Supporting Information

BODIPY(aryl)iodonium Salts in the Efficient Synthesis of Diversely Functionalized BODIPYs and Selective Detection of Serum Albumin

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I. Experimental section

Materials and methods

The reagents and solvents were procured from commercial sources sigma-aldrich and spectrochem and used. Dichloromethane was freshly distilled in presence of calcium hydride prior to use. For studying interaction with serum albumin aqueous solution was prepared using purified water, collected from an Elix 10 water purification system (Millipore India Pvt. Ltd). Protease-free, heat shock fraction, BSA was obtained from Sigma-Aldrich (Cat. No. B4287, Mol. Wt. ~66 kDa). Other biomolecules used in this study viz. N-acetyl-L-Cystine (SRL India, cat. no. 47866, MW=163.20 g/mol); Fibrinogen (Sigma, Product No. F4883, MW=340 kDa); Glutathione (SRL India, cat. no. 48938, MW=307.32 g/mol); Lysozyme (Thermo Scientific, Product No. 89833, MW=14.38 kDa); Collagen, Sigma, Product No. C8374, MW=161 kDa) were used as received. Silica gel for chromatography and TLC plates (60 F_{254}) was procured from Merck. Melting points were recorded on E-Z melting apparatus. NMR spectra were measured on a Brucker Advance II (400 MHz for ^{1}H and 100 MHz for ^{13}C) instrument using solvents DMSO-d_6 and $CDCl_3$. HRMS spectra were obtained on a 6200 series TOF (Q-TOF, B.06.01 (B6172 SP1). Steady-state absorption spectra were recorded on a Perkin-Elmer model Lambda25 absorption spectrophotometer. Fluorescence spectra were taken in a Hitachi model FL4500 spectrofluorimeter and all the spectra were corrected for the instrument response function. The relative experimental error in the measured photophysical parameters was estimated within ±5%.

Time-resolved fluorescence experiment

The time-resolved fluorescence decay was measured using a fluorescence spectrometer (QM-40, PTI, USA) outfitted with a TCSPC fluorescence lifetime detection device (PM-3). The instrument response function (IRF), which was collected at the excitation wavelength using a scattering solution, was used to fit the experimentally obtained decay traces using the iterative deconvolution technique based on the Levenberg-Marquardt algorithm

$$I(t) = \sum_i \alpha_i \times \exp\left(\frac{t}{\tau_i}\right)$$

Where α_i is the amplitude of the i^{th} component associated with fluorescence lifetime τ_i such that $\Sigma\alpha_i = 1$. The average fluorescence lifetime for the multi-exponential fluorescence decay function

was calculated as the fractional input of each individual decay component (f_i) to the steady-state intensity.

$$\tau_{av} = \sum_i f_i = \frac{\sum_i \alpha_i \tau_i^2}{\sum_i \alpha_i \tau_i}$$

Additionally, using known quantum yield (ϕ_f) and average lifetime (τ_{av}) values, the radiative (k_r) and total non-radiative (Σk_{nr}) decay rate constants in each instance were calculated using the following relations:

$$k_r = \frac{\phi_f}{\tau_{av}}; \quad \sum k_{nr} = \frac{(1-\phi_f)}{\tau_{av}}$$

Fluorescence anisotropy studies

Fluorescence anisotropy for the BODIPY-BSA interaction was calculated using the following equation:

$$r = \frac{I_{VV} - GI_{VH}}{I_{VV} + 2GI_{VH}}$$

The fluorescence spectral intensities produced by aligning the excitation and emission polarizers in parallel or perpendicular orientations, respectively, are represented by I_{VV} and I_{VH}. G is the instrument geometry factor.

II. Single Crystal XRD Experiments

The single crystal XRD data collection and data reduction were performed using CrysAlis PRO on a single crystal Rigaku Oxford XtaLab Pro Kappa dual home/near diffractometer. The crystals were kept at 93 K during data collection using CuKα (λ = 1.54184 Å) radiation. Using Olex2, the structure was solved with the ShelXT structure solution program using Intrinsic Phasing and refined with the ShelXL refinement package using Least Squares minimization.

X-ray Single Crystal Data for compound 4e (CCDC: 2294690)

The single crystal of compound (**4e**) $C_{38}H_{41}BCl_3F_2IN_2O_3S$ was crystalized as a red block through the slow evaporation of $CHCl_3$ solution at room temperature. The compound **4e** was crystallized in the $P\bar{1}$ space group and the asymmetric unit contains one molecule of **4e** and half of molecule

of chloroform ($CHCl_3$). Crystal Data for $C_{38}H_{41}BCl_3F_2IN_2O_3S$ (M =887.85 g/mol): triclinic, space group P-1 (no. 2), a = 8.40960(10) Å, b = 14.7442(2) Å, c = 17.5925(2) Å, α = 109.4650(10)°, β = 94.5770(10)°, γ = 105.5260(10)°, V = 1947.03(4) Å3, Z = 2, T = 93(2) K, μ(Cu Kα) = 9.258 mm^{-1}, Dcalc = 1.514 g/cm^3, 21257 reflections measured (6.886° ≤ 2Θ ≤ 159.76°), 8171 unique (R_{int} = 0.0381, Rsigma = 0.0414) which were used in all calculations. The final R_1 was 0.0429 (I > 2σ(I)) and wR_2 was 0.1176 (all data). The crystallographic details of the compound **4e** are deposited to the Cambridge Crystallographic (CCDC 2294690). The ORTEP diagram as crystal structure of (**4e**) is illustrated in Fig. S1.

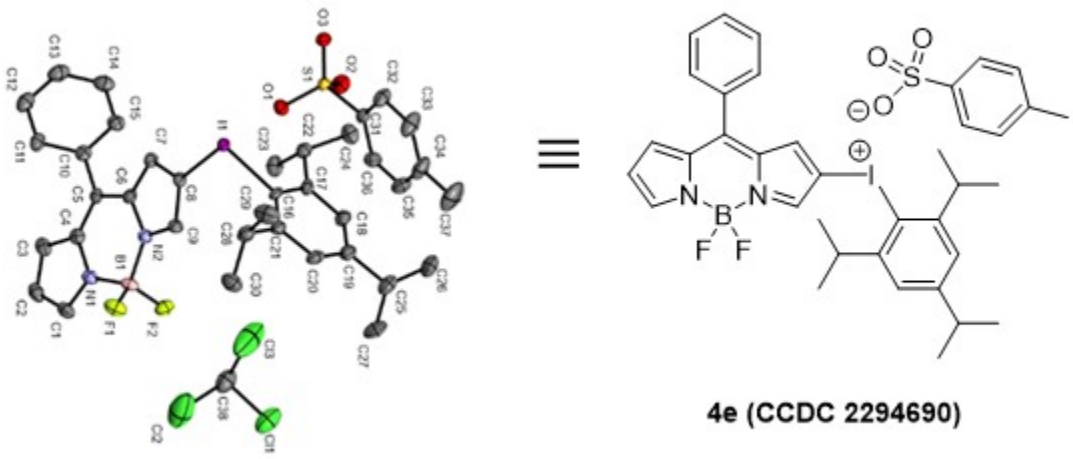

Fig. S1: The ORTEP diagram of compound (**4e**) (CCDC 2294690). (The thermal ellipsoid is drawn at the 50 % probability level.)

Table S1 Crystal data and structure refinement for compound 4e (exp_814_C-H).

Identification code	**4e** (exp_814_C-H)
Empirical formula	$C_{38}H_{41}BCl_3F_2IN_2O_3S$
Formula weight	887.85
Temperature/K	93(2)
Crystal system	triclinic
Space group	P-1
a/Å	8.40960(10)
b/Å	14.7442(2)
c/Å	17.5925(2)
α/°	109.4650(10)
β/°	94.5770(10)
γ/°	105.5260(10)
Volume/$Å^3$	1947.03(4)
Z	2

ρ_{calc}g/cm^3	1.514
μ/mm^{-1}	9.258
F(000)	900.0
Crystal size/mm^3	0.15 × 0.05 × 0.03
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.886 to 159.76
Index ranges	-10 ≤ h ≤ 10, -18 ≤ k ≤ 13, -22 ≤ l ≤ 22
Reflections collected	21257
Independent reflections	8171 [R_{int} = 0.0381, R_{sigma} = 0.0414]
Data/restraints/parameters	8171/0/467
Goodness-of-fit on F^2	1.114
Final R indexes [I>=2σ (I)]	R_1 = 0.0429, wR_2 = 0.1170
Final R indexes [all data]	R_1 = 0.0438, wR_2 = 0.1176
Largest diff. peak/hole / e Å^{-3}	2.86/-1.90

Table S2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for exp_814_C-H. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
I1	4478.8(2)	1753.9(2)	5780.5(2)	17.32(8)
S1	4606.3(10)	-538.2(6)	6307.9(5)	18.82(16)
Cl1	2035.2(18)	6551.9(12)	9477.8(7)	58.4(3)
Cl2	4557(2)	7356.1(19)	8674.5(11)	96.1(7)
Cl3	3581(4)	5227(2)	8460.0(13)	125.2(11)
F2	2232(3)	5537.0(17)	6736.6(13)	28.1(4)
F1	4912(3)	6117.7(17)	6573.2(15)	31.6(5)
O3	5110(3)	-1386.1(19)	5812.0(15)	23.5(5)
O1	5490(3)	404.5(19)	6211.7(16)	26.7(5)
O2	2805(3)	-744(2)	6208.8(17)	29.5(6)
N2	3320(4)	4379(2)	5757.6(17)	20.4(5)
N1	2678(4)	5781(2)	5471.8(19)	22.2(6)
C6	2701(4)	3771(3)	4940(2)	19.9(6)
C31	5345(4)	-352(3)	7339(2)	21.8(7)
C5	1972(4)	4126(3)	4385(2)	19.6(6)
C16	3778(4)	2101(3)	6955.3(19)	19.6(6)
C7	2993(4)	2838(3)	4795(2)	19.8(6)
C1	2542(4)	6687(3)	5561(3)	26.4(7)
C22	779(4)	917(3)	6241(2)	23.7(7)
C4	1974(4)	5126(3)	4658(2)	21.7(6)
C21	5015(5)	2758(3)	7646(2)	23.2(7)
C18	1727(5)	1802(3)	7777(2)	25.7(7)
C17	2124(4)	1609(3)	6990(2)	20.5(6)

C9	3977(4)	3858(3)	6132(2)	20.4(6)
C10	1221(4)	3435(3)	3532(2)	22.1(7)
C32	6328(5)	-896(3)	7524(2)	31.3(8)
C3	1361(4)	5694(3)	4254(2)	26.1(7)
C2	1739(5)	6662(3)	4818(3)	28.8(8)
C36	4976(5)	383(3)	7966(2)	31.0(8)
C24	-503(5)	71(3)	6396(3)	30.2(8)
C15	103(5)	2472(3)	3367(2)	25.9(7)
C8	3784(4)	2904(3)	5548(2)	19.4(6)
C23	-127(5)	1532(3)	5915(3)	30.9(8)
C20	4524(5)	2907(3)	8412(2)	26.8(7)
C19	2913(5)	2429(3)	8487(2)	28.1(8)
C11	1602(5)	3738(3)	2875(2)	25.5(7)
C12	862(5)	3096(3)	2076(2)	33.0(8)
C33	6942(6)	-692(4)	8339(3)	41.6(10)
C14	-659(5)	1837(3)	2571(3)	32.1(8)
C35	5603(6)	574(3)	8773(2)	38.4(9)
C28	6833(5)	3251(3)	7625(2)	29.9(8)
B1	3325(5)	5486(3)	6181(3)	22.6(7)
C13	-277(6)	2148(3)	1926(2)	36.1(9)
C25	2522(6)	2608(4)	9343(3)	38.1(9)
C34	6589(6)	36(4)	8970(2)	40.5(10)
C29	7918(5)	2660(4)	7830(3)	44.2(11)
C30	7521(6)	4363(3)	8192(3)	40.1(10)
C38	2929(7)	6273(4)	8590(3)	45.6(11)
C27	2159(9)	3604(4)	9699(3)	58.1(15)
C37	7269(8)	245(6)	9856(3)	63.0(17)
C26	1121(10)	1754(5)	9396(3)	70(2)

Table S3 Anisotropic Displacement Parameters ($Å^2×10^3$) for exp_814_C-H. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
I1	20.68(12)	18.18(12)	16.13(12)	7.42(8)	5.65(7)	8.87(8)
S1	22.3(4)	19.8(4)	17.5(3)	7.4(3)	6.0(3)	10.3(3)
Cl1	61.5(8)	82.8(10)	34.1(6)	18.9(6)	12.0(5)	30.0(7)
Cl2	72.7(11)	125.6(17)	58.6(9)	33.3(10)	7.0(8)	-16.2(11)
Cl3	237(3)	162(2)	83.7(13)	83.3(15)	89.0(17)	166(2)
F2	30.5(11)	30.7(11)	24.6(10)	6.8(9)	6.9(8)	16.0(9)
F1	22.6(10)	24.8(11)	40.0(13)	6.1(9)	-5.1(9)	6.1(8)
O3	32.1(13)	21.3(12)	20.0(11)	7.1(9)	8.1(10)	12.5(10)
O1	35.5(14)	22.6(12)	28.7(13)	13.4(10)	10.6(11)	13.4(11)
O2	23.5(12)	37.0(15)	28.9(13)	11.7(11)	4.8(10)	11.7(11)

N2	24.3(14)	19.2(14)	18.8(13)	6.9(11)	3.7(11)	8.7(11)
N1	20.6(13)	20.1(14)	26.7(15)	7.6(11)	5.6(11)	8.6(11)
C6	21.7(15)	23.0(16)	18.4(15)	8.4(13)	6.4(12)	10.4(13)
C31	24.4(16)	24.7(17)	18.9(15)	9.6(13)	8.2(13)	8.7(13)
C5	18.4(15)	22.2(16)	20.1(15)	9.5(13)	6.0(12)	6.8(12)
C16	27.6(17)	22.6(16)	11.5(14)	5.6(12)	7.0(12)	12.3(13)
C7	22.9(16)	21.8(16)	18.3(15)	8.9(12)	3.9(12)	10.7(13)
C1	21.9(16)	18.0(16)	39(2)	9.1(14)	7.4(14)	6.5(13)
C22	24.2(16)	26.0(17)	22.7(16)	8.7(14)	6.1(13)	10.8(14)
C4	18.2(15)	24.2(17)	24.5(16)	10.5(13)	4.2(12)	7.2(13)
C21	29.4(18)	22.8(16)	17.4(15)	6.2(13)	4.0(13)	9.6(14)
C18	26.5(17)	29.0(18)	25.8(17)	10.6(14)	11.6(14)	12.9(14)
C17	22.5(16)	25.0(16)	22.4(16)	13.8(13)	10.7(13)	12.6(13)
C9	22.7(16)	19.8(16)	21.6(16)	7.6(13)	5.2(12)	11.0(13)
C10	21.0(16)	26.0(17)	23.2(16)	10.1(14)	4.4(13)	12.1(13)
C32	37(2)	43(2)	22.9(18)	15.4(16)	9.9(15)	22.2(18)
C3	20.9(16)	27.9(18)	36.2(19)	17.3(15)	7.7(14)	10.8(14)
C2	26.5(18)	25.6(18)	42(2)	18.8(16)	10.6(16)	11.5(14)
C36	42(2)	24.1(18)	26.1(18)	6.4(15)	8.6(16)	12.3(16)
C24	22.9(17)	31.2(19)	39(2)	16.2(16)	5.0(15)	7.8(15)
C15	26.3(17)	25.0(18)	29.3(18)	9.9(14)	6.4(14)	12.6(14)
C8	23.1(16)	21.2(16)	21.4(15)	11.7(13)	7.2(12)	13.2(13)
C23	26.1(18)	40(2)	35(2)	21.2(17)	5.6(15)	13.6(16)
C20	33.7(19)	28.4(18)	15.8(15)	3.0(13)	3.7(14)	12.6(15)
C19	37(2)	29.3(19)	23.8(17)	10.1(14)	11.7(15)	16.8(16)
C11	26.5(17)	32.9(19)	24.0(17)	15.1(15)	5.1(14)	14.1(15)
C12	35(2)	44(2)	26.2(19)	16.4(17)	6.4(16)	18.3(18)
C33	37(2)	70(3)	31(2)	27(2)	8.3(17)	27(2)
C14	29.2(19)	27.9(19)	33(2)	5.3(16)	-1.2(15)	9.1(15)
C35	52(3)	34(2)	21.5(18)	3.6(16)	9.5(17)	10.0(19)
C28	28.0(18)	33(2)	22.0(17)	5.3(15)	4.4(14)	5.3(15)
B1	21.2(18)	17.4(17)	27.9(19)	4.9(15)	3.1(15)	8.8(14)
C13	40(2)	40(2)	23.4(18)	5.2(16)	-2.5(16)	15.6(18)
C25	45(2)	48(3)	24.0(19)	12.9(18)	13.7(17)	18(2)
C34	35(2)	61(3)	18.9(18)	14.9(18)	3.4(16)	6(2)
C29	26(2)	34(2)	63(3)	6(2)	8.6(19)	9.1(17)
C30	39(2)	27(2)	44(2)	8.5(18)	1.7(19)	1.8(17)
C38	49(3)	61(3)	34(2)	22(2)	10(2)	23(2)
C27	85(4)	50(3)	40(3)	7(2)	37(3)	28(3)
C37	54(3)	101(5)	24(2)	24(3)	-3(2)	12(3)
C26	118(6)	52(3)	37(3)	18(2)	39(3)	10(3)

Table S4 Bond Lengths for exp_814_C-H.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
I1	C16	2.129(3)	C22	C17	1.519(5)
I1	C8	2.084(3)	C22	C24	1.532(5)
S1	O3	1.456(2)	C22	C23	1.541(5)
S1	O1	1.462(3)	C4	C3	1.427(5)
S1	O2	1.447(3)	C21	C20	1.405(5)
S1	C31	1.774(4)	C21	C28	1.517(5)
Cl1	C38	1.760(5)	C18	C17	1.404(5)
Cl2	C38	1.757(6)	C18	C19	1.396(6)
Cl3	C38	1.723(6)	C9	C8	1.395(5)
F2	B1	1.392(5)	C10	C15	1.396(5)
F1	B1	1.372(4)	C10	C11	1.402(5)
N2	C6	1.384(4)	C32	C33	1.386(6)
N2	C9	1.356(4)	C3	C2	1.374(6)
N2	B1	1.550(5)	C36	C35	1.382(6)
N1	C1	1.329(5)	C15	C14	1.382(5)
N1	C4	1.404(5)	C20	C19	1.389(6)
N1	B1	1.556(5)	C19	C25	1.518(5)
C6	C5	1.422(5)	C11	C12	1.385(6)
C6	C7	1.405(5)	C12	C13	1.392(6)
C31	C32	1.386(5)	C33	C34	1.379(7)
C31	C36	1.388(5)	C14	C13	1.389(6)
C5	C4	1.390(5)	C35	C34	1.387(7)
C5	C10	1.474(5)	C28	C29	1.518(6)
C16	C21	1.404(5)	C28	C30	1.526(6)
C16	C17	1.403(5)	C25	C27	1.517(7)
C7	C8	1.394(5)	C25	C26	1.511(8)
C1	C2	1.408(6)	C34	C37	1.516(6)

Table S5 Bond Angles for exp_814_C-H.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C8	I1	C16	93.99(13)	N2	C9	C8	108.1(3)
O3	S1	O1	111.88(15)	C15	C10	C5	120.5(3)
O3	S1	C31	104.98(16)	C15	C10	C11	119.0(3)
O1	S1	C31	105.04(16)	C11	C10	C5	120.5(3)
O2	S1	O3	113.61(16)	C31	C32	C33	119.3(4)
O2	S1	O1	113.41(16)	C2	C3	C4	107.0(3)
O2	S1	C31	107.04(16)	C3	C2	C1	107.5(3)
C6	N2	B1	126.4(3)	C35	C36	C31	119.8(4)
C9	N2	C6	108.7(3)	C14	C15	C10	120.8(4)

C9	N2	B1	124.9(3)	C7	C8	I1	125.9(3)
C1	N1	C4	108.2(3)	C7	C8	C9	108.8(3)
C1	N1	B1	124.9(3)	C9	C8	I1	125.2(2)
C4	N1	B1	126.6(3)	C19	C20	C21	122.2(3)
N2	C6	C5	121.5(3)	C18	C19	C25	122.7(4)
N2	C6	C7	108.6(3)	C20	C19	C18	118.9(3)
C7	C6	C5	129.8(3)	C20	C19	C25	118.3(4)
C32	C31	S1	121.3(3)	C12	C11	C10	120.3(4)
C32	C31	C36	119.9(3)	C11	C12	C13	119.7(4)
C36	C31	S1	118.7(3)	C34	C33	C32	121.5(4)
C6	C5	C10	120.0(3)	C15	C14	C13	119.7(4)
C4	C5	C6	119.2(3)	C36	C35	C34	121.0(4)
C4	C5	C10	120.9(3)	C21	C28	C29	110.0(3)
C21	C16	I1	118.3(2)	C21	C28	C30	113.2(3)
C17	C16	I1	117.4(2)	C29	C28	C30	110.3(4)
C17	C16	C21	124.2(3)	F2	B1	N2	110.4(3)
C8	C7	C6	105.8(3)	F2	B1	N1	109.6(3)
N1	C1	C2	110.1(3)	F1	B1	F2	110.0(3)
C17	C22	C24	113.2(3)	F1	B1	N2	111.2(3)
C17	C22	C23	110.8(3)	F1	B1	N1	110.6(3)
C24	C22	C23	110.1(3)	N2	B1	N1	104.9(3)
N1	C4	C3	107.2(3)	C14	C13	C12	120.5(4)
C5	C4	N1	120.7(3)	C27	C25	C19	111.4(4)
C5	C4	C3	132.1(3)	C26	C25	C19	114.1(4)
C16	C21	C20	116.2(3)	C26	C25	C27	110.2(5)
C16	C21	C28	125.0(3)	C33	C34	C35	118.5(4)
C20	C21	C28	118.6(3)	C33	C34	C37	120.7(5)
C19	C18	C17	122.2(3)	C35	C34	C37	120.9(5)
C16	C17	C22	124.1(3)	Cl2	C38	Cl1	108.5(3)
C16	C17	C18	116.2(3)	Cl3	C38	Cl1	109.7(3)
C18	C17	C22	119.7(3)	Cl3	C38	Cl2	113.4(3)

Table S6 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for exp_814_C-H.

Atom	*x*	*y*	*z*	U(eq)
H7	2710.24	2278.01	4288.86	24
H1	2932.03	7266.68	6054.85	32
H22	1353.36	588.77	5801.44	28
H18	614.25	1494.42	7828.14	31
H9	4481.06	4098.94	6694.32	24
H32	6577.88	-1404.33	7098.14	38
H3	799.33	5447.98	3700.88	31

H2	1500.5	7214.68	4723.96	35
H36	4293.68	752.44	7840.54	37
H24A	87.42	-295.37	6626.48	45
H24B	-1249.64	-398.55	5877.73	45
H24C	-1168.06	366.25	6783.98	45
H15	-137.33	2251.69	3806.36	31
H23A	-737.61	1843.68	6325.58	46
H23B	-921.05	1080.5	5406.03	46
H23C	700.87	2061.72	5807.36	46
H20	5321.49	3350.44	8895.21	32
H11	2371.26	4387.97	2978.32	31
H12	1129.9	3301.28	1631.44	40
H33	7622.03	-1061.92	8465.75	50
H14	-1440.91	1190.53	2465.72	38
H35	5354.9	1082.17	9200.72	46
H28	6897.65	3216.25	7050.96	36
H13	-795.94	1710.68	1378.05	43
H25	3558.15	2663.03	9699.67	46
H29A	7889.91	2687.84	8393.14	66
H29B	9077.62	2957.66	7780.79	66
H29C	7488.11	1952.96	7449.22	66
H30A	6775.71	4727.63	8072.69	60
H30B	8646.22	4660.22	8102.47	60
H30C	7581.12	4414.21	8763.79	60
H38	2047.62	6109.23	8106.27	55
H27A	3109.73	4157.09	9694.8	87
H27B	1991.95	3719.72	10264.62	87
H27C	1142.42	3578.3	9368.42	87
H37A	6888.67	-378.96	9967.25	95
H37B	6858.62	763.32	10218.3	95
H37C	8499.33	486.82	9955.48	95
H26A	55.87	1719.39	9098.85	106
H26B	1043.3	1877.97	9972.86	106
H26C	1353.45	1112.65	9151.3	106

Refinement model description

Number of restraints - 0, number of constraints - unknown.

