

Supplementary Information

for

Zn-Templated Synthesis of Substituted (2,6-Diimine)pyridines Proligands and Evaluation of Their Iron Complexes as Anolytes for Flow Battery Applications

*Jason D. Braun, Paul A. Gray[#], Baldeep K. Sidhu[#], Dion B. Nemez and David E. Herbert**

Department of Chemistry and the Manitoba Institute for Materials, University of Manitoba, 144

Dysart Road, Winnipeg, Manitoba, R3T 2N2, Canada

*david.herbert@umanitoba.ca

[#]These authors contributed equally to this work.

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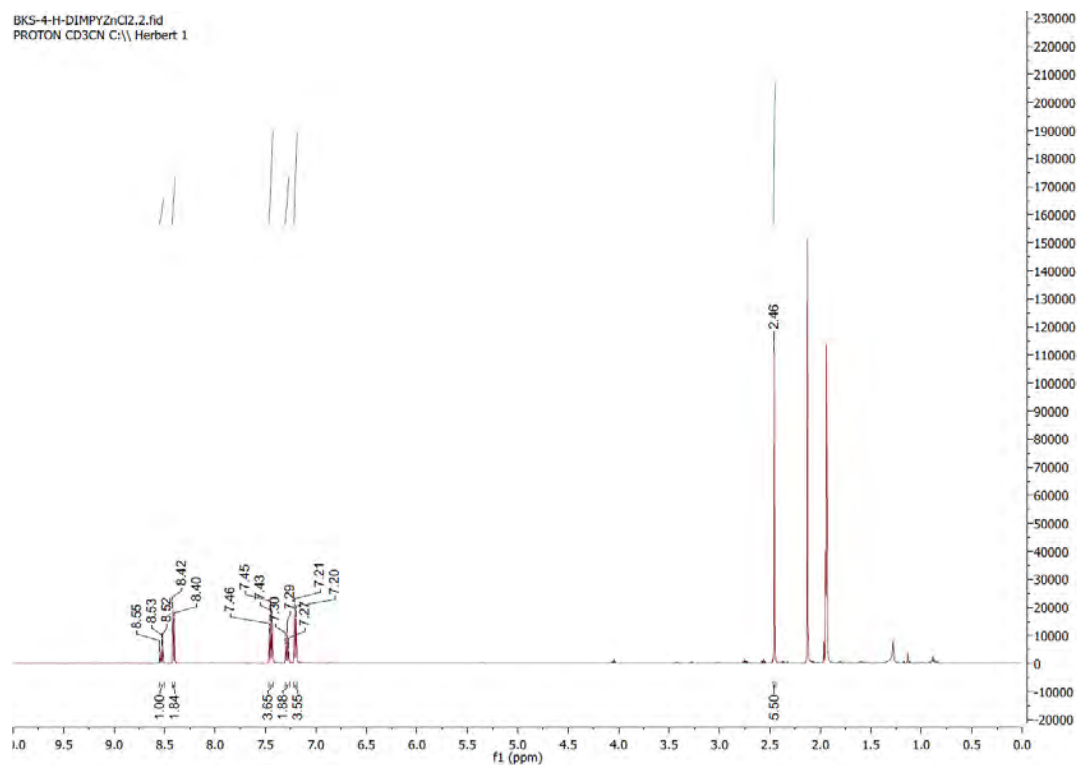


Figure S1. ^1H NMR (CD_3CN , 500 MHz, 25°C , ppm) of **1a**.

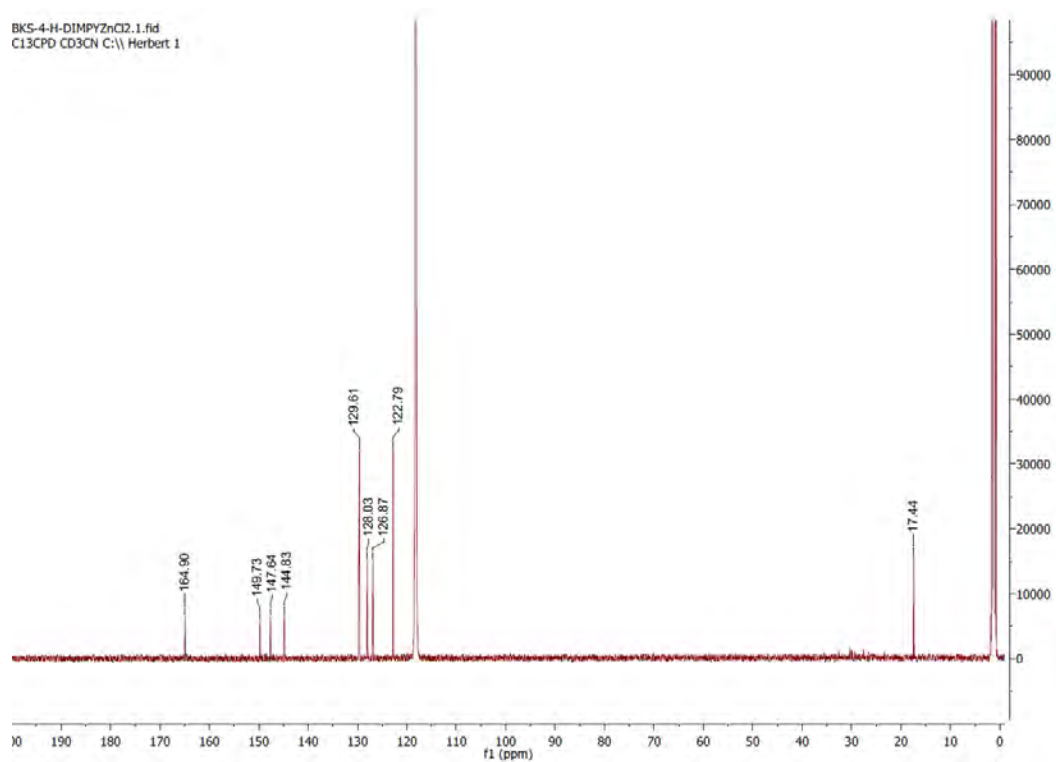


Figure S2. $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3CN , 125 MHz, 25°C , ppm) of **1a**.

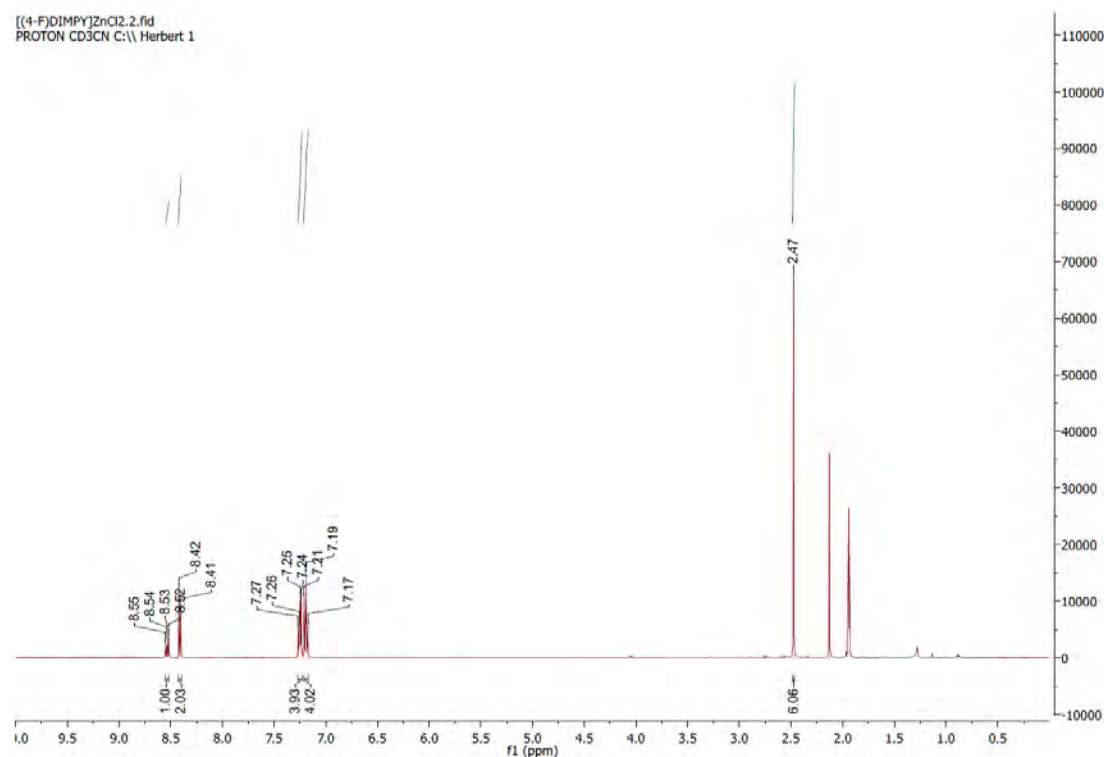


Figure S3. ^1H NMR (CD_3CN , 500 MHz, 25°C , ppm) of **1b**.

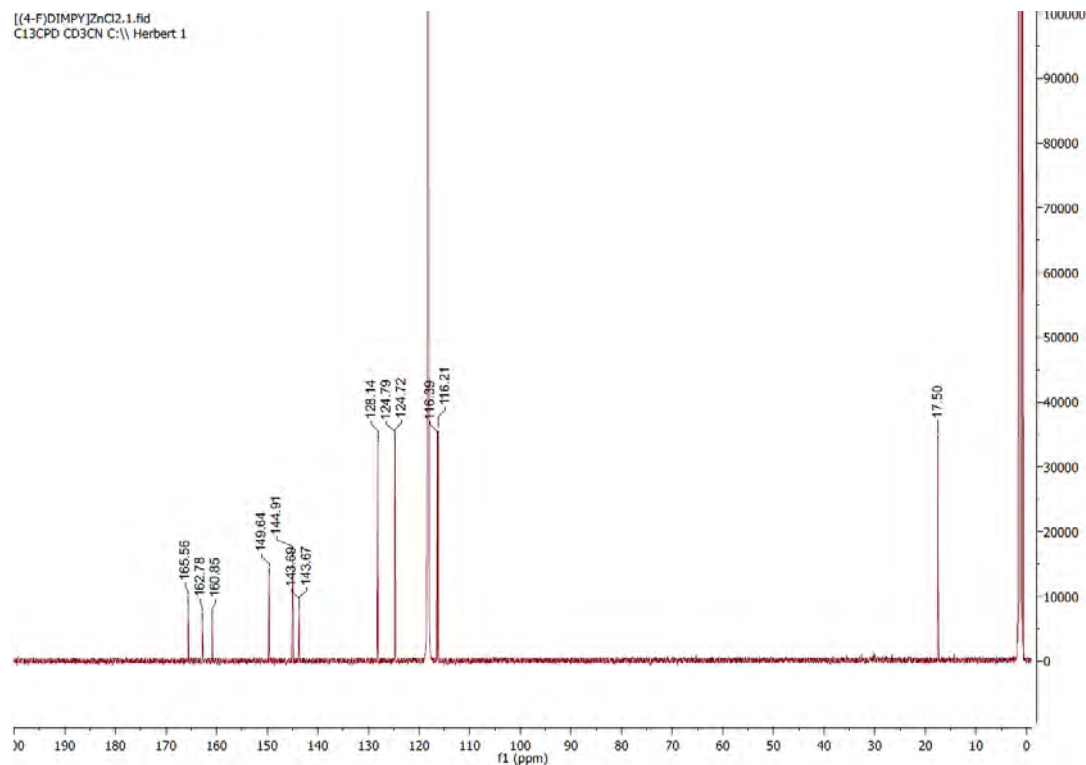


Figure S4. $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3CN , 125 MHz, 25°C , ppm) of **1b**.

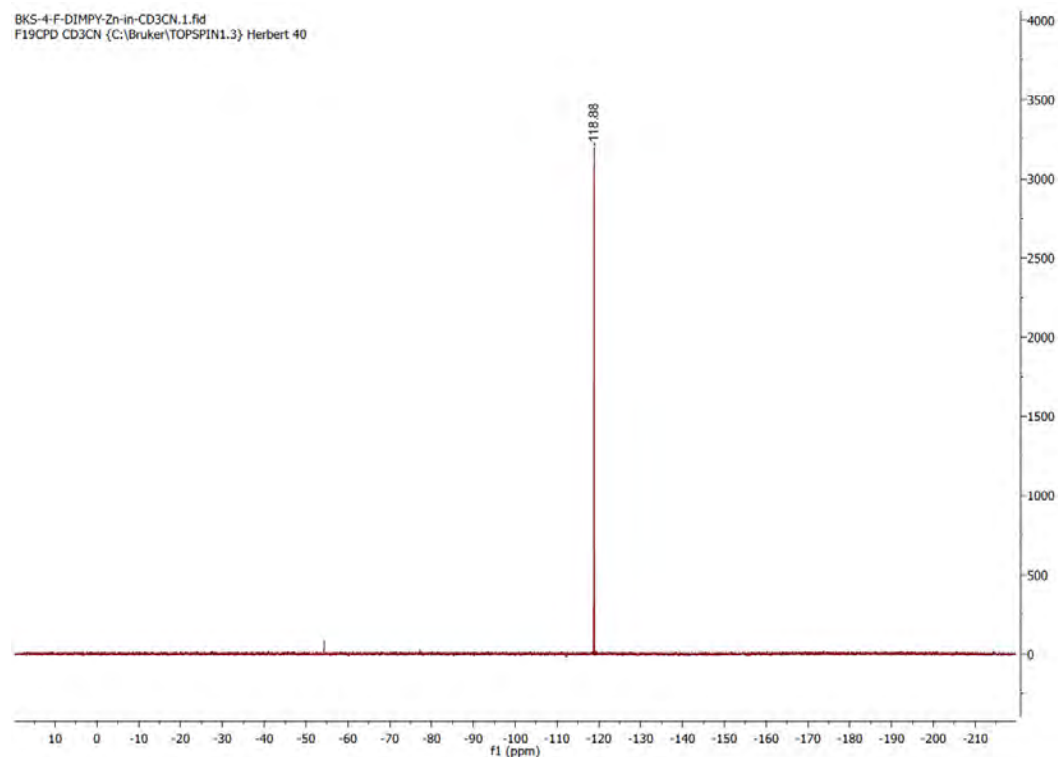


Figure S5. $^{19}\text{F}\{^1\text{H}\}$ NMR (CD_3CN , 282 MHz, 25°C, ppm) of **1b**.

