

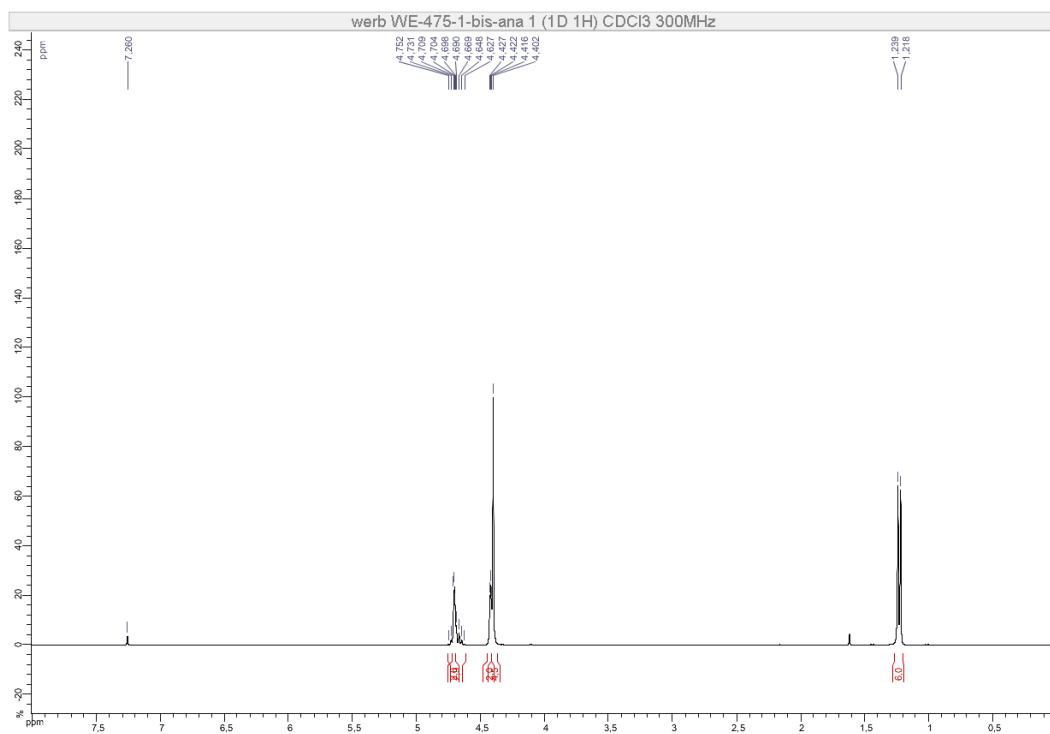
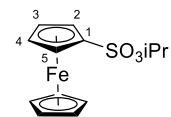
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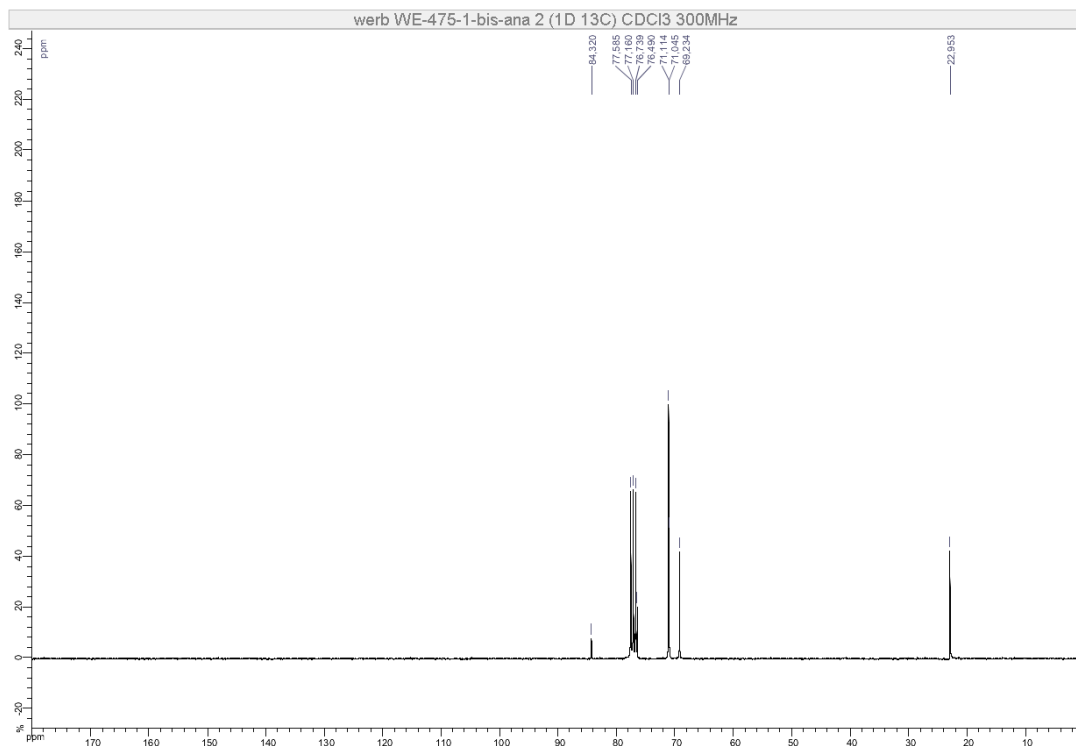
NMR Spectra

O-Isopropylferrocenesulfonate (1)

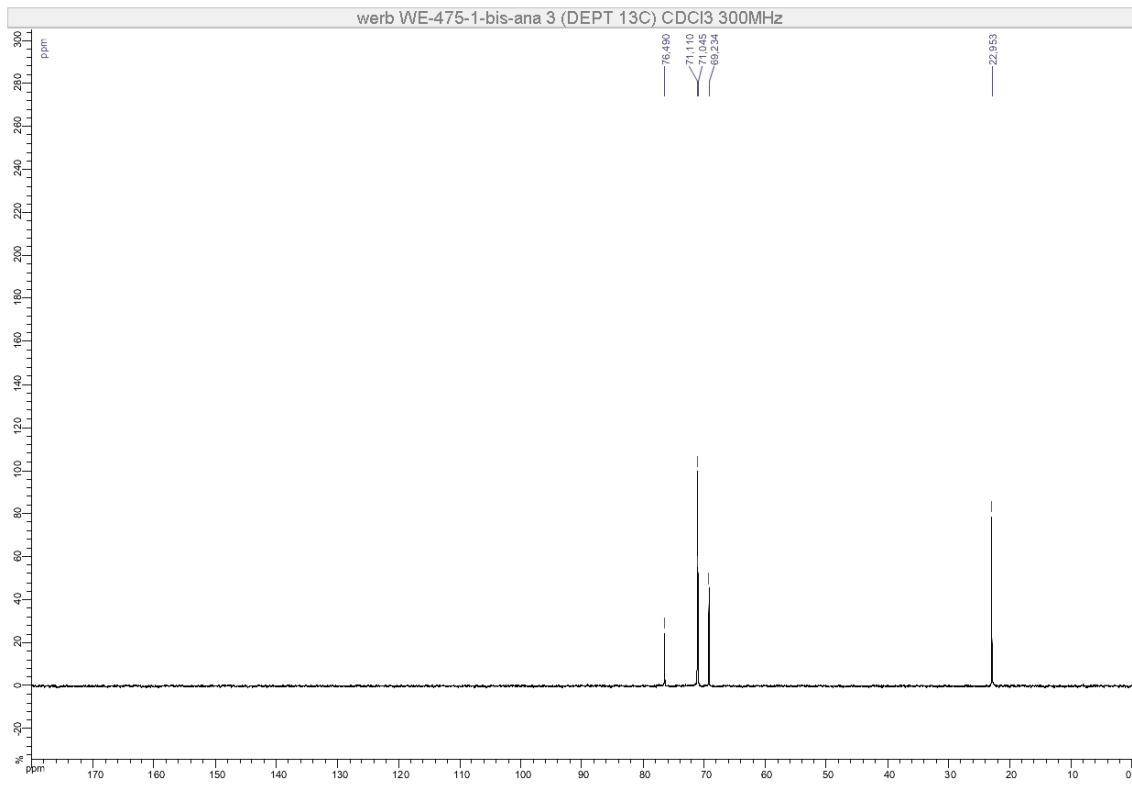
^1H NMR (300 MHz, CDCl_3)



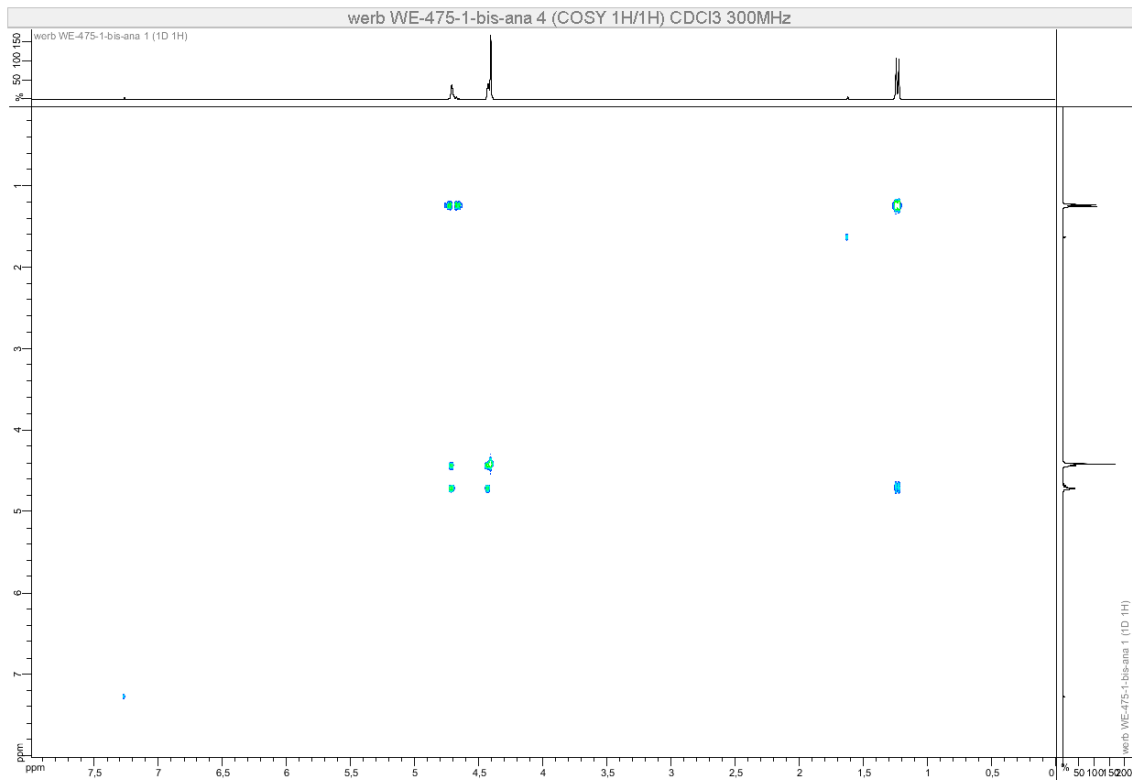
^{13}C NMR (75 MHz, CDCl_3)



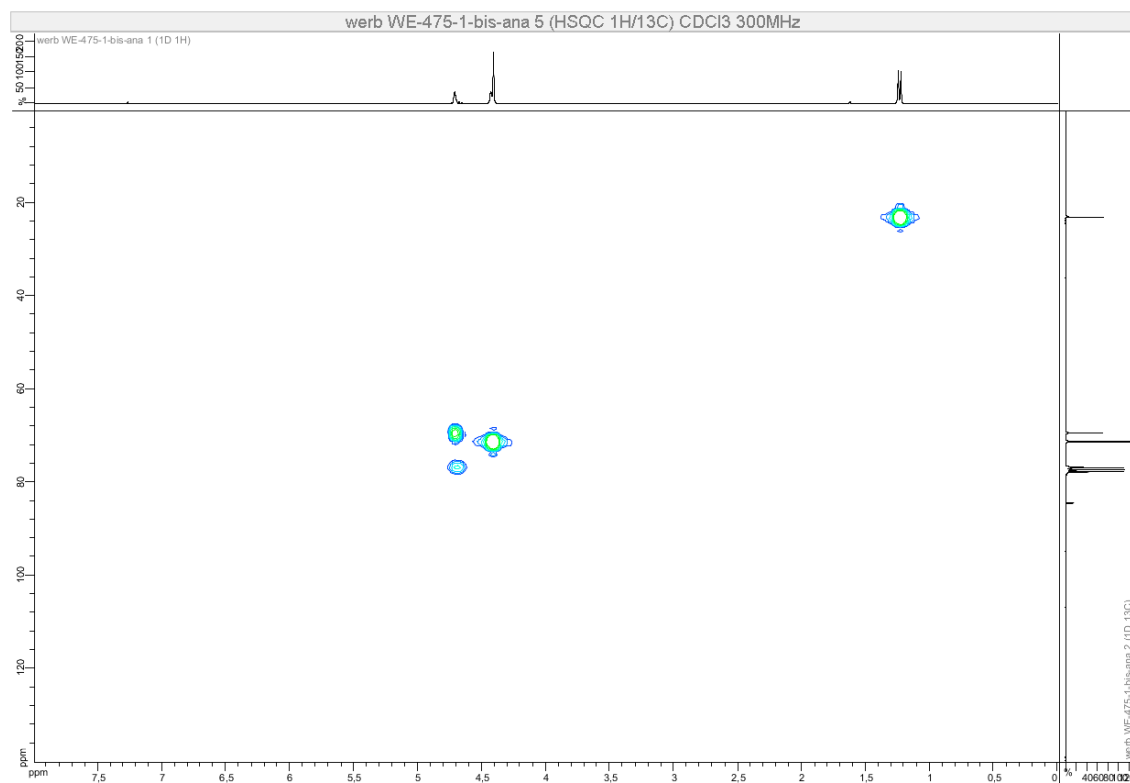
DEPT 135 (75 MHz, CDCl₃)



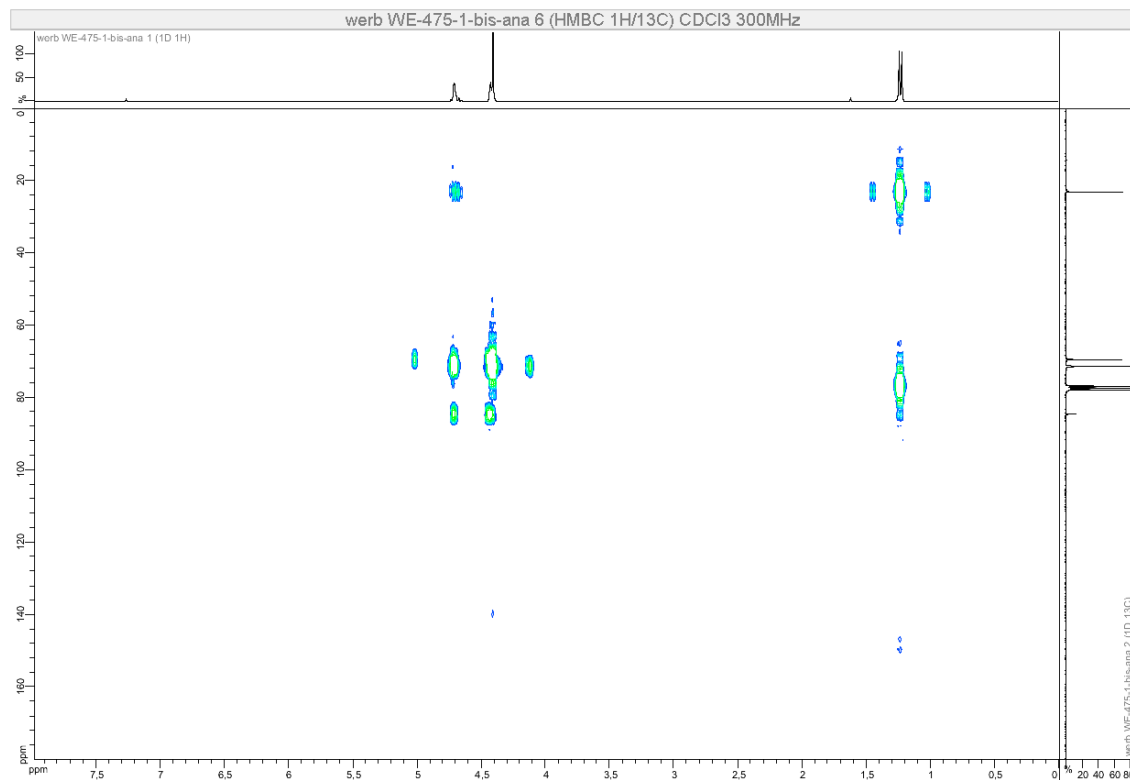
COSY (300 MHz, CDCl₃)



HSQC (300 MHz, CDCl₃)



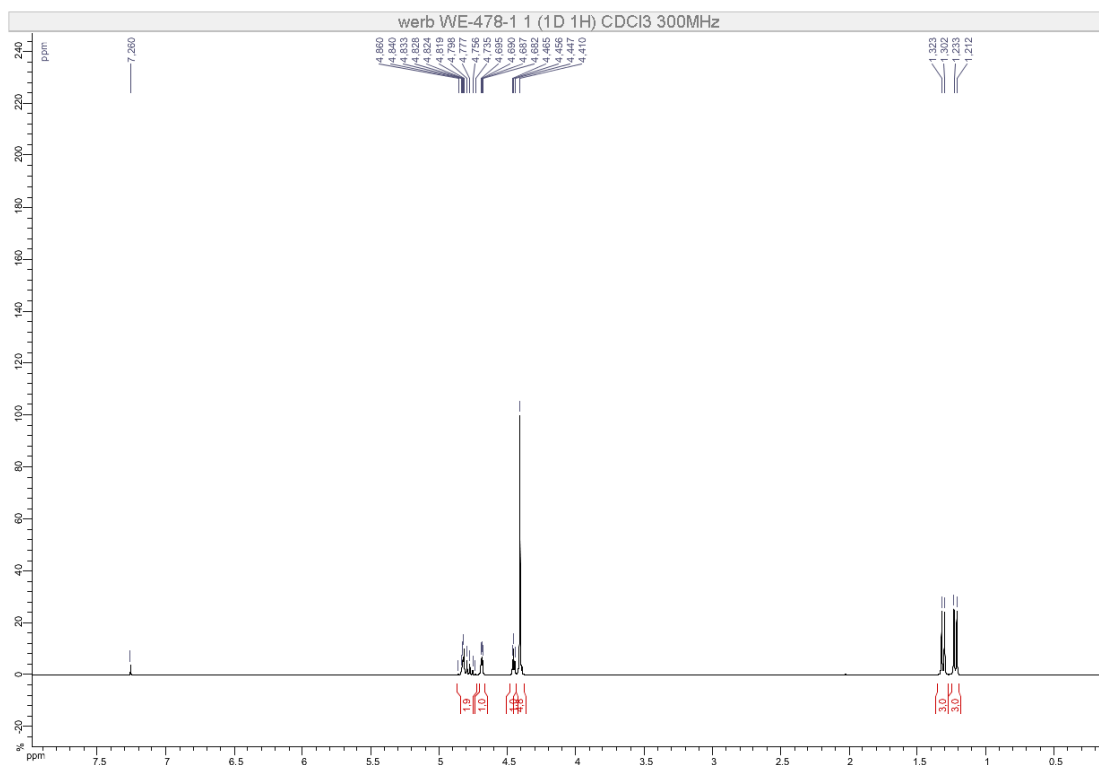
HMBC (300 MHz, CDCl₃)



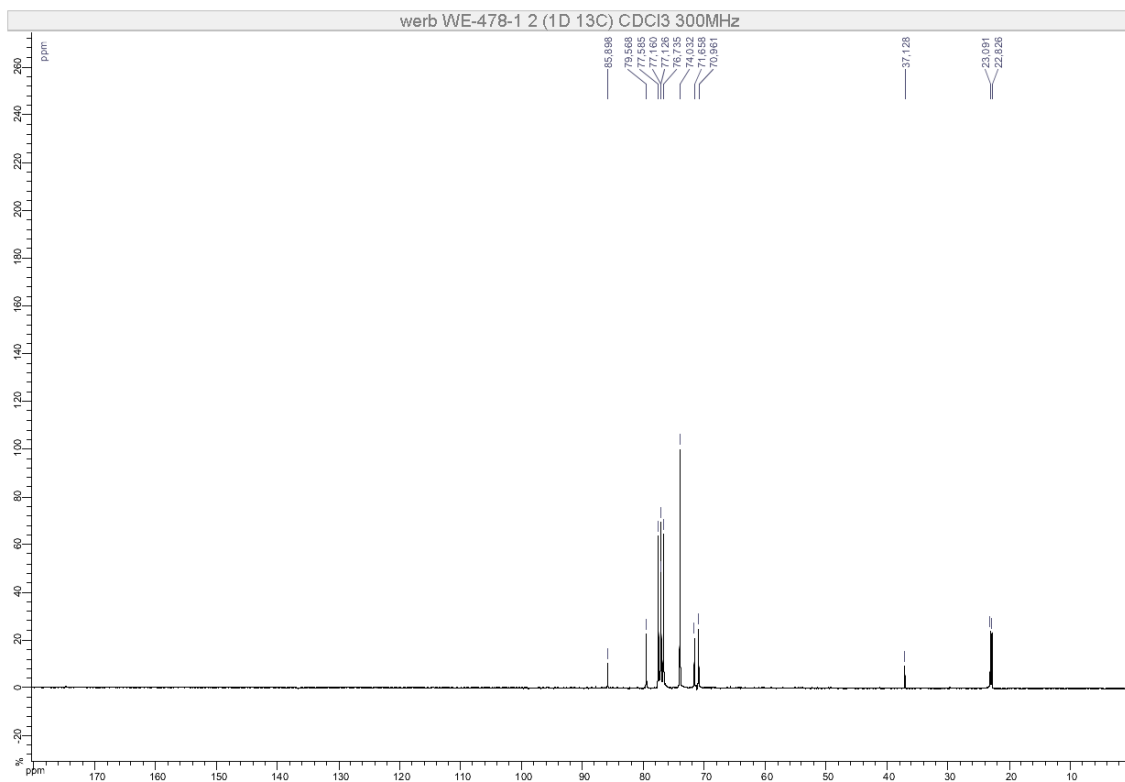
2-Iodo-*O*-isopropylferrocenesulfonate (3, racemic mixture)



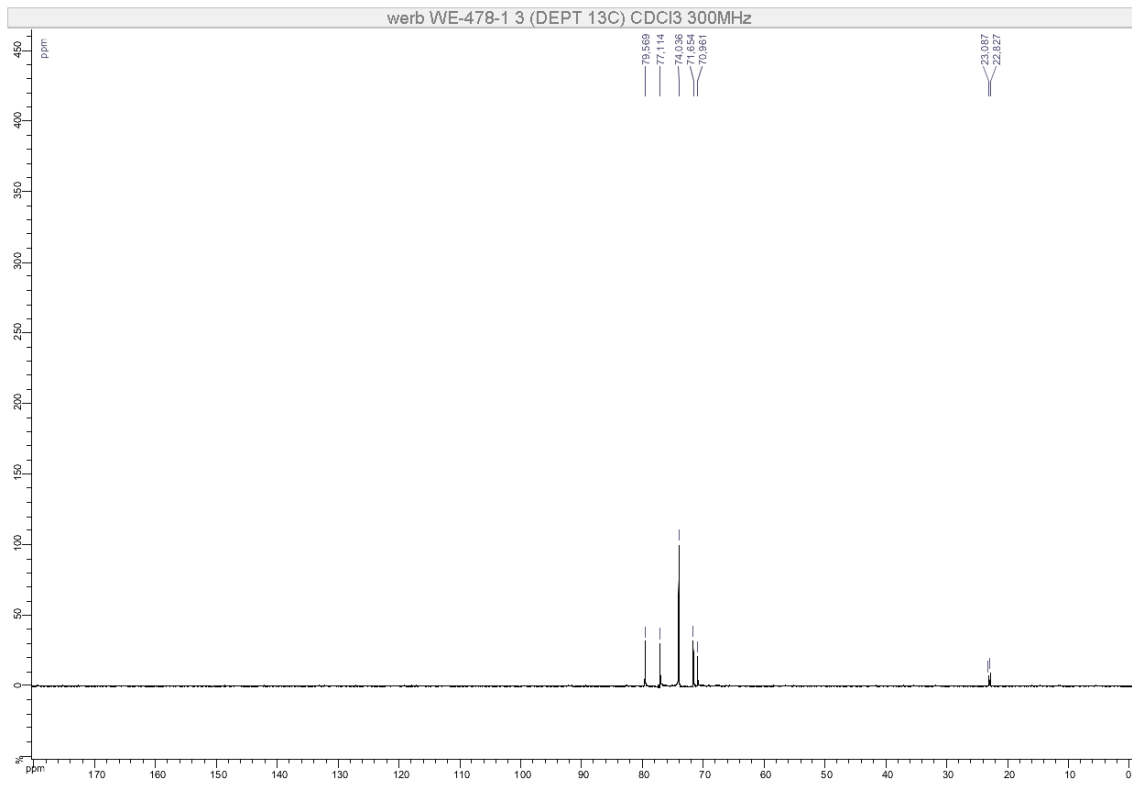
^1H NMR (300 MHz, CDCl_3)



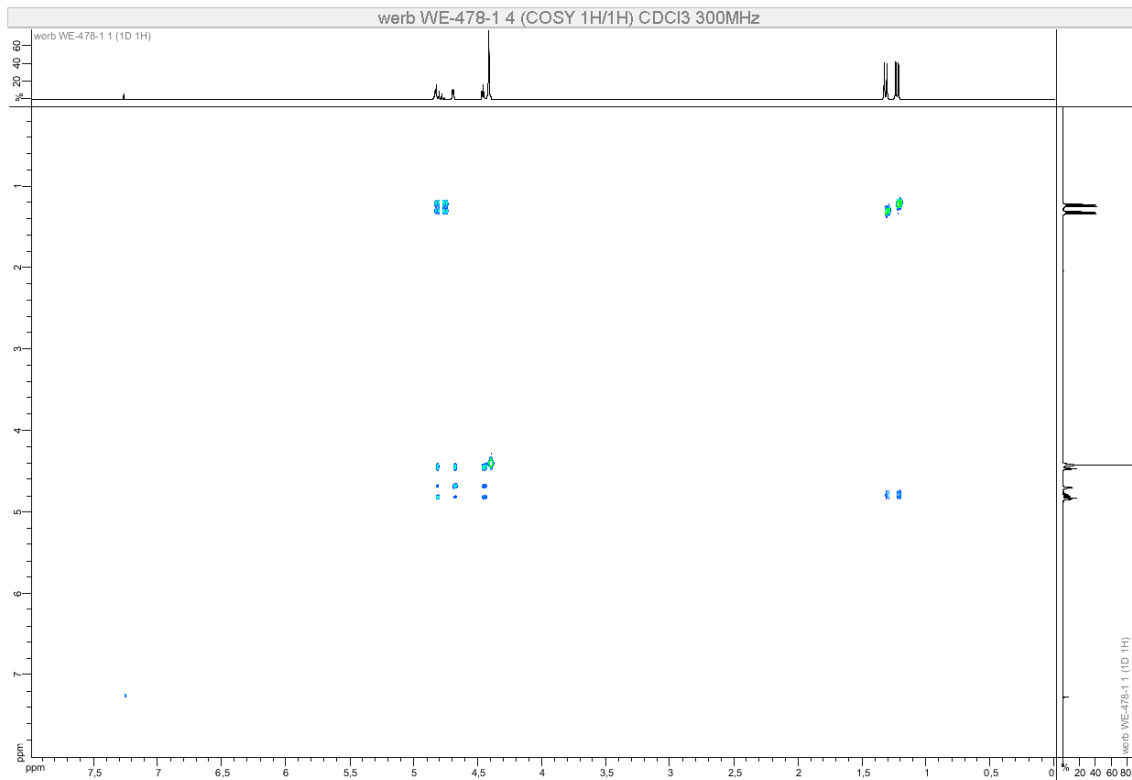
^{13}C NMR (75 MHz, CDCl_3)



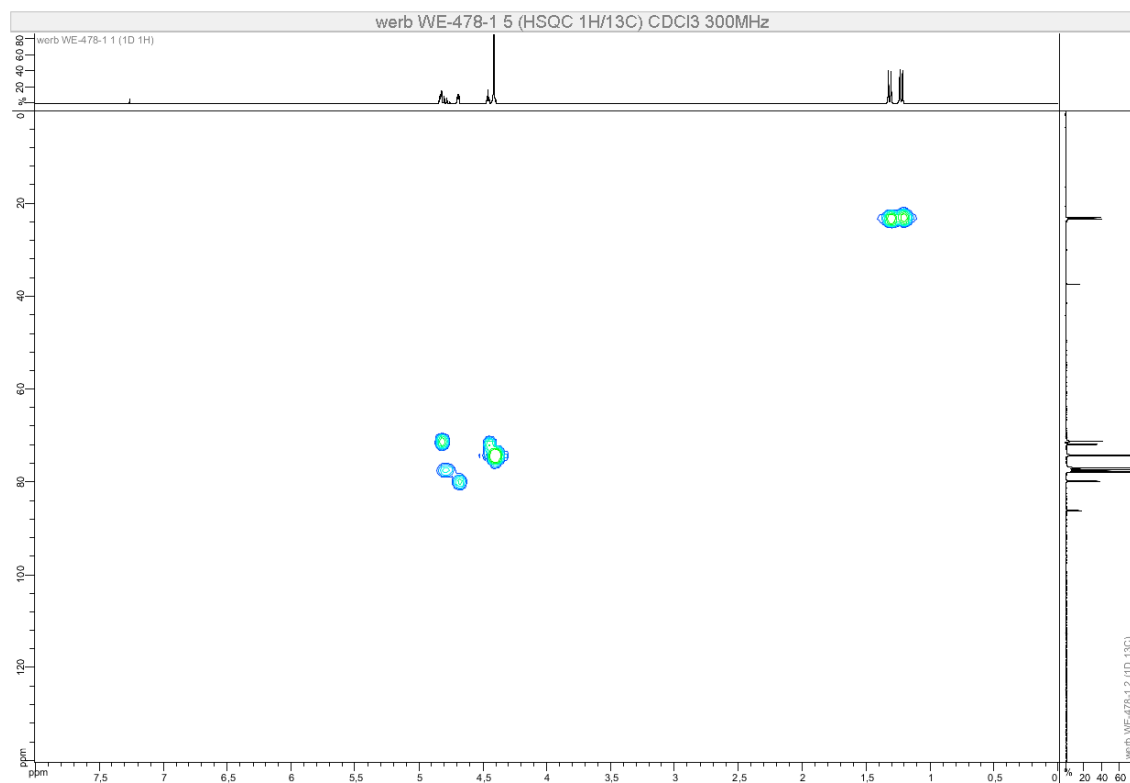
DEPT 135 (75 MHz, CDCl₃)



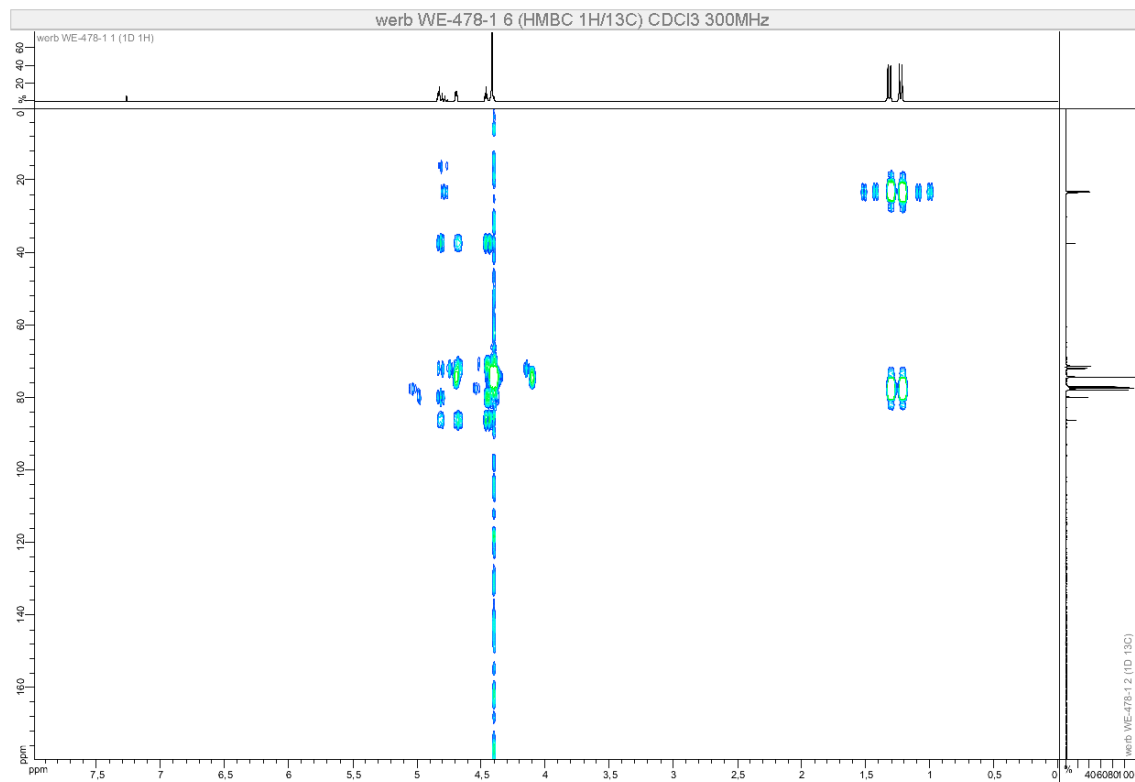
COSY (300 MHz, CDCl₃)



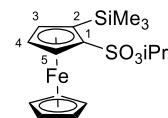
HSQC (300 MHz, CDCl₃)



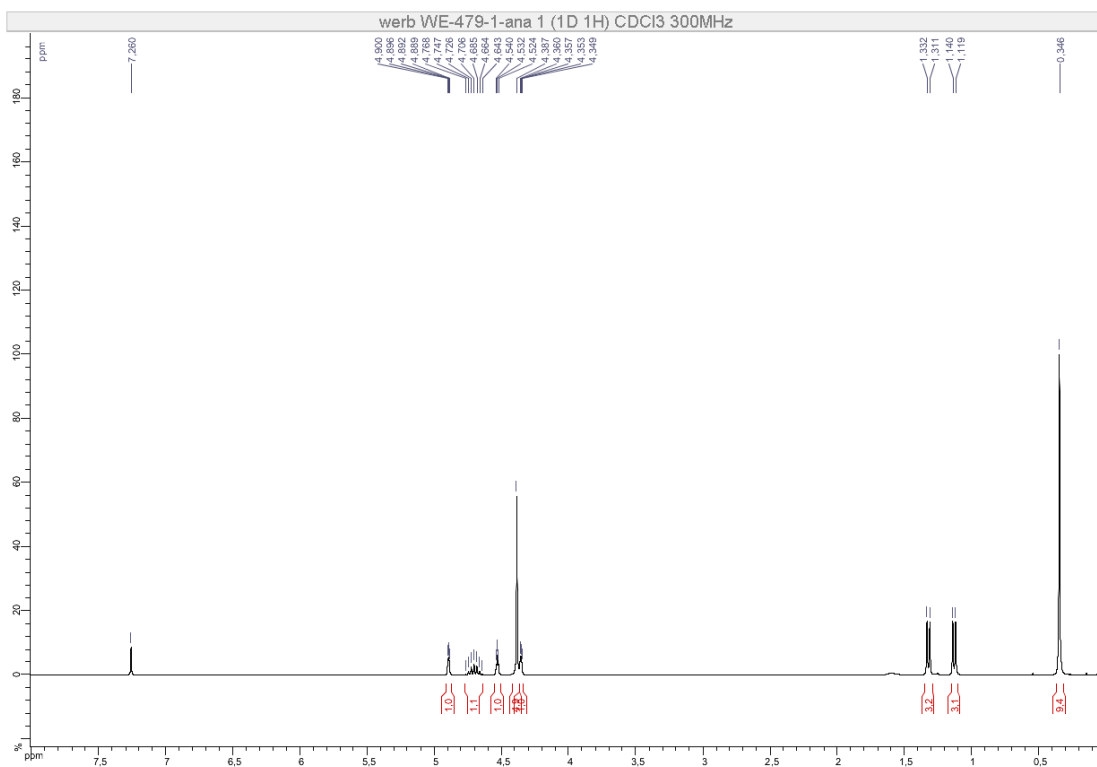
HMBC (300 MHz, CDCl₃)



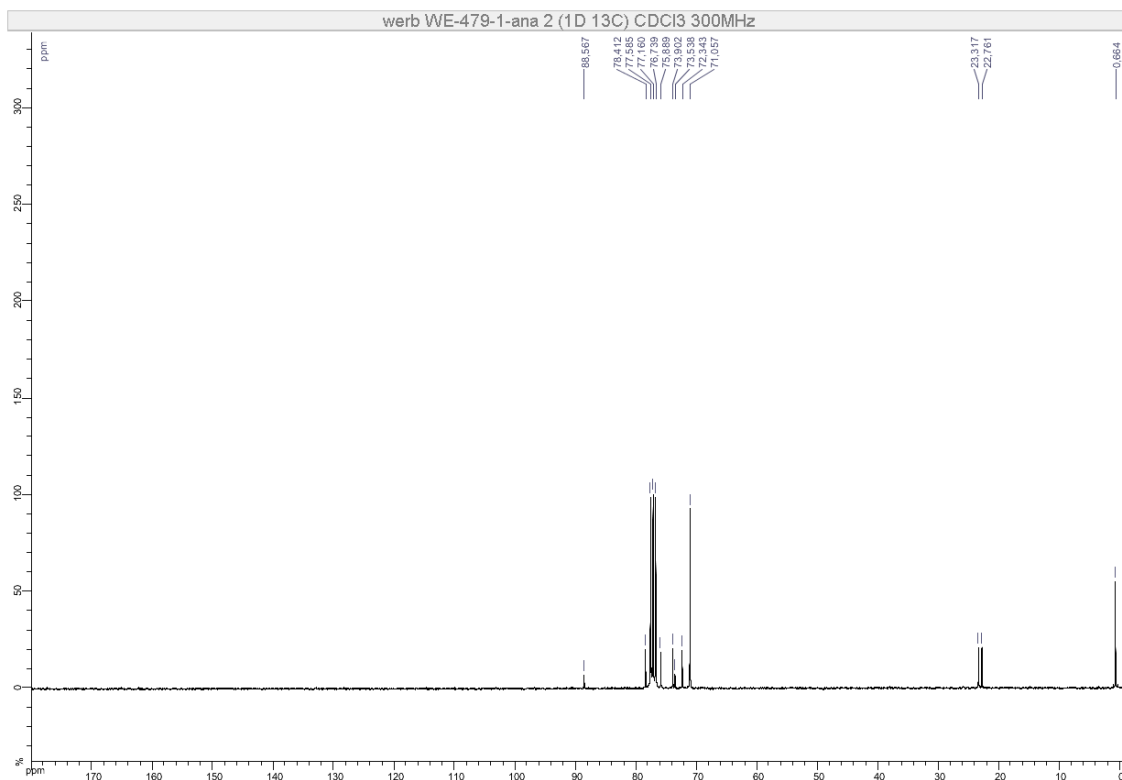
O-Isopropyl-2-(trimethylsilyl)ferrocenesulfonate (4, racemic mixture)



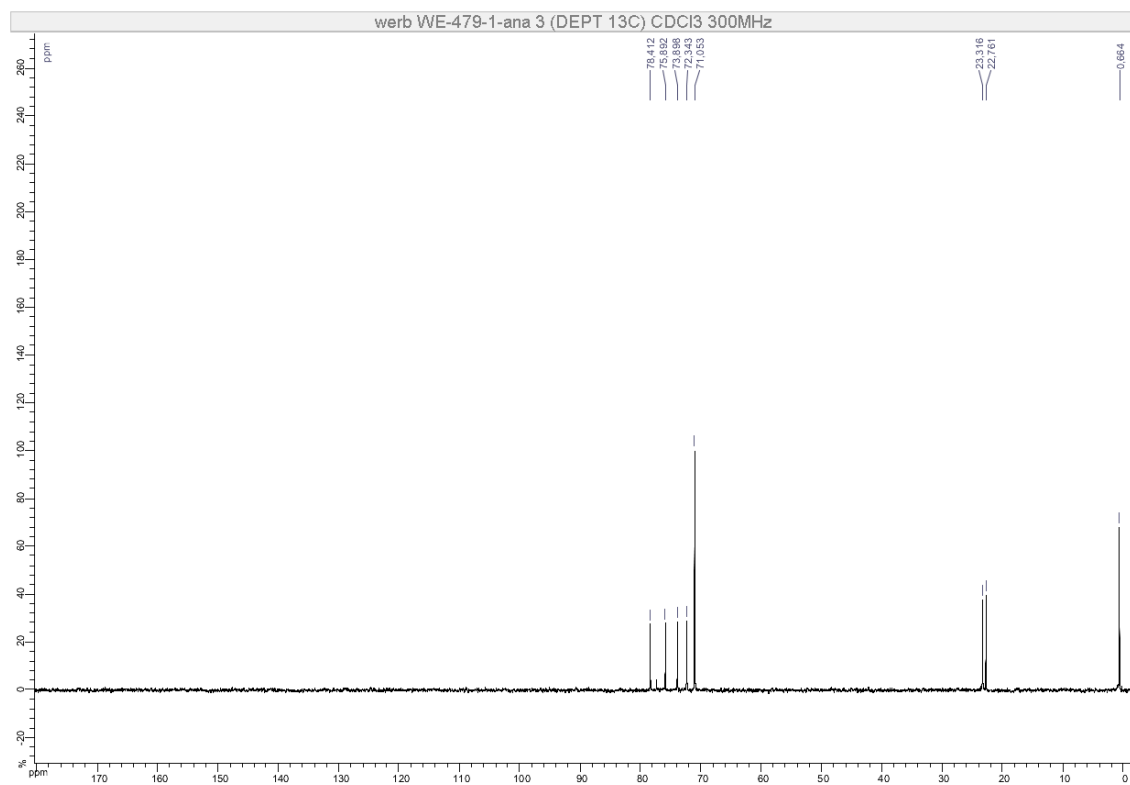
^1H NMR (300 MHz, CDCl_3)



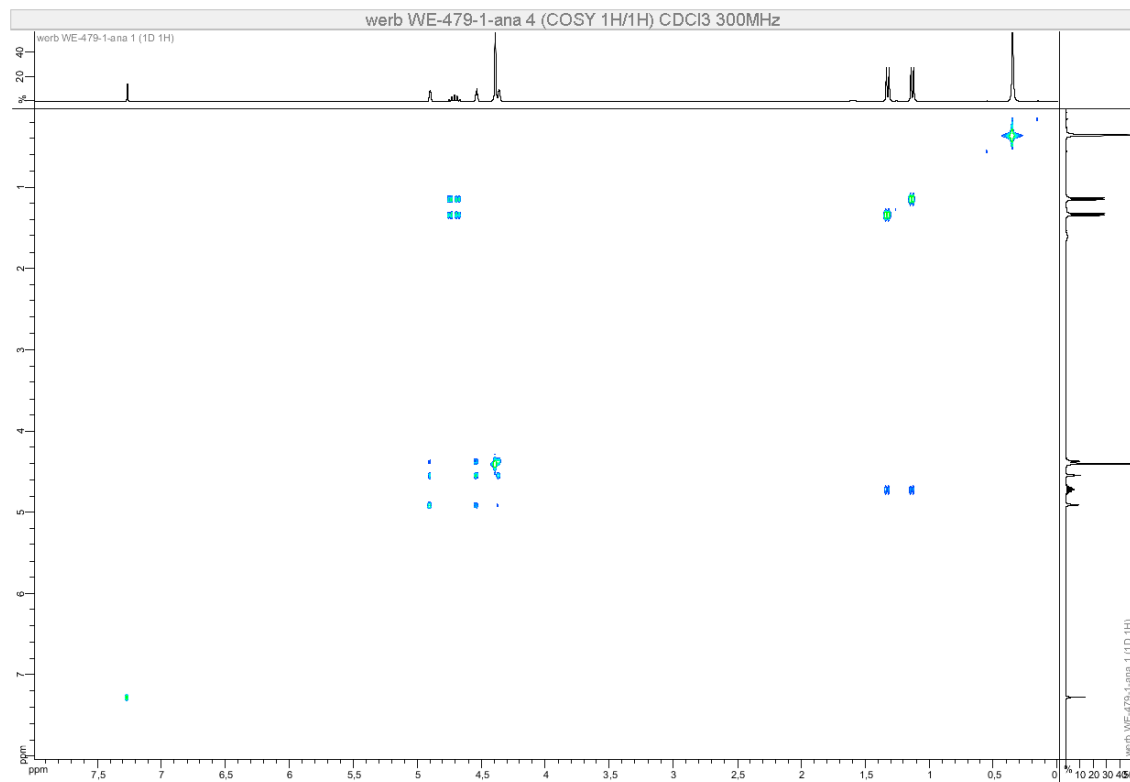
^{13}C NMR (75 MHz, CDCl_3)



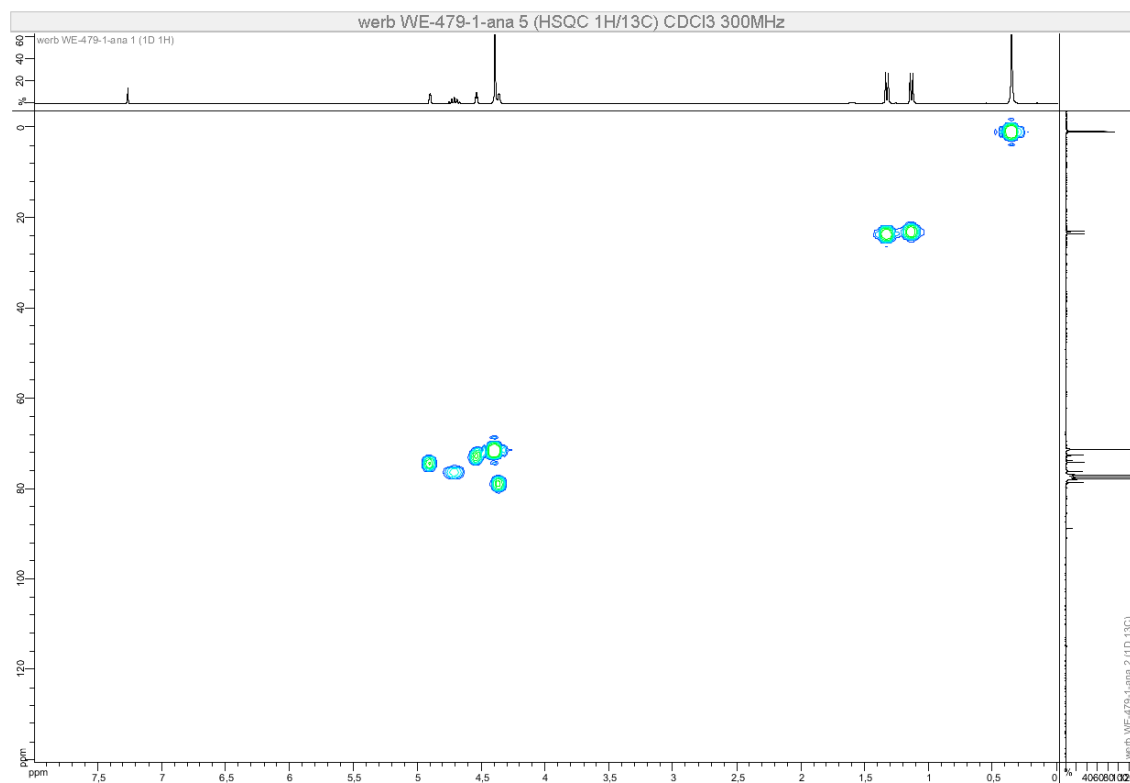
DEPT 135 (75 MHz, CDCl₃)



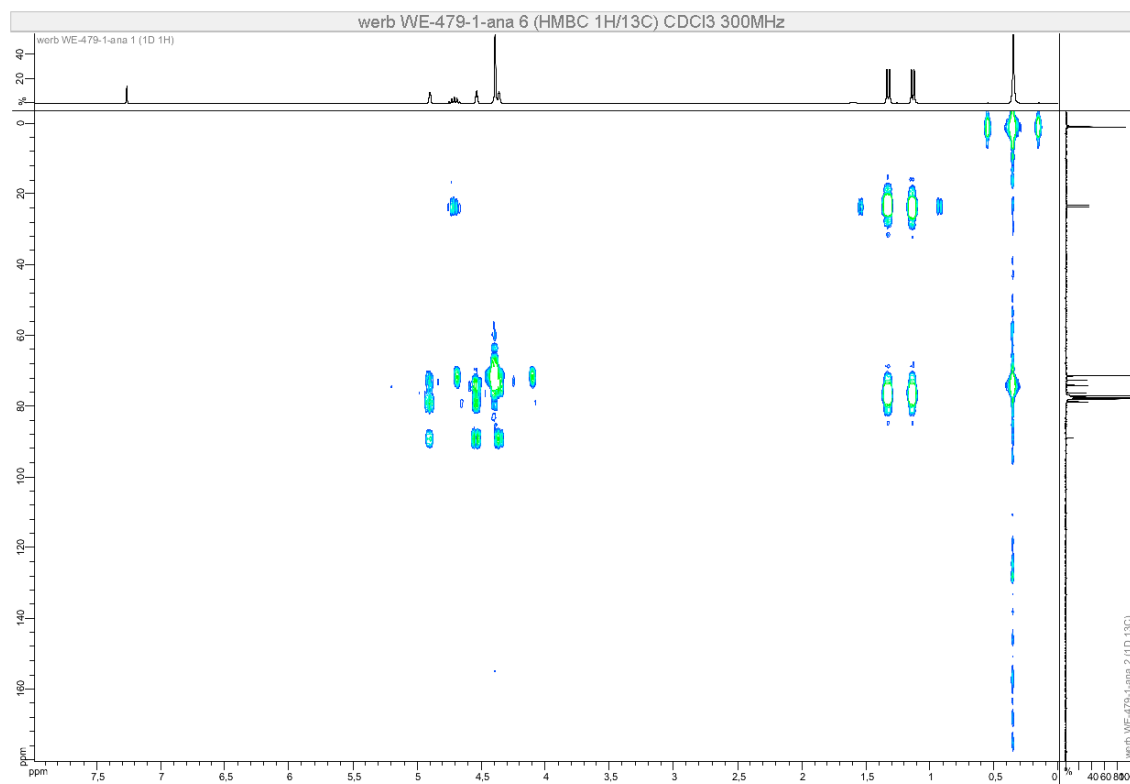
COSY (300 MHz, CDCl₃)



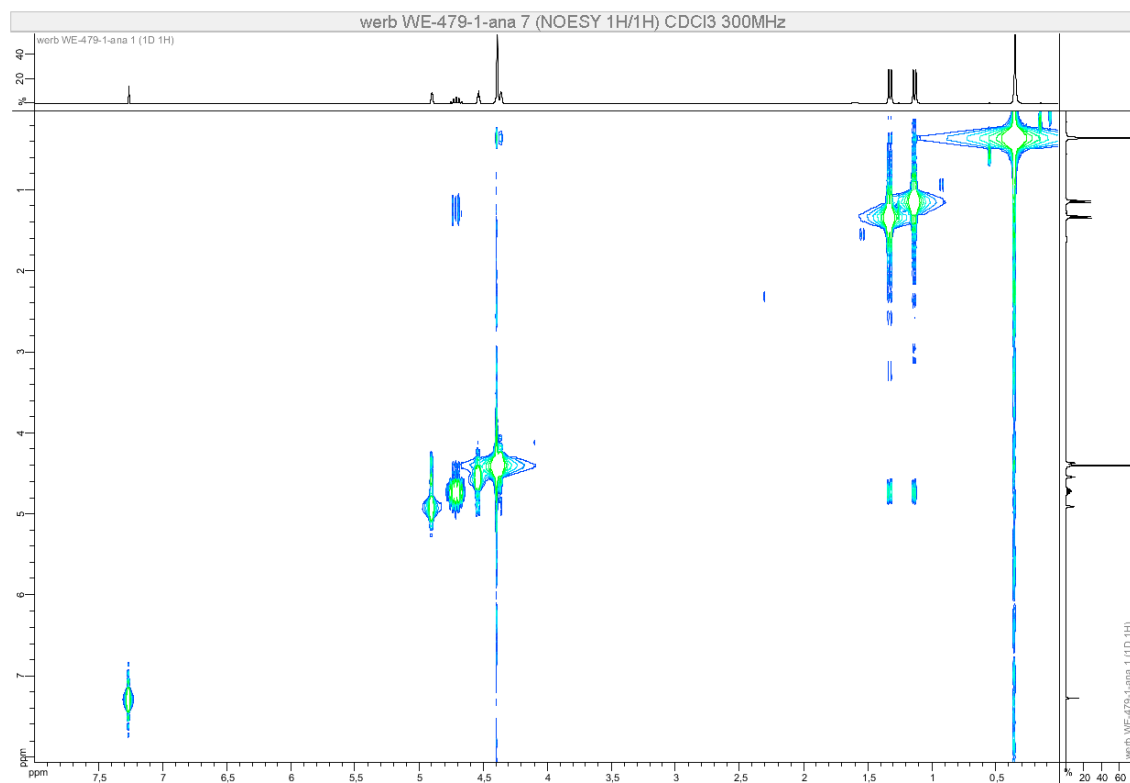
HSQC (300 MHz, CDCl₃)



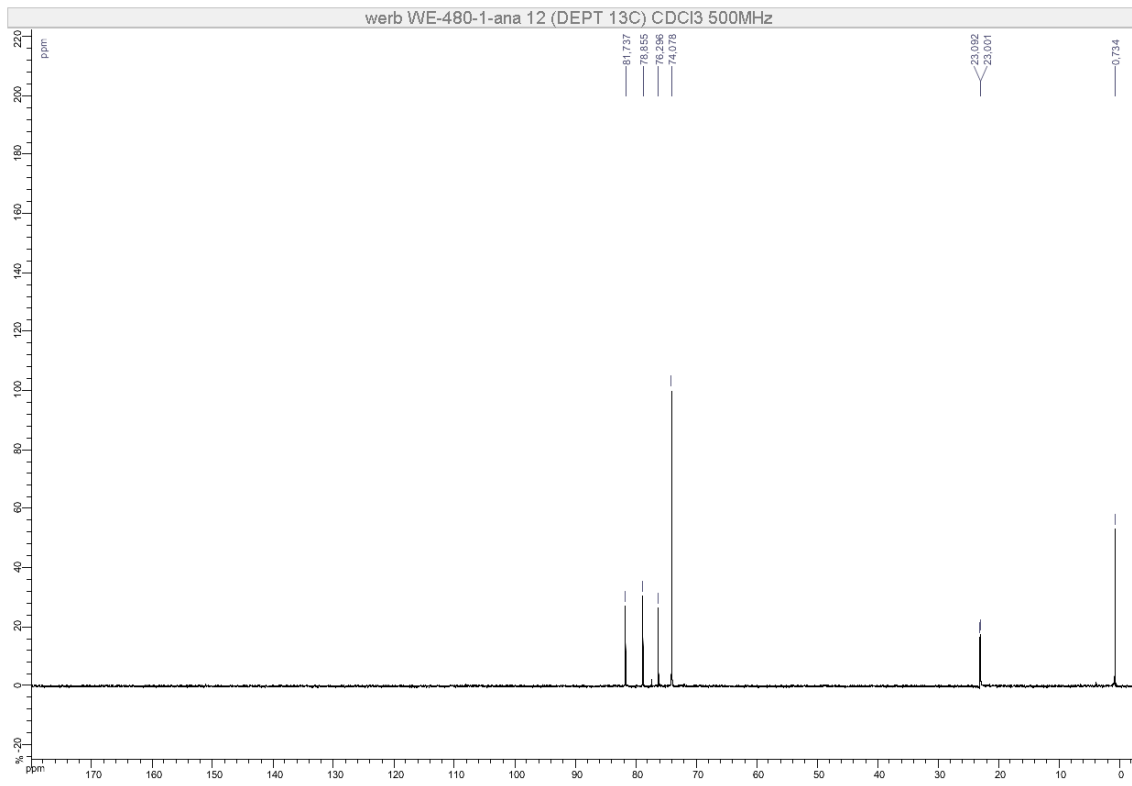
HMBC (300 MHz, CDCl₃)



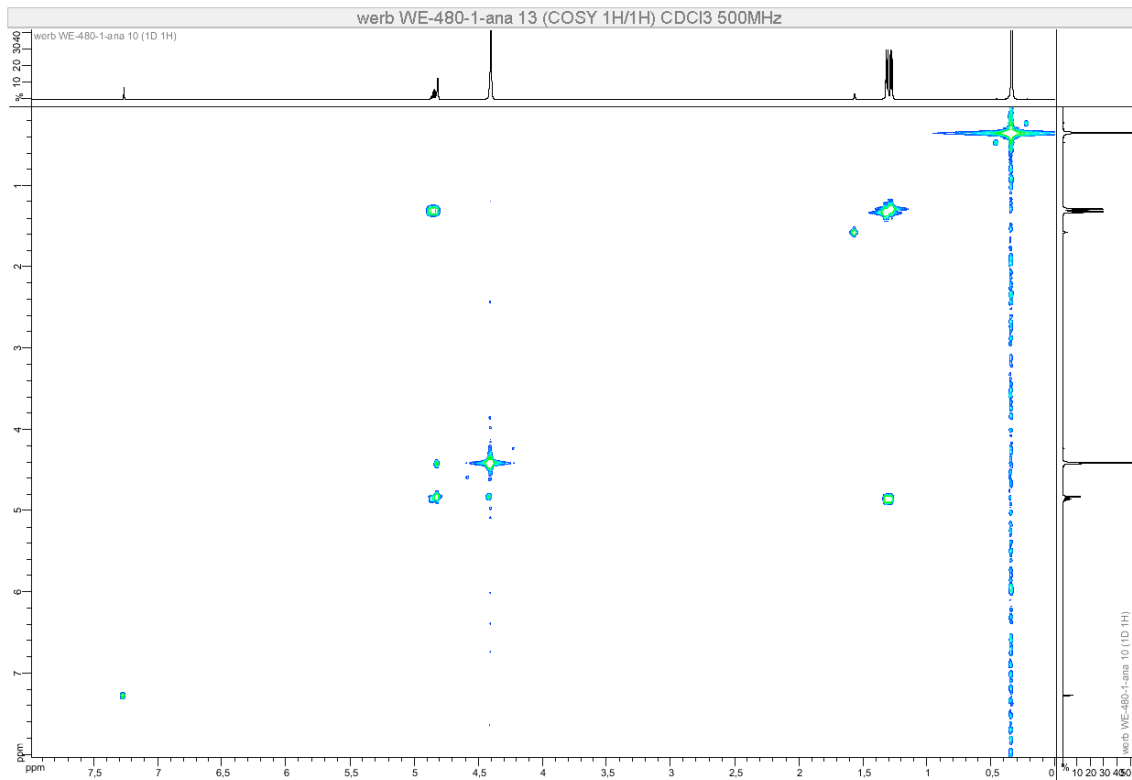
NOESY (300 MHz, CDCl₃)



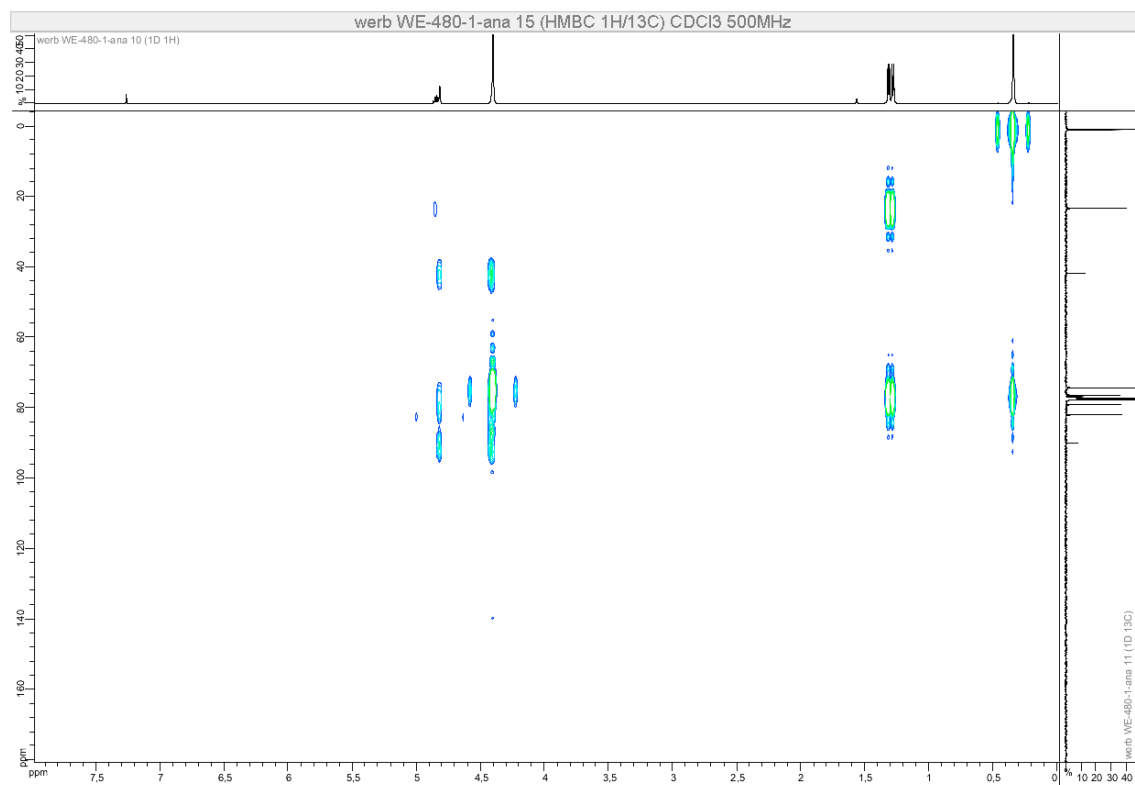
DEPT 135 (126 MHz, CDCl₃)



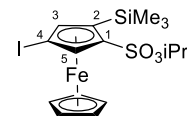
COSY (500 MHz, CDCl₃)



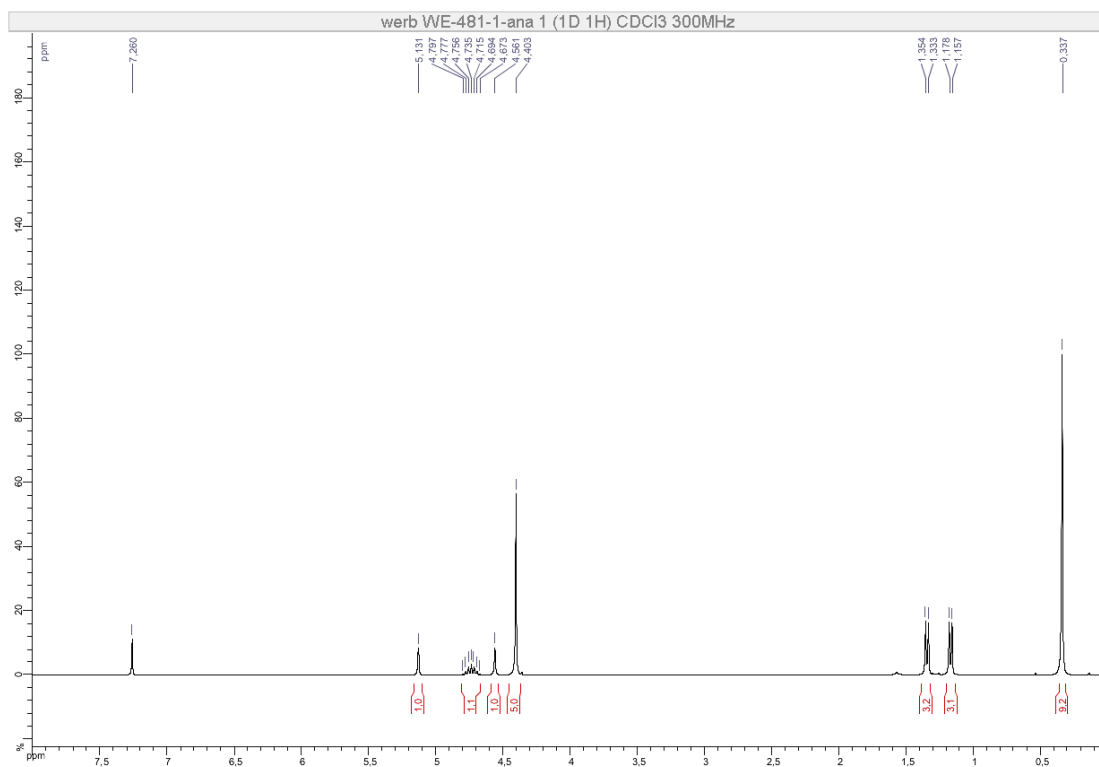
HMBC (500 MHz, CDCl₃)



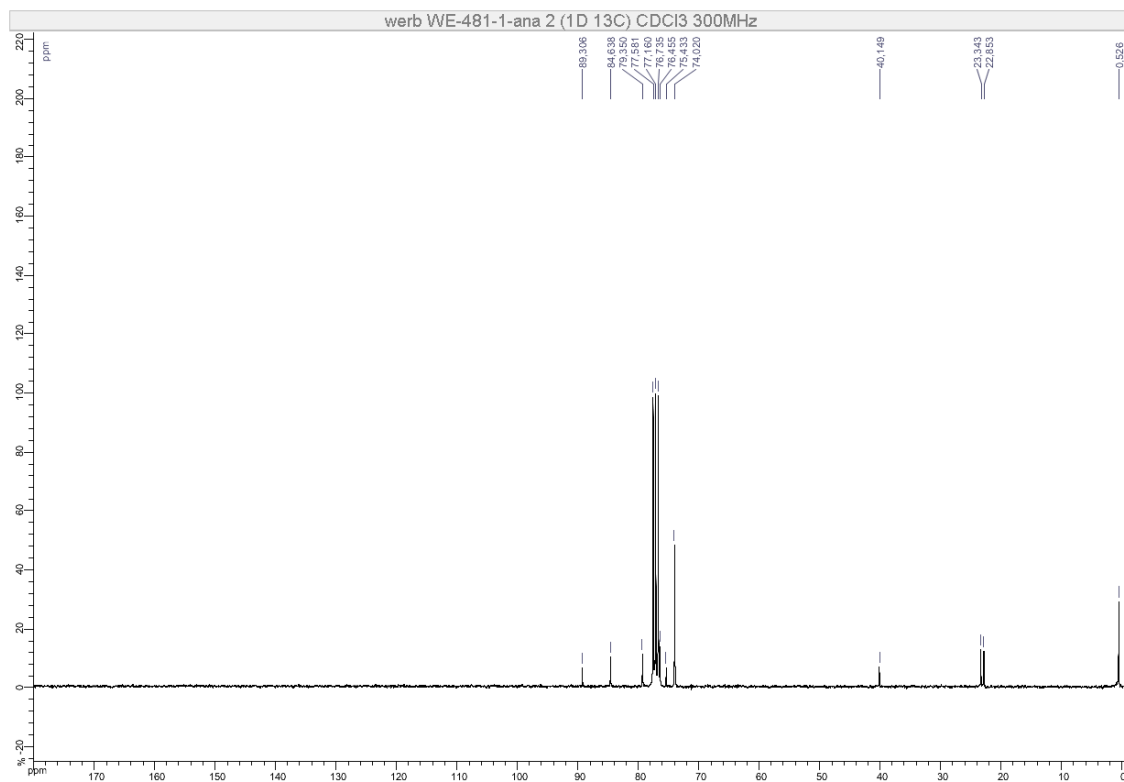
4-Iodo-*O*-isopropyl-2-(trimethylsilyl)ferrocenesulfonate (6, racemic mixture)



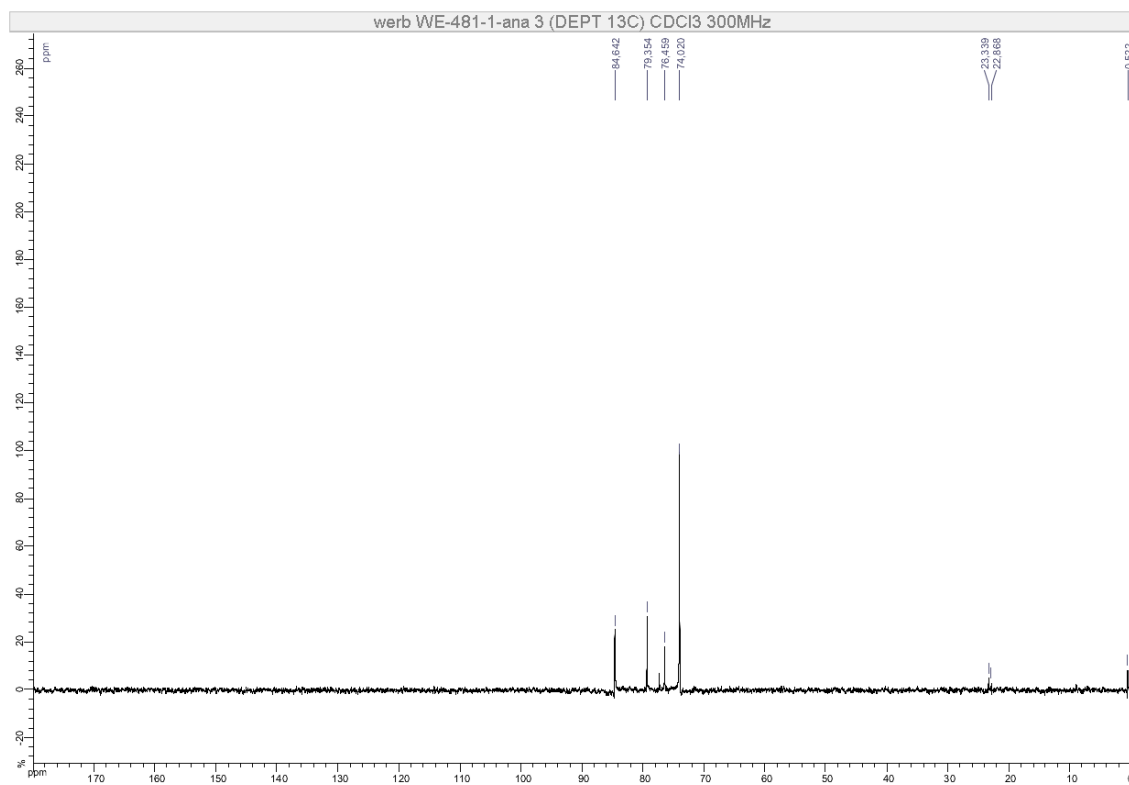
^1H NMR (300 MHz, CDCl_3)



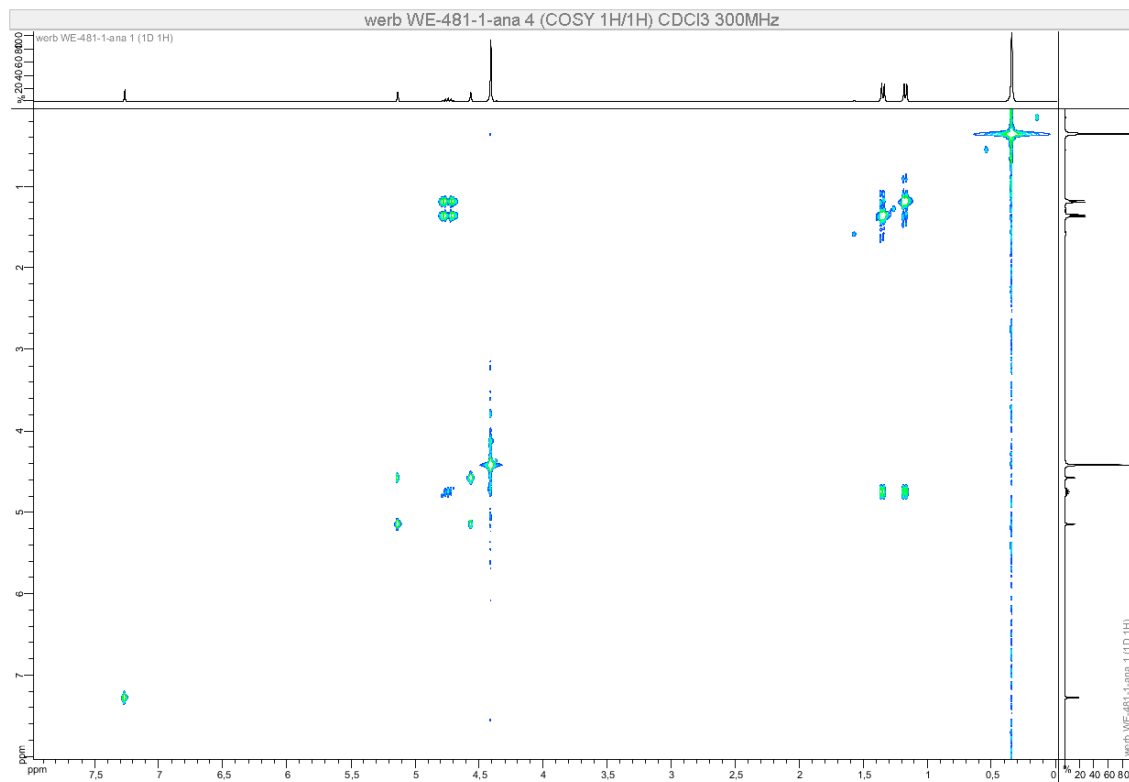
^{13}C NMR (75 MHz, CDCl_3)



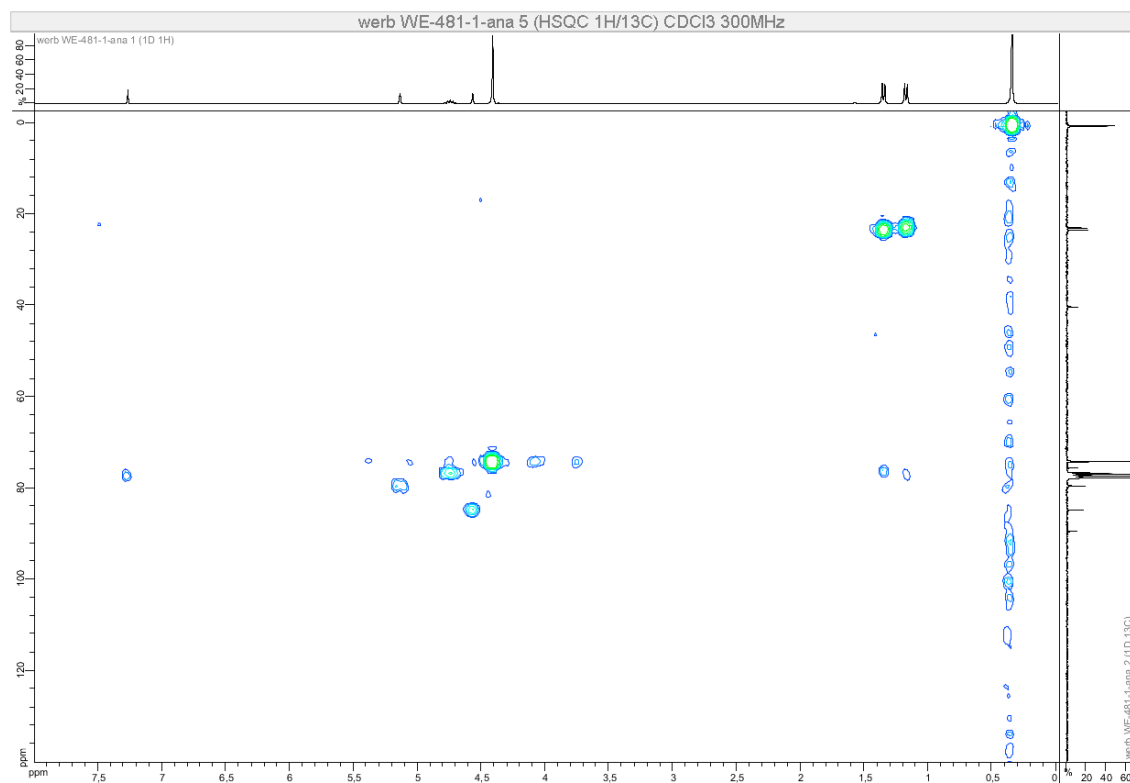
DEPT 135 (75 MHz, CDCl₃)



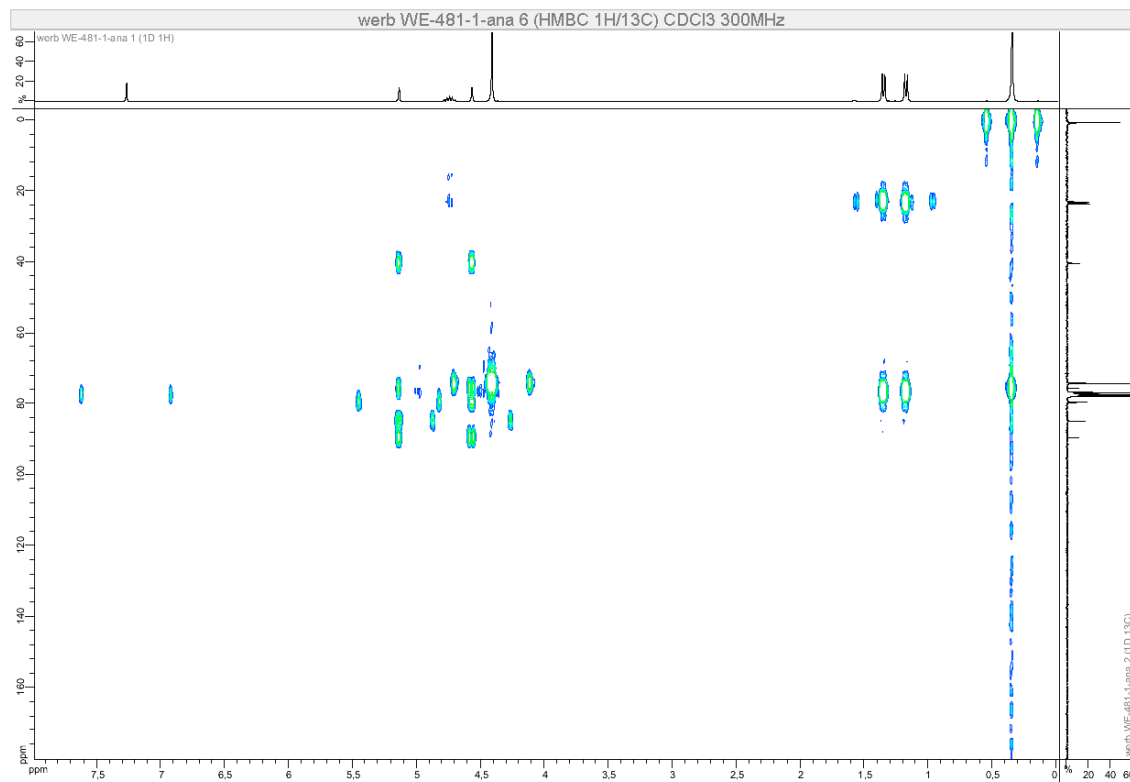
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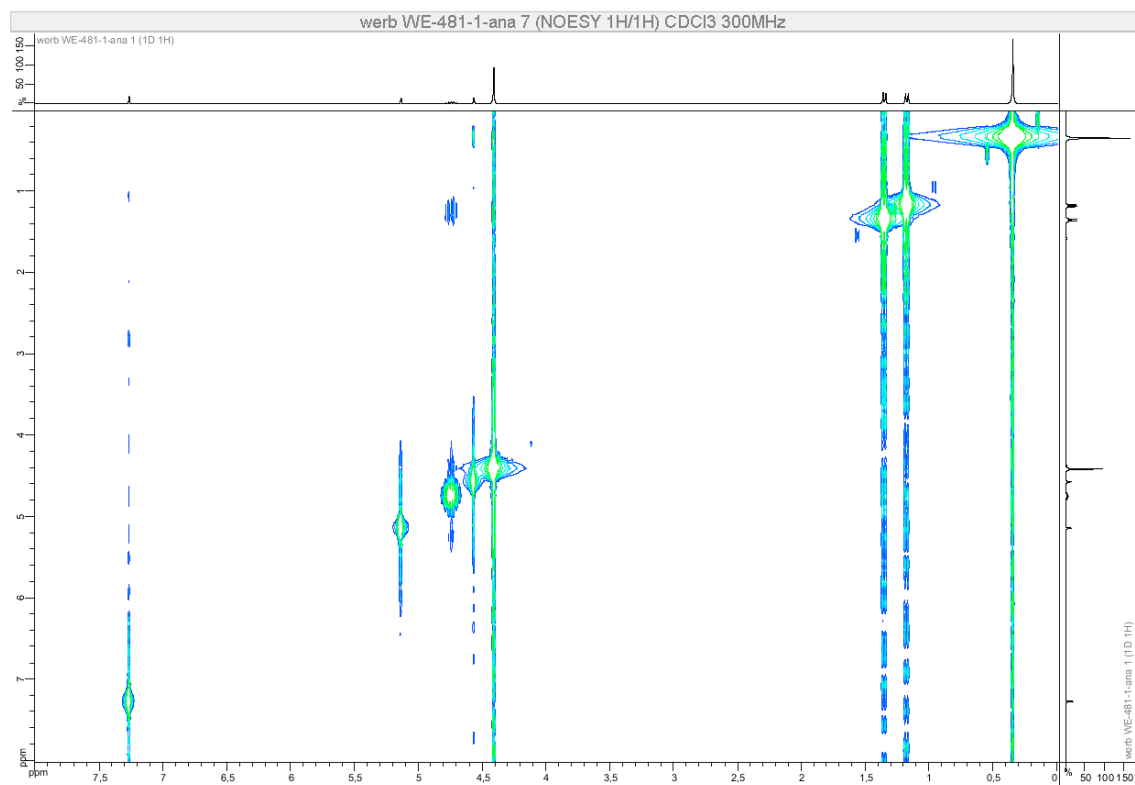
HSQC (300 MHz, CDCl₃)



HMBC (300 MHz, CDCl₃)

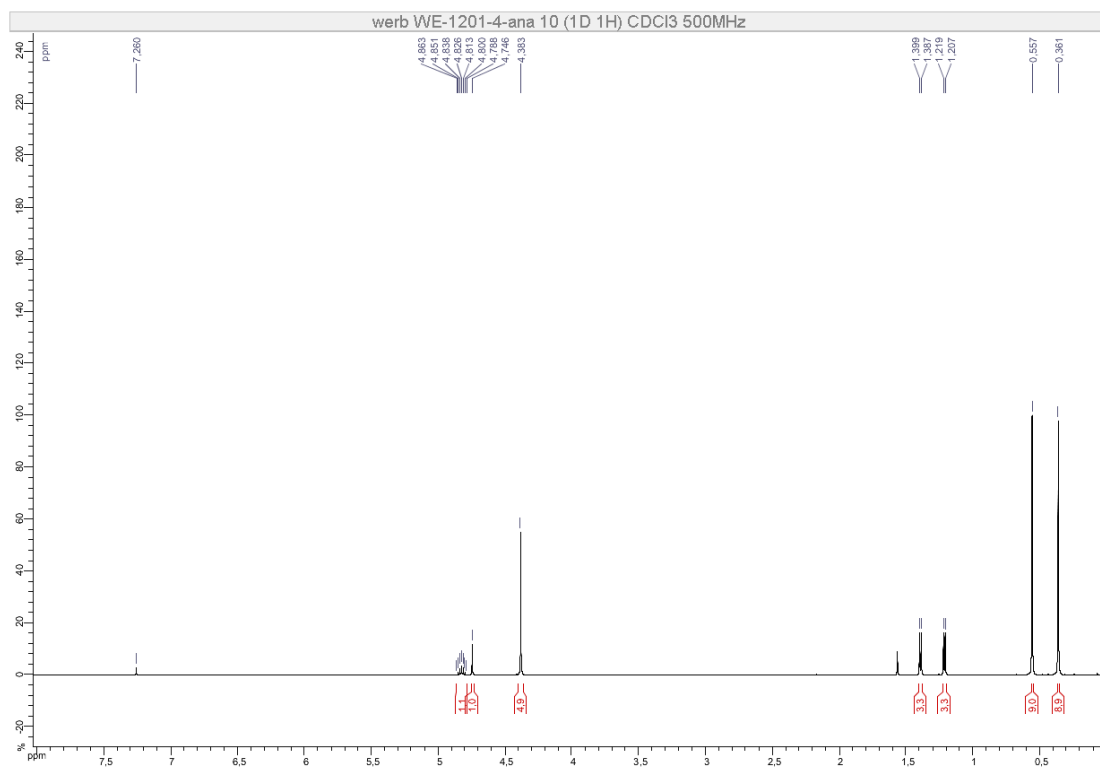
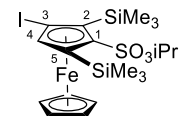


NOESY (300 MHz, CDCl₃)

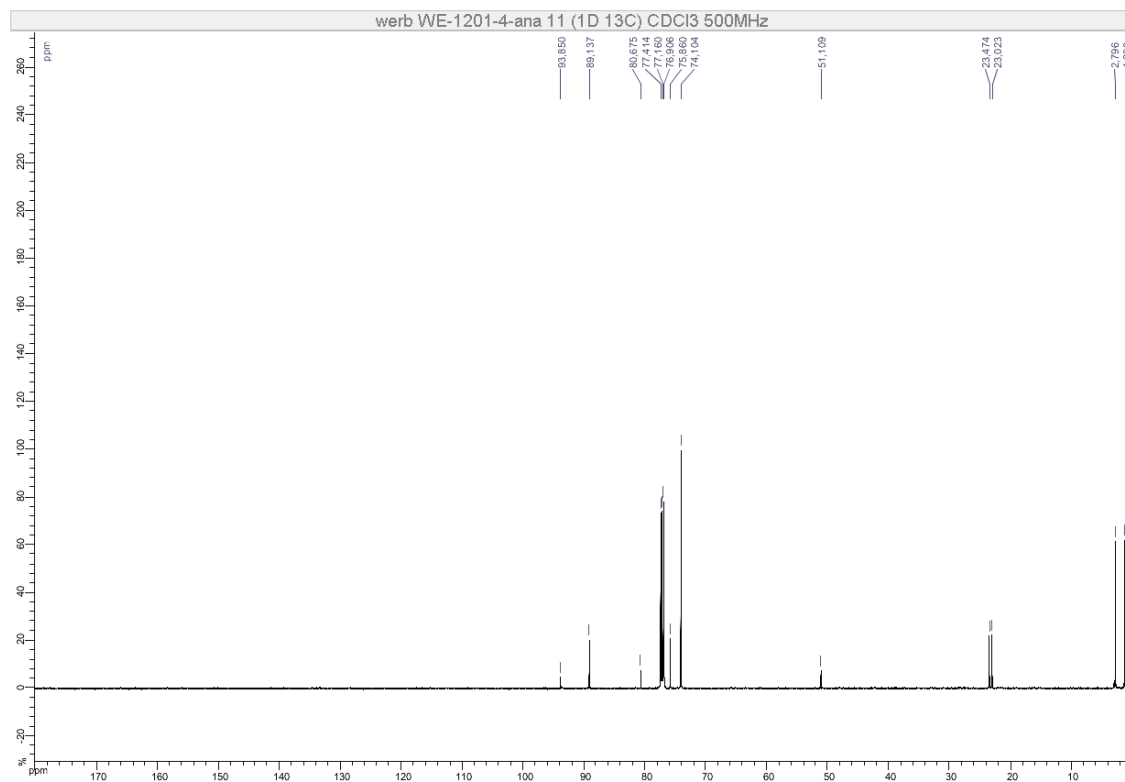


3-Iodo-*O*-isopropyl-2,5-bis(trimethylsilyl)ferrocenesulfonate (7, racemic mixture)

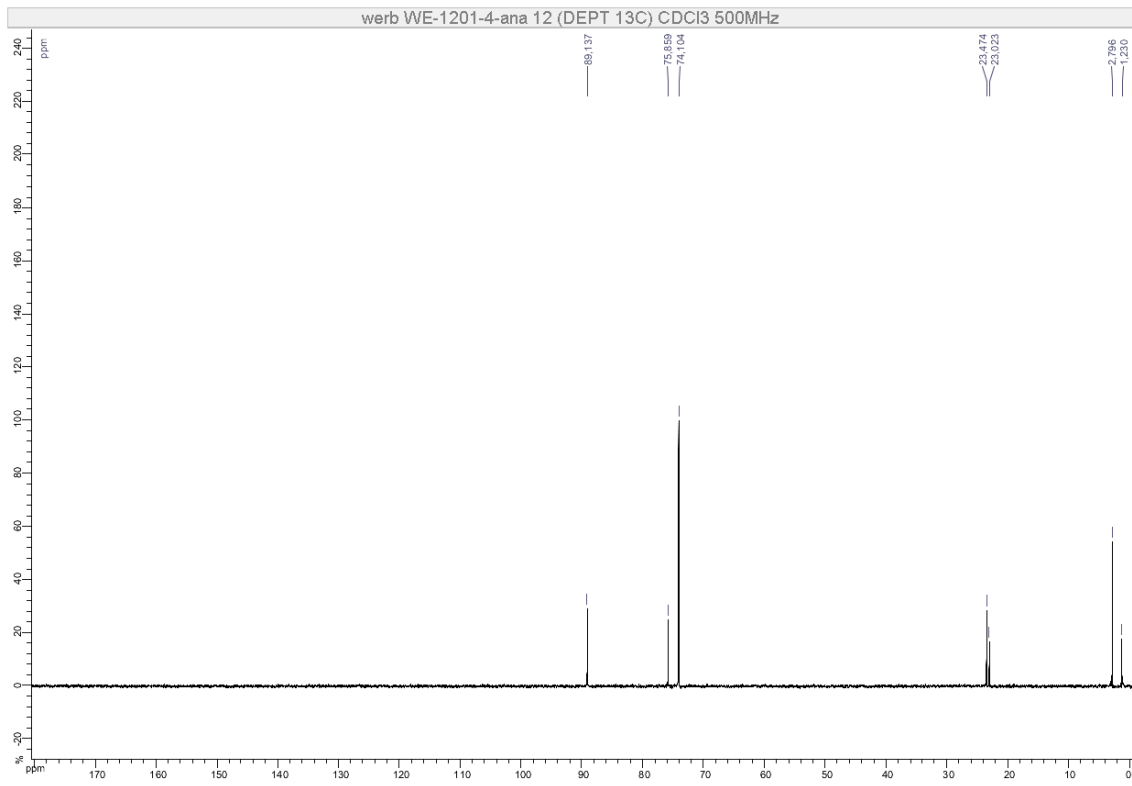
^1H NMR (500 MHz, CDCl_3)



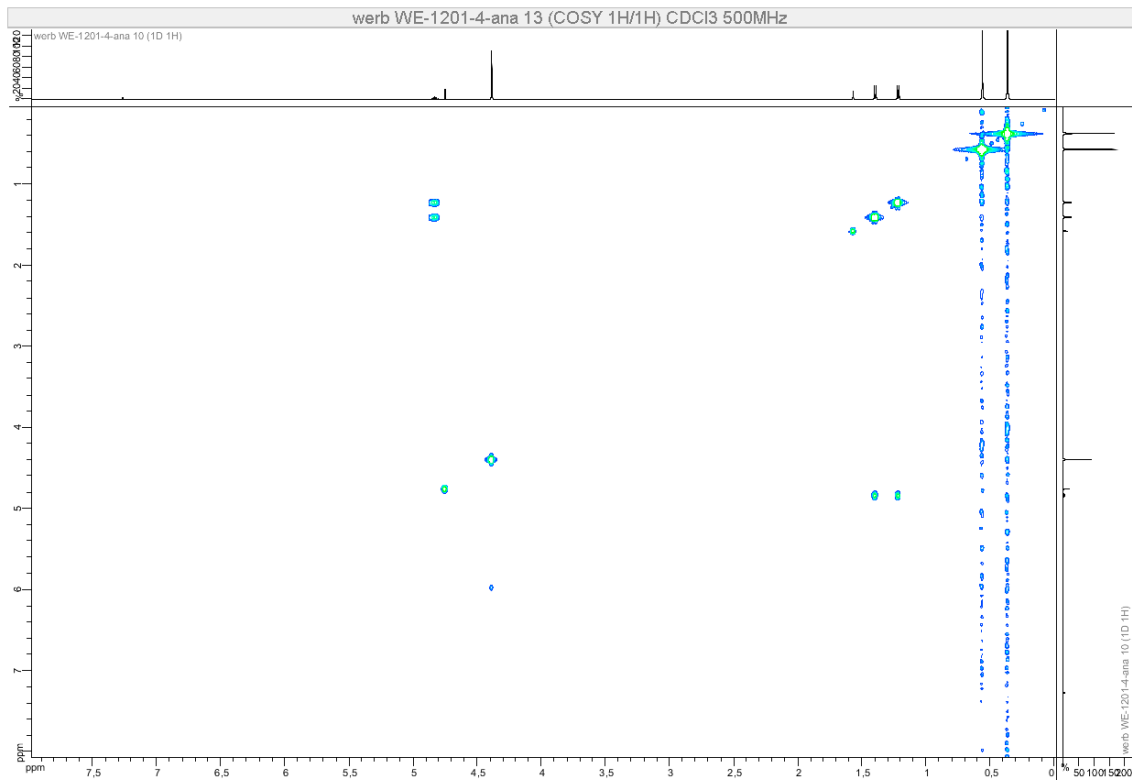
^{13}C NMR (126 MHz, CDCl_3)



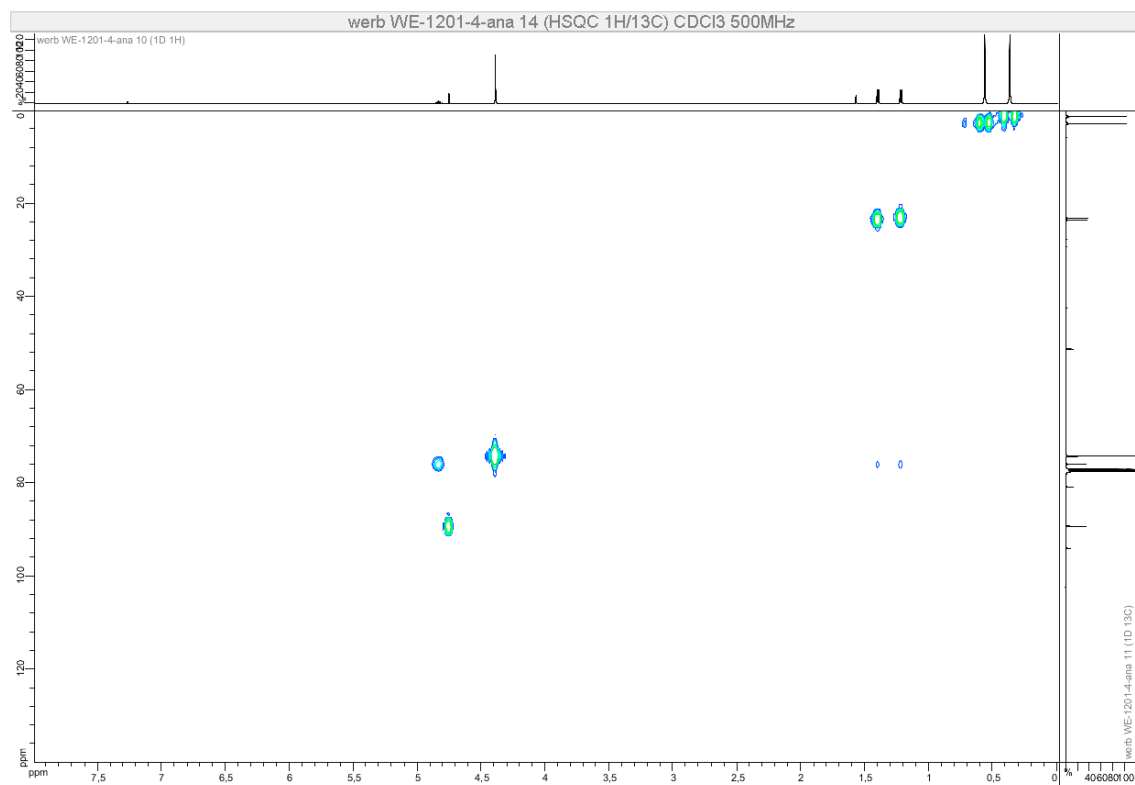
DEPT 135 (126 MHz, CDCl₃)



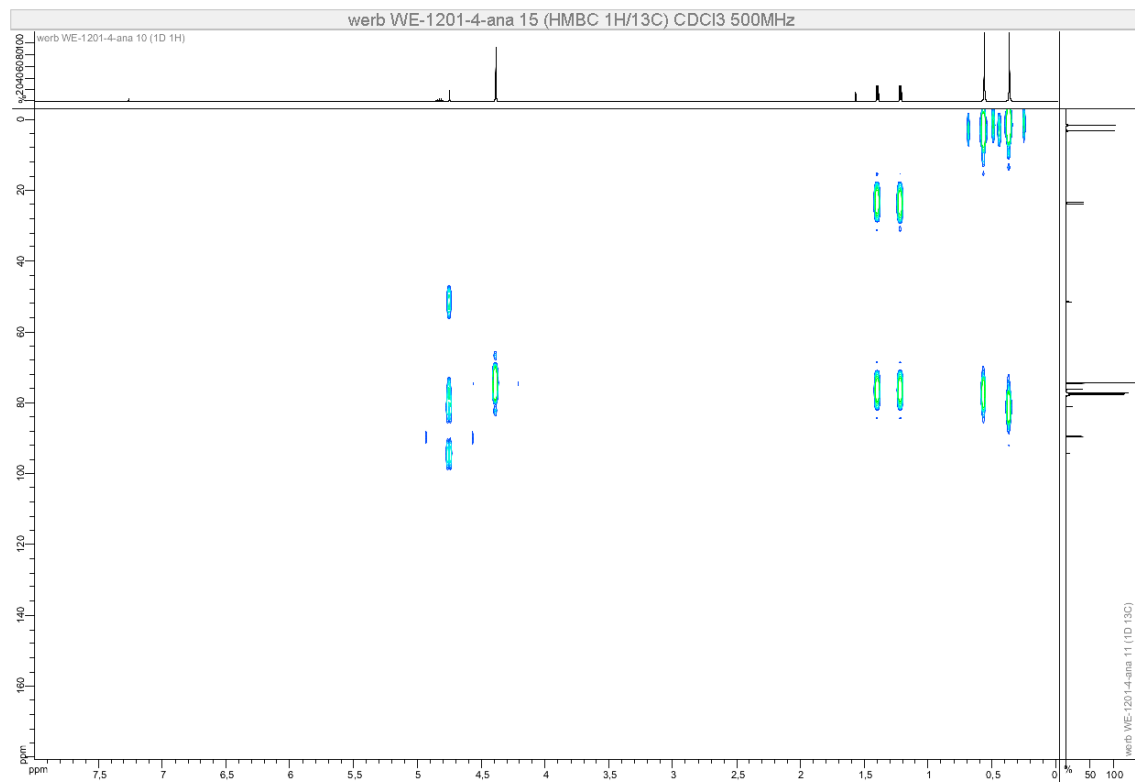
COSY (500 MHz, CDCl₃)



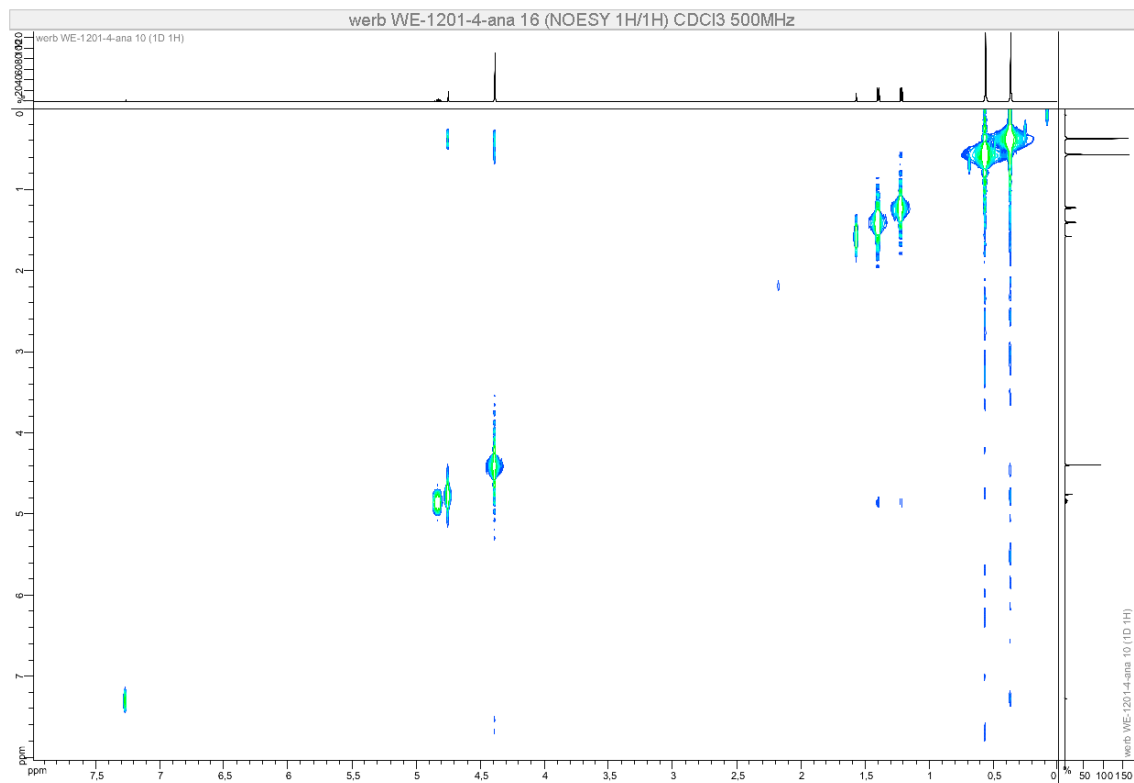
HSQC (500 MHz, CDCl₃)



HMBC (500 MHz, CDCl₃)

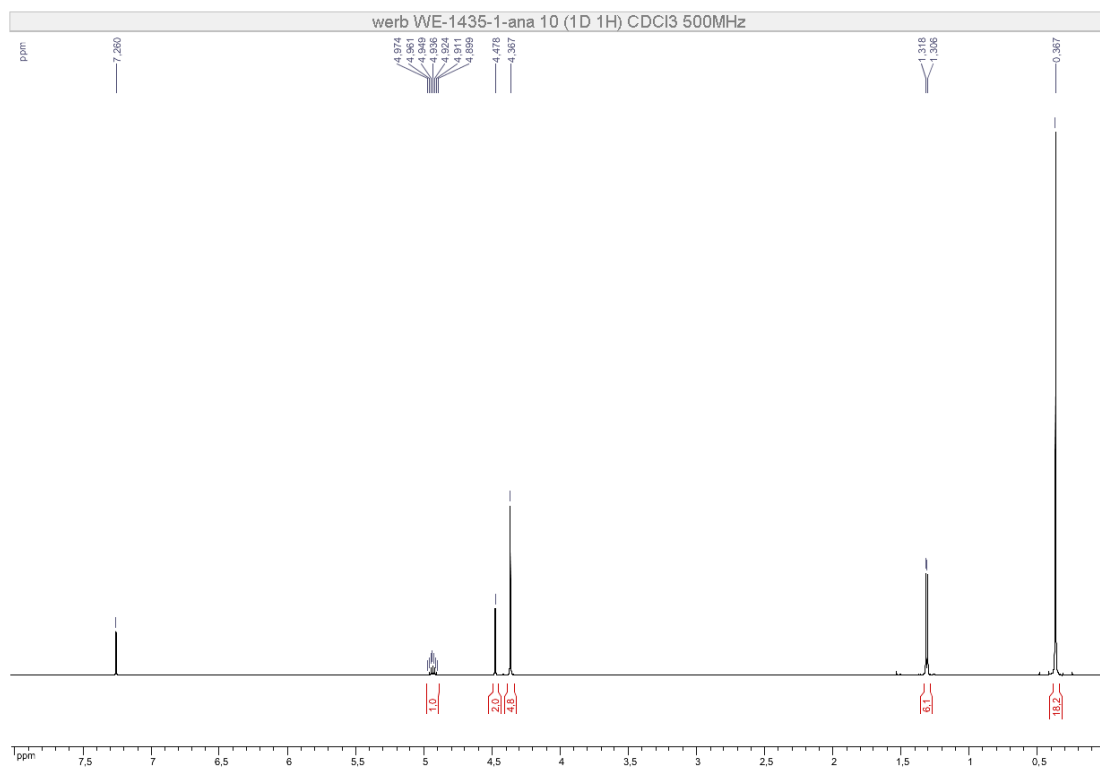
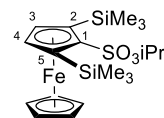


NOESY (500 MHz, CDCl₃)

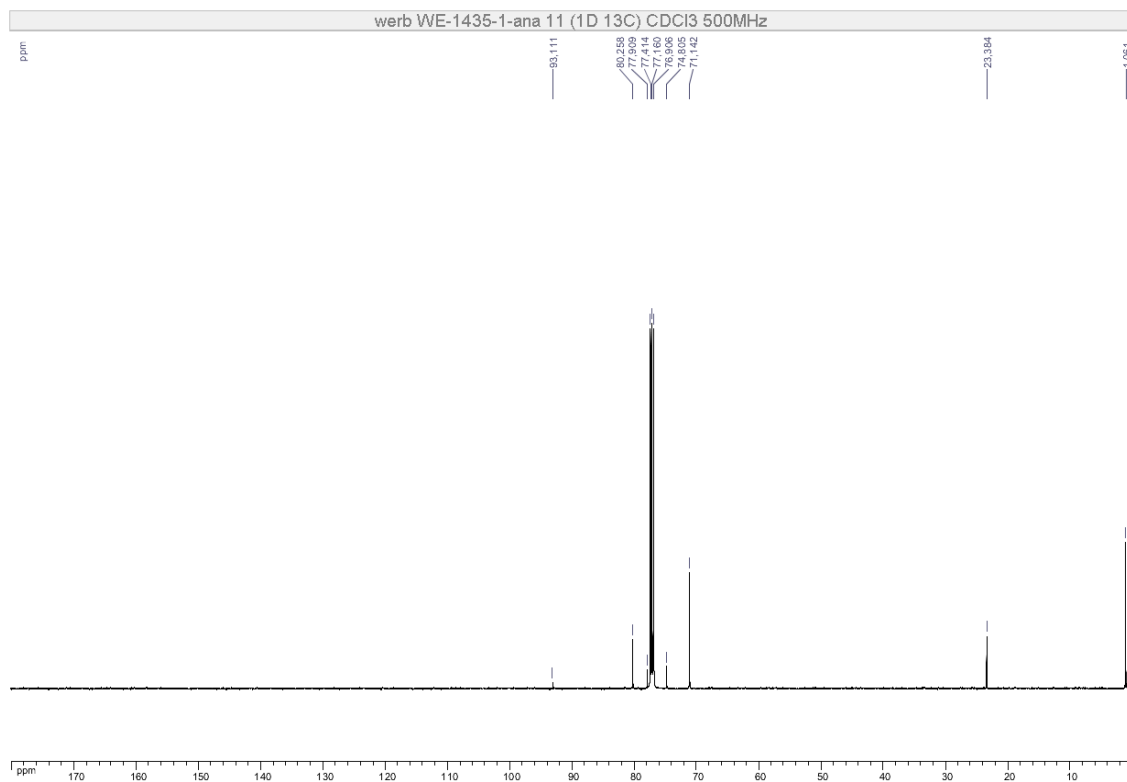


O-Isopropyl-2,5-bis(trimethylsilyl)ferrocenesulfonate (7')

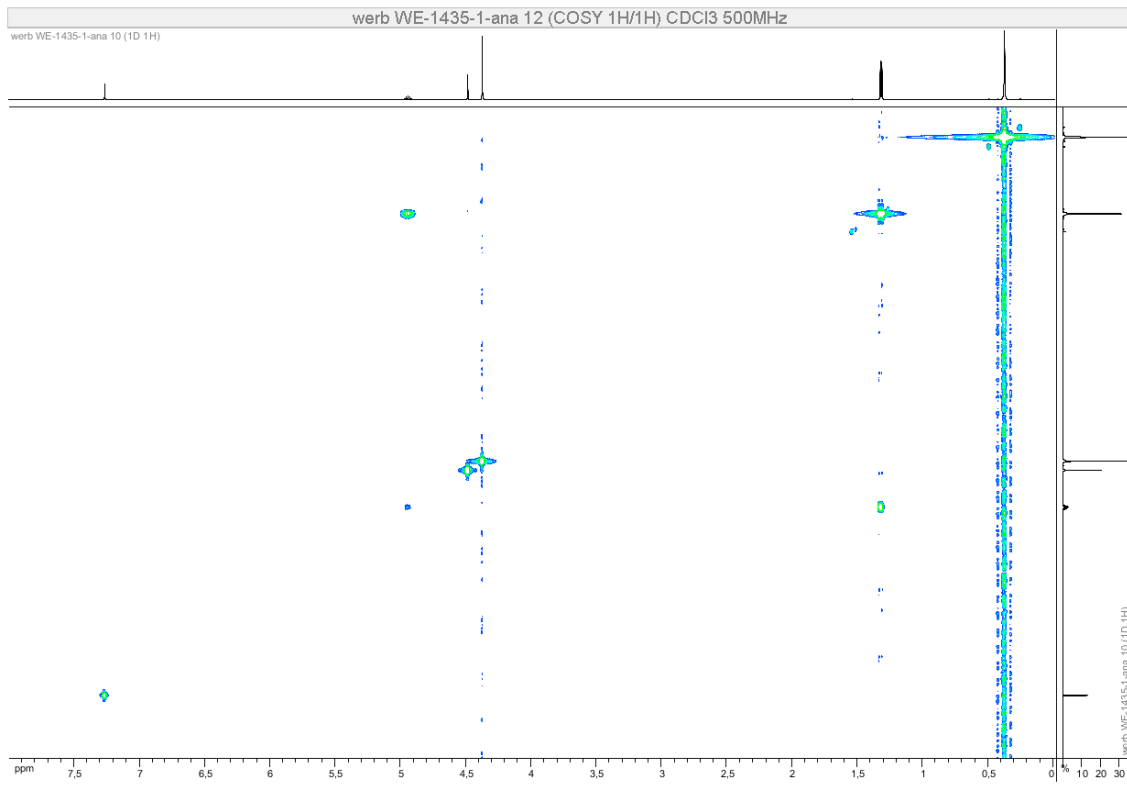
¹H NMR (500 MHz, CDCl₃)



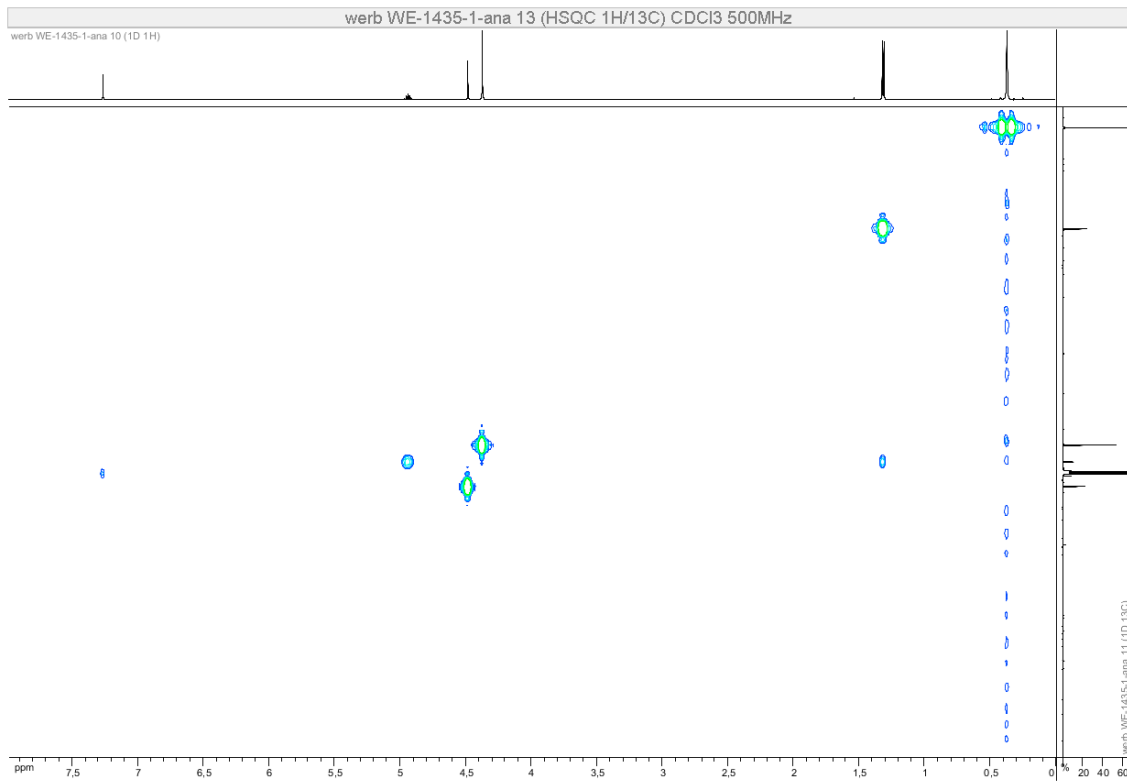
¹³C NMR (126 MHz, CDCl₃)



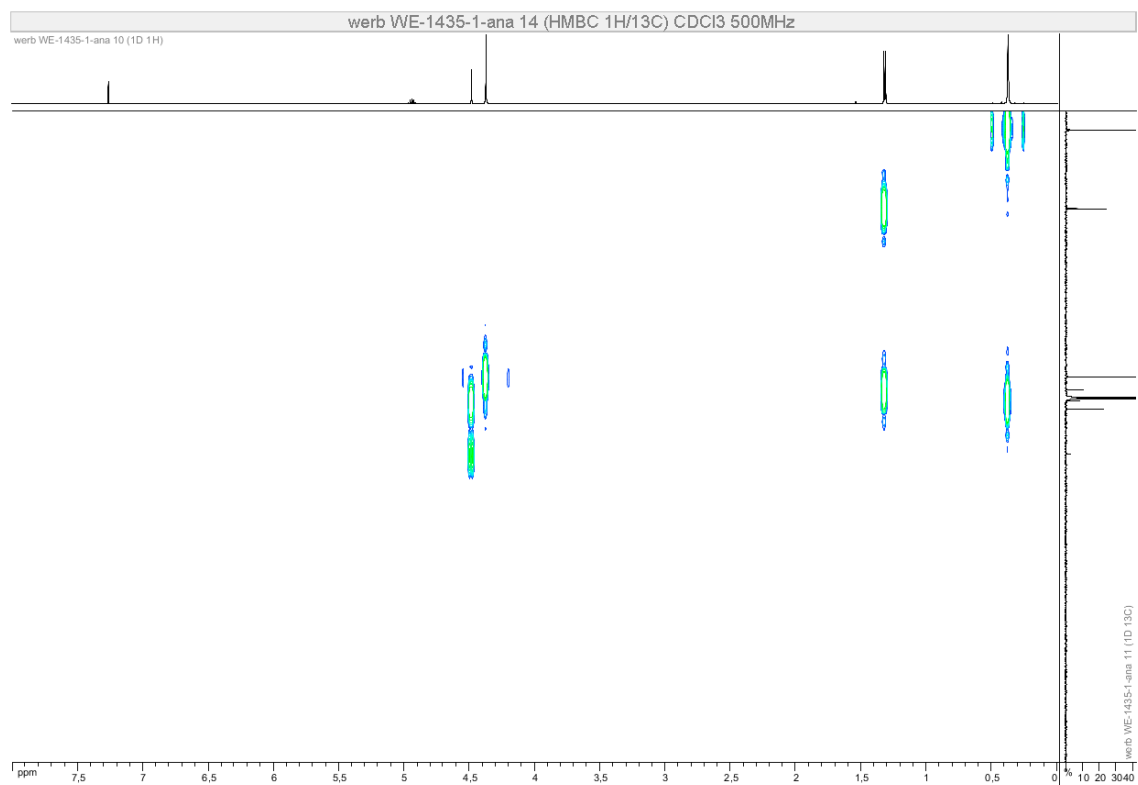
COSY (500 MHz, CDCl₃)



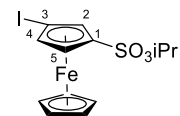
HSQC (500 MHz, CDCl₃)



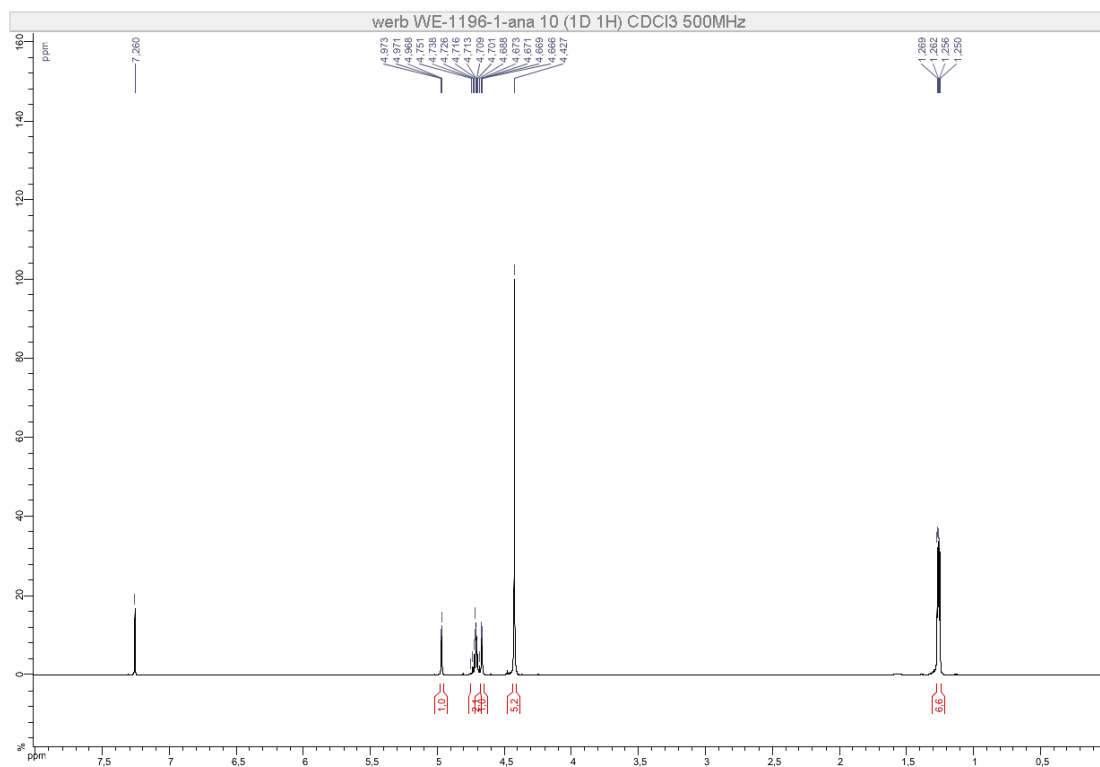
HMBC (500 MHz, CDCl₃)



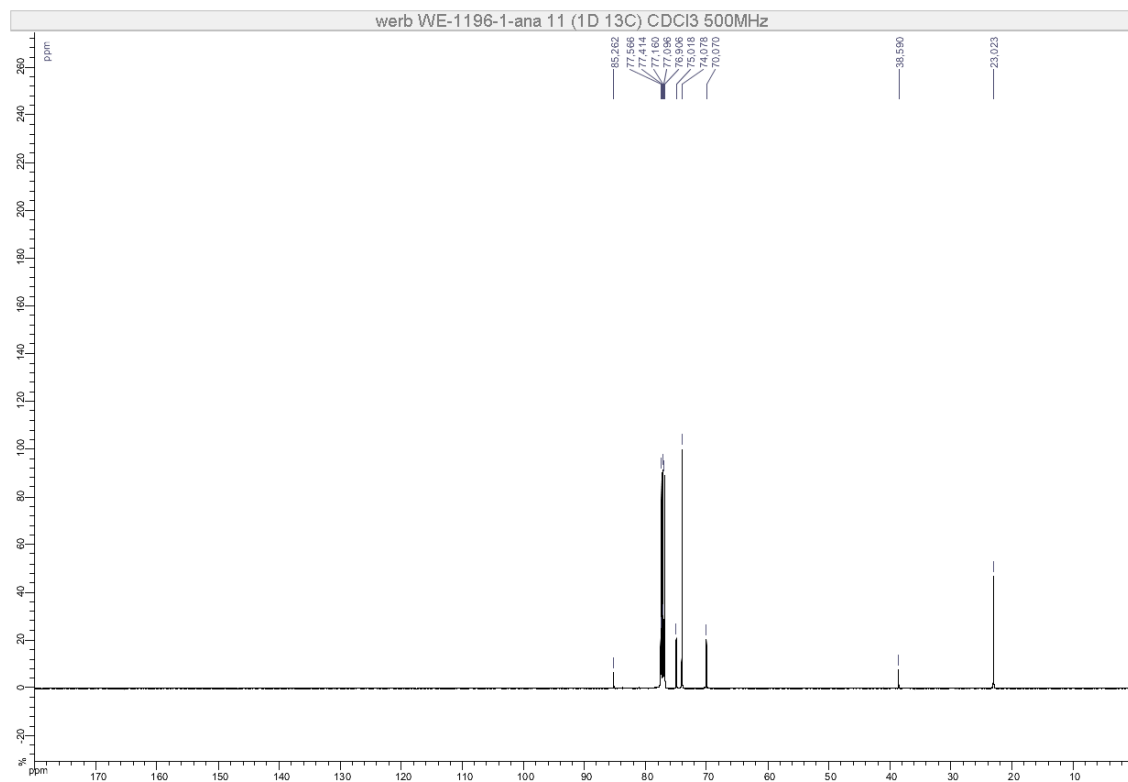
3-Iodo-*O*-isopropylferrocenesulfonate (**8**, racemic mixture)



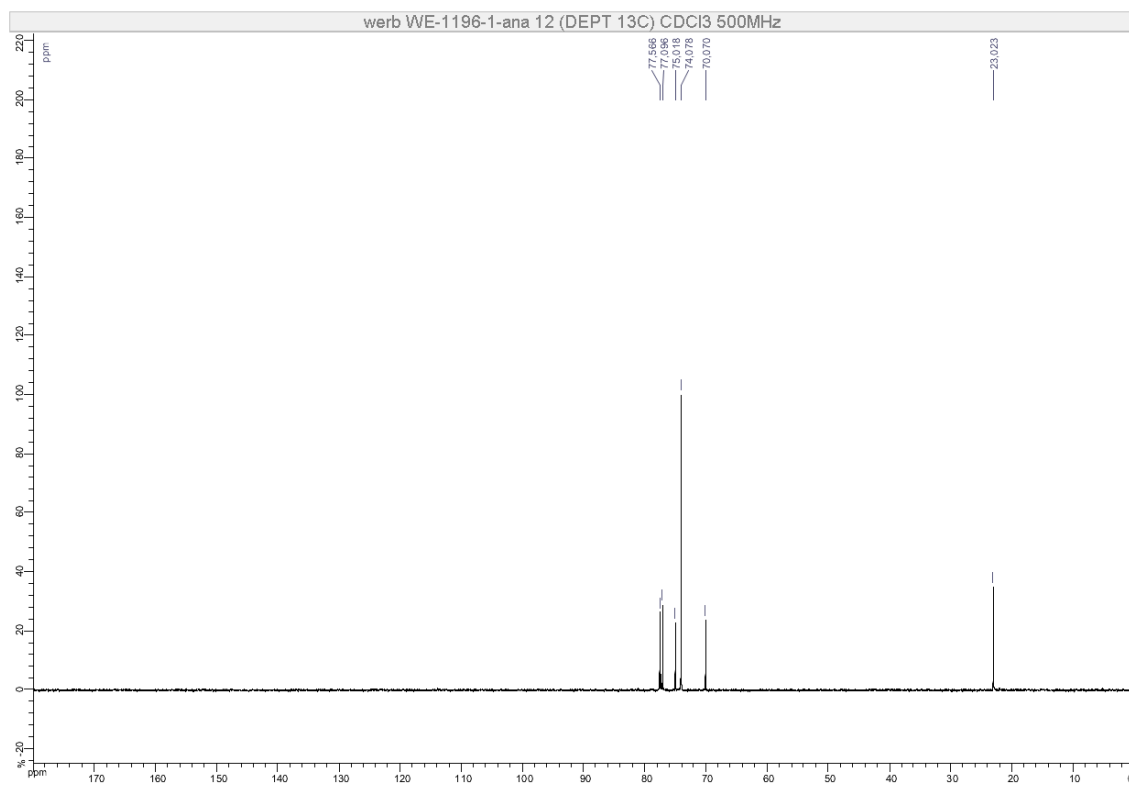
¹H NMR (500 MHz, CDCl₃)



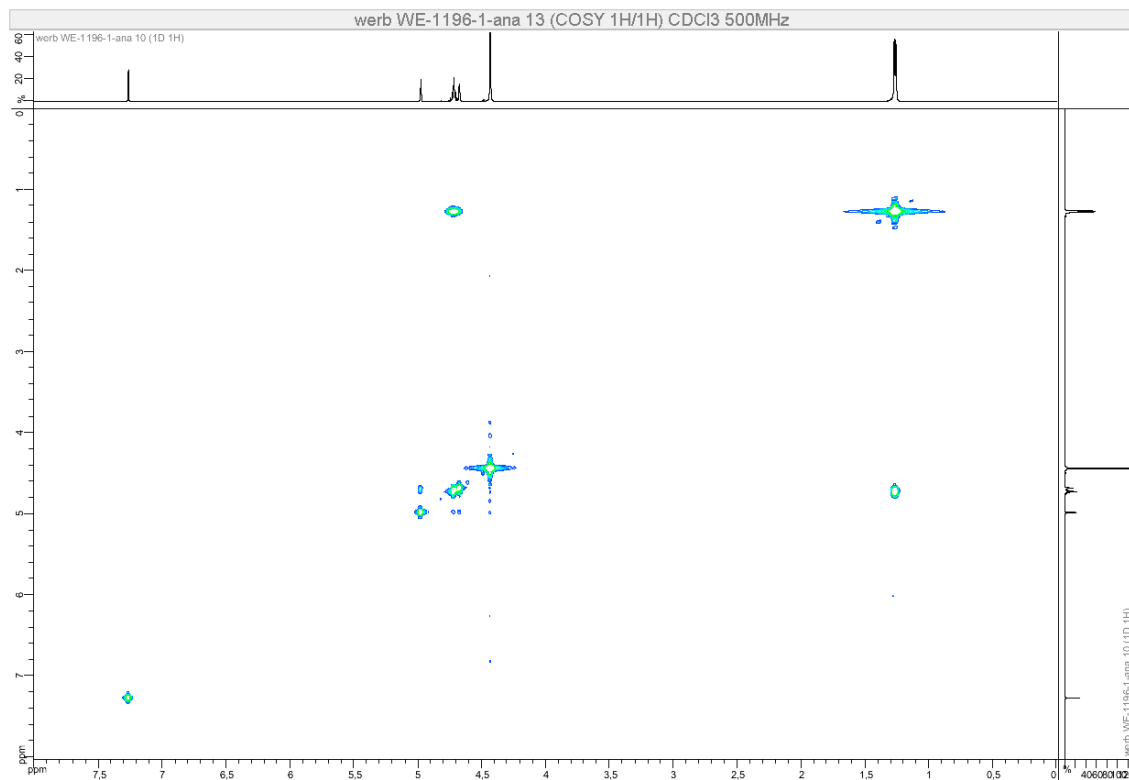
¹³C NMR (126 MHz, CDCl₃)



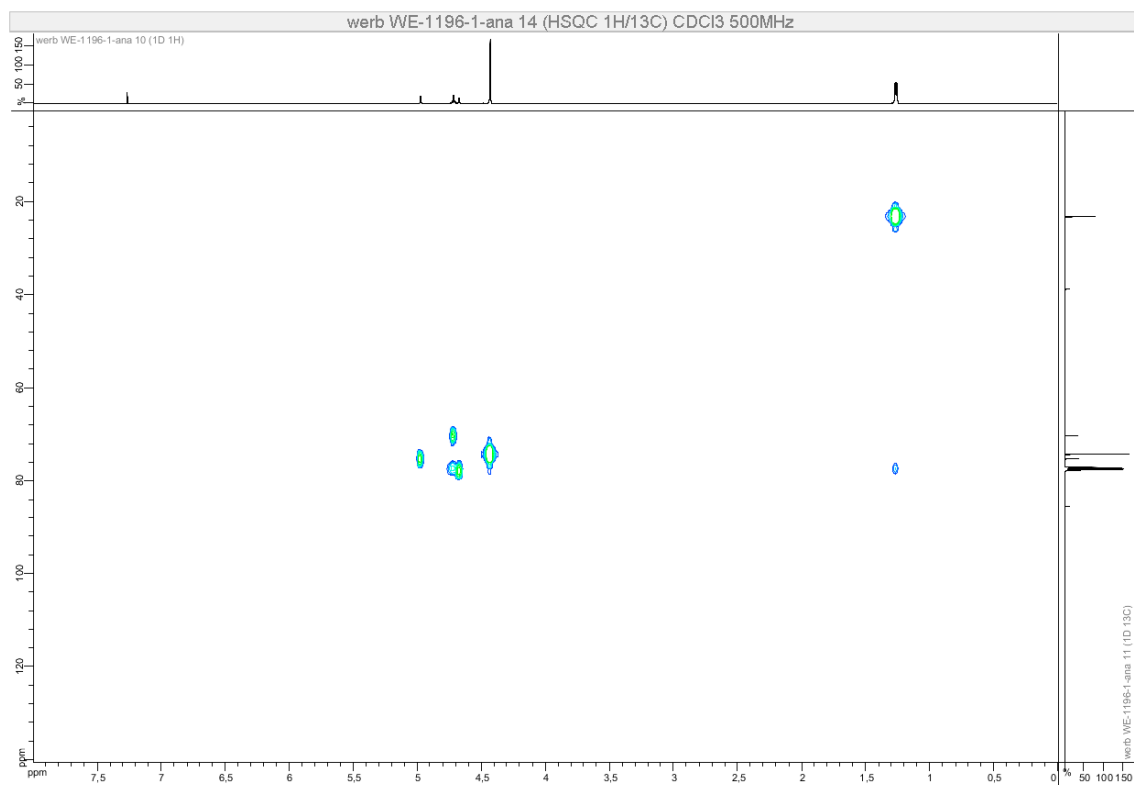
DEPT 135 (126 MHz, CDCl₃)



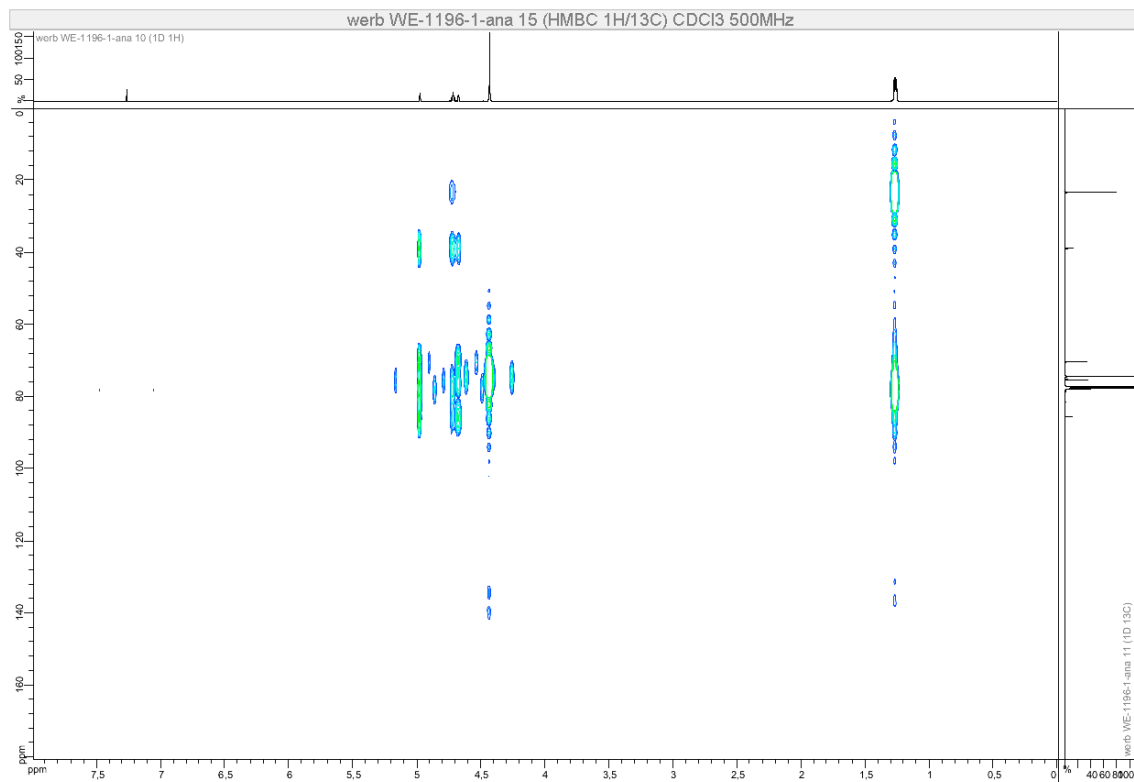
COSY (500 MHz, CDCl₃)



HSQC (500 MHz, CDCl₃)

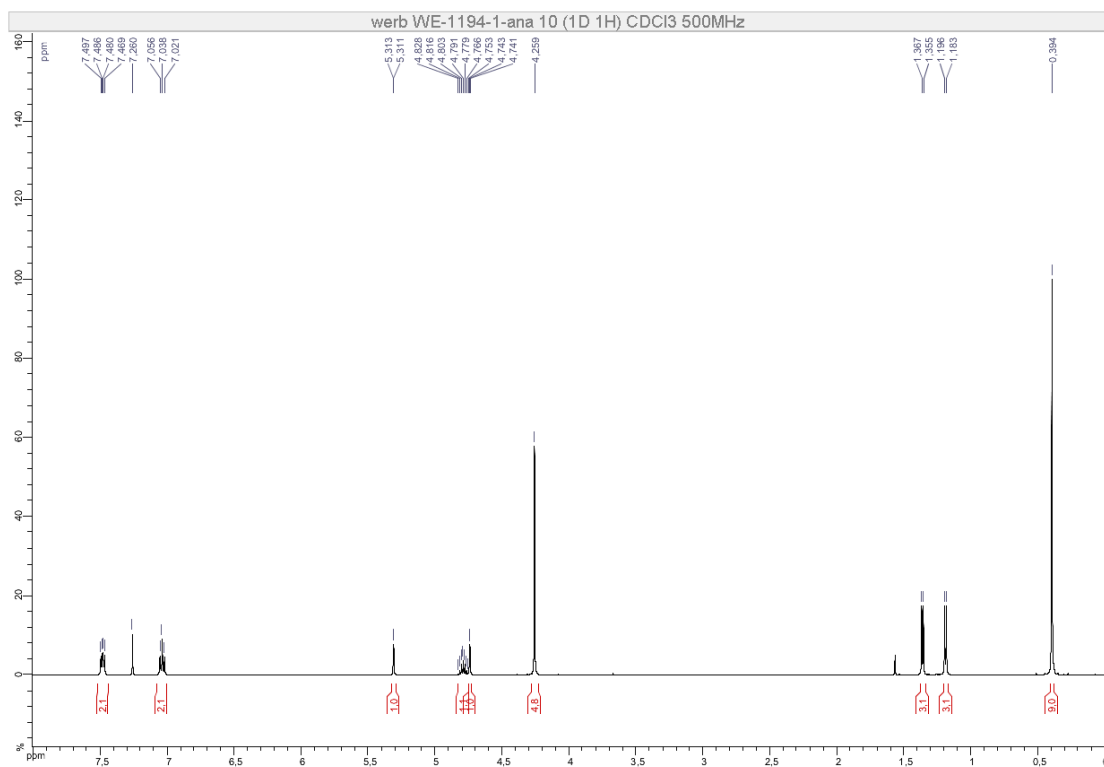
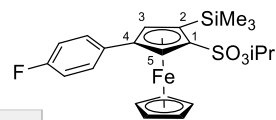


HMBC (500 MHz, CDCl₃)

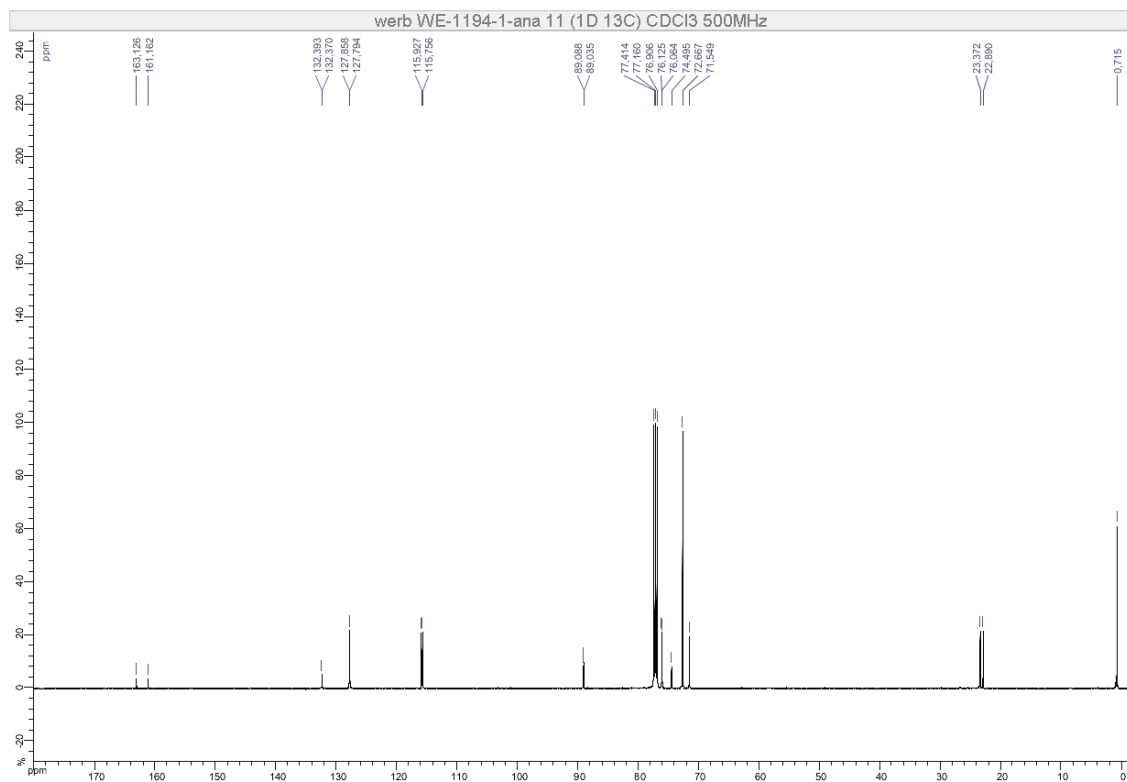


4-(4-Fluorophenyl)-*O*-isopropyl-2-(trimethylsilyl)ferrocenesulfonate (9, racemic mixture)

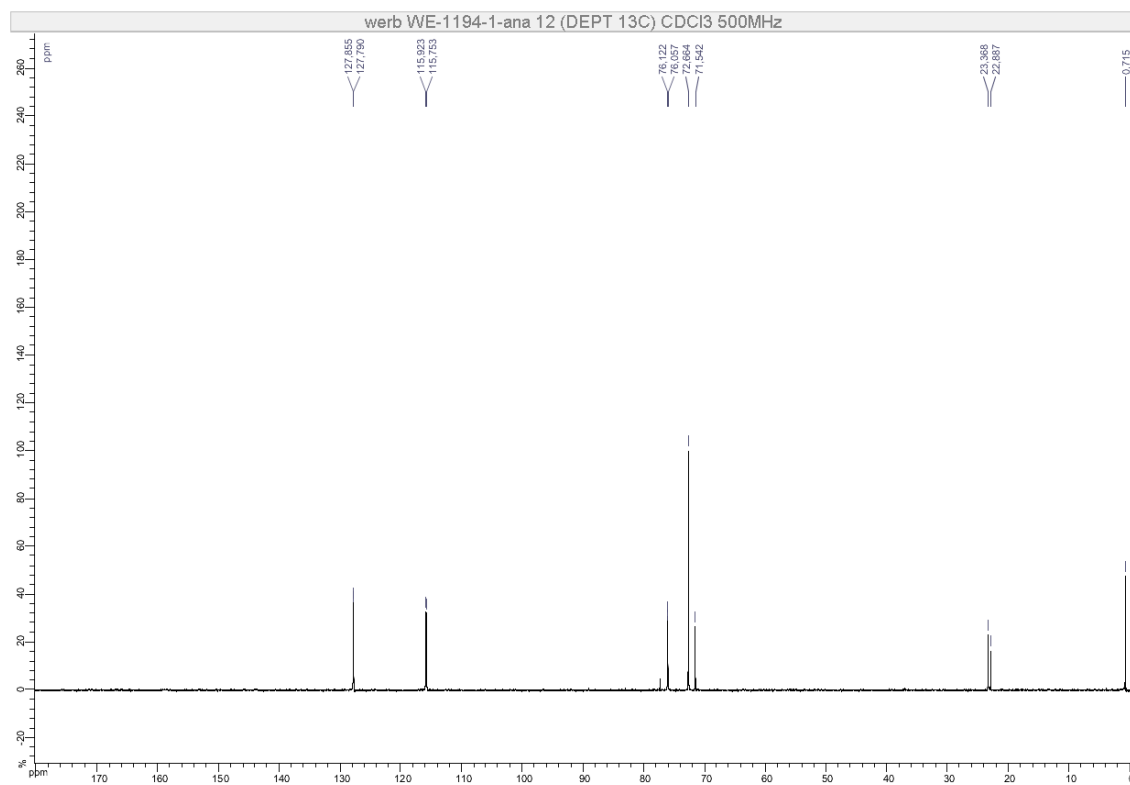
^1H NMR (500 MHz, CDCl_3)



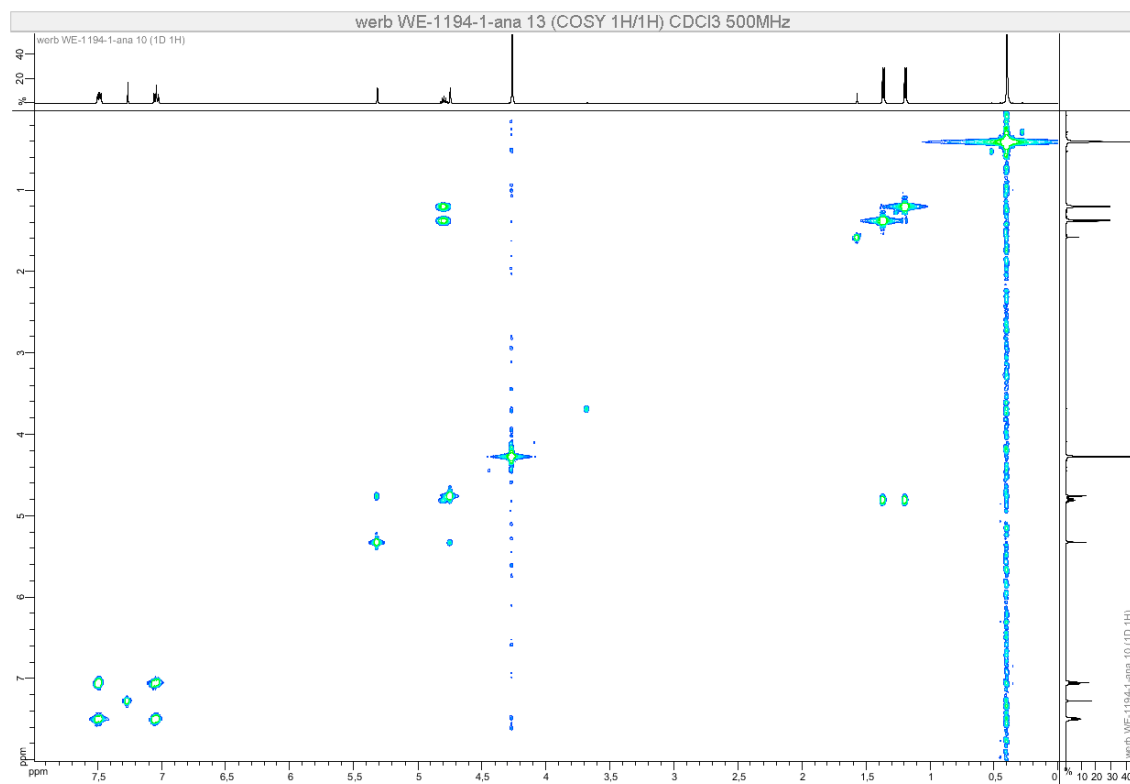
^{13}C NMR (126 MHz, CDCl_3)



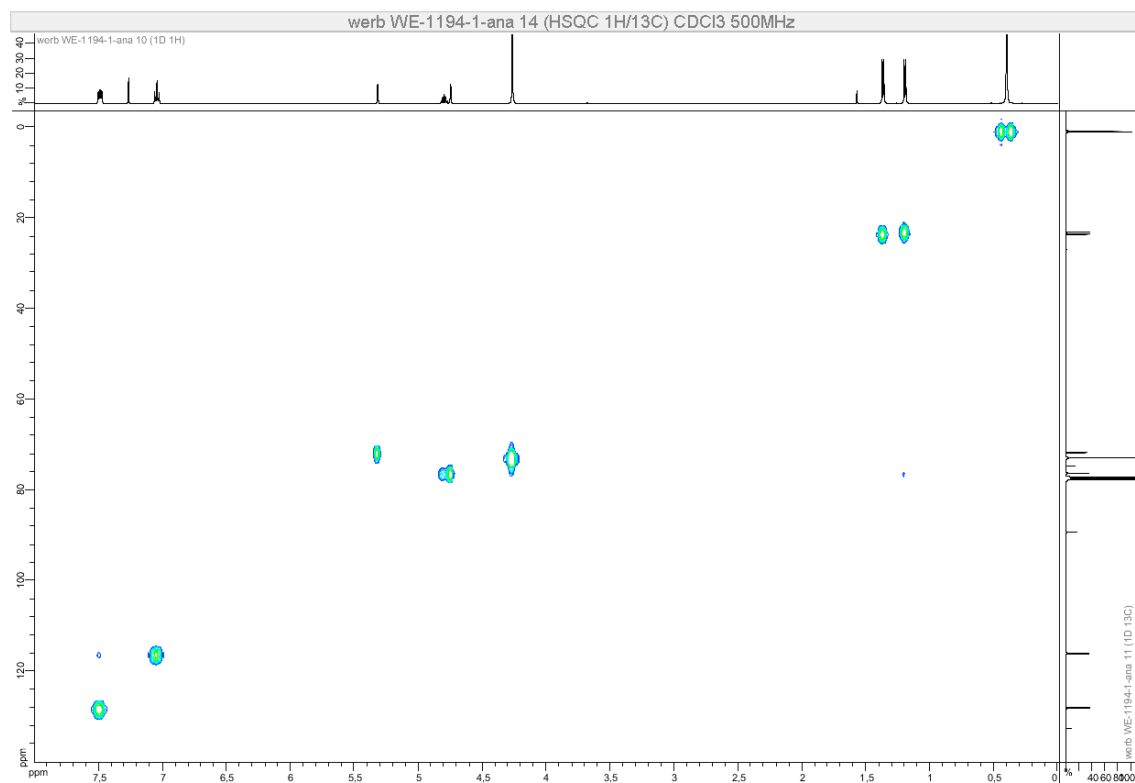
DEPT 135 (126 MHz, CDCl₃)



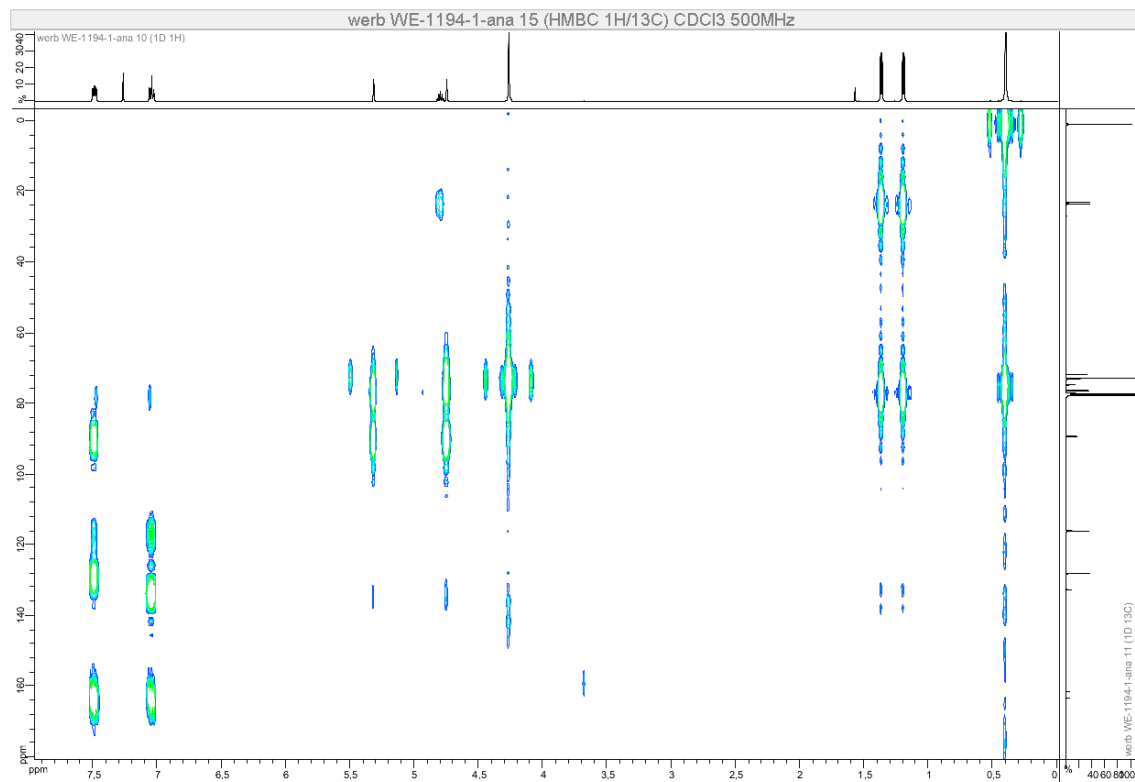
COSY (500 MHz, CDCl₃)



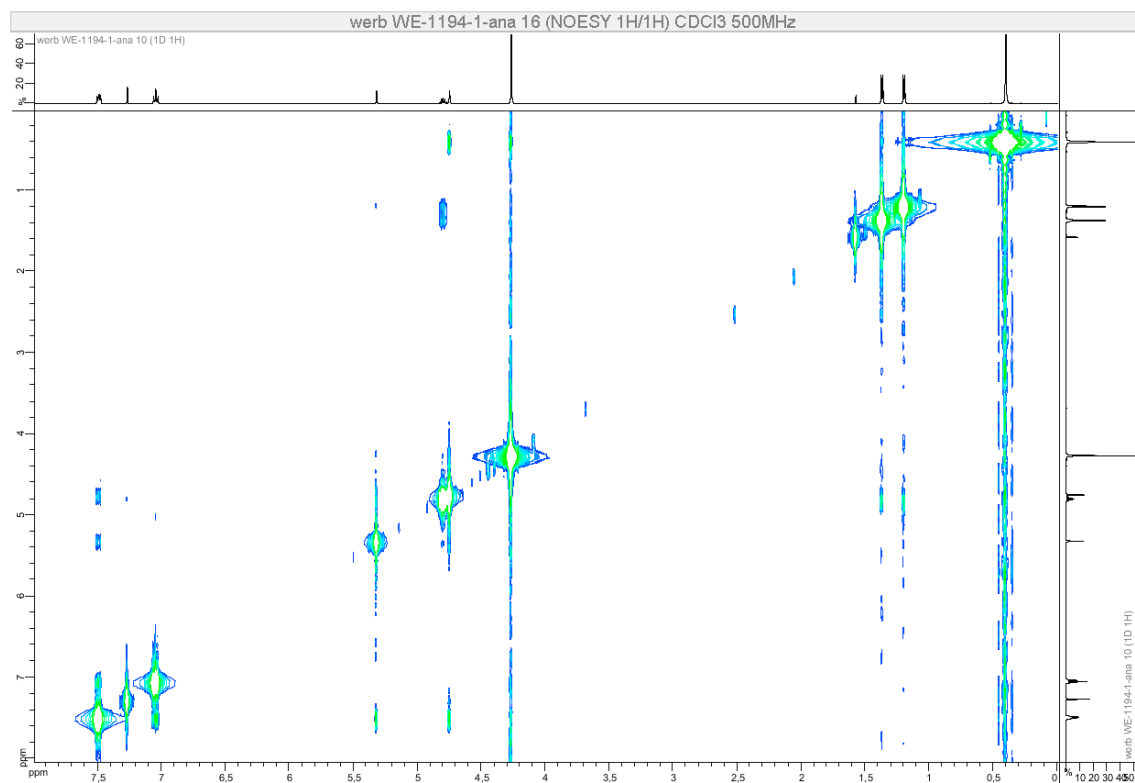
HSQC (500 MHz, CDCl₃)



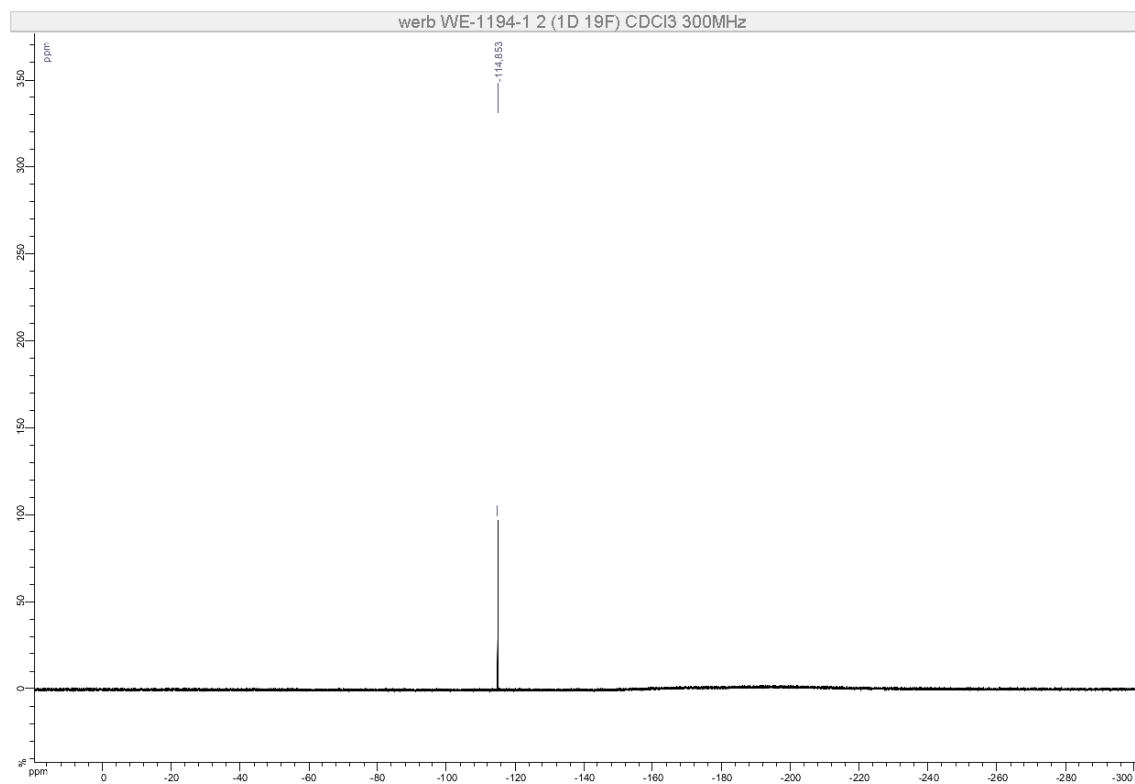
HMBC (500 MHz, CDCl₃)



NOESY (500 MHz, CDCl₃)

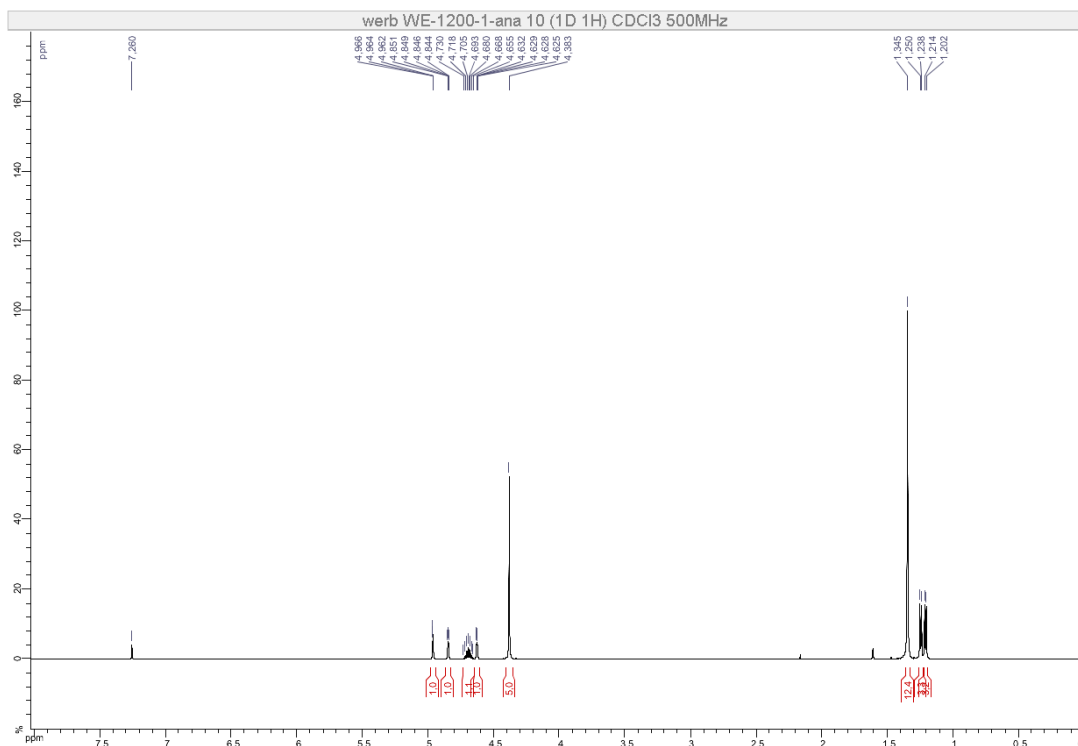
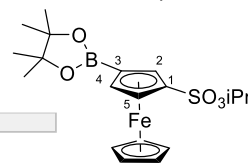


¹⁹F (282 MHz, CDCl₃)

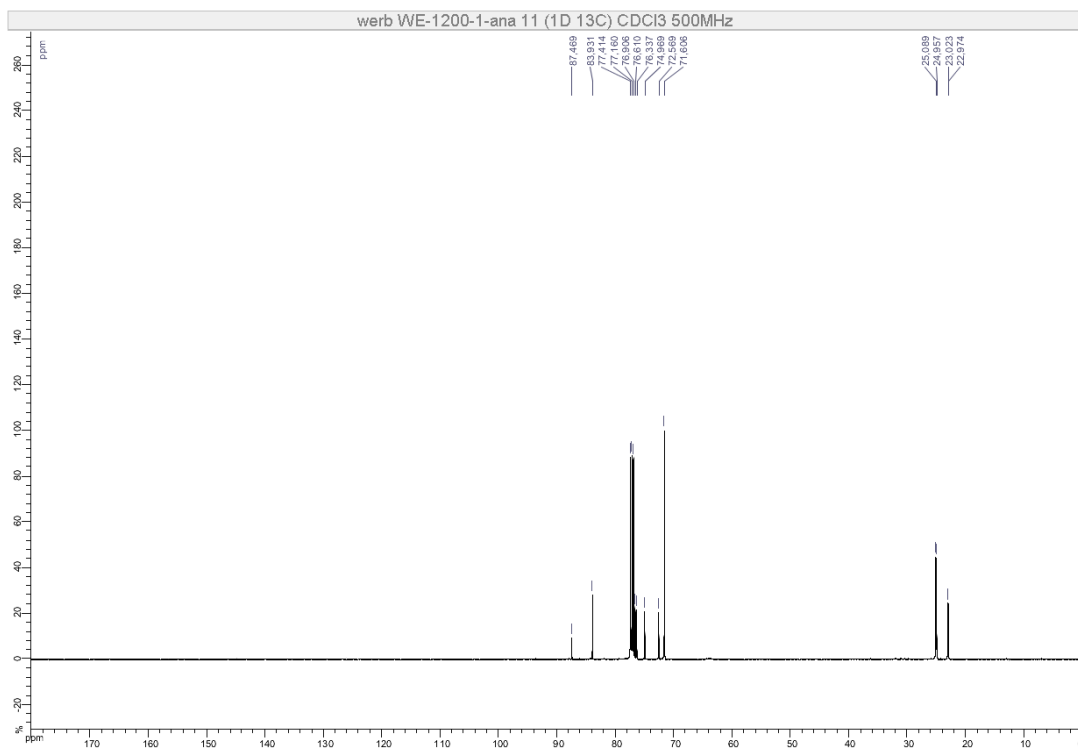


O-Isopropyl-3-[4,4,5,5-tetramethyl-2-(1,3,2-dioxaborolyl)]ferrocenesulfonate (10, racemic mixture)

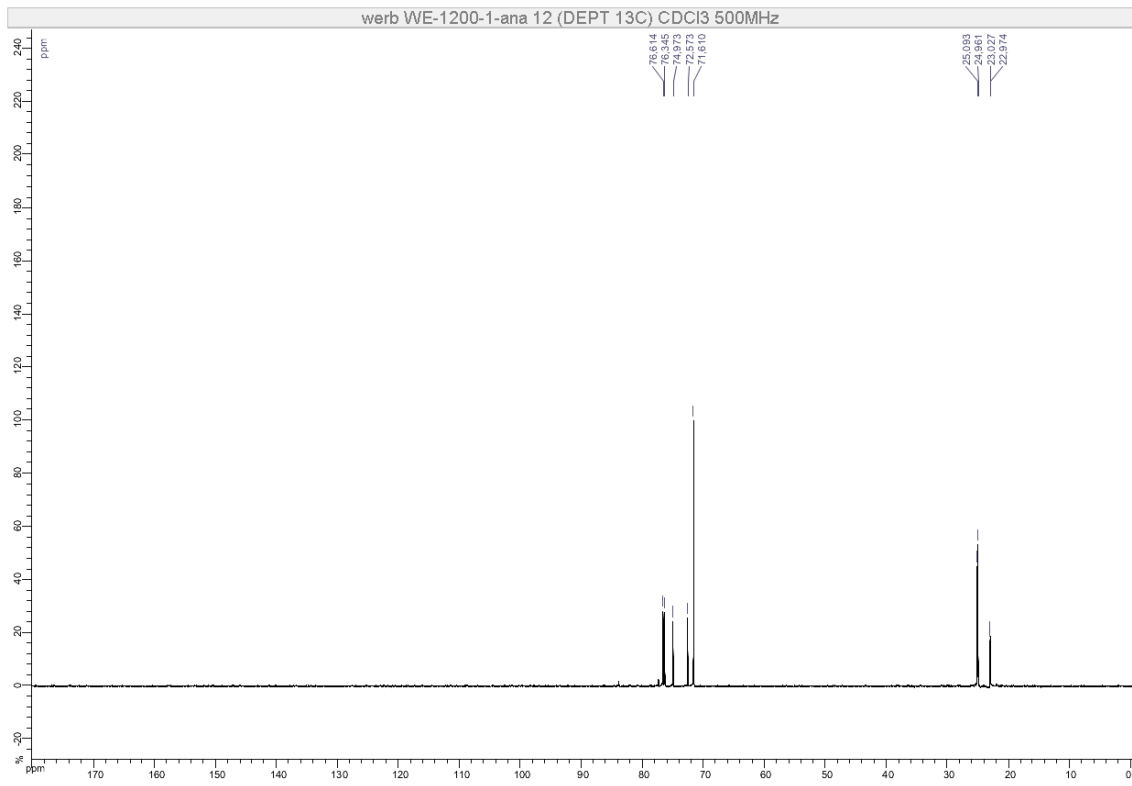
^1H NMR (500 MHz, CDCl_3)



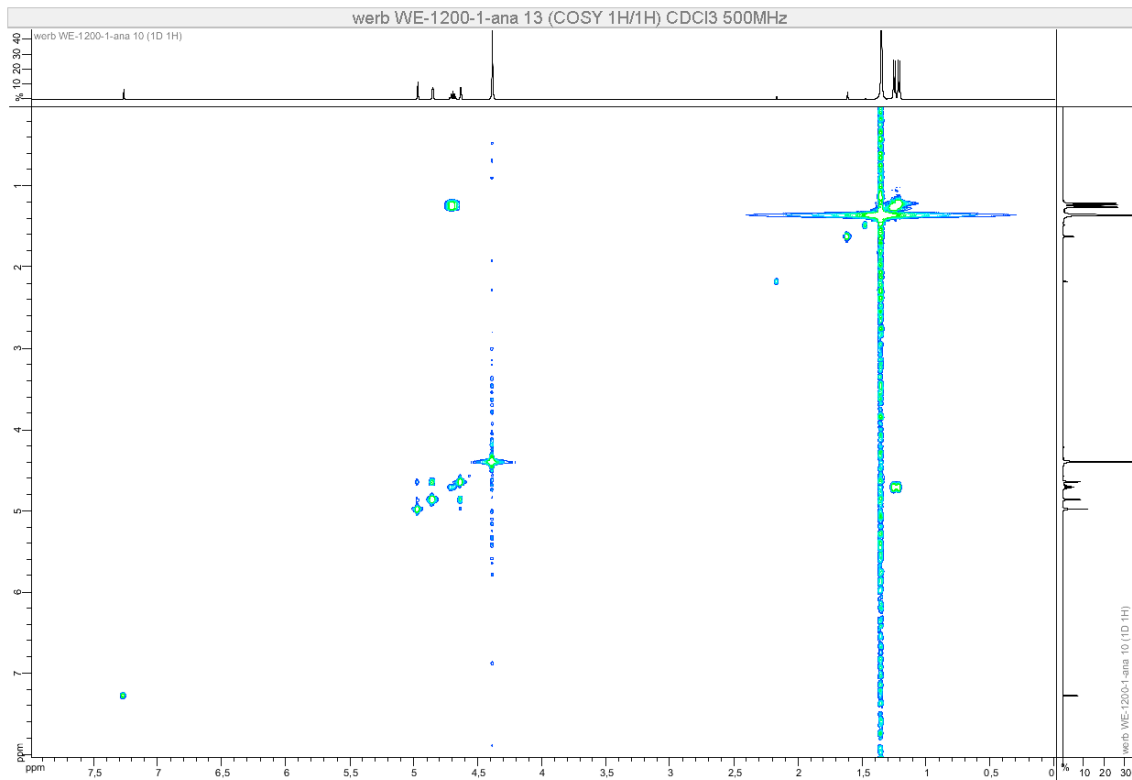
^{13}C NMR (126 MHz, CDCl_3)



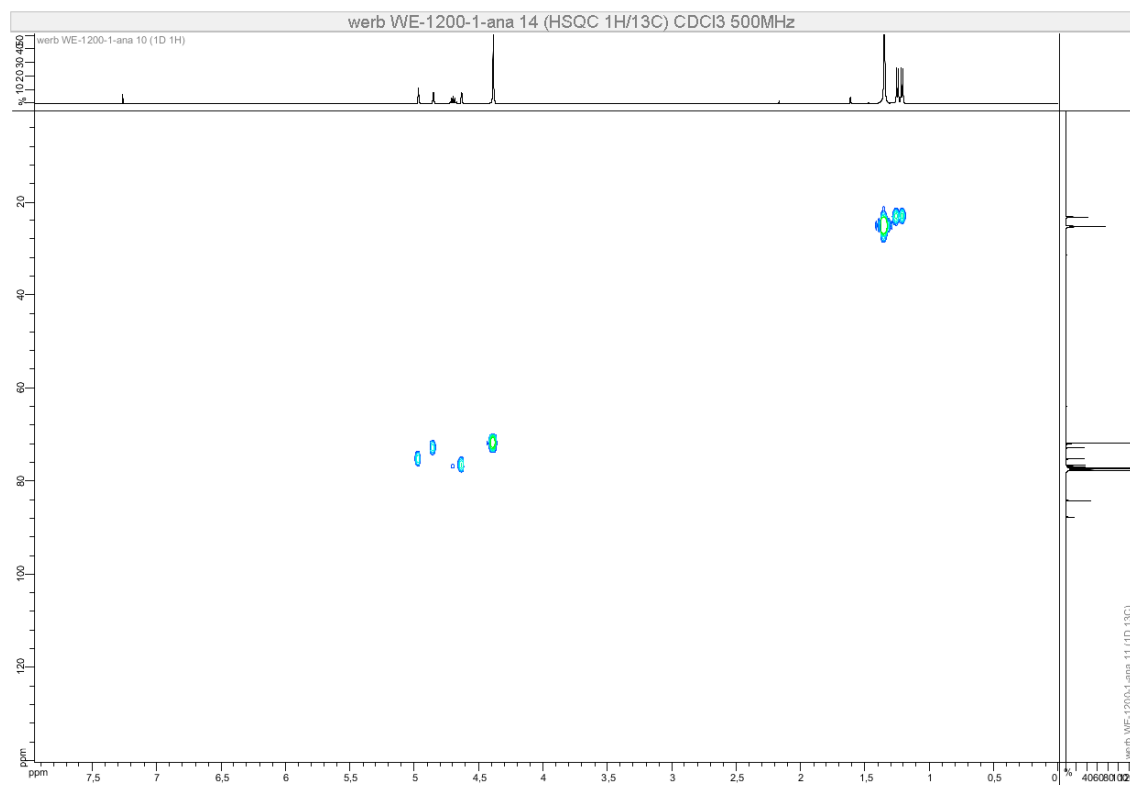
DEPT 135 (126 MHz, CDCl₃)



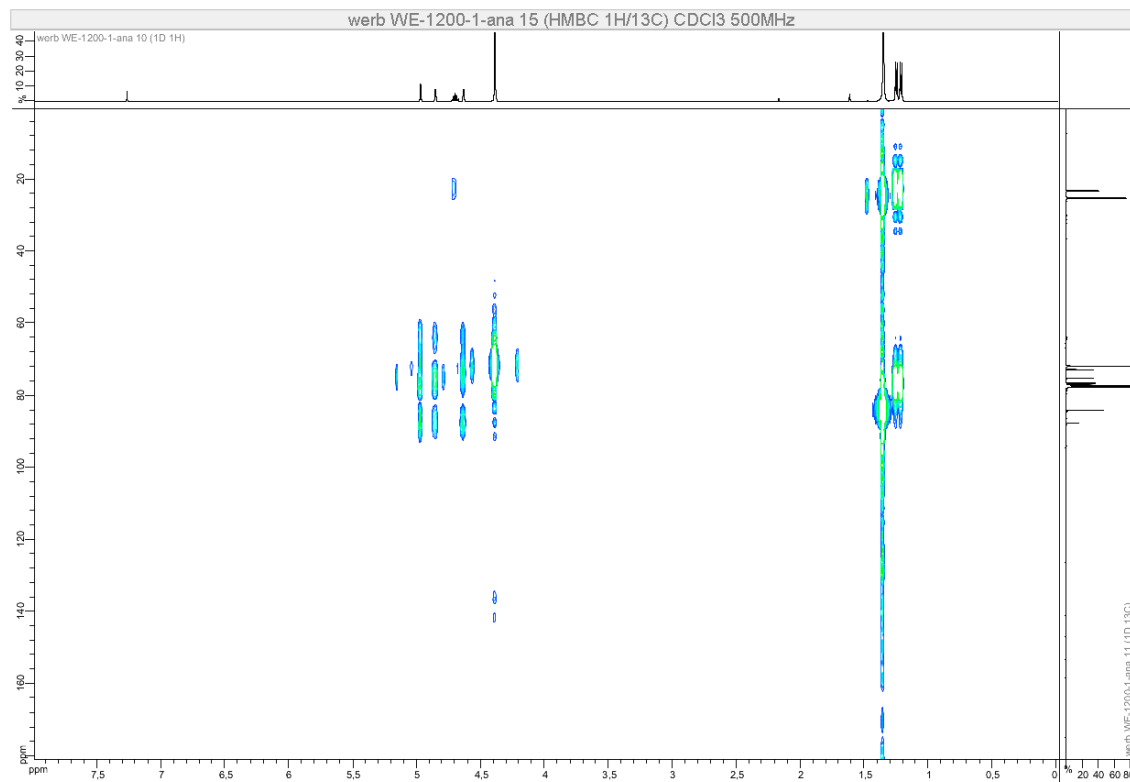
COSY (500 MHz, CDCl₃)



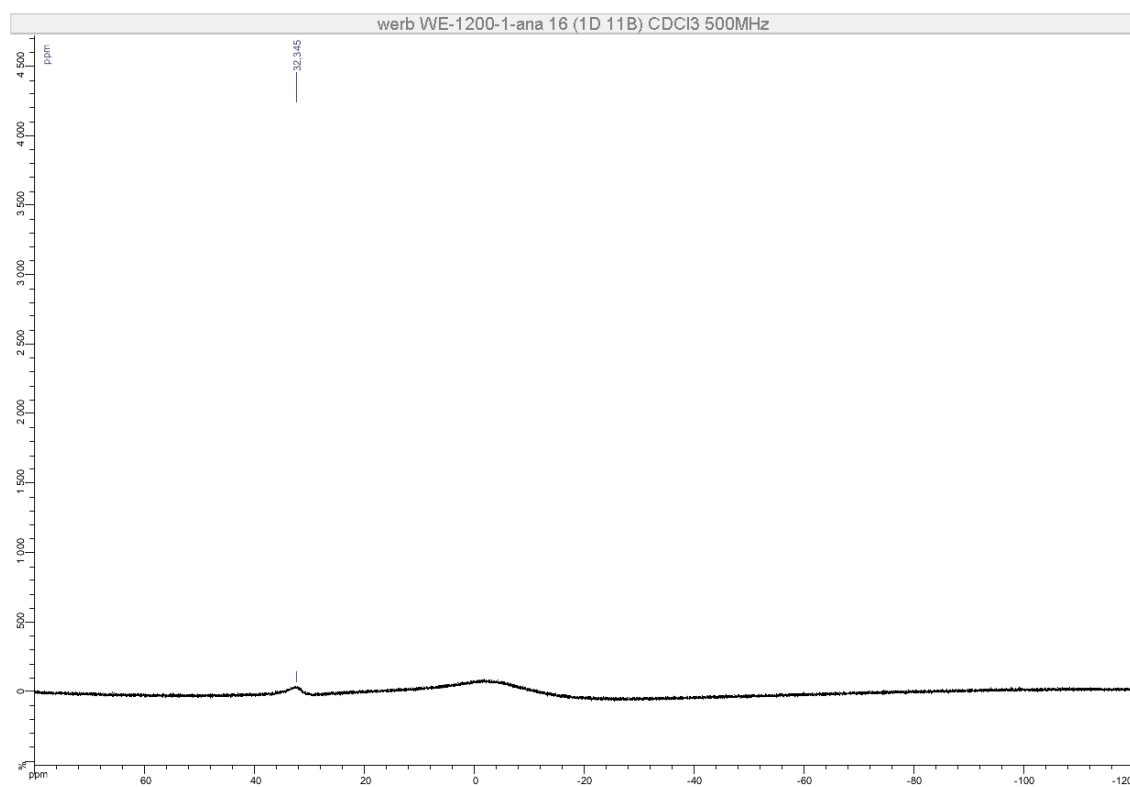
HSQC (500 MHz, CDCl₃)



HMBC (500 MHz, CDCl₃)

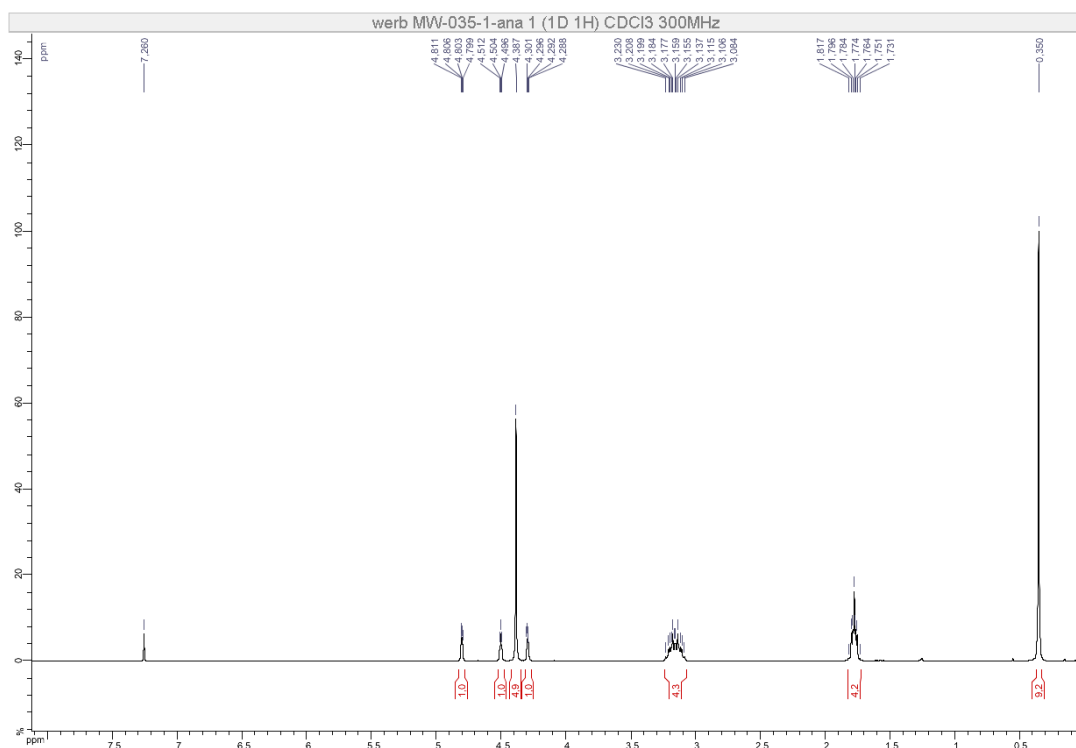


^{11}B (96 MHz, CDCl_3)

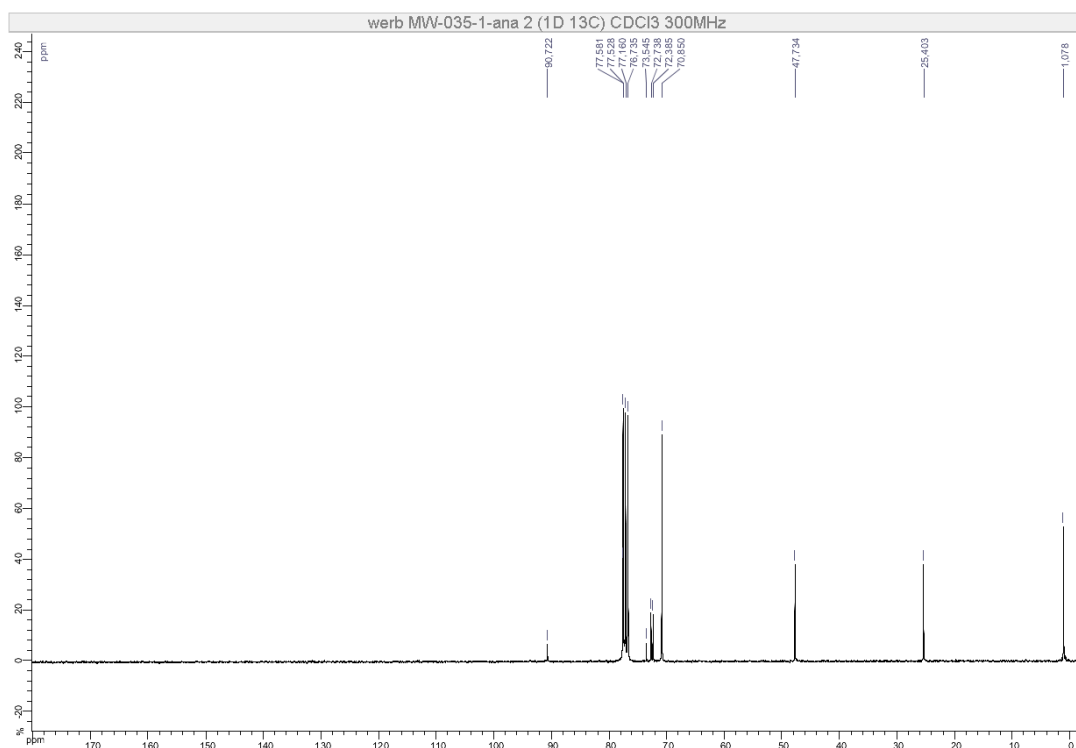


1-(*N*-Pyrrolidino)sulfonyl-2-(trimethylsilyl)ferrocene (racemic mixture)

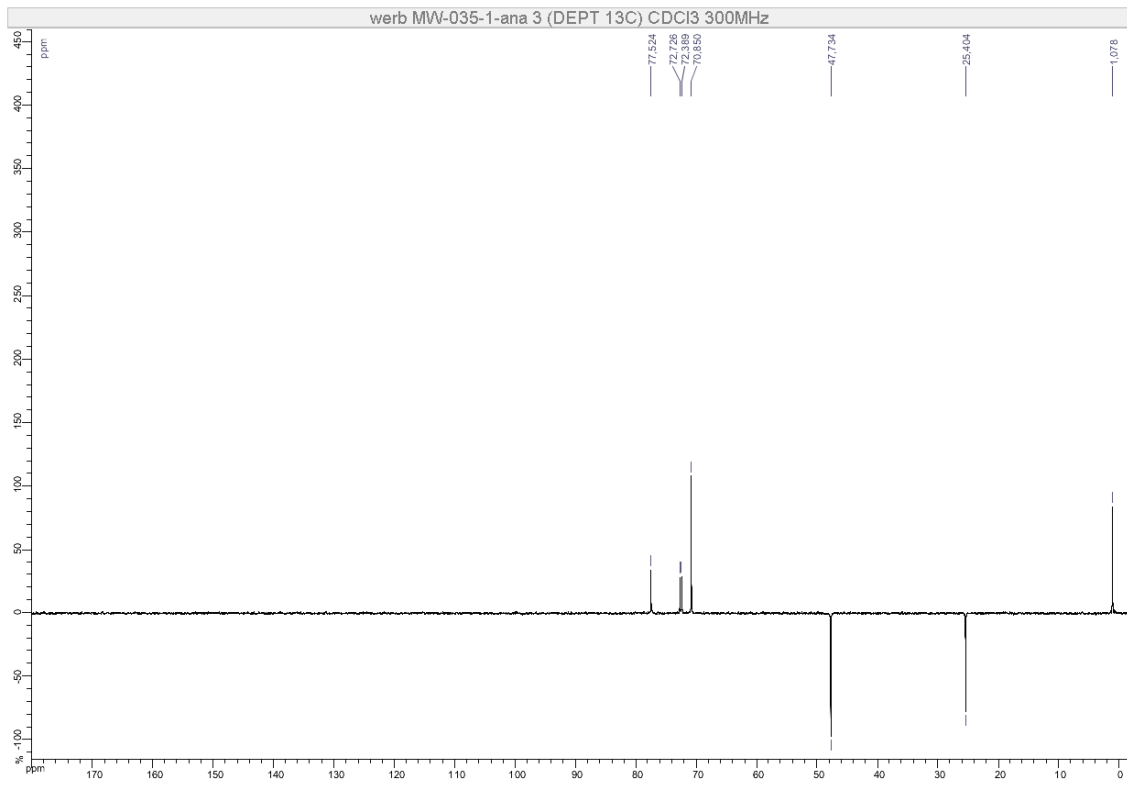
^1H NMR (300 MHz, CDCl_3)



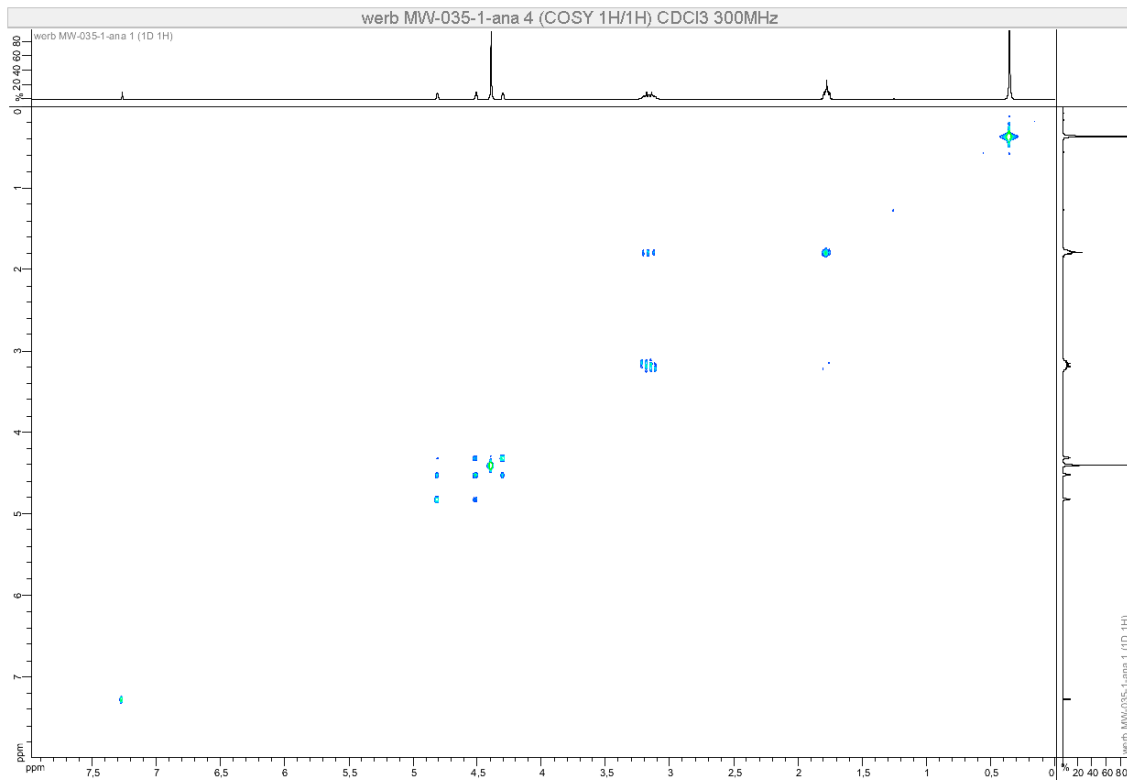
^{13}C NMR (75 MHz, CDCl_3)



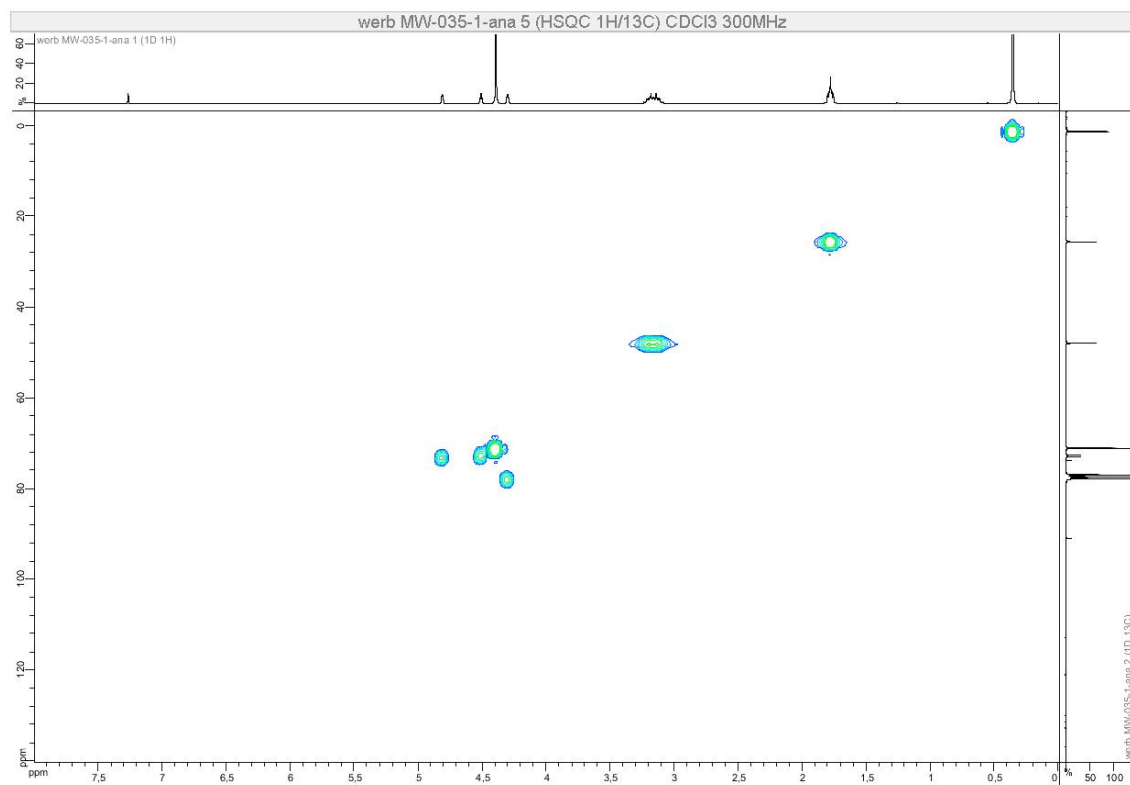
DEPT 135 (75 MHz, CDCl₃)



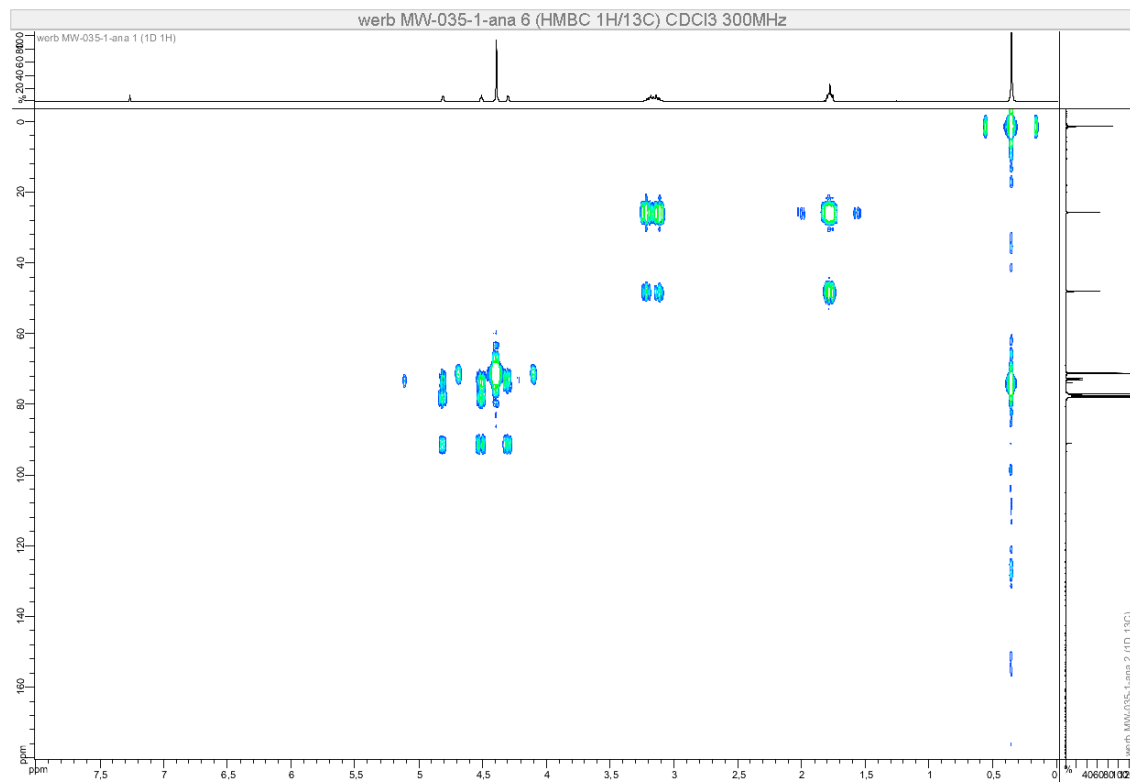
COSY (300 MHz, CDCl₃)



HSQC (300 MHz, CDCl₃)

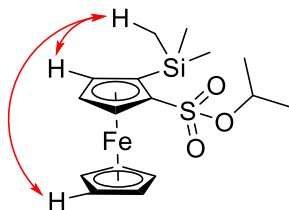


HMBC (300 MHz, CDCl₃)

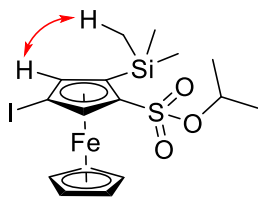


Selected NOESY correlations observed

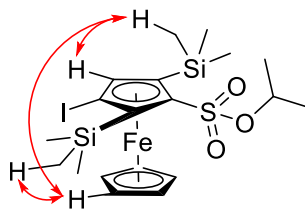
Compound *rac-4*



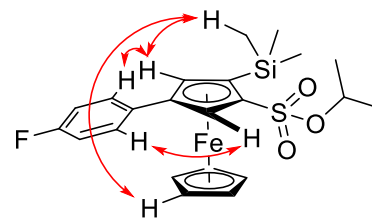
Compound *rac-6*



Compound *rac-7*

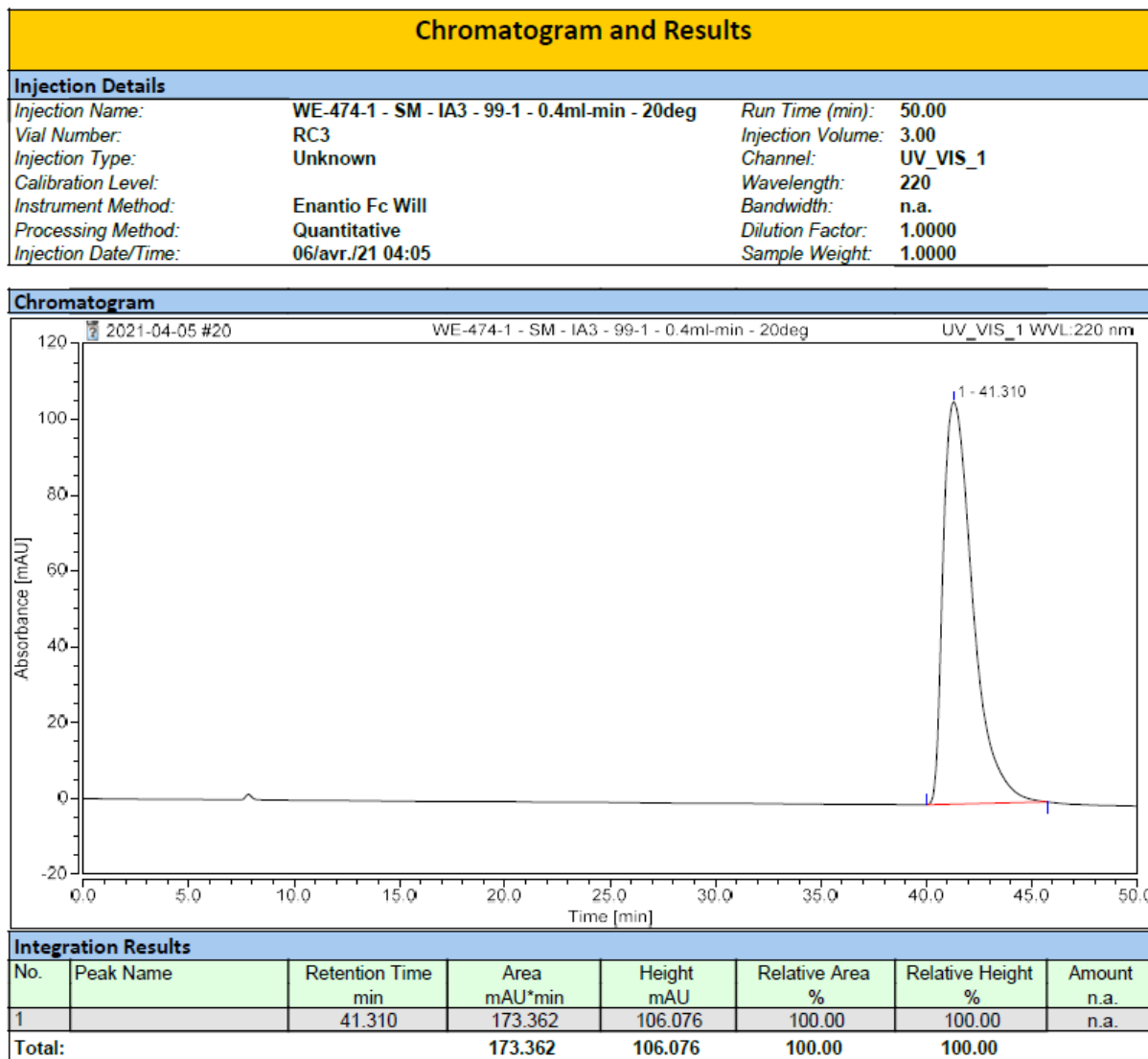


Compound *rac-9*

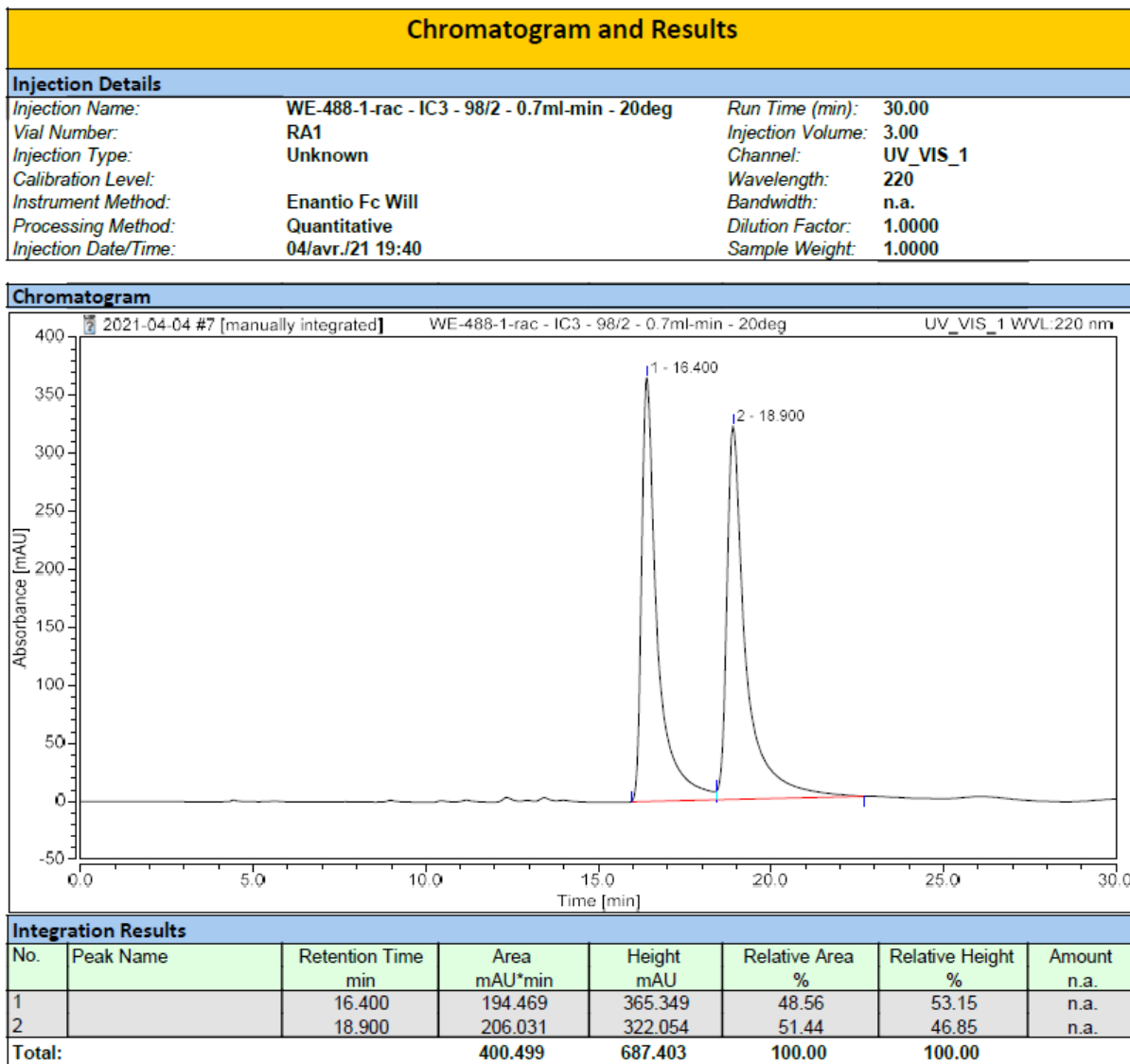


HPLC Chromatograms

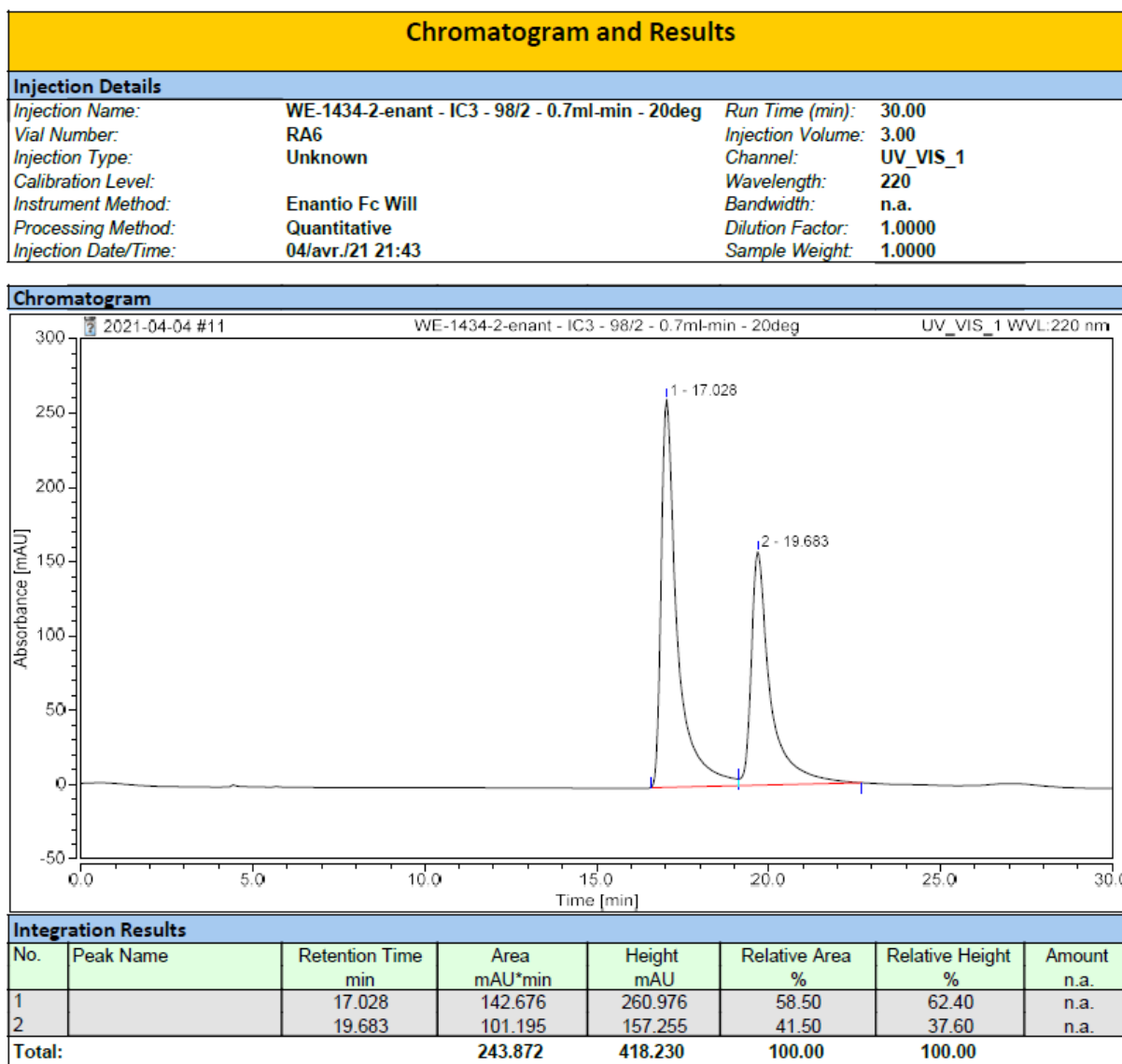
O-Isopropylferrocenesulfonate (1)



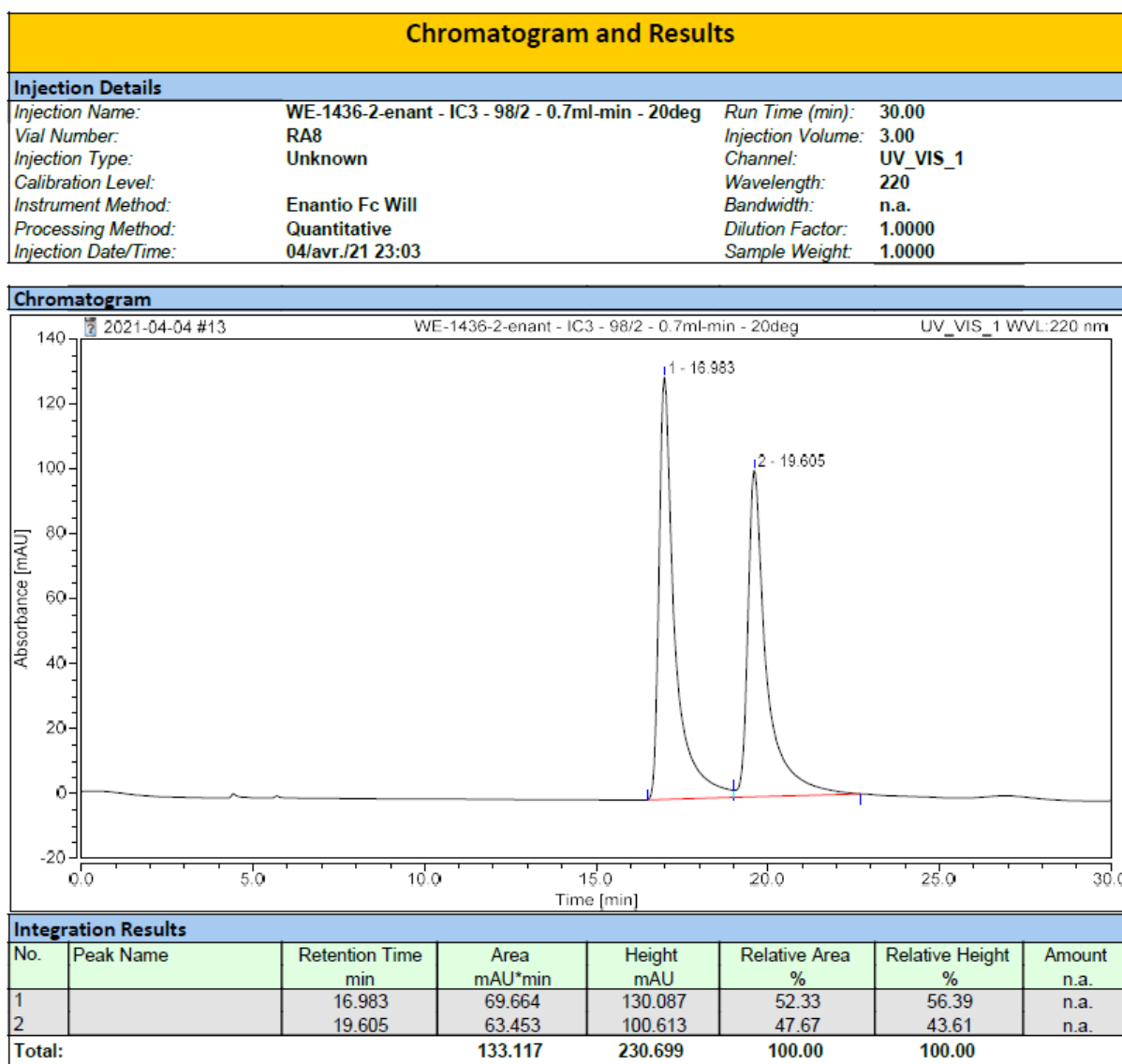
Compound (±)-*O*-isopropyl-2-(trimethylsilyl)ferrocenesulfonate (4)



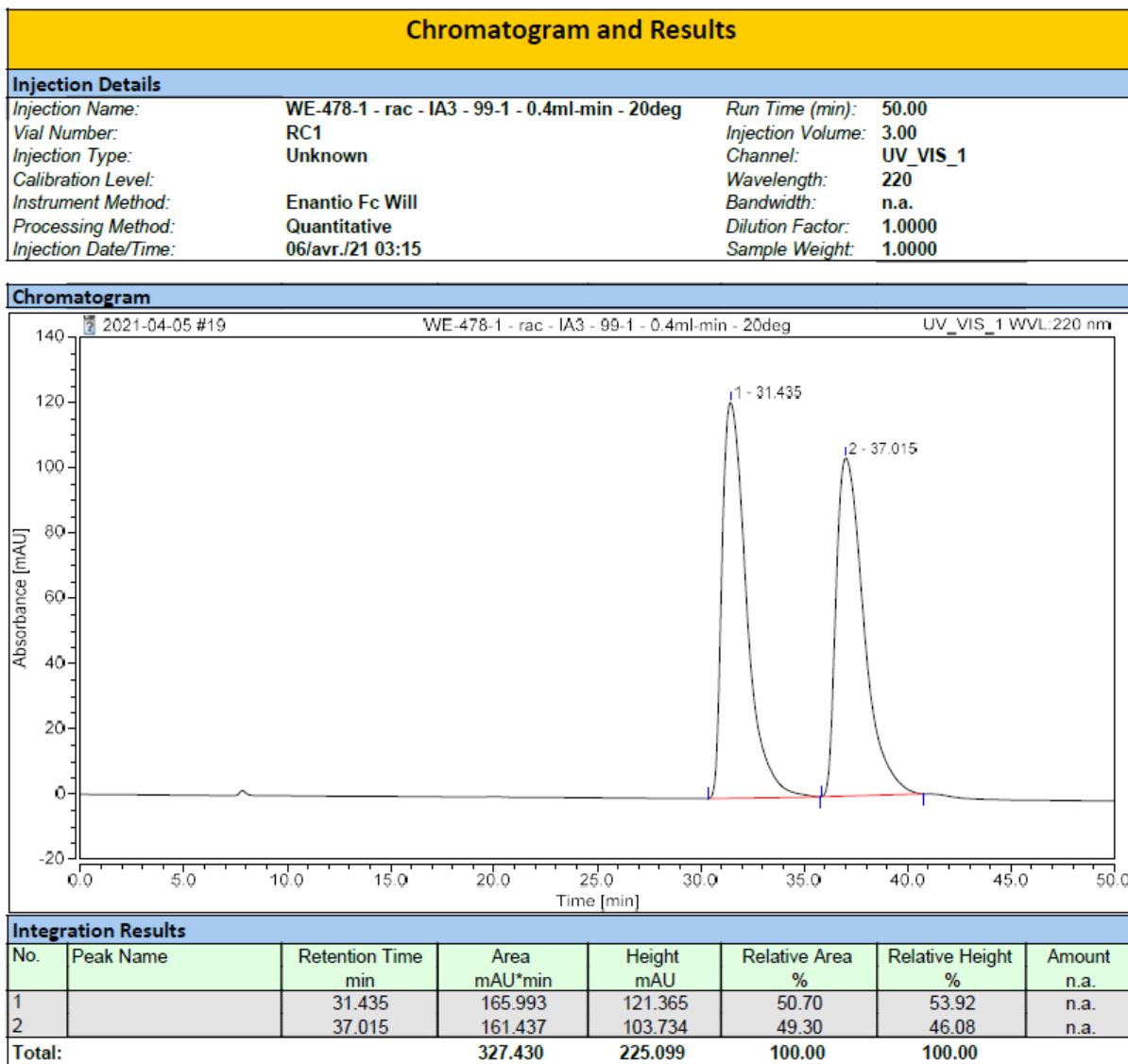
Deprotonation of *O*-isopropylferrocenesulfonate (1) with *s*BuLi·TMEDA using chlorotrimethylsilane as electrophile



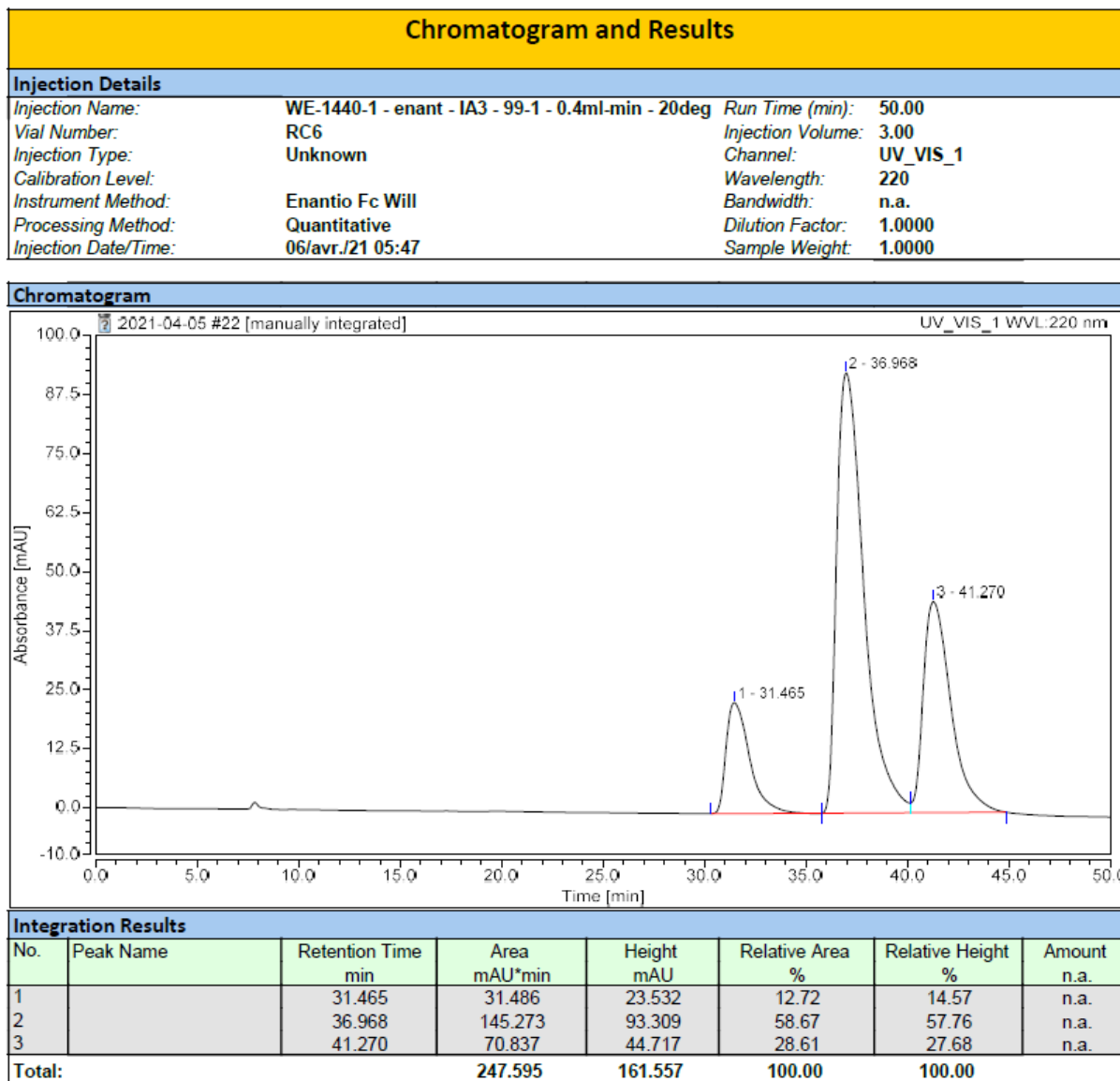
Deprotonation of *O*-isopropylferrocenesulfonate (1) with PEALi using chlorotrimethylsilane as *in situ* trap



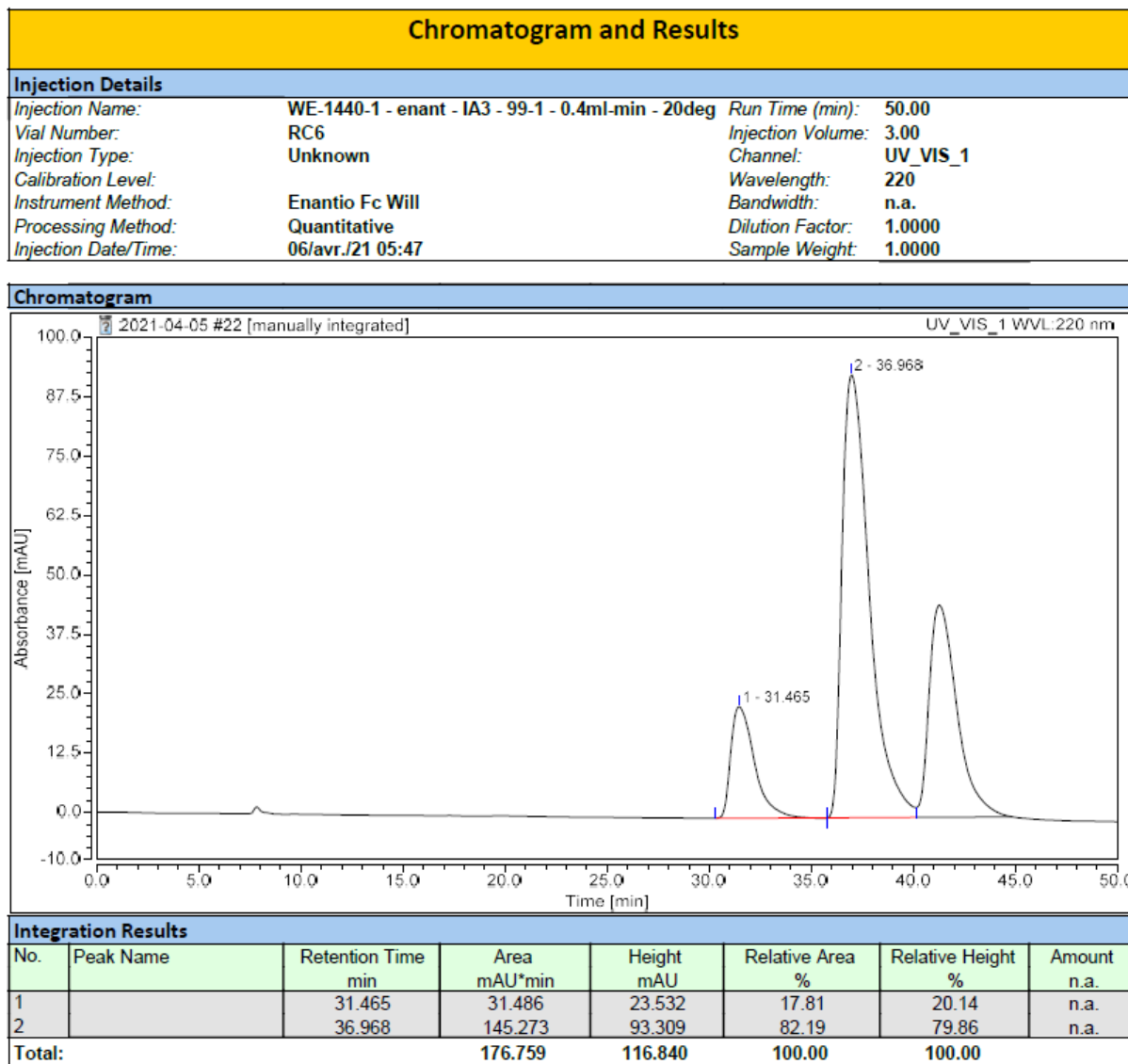
Compound (±)-2-iodo-*O*-isopropylferrocenesulfonate (3)



Deprotonation of *O*-isopropylferrocenesulfonate (1) with PEALi using (PEA)₂Zn as *in situ* trap



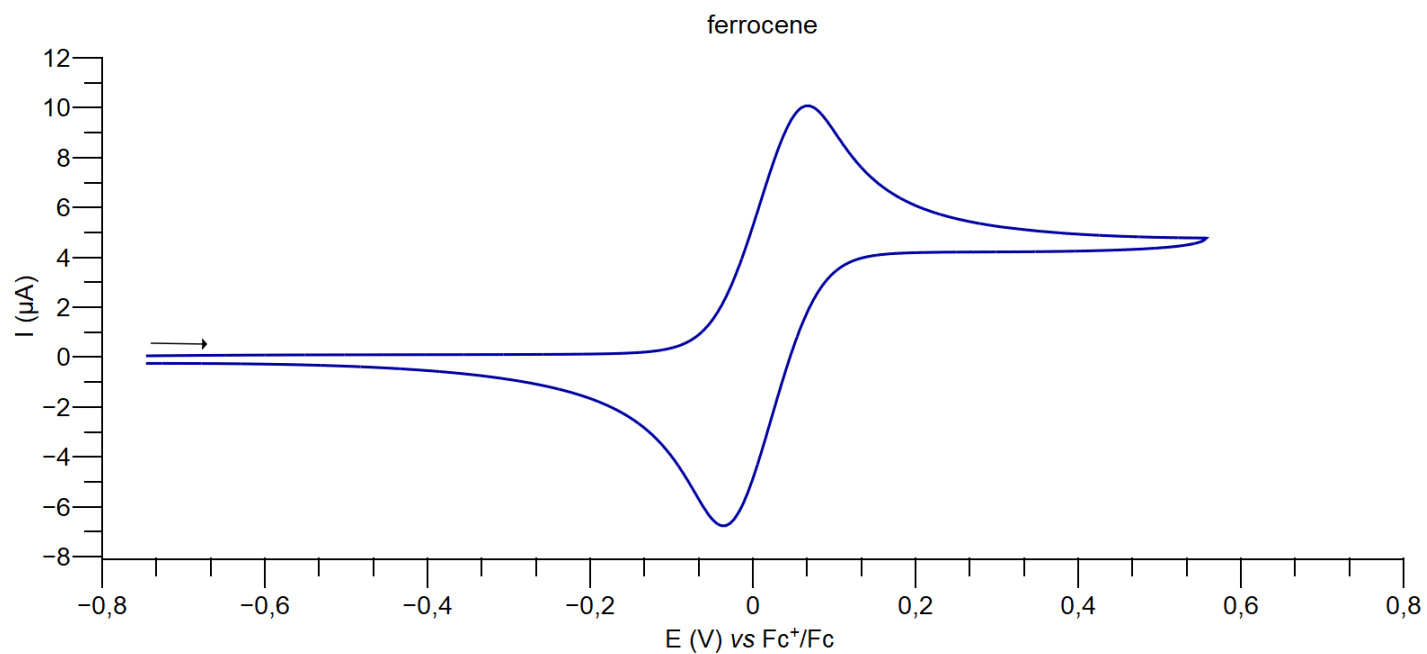
Deprotonation of *O*-isopropylferrocenesulfonate (1) with PEALi using (PEA)₂Zn as *in situ* trap



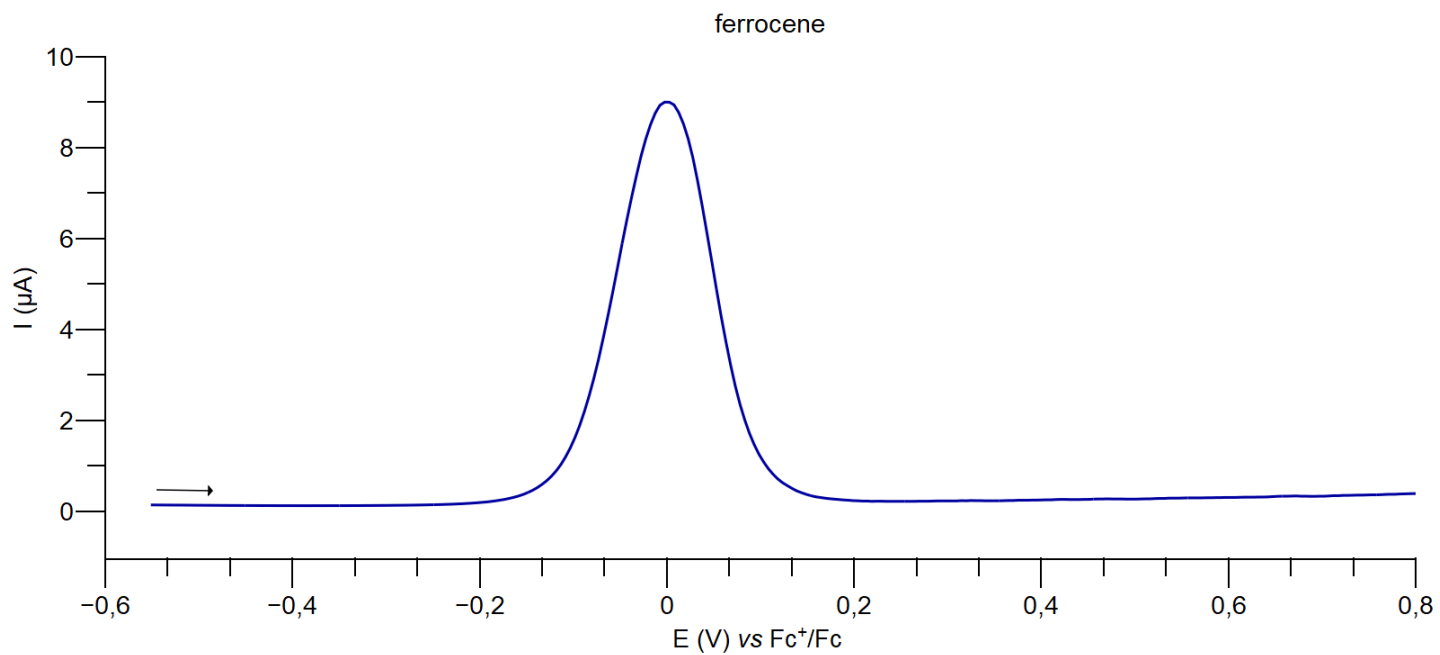
Electrochemical measurements

Ferrocene

Cyclic voltammetry

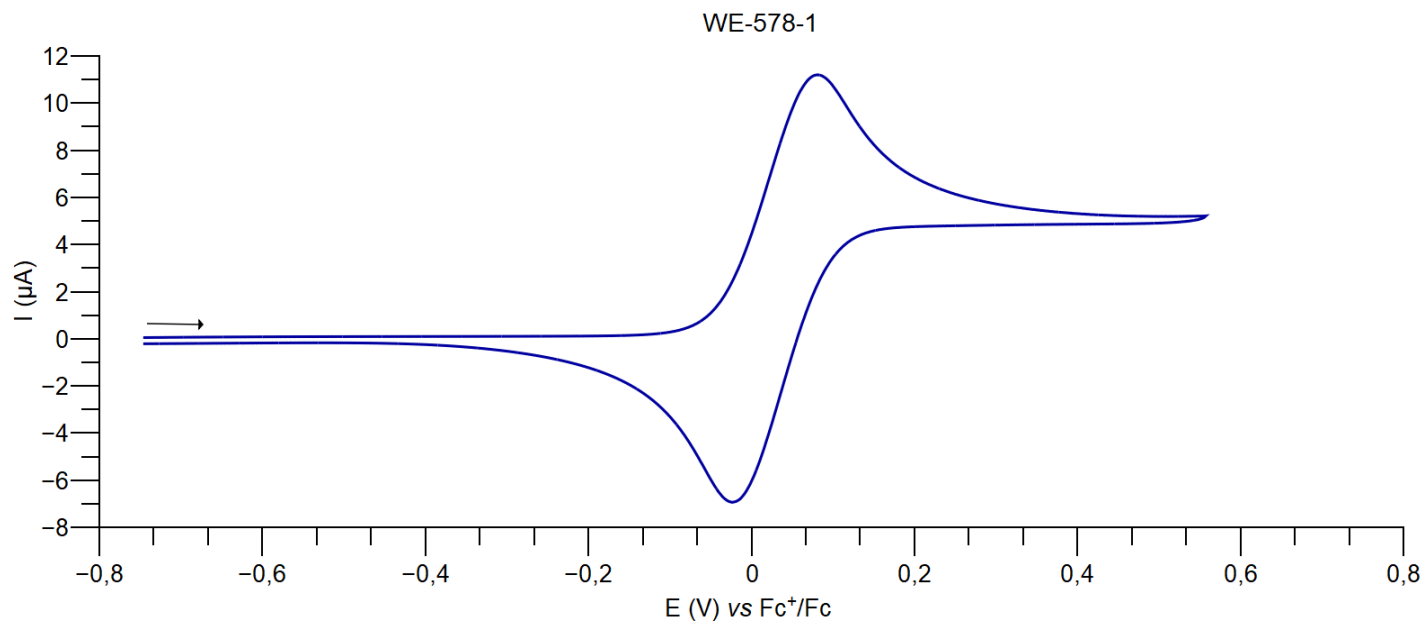


Differential pulse voltammetry

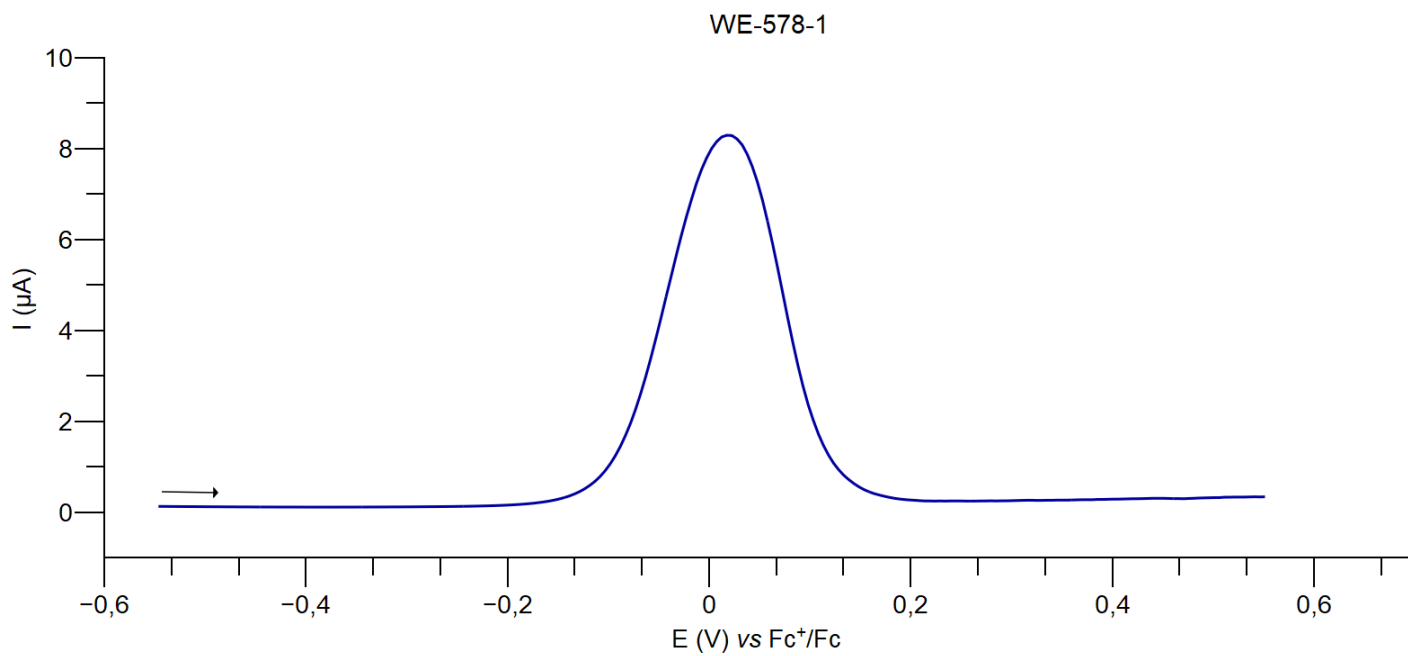


(Trimethylsilyl)ferrocene

Cyclic voltammetry

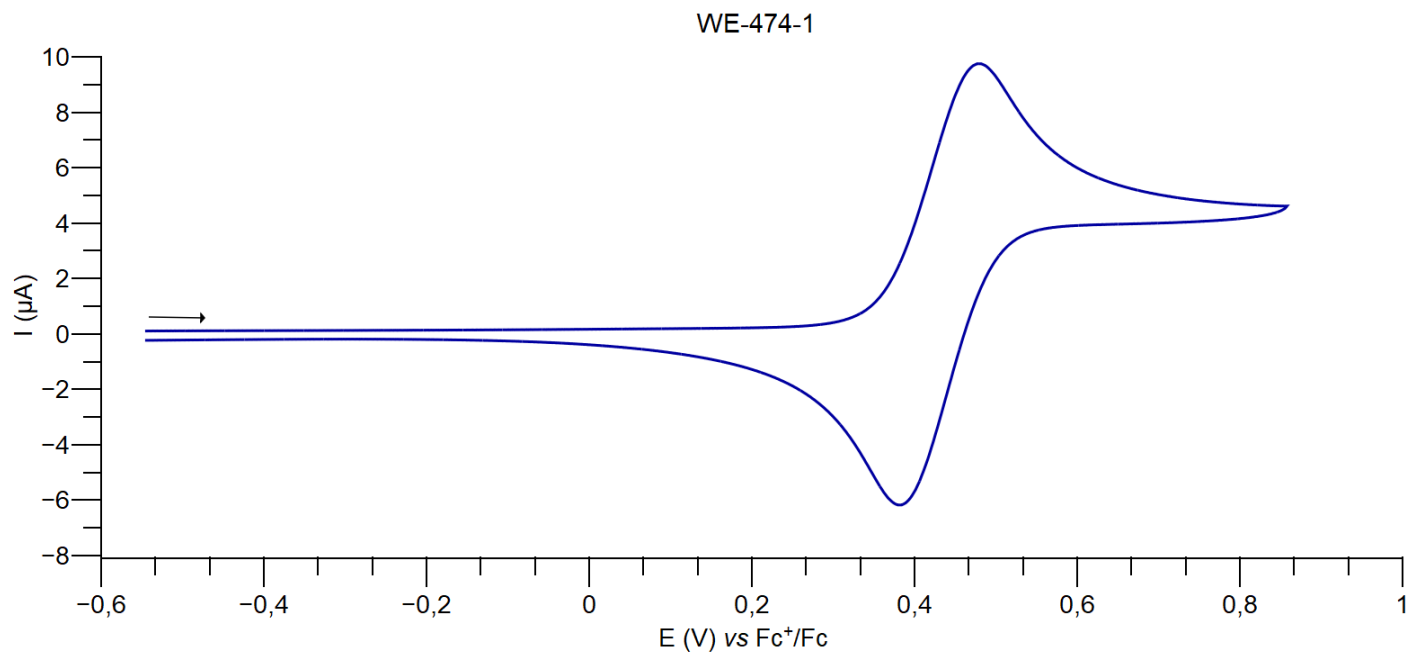


Differential pulse voltammetry

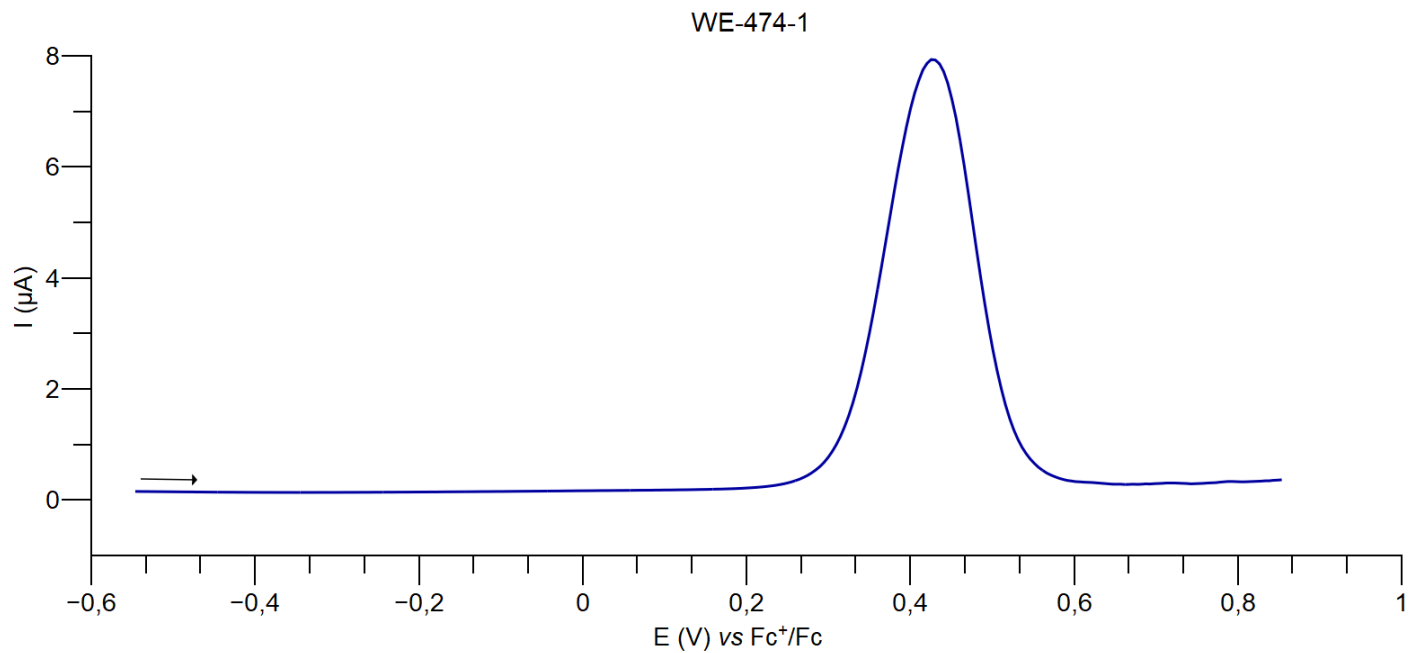


***O*-Isopropylferrocenesulfonate (1)**

Cyclic voltammetry

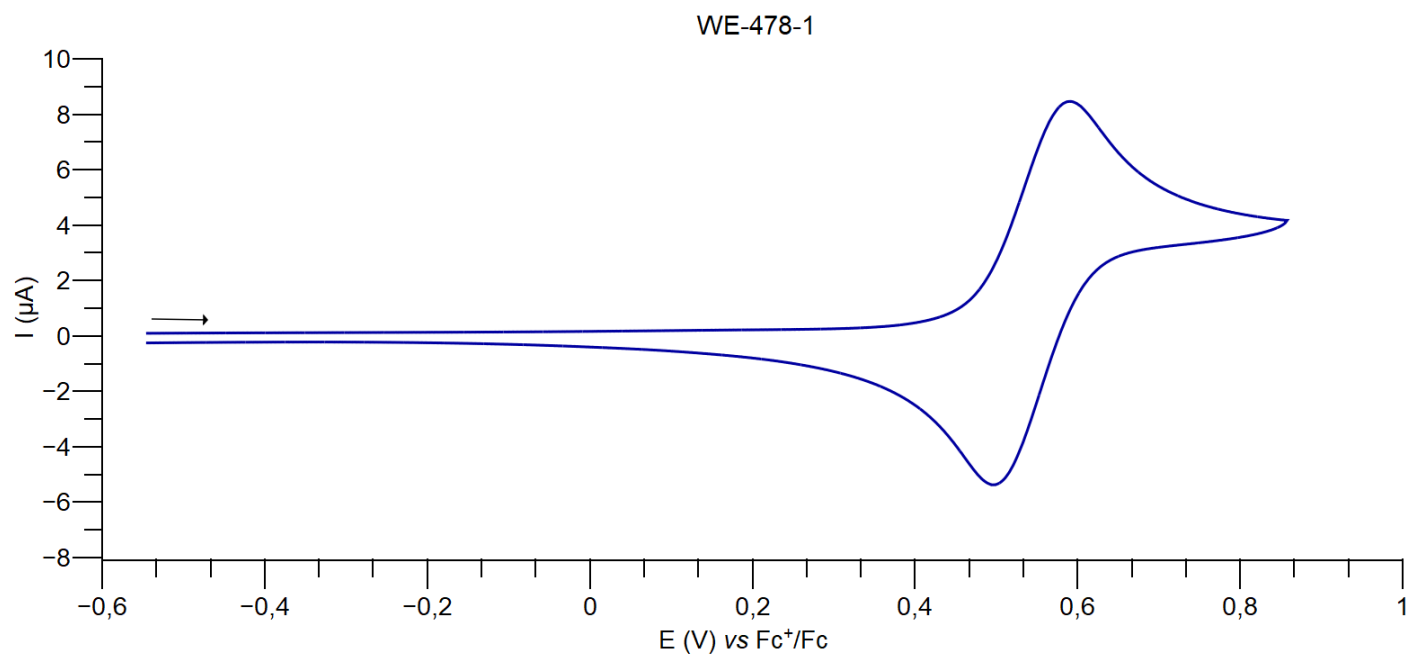


Differential pulse voltammetry

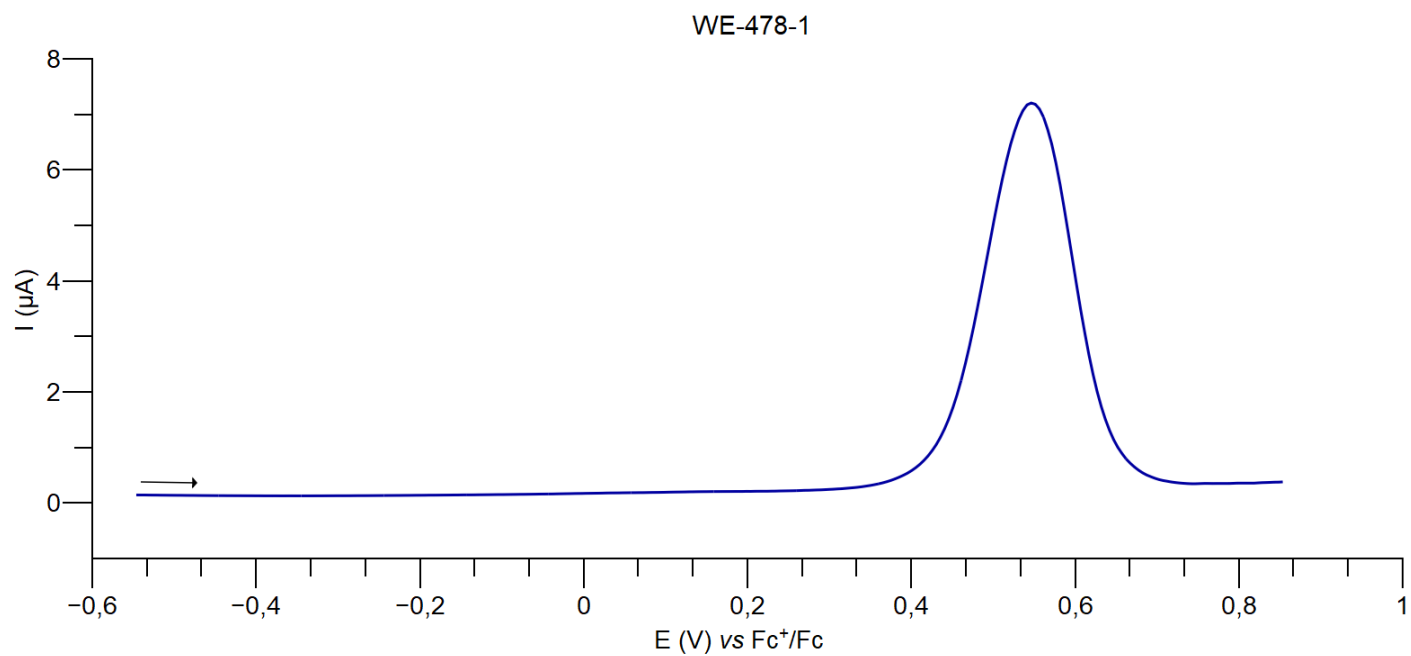


2-Iodo-*O*-isopropