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

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[#]These authors contributed equally to this work.

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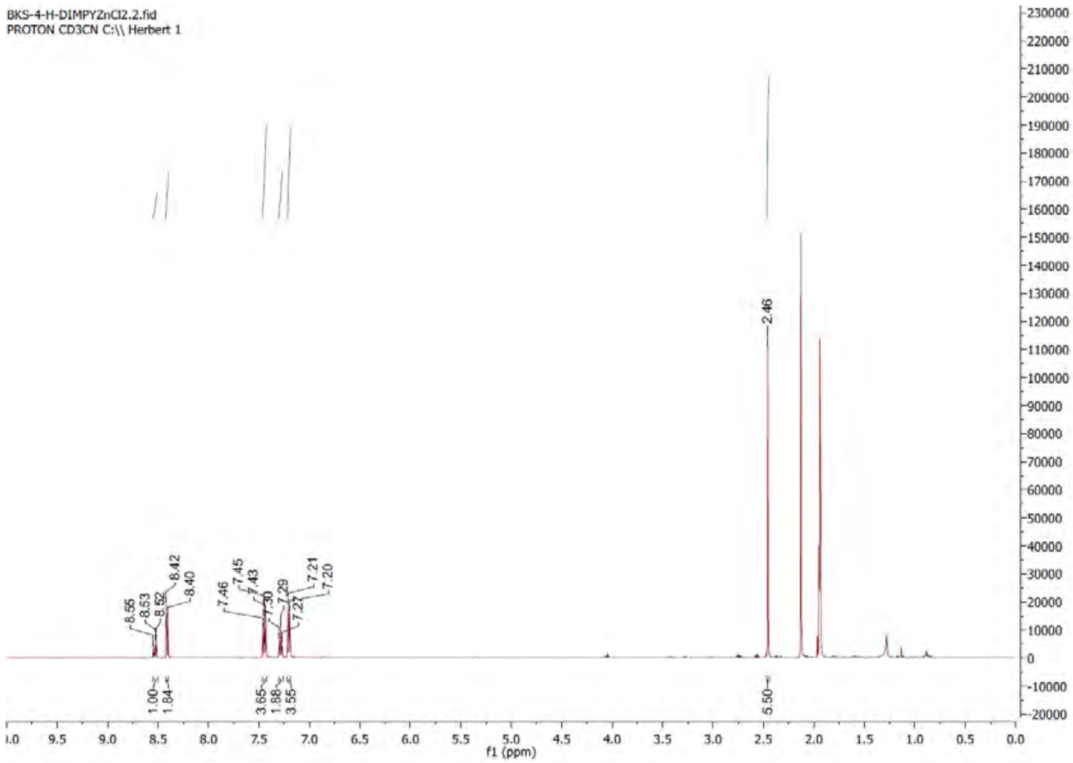

Figure S1. ^{1}H NMR (CD_3CN, 500 MHz, 25°C, ppm) of **1a**.

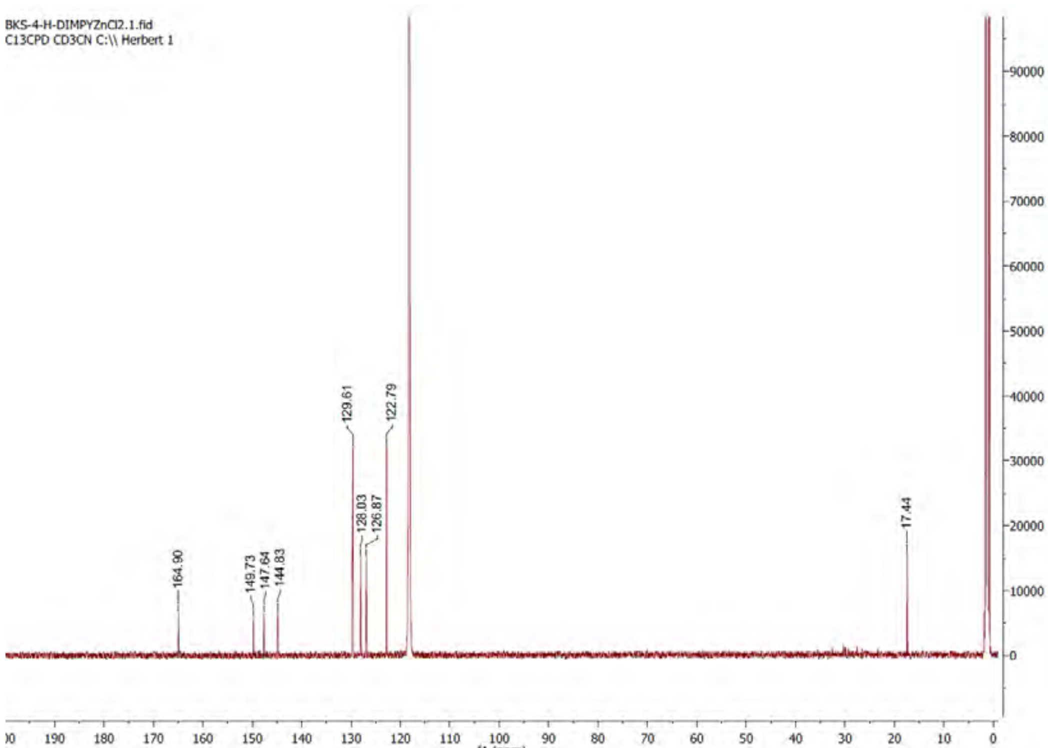

Figure S2. ^{13}C{^{1}H} NMR (CD_3CN, 125 MHz, 25°C, ppm) of **1a**.

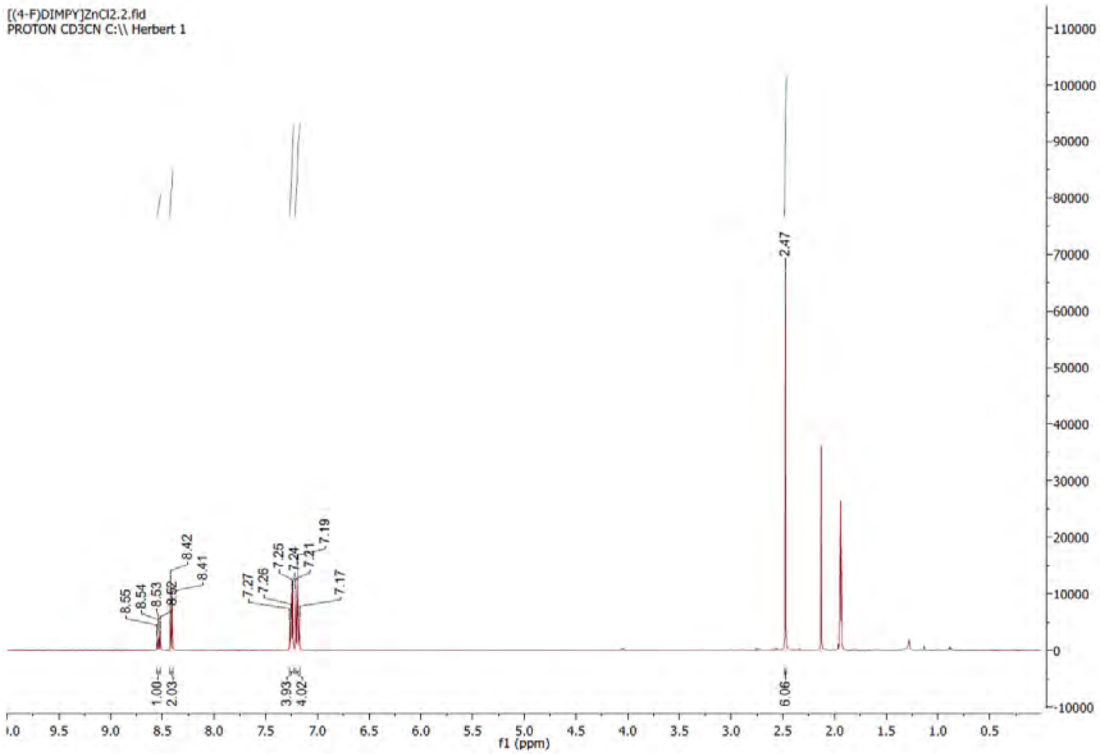

Figure S3. ^{1}H NMR (CD_3CN, 500 MHz, 25°C, ppm) of **1b**.

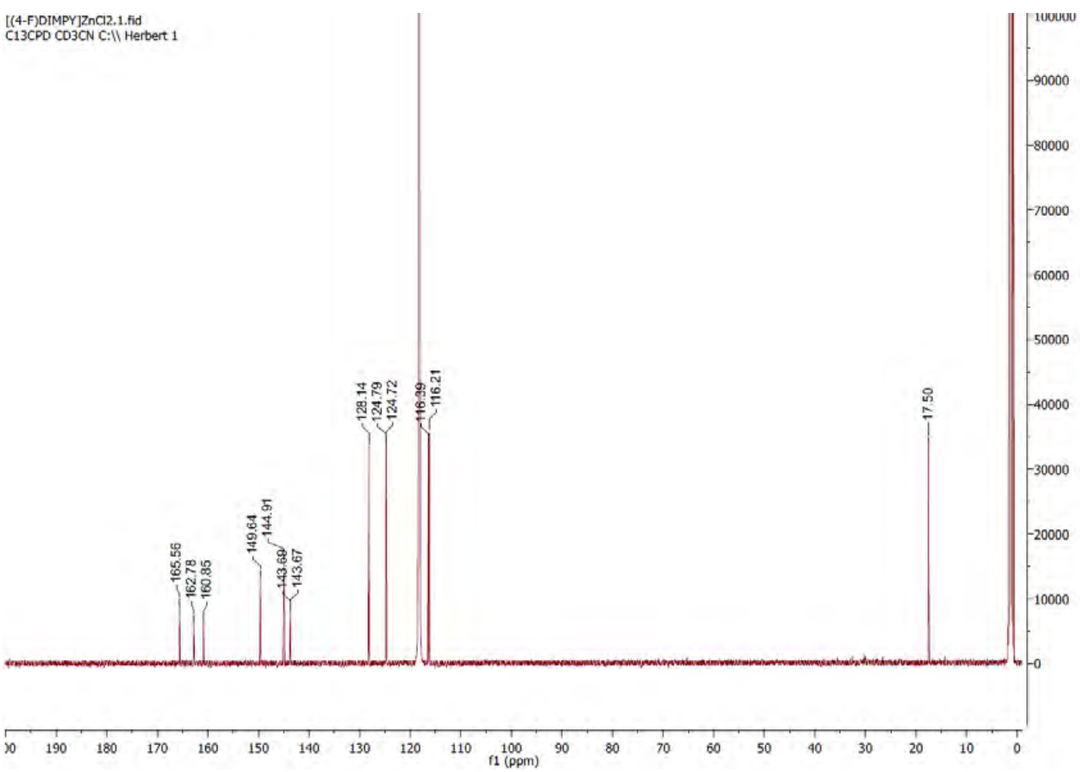

Figure S4. $^{13}C\{^{1}H\}$ NMR (CD_3CN, 125 MHz, 25°C, ppm) of **1b**.

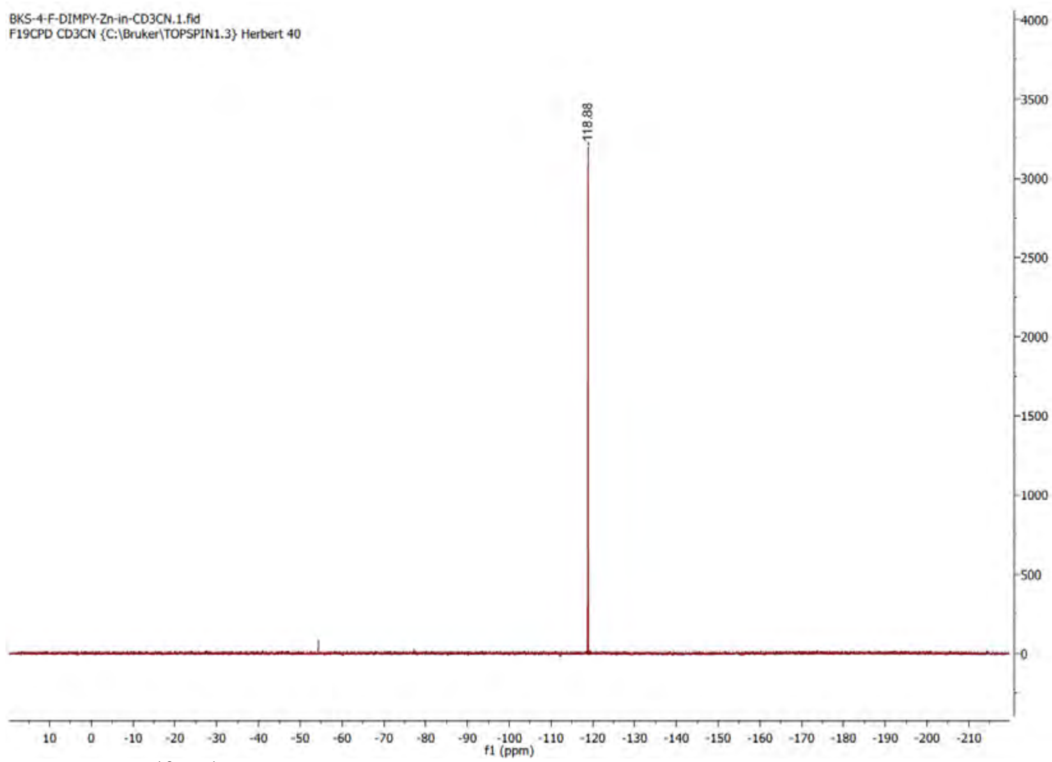

Figure S5. $^{19}F\{^{1}H\}$ NMR (CD_3CN, 282 MHz, 25°C, ppm) of **1b**.