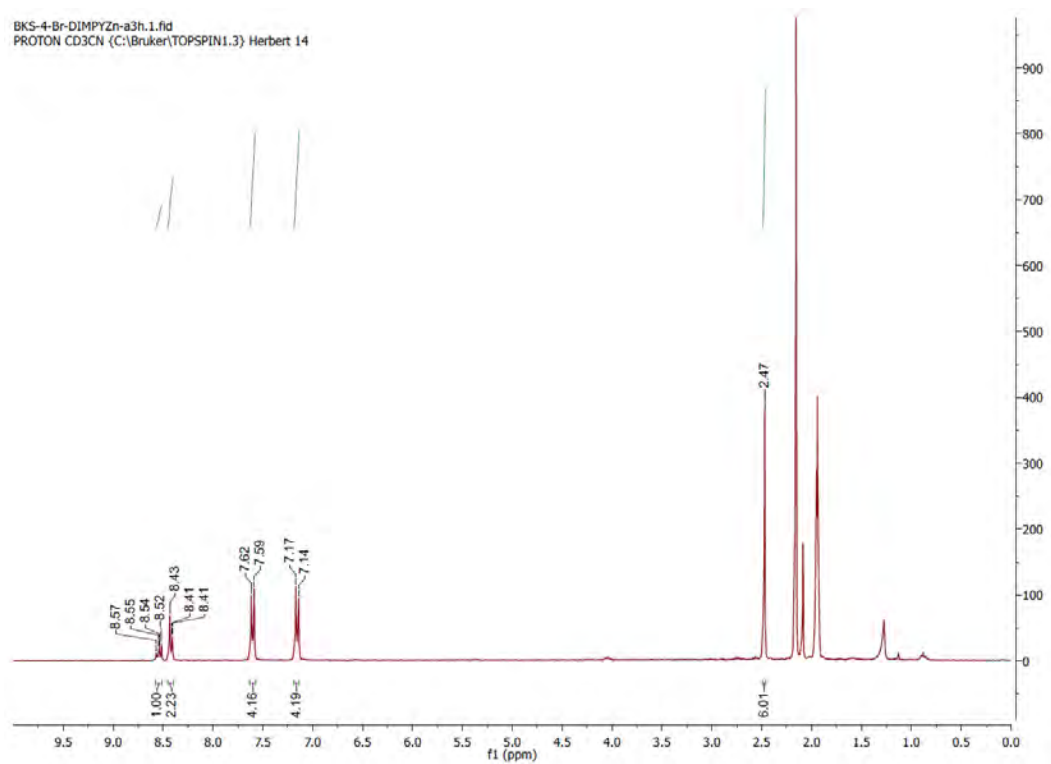
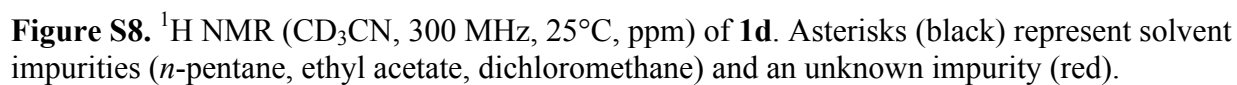
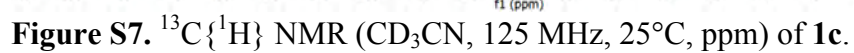


Figure S6. ^1H NMR (CD_3CN , 300 MHz, 25°C, ppm) of **1c**.



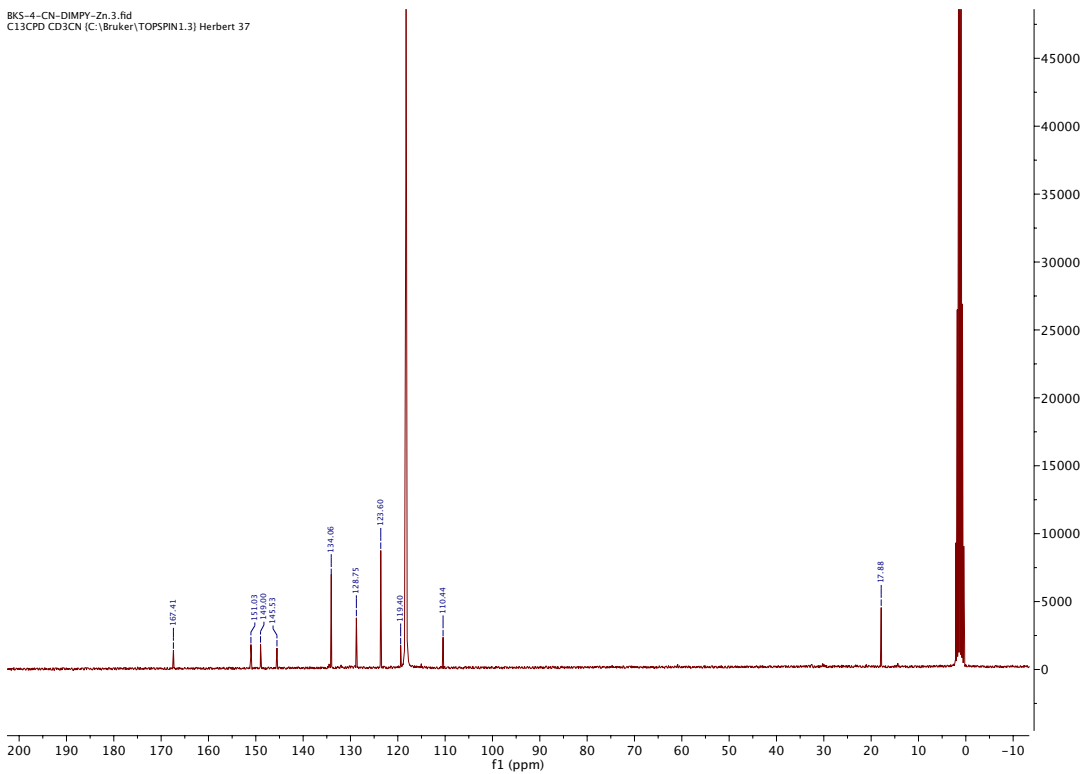


Figure S9. $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3CN , 125 MHz, 25°C, ppm) of **1d**.

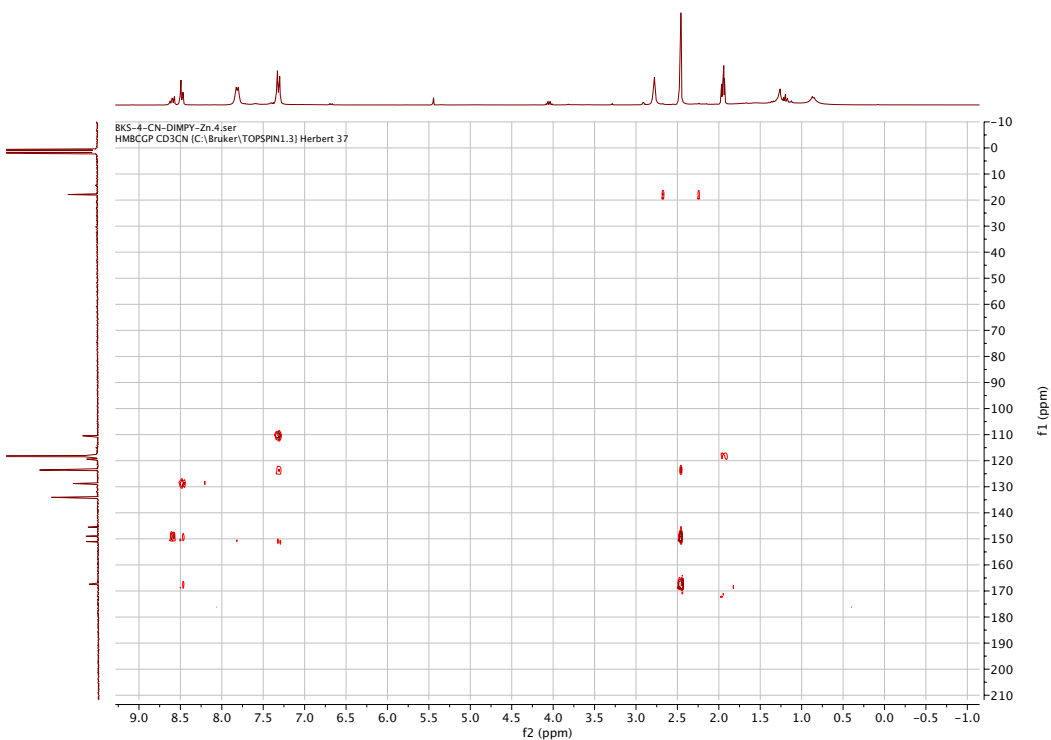


Figure S10. HMBC NMR (CD_3CN , 300/75 MHz, 25°C, ppm) of **1d**.

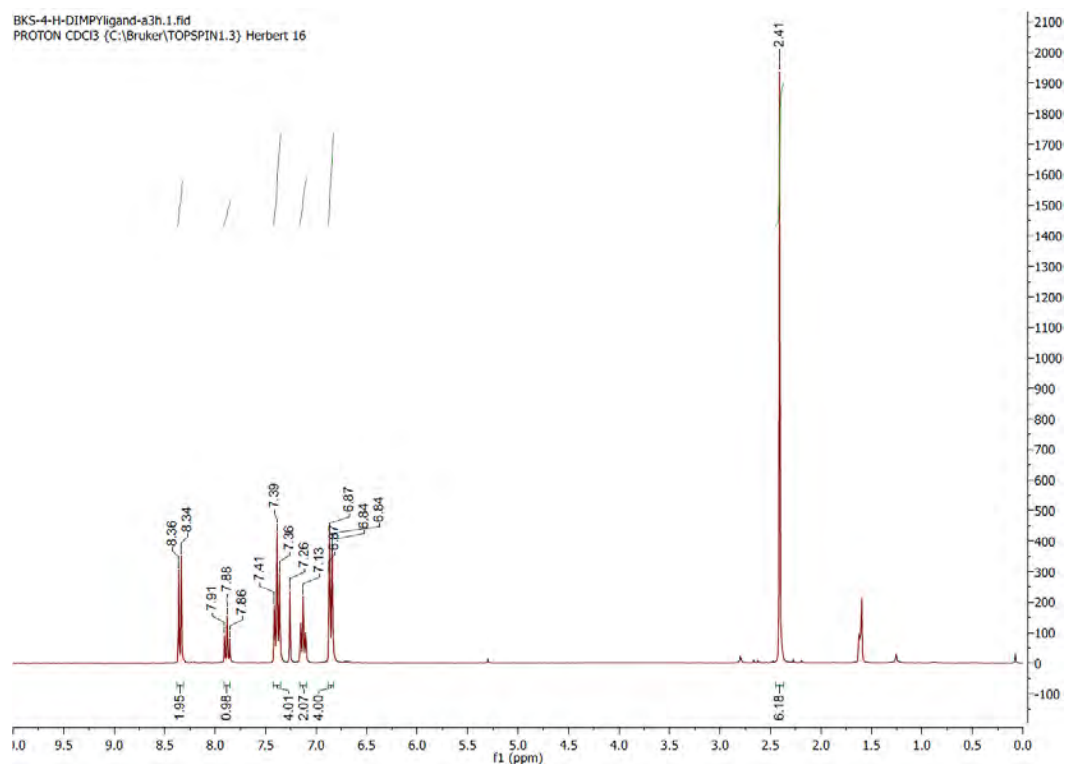


Figure S11. ^1H NMR (CDCl_3 , 300 MHz, 25°C, ppm) of **2a**.

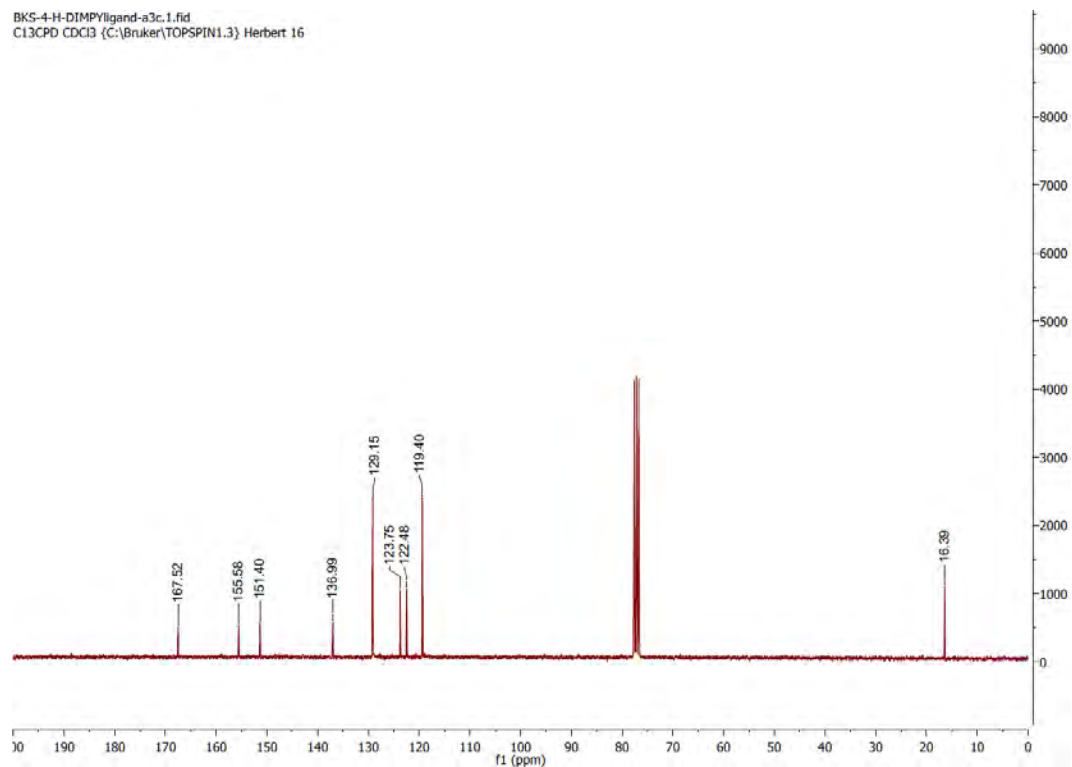


Figure S12. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz, 25°C, ppm) of **2a**.

BKS-4-F-DIMPYligand-a3h.1.fid
 PROTON CDCl₃ (C:\Bruker\TOPSPIN1.3) Herbert 15

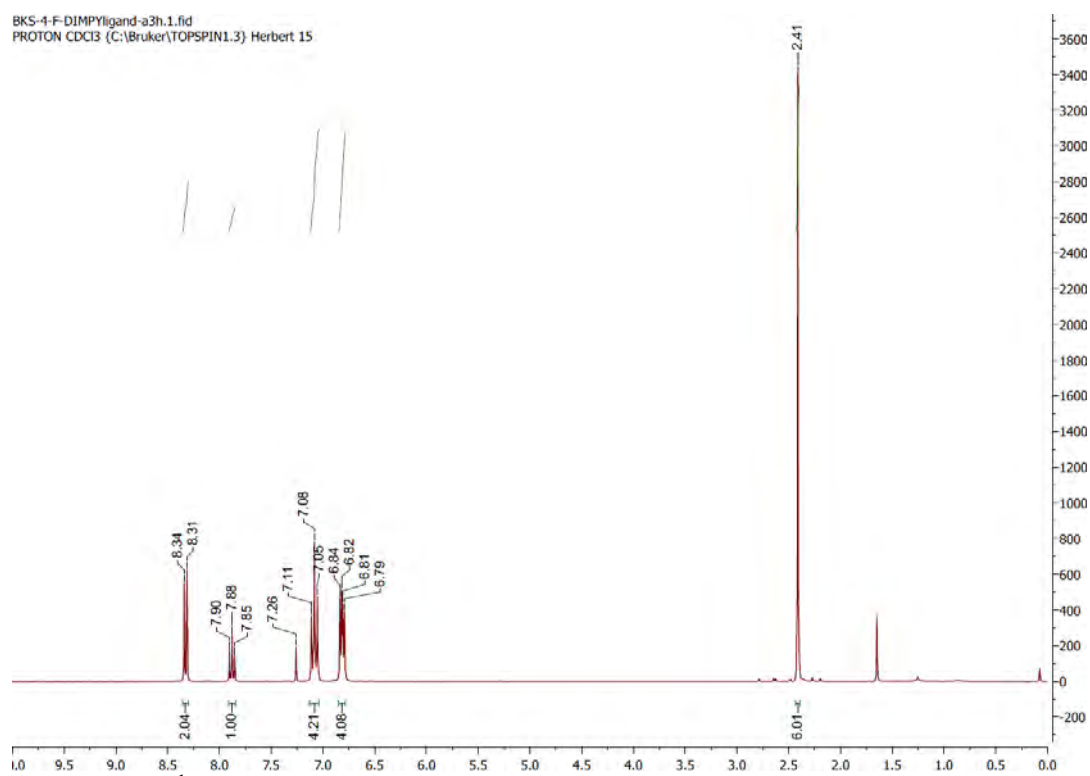


Figure S13. ¹H NMR (CDCl₃, 300 MHz, 25°C, ppm) of **2b**.

