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Synthesis and Regioselective Functionalization of Perhalogenated BODIPYs

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1. Experimental Section

1.1 General

Reagents and solvents used were purchased from Sigma-Aldrich, Fisher Scientific or VWR and used without further purification. To monitor reactions, 0.2 mm silica gel plates (254 indicator, polyester backed, 60Å, precoated) and UV lamp (UVGL-58, UVP) were used. Liquid chromatography was performed using preparative TLC plates (60G, f254, VWR) or silica gel for column chromatography (60Å, 230-400 mesh, Sorbent Technologies). All the NMR spectra were obtained on a Bruker AV-400 nanobay, an AV-400 liquid, or an AV-500 spectrometer at room temperature, at the LSU NMR Facility. Chemical shifts (δ) are given in parts per million (ppm) in $CDCl_3$ (7.27 ppm for ^{1}H NMR and 77.0 ppm for ^{13}C NMR); coupling constants (J) are reported in Hz. High-resolution mass spectra (HRMS) were obtained on a 6210 ESI-TOF Mass Spectrometer (Agilent Technologies) at the LSU Mass Spectrometry Facility.

1.2 Spectroscopic Methods

UV-Visible spectra and fluorescence spectra were recorded using a Varian Cary spectrophotometer and a Perkin Elmer LS55 spectrophotometer at room temperature. Quartz cuvettes (10 mm path length) and ACS grade solvents were used for both measurements. For the determination of quantum yields, dilute solutions with different absorbance between 0.02-0.08 at the particular excitation wavelength were used. Molar absorption coefficients (ε) was determined from the plots of integrated absorbance vs concentrations. Rhodamine B in methanol (0.4)[1], crystal violet perchlorate in methanol (0.55 in methanol)[2], and methylene blue (0.03 in methanol)[2] were used as external standards for all the BODIPY derivatives. The following equation was used for the calculations of the relative fluorescence quantum yields (Φ_f)[3]:

$$\Phi_s = \Phi_{st} \times (Grad_x/Grand_{st}) \times (n_x^2/n_{st}^2)$$

where Φ and n are the fluorescence quantum yields and refractive indexes, respectively; Grad represents gradient of integrated fluorescence intensity vs absorbance at the particular wavelength, subscripts s and x refer to the standards and the tested samples.

1.3 X-ray methods: Crystal structures of **1b**, **2b**, **3b**, **4a**, **4b**, **5a** and **5b** were determined from data collected at T=90K using MoKα radiation (CuKα for **5a**) on Bruker Apex-II or Nonius KappaCCD diffractometers. **1b** has 13% Br substituted in the Cl site at the meso position. **4b** has all three thiophenes disordered and **5b** has 4 of the 5 thiophenes disordered. **5a** has two independent molecules, one of which has all phenyl groups ordered while the other has 4 of the 5 disordered. *Crystal data*: **1b**, $C_9BBr_{6.13}Cl_{0.87}F_2N_2$, monoclinic, a = 8.4388(3), b = 8.4196(2), c = 21.5892(6) Å, β = 99.574(2)°, space group $P2_1$/n, Z = 4, 29024 reflections measured, θ_{max} = 36.4°, 7099 unique (R_{int} = 0.036), which were used in all calculations, final R = 0.028 (5672 I>2σ(I) data), w$R(F^2)$ 0.057 (all data), CCDC 1453168; **2b**, $C_9BBr_4Cl_3F_2N_2$, monoclinic, a = 8.3531(5), b = 8.5259(5), c = 20.7030(15) Å, β = 99.009(5)°, space group $P2_1$/n, Z = 4, 39613 reflections measured, θ_{max} = 40.0°, 9029 unique (R_{int} = 0.036), final R = 0.030 (7111 I>2σ(I) data), w$R(F^2)$ 0.055 (all data) , CCDC 1453169; **3b**, $C_9BBr_2Cl_5F_2N_2$, triclinic, a = 8.775(2), b = 9.170(3), c = 9.710(3) Å, α = 98.378(17), β = 106.86(2), γ = 105.71(2)°, space group P-1, Z = 2, 6598 reflections measured, θ_{max} = 28.3°, 3450 unique (R_{int} = 0.025), final R = 0.035 (2962 I>2σ(I) data), w$R(F^2)$ 0.086 (all data), CCDC 1453170; **4a**, $C_{27}H_{15}BCl_4F_2N_2$, monoclinic, a = 12.0397(3), b = 9.5581(2), c = 21.4720(5) Å, β = 105.7660(10)°, space group $P2_1$/n, Z = 4, 22356 reflections measured, θ_{max} = 28.7°, 6116 unique (R_{int} = 0.043), final R = 0.039 (4471 I>2σ(I) data), w$R(F^2)$ 0.086 (all data) CCDC 1453171; **4b**, $C_{21}H_9BCl_4F_2N_2S_3$, triclinic, a = 10.0519(9), b = 10.7177(9), c = 11.8528(10) Å, α =

102.040(4), β = 91.199(4), γ = 91.199(4)°, space group *P*-1, *Z* = 2, 36429 reflections measured, θ_{max} = 33.2°, 8575 unique (R_{int} = 0.029), final R = 0.042 (7372 I>2σ(I) data), w$R(F^2)$ 0.132 (all data), CCDC 1453172; **5a**, $C_{39}H_{25}BCl_2F_2N_2$, monoclinic, *a* = 26.1253(10), *b* = 12.6428(5), *c* = 18.6230(7) Å, β = 91.840(2)°, space group $P2_1/c$, *Z* = 8, 34476 reflections measured, θ_{max} = 61.0°, 9079 unique (R_{int} = 0.039), final R = 0.044 (7087 I>2σ(I) data), w$R(F^2)$ 0.117 (all data), CCDC 1453173; **5b**, $C_{29}H_{15}BCl_2F_2N_2S_5$, monoclinic, *a* = 9.9110(2), *b* = 24.3651(5), *c* = 12.2192(3) Å, β = 110.9070(10)°, space group $P2_1/c$, *Z* = 4, 41084 reflections measured, θ_{max} = 28.4°, 6904 unique (R_{int} = 0.038), final R = 0.114 (5832 I>2σ(I) data), w$R(F^2)$ 0.296 (all data), CCDC 1453174.

1.4 Synthesis and characterization of BODIPYs

BODIPY **1-3a** were synthesized according to a published procedure.[4]

General procedure for BODIPY 3a-b:

BODIPY **1-3a** (0.1 mmol) was dissolved in 2 ml DCM. Br_2 (1.02ml, 20 mmol) was added into the flask. The mixture was stirred at room temperature overnight. TLC was used to monitor the reaction. The mixture was poured into saturated $Na_2S_2O_3$ (aq) (100 ml) and extracted by CH_2Cl_2 (20 ml* 3). The organic layers were combined and washed with brine then water. The solvent were removed under reduced pressure. The residue was purified by using column chromatography (CH_2Cl_2/Hexanes 1:1 as eluents) to provide the pure compounds.

BODIPY **1b**: Yield: 58 mg, 83%; ^{1}H NMR (400 MHz, $CDCl_3$): no peaks; ^{13}C NMR (125 MHz, $CDCl_3$): 138.1, 134.6, 129.9, 122.5, 118.4; ^{11}B NMR (128 MHz, $CDCl_3$) δ -0.17 (t, $J_{(B,F)}$ = 26.9 Hz); HRMS (ESI-TOF) m/z 692.4972 $[M]^-$; calculated for $C_9BBr_6ClF_2N_2$: 692.4948.

BODIPY **2b:** Yield: 47.6 mg, 78%; ^{1}H NMR (400 MHz, $CDCl_3$): no peaks; ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.6, 132.3, 128.9, 128.7, 119.2; ^{11}B NMR (128 MHz, $CDCl_3$) δ -0.19 (t, $J_{(B,F)}$ = 27.1 Hz); HRMS (ESI-TOF) m/z 604.5946 $[M]^-$; calculated for $C_9BBr_4Cl_3F_2N_2$: 604.5958.

BODIPY **3b:** Yield: 43.8 mg, 84%; ^{1}H NMR (400 MHz, $CDCl_3$): no peaks; ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.5, 138.8, 126.8, 125.4, 119.6; ^{11}B NMR (128 MHz, $CDCl_3$) δ -0.31 (t, $J_{(B,F)}$ = 26.4 Hz); HRMS (ESI-TOF) m/z 516.6980 $[M]^-$; calculated for $C_9BBr_2Cl_5F_2N_2$: 516.6968 .

General procedure for BODIPY 4a-b

BODIPY **3b** (15.7 mg, 0.03 mmol) and $Pd(PPh_3)_4$ (3 mol%) were added into a 25 ml round-bottomed flask. The flask was evacuated and refilled with nitrogen for three times. Toluene (5 ml) and organostananne reagents (0.14 mmol, 4 equiv) were purged into the flask, and the mixture was heated to 90-100 ^oC and stirred for 6 hours. The reaction was stopped when **4a-b** was showed as major products according to TLC. The solvents were removed under reduced pressure. Then, the crude product was purified by using column chromatography (Ethyl acetate/Hexanes 1: 10 as eluents) to provide the desired products.

BODIPY 4a: Yield: 8.9 mg, 57%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.94-6.97 (m, 2H), 6.87–6.90 (m, 4H), 6.63–6.68 (m, 7H), 6.42–6.45 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.3, 143.7, 142.3, 131.2, 131.0, 129.5, 129.3, 129.2, 128.9, 127.5, 127.4, 126.8, 121.9; ^{11}B NMR (128 MHz, $CDCl_3$) δ 0.13 (t, $J_{(B,F)}$ = 27.7 Hz); HRMS (ESI-TOF) m/z 555.0100 $[M]^-$; calculated for $C_{27}H_{15}BCl_4F_2N_2$: 555.0092.

BODIPY 4b: Yield: 12.3 mg, 71%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17-7.18 (dd, $J_{(H,H)}$ = 5.1, 1.2 Hz, 2H), 6.93-6.94 (dd, $J_{(H,H)}$ = 5.0, 1.3 Hz, 1H), 6.67-6.70 (m, 3H), 6.45-6.46 (dd, $J_{(H,H)}$ = 3.6, 1.2 Hz, 2H), 6.30-

6.32 (dd, $J_{(H,H)}$ = 5.0, 3.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.0, 138.3, 136.8, 134.0, 131.5, 130.6, 130.4, 130.3, 129.4, 127.9, 126.8, 126.6, 123.4; ^{11}B NMR (128 MHz, $CDCl_3$) δ -0.02 (t, $J_{(B,F)}$ = 27.5 Hz); HRMS (ESI-TOF) m/z 572.8774 $[M]^-$; calculated for $C_{21}H_9BCl_4F_2N_2S_3$: 572.8779.

General procedure for BODIPY 5a-b

BODIPY **4a-b** (0.02 mmol) and $Pd(PPh_3)_4$ (3 mol%) were added into a 25 ml round-bottomed flask. The flask was evacuated and refilled with nitrogen for three times. Toluene (5 ml) and organostananne reagents (0.2 mmol, 10 equiv) were purged into the flask, and the mixture was reflux overnight. The reaction was stopped when **5a-b** was showed as major products according to TLC. The solvents were removed under reduced pressure. Then, the crude product was purified by using column chromatography (Ethyl acetate/Hexanes 1: 4 as eluents) to provide the desired products.

BODIPY **5a**: Yield: 9.6 mg, 75%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70-7.72 (m, 4H), 7.44-7.48 (m, 6H), 6.88-6.95 (m, 6H), 6.79-6.81 (m, 2H), 6.73-6.76 (m, 4H), 6.62-6.64 (m, 1H), 6.45-6.48 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.6, 147.2, 143.1, 132.5, 131.2, 130.7, 130.2, 130.1, 129.8, 129.7, 129.6, 129.0, 127.9, 127.3, 126.9, 126.7, 123.4; ^{11}B NMR (128 MHz, $CDCl_3$) δ 0.62 (t, $J_{(B,F)}$ = 30.0 Hz); HRMS (ESI-TOF) m/z 639.1475 $[M]^-$; calculated for $C_{39}H_{25}BCl_2F_2N_2$: 639.1498.

BODIPY 5b: Yield: 12.4 mg, 92%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90-7.91 (dd, $J_{(H,H)}$ = 3.8, 1.2 Hz, 2H), 7.64-7.65 (dd, $J_{(H,H)}$ = 5.1, 1.2 Hz, 2H), 7.20-7.22 (dd, $J_{(H,H)}$ = 5.0, 3.8 Hz, 2H), 7.16-7.17 (dd, J = 5.1, 1.2 Hz, 2H), 6.91-6.92 (dd, $J_{(H,H)}$ = 5.0, 1.2 Hz, 1H), 6.66 – 6.68 (m (overlap), 3H), 6.46-6.47 (dd, $J_{(H,H)}$ = 3.6, 1.2 Hz, 2H), 6.28-6.30 (dd, $J_{(H,H)}$ = 5.0, 3.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.8, 137.0, 136.0, 133.67(t, overlap), 133.62, 132.6, 132.5, 131.5, 130.9, 129.5, 129.25, 129.21, 127.5, 127.1, 126.6, 126.3, 125.8; ^{11}B NMR (128 MHz, $CDCl_3$) δ 0.76 (t, $J_{(B,F)}$ =30.7 Hz); HRMS (ESI-TOF) m/z 668.9313 $[M]^-$; calculated for $C_{29}H_{15}BCl_2F_2N_2S_5$: 668.9319.

