Supporting Information

Heteroatom connected ferrocenyl BODIPYs: synthesis, structure and properties

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EXPERIMENTAL SECTION

Electrochemical Characterizations

Electrochemical characterization of all compounds was done by cyclic voltametry (CV) and Differential pulse voltametry (DPV). Voltamograms were recorded on a CHI620D electrochemical analyzer using glassy carbon as working electrode, Pt wire as the counter electrode, and saturated calomel electrode as the reference electrode (SCE). The scan speed was 100 mVS^{-1}. A solution of tetrabutylammonium- hexafluorophosphate ($TBAPF_6$) in anhydrous CH_2Cl_2 (0.1 M) was employed as the supporting electrolyte. The half-wave oxidation potentials were corrected to ferrocene as per IUPAC guidelines.[1]

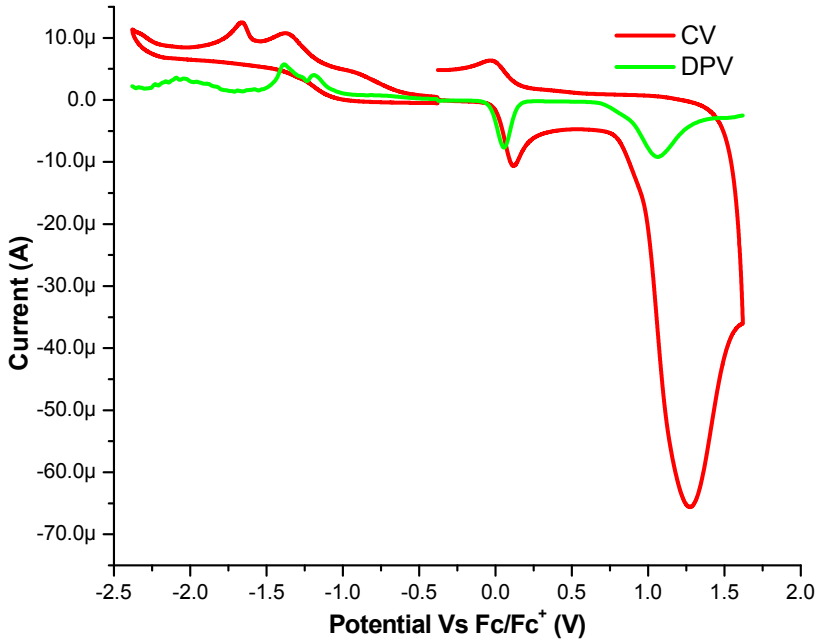


Figure S1. CV and DPV plots of Heteroatom connectedferrocenyl BODIPY **2a.**

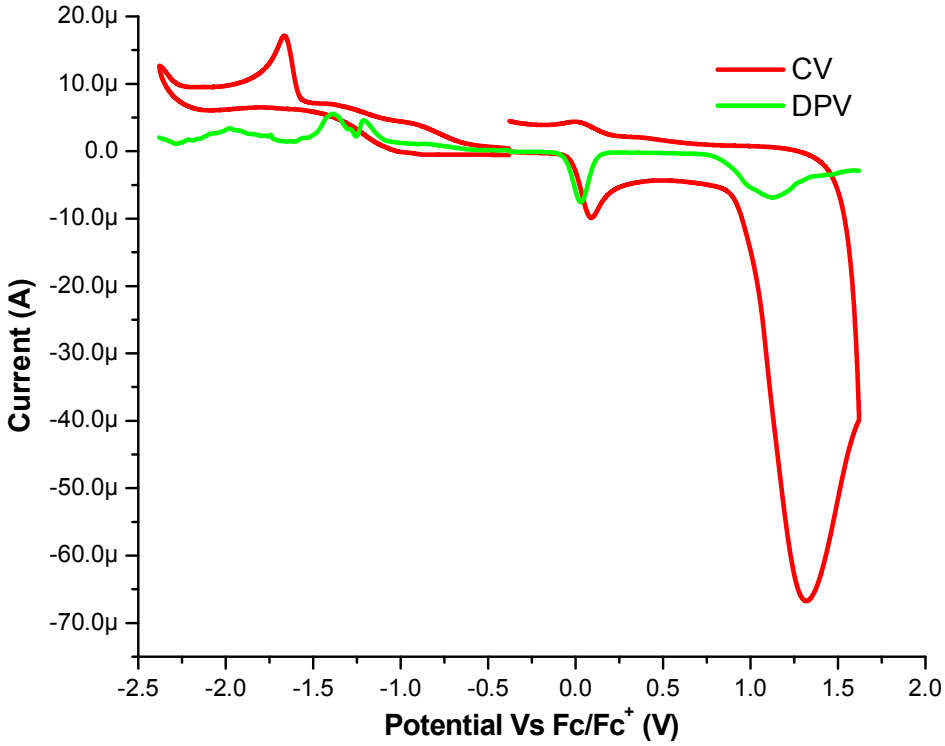


Figure S2. CV and DPV plots of heteroatom connected ferrocenyl BODIPY **2b.**

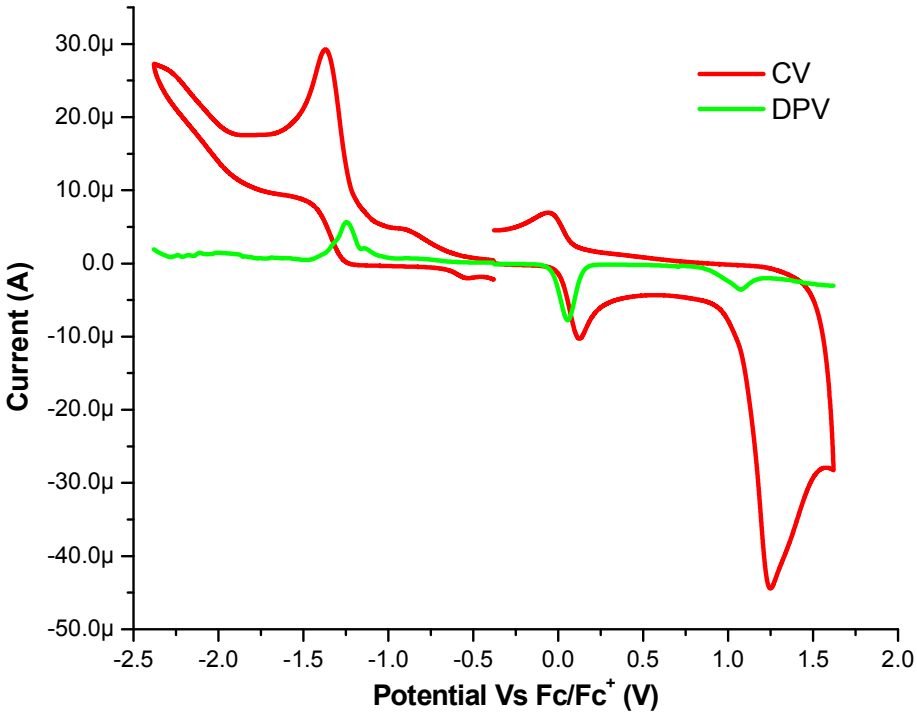


Figure S3. CV and DPV plots of heteroatom connected ferrocenyl BODIPY **3c.**

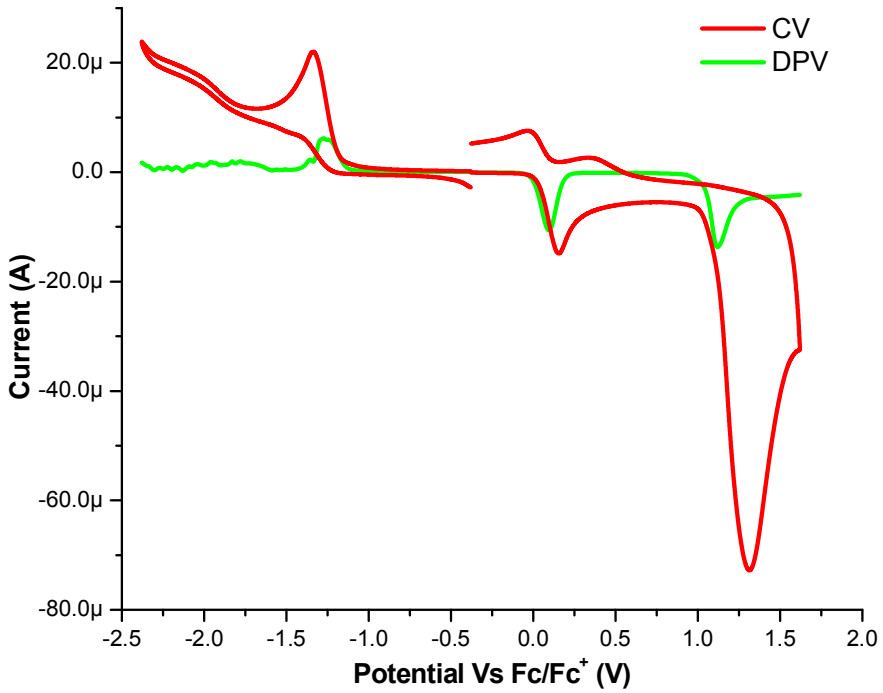


Figure S4. CV and DPV plots of heteroatom connected ferrocenyl BODIPY **3d.**

Single Crystal X-ray Diffraction Studies.

Single crystal X-ray structural studies of **2a, 2b, 3c** and **3d** were performed on a 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 CCDC numbers 973244, 973245, 973246 and 973247 contain

the supplementary crystallographic data for **2a, 2b, 3c** and **3d** 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	**2a**	**2b**	**3c**	**3d**
Empirical formula	$C_{50}H_{40}B_2F_4Fe_2N_6$	$C_{50}H_{40}B_2F_4Fe_2N_6$	$C_{50}H_{38}B_2F_4Fe_2N_4O_2$	$C_{50}H_{38}B_2F_4Fe_2N_4O_2$
Formula weight	934.20	934.20	936.16	936.16
Temperature/K	150(2)	150(2)	150(2)	150(2)
Crystal system	Monoclinic	Triclinic	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P2_12_12_1$
Unit cell dimensions				
a/Å	20.5133(6)	11.3486(3)	7.88490(10)	11.0633(4)
α/°	90	88.981(2)	90	90
b/ Å	15.1810(4)	13.7482(3)	10.0374(2)	14.4288(6)
β/°	110.808(3)	88.659(2)	94.228(2)	90
c/ Å	14.5953(4)	13.9193(4)	26.0231(5)	26.8755(13)
γ/°	90	69.607(2)	90	90
Volume/ $Å^3$	4248.7(2)	2034.95(9)	2053.96(6)	4290.1(3)
Z	4	2	2	4
Calculated density/ Mg/m^3	1.460	1.525	1.514	1.449
Absorption coefficient/mm^{-1}	0.745	0.778	0.773	5.957
F(000)	1920	960	960	1920
Crystal size/mm	0.23 x 0.18 x 0.13	0.36 x 0.32 x 0.24	0.23 x 0.15 x 0.12	0.33 x 0.27 x 0.21
θ range from data collection/°	3.10 to 25.00	3.16 to 25.00	3.11 to 25.00	3.29 to 71.89
Reflections collected/unique	27023 / 7447 [R(int) = 0.0450]	16060 / 7157 [R(int) = 0.0146]	16172 / 3617 [R(int) = 0.0275]	30197 / 8322 [R(int) = 0.0949]
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Data/restraints/parameters	7447 / 0 / 577	7157 / 0 / 577	3617 / 0 / 289	8322 / 0 / 578
Goodness-of-fit on F^2	1.099	1.109	1.054	0.987
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0450, wR_2 = 0.1082	R_1 = 0.0293, wR_2 = 0.0759	R_1 = 0.0270, wR_2 = 0.0675	R_1 = 0.0619, wR_2 = 0.1514
R indices (all data)	R_1 = 0.0618, wR_2 = 0.1202	R_1 = 0.0309, wR_2 = 0.0768	R_1 = 0.0284, wR_2 = 0.0685	R_1 = 0.0956, wR_2 = 0.1823
Largest diff. peak and hole/e $Å^{-3}$	0.370 and -0.323	0.383 and -0.378	0.288 and -0.319	0.743 and -0.696
CCDC number	973244	973245	973246	973247