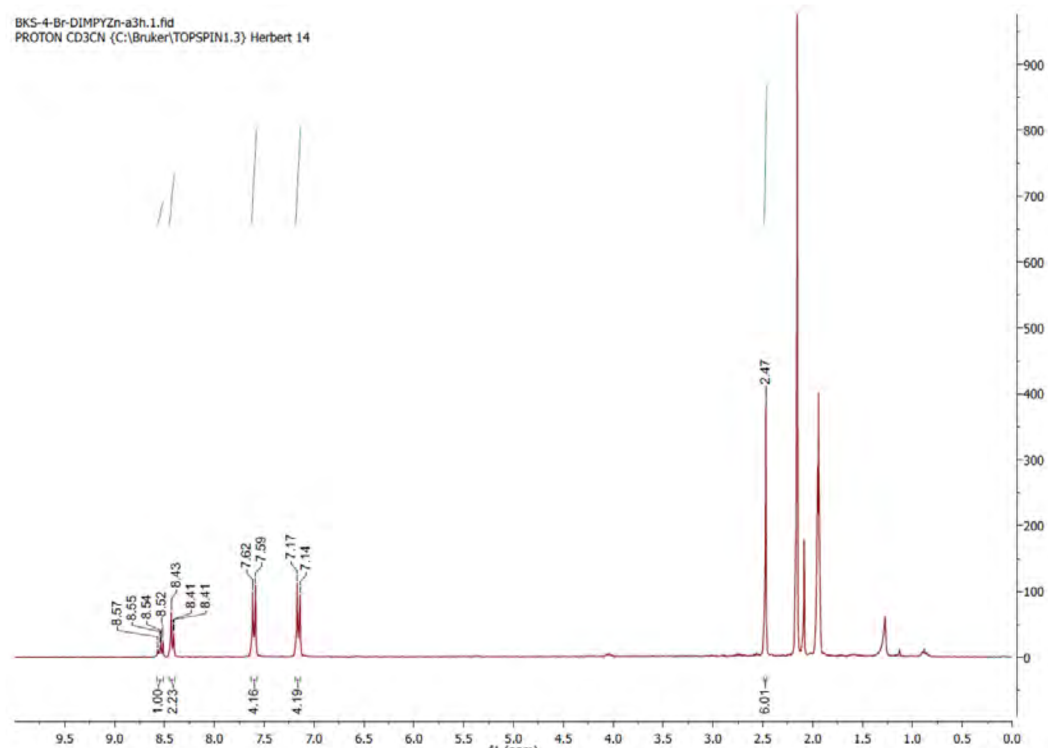

Figure S6. ^{1}H NMR (CD_3CN, 300 MHz, 25°C, ppm) of **1c**.

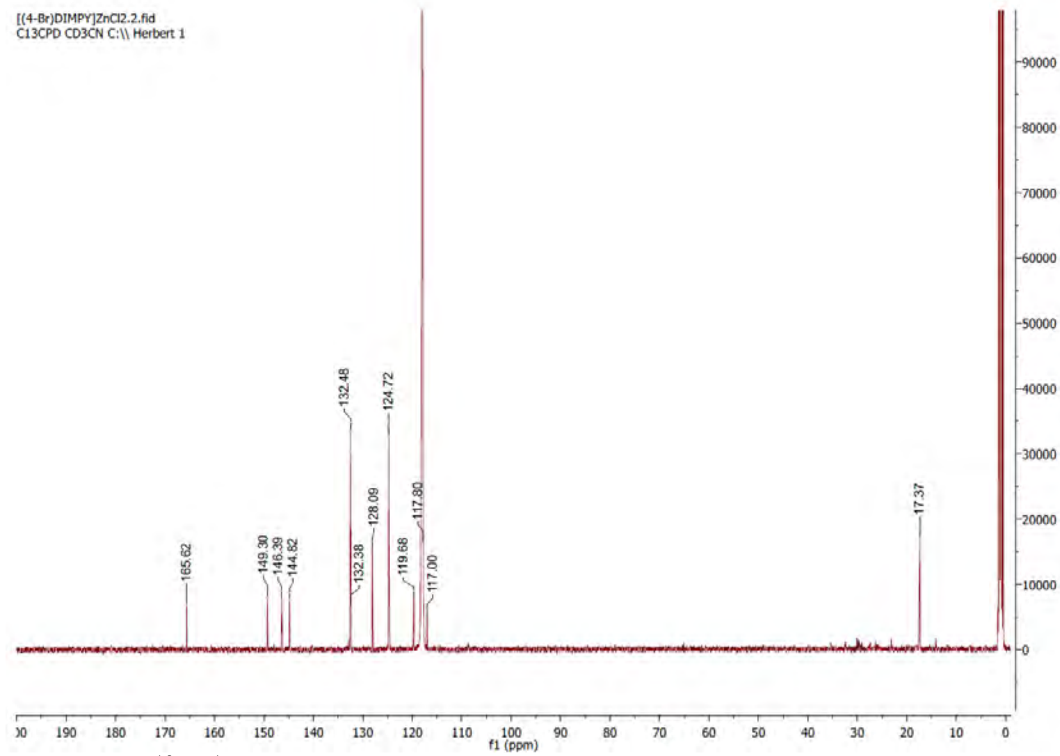

Figure S7. $^{13}C\{^{1}H\}$ NMR (CD_3CN, 125 MHz, 25°C, ppm) of **1c**.

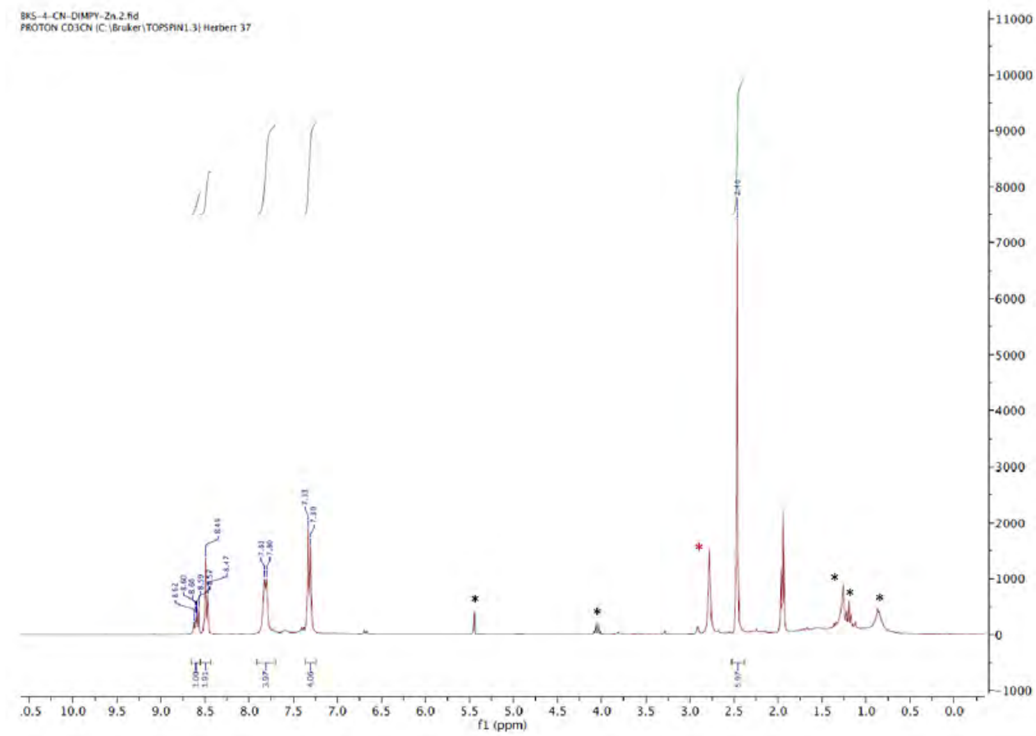

Figure S8. ^{1}H NMR (CD_3CN, 300 MHz, 25°C, ppm) of **1d**. Asterisks (black) represent solvent impurities (*n*-pentane, ethyl acetate, dichloromethane) and an unknown impurity (red).

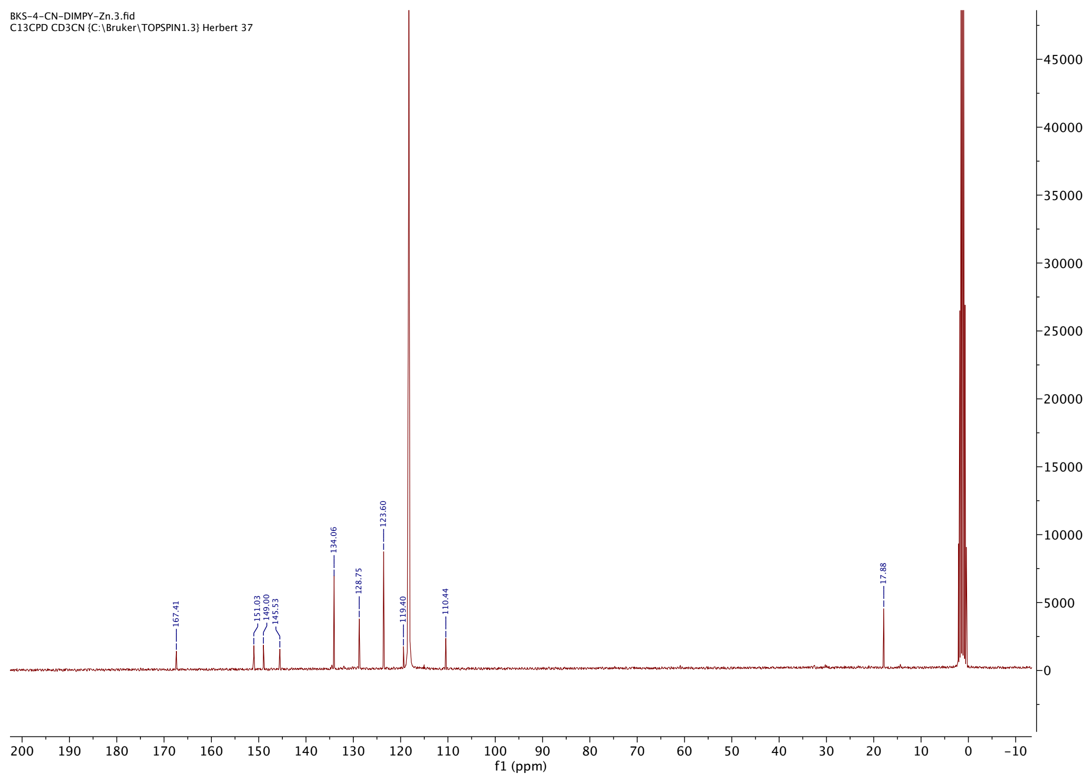

Figure S9. $^{13}C\{^{1}H\}$ NMR (CD_3CN, 125 MHz, 25°C, ppm) of **1d**.

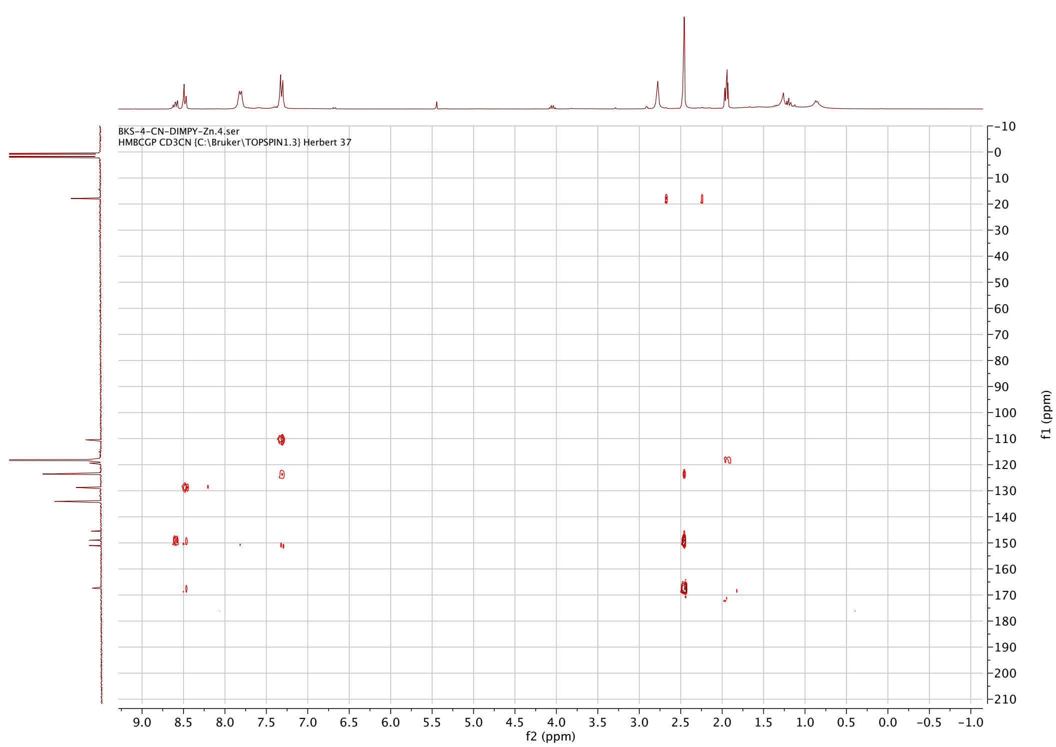

Figure S10. HMBC NMR (CD_3CN, 300/75 MHz, 25°C, ppm) of **1d**.

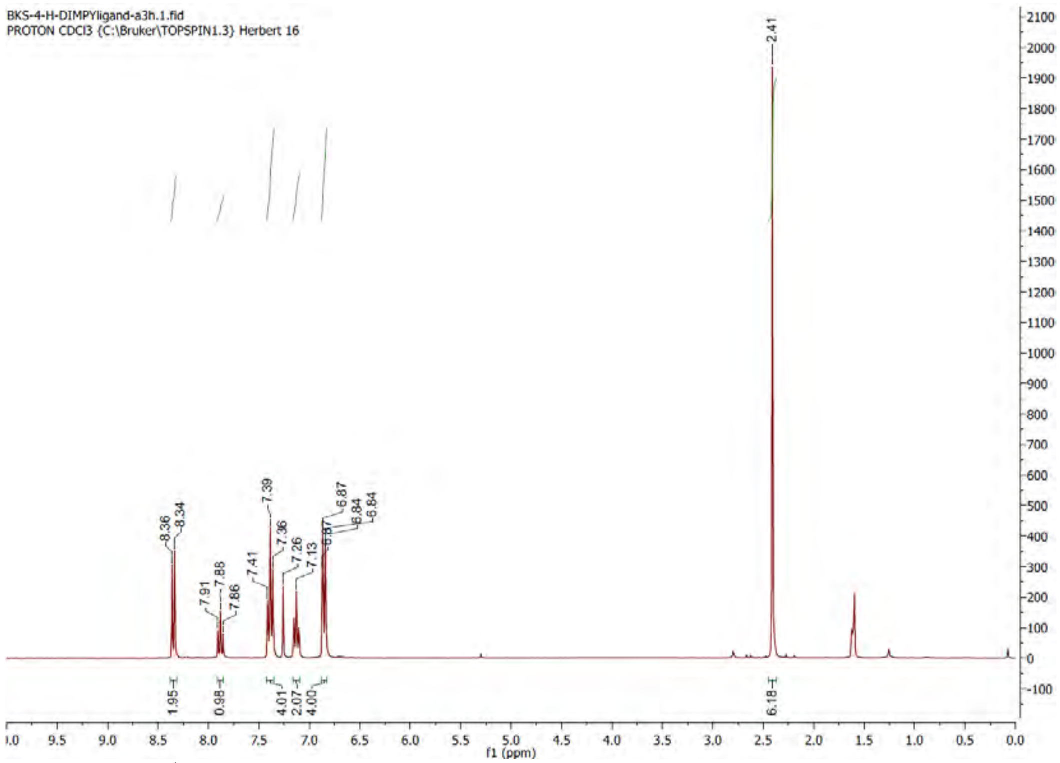

Figure S11. ^{1}H NMR ($CDCl_3$, 300 MHz, 25°C, ppm) of **2a**.