General procedure for BODIPY 6a-b

BODIPY **5a-b** (0.02 mmol) and $Pd(PCy_3)G2$ (3 mol%) were added into a 25 ml round-bottomed flask. The flask was evacuated and refilled with nitrogen for three times. Toluene (5 ml) and 2-(tributylstannyl)-thiophene (74.6 mg, 0.2 mmol) were purged into the flask, and the mixture was reflux overnight. The reaction was stopped when **6a-b** was showed as major products according to TLC. The solvents were removed under reduced pressure. Then, the crude product was purified by using column chromatography (Ethyl acetate/Hexanes 1: 2 as eluents) to provide the desired products.

BODIPY 6a: Yield: 11.2 mg, 76%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.51 (m, 4H), 7.30-7.39 (m, 6H), 6.93-6.94 (dd, $J_{(H,H)}$ = 5.1, 1.2 Hz, 2H), 6.77-6.88 (m, 8H), 6.65-6.67 (m, 4H), 6.58-6.62 (m (overlap), 3H), 6.42-6.45 (m, 2H), 6.12-6.13 (dd, $J_{(H,H)}$ = 3.6, 1.2 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.1, 147.4, 143.9, 134.22, 134.19, 132.2, 131.5, 131.3, 130.6, 130.4, 130.1, 129.1, 128.6, 128.0, 127.8, 127.7, 127.2, 126.5, 126.3, 126.1, 125.7; ^{11}B NMR (128 MHz, $CDCl_3$) δ 0.85 (t, J = 30.3 Hz); HRMS (ESI-TOF) m/z 735.2011 $[M]^-$; calculated for $C_{47}H_{31}BF_2N_2S_2$: 735.2032.

BODIPY 6b: Yield: 14.6 mg, 95%; ^{1}H NMR (500 MHz,$CDCl_3$) δ 7.65-7.66 (m, 2H), 7.45-7.46 (dd, $J_{(H,H)}$ = 5.1, 1.2 Hz, 2H), 7.19-7.20 (dd, $J_{(H,H)}$ = 5.1, 1.2 Hz, 2H), 7.06-7.08 (dd, $J_{(H,H)}$ = 5.0, 3.7 Hz, 2H), 6.99-7.00 (dd, $J_{(H,H)}$ = 5.1, 1.2 Hz, 2H), 6.88-6.89 (dd, $J_{(H,H)}$ = 5.0, 1.3 Hz, 1H), 6.82-6.83 (dd, $J_{(H,H)}$ = 5.1, 3.6 Hz, 2H), 6.66-6.67 (dd, $J_{(H,H)}$ = 3.6, 1.3 Hz, 1H), 6.58-6.59 (dd, $J_{(H,H)}$ = 3.6, 1.2 Hz, 1H), 6.53-6.55 (dd, $J_{(H,H)}$ = 5.1, 3.5 Hz, 1H), 6.36-6.37 (dd, $J_{(H,H)}$ = 3.5, 1.2 Hz, 2H), 6.25-6.27 (dd, $J_{(H,H)}$ = 5.1, 3.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.4, 137.7, 137.4, 134.3, 134.1, 133.41, 133.37, 133.0(t), 132.1, 131.2,

130.53, 130.50, 130.2, 129.4, 129.2, 129.0, 127.1, 126.5, 126.3, 126.2; ^{11}B NMR (128 MHz, $CDCl_3$) δ 0.96 (t, $J_{(B,F)}$=30.7 Hz); HRMS (ESI-TOF) m/z 764.9862 $[M]^-$; calculated for $C_{37}H_{21}BF_2N_2S_7$: 764.9853.

General procedure for BODIPY 7a-b

BODIPY **6a-b** (0.01 mmol) was dissolved in dry CH_2Cl_2 (2 ml). $BF_3{\cdot}OEt_2$ (12.3 μl, 0.1 mmol) and trimethylsilyl cyanide (26.8 μl, 0.2 mmol) were added into the flask. The mixture was stirred at room temperature for 1h. The reaction was quenched with H_2O (2ml), and extract byCH_2Cl_2 (20 ml* 3). The organic layers were combined and washed with brine then water. The solvent were removed under reduced pressure. The residue was purified by using column chromatography (CH_2Cl_2/Hexanes 2:1 as eluents) to provide the pure compounds.

BODIPY 7a: Yield: 6.9 mg, 92%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60-7.63 (m, 4H), 7.41-7.46 (m, 6H), 6.93-6.95 (dd, $J_{(H,H)}$ = 5.1, 1.2 Hz, 2H), 6.88-6.92 (m, 2H), 6.81-6.85 (m, 6H), 6.68-6.70 (m, 4H), 6.62-6.66 (m, 1H), 6.56-6.59 (dd, $J_{(H,H)}$ = 5.1, 3.7 Hz, 2H), 6.46-6.50 (m, 2H), 6.14-6.16 (dd, $J_{(H,H)}$ = 3.7, 1.2 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.1, 148.4, 144.7, 133.5, 133.1, 131.1, 130.9, 130.7, 130.4, 130.1, 129.7, 129.3, 129.0, 128.37, 128.0, 127.5, 126.8, 126.7, 126.1; ^{11}B NMR (128 MHz, $CDCl_3$) δ -16.30 (s); HRMS (ESI-TOF) m/z 749.2126 $[M]^-$; calculated for $C_{49}H_{31}BN_2S_2$: 749.2125.

BODIPY 7b: Yield: 7.3 mg, 93%; ^{1}H NMR (400 MHz,$CDCl_3$) δ 7.80-7.81 (dd, $J_{(H,H)}$ = 3.7, 1.2 Hz, 2H), 7.57-7.59 (dd, $J_{(H,H)}$ = 5.1, 1.2 Hz, 2H), 7.17-7.20 (dd, $J_{(H,H)}$ = 5.0, 3.7 Hz, 2H), 7.15-7.17 (dd, $J_{(H,H)}$ = 5.1, 1.2 Hz, 2H), 7.06-7.08 (dd, $J_{(H,H)}$ = 5.0, 1.2 Hz, 2H), 6.94-6.96 (dd, $J_{(H,H)}$ = 5.0, 1.3 Hz, 1H), 6.77-6.79 (dd, $J_{(H,H)}$ = 5.1, 3.6 Hz, 2H), 6.71-6.72 (dd, $J_{(H,H)}$ = 3.6, 1.3 Hz, 1H), 6.59-6.61 (dd, $J_{(H,H)}$ = 5.1, 3.5 Hz, 2H), 6.54-6.56 (dd, $J_{(H,H)}$ = 3.7, 1.2 Hz, 2H), 6.43-6.44 (dd, $J_{(H,H)}$ = 3.6, 1.2 Hz, 2H), 6.30-6.32 (dd, $J_{(H,H)}$ = 5.0, 3.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.5, 139.7, 137.7, 133.85, 133.77, 133.4, 132.8, 132.24, 132.22, 131.2, 130.8, 129.8, 129.6, 129.4, 129.2, 127.6, 127.4, 127.3, 126.6, 126.5, 126.4; ^{11}B NMR (128 MHz, $CDCl_3$) δ -16.12 (s); HRMS (ESI-TOF) m/z 778.9926 $[M]^-$; calculated for $C_{39}H_{21}BN_4S_7$: 778.9946.

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2. J. Olmsted, *J Phys. Chem.,* 1979, **83**, 2581.

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4. N. Zhao, S. Xuan, F. R. Fronczek, K. M. Smith and M. G. H. Vicente, *J. Org. Chem.,* 2015, **80**, 8377.

2. Spectroscopic data

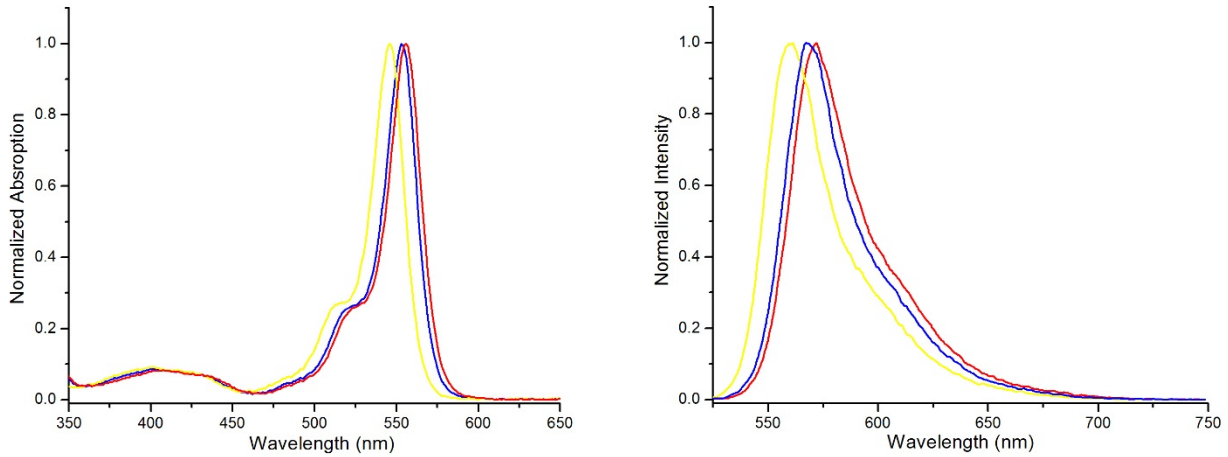


Figure S1: Normalized UV-Vis and fluorescence spectra spectra of BODIPYs **1b** (red), **2b** (blue), and **3b** (yellow) in CH_2Cl_2 at room temperature.

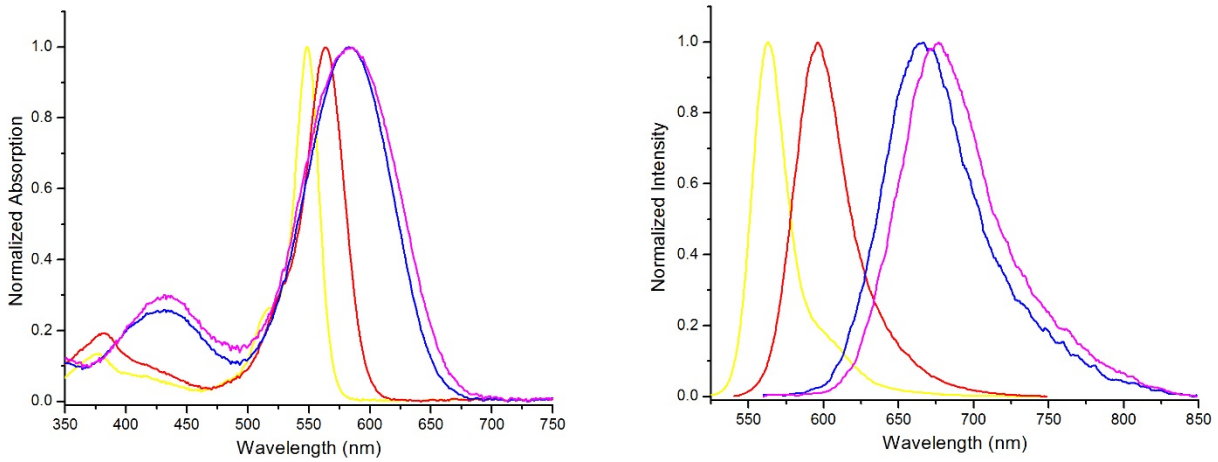


Figure S2: Normalized UV-Vis and fluorescence spectra spectra of BODIPYs **4a** (yellow), **5a** (red), **6a** (blue), and **7a** (purple) in CH_2Cl_2 at room temperature.

