Supporting Information for New Journal of Chemistry

Formation of Iron(III)-Thiolate Metallocyclophane Using a Ferrocene-Based Bis-Isocyanide

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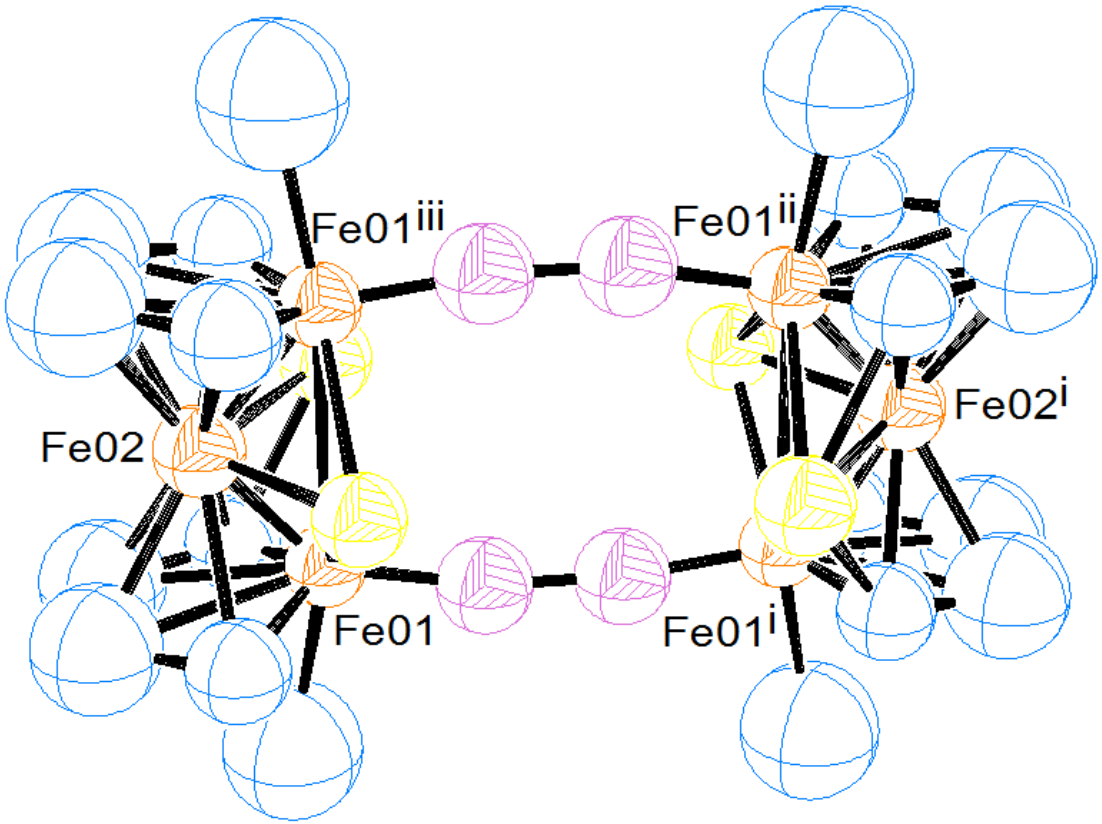

Figure S1. ORTEP representation of the crystal structure of the cation of **3**$[BF_4]_2$ which exist highly disorder due to the positional packing of Cp-Fe fragments, ferrocene moiety, and iron-thiolate core. (50% ellipsoid; all H atoms and anions are omitted for clarity).

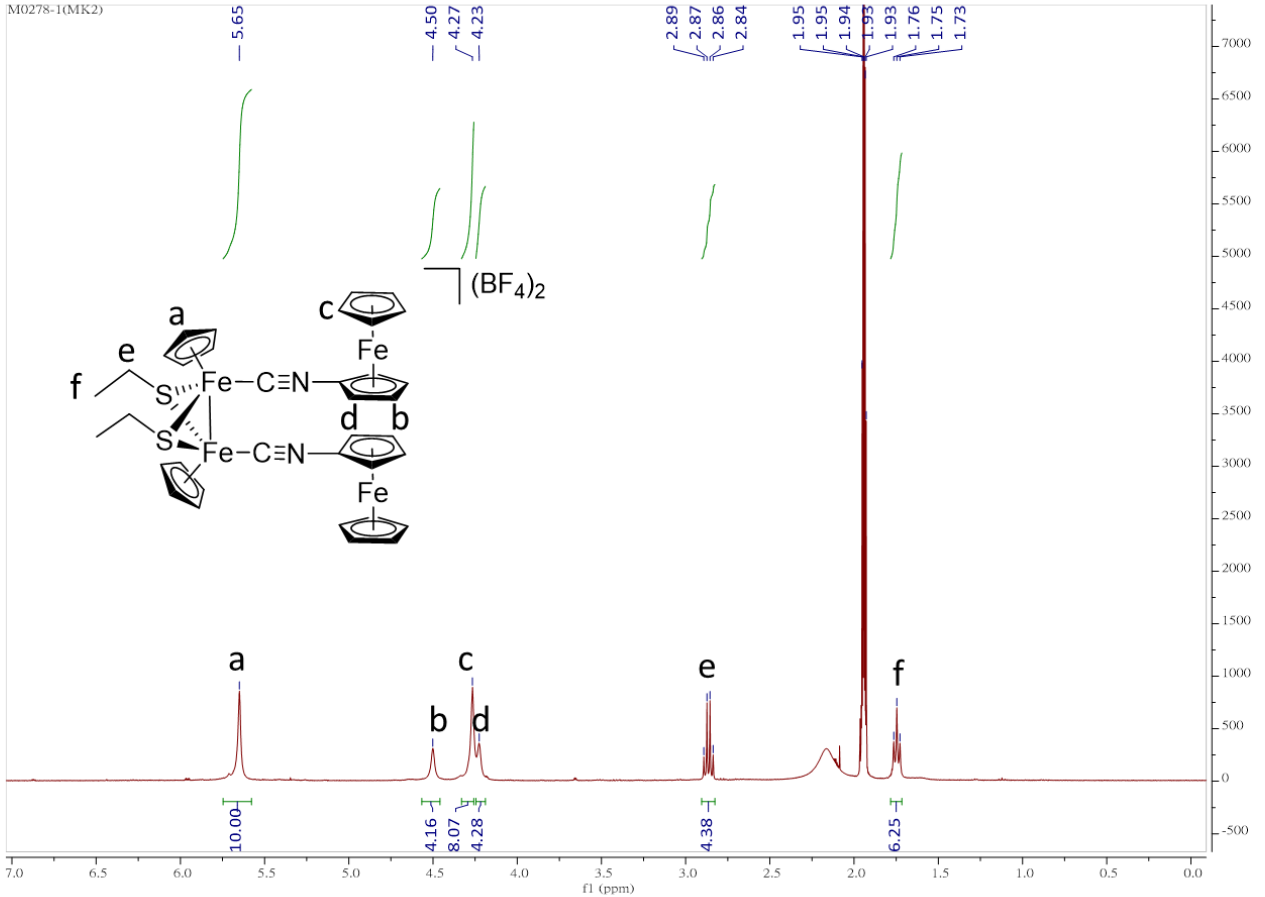

Figure S2. ^{1}H NMR spectrum of **2**$[BF_4]_2$ in CD_3CN.

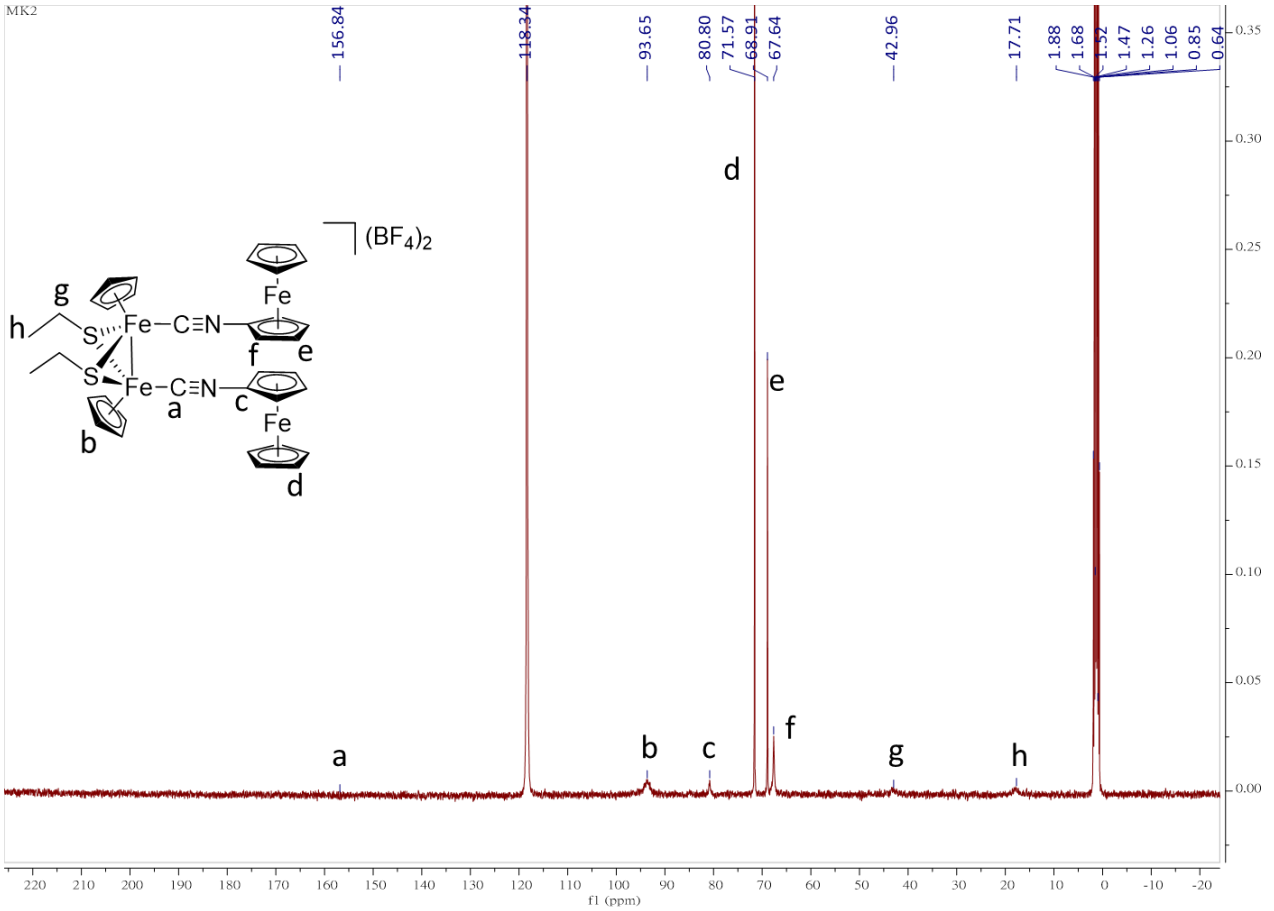

Figure S3. $^{13}C\{^{1}H\}$ NMR spectrum of **2**$[BF_4]_2$ in CD_3CN.

