Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Meso enyne substituted BODIPYs: synthesis, structure and properties

*Bhausaheb Dhokale, Thaksen Jadhav, Shaikh M. Mobin, and Rajneesh Misra**

*E-mail: rajneeshmisra@iiti.ac.in

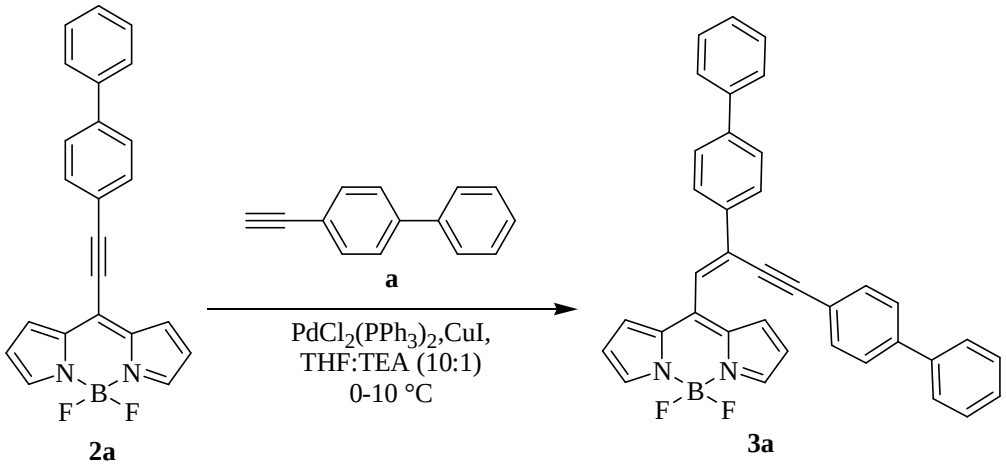
Department of Chemistry,

Indian Institute of Technology Indore,

Indore- 452 017, India.

Table of Contents

Table S1. Optimization of reaction conditions for synthesis of BODIPY **3a** (Method B)[a].



2a **3a**

Sr. No.	Solvent	Base	$Pd(PPh_3)_2Cl_2$	CuI	Yield
1	Tetrahydrofuran	TEA	5 mol %	10 mol %	60 % (89 mg)
2	Toluene	TEA	5 mol %	10 mol %	57 % (84 mg)
3	Dichloromethane	TEA	5 mol %	10 mol %	57 % (84 mg)
4	Tetrahydrofuran	TEA	-	10 mol %	No expected product
5	Tetrahydrofuran	TEA	5 mol %	-	No expected product

[a] Pd-Cu catalyzed hydroalkynylation reaction across –C≡C– bond; all reactions were performed in inert atmosphere.

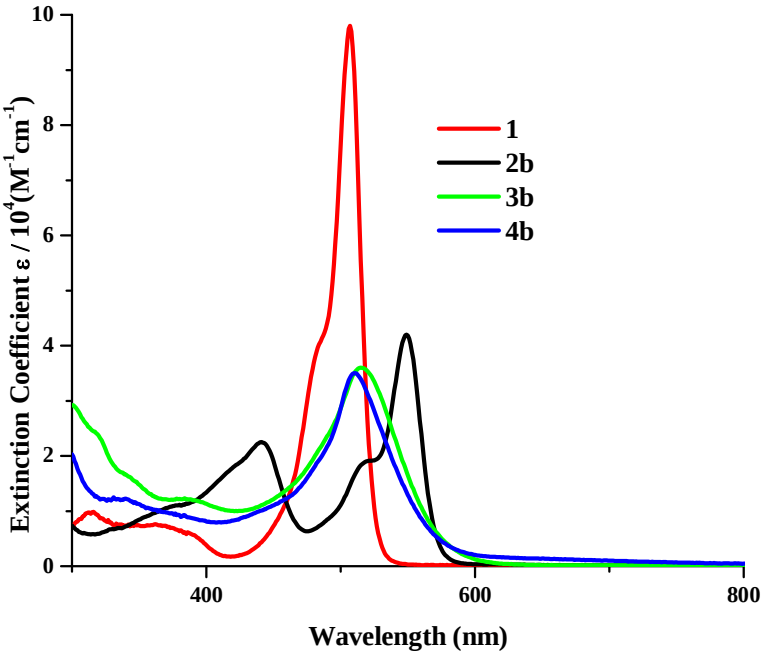


Figure S1. Electronic absorption spectra of BODIPYs **1, 2b, 3b** and **4b** recorded in toluene.

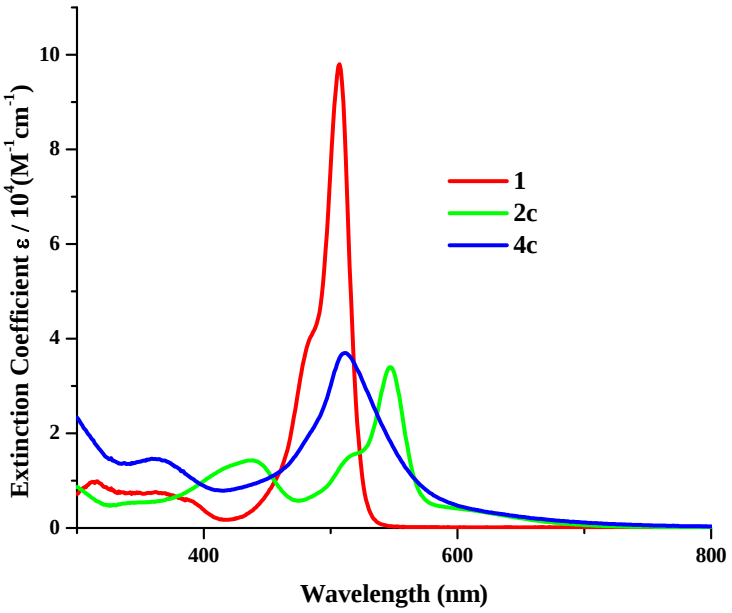


Figure S2. Electronic absorption spectra of BODIPYs **1, 2c** and **4c** recorded in toluene.

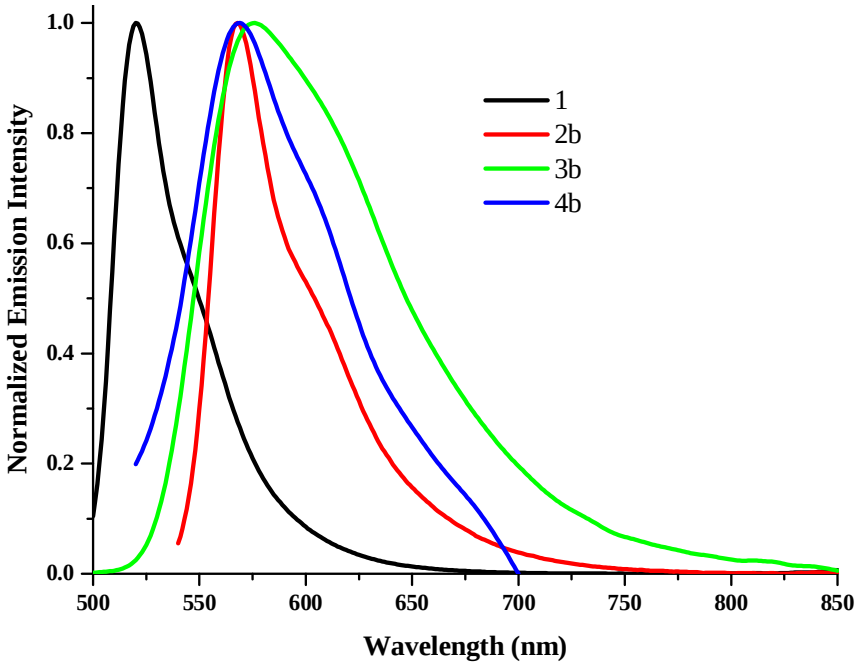


Figure S3. Normalized emission spectra of BODIPYs **1, 2b, 3b** and **4b** recorded in toluene.

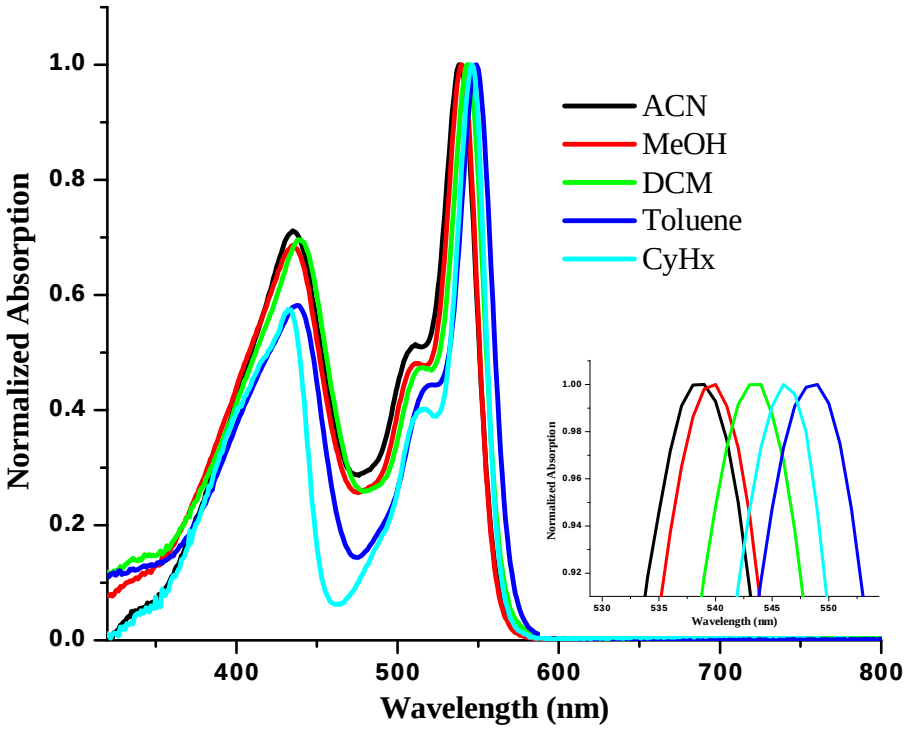


Figure S4. Normalized electronic absorption spectra of BODIPY **2a** in different solvents (Insec shows enlarged view).

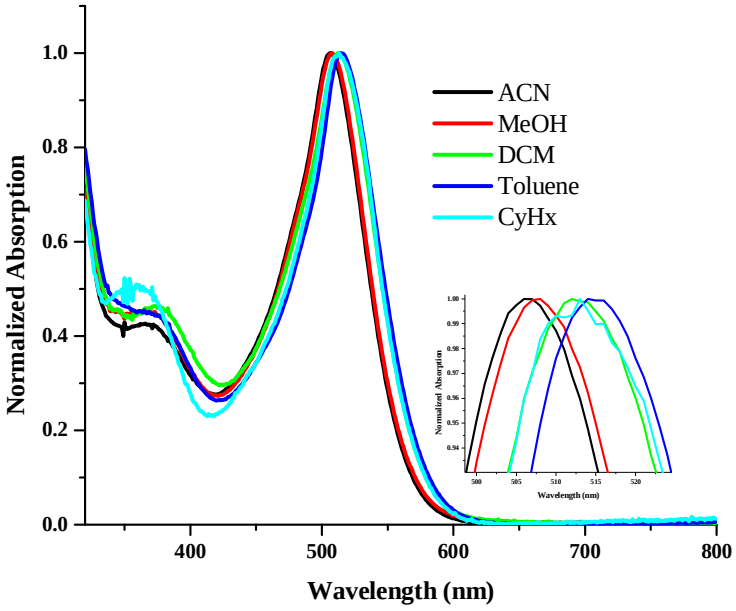


Figure S5. Normalized electronic absorption spectra of BODIPY **3a** in different solvents (Insec shows enlarged view).

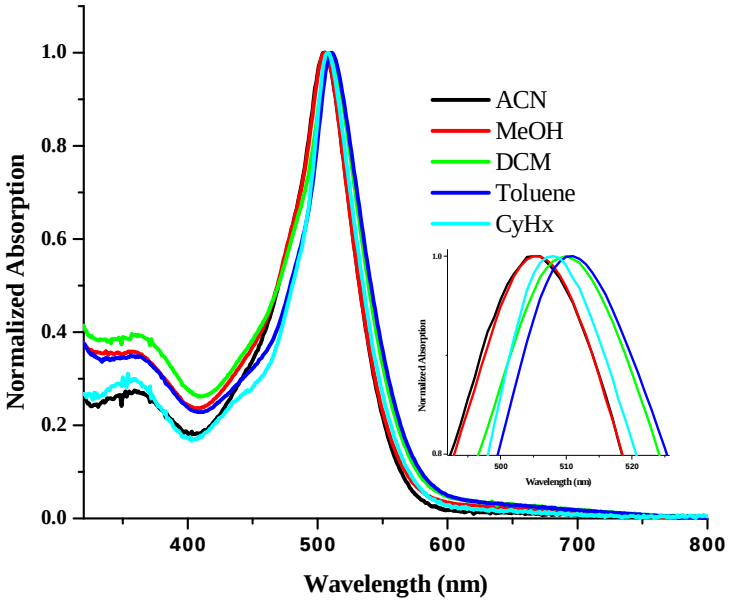


Figure S6. Normalized electronic absorption spectra of BODIPY **4a** in different solvents (Insec shows enlarged view).

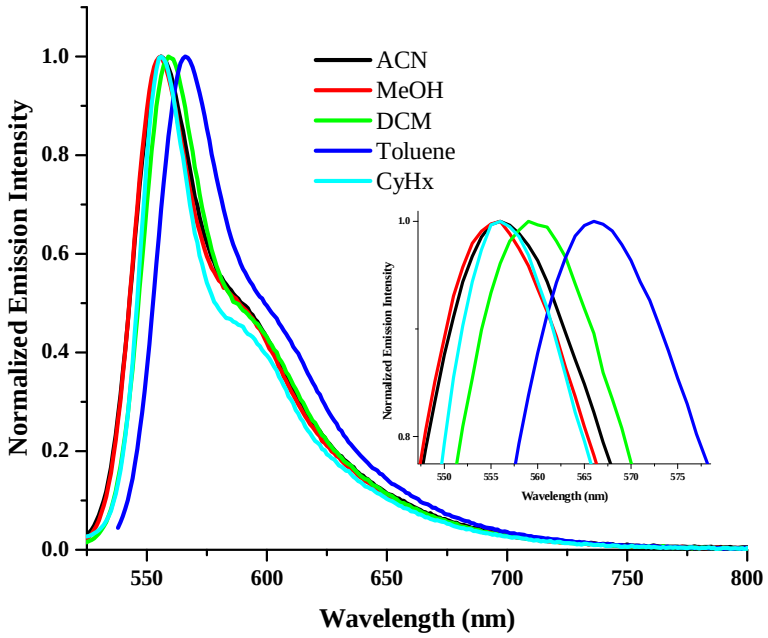


Figure S7. Normalized emission spectra of BODIPY **2a** in different solvents.

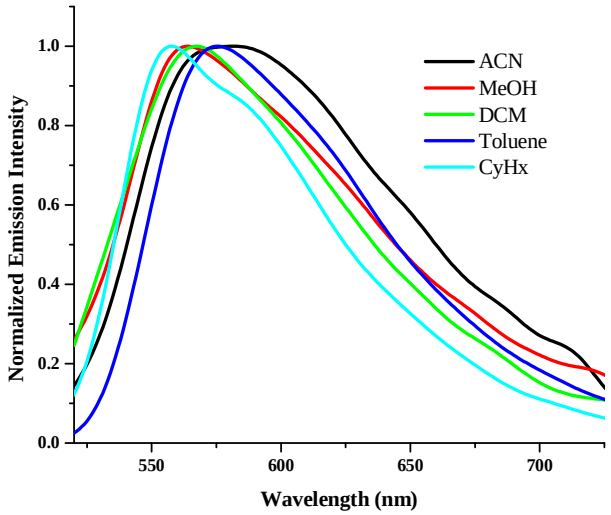


Figure S8. Normalized emission spectra of BODIPY **3a** in different solvents.

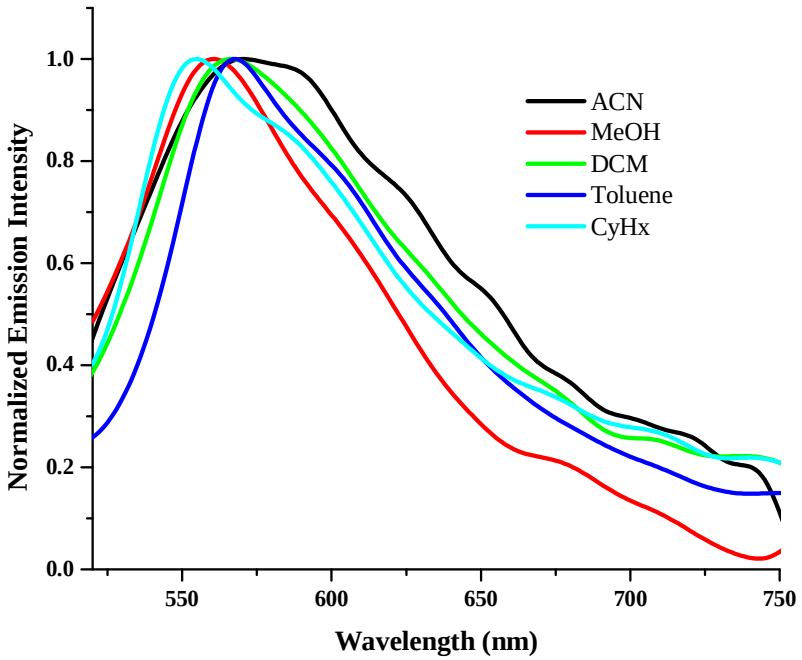


Figure S9. Normalized emission spectra of BODIPY **4a** in different solvents.

Electrochemical Data

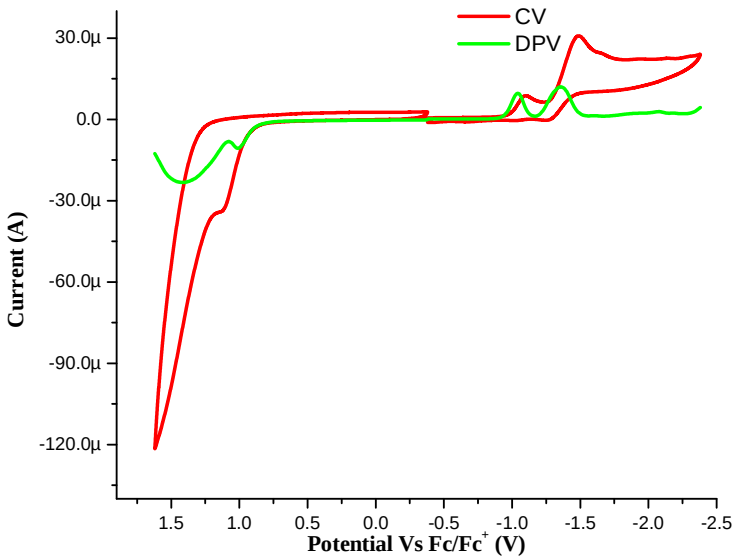


Figure S10. CV and DPV plots of BODIPY **3a**.

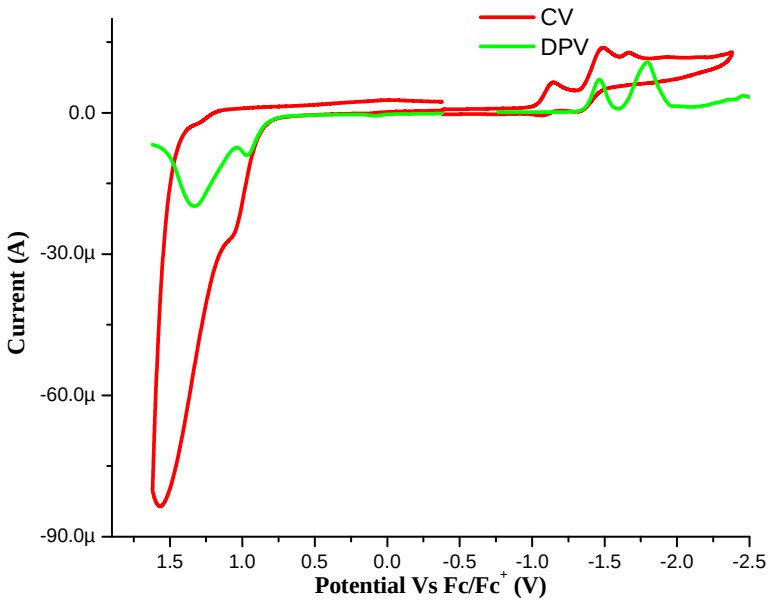


Figure S11. CV and DPV plots of BODIPY **3b.**

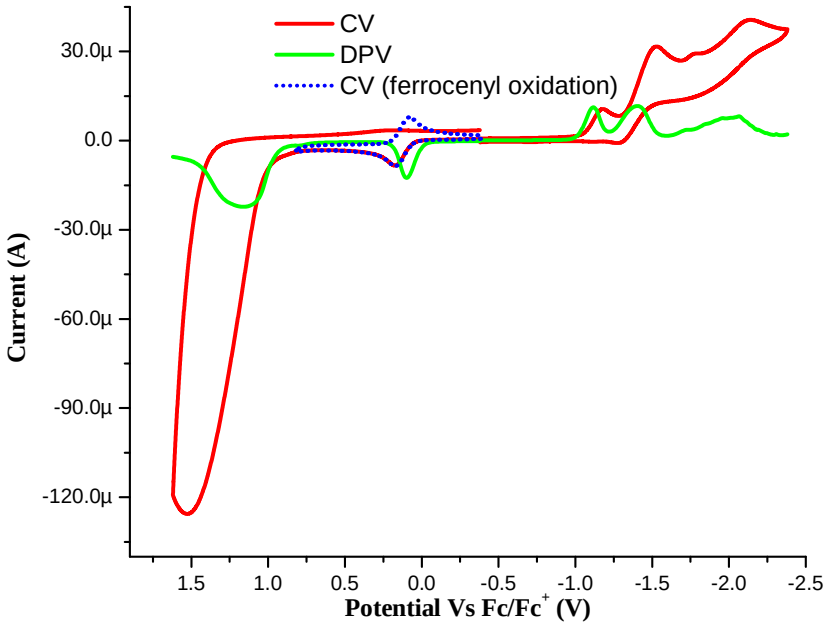


Figure S12. CV and DPV plots of BODIPY **4a.**

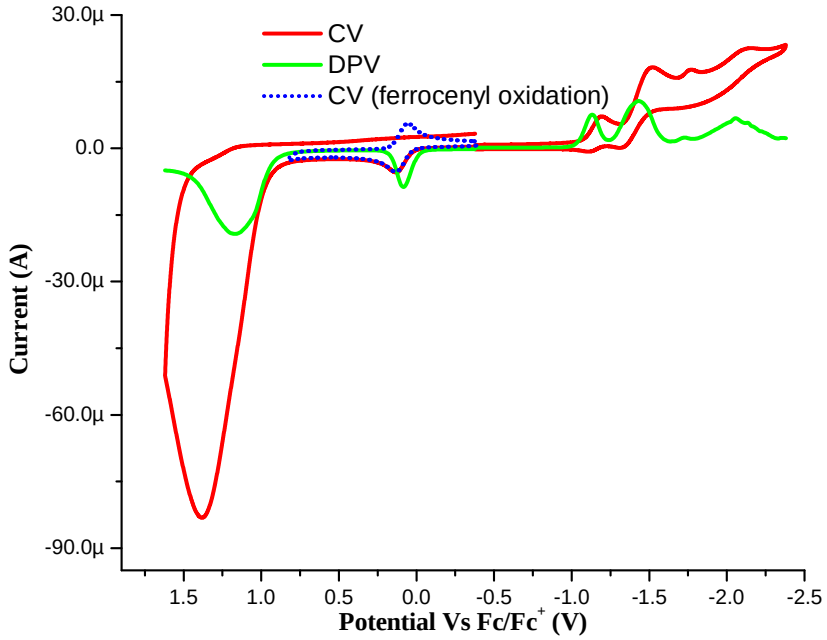


Figure S13. CV and DPV plots of BODIPY **4b.**

Single Crystal X-ray Diffraction Studies.

