Supporting Information

Meso enamine substituted BODIPYs

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

Experimental Section

General methods.

Chemicals were used as received unless otherwise indicated. All oxygen or moisture sensitive reactions were performed under nitrogen/argon atmosphere using standard schlenk method. ^{1}H NMR (400 MHz), and ^{13}C NMR (100MHz) spectra were recorded on 100 MHz instrument by using $CDCl_3$ as solvent. ^{1}H NMR chemical shifts are reported in parts per million (ppm) relative to the solvent residual peak ($CDCl_3$, 7.26 ppm). Multiplicities are given as: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), m (multiplet), and the coupling constants, *J*, are given in Hz. ^{13}C NMR chemical shifts are reported relative to the solvent residual peak ($CDCl_3$, 77.36 ppm). UV-visible absorption spectra of all compounds were recorded on UV-visible Spectrophotometer. HRMS were recorded on TOF-Q mass spectrometer.

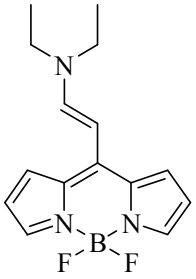
Synthesis and Characterization-

Reaction Procedure-

8-chloro BODIPY (200mg, 0.88 mmol), was dissolved in the 20 ml dry DCM and, respective tertiary amine (3.54 mmol) was added. The reaction mixture was stirred at room temperature; and the progress of the reaction was monitored by TLC. After completion of reaction the solvent was removed at the reduced pressure without heating, and the crude product was purified by column chromatography by using DCM: hexane (2:1).

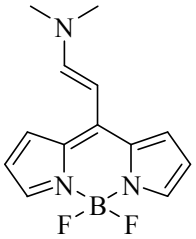
All the products were characterized by ^{1}H, ^{13}C NMR and HRMS techniques. The BODIPYs **2, 4a,4b** and **5a** were also characterized by single crystal X-ray analysis.

2



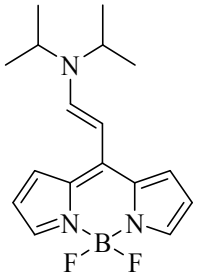
Yellow-red crystalline solid. Yield: 31% (79 mg); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.89 (d, *J* = 12 Hz, 1H), 7.60 (s, 2H), 6.98 (d, *J* = 4 Hz, 2H), 6.41 (m, 2H), 6.03 (d, *J* = 12 Hz, 1H), 3.50 (m, 4H), 1.35 (t, *J* = 8 Hz. 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): 155.4, 147.7, 134.5, 131.3, 121.0, 114.4, 96.3, 52.0, 44.2, 15.0, 12.7. ^{11}B NMR ($CDCl_3$, 128 MHz, ppm) 0.41 (t, $J_{B\text{-}F}$ = 29.5 Hz); UV/vis (DCM): λ_{max} (ε [$M^{-1}cm^{-1}$]) 477 (3.38×10^4). HRMS (ESI-TOF) m/z = calculated for $C_{15}H_{18}BF_2N_3$ = 312.1457 $[M+Na]^+$, measured 312.1471 $[M+Na]^+$.

3



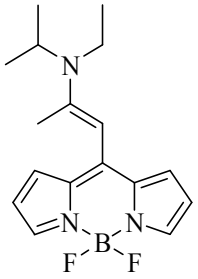
Yellow-red crystalline solid. Yield: 18% (42 mg);. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.83 (d, *J* = 12 Hz, 1H), 7.61 (s, 2H), 6.99 (d, *J* = 4 Hz, 2H), 6.41 (m, 2H), 5.93 (d, *J* = 12 Hz, 1H), 3.29 (s, 3H), 3.12 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): 156.0, 147.7, 134.3, 131.2, 120.7, 114.3, 96.4, 53.8, 27.5, 24.4. UV/vis (DCM): λ_{max} (ε [$M^{-1}cm^{-1}$]) 476 (3.34×10^4). HRMS (ESI-TOF) m/z = calculated for $C_{13}H_{14}BF_2N_3$ = 284.1143 $[M+Na]^+$, measured 284.1147 $[M+Na]^+$.

4a



Yellow-red crystalline solid. Yield: 13% (36 mg); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.01 (d, *J* = 12 Hz, 1H), 7.60 (s, 2H), 6.94 (d, *J* = 4 Hz, 2H), 6.42 (m, 2H), 6.21 (d, *J* = 12 Hz, 1H), 4.32 (m, 1H), 4.82 (m, 1H), 1.38 (d, *J* = 4 Hz, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): 153.0, 147.9, 134.0, 131.1, 120.6, 114.2, 96.8, 51.4, 49.2, 23.8, 20.3; UV/vis (DCM): λ_{max} (ε [$M^{-1}cm^{-1}$]) 477 (3.87×10^4). HRMS (ESI-TOF) m/z = calculated for $C_{16}H_{18}BF_2N_3$ = 340.1770 $[M+Na]^+$, measured 340.1763 $[M+Na]^+$.

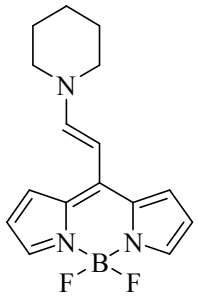
4b



Yellow-red crystalline solid. Yield: 9% (25 mg); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.56 (s, 2H), 6.84 (s, 2H), 6.37 (s, 2H), 6.03 (s, 1H), 4.38 (m, 1H), 3.54 (m, 1H), 2.45 (s, 1H), 1.37 (m, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): 145.0, 139.6, 134.0, 132.3, 121.6, 119.1, 114.1, 52.0, 40.2, 34.6, 21.6, 20.9, 14.9. UV/vis (DCM): λ_{max} (ε [$M^{-1}cm^{-1}$]) 504 (3.40×10^4) and 466 (2.99×

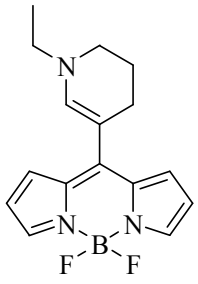
10^4). HRMS (ESI-TOF) m/z = calculated for $C_{17}H_{22}BF_2N_3$ = 340.1770 $[M+Na]^+$, measured 340.1771 $[M+Na]^+$.

5a



Yellow-red crystalline solid. Yield: 12% (32 mg); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.84 (d, *J* = 12 Hz, 1H), 7.59 (s, 2H), 6.97 (d, *J* = 4 Hz, 2H), 6.40 (m, 2H), 6.06 (d, *J* = 12 Hz, 1H), 3.54 (m, 4H), 1.77 (m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): 156.0, 147.7, 134.3, 131.2, 120.9, 114.3, 96.0, 53.8, 27.1, 24.0. UV/vis (DCM): λ_{max} (ε [$M^{-1}cm^{-1}$]) 477 (3.14×10^4). HRMS (ESI-TOF) m/z = calculated for $C_{16}H_{18}BF_2N_3$ = 324.1457 $[M+Na]^+$, measured 324.1444 $[M+Na]^+$.

5b



Yellow-red crystalline solid. Yield: 7% (18 mg); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.78 (s, 1H), 7.61 (s, 2H), 6.84 (d, *J* = 4 Hz, 2H), 6.41 (m, 2H), 3.44 (m, 4H), 2.80 (t, *J* = 8H, 2H), 2.15 (p, *J* = 8 Hz, 2H), 1.33 (t, *J* = 8 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): 155.6, 147.7, 133.8,

131.4, 123.8, 113.9, 110.2 52.6, 47.0, 25.7, 21.8, 14.0; UV/vis (DCM): λ_{max} (ε [$M^{-1}cm^{-1}$]) 447 (3.9×10^4). HRMS (ESI-TOF) m/z = calculated for $C_{16}H_{18}BF_2N_3$ = 324.1457 $[M+Na]^+$, measured 324.1556 $[M+Na]^+$.

Single Crystal X-ray Diffraction Studies.

Single crystal X-ray structural studies of **3**, **4a, 4b** and **5b** were performed on a CCD Agilent Technologies (Oxford Diffraction) SUPER NOVA diffractometer. Data were collected at 150(2) K using graphite-monochromated CuK\α radiation (λ_α = 1.5418 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 structure, and dat refinement parameters are summarized in Table 1. The CCDC numbers 1001550-1001553 contain the supplementary crystallographic data for **2, 4a, 4b** and **5a** respectively. 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 S1. Crystal structure and data refinement parameters

BODIPY	**2**	**4a**	**4b**	**5a**
Empirical formula	C_{15} H_{18} B F_2 N_3	C_{17} H_{22} B F_2 N_3	C_{17} H_{22} B F_2 N_3	C_{16} H_{18} B F_2 N_3
Formula weight	289.13	317.19	317.19	301.14
Temperature/K	150(2)	150(2)	150(2)	150(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic,
Space group	*P* $2_1/n$	*P* $2_1/c$	*P* $2_1/n$	P $2_1/c$
Unit cell dimensions				
a/Å	a = 8.3942(3)	9.2376(16)	11.1777(8)	a = 7.8218(4)
α/°	90	90	90	90
b/ Å	12.6829(4)	14.7140(12)	11.3773(5)	b = 23.1144(9)
β/°	95.074(3)	127.73(3)	109.830(8)	110.867(6)
c/ Å	14.0136(4)	15.929(3)	14.4649(9)	c = 8.5337(4)
γ/°	90	90	90	90
Volume/ $Å^3$	1486.08(8)	1712.2(5)	1730.45(18)	1441.66(11)
Z	4	4	4	4
Calculated density/ Mg/m^3	1.292	1.230	1.217	1.387
Absorption coefficient/mm^{-1}	0.785	0.088	0.087	0.101
F(000)	608	672	672	632
Crystal size/mm	0.26 x 0.18 x 0.13	0.33 x 0.26 x 0.21	0.33 x 0.28 x 0.21	0.33 x 0.26 x 0.21
θ range from data collection/°	4.71 to 72.08	3.02 to 24.99	3.34 to 25.00	3.10 to 25.00
Reflections collected/unique	9691 / 2895 [R(int) = 0.0210]	13178 / 3000 [R(int) = 0.0417]	9413 / 3022 [R(int) = 0.0609]	11087 / 2523 [R(int) = 0.0371]
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Data/restraints/parameters	2895 / 0 / 190	3000 / 0 / 212	3022 / 0 / 212	2523 / 0 / 199
Goodness-of-fit on F^2	1.044	1.108	1.020	1.127
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0550, wR_2 = 0.1567	R_1 = 0.0515, wR_2 = 0.1262	R_1 = 0.0550, wR_2 = 0.1179	R_1 = 0.0374, wR_2 = 0.0857
R indices (all data)	R_1 = 0.0606, wR_2 = 0.1627	R_1 = 0.0632, wR_2 = 0.1352	R_1 = 0.0979, wR_2 = 0.1443	R_1 = 0.0445, wR_2= 0.0889
Largest diff. peak and hole/e $Å^{-3}$	0.300 and -0.261	0.302 and -0.261	0.186 and -0.202	0.198 and -0.209
CCDC number	1001550	1001551	1001552	1001553