Details:

```
1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups
 At 1.5 times of:
  All C(H,H,H) groups
2.a Ternary CH refined with riding coordinates:
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 C22(H22), C28(H28), C25(H25), C38(H38)
2.b Aromatic/amide H refined with riding coordinates:
 C7(H7), C1(H1), C18(H18), C9(H9), C32(H32), C3(H3), C2(H2), C36(H36),
 C15(H15), C20(H20), C11(H11), C12(H12), C33(H33), C14(H14), C35(H35), C13(H13)
2.c Idealised Me refined as rotating group:
 C24(H24A,H24B,H24C), C23(H23A,H23B,H23C), C29(H29A,H29B,H29C), C30(H30A,H30B,
 H30C), C27(H27A,H27B,H27C), C37(H37A,H37B,H37C), C26(H26A,H26B,H26C)
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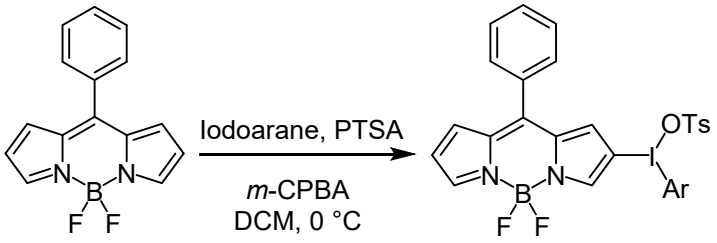
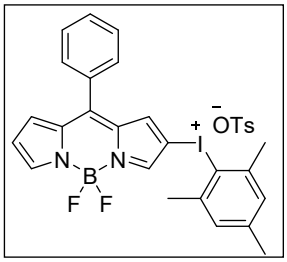
III. General experimental procedure

General procedure for the synthesis of Bodipy(aryl)iodonium salts 4a-g:



To a stirred solution of iodoarenes(0.37 mmol) in dichloromethane (2 mL) at 0 ºC was added *m*-CPBA (0.45 mmol) and PTSA (0.45 mmol). The resulting suspension was allowed to stir at 0 ºC for 20 min and then a solution of BODIPY **1** (0.1 g, 0.37 mmol) in dichloromethane (1 mL) was added dropwise to the reaction mixture and continued the stirring at 0 ºC for 2 h. The progress of the reaction was monitored by TLC. After completion of the reaction, removed the excess of solvent at low temperature. The residue so obtained was taken into in cold diethyl ether and stirred at 0 ºC for 20 min. The solid product was filtered, washed with cold diethyl ether and dried under vacuum to obtain yellowish solid products **4a-g**.

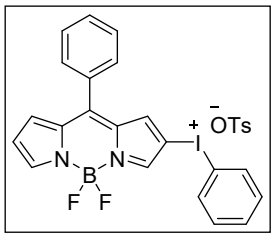
5,5-difluoro-10-phenyl-5*H*-4λ^4,5λ^{4}4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinin-2-yl)-(mesityl)iodonium 4-methylbenzenesulfonate (4a):



Yellow colour, 93% yield, M.pt- 247-248 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.57 (s, 2H), 7.77 – 7.71 (m, 1H), 7.64 (d, J = 3.9 Hz, 4H), 7.49 – 7.42 (m, 3H), 7.30 – 7.24 (d, J = 3.4 Hz, 1H), 7.16 (s, 2H), 7.10 (d, J = 7.5 Hz, 2H), 6.92 (d, J = 2.9 Hz, 1H), 2.63 (s, 6H), 2.27 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 152.2, 147.9, 146.0, 144.2, 143.2, 141.7, 138.1, 136.7, 134.3, 133.2, 132.6, 132.2, 131.2, 130.0, 129.4, 128.5, 125.9, 124.2, 123.5, 92.2, 65.4, 26.9,

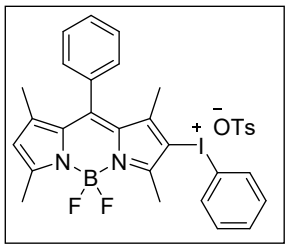
21.2, 20.93 15.6. ^{19}F NMR (376 MHz, DMSO-d_6) δ -141.2 (dd, J = 56.5, 28.1 Hz); HRMS (ESI) *m/z* calcd for $C_{24}H_{21}BF_2IN_2$ $[M]^+$ 513.0797; found 513.0809.

(5,5-difluoro-10-phenyl-5*H*-4λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinin-2-yl)(phenyl)-iodonium 4-methylbenzenesulfonate (4b):



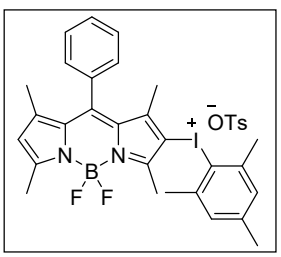
Yellow colour, 89% yield, M.pt- 207-208 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.62 (s, 1H), 8.54 (s, 1H), 8.18 (d, J = 7.8 Hz, 2H), 7.74 (dq, J = 8.1, 4.0 Hz, 1H), 7.66 (d, J = 4.3 Hz, 4H), 7.62 – 7.56 (m, 2H), 7.52 – 7.46 (m, 4H), 7.28 (d, J = 4.2 Hz, 1H), 7.12 (d, J = 7.8 Hz, 2H), 6.91 (d, J = 4.0 Hz, 1H), 2.29 (s, 3H).^{13}C NMR (100 MHz, DMSO-d_6) δ 151.83, 148.02, 146.14, 144.56, 138.11, 136.49, 136.46, 135.04, 133.78, 133.76, 132.67, 132.24, 131.96, 131.90, 131.23, 129.43, 128.53, 125.96, 123.26, 123.24, 119.86, 21.25.; HRMS (ESI) *m/z* calcd for $C_{21}H_{15}BF_2IN_2$ $[M]^+$ 471.0345; found 471.0339.

(5,5-difluoro-1,3,7,9-tetramethyl-10-phenyl-5*H*-4λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1'*f*][1,3,2]-diaza-borinin-2-yl)(phenyl)iodonium 4-methyl-benzenesulfonate (4c):



Yellow colour, 83% yield, M.pt- 131-134 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.09 (d, J = 7.9 Hz, 2H), 7.61 (bs, 3H), 7.49 (m, 5H), 7.49 (m, 2H), 7.12 (d, J = 7.7 Hz, 2H), 6.50 (s, 1H), 2.71 (s, 3H), 2.56 (s, 3H), 2.28 (s, 3H), 1.50 (s, 3H), 1.39 (s, 3H).^{13}C NMR (100 MHz, DMSO-d_6) δ 164.5, 151.7, 149.1, 146.2, 143.1, 140.6, 138.0, 135.0, 134.2, 133.4, 132.4, 132.3, 130.3, 130.1, 129.3, 128.5, 128.1, 125.9, 125.6, 117.3, 102.9, 21.2, 15.4, 15.2, 15.0, 14.9; ^{19}F NMR (376 MHz, DMSO-d_6) δ -^{19}F NMR (376 MHz, DMSO) δ -142.89, -142.98, -143.07, -143.15. (dd, J = 64.4, 31.7 Hz); HRMS (ESI) *m/z* calcd for $C_{25}H_{23}BF_2IN_2$ $[M]^+$ 527.0965; found 527.0966.