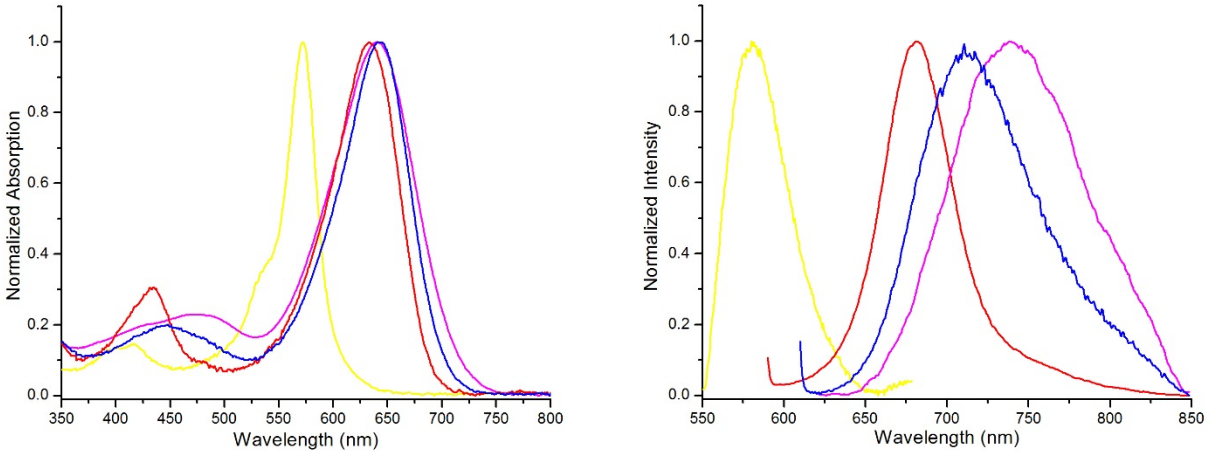
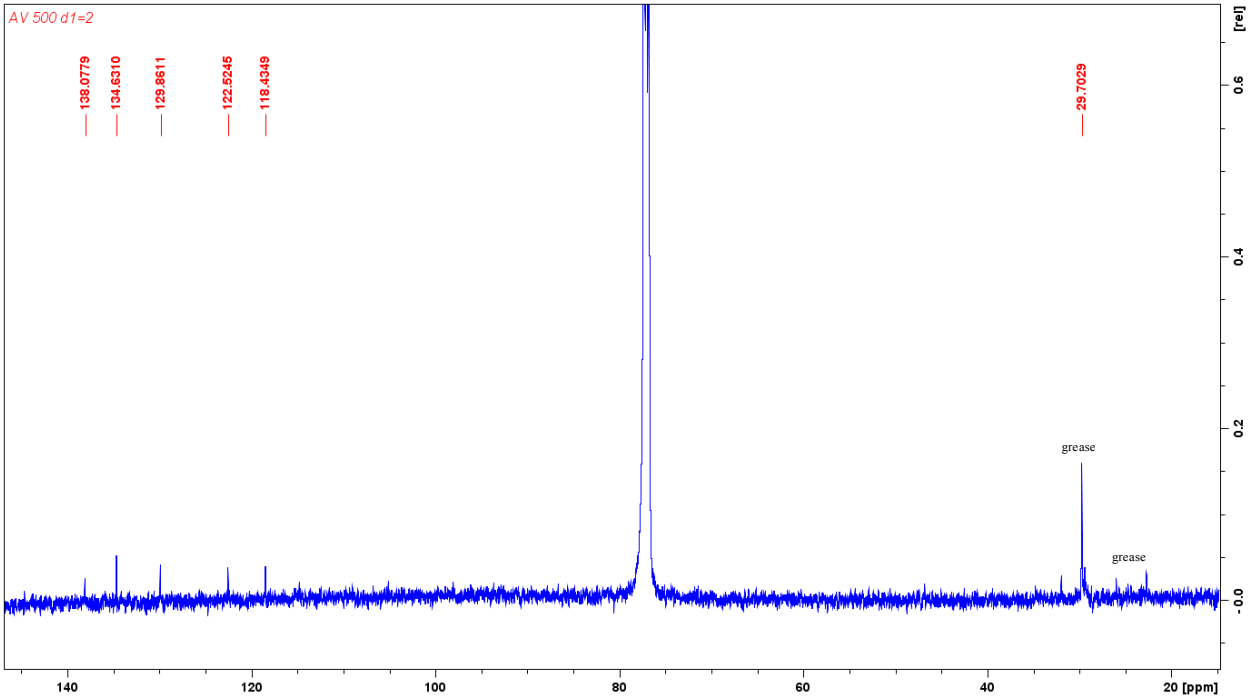


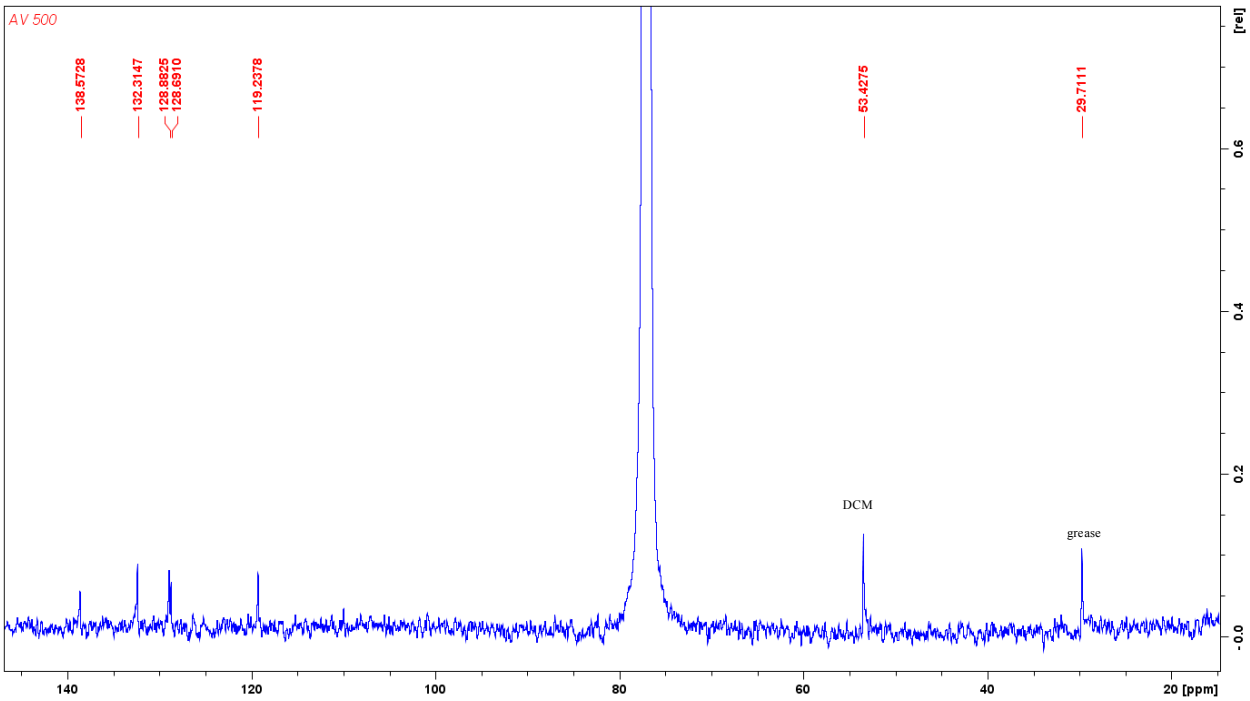
Figure S3: Normalized UV-Vis and fluorescence spectra spectra of BODIPYs **4b** (yellow), **5b** (red), **6b** (blue), and **7b** (purple) in CH_2Cl_2 at room temperature.