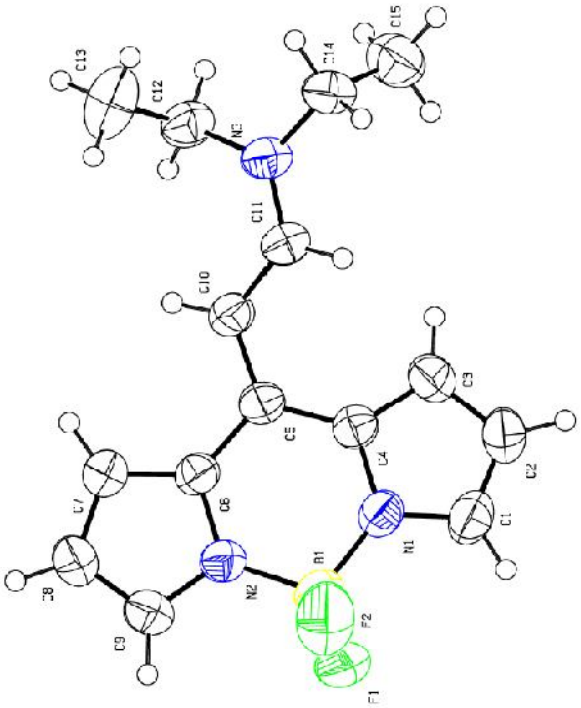


Figure S1. Crystal structure of BODIPY **2**

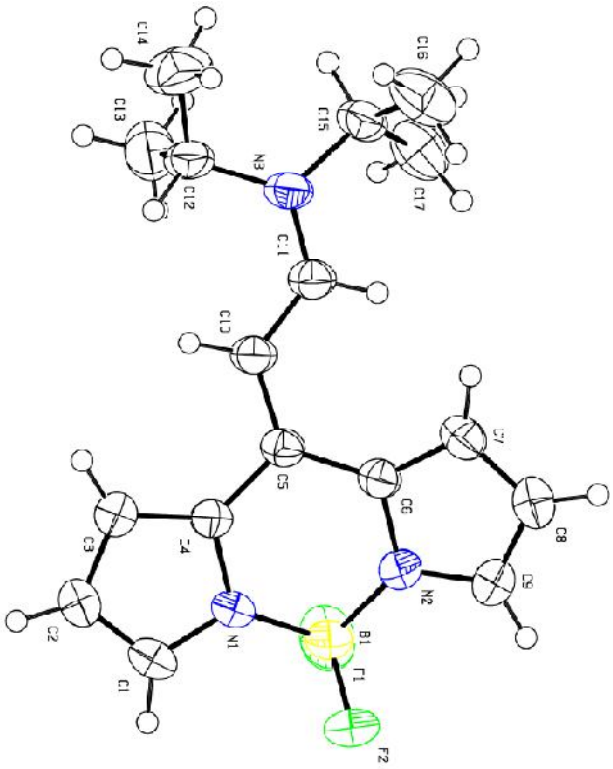


Figure S2. Crystal structure of BODIPY **4a**

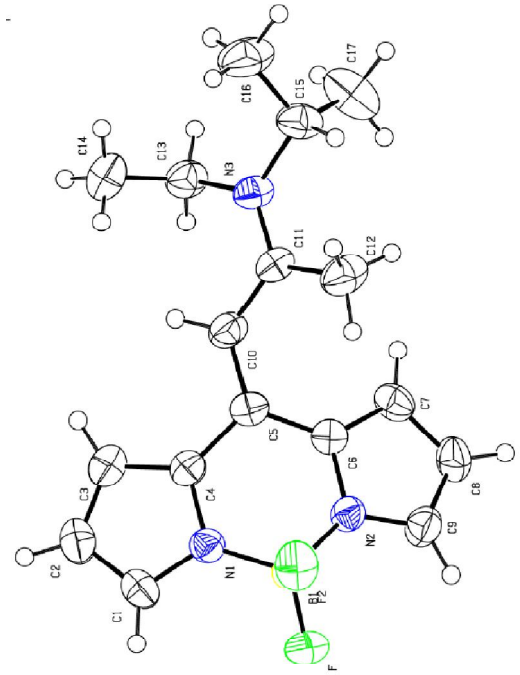


Figure S3. Crystal structure of BODIPY **4b**

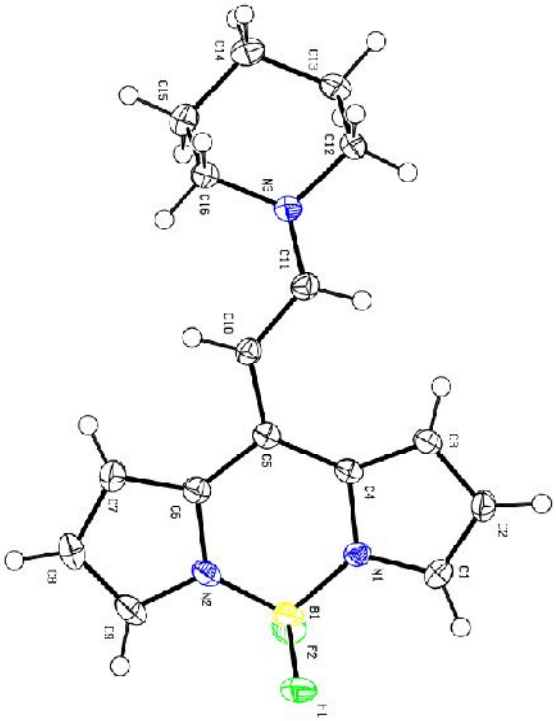
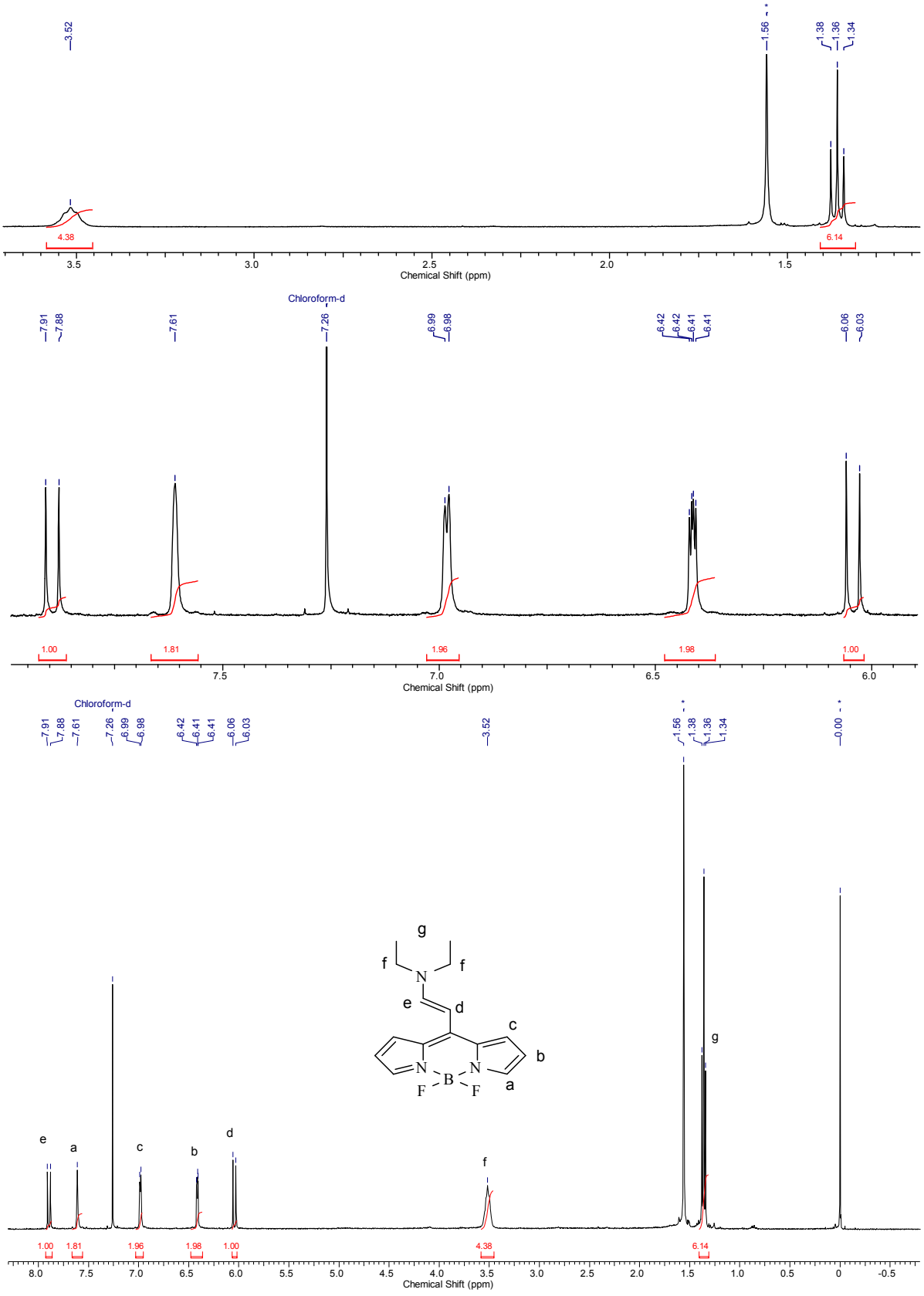
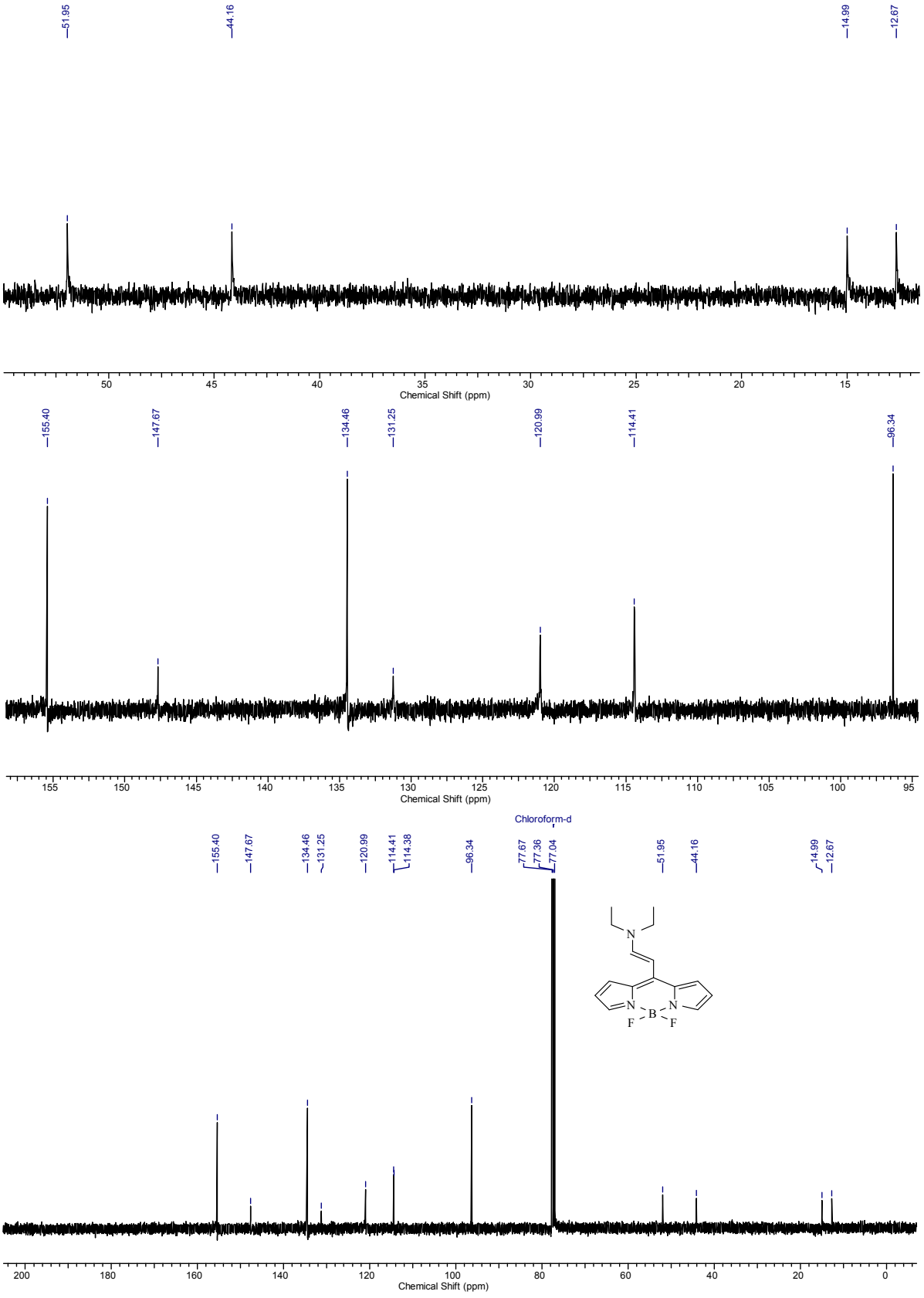