Single crystal X-ray structural studies of **2a**, **3b** and **3a** were performed on a CCD Agilent Technologies (Oxford Diffraction) SUPER NOVA diffractometer. Data were collected at 293(2) K using graphite-monochromated Mo Kα radiation (λ_α = 0.71073 Å). The strategy for the Data collection was evaluated by using the CrysAlisPro CCD software. The data were collected by the standard 'phi-omega scan techniques, and were scaled and reduced using CrysAlisPro RED software. The structures were solved by direct methods using SHELXS-97, and refined by full matrix least-squares with SHELXL-97, refining on $F^{2.1}$. The positions of all the atoms were obtained by direct methods. All non-hydrogen atoms were refined anisotropically. The remaining hydrogen atoms were placed in geometrically constrained positions, and refined with isotropic temperature factors, generally 1.2U_{eq} of their parent atoms. The crystal, and refinement data are summarized in Table 1. The CCDC numbers 1018403 – 1018405 for **2a, 3b** and **4a** respectively and 1041639 for **2d** contain the supplementary crystallographic data. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 union Road, Cambridge CB21 EZ, UK; Fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

Table S2. Crystal structure and data refinement parameters

BODIPY	**2a**	**3b**	**4a**	**2d**
Empirical formula	C_{69} H_{45} B_3 F_6 N_6	C_{33} H_{21} B F_2 N_2	C_{35} H_{25} B F_2 Fe N_2	C_{17} H_{11} B F_2 N_2
Formula weight	1104.54	494.33	578.23	292.09
Temperature/K	150(2) K	150(2) K	150(2) K	273(2)
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	*C*2/c	*P*-1	*P*-1	$P2_1/c$
Unit cell dimensions				
a/Å	a = 17.0474(6)	a = 9.3787(5)	a = 9.0180(3)	a = 8.9615(3)
α/°	90	97.430(5)	75.968(4)	90
b/ Å	b = 13.3497(4)	b = 9.6798(8)	b = 9.7850(4)	b = 10.2059(2)
β/°	91.859 (3)	90.537(4)	86.559(3)	105.796(3)
c/ Å	c = 49.6003(15)	c = 14.6648(8)	c = 17.3902(7)	c = 15.7879(4)
γ/°	90	107.816(6)	70.319(4)	90
Volume/ $Å^3$	11282.0(6)	1255.15(14)	1401.38(9)	1389.44(6)
Z	8	2	2	4
Calculated density/ Mg/m^3	1.301	1.308	1.370	1.396
Absorption coefficient/mm^{-1}	0.090	0.086	0.579	0.840
F(000)	4560	512	596	600
Crystal size/mm	0.31 x 0.18 x 0.13	0.23 x 0.18 x 0.13	0.33 x 0.26 x 0.21	0.33 x 0.26 x 0.21
θ range from data collection/°	3.08 to 25.00	3.09 to 25.00	3.15 to 25.00	5.13 to 71.34
Reflections collected/unique	38792 / 9903 [R(int) = 0.0571]	9380 / 4415 [R(int) = 0.0355]	9666 / 4930 [R(int) = 0.0227]	8592 / 2672 [R(int) = 0.0204]
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Data/restraints/parameters	9903 / 0 / 758	4415 / 0 / 343	4930 / 0 / 370	2672 / 0 / 199
Goodness-of-fit on F^2	1.040	1.044	1.080	1.075
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0626, wR_2 = 0.1305	R_1 = 0.0500, wR_2 = 0.1044	R_1 = 0.0347, wR_2 = 0.0911	R_1 = 0.0363, wR_2 = 0.0956
R indices (all data)	R_1 = 0.0984, wR_2 = 0.1526	R_1 = 0.0938, wR_2 = 0.1259	R_1 = 0.0380, wR_2 = 0.0942	R_1 = 0.0377, wR_2 = 0.0968
Largest diff. peak and hole/e $Å^{-3}$	0.195 and -0.164	0.139 and -0.169	0.275 and -0.340	0.220 and -0.231
CCDC number	1018403	1018404	1018405	1041639

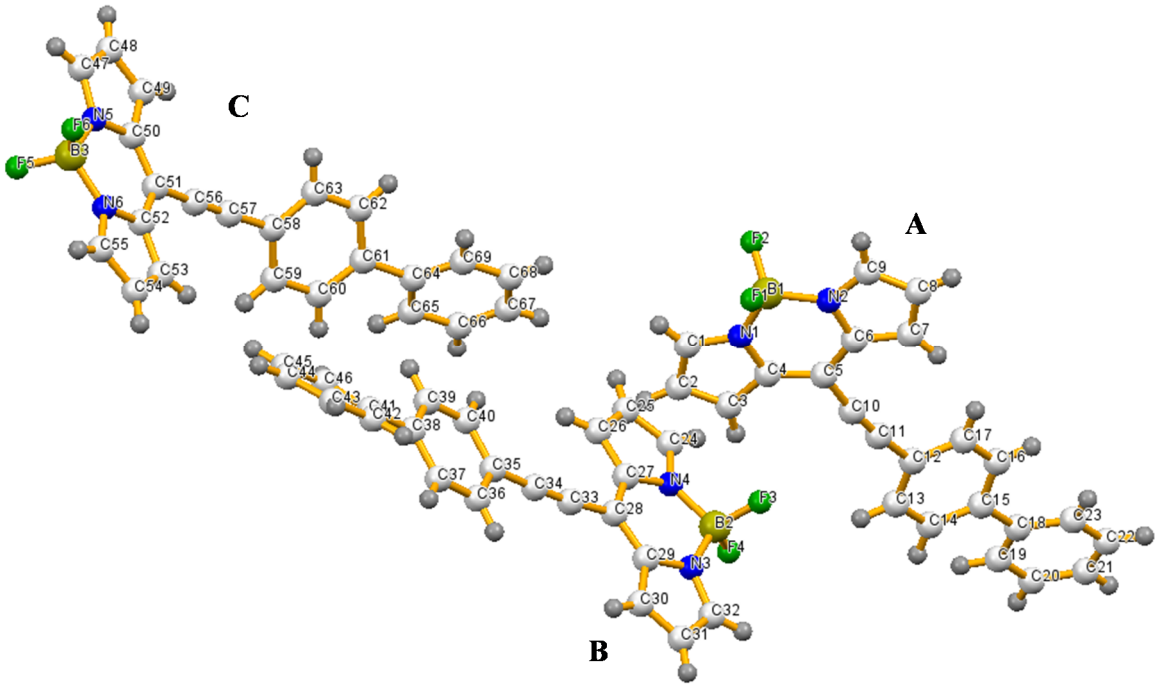


Figure S14. Crystal structure of BODIPY **2a** showing three molecules (**A, B, C**) in an asymmetric unit

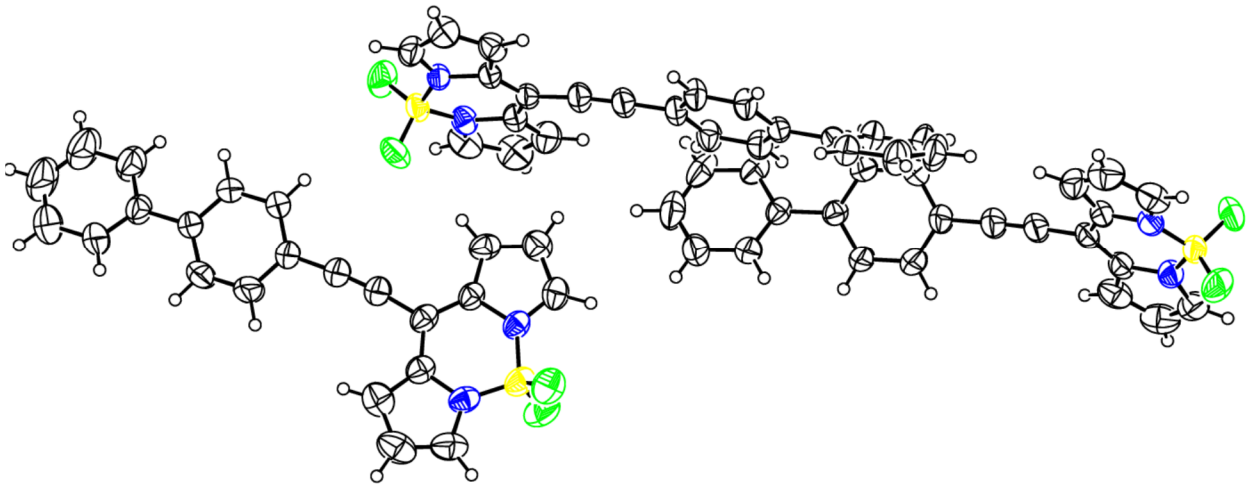


Figure S15. Crystal structure of BODIPY **2a**

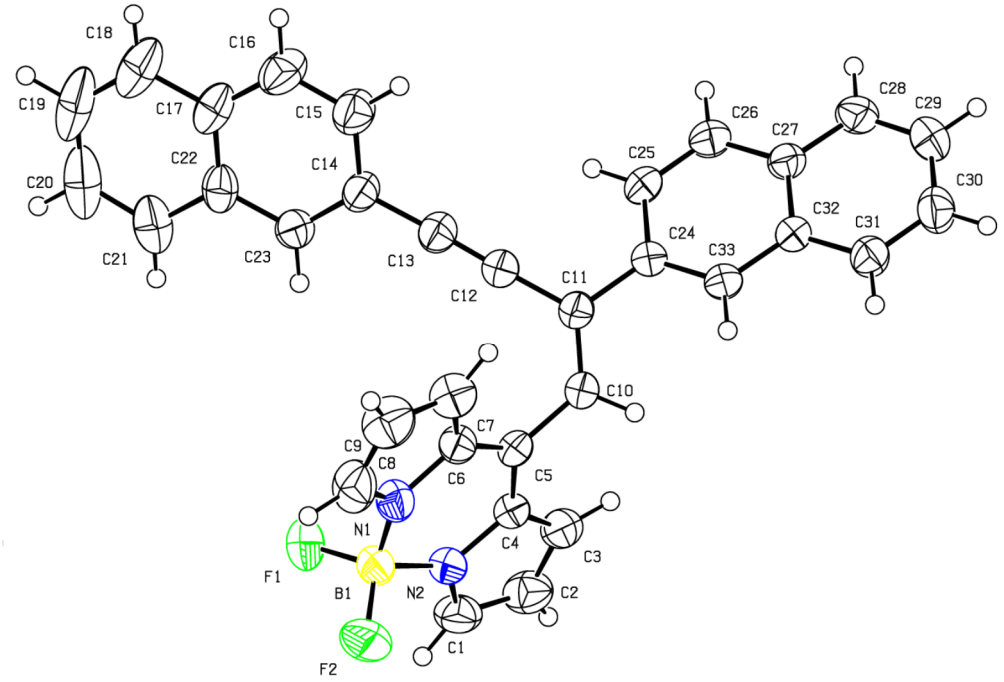


Figure S16. Crystal structure of BODIPY **3b**

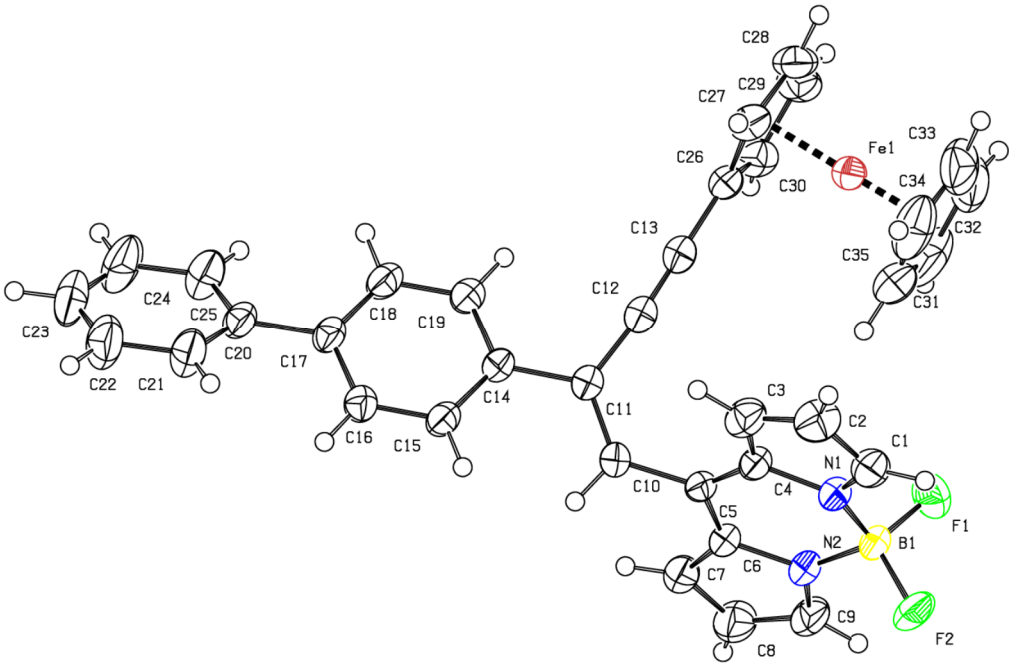


Figure S17. Crystal structure of BODIPY **4a**

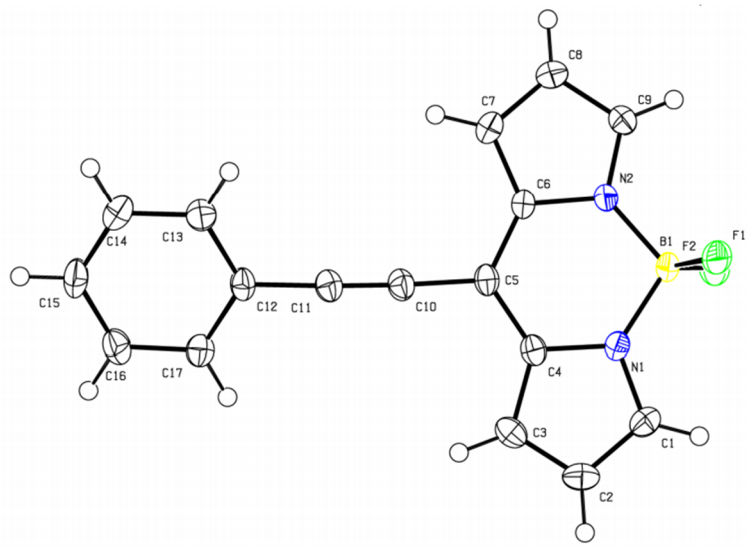


Figure S18. Crystal Structure of BODIPY **2d.**

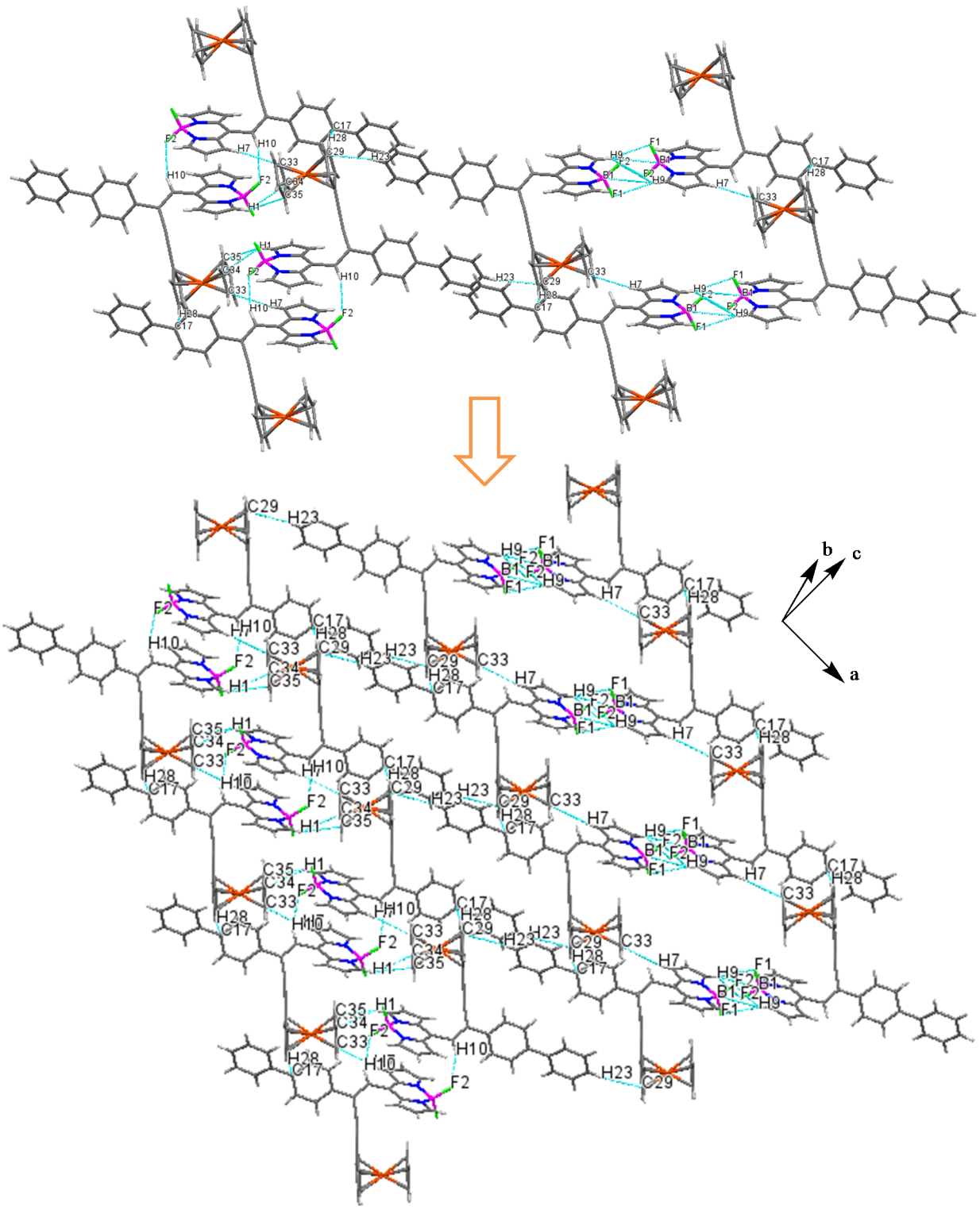


Figure S19. Crystal structure packing of BODIPY **4a**.