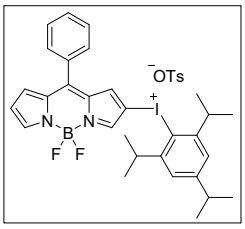
(5,5-difluoro-1,3,7,9-tetramethyl-10-phenyl-5*H*-4λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]-diaza-borinin-2-yl)(mesityl)iodonium (4d):



Yellow colour, 69% yield, M.pt- 150-153 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.60 (s, 3H), 7.46 (d, J = 7.2 Hz, 2H), 7.40 (s, 2H), 7.17 (s, 2H), 7.10 (d, J = 7.0 Hz, 2H), 6.50 (s, 1H), 2.57 (d, J = 8.7 Hz, 6H), 2.52 (s, 6H), 2.28 (s, 6H), 1.38 (d, J = 6.3 Hz, 6H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 164.4, 151.6, 149.1, 146.1, 143.1, 143.0, 141.7, 140.6, 138.0, 134.2, 133.4, 130.4, 130.3, 130.1, 128.5, 128.1, 125.9, 125.6, 121.4, 99.6, 26.3, 21.2, 20.9, 15.4, 15.1, 14.9; ^{19}F NMR

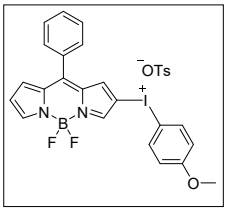
(376 MHz, DMSO-d_6) δ -143.0 (dd, J = 64.4, 31.7 Hz); HRMS (ESI) *m/z* calcd for $C_{28}H_{29}BF_2IN_2$ $[M]^+$ 569.1438; found 569.1436.

(5,5-difluoro-10-phenyl-5*H*-4λ⁴,5λ⁴-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinin-2-yl)-(2,4,6-triisopropylphenyl)iodonium-4-methylbenzenesulfonate (4e):



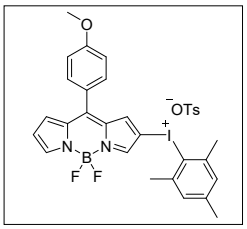
Yellow colour, 81% yield, M.pt- 287-288 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.58 (s, 1H), 8.51 (s, 1H), 7.73 (t, J = 6.2 Hz, 1H), 7.66 – 7.59 (m, 4H), 7.48 (d, J = 7.7 Hz, 2H), 7.28 (dd, J = 27.9, 10.4 Hz, 4H), 7.11 (d, J = 7.6 Hz, 2H), 6.93 (d, J = 3.5 Hz, 1H), 3.50 (dt, J = 12.6, 6.2 Hz, 2H), 2.95 (dt, J = 13.7, 6.7 Hz, 1H), 2.29 (s, 3H), 1.24 (d, J = 6.0 Hz, 12H), 1.19 (d, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 154.5, 152.6, 151.1, 147.8, 146.2, 143.5, 138.1, 136.8, 134.4, 132.5, 132.4, 132.2, 131.2, 129.3, 128.5, 125.9, 125.7, 124.8, 123.6, 123.6, 92.8, 40.0, 38.9, 33.8, 24.4, 24.0, 21.2; ^{19}F NMR (376 MHz, DMSO-d_6) δ -141.3 (dd, J = 56.8, 28.3 Hz); HRMS (ESI) *m/z* calcd for $C_{30}H_{33}BF_2IN_2$ $[M]^+$ 597.1685; found 597.1749.

(5,5-difluoro-10-phenyl-5H-4λ⁴,5λ⁴-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinin-2-yl)(4-methoxyphenyl)iodonium-4-methylbenzenesulfonate (4f):



Yellow colour, 80% yield, M.pt- 242-245 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.62 (s, 1H), 8.54 (s, 1H), 8.12 (d, J = 8.64 Hz, 1H), 7.75 – 7.65 (m, 5H), 7.57 (s, 1H), 7.49 (d, J =7.72 Hz, 2H), 7.29 (d, J = 4.52 Hz, 1H), 7.13 (d, J = 7.76 Hz, 2H), 7.05 (d, J = 8.2 Hz, 2H), 6.92 (d, J = 4.6 Hz, 1H), 3.77 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 162.3, 152.3, 148.0, 145.6, 144.1, 138.4, 137.2, 136.7, 133.3, 132.5, 132.3, 131.2, 129.5, 128.6, 125.9, 123.6, 117.8, 107.1, 56.1, 21.2; ^{19}F NMR (376 MHz, DMSO-d_6) δ -141.3 (dd, J = 56.6, 28.1 Hz); HRMS (ESI) *m/z* calcd for $C_{22}H_{17}BF_2IN_2O$ $[M]^+$ 501.0442; found 501.0430.

(5,5-difluoro-10-(4-methoxyphenyl)-5H-4λ⁴,5λ⁴-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinin-2-yl)(mesityl)iodonium-4-methylbenzenesulfonate (4g):



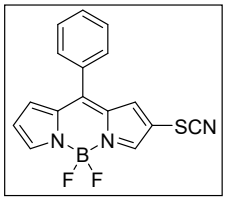
Yellow colour, 65% yield, M.pt- 283-286 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.56 (s, 1H), 8.49 (s, 1H), 7.66 (d, J = 8.48 Hz, 2H), 7.49 – 7.46 (m, 3H), 7.32 (d, J = 4.5 Hz, 1H), 7.22-7.17 (m, 4H), 7.12 (d, J = 7.7 Hz, 2H), 6.91 (d, J = 4.5 Hz, 1H), 3.90 (s, 3H), 2.63 (s, 6H), 2.28 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 154.5,

152.6, 151.1, 147.8, 146.2, 143.5, 138.1, 136.8, 134.4, 132.5, 132.4, 132.2, 131.2, 129.3, 128.5, 125.9, 125.7, 124.8, 123.6, 123.6, 92.8, 40.0, 38.9, 33.8, 24.4, 24.0, 21.2; ^{19}F NMR (376 MHz, DMSO-d_6) δ -143.2 (dd, J = 55.7, 27.6 Hz); HRMS (ESI) *m/z* calcd for $C_{25}H_{23}BF_2IN_2O$ $[M]^+$ 543.0911; found 543.0927.

General experimental procedure

To a stirred solution of **4a** (100 mg, 0.42 mmol) in acetonitrile (5 mL), appropriate nucleophiles (0.48 mmol) and cesium carbonate (1.20 mmol) were added and stirred the contents at room temperature for 1-2 h. Upon completion of the reaction, water (25 mL) was added, and extracted the mixture with dichloromethane (3 × 25 mL). The organic phase was dried over anhydrous sodium sulphate and concentrated under reduced pressure. Purification by column chromatography (chloroform and hexane 70:30) afforded the desired products **5a-c**.