BKS-4-F-DIMPYligand-a3c.1.fid
 C13CPD CDCl₃ (C:\Bruker\TOPSPIN1.3) Herbert 15

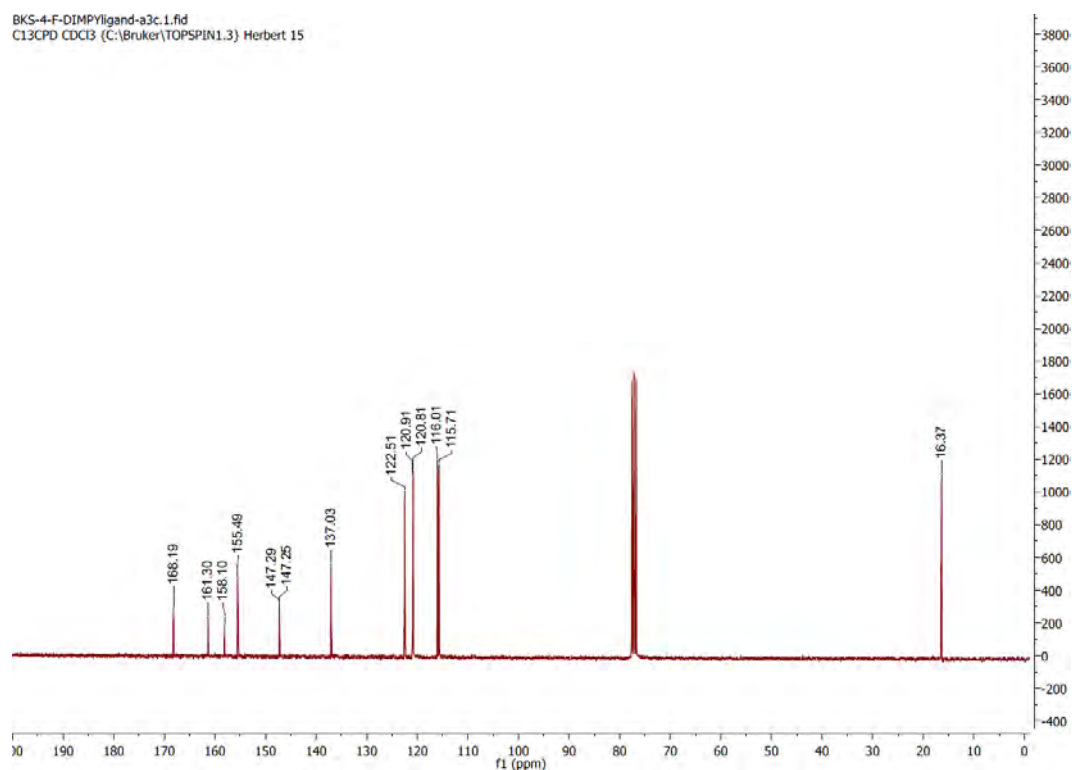


Figure S14. ¹³C{¹H} NMR (CDCl₃, 75 MHz, 25°C, ppm) of **2b**.

BKS-02-025-f3f.1.fid
 Dezincated 4-F-DIMPY
 Washed with water 2x
 F19CPD CDCl3 (C:\Bruker\TOPSPIN1.3) Herbert 49

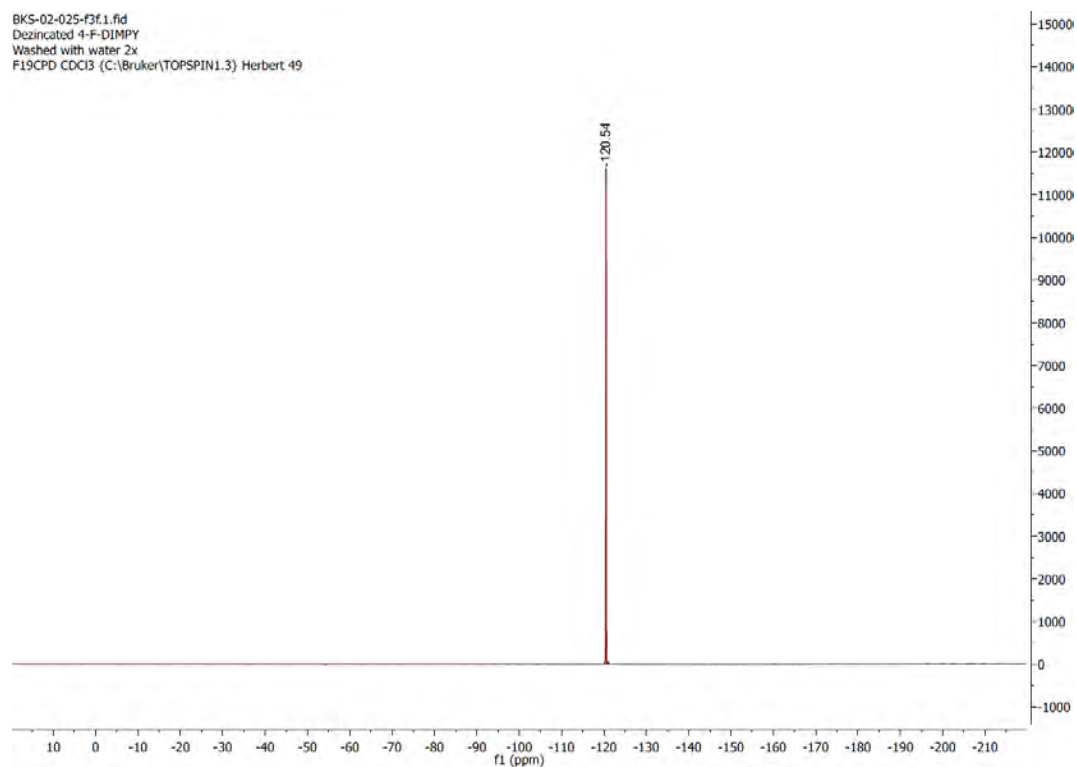


Figure S15. $^{19}\text{F}\{^1\text{H}\}$ NMR (CDCl_3 , 282 MHz, 25°C, ppm) of **2b**.

BKS-4-Br-DIMPYligand-a3h.1.fid
 PROTON CDCl3 (C:\Bruker\TOPSPIN1.3) Herbert 17

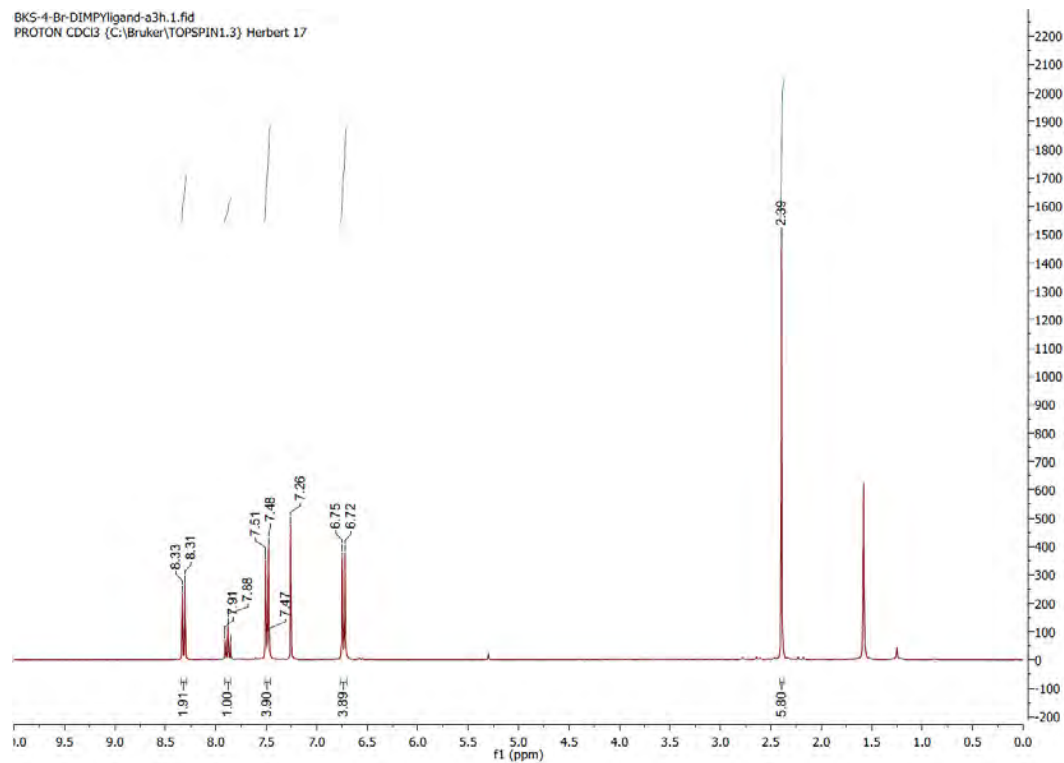


Figure S16. ^1H NMR (CDCl_3 , 300 MHz, 25°C, ppm) of **2c**.

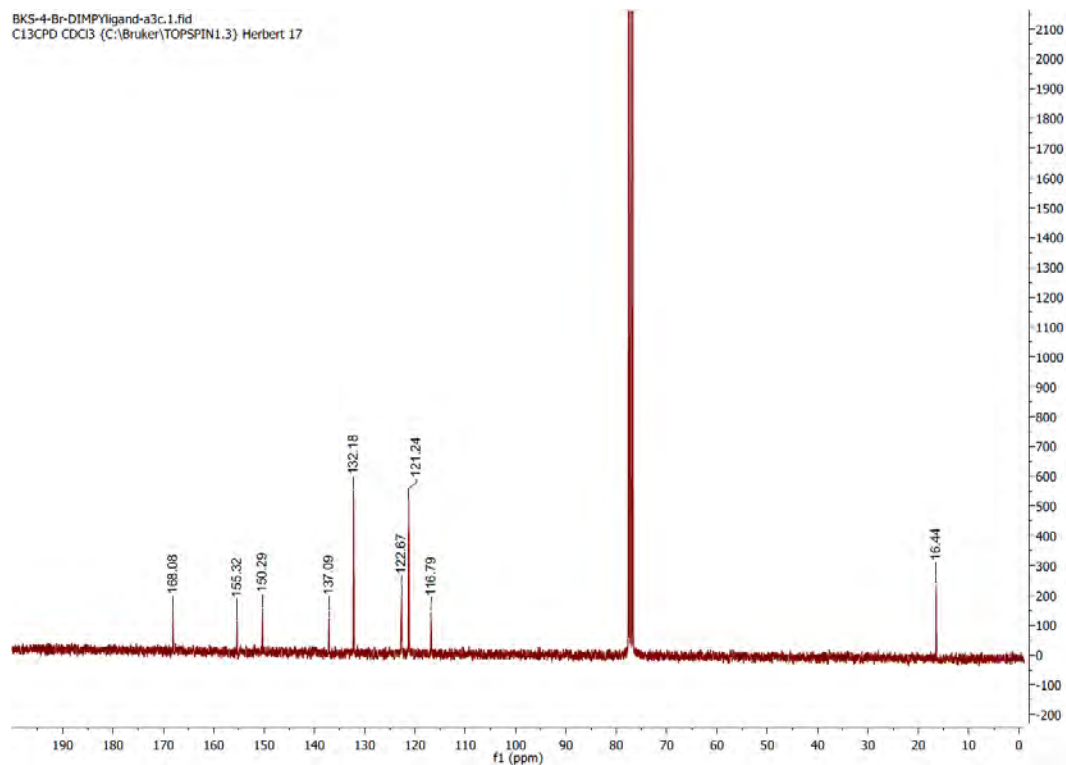


Figure S17. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz, 25°C, ppm) of **2c**.

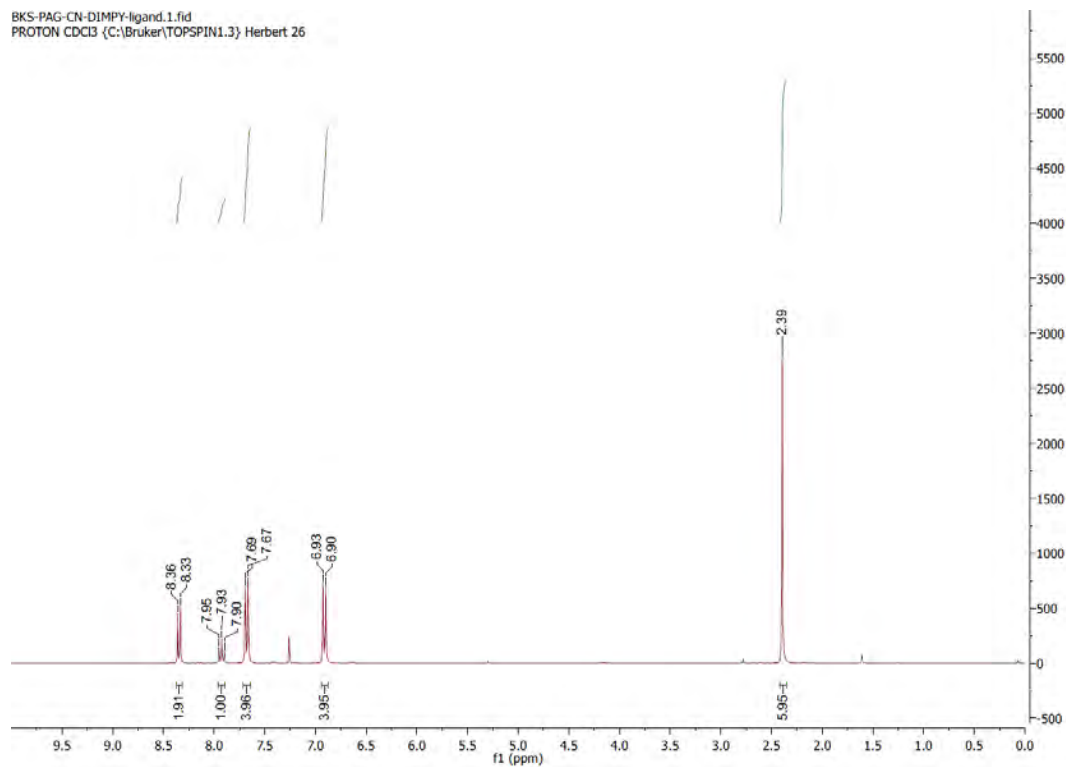


Figure S18. ^1H NMR (CDCl_3 , 300 MHz, 25°C, ppm) of **2d**.