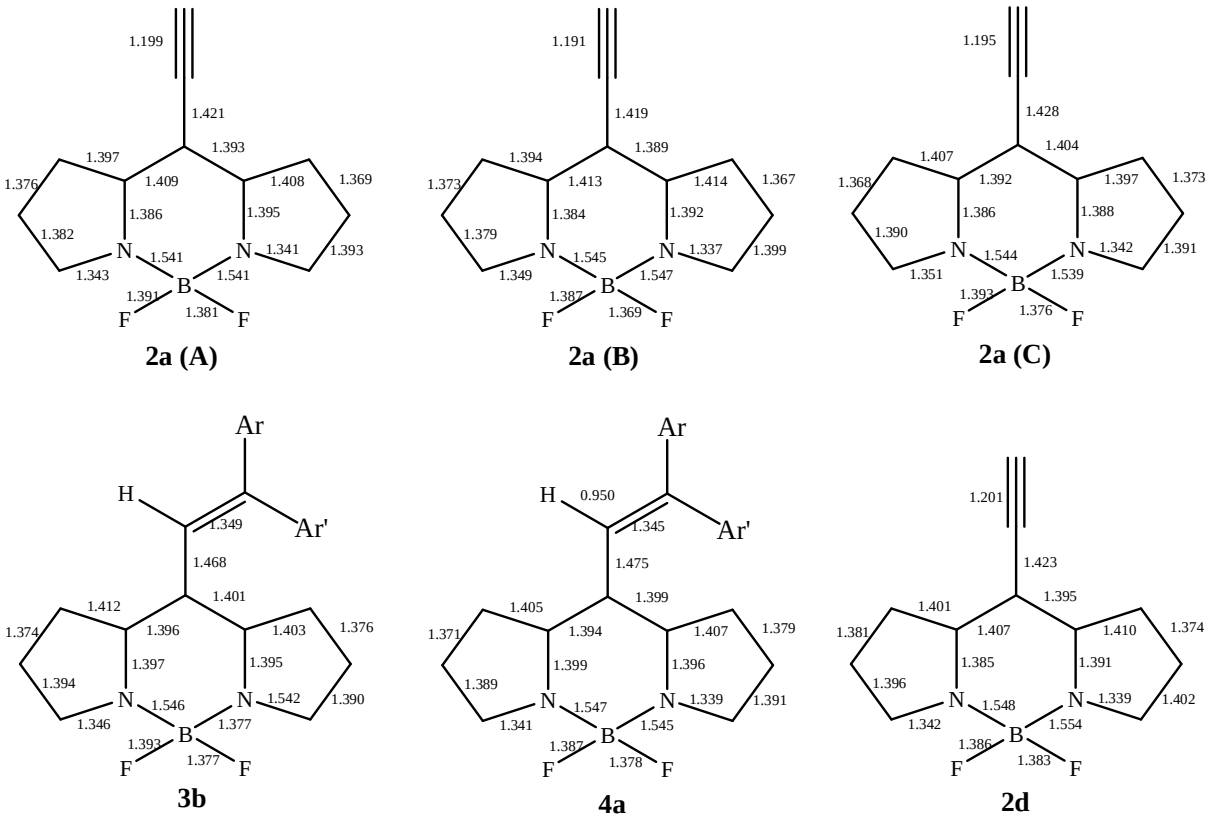


Figure S20. Comparison of selected bond lengths of the crystal structures of BODIPYs **2a, 3b, 4a** and **2d** (A, B and C represent three different molecules in an asymmetric unit of **2a**).

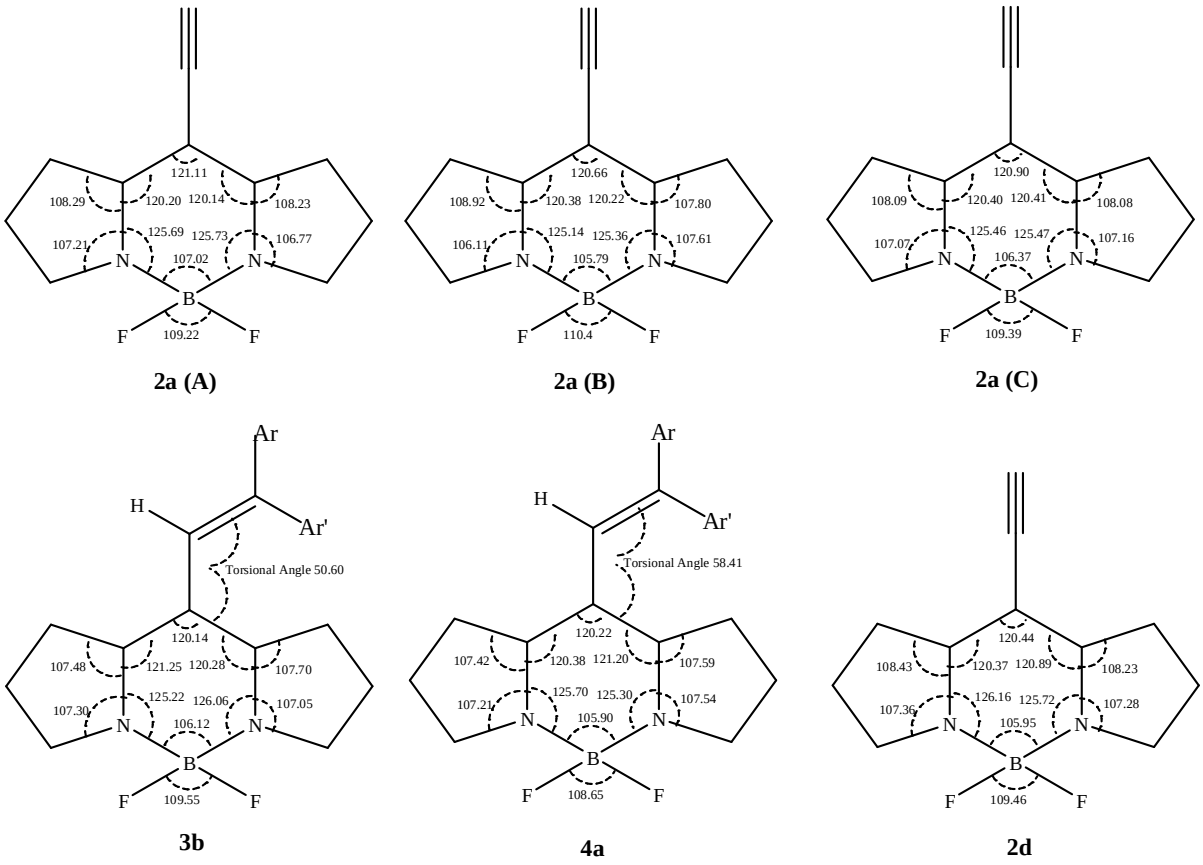


Figure S21. Comparison of selected bond angles of the crystal structures of BODIPYs **2a, 3b, 4a** and **2d** (A, B and C represent three different molecules in an asymmetric unit of **2a**).

Table S3. Selected bond lengths [A] and angles [deg] for the crystal structure of **2a**.

B(1)-F(1)	1.380(4)	F(1)-B(1)-F(2)	109.2(3)	N(5)-C(47)-C(48)	110.5(3)
B(1)-F(2)	1.391(4)	F(1)-B(1)-N(2)	110.1(3)	C(49)-C(48)-C(47)	106.9(3)
B(1)-N(2)	1.540(5)	F(2)-B(1)-N(2)	110.2(3)	C(48)-C(49)-C(50)	107.4(3)
B(1)-N(1)	1.541(4)	F(1)-B(1)-N(1)	110.5(3)	N(5)-C(50)-C(51)	120.4(3)
B(2)-F(4)	1.369(3)	F(2)-B(1)-N(1)	109.8(3)	N(5)-C(50)-C(49)	108.1(3)
B(2)-F(3)	1.388(4)	N(2)-B(1)-N(1)	107.0(2)	C(51)-C(50)-C(49)	131.5(3)
B(2)-N(4)	1.545(4)	F(4)-B(2)-F(3)	110.0(2)	C(52)-C(51)-C(50)	120.9(3)
B(2)-N(3)	1.546(4)	F(4)-B(2)-N(4)	111.0(3)	C(52)-C(51)-C(56)	119.9(3)
B(3)-F(6)	1.376(4)	F(3)-B(2)-N(4)	109.2(3)	C(50)-C(51)-C(56)	119.2(3)
B(3)-F(5)	1.393(4)	F(4)-B(2)-N(3)	110.9(3)	N(6)-C(52)-C(51)	120.4(3)
B(3)-N(5)	1.538(4)	F(3)-B(2)-N(3)	109.7(2)	N(6)-C(52)-C(53)	108.1(3)
B(3)-N(6)	1.544(4)	N(4)-B(2)-N(3)	105.8(2)	C(51)-C(52)-C(53)	131.4(3)
N(1)-C(1)	1.341(4)	F(6)-B(3)-F(5)	109.4(3)	C(54)-C(53)-C(52)	107.4(3)
N(1)-C(4)	1.395(3)	F(6)-B(3)-N(5)	110.7(3)	C(53)-C(54)-C(55)	107.2(3)
N(2)-C(9)	1.343(4)	F(5)-B(3)-N(5)	109.6(3)	N(6)-C(55)-C(54)	110.2(3)
N(2)-C(6)	1.386(4)	F(6)-B(3)-N(6)	111.2(3)	C(57)-C(56)-C(51)	177.6(3)
N(3)-C(32)	1.337(4)	F(5)-B(3)-N(6)	109.6(3)	N(4)-C(24)-C(25)	111.0(3)
N(3)-C(29)	1.392(3)	N(5)-B(3)-N(6)	106.4(2)	C(26)-C(25)-C(24)	106.8(3)
N(4)-C(24)	1.349(4)	C(1)-N(1)-C(4)	106.8(2)	C(25)-C(26)-C(27)	107.2(3)

N(4)-C(27)	1.384(3)	C(1)-N(1)-B(1)	127.5(3)	N(4)-C(27)-C(26)	108.9(3)
N(5)-C(47)	1.342(4)	C(4)-N(1)-B(1)	125.7(3)	N(4)-C(27)-C(28)	120.4(3)
N(5)-C(50)	1.389(3)	C(9)-N(2)-C(6)	107.2(3)	C(26)-C(27)-C(28)	130.7(3)
N(6)-C(55)	1.351(4)	C(9)-N(2)-B(1)	127.1(3)	C(29)-C(28)-C(27)	120.6(2)
N(6)-C(52)	1.386(3)	C(6)-N(2)-B(1)	125.7(3)	C(29)-C(28)-C(33)	121.1(3)
C(1)-C(2)	1.393(4)	C(32)-N(3)-C(29)	107.6(2)	C(27)-C(28)-C(33)	118.3(3)
C(2)-C(3)	1.369(4)	C(32)-N(3)-B(2)	126.8(3)	C(28)-C(29)-N(3)	120.2(2)
C(3)-C(4)	1.408(4)	C(29)-N(3)-B(2)	125.4(2)	C(28)-C(29)-C(30)	131.8(3)
C(3)-H(3)	0.9500	C(24)-N(4)-C(27)	106.1(3)	N(3)-C(29)-C(30)	107.8(2)
C(4)-C(5)	1.394(4)	C(24)-N(4)-B(2)	128.3(3)	C(31)-C(30)-C(29)	107.1(3)
C(5)-C(6)	1.409(4)	C(27)-N(4)-B(2)	125.1(2)	C(30)-C(31)-C(32)	107.5(3)
C(5)-C(10)	1.421(4)	C(47)-N(5)-C(50)	107.1(3)	N(3)-C(32)-C(31)	110.0(3)
C(6)-C(7)	1.397(4)	C(47)-N(5)-B(3)	127.3(3)	C(34)-C(33)-C(28)	174.2(3)
C(7)-C(8)	1.375(5)	C(50)-N(5)-B(3)	125.5(3)	C(33)-C(34)-C(35)	178.1(3)
C(8)-C(9)	1.382(5)	C(55)-N(6)-C(52)	107.1(3)		
C(25)-C(26)	1.373(5)	C(55)-N(6)-B(3)	127.3(3)		
C(26)-C(27)	1.394(4)	C(52)-N(6)-B(3)	125.5(3)		
C(27)-C(28)	1.413(4)	N(1)-C(1)-C(2)	110.6(3)		
C(28)-C(29)	1.389(4)	C(3)-C(2)-C(1)	107.2(3)		
C(28)-C(33)	1.419(4)	C(2)-C(3)-C(4)	107.2(3)		
C(47)-C(48)	1.391(5)	C(5)-C(4)-N(1)	120.1(3)		
C(48)-C(49)	1.373(5)	C(5)-C(4)-C(3)	131.6(3)		
C(49)-C(50)	1.403(4)	N(1)-C(4)-C(3)	108.2(3)		
C(50)-C(51)	1.397(4)	C(4)-C(5)-C(6)	121.1(3)		
C(51)-C(52)	1.392(4)	C(4)-C(5)-C(10)	121.0(3)		
C(51)-C(56)	1.428(4)	C(6)-C(5)-C(10)	117.9(3)		
		N(2)-C(6)-C(7)	108.3(3)		
		N(2)-C(6)-C(5)	120.2(3)		
		C(7)-C(6)-C(5)	131.4(3)		
		C(8)-C(7)-C(6)	107.0(3)		
		C(7)-C(8)-C(9)	107.5(4)		
		N(2)-C(9)-C(8)	110.1(3)		
		C(11)-C(10)-C(5)	172.0(3)		
		C(10)-C(11)-C(12)	174.9(3)		

Table S4. Selected bond lengths [A] and angles [deg] for the crystal structure of **3b**.

F(1)-B(1)	1.393(3)	F(2)-B(1)-F(1)	109.52(19)
F(2)-B(1)	1.377(3)	F(2)-B(1)-N(1)	110.8(2)
B(1)-N(1)	1.541(4)	F(1)-B(1)-N(1)	109.8(2)
B(1)-N(2)	1.546(4)	F(2)-B(1)-N(2)	110.9(2)
N(1)-C(9)	1.341(3)	F(1)-B(1)-N(2)	109.6(2)
N(1)-C(6)	1.396(3)	N(1)-B(1)-N(2)	106.14(18)
N(2)-C(1)	1.346(3)	C(9)-N(1)-C(6)	107.1(2)
N(2)-C(4)	1.396(3)	C(9)-N(1)-B(1)	126.9(2)
C(1)-C(2)	1.394(3)	C(6)-N(1)-B(1)	126.0(2)
C(2)-C(3)	1.373(3)	C(1)-N(2)-C(4)	107.3(2)
C(3)-C(4)	1.405(3)	C(1)-N(2)-B(1)	127.3(2)
C(4)-C(5)	1.395(3)	C(4)-N(2)-B(1)	125.2(2)
C(5)-C(6)	1.401(3)	N(2)-C(1)-C(2)	110.5(2)
C(5)-C(10)	1.468(3)	C(3)-C(2)-C(1)	106.6(2)
C(6)-C(7)	1.403(3)	C(2)-C(3)-C(4)	108.1(2)
C(7)-C(8)	1.377(3)	C(5)-C(4)-N(2)	121.3(2)
C(8)-C(9)	1.390(4)	C(5)-C(4)-C(3)	131.1(2)
C(10)-C(11)	1.349(3)	N(2)-C(4)-C(3)	107.5(2)

C(11)-C(12)	1.435(3)	C(4)-C(5)-C(6)	120.1(2)
		C(4)-C(5)-C(10)	117.3(2)
		C(6)-C(5)-C(10)	122.5(2)
		N(1)-C(6)-C(5)	120.3(2)
		N(1)-C(6)-C(7)	107.7(2)
		C(5)-C(6)-C(7)	131.7(2)
		C(8)-C(7)-C(6)	107.9(2)
		C(7)-C(8)-C(9)	106.4(3)
		N(1)-C(9)-C(8)	110.9(2)
		C(11)-C(10)-C(5)	126.98(19)
		C(10)-C(11)-C(12)	122.62(19)
		C(13)-C(12)-C(11)	177.0(3)

Table S5. Selected bond lengths [A] and angles [deg] for the crystal structure of **4a**.

B(1)-F(1)	1.378(3)	F(1)-B(1)-F(2)	108.66(16)
B(1)-F(2)	1.387(3)	F(1)-B(1)-N(2)	111.25(18)
B(1)-N(2)	1.544(3)	F(2)-B(1)-N(2)	110.34(18)
B(1)-N(1)	1.547(3)	F(1)-B(1)-N(1)	110.22(17)
Fe(1)-C(34)	2.013(3)	F(2)-B(1)-N(1)	110.46(18)
Fe(1)-C(35)	2.016(3)	N(2)-B(1)-N(1)	105.89(15)
Fe(1)-C(33)	2.023(3)	C(1)-N(1)-C(4)	107.21(17)
Fe(1)-C(31)	2.028(3)	C(1)-N(1)-B(1)	126.95(17)
Fe(1)-C(30)	2.032(2)	C(4)-N(1)-B(1)	125.71(17)
Fe(1)-C(26)	2.0326(19)	C(9)-N(2)-C(6)	107.52(18)
Fe(1)-C(27)	2.035(2)	C(9)-N(2)-B(1)	127.05(17)
Fe(1)-C(32)	2.033(3)	C(6)-N(2)-B(1)	125.34(17)
Fe(1)-C(29)	2.036(2)	N(1)-C(1)-C(2)	110.59(19)
Fe(1)-C(28)	2.038(2)	C(3)-C(2)-C(1)	106.9(2)
N(1)-C(1)	1.341(3)	C(2)-C(3)-C(4)	107.87(19)
N(1)-C(4)	1.399(2)	C(5)-C(4)-N(1)	120.37(18)
N(2)-C(9)	1.339(3)	C(5)-C(4)-C(3)	131.87(18)
N(2)-C(6)	1.396(2)	N(1)-C(4)-C(3)	107.45(18)
C(1)-C(2)	1.389(3)	C(4)-C(5)-C(6)	120.20(17)
C(1)-H(1)	0.9500	C(4)-C(5)-C(10)	121.90(18)
C(2)-C(3)	1.371(3)	C(6)-C(5)-C(10)	117.80(18)
C(2)-H(2)	0.9500	N(2)-C(6)-C(5)	121.19(18)
C(3)-C(4)	1.404(3)	N(2)-C(6)-C(7)	107.66(18)
C(3)-H(3)	0.9500	C(5)-C(6)-C(7)	131.14(18)
C(4)-C(5)	1.394(3)	C(8)-C(7)-C(6)	107.40(19)
C(5)-C(6)	1.399(3)	C(7)-C(8)-C(9)	107.0(2)
C(5)-C(10)	1.475(2)	N(2)-C(9)-C(8)	110.43(19)
C(6)-C(7)	1.406(3)	C(11)-C(10)-C(5)	127.06(18)
C(7)-C(8)	1.379(3)	C(10)-C(11)-C(12)	122.32(17)
C(7)-H(7)	0.9500	C(10)-C(11)-C(14)	120.86(17)
C(8)-C(9)	1.390(3)	C(12)-C(11)-C(14)	16.58(17)
C(8)-H(8)	0.9500	C(13)-C(12)-C(11)	173.6(2)
C(9)-H(9)	0.9500	C(12)-C(13)-C(26)	178.5(3)
C(10)-C(11)	1.344(3)		
C(10)-H(10)	0.9500		
C(11)-C(12)	1.437(3)		
C(11)-C(14)	1.493(2)		
C(12)-C(13)	1.193(3)		

Table S6. Selected bond lengths [A] and angles [deg] for the crystal structure of **2d**.

F(1)-B(1)	1.3831(15)	F(1)-B(1)-F(2)	109.47(10)
F(2)-B(1)	1.3858(15)	F(1)-B(1)-N(2)	110.26(10)
B(1)-N(2)	1.5476(16)	F(2)-B(1)-N(2)	109.91(10)
B(1)-N(1)	1.5538(16)	F(1)-B(1)-N(1)	110.87(10)
N(2)-C(9)	1.3420(16)	F(2)-B(1)-N(1)	110.34(10)
N(2)-C(6)	1.3854(14)	N(2)-B(1)-N(1)	105.94(9)
N(1)-C(1)	1.3394(16)	C(9)-N(2)-C(6)	107.35(10)
N(1)-C(4)	1.3913(14)	C(9)-N(2)-B(1)	126.45(10)
C(1)-C(2)	1.4024(18)	C(6)-N(2)-B(1)	126.17(10)
C(2)-C(3)	1.3735(18)	C(1)-N(1)-C(4)	107.28(10)
C(3)-C(4)	1.4095(17)	C(1)-N(1)-B(1)	126.97(10)
C(4)-C(5)	1.3947(17)	C(4)-N(1)-B(1)	125.72(9)
C(5)-C(6)	1.4070(17)	N(1)-C(1)-C(2)	110.33(11)
C(5)-C(10)	1.4226(16)	C(3)-C(2)-C(1)	106.97(11)
C(6)-C(7)	1.4013(17)	C(2)-C(3)-C(4)	107.19(11)
C(7)-C(8)	1.3810(19)	N(1)-C(4)-C(5)	120.89(10)
C(8)-C(9)	1.3964(18)	N(1)-C(4)-C(3)	108.23(10)
C(10)-C(11)	1.2007(18)	C(5)-C(4)-C(3)	130.88(11)
		C(4)-C(5)-C(6)	120.44(10)
		C(4)-C(5)-C(10)	120.56(11)
		C(6)-C(5)-C(10)	118.91(11)
		N(2)-C(6)-C(7)	108.43(10)
		N(2)-C(6)-C(5)	120.37(10)
		C(7)-C(6)-C(5)	130.94(11)
		C(8)-C(7)-C(6)	107.17(11)
		C(7)-C(8)-C(9)	106.77(11)
		N(2)-C(9)-C(8)	110.27(11)
		C(11)-C(10)-C(5)	175.46(13)