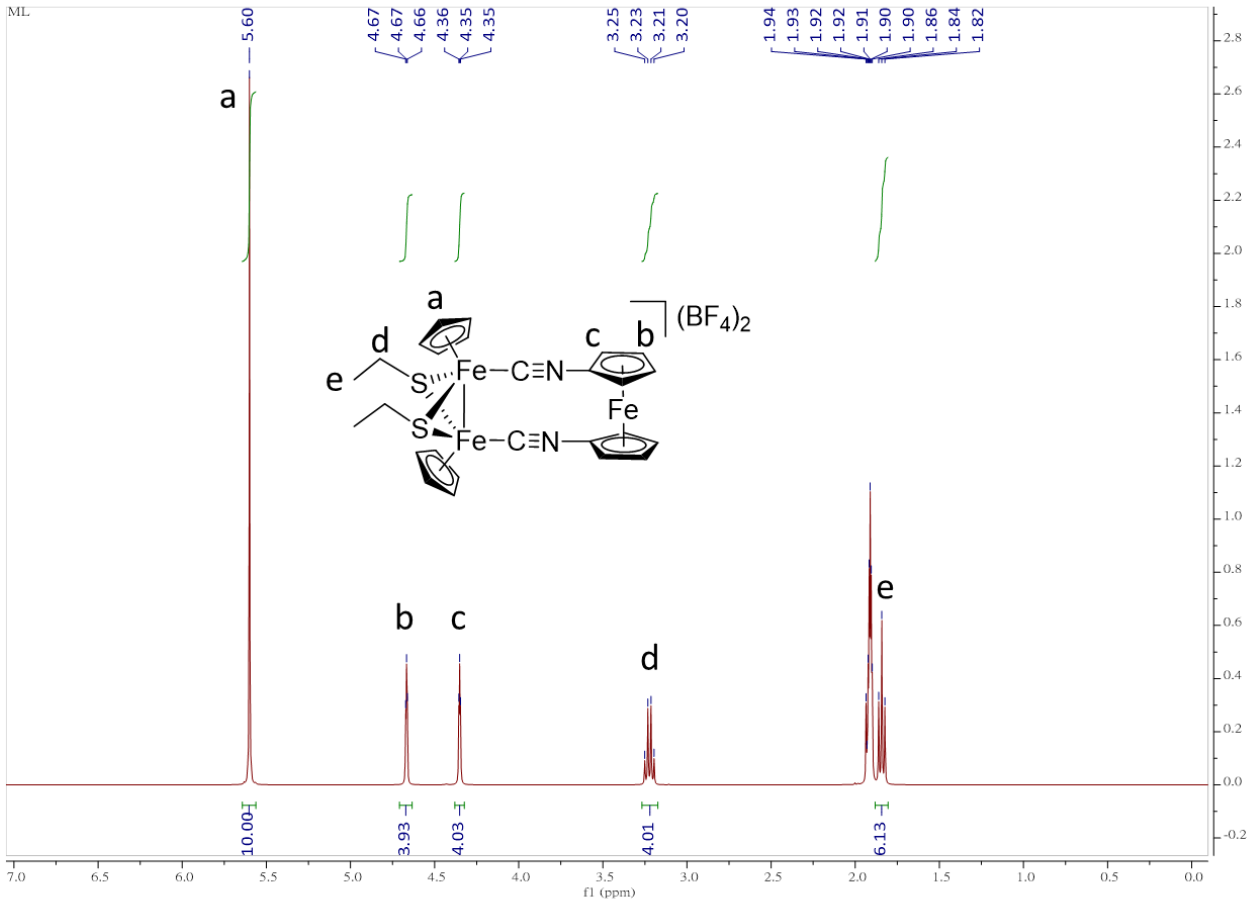

Figure S4. ^{1}H NMR spectrum of **3**$[BF_4]_2$ in CD_3CN.

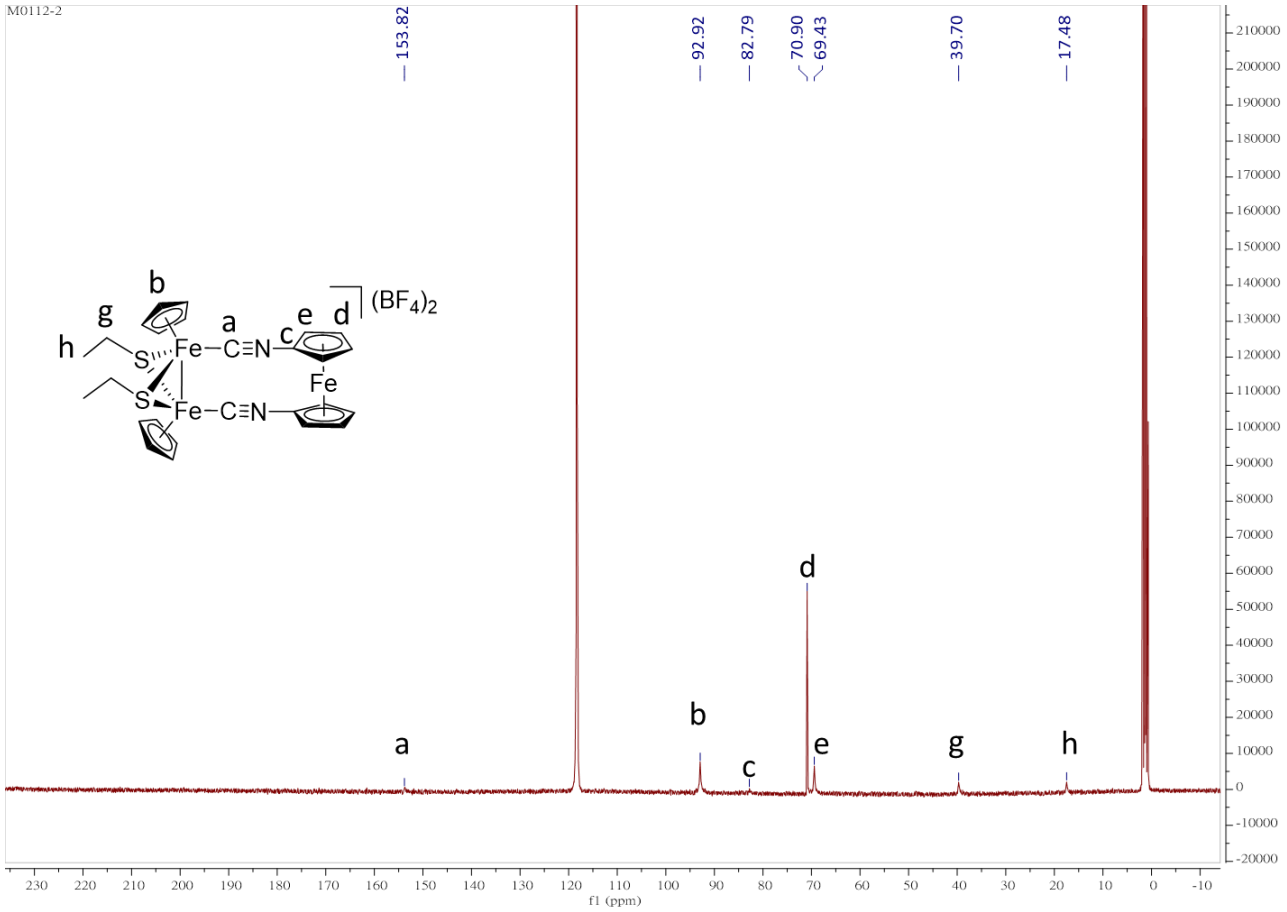

Figure S5. $^{13}C\{^{1}H\}$ NMR spectrum of **3**$[BF_4]_2$ in CD_3CN.