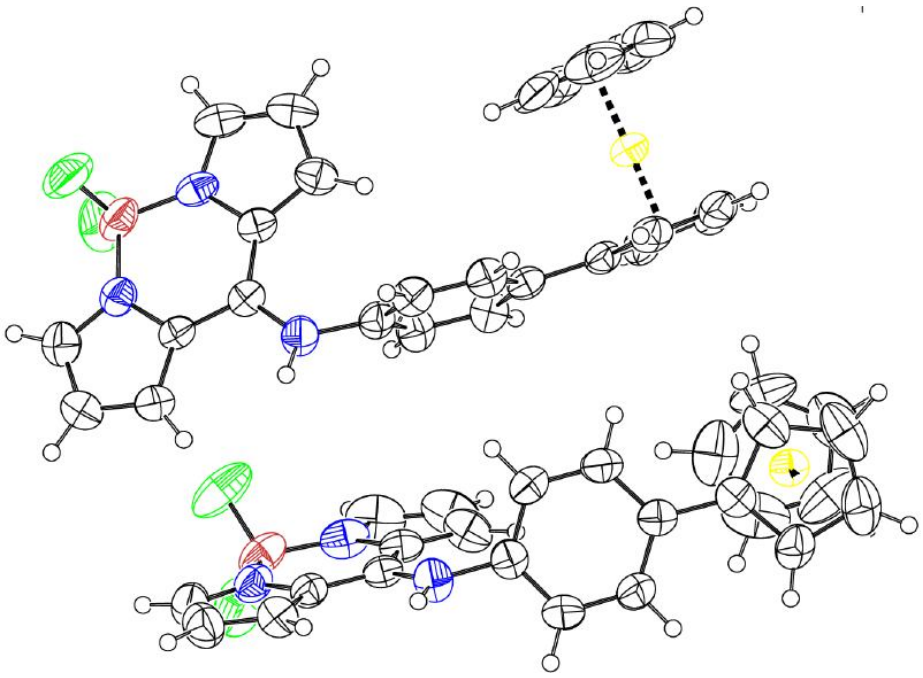


Figure S5. Crystal structure of heteroatom connected ferrocenyl BODIPY **2a**

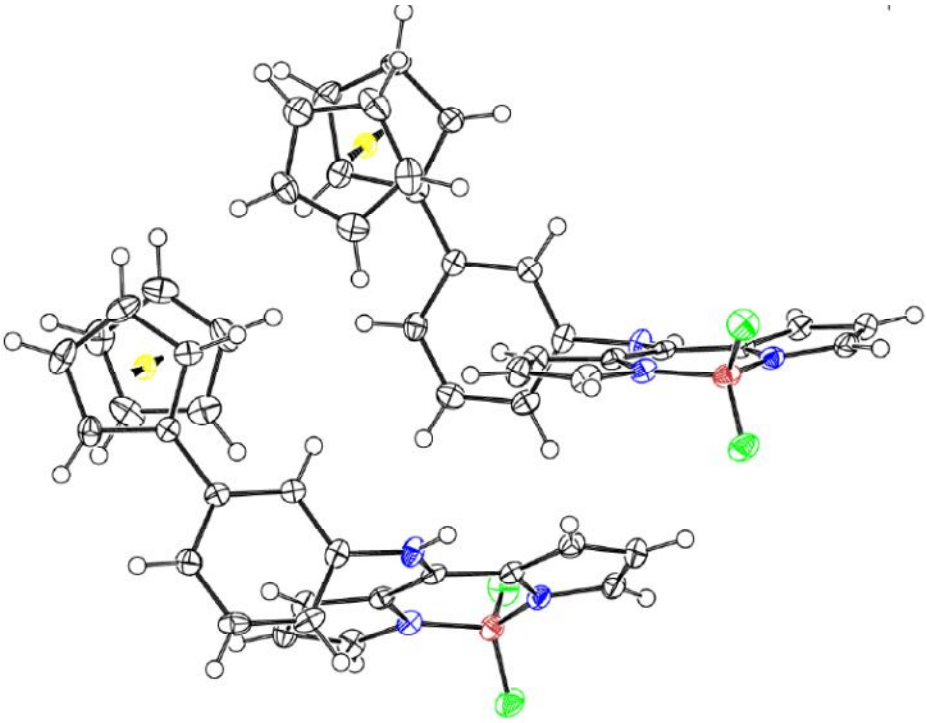


Figure S6. Crystal structure of heteroatom connected ferrocenyl BODIPY **2b**

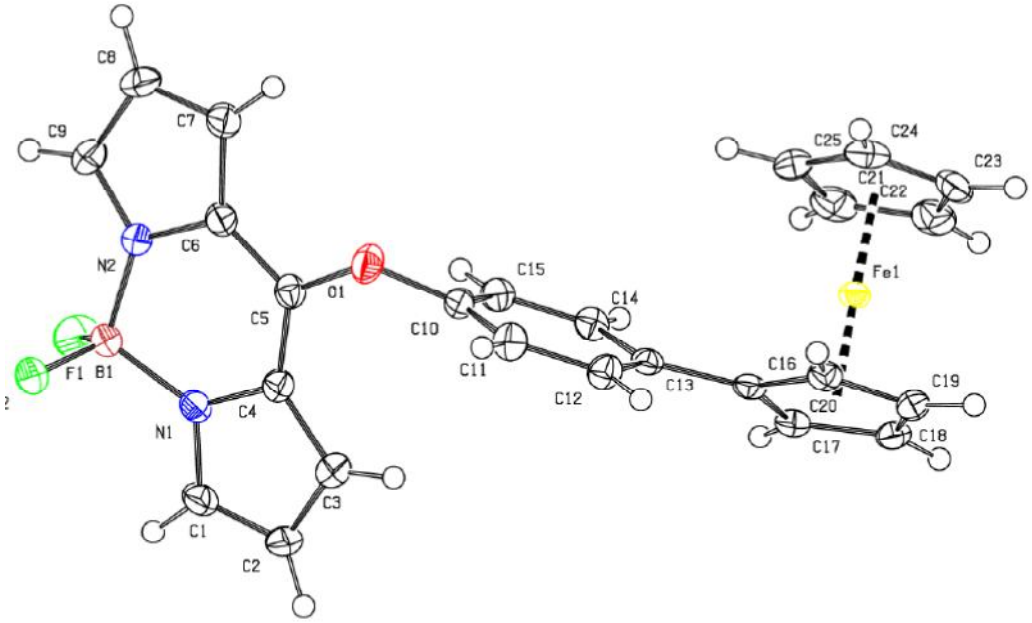


Figure S7. Crystal structure of heteroatom connected ferrocenyl BODIPY **3c**

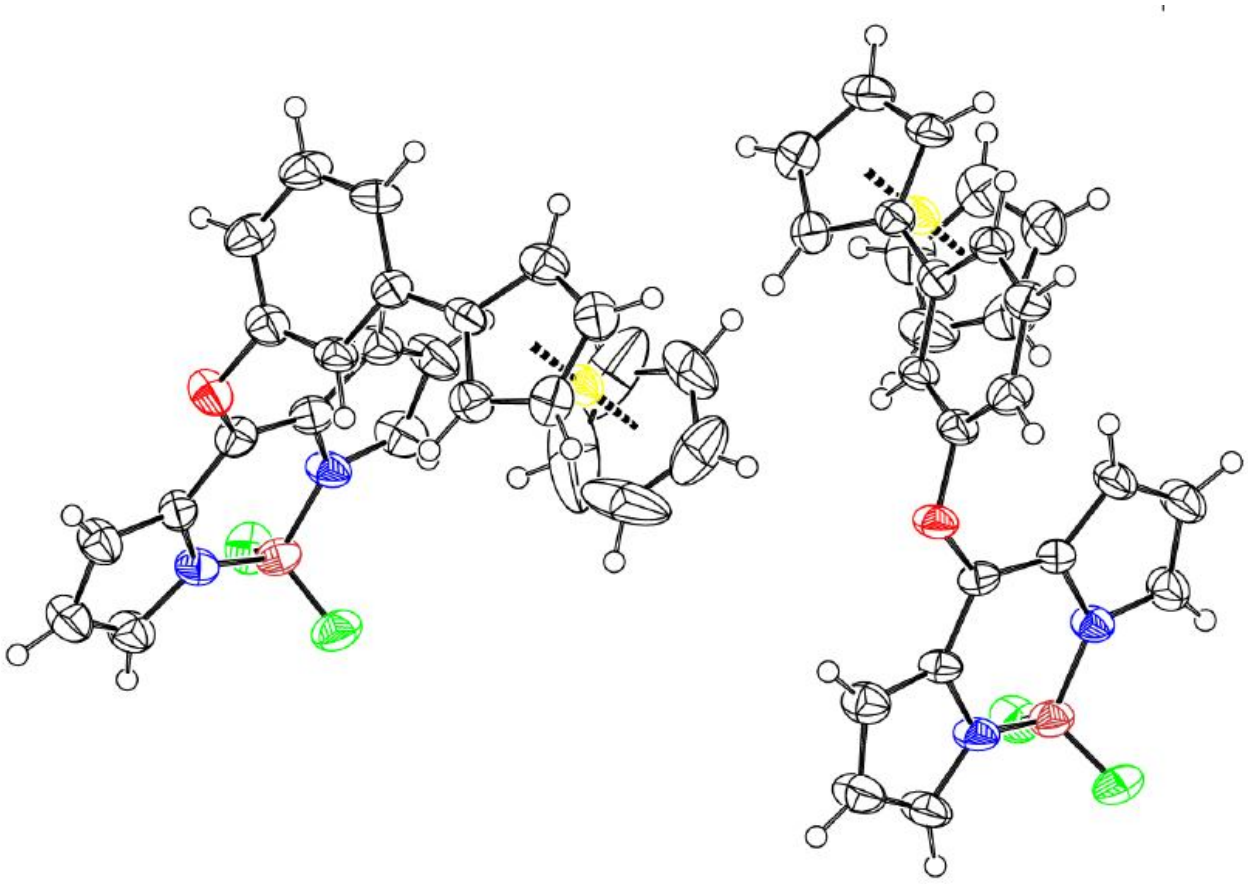


Figure S8. Crystal structure of heteroatom connected ferrocenyl BODIPY **3d**

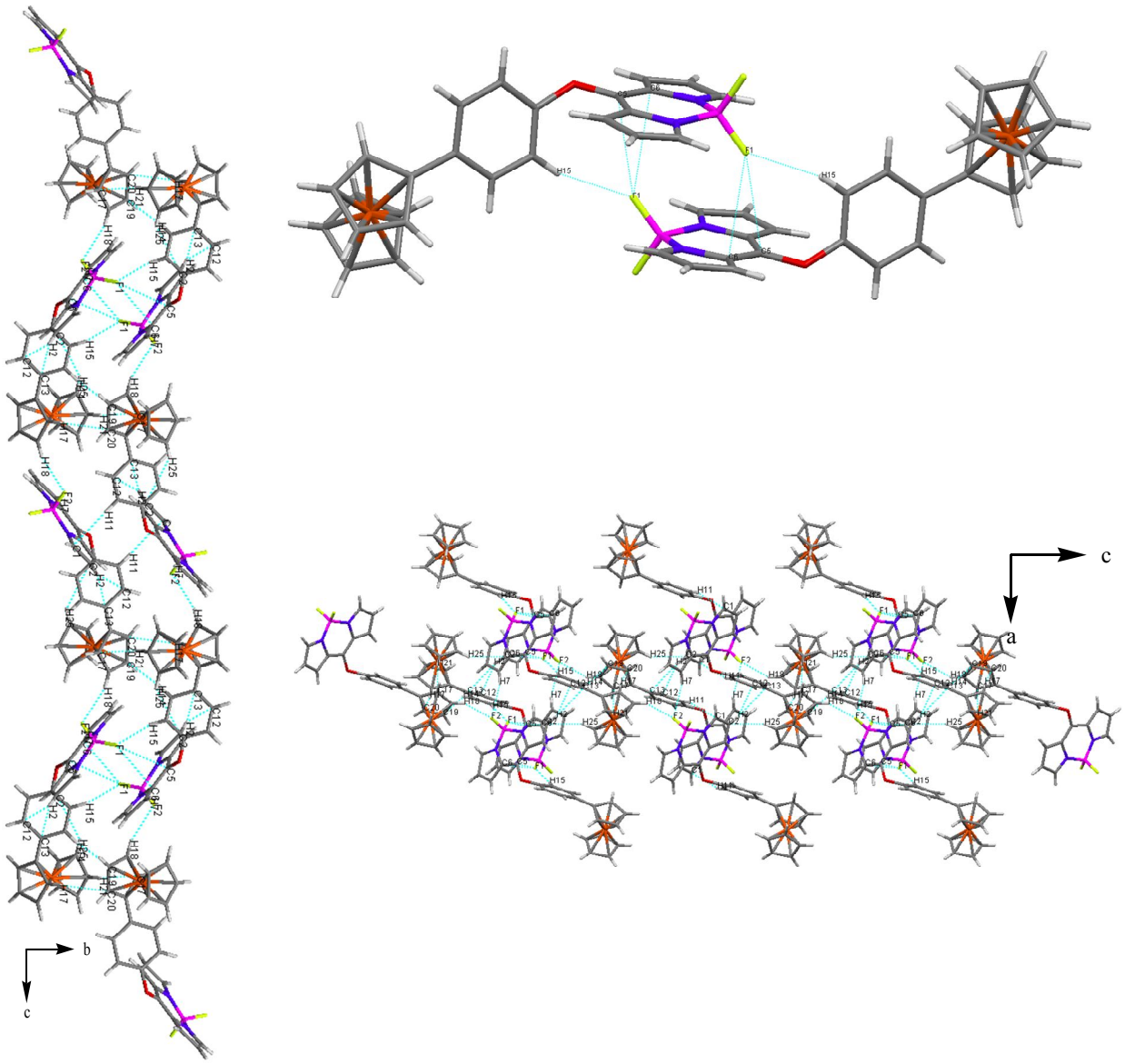


Figure S9. Packing diagram of the heteroatom connected ferrocenyl BODIPY **3c**.

DFT Calculations.

Calculation method: B3LYP/6-31G** for C, N, B, F, H, O and Lanl2DZ for Fe level with Gaussian 09[2]

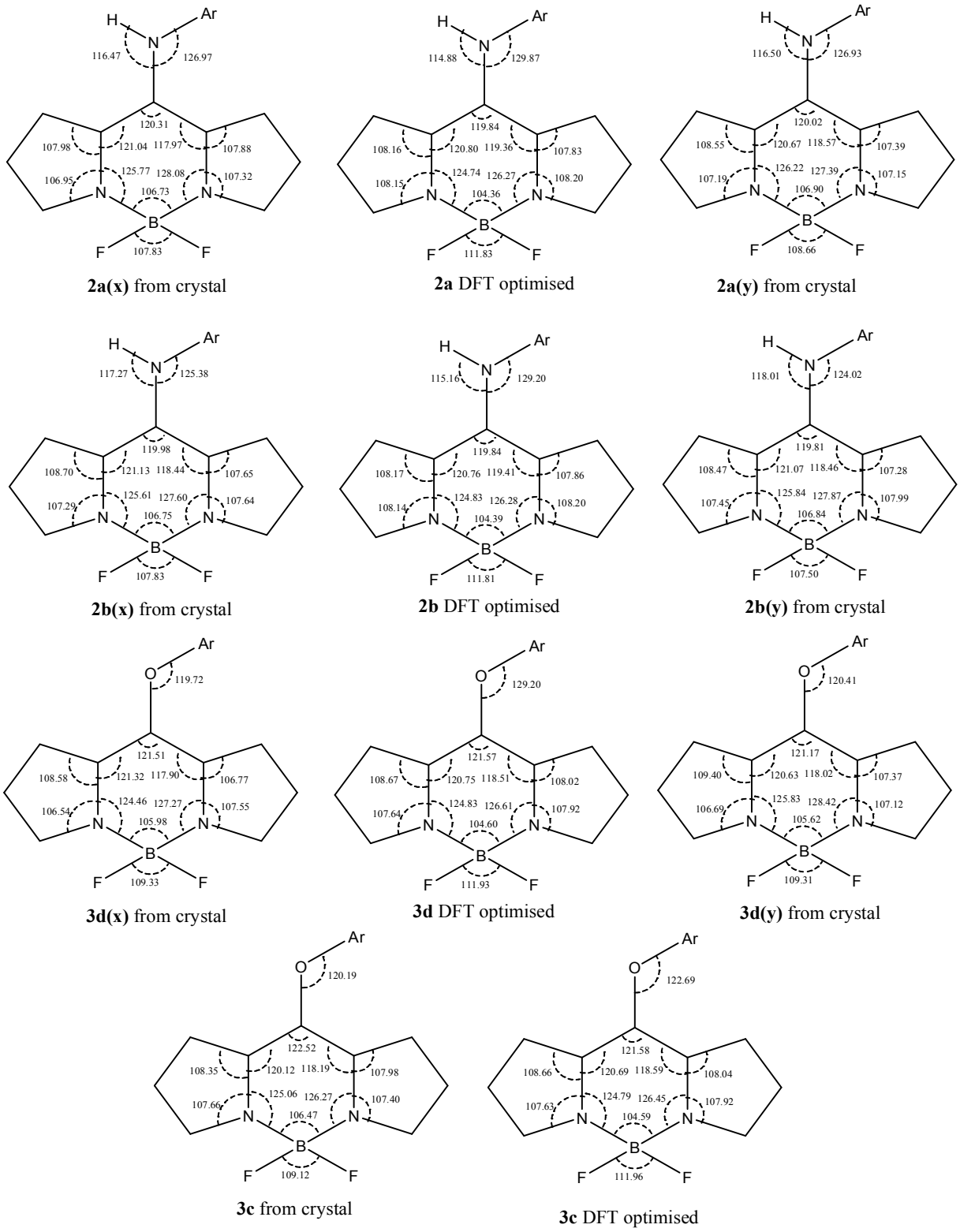


Figure S10. Comparison of selected bond angles of the crystal structures and DFT optimized structures of the heteroatom connected ferrocenyl BODIPYs **2a, 2b, 3c** and **3d** (x and y represents two different molecules in an asymmetric unit)**.**

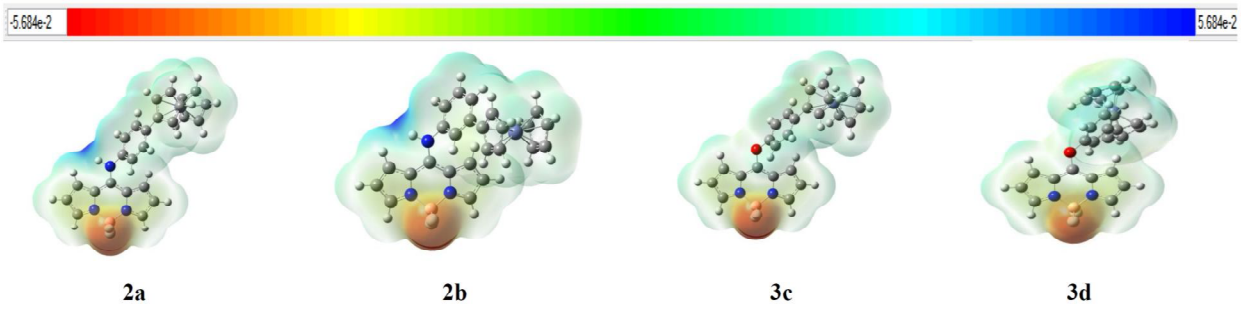


Figure S11. Electrostatic potential map of heteroatom connected ferrocenyl BODIPYs **2a, 2b, 3c** and **3d**. Red = lowest potential (electron-rich) and blue = highest potential (electron-poor). Calculated by Gaussian 09W.

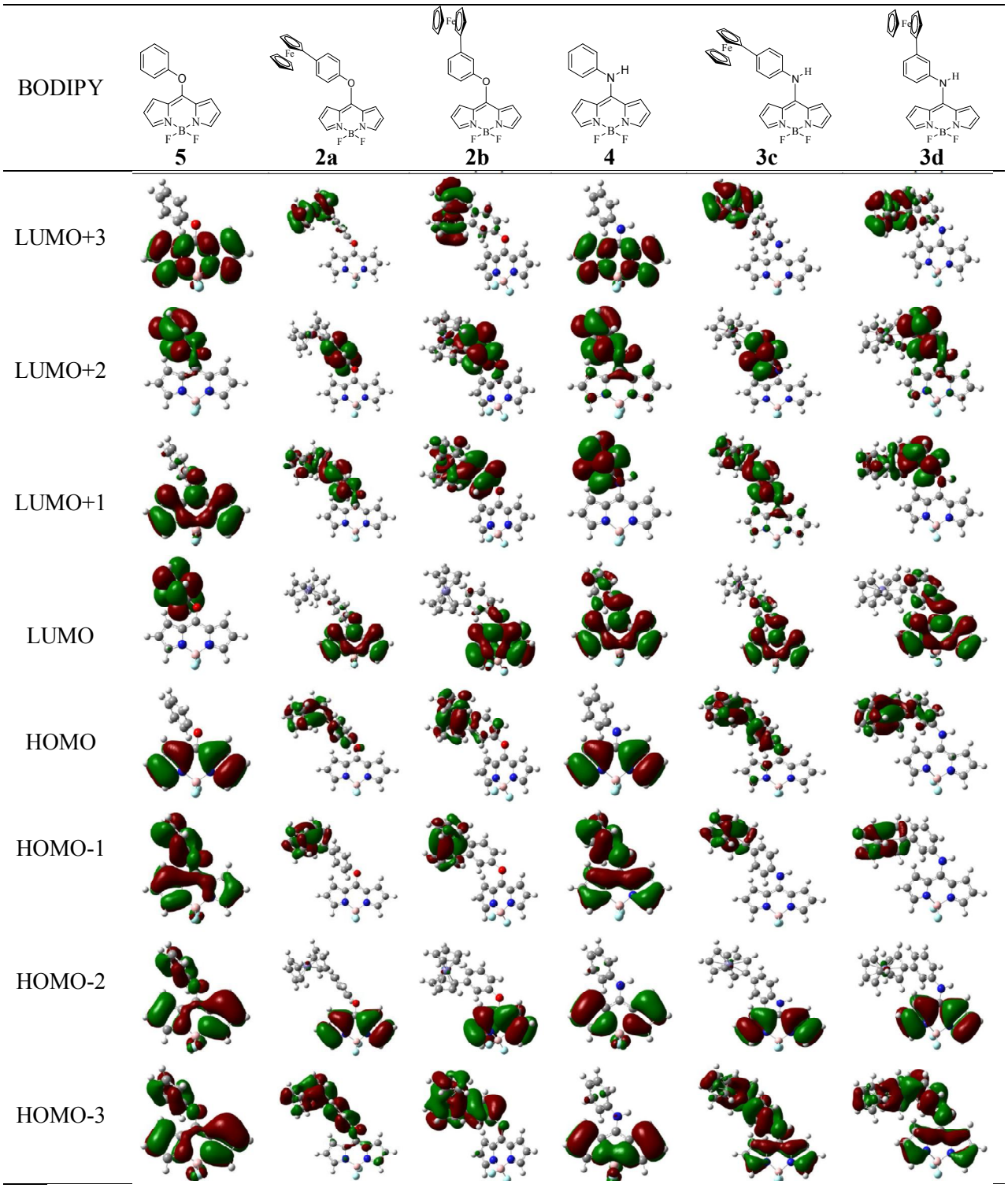


Figure S12. HOMO, and LUMO frontier orbitals of heteroatom connected ferrocenyl BODIPYs **2a, 2b, 3c** and **3d** at the B3LYP/6-31 G** for C, N, B, F, H, O and Lanl2DZ for Fe level.