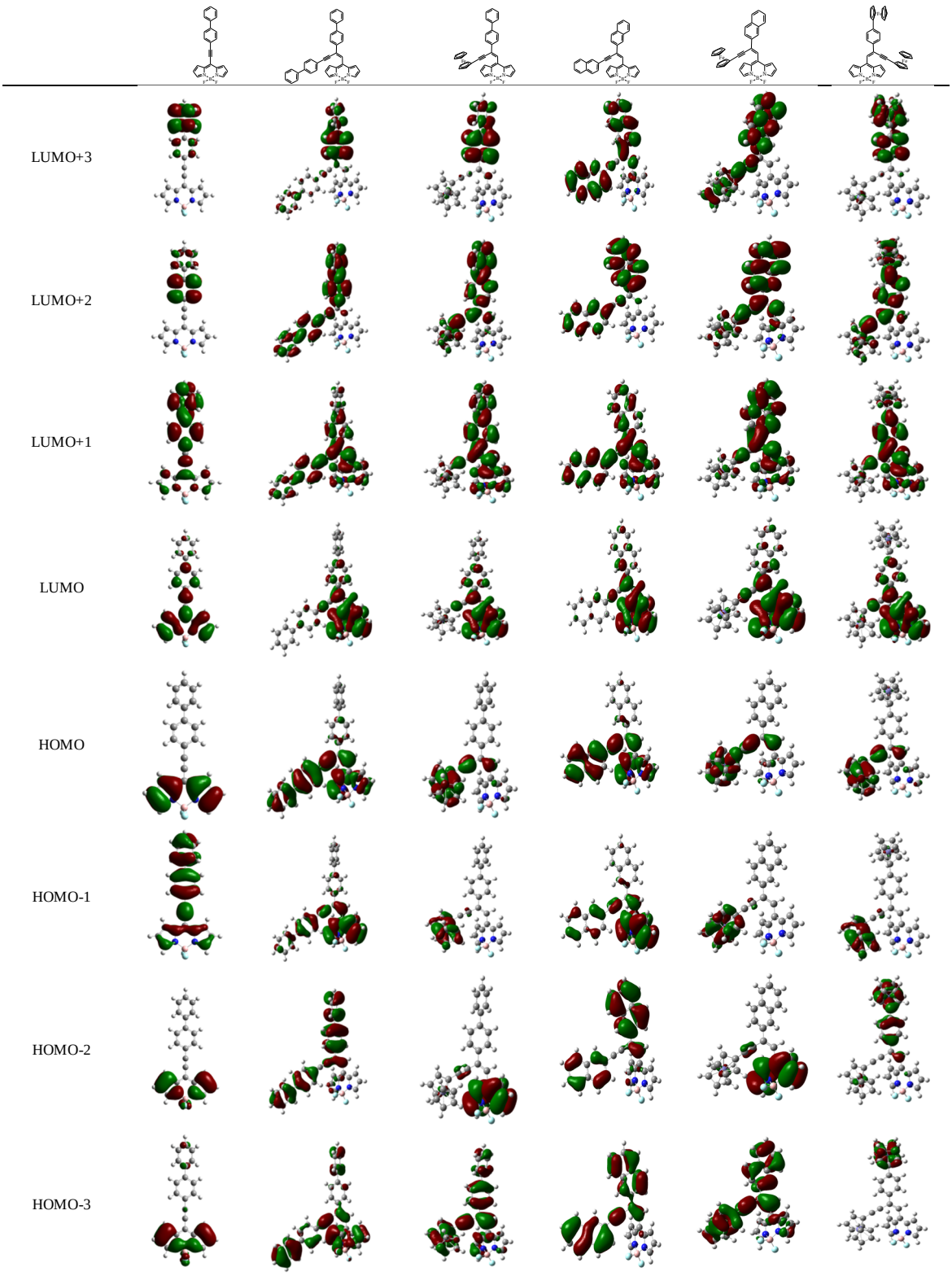


Figure S22. Frontier molecular orbital plots of BODIPYs **2a, 3a, 4a, 2b, 3b, 4b, 2c** and **4c** calculated at B3LYP/6-31G* level for C, N, B, F, H, and Lanl2DZ level for Fe[1]

BODIPY 3a

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	5	0	-2.489139	3.954147	-0.064316
2	9	0	-3.232064	2.954298	-0.692262
3	9	0	-3.264221	5.048936	0.251381
4	7	0	-1.816524	3.360293	1.212754
5	7	0	-1.288014	4.363032	-0.980079
6	6	0	-2.366753	3.193190	2.424065
7	1	0	-3.347816	3.595426	2.638774
8	6	0	-1.492293	2.466583	3.258384
9	1	0	-1.674420	2.205716	4.291819
10	6	0	-0.364096	2.179120	2.500890
11	1	0	0.525949	1.654313	2.817365
12	6	0	-0.569608	2.740611	1.213474
13	6	0	0.297413	2.866899	0.110044
14	6	0	-0.044373	3.736992	-0.946616
15	6	0	0.691966	4.166873	-2.078903
16	1	0	1.698154	3.859610	-2.329816
17	6	0	-0.113295	5.062417	-2.775337
18	1	0	0.132761	5.601420	-3.679881
19	6	0	-1.330069	5.144883	-2.070541
20	1	0	-2.221048	5.713498	-2.301155
21	6	0	1.568480	2.139778	0.063286
22	1	0	2.455862	2.721777	-0.168005
23	6	0	1.688774	0.780629	0.159332
24	6	0	0.526012	-0.041109	0.181560
25	6	0	-0.497629	-0.697752	0.125612
26	6	0	3.016420	0.113494	0.125504
27	6	0	4.178800	0.770055	0.564653
28	1	0	4.110741	1.774735	0.971741
29	6	0	5.418717	0.144697	0.508977
30	1	0	6.301401	0.686013	0.837090
31	6	0	5.553058	-1.166970	0.020181
32	6	0	4.386282	-1.826149	-0.402463
33	1	0	4.449735	-2.851241	-0.755898
34	6	0	3.144657	-1.202839	-0.346761
35	1	0	2.257098	-1.736616	-0.671956
36	6	0	6.877300	-1.833452	-0.038184
37	6	0	7.835343	-1.629035	0.969802
38	1	0	7.591940	-0.995920	1.818529
39	6	0	9.079378	-2.255172	0.913324
40	1	0	9.801163	-2.089145	1.708711
41	6	0	9.393991	-3.099800	-0.152849
42	1	0	10.363831	-3.587719	-0.197004
43	6	0	8.452788	-3.312623	-1.161777
44	1	0	8.690179	-3.961234	-2.000886
45	6	0	7.208612	-2.686883	-1.104784
46	1	0	6.494508	-2.838848	-1.909361
47	6	0	-1.743861	-1.378636	0.056657

48	6	0	-1.828173	-2.770851	0.255359
49	6	0	-2.926801	-0.659009	-0.217747
50	6	0	-3.053308	-3.420358	0.183000
51	1	0	-0.925373	-3.331671	0.478020
52	6	0	-4.145116	-1.322624	-0.287488
53	1	0	-2.882882	0.413939	-0.382603
54	6	0	-4.238191	-2.712672	-0.090420
55	1	0	-3.099756	-4.489671	0.367693
56	1	0	-5.039625	-0.755351	-0.526973
57	6	0	-5.544486	-3.411383	-0.168508
58	6	0	-5.643628	-4.698415	-0.725162
59	6	0	-6.718167	-2.804685	0.311690
60	6	0	-6.870829	-5.355024	-0.798925
61	1	0	-4.755177	-5.175530	-1.129331
62	6	0	-7.945333	-3.461453	0.238662
63	1	0	-6.662390	-1.821087	0.769454
64	6	0	-8.027580	-4.739724	-0.316823
65	1	0	-6.924541	-6.345884	-1.242314
66	1	0	-8.838160	-2.975985	0.623846
67	1	0	-8.984529	-5.251280	-0.374071

Total energy (Sum of electronic and zero-point energies): -1759.1599841 Hartree

BODIPY 3b

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	5	0	3.305221	-2.938519	-0.067081
2	9	0	3.742837	-1.811028	-0.761545
3	9	0	4.347077	-3.782310	0.251595
4	7	0	2.545618	-2.481985	1.217829
5	7	0	2.220428	-3.682662	-0.914741
6	6	0	3.075798	-2.123568	2.396032
7	1	0	4.135463	-2.244029	2.577615
8	6	0	2.071150	-1.617684	3.246833
9	1	0	2.215560	-1.273524	4.261665
10	6	0	0.880265	-1.670416	2.534154
11	1	0	-0.104781	-1.385753	2.875207
12	6	0	1.179964	-2.212910	1.256953
13	6	0	0.337995	-2.607946	0.198969
14	6	0	0.858303	-3.400673	-0.845436
15	6	0	0.220734	-4.054225	-1.929580
16	1	0	-0.838916	-4.029455	-2.144848
17	6	0	1.207230	-4.738244	-2.632704
18	1	0	1.079174	-5.360099	-3.508008
19	6	0	2.427101	-4.472301	-1.980435
20	1	0	3.426967	-4.799753	-2.232192
21	6	0	-1.082172	-2.246109	0.192679
22	1	0	-1.788172	-3.055284	0.030872
23	6	0	-1.557506	-0.965032	0.247278

24	6	0	-0.653178	0.134219	0.186158
25	6	0	0.154968	1.036262	0.064153
26	6	0	-3.015239	-0.674592	0.254302
27	6	0	-3.491509	0.544638	-0.198925
28	6	0	-3.952994	-1.640359	0.727200
29	6	0	-4.877503	0.839890	-0.227688
30	1	0	-2.788850	1.293820	-0.552497
31	6	0	-5.301154	-1.382445	0.714649
32	1	0	-3.593183	-2.580658	1.133199
33	6	0	-5.372940	2.084349	-0.703650
34	6	0	-5.809612	-0.144457	0.234656
35	1	0	-6.000640	-2.126065	1.089105
36	6	0	-6.724971	2.343274	-0.720615
37	1	0	-4.663639	2.829343	-1.055986
38	6	0	-7.196474	0.153484	0.206560
39	6	0	-7.645198	1.369297	-0.261059
40	1	0	-7.092244	3.297807	-1.087340
41	1	0	-7.901208	-0.595498	0.560064
42	1	0	-8.709779	1.585981	-0.279527
43	6	0	1.177314	2.014203	-0.087168
44	6	0	0.907534	3.367785	0.074643
45	6	0	2.506603	1.592612	-0.414914
46	6	0	1.923311	4.341453	-0.079176
47	1	0	-0.099987	3.688116	0.325829
48	6	0	3.503378	2.522802	-0.568513
49	1	0	2.717949	0.534550	-0.538624
50	6	0	1.668293	5.731174	0.083298
51	6	0	3.251661	3.913865	-0.409291
52	1	0	4.510619	2.198044	-0.817569
53	6	0	2.676335	6.654865	-0.073753
54	1	0	0.660026	6.051938	0.334621
55	6	0	4.267387	4.892606	-0.564711
56	6	0	3.988318	6.231698	-0.401255
57	1	0	2.469443	7.714025	0.052870
58	1	0	5.273719	4.566028	-0.815805
59	1	0	4.775686	6.970557	-0.523188

Total energy (Sum of electronic and zero-point energies): -1604.333007 Hartree

BODIPY 4a

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	5	0	-3.718796	2.882950	0.019948
2	26	0	-2.814565	-2.931940	-0.266684
3	9	0	-4.296953	1.792286	-0.632094
4	9	0	-4.668114	3.820597	0.370440
5	7	0	-2.942440	2.389816	1.279288
6	7	0	-2.620280	3.515344	-0.892902
7	6	0	-3.462877	2.099635	2.481527
8	1	0	-4.512375	2.272956	2.678394

9	6	0	-2.459678	1.596008	3.335096
10	1	0	-2.593282	1.304934	4.367970
11	6	0	-1.279182	1.585220	2.600053
12	1	0	-0.298146	1.286223	2.939136
13	6	0	-1.584958	2.077901	1.305485
14	6	0	-0.747930	2.404228	0.216076
15	6	0	-1.270101	3.179029	-0.846409
16	6	0	-0.637907	3.761195	-1.974324
17	1	0	0.412251	3.684221	-2.220438
18	6	0	-1.615307	4.455909	-2.680808
19	1	0	-1.485983	5.034280	-3.585203
20	6	0	-2.825191	4.270027	-1.985292
21	1	0	-3.817090	4.631195	-2.221554
22	6	0	0.658257	2.019092	0.169550
23	1	0	1.338556	2.778326	-0.203019
24	6	0	1.179602	0.770614	0.392999
25	6	0	0.351065	-0.357325	0.642397
26	6	0	-0.374968	-1.321168	0.804751
27	6	0	2.643705	0.529218	0.278357
28	6	0	3.578481	1.548121	0.532889
29	1	0	3.236520	2.528268	0.851881
30	6	0	4.943522	1.315780	0.409496
31	1	0	5.638900	2.128944	0.596465
32	6	0	5.438145	0.054700	0.031424
33	6	0	4.501559	-0.965636	-0.208367
34	1	0	4.850094	-1.960454	-0.470406
35	6	0	3.135922	-0.736786	-0.080880
36	1	0	2.434640	-1.546131	-0.257852
37	6	0	6.895314	-0.192605	-0.096996
38	6	0	7.810983	0.403704	0.787688
39	1	0	7.443704	1.032905	1.593689
40	6	0	9.180059	0.169952	0.666711
41	1	0	9.868573	0.634277	1.367770
42	6	0	9.664755	-0.665031	-0.342217
43	1	0	10.731752	-0.847159	-0.436635
44	6	0	8.767503	-1.264415	-1.228697
45	1	0	9.134398	-1.909294	-2.022830
46	6	0	7.398416	-1.031153	-1.107063
47	1	0	6.711940	-1.481608	-1.818503
48	6	0	-1.296502	-2.369472	1.037303
49	6	0	-2.587983	-2.214374	1.663822
50	1	0	-2.991325	-1.279124	2.026399
51	6	0	-3.211543	-3.491224	1.703918
52	1	0	-4.199297	-3.699953	2.092942
53	6	0	-2.333938	-4.440423	1.095024
54	1	0	-2.542829	-5.490898	0.941938
55	6	0	-1.156769	-3.758344	0.679245
56	1	0	-0.307236	-4.189667	0.167536
57	6	0	-2.675841	-3.286725	-2.309996
58	1	0	-1.903104	-3.888846	-2.770012
59	6	0	-3.927309	-3.762945	-1.811982
60	1	0	-4.269255	-4.789659	-1.826981
61	6	0	-4.626539	-2.651946	-1.248888
62	1	0	-5.591438	-2.691990	-0.760491

63	6	0	-3.812070	-1.488242	-1.396633
64	1	0	-4.045825	-0.489006	-1.051870
65	6	0	-2.607461	-1.884243	-2.052701
66	1	0	-1.766232	-1.238796	-2.269464

Total energy (Sum of electronic and zero-point energies): -1806.3436029 Hartree

BODIPY 4b

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	5	0	-2.419238	3.357416	0.162518
2	26	0	-2.986511	-2.513793	-0.238216
3	9	0	-3.124343	2.516568	-0.700249
4	9	0	-3.225938	4.344662	0.686978
5	7	0	-1.776058	2.503494	1.299444
6	7	0	-1.198468	3.976108	-0.596387
7	6	0	-2.364277	2.065630	2.423488
8	1	0	-3.361786	2.395202	2.682228
9	6	0	-1.496189	1.197871	3.118393
10	1	0	-1.703272	0.721535	4.066881
11	6	0	-0.330834	1.110219	2.363543
12	1	0	0.568142	0.558493	2.599186
13	6	0	-0.509964	1.931926	1.221075
14	6	0	0.398810	2.324404	0.216535
15	6	0	0.064863	3.389045	-0.642799
16	6	0	0.827608	4.069375	-1.625982
17	1	0	1.851550	3.844995	-1.892206
18	6	0	0.018365	5.071064	-2.151310
19	1	0	0.277783	5.795654	-2.910802
20	6	0	-1.226476	4.970280	-1.497234
21	1	0	-2.126989	5.552285	-1.641257
22	6	0	1.703616	1.663519	0.092537
23	1	0	2.585160	2.297999	0.114957
24	6	0	1.860964	0.330892	-0.169989
25	6	0	0.730527	-0.469143	-0.499032
26	6	0	-0.261263	-1.061026	-0.885232
27	6	0	-1.457553	-1.652180	-1.354189
28	6	0	-1.661237	-3.024016	-1.750141
29	1	0	-0.922267	-3.810679	-1.681350
30	6	0	-2.997079	-3.149958	-2.221832
31	1	0	-3.462385	-4.064179	-2.565904
32	6	0	-3.632634	-1.873479	-2.114940
33	1	0	-4.663142	-1.656311	-2.362724
34	6	0	-2.697782	-0.947131	-1.578701
35	1	0	-2.868628	0.098286	-1.354768
36	6	0	-3.696232	-1.714908	1.543771
37	1	0	-3.841938	-0.656215	1.709987
38	6	0	-4.653436	-2.623706	0.998218
39	1	0	-5.657730	-2.374638	0.681357
40	6	0	-4.035384	-3.906683	0.893427
41	1	0	-4.490255	-4.800073	0.485800

42	6	0	-2.695143	-3.791420	1.375053
43	1	0	-1.958483	-4.583625	1.401633
44	6	0	-2.487879	-2.437489	1.778062
45	1	0	-1.561657	-2.013791	2.142425
46	6	0	3.209561	-0.293401	-0.239262
47	6	0	4.257993	0.177595	0.534847
48	6	0	3.439780	-1.401520	-1.105619
49	6	0	5.551484	-0.398241	0.465135
50	1	0	4.091522	0.991575	1.235901
51	6	0	4.682818	-1.979185	-1.196688
52	1	0	2.614575	-1.777518	-1.702012
53	6	0	6.634184	0.078143	1.254972
54	6	0	5.774999	-1.500566	-0.423275
55	1	0	4.845438	-2.818161	-1.869104
56	6	0	7.879470	-0.501738	1.165263
57	1	0	6.461720	0.912562	1.930743
58	6	0	7.070918	-2.076972	-0.491215
59	6	0	8.100293	-1.589204	0.283335
60	1	0	8.699645	-0.127407	1.771673
61	1	0	7.237480	-2.912528	-1.166951
62	1	0	9.087856	-2.038191	0.222083

Total energy (Sum of electronic and zero-point energies): -1728.9296497 Hartree

BODIPY 4c

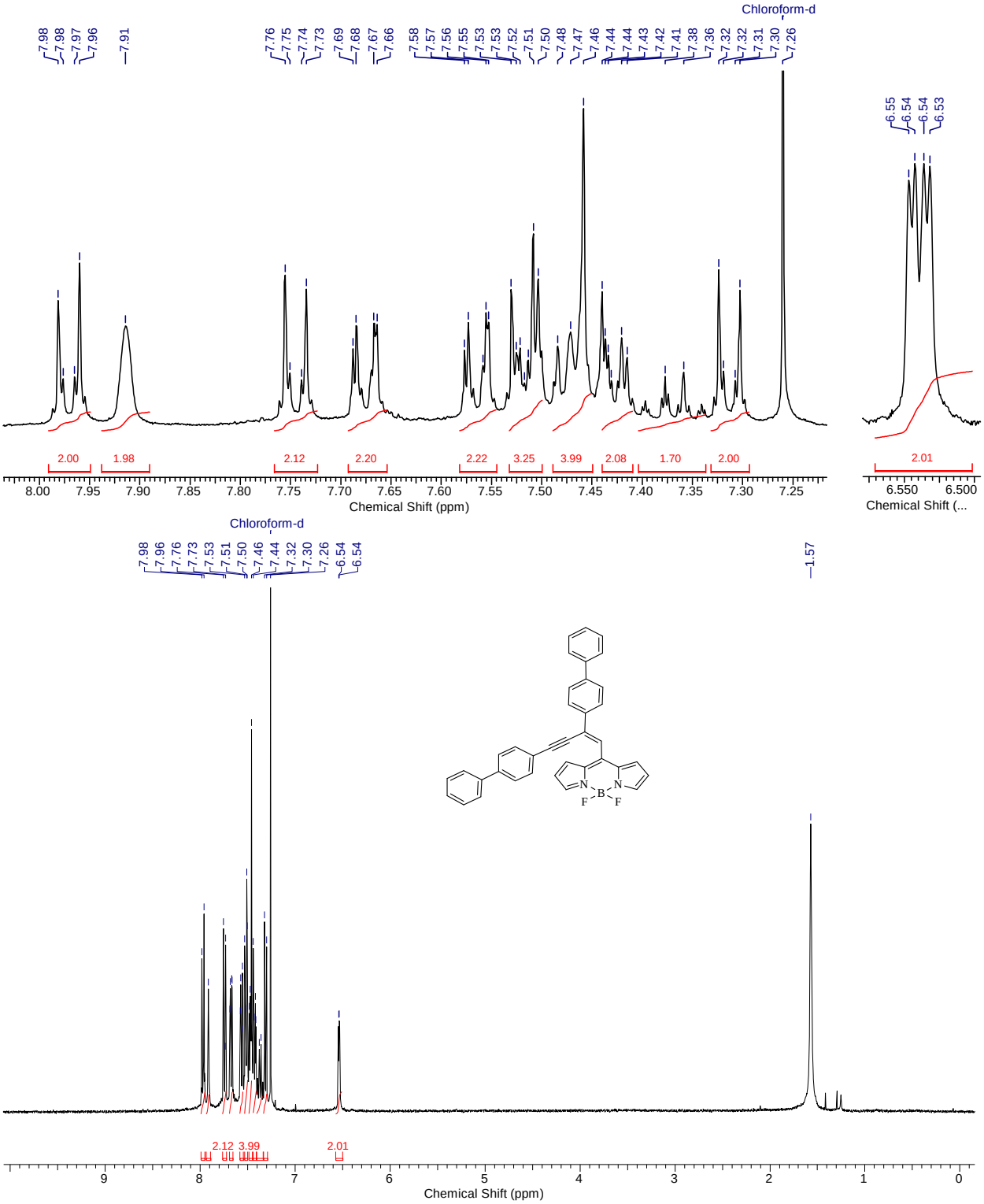
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	5	0	-5.009916	2.862190	0.403328
2	26	0	-4.145991	-2.927077	-0.226669
3	9	0	-5.685694	1.793316	-0.188255
4	9	0	-5.891547	3.786289	0.925549
5	7	0	-4.051868	2.329188	1.512420
6	7	0	-4.062055	3.527144	-0.645023
7	6	0	-4.384209	1.999752	2.770169
8	1	0	-5.392020	2.160772	3.128765
9	6	0	-3.262772	1.477415	3.446564
10	1	0	-3.238213	1.154115	4.478205
11	6	0	-2.206900	1.496228	2.541524
12	1	0	-1.185455	1.193222	2.719119
13	6	0	-2.705488	2.025386	1.323731
14	6	0	-2.041899	2.392579	0.132038
15	6	0	-2.719653	3.198756	-0.813056
16	6	0	-2.265426	3.821990	-2.002900
17	1	0	-1.264018	3.760719	-2.406344
18	6	0	-3.339317	4.532709	-2.531102
19	1	0	-3.348584	5.141199	-3.424875
20	6	0	-4.430405	4.315822	-1.668543
21	1	0	-5.447237	4.677659	-1.740684
22	6	0	-0.657039	2.022930	-0.134439
23	1	0	-0.044380	2.799795	-0.580434
24	6	0	-0.098841	0.774460	-0.024601