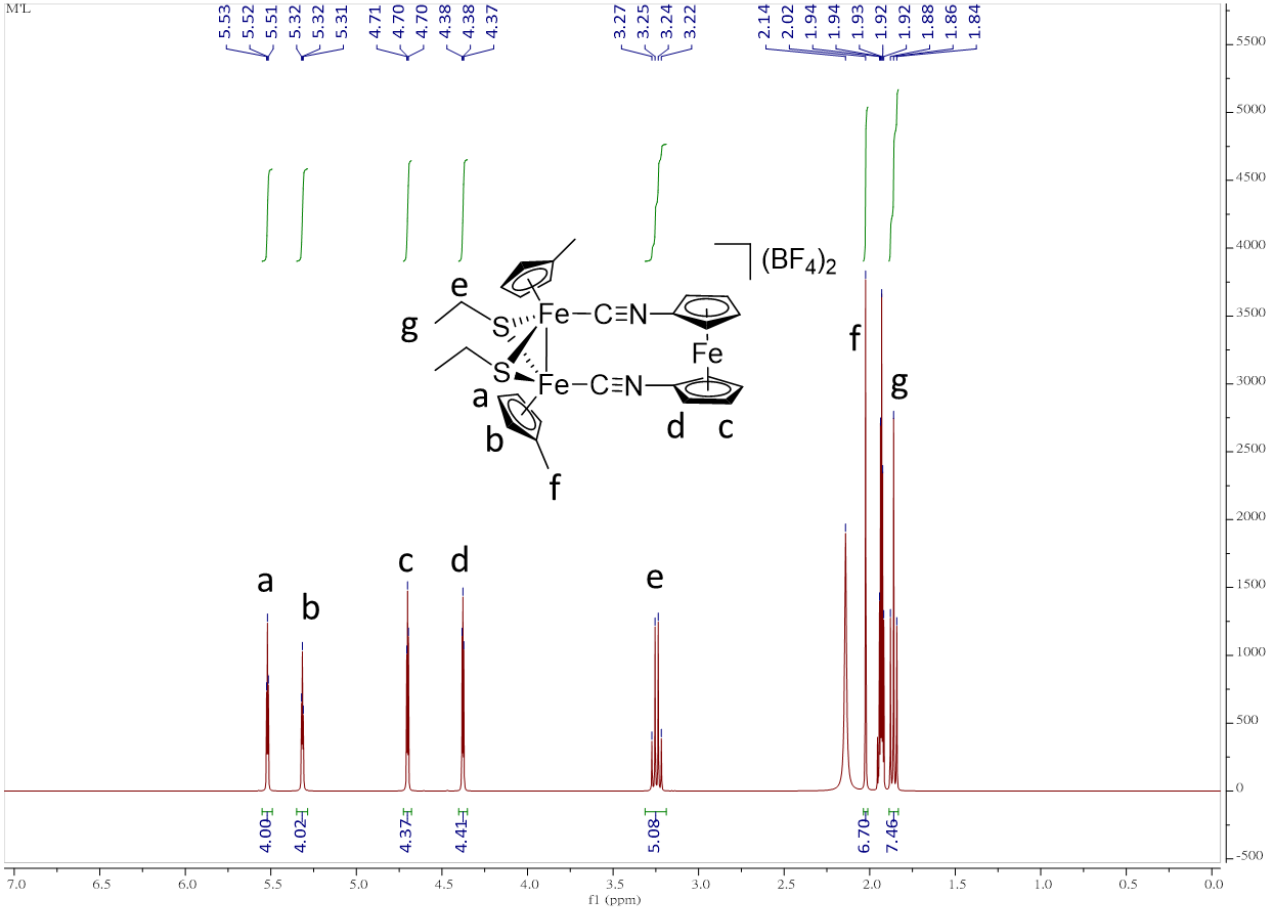

Figure S6. ^{1}H NMR spectrum of **3'**$[BF_4]_2$ in CD_3CN.

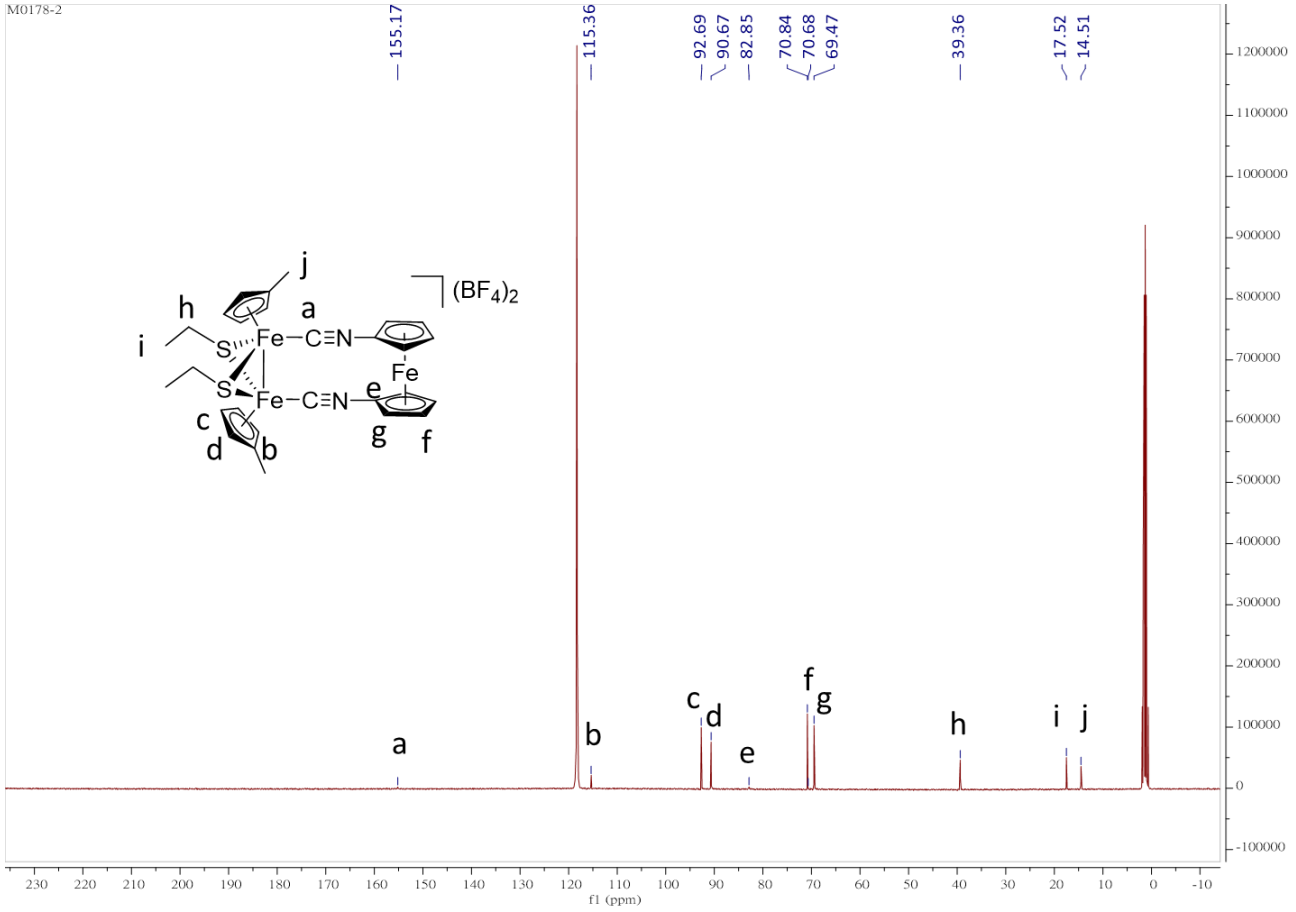

Figure S7. $^{13}C\{^{1}H\}$ NMR spectrum of **3'**$[BF_4]_2$ in CD_3CN.

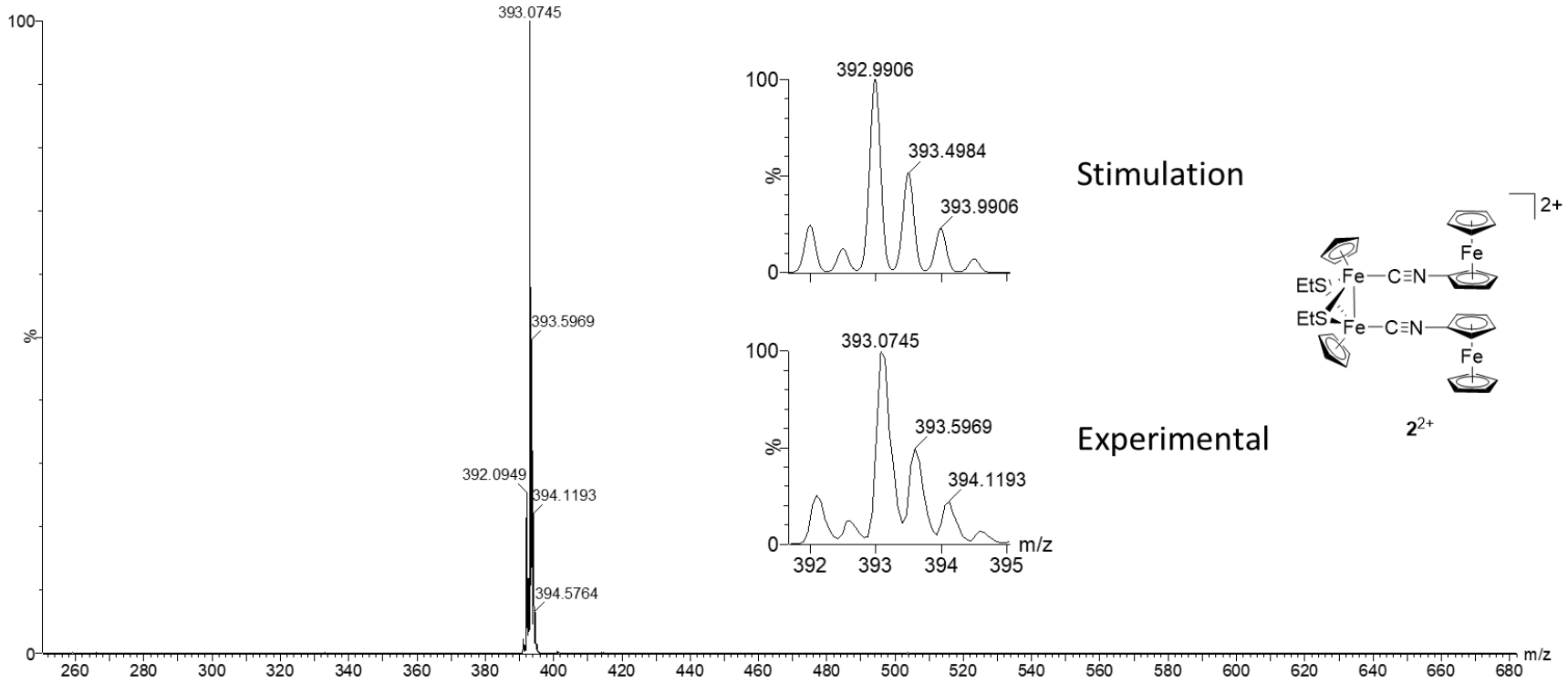

Figure S8. ESI-MS of **2**$[BF_4]_2$ in CH_3CN.