TD-DFT data:

Table S2. Computed vertical transitions and their oscillator strengths and configurations.

Compound	DCM		
	λ_{max}[nm]	*f*	Configuration
3c	423.65	0.0509	HOMO-2→LUMO (0.55073) HOMO-3→LUMO (-0.42994)
	409.28	0.6567	HOMO-2→LUMO (0.42888) HOMO-3→LUMO (0.55294)

Excitation energies and oscillator strengths:

Excited State 1: Singlet-A 0.9169 eV 1352.17 nm f=0.0006 <S**2>=0.000
114 ->118 -0.45359
115 ->117 -0.48339
115 ->120 -0.23151
This state for optimization and/or second-order correction.
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 0.9206 eV 1346.72 nm f=0.0000 <S**2>=0.000
114 ->117 0.47296
114 ->120 0.22546
115 ->118 -0.46954

Excited State 3: Singlet-A 1.5526 eV 798.56 nm f=0.0006 <S**2>=0.000
110 ->117 -0.31860
110 ->120 -0.16215
114 ->118 -0.46499
115 ->117 0.34642
115 ->120 0.15473

Excited State 4: Singlet-A 1.5676 eV 790.90 nm f=0.0000 <S**2>=0.000
110 ->118 0.33626
114 ->117 0.37434
114 ->120 0.16376
115 ->118 0.45207

Excited State 5: Singlet-A 2.3299 eV 532.15 nm f=0.0096 <S**2>=0.000
115 ->116 0.69974

Excited State 6: Singlet-A 2.3884 eV 519.12 nm f=0.0000 <S**2>=0.000
114 ->116 0.70155

Excited State 7: Singlet-A 2.5588 eV 484.54 nm f=0.0005 <S**2>=0.000
110 ->117 0.52501
110 ->120 0.24077
114 ->118 -0.28255
115 ->117 0.24489

Excited State 8: Singlet-A 2.6364 eV 470.28 nm f=0.0000 <S**2>=0.000
109 ->118 0.10819
110 ->118 0.59099
114 ->117 -0.24405
115 ->118 -0.26769

Excited State 9: Singlet-A 2.9265 eV 423.65 nm f=0.0509 <S**2>=0.000
112 ->116 0.55073
113 ->116 -0.42994

Excited State 10: Singlet-A 3.0293 eV 409.28 nm f=0.6567 <S**2>=0.000
112 ->116 0.42888
113 ->116 0.55294
SavETr: write IOETrn= 770 NScale= 10 NData= 16 NLR=1 LETran= 180.

DFT Data for heteroatom connected ferrocenyl BODIPY **2a**

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.967181	-2.499583	-0.660969
2	1	0	4.325252	-3.345820	-0.870909
3	6	0	6.363589	-2.517296	-0.641294
4	1	0	7.008306	-3.363138	-0.832989
5	6	0	6.778289	-1.215584	-0.325752
6	1	0	7.776059	-0.822064	-0.192599
7	7	0	5.706657	-0.415908	-0.169702
8	5	0	5.717943	1.033653	0.415643
9	6	0	2.560339	3.003971	-0.159134
10	6	0	2.058621	1.712105	-0.302093

11	1	0	1.040730	1.436123	-0.529420
12	6	0	3.145196	0.821959	-0.127039
13	6	0	3.271474	-0.581965	-0.313867
14	6	0	4.567181	-1.177297	-0.370129
15	7	0	4.284716	1.583177	0.117664
16	9	0	5.934192	0.982923	1.783179
17	6	0	3.935018	2.879469	0.098907
18	1	0	4.679553	3.645683	0.262693
19	9	0	6.665315	1.808302	-0.225965
20	1	0	2.009931	3.930404	-0.241763
21	7	0	2.203978	-1.400320	-0.529186
22	1	0	2.437552	-2.320398	-0.874735
23	6	0	0.838341	-1.229576	-0.172942
24	6	0	-0.149510	-1.665824	-1.064203
25	6	0	0.459819	-0.723327	1.076369
26	6	0	-1.494234	-1.582620	-0.716880
27	1	0	0.139948	-2.054772	-2.036650
28	6	0	-0.887675	-0.634669	1.409431
29	1	0	1.218672	-0.407932	1.783984
30	6	0	-1.894754	-1.058142	0.523786
31	1	0	-2.246469	-1.906108	-1.429346
32	1	0	-1.162658	-0.261917	2.391030
33	6	0	-3.315596	-0.985557	0.908009
34	26	0	-4.826722	0.149486	0.012443
35	6	0	-4.375197	-1.830726	0.429628
36	6	0	-3.900444	-0.082331	1.859243
37	6	0	-5.583525	-1.459276	1.087224
38	6	0	-5.290430	-0.377066	1.970090
39	6	0	-4.011246	1.249592	-1.552715
40	6	0	-4.603404	2.126236	-0.594455
41	6	0	-5.989454	1.797788	-0.493279
42	6	0	-6.253970	0.718101	-1.389046
43	6	0	-5.030812	0.378515	-2.043406
44	1	0	-4.271190	-2.621172	-0.300566
45	1	0	-3.382237	0.716058	2.372067
46	1	0	-6.556029	-1.902467	0.923205
47	1	0	-6.003711	0.153571	2.585420
48	1	0	-2.965786	1.222787	-1.827896
49	1	0	-4.086943	2.885868	-0.023914
50	1	0	-6.705540	2.262419	0.170472
51	1	0	-7.205595	0.222581	-1.523965
52	1	0	-4.896597	-0.415641	-2.765092

Total Energy = -1477.1224778 HF

DFT Data for heteroatom connected ferrocenyl BODIPY **2b**

Standard orientation:

Center	Atomic	Atomic	Coordinates (Angstroms)

Number	Number	Type	X	Y	Z
1	6	0	-4.915671	2.027843	0.709757
2	1	0	-4.602195	3.064090	0.721786
3	6	0	-6.163392	1.545930	1.111497
4	1	0	-6.995525	2.123301	1.488386
5	6	0	-6.136257	0.156036	0.928330
6	1	0	-6.895892	-0.582974	1.140425
7	7	0	-4.945233	-0.219189	0.425466
8	5	0	-4.423182	-1.687014	0.295323
9	6	0	-1.394435	-2.110225	-1.902349
10	6	0	-1.276179	-0.754505	-1.600141
11	1	0	-0.514181	-0.077692	-1.953658
12	6	0	-2.372224	-0.416582	-0.771020
13	6	0	-2.854025	0.829920	-0.283149
14	6	0	-4.163362	0.914584	0.277051
15	7	0	-3.136021	-1.564874	-0.584062
16	9	0	-4.098391	-2.180758	1.548638
17	6	0	-2.552658	-2.570815	-1.255874
18	1	0	-2.993294	-3.557732	-1.247583
19	9	0	-5.358739	-2.479227	-0.342008
20	1	0	-0.739248	-2.698474	-2.529272
21	7	0	-2.148306	1.988110	-0.396615
22	1	0	-2.674012	2.831032	-0.213681
23	6	0	-0.743545	2.176136	-0.547654
24	6	0	-0.286470	3.131869	-1.458755
25	6	0	0.159579	1.479913	0.262300
26	6	0	1.085636	3.370621	-1.560881
27	1	0	-0.994676	3.668303	-2.083080
28	6	0	1.539543	1.693648	0.144374
29	1	0	-0.220897	0.776317	0.993695
30	6	0	1.989132	2.655650	-0.780598
31	1	0	1.449959	4.109740	-2.268183
32	1	0	3.053777	2.832651	-0.893146
33	6	0	2.481975	0.952499	1.002922
34	26	0	3.863025	-0.493475	0.402324
35	6	0	3.819070	1.350637	1.349818
36	6	0	2.230898	-0.294400	1.671353
37	6	0	4.370504	0.370431	2.224410
38	6	0	3.389387	-0.646851	2.422080
39	6	0	3.676679	-0.788763	-1.645292
40	6	0	3.447843	-2.015145	-0.951481
41	6	0	4.627509	-2.328049	-0.209973
42	6	0	5.652597	-1.127722	-0.447037
43	6	0	4.996692	-0.342669	-1.332203
44	1	0	4.321347	2.245521	1.009737
45	1	0	1.332129	-0.889130	1.585209
46	1	0	5.368911	0.382013	2.639341
47	1	0	3.515675	-1.548585	3.004960
48	1	0	2.959862	-0.264994	-2.262718
49	1	0	2.529973	-2.586728	-0.957599
50	1	0	4.759224	-3.179347	0.443630

51	1	0	6.623875	-0.998931	0.010592
52	1	0	5.460601	0.568618	-1.684005

Total Energy = -1477.1227491 HF

DFT Data for heteroatom connected ferrocenyl BODIPY **3c**

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.966530	-2.503608	-0.673771
2	1	0	4.324055	-3.348591	-0.887062
3	6	0	6.362931	-2.522230	-0.654462
4	1	0	7.007106	-3.367656	-0.849779
5	6	0	6.778469	-1.222076	-0.333643
6	1	0	7.776501	-0.829699	-0.199079
7	7	0	5.707344	-0.422415	-0.174072
8	5	0	5.719612	1.024713	0.417243
9	6	0	2.563059	2.999255	-0.148742
10	6	0	2.060544	1.708287	-0.296920
11	1	0	1.042443	1.433849	-0.525169
12	6	0	3.146628	0.816784	-0.125767
13	6	0	3.272033	-0.586433	-0.318408
14	6	0	4.567375	-1.182296	-0.377397
15	7	0	4.286650	1.576311	0.121834
16	9	0	5.936116	0.968216	1.784512
17	6	0	3.937717	2.872876	0.108496
18	1	0	4.682741	3.637967	0.275282
19	9	0	6.667311	1.801439	-0.221365
20	1	0	2.013183	3.926347	-0.227433
21	6	0	0.838546	-1.233178	-0.179643
22	6	0	-0.149749	-1.665162	-1.072486
23	6	0	0.460584	-0.731860	1.071825
24	6	0	-1.494351	-1.582593	-0.724541
25	1	0	0.139276	-2.050267	-2.046590
26	6	0	-0.886788	-0.643777	1.405533
27	1	0	1.219771	-0.419835	1.780574
28	6	0	-1.894303	-1.062998	0.518361
29	1	0	-2.246926	-1.902695	-1.438176
30	1	0	-1.161346	-0.274913	2.388719
31	6	0	-3.315021	-0.991156	0.903179
32	26	0	-4.825659	0.148466	0.012619
33	6	0	-4.375223	-1.833717	0.421540
34	6	0	-3.899135	-0.091513	1.858252
35	6	0	-5.583193	-1.464265	1.080917
36	6	0	-5.289272	-0.385879	1.968175
37	6	0	-4.009856	1.254532	-1.548161
38	6	0	-4.601294	2.127568	-0.586170

39	6	0	-5.987518	1.799528	-0.486058
40	6	0	-6.252860	0.723700	-1.386214
41	6	0	-5.030040	0.386090	-2.042225
42	1	0	-4.271836	-2.621207	-0.311929
43	1	0	-3.380348	0.704448	2.374255
44	1	0	-6.555994	-1.906200	0.915276
45	1	0	-6.002110	0.142639	2.585838
46	1	0	-2.964469	1.228243	-1.823670
47	1	0	-4.084264	2.884535	-0.012611
48	1	0	-6.703190	2.261842	0.179753
49	1	0	-7.204807	0.229304	-1.522975
50	1	0	-4.896447	-0.405162	-2.767208
51	8	0	2.204008	-1.403261	-0.536875

Total Energy = -1496.9737685 HF

DFT Data for heteroatom connected ferrocenyl BODIPY **3d**

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.336048	-2.207188	-0.501687
2	1	0	1.489409	-2.394890	-1.143838
3	6	0	3.035621	-3.138850	0.257922
4	1	0	2.840316	-4.199069	0.332298
5	6	0	4.066313	-2.440403	0.914133
6	1	0	4.823863	-2.808992	1.591702
7	7	0	4.025398	-1.140125	0.589408
8	5	0	4.956982	-0.020296	1.176846
9	6	0	4.923310	3.254378	-0.703334
10	6	0	3.783793	2.654071	-1.231396
11	1	0	3.089545	3.062314	-1.951348
12	6	0	3.706586	1.361913	-0.662642
13	6	0	2.792228	0.316379	-0.885604
14	6	0	2.962620	-0.952268	-0.293886
15	7	0	4.782602	1.189670	0.198232
16	9	0	4.520610	0.335861	2.441335
17	6	0	5.505135	2.321579	0.177150
18	1	0	6.390467	2.416446	0.790574
19	9	0	6.267137	-0.454144	1.185477
20	1	0	5.305347	4.241415	-0.921893
21	6	0	0.716367	-0.224619	-1.566652
22	6	0	0.521682	-1.259939	-2.474965
23	6	0	-0.192149	0.044826	-0.546376
24	6	0	-0.620333	-2.052169	-2.334056
25	1	0	1.248012	-1.430999	-3.261748
26	6	0	-1.341057	-0.748306	-0.406277
27	1	0	0.006425	0.856264	0.144420

28	6	0	-1.537770	-1.804294	-1.316573
29	1	0	-0.794305	-2.867670	-3.029621
30	1	0	-2.425859	-2.422053	-1.237274
31	6	0	-2.299874	-0.481439	0.682258
32	26	0	-4.224154	0.309728	0.497532
33	6	0	-3.279452	-1.396159	1.202036
34	6	0	-2.421884	0.733164	1.439939
35	6	0	-3.977208	-0.756486	2.266538
36	6	0	-3.447812	0.560136	2.412816
37	6	0	-4.603746	0.674554	-1.512650
38	6	0	-4.688314	1.890774	-0.770372
39	6	0	-5.710869	1.736036	0.214601
40	6	0	-6.258252	0.424285	0.080449
41	6	0	-5.572823	-0.232546	-0.986997
42	1	0	-3.457427	-2.402379	0.849334
43	1	0	-1.858525	1.641834	1.280359
44	1	0	-4.786282	-1.185337	2.841421
45	1	0	-3.788744	1.309989	3.112990
46	1	0	-3.896417	0.461082	-2.302431
47	1	0	-4.066274	2.764362	-0.908813
48	1	0	-5.997595	2.471283	0.953770
49	1	0	-7.031976	-0.007813	0.700038
50	1	0	-5.741207	-1.247486	-1.320660
51	8	0	1.819953	0.605426	-1.777548

Total Energy = -1496.9741398 HF

DFT Data for BODIPY **4**

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.326931	-2.769188	-0.130235
2	1	0	0.533365	-3.502897	-0.205148
3	6	0	2.692627	-3.047523	-0.047566
4	1	0	3.161823	-4.021729	-0.049203
5	6	0	3.350504	-1.812200	0.035655
6	1	0	4.405242	-1.596168	0.135559
7	7	0	2.454775	-0.808846	-0.007148
8	5	0	2.744556	0.697315	0.298448
9	6	0	0.033015	3.083031	-0.770386
10	6	0	-0.708254	1.906365	-0.694132
11	1	0	-1.758552	1.789912	-0.914572
12	6	0	0.183089	0.877104	-0.307089
13	6	0	0.035555	-0.533619	-0.222056
14	6	0	1.189616	-1.364289	-0.110118
15	7	0	1.446700	1.442119	-0.155506
16	9	0	2.941616	0.867453	1.658714
17	6	0	1.354881	2.752666	-0.430775