Copies of ^{1}H and ^{13}C NMR spectra of new BODIPYs

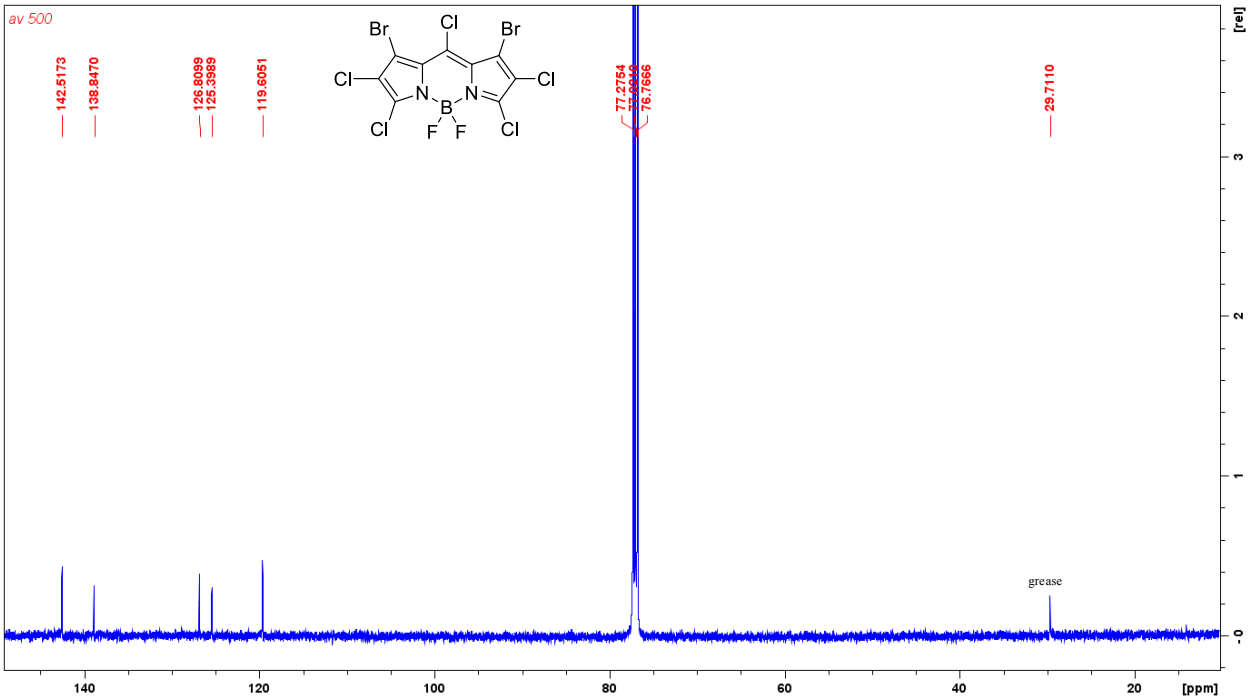
^{13}C NMR of BODIPY **1b**



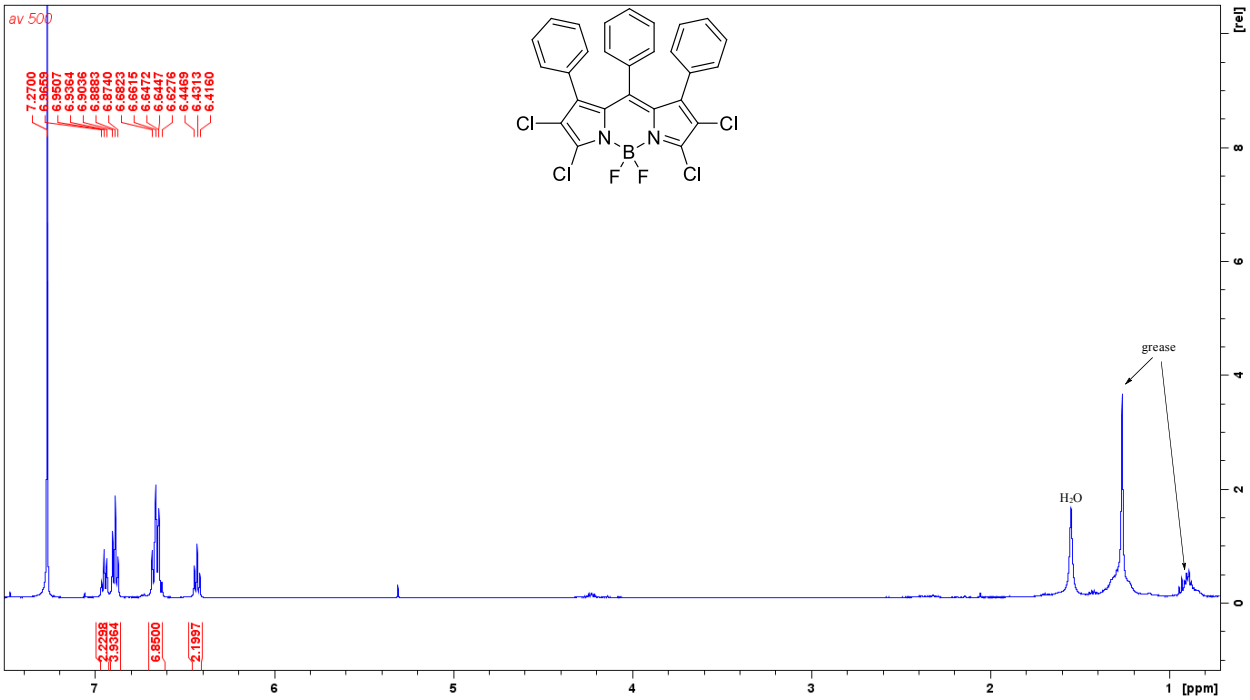
^{13}C NMR of BODIPY **2b**



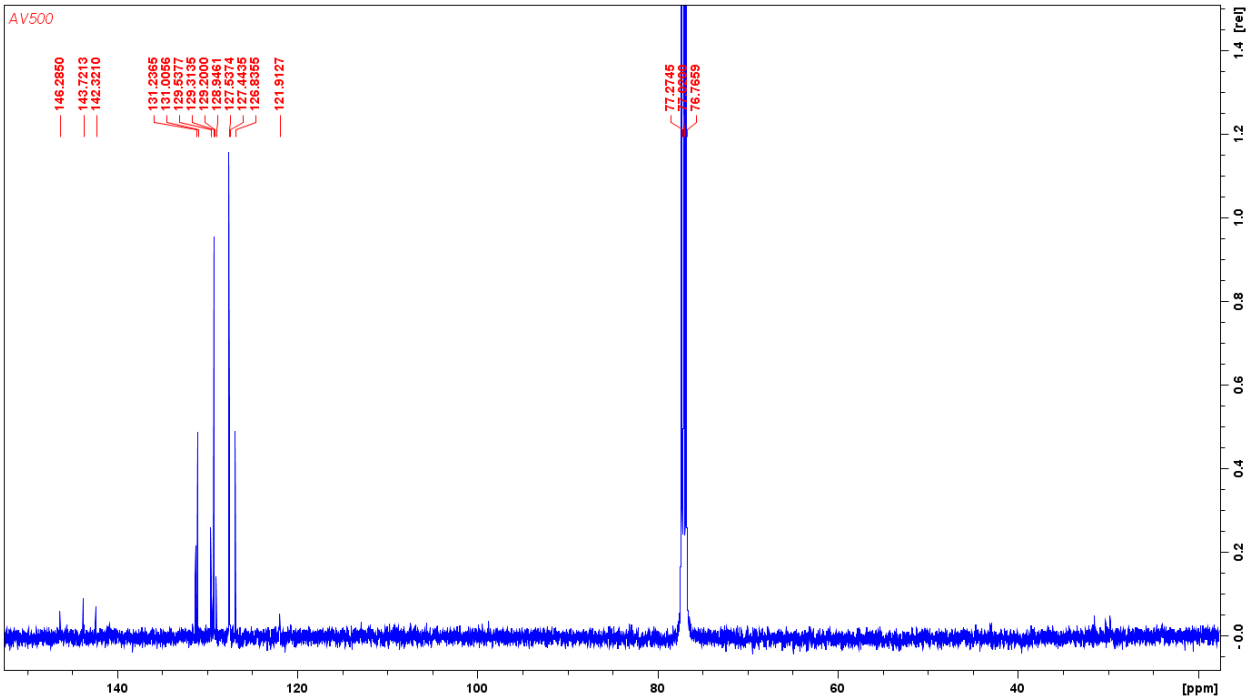
^{13}C NMR of BODIPY **3b**



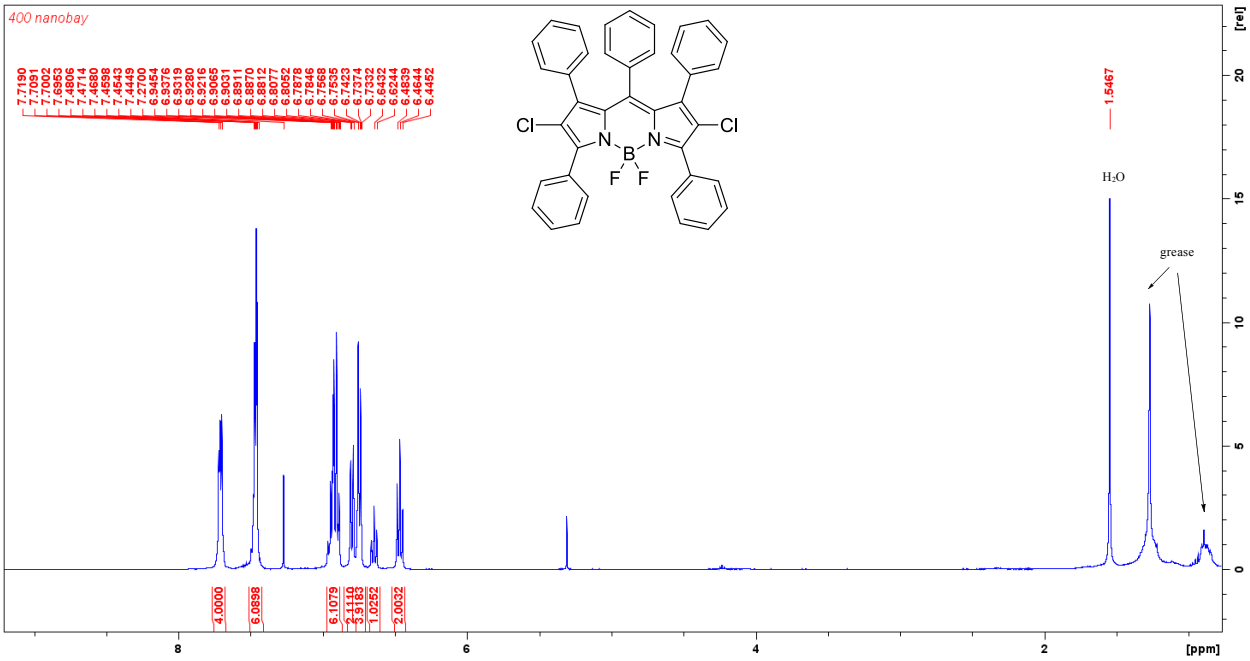
^{1}H NMR of BODIPY **4a**



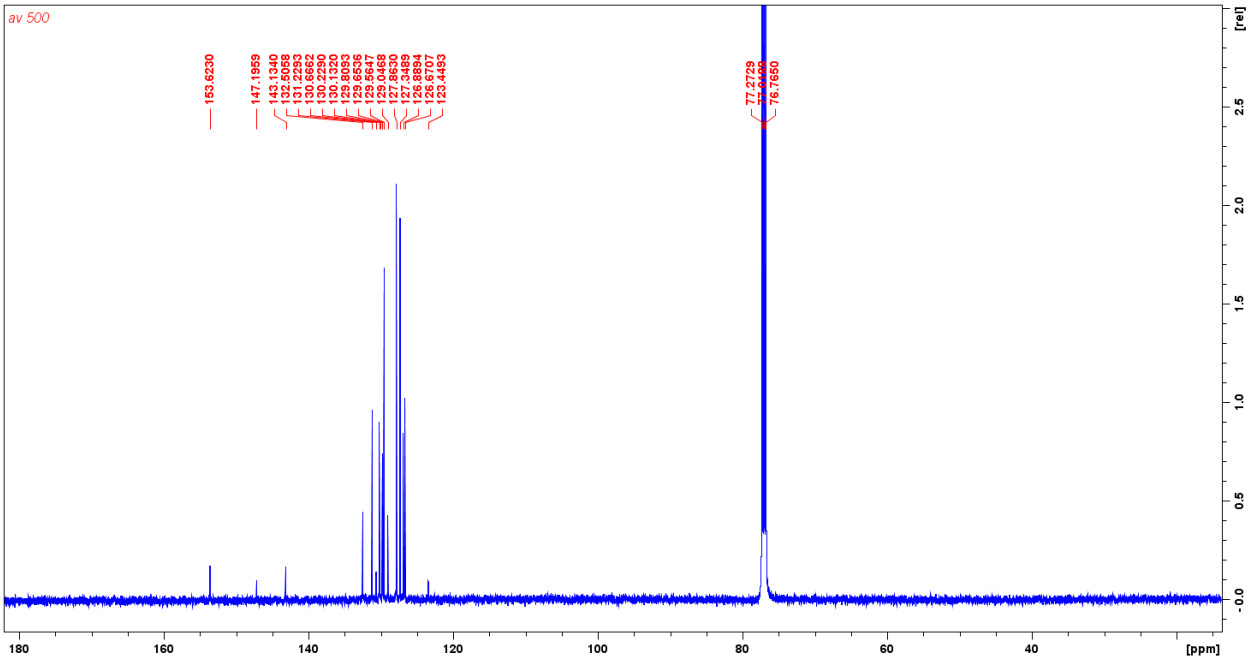
^{13}C NMR of BODIPY **4a**



