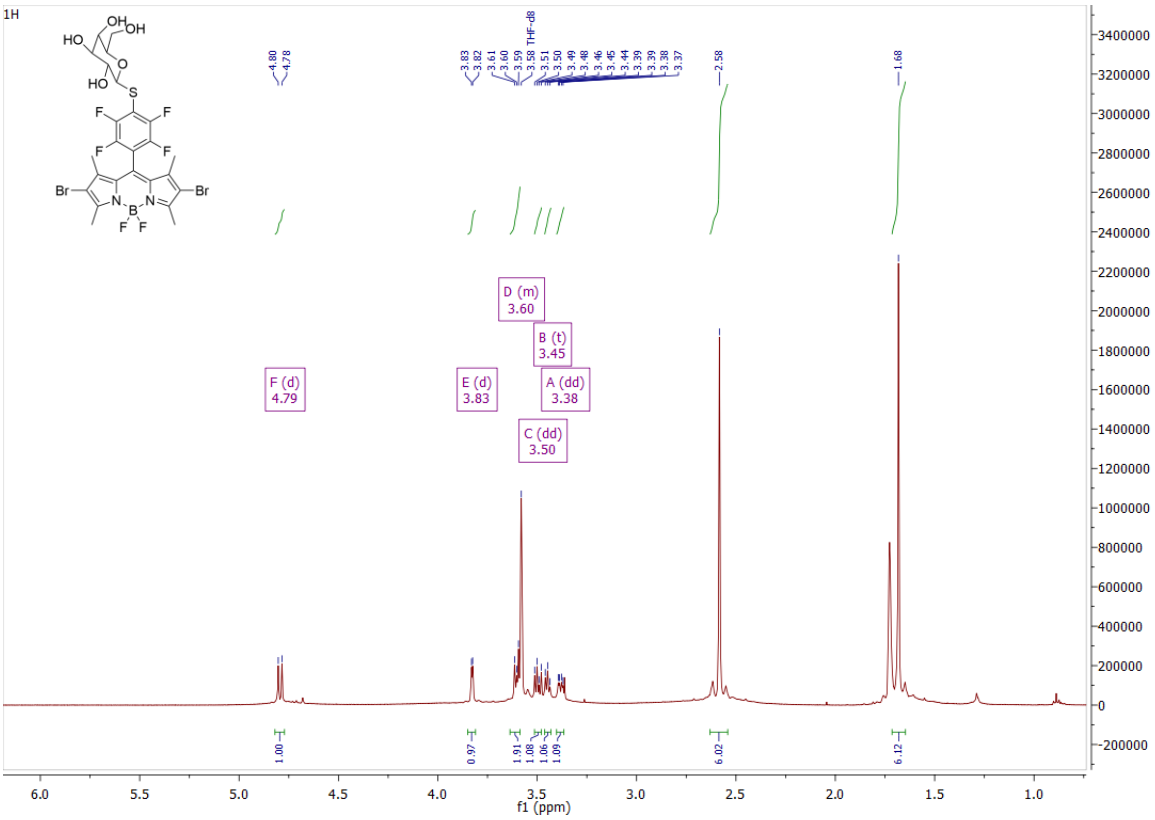

Figure S206: ^{1}H NMR (500 MHz, THF-d_8) spectrum of BODIPY **46**.

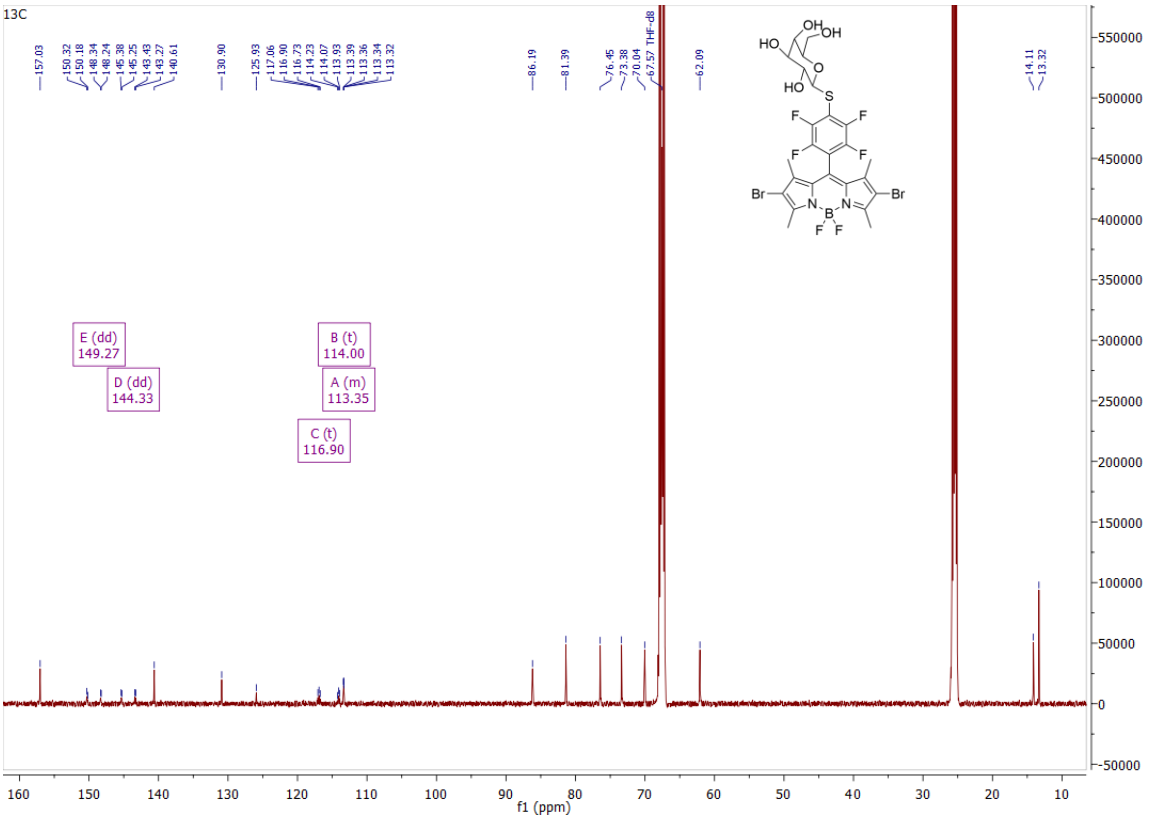

Figure S207: ^{13}C NMR (126 MHz, THF-d_8) spectrum of BODIPY **46**.