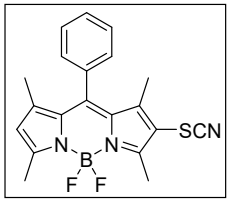
5,5-difluoro-10-phenyl-2-thiocyanato-5*H*-4λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diaza-



borinine 5a:

Orange colour, 72% yield, M.pt- 212-214 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.62 (s, 1H), 8.54 (s, 1H), 8.06 (d, J = 8.3 Hz, 2H), 7.74 (dd, J = 9.0, 4.5 Hz, 1H), 7.66 (d, J = 4.4 Hz, 4H), 7.56 (s, 1H), 7.32 – 7.27 (m, 3H), 6.91 (d, J = 5.8 Hz, 1H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 151.8, 148.0, 144.5, 142.4, 136.6, 136.5, 135.0, 134.3, 133.6, 132.7, 132.5, 132.2, 131.2, 131.1, 131.1, 129.4, 129.3, 129.3, 128.4, 123.3, 123.2, 116.1, 96.7, 21.3; HRMS (ESI) *m/z* calcd for $C_{16}H_{10}BF_2N_3S$ $[M+H]^+$ 306.0667; found 306.0670.

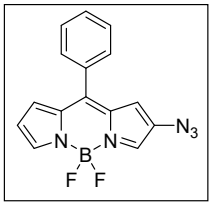
5,5-difluoro-1,3,7,9-tetramethyl-10-phenyl-2-thiocyanato-5*H*-4λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1'-



***f*][1,3,2]diazaborinine 5b:**

Orange colour, 81% yield, M.pt- 176-178 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.68 (s, 3H), 8.58 (s, 3H), 8.20 (d, J = 7.9 Hz, 6H), 7.66 (dd, J = 10.4, 5.9 Hz, 18H), 7.53 (t, J = 7.7 Hz, 7H), 7.30 (d, J = 4.3 Hz, 3H), 6.93 (d, J = 4.2 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 152.5, 148.0, 144.3, 136.9, 136.8, 135.1, 134.4, 133.6, 132.6, 132.4, 132.2, 132.1, 131.2, 129.4, 123.6, 122.7, 119.5, 118.2, 94.1; HRMS (ESI) *m/z* calcd for $C_{20}H_{18}BF_2N_3S$ $[M+H]^+$ 382.1345; found 382.1359.

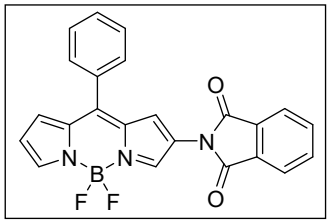
2-azido-5,5-difluoro-10-phenyl-5*H*-4λ⁴,5λ⁴-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinine 5c:



Dark black colour, 70% yield, M.pt- 176-178 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.69 (s, 1H), 7.67 – 7.61 (m, 1H), 7.58 (d, J = 4.4 Hz, 4H), 6.97 (d, J = 4.2 Hz, 1H), 6.58 (d, J = 8.2 Hz, 2H);^{13}C NMR (100 MHz, $CDCl_3$) δ 146.8, 146.6, 146.0, 136.2, 135.8, 135.2, 133.4, 133.2, 133.2 131.11, 130.4, 128.6, 119.6; HRMS (ESI) *m/z* calcd for $C_{15}H_{10}BF_2N_5$ $[M+H]^+$ 310.1065; found 310.1073.

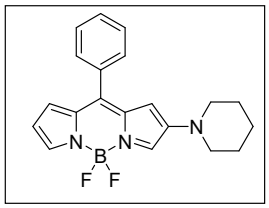
Cu-catalyzed nucleophilic substitution of BODIPYs 5d-f: To a stirred solution of **4a** (100 mg, 0.42 mmol) and appropriate amines (0.48 mmol) in acetonitrile (5 mL) was added CuI (0.04 mmol) and allowed to contents to stir at room temperature for 3-4 h. Upon completion the reaction, water (25 mL) was added, and extracted the mixture with dichloromethane (3 × 25 mL). The organic phase was dried over sodium sulphate and concentrated under reduced pressure. Purification by column chromatography (chloroform and hexane 70:30) afforded **5d, 5e** and **5g**.

2-(5,5-difluoro-10-phenyl-5*H*-4λ⁴,5λ⁴-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinin-2-yl) isoindoline-1,3-dione 5d:



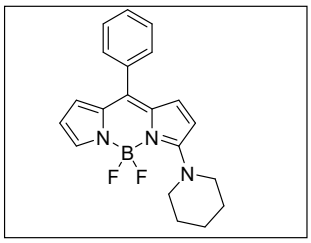
Purple colour, 56% yield, M.pt- 237-238 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.65 (s, 1H), 8.03 (s, 1H), 7.94-7.92 (m, 2H), 7.80 – 7.78 (m, 2H), 7.64-7.56 (m, 5H), 7.46 (s, 1H), 7.02 (d, J = 4.28 Hz, 1H), 6.61 (d, J = 4.08 Hz, 1H) ; ^{13}C NMR (100 MHz, DMSO-d_6) δ 152.4, 148.0, 144.1, 137.0, 136.9, 134.9, 134.2, 133.4, 132.4, 132.4, 131.2, 131.0, 129.5, 129.3, 126.4, 123.7, 122.5, 119.3, 94.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -136.8 (dd, J = 56.7, 28.3 Hz); HRMS (ESI) *m/z* calcd for $C_{23}H_{14}BF_2N_3O_2$ $[M+H]^+$ 414.1219; found 414.1224.

5,5-difluoro-10-phenyl-2-(piperidin-1-yl)-5*H*-4λ⁴,5λ⁴-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]-diazaborinine 5e:



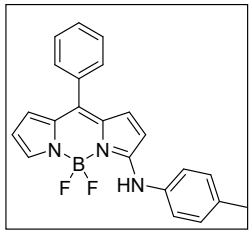
Yellowish brown colour, 58% yield, M.pt- 69-71 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (m, 6H), 7.41 (s, 1H), 6.92 (d, J = 5.28 Hz, 1H), 6.38 (t, J = 5.36 Hz, 2H), 3.95 (m, 4H), 1.84 – 1.74 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.14, 134.82, 134.42, 130.36, 128.98, 128.22, 122.98, 114.88, 52.04, 26.39, 24.12; ^{19}F NMR (376 MHz, $CDCl_3$) δ -134.9 (dd, J = 66.4, 32.7 Hz). HRMS (ESI) *m/z* calcd for $C_{20}H_{20}BF_2N_3$ $[M+H]^+$ 351.1718; found 352.1789.

5,5-difluoro-10-phenyl-2-(piperidin-1-yl)-5*H*-4λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]-diazaborinine 5f:



