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Supporting Information

Ferrocenyl BODIPYs: Synthesis, Structure and Properties

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General: Chemicals were used as received unless otherwise indicated. All oxygen or moisture sensitive reactions were performed under nitrogen/argon atmosphere using standard schlenk method. Triethylamine (TEA) was received from commercial source, and distilled on KOH prior to use. ^{1}H NMR (400 MHz), and ^{13}C NMR (100MHz) spectra were recorded on the Bruker Avance (III) 400 MHz, using $CDCl_3$ as solvent. Tetramethylsilane (TMS) was used as reference for recording ^{1}H (of residual proton; δ = 7.26 ppm), and ^{13}C (δ = 77.0 ppm) spectra in $CDCl_3$. UV-visible absorption spectra of all compounds in toluene were recorded on a Carry-100 Bio UV-visible Spectrophotometer. Cyclic voltamograms (CVs) were recorded on a CHI620D electrochemical analyzer using Glassy carbon as working electrode, Pt wire as the counter electrode, and Saturated Calomel Electrode (SCE) as the reference electrode. HRMS was recorded on Brucker-Daltonics, micrO TOF-Q II mass spectrometer.

General procedure for synthesis of 3a-3d. 2,6-diiodo BODIPY **2** (0.087 mmol), $Pd(PPh_3)_2Cl_2$ (0.005 mmol), and CuI (0.01 mmol) were dissolved in THF (10ml), and Et_3N (10ml) in 1:1 ratio. The mixture was degassed with Ar for 45 min. Appropriate ferrocenyl alkyne intermediate (0.261 mmol) was added to the solution, and the resulting mixture was stirred for 12 h at 60 $^{\circ}$C. Upon completion, the mixture was evaporated to dryness, and the crude product was dissolved in CH_2Cl_2, and then passed through a pad of silica to remove insoluble material. The filtrate was evaporated to dryness, and the crude product was chromatographed on silica (1:1 hexanes/CH_2Cl_2), and finally recrystallized from chloroform: ethanol mixture to give **3a-3d** (yield 40-60%) crystalline solid.

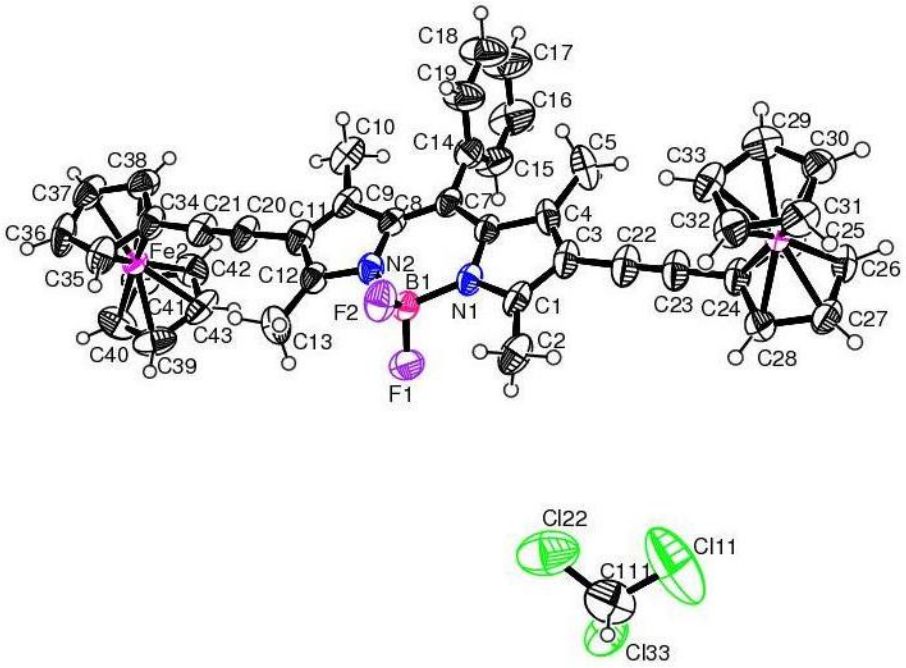
3a: purple solid (39 mg, Yield: 60%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52-7.51 (m, 3H), 7.30-7.27 (m, 2H), 4.44 (s, 4H), 4.22-4.19 (m, 14), 2.69 (s, 6H), 1.49 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.1, 148.0, 143.4, 142.0, 134.8, 131.2, 129.3, 127.9, 116.9, 95.1, 77.5, 71.5, 70.0, 68.9, 65.4, 13.7, 13.5; HRMS ($C_{43}H_{35}BF_2Fe_2N_2$) calcd 740.1564 [M^+], found 740.1571 [M^+]; UV/Vis (toluene): λ_{max} (ε [$M^{-1}cm^{-1}$]) 583 nm (15500); X-ray: see Figure 3.

3b: purple solid (30 mg, Yield: 40%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54-7.51 (m, 5H), 7.36 (d, 4H, *J* = 8Hz), 7.31-7.28 (m, 4H), 4.69 (s, 4H), 4.38 (s,4H), 4.06 (s, 10H), 2.73 (s, 6H), 1.24 (s, 6H); HRMS ($C_{55}H_{43}BF_2Fe_2N_2$) calcd 892.2192 [M^+], found 892.2214 [M^+]; UV/Vis (toluene): λ_{max} (ε [$M^{-1}cm^{-1}$]) 590 (42800); X-ray: see Figure 3. Due to poor solubility of this compound the ^{13}C NMR could not be obtained.

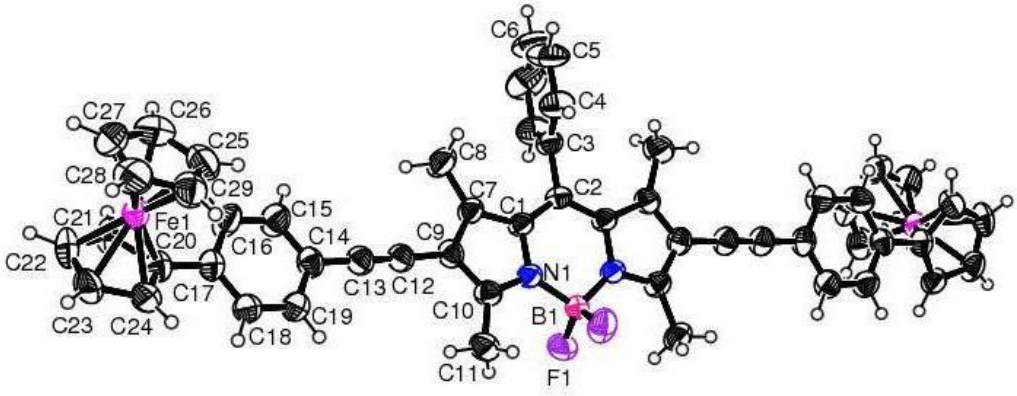
3c: purple solid (38 mg, Yield: 50%).^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56-7.53 (m, 5H), 7.5 (s, 2H), 7.39 (d, 2H, *J* = 8Hz), 7.33-7.30 (m, 2H), 7.22 (d, 2H, *J* = 8Hz), 4.67 (s, 4H), 4.35 (s, 4H), 4.07 (s, 10H), 2.75 (s, 6H), 1.55(s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.5, 144.1, 142.5, 141.8, 139.8, 134.5, 131.3, 129.4, 128.9, 128.6, 128.4, 127.9, 126.1, 123.4, 116.3, 96.7, 84.5, 81.4, 69.7, 69.2, 66.6, 13.8, 13.5; HRMS ($C_{55}H_{43}BF_2Fe_2N_2$) calcd 892.2192 [M^+], found 892.2198 [M^+]; UV/Vis (toluene): λ_{max} (ε [$M^{-1}cm^{-1}$]) 576 (69600).