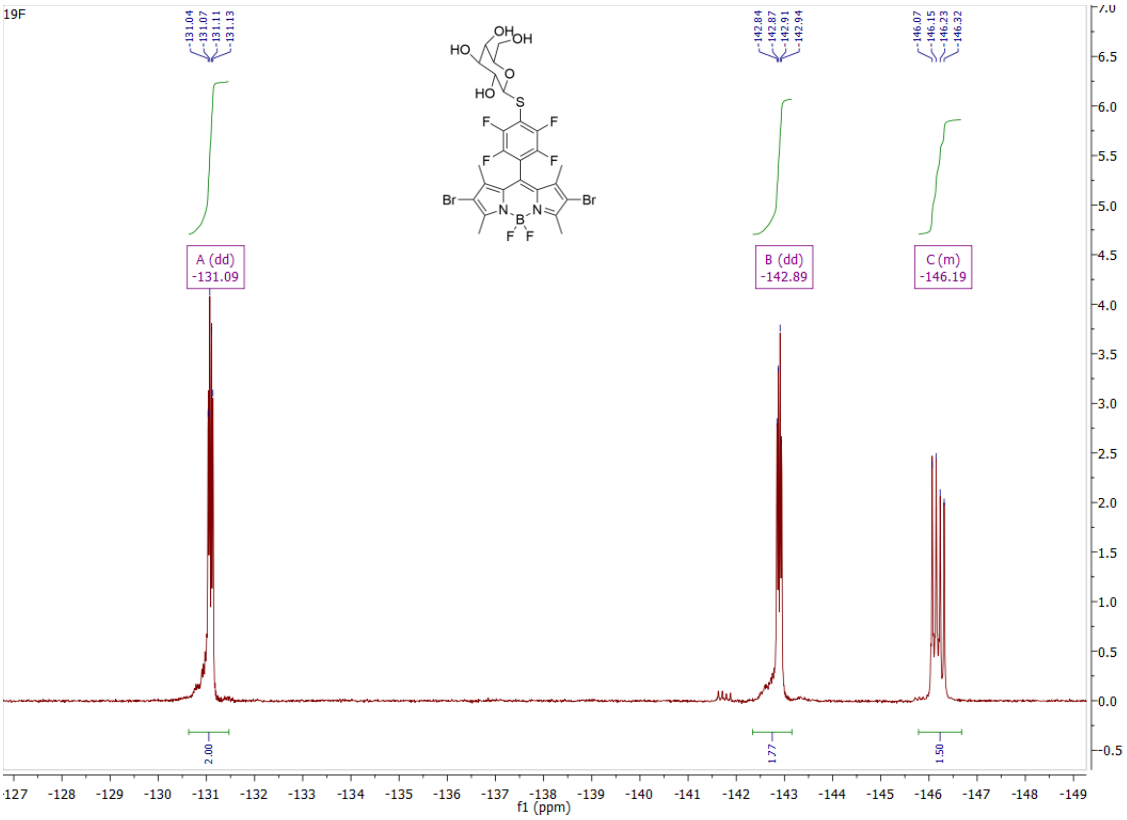

Figure S208: ^{19}F NMR (376 MHz, THF-d_8) spectrum of BODIPY **46**.

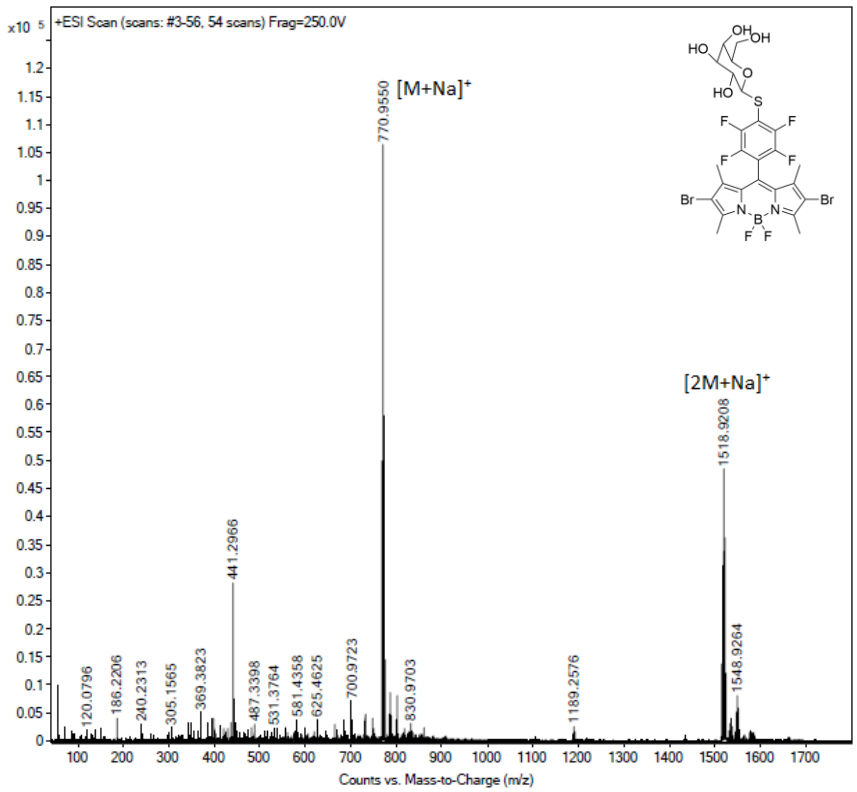

Figure S209: HRMS spectrum (ESI+) of BODIPY **46**.