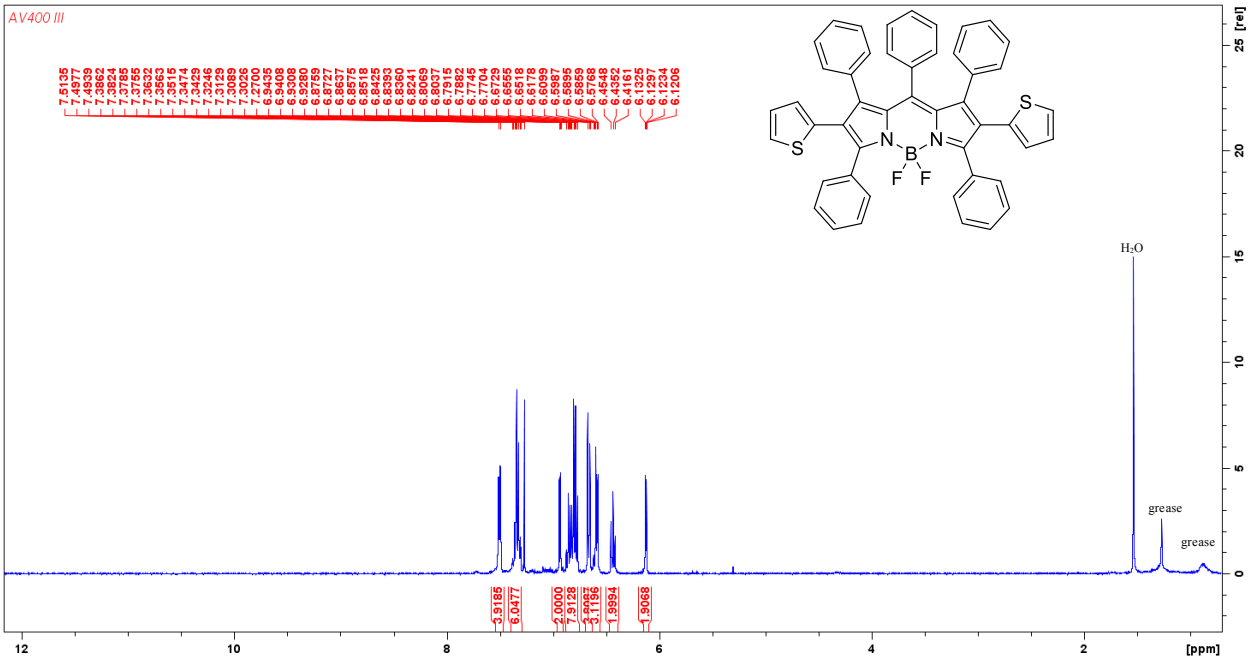
^{1}H NMR of BODIPY **5a**



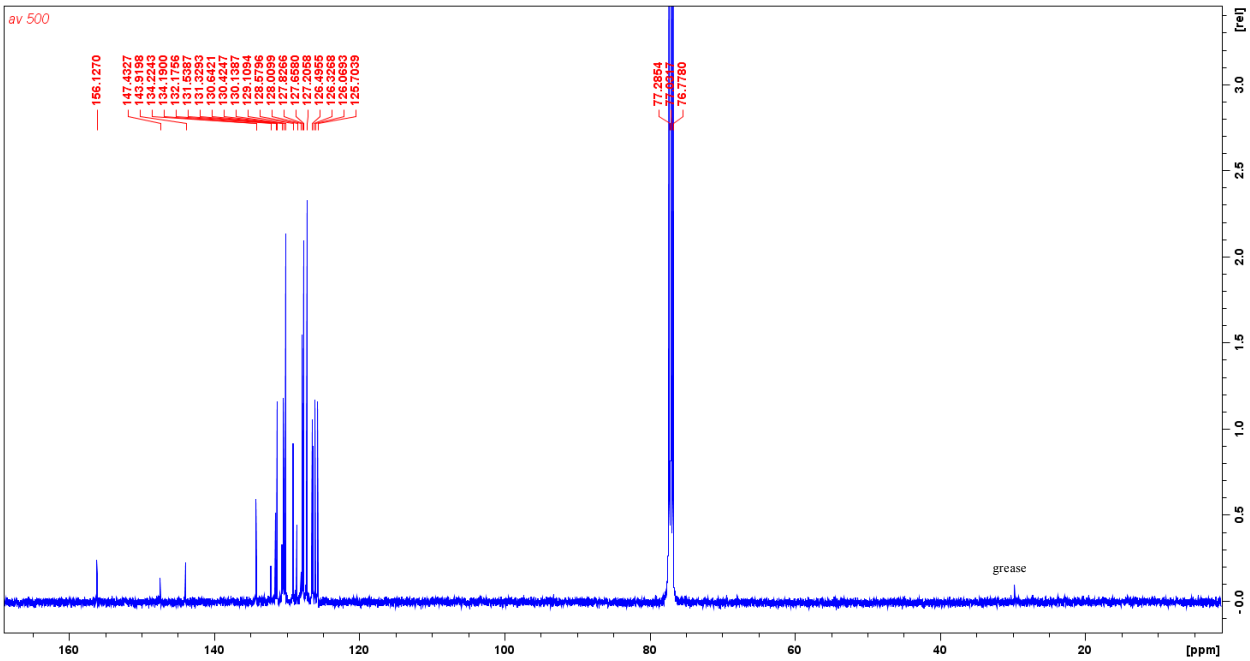
^{13}C NMR of BODIPY **5a**



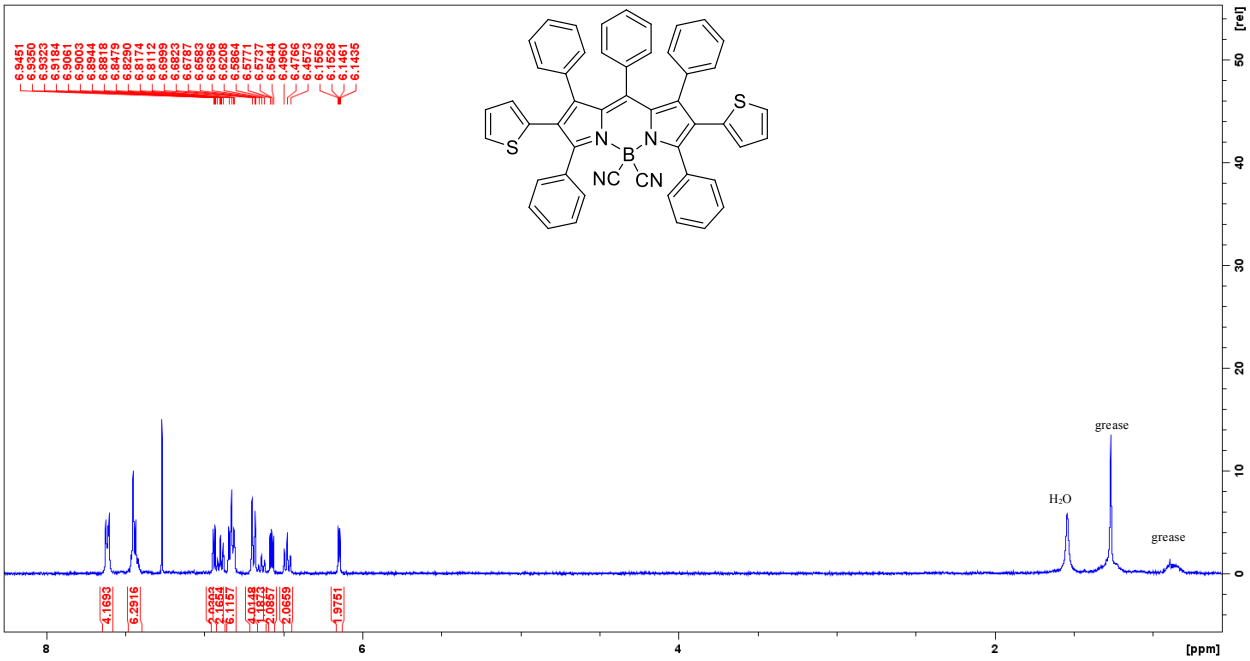
^{1}H NMR of BODIPY **6a**



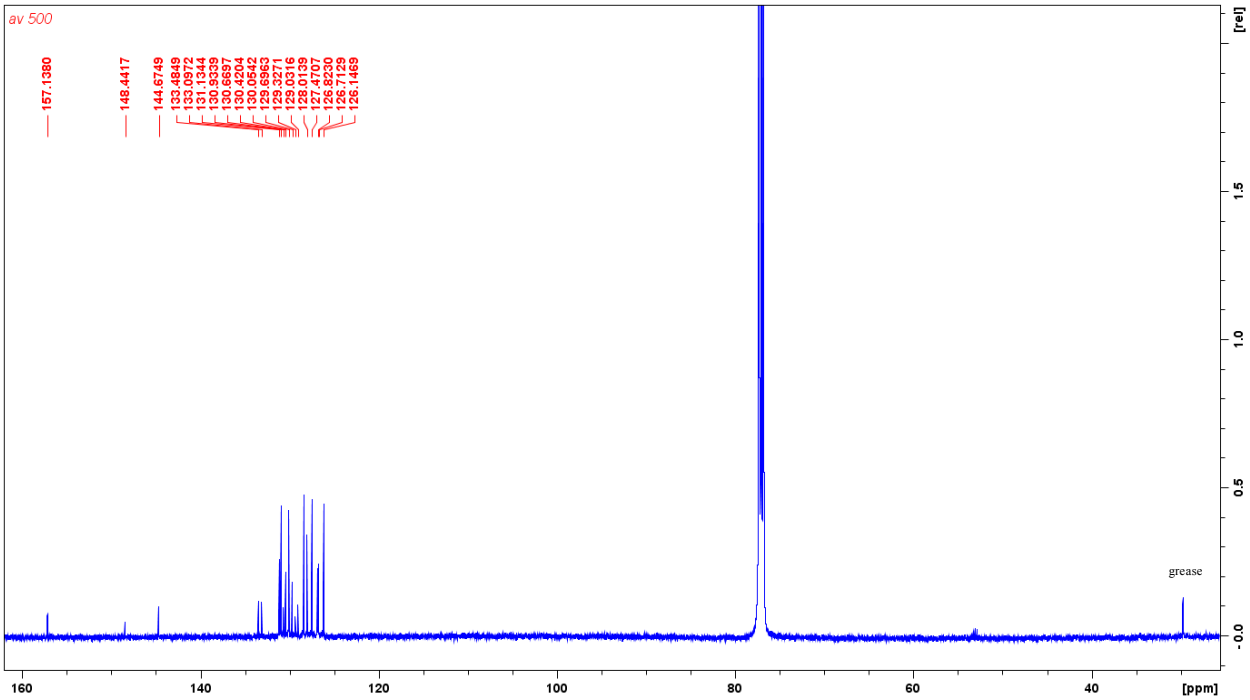
^{13}C NMR of BODIPY **6a**



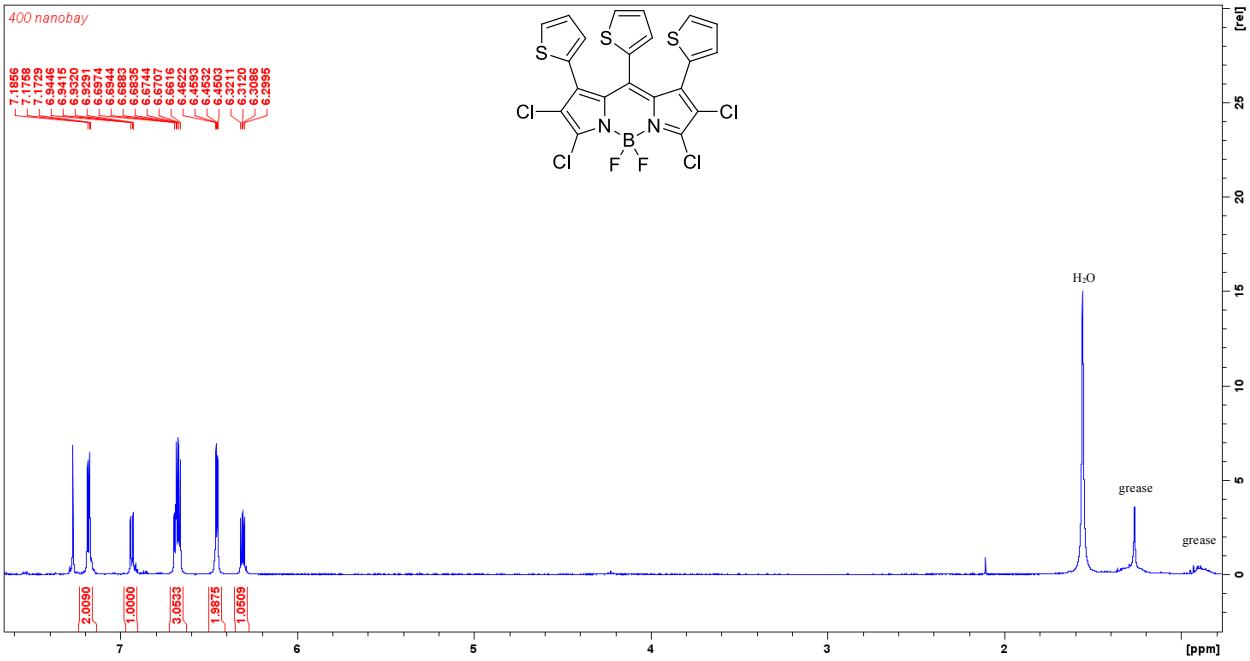
^{1}H NMR of BODIPY **7a**



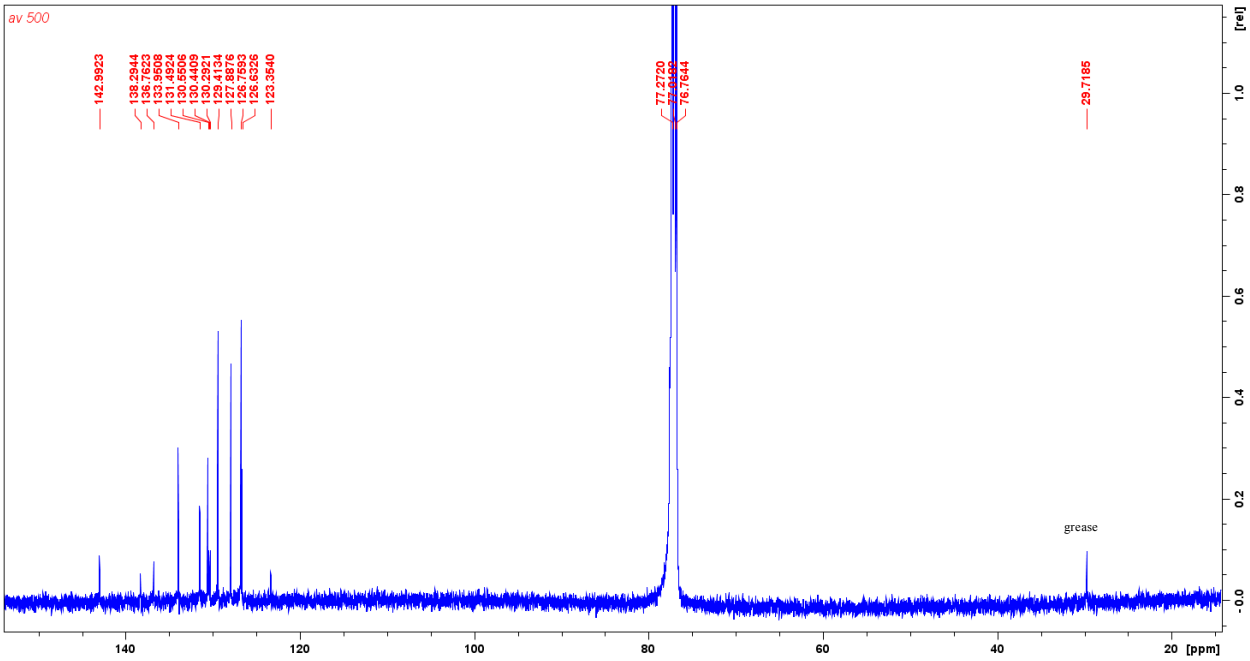
^{13}C NMR of BODIPY **7a**