18	1	0	2.233251	3.381121	-0.378996
19	9	0	3.826568	1.141591	-0.436105
20	1	0	-0.326581	4.064000	-1.049239
21	7	0	-1.171160	-1.158968	-0.327561
22	1	0	-1.120447	-2.155914	-0.489058
23	6	0	-2.478898	-0.669356	-0.052505
24	6	0	-3.528577	-1.064789	-0.889040
25	6	0	-2.741649	0.118844	1.075604
26	6	0	-4.835078	-0.667674	-0.602903
27	1	0	-3.316315	-1.673166	-1.764351
28	6	0	-4.047018	0.525327	1.342332
29	1	0	-1.928258	0.408757	1.732131
30	6	0	-5.098182	0.133682	0.508515
31	1	0	-5.644427	-0.979283	-1.257067
32	1	0	-4.244729	1.138771	2.216812
33	1	0	-6.114385	0.448209	0.727117

Total Energy = - 967.8060115 HF

DFT Data BODIPY **5**

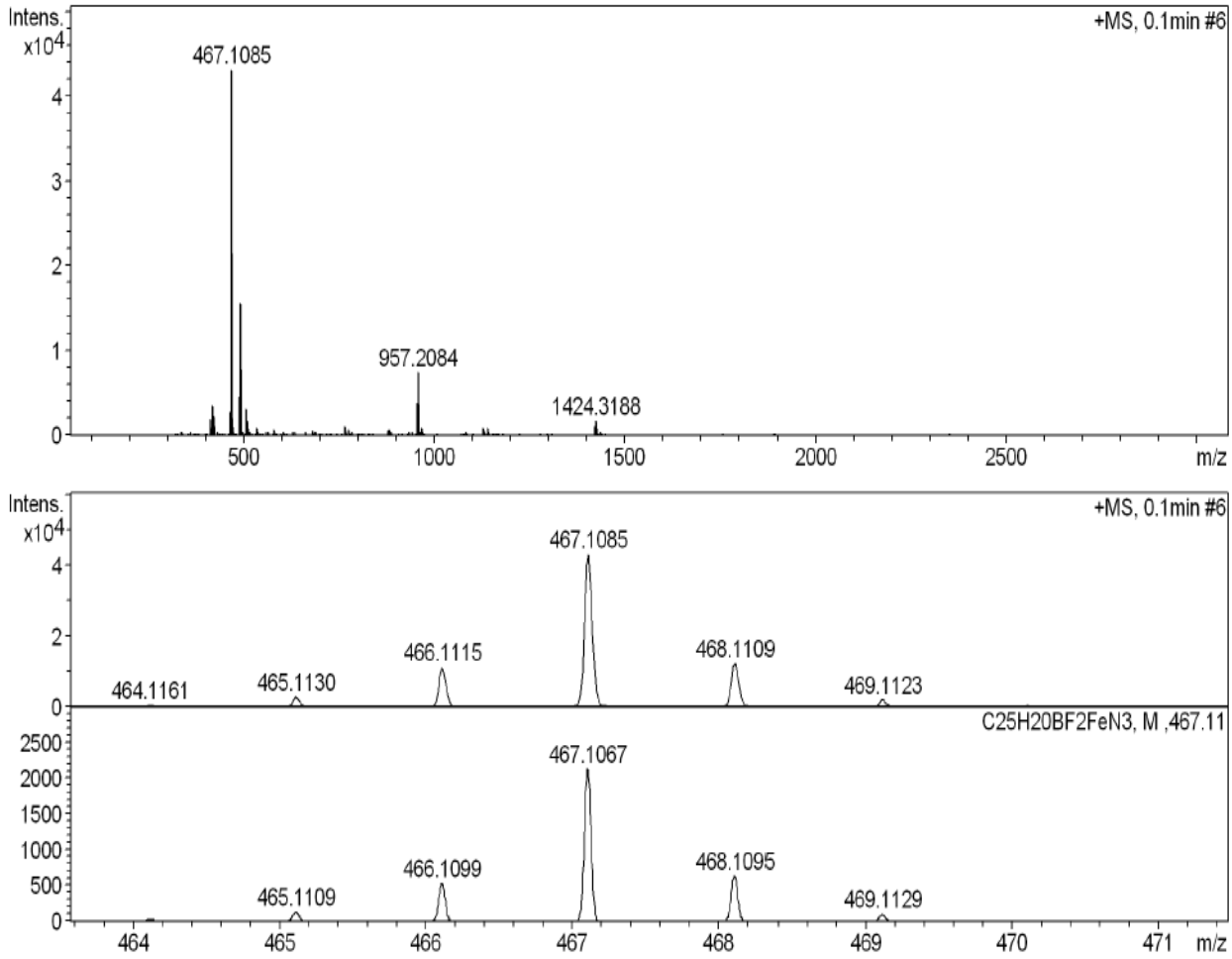
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.288437	-2.754176	-0.241087
2	1	0	0.477187	-3.453208	-0.387353
3	6	0	2.645037	-3.033019	-0.105667
4	1	0	3.119476	-4.004627	-0.118593
5	6	0	3.302235	-1.796485	0.045369
6	1	0	4.354010	-1.590446	0.191551
7	7	0	2.415242	-0.789895	-0.002447
8	5	0	2.685666	0.719430	0.315326
9	6	0	-0.080782	3.103275	-0.645849
10	6	0	-0.796361	1.910961	-0.648637
11	1	0	-1.845267	1.783557	-0.869706
12	6	0	0.121175	0.878107	-0.328790
13	6	0	0.020662	-0.528403	-0.312941
14	6	0	1.155106	-1.347806	-0.177599
15	7	0	1.374102	1.459280	-0.132252
16	9	0	2.874814	0.883190	1.675994
17	6	0	1.250081	2.780360	-0.322750
18	1	0	2.110942	3.427439	-0.223215
19	9	0	3.759781	1.185246	-0.414539
20	1	0	-0.460600	4.093151	-0.858052
21	6	0	-2.377717	-0.714551	-0.126056
22	6	0	-3.403901	-0.752364	-1.066090
23	6	0	-2.602729	-0.309442	1.189233
24	6	0	-4.685956	-0.354883	-0.681563
25	1	0	-3.189863	-1.088258	-2.075580
26	6	0	-3.887695	0.089390	1.556457

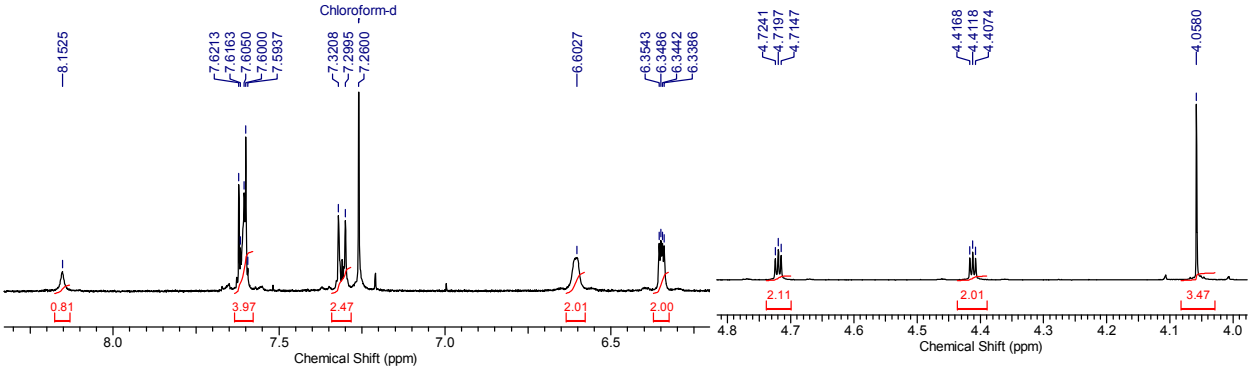
27	1	0	-1.787860	-0.306427	1.905891
28	6	0	-4.929806	0.070019	0.625748
29	1	0	-5.492890	-0.378348	-1.408365
30	1	0	-4.073827	0.409803	2.577532
31	8	0	-1.131877	-1.202128	-0.525016
32	1	0	-5.928096	0.379716	0.920514

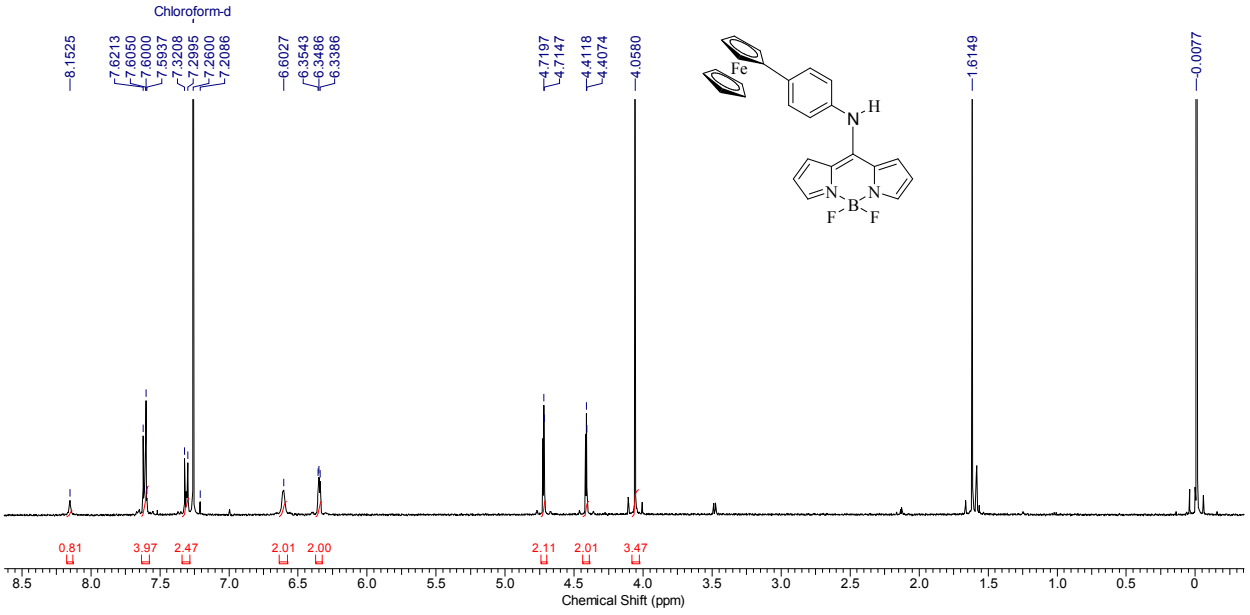
Total Energy = -987.6577199 HF

HRMS of **2a**

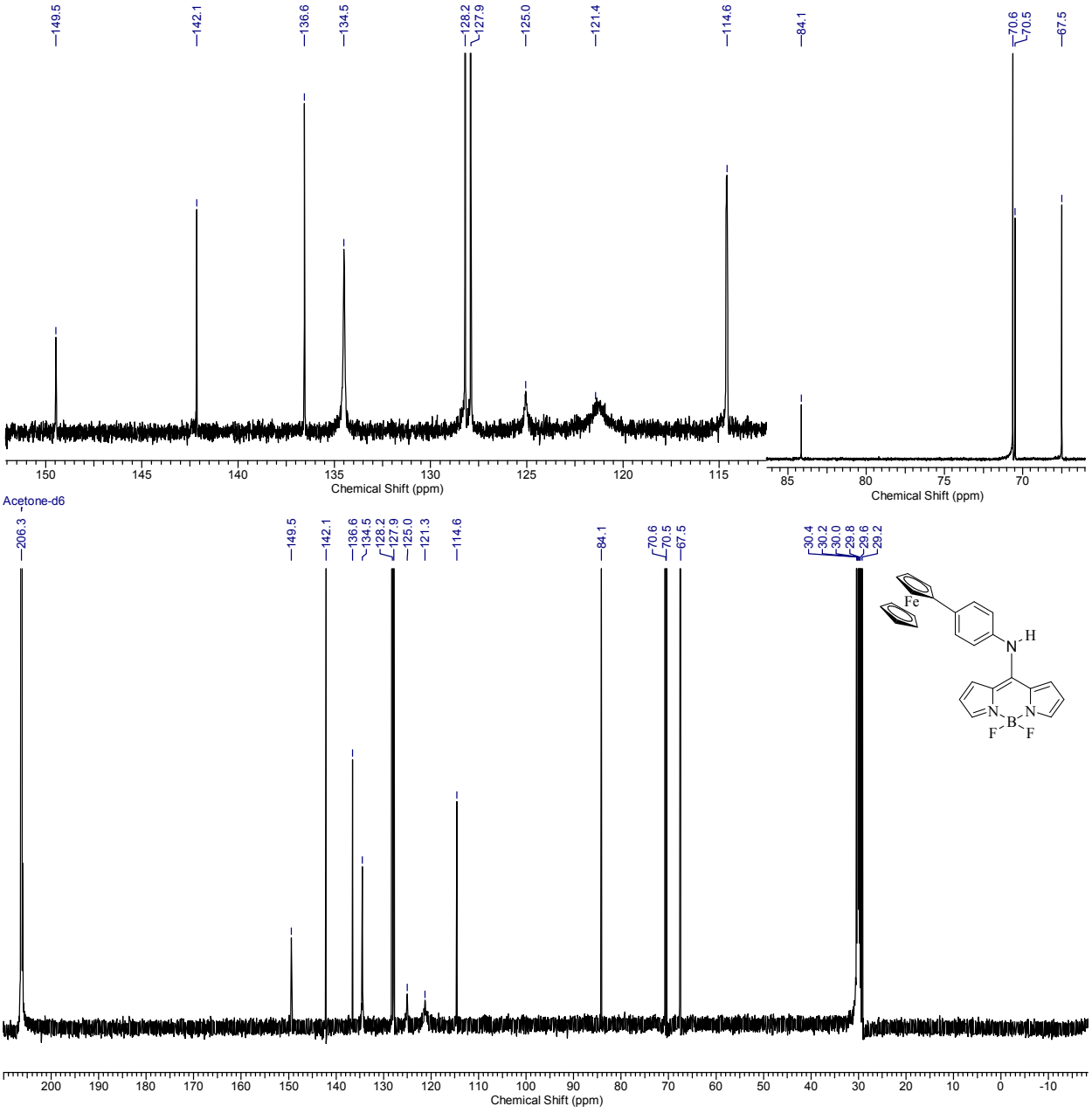


^{1}H NMR of **2a**

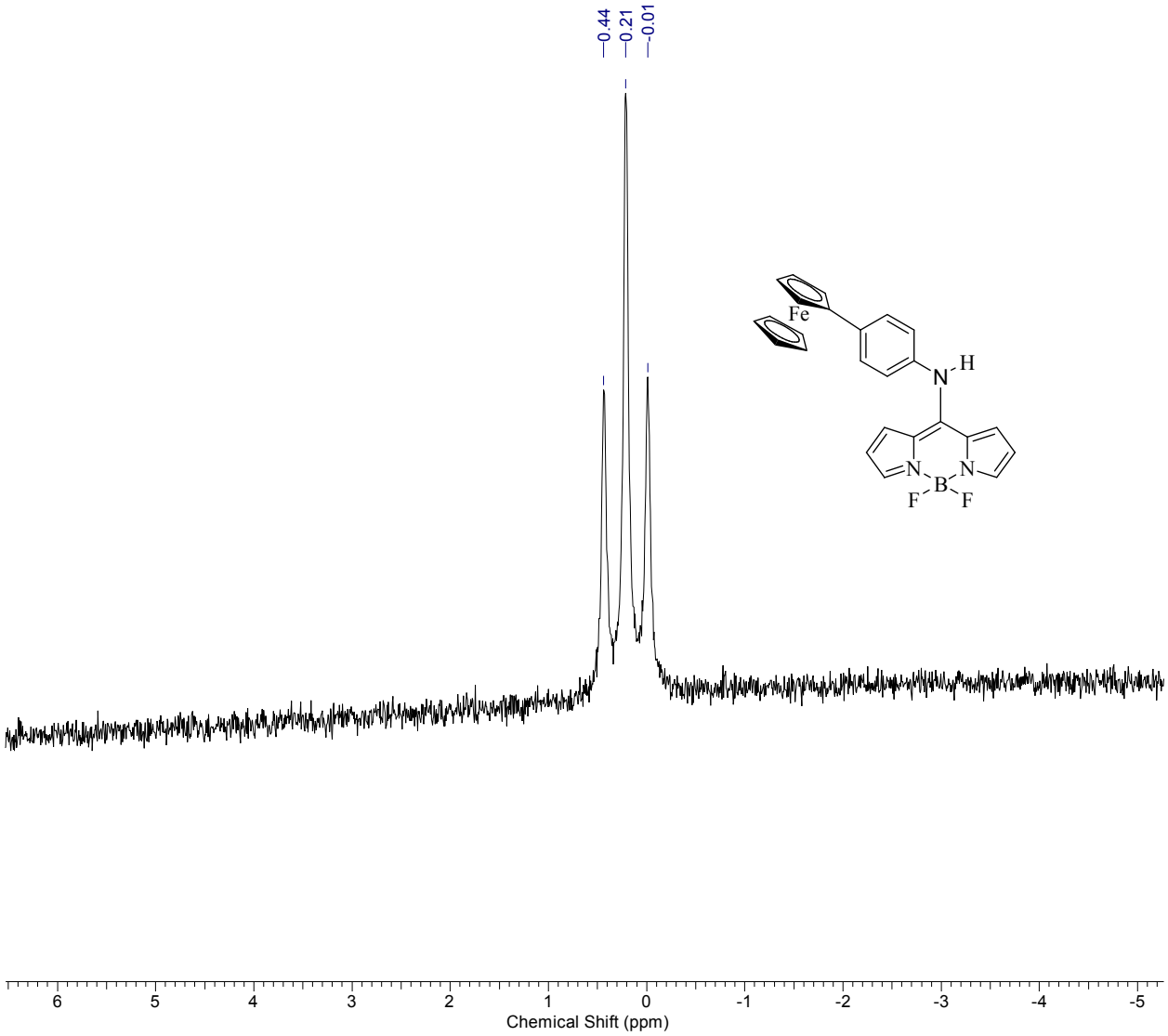

Chloroform-d
8.1525
7.6213
7.6163
7.6050
7.6000
7.5937
7.3208
7.2995
7.2600
6.6027
6.3543
6.3486
6.3442
6.3386
4.7241
4.7197
4.7147
4.4168
4.4118
4.4074
4.0580
0.81
3.97
2.47
2.01
2.00
2.11
2.01
3.47
Chemical Shift (ppm)
Chemical Shift (ppm)