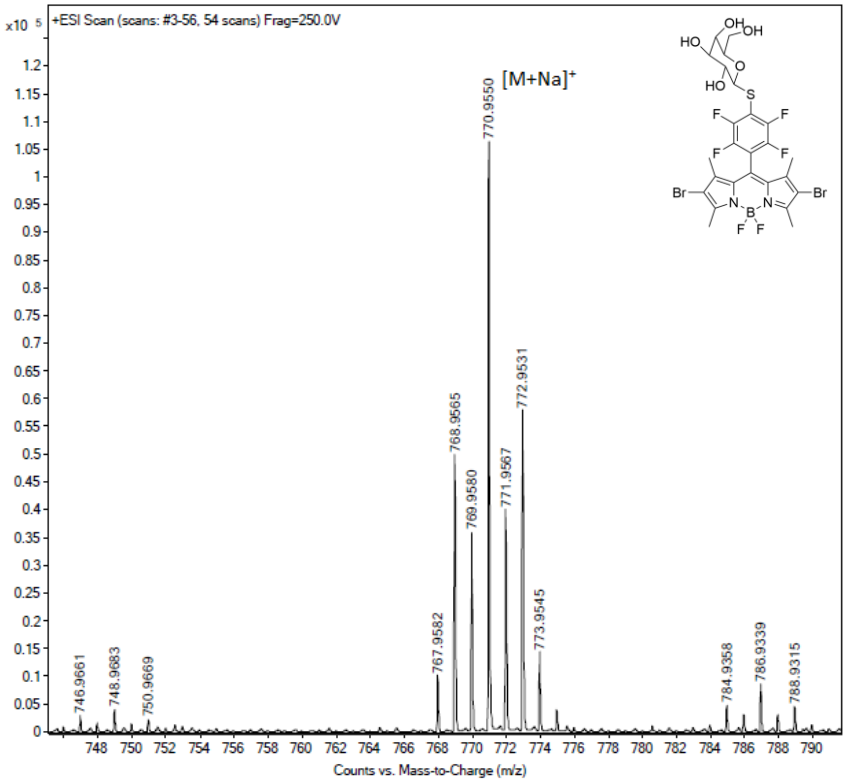

Figure S210: Zoom in from HRMS spectrum (ESI+) of BODIPY **46**.

2,6-Dibromo-8-[3-nitro-4-(1'-thio-β-D-glucosyl)phenyl]-1,3,5,7-tetramethyl-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (**49**):

BODIPY **49** was prepared according to the general synthetic procedure. BODIPY **47** (100 mg, 0.18 mmol) and NBS (79 mg, 0.44 mmol) were dissolved in HFIP. After column chromatography (silica gel, DCM/MeOH = 9/1, v/v) BODIPY **49** was obtained as a red-orange solid (44 mg, 61 mmol, 35 %).

^{1}H NMR (500 MHz, THF-d$_8$): δ (ppm) = 1.50 (d, *J* = 6.1 Hz, 6H, Me), 2.57 (s, 6H, Me), 3.34–3.38 (m, 3H, 2´-H + 3´-H + 4´-H), 3.43 (ddd, *J* = 8.6, 5.7, 2.1 Hz, 1H, 5´-H), 3.56 (d, *J* = 7.1 Hz, 1H, 6´-H), 3.81 (dd, *J* = 11.9, 2.5 Hz, 1H, 6´-H), 4.57 (br s, 1H, OH), 4.81 (br s, 1H, OH), 4.90–4.92 (m, 1H, 1´-H), 5.06 (br s, 1H, OH), 7.66 (dd, *J* = 8.3, 2.0 Hz, 1H, Ar-H$_{meta}$), 8.16 (d, *J* = 8.3 Hz, 1H, Ar-H$_{ortho}$), 8.26 (d, *J* = 2.0 Hz, 1H, Ar-H$_{ortho}$).

^{13}C NMR (126 MHz, THF-d$_8$): δ (ppm) = 13.9 (Me), 14.8 (Me), 63.1 (6´-C), 71.3 (4´-C), 73.96 (2´-C), 80.3 (3´-C), 83.3 (5´-C), 86.6 (1´-C), 112.6 (C$_{Br}$), 126.6 (Ar-C$_{ortho}$), 131.5 (Ar-C$_{meta}$), 132.4 (C$_{pyrrole}$), 134.3 (Ar-C$_{ortho}$), 139.3 (Ar-C$_{para}$), 140.5*, 141.2 (C$_{pyrrole}$), 141.3*, 148.5 (C$_{meso}$), 155.4 (C$_{pyrrole}$). *These signals could not be assigned exactly to corresponding carbon atoms. They belong to the Ar-C$_{ipso}$ and the Ar-C$_{nitro}$ of the aryl residue.

^{19}F NMR (376 MHz, THF-d$_8$): δ (ppm) = -146.46 – -146.22 (m$_c$, 2F, BF$_2$).

HRMS (ESI-TOF): *m/z* calcd. for $C_{25}H_{26}BBr_2F_2N_3O_7SNa^+$ $[M+Na]^+$: 743.9791, found: 743.9789.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3371 [ν(OH), 1608 [ν(C=C)], 1541 [$\nu_{as}(NO_2)$], 1461 [δ(Me)], 1346 [$\nu_{sym}(NO_2)$], 1176 and 1101 [ν(BF), ν(CBr)].

UV/Vis (MeOH): λ_{max} (nm) [log (ε/L mol^{-1} cm^{-1})] = 372 [4.04], 530 [4.72].

Fluorescence (DCM): λ_{max} (nm) = 549 at $\lambda_{Excitation}$ (nm) = 310, 520.

M.P.(°C): >250.