Figure S4. Crystal structure of BODIPY **5a**

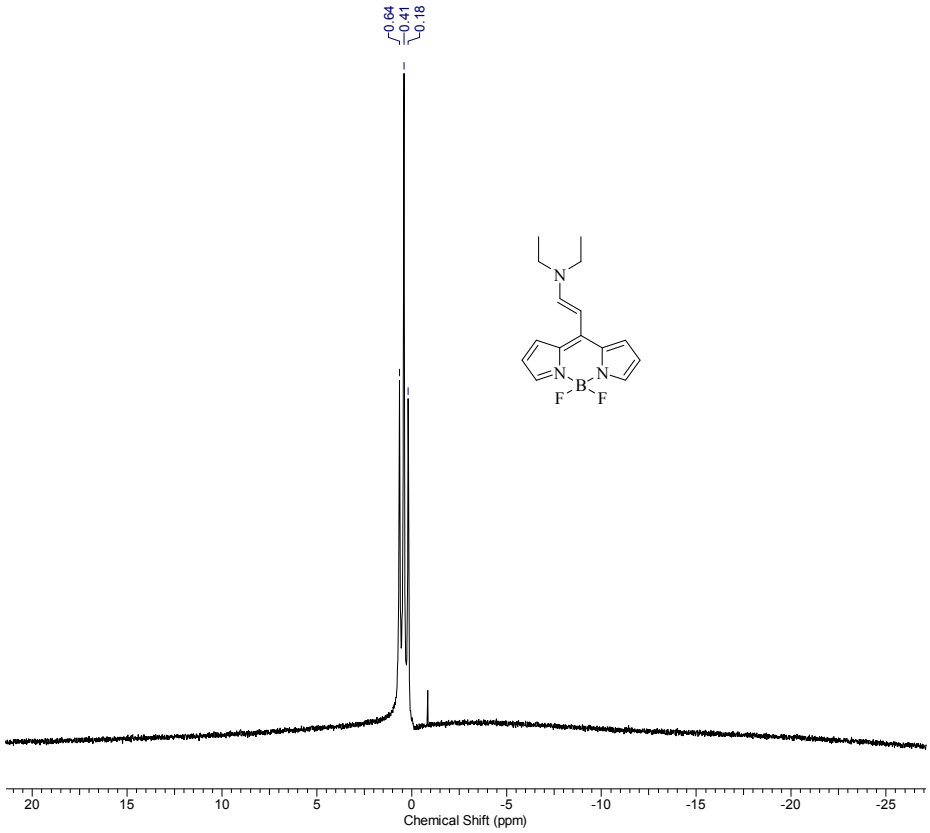
^{1}H NMR of BODIPY **2**



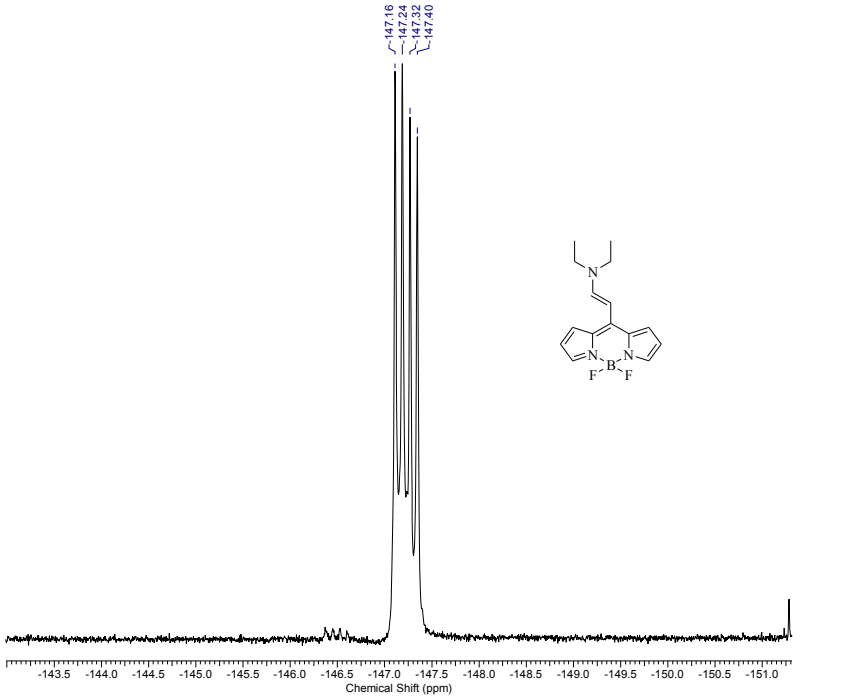
^{13}C NMR of BODIPY **2**



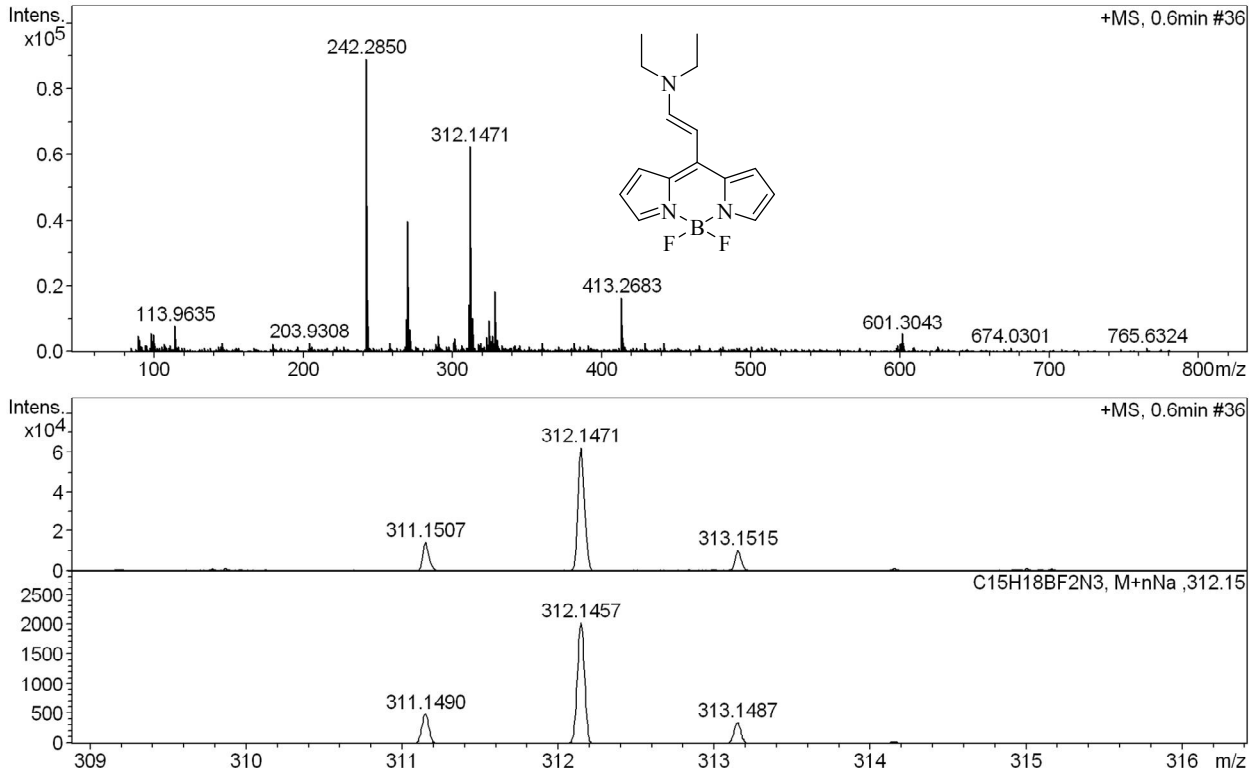
^{11}B NMR of BODIPY **2**