Chloroform-d
8.1525
7.6213
7.6050
7.6000
7.5937
7.3208
7.2995
7.2600
7.2086
6.6027
6.3543
6.3486
6.3386
4.7197
4.7147
4.4118
4.4074
4.0580
1.6149
0.0077
Fe
N
H
N
B
N
F
F
0.81
3.97
2.47
2.01
2.00
2.11
2.01
3.47
Chemical Shift (ppm)

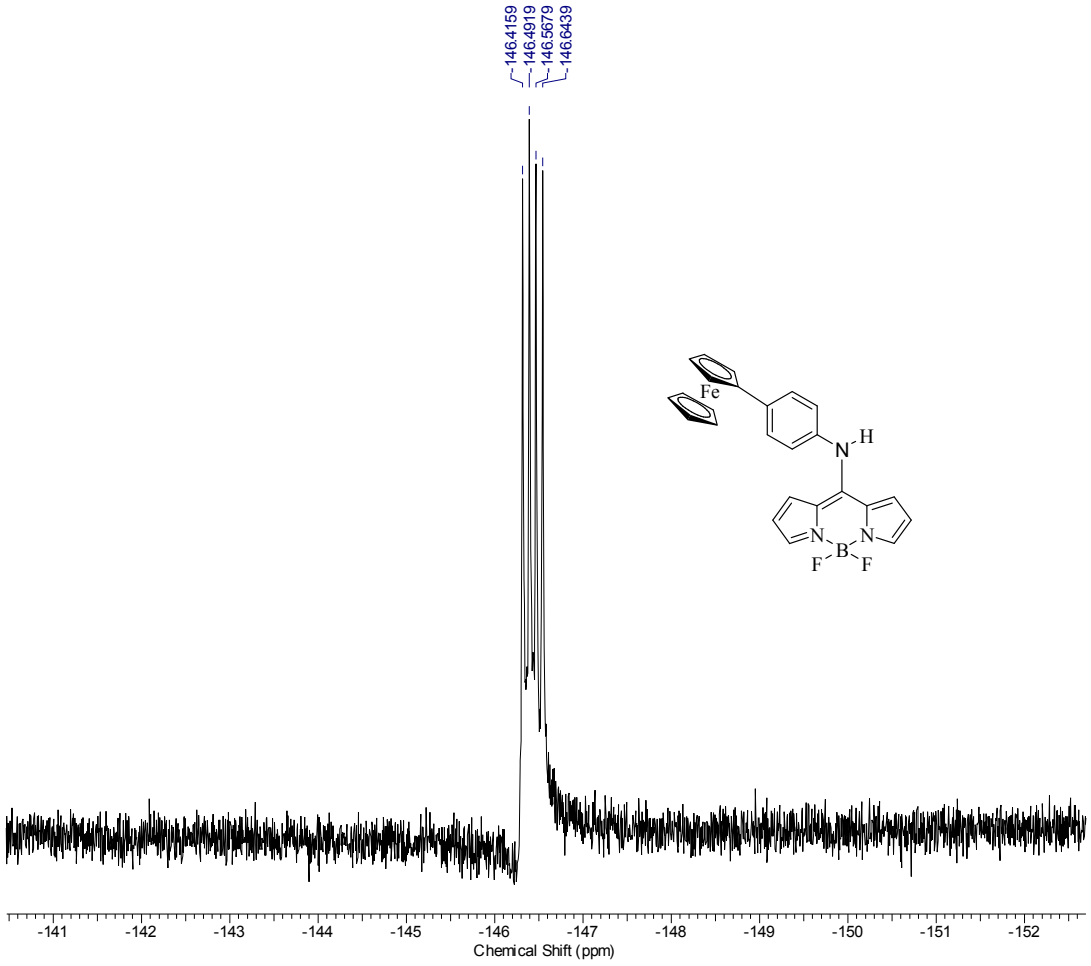
^{13}C NMR of **2a**


149.5
142.1
136.6
134.5
128.2
127.9
125.0
121.4
114.6
84.1
70.6
70.5
67.5
Chemical Shift (ppm)
Acetone-d6
206.3
149.5
142.1
136.6
134.5
128.2
127.9
125.0
121.3
114.6
84.1
70.6
70.5
67.5
30.4
30.2
30.0
29.8
29.6
29.2
Fe
H
N
B
F
Chemical Shift (ppm)

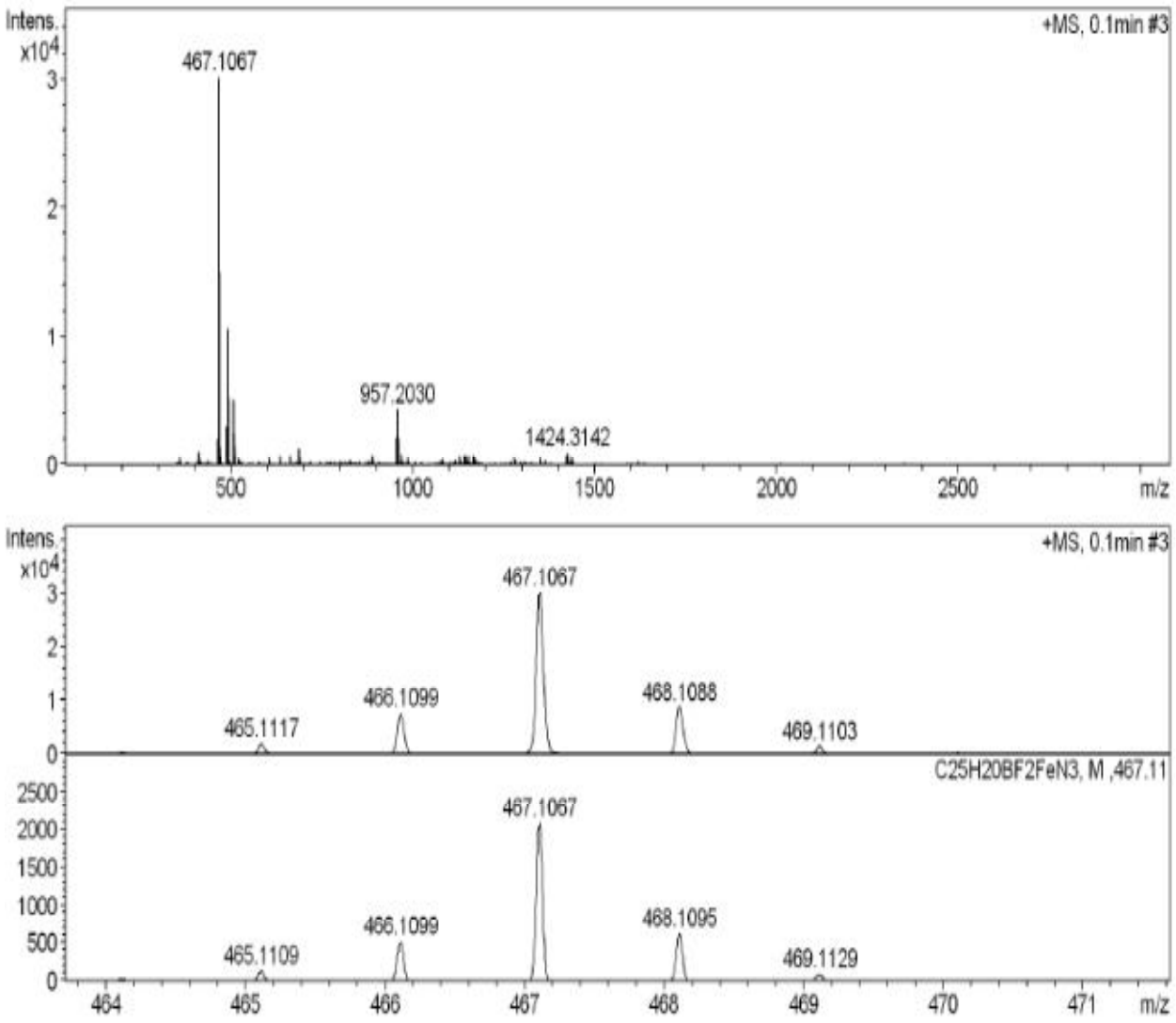
^{11}B NMR of **2a**



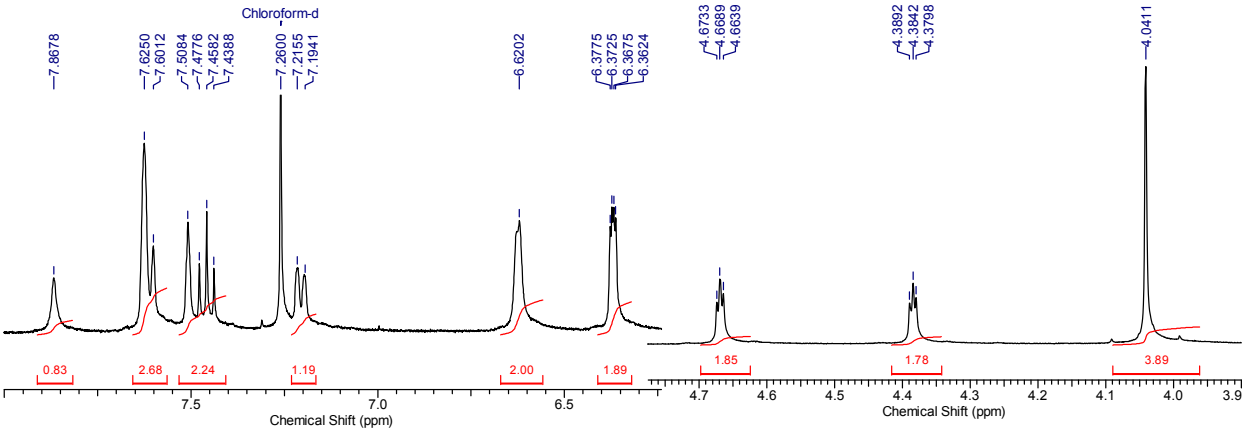
^{19}F NMR of **2a**

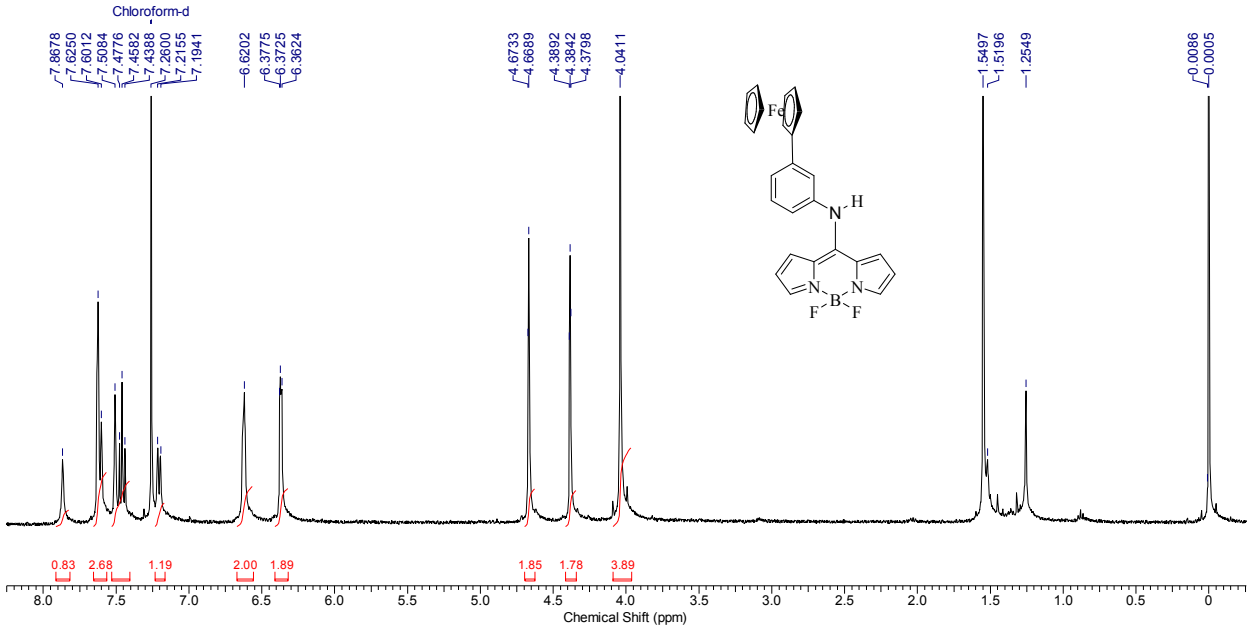

-146.4159
-146.4919
-146.5679
-146.6439
Fe
N
H
N
B
N
F
F
-141
-142
-143
-144
-145
-146
-147
-148
-149
-150
-151
-152
Chemical Shift (ppm)

HRMS of **2b**

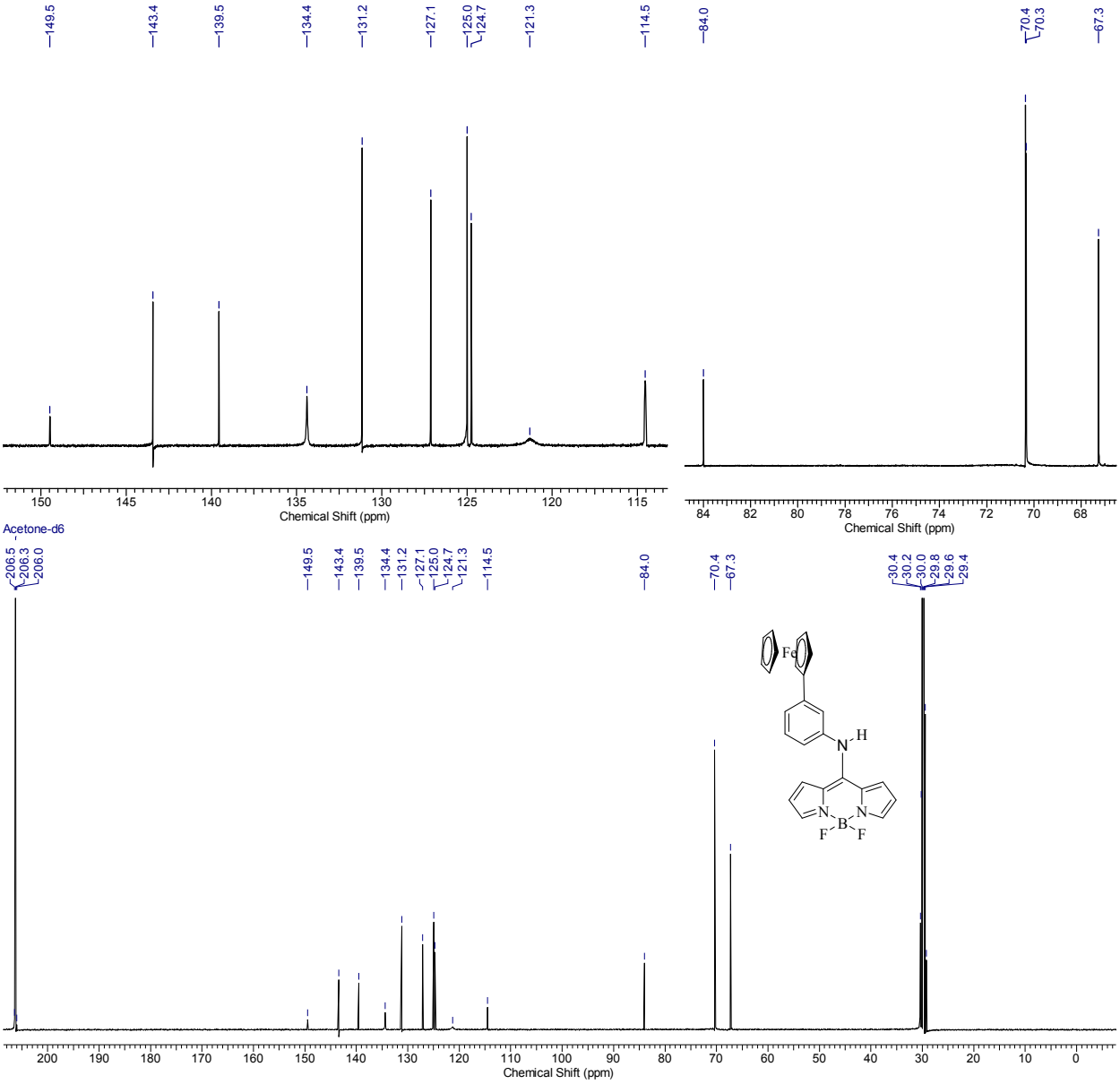

Intens.
x10^4
+MS, 0.1min #3
467.1067
957.2030
1424.3142
m/z
Intens.
x10^4
+MS, 0.1min #3
467.1067
466.1099
468.1088
465.1117
469.1103
C25H20BF2FeN3, M ,467.11
467.1067
466.1099
468.1095
465.1109
469.1129
m/z