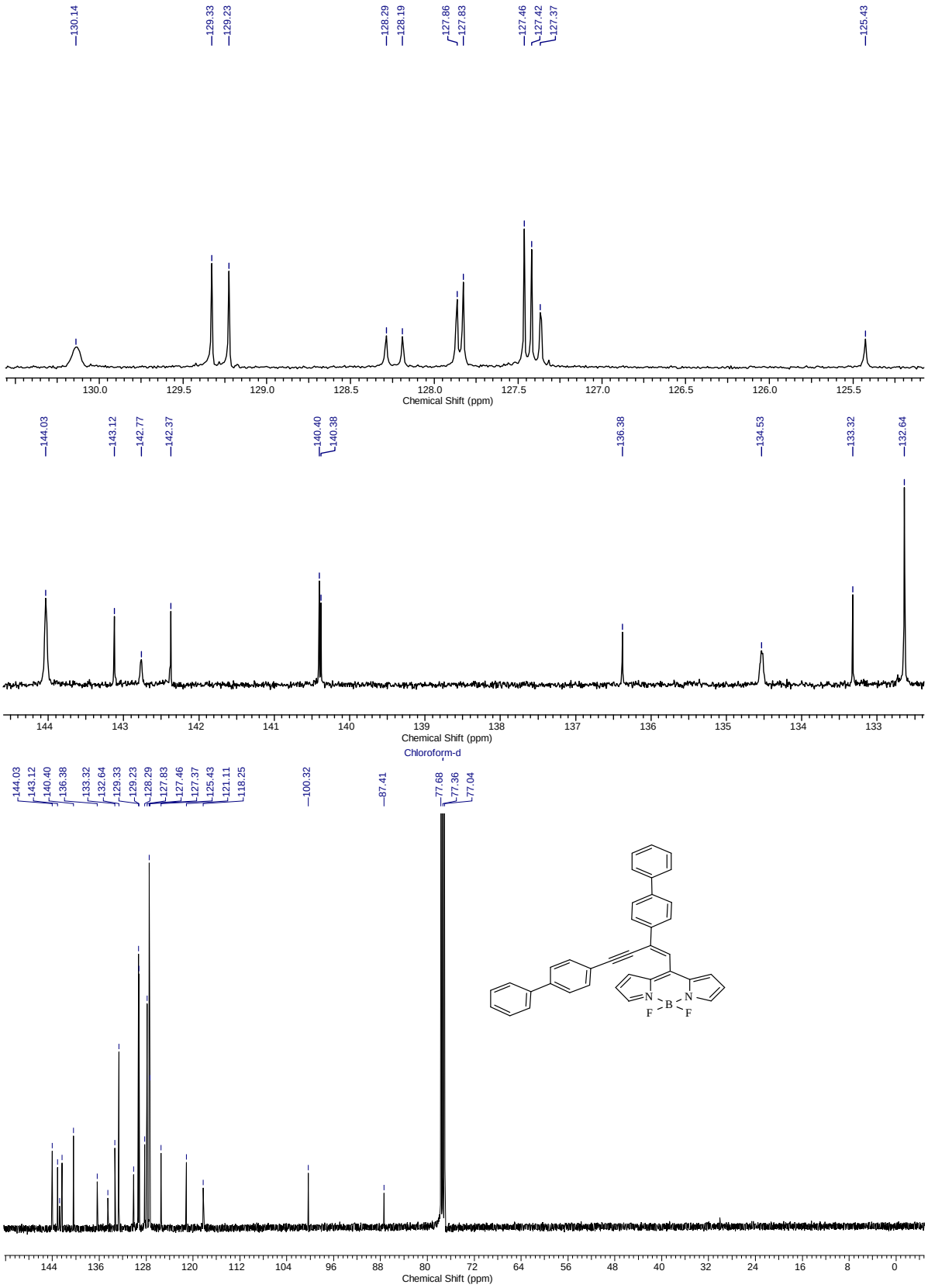
25	6	0	-0.879485	-0.368178	0.302791
26	6	0	-1.575204	-1.340200	0.534124
27	6	0	1.336487	0.551845	-0.341390
28	6	0	2.287188	1.581999	-0.214298
29	1	0	1.983014	2.555255	0.159384
30	6	0	3.625775	1.364892	-0.512112
31	1	0	4.335370	2.175378	-0.374782
32	6	0	4.083344	0.107511	-0.949972
33	6	0	3.132503	-0.919571	-1.075005
34	1	0	3.443709	-1.897174	-1.431027
35	6	0	1.792989	-0.706530	-0.767103
36	1	0	1.081899	-1.520396	-0.868251
37	6	0	-2.457153	-2.396905	0.863084
38	6	0	-3.646951	-2.261439	1.670377
39	1	0	-3.996102	-1.336382	2.107400
40	6	0	-4.260500	-3.540484	1.763702
41	1	0	-5.184321	-3.761426	2.281748
42	6	0	-3.479725	-4.471005	1.010937
43	1	0	-3.710324	-5.517254	0.859900
44	6	0	-2.371758	-3.775522	0.451904
45	1	0	-1.604024	-4.190834	-0.186604
46	6	0	-4.300390	-3.217618	-2.278975
47	1	0	-3.601698	-3.801454	-2.863940
48	6	0	-5.467525	-3.715176	-1.622113
49	1	0	-5.807360	-4.742695	-1.619653
50	6	0	-6.079731	-2.625621	-0.930610
51	1	0	-6.965075	-2.685389	-0.311008
52	6	0	-5.294827	-1.454130	-1.156037
53	1	0	-5.477720	-0.467531	-0.749855
54	6	0	-4.196495	-1.823528	-1.990048
55	1	0	-3.394845	-1.167230	-2.302696
56	6	0	5.501073	-0.124008	-1.274724
57	26	0	7.103203	-0.186048	0.068607
58	6	0	6.480772	0.877896	-1.598720
59	6	0	6.170601	-1.394034	-1.341932
60	6	0	7.719703	0.230742	-1.873805
61	6	0	7.528335	-1.174265	-1.713464
62	6	0	7.005609	-1.133886	1.918071
63	6	0	8.368637	-0.936344	1.540334
64	6	0	8.583111	0.465622	1.378024
65	6	0	7.352247	1.134973	1.655164
66	6	0	6.377759	0.146166	1.989250
67	1	0	6.306661	1.944835	-1.633370
68	1	0	5.730377	-2.354305	-1.109134
69	1	0	8.649239	0.722679	-2.128026
70	1	0	8.289065	-1.936831	-1.816502
71	1	0	6.524742	-2.087978	2.089283
72	1	0	9.101867	-1.714806	1.374472
73	1	0	9.506685	0.935714	1.066655
74	1	0	7.181935	2.201902	1.595499
75	1	0	5.334857	0.330584	2.211242