BKS-PAG-CN-DIMPY-ligand.2.fid
C13CPD CDCl3 (C:\Bruker\TOPSPIN1.3) Herbert 26

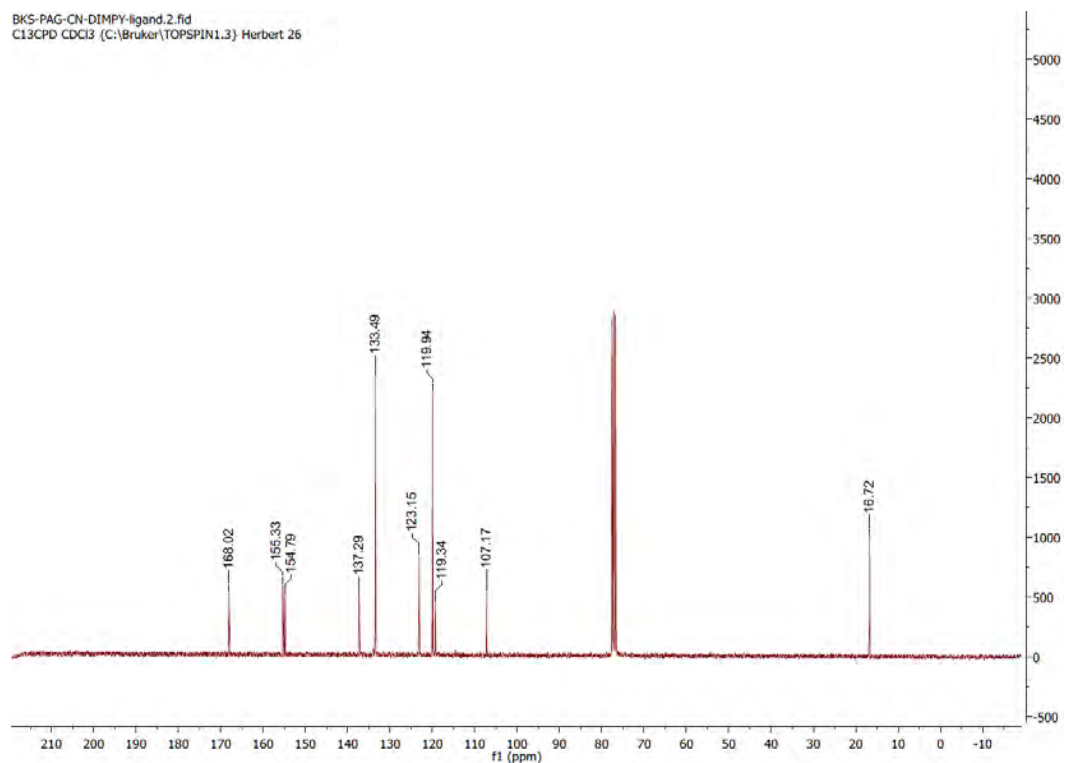


Figure S19. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz, 25°C, ppm) of **2d**.

PAG-02-47-A3H
H-Dip2Fe (PF6)2
PROTON CD3CN (C:\Bruker\TOPSPIN1.3) Herbert 10

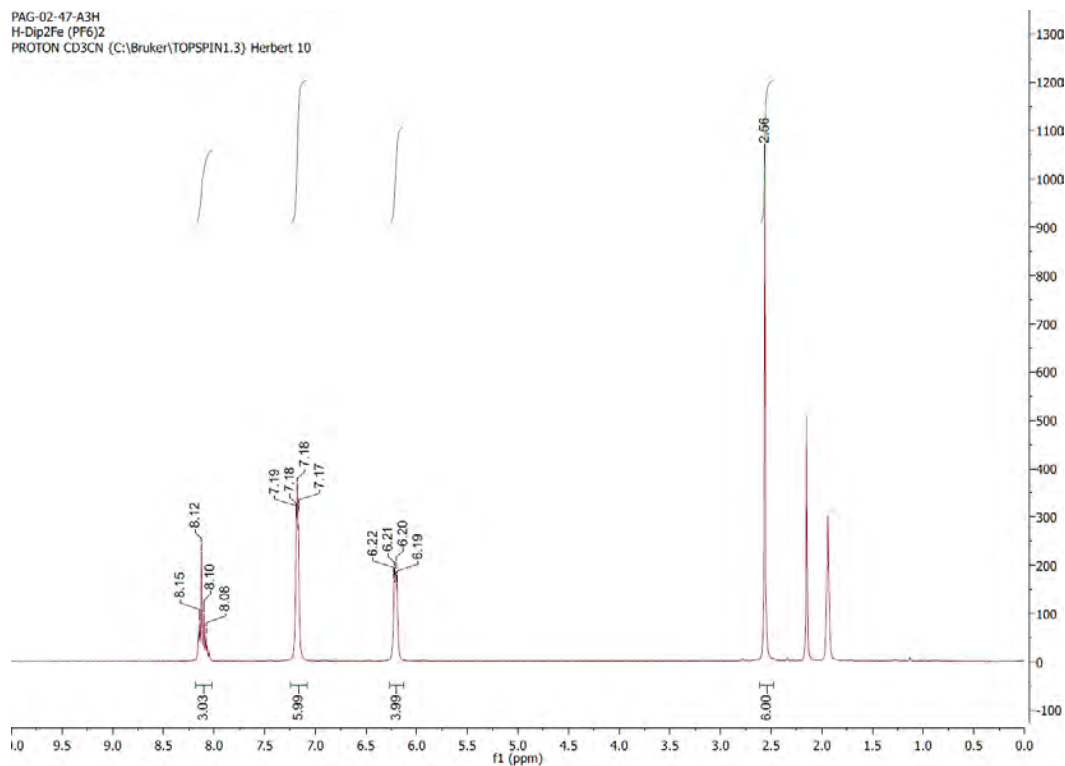


Figure S20. ^1H NMR (CD_3CN , 300 MHz, 25°C, ppm) of **3a**.

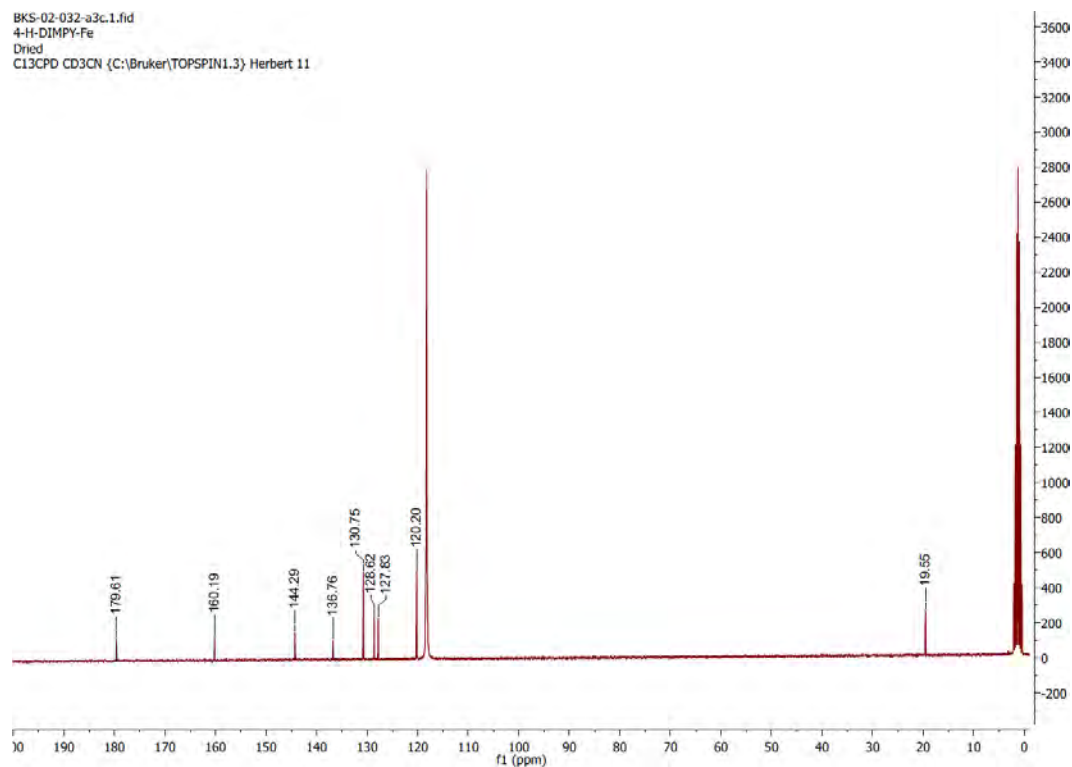


Figure S21. $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3CN , 75 MHz, 25°C, ppm) of **3a**.

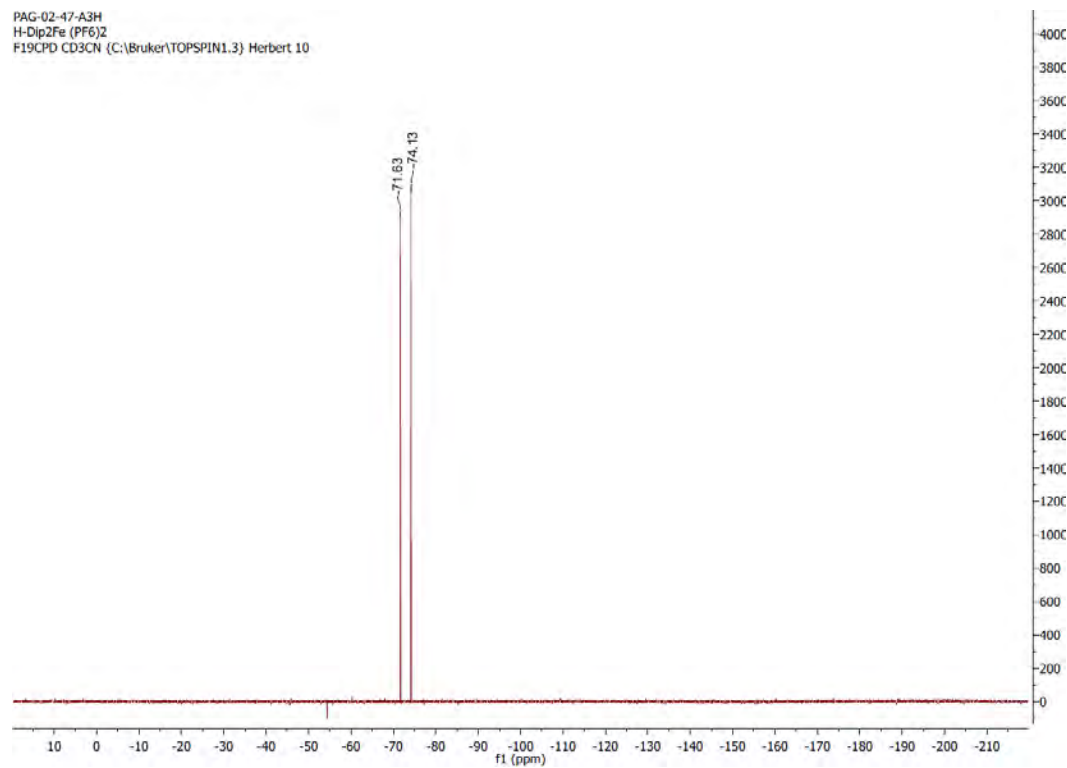


Figure S22: $^{19}\text{F}\{^1\text{H}\}$ NMR (CD_3CN , 282 MHz, 25°C, ppm) of **3a**.

PAG-02-47-A3H
H-Dip2Fe (PF₆)₂
P31CPD CD3CN (C:\Bruker\TOPSPIN1.3} Herbert 10

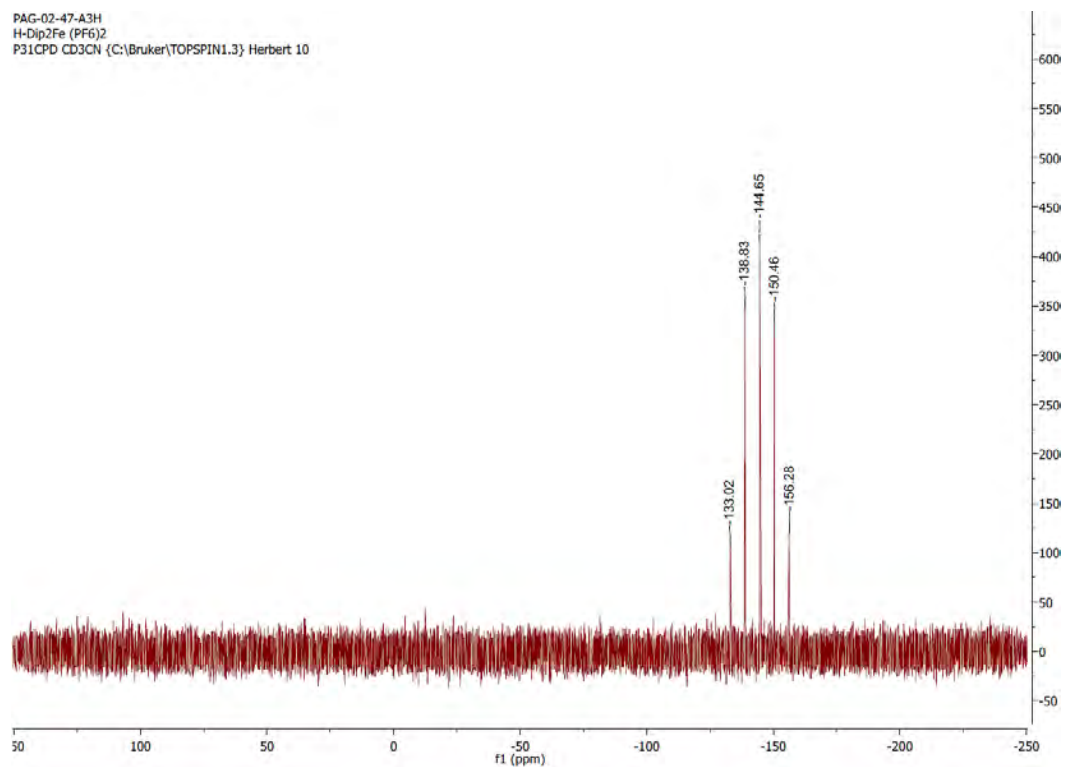


Figure S23. ³¹P{¹H} NMR (CD₃CN, 121 MHz, 25°C, ppm) of **3a**.

PAG-02-087-A3H
Iron-DIMPY in CD3CN
PROTON CD3CN (C:\Bruker\TOPSPIN1.3} Herbert 31

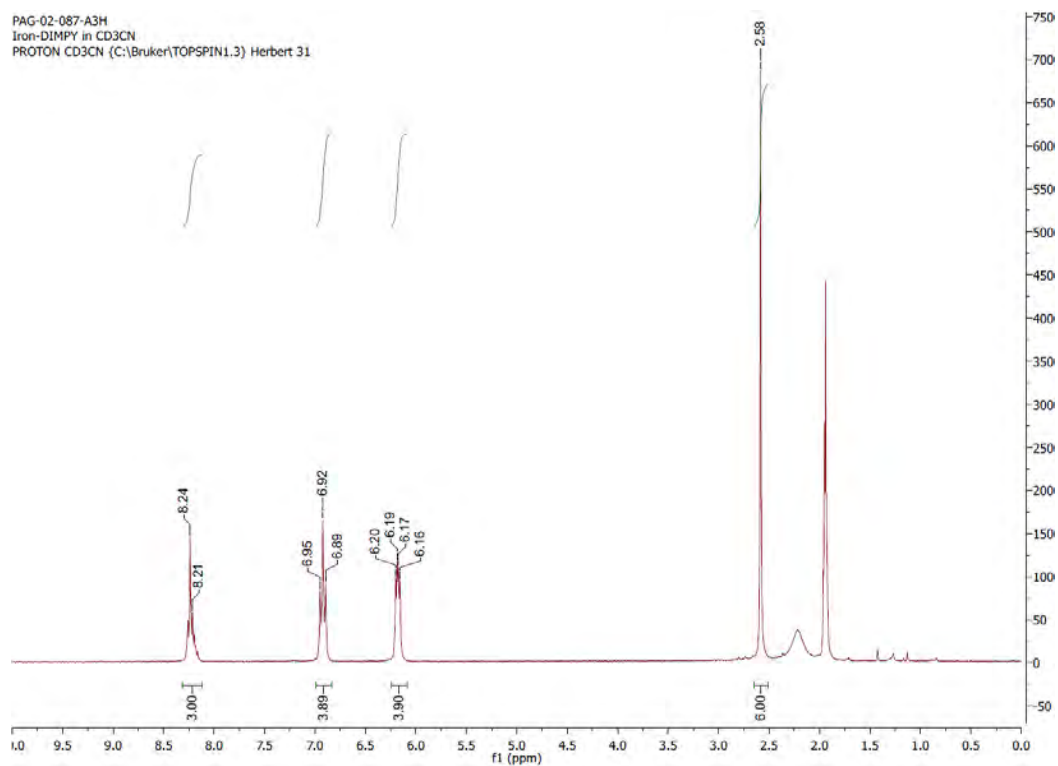


Figure S24. ¹H NMR (CD₃CN 300 MHz, 25°C, ppm) of **3b**.