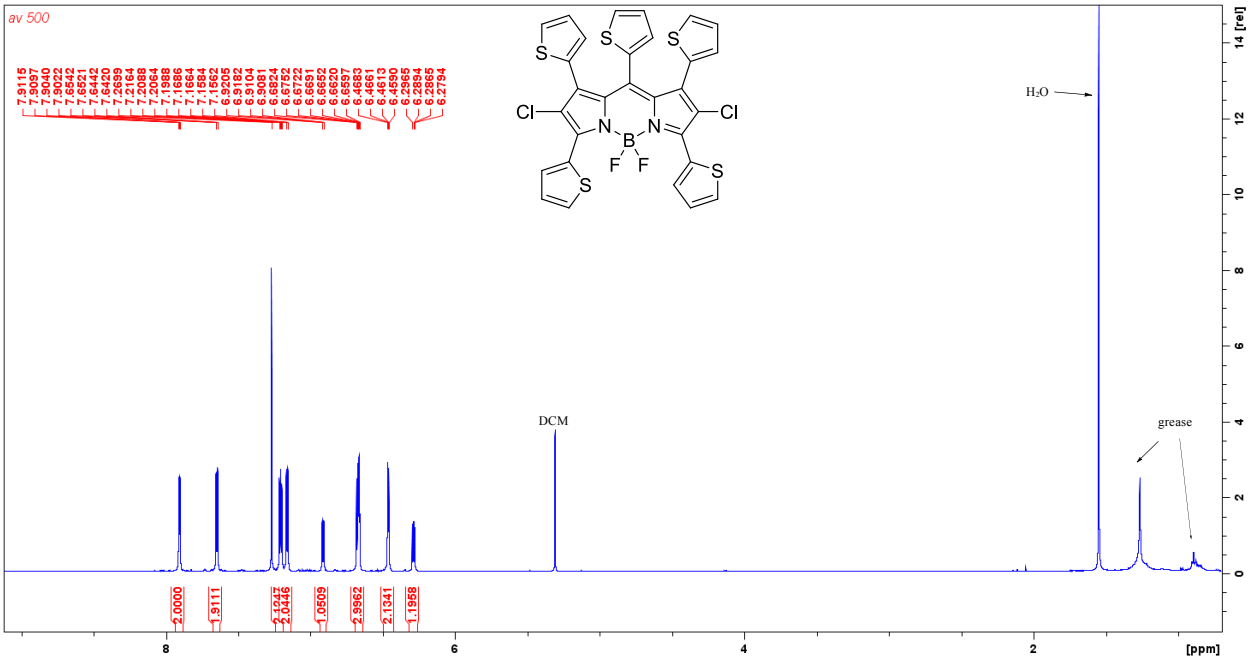
^{1}H NMR of BODIPY **4b**



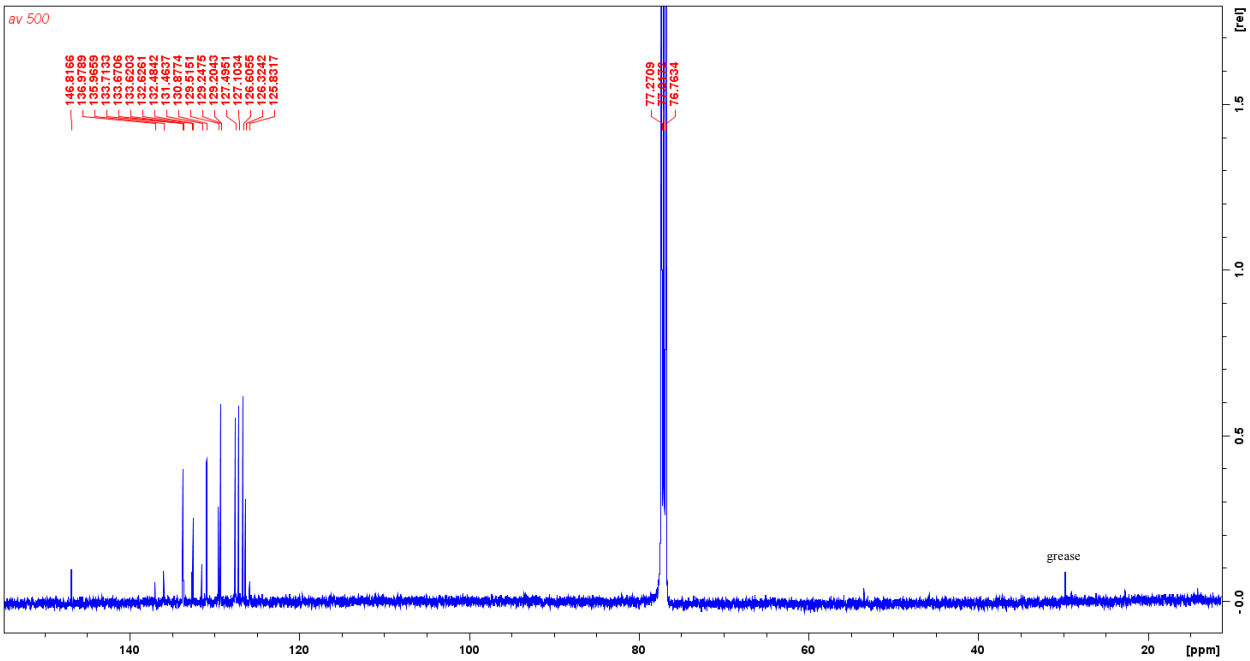
^{13}C NMR of BODIPY **4b**



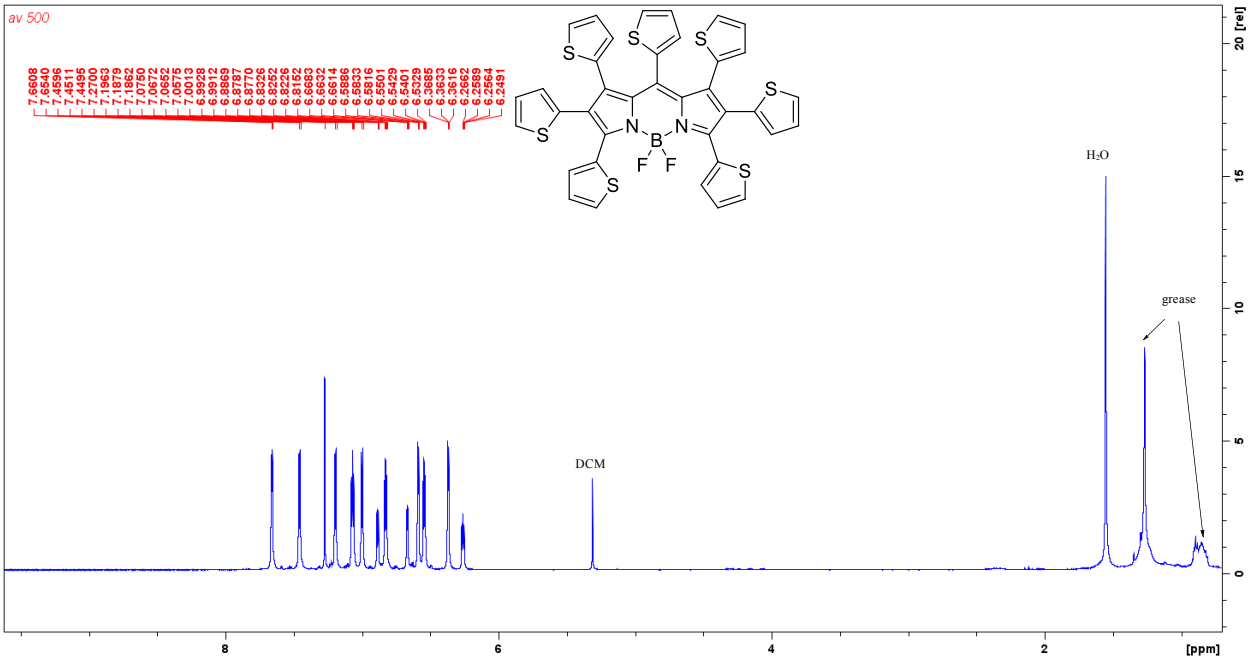
^{1}H NMR of BODIPY **5b**



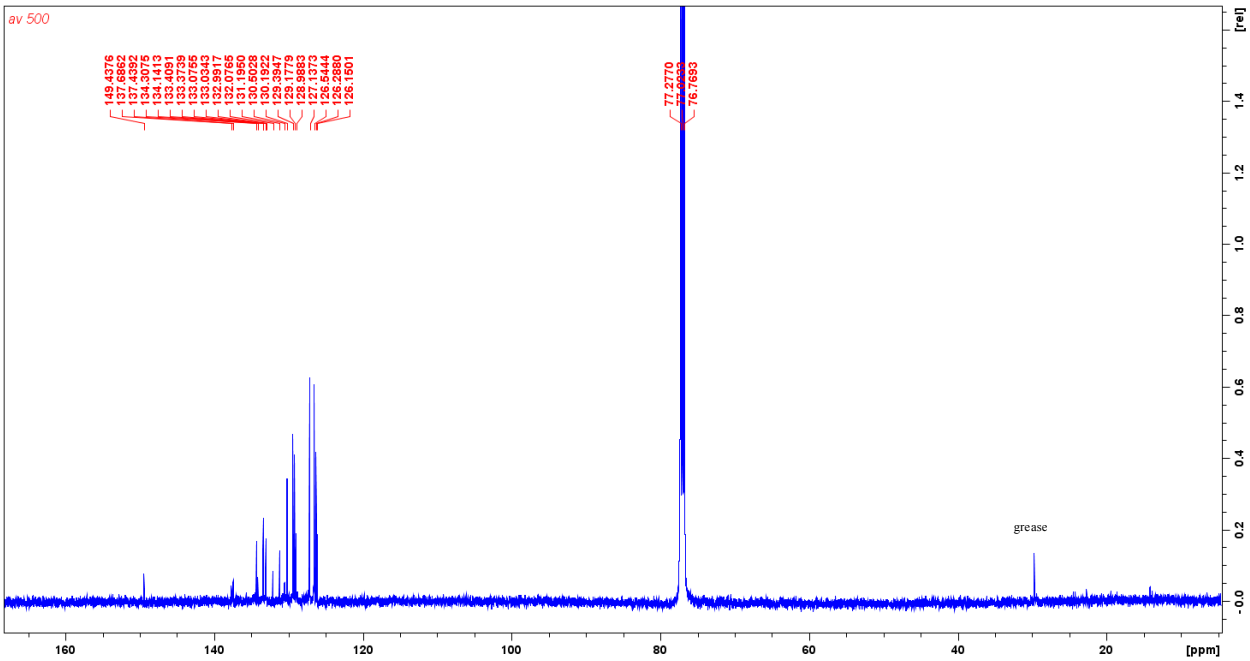
^{13}C NMR of BODIPY **5b**



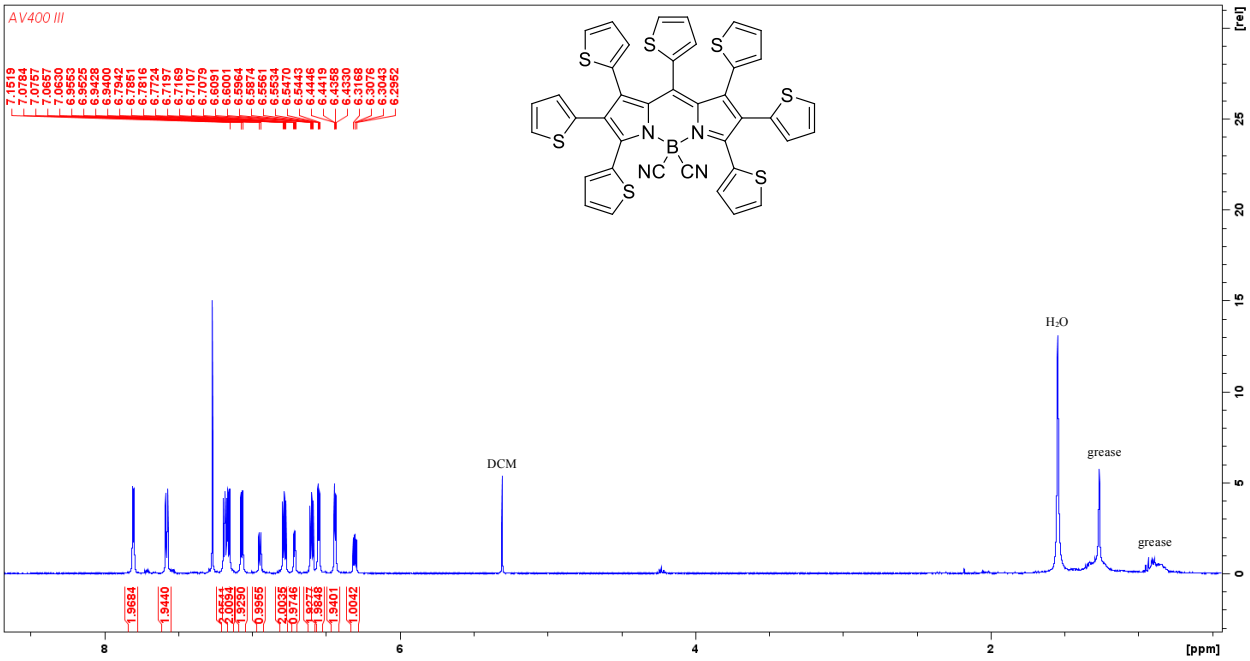
^{1}H NMR of BODIPY **6b**



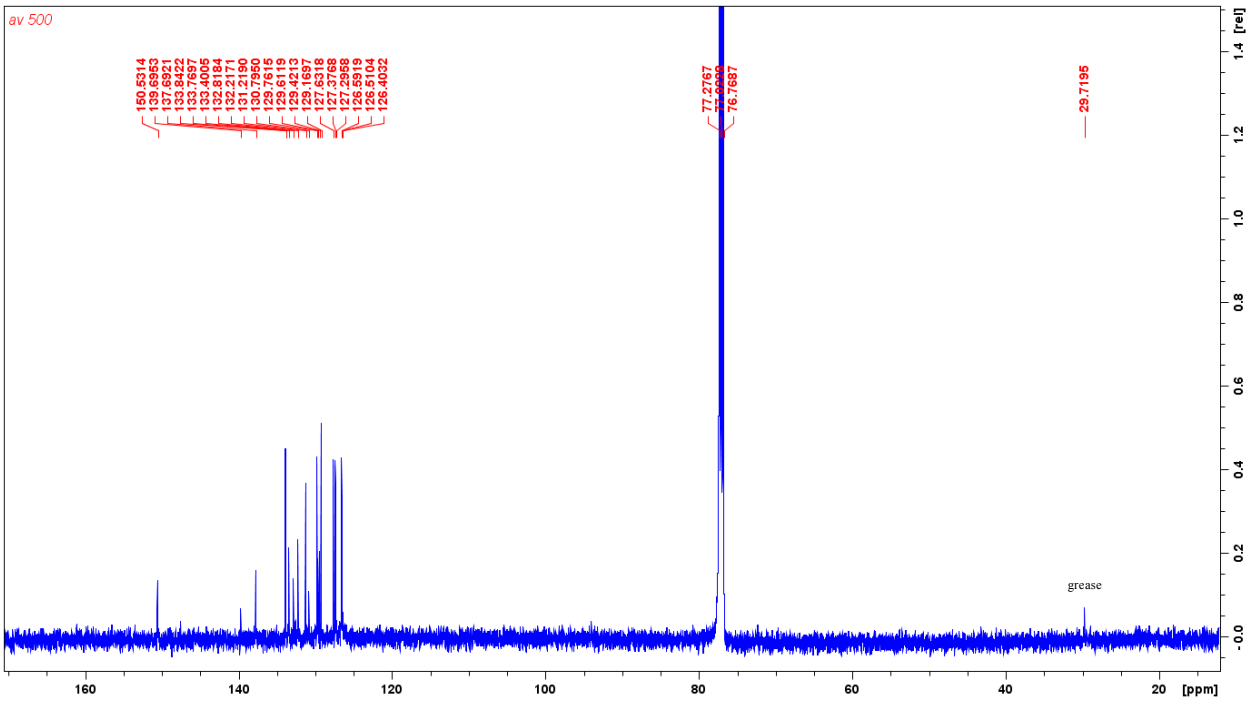
^{13}C NMR of BODIPY **6b**