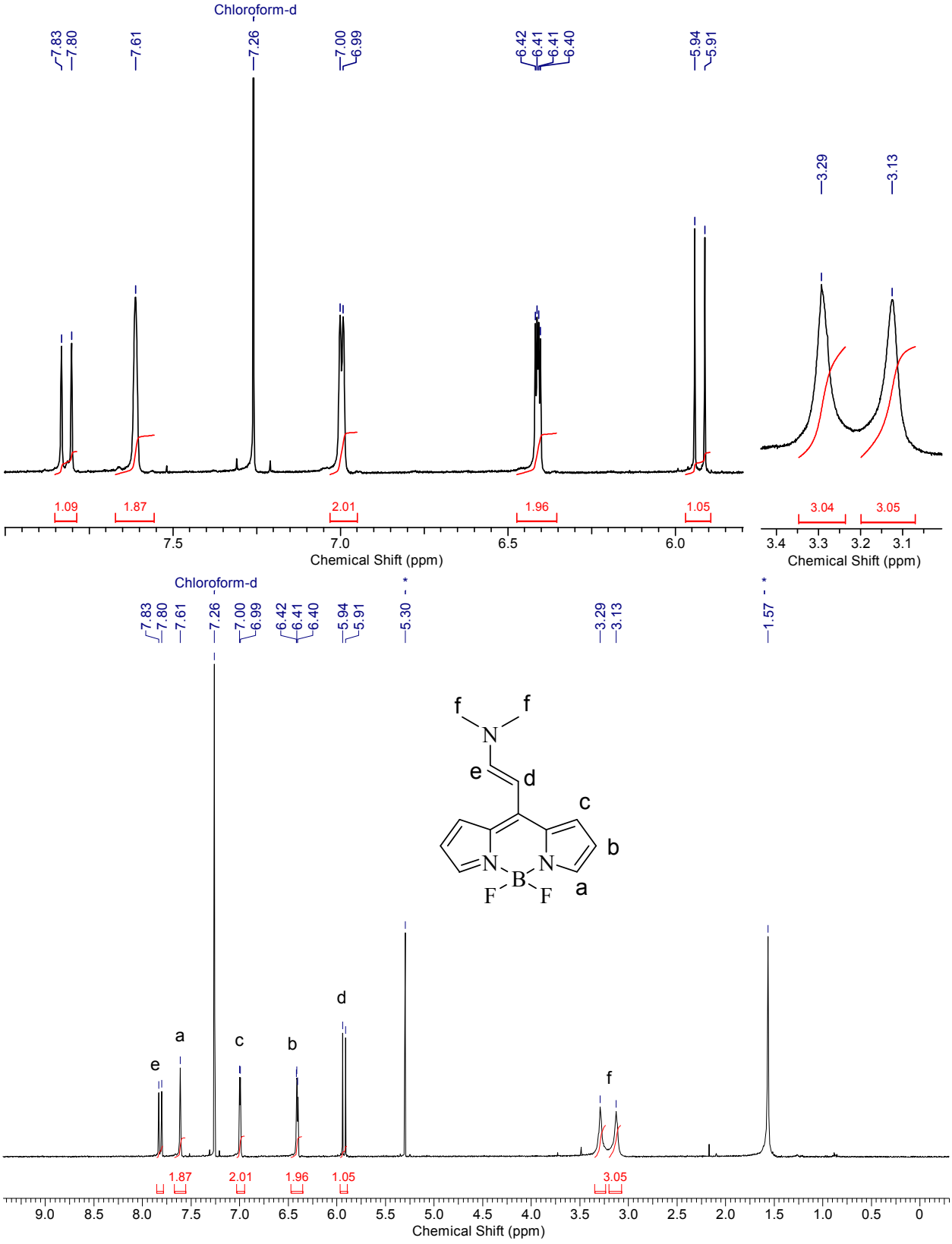
^{19}F NMR of BODIPY **2**



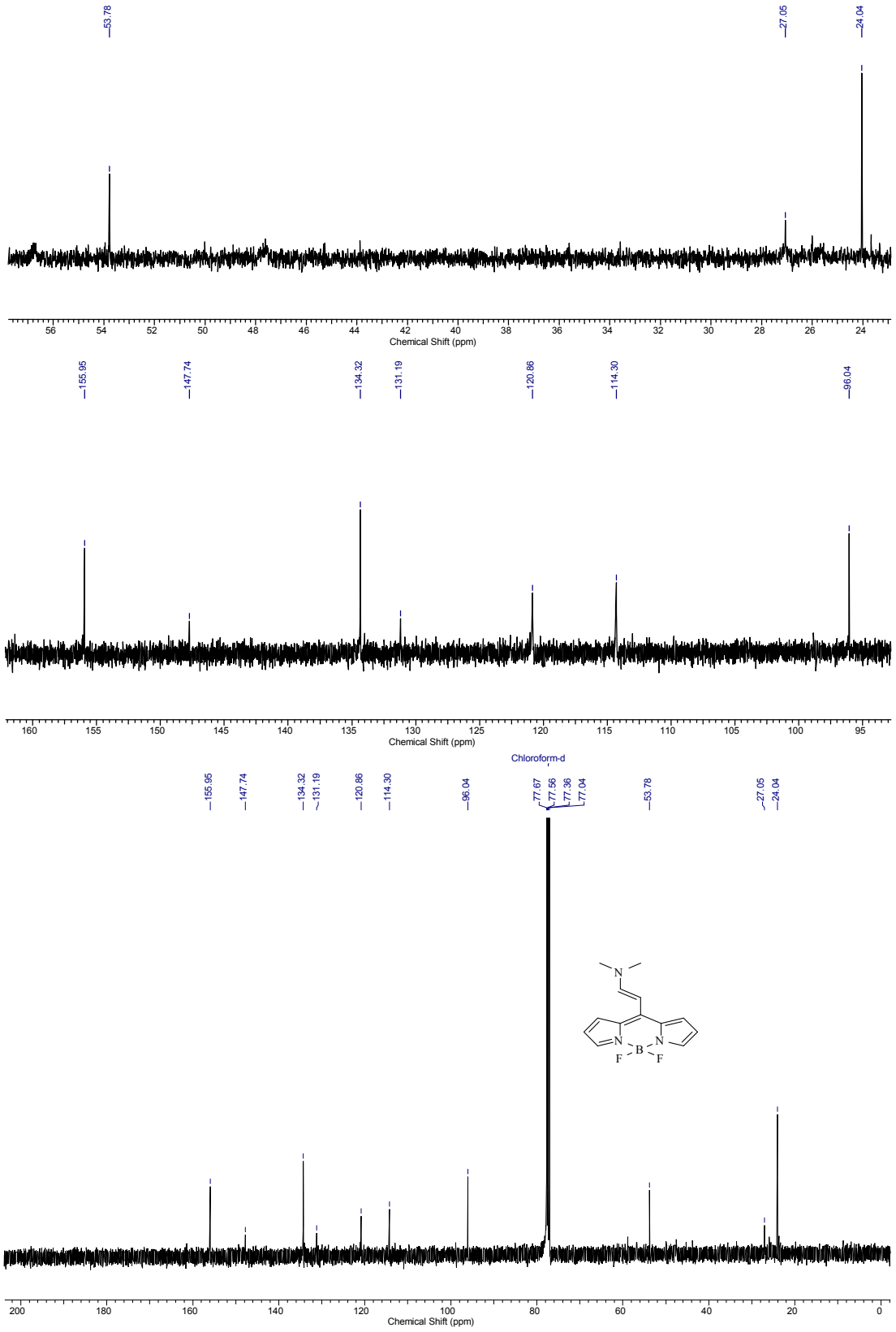
HRMS of BODIPY **2**



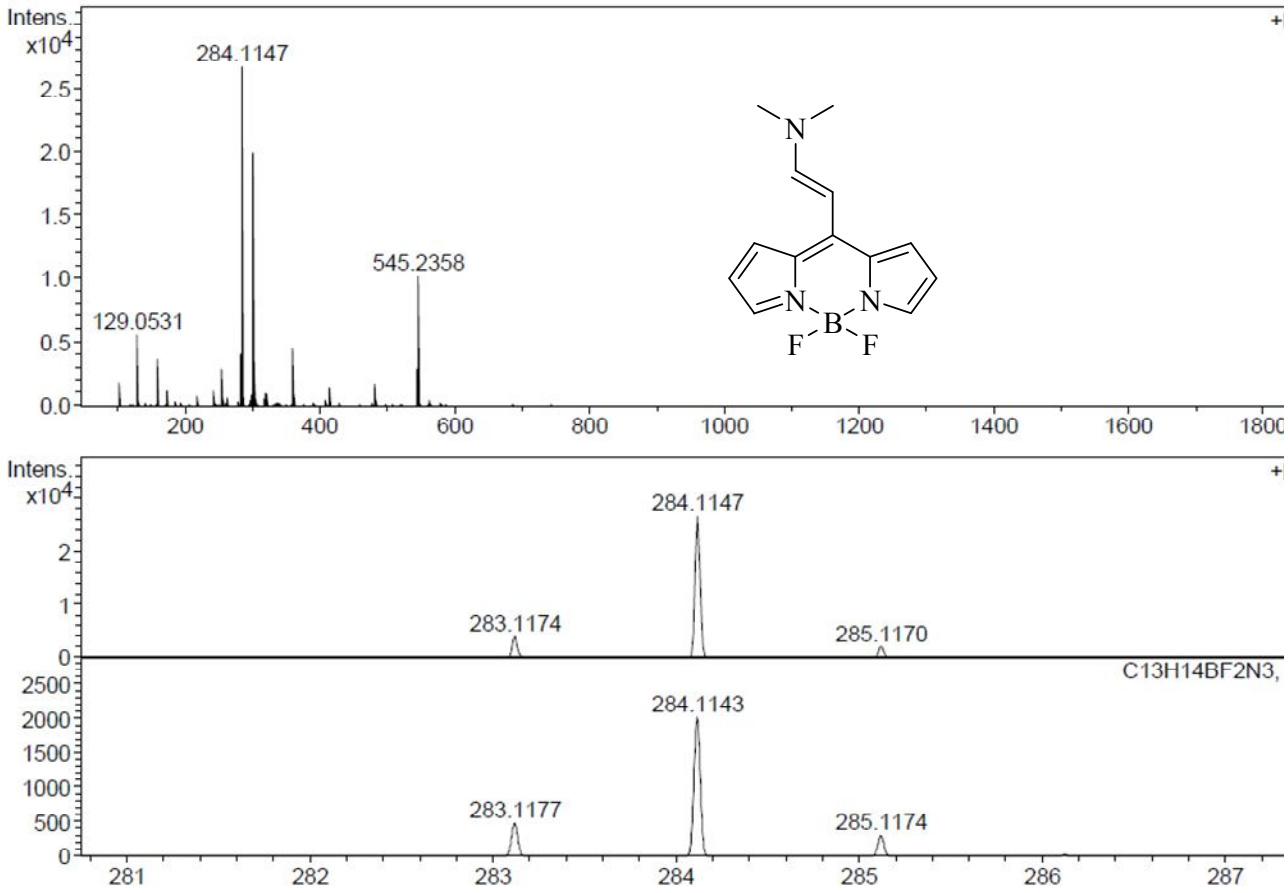
^{1}H NMR of BODIPY **3**



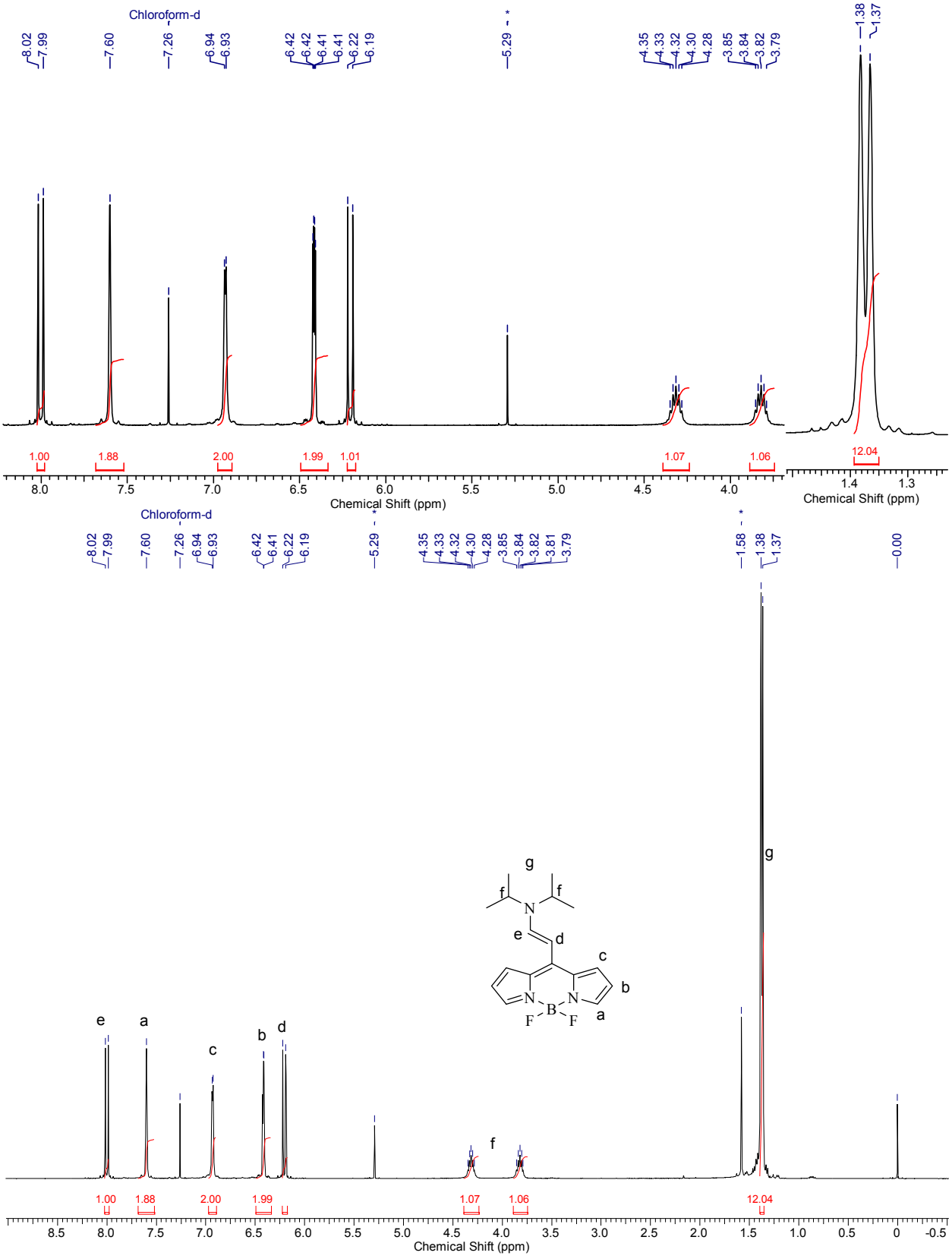
^{13}C NMR of BODIPY **3**