Yellowish brown colour, 77% yield, M.pt- 65-68 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (m, 6H), 6.90 (s, 1H), 6.35 (s, 2H), 6.30 (d, J = 5.12 Hz, 1H), 3.94 (m, 4H), 1.83 – 1.81 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.04, 135.66, 135.34, 131.51, 130.62, 130.47, 128.79, 128.08, 117.91, 113.80, 113.29, 51.87, 26.38, 24.23. HRMS (ESI) *m/z* calcd for $C_{20}H_{20}BF_2N_3$ $[M+H]^+$ 351.1718; found 352.1791.

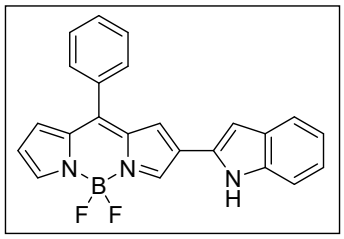
5,5-difluoro-10-phenyl-*N*-(*p*-tolyl)-5*H*-4λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinin-2-amine 5g:



Dark reddish colour, 80% yield, M.pt- 187-190 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.46 (m, 6H), 7.27 – 7.18 (m, 5H), 6.99 (d, J = 5.0 Hz, 1H), 6.56 (s, 1H), 6.41 (d, J = 5.0 Hz, 1H), 2.40 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 136.9, 136.4, 135.8, 134.4, 134.0, 133.6, 130.4, 130.2, 129.5, 128.4, 126.0, 123.3, 112.8, 21.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -136.8 (dd, J = 58.0, 28.4 Hz); HRMS (ESI) *m/z* calcd for $C_{22}H_{18}BF_2N_3$ $[M+H]^+$ 373.1562; found 373.1555.

Pd-catalyzed nucleophilic substitution of BODIPYs: To a solution of **4a** (100 mg, 0.42 mmol) and appropriate nucleophiles (0.48 mmol) in dry acetonitrile (5 mL), was added $Pd(OAc)_2$ (0.04 mmol) and the contents were stirred at 80 ˚C for 2-4 h. After completion of the reaction, the contents were poured into water (50 mL) and extracted with dichloromethane (3 × 100 mL). The organic layer was dried over anhydrous sodium sulphate and concentrated under reduce pressure. Purification by column chromatography (chloroform and hexane 80:20) afforded the desired product.

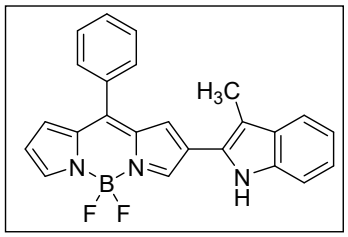
5,5-difluoro-2-(1*H*-indol-2-yl)-10-phenyl-5*H*-4λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1'*f*][1,3,2]-diazaborinine 5h:



Golden brown colour, 57% yield, M.pt- 240-242 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 2H), 8.00 (s, 1H), 7.67 (m, 1H), 7.63 (m, 5H), 7.32 (d, J = 8.0 Hz, 1H), 7.2 (m, 2H), 6.99 (s, 1H), 6.96 (d, J = 4.04,

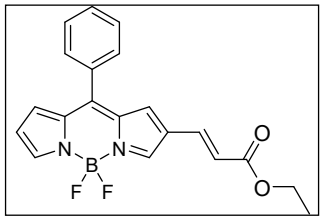
1H), 6.69 (s, 1H), 6.60 (dd, J = 4.00, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.66, 144.58, 141.64, 136.58, 135.43, 135.33, 133.70, 131.78, 131.03, 130.88, 130.46, 129.03, 128.58, 126.36, 123.33, 122.54, 120.53, 120.43, 118.84, 110.73, 100.18; HRMS (ESI) *m/z* calcd for $C_{23}H_{16}BF_2N_3$ $[M+H]^+$ 384.1465; found 384.1482.

5,5-difluoro-2-(3-methyl-1*H*-indol-2-yl)-10-phenyl-5*H*-4λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1'*f*]-[1,3,2]diazaborinine 5i:



Golden brown colour, 77% yield, M.pt- 235-239 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.20 (s, 1H), 8.58 (s, 1H), 8.21 (s, 1H), 7.79 (m, 6H), 7.52 (d, J = 7.88 Hz, 1H), 7.33 (s, 1H), 7.30 (d, J = 8 Hz 1H), 7.11 (m, 1H), 7.06 (d, 1H), 7.02 (m, 1H), 6.74 (dd, J = 4.2, 1.84 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 158.98, 140.22, 138.92, 138.07, 132.47, 130.89, 130.22, 126.45, 125.30, 123.61, 123.00, 122.69, 122.36, 120.96, 118.13,115.58, 111.96, 109.37, 84.19, 22.04; HRMS (ESI) *m/z* calcd for $C_{24}H_{18}BF_2N_3$ $[M+H]^+$ 398.1606; found 398.1639.

5,5-difluoro-2-(3-methyl-1*H*-indol-2-yl)-10-phenyl-5*H*-4λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1'*f*]-[1,3,2]diazaborinine 5j:

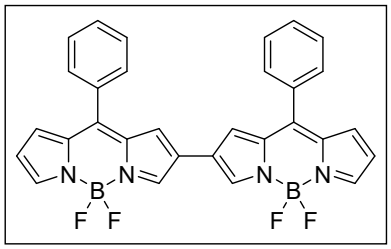


Pink colour, 50% yield, M.pt-75-78 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 8.05 (s, 1H), 7.65-7.58 (m, 5H), 7.57 (d, J = 16 Hz, 1H), 7.05 (d, J = 4.4 Hz, 1H), 7.02 (s, 1H), 6.64 (d, J = 3.48 Hz, 1H), 6.26 (d, J = 15.96 Hz, 1H), 4.27 (q, J = 7.16, 14.28 Hz, 2H), 1.34 (t, J = 7.16 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 147.8, 146.4, 142.5, 135.8, 135.6, 135.1, 133.4, 133.1, 131.2, 130.1, 128.7, 128.5, 127.8, 119.8, 117.9, 60.5, 14.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -145.05 (dd, J = 56.8, 28.4 Hz); HRMS (ESI) *m/z* calcd for $C_{20}H_{18}BF_2N_2O_2$ $[M+H]^+$ 367.1429; found 367.1432.

General procedure for the synthesis of BODIPY dimer

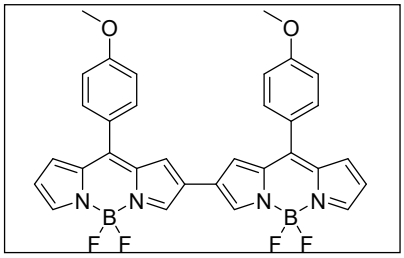