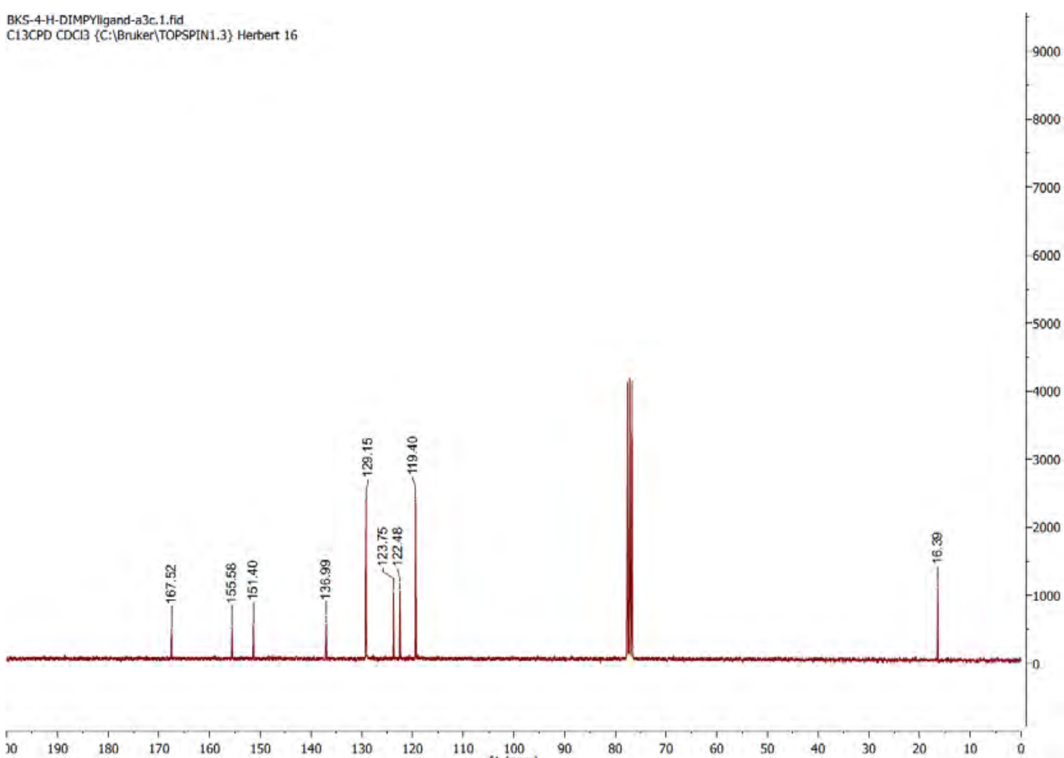

Figure S12. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 75 MHz, 25°C, ppm) of **2a**.

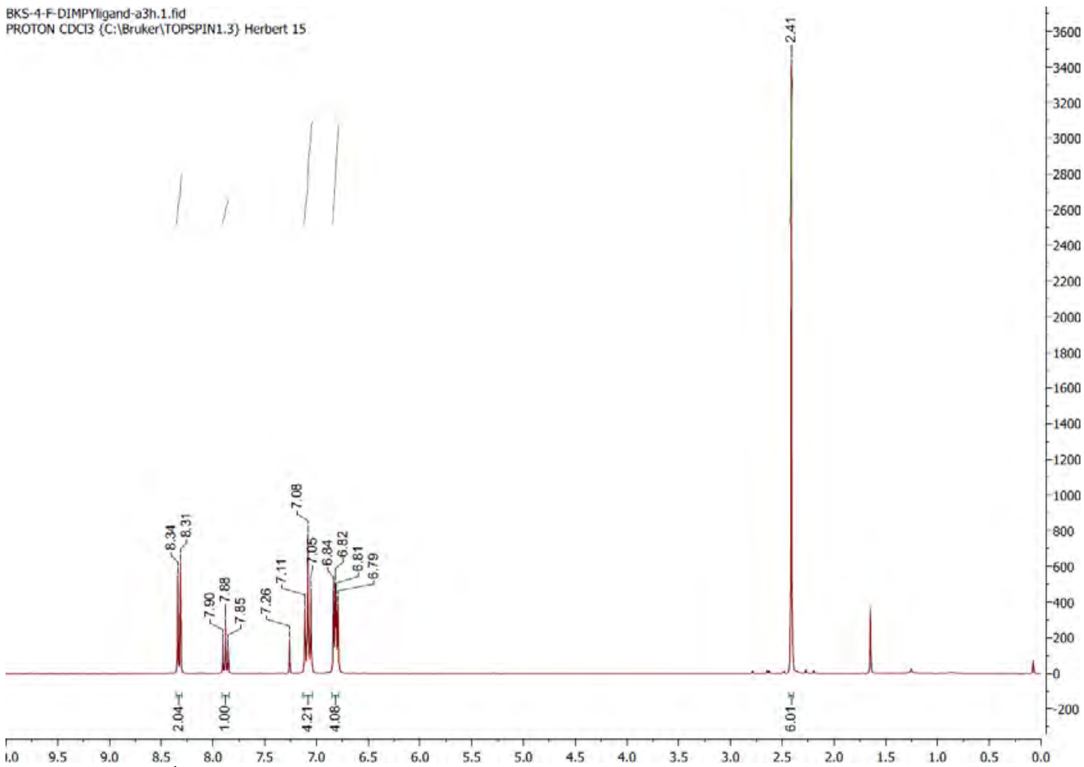

Figure S13. ^{1}H NMR ($CDCl_3$, 300 MHz, 25°C, ppm) of **2b**.

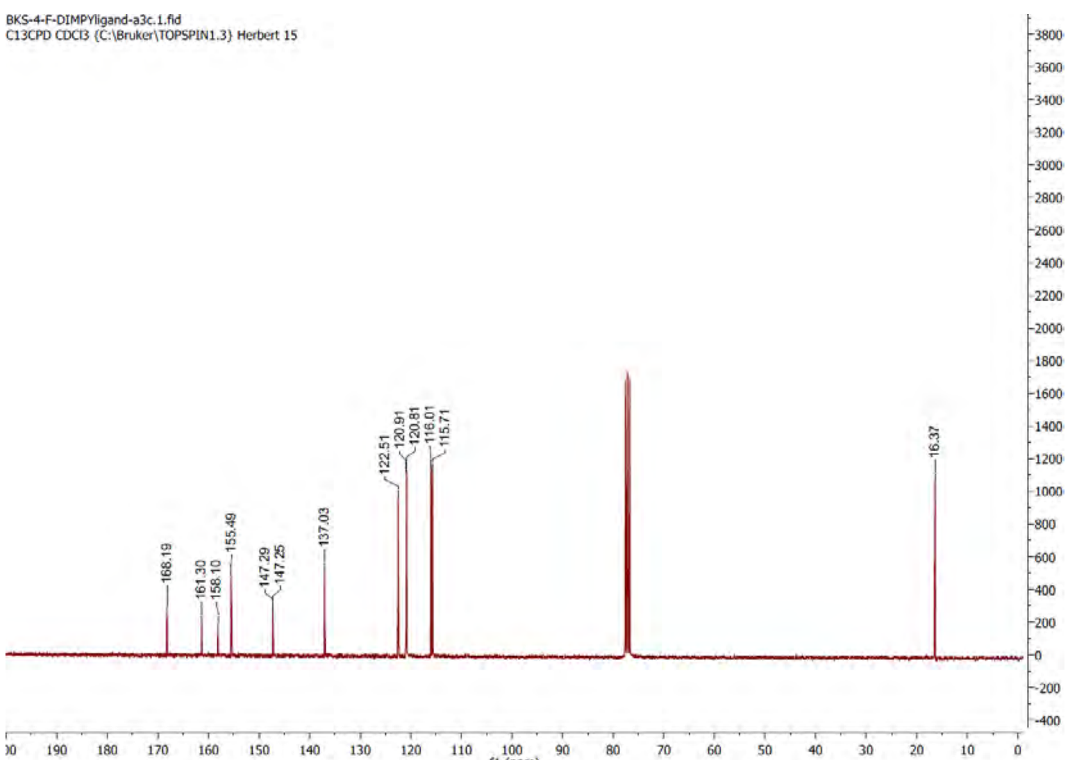

Figure S14. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz, 25°C, ppm) of **2b**.

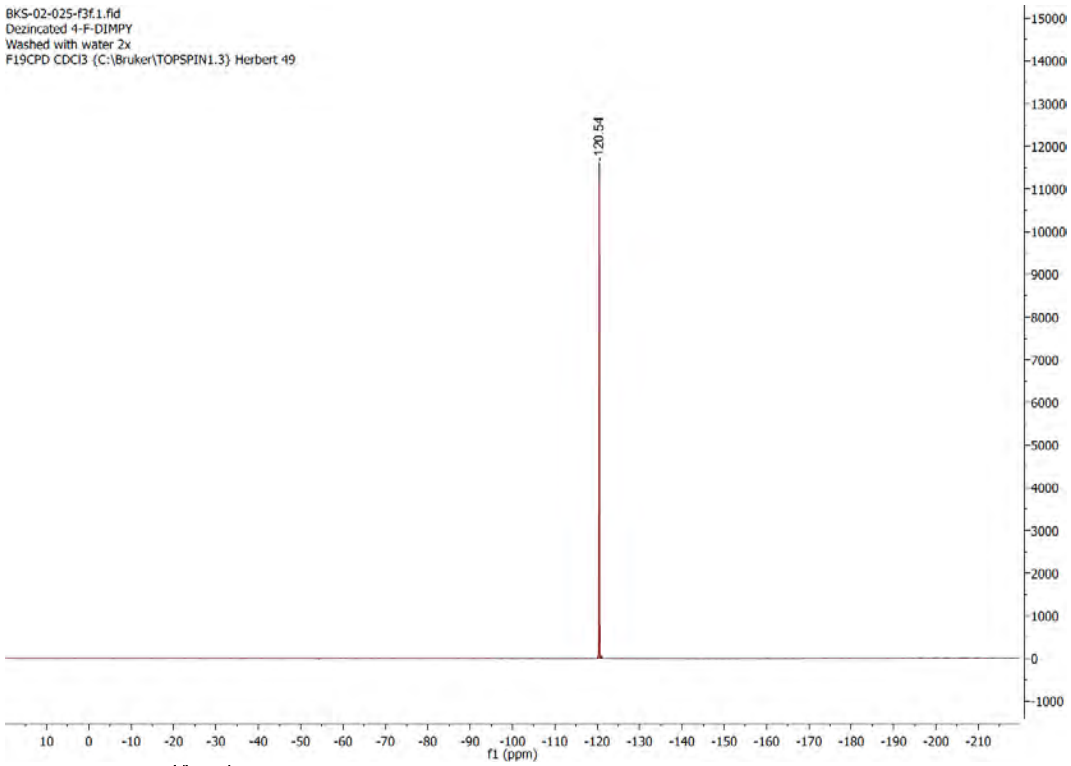

Figure S15. $^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 282 MHz, 25°C, ppm) of **2b**.

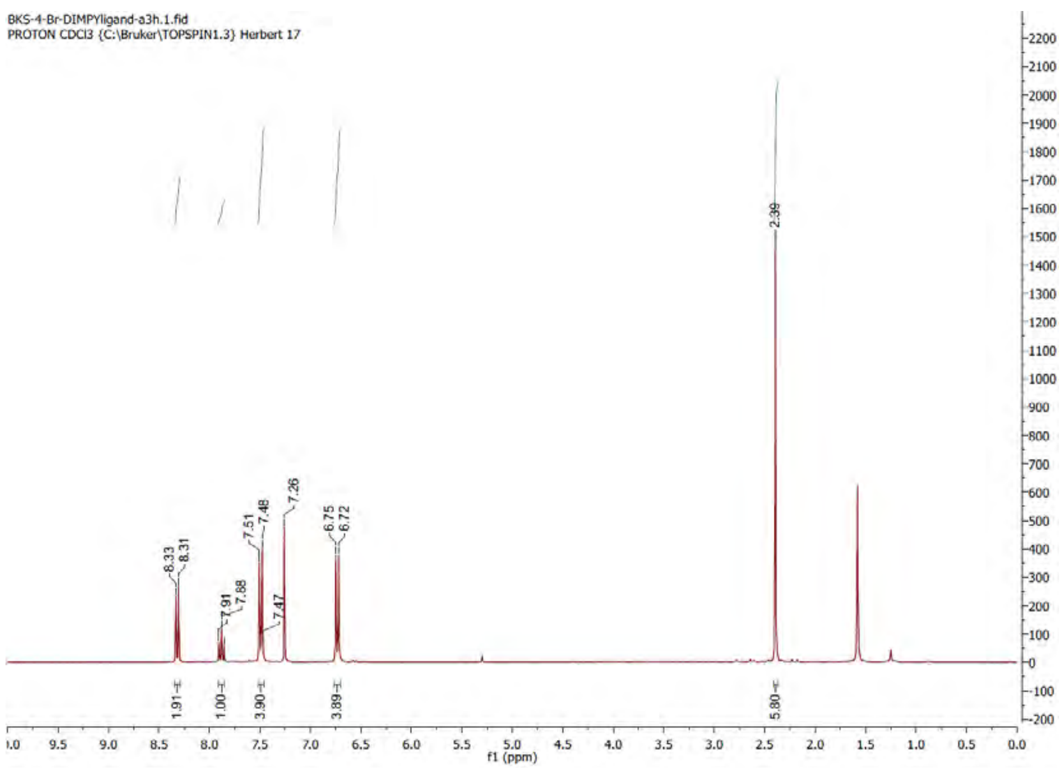

Figure S16. ^{1}H NMR ($CDCl_3$, 300 MHz, 25°C, ppm) of **2c**.

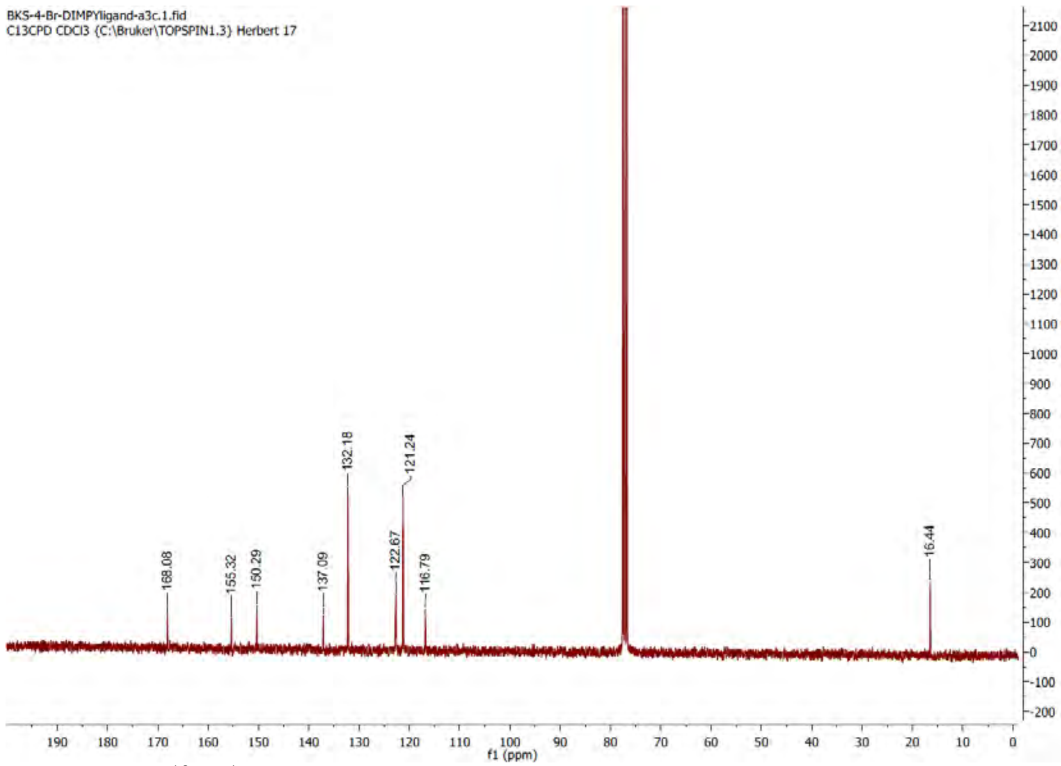

Figure S17. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz, 25°C, ppm) of **2c**.

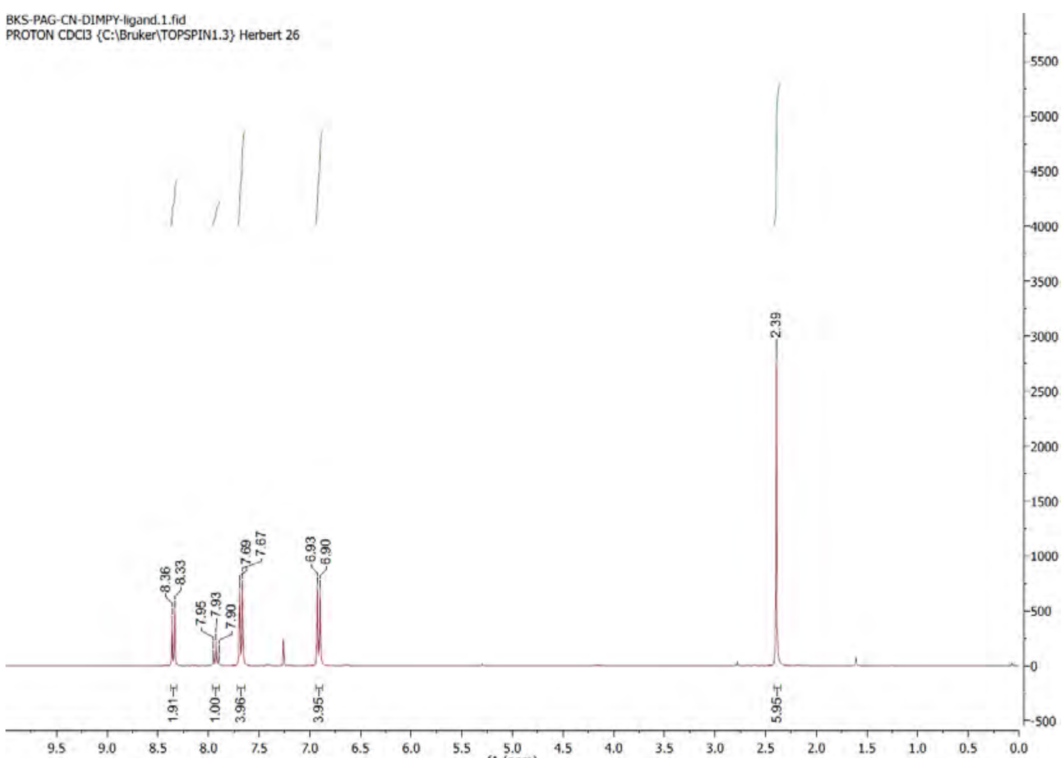

Figure S18. ^1H NMR ($CDCl_3$, 300 MHz, 25°C, ppm) of **2d**.

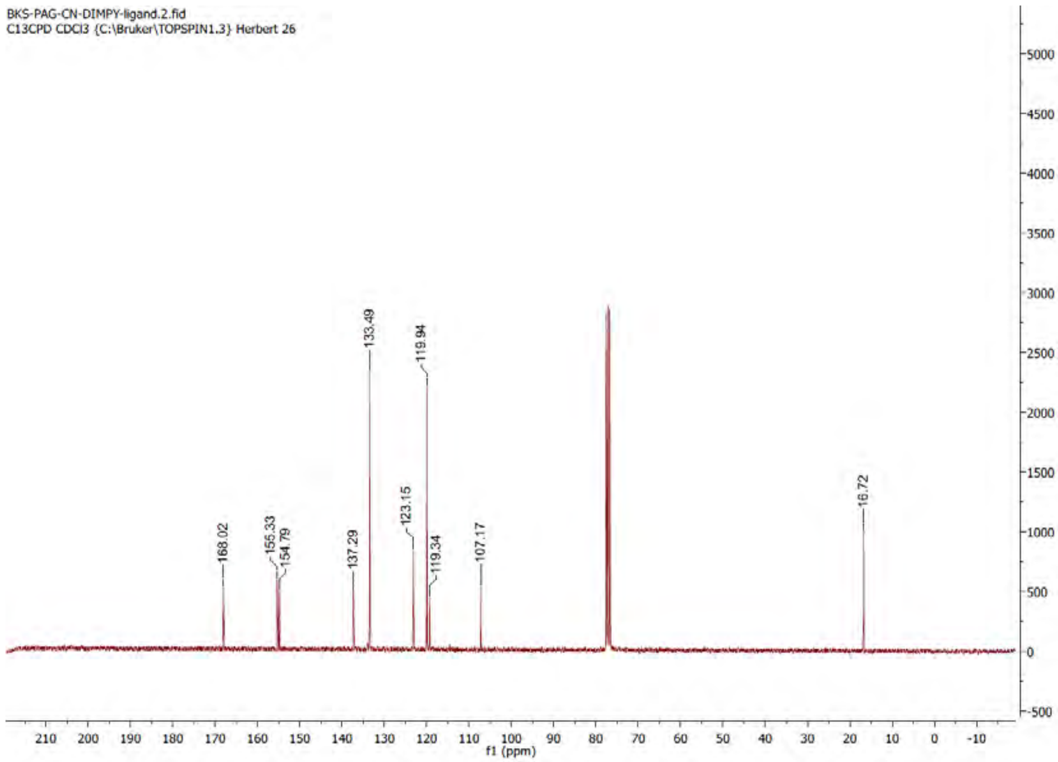

Figure S19. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 75 MHz, 25°C, ppm) of **2d**.

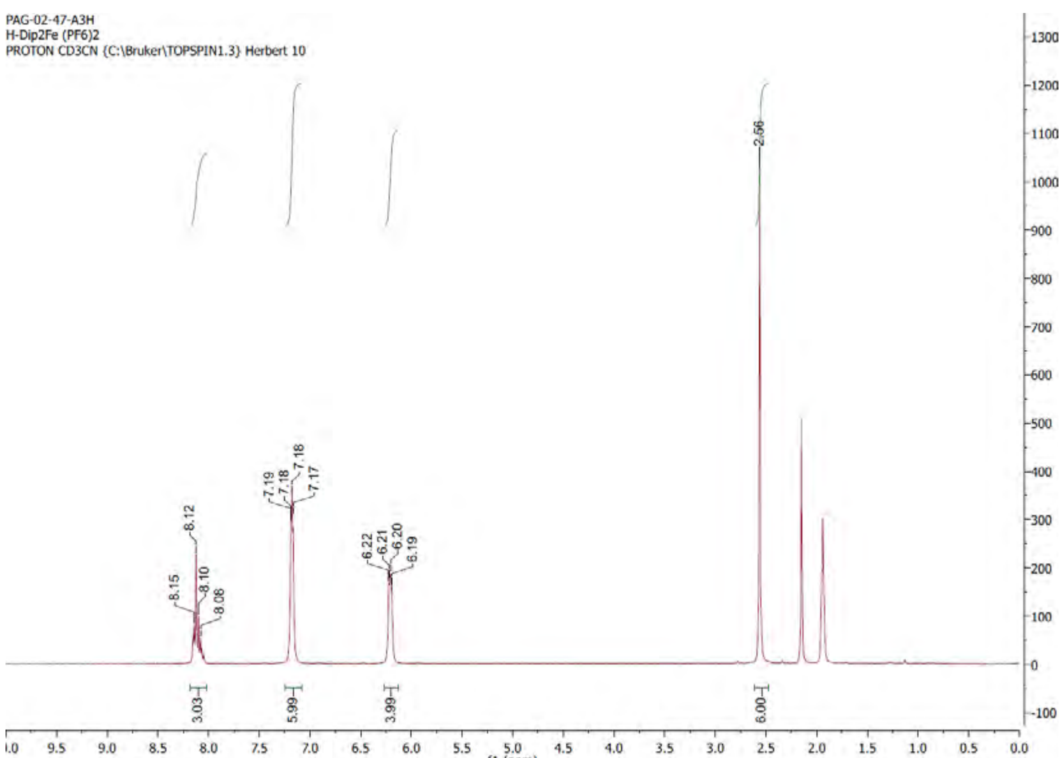

Figure S20. ^{1}H NMR (CD_3CN, 300 MHz, 25°C, ppm) of **3a**.

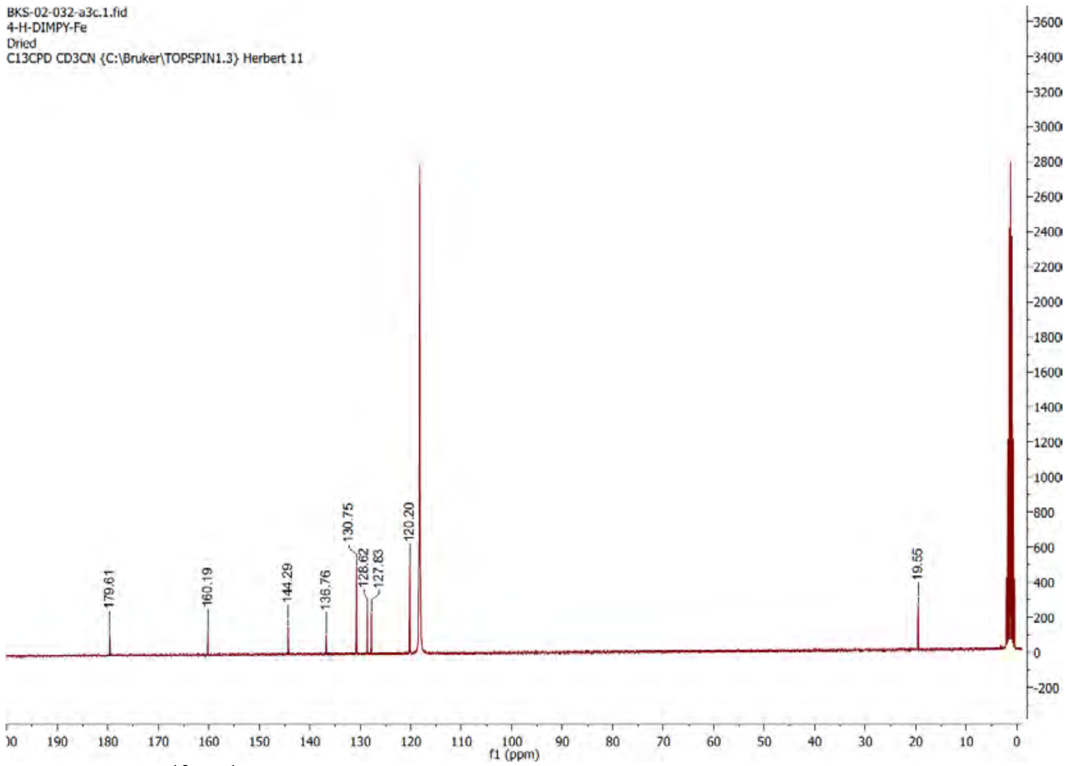

Figure S21. $^{13}C\{^1H\}$ NMR (CD_3CN, 75 MHz, 25°C, ppm) of **3a**.

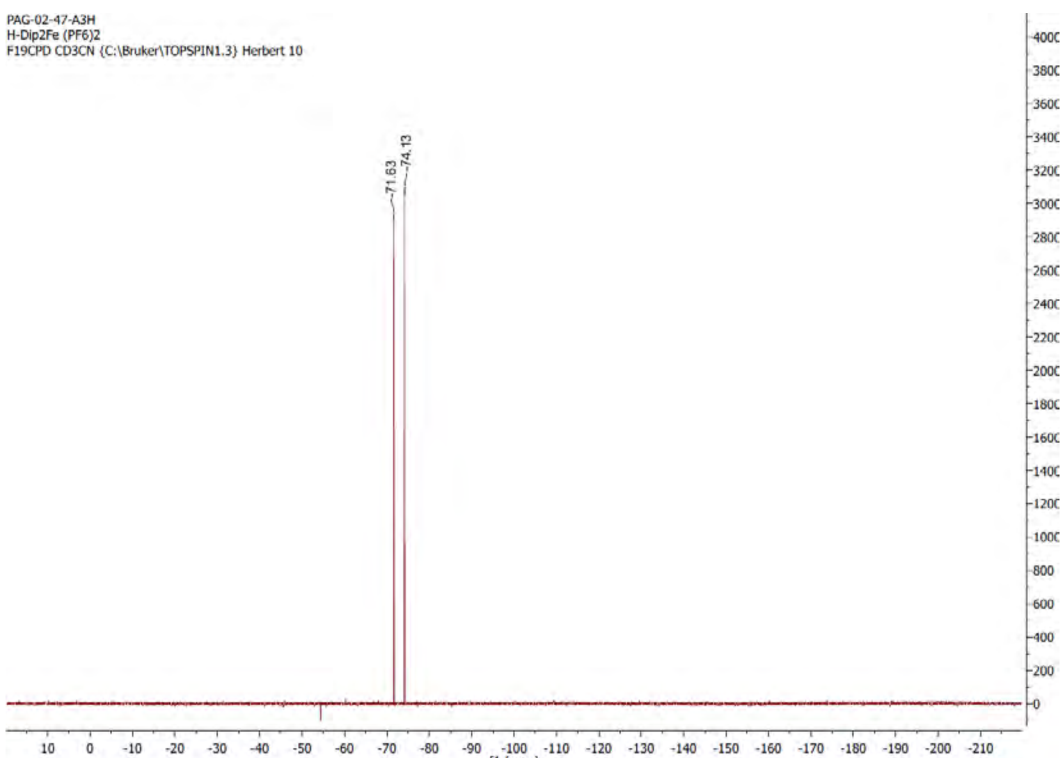

Figure S22: $^{19}F\{^1H\}$ NMR (CD_3CN, 282 MHz, 25°C, ppm) of **3a**.

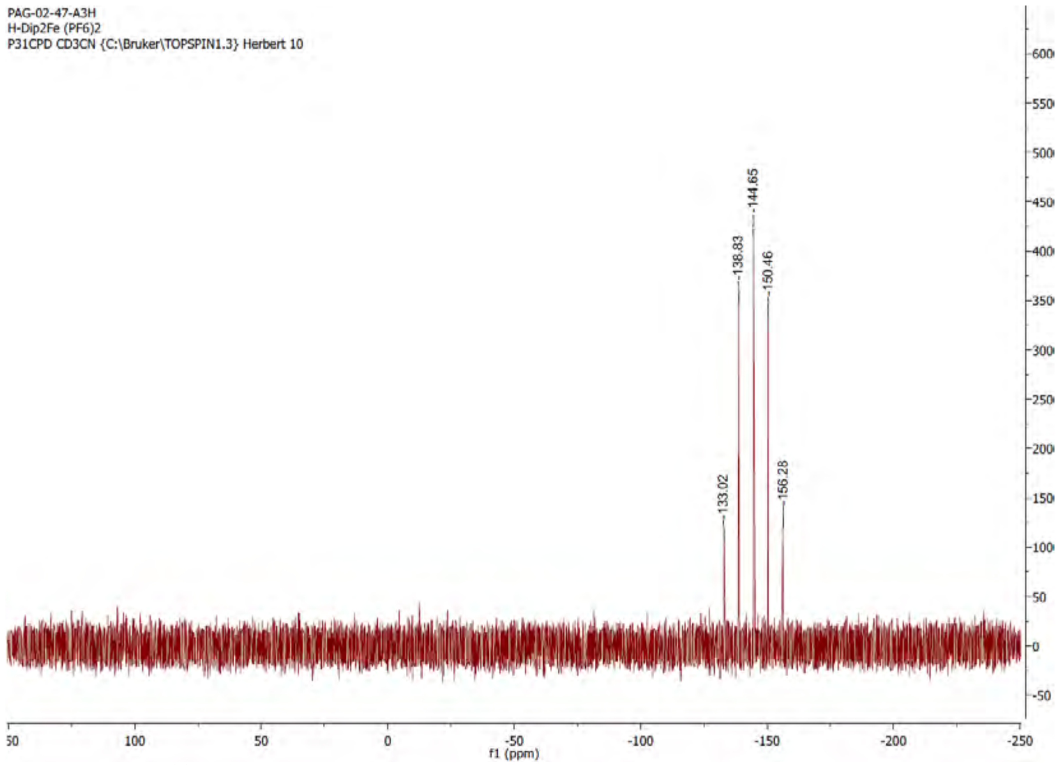

Figure S23. $^{31}P\{^1H\}$ NMR (CD_3CN, 121 MHz, 25°C, ppm) of **3a**.

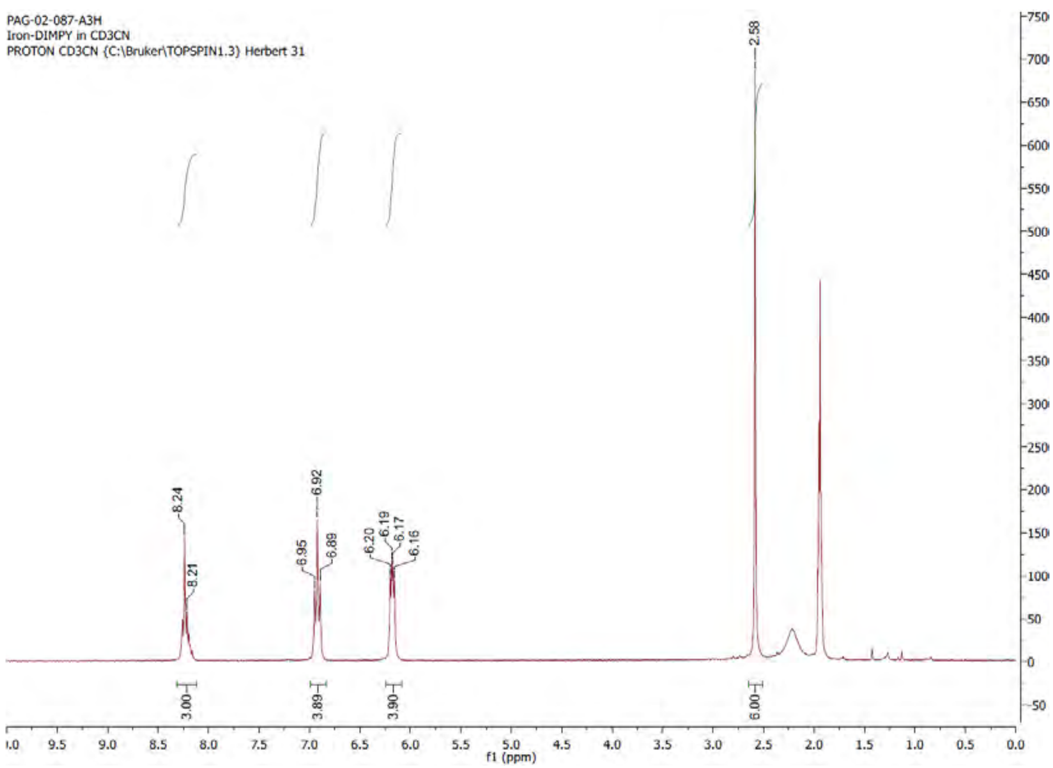

Figure S24. ^1H NMR (CD_3CN 300 MHz, 25°C, ppm) of **3b**.

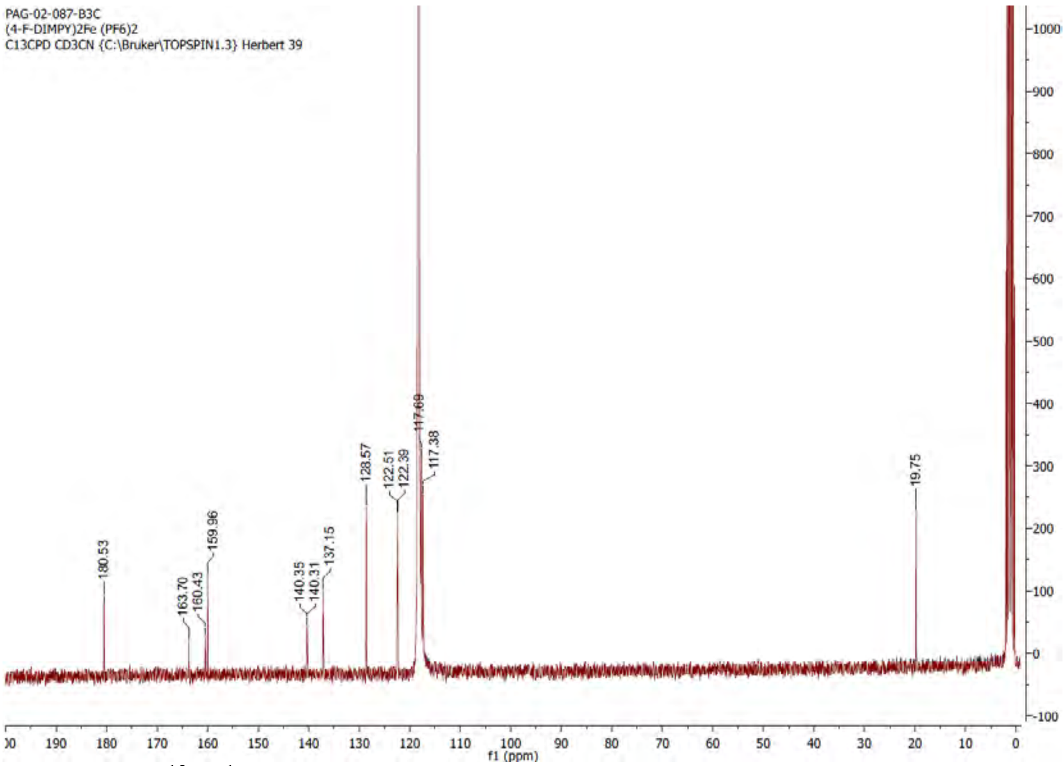

Figure S25. $^{13}C\{^{1}H\}$ NMR (CD_3CN, 75 MHz, 25°C, ppm) of **3b**.

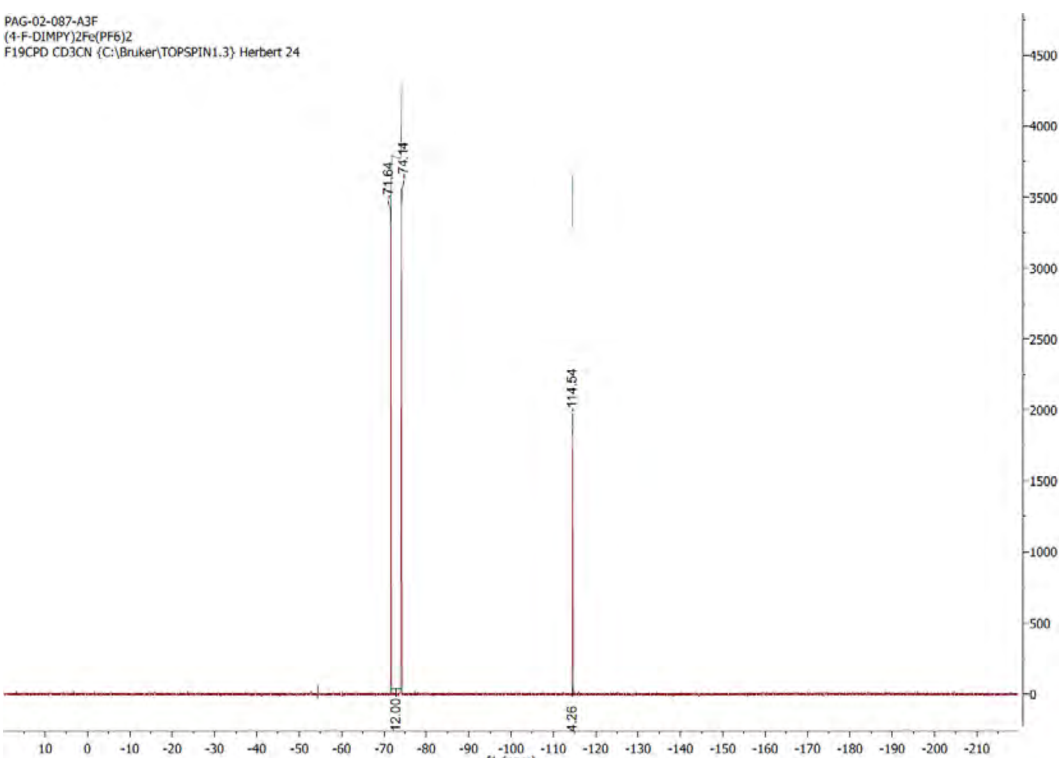

Figure S26. $^{19}F\{^{1}H\}$ NMR (CD_3CN, 282 MHz, 25°C, ppm) of **3b**.

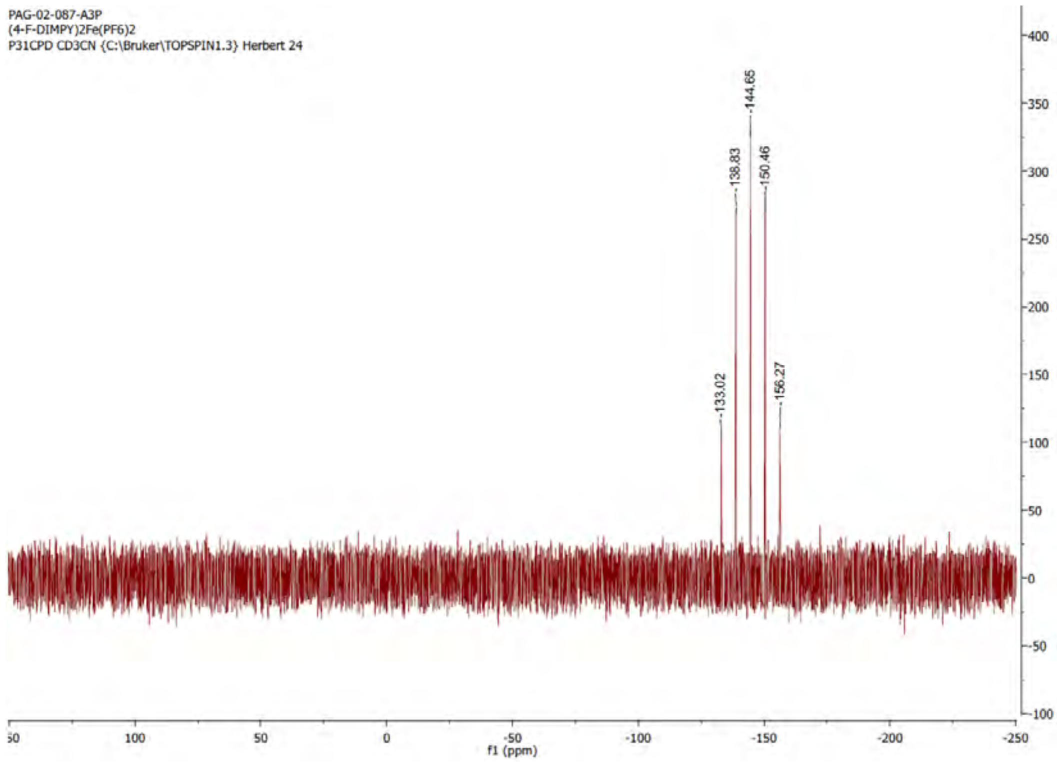

Figure S27. $^{31}P\{^{1}H\}$ NMR (CD_3CN, 121 MHz, 25°C, ppm) of **3b**.

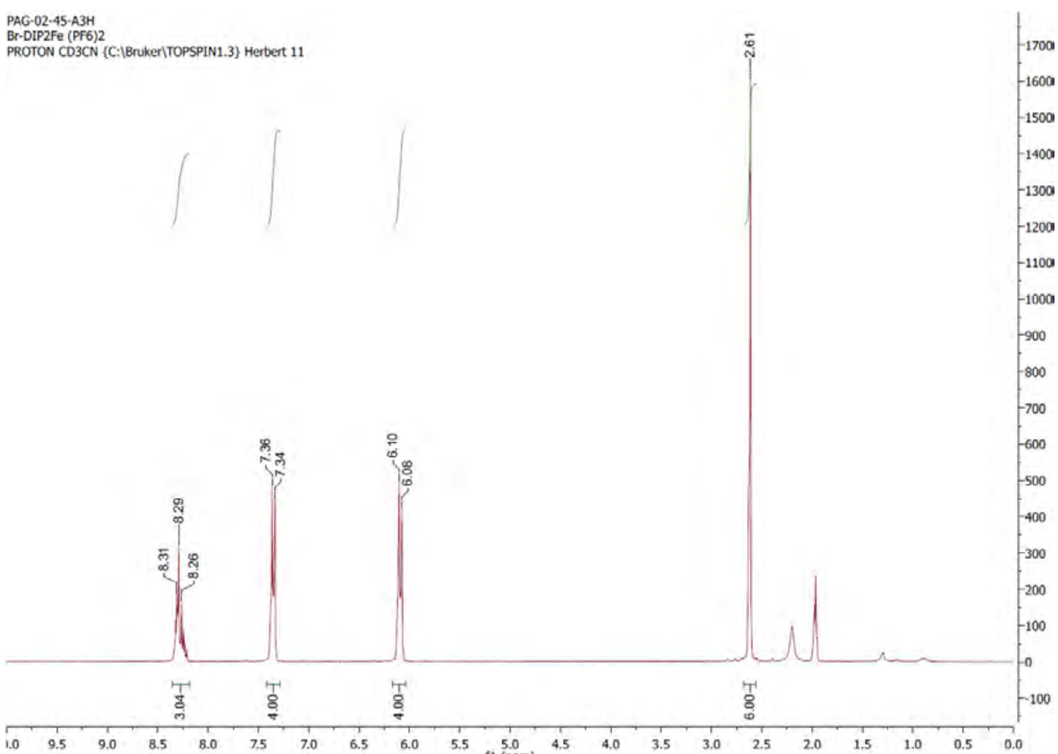

Figure S28. ^{1}H NMR (CD_3CN, 300 MHz, 25°C, ppm) of **3c**.

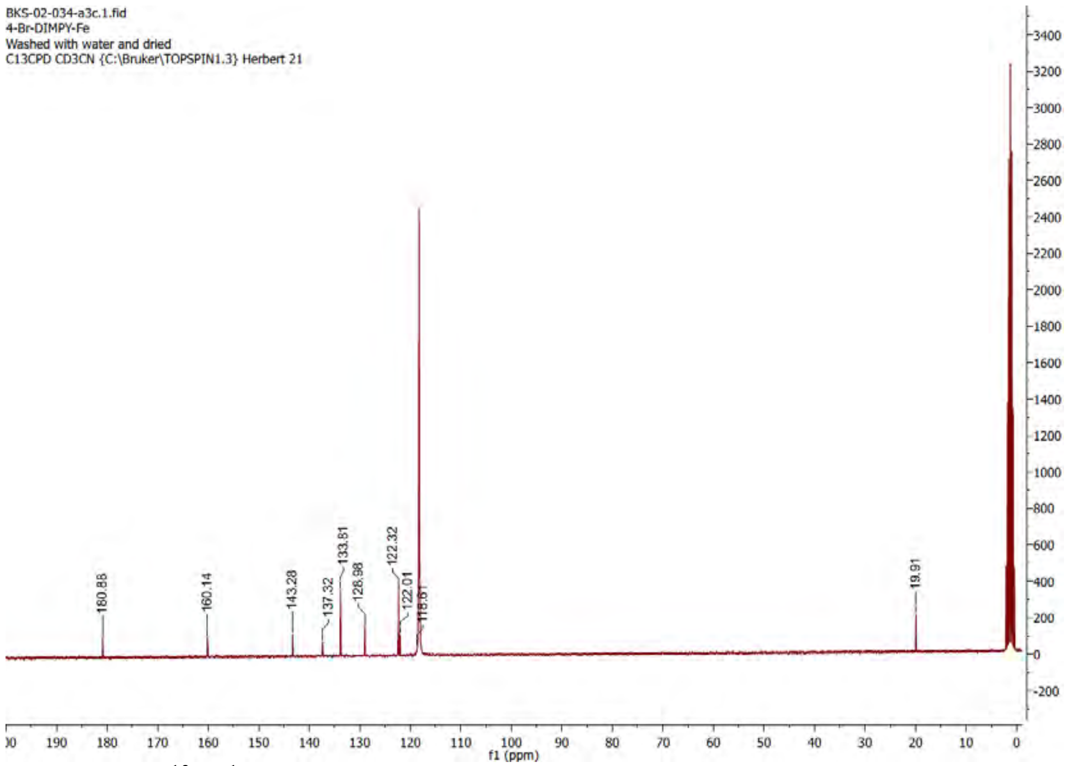

Figure S29. $^{13}C\{^1H\}$ NMR (CD_3CN, 75 MHz, 25°C, ppm) of **3c**.

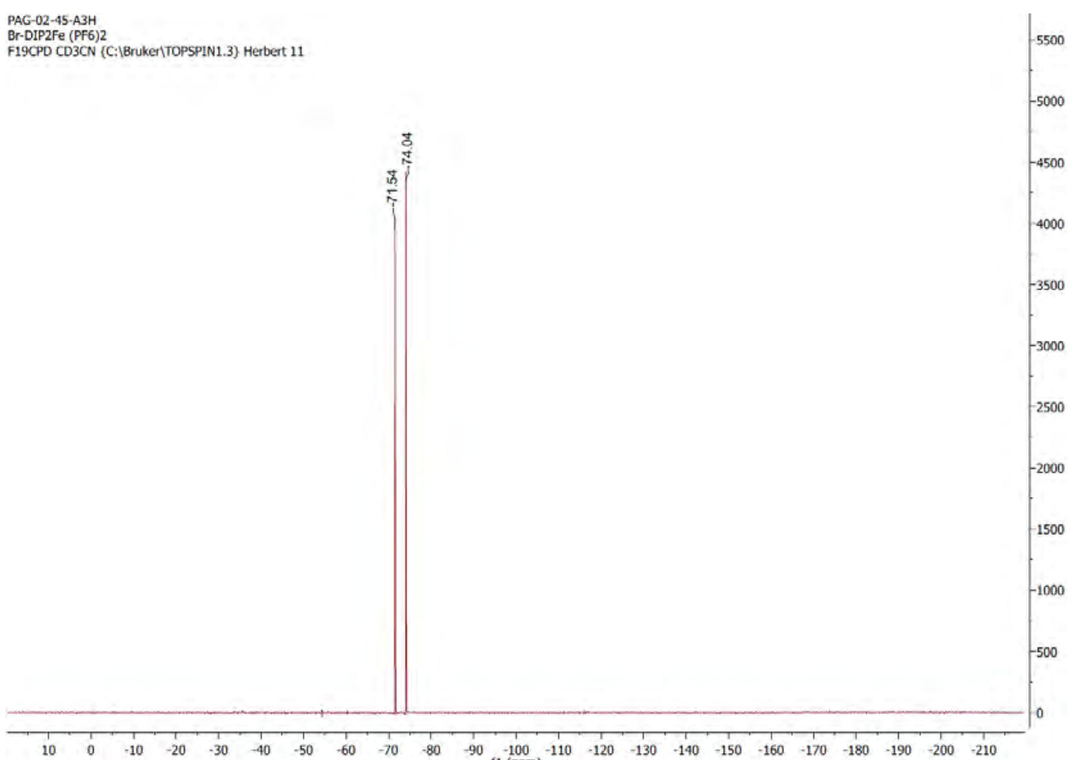

Figure S30. $^{19}F\{^1H\}$ NMR (CD_3CN, 282 MHz, 25°C, ppm) of **3c**.

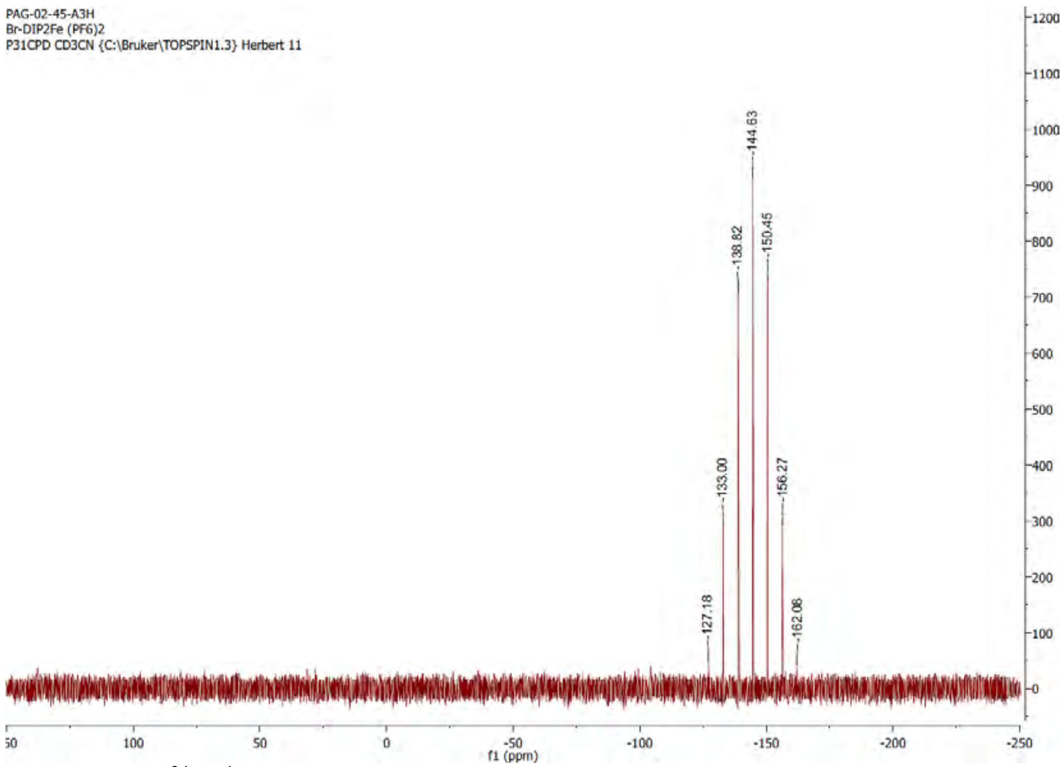

Figure S31. $^{31}P\{^1H\}$ NMR (CD_3CN, 121 MHz, 25°C, ppm) of **3c**.

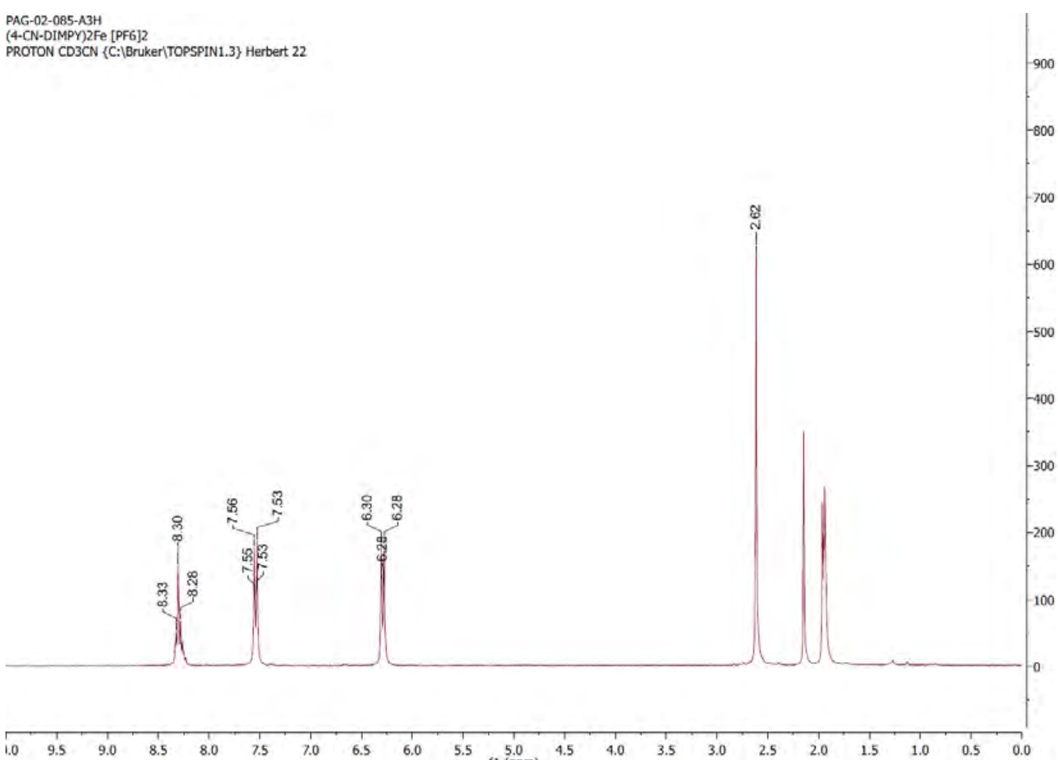

Figure S32. ^1H NMR (CD_3CN, 300 MHz, 25°C, ppm) of **3d**.

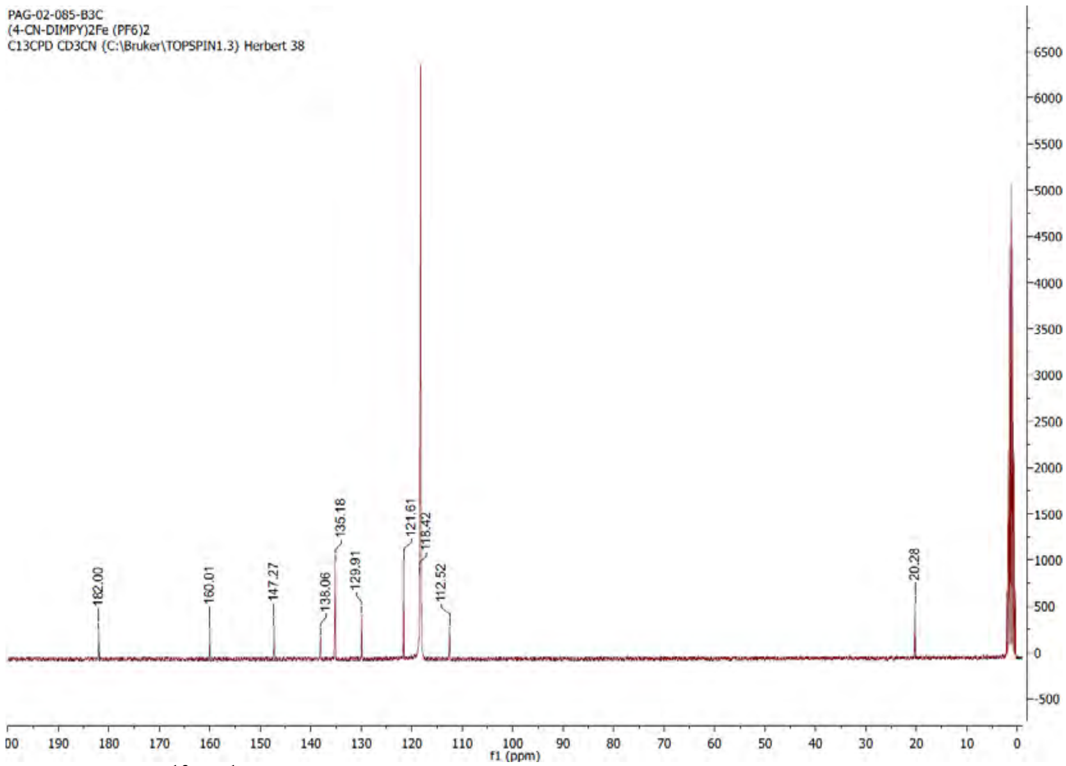

Figure S33. $^{13}C\{^{1}H\}$ NMR (CD_3CN, 75 MHz, 25°C, ppm) of **3d**.

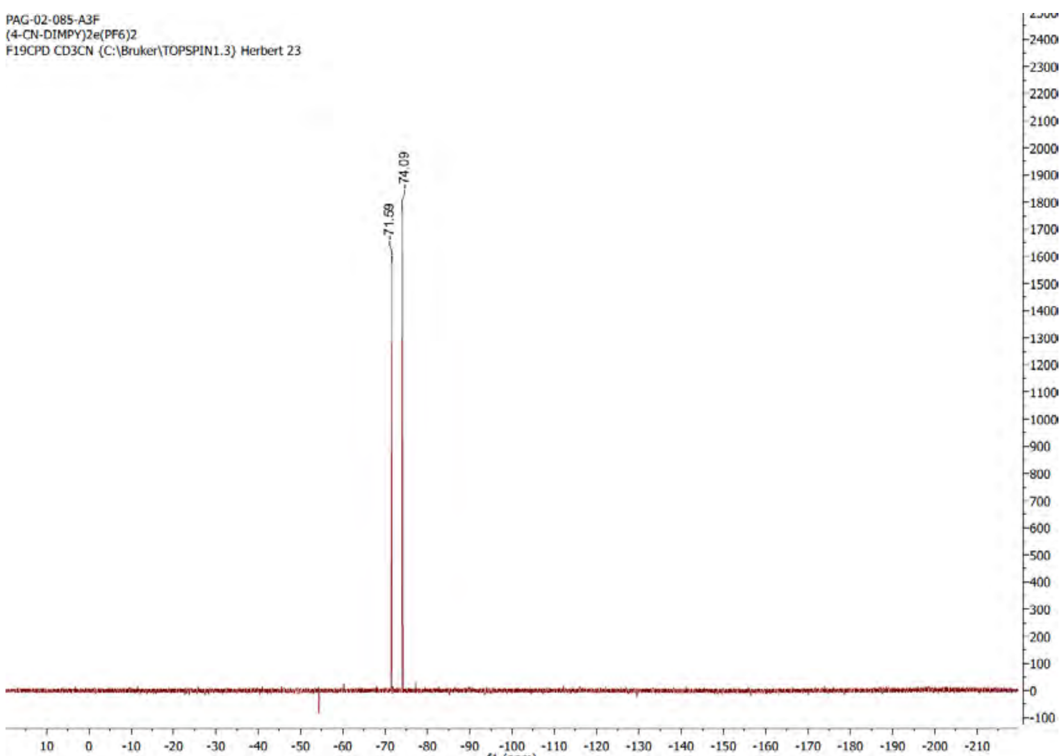

Figure S34. $^{19}F\{^{1}H\}$ NMR (CD_3CN, 282 MHz, 25°C, ppm) of **3d**.

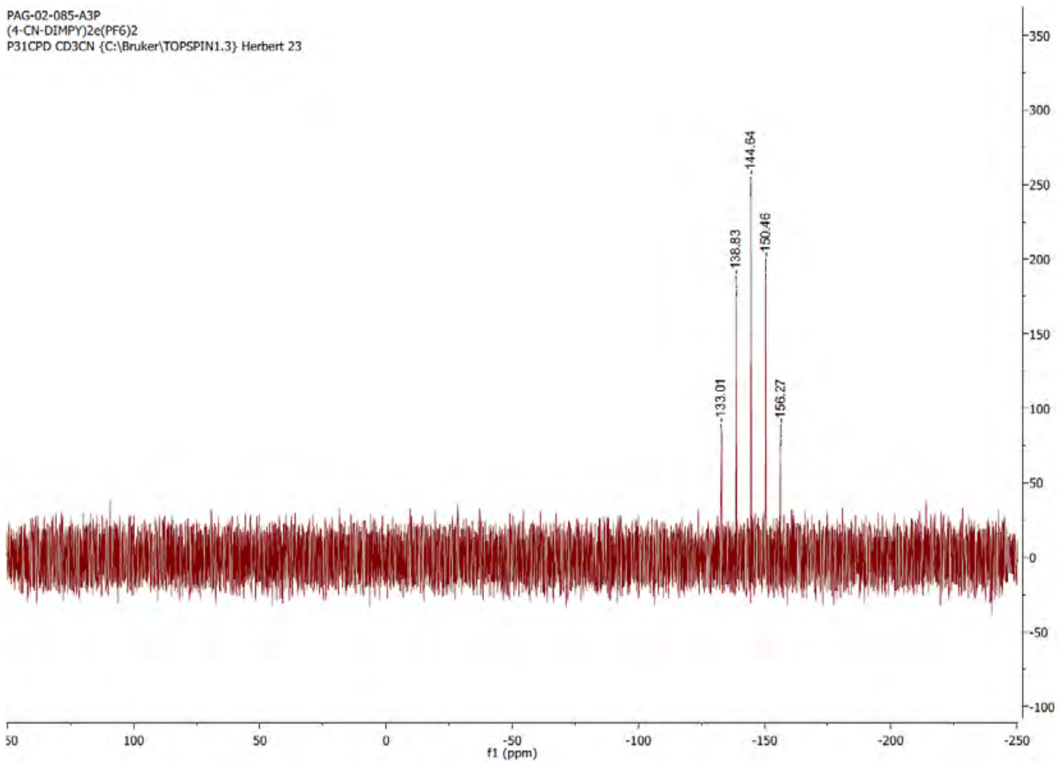

Figure S35. $^{31}P\{^{1}H\}$ NMR (CD_3CN, 121 MHz, 25°C, ppm) of **3d**.

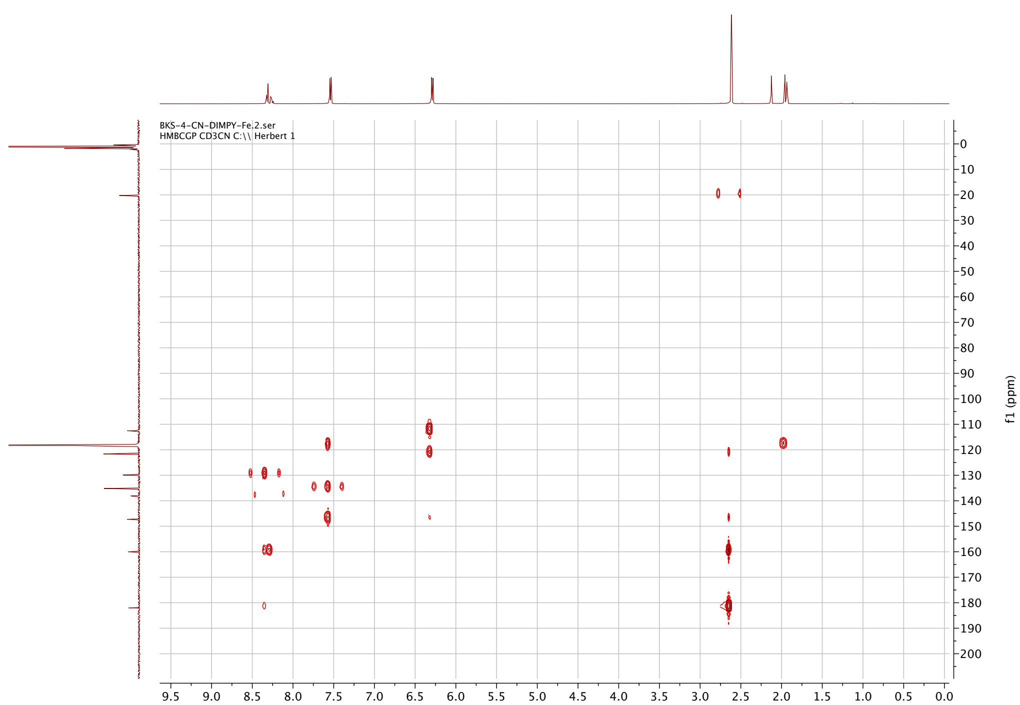

Figure S36. HMBC NMR (CD_3CN, 300/75 MHz, 25°C, ppm) of **1d**.

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

	1b	**1c**	**1d**	**3c**	**3d**
M – N$_{pyr}$					
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)
M – N$_{imine}$					
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)
C$_{imine}$ – N$_{imine}$					
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)
C$_{Ar}$ – N$_{imine}$					
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
Intraligand angles					
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)	-	-	-
Interligand angles					
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] $\tau_5 = (\beta-\alpha)/60°$ 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)

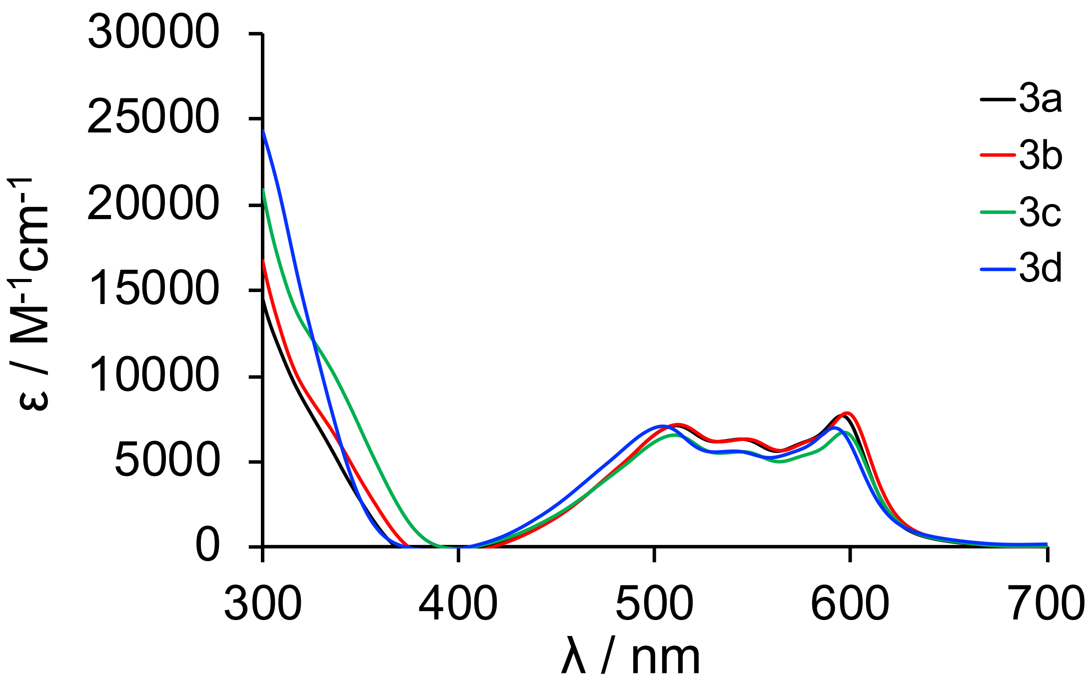

Figure S37. UV-vis spectra of **3(a-d)** in CH_3CN.

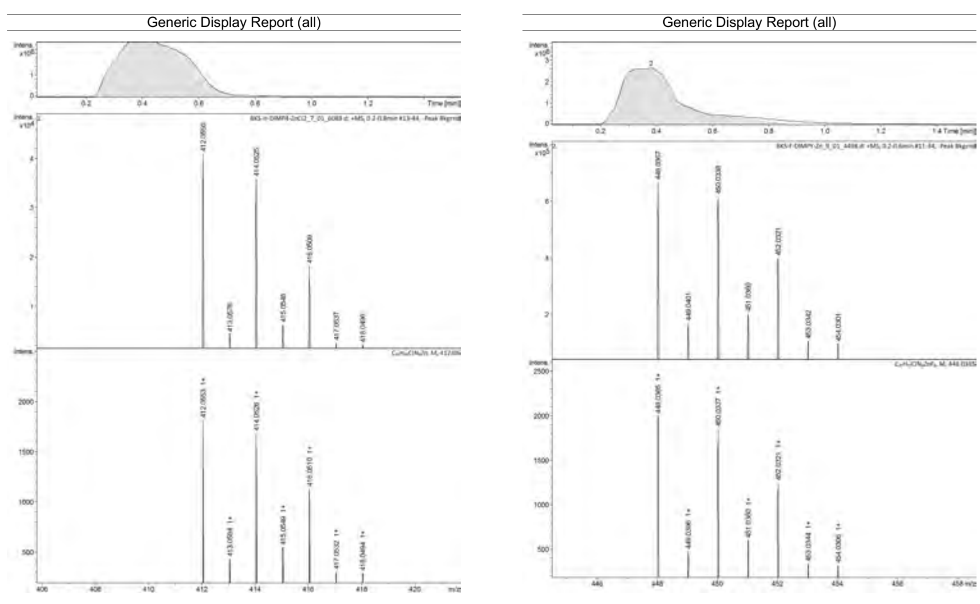

Figure S38. MS (ESI-TOF/MS, m/z) for **1a** and **1b**.

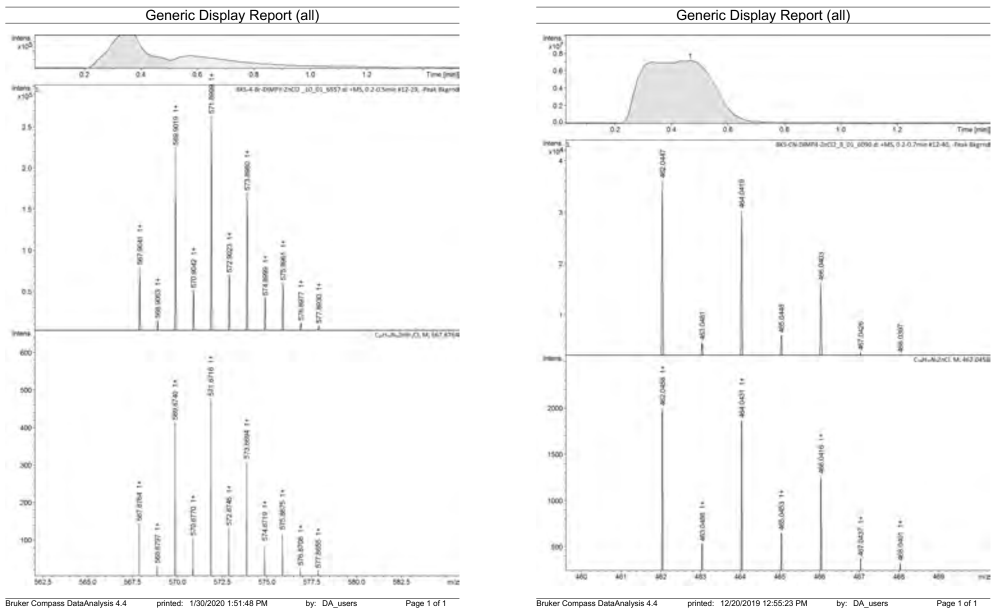

Figure S39. MS (ESI-TOF/MS, m/z) for **1c** and **1d**.