^{1}H NMR of BODIPY **7b**

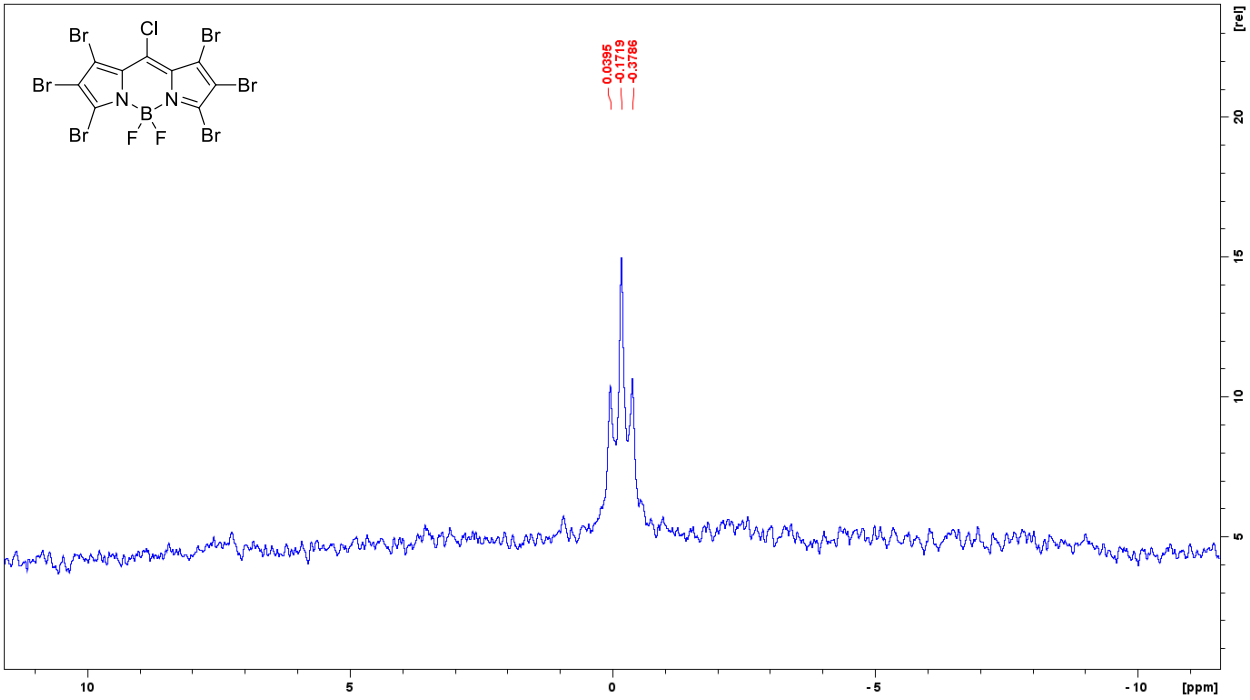


^{1}H NMR of BODIPY **7b**

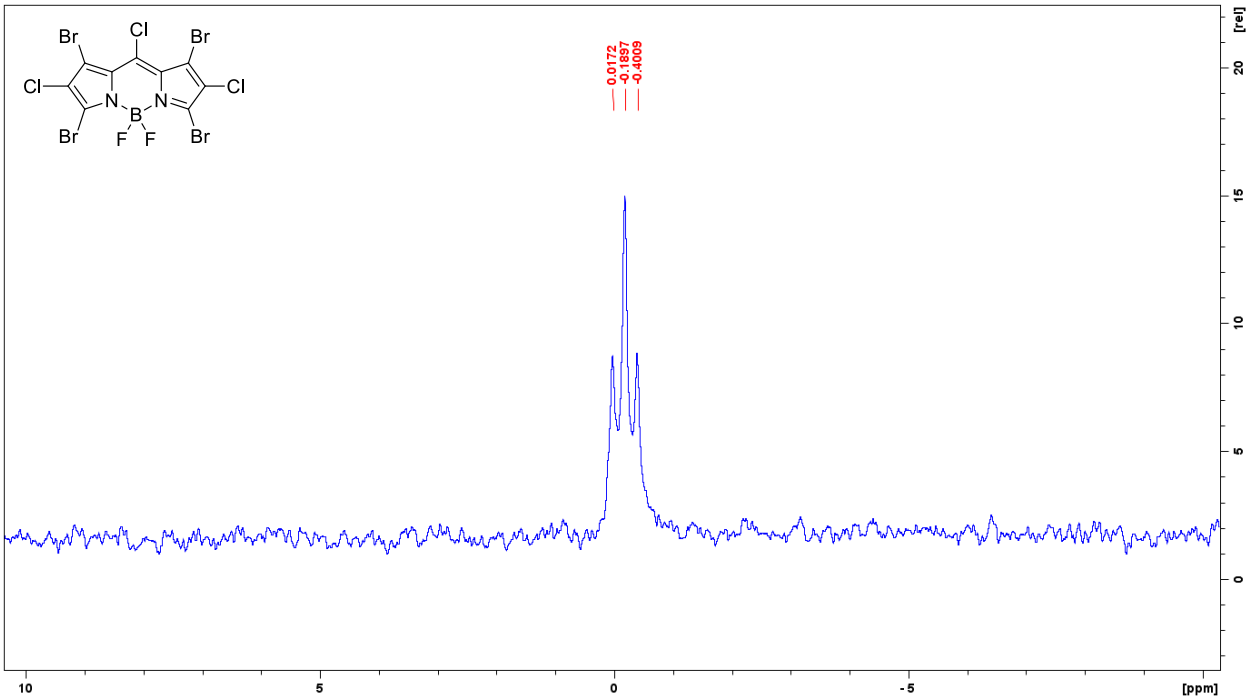


Copies of ^{11}B NMR of new BODIPYs

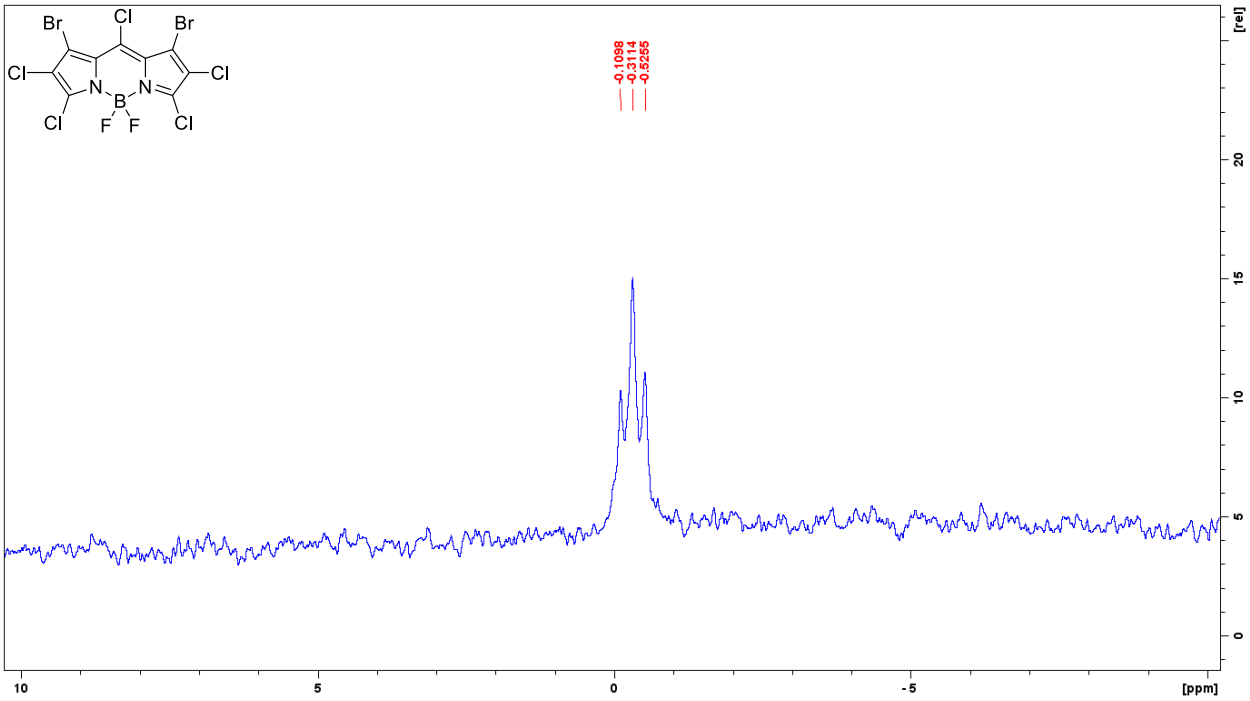
^{11}B NMR of BODIPY **1b**



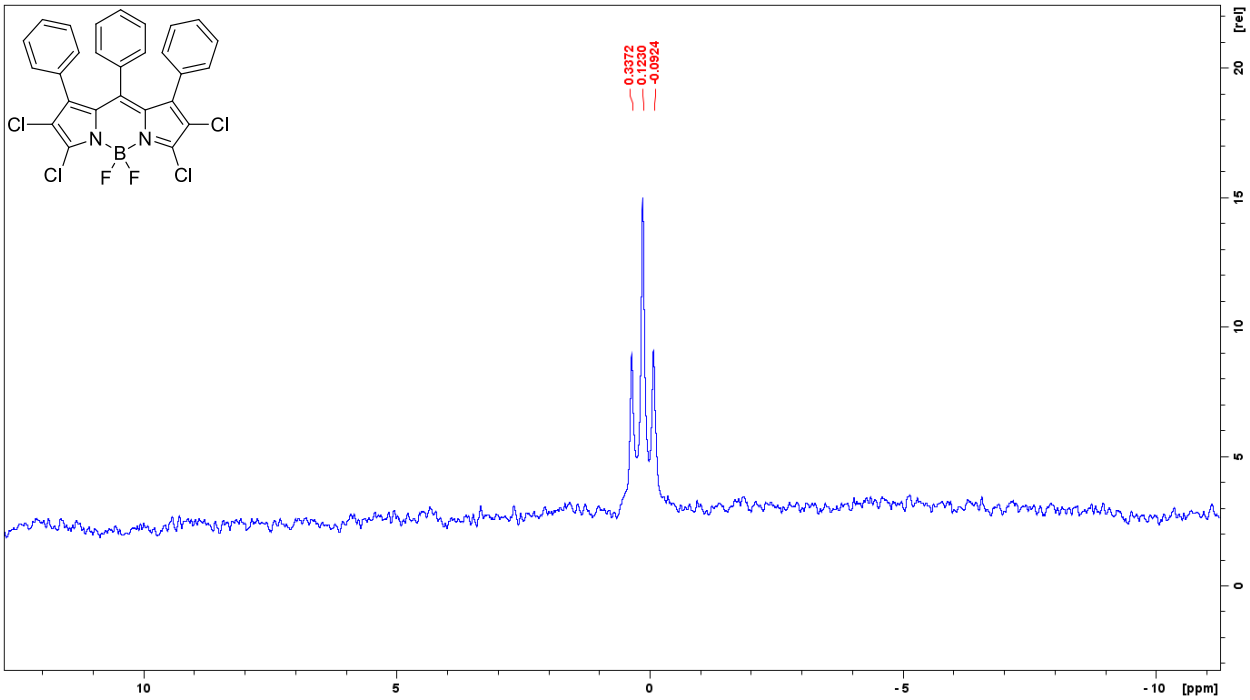
^{11}B NMR of BODIPY **2b**



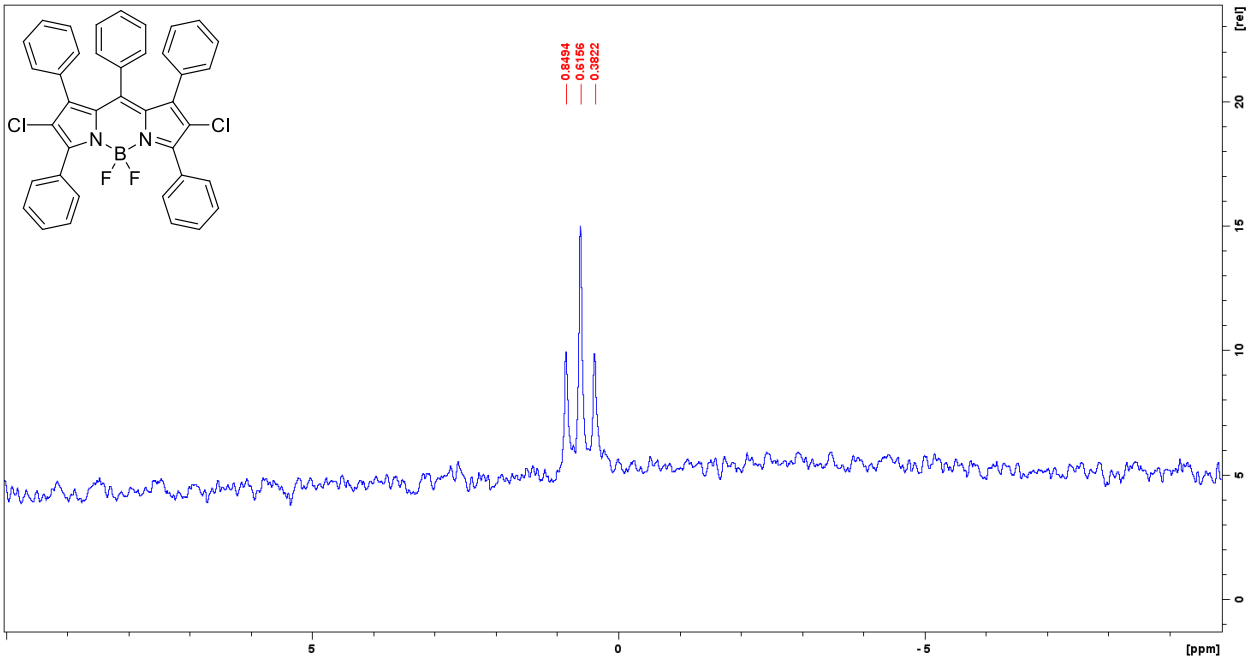
^{11}B NMR of BODIPY **3b**



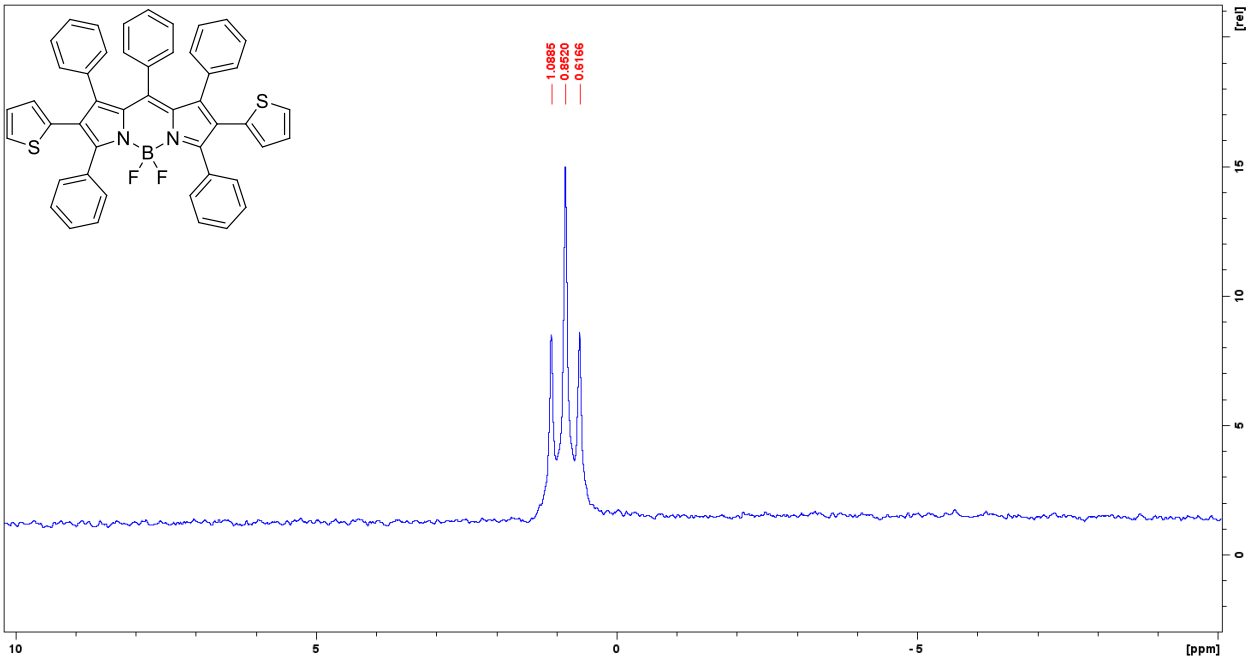