To a 10 mL vial with magnetic stir bar BODIPY iodonium salts **4a**/**4g** (100 mg, 0.146 mmol), catalytic amount of $Pd(OAc)_2$ (5 mol%) and PEG-400 (2 mL) were added. The reaction vial was kept under MW irradiation for 20 min at 80 ºC. Completion of the reaction was confirmed by TLC and the resulting contents were taken into water, extracted with ethyl acetate (3×3 mL) and dried the combined organic layer over anhydrous sodium sulfate. After removal of the organic solvent, the residue so obtained was purified by column chromatography and afforded the desired product **5k** and **5l** in 79-82% yield.

5,5,5',5'-tetrafluoro-10,10'-diphenyl-5*H*,5'*H*-4λ⁴,5λ⁴,5'λ⁴,6'λ⁴-2,2'-bidipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinine 5k:



Purple colour, 79% yield, M.pt- 237-238 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.89 (s, 2H), 8.13 (s, 2H), 7.72-7.68 (m, 6H), 7.65 – 7.61 (m, 4H), 7.53 (s, J = 7.7 Hz, 2H), 6.99 (d, J = 3.92, 10.4 Hz, 2H), 6.70 (dd, J = 1.88, 4.2 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 146.72, 144.73, 135.36, 134.83, 133.47, 131.80, 131.47, 131.14, 129.19, 127.26, 126.32, 119.53; ^{19}F NMR (376 MHz, $CDCl_3$) δ -136.8 (dd, J = 58.0, 28.4 Hz). HRMS (ESI) *m/z* calcd for $C_{30}H_{20}B_2F_2N_4$ $[M+H]^+$ 535.1890; found 535.1893.

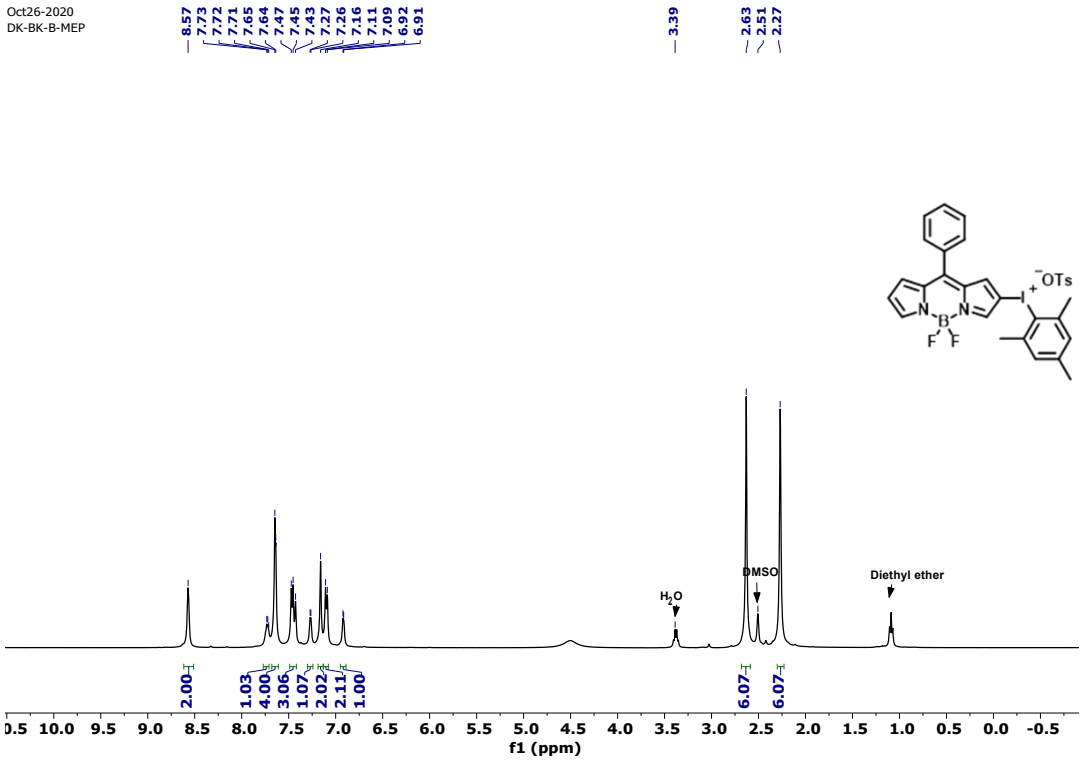
5,5,5',5'-tetrafluoro-10,10'-diphenyl-5*H*,5'*H*-4λ⁴,5λ⁴,5'λ⁴,6'λ⁴-2,2'-bidipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinine 5l:



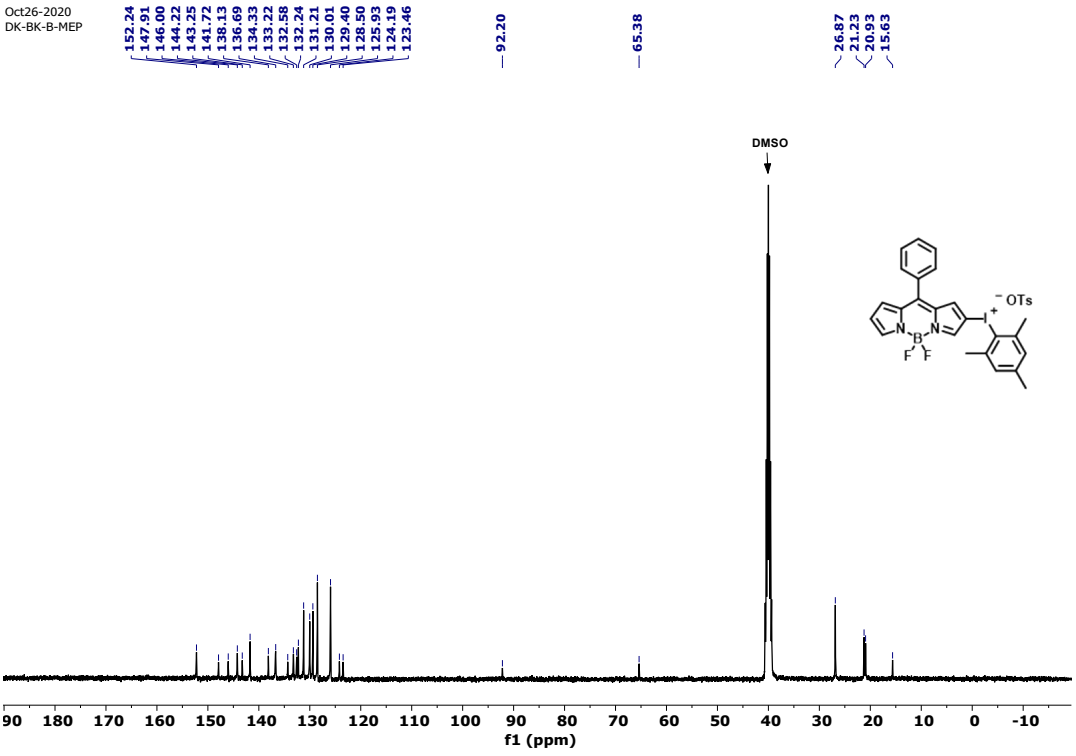
Purple colour, 82% yield, M.pt- 235-238 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 2H), 7.95 (s, 2H), 7.61 (d, J = 27.9, 10.4 Hz, 4H), 7.12 (d, J = 8.6, 4H), 7.02 (m, 4H), 6.59 (dd, J = 4.0 ,1.2 Hz, 2H), 3.96 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 152.6, 151.1, 147.8, 146.2, 143.5, 138.1, 136.8, 134.4, 132.5, 132.4, 132.2, 131.2, 129.3, 128.5, 125.9, 125.7, 124.8, 123.6, 123.6, 92.8, 40.0, 38.9, 33.8, 24.4, 24.0, 21.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -145.0 (dd, J = 57.4, 29.8 Hz). HRMS (ESI) *m/z* calcd for $C_{32}H_{25}B_2F_4N_4O_2$ $[M+H]^+$ 595.2021; found 595.2118.

IV. Spectra (^{1}H, ^{13}C NMR and HRMS) of the synthesized compounds

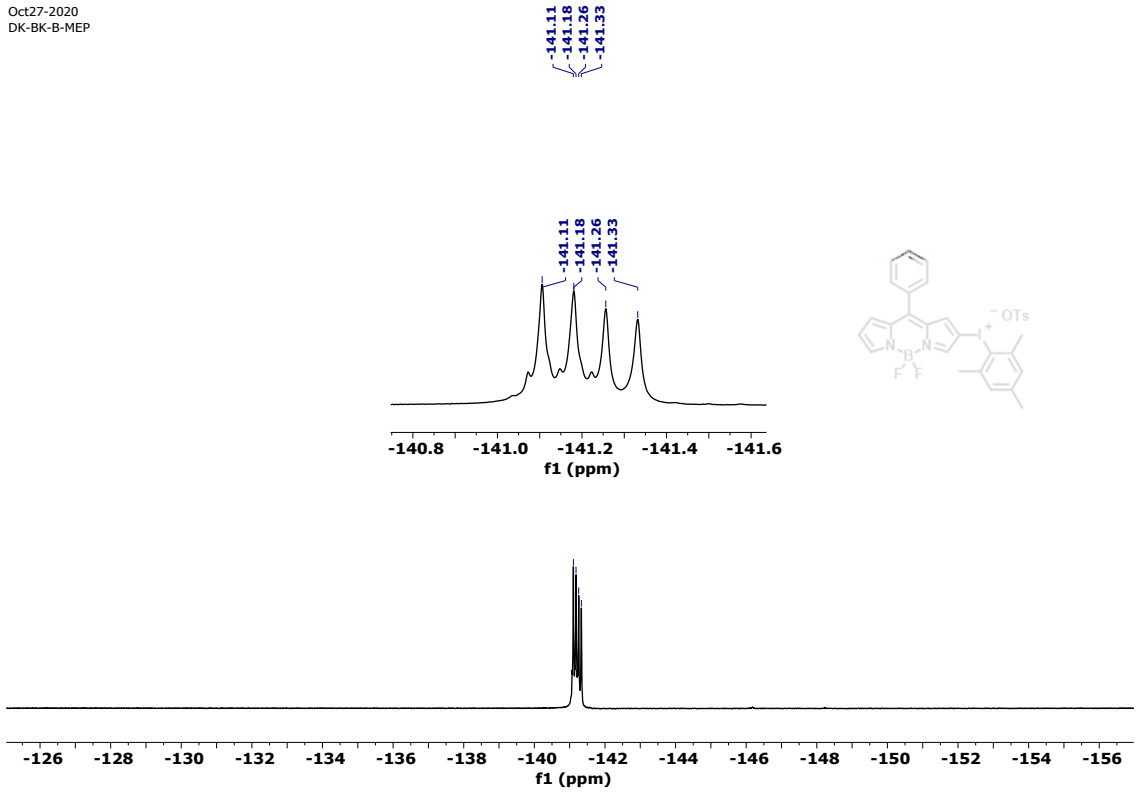
^{1}H NMR spectrum of 4a



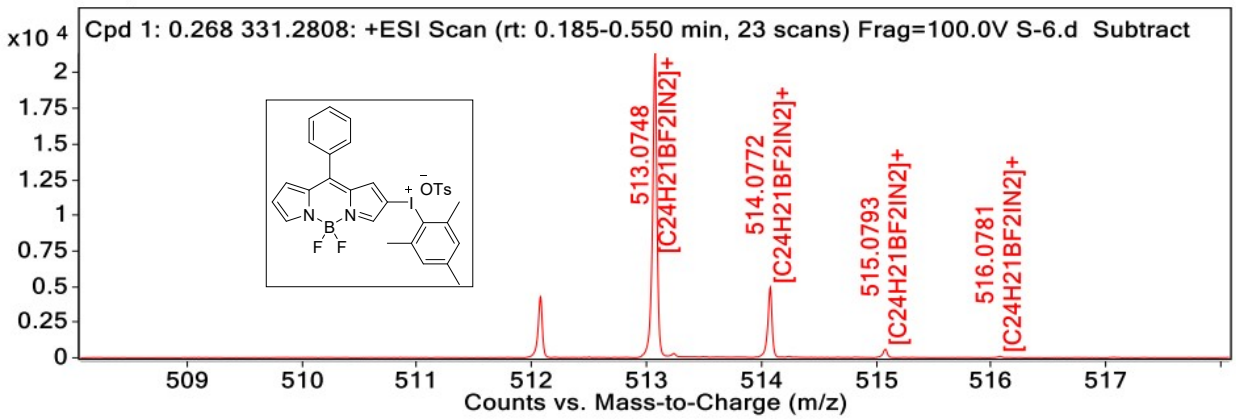
^{13}C NMR spectrum of 4a



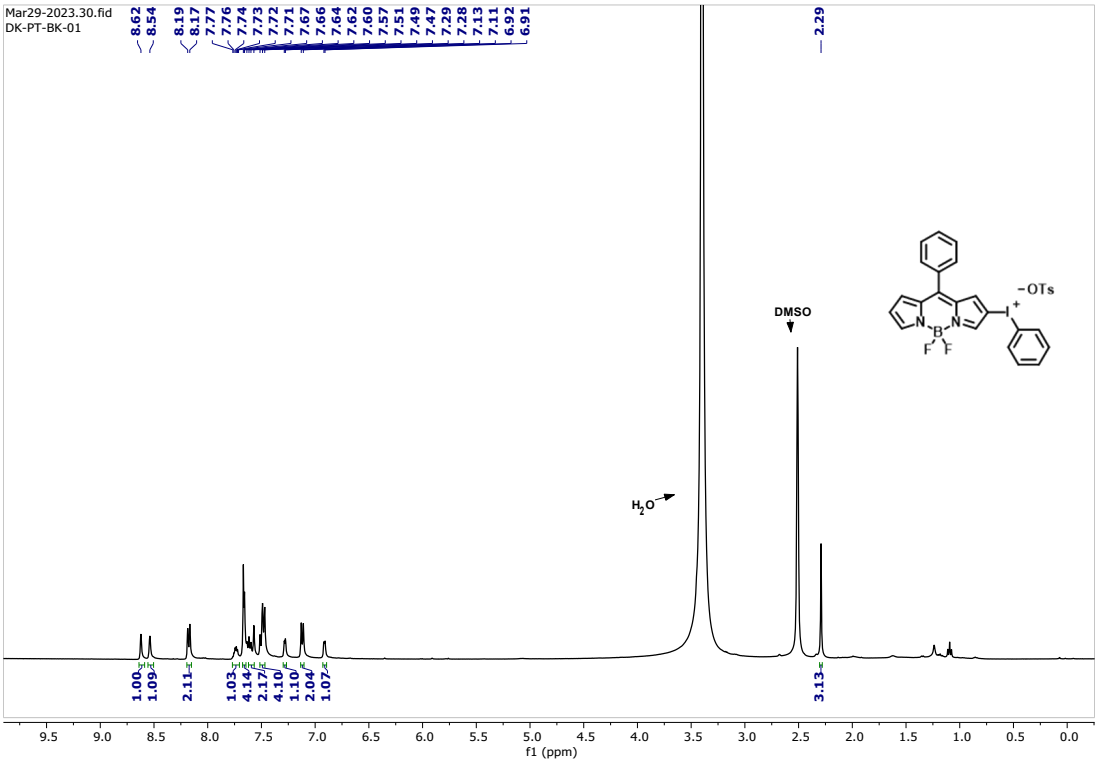
^{19}F NMR spectrum of 4a



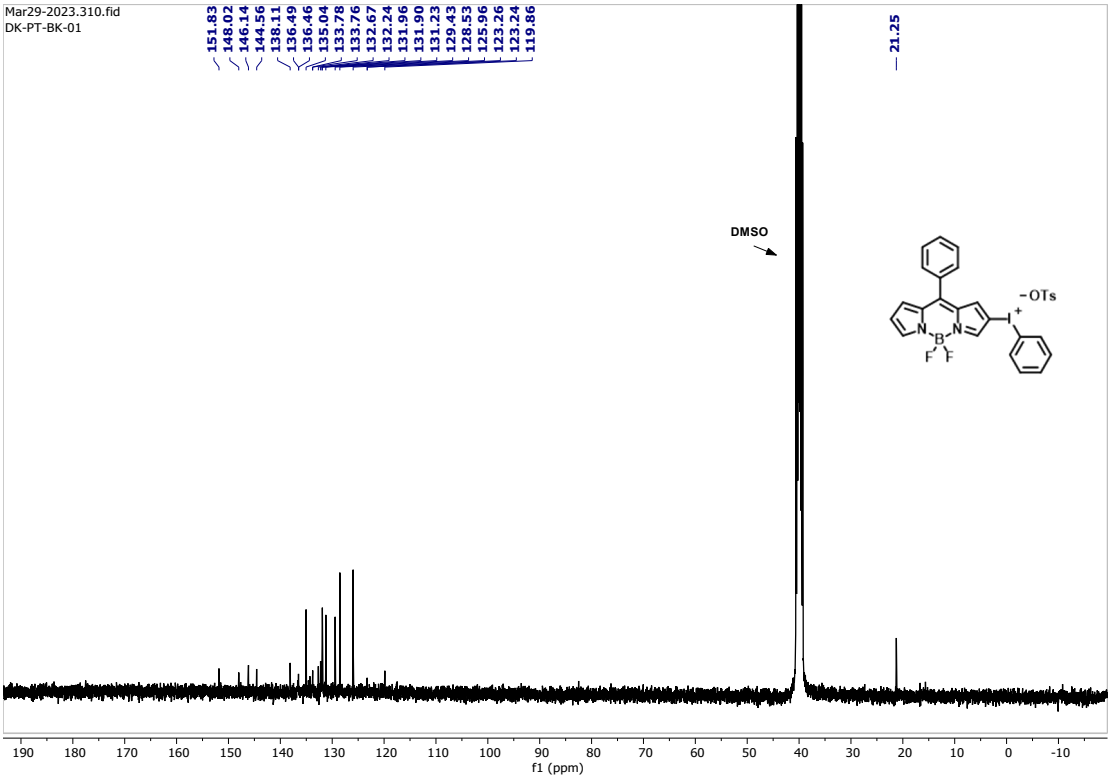
HRMS spectrum of 4a



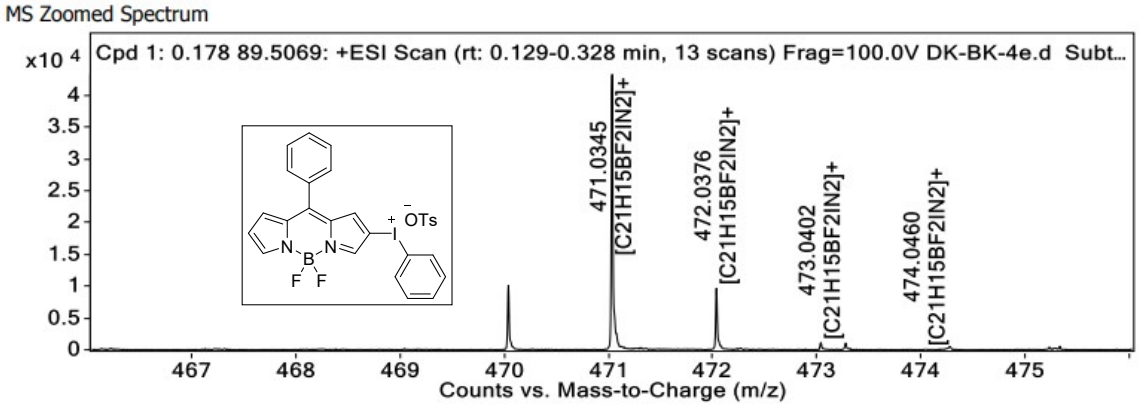
^{1}H NMR spectrum of 4b



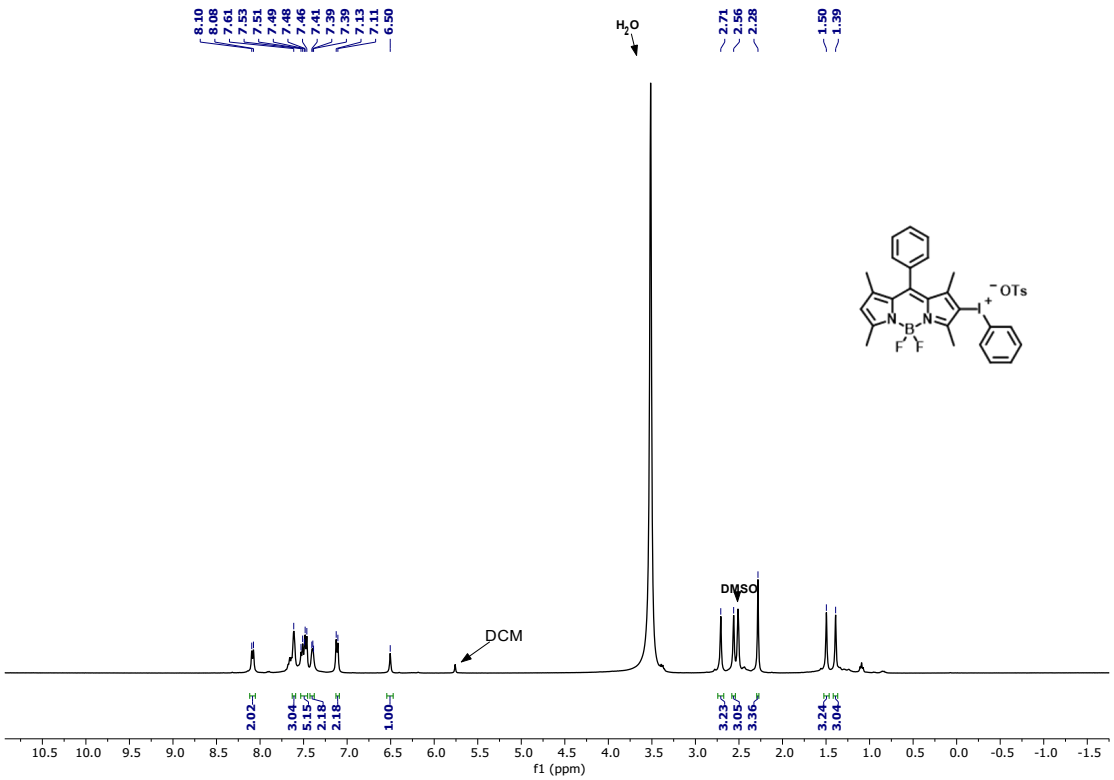
^{13}C NMR spectrum of 4b



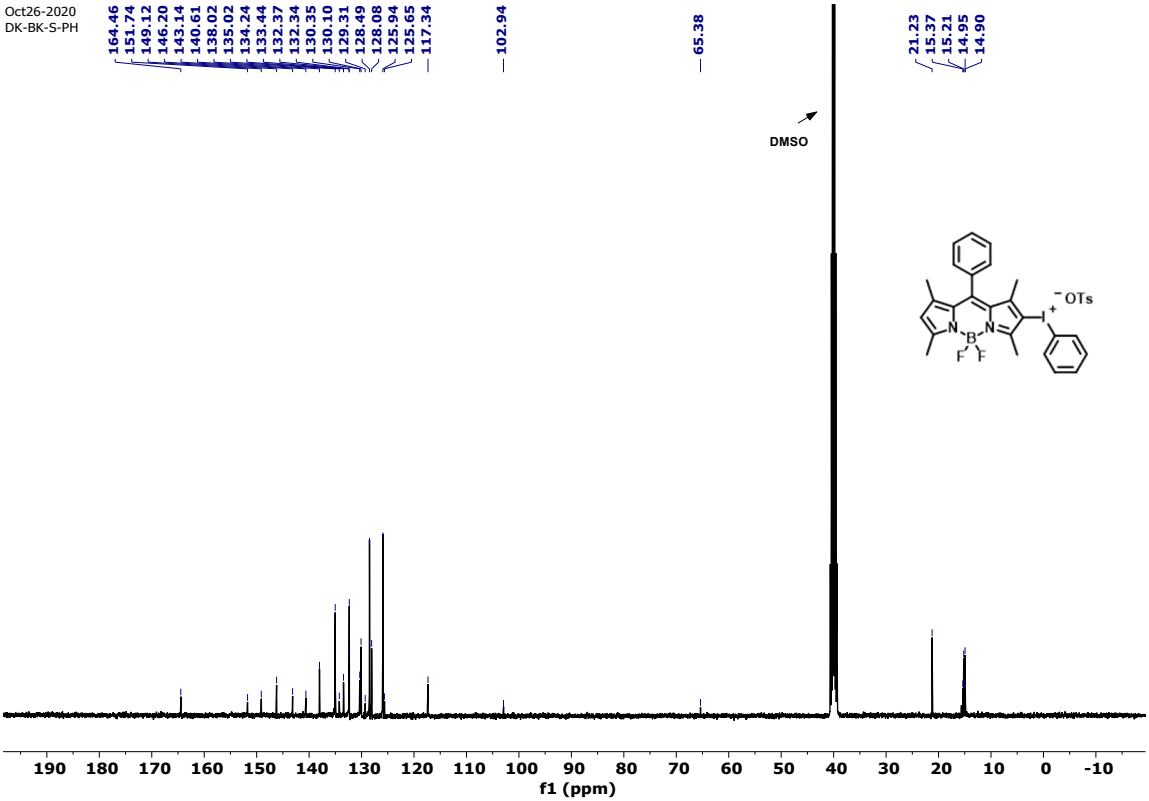
HRMS spectrum of 4b



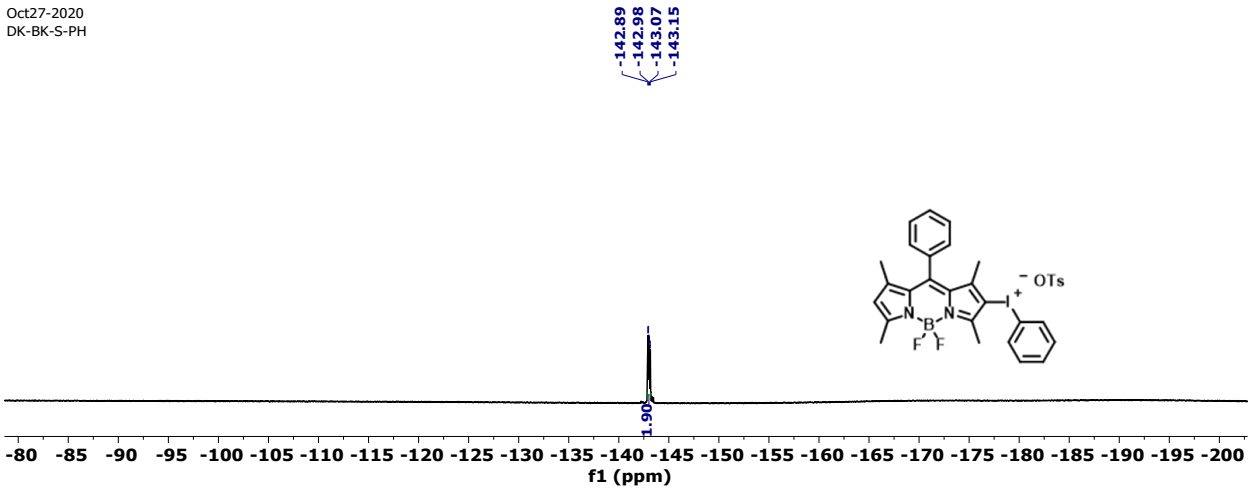
^{1}H NMR spectrum of 4c



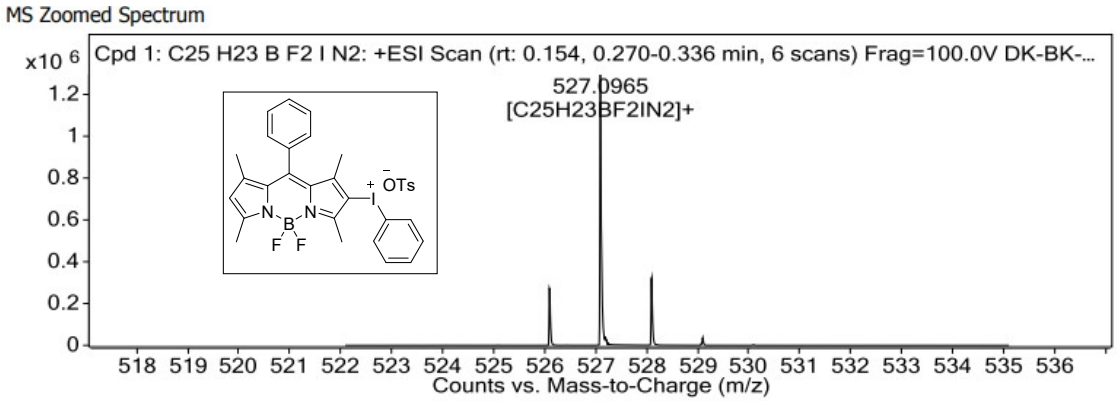
^{13}C NMR spectrum of 4c



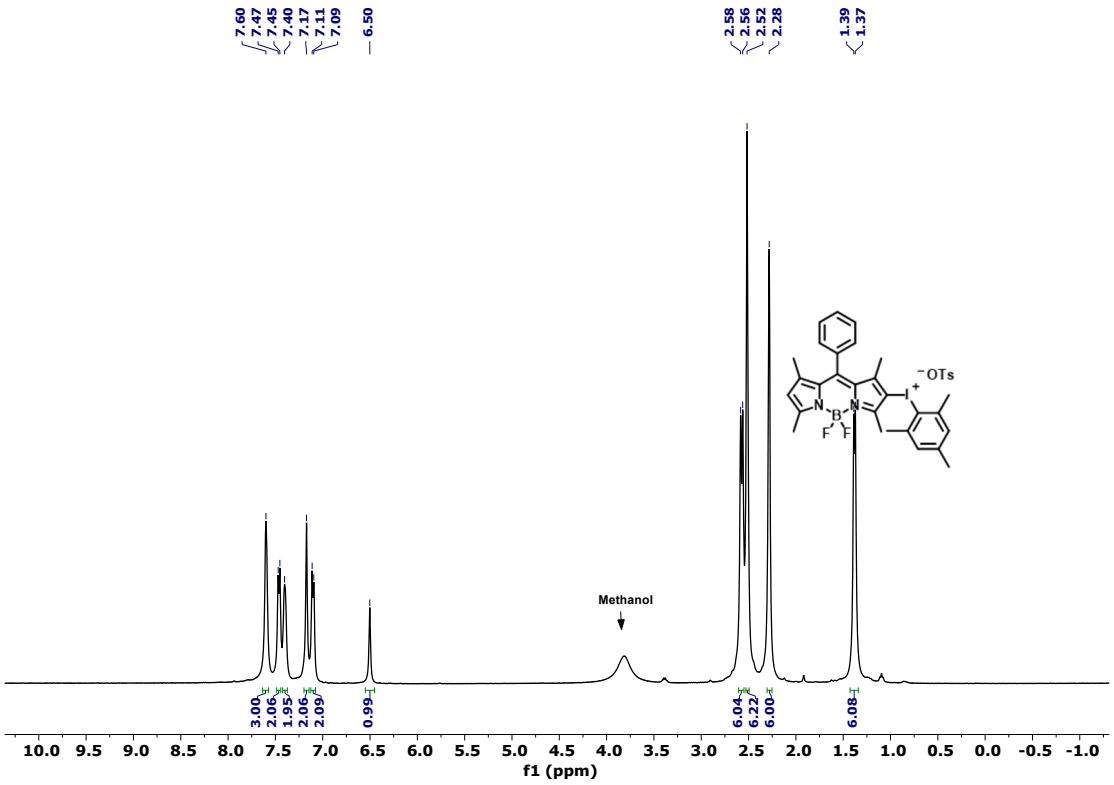
^{19}F NMR spectrum of 4c



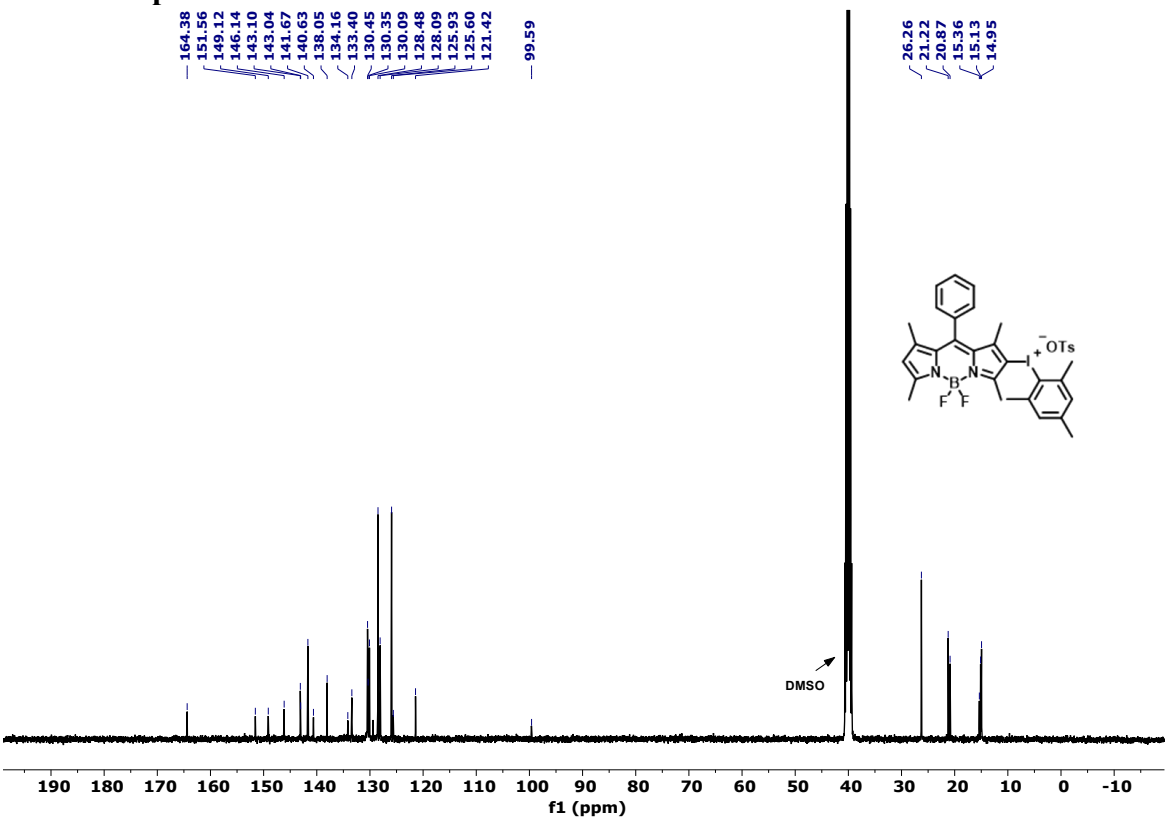
HRMS spectrum of 4c



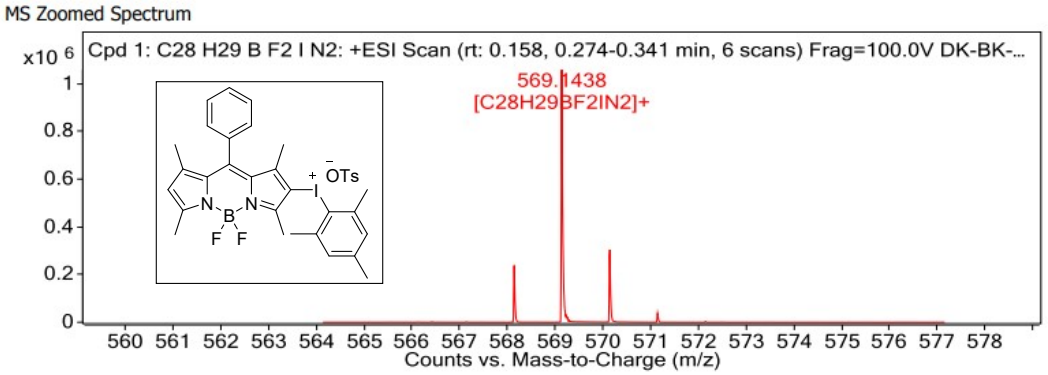
^{1}H NMR spectrum of 4d



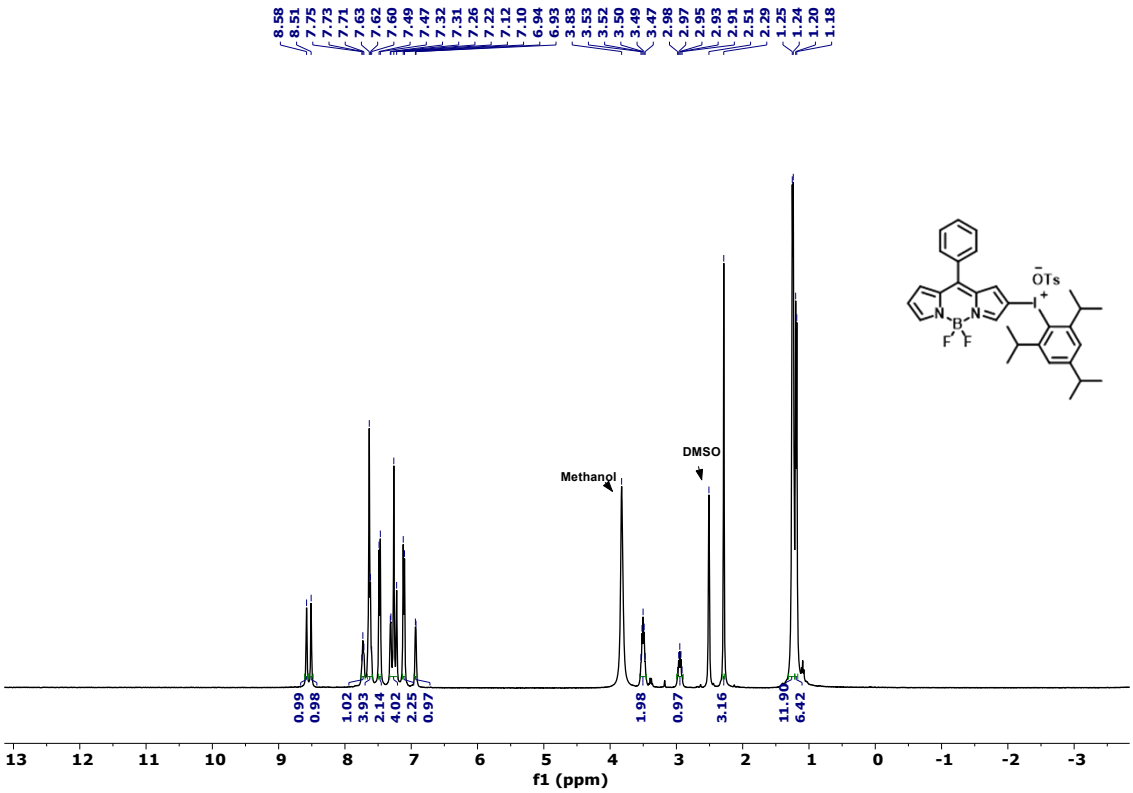
^{13}C NMR spectrum of 4d



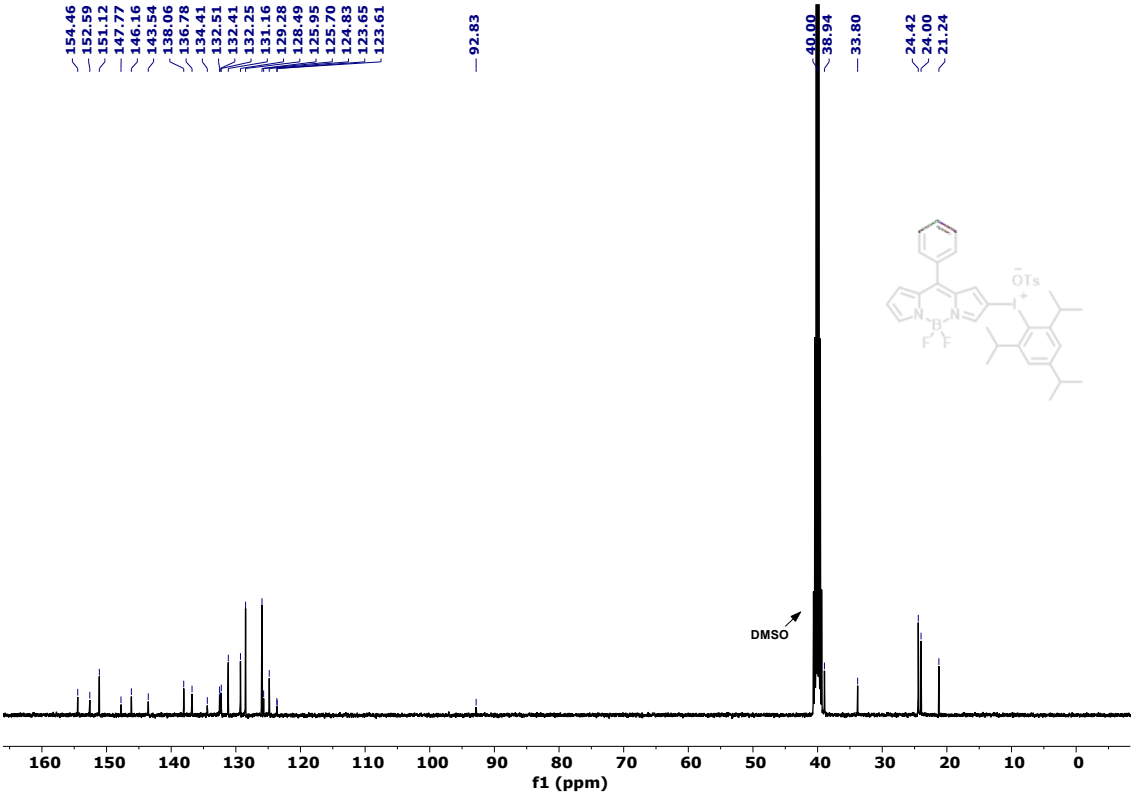
HRMS spectrum of 4d



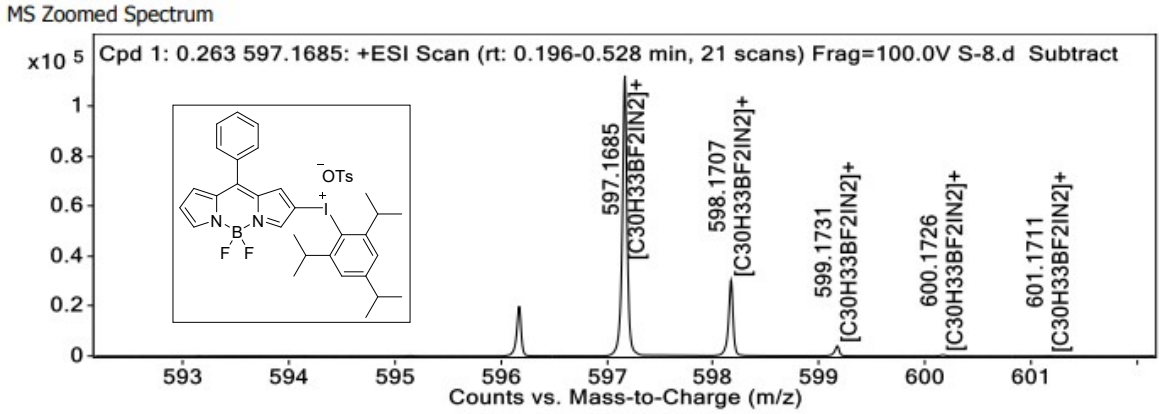
^{1}H NMR spectrum of 4e



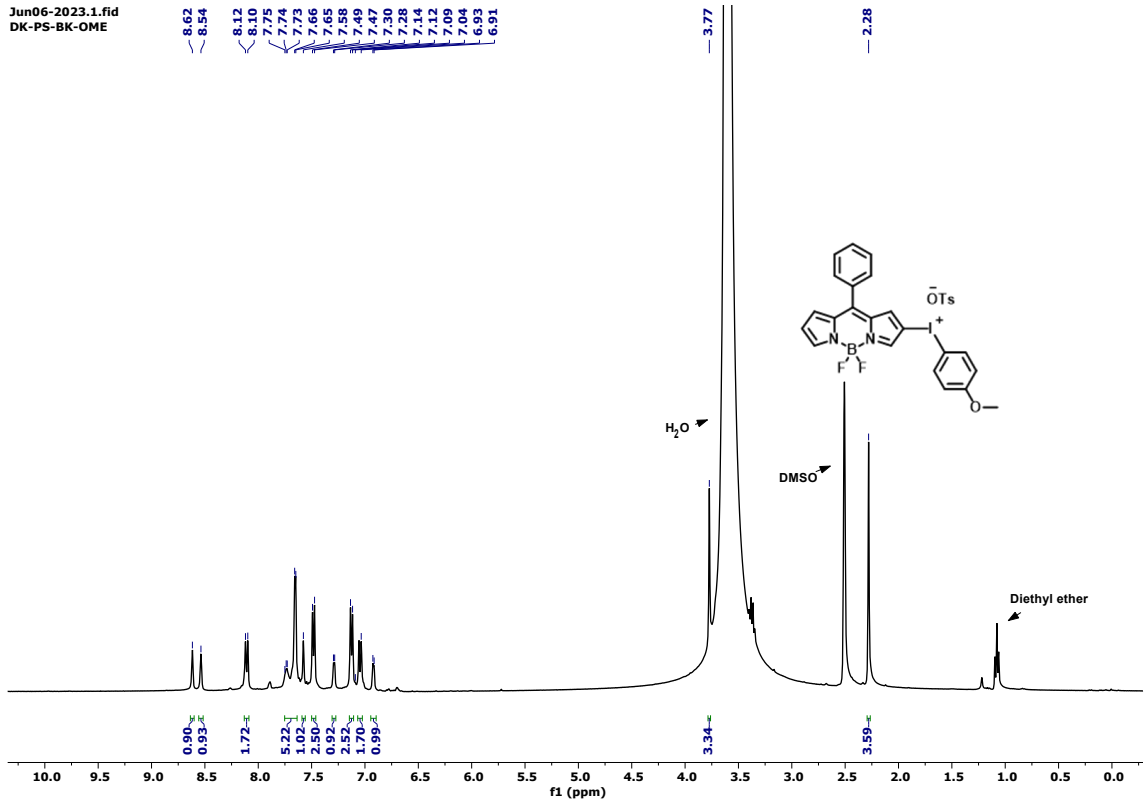
^{13}C NMR spectrum of 4e



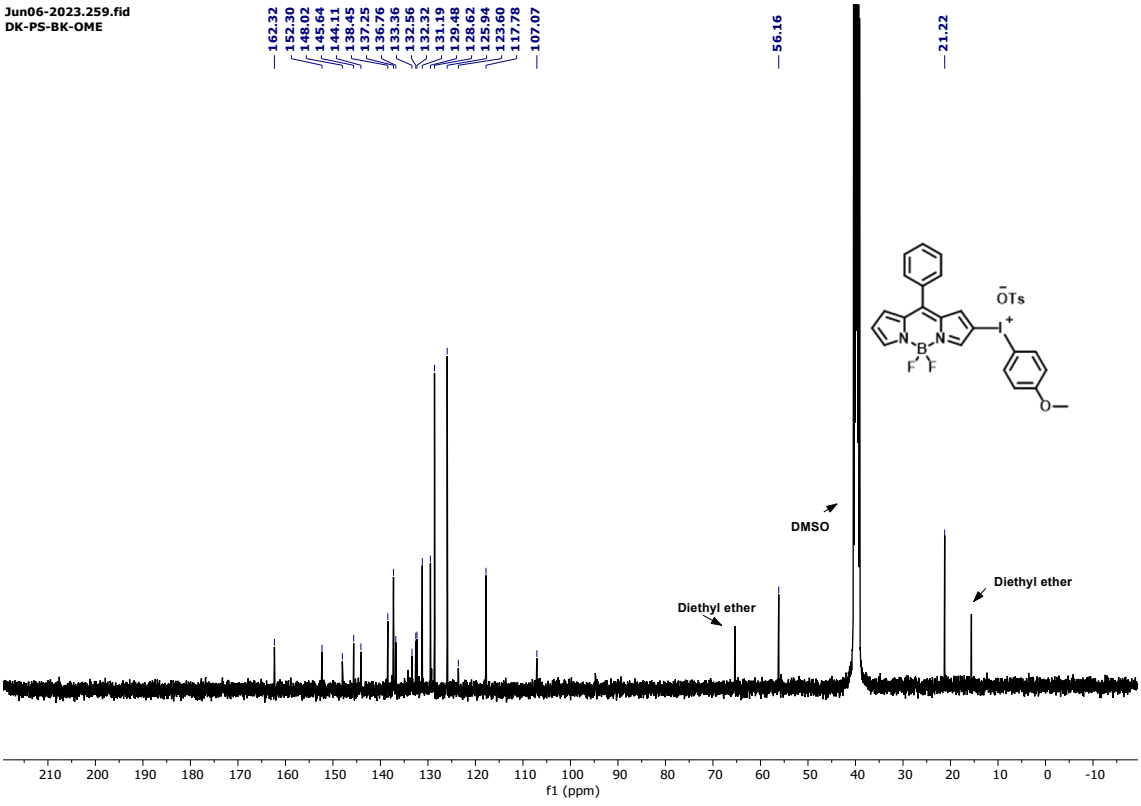
HRMS spectrum of 4e



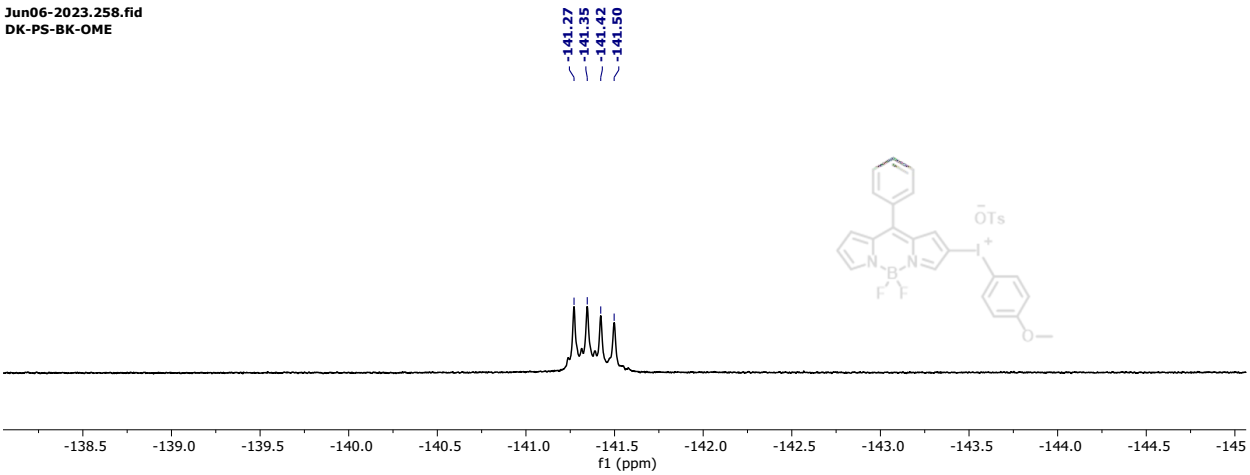
^{1}H NMR spectrum of 4f



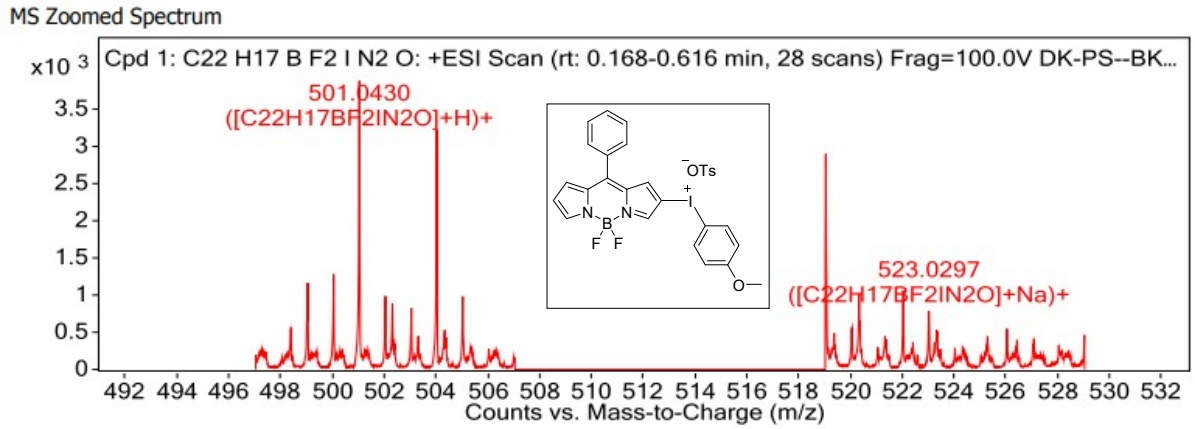
^{13}C NMR spectrum of 4f



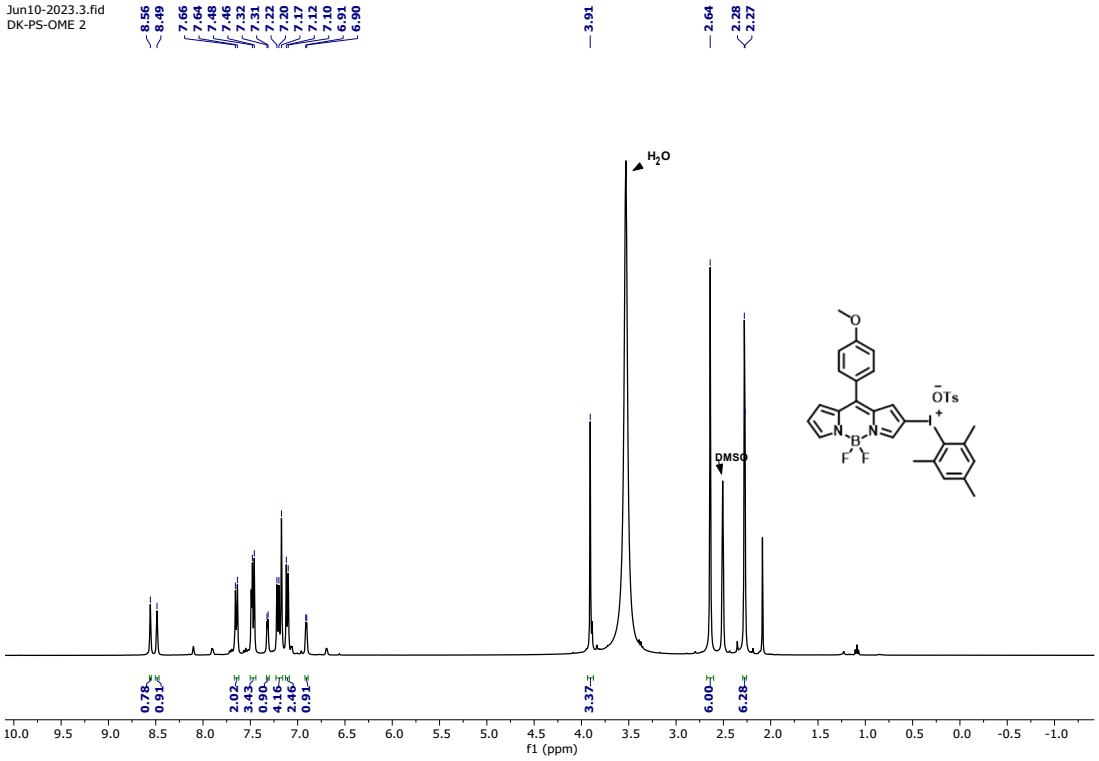
^{19}F NMR spectrum of 4f



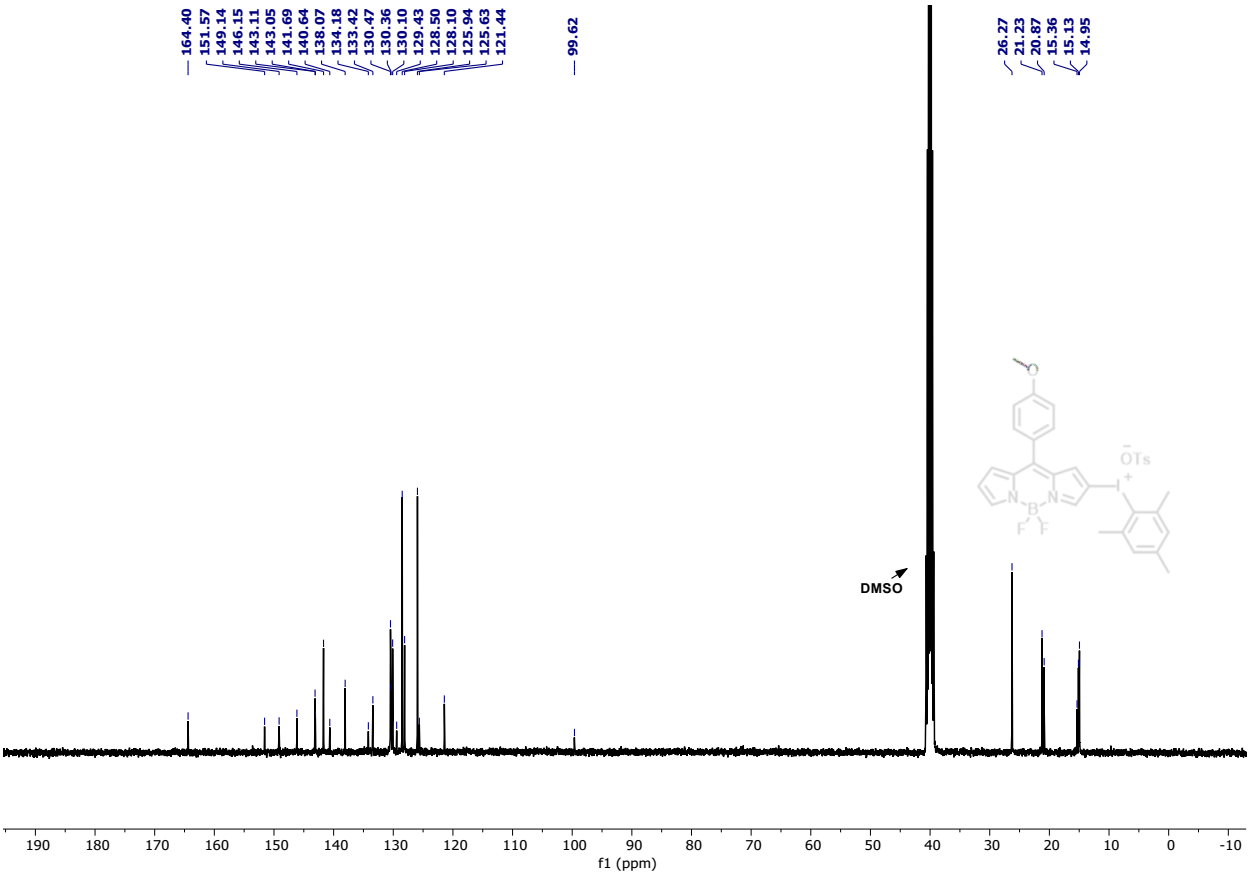
HRMS spectrum of 4f



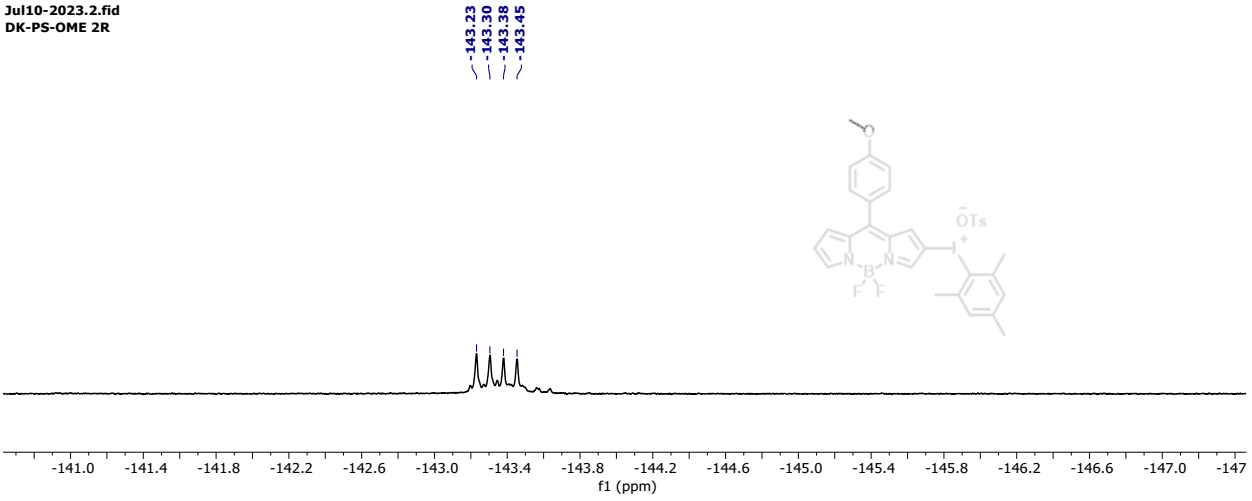
^{1}H NMR spectrum of 4g



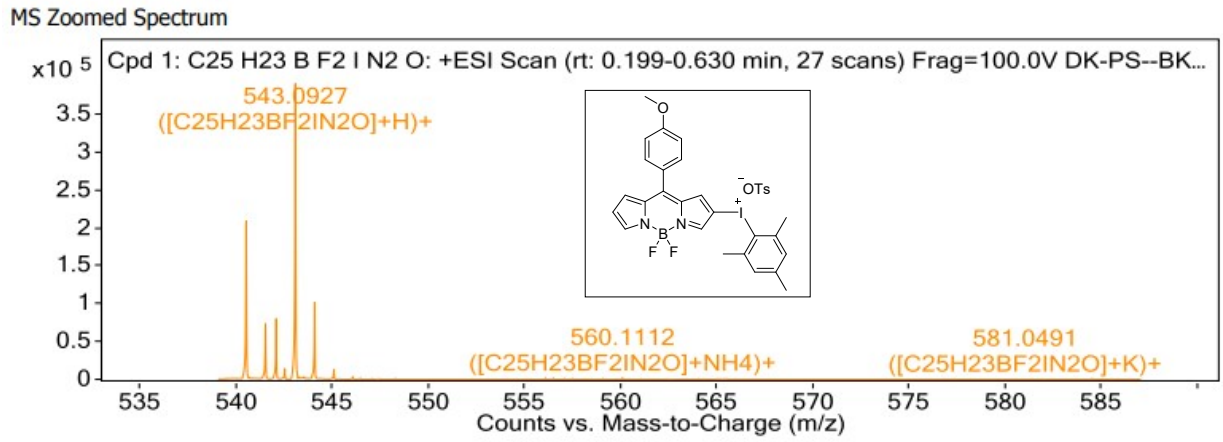
^{13}C NMR spectrum of 4g



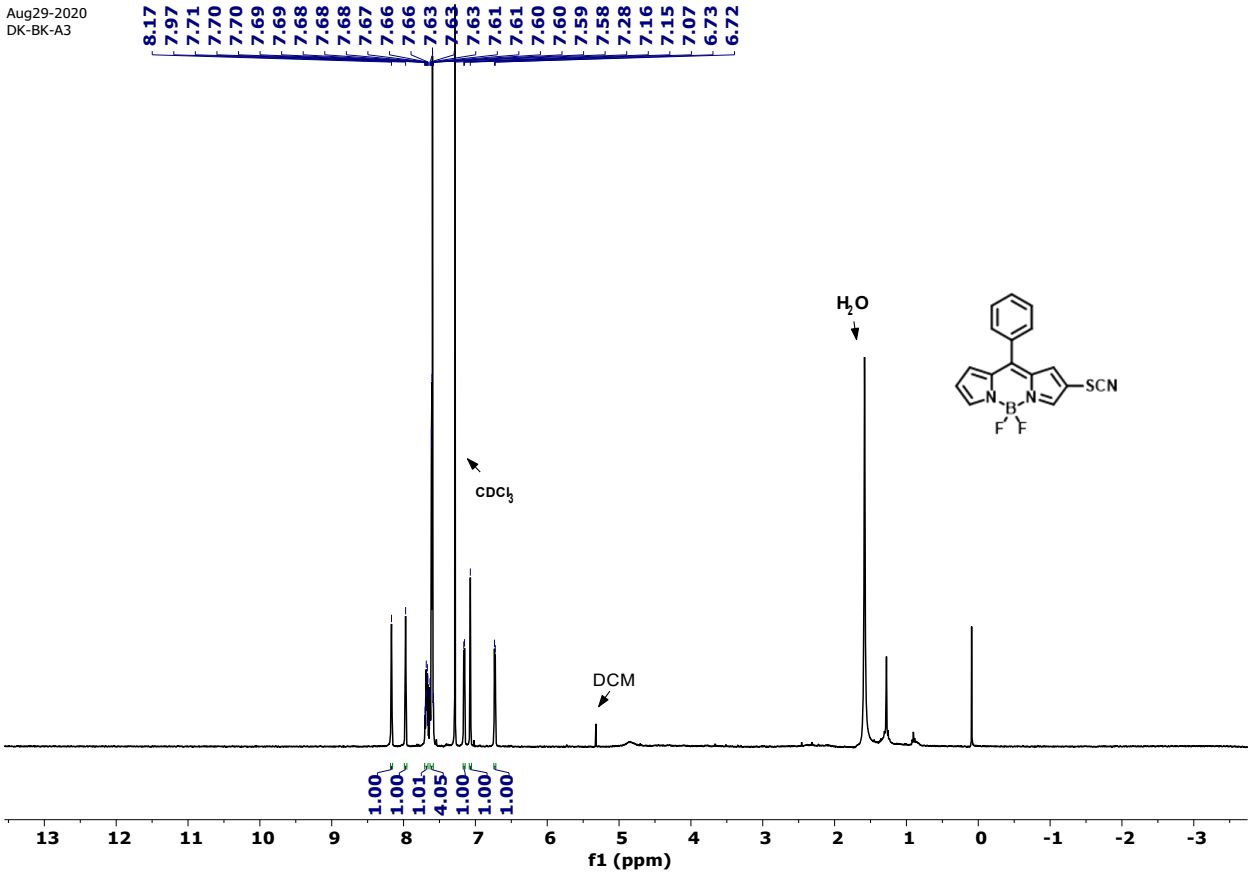
^{19}F NMR spectrum of 4g



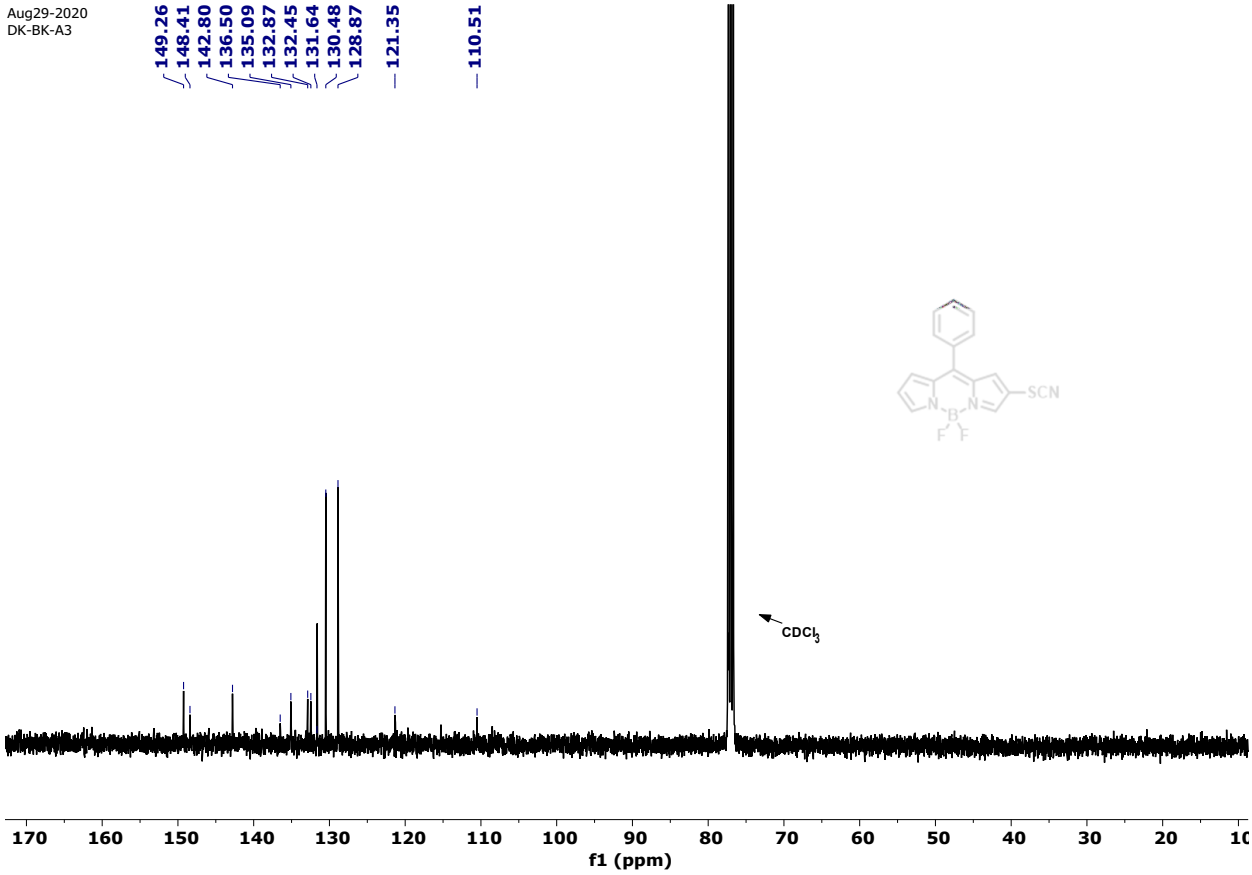
HRMS spectrum of 4g



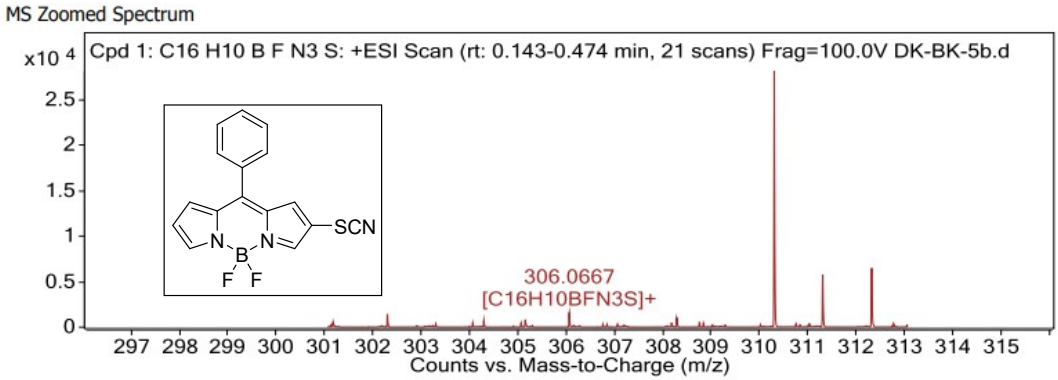
^{1}H NMR spectrum of 5a



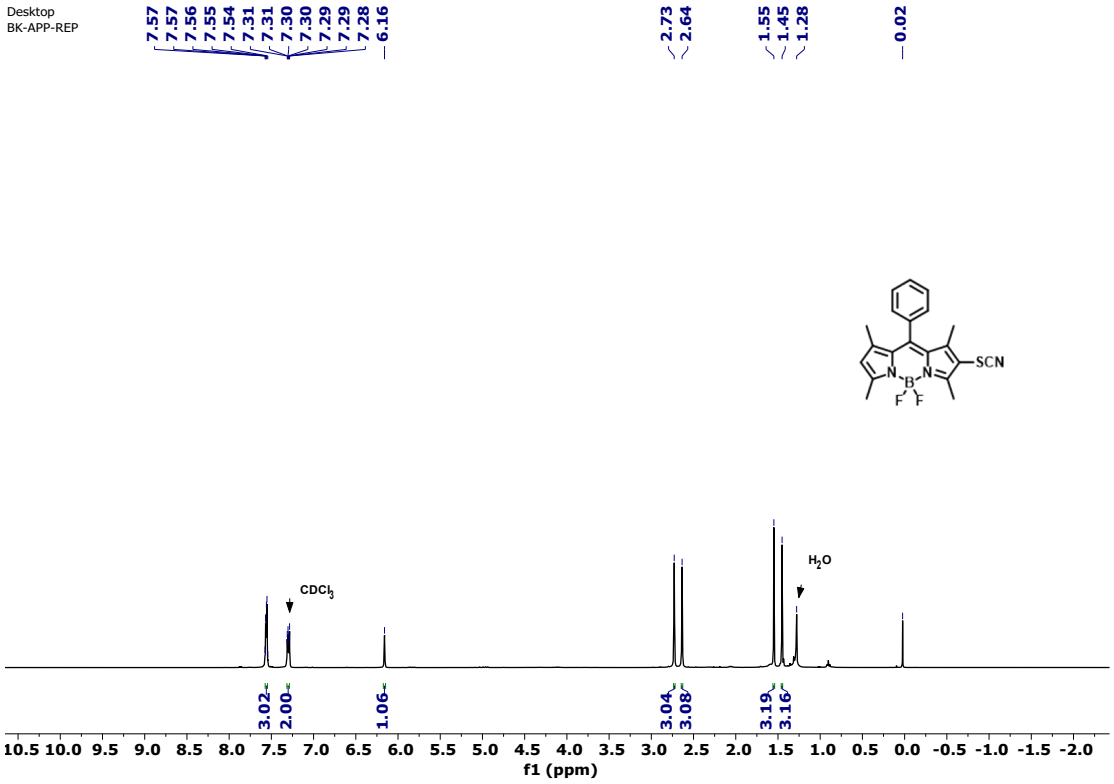
^{13}C NMR spectrum of 5a



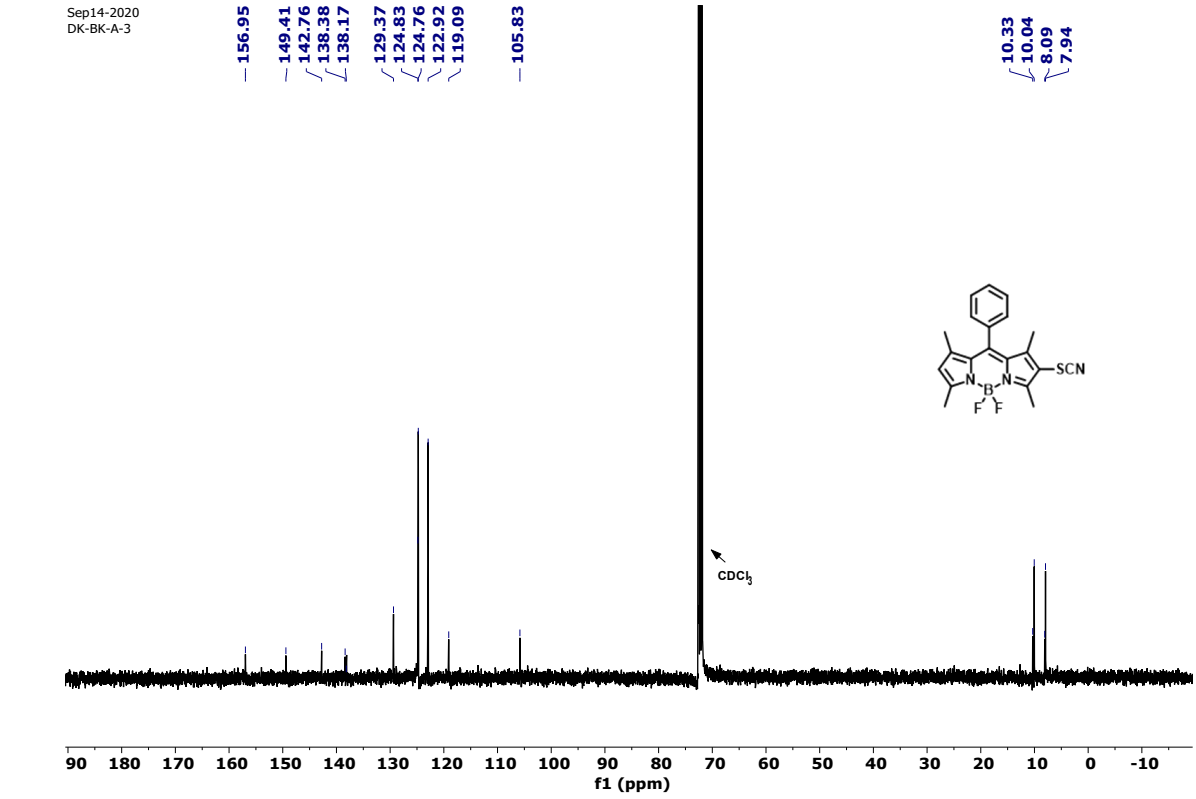
HRMS spectrum of 5a



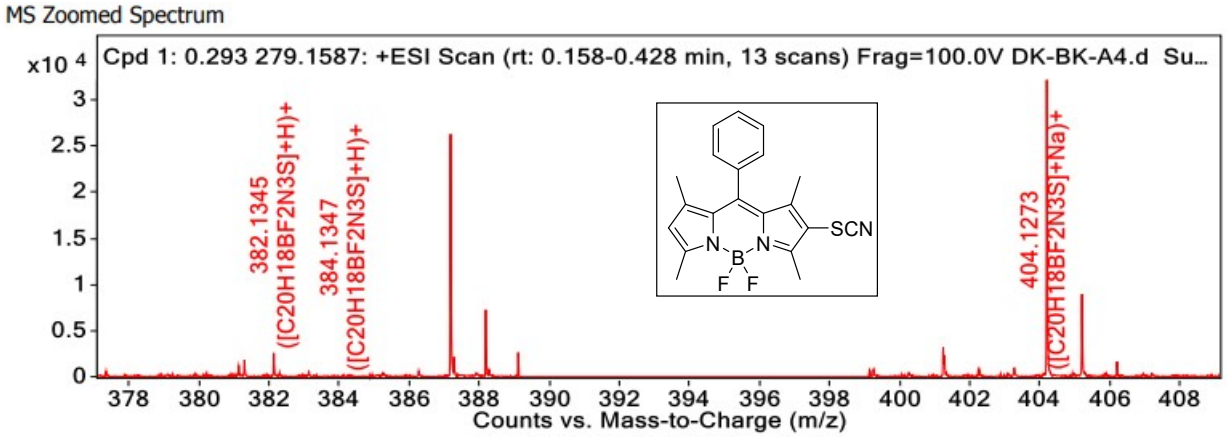
^{1}H NMR spectrum of 5b