HRMS of BODIPY **3**



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



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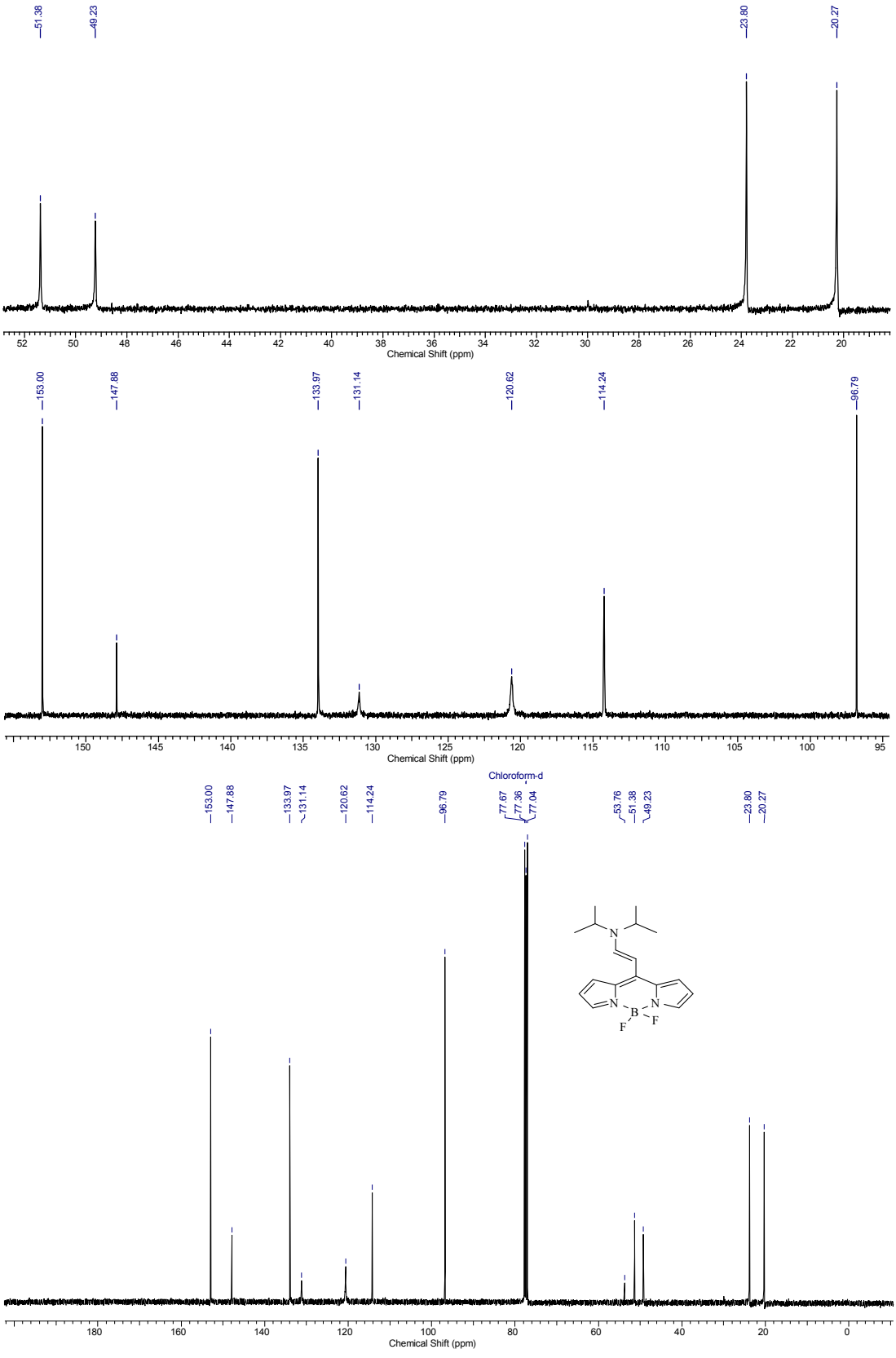
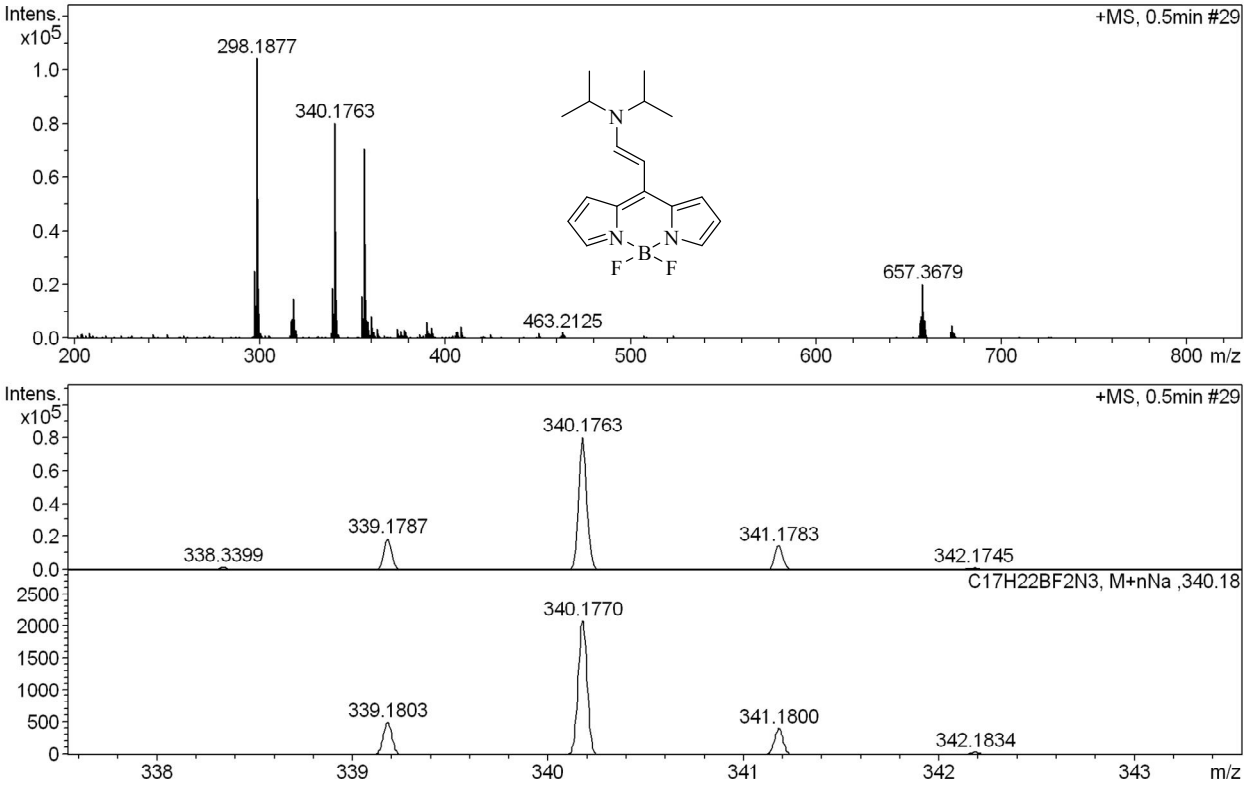
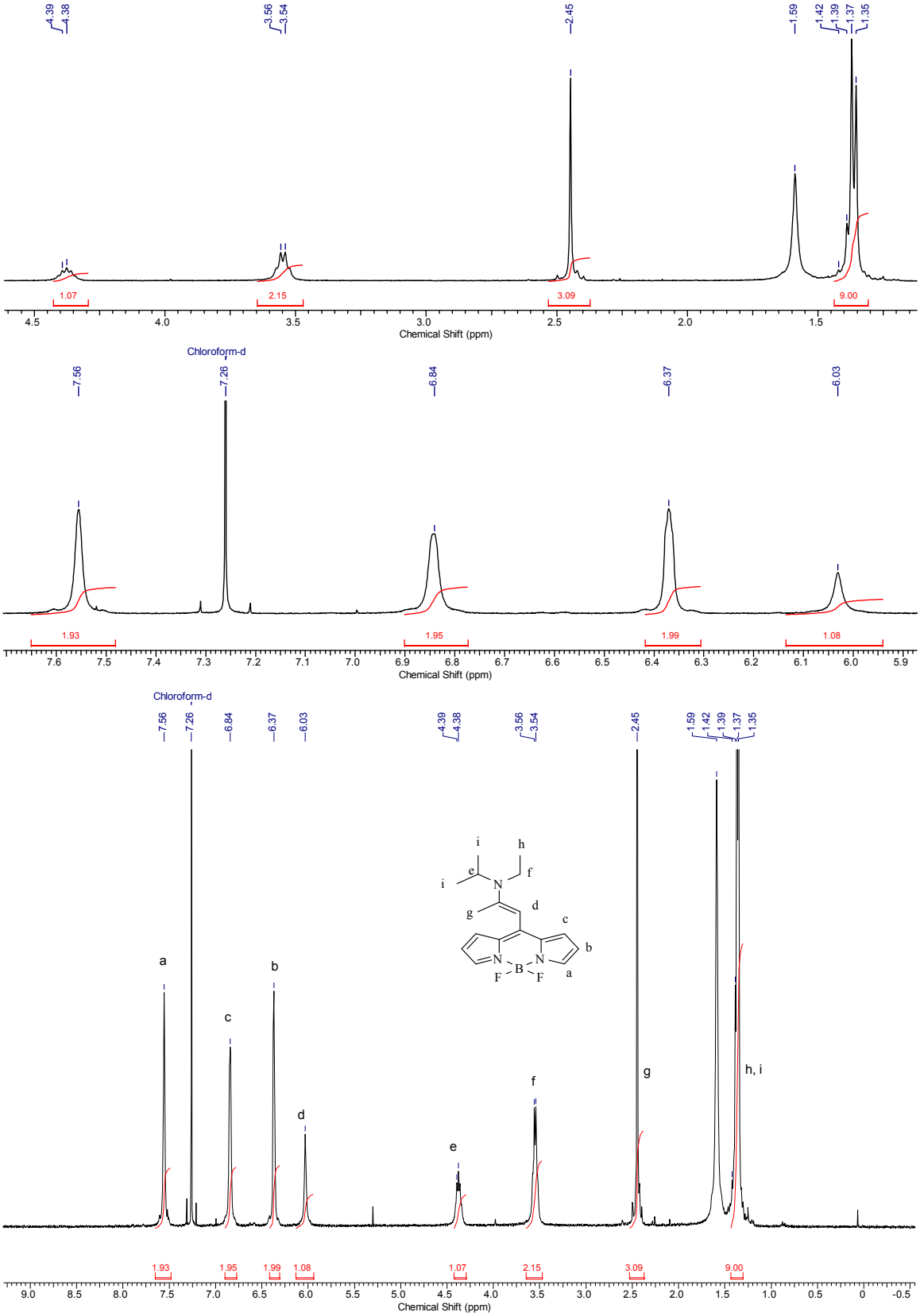