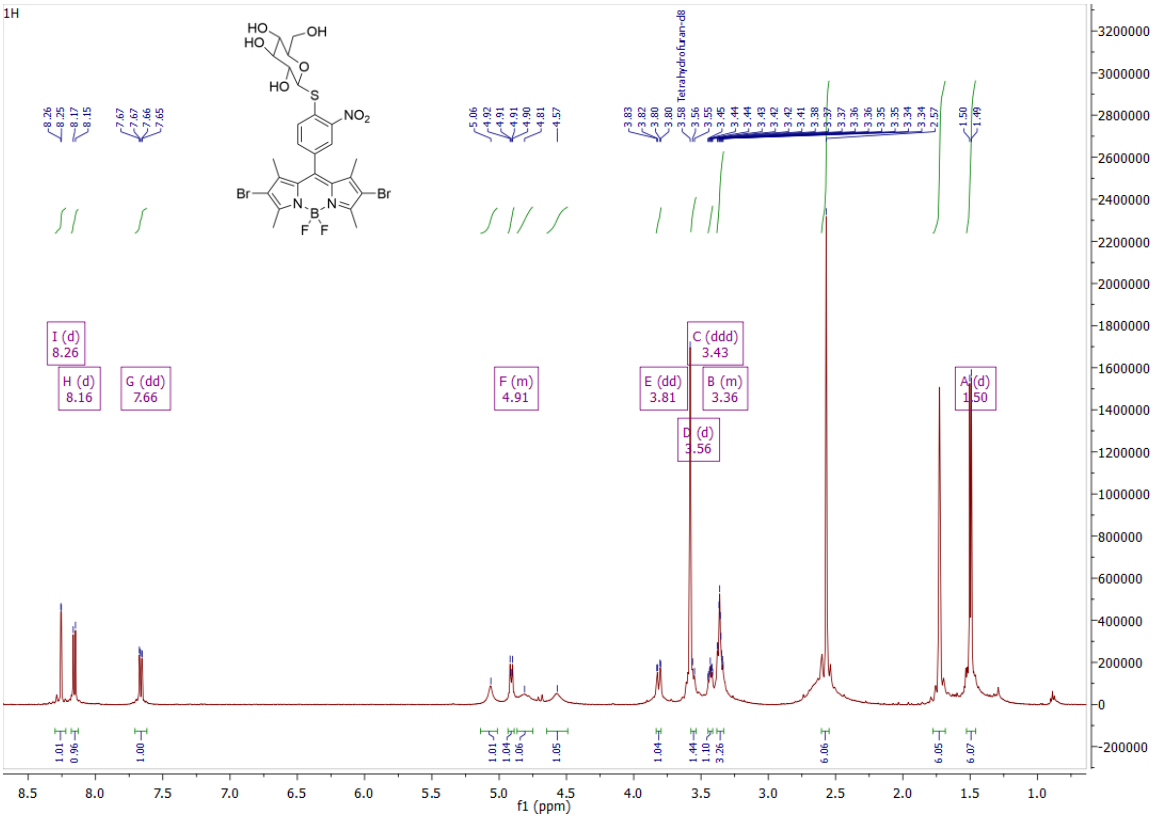

Figure S211: ^{1}H NMR (500 MHz, THF-d_8) spectrum of BODIPY **49**.

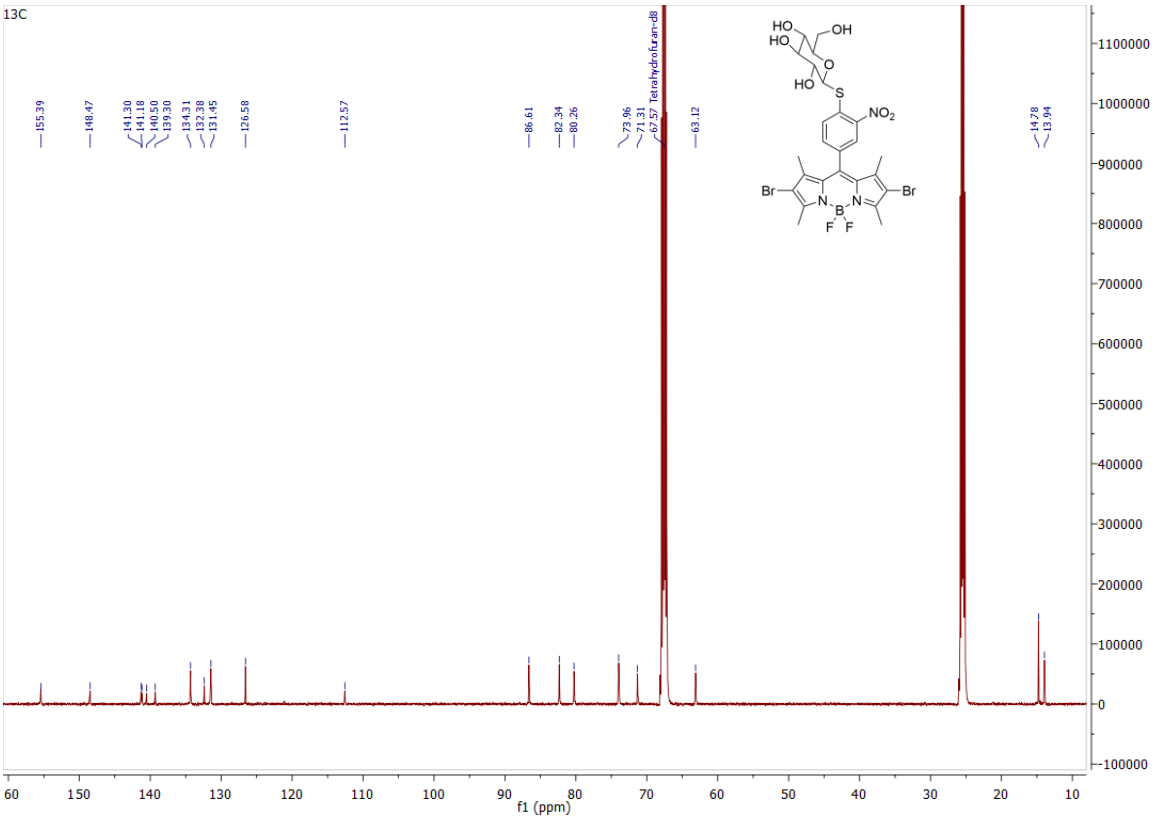

Figure S212: ^{13}C NMR (126 MHz, THF-d_8) spectrum of BODIPY **49**.