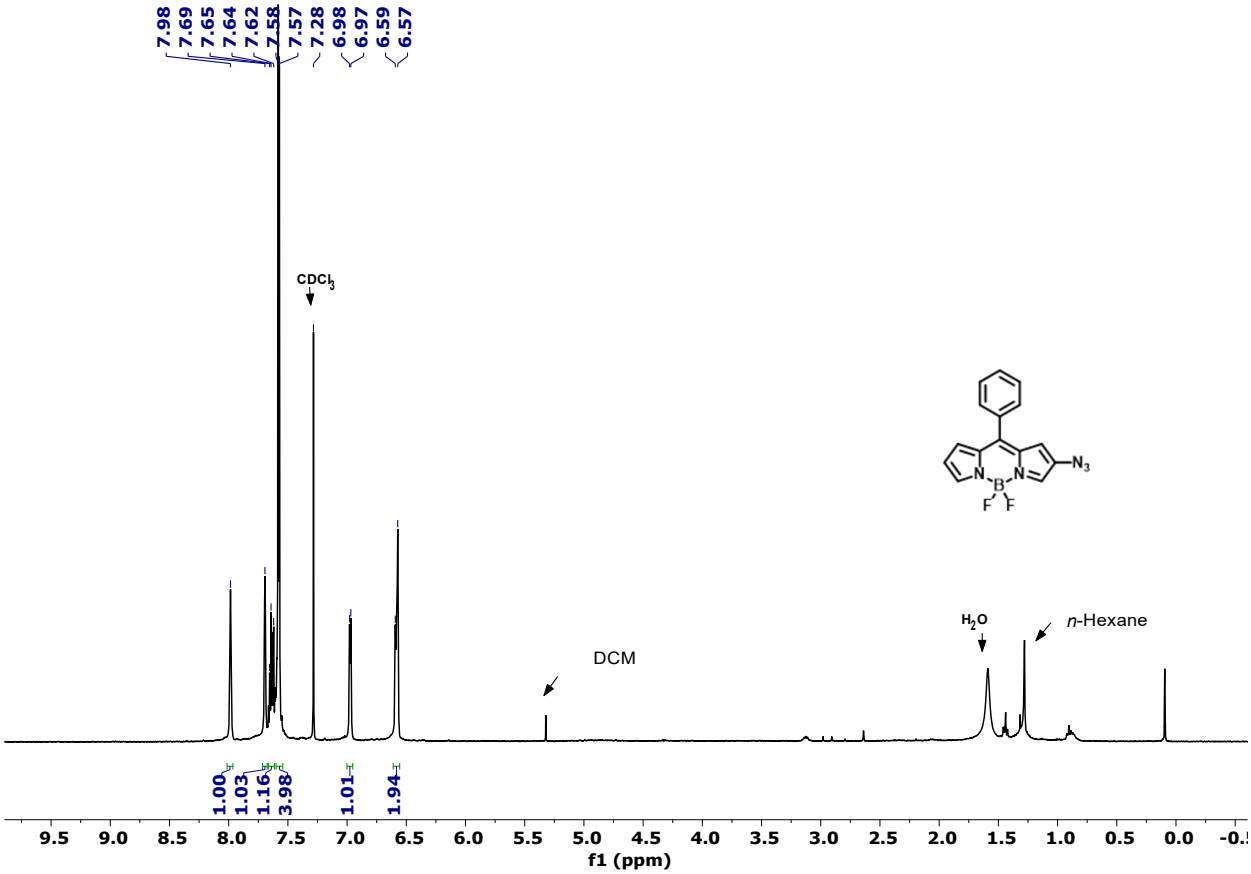
^{13}C NMR spectrum of 5b



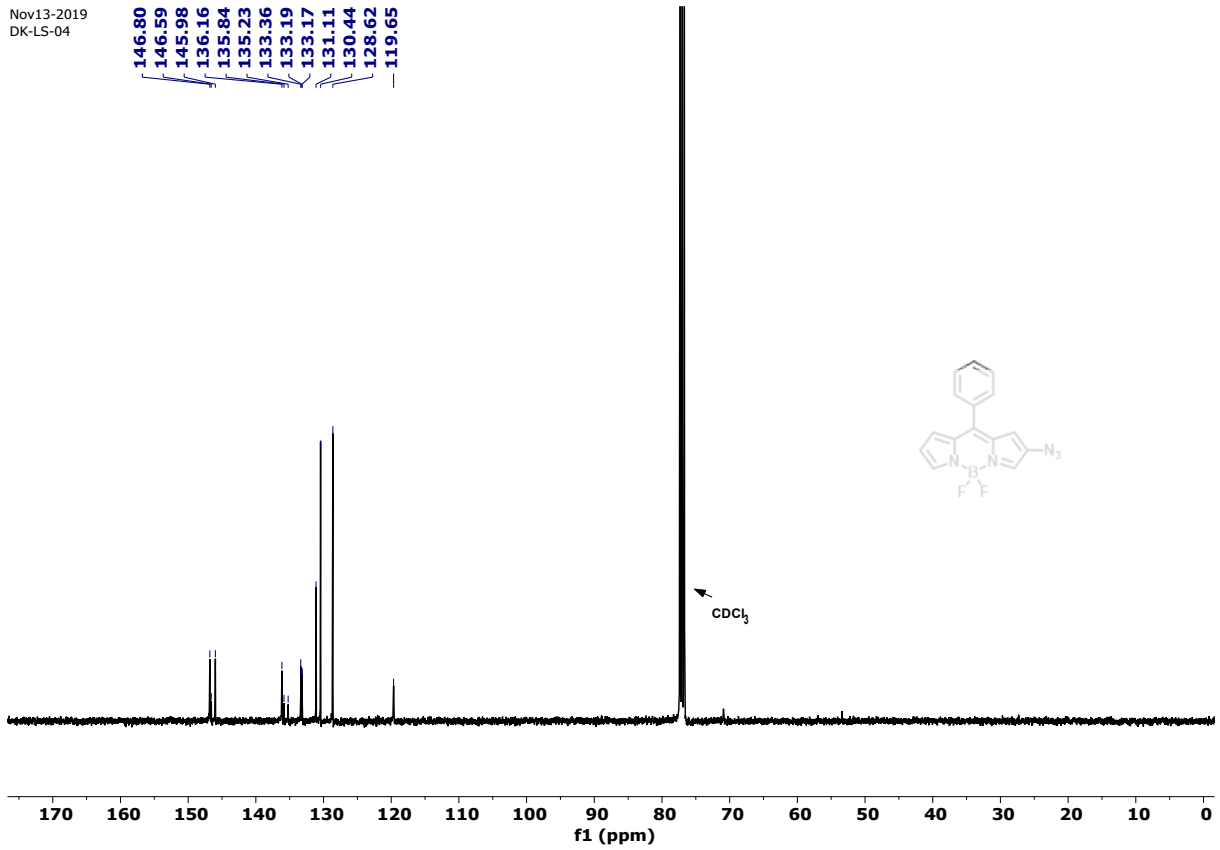
HRMS spectrum of 5b



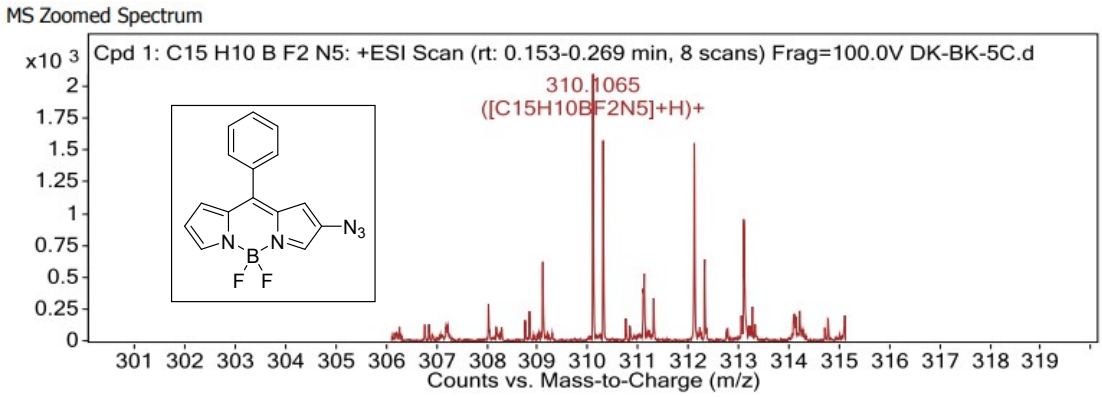
^{1}H NMR spectrum of 5c



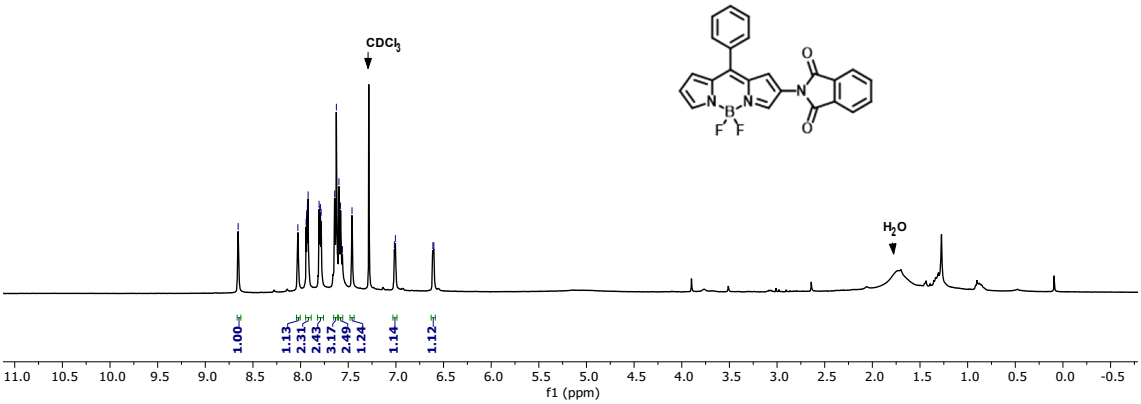
^{13}C NMR spectrum of 5c



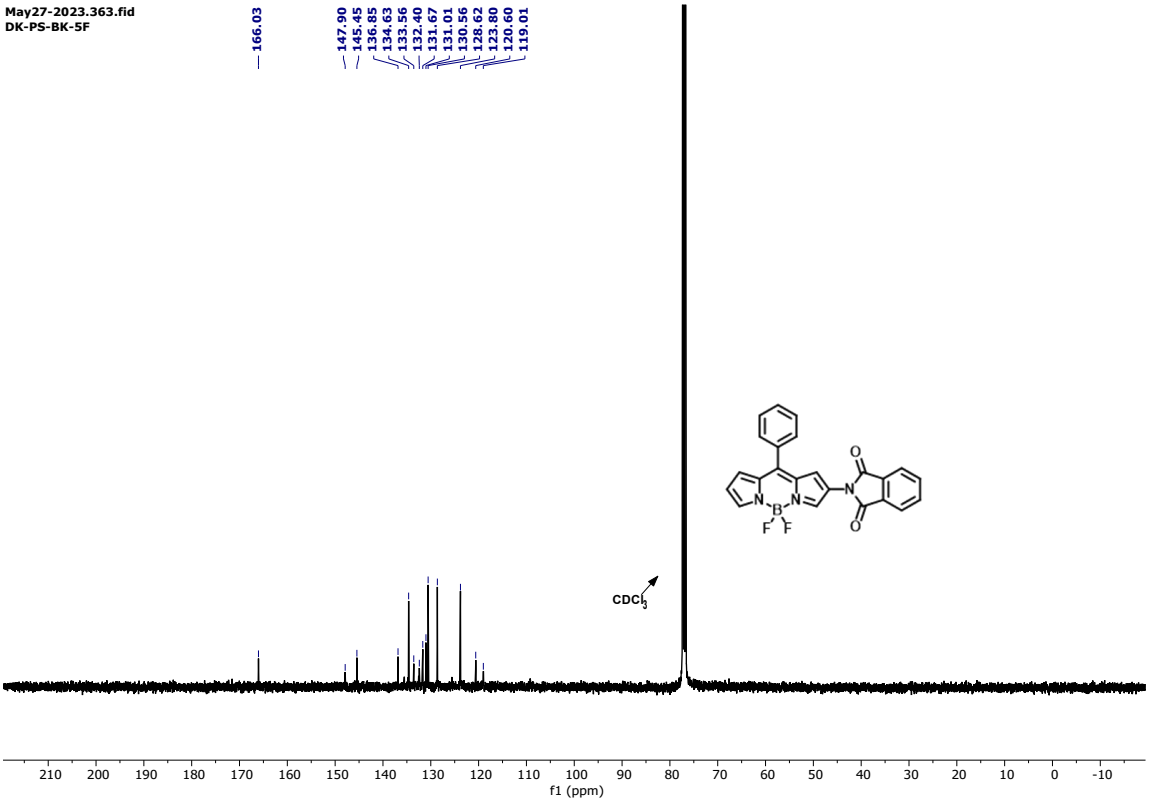
HRMS spectrum of 5c



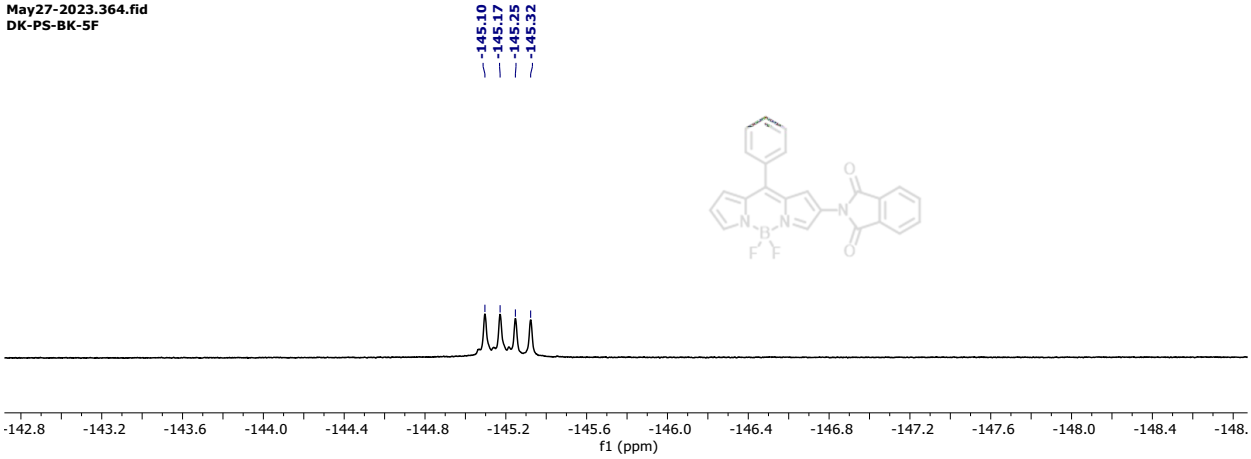
^{1}H NMR spectrum of 5d



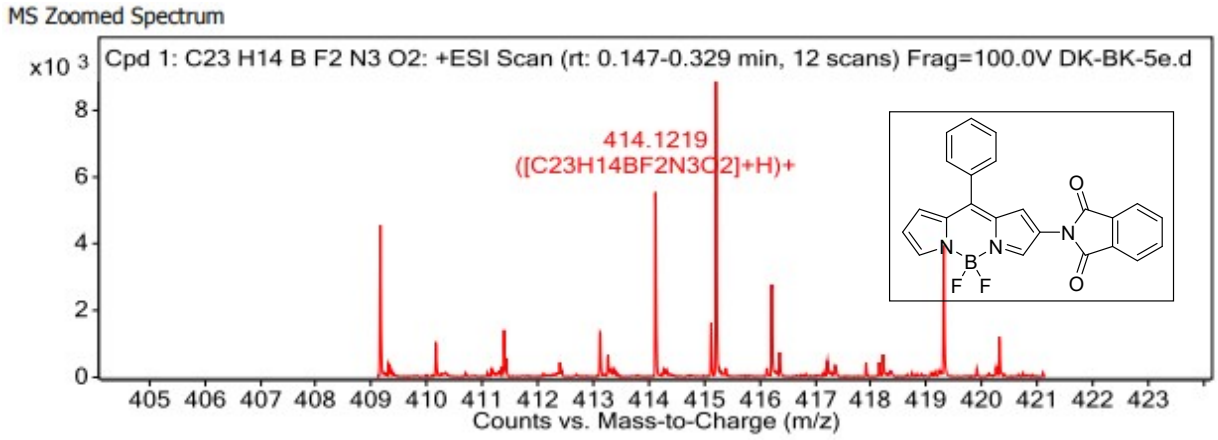
^{13}C NMR spectrum of 5d



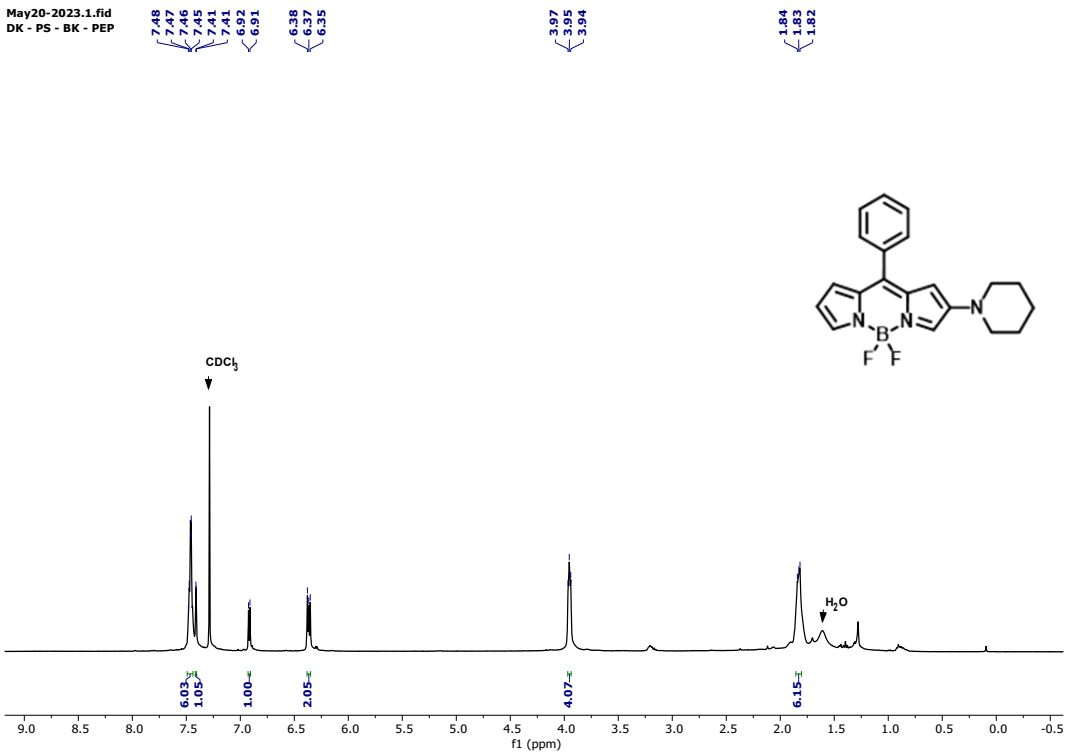
^{19}F NMR spectrum of 5d



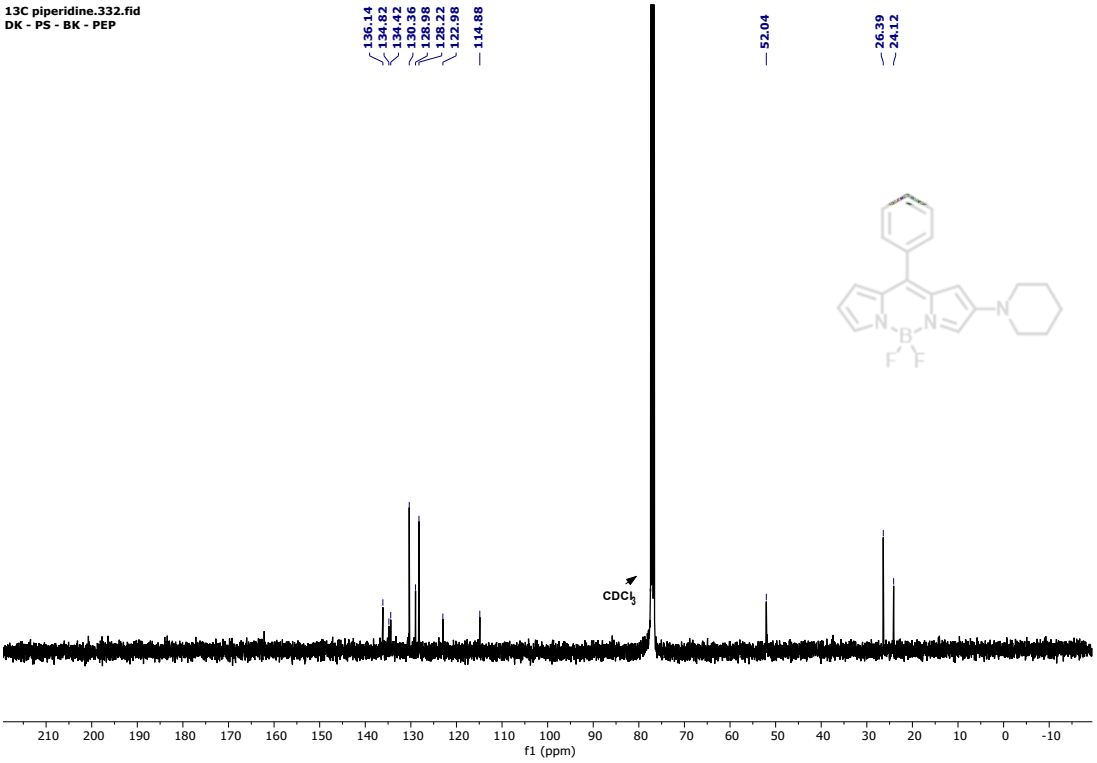
HRMS spectrum of 5d



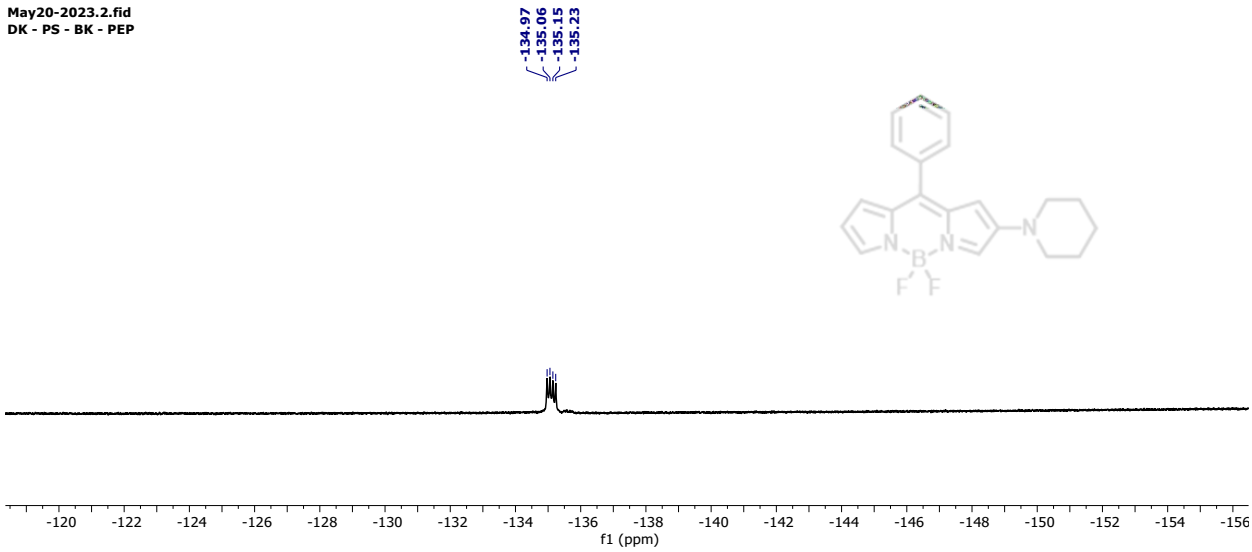
^{1}H NMR spectrum of 5e



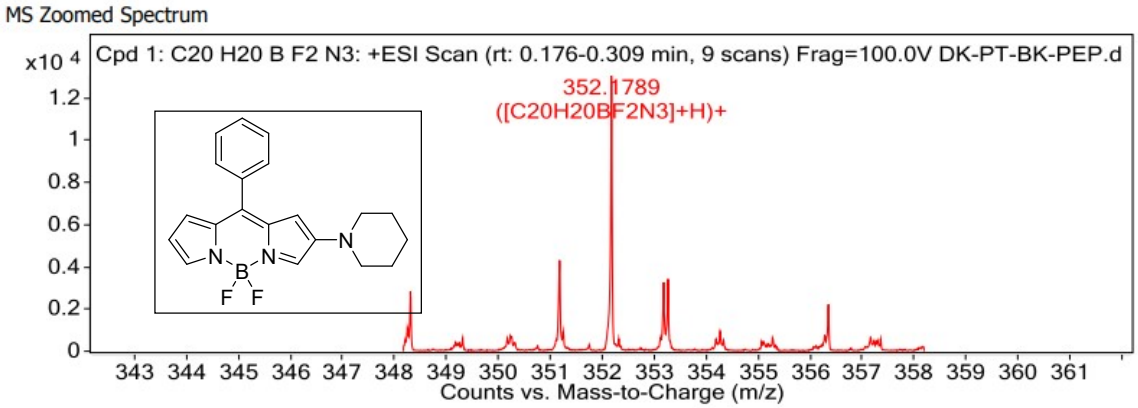
^{13}C NMR spctrum of 5e



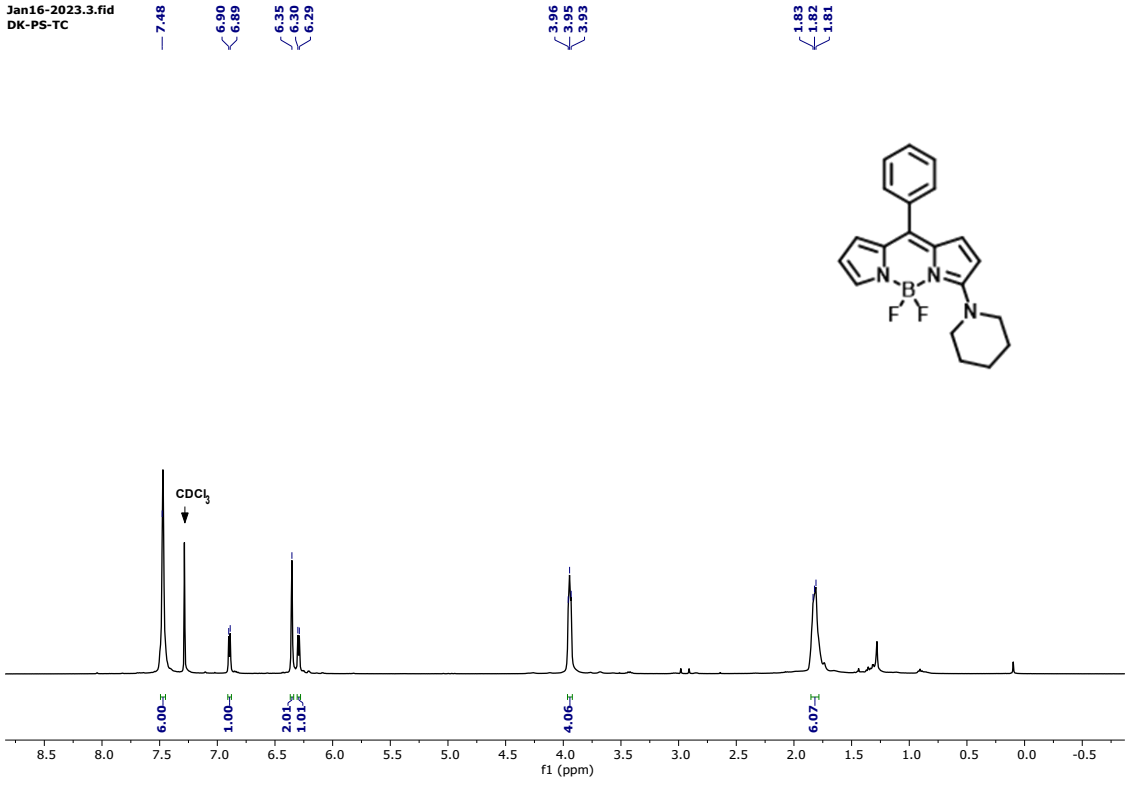
^{19}F NMR spectrum of 5e



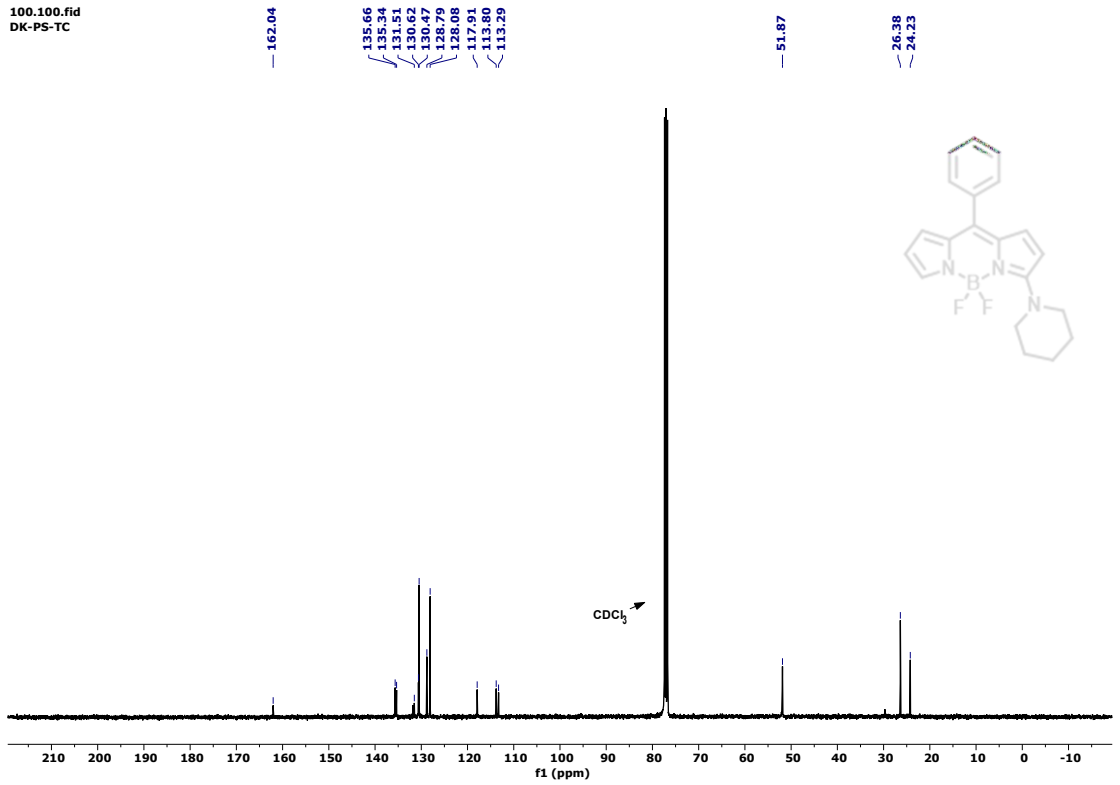
HRMS spectrum of 5e



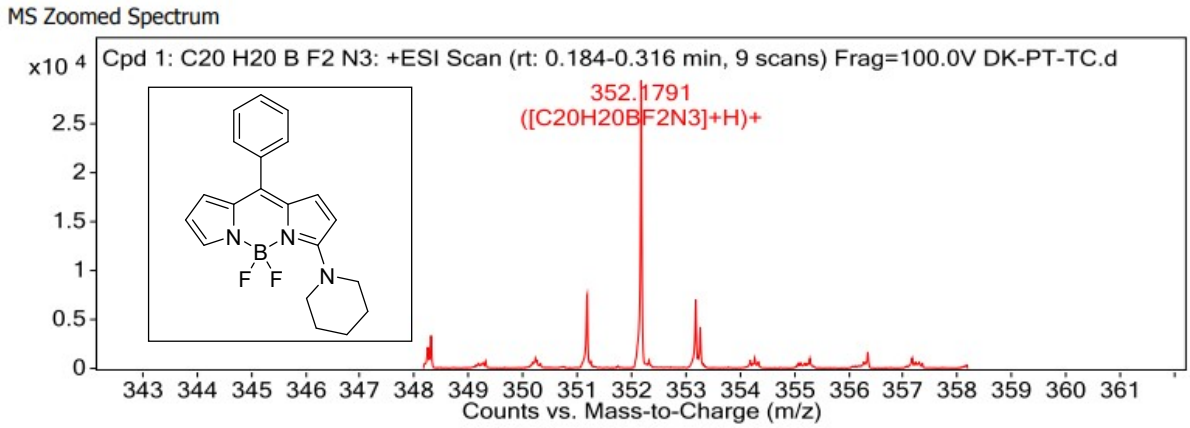
^{1}H NMR spectrum of 5f



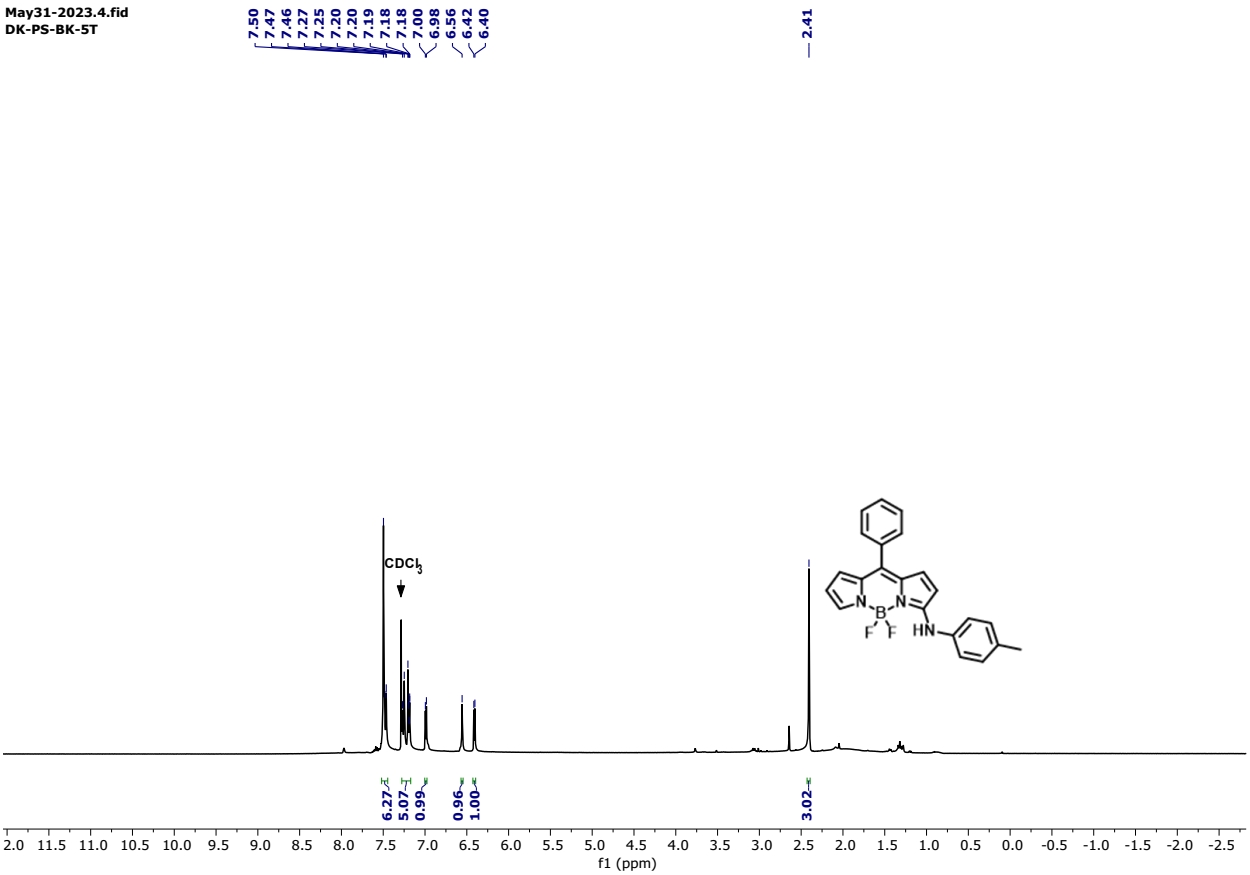
^{13}C NMR spectrum of 5f



HRMS spectrum of 5f



^{1}H NMR spectrum of 5g



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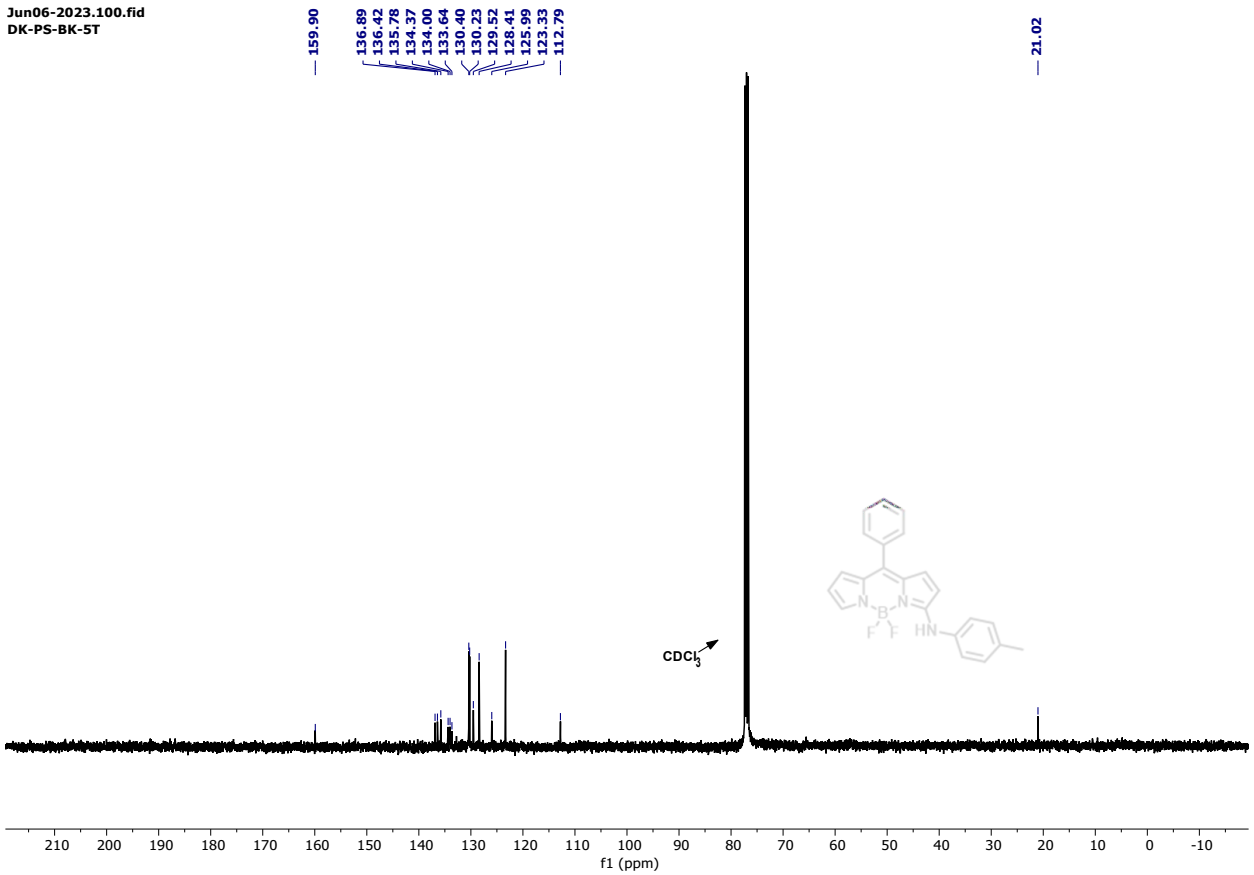
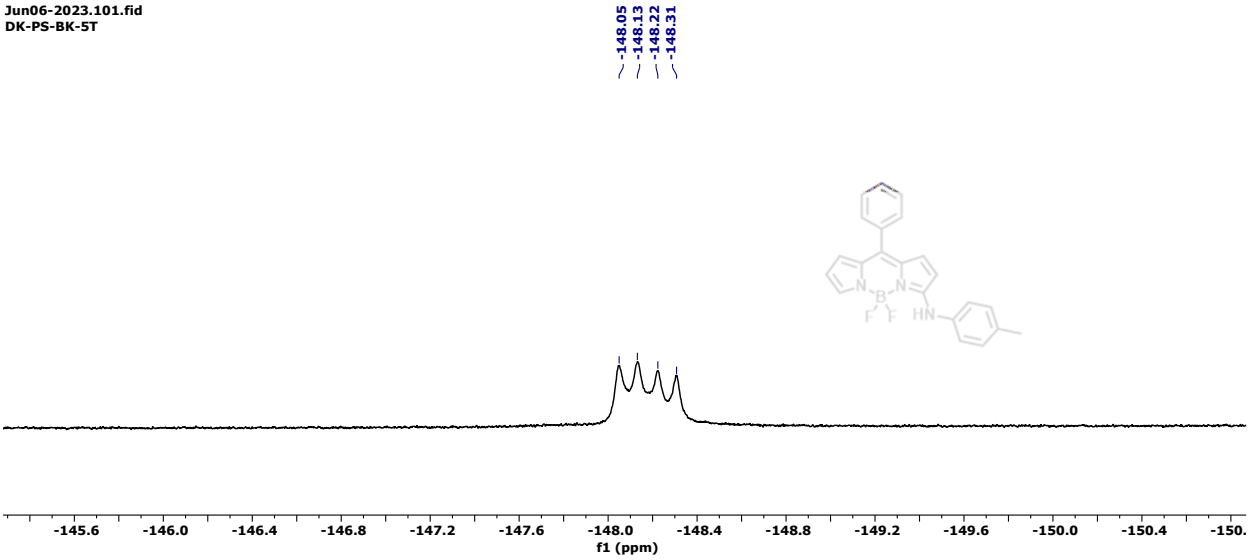
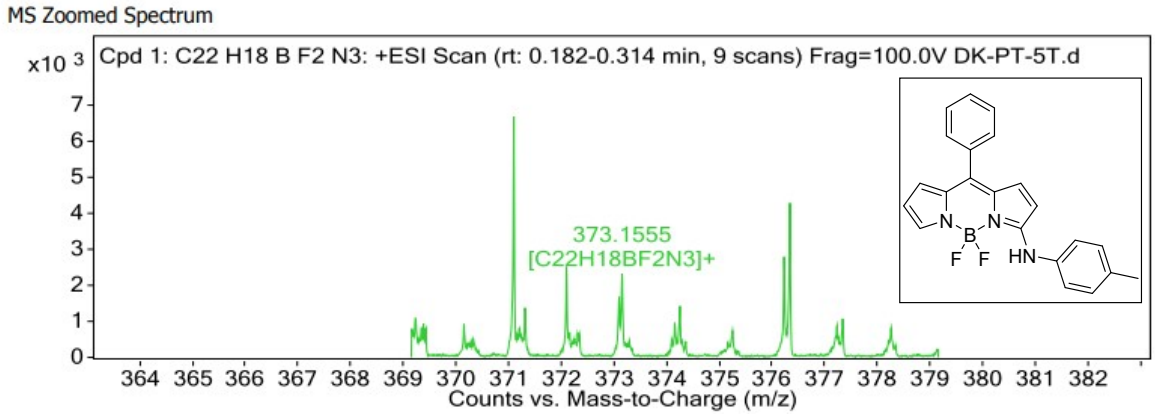


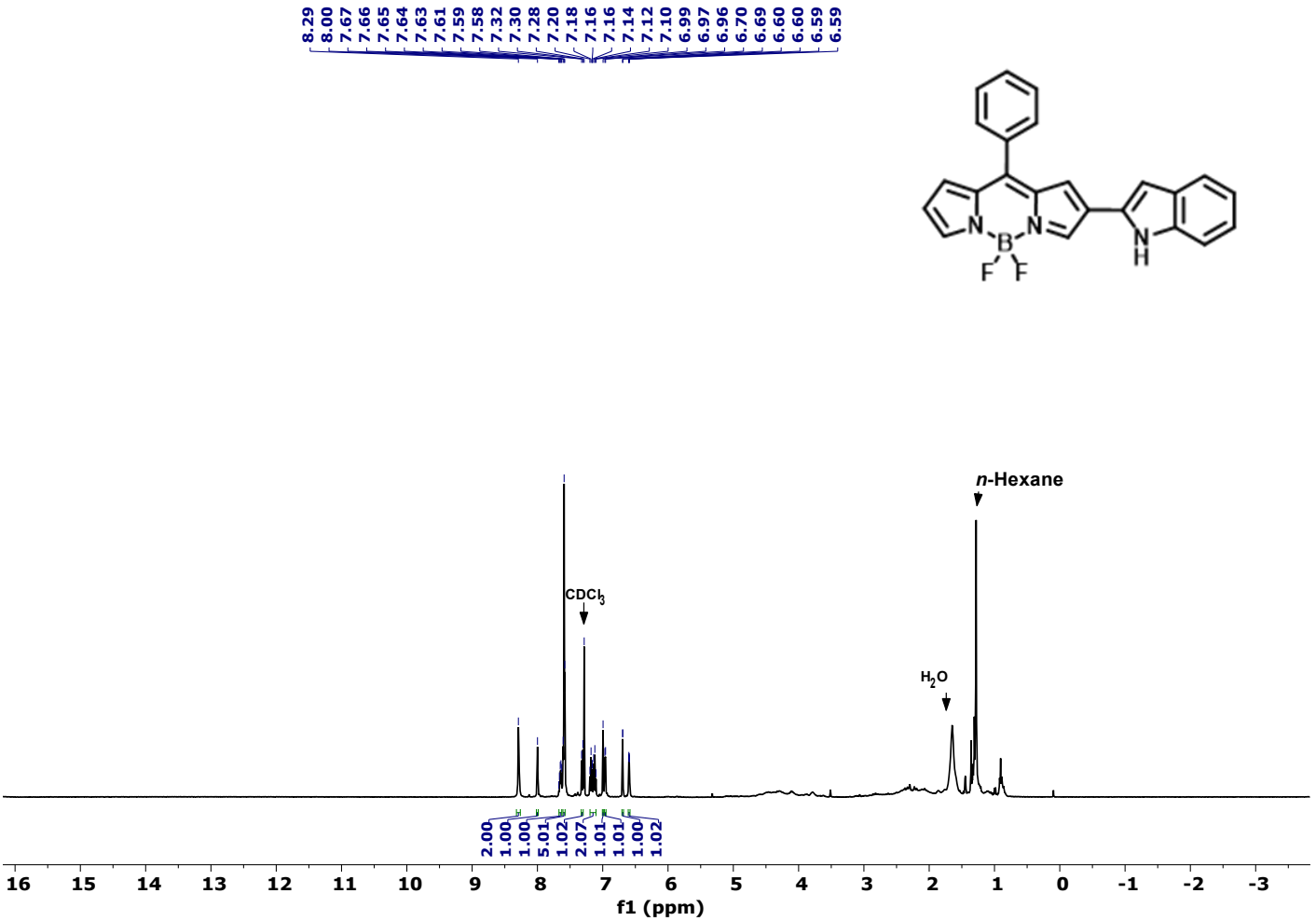
^{19}F NMR spectrum of 5g



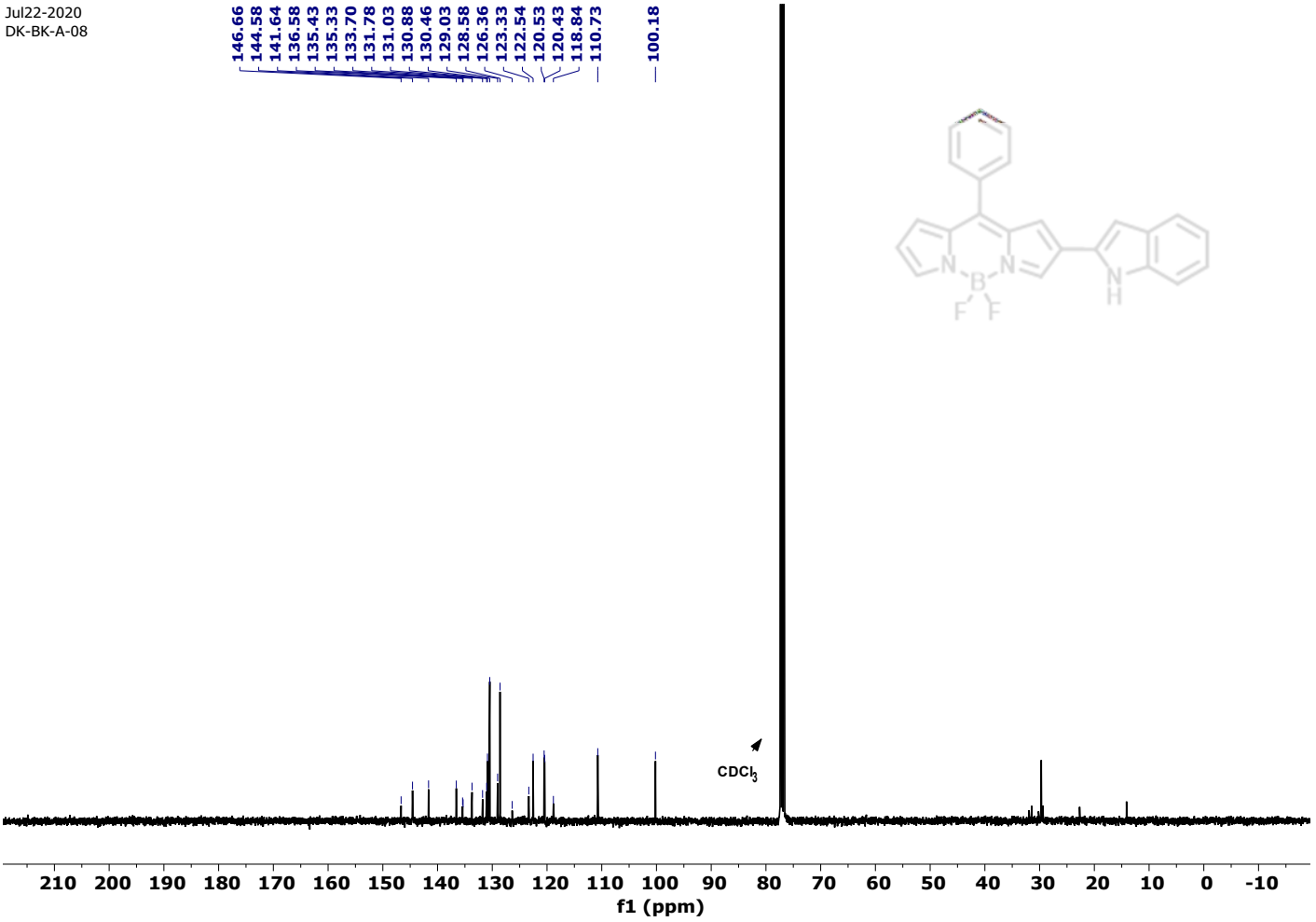
HRMS spectrum of 5g



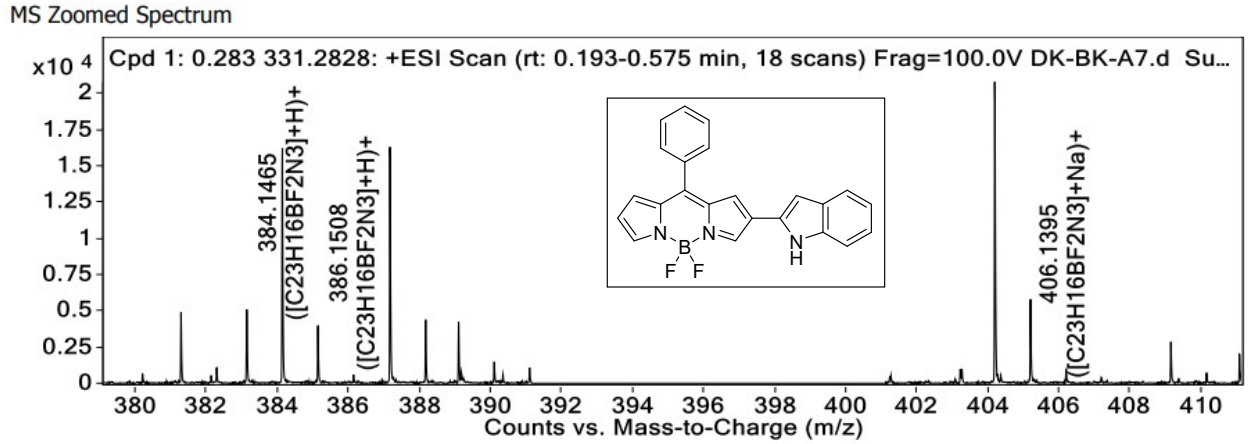
^{1}H NMR spectrum of 5h



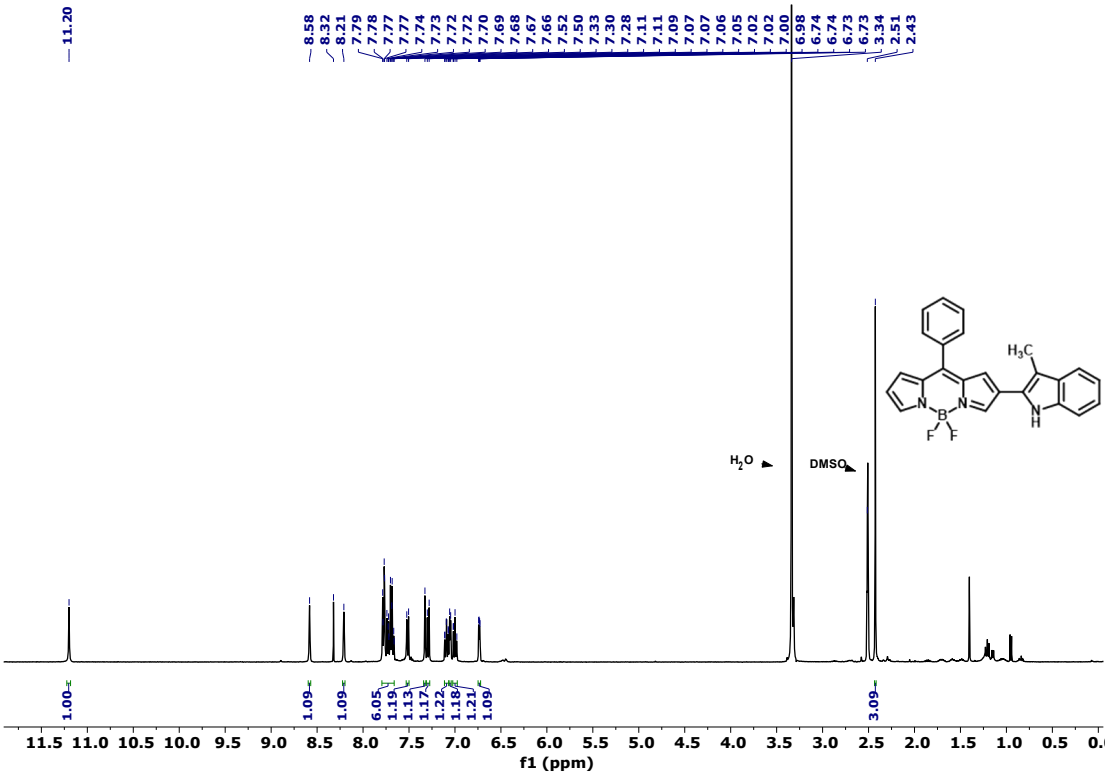
^{13}C NMR spectrum of 5h



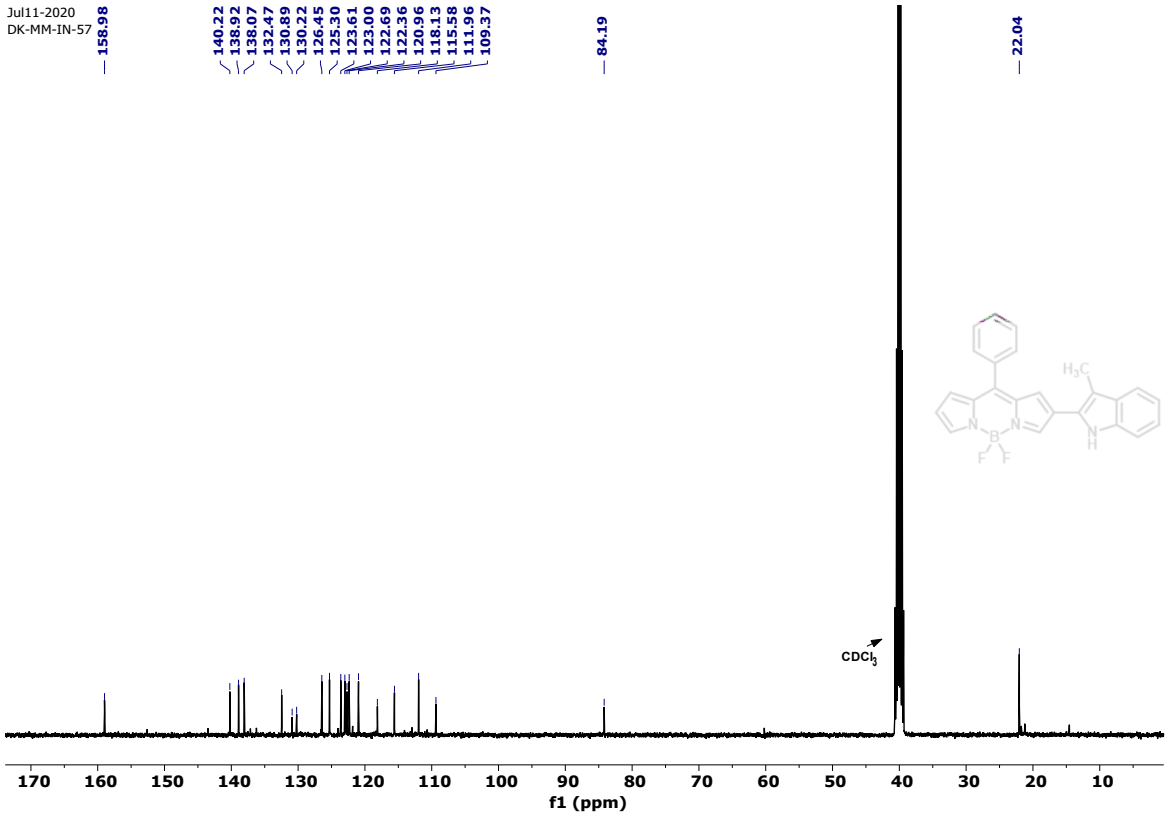
HRMS spectrum of 5h



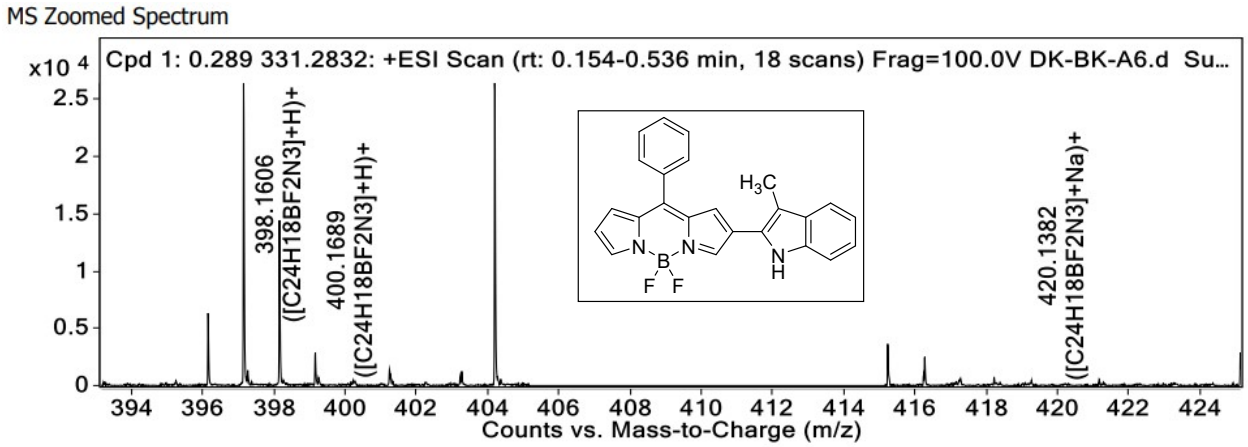
^{1}H NMR spectrum of 5i



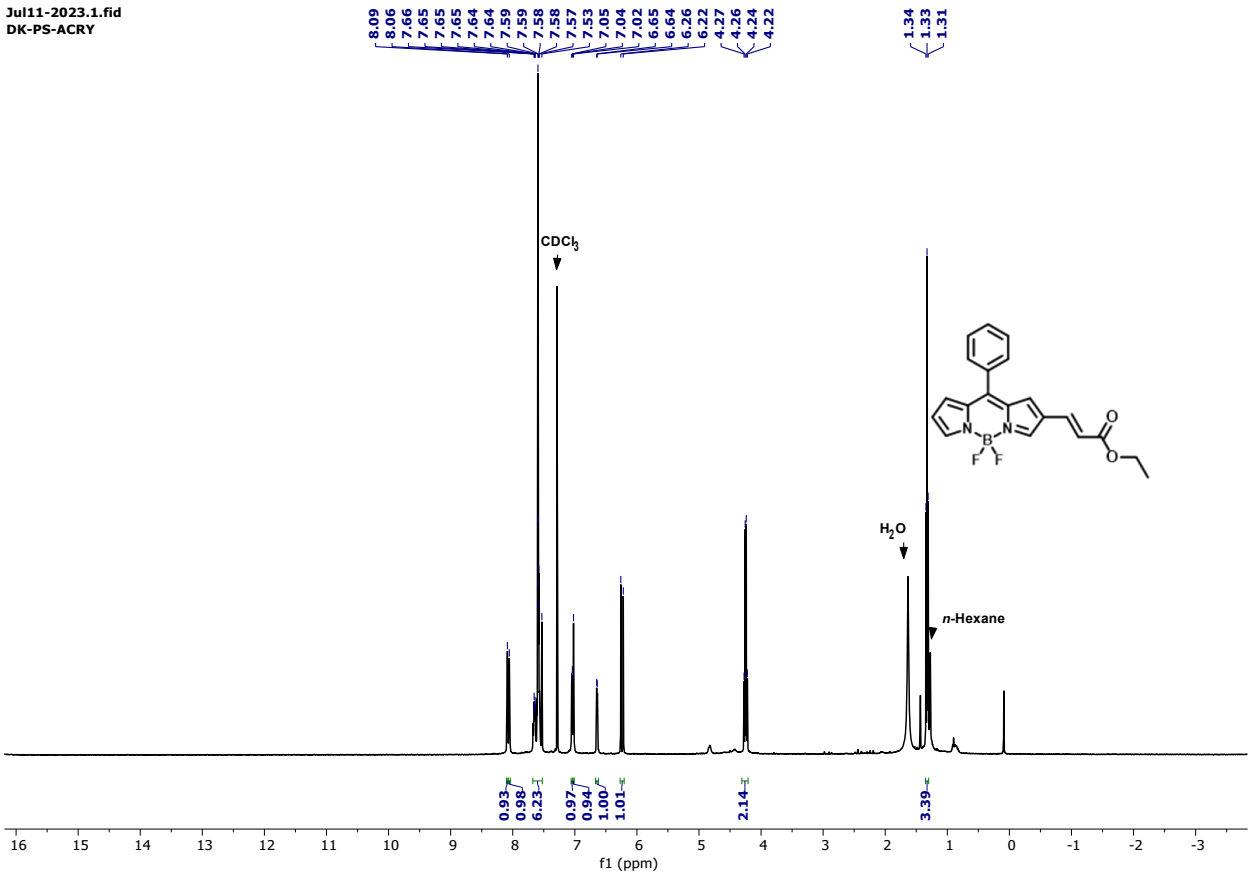
^{13}C NMR spectrum of 5i



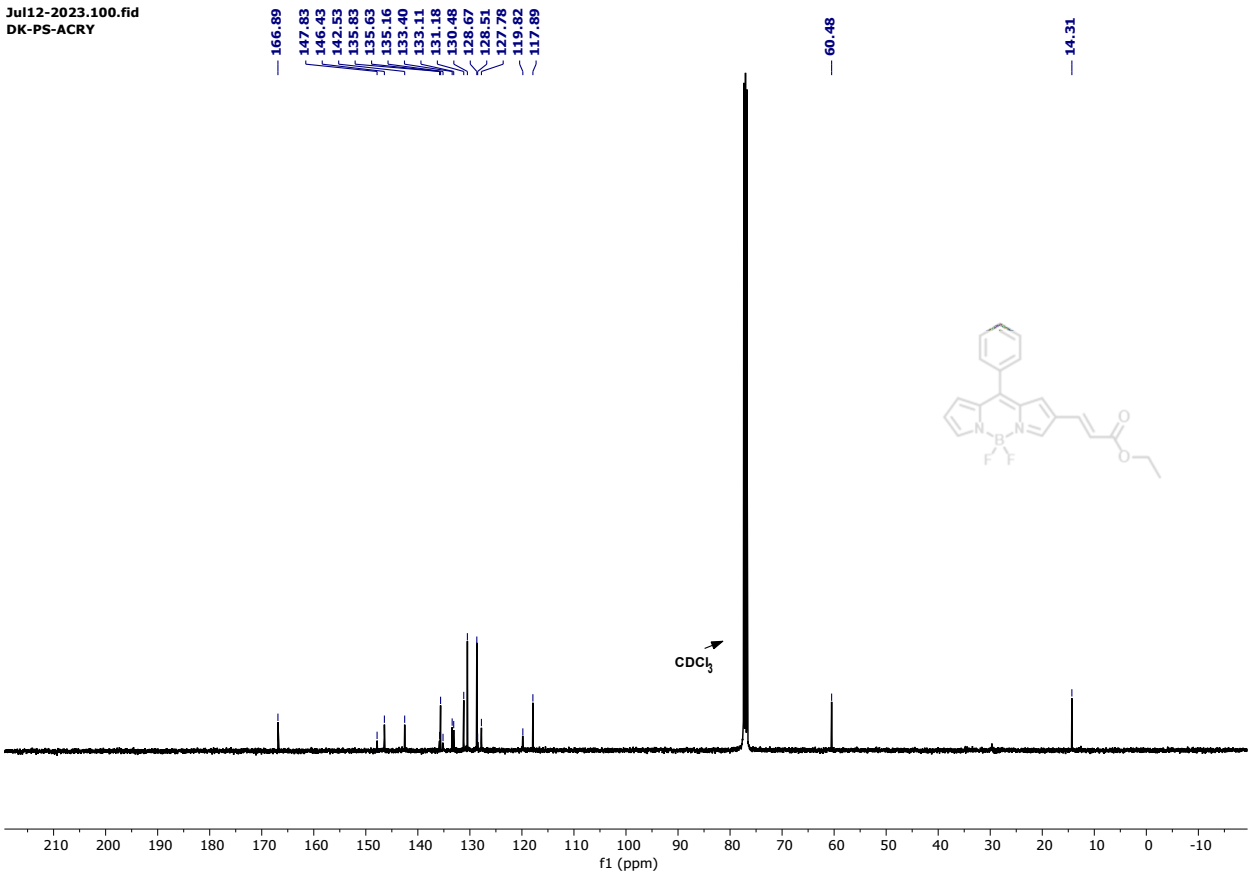
HRMS spectrum of 5i



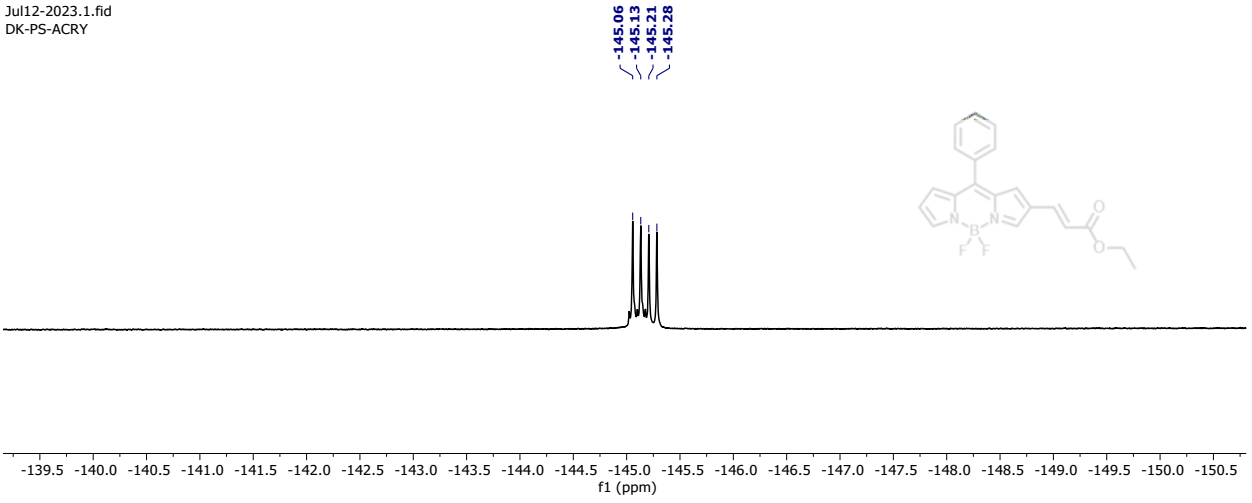
^{1}H NMR spectrum of 5j



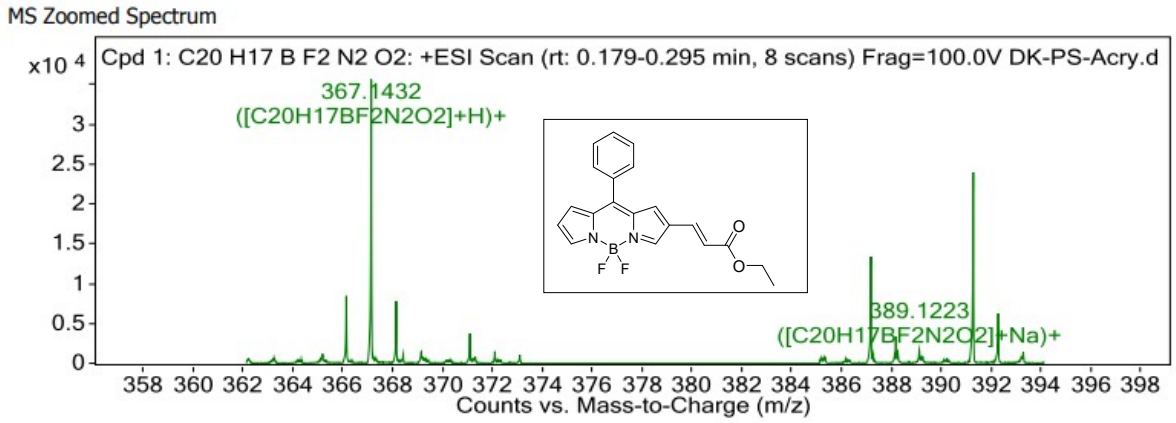
^{13}C NMR spectrum of 5j



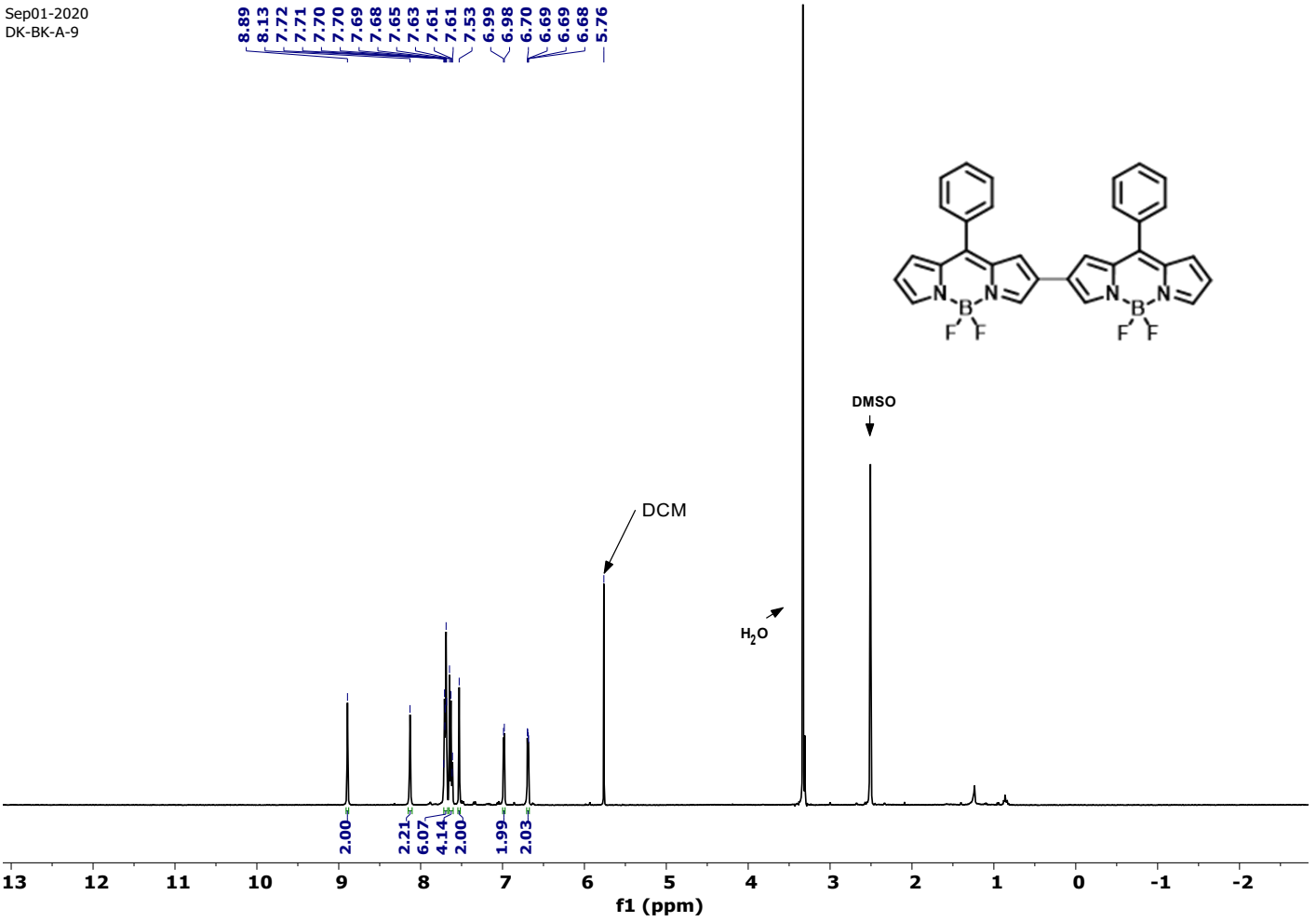
^{19}F NMR spectrum of 5j



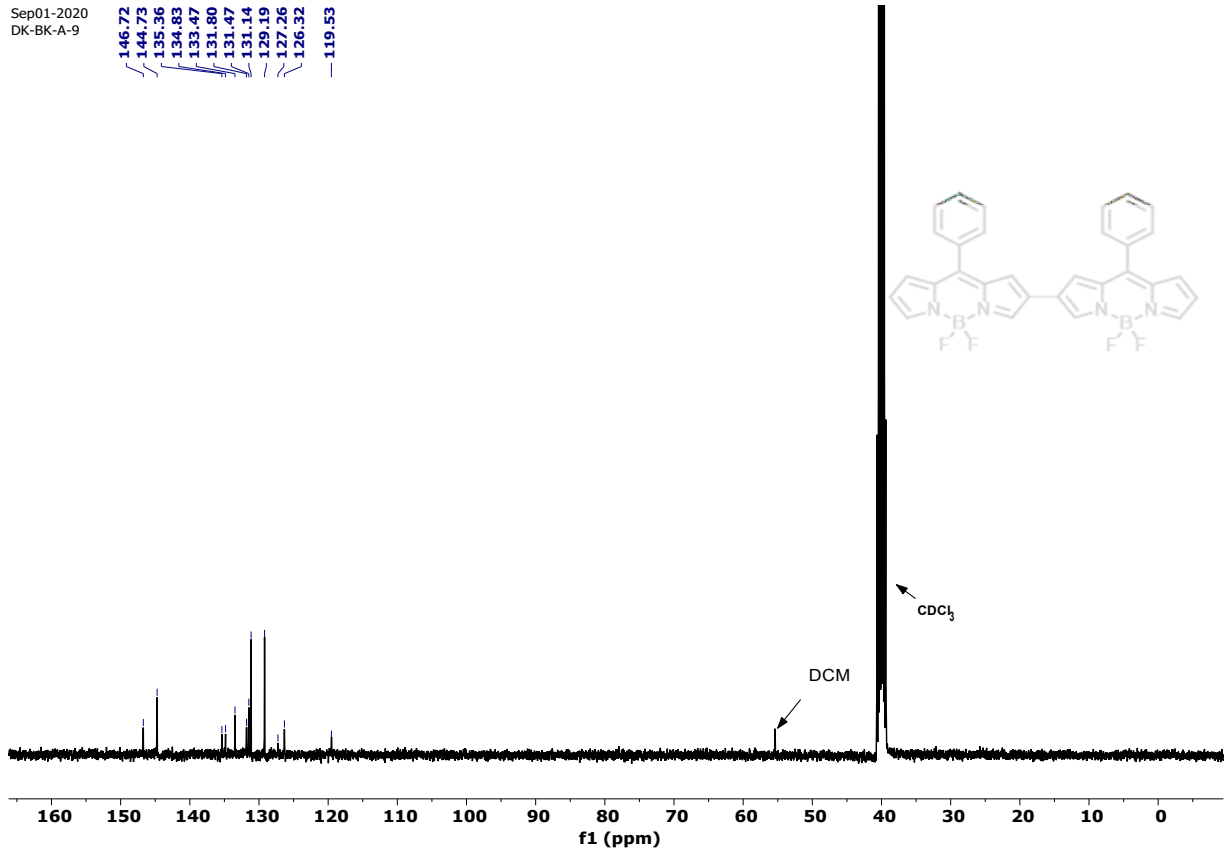
HRMS spectrum of 5j



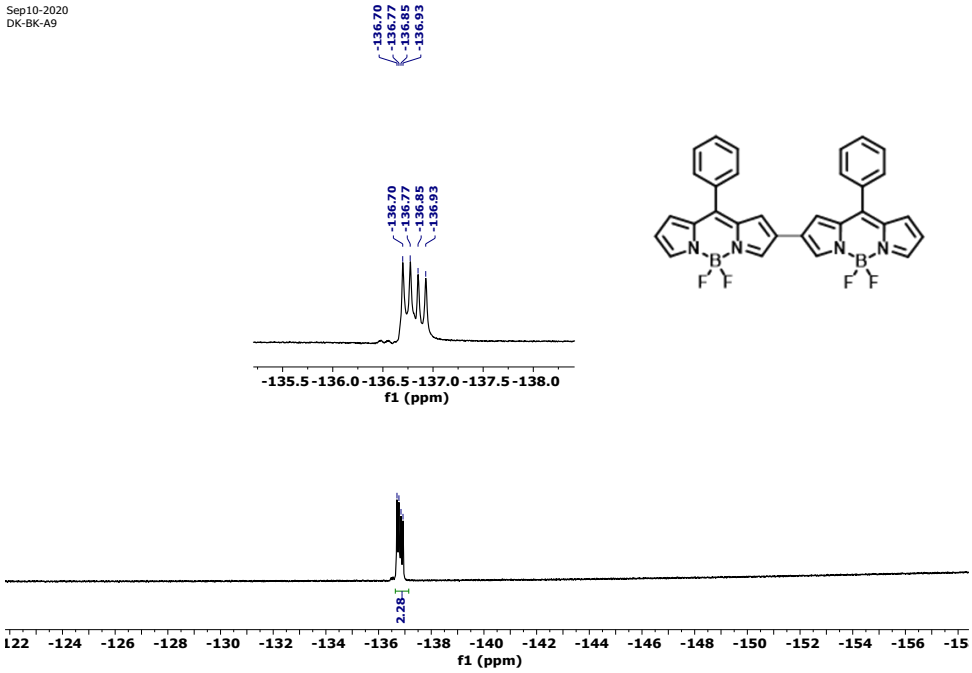
^{1}H NMR spectrum of 5k



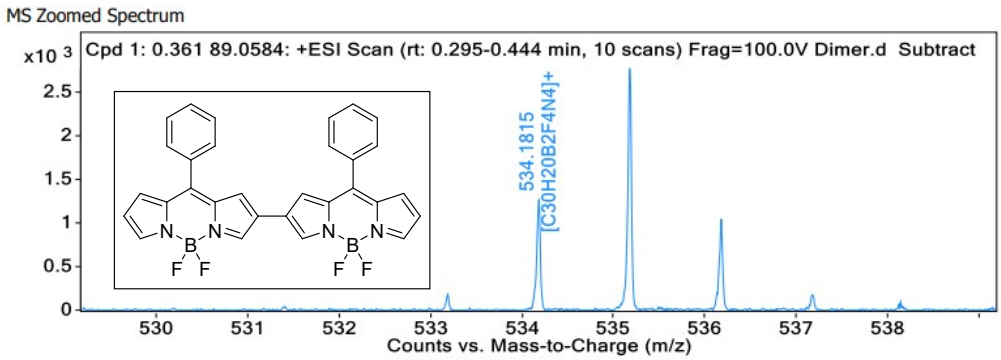
^{13}C NMR spectrum of 5k



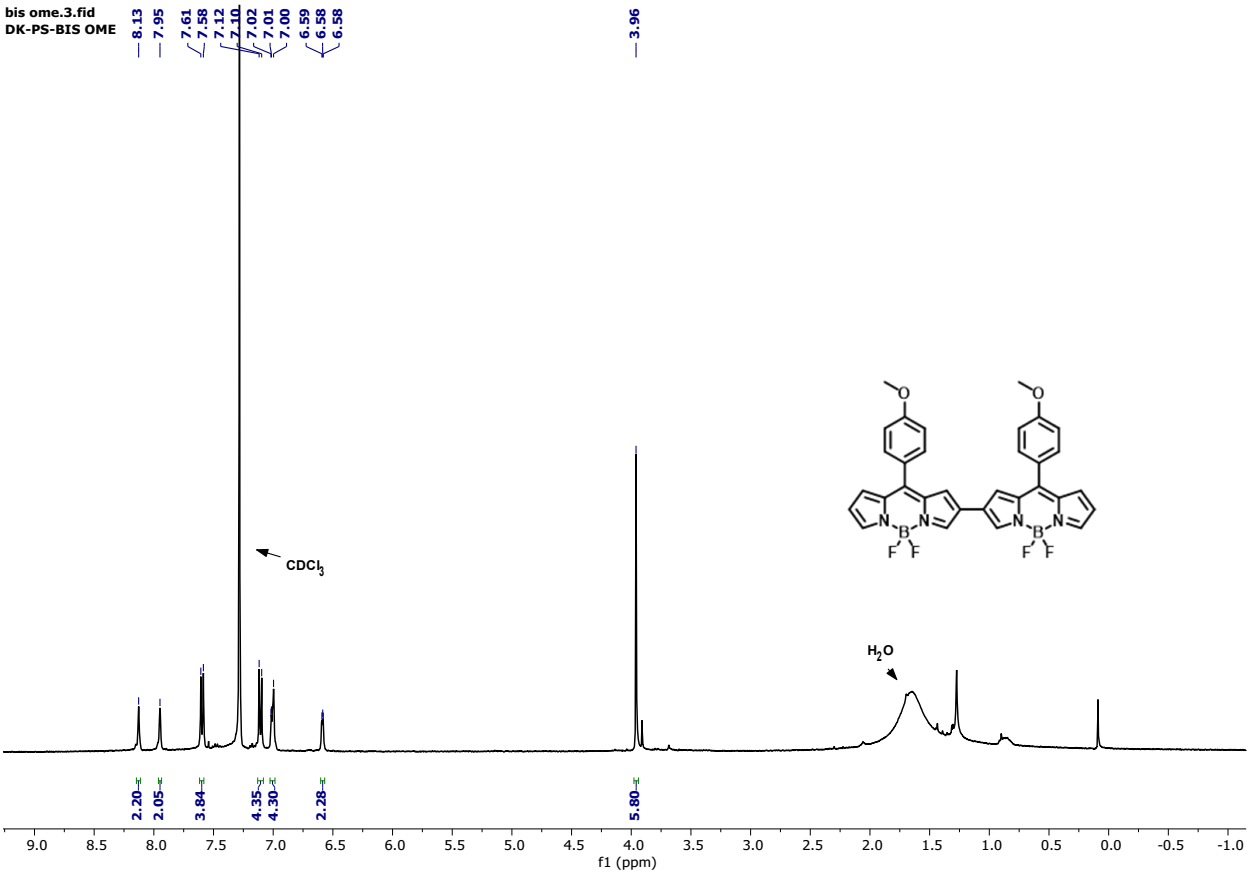
^{19}F NMR spectrum of 5k



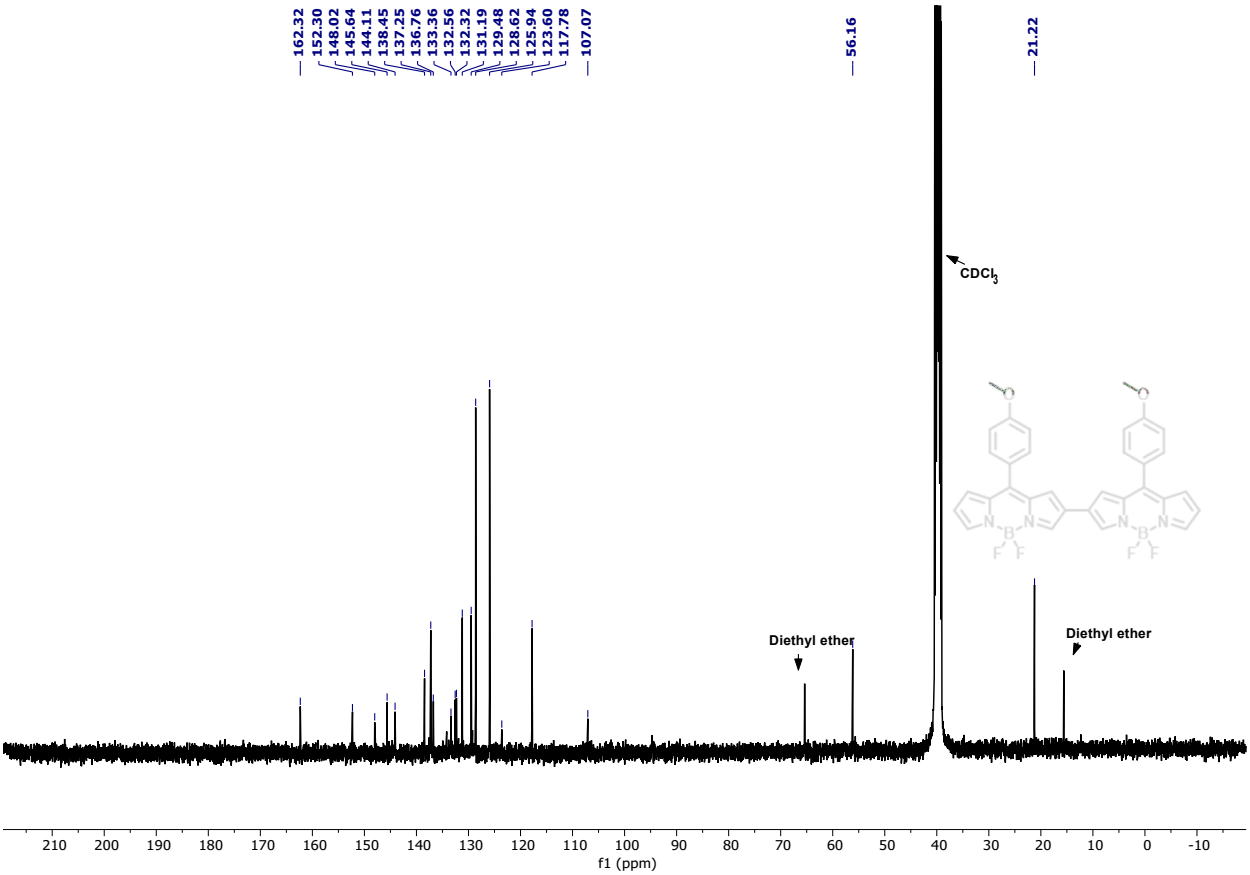
HRMS spectrum of 5k



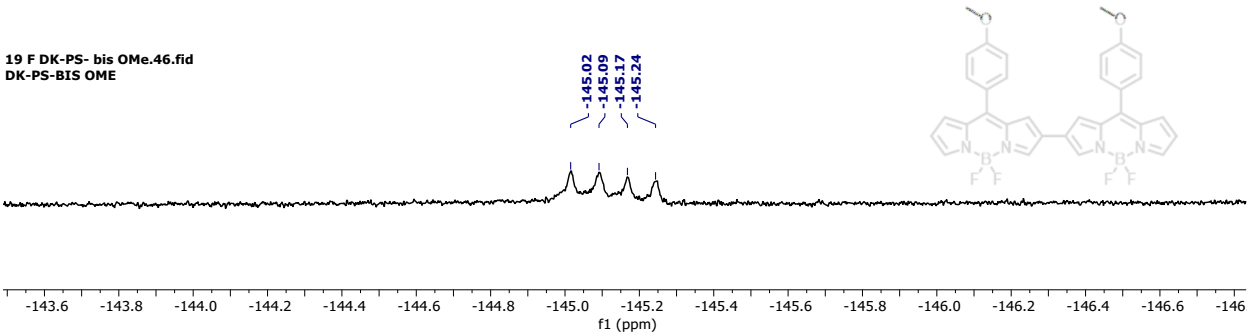
^{1}H NMR spectrum of 5l



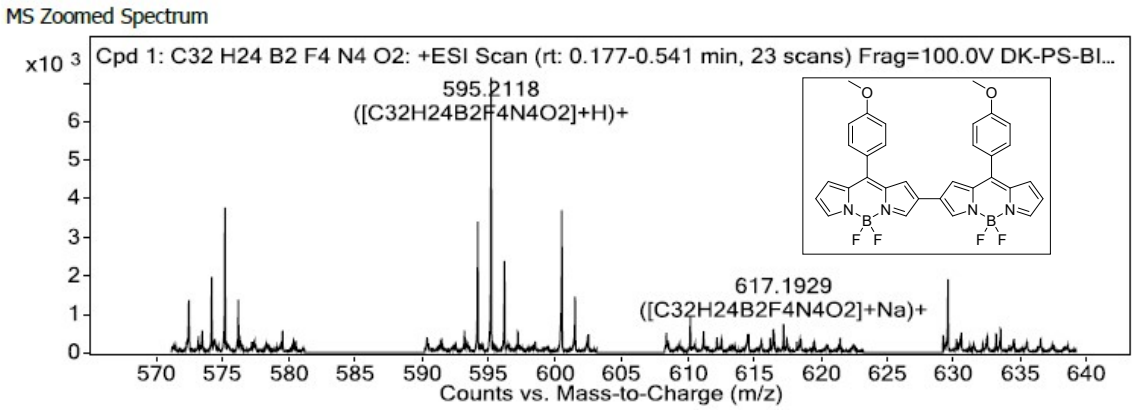
^{13}C NMR spectrum of 5l



^{19}F NMR spectrum of 5l



HRMS spectrum of 5l



V. Photophysical properties

Table S7. Photophysical properties of **4e**, **5h** and **5i** (10 μM) in dichloromethane

Compound.	λ_{abs} (nm)	ε (M^{-1} cm^{-1})	λ_{em} (nm)	ϕ_f	Stoke′s shift (nm)
4e	493	137320	518	0.06	25
	359	41570	-	-	-
5h	590	132870	611	0.021	21
	436	106930	-	-	-
	354	94580	-	-	-
5i	600	110080	665	0.022	65
	450	112790	-	-	-
	354	78050	-	-	-

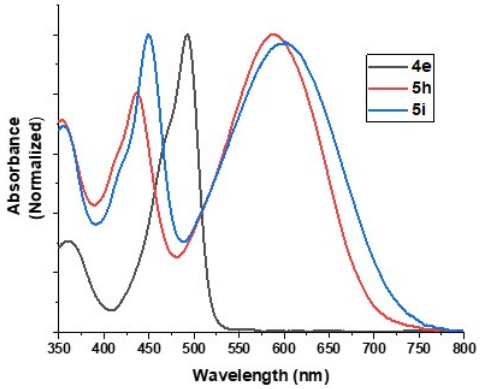


Fig. S2a. Normalized UV-Visible absorption spectra of **4e**, **5h** and **5i** in dichloromethane (10 μM)

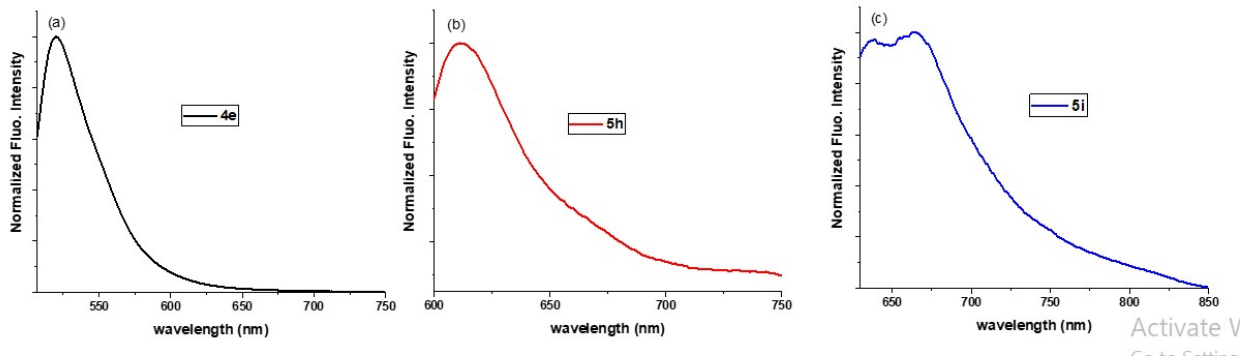


Fig. S2b. Normalized emission spectra of **4e** (λ_{ex}: 490 nm), **5h** (λ_{ex}: 580 nm) and **5i** (λ_{ex}: 615 nm) in dichloromethane (10 μM); slit width: 5 nm

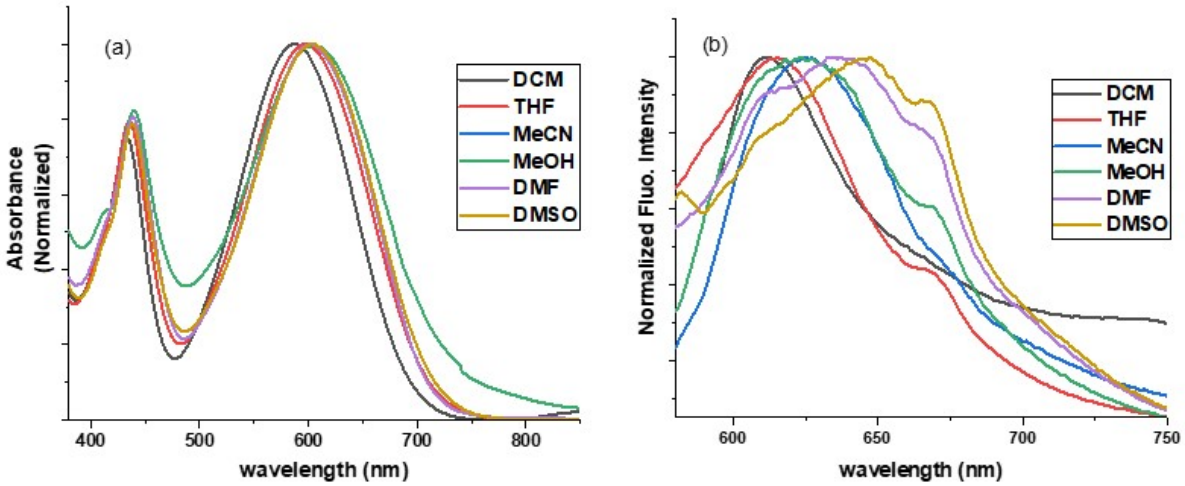


Fig. S3. UV-Visible (a) Normalized absorption spectra (b) Normalized emission spectra of **5h** (10 μM) in different solvents (λ_{ex}: 580 nm; slit width: 5 nm)

Table S8. Photophysical properties of **5h** (10 μM) in different solvents

Solvent	λ_{abs}/nm	λ_{em}/nm	Stoke′s shift/nm
DCM	590	611	21
THF	598	615	17
MeCN	600	624	24
MeOH	600	625	25
DMF	601	633	32
DMSO	603	647	44

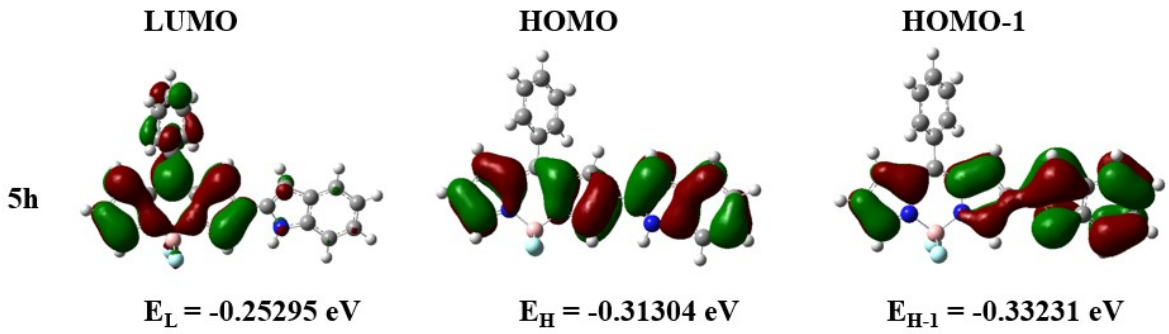


Fig. S4. DFT calculated frontier molecular orbitals

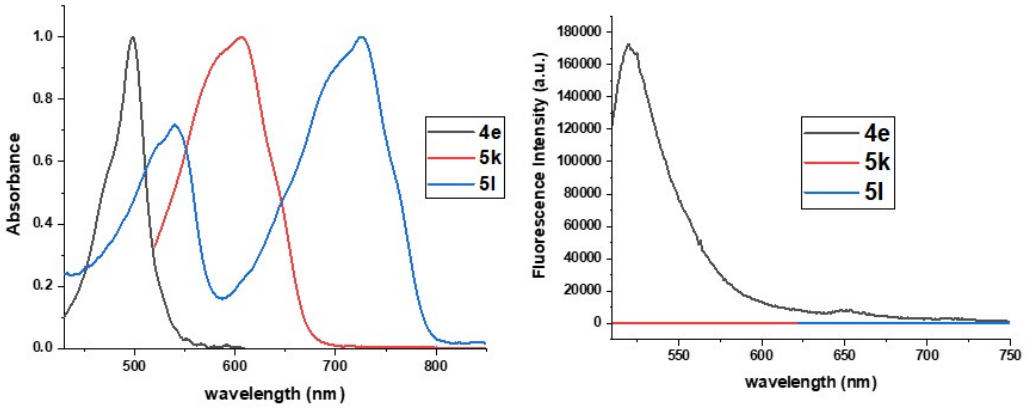


Fig. S5. UV-Visible (a) Absorption spectra (b) Emission spectra of **4e, 5k** and **5l** in dichloromethane

Table S9. Summary of photophysical properties of BODIPY derivatives **4(a-e)** in different solvents.

Compound	Solvent	$\lambda_{,abs}$ /nm	ν_{abs} /cm^{-1}	λ_{em} /nm	ν_{em} /cm^{-1}	Stokes shift /cm^{-1}	ϕ_f /10^{-2}	τ_{av} /ns	κ_r /ns^{-1}	$\Sigma\kappa_{nr}$ /ns^{-1}