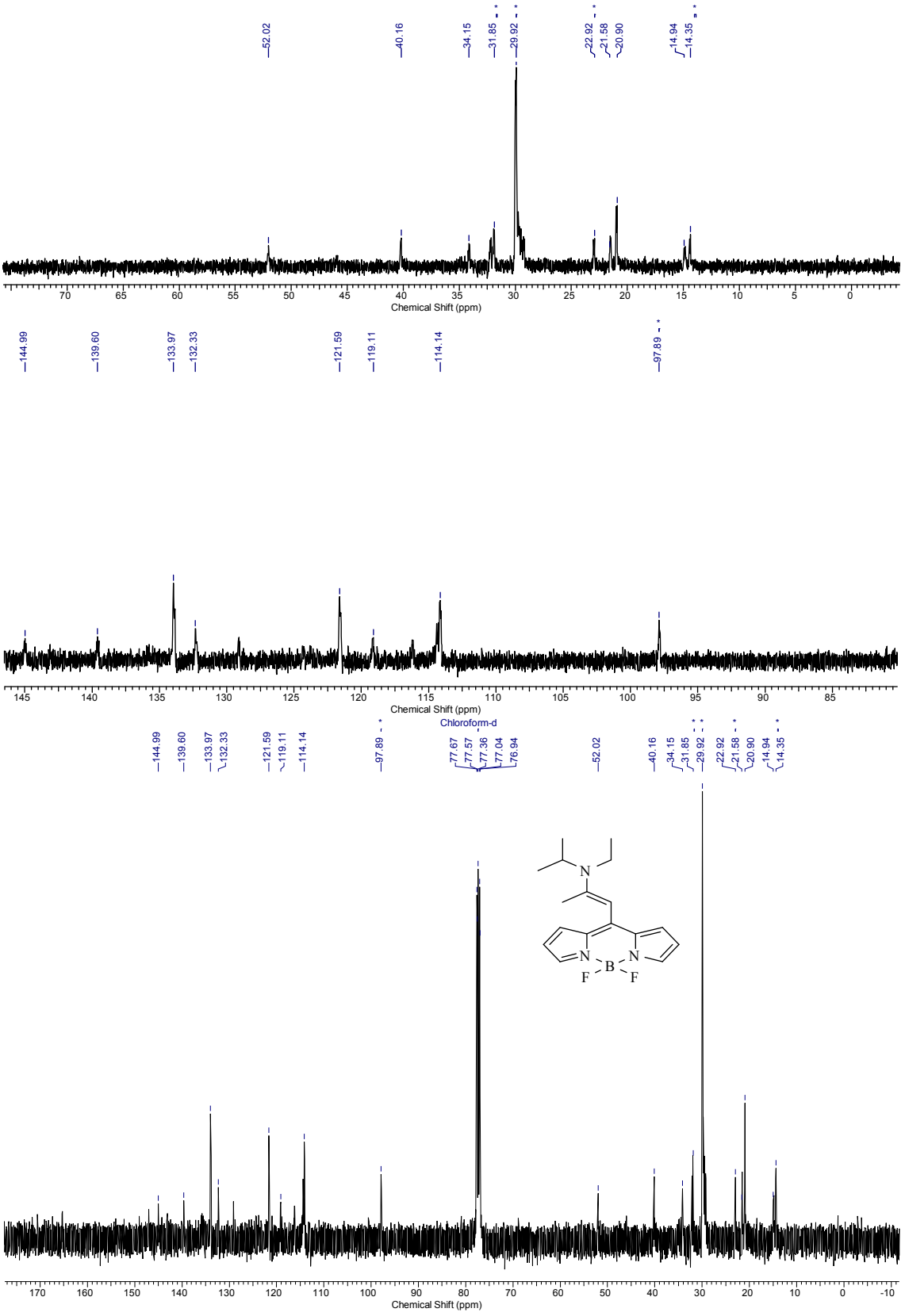
HRMS of BODIPY **4a**



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



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