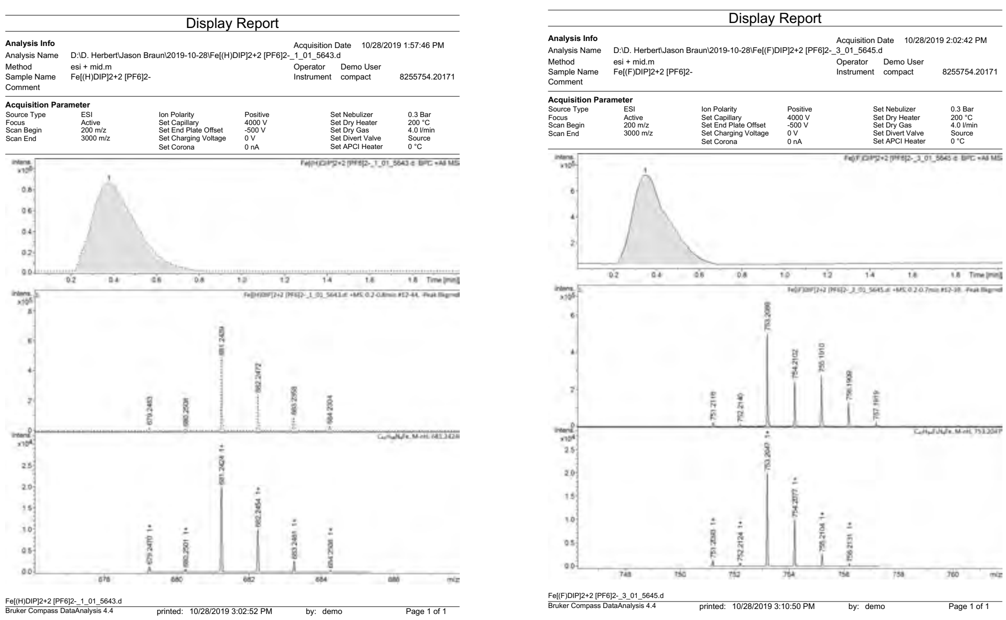

Figure S40. MS (ESI-TOF/MS, m/z) for **3a** and **3b**.

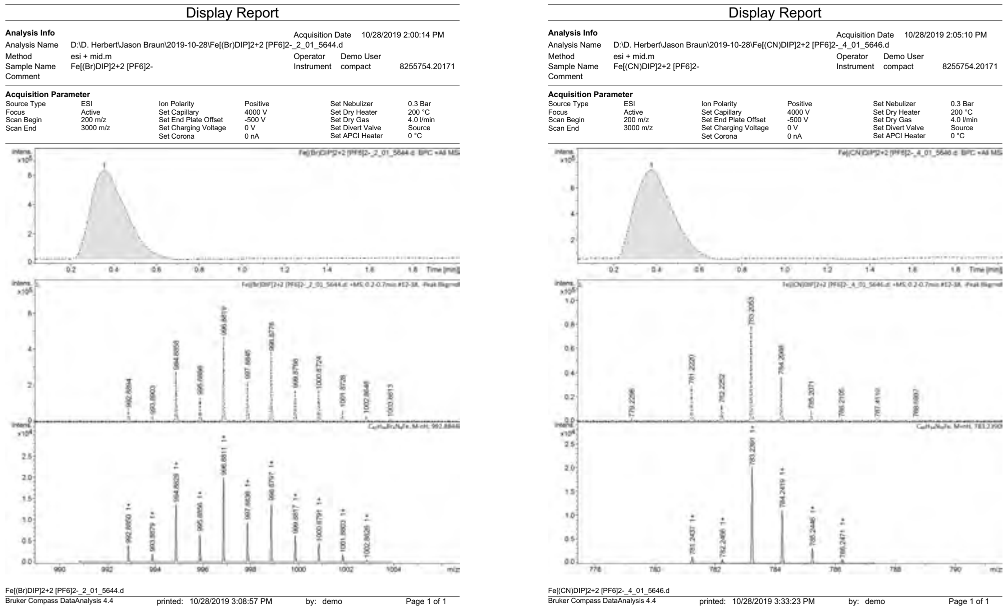

Figure S41. MS (ESI-TOF/MS, m/z) for **3c** and **3d**.

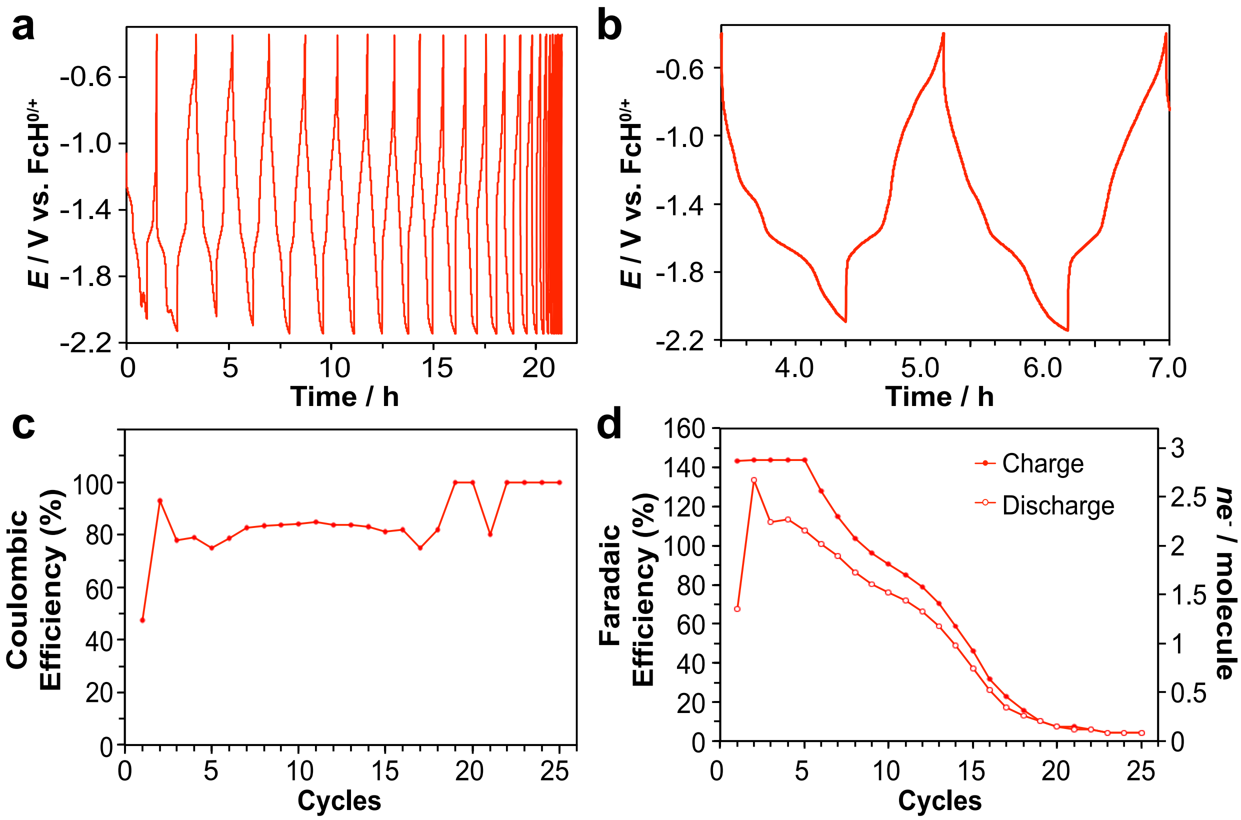

Figure S42. (a, b) Total cell voltage, (c) Coulombic efficiency (% CE), and (d) capacity retention for **3b**. Anodic and cathodic current set to 7 mA with a charging rate of 1C. Voltage limits set according to previously obtained CVs in order to limit access or irreversible redox events; in 0.3 M nBu_4PF_6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

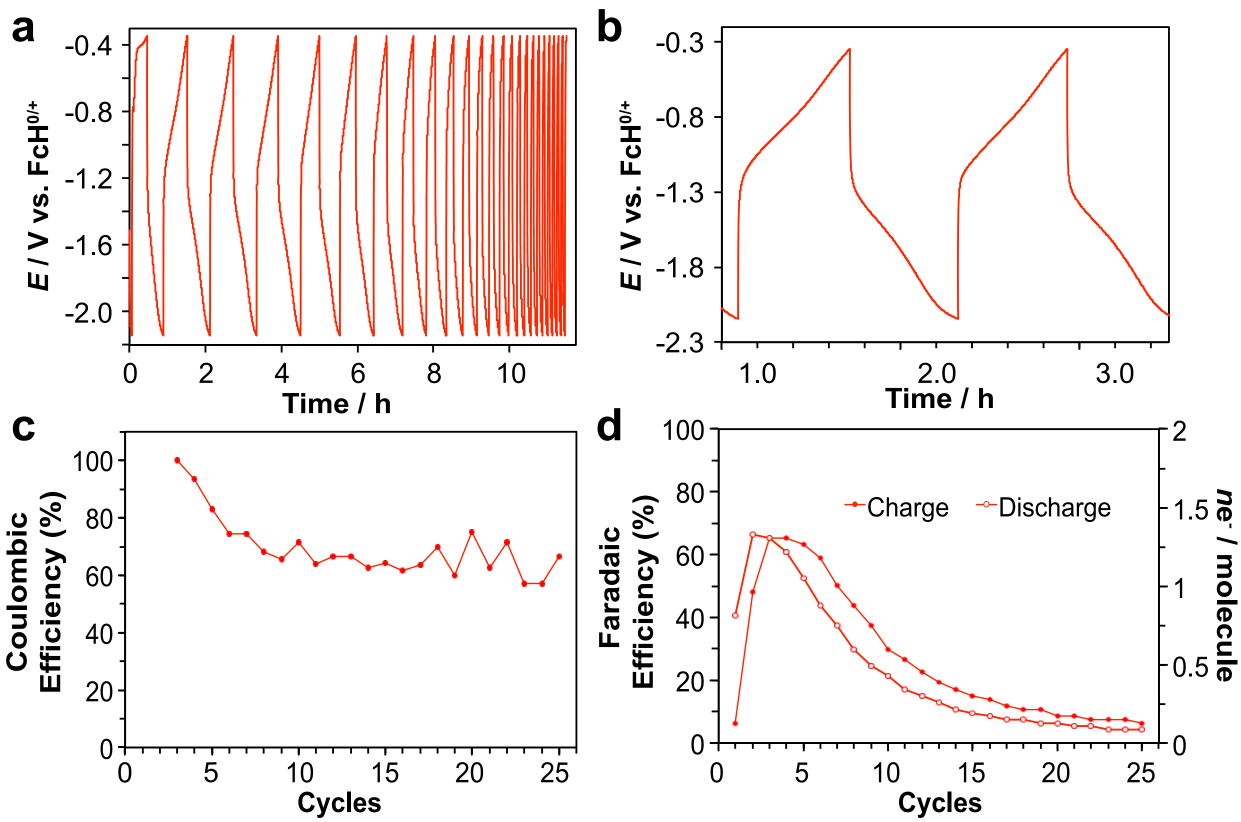

Figure S43. (a, b) Total cell voltage, (c) Coulombic efficiency (% CE), and (d) capacity retention for **3c**. Anodic and cathodic current set to 2 mA with a charging rate of 1C. Voltage limits set according to previously obtained CVs in order to limit access or irreversible redox events; in 0.3 M nBu_4PF_6 acetonitrile solution.

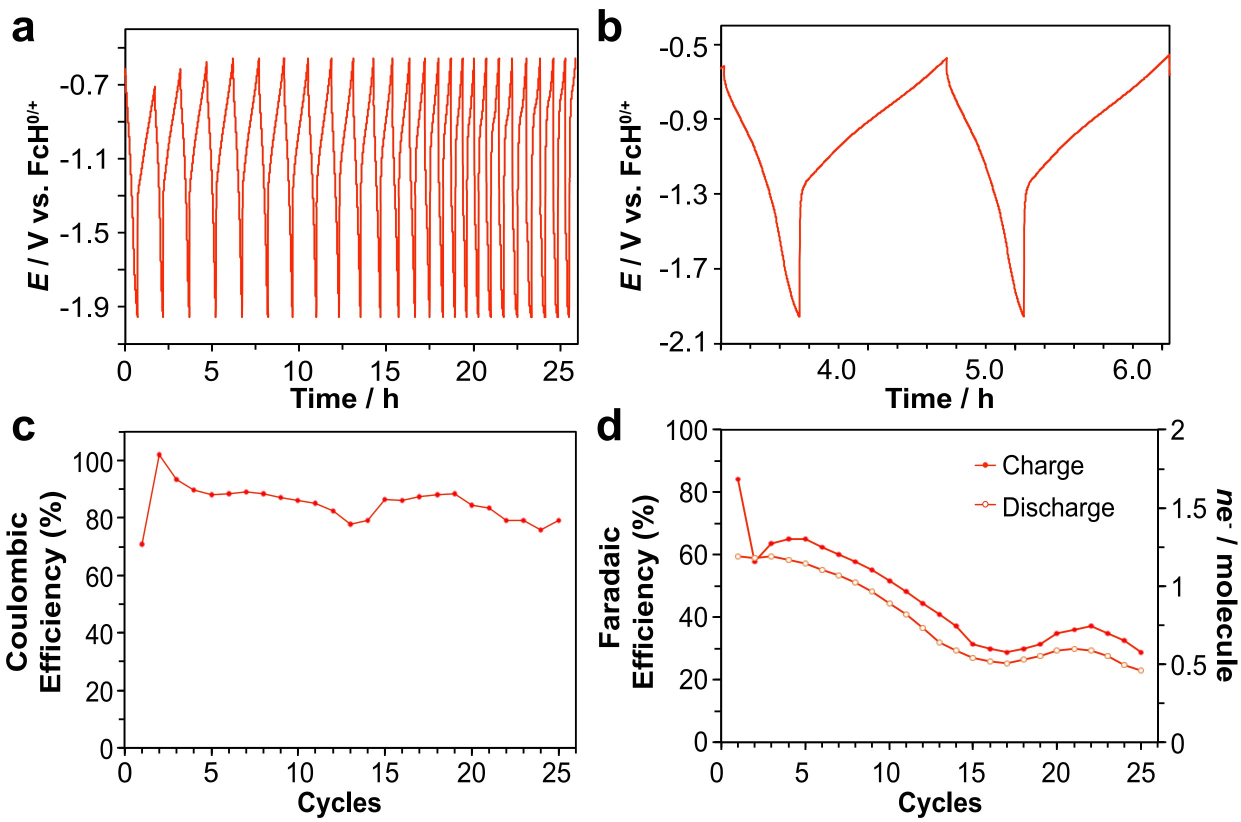

Figure S44. (a, b) Total cell voltage, (c) Coulombic efficiency (% CE), and (d) capacity retention for **3d**. Anodic and cathodic current set to 3 mA with a charging rate of 1C. Voltage limits set according to previously obtained CVs in order to limit access or irreversible redox events; in 0.3 M nBu_4PF_6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

REFERENCES

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