PAG-02-087-B3C
(4-F-DIMPY)2Fe (PF6)2
C13CPD CD3CN (C:\Bruker\TOPSPIN1.3} Herbert 39

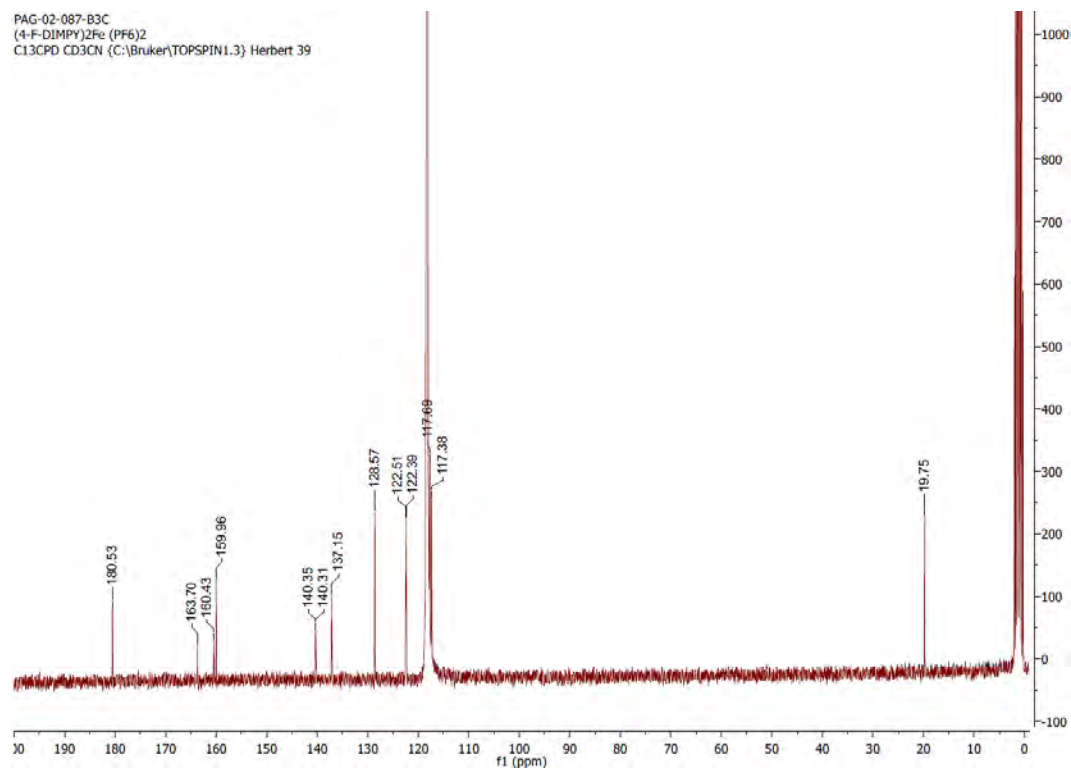


Figure S25. $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3CN , 75 MHz, 25°C, ppm) of **3b**.

PAG-02-087-A3F
(4-F-DIMPY)2Fe(PF6)2
F19CPD CD3CN (C:\Bruker\TOPSPIN1.3} Herbert 24

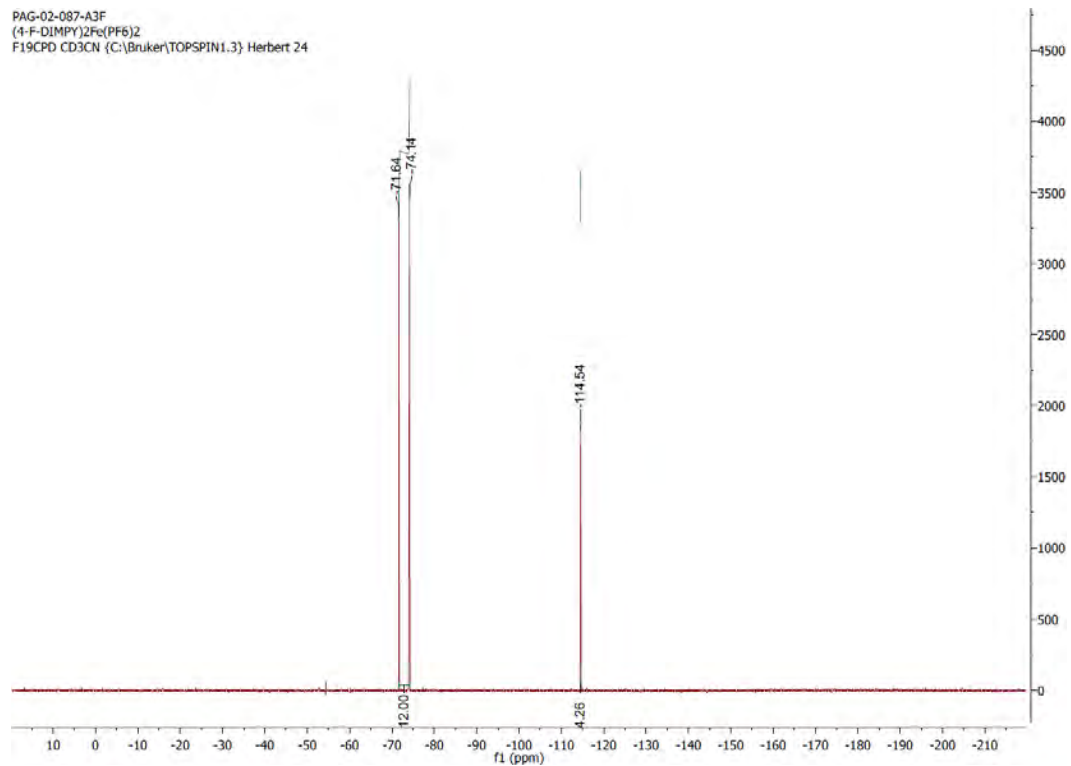


Figure S26. $^{19}\text{F}\{^1\text{H}\}$ NMR (CD_3CN , 282 MHz, 25°C, ppm) of **3b**.

PAG-02-087-A3P
(4-F-DIMPY)2Fe(PF6)2
P31CPD CD3CN (C:\Bruker\TOPSPIN1.3) Herbert 24

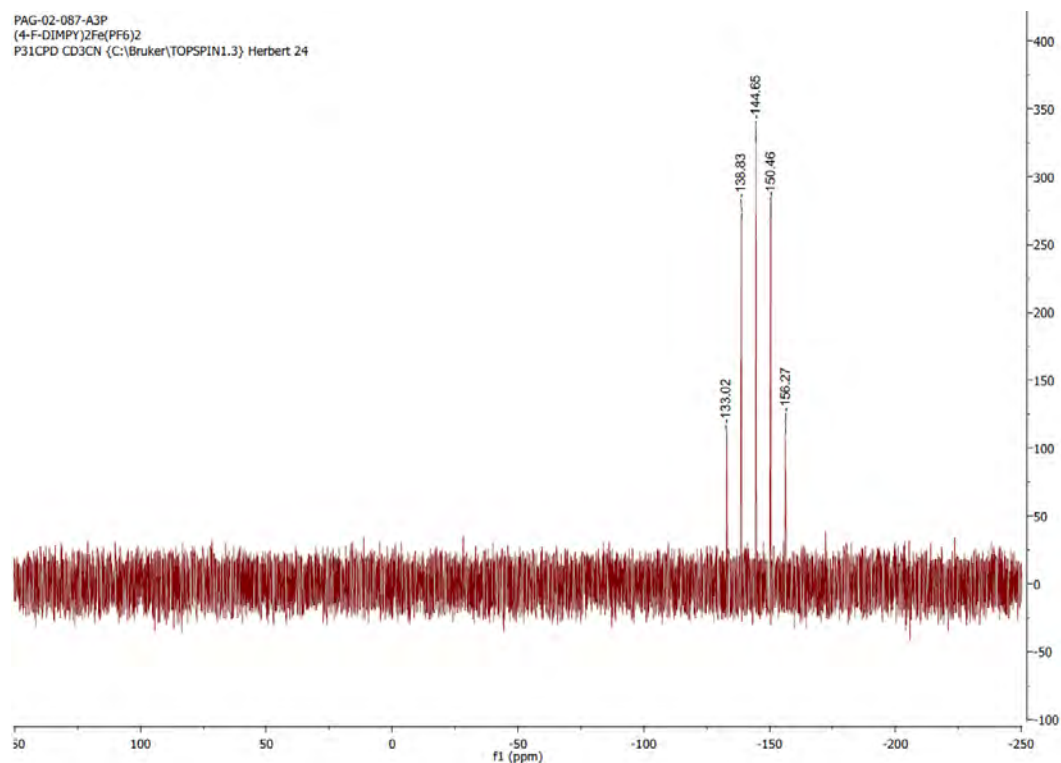


Figure S27. $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_3CN , 121 MHz, 25°C, ppm) of **3b**.

PAG-02-15-A3H
Br-DIP2Fe (PF6)2
PROTON CD3CN (C:\Bruker\TOPSPIN1.3) Herbert 11

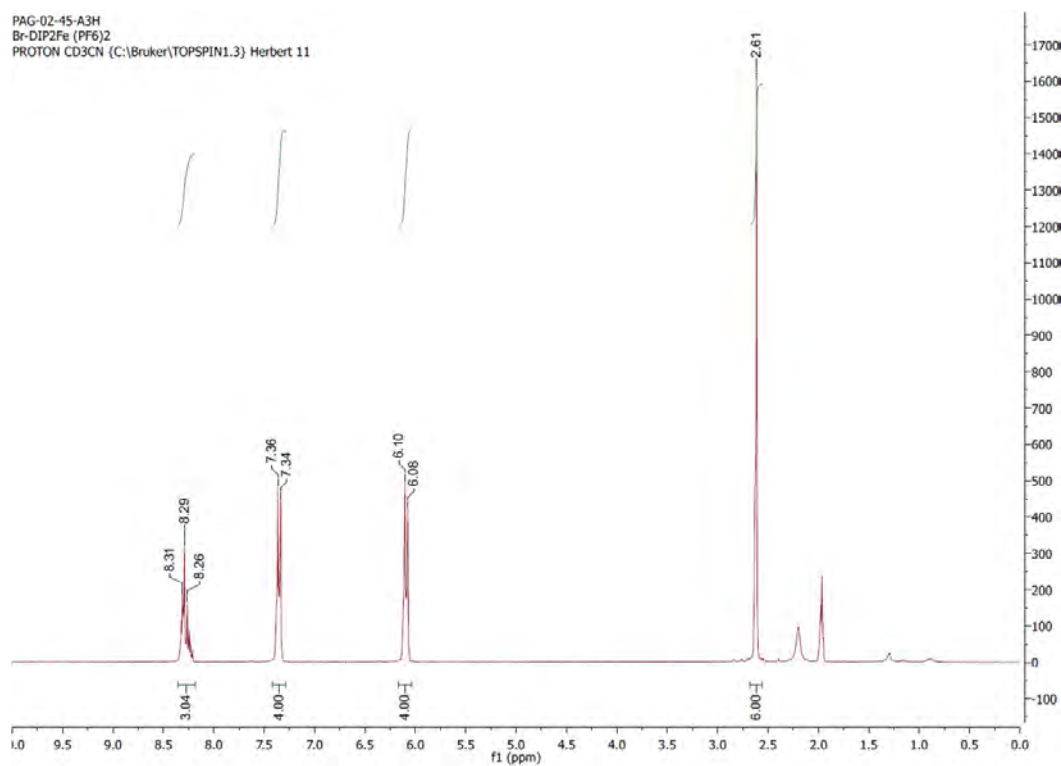


Figure S28. ^1H NMR (CD_3CN , 300 MHz, 25°C, ppm) of **3c**.

BKS-02-034-a3c.1.fid
 4-Br-DIMPY-Fe
 Washed with water and dried
 C13CPD CD3CN (C:\Bruker\TOPSPIN1.3) Herbert 21

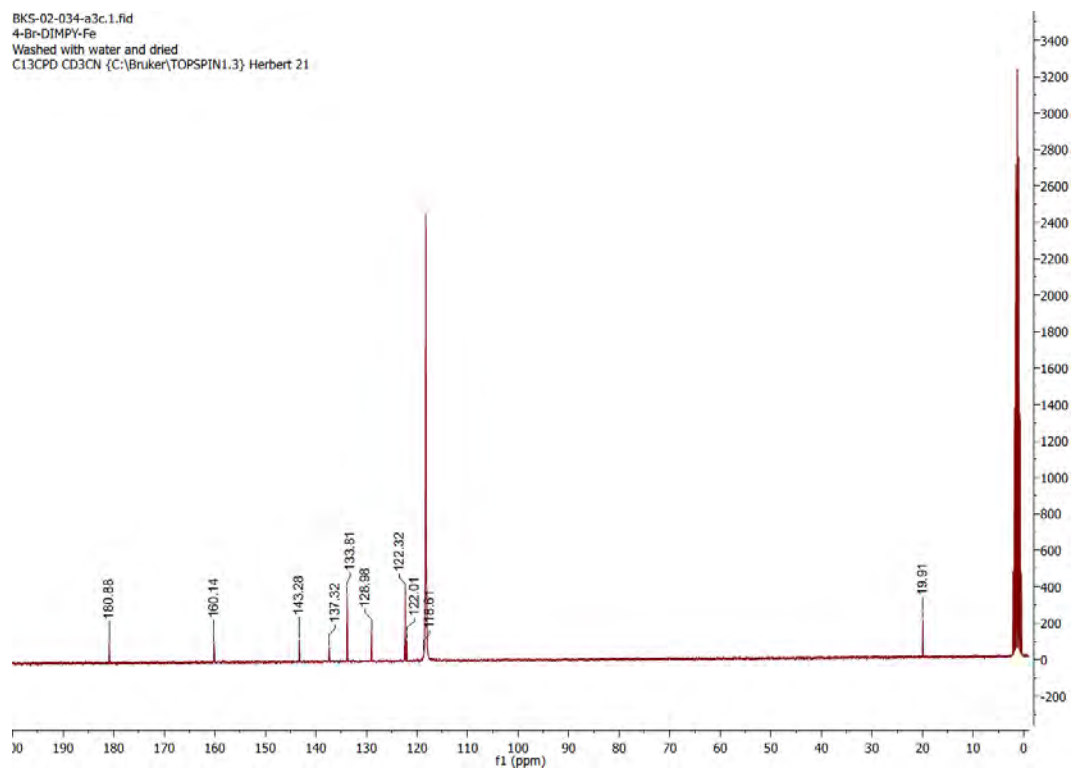


Figure S29. $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3CN , 75 MHz, 25°C, ppm) of **3c**.