4a	DCM	495	20202	519	19268	934	30.08	0.22	1.37	3.18
	DMSO	496	20161	519	19268	893	6.21	0.07	0.89	13.40
	Methanol	488	20492	510	19608	884	9.98	0.16	0.62	5.63
	Water	482	20747	511	19569	1177	14.79	0.15	0.99	5.68
4b	DCM	507	19724	515	19417	306	79.33	1.79	0.44	0.12
	DMSO	502	19920	515	19417	503	7.27	2.47	0.03	0.38
	Methanol	487	20534	530	18868	1666	7.19	0.69	0.10	1.35
	Water	495	20202	513	19493	709	13.19	2.33	0.06	0.37
4c	DCM	489	20450	507	19724	726	5.30	1.51	0.04	0.63
	DMSO	492	20325	508	19685	640	7.56	0.70	0.11	1.32
	Methanol	484	20661	526	19011	1650	4.91	2.84	0.02	0.33
	Water	488	20492	526	19011	1480	1.39	2.43	0.01	0.41
4d	DCM	492	20325	508	19685	640	40.09	1.27	0.32	0.47
	DMSO	493	20284	509	19646	638	30.88	0.79	0.39	0.87
	Methanol	485	20619	500	20000	619	18.22	1.38	0.13	0.59
	Water	485	20619	500	20000	619	7.85	1.22	0.06	0.75
4e	DCM	493	20284	518	19305	979	6.50	0.36	0.18	2.60
	DMSO	496	20161	516	19380	781	1.50	0.35	0.04	2.81
	Methanol	488	20492	511	19569	922	3.80	0.25	0.15	3.85
	Water	487	20534	510	19608	926	5.00	0.16	0.31	5.94

Table S10. Binding constant (K_a) and values of thermodynamic parameters ΔG, ΔH and ΔS for the interaction of BODIPY-BSA at different temperatures.

Compound	Temp /K	$K_a/10^5$ M^{-1}	ΔG/ kJ mol^{-1}	ΔH/ kJ mol^{-1}	ΔS/ kJ $K^{-1}mol^{-1}$
4a	298	4.58 ± 0.8	-32.46	-112.92 ± 0.2	-0.27 ± 0.003
	303	3.55 ± 0.5	-31.11		
	308	2.56 ± 0.6	-29.76		
	313	3.27 ± 0.3	-28.41		
	318	4.62 ± 0.2	-27.06		
4c	298	2.17 ± 0.8	-29.78	-41.70± 0.6	-0.04 ± 0.001
	303	1.80 ± 0.8	-29.58		
	308	2.22 ± 0.4	-29.38		
	313	0.80 ± 0.1	-29.18		
	318	0.84 ± 0.1	-28.98		
4d	298	0.25 ± 0.2	-28.04	-51.88± 0.5	-0.08 ± 0.002
	303	0.48 ± 0.1	-27.64		
	308	0.37 ± 0.1	-27.24		
	313	0.29 ± 0.1	-26.84		
	318	0.18 ± 0.2	-26.44		
4e	298	0.61 ± 0.2	-27.36	47.14±0.10	0.25±0.003
	303	1.73 ± 0.3	-28.61		
	308	1.41±0.5	-29.86		
	313	1.96±0.1	-31.11		
	315	1.84±0.3	-32.36		

Table S11: Lifetime decay parameters of **4a**, **4c**, **4d** and **4e** with increasing concentration of BSA.

Compound	[BSA]/ μM	α_1	τ_1 /ns	α_2	τ_2 /ns	τ_{av} /ns
4a	0	100.00	0.16	0.00	0.00	0.16
	1	99.75	0.15	0.25	2.65	0.26
	3	99.72	0.15	0.28	3.10	0.31
	5	99.44	0.16	0.56	3.25	0.48
	10	99.02	0.19	0.98	3.32	0.65
	15	98.20	0.23	1.81	3.06	0.78
	20	98.35	0.25	1.65	3.27	0.79
	25	97.97	0.30	2.03	3.40	0.89
	30	97.20	0.34	2.80	3.37	1.02
4c	0	59.73	0.72	40.27	3.94	3.25
	1	64.66	1.43	35.34	4.81	3.62
	3	62.35	1.15	37.65	4.67	3.66
	5	65.87	1.09	34.13	4.61	3.51
	10	69.11	1.03	30.89	4.58	3.39
	15	72.23	0.95	27.77	4.37	3.14
	20	72.17	1.06	27.83	4.47	3.17
	25	73.86	1.12	26.14	4.46	3.07
	30	73.75	1.08	26.25	4.43	3.07
	35	74.35	0.98	25.65	4.24	2.93
4d	0	64.16	3.69	35.84	1.11	3.32
	1	51.05	3.54	48.95	0.71	3.08
	3	58.31	3.55	41.69	0.78	3.18
	5	57.40	3.85	42.60	0.99	3.39
	10	53.15	0.86	46.85	3.86	3.25
	15	64.82	0.76	35.18	4.00	3.16
	20	70.18	0.75	29.82	3.92	2.93
	25	74.49	0.86	25.51	4.01	2.80
	28	76.56	0.90	23.44	3.98	2.67
	30	75.86	0.93	24.14	4.01	2.71
	35	72.22	0.92	27.78	3.96	2.82
	40	72.19	0.85	27.81	3.80	2.72
4e	0	88.71	0.15	11.29	0.01	0.14
	1	98.79	0.14	1.211	1.86	0.38
	3	95.49	0.15	4.509	2.12	0.94
	5	90.41	0.20	9.591	2.23	1.30
	10	80.71	0.31	19.29	2.37	1.64
	15	75.56	0.41	24.44	2.43	1.74
	20	68.29	0.37	31.71	2.25	1.76
	25	67.7	0.49	32.3	2.41	1.83
	28	66.68	0.49	33.32	2.39	1.84
	30	69.22	0.63	30.78	2.51	1.83
	35	66.83	0.74	33.17	2.53	1.87
	40	66.17	0.79	33.83	2.57	1.90

Table S12. Thermodynamic parameters obtained from ITC measurements.

Compound	Ka/10^3 M^{-1}	ΔG/ kJ mol^{-1}	ΔH/10^4 kJ mol^{-1}	ΔS/10^2 kJ $K^{-1}mol^{-1}$
4a	1.19 ± 0.1	-174	-7.08 ± 0.2	-2.37
4c	1.03 ± 0.1	-286	-7.27± 0.4	-2.43
4d	0.52 ± 0.05	-580	-54.89± 0.9	-18.40
4e	0.98 ± 0.02	-338	-6.58± 0.2	-2.20

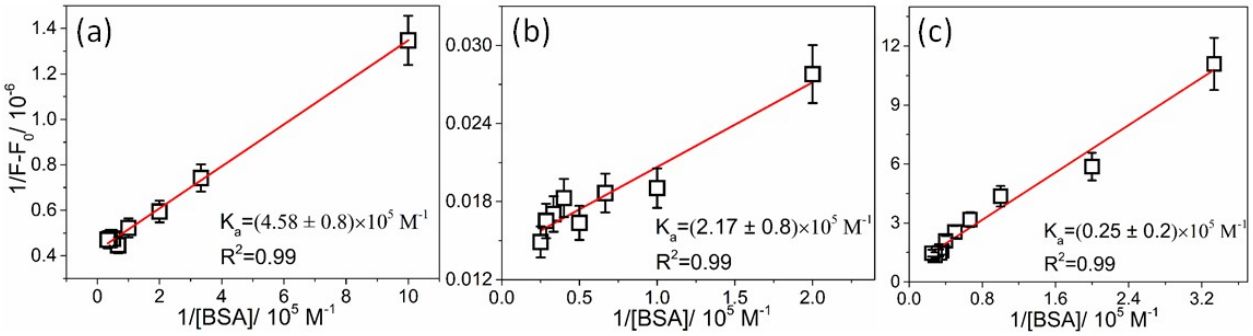


Fig. S6. B-H plot for calculation of binding constant of **4a**, **4c** and **4d** with BSA.

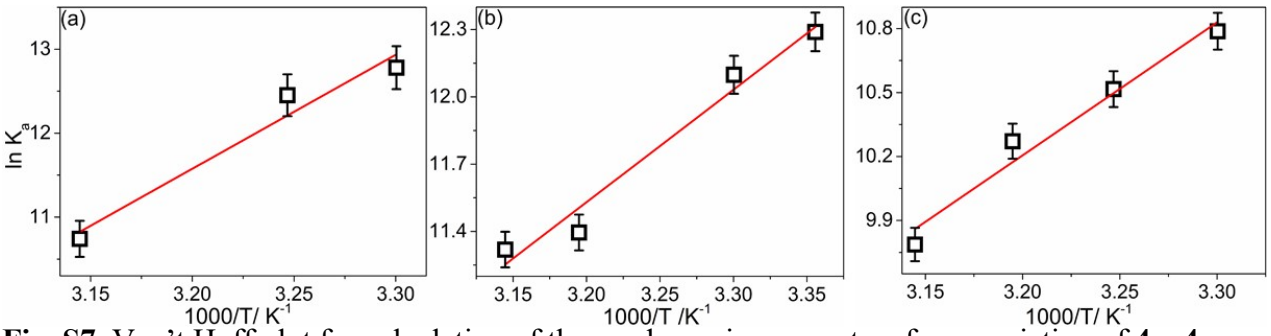


Fig. S7. Van't Hoff plot for calculation of thermodynamic parameters for association of **4a**, **4c** and **4d** with BSA.

Table S13. Calculated values of LOD and LOQ for detection of BSA for the compounds **4a**, **4c**, **4d** and **4e.**

	LOD/ mg ml^{-1}	LOQ/ mg ml^{-1}
4a	0.21	0.71
4c	0.007	0.02
4d	0.32	1.08
4e	0.02	0.05