3d: purple solid (45 mg, Yield: 55%).^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54-7.53 (m, 3H), 7.45-7.37 (m, 8H), 7.31-7.28 (m, 2H), 4.49 (s, 4H), 4.25-4.23 (m, 14H), 2.72 (s, 6H), 1.52 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.6, 147.7, 143.7, 141.1, 134.4, 131.3, 131.2, 129.4, 127.9, 123.7, 122.5, 116.2, 101.8, 96.5, 90.6, 85.6, 83.3, 71.5, 70.0, 69.0, 64.9, 13.8, 13.4; HRMS ($C_{59}H_{43}BF_2Fe_2N_2$) calcd 940.2193 [M^+], found 940.2191 [M^+]; UV/Vis (toluene): λ_{max} (ε [$M^{-1}cm^{-1}$]) 586 (696200).

II. Crystallographic data



3a



3b

Figure S1. ORTEP view of **3a** and **3b**, and the atom-labelling scheme. Thermal ellipsoids are plotted at the 50 % level.

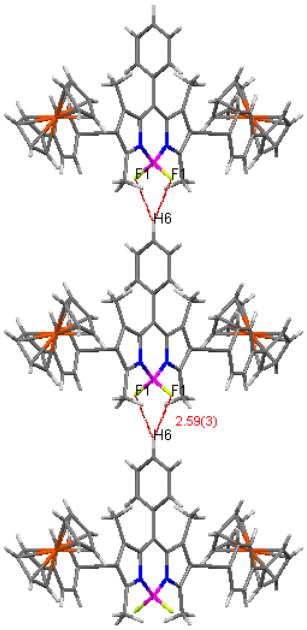
Table S1. Selected bond lengths [Å] and bond angles [°] for BODIPYs **3a** and **3b**.

	Bond lengths [Å]	**Bond angles [°]**	
For **3a**			
B1-F1	1.372(7)	N1-B1-N2	105.6(4)
B1-F2	1.407(7)	F1-B1-F2	109.0(5)
B1-N1	1.557(7)	N1-B1-F1	111.1(5)
B1-N2	1.544(7)	N2-B1-F2	110.2(4)
N1-C1	1.357(6)	N1-B1-F2	109.3(4)
N1-C6	1.406(6)	N2-B1-F1	111.5(5)
N2-C8	1.412(6)		
N2-C12	1.361(6)		
C22-C23	1.187(8)		
C20-C21	1.194(8)		
For **3b**			
B1-F1	1.375(4)	N1-B1-N1	107.4(4)
B1-N1	1.537(4)	N1-B1-F1	109.9(4)
N1-C1	1.407(4)	F1-B1-F1	110.2(4)

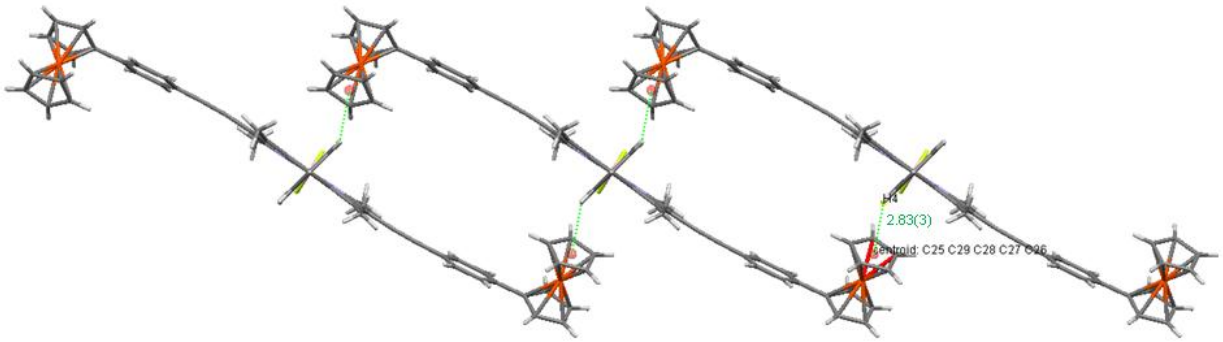
Table S2. Bond angle and bond distance for intermolecular interactions in **3b.**

No.	**Intermolecular interaction**	**H···A Distance (Å)**	**D···H···A Angle (°)**
3a	C-H···F (C111-H111···F2*)	2.46(3)	141(7)
3b			
1	C-H···F (C6-H6···F1**)	2.59(2)	154(4)
2	C-H···π (C4-H4···C25,C26,C27,C28,C29***)	2.83(3)	151(1)

* F1 at equivalent position (1-x, 1-y,1-z); ** F1 at equivalent position (x, -1+y, z); *** (C25,C26,C27,C28,C29) at equivalent position (2-x, y, 3/2-z).



(a)



(b)

Figure S2a. Crystal structure of **3b** showing intermolecular C-H---F interactions (a) along the *c*-axis, and C-H---π interactions along the *b*-axis.

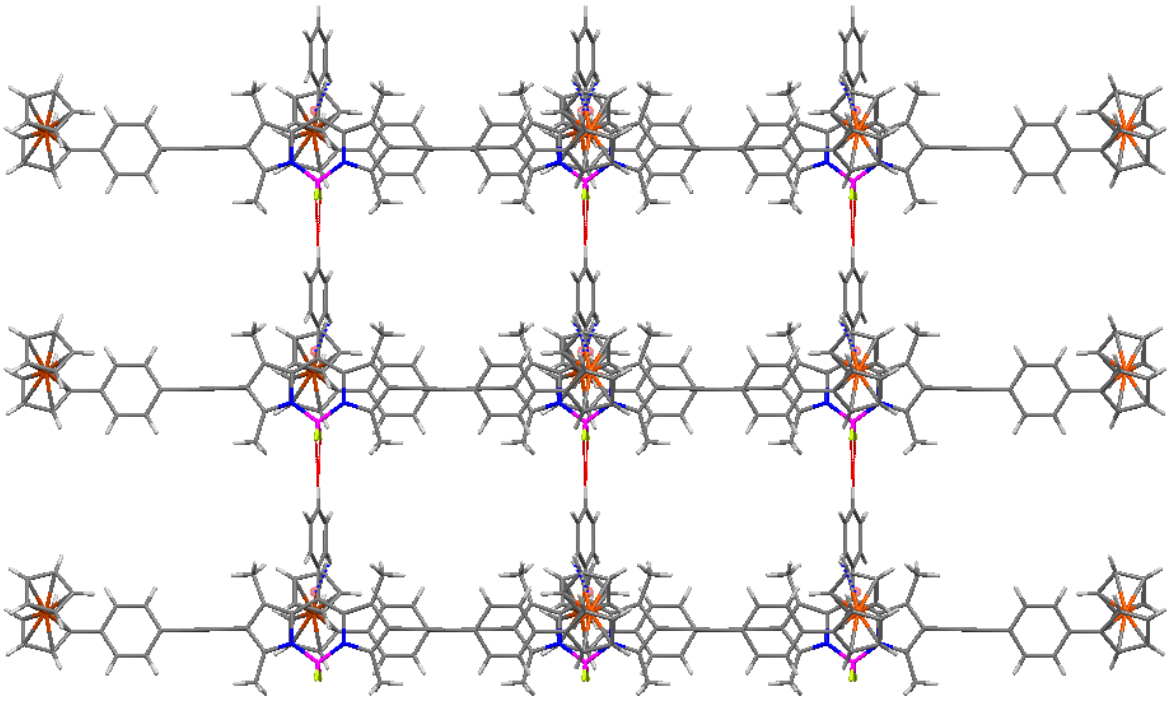


Figure S2b. Crystal structure of **3b** showing intermolecular C-H---F, and C-H---π interactions in 2D network.

Single crystal X-ray structural studies of **3a** and **3b** 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 **891093** and **891094** contain the supplementary crystallographic data for **3a** and **3b** respectively. These data can be obtained free of charge via www.ccdc.cam.ac.uk (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 S3. Crystal data and refinement parameters for the BODIPY dyes **3a** and **3b**

	3a	**3b**
Empirical formula	$C_{44}\,H_{36}\,B\,Cl_3\,F_2\,Fe_2\,N_2$	$C_{55}\,H_{43}\,B\,F_2\,Fe_2\,N_2$
Formula weight (g mol^{-1})	859.61	892.42
Crystal size (mm)	0.23 x 0.18 x 0.13	0.30 x 0.24 x 0.18
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$C2/c$
Z	4	4
***a*/ (Å)**	12.2026(10)	29.777(3)
***b*/ (Å)**	15.5375(13)	11.2969(6)
***c*/ (Å)**	20.834(2)	14.2126(10)
α /(°)	90	90.00
β/ (°)	90.456(8)	117.784(10)
γ/ (°)	90	90.00
Volume /(Å^3)	3950.0(6)	4229.8(5)
Calculated density/ (Mg m^{-3})	1.445 Mg/m^{-3}	1.401 Mg/m^{-3}
Absorption coefficient /(mm^{-1})	0.981	0.737
***T* (K)**	293(2)	150(2) K

***F*(000)**	1760	1848
θ range for data collection/(°)	3.11 to 25.00	2.94 to 25.00
Total reflections measured	29958	19402
Independent reflections [R(int)]	6955 [0.1052]	3717 [0.0760]
Completeness to θmax	θ = 25.00; 99.8 %	θ= 25.00; 99.8 %
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / Restraints /	6955 / 0 / 491	3717 / 0 / 284
Parameters		
Final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0826	R1 = 0.0529
	wR2 = 0.2261	wR2 = 0.1379
***R* indices all data**	R1 = 0.1026	R1 = 0.0841
	wR2 = 0.2555	wR2 = 0.1646
Goodness-of-fit on F^2	1.070	1.060
Largest diff. peak and hole ($eÅ^{-3}$)	1.105 and -0.953	0.291 and -0.368

Electrochemical Data for 1 , and 3a-3d.

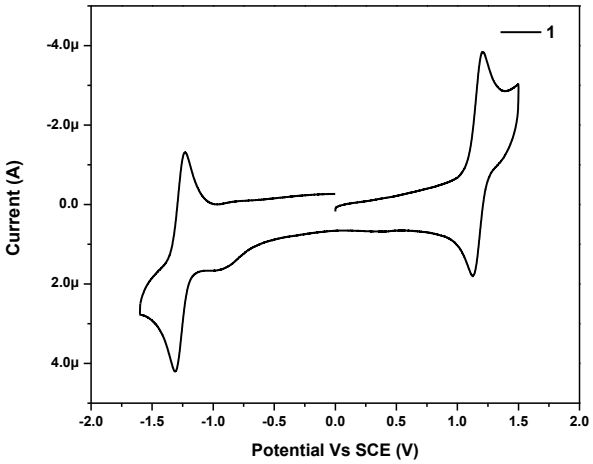


Figure S3. Cyclic voltammogram of BODIPY **1.**

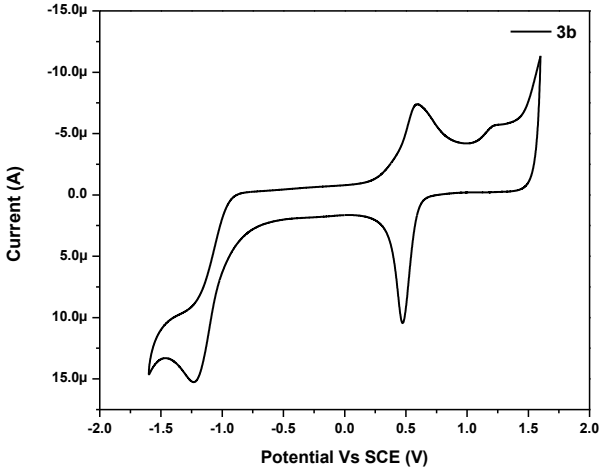


Figure S5. Cyclic voltammogram of BODIPY **3b.**

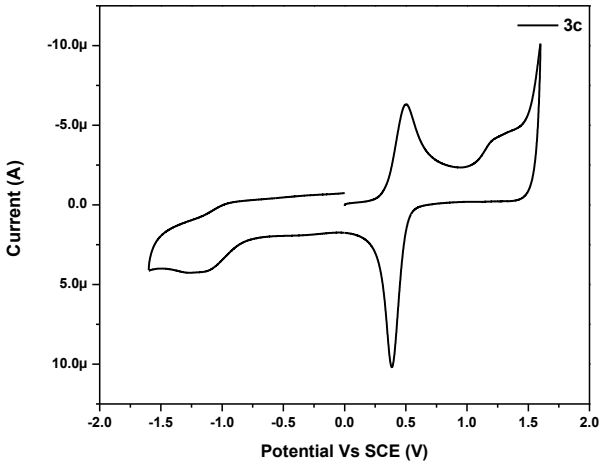


Figure S6. Cyclic voltammogram of BODIPY **3c.**