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

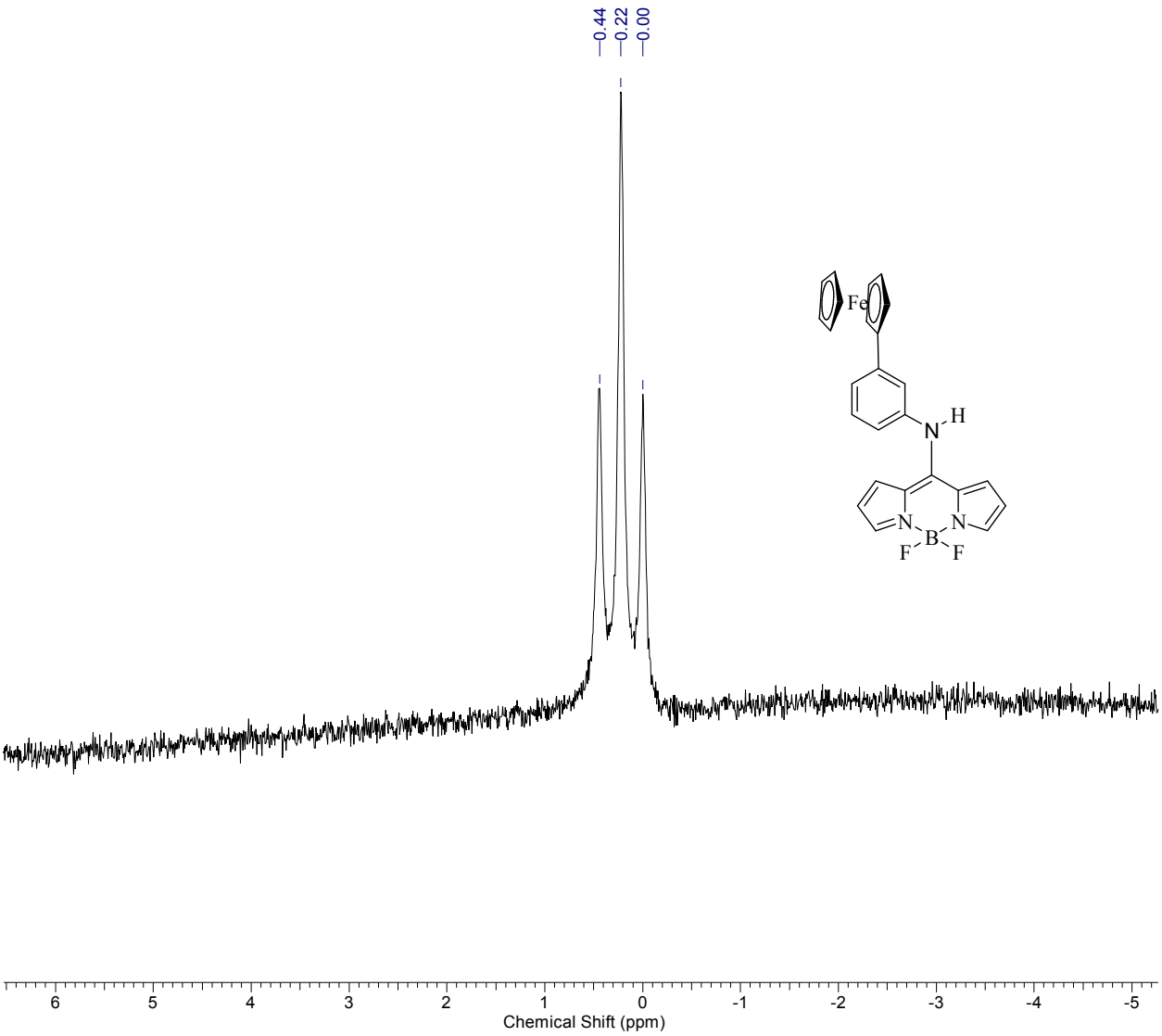

Chloroform-d
7.8678
7.6250
7.6012
7.5084
7.4776
7.4582
7.4388
7.2600
7.2155
7.1941
6.6202
6.3775
6.3725
6.3675
6.3624
4.6733
4.6689
4.6639
4.3892
4.3842
4.3798
4.0411
0.83
2.68
2.24
1.19
2.00
1.89
1.85
1.78
3.89
Chemical Shift (ppm)
Chemical Shift (ppm)


Chloroform-d
7.8678
7.6250
7.6012
7.5084
7.4776
7.4582
7.4388
7.2600
7.2155
7.1941
6.6202
6.3775
6.3725
6.3624
4.6733
4.6689
4.3892
4.3842
4.3798
4.0411
1.5497
1.5196
1.2549
0.0086
0.0005
Fe
N
H
N
B
N
F
F
0.83
2.68
1.19
2.00
1.89
1.85
1.78
3.89
Chemical Shift (ppm)

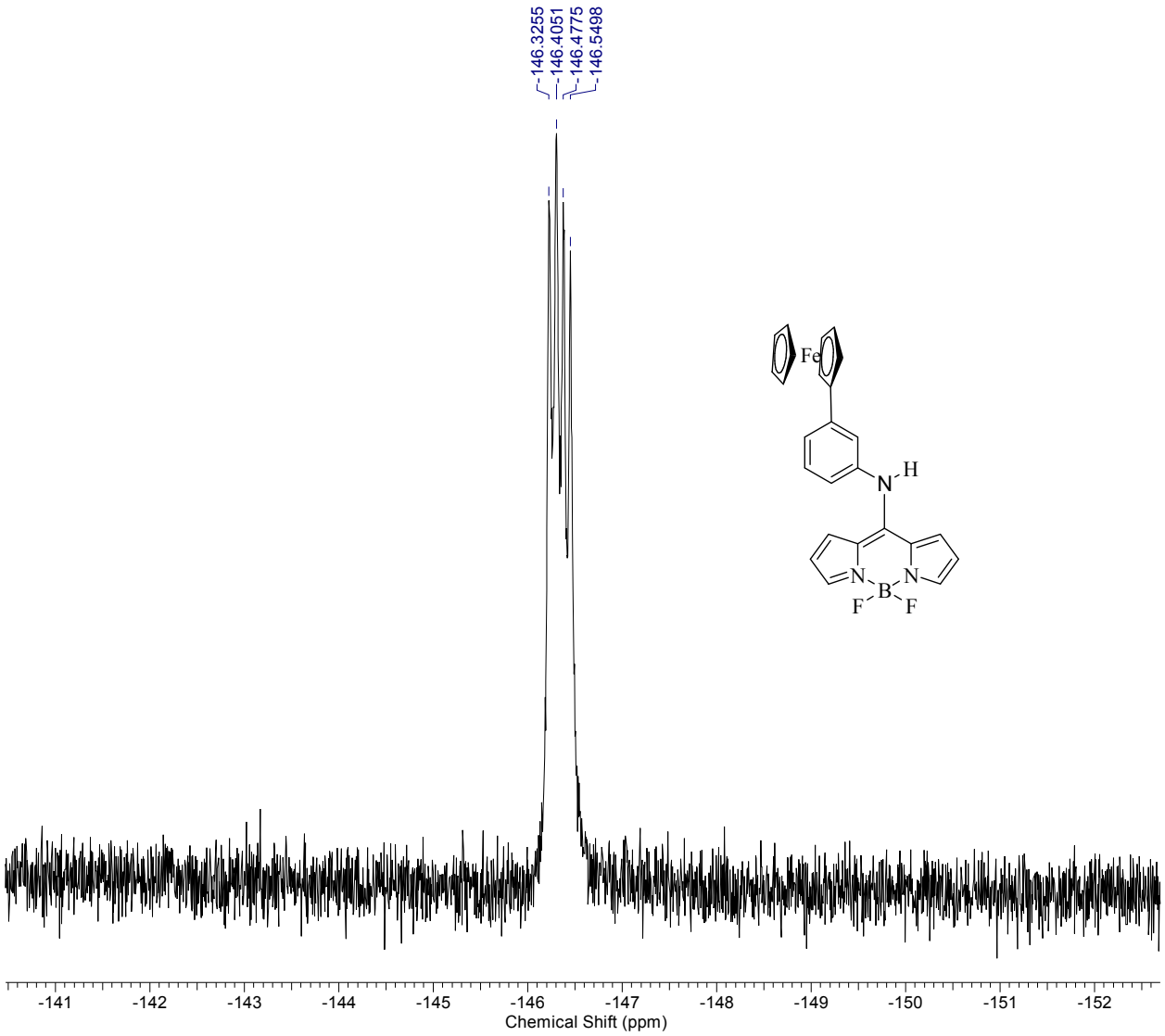
^{13}C NMR of **2b**


149.5
143.4
139.5
134.4
131.2
127.1
125.0
124.7
121.3
114.5
84.0
70.4
70.3
67.3
Chemical Shift (ppm)
Acetone-d6
206.5
206.3
206.0
30.4
30.2
30.0
29.8
29.6
29.4
Fc
N
H
B
F

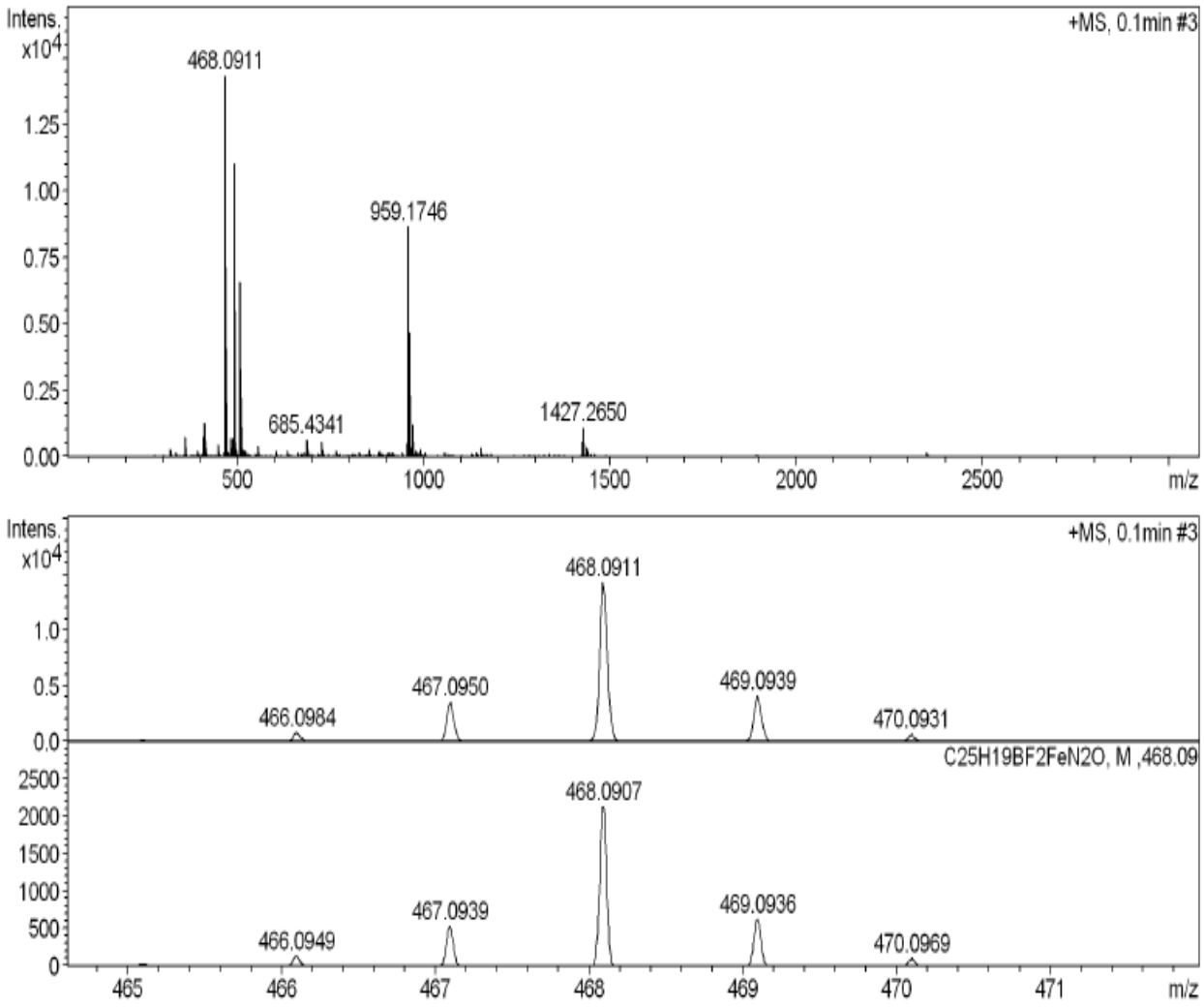
^{11}B NMR of **2b**



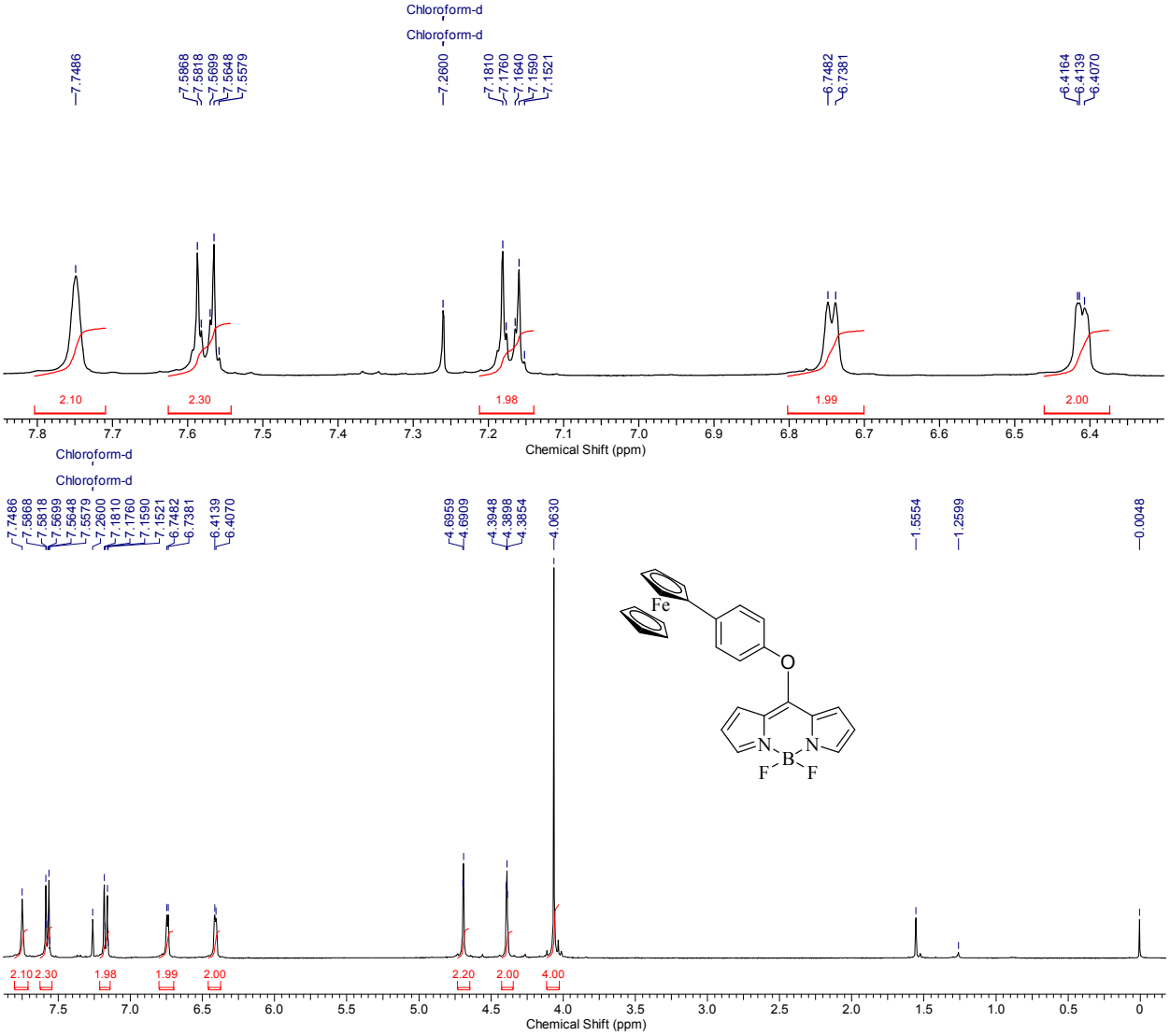
^{19}F NMR of **2b**


-146.3255
-146.4051
-146.4775
-146.5498
Fe
N
H
N
B
N
F
F
-141
-142
-143
-144
-145
-146
-147
-148
-149
-150
-151
-152
Chemical Shift (ppm)