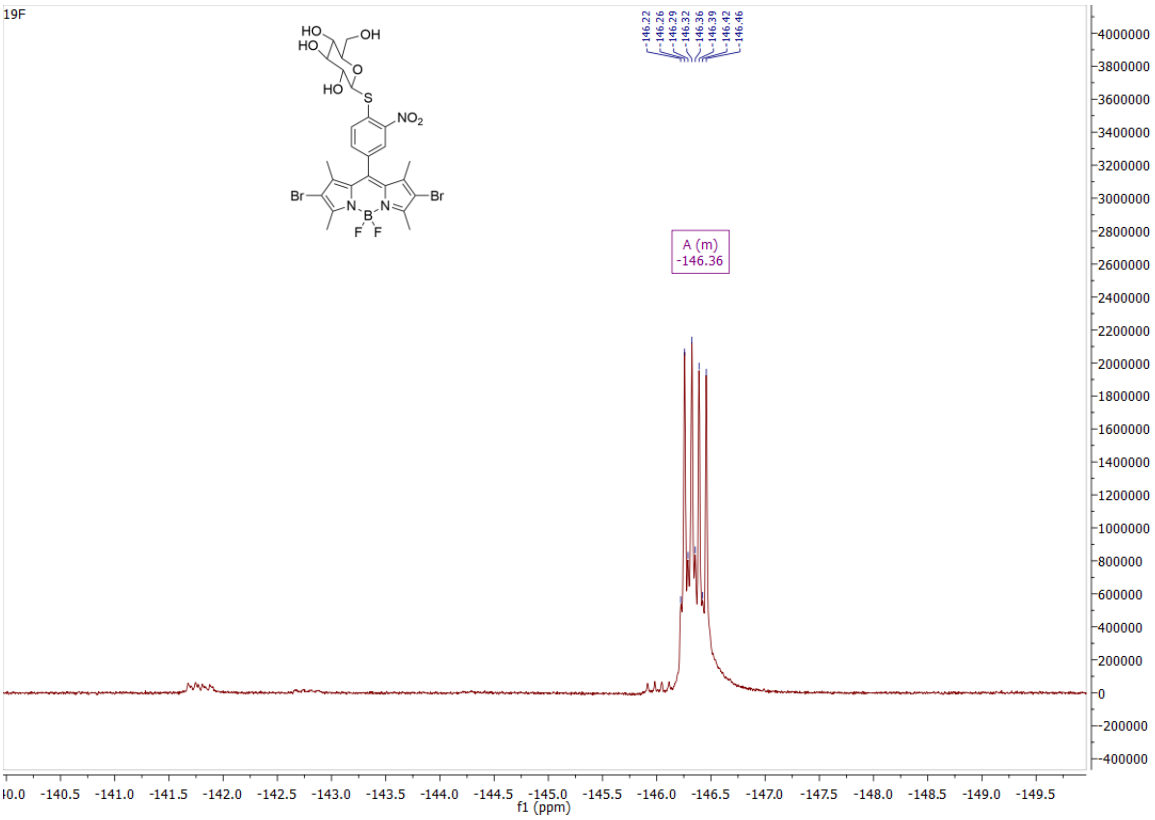

Figure S213: ^{19}F NMR (376 MHz, THF-d_8) spectrum of BODIPY **49**.

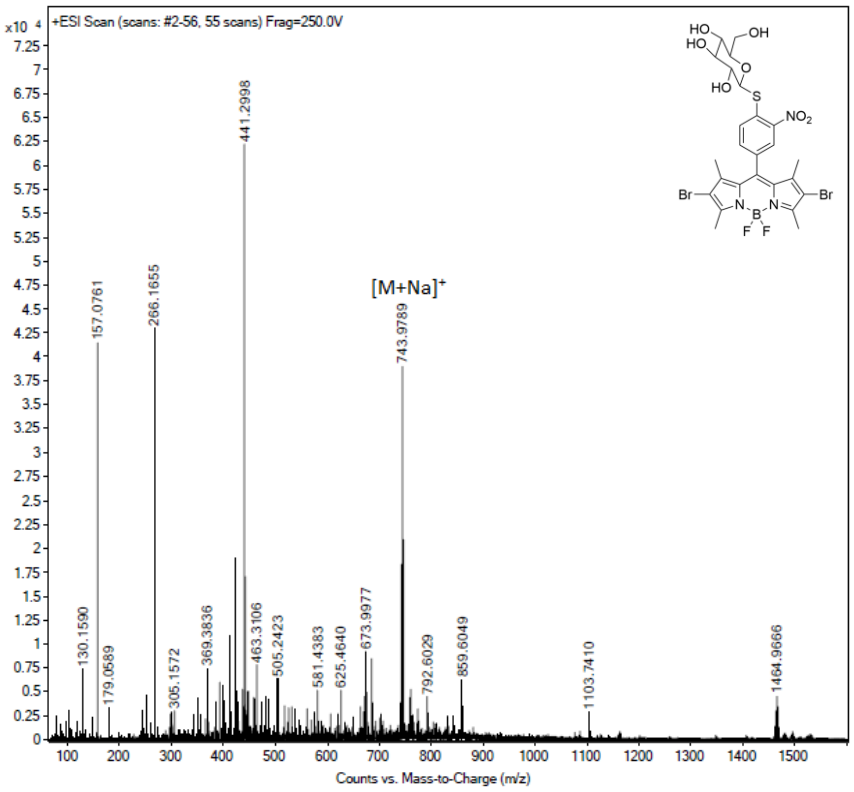

Figure S214: HRMS spectrum (ESI+) of BODIPY **49**.