PAG-02-45-A3H
 Br-DIP2Fe (PF6)2
 F19CPD CD3CN (C:\Bruker\TOPSPIN1.3) Herbert 11

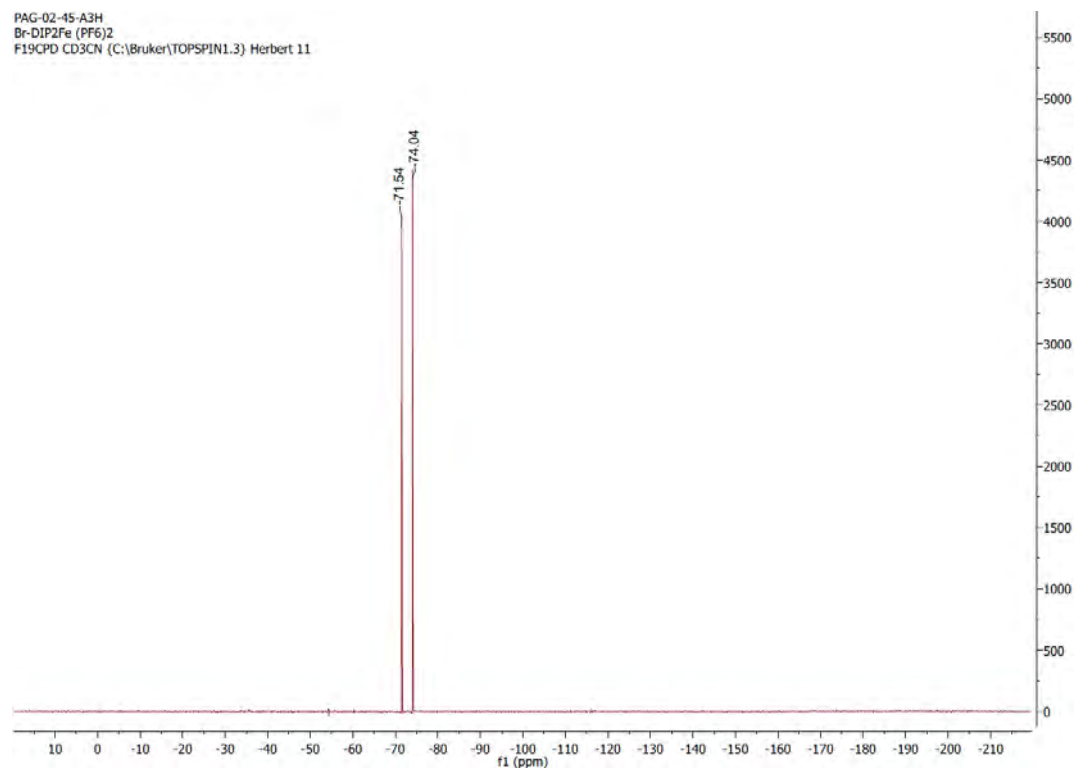


Figure S30. $^{19}\text{F}\{^1\text{H}\}$ NMR (CD_3CN , 282 MHz, 25°C, ppm) of **3c**.

PAG-02-45-A3H
Br-DIP2Fe (PF6)2
P31CPD CD3CN {C:\Bruker\TOPSPIN1.3} Herbert 11

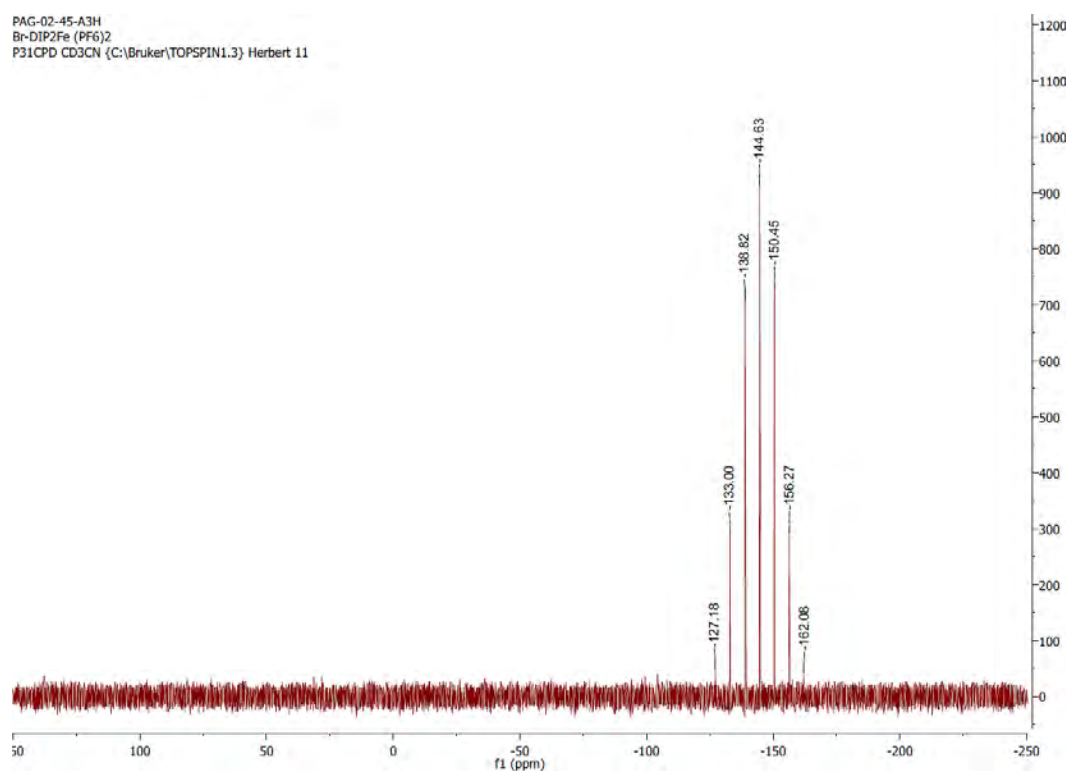


Figure S31. $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_3CN , 121 MHz, 25°C, ppm) of **3c**.

PAG-02-085-A3H
(4-CN-DIMPY)2Fe [PF6]2
PROTON CD3CN {C:\Bruker\TOPSPIN1.3} Herbert 22

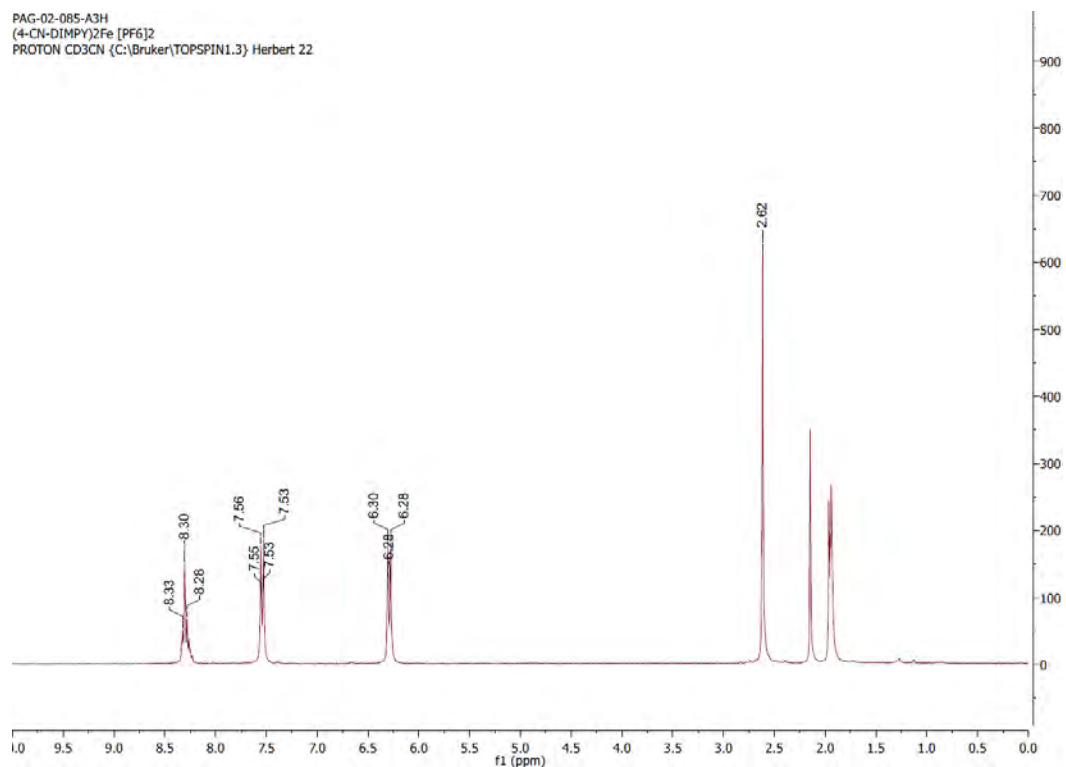


Figure S32. ^1H NMR (CD_3CN , 300 MHz, 25°C, ppm) of **3d**.

PAG-02-085-B3C
 (4-CN-DIMPY)2Fe (PF6)2
 C13CPD CD3CN (C:\Bruker\TOPSPIN1.3) Herbert 38

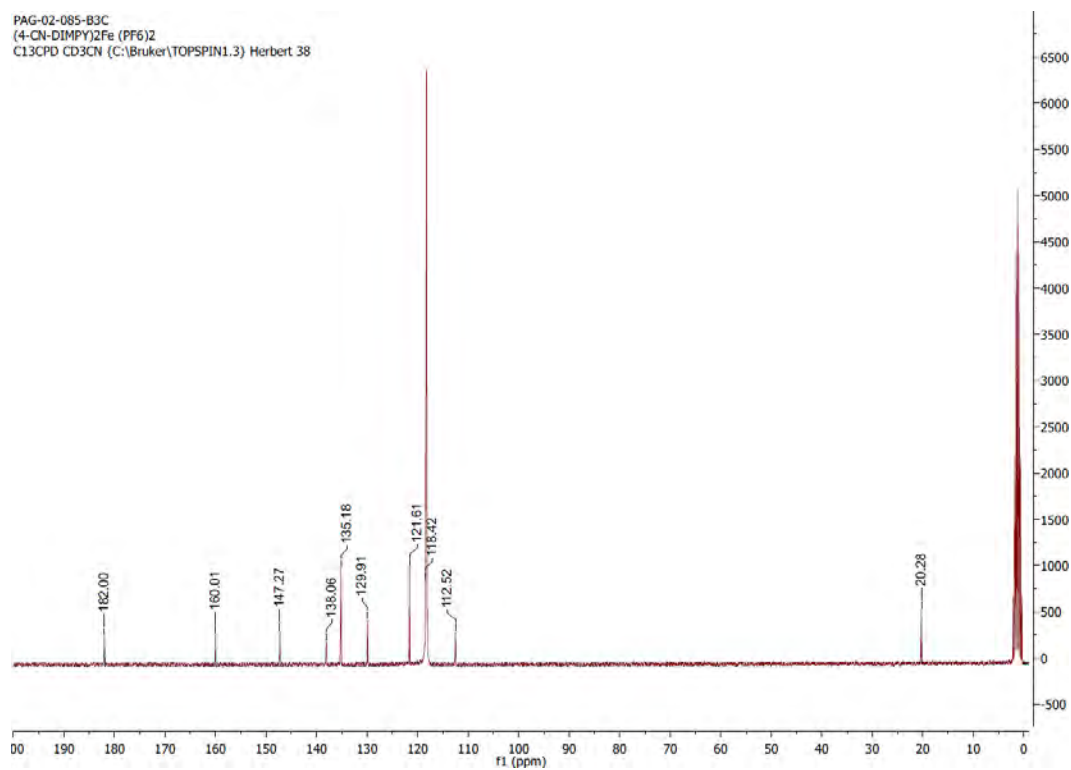


Figure S33. $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3CN , 75 MHz, 25°C, ppm) of **3d**.

PAG-02-085-A3F
 (4-CN-DIMPY)2e(PF6)2
 F19CPD CD3CN (C:\Bruker\TOPSPIN1.3) Herbert 23

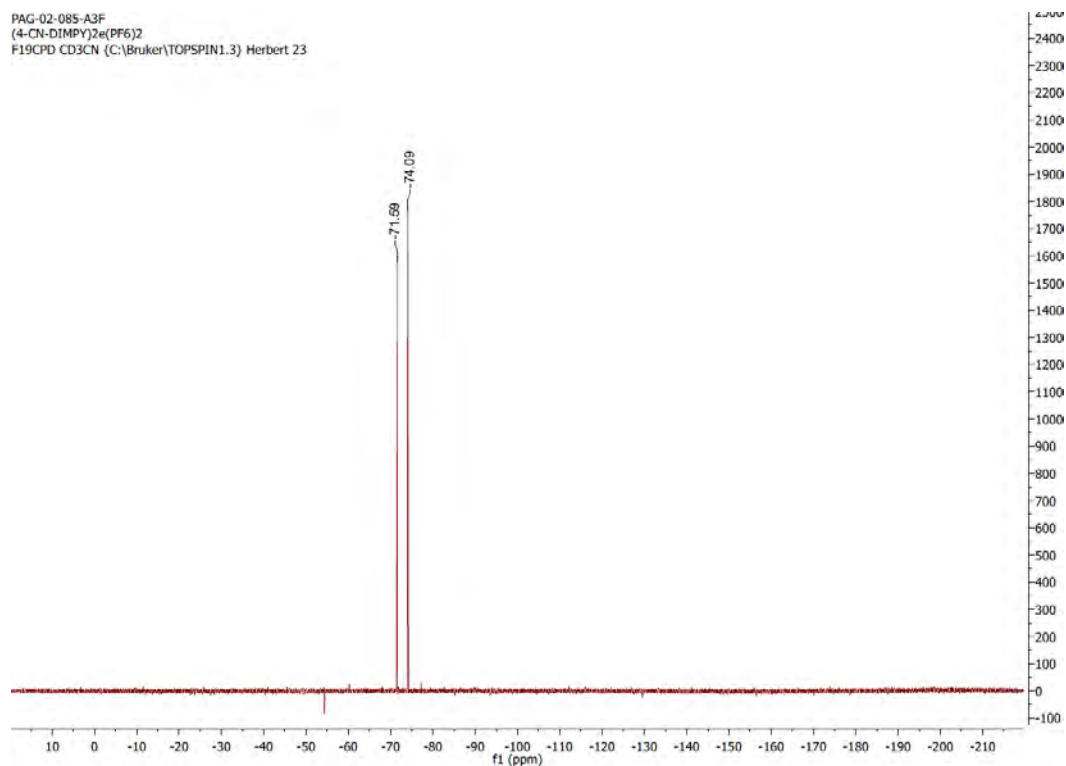


Figure S34. $^{19}\text{F}\{^1\text{H}\}$ NMR (CD_3CN , 282 MHz, 25°C, ppm) of **3d**.

PAG-02-085-A3P
 (4-CN-DIMPY)2e(PF6)2
 P31CPD CD3CN {C:\Bruker\TOPSPIN1.3} Herbert 23

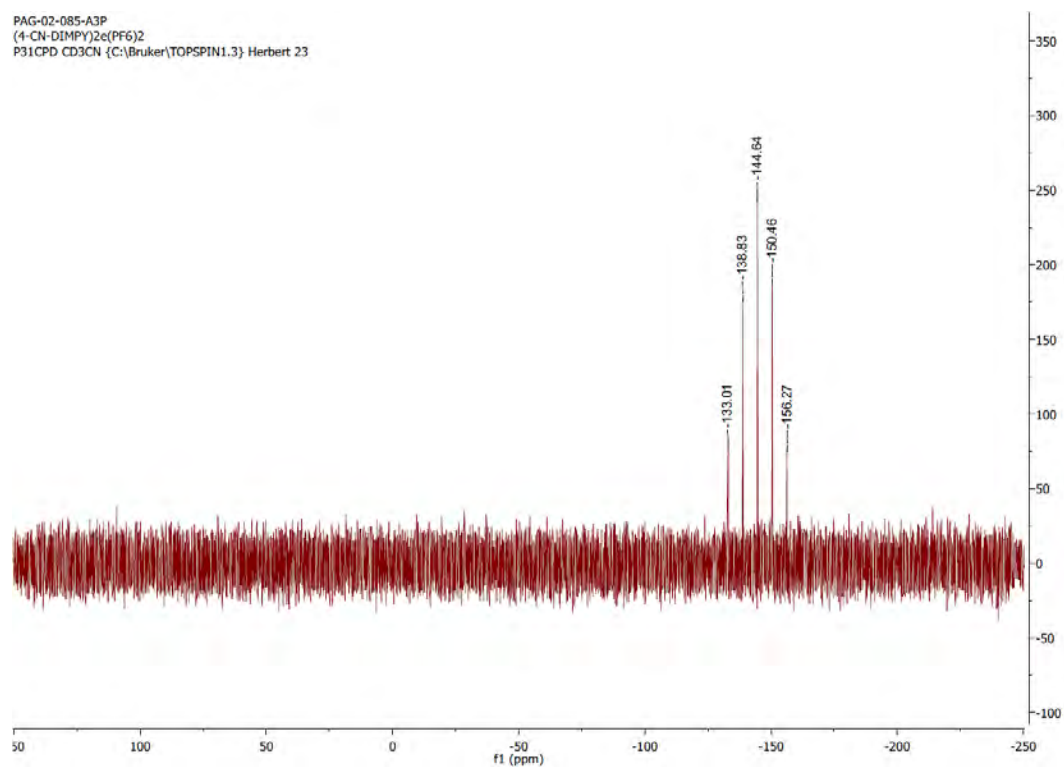


Figure S35. $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_3CN , 121 MHz, 25°C, ppm) of **3d**.

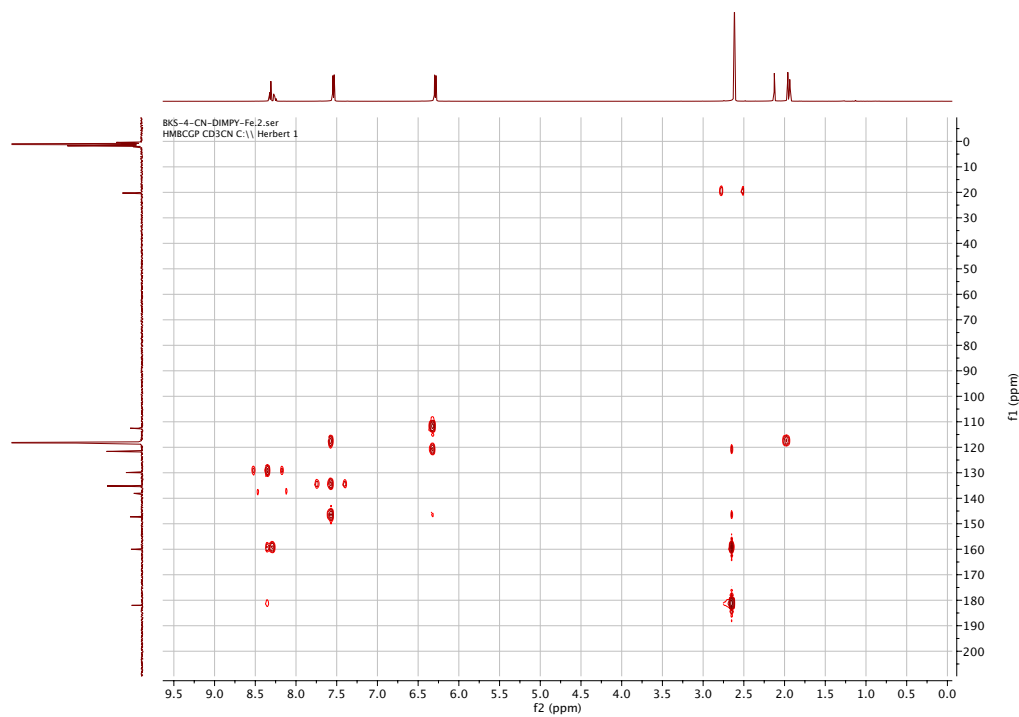


Figure S36. HMBC NMR (CD_3CN , 300/75 MHz, 25°C, ppm) of **1d**.

Table S1. Selected bond distances (Å) for **1b-d** (Zn) and **3c-d** (Fe).

	1b	1c	1d	3c	3d
<i>M</i> – <i>N</i> _{pyr}					
M1 – N2	2.080(3)	2.081(4)	2.084(4)	1.870(3)	1.860(3)
M1 – N5(7)	-	-	-	1.867(3)	1.865(3)
<i>M</i> – <i>N</i> _{imine}					
M1 – N1	2.210(3)	2.234(4)	2.245(4)	1.985(3)	1.981(3)
M1 – N3	2.258(3)	2.245(4)	2.240(4)	1.968(3)	1.963(3)
M1 – N4(6)	-	-	-	1.998(3)	1.977(4)
M1 – N6(8)	-	-	-	1.992(3)	1.980(4)
<i>C</i> _{imine} – <i>N</i> _{imine}					
C1 – N1	1.273(5)	1.271(6)	1.280(6)	1.303(5)	1.305(5)
C8 – N3	1.281(5)	1.273(6)	1.281(6)	1.298(4)	1.302(5)
C22(23) – N4(6)	-	-	-	1.299(5)	1.299(5)
C29(31) – N6(8)	-	-	-	1.297(5)	1.299(5)
<i>C</i> _{Ar} – <i>N</i> _{imine}					
C10 – N1	1.434(5)	1.422(7)	1.421(6)	1.433(3)	1.441(5)
C16(17) – N3	1.429(5)	1.420(7)	1.419(6)	1.435(5)	1.441(5)
C31(33) – N4(6)	-	-	-	1.437(5)	1.442(5)
C37(40) – N6(8)	-	-	-	1.439(5)	1.440(5)
Zn-Cl					
Zn1-Cl1	2.2570(10)	2.2439(14)	2.2437(11)	-	-
Zn1-Cl2	2.2375(10)	2.2324(13)	2.2316(13)	-	-
Zn2-Cl3	2.2433(10)	2.2337(14)	-	-	-
Zn2-Cl4	2.2526(10)	2.2300(14)	-	-	-

Table S2. Selected bond angles (°) for **1b-d** (Zn) and **3c-d** (Fe).

	1b	1c	1d	3c	3d
<i>Intraligand angles</i>					
N1 – M1 – N3	147.86(11)	147.58(15)	147.44(15)	159.71(12)	159.98(14)
N1 – M1 – N2	74.00(11)	73.75(16)	73.80(15)	80.16(12)	79.97(14)
N2 – M1 – N3	73.87(11)	73.90(16)	73.72(15)	79.56(12)	80.05(14)
N4(6) – Fe1 – N6(8) ^a	-	-	-	158.95(12)	160.18(14)
N4(6) – Fe1 – N5(7) ^a	-	-	-	79.52(13)	80.44(15)
N5(7) – Fe1 – N6(8) ^a	-	-	-	79.68(13)	79.75(15)
N4 – Zn2 – N6	147.49(11)	147.90(15)	-	-	-
N4 – Zn2 – N5	74.24(11)	74.19(15)	-	-	-
N5 – Zn2 – N6	73.29(11)	73.81(15)	-	-	-
<i>Interligand angles</i>					
N2 – M1 – N5(7)	-	-	-	173.65(14)	177.45(15)
N1 – M1 – N6(8)	-	-	-	91.42(12)	90.99(14)
N2 – M1 – N4(6)	-	-	-	94.82(12)	101.45(14)
N2 – M1 – N6(8)	-	-	-	106.10(13)	98.34(14)
N1 – M1 – N5(7)	-	-	-	102.58(13)	101.70(14)
N3 – M1 – N5(7)	-	-	-	97.65(12)	98.31(14)
N3 – M1 – N4(6)	-	-	-	92.28(12)	89.29(14)
N1 – Zn1 – Cl1	95.97(8)	96.97(11)	93.02(10)	-	-
N1 – Zn1 – Cl2	98.82(8)	99.72(11)	100.05(11)	-	-
N2 – Zn1 – Cl1	114.79(8)	111.14(12)	116.75(10)	-	-
N2 – Zn1 – Cl2	128.78(8)	129.44(12)	123.28(10)	-	-
N3 – Zn1 – Cl1	97.03(9)	96.55(12)	99.49(10)	-	-
N3 – Zn1 – Cl2	101.44(8)	99.01(11)	99.47(11)	-	-
Cl1 – Zn1 – Cl2	116.40(4)	119.41(5)	119.88(5)	-	-
N4 – Zn2 – Cl3	99.14(8)	98.37(11)	-	-	-
N4 – Zn2 – Cl4	97.84(8)	97.51(11)	-	-	-
N5 – Zn2 – Cl3	126.73(8)	122.22(12)	-	-	-
N5 – Zn2 – Cl4	115.97(8)	117.26(12)	-	-	-
N6 – Zn2 – Cl3	98.79(8)	96.45(12)	-	-	-
N6 – Zn2 – Cl4	97.69(8)	99.19(11)	-	-	-
Cl3 – Zn2 – Cl4	117.30(4)	120.52(6)	-	-	-
τ_5^b	0.32, 0.35	0.30, 0.31	0.40	-	-

^a Atom labels in parentheses are for cyano derivatives **1d** and **3d**^b $\tau_5 = (\beta - \alpha)/60^\circ$ where β and α are the largest valence angles (bolded in table) and $\beta > \alpha$.¹ Where two values are given, values correspond to the two molecules in asymmetric unit (Zn1 and Zn2)

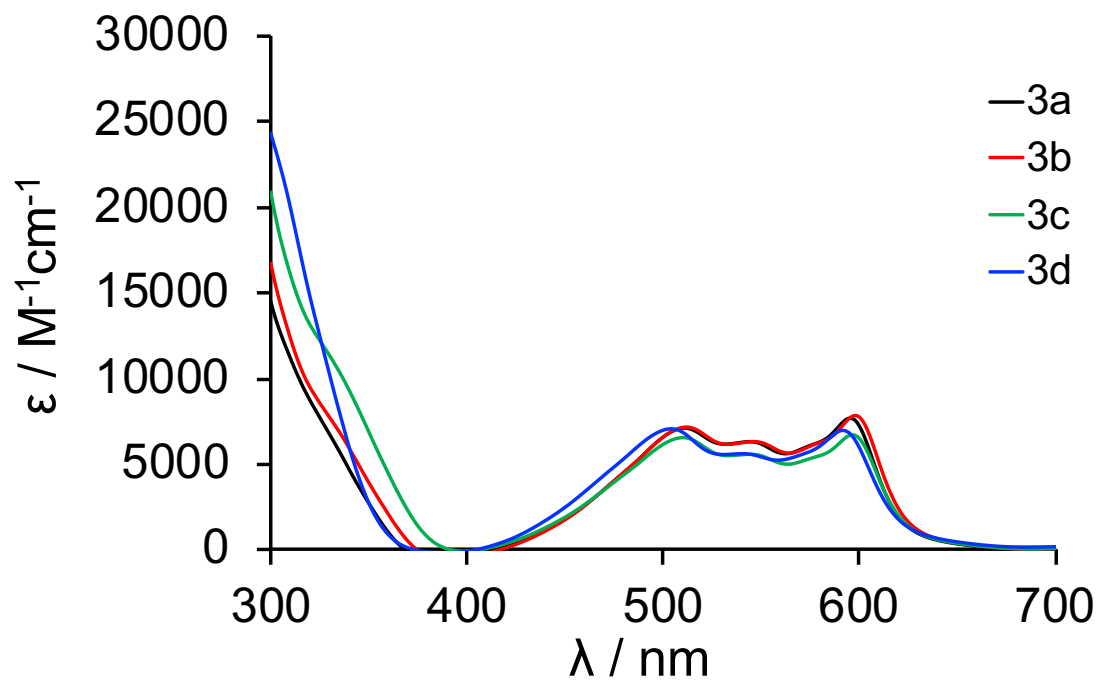


Figure S37. UV-vis spectra of **3(a-d)** in CH₃CN.

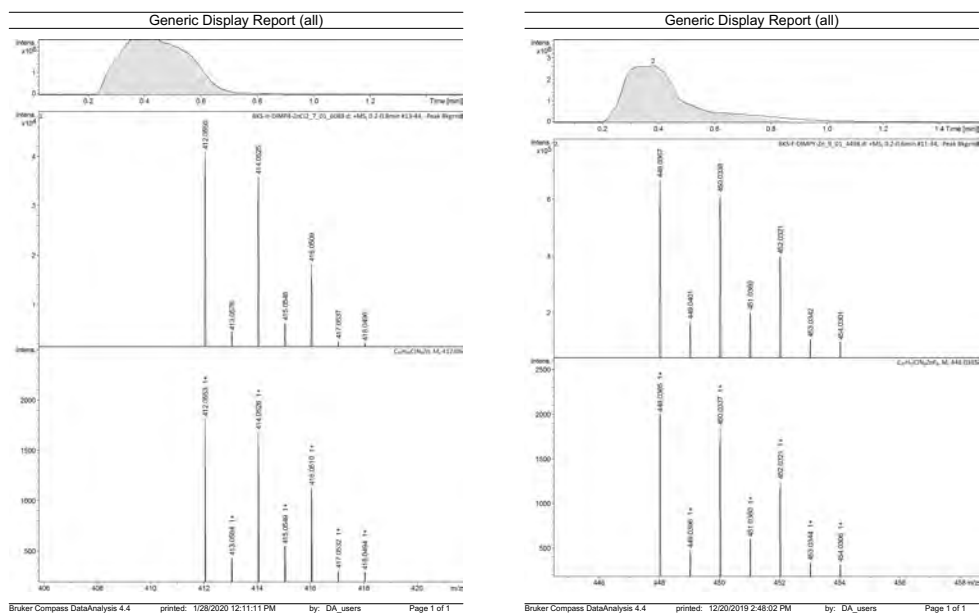


Figure S38. MS (ESI-TOF/MS, m/z) for **1a** and **1b**.

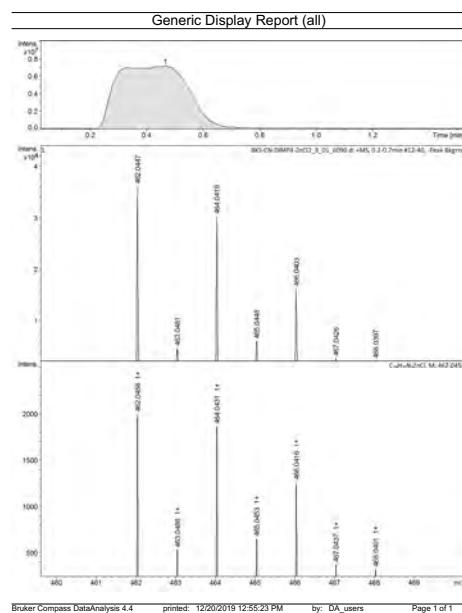
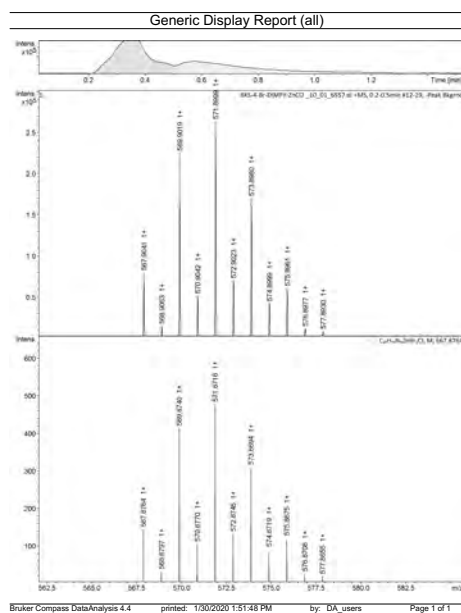


Figure S39. MS (ESI-TOF/MS, m/z) for **1c** and **1d**.