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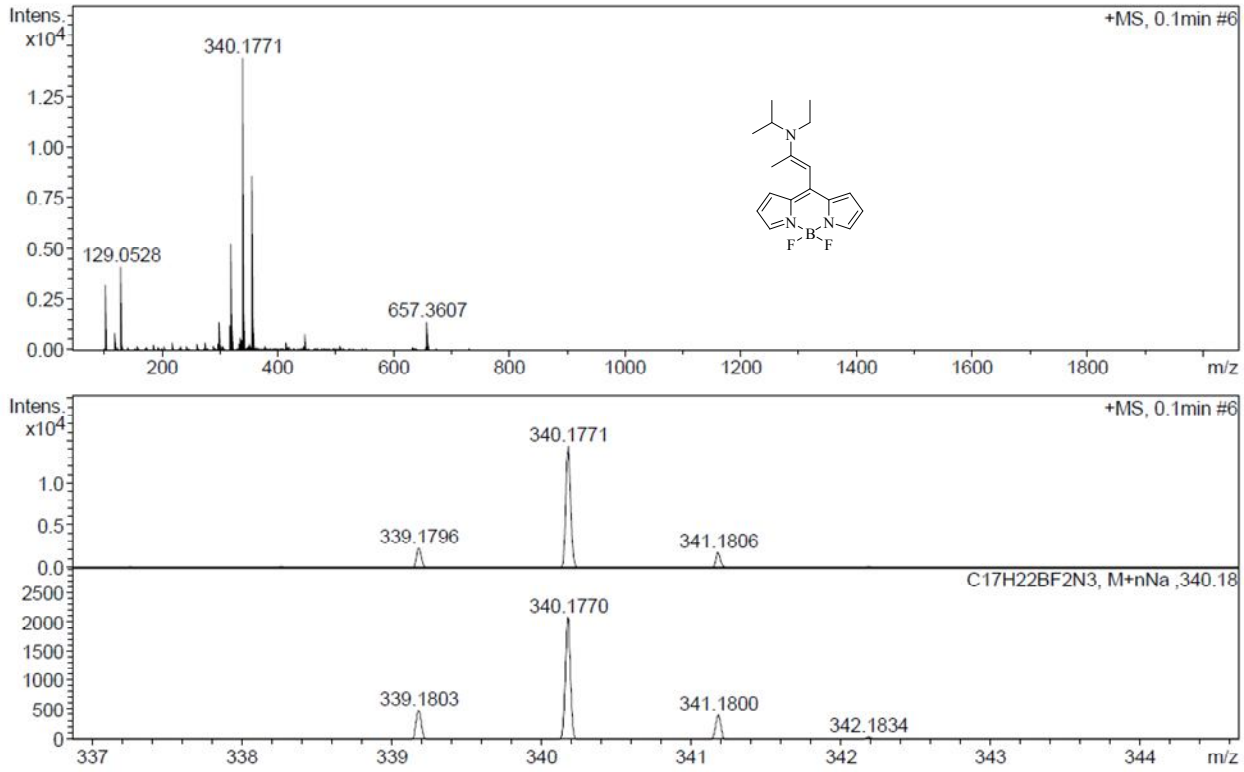
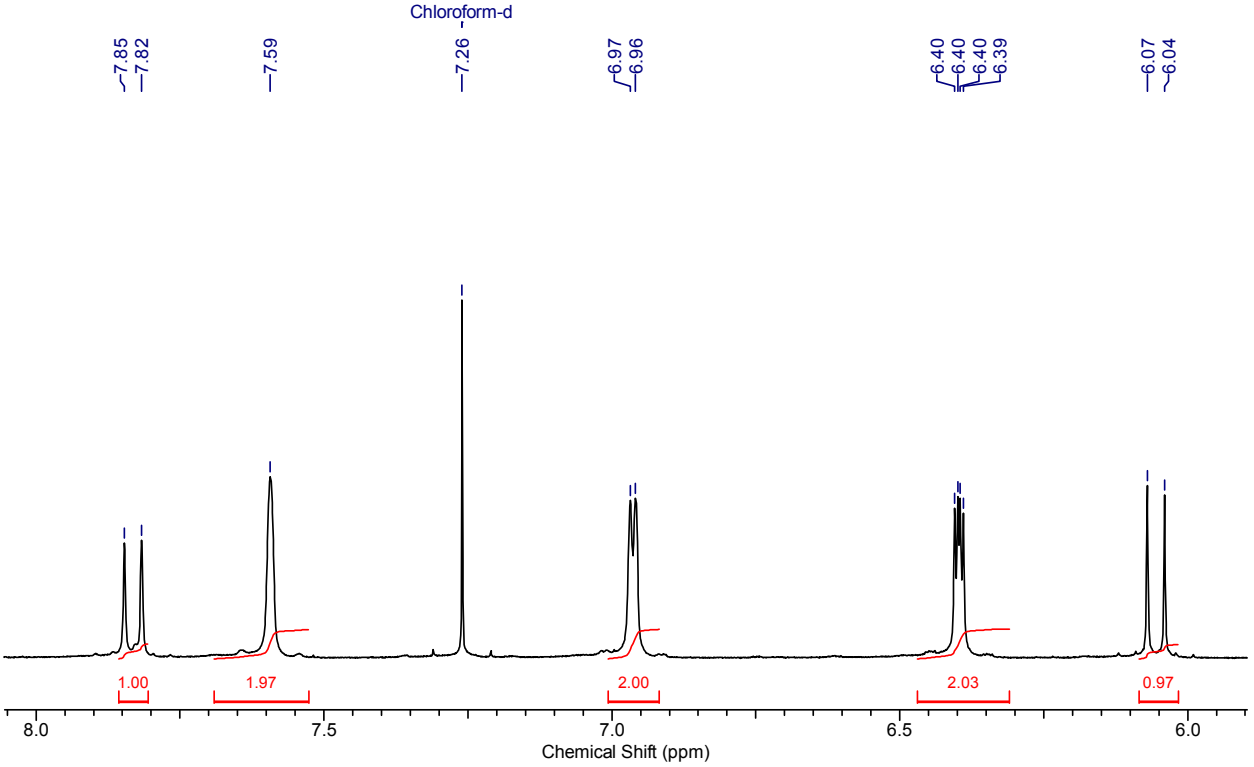
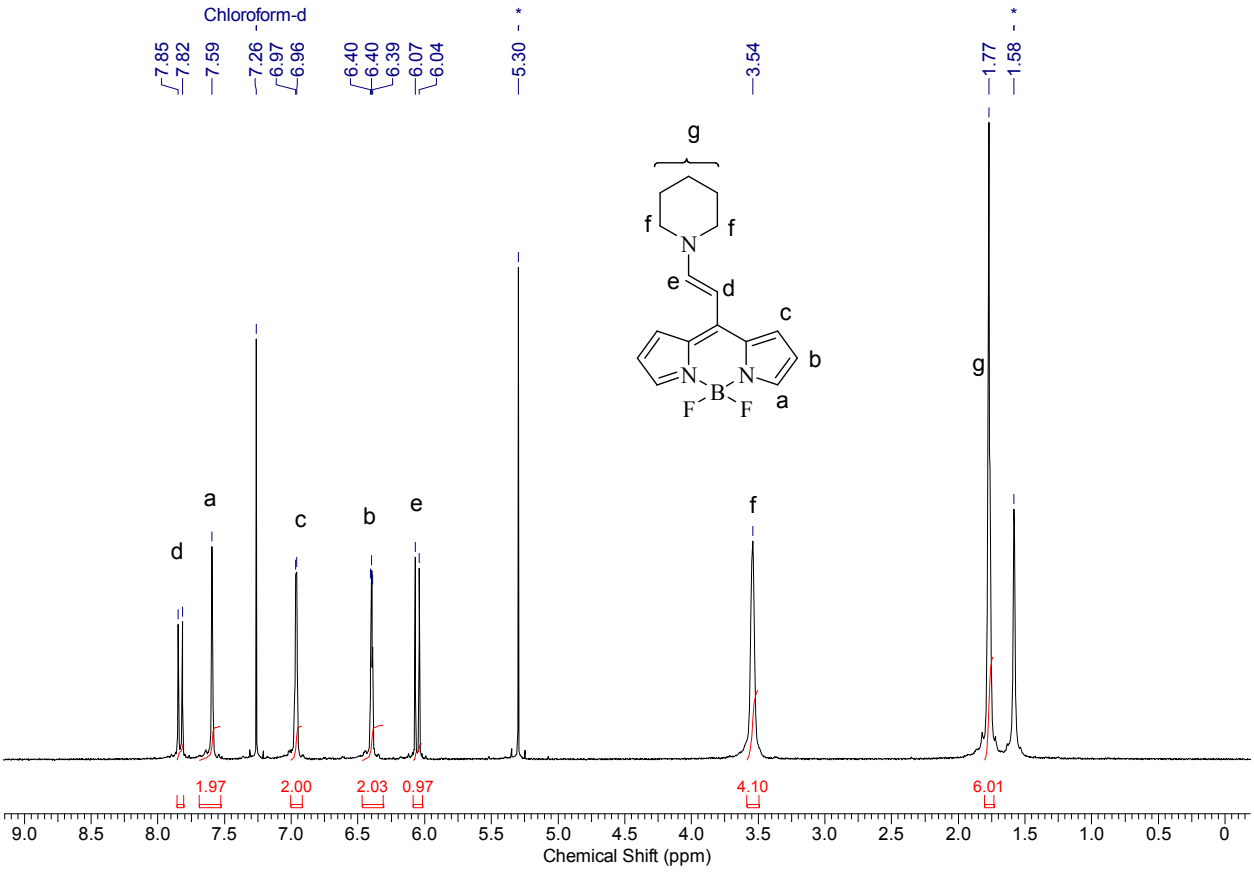
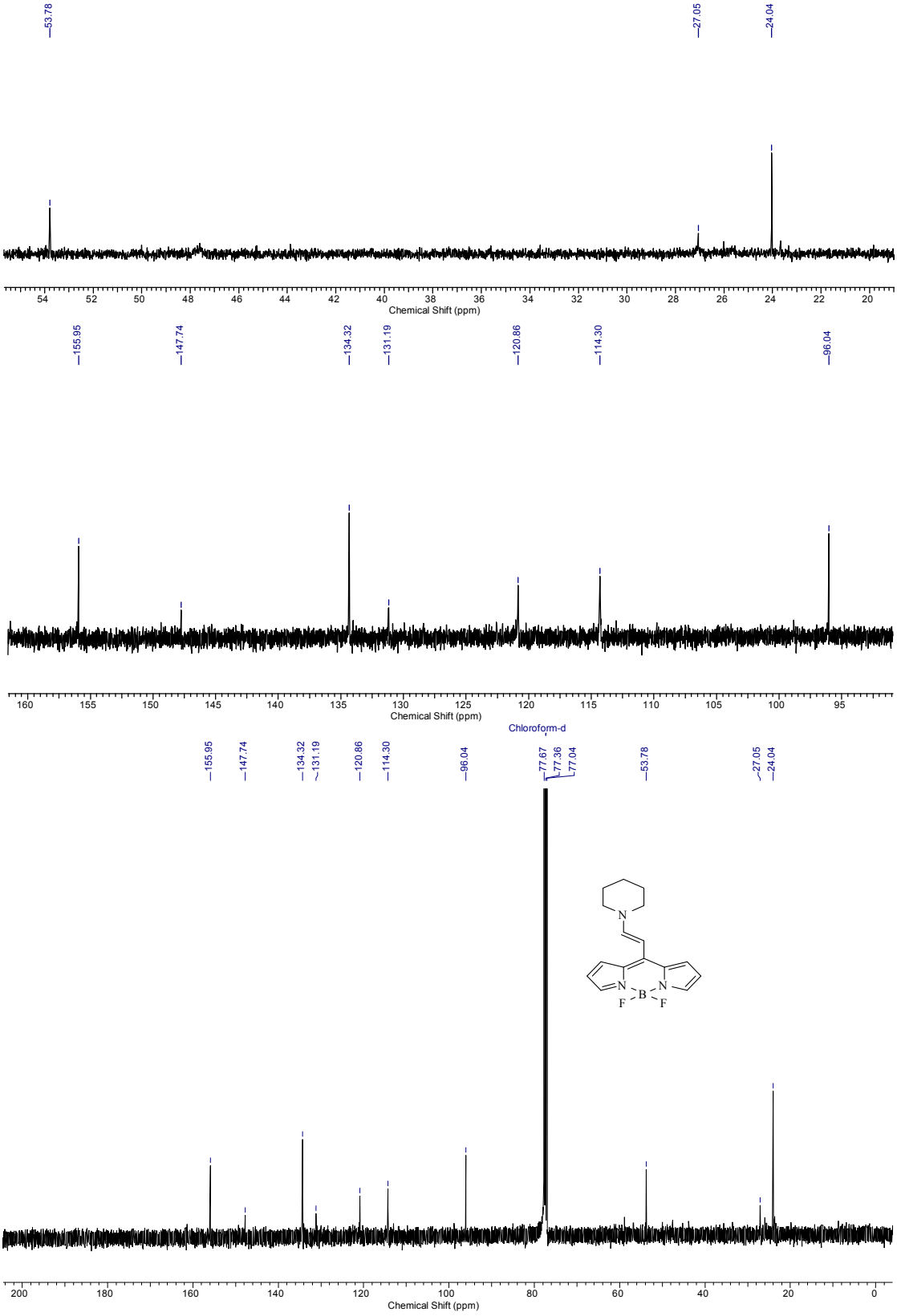