Total energy (Sum of electronic and zero-point energies): -2084.6118279 Hartree

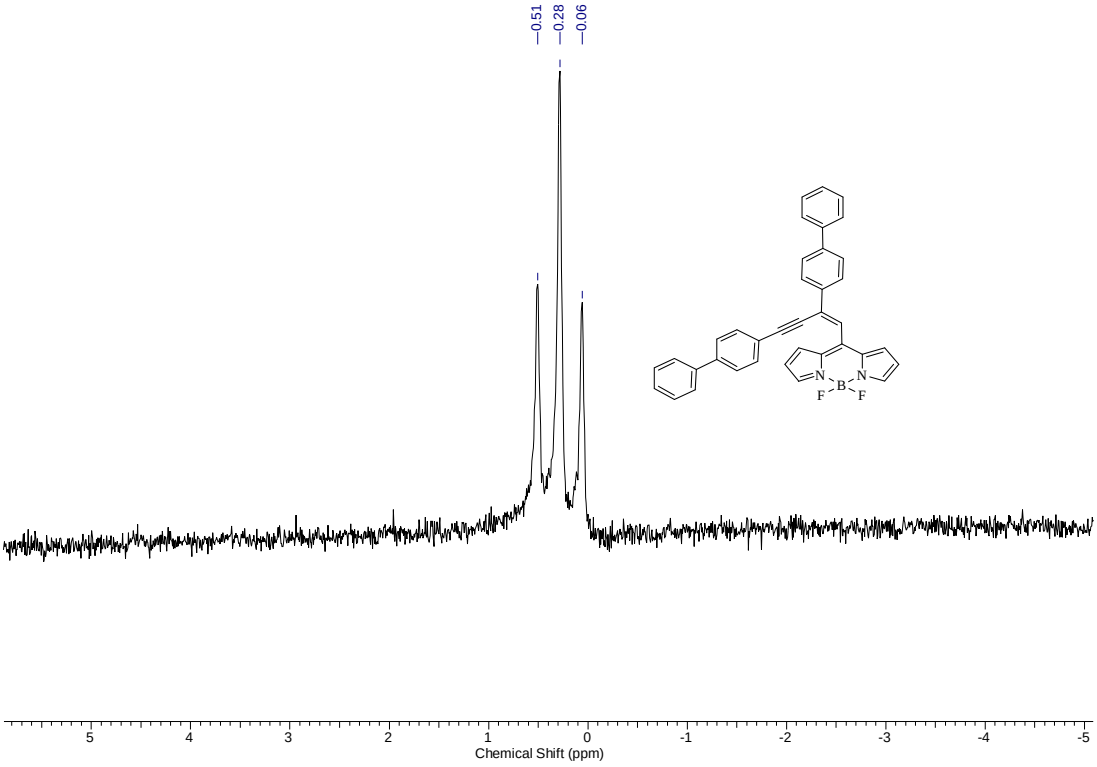
^{1}H NMR of BODIPY **3a**



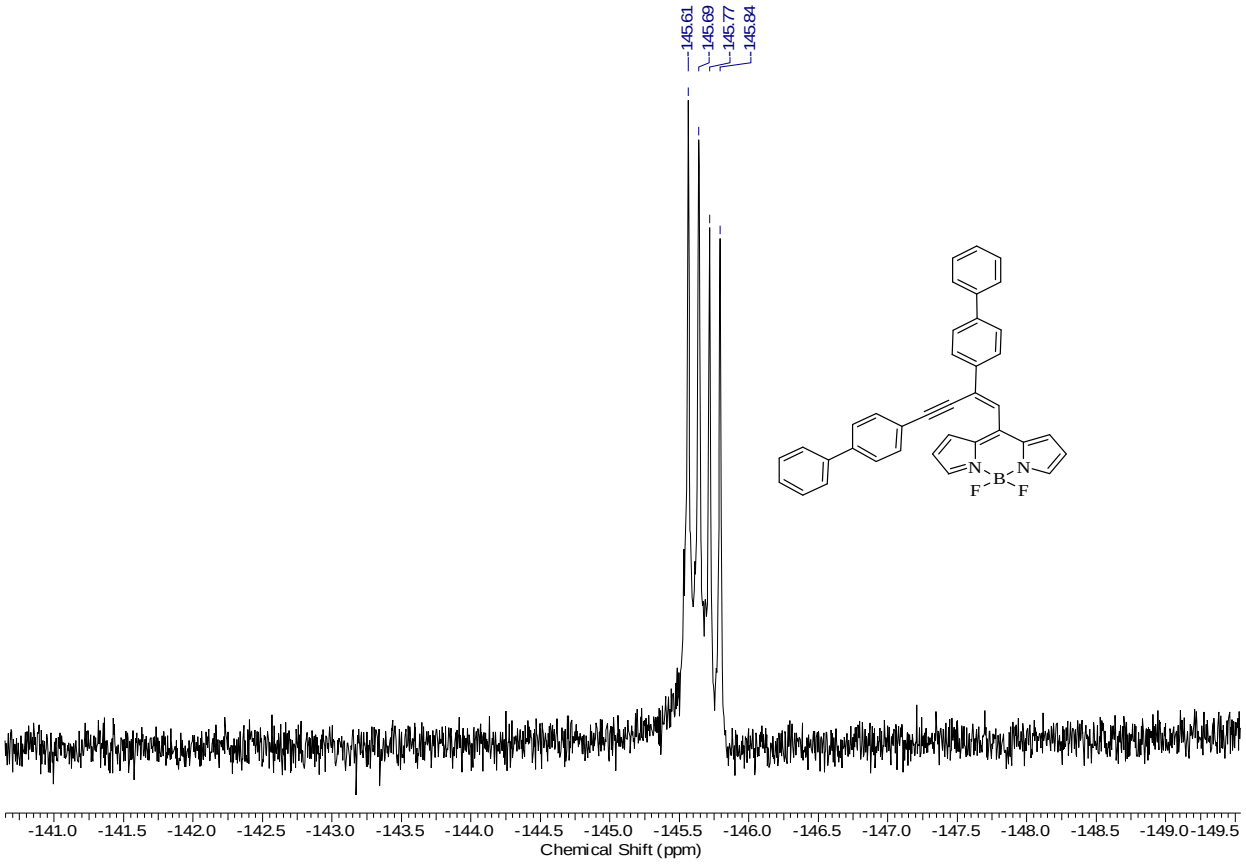
^{13}C NMR of BODIPY **3a**



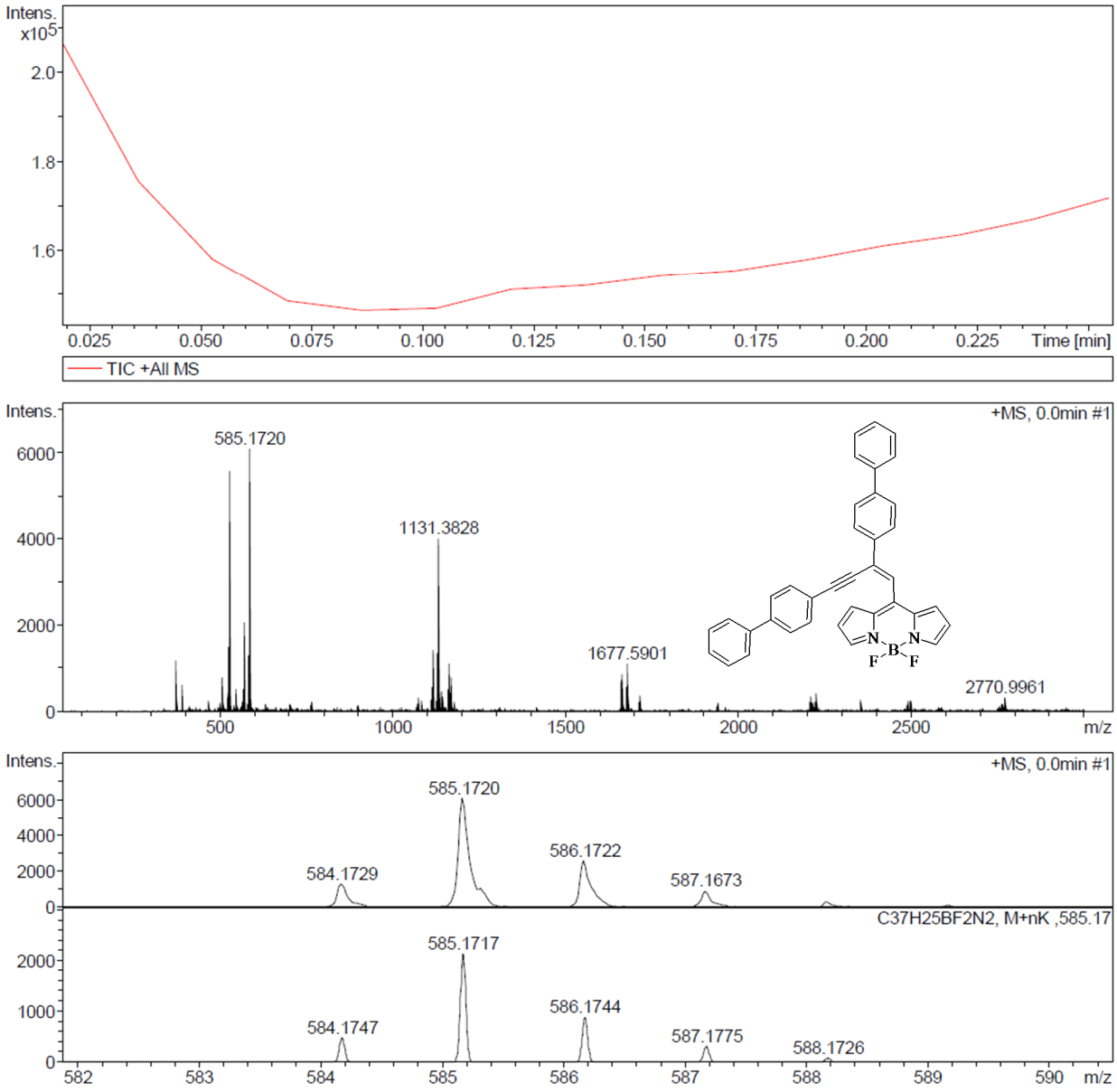
^{11}B NMR of BODIPY **3a**



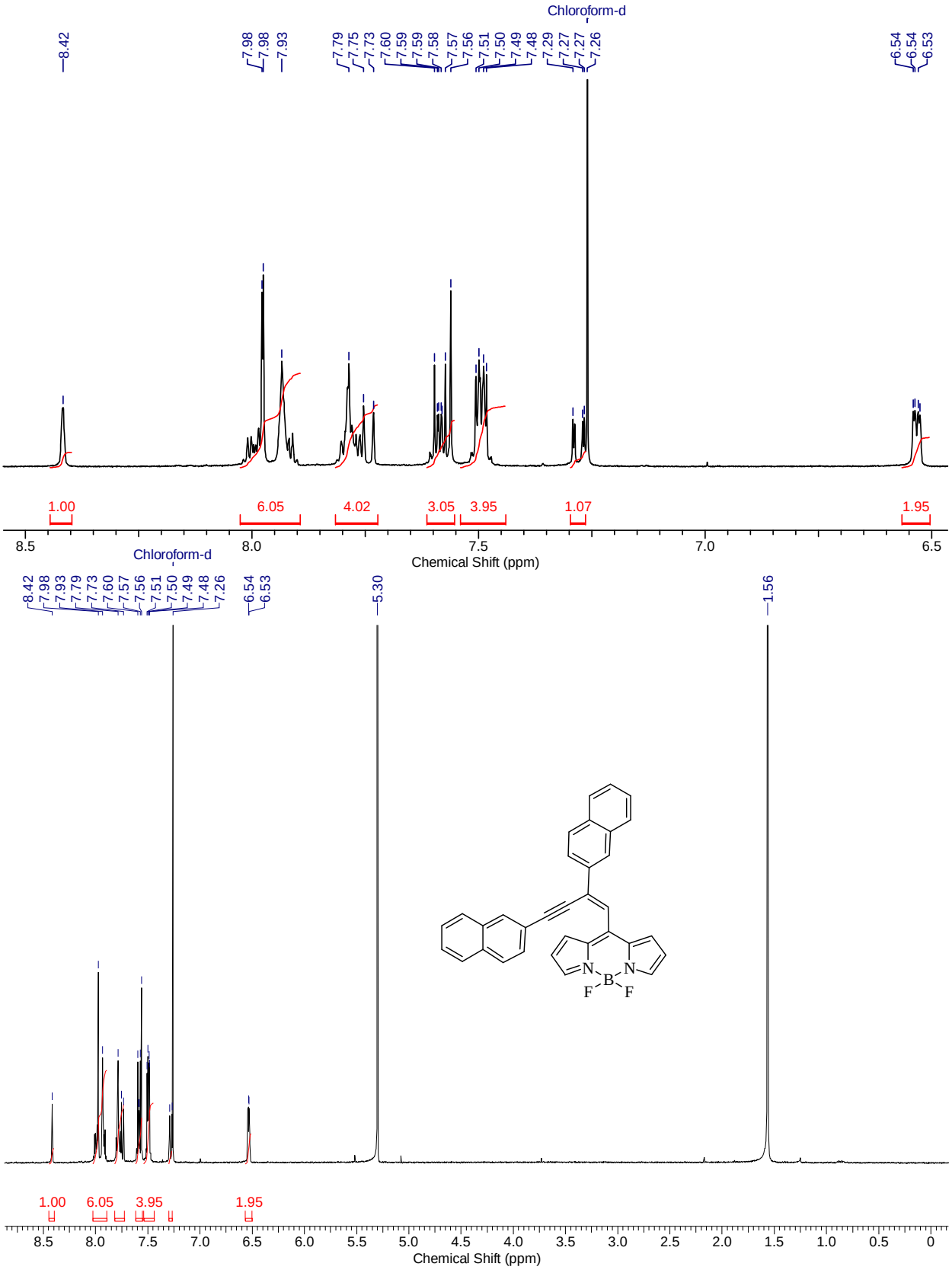
^{19}F NMR of BODIPY **3a**



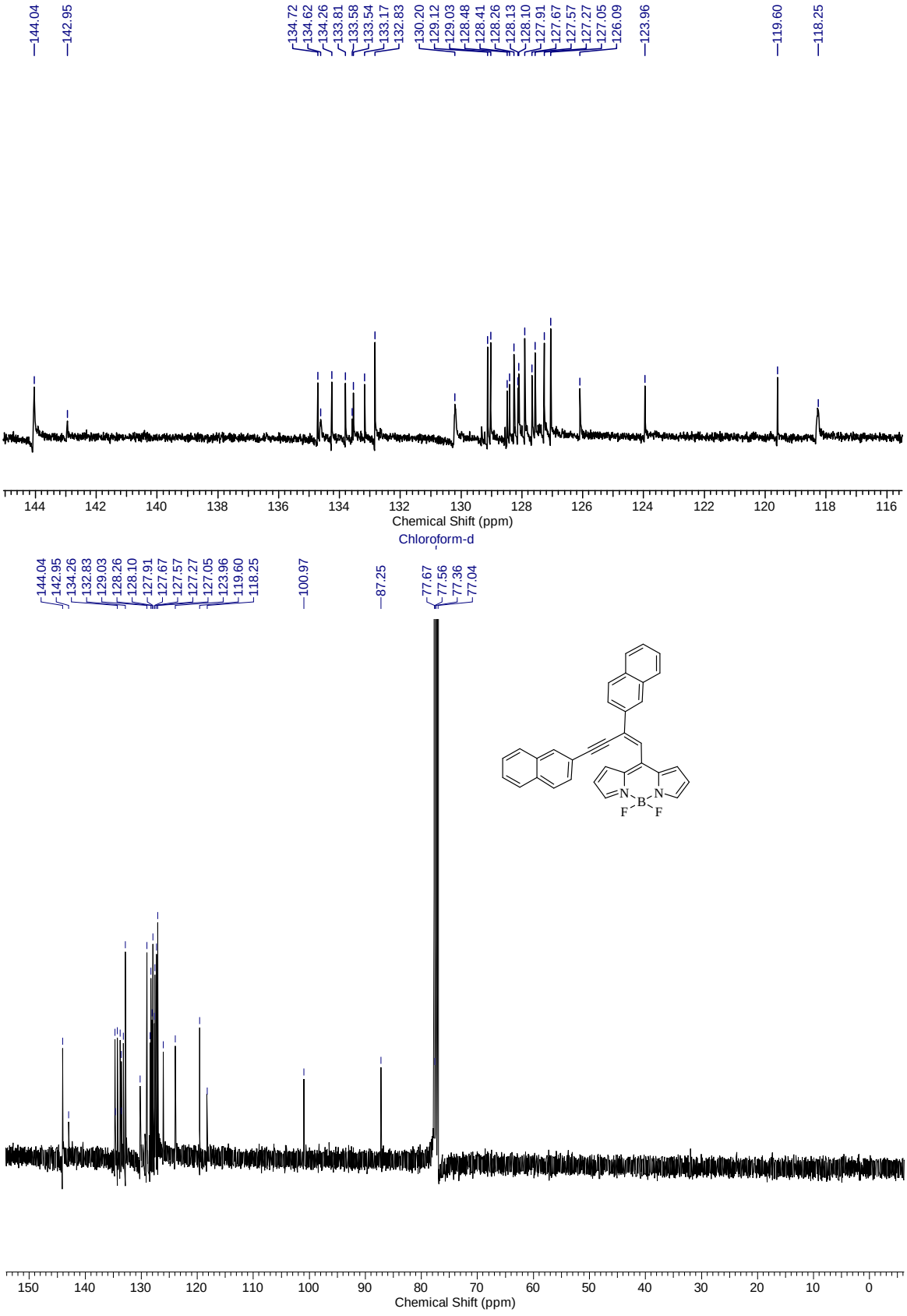
HRMS of BODIPY **3a**



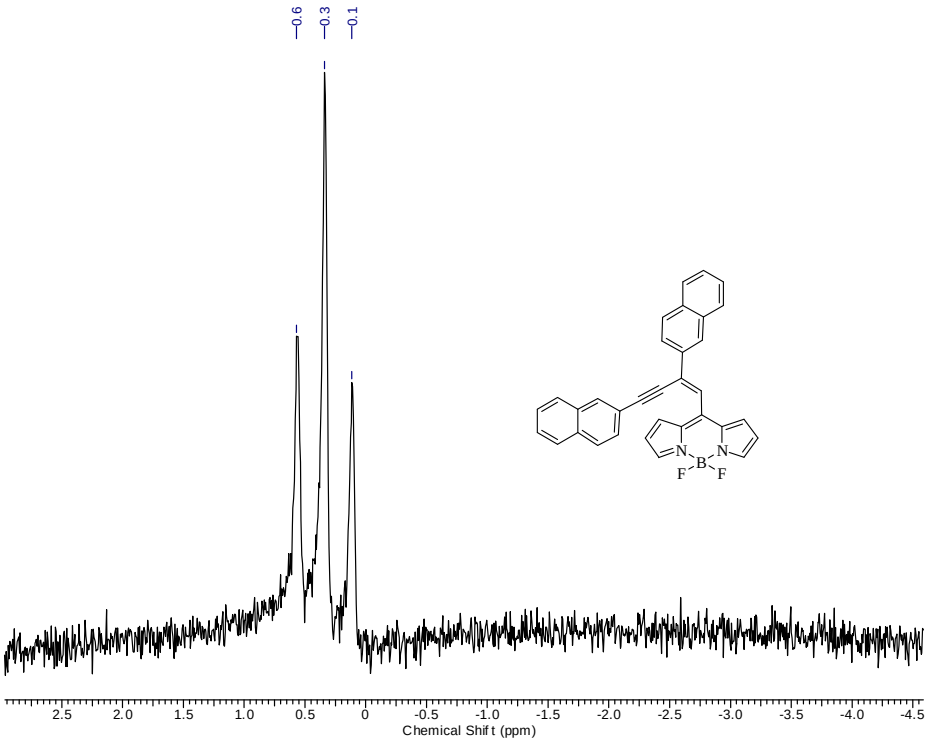
^{1}H NMR of BODIPY **3b**



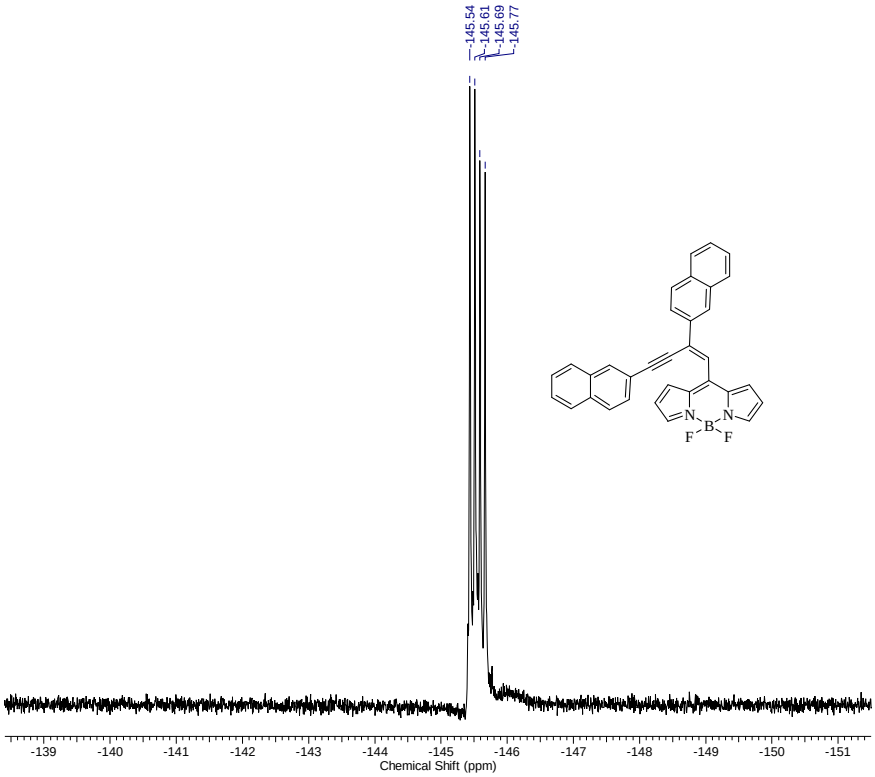
^{13}C NMR of BODIPY **3b**



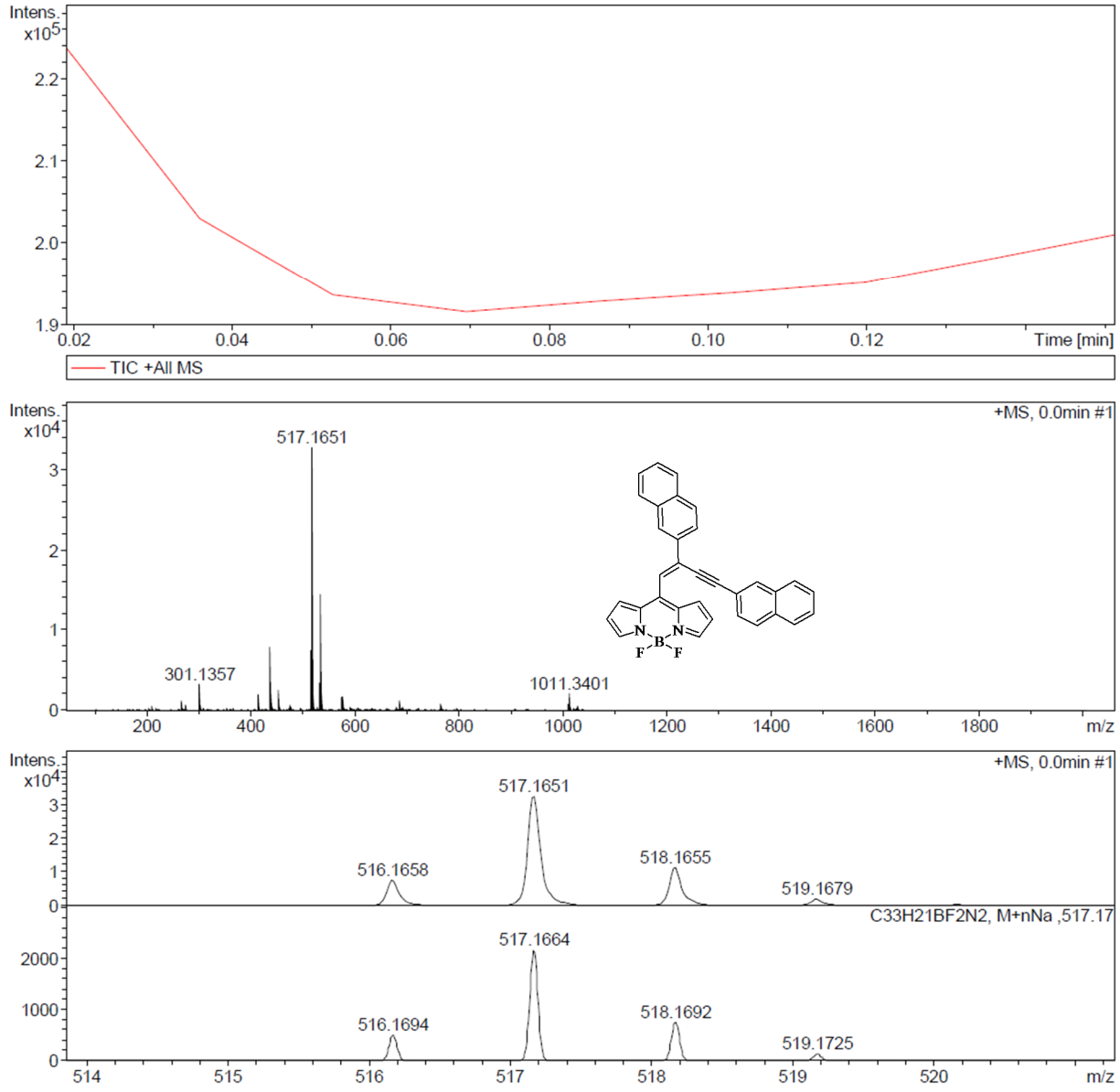
^{11}B NMR of BODIPY **3b**



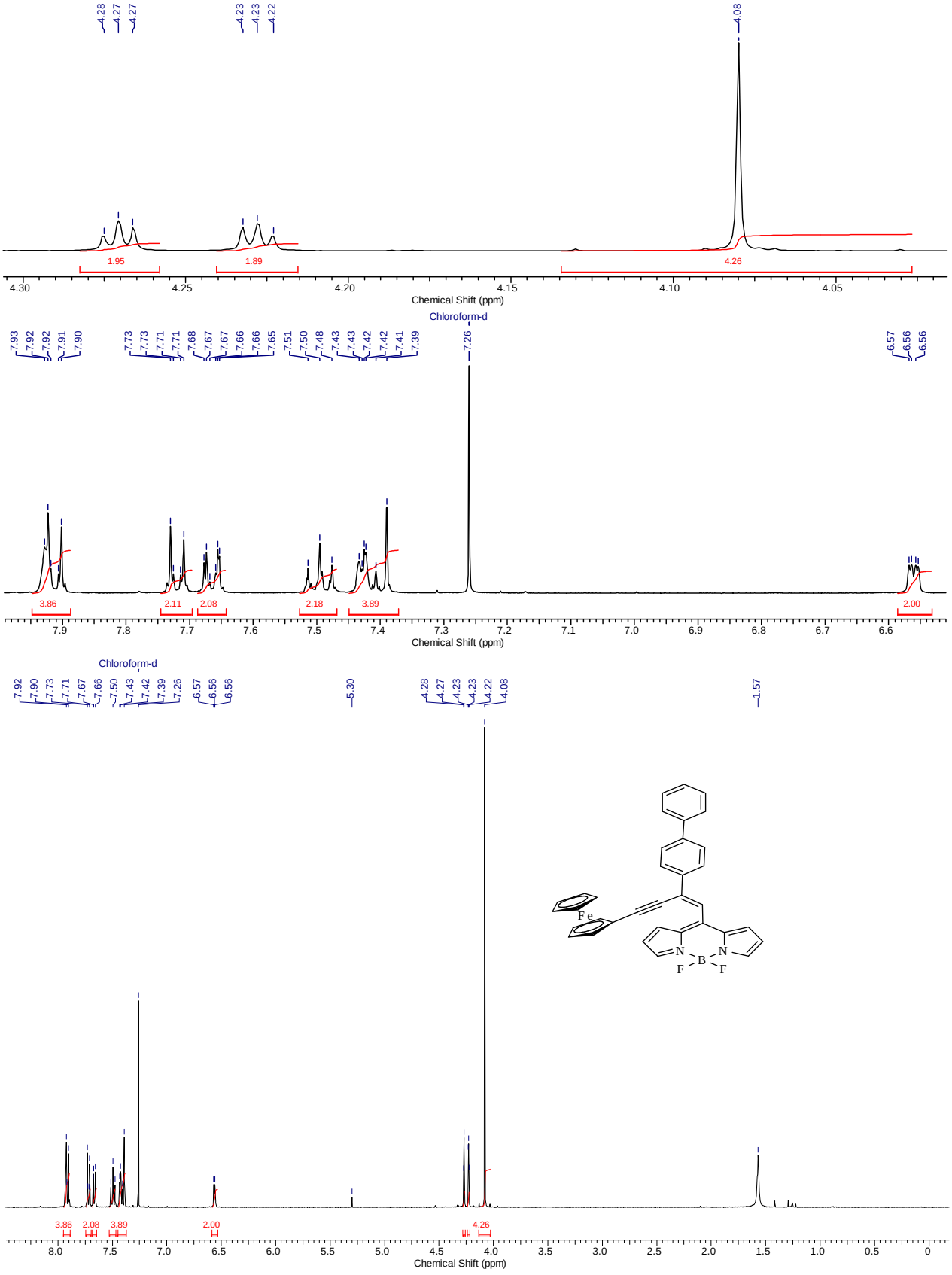
^{19}F NMR of BODIPY **3b**



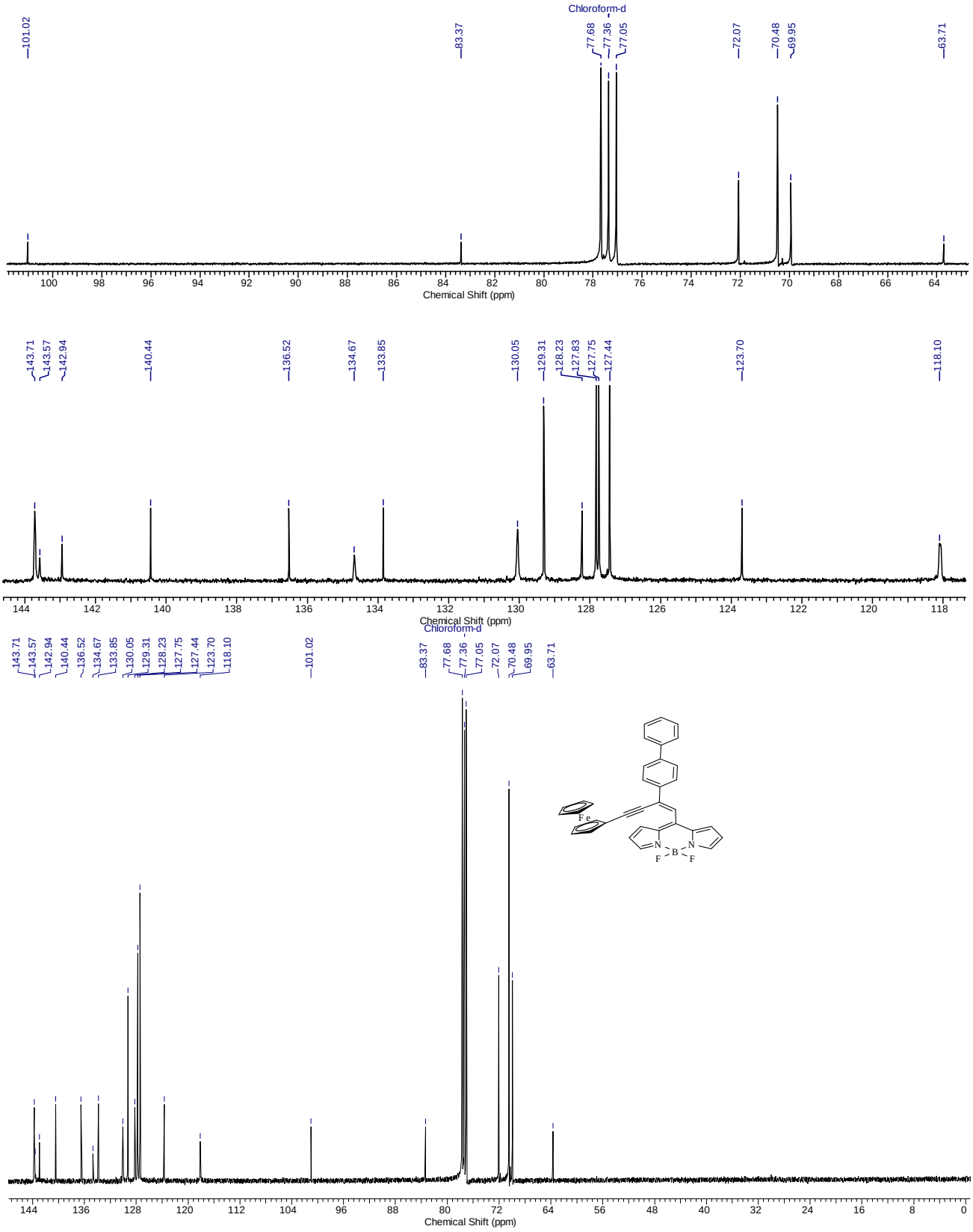