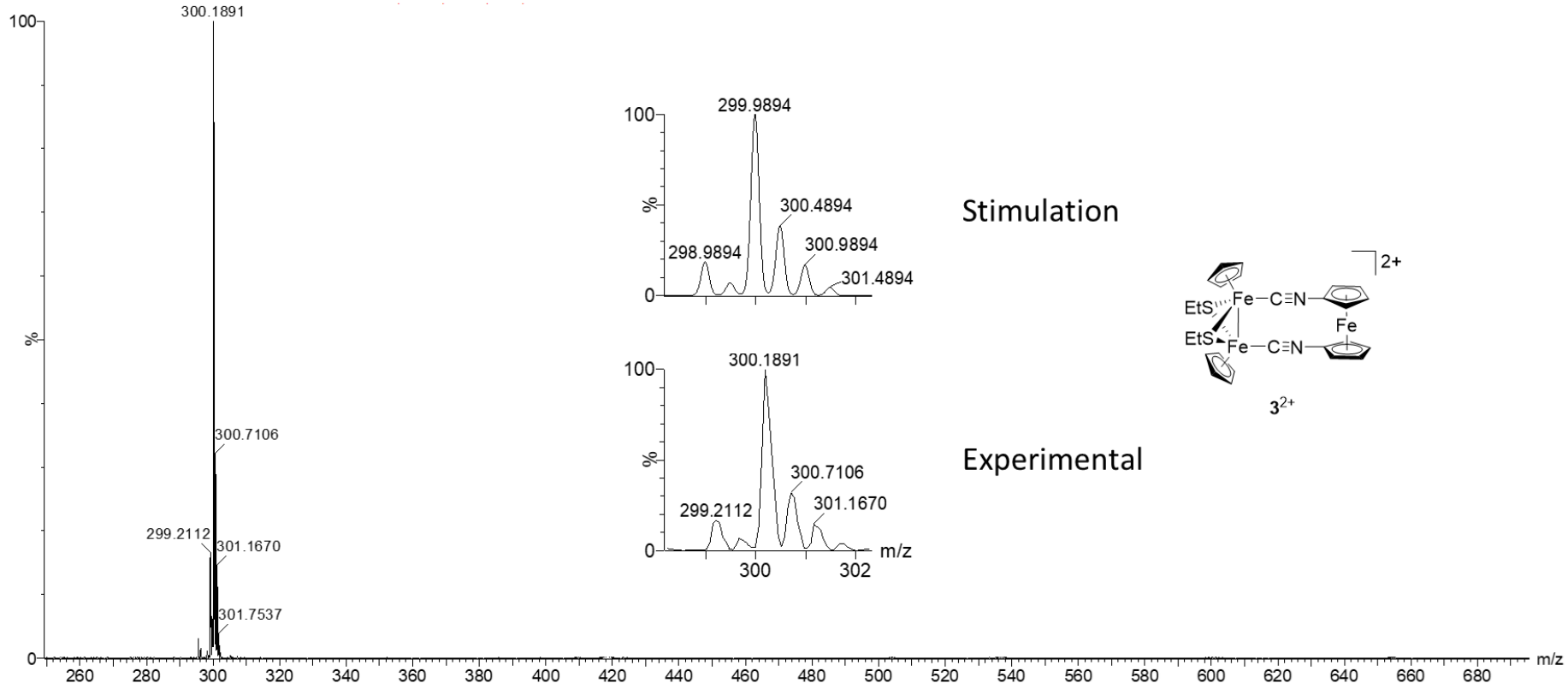

Figure S9. ESI-MS of **3**$[BF_4]_2$ in CH_3CN.

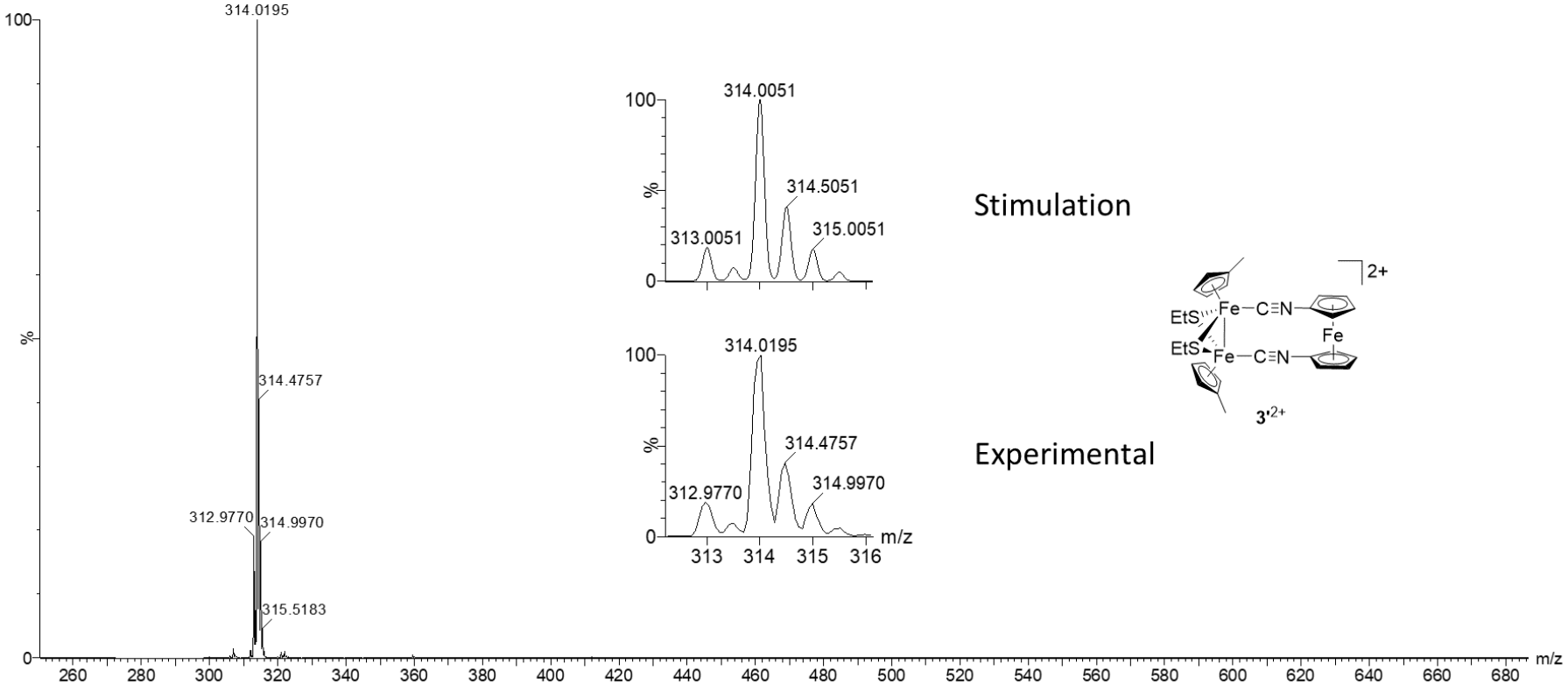

Figure S10. ESI-MS of **3'**$[BF_4]_2$ in CH_3CN.

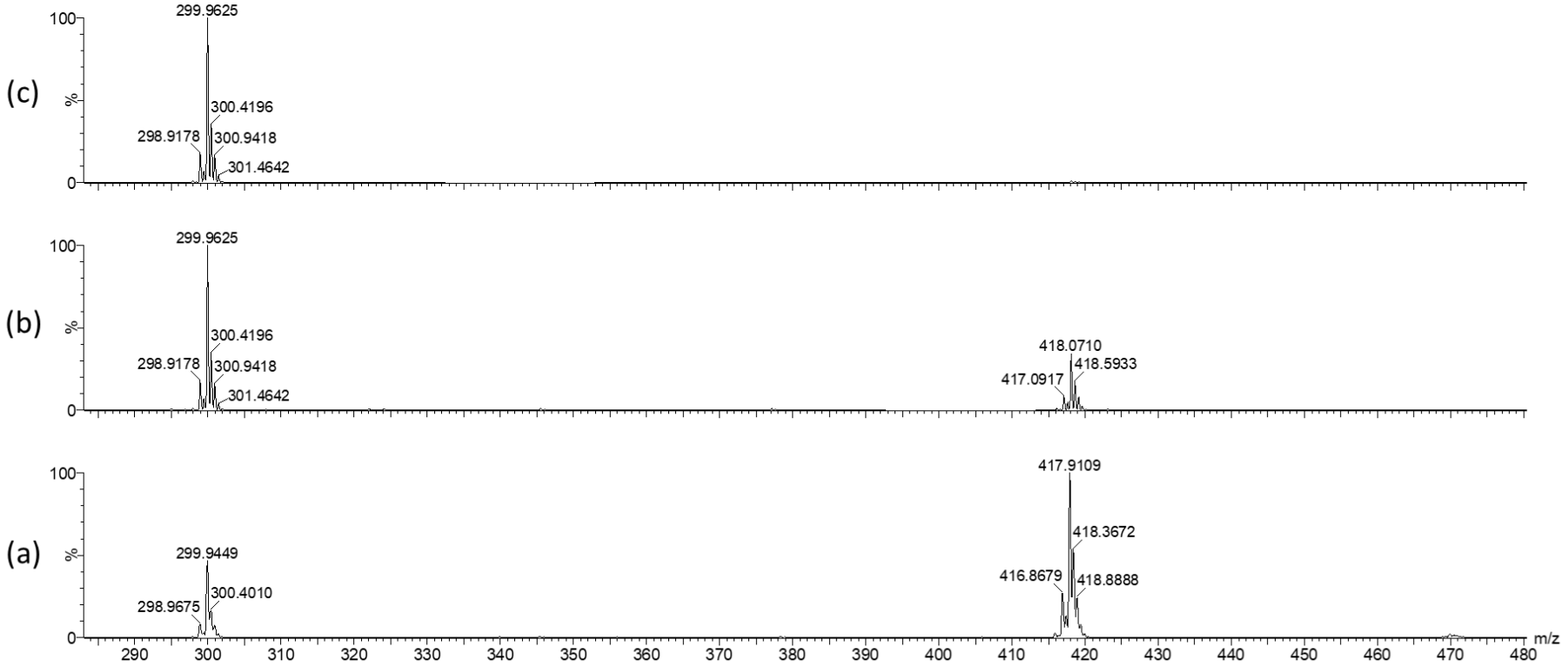

Figure S11. Reaction tracing ESI-MS of **4**$[BF_4]_2$ which mixed **1**$[BF_4]_2$ with excess $(CN)_2$-Fc for (a) 10 min, (b) 2 hrs, and (c) 6 hrs in CH_3CN.