^{1}H NMR of BODIPY **5a**





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



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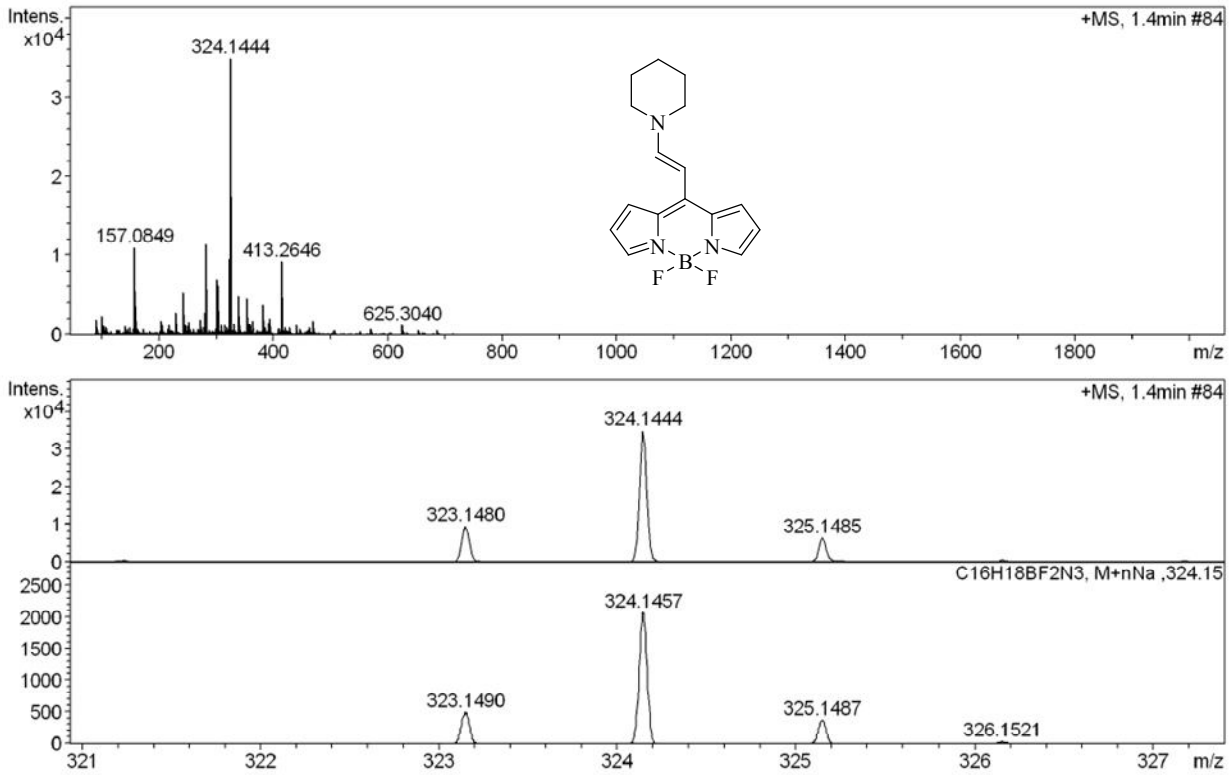
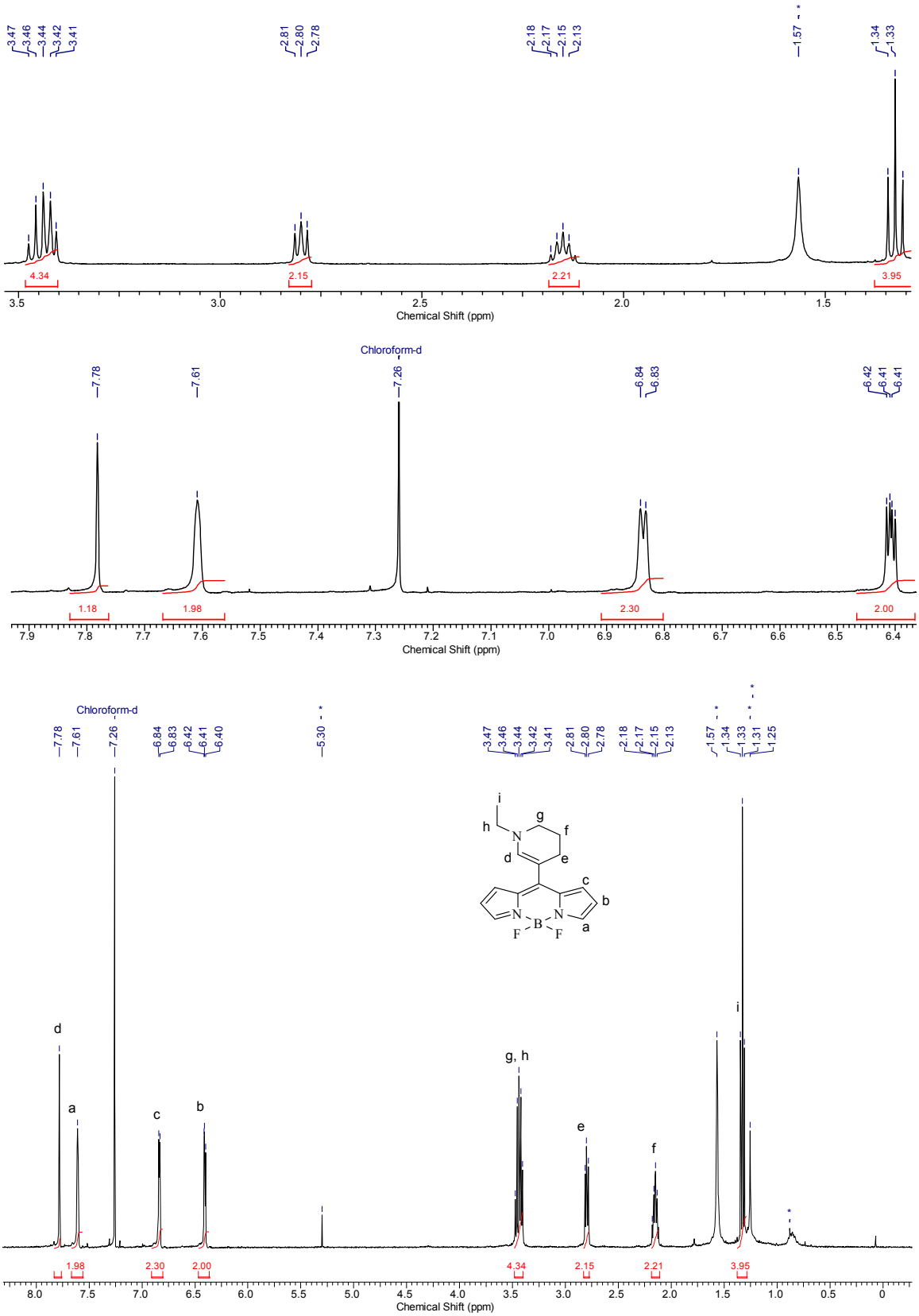
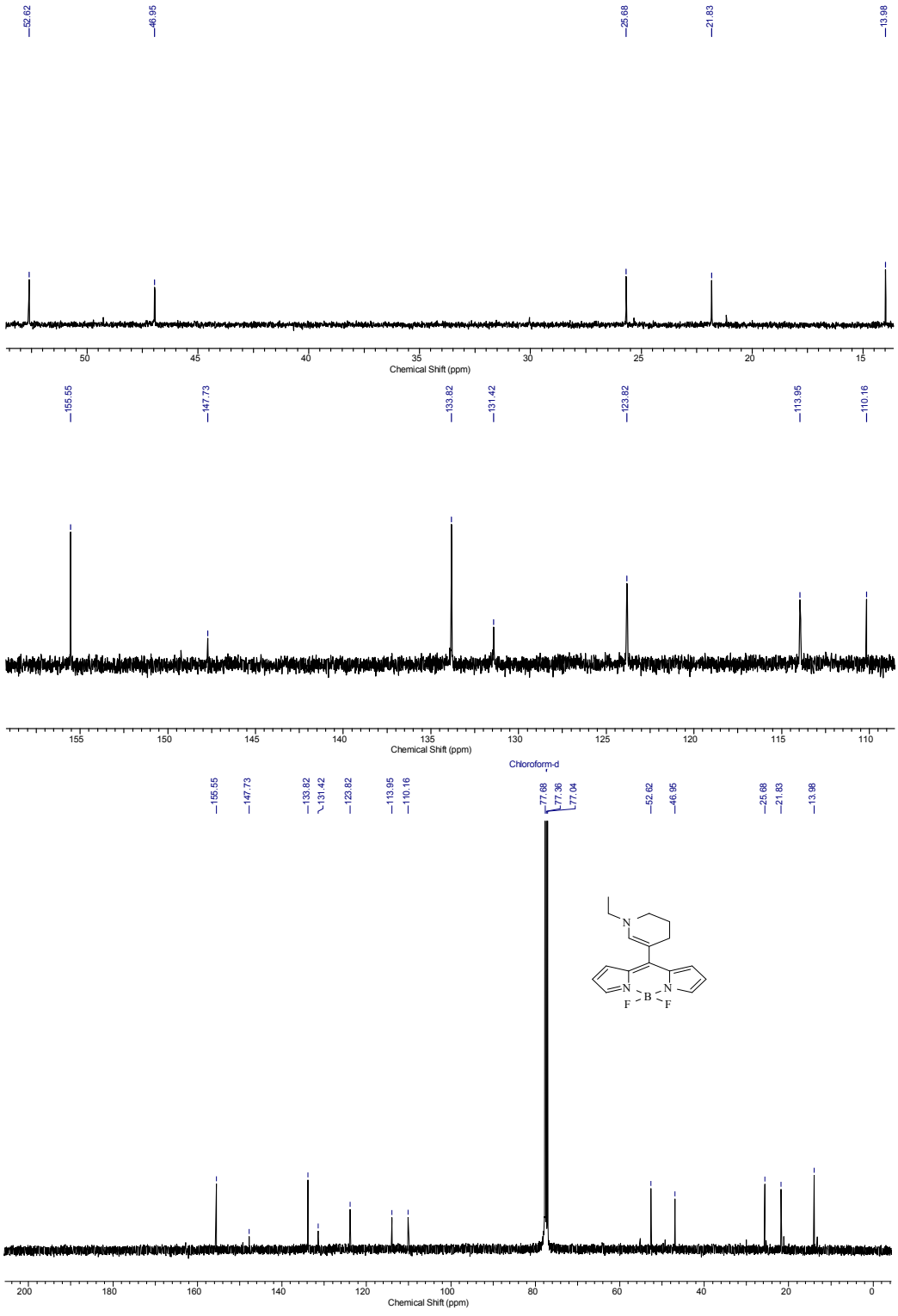


^{1}H NMR of BODIPY **5b**



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



HRMS of BODIPY **5b**