HRMS of BODIPY **3b**



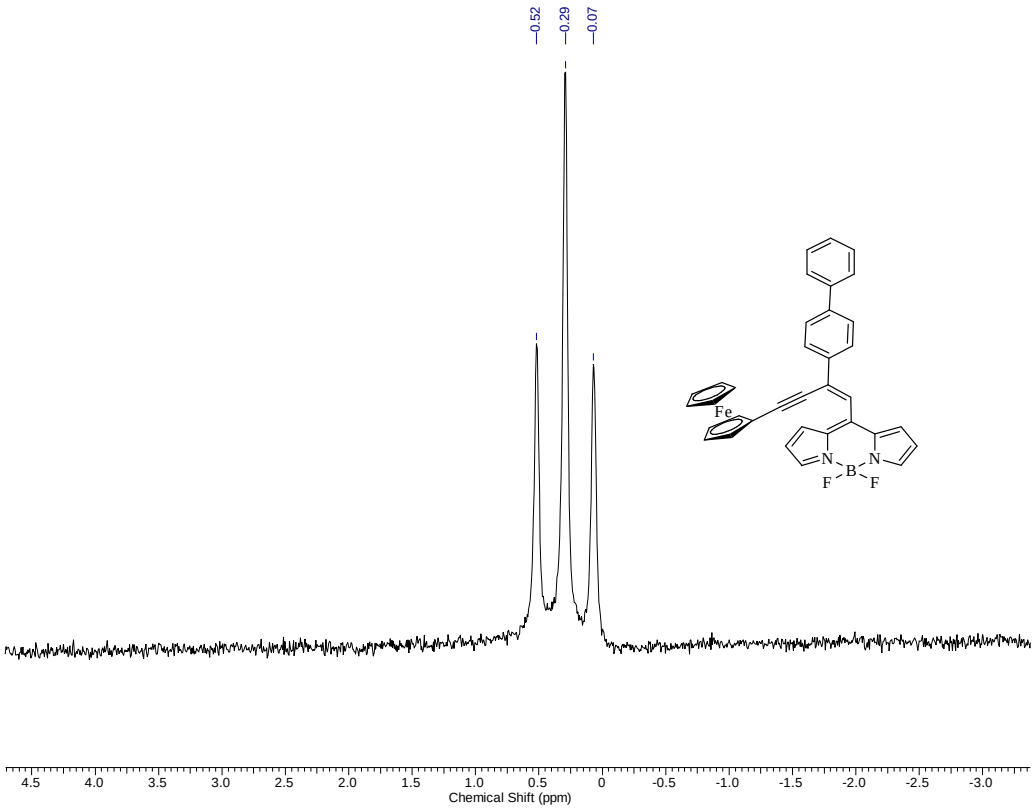
^{1}H NMR of BODIPY **4a**



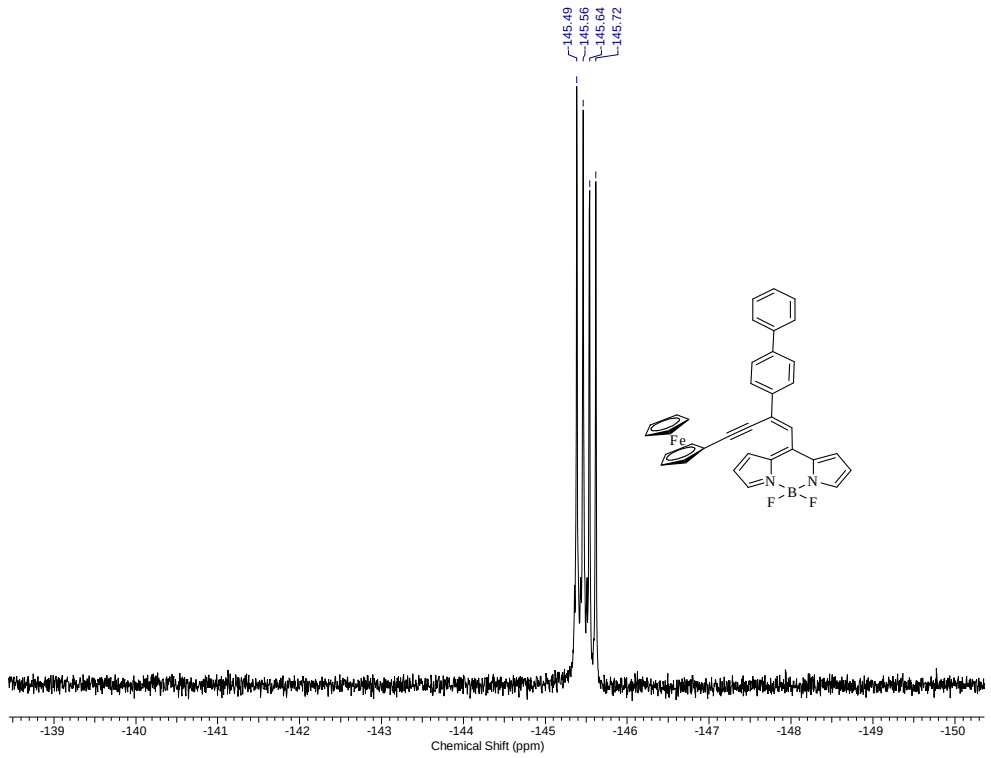
^{13}C NMR of BODIPY **4a**



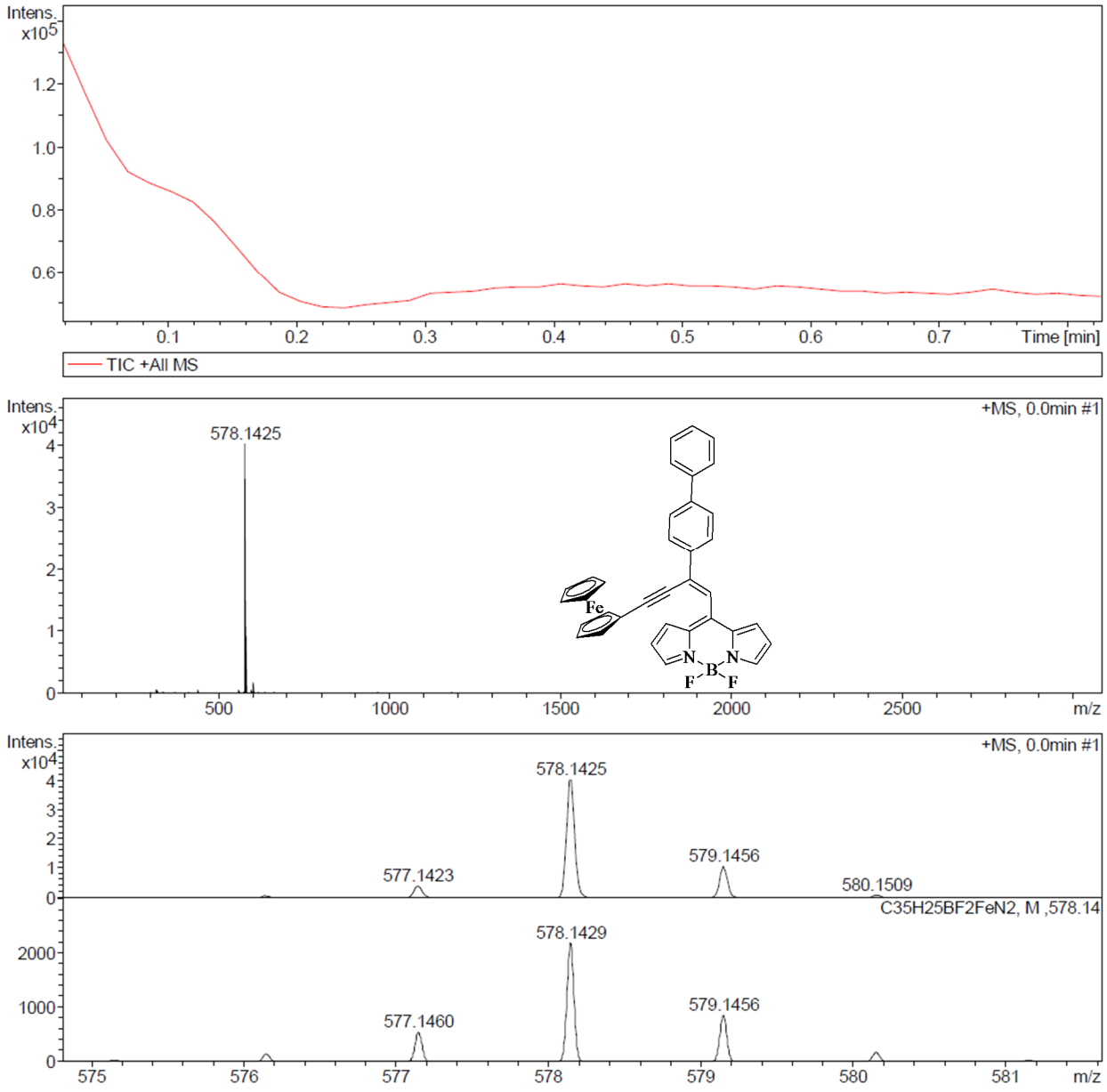
^{11}B NMR of BODIPY **4a**



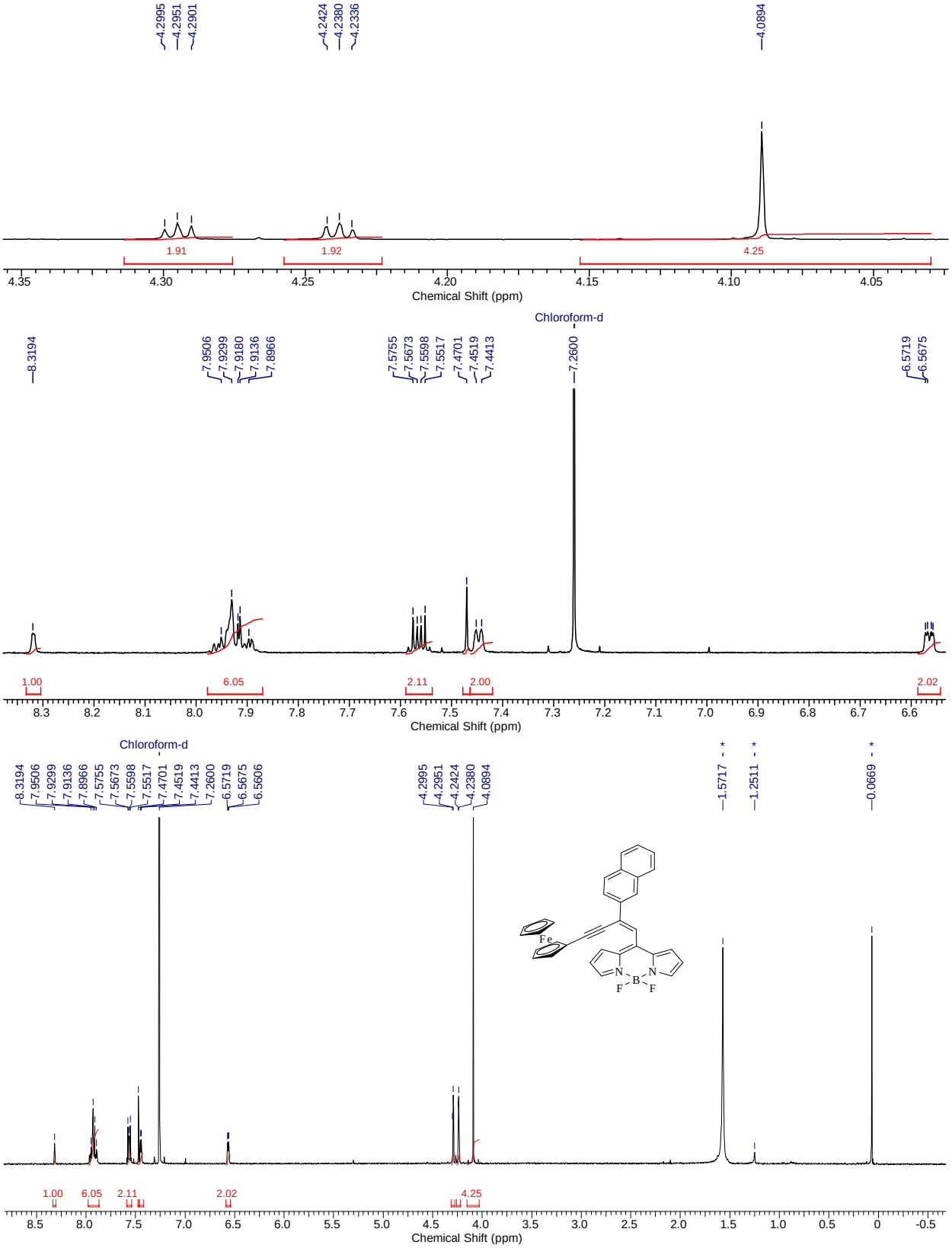
^{19}F NMR of BODIPY **4a**



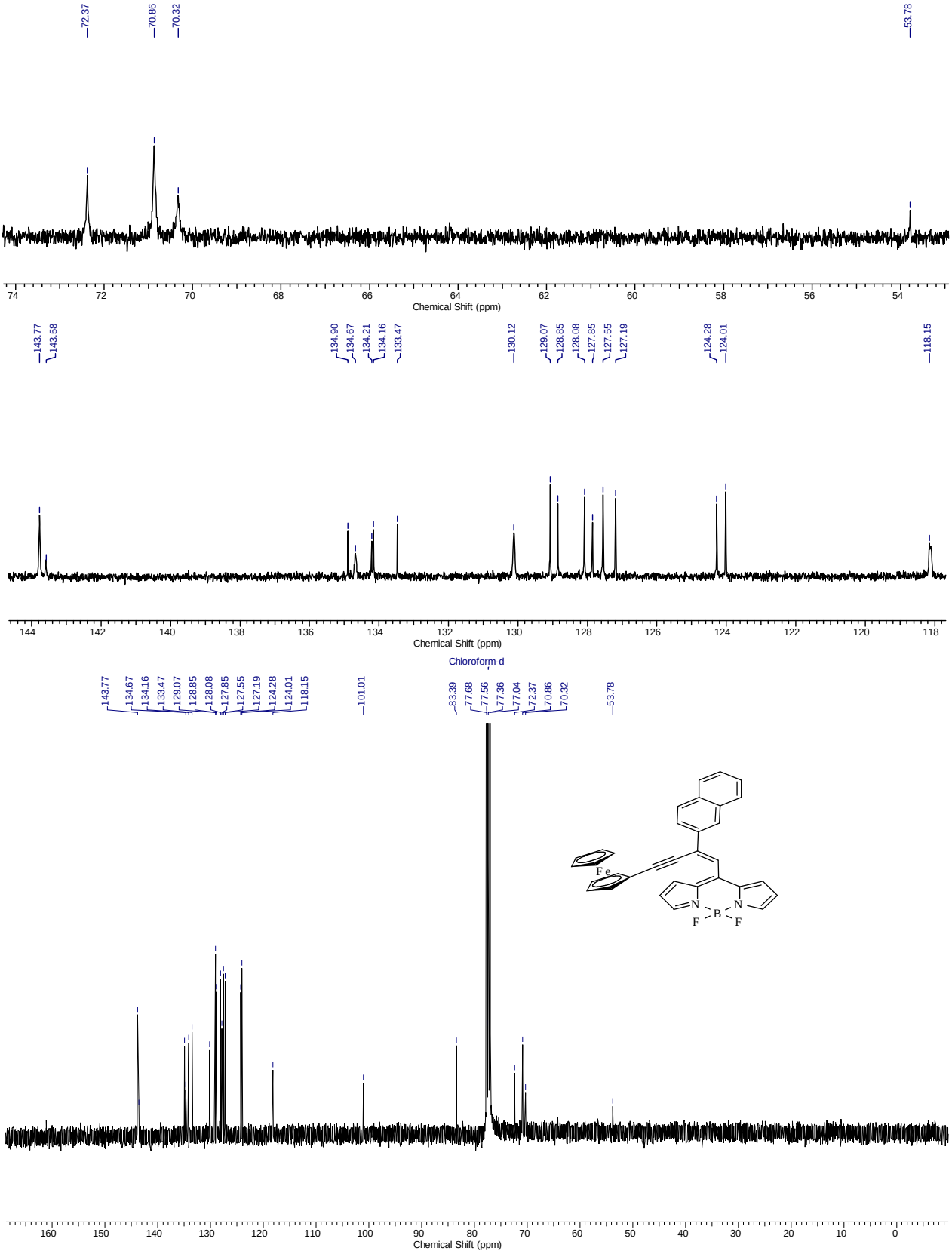
HRMS of BODIPY **4a**



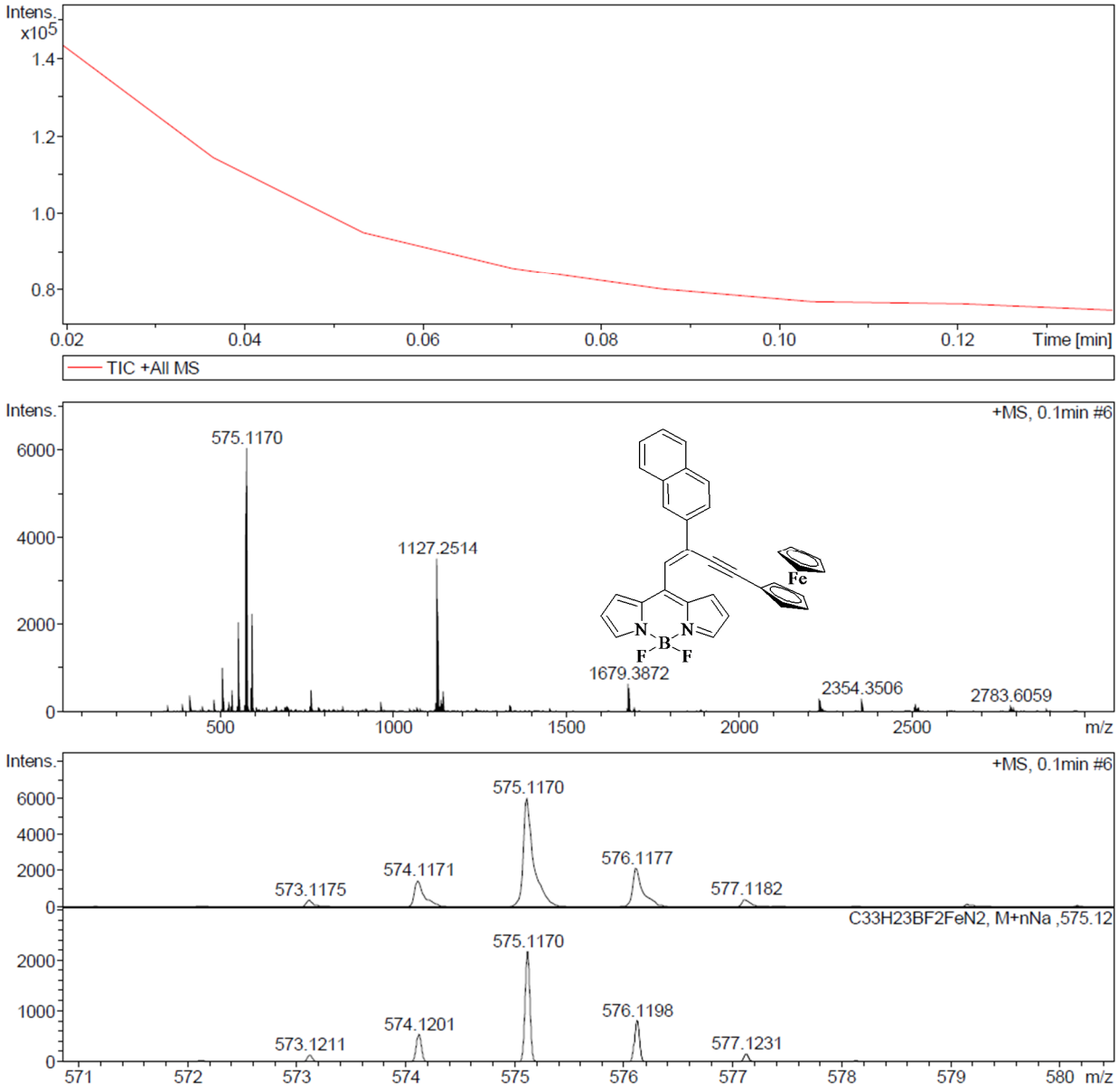
^{1}H NMR of BODIPY **4b**



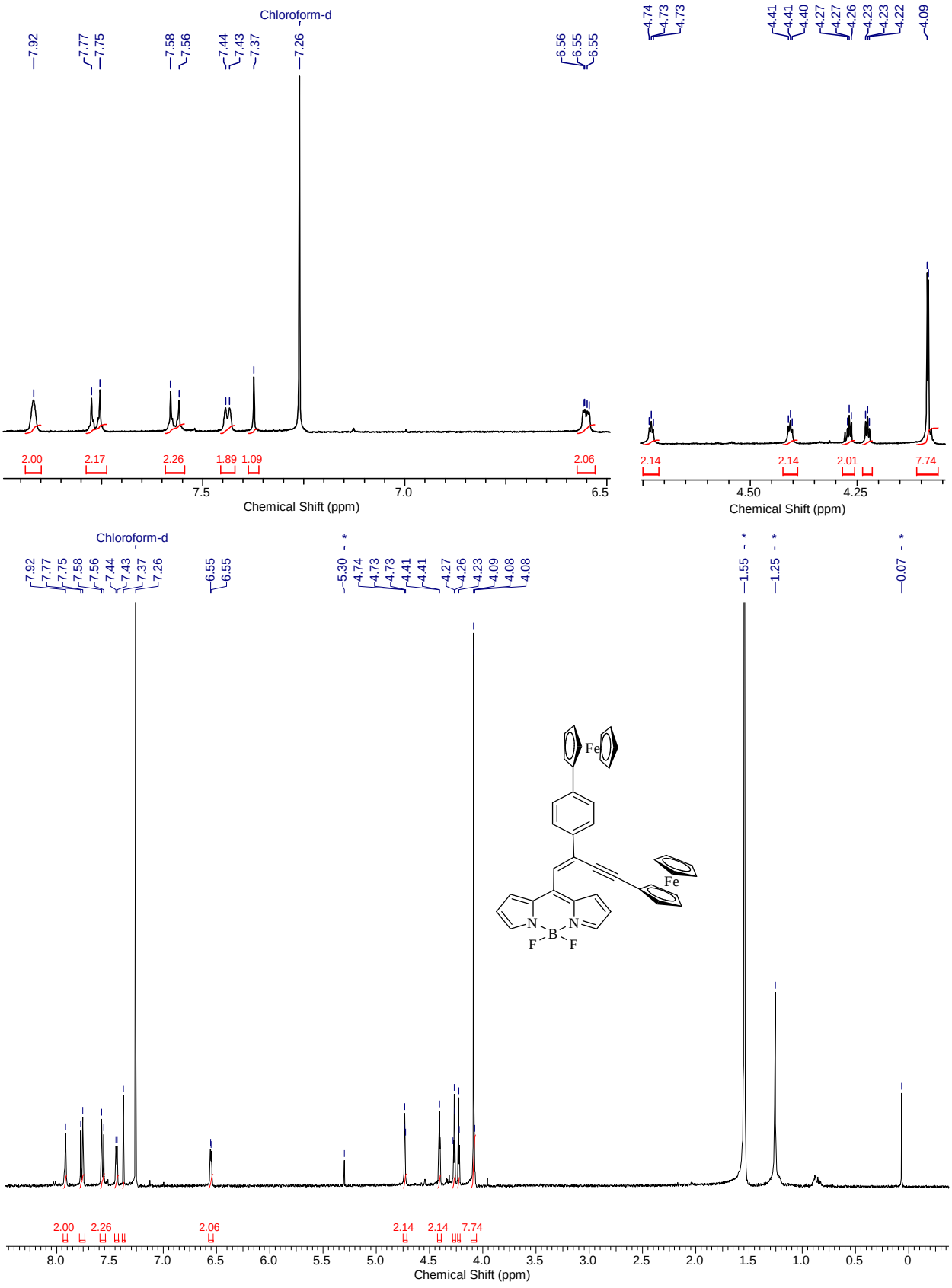
^{13}C NMR of BODIPY **4b**



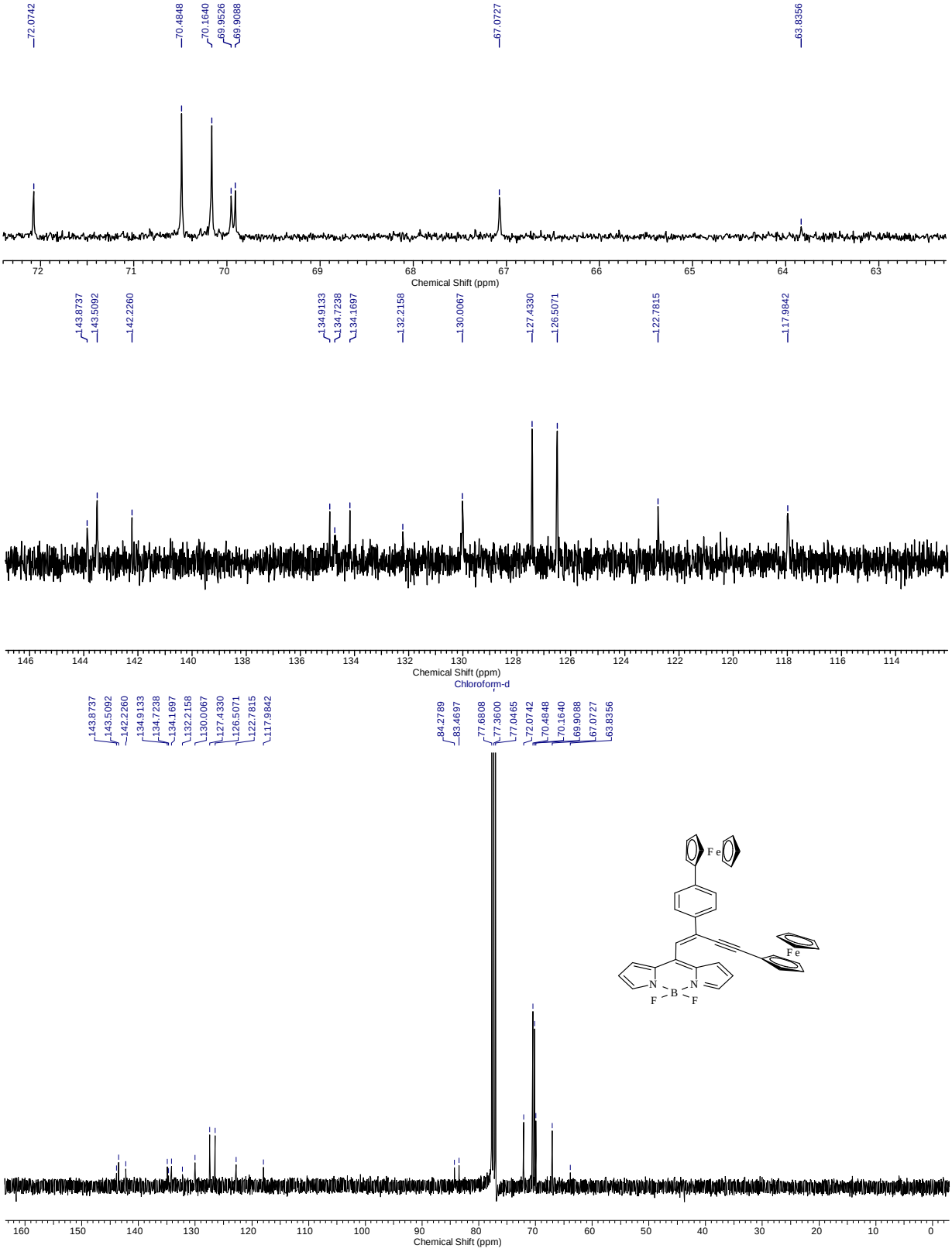
HRMS of BODIPY **4b**



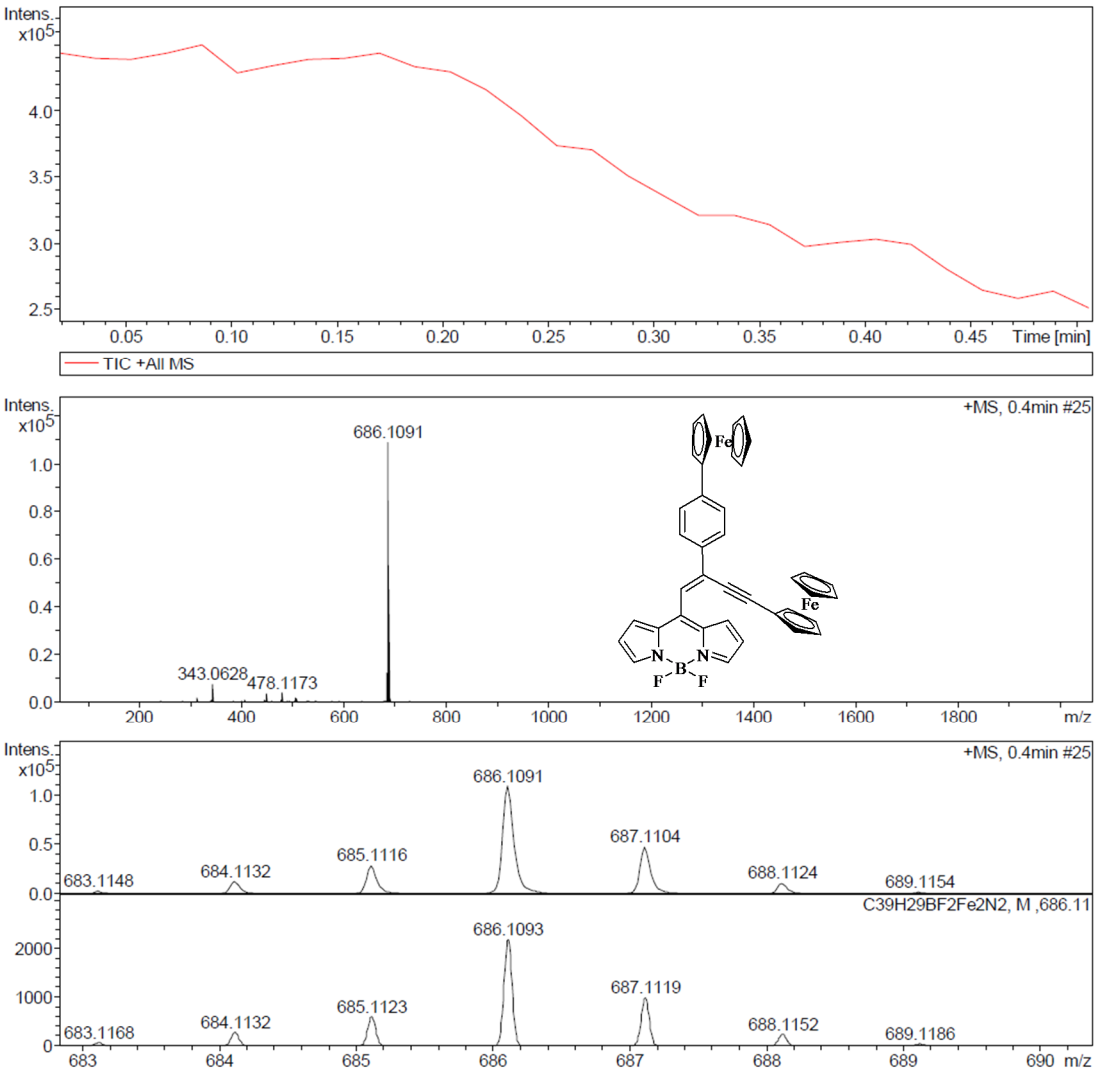
^{1}H NMR of BODIPY **4c**



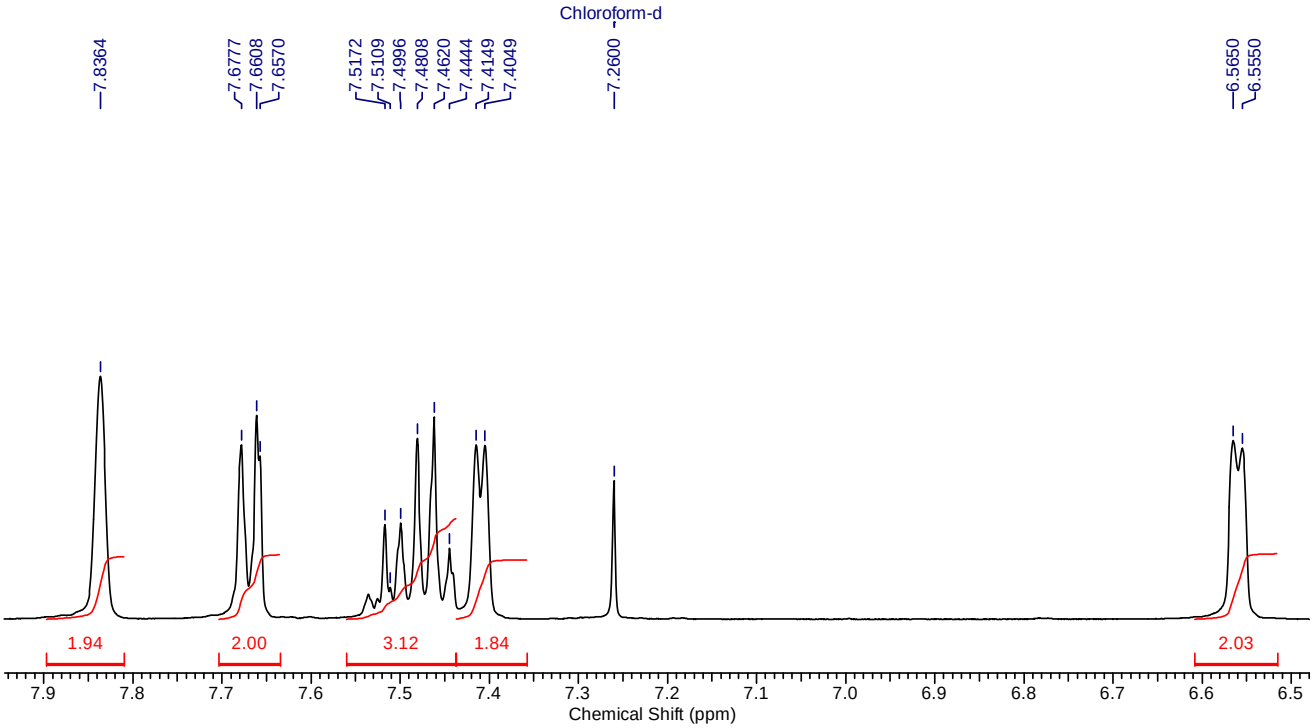
^{13}C NMR of BODIPY **4c**

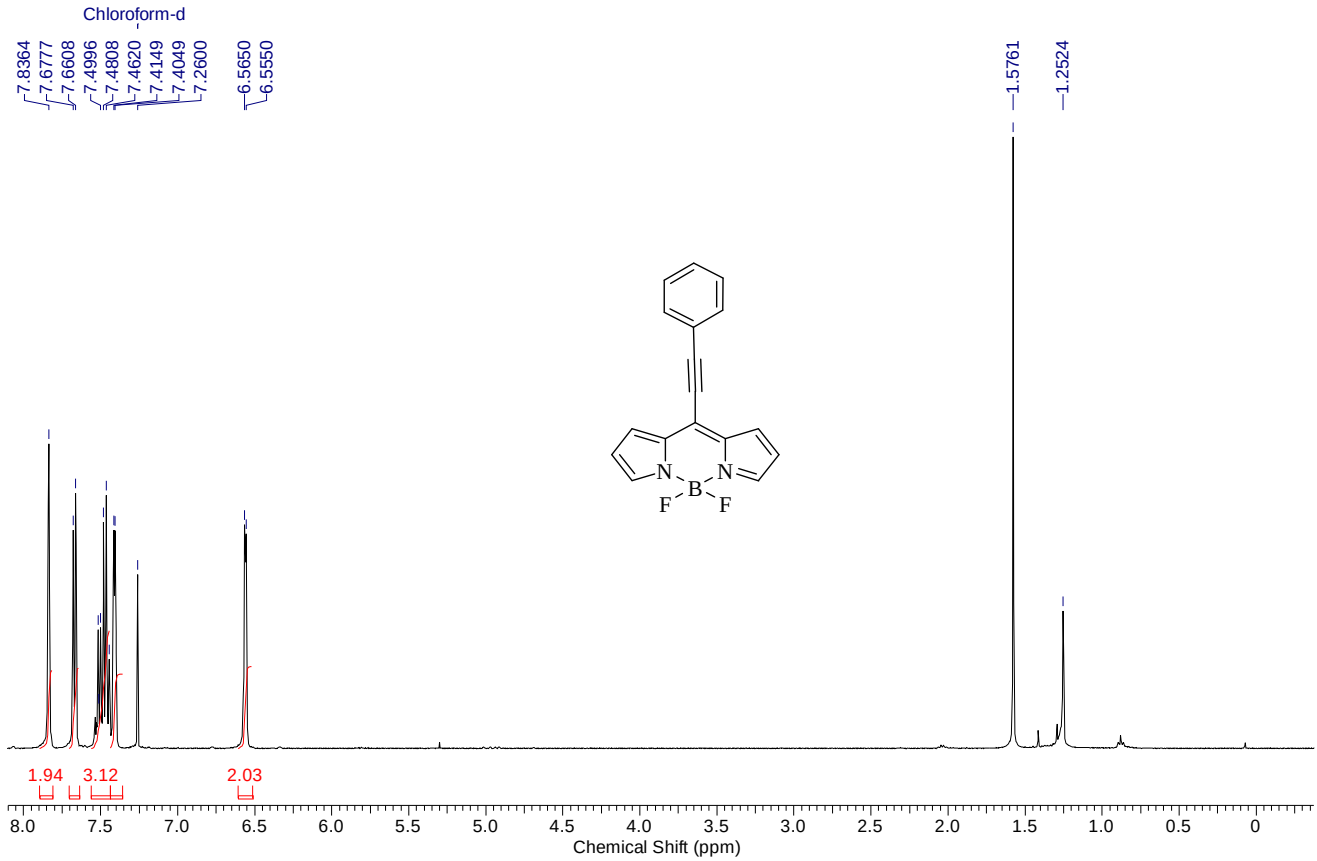