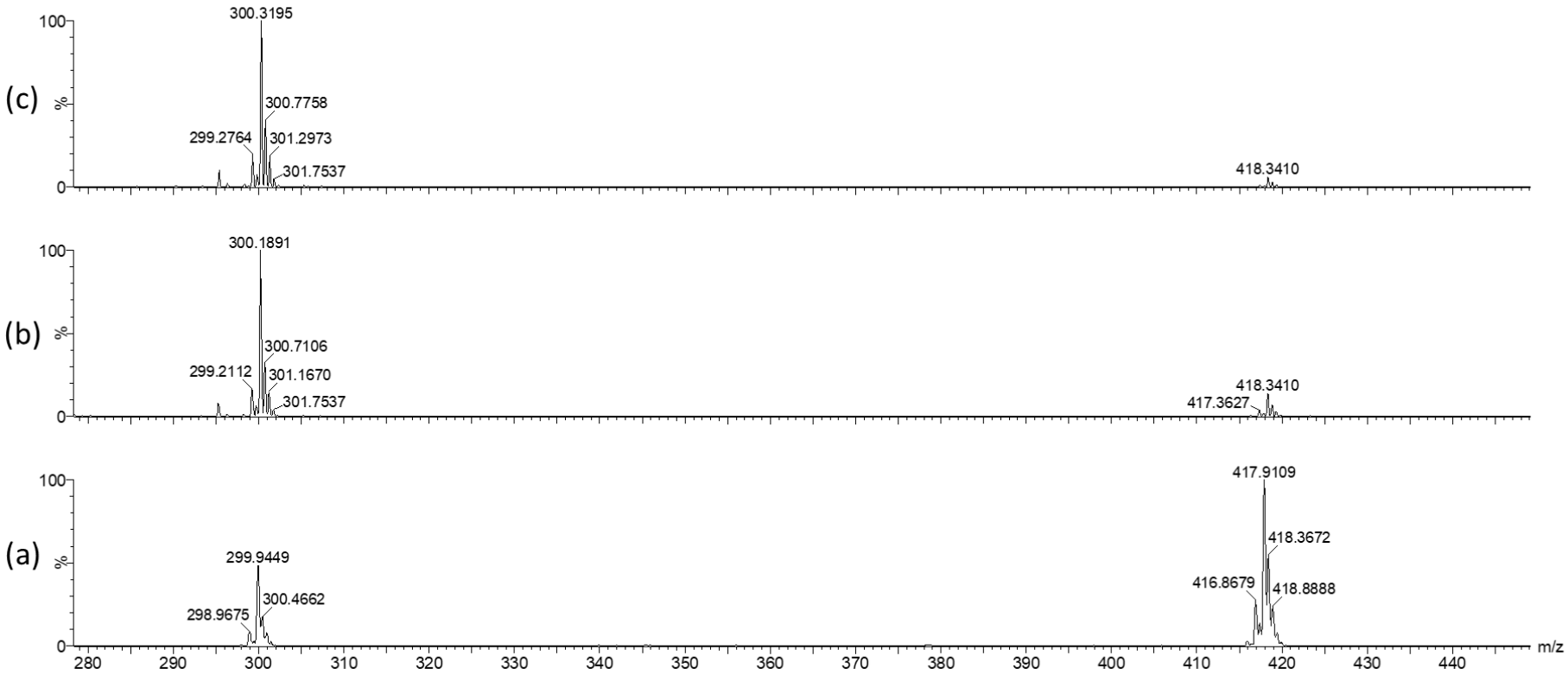

Figure S12. ESI-MS of **4**$[BF_4]_2$ for (a) fresh prepared, (b) 45 min, and (c) fresh prepared added 1eq of **1**$[BF_4]_2$ for 30 min in CH_3CN.

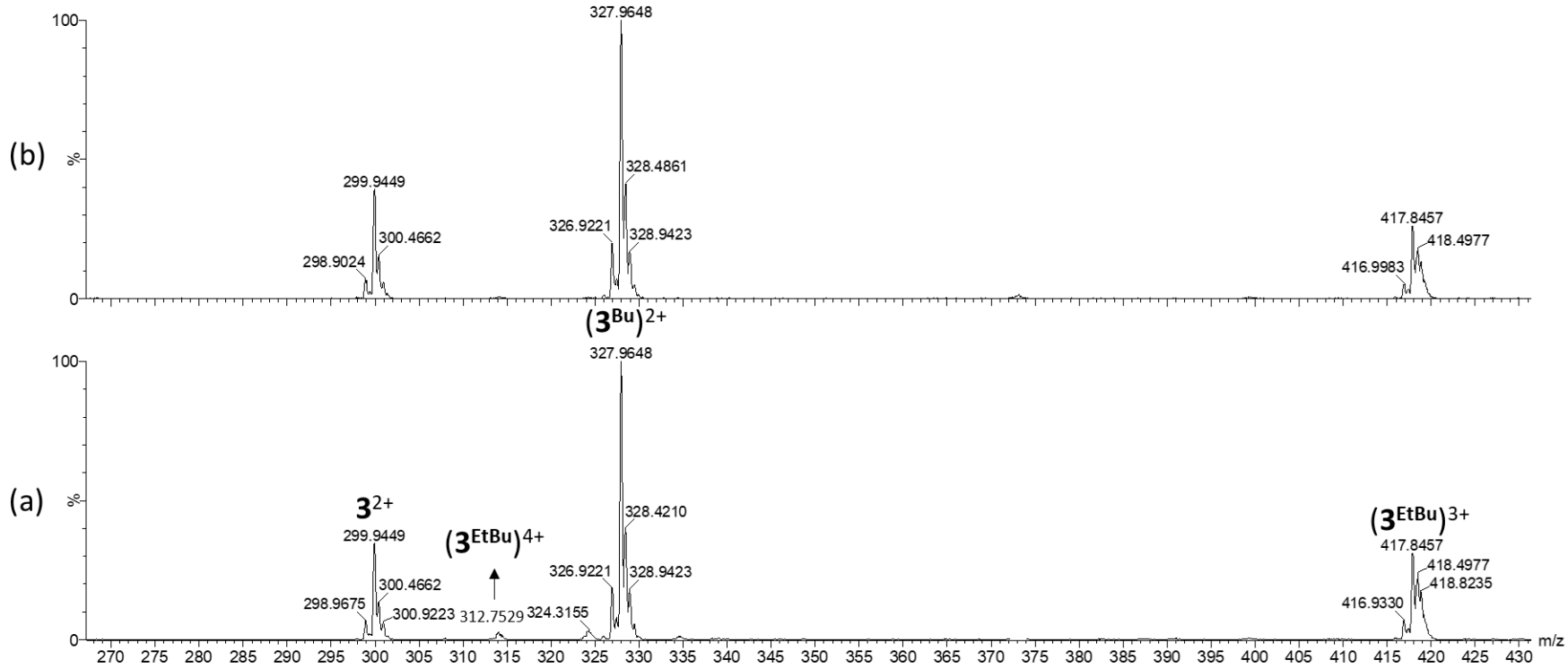

Figure S13. ESI-MS of the mixture $\mathbf{1}^{\mathbf{Bu}}(BF_4)_2$) with fresh made $\mathbf{4}[BF_4]_2$ in (a) 10min and (b) 1 hr.

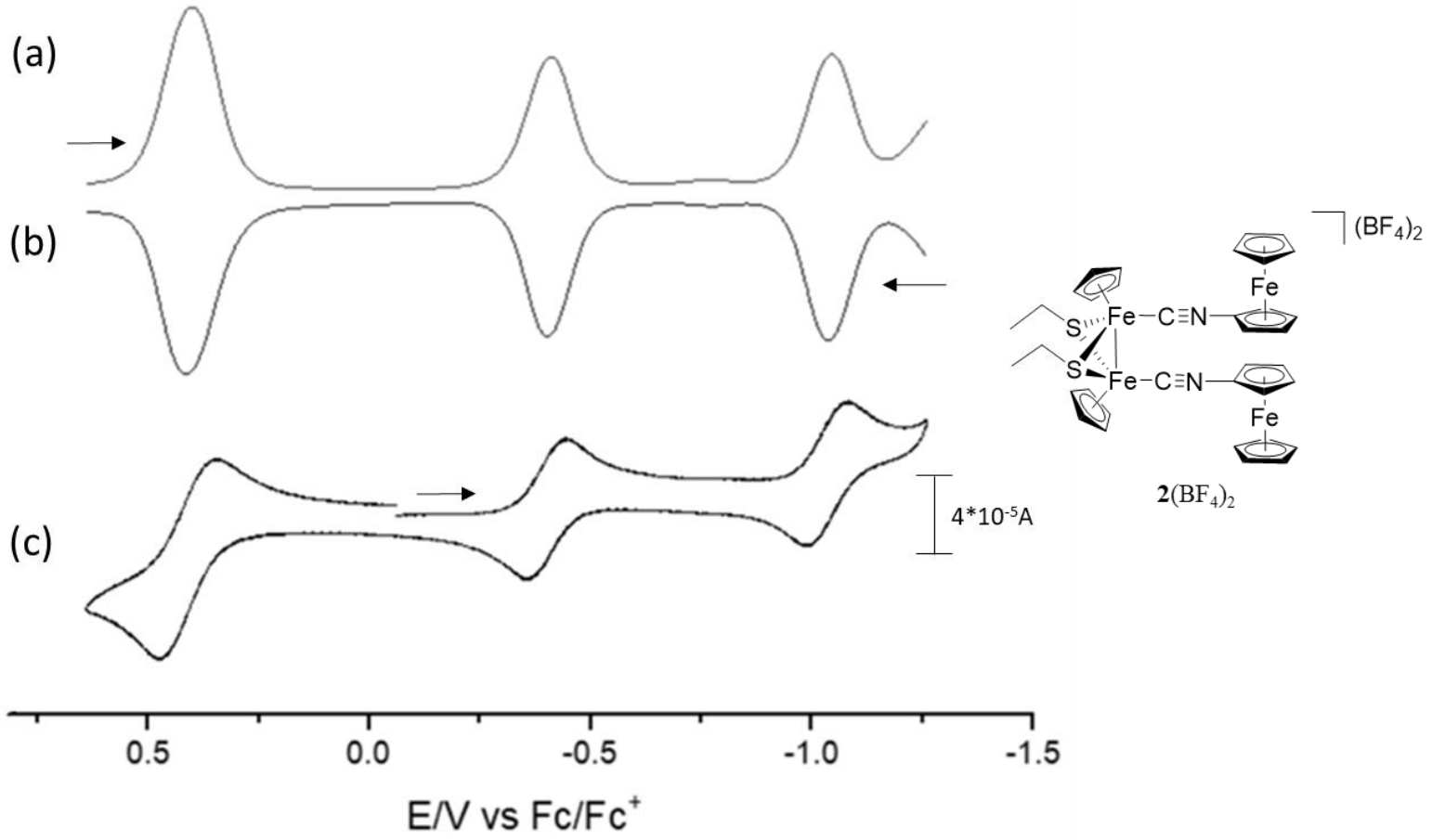

Figure S14. (a) Reduce wave, (b) oxidize wave of DPV and (c) CV result of **2**$(BF_4)_2$ in CH_3CN ($2*10^{-4}$M). Scan rate = 100mVs^{-1}; working electrode = glassy carbon electrode.