^{11}B NMR of BODIPY **4a**



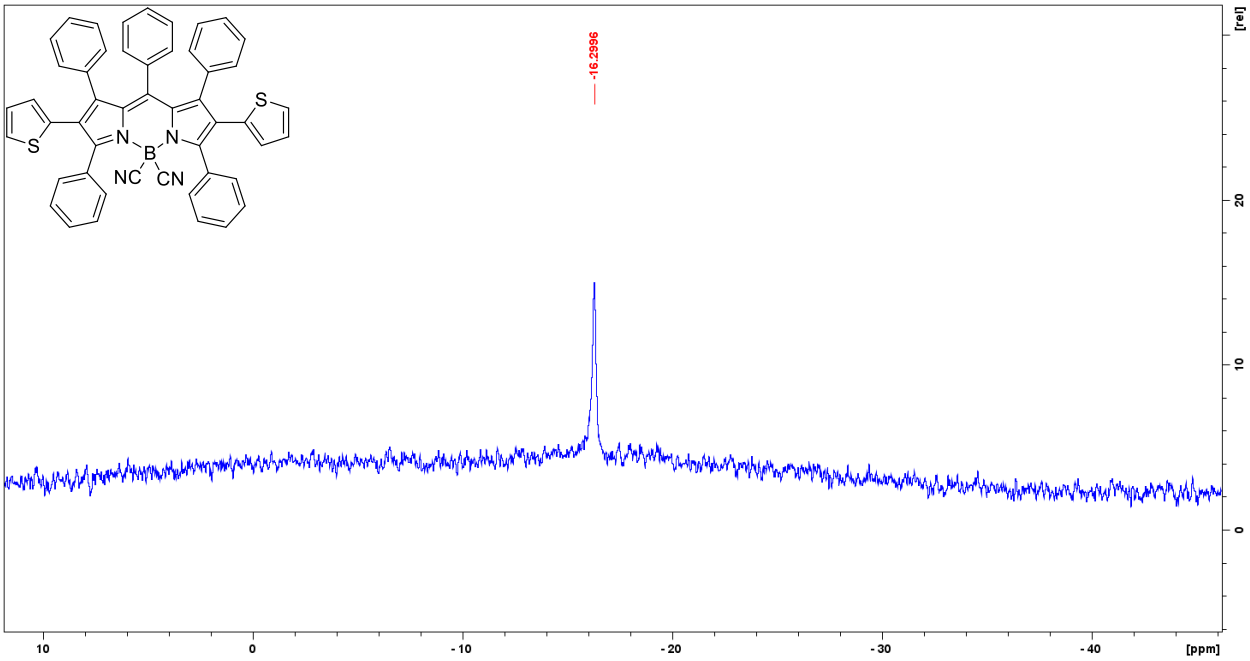
^{11}B NMR of BODIPY **5a**



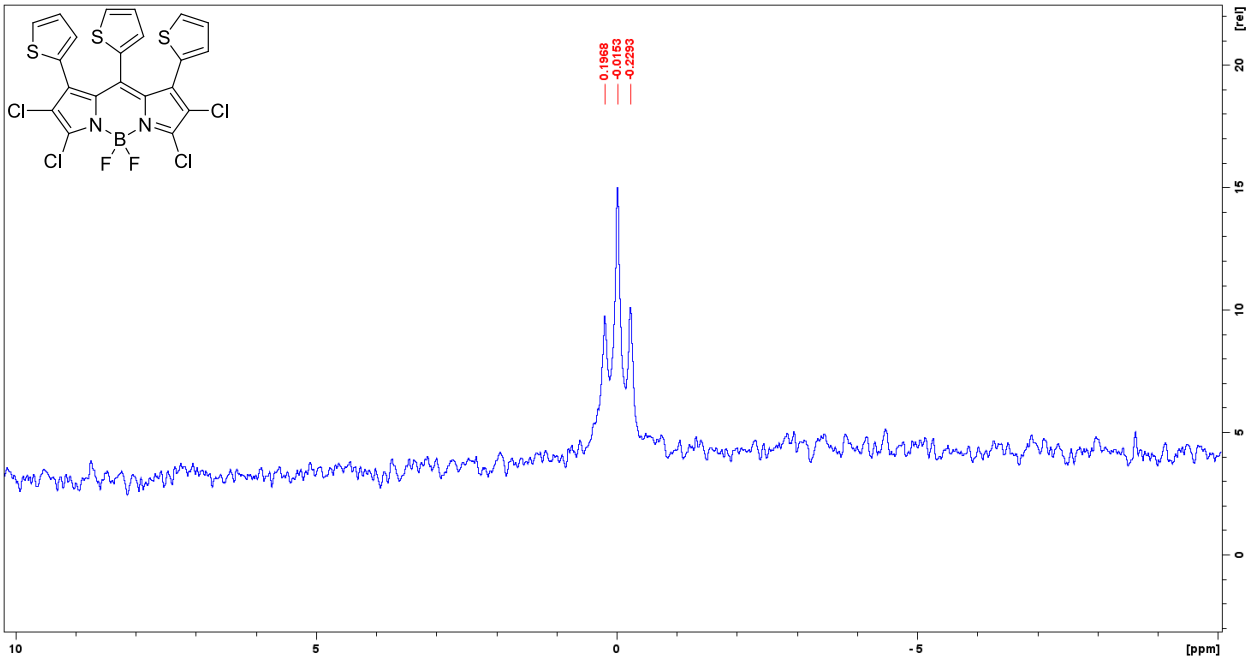
^{11}B NMR of BODIPY **6a**



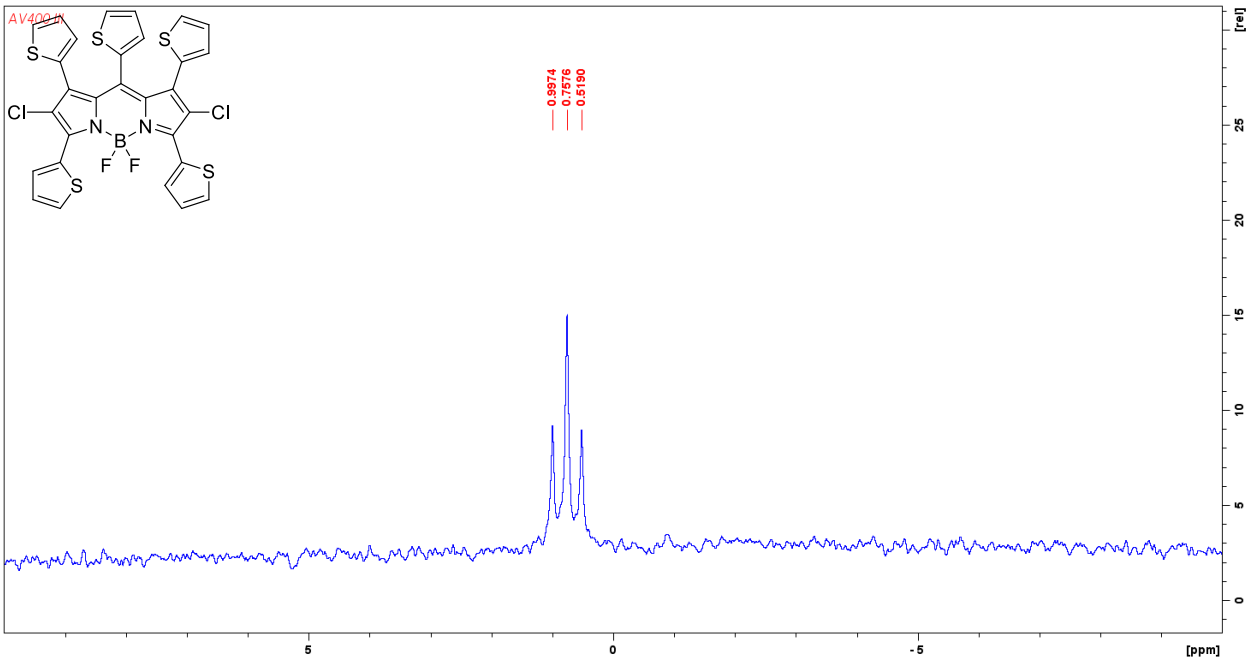
^{11}B NMR of BODIPY **7a**



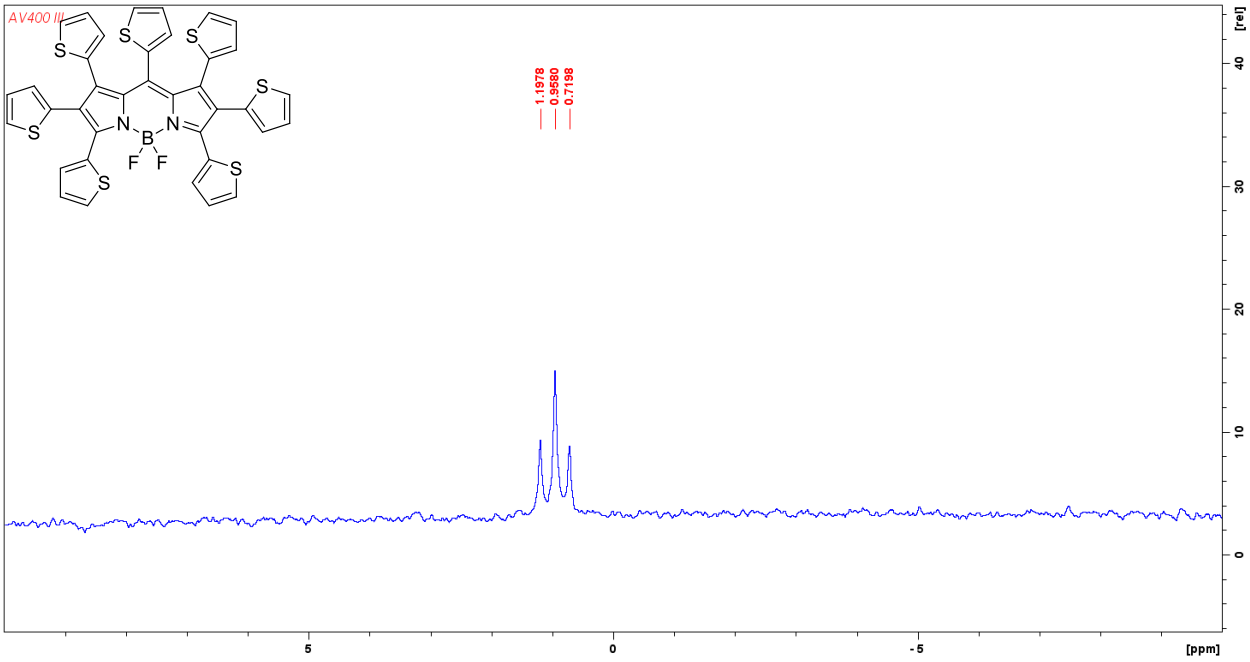
^{11}B NMR of BODIPY **4b**



^{11}B NMR of BODIPY **5b**



^{11}B NMR of BODIPY **6b**



^{11}B NMR of BODIPY **7b**