HRMS of BODIPY **4c**

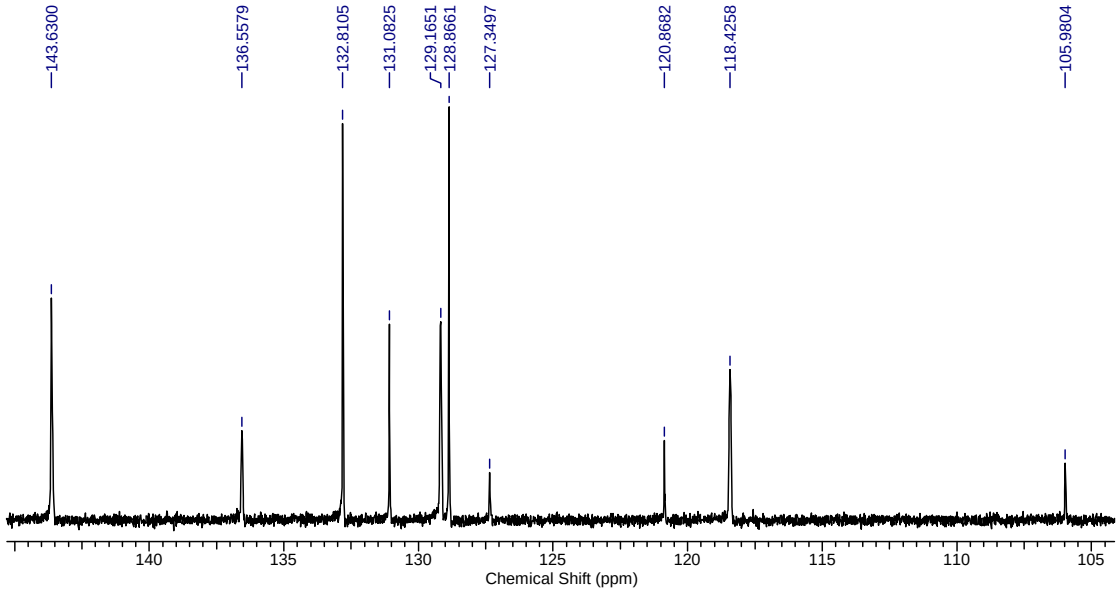


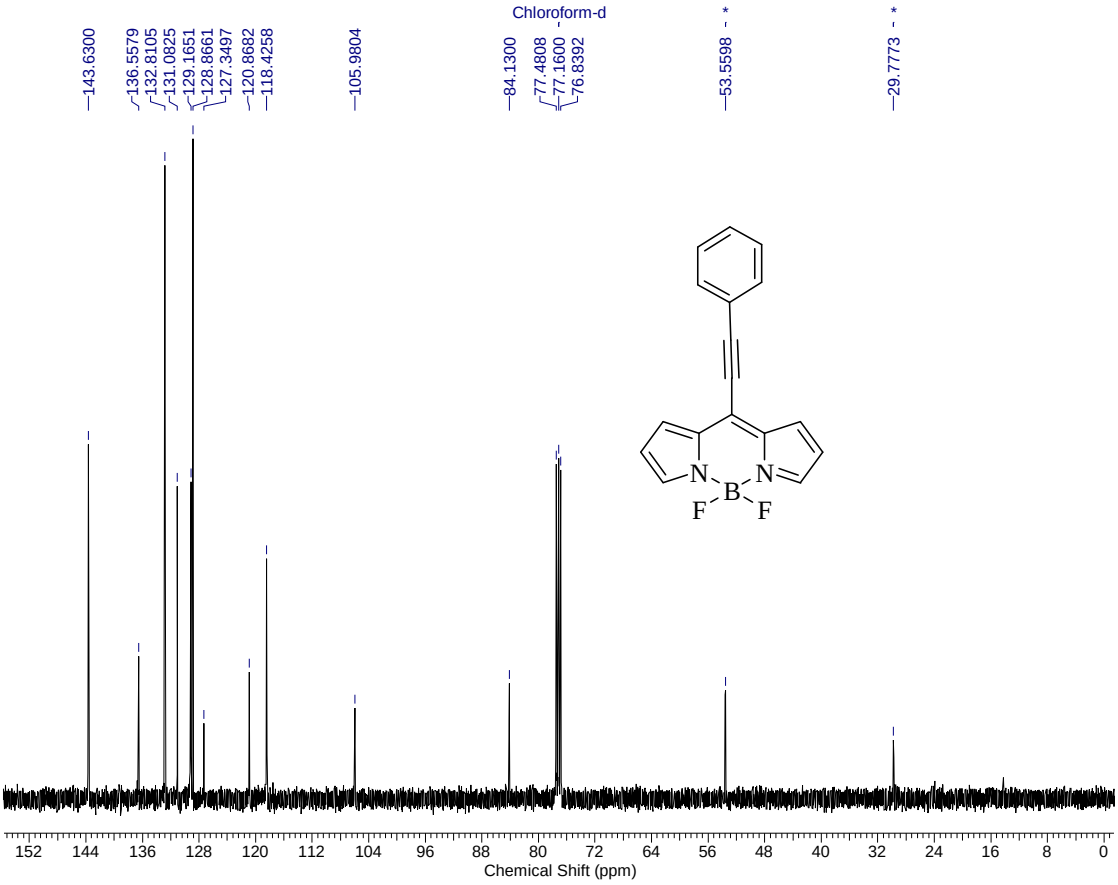
^{1}H NMR of BODIPY **2d**



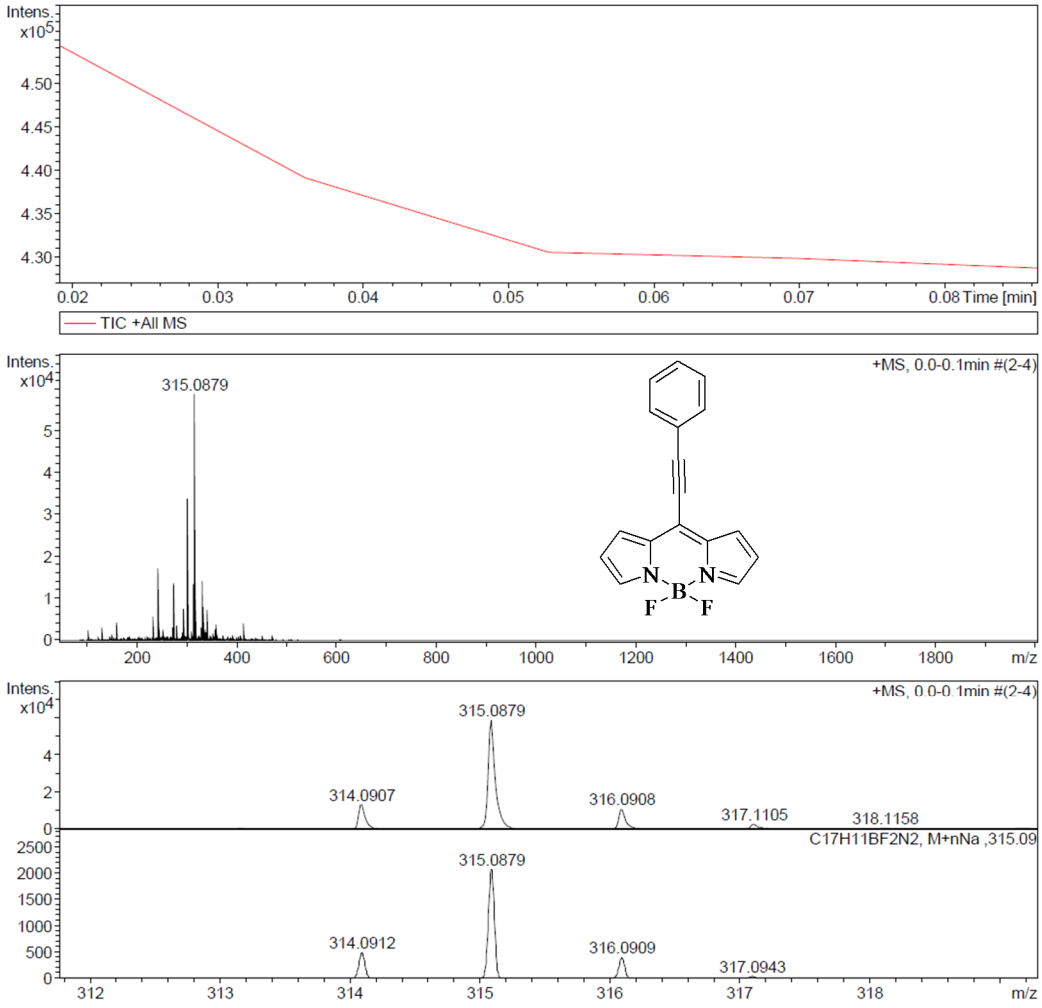


^{13}C NMR data of BODIPY **2d**





HRMS of BODIPY **2d**



[1] (a) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Jr. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian 09, revision A.02; Gaussian, Inc.: Wallingford, CT, **2009**; (b) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785− 789; (c) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 1372−1377; (c) P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 270-283; (d) M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. Defrees and J. A. Pople, *J. Chem. Phys.*, 1982, **77**, 3654-3665.