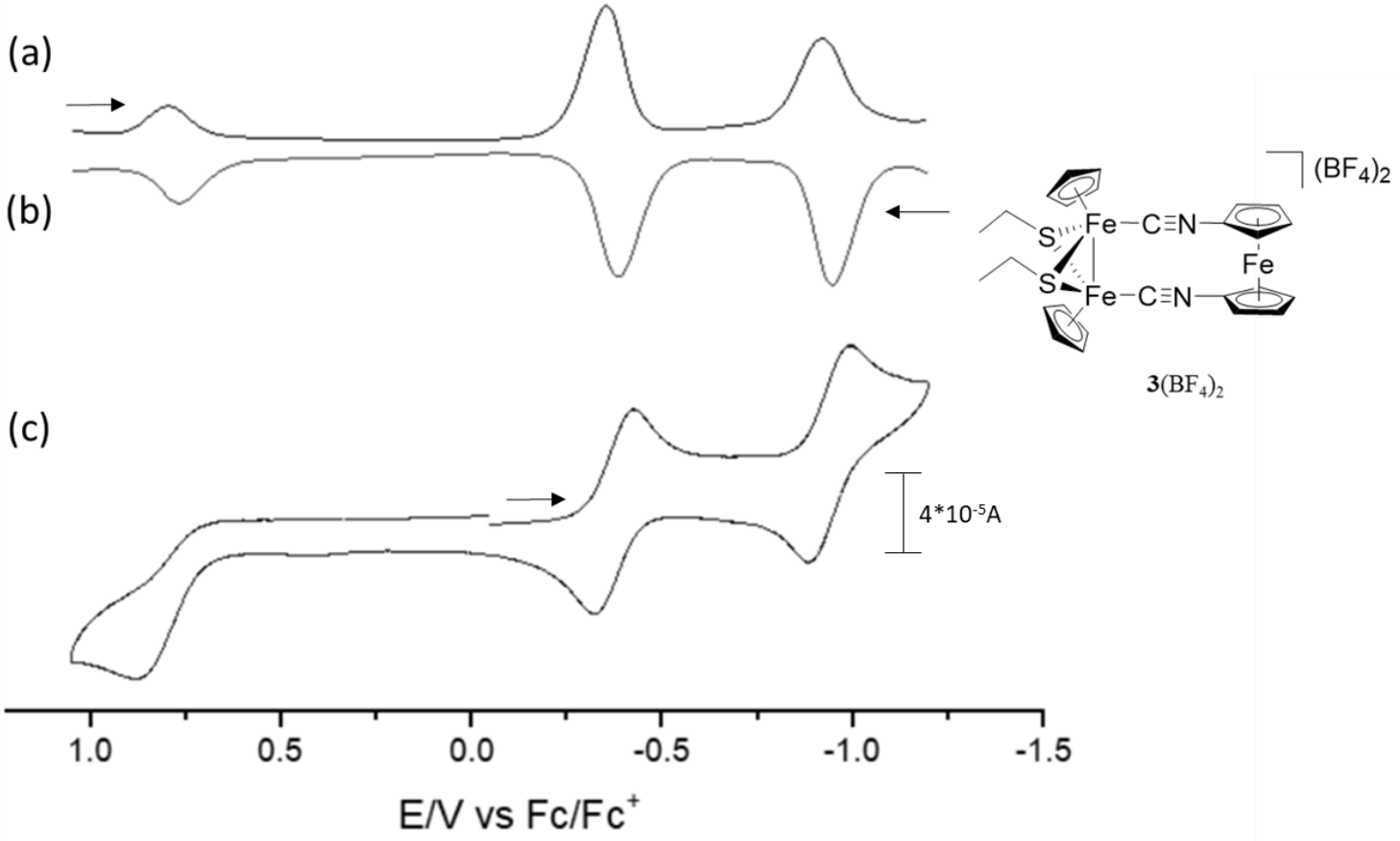

Figure S15. (a) Reduce wave, (b) oxidize wave of DPV and (c) CV result of **3**$[BF_4]_2$ in CH_3CN ($2*10^{-4}$M). Scan rate = 100mVs^{-1}; working electrode = glassy carbon electrode.

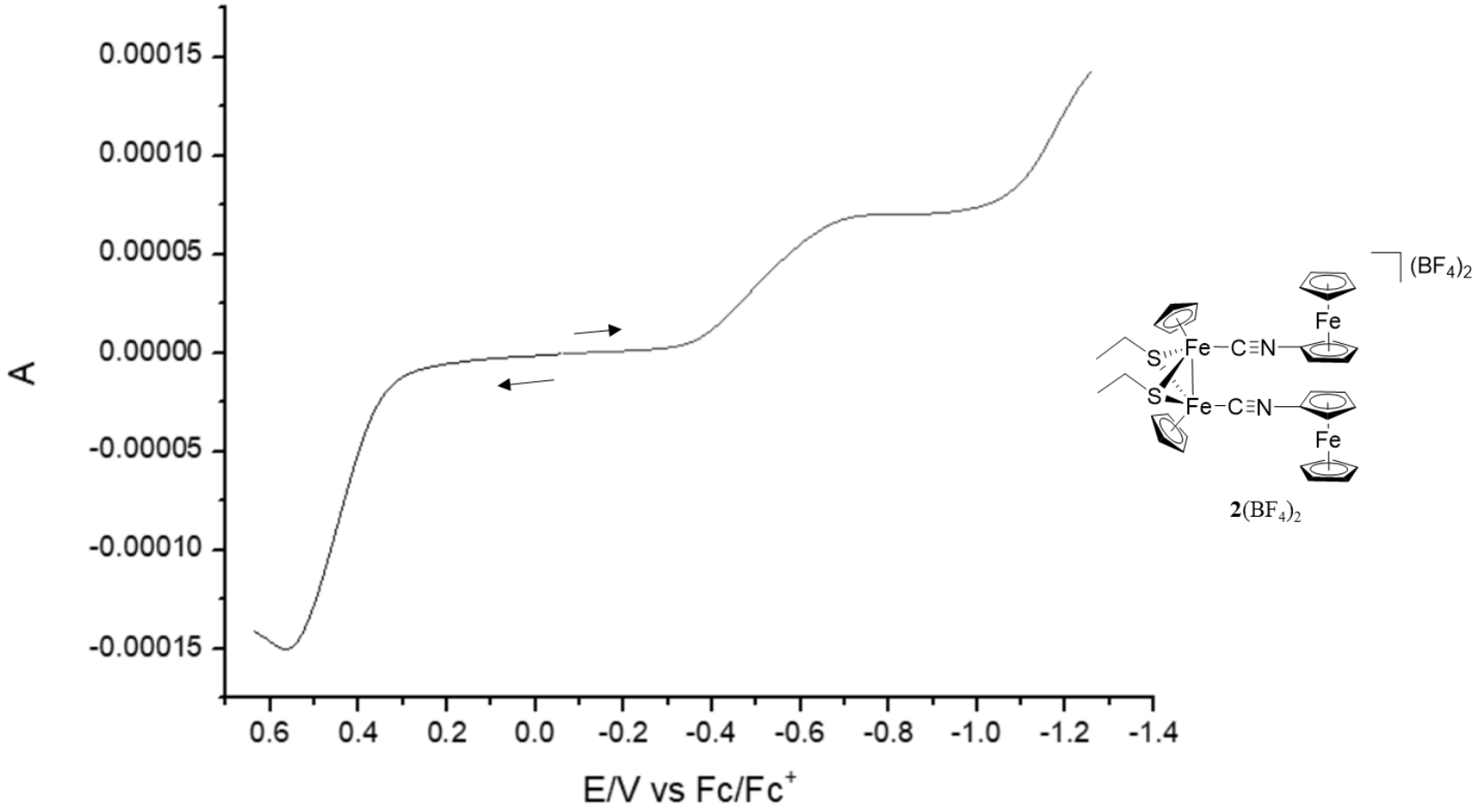

Figure S16. NPV result of **2**$[BF_4]_2$ in CH_3CN ($2*10^{-4}$M); working electrode = glassy carbon electrode.

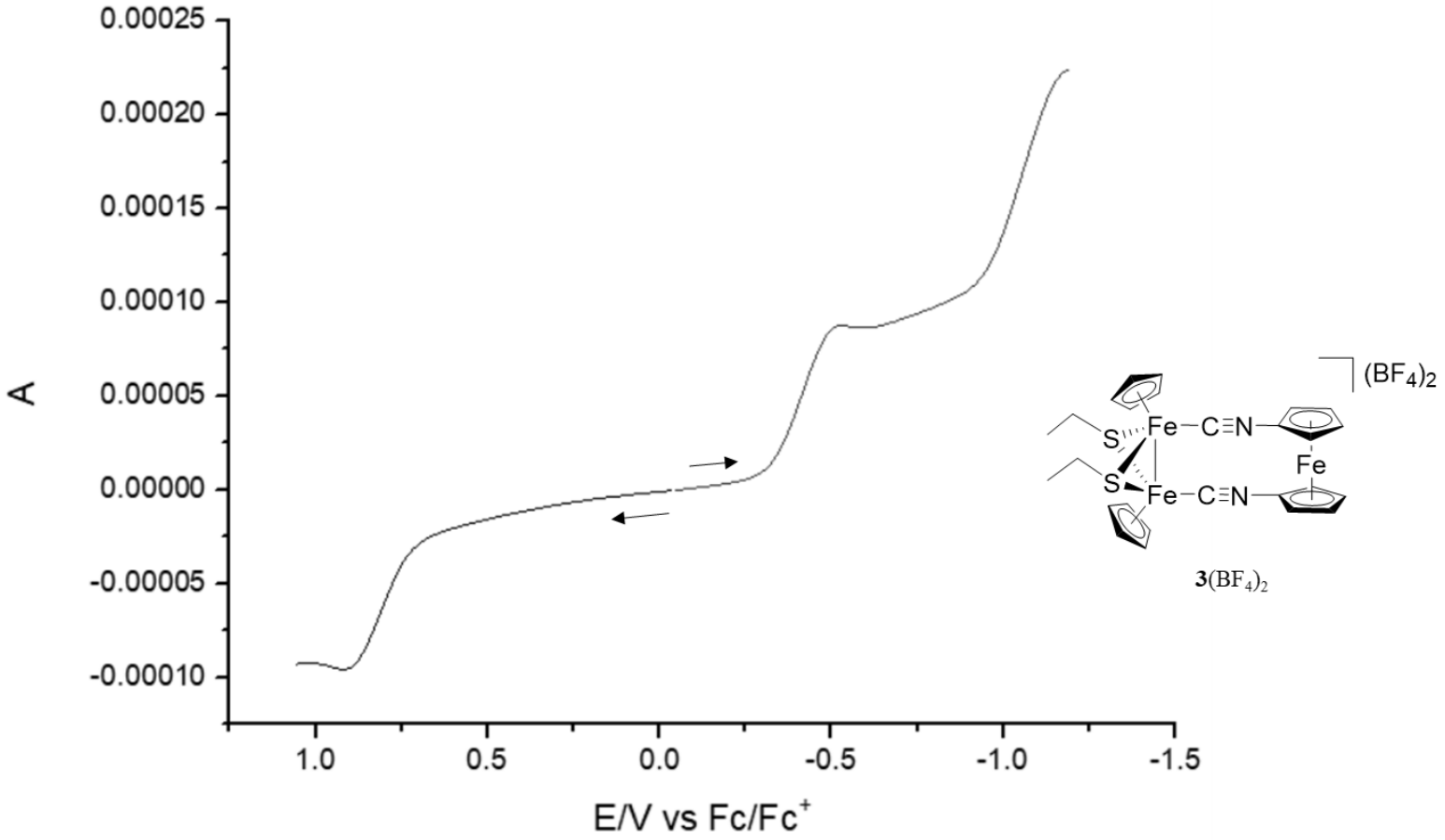

Figure S17. NPV result of **3**$[BF_4]_2$ in CH_3CN ($2*10^{-4}$M). Scan rate = 100mVs^{-1}; working electrode = glassy carbon electrode.

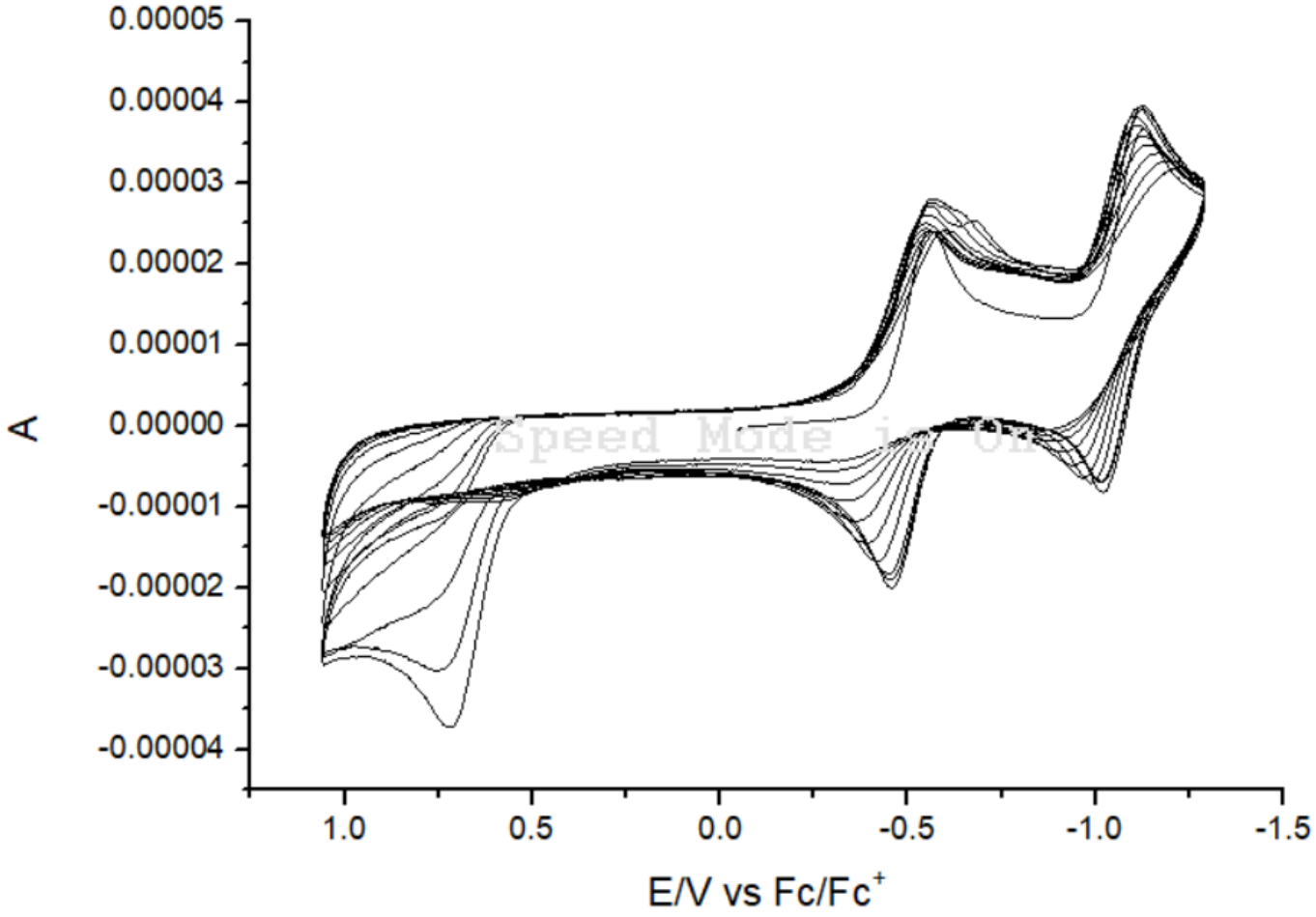

Figure S18. CV result (10 cycles scan) of **3**$[BF_4]_2$ in CH_3CN ($2*10^{-4}$M). Scan rate = 100mVs^{-1}; working electrode = glassy carbon electrode.

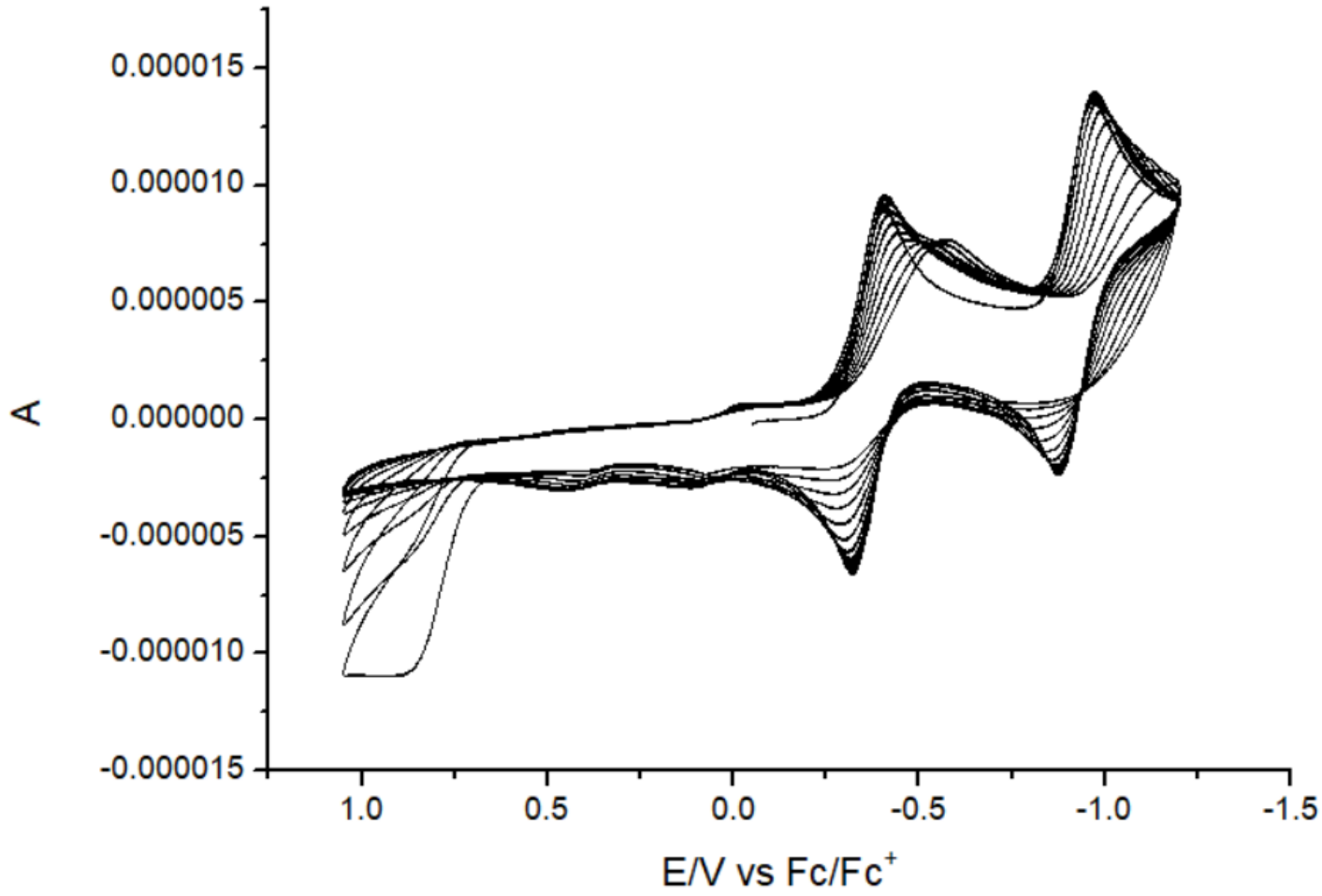

Figure S19. CV result (10 cycles scan) of **3**$[BF_4]_2$ in CH_3CN ($2*10^{-4}$M). Scan rate = 100mVs^{-1}; working electrode = Pt electrode.