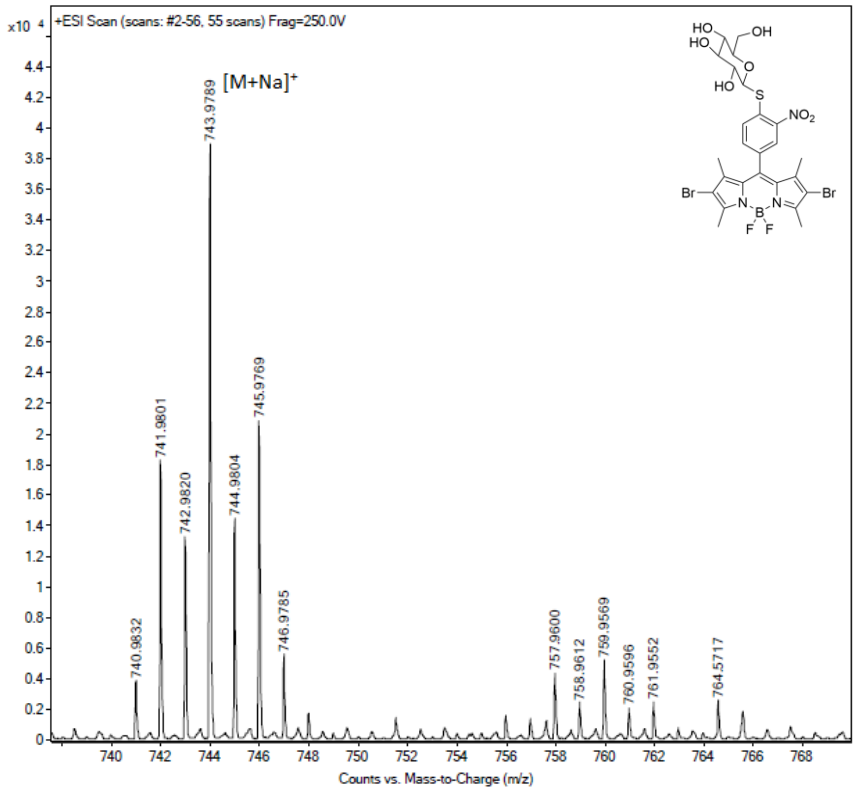

Figure S215: Zoom in from HRMS spectrum (ESI+) of BODIPY **49**.

2,6-Dibromo-8-[3-nitro-4-(1'-thio-β-D-galactosyl)phenyl]-1,3,5,7-tetramethyl-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (**50**):

BODIPY **50** was prepared according to the general synthetic procedure. BODIPY **48** (100 mg, 0.18 mmol) and NBS (79 mg, 0.44 mmol) were dissolved in HFIP. After column chromatography (silica gel, DCM/MeOH = 9/1, v/v) BODIPY **50** was obtained as a red solid (58 mg, 80 µmol, 45 %).

^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) = 1.40 (s, 6H, Me), 2.47 (s, 6H, Me), 3.39–3.46 (m, 3H, 3´-H + 6´-H + H_2O), 3.54–3.62 (m, 3H, 2´-H + 5´-H + H_2O), 3.72 (br s, 1H, 4´-H), 4.90 (d, J = 9.4 Hz, 1H, 1´-H), 7.73 (d, J = 7.0 Hz, 1H, Ar-H_{ortho}), 8.03 (d, J = 8.0 Hz, 1H, Ar-H_{meta}), 8.27 (br s, 1H, Ar-H_{ortho}).

^{13}C NMR (126 MHz, DMSO-d_6): δ (ppm) = 13.5 (Me), 14.1 (Me), 60.3 (6´-C), 68.2 (4´-C), 69.1 (2´-C), 74.6 (3´-C), 79.2 (5´-C), 84.9 (1´-C), 111.5–111.6 (m, C_{Br}), 125.4 (Ar-C_{ortho}), 129.9*, 130.1 (Ar-C_{meta}), 130.3 ($C_{pyrrole}$), 133.3 (Ar-C_{ortho}), 136.99*, 139.4 (Ar-C_{para}), 140.2 ($C_{pyrrole}$), 146.8 (C_{meso}), 153.7 ($C_{pyrrole}$).*These signals could not be assigned exactly to corresponding carbon atoms. They belong to the Ar-C_{ipso} and the Ar-C_{nitro} of the aryl residue.

^{19}F NMR (376 MHz, DMSO-d_6): δ (ppm) = -143.39 – -143.15 (m_c, 2F, BF_2).

HRMS (ESI-TOF): *m/z* calcd. for $C_{25}H_{26}BBr_2F_2N_3O_7SNa^+$ $[M+Na]^+$: 743.9791, found: 743.9849.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3375 [ν(OH), 2925 [ν(Me)], 1610 [ν(C=C)], 1540 [$\nu_{as}(NO_2)$], 1461 [δ(Me)], 1345 [$\nu_{sym}(NO_2)$], 1173 and 1112 [ν(BF), ν(CBr)].

UV/Vis (MeOH): λ_{max} (nm) [log (ε/L mol^{-1} cm^{-1})] = 371 [4.08], 530 [4.80].

Fluorescence (DCM): λ_{max} (nm) = 548 at $\lambda_{Excitation}$ (nm) = 360, 510.

M.P.(°C): >250.

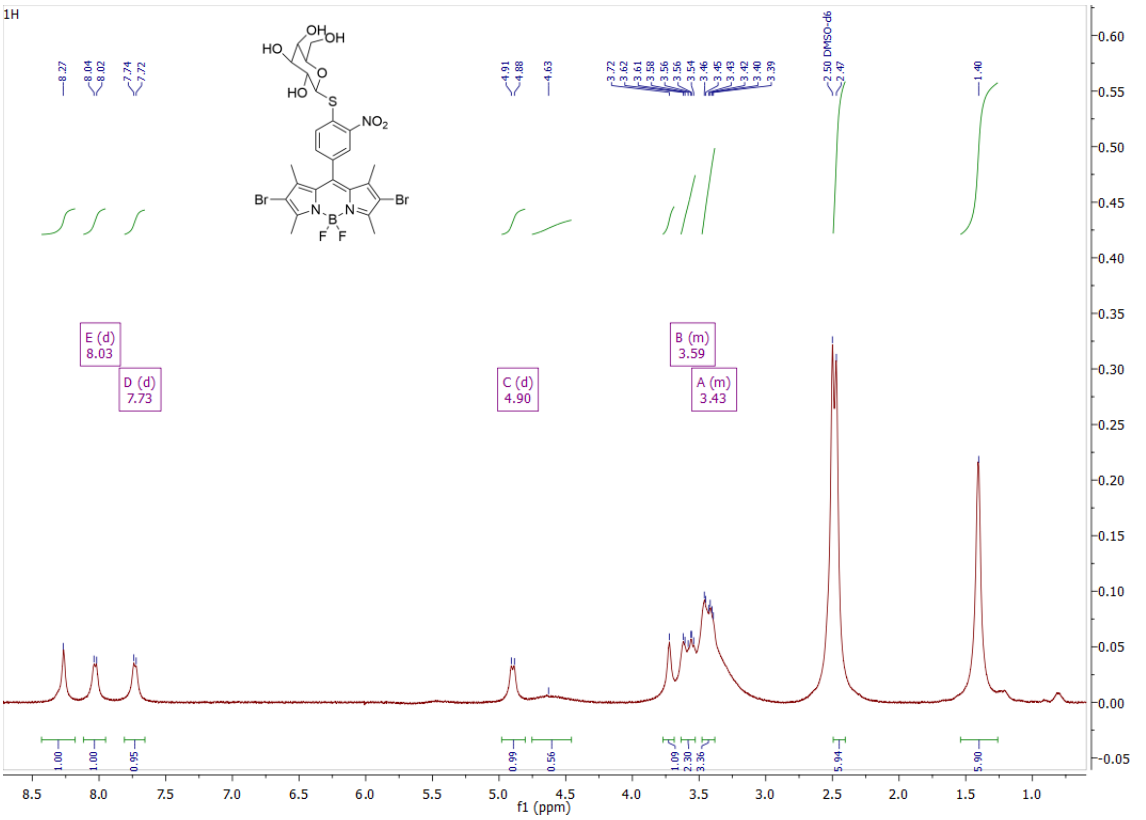

Figure S216: ^{1}H NMR (500 MHz, DMSO-d_6) spectrum of BODIPY **50**.

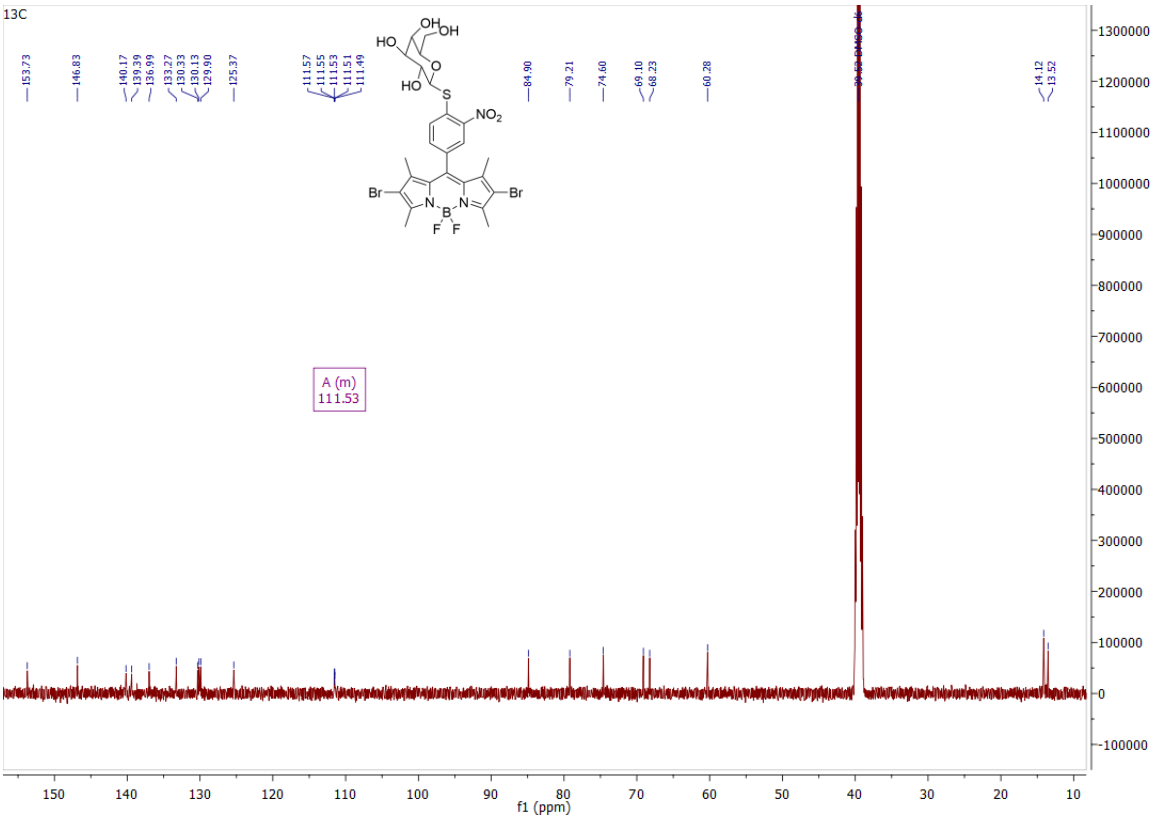

Figure S217: ^{13}C NMR (126 MHz, DMSO-d_6) spectrum of BODIPY **50**.

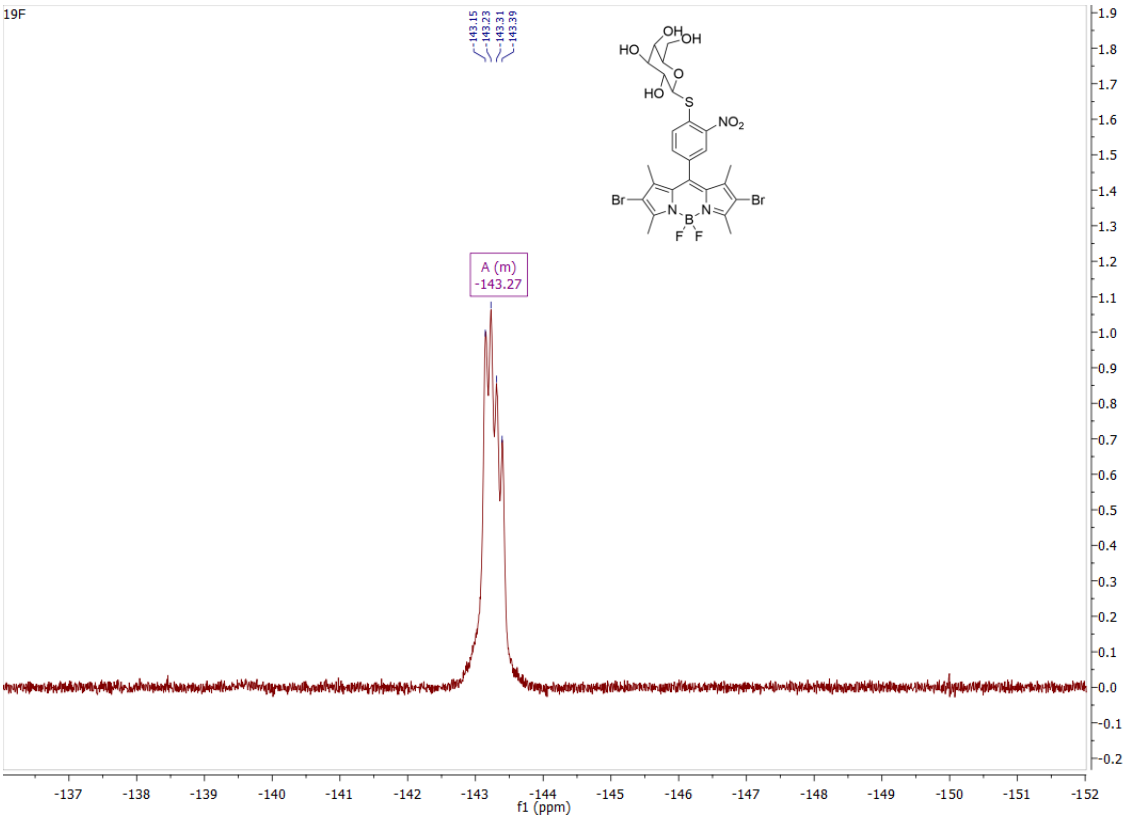

Figure S218: ^{19}F NMR (376 MHz, DMSO-d_6) spectrum of BODIPY **50**.

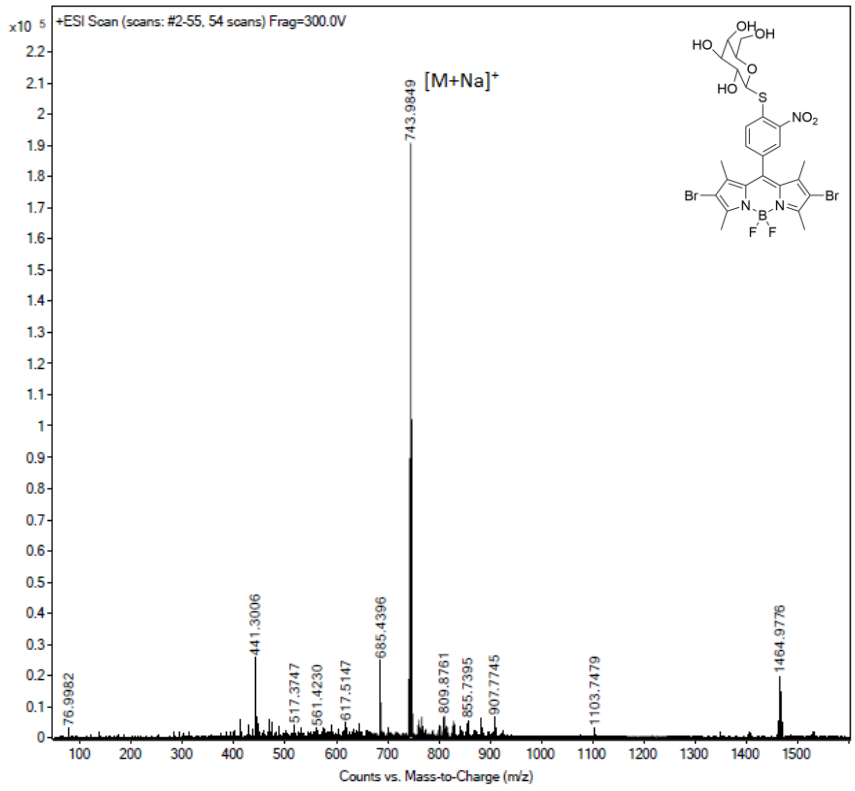

Figure S219: HRMS spectrum (ESI+) of BODIPY **50**.

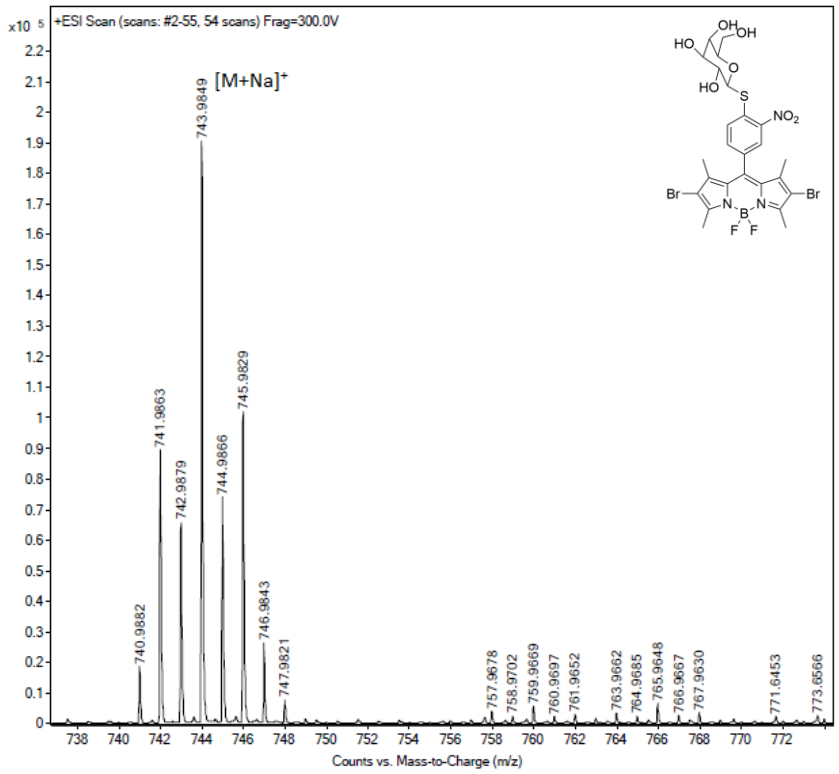

Figure S220: Zoom in from HRMS spectrum (ESI+) of BODIPY **50**.

14. References

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