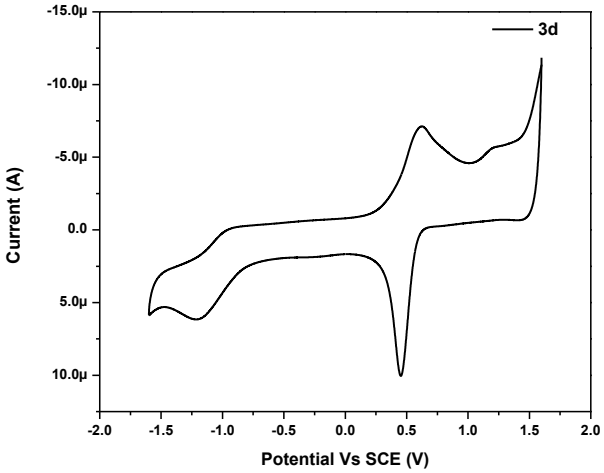


Figure S7. Cyclic voltammogram of BODIPY **3d.**

Copies of ^{1}H NMR, ^{13}C NMR and HRMS Spectra of the New Compounds

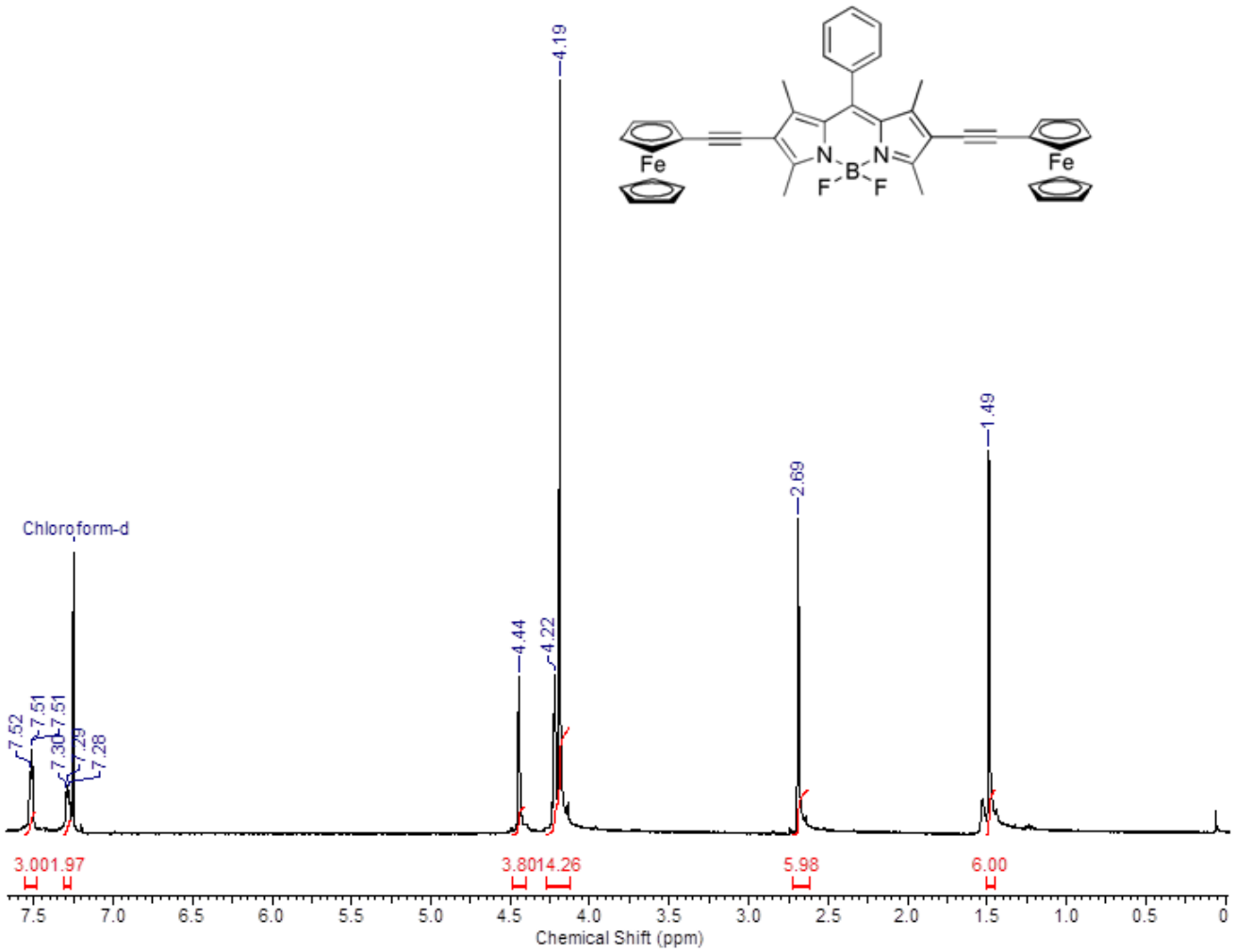


Figure S8. ^{1}H NMR Spectra of **3a.**