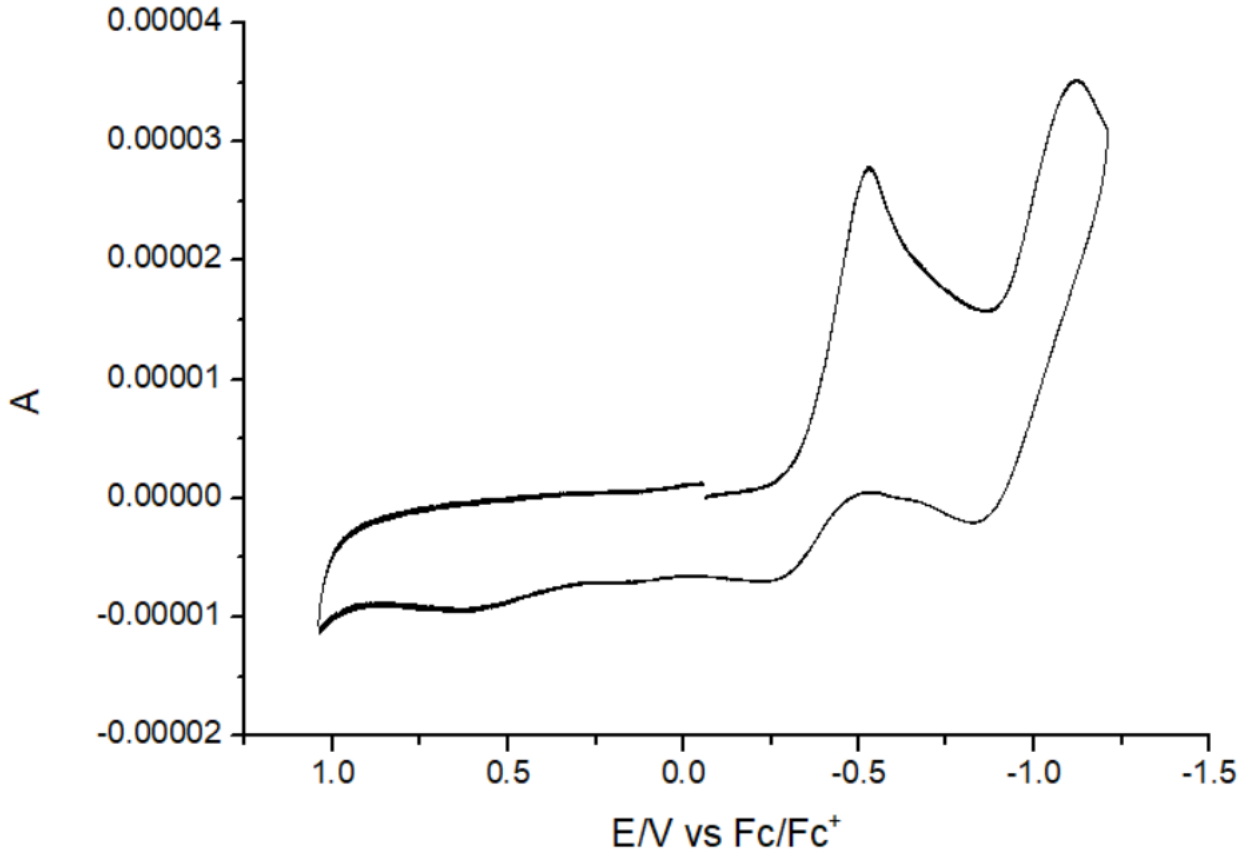

Figure S20. CV result of the insoluble material adsorbed on electrode surface in CH_3CN. Scan rate = 100mVs^{-1}; working electrode = glassy carbon electrode.

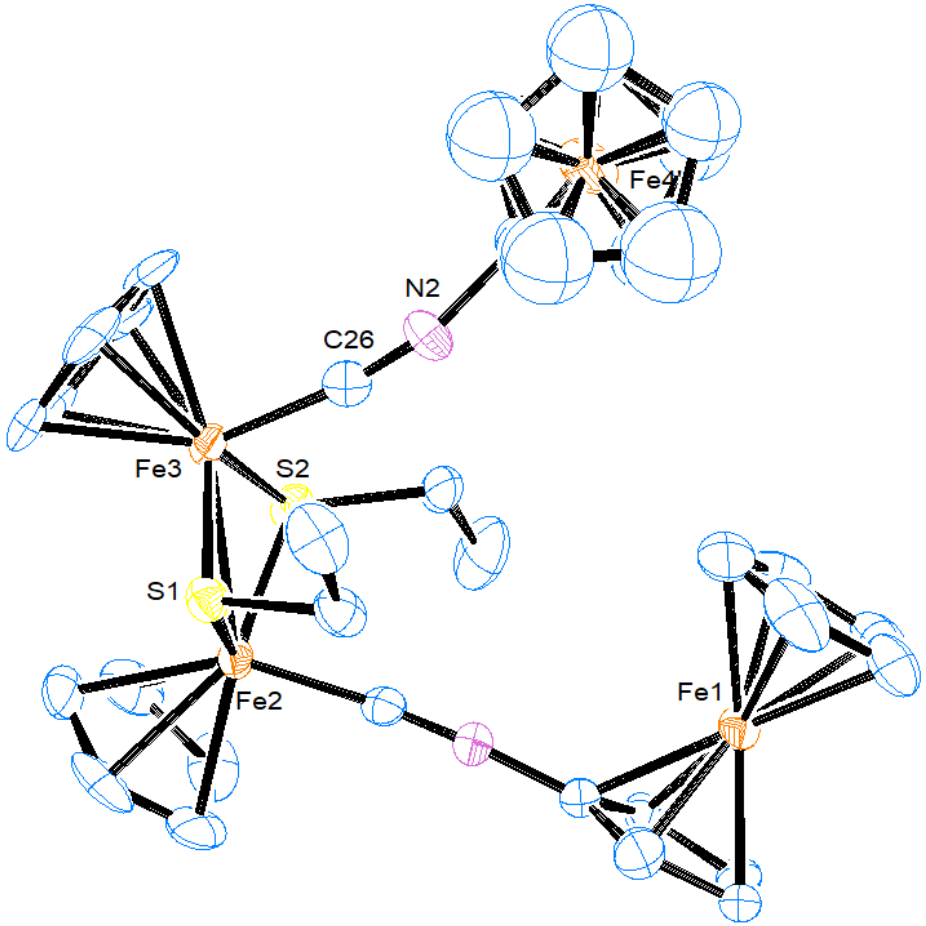

Figure S21. ORTEP representation of the crystal structure of the cation of **2**$[BF_4]_2$ contains 40% disorder Fe4-ferrocene unit. (50% ellipsoid; all H atoms and anions are omitted for clarity).

Table S1. Selected bond lengths (Å) and angles (°) of **2**$(BF_4)_2$, **3'**$(BF_4)_2$, and related $Fe_2(\mu\text{-}SEt)_2$ core complexes.

Complexes	Fe–Fe	Fe–S	Fe–CNR	C≡Ns	S–Fe–S	Fe–S–Fe	Ref.
$[(CpFe)_2(\mu\text{-}SEt)_2(CNCH_3)_2][BF_4]_2$	2.6467(8)	2.1996(11) 2.2068(12) 2.2086(11) 2.2110(11)	1.867(4) 1.855(4)	1.151(5) 1.148(5)	102.49(4) 102.80(4)	73.66(4) 73.75(4)	[15]
$[(CpFe)_2(\mu\text{-}SEt)_2(1,4\text{-}CNC_6H_4NC)_2][BF_4]_2$	2.633(3)	2.191(4) 2.19(4) 2.205(4) 2.230(4)	1.809(15) 1.862(16)	1.126(15)[a] 1.097(15)[a] 1.124(19)[b] 1.14(2)[b]	105.79(17) 104.17(17)	73.00(14) 73.59(13)	[16]
$[(CpFe)_2(\mu\text{-}SEt)_2(1,4\text{-}CNCH_2C_6H_4CH_2NC)_2][BF_4]_2$	2.641(3)	2.206(3) 2.194(2) 2.201(2) 2.206(3)	1.856(8) 1.846(8)	1.147(8)[a] 1.157(8)[a] 1.147(12)[b] 1.15(2)[b], [c] 1.24(3)[b], [c]	104.24(6) 104.37(6)	73.65(10) 73.77(10)	[17]
$[(CpFe)_2(\mu\text{-}SEt)_2(4,4'\text{-}CNC_6H_4OC_6H_4NC))_2][BF_4]_2$	2.6390(8)	2.205(1) 2.205(1) 2.208(1) 2.207(1)	1.856(4) 1.852(4)	1.134(6)[a] 1.144(6)[a] 1.130(8)[b] 1.137(8)[b]	104.21(5) 104.25(5)	73.52(4) 73.41(4)	[17]
2$[BF_4]_2$	2.6422(17)	2.204(2) 2.213(3) 2.207(3) 2.205(3)	1.858(9) 1.859(10)	1.145(11) 1.146(12)	103.35(9) 103.46(10)	73.60(8) 73.46(8)	This work
3'$[BF_4]_2$	2.6495(8)	2.2083(12) 2.2090(12) 2.1982(12) 2.2092(12)	1.834(4) 1.842(4)	1.160(6) 1.158(5)	105.18(4) 105.51(4)	73.71(4) 73.94(4)	This work
$Fc(NC)_2$				1.161(19)			This work

[a] For Fe-CNR. [b] For free CNR. [c] For disorder free CNR.

Table S2. Crystallographic Data for $Fc(NC)_2$ and Iron-thiolate Core Complexes **2**$[BF_4]_2$ and **3**$[BF_4]_2$.

	$Fc(NC)_2$	**2**$[BF_4]_2$	**3'**$[BF_4]_2$
empirical formula	$C_{12}H_8FeN_2O$	$C_{38}H_{41}B_2F_8Fe_4N_3S_2$	$C_{28}H_{32}B_2F_8Fe_3N_2S_2$
fw	252.05	1000.88	801.85
T (K)	200(2)	200(2)	200(2)
cystal size (mm^3)	0.08 x 0.05 x 0.02	0.38 x 0.26 x 0.03	0.24 x 0.20 x 0.03
cryst syst	Monoclinic	Monoclinic	Monoclinic
space group	C2/c	$P2_1/c$	$P2_1/c$
a (Å)	9.076(5)	22.5056(13)	10.1086(3)
b (Å)	8.347(4)	9.8715(4)	10.8254(3)
c (Å)	13.309(9)	20.6103(9)	28.7588(7)
α (deg)	90	90	90
β (deg)	108.19(2)	116.551(2)	94.8810(10)
γ (deg)	90	90	90
V ($Å^3$)	957.8(9)	4096.0(3)	3135.65(15)
Z	4	4	4
Dcalcd (g cm^{-3})	1.762	1.623	1.699
μ (mm^{-1})	1.548	1.560	1.574
reflns measd/indep	3616 / 843	27606 / 7280	50107 / 5535
data/restraints/params	843 / 7 / 97	7280 / 6 / 477	5535 / 0 / 394
GOF	1.172	1.070	1.019
Rint	0.0723	0.0728	0.0384
R1 [I > 2σ] (all data)	0.0773 (0.2046)	0.0978 (0.214)	0.0490 (0.1222)
wR2 [I > 2σ] (all data)	0.1013 (0.2250)	0.1518 (0.2472)	0.0581 (0.1312)
max peak/hole (e/$Å^3$)	0.574 / -1.101	1.632 / -2.065	1.769 / -1.584

Note: The B-level alert message for the somewhat low C-C bond precision in **2**$[BF_4]_2$ resulted from the weak diffraction data (less than half of the data with I>2σ(I)). This is the disorder nature of terminal ferrocene groups in the sample crystal. The current result is the best we can get.