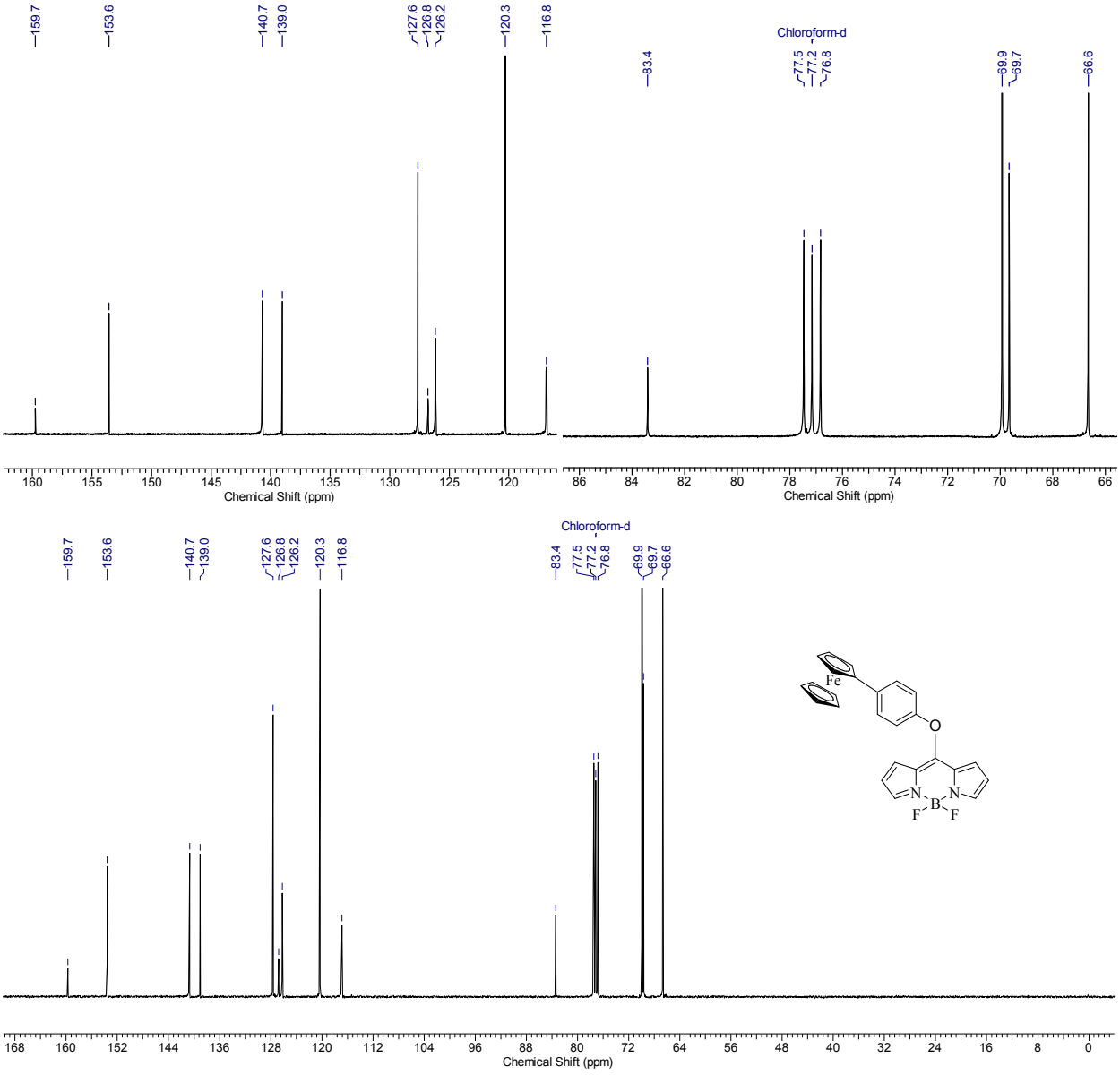
HRMS of **3c**


Intens.
x10^4
+MS, 0.1min #3
468.0911
959.1746
685.4341
1427.2650
m/z
Intens.
x10^4
+MS, 0.1min #3
468.0911
467.0950
469.0939
466.0984
470.0931
C25H19BF2FeN2O, M ,468.09
468.0907
467.0939
469.0936
466.0949
470.0969
m/z

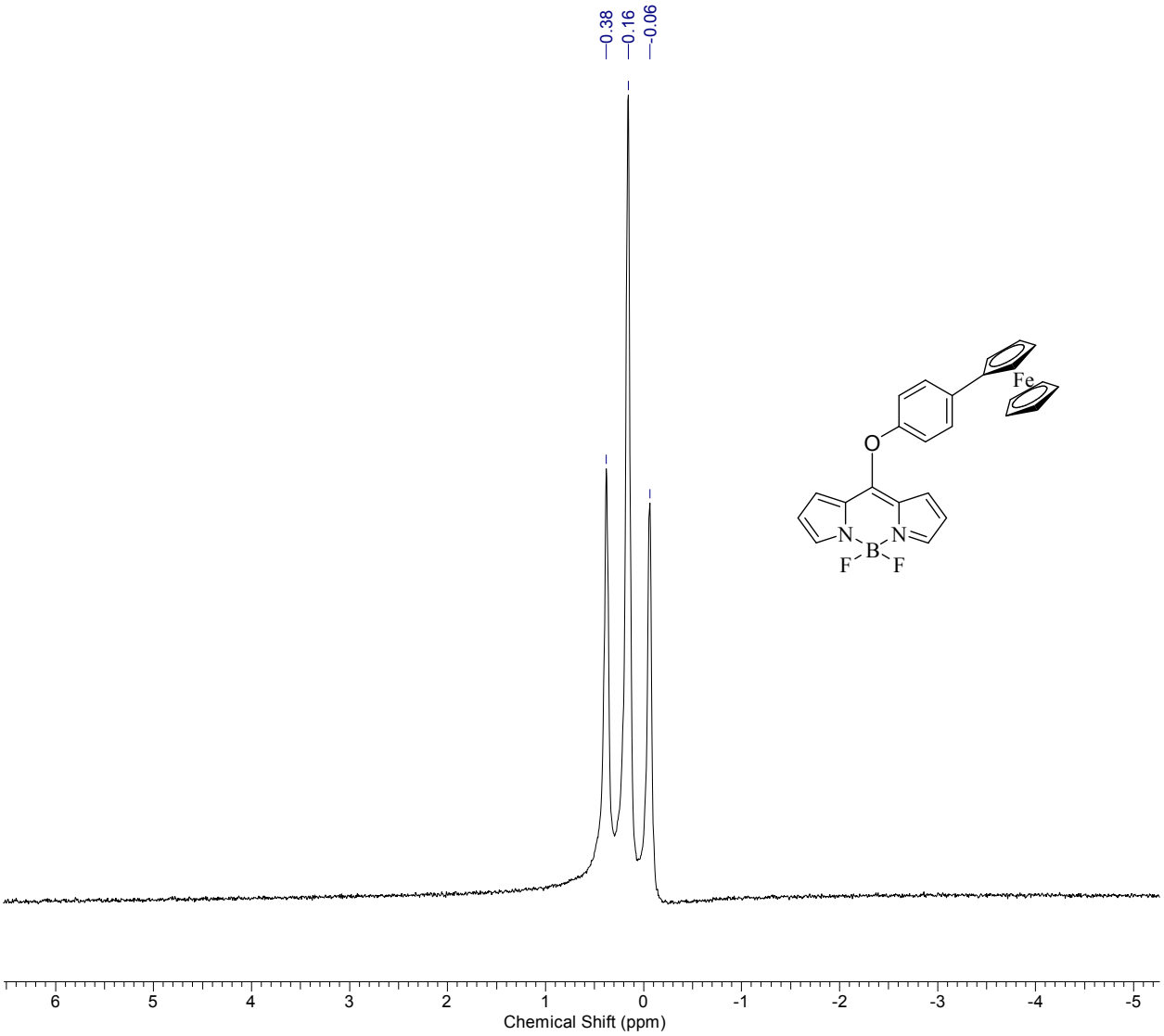
^{1}H NMR of **3c**


Chloroform-d
Chloroform-d
7.7486
7.5868
7.5818
7.5699
7.5648
7.5579
7.2600
7.1810
7.1760
7.1640
7.1590
7.1521
6.7482
6.7381
6.4164
6.4139
6.4070
2.10
2.30
1.98
1.99
2.00
Chemical Shift (ppm)
Chloroform-d
Chloroform-d
4.6959
4.6909
4.3948
4.3898
4.3854
4.0630
1.5554
1.2599
0.0048
Fe
O
N
B
N
F
F
2.10
2.30
1.98
1.99
2.00
2.20
2.00
4.00
Chemical Shift (ppm)

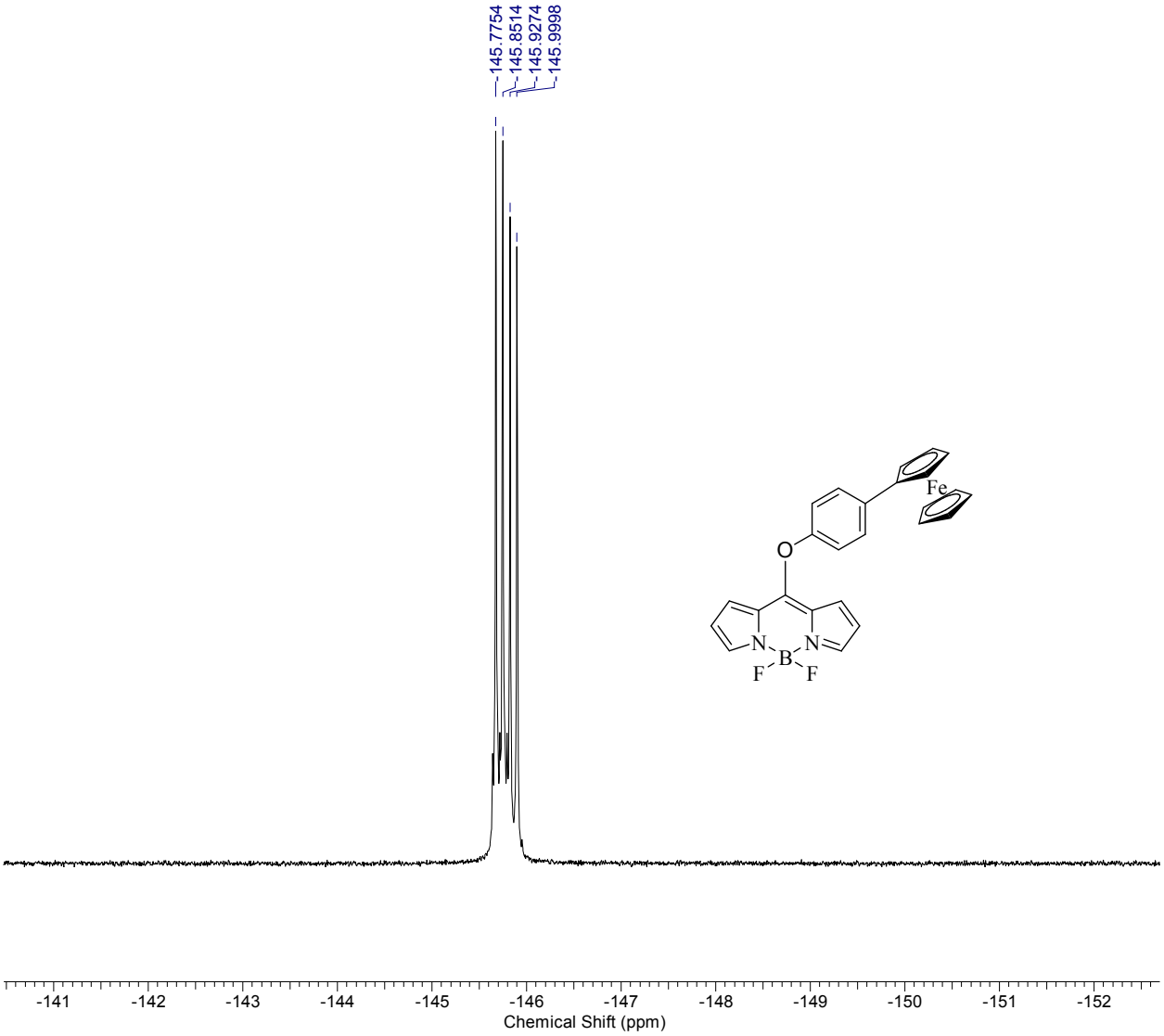
^{13}C NMR of **3c**


159.7
153.6
140.7
139.0
127.6
126.8
126.2
120.3
116.8
83.4
Chloroform-d
77.5
77.2
76.8
69.9
69.7
66.6
Chemical Shift (ppm)
Fe
O
N
B
F

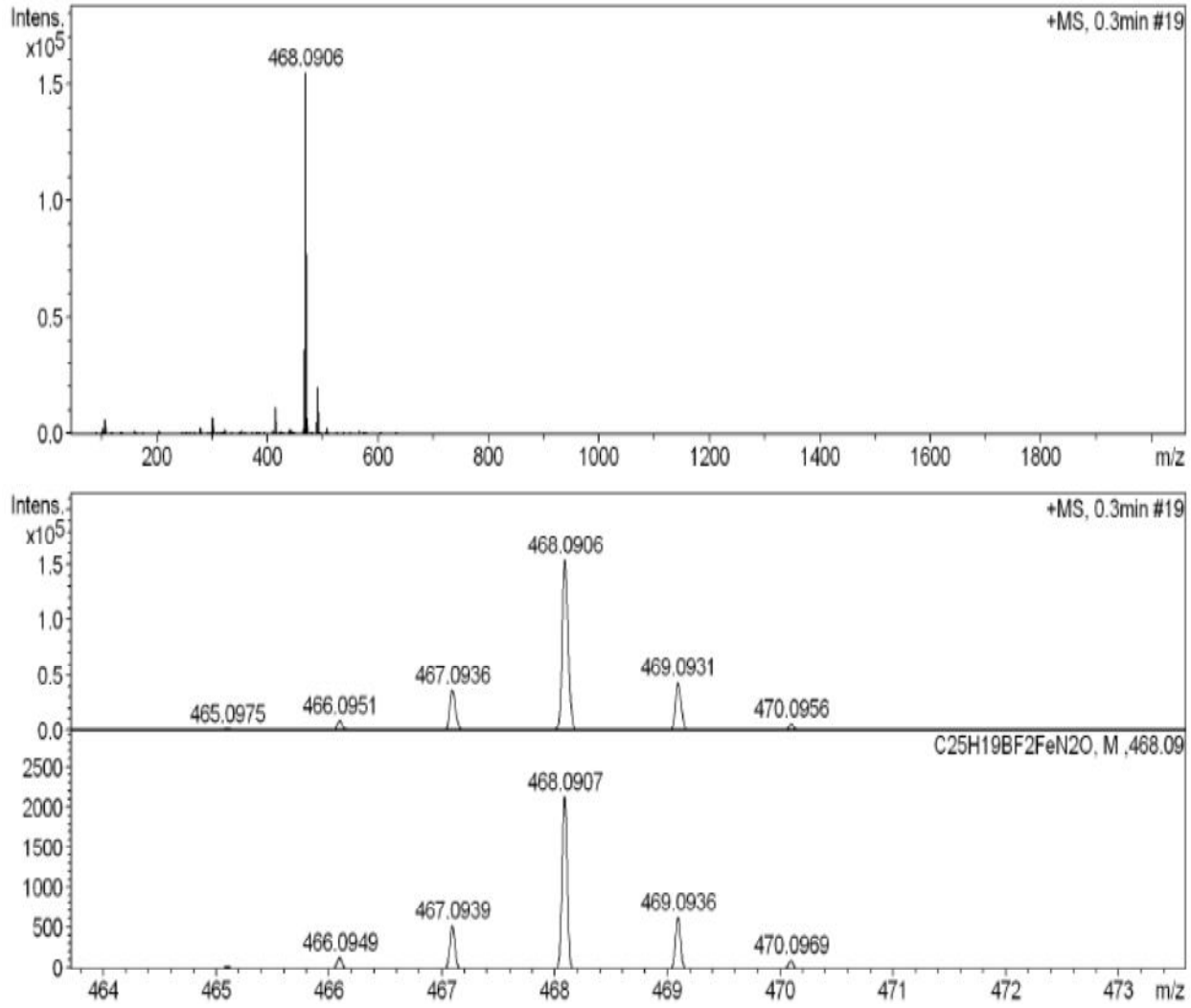
^{11}B NMR of **3c**



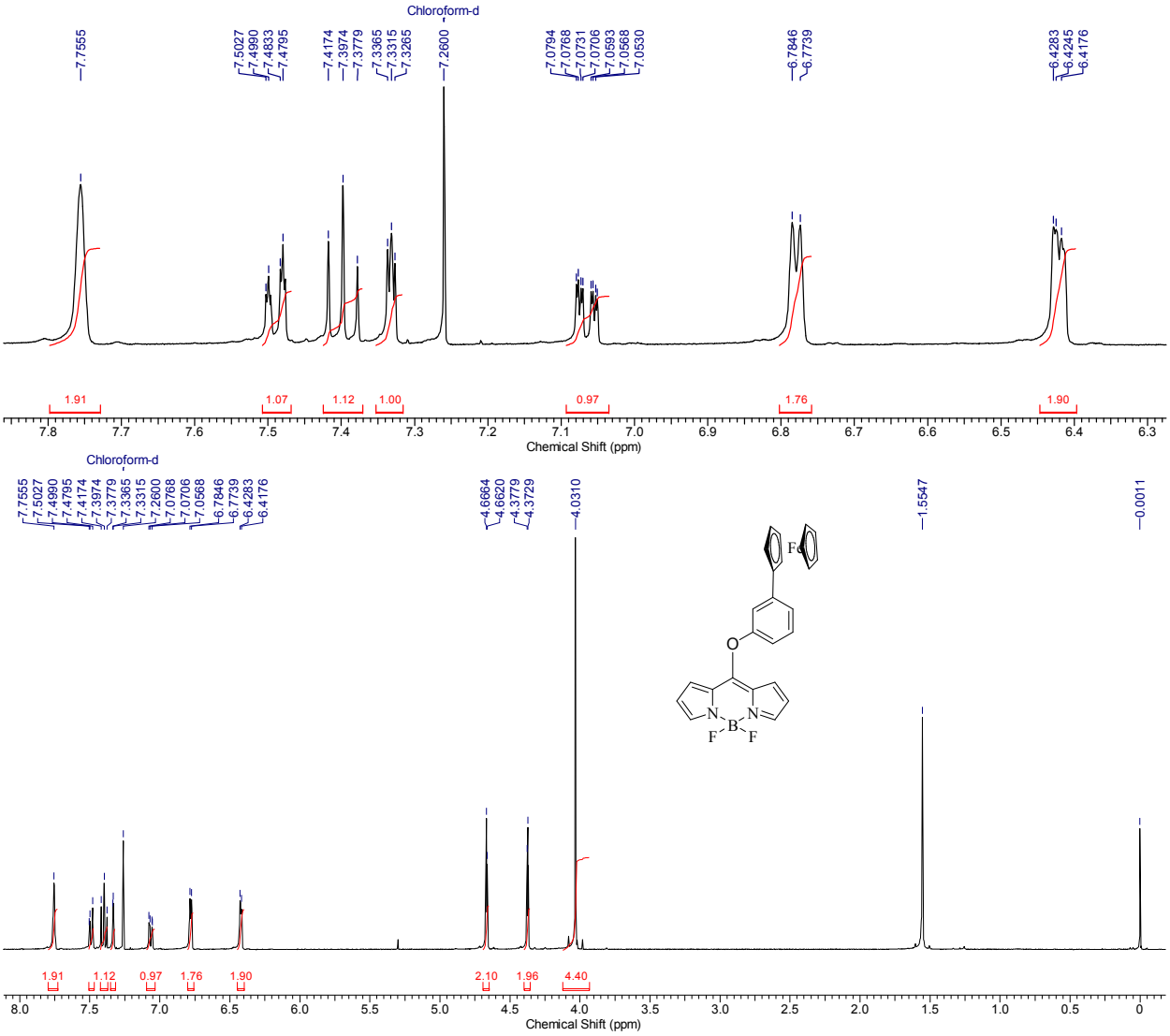
^{19}F NMR of **3c**


-145.7754
-145.8514
-145.9274
-145.9998
Fe
O
N
B
N
F
F
-141
-142
-143
-144
-145
-146
-147
-148
-149
-150
-151
-152
Chemical Shift (ppm)

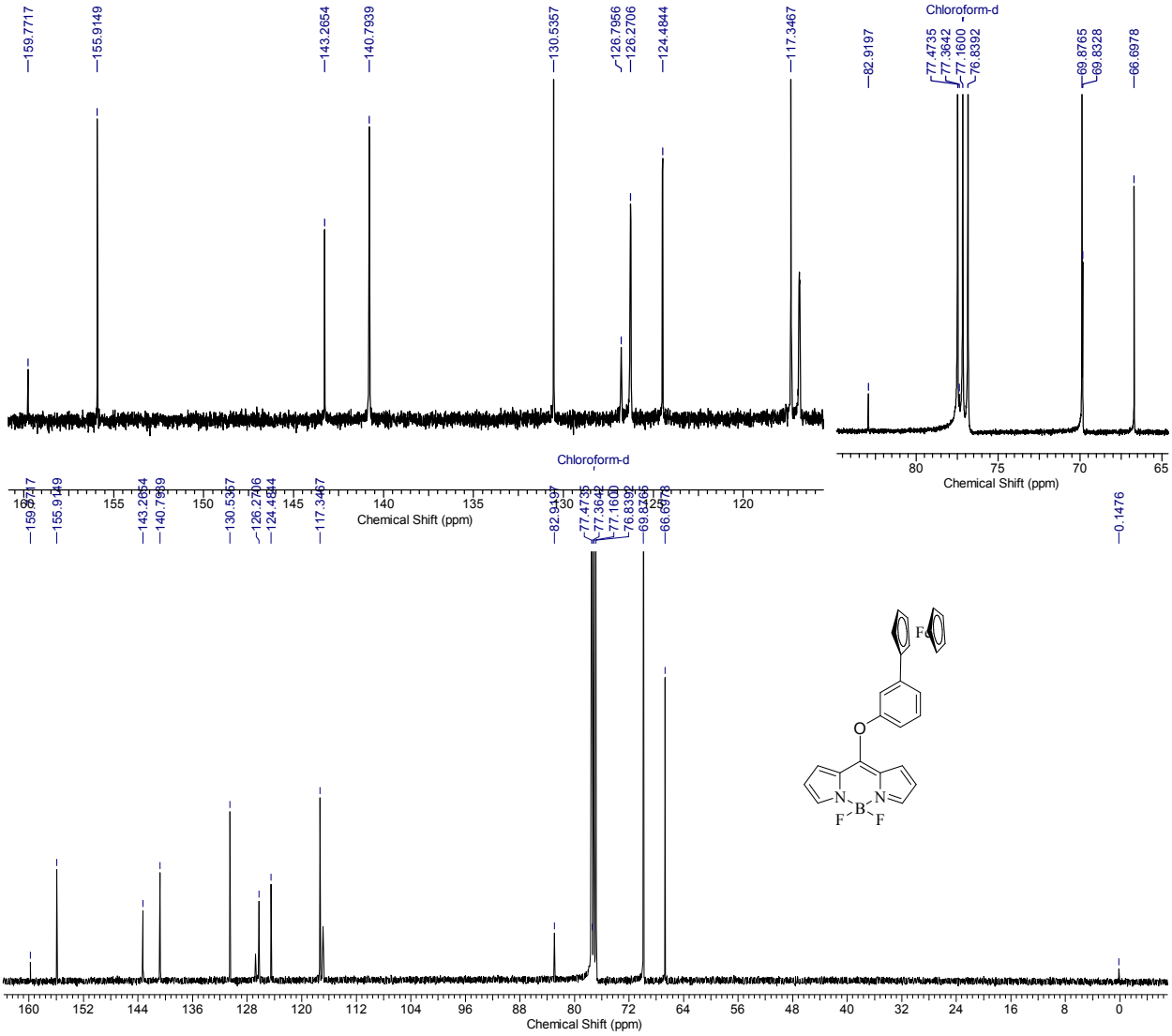
HRMS of **3d**


Intens.
x10^5
+MS, 0.3min #19
468.0906
1.5
1.0
0.5
0.0
200
400
600
800
1000
1200
1400
1600
1800
m/z
Intens.
x10^5
+MS, 0.3min #19
468.0906
467.0936
469.0931
465.0975
466.0951
470.0956
C25H19BF2FeN2O, M ,468.09
2500
2000
1500
1000
500
0
468.0907
467.0939
469.0936
466.0949
470.0969
464
465
466
467
468
469
470
471
472
473
m/z

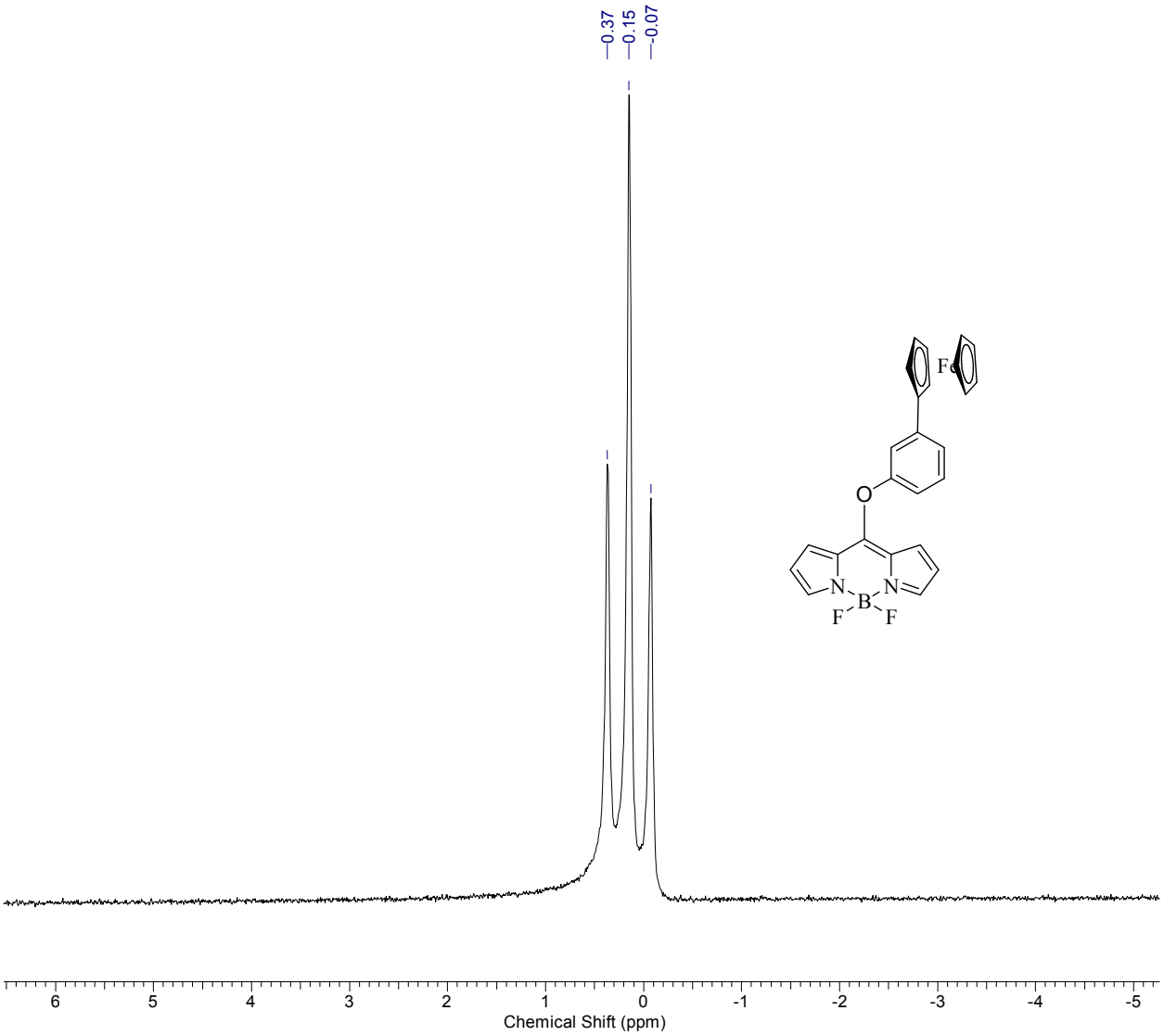
^{1}H NMR of **3d**


Chloroform-d
7.7555
7.5027
7.4990
7.4833
7.4795
7.4174
7.3974
7.3779
7.3365
7.3315
7.3265
7.2600
7.0794
7.0768
7.0731
7.0706
7.0593
7.0568
7.0530
6.7846
6.7739
6.4283
6.4245
6.4176
1.91
1.07
1.12
1.00
0.97
1.76
1.90
Chemical Shift (ppm)
Chloroform-d
7.7555
7.5027
7.4990
7.4795
7.4174
7.3974
7.3779
7.3365
7.3315
7.2600
7.0768
7.0706
7.0568
6.7846
6.7739
6.4283
6.4176
4.6664
4.6620
4.3779
4.3729
4.0310
1.5547
0.0011
Fe
O
N
B
N
F
F
1.91
1.12
0.97
1.76
1.90
2.10
1.96
4.40
Chemical Shift (ppm)

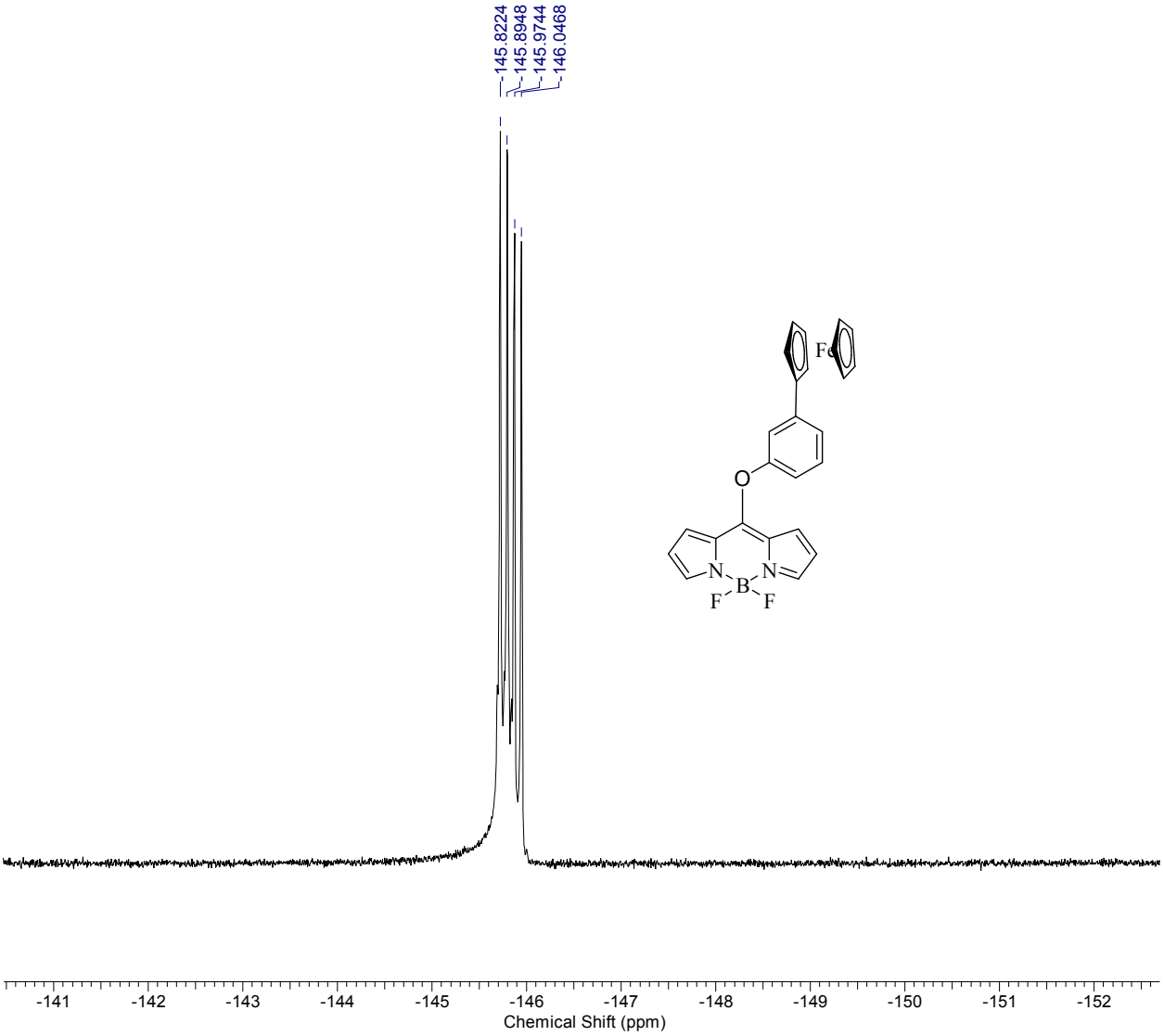
^{13}C NMR of **3d**


159.7717
155.9149
143.2654
140.7939
130.5357
126.7956
126.2706
124.4844
117.3467
82.9197
77.4735
77.3642
77.1600
76.8392
69.8765
69.8328
66.6978
Chloroform-d
Chemical Shift (ppm)
0.1476
F
O
N
B
F

^{11}B NMR of **3d**



^{19}F NMR of **3d**



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(2) (a) Becke, A. D. *J. Chem. Phys.* 1993, **98**, 5648-5652. (b) Lee, C. T.; Yang, W. T.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785-789. (c) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270-283. (d) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M.S.; Defrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654-3665.