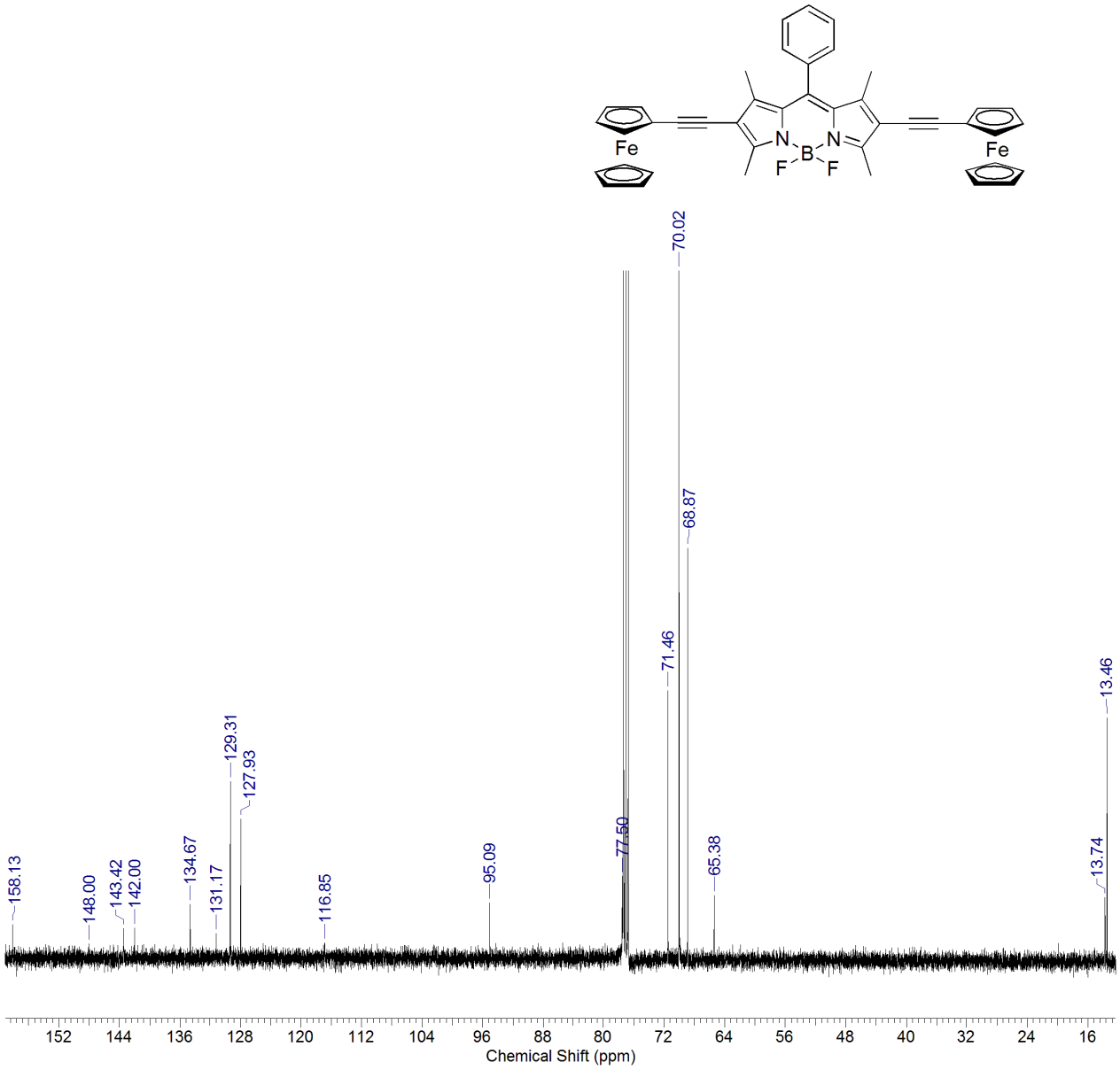


Figure S9. ^{13}C NMR Spectra of **3a.**

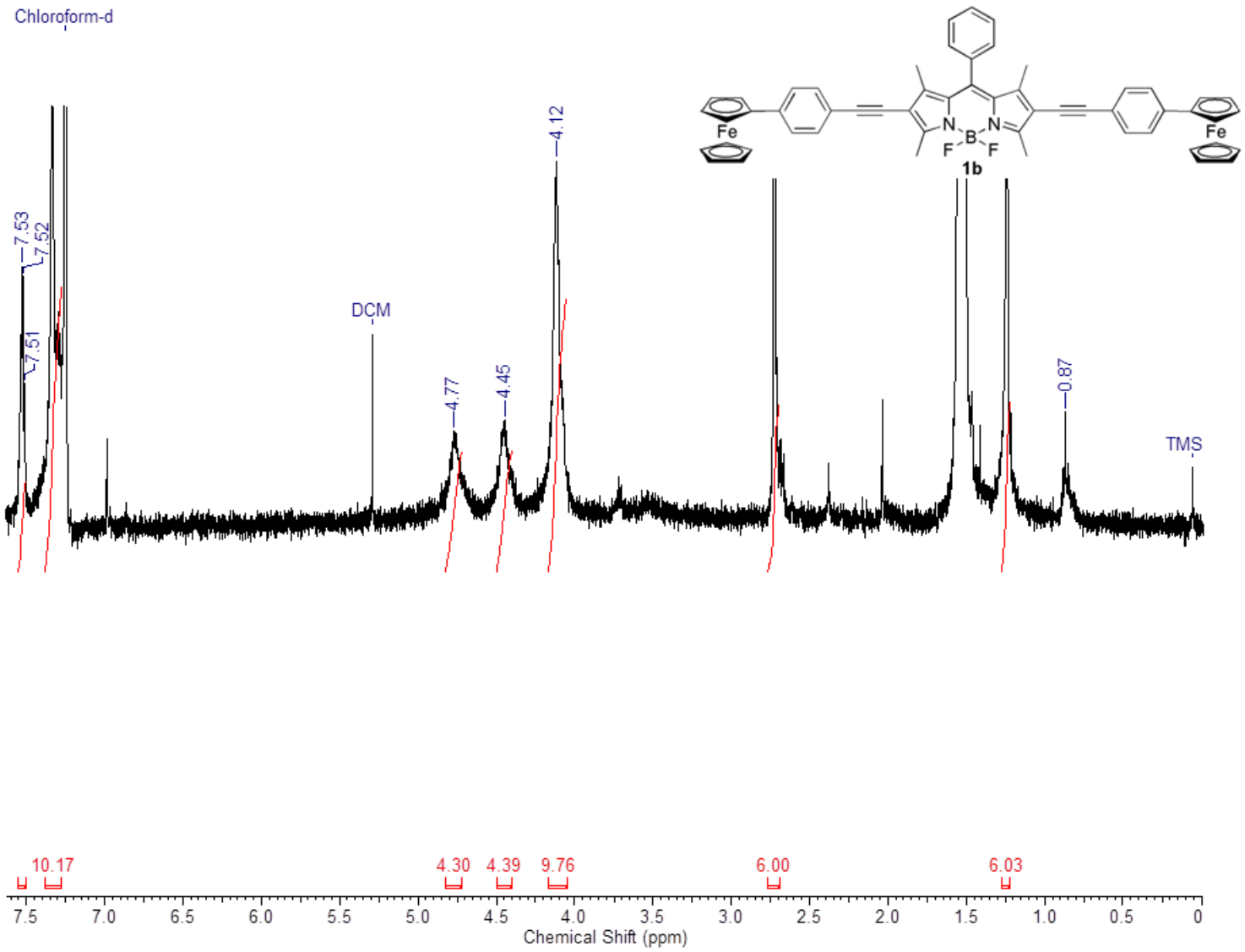


Figure S10. ^{1}H NMR Spectra of **3b.**

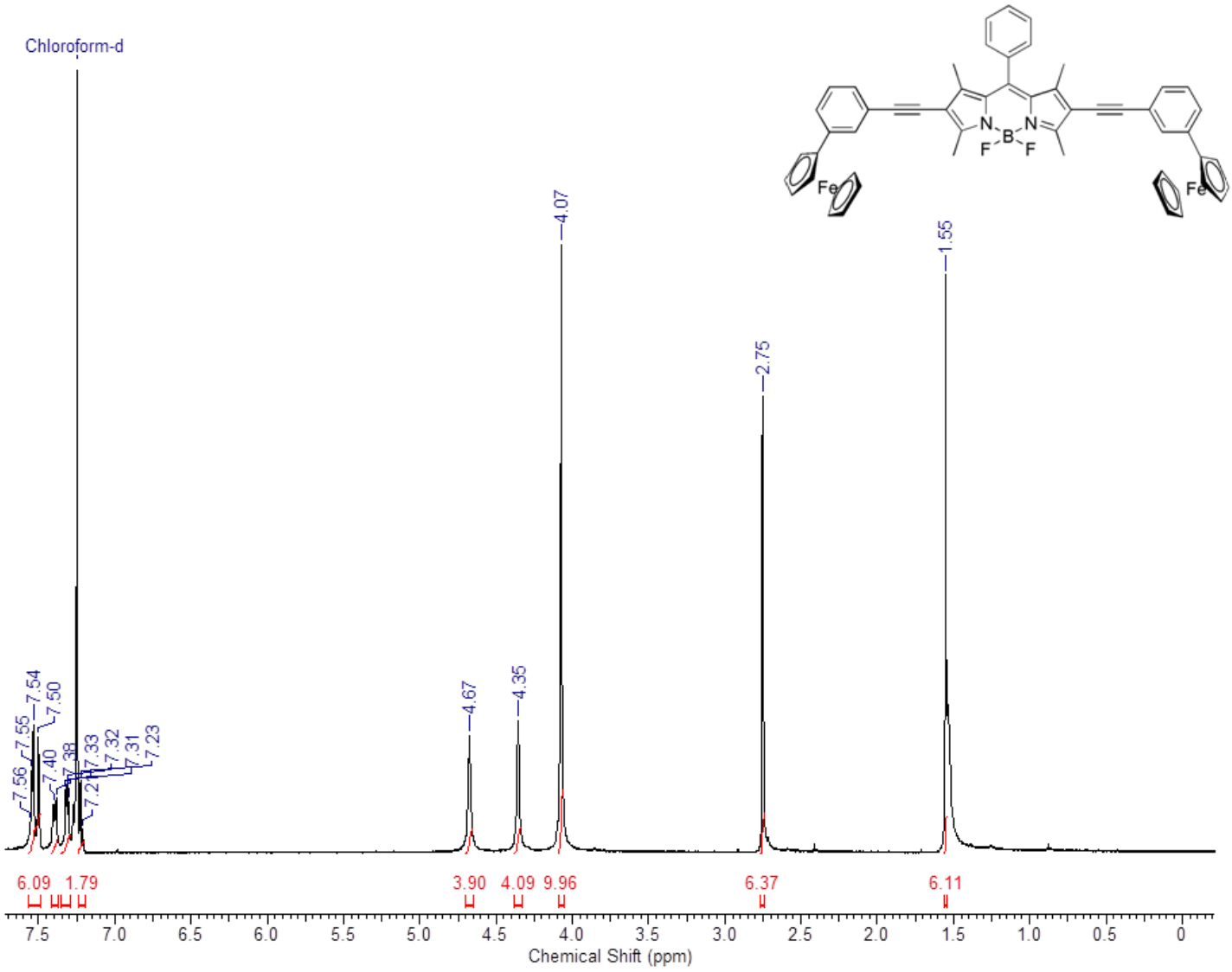


Figure S11. ^{1}H NMR Spectra of **3c.**

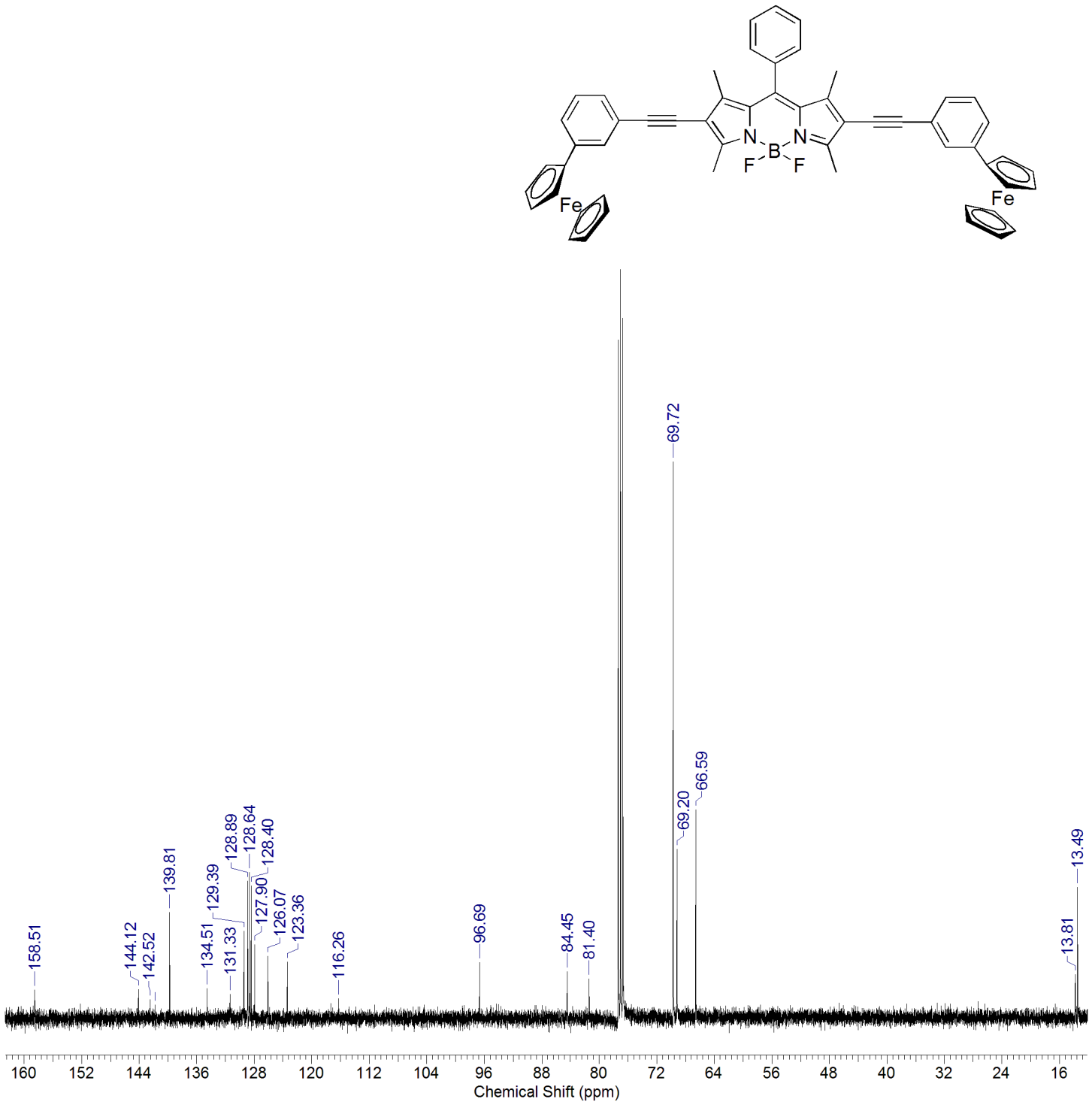


Figure S12. ^{13}C NMR Spectra of **3c.**

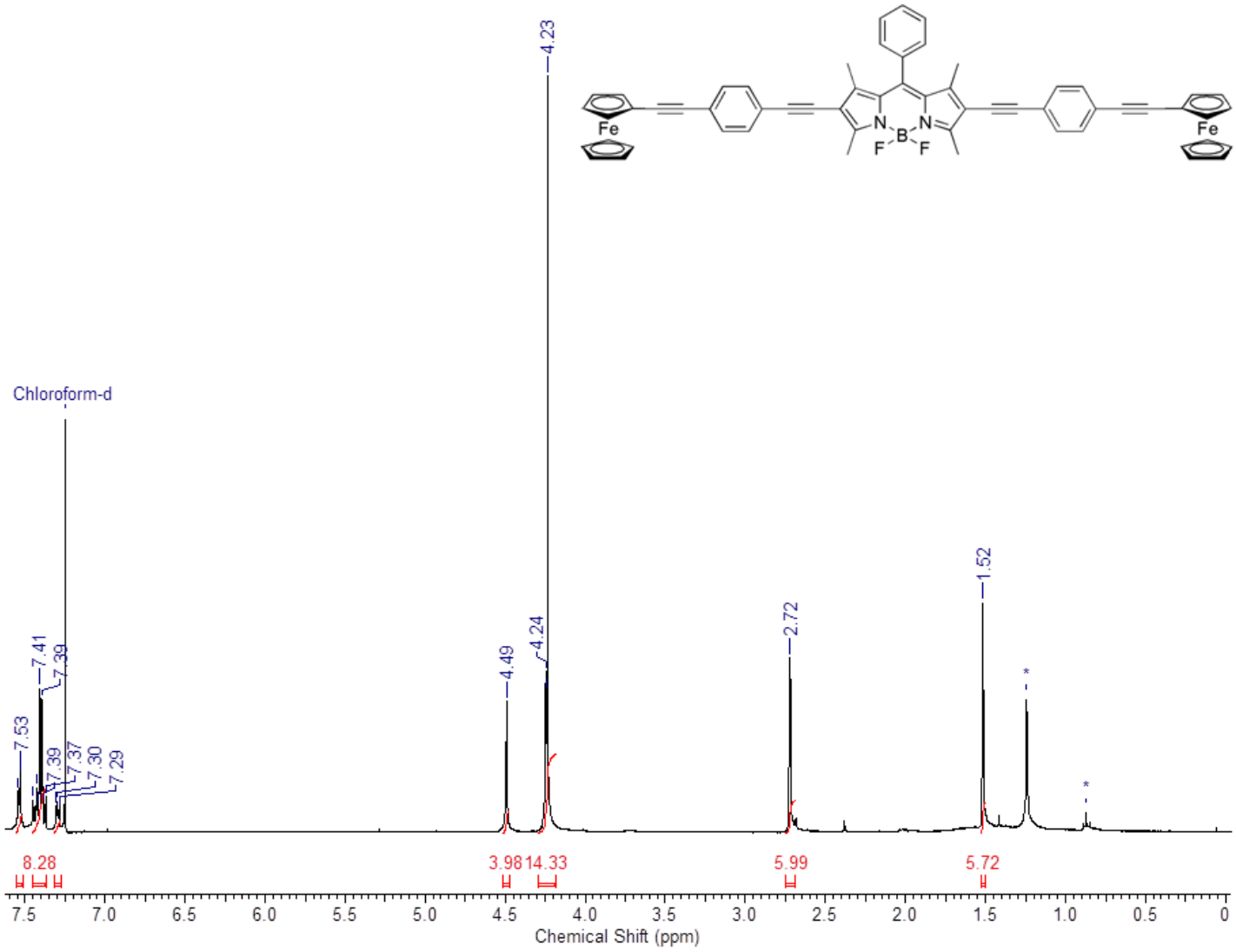


Figure S13. ^{1}H NMR Spectra of **3d.**

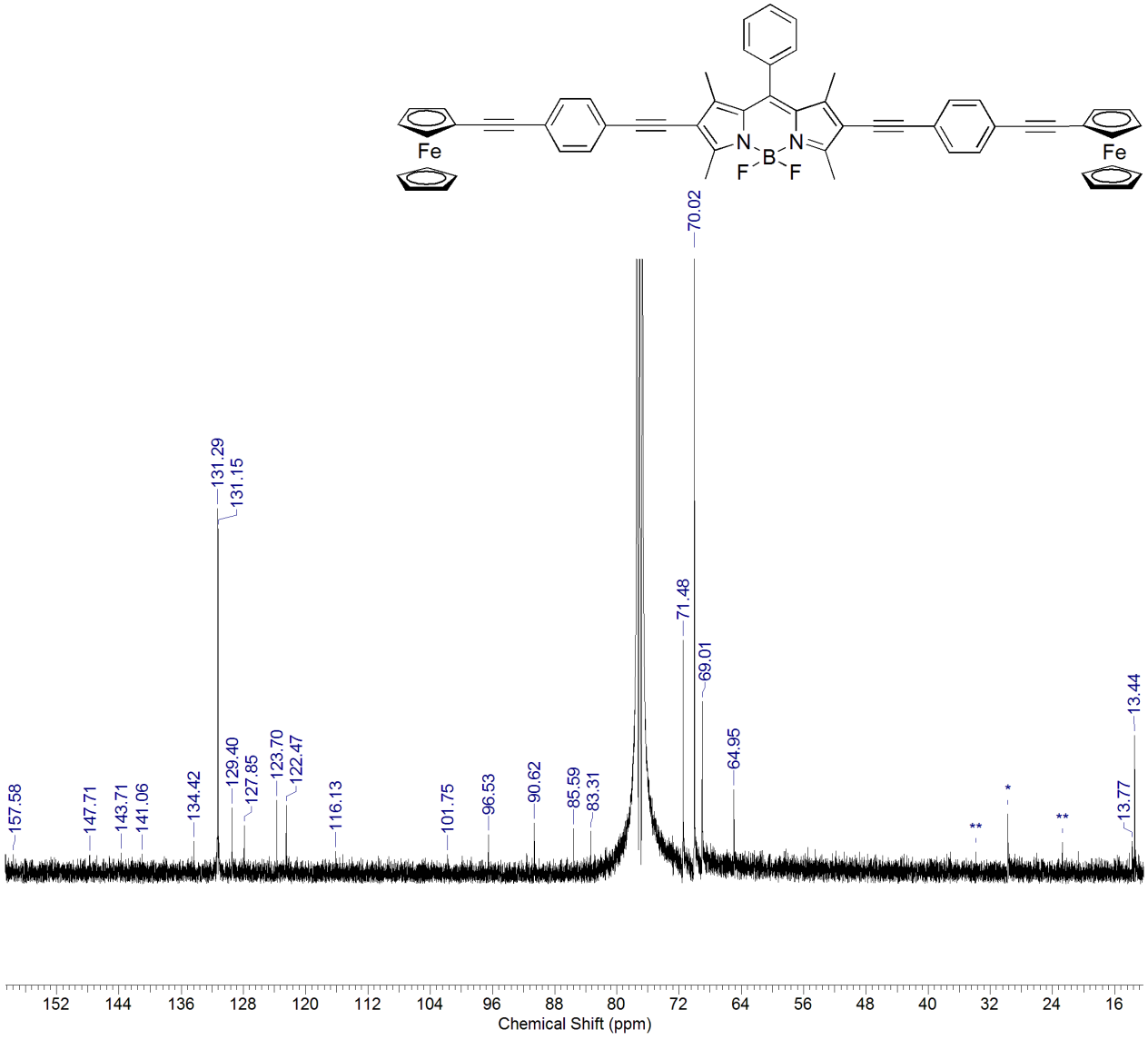


Figure S14. ^{13}C NMR Spectra of **3d.**

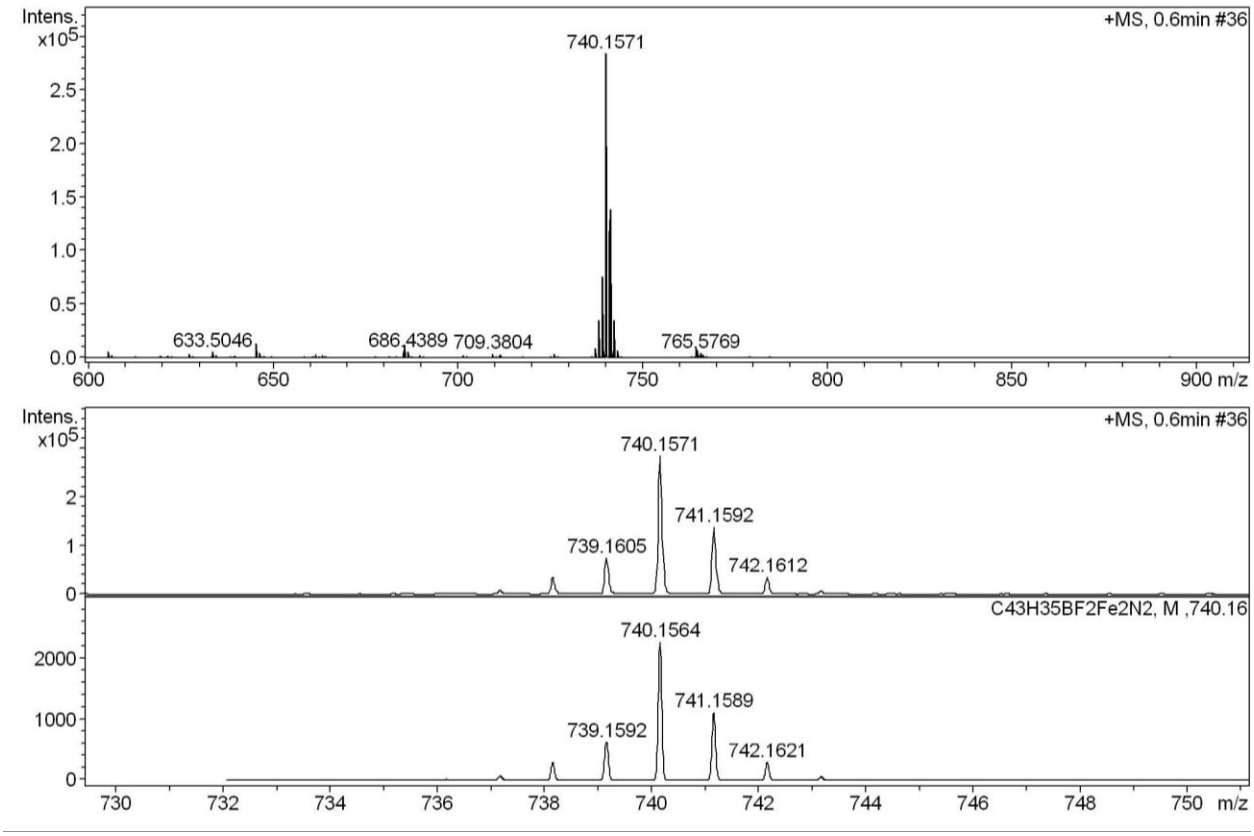


Figure S15. HRMS Spectra of **3a.**

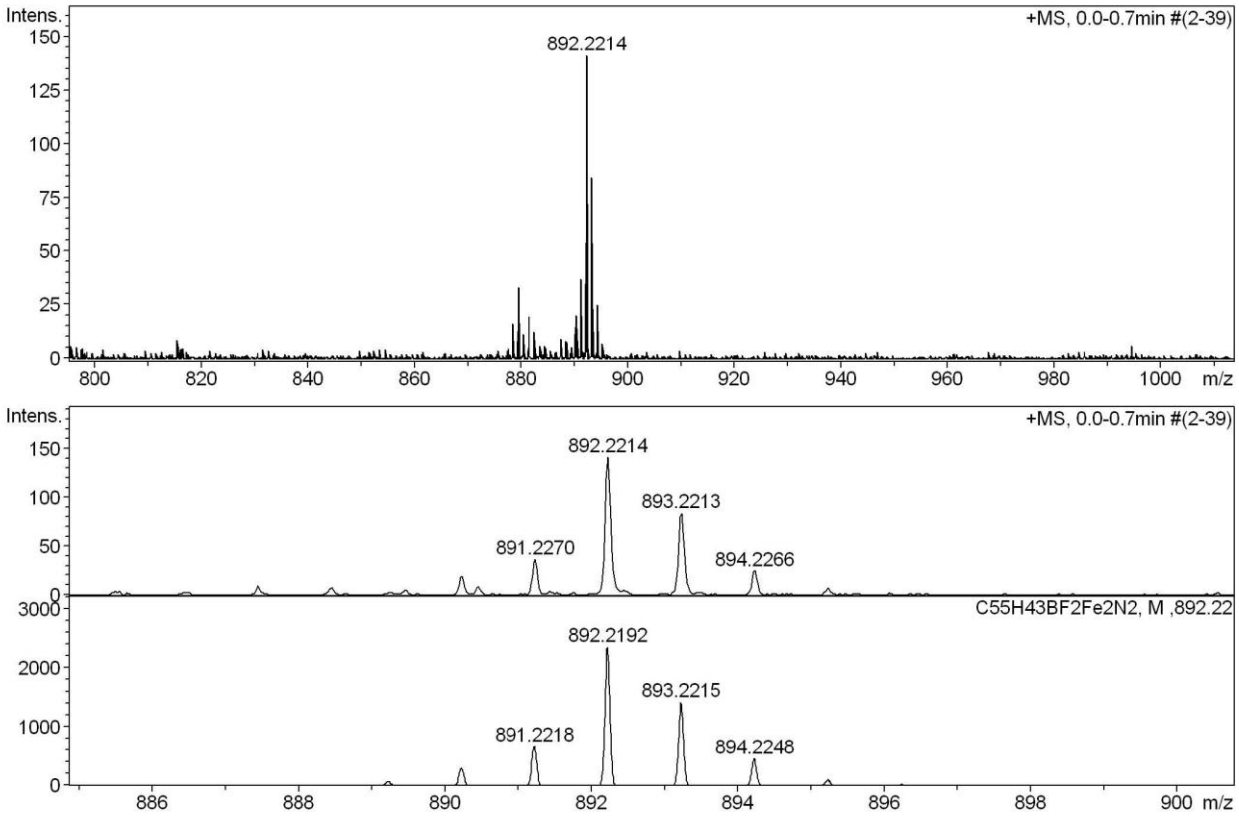


Figure S16. HRMS Spectra of **3b.**

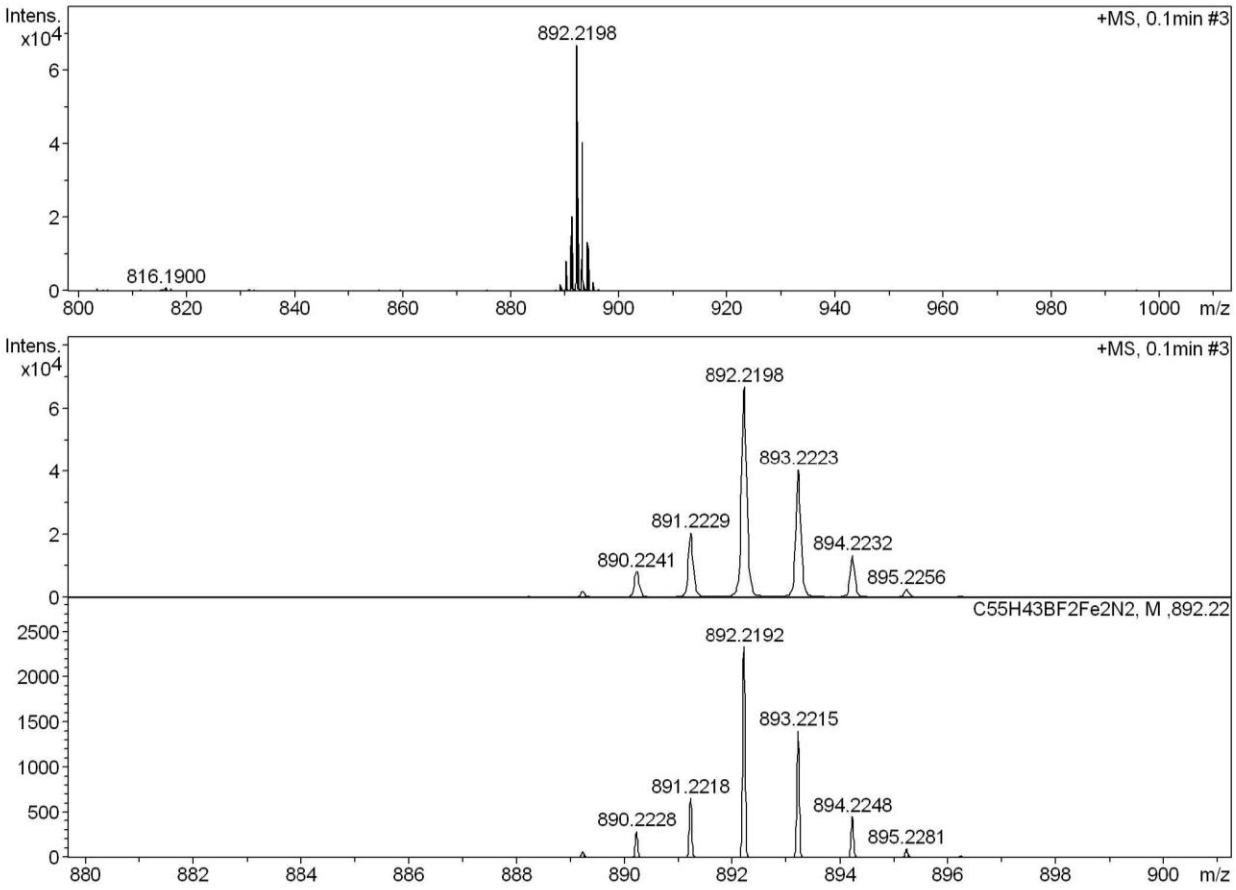


Figure S17. HRMS Spectra of **3c.**

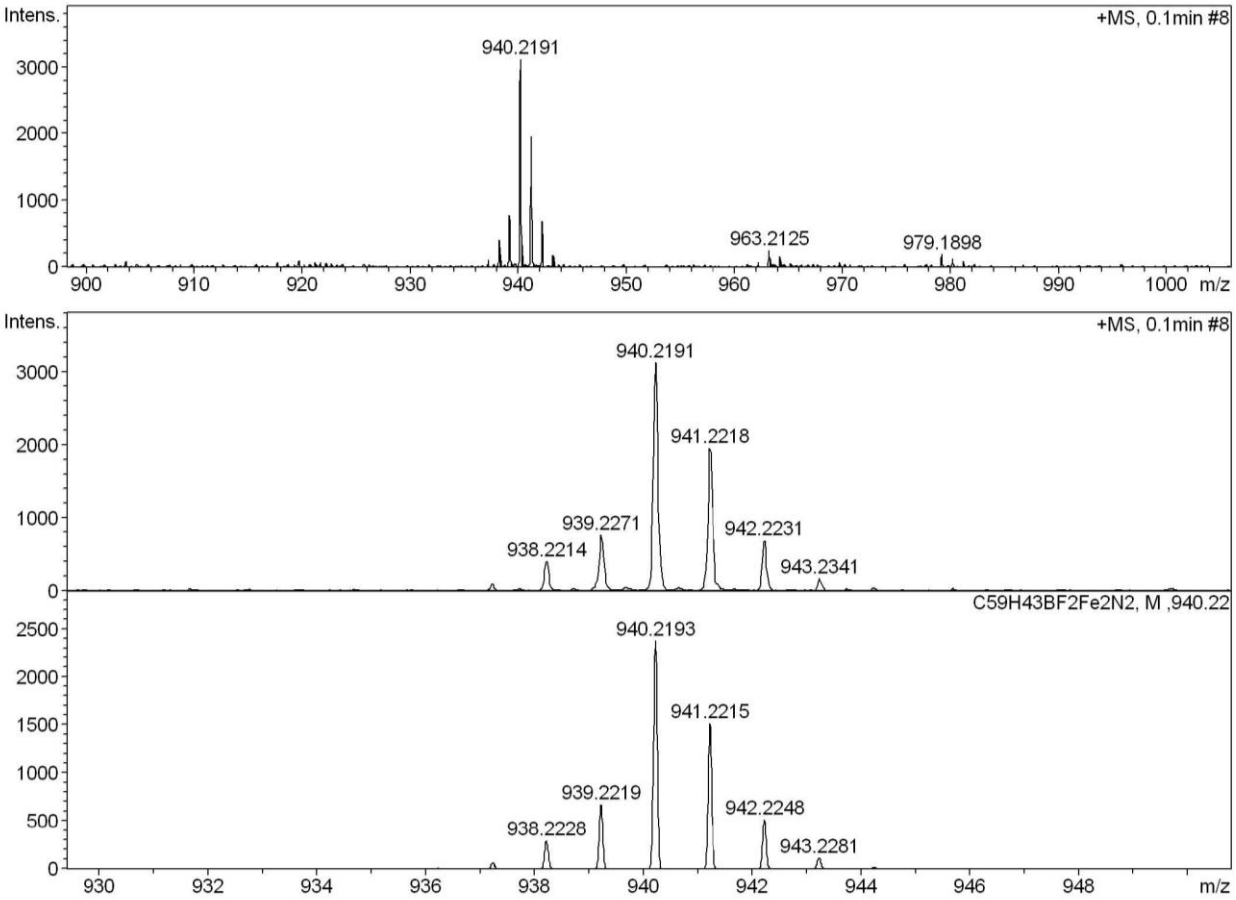


Figure S18. HRMS Spectra of **3d.**