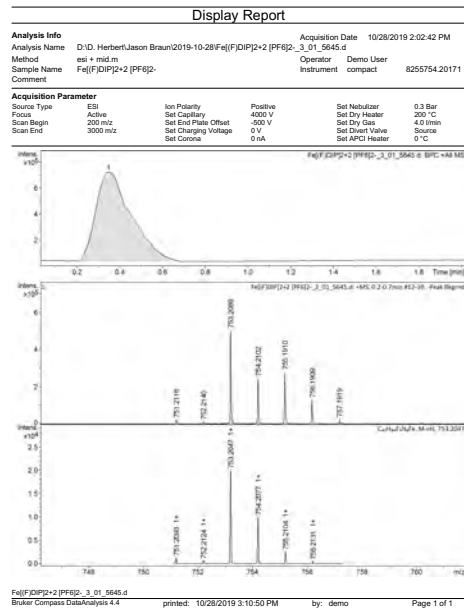
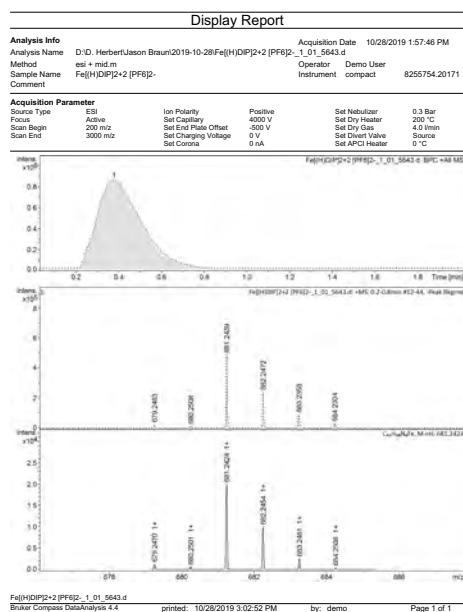
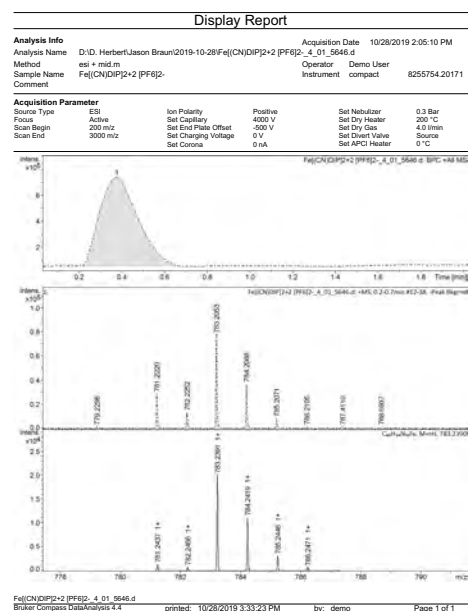
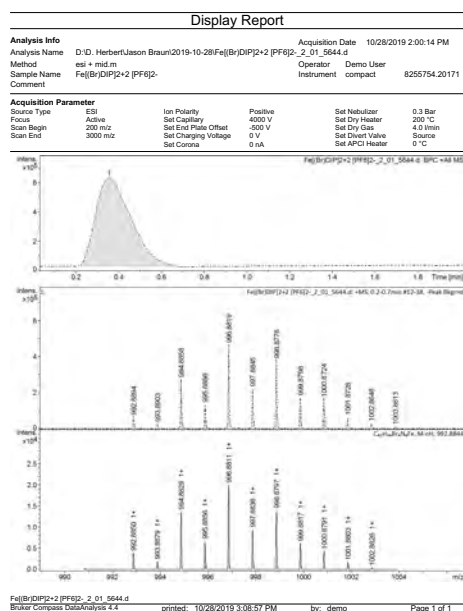


Figure S40. MS (ESI-TOF/MS, m/z) for **3a** and **3b**.



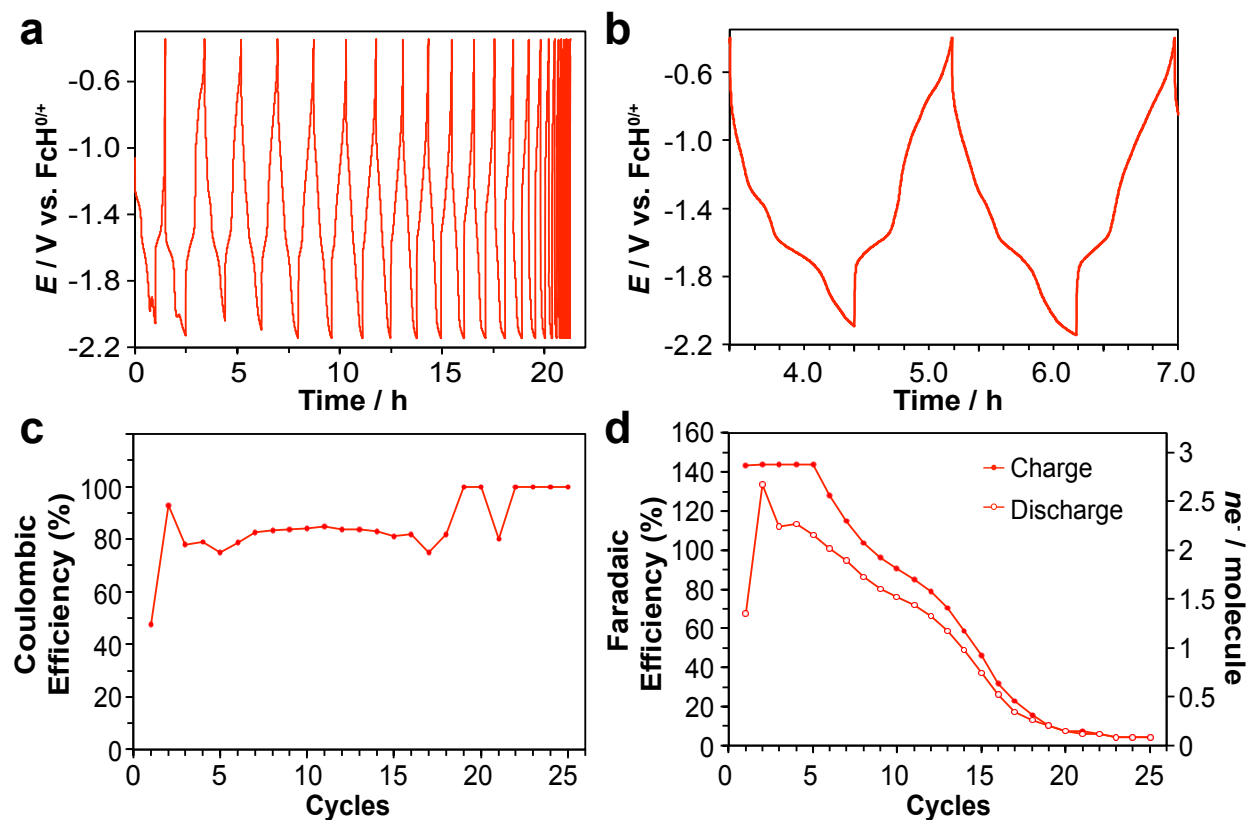


Figure S42. (a, b) Total cell voltage, (c) Coulombic efficiency (% CE), and (d) capacity retention for **3b**. Anodic and cathodic current set to 7 mA with a charging rate of 1C. Voltage limits set according to previously obtained CVs in order to limit access or irreversible redox events; in 0.3 M nBu_4PF_6 acetonitrile solution.

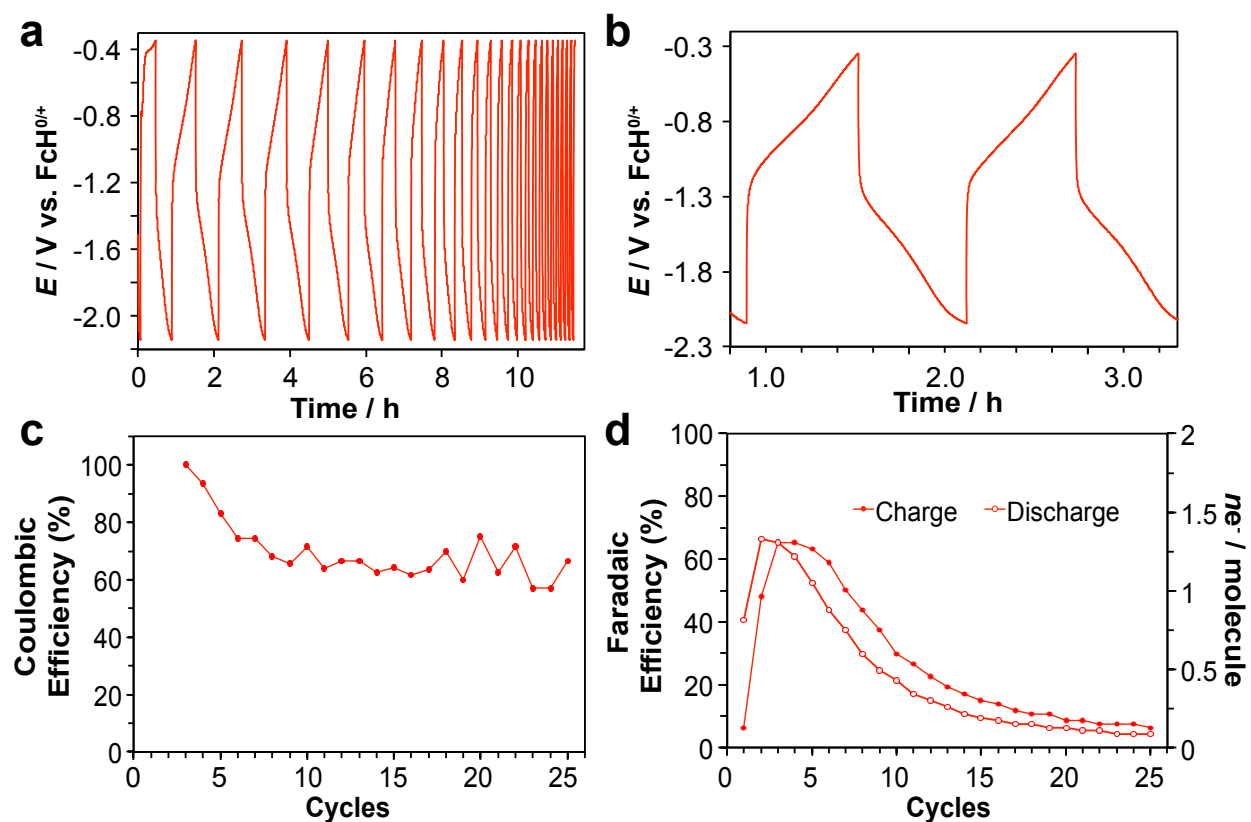


Figure S43. (a, b) Total cell voltage, (c) Coulombic efficiency (% CE), and (d) capacity retention for **3c**. Anodic and cathodic current set to 2 mA with a charging rate of 1C. Voltage limits set according to previously obtained CVs in order to limit access or irreversible redox events; in 0.3 M $n\text{Bu}_4\text{PF}_6$ acetonitrile solution.

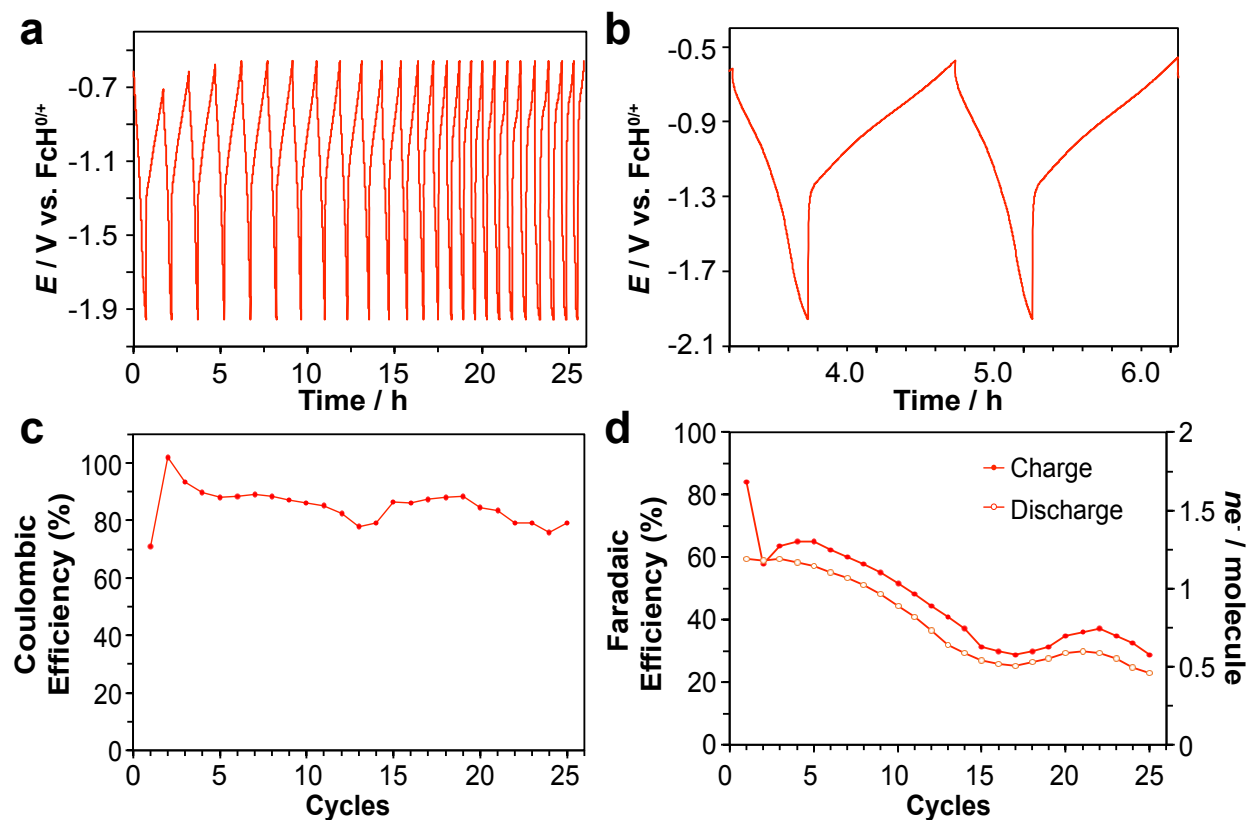


Figure S44. (a, b) Total cell voltage, (c) Coulombic efficiency (% CE), and (d) capacity retention for **3d**. Anodic and cathodic current set to 3 mA with a charging rate of 1C. Voltage limits set according to previously obtained CVs in order to limit access or irreversible redox events; in 0.3 M nBu_4PF_6 acetonitrile solution.

REFERENCES

- [1] A. W. Addison, T. N. Rao, J. Reedijk, J. van Rijn and G. C. Verschoor, *J. Chem. Soc. Dalton Trans.*, 1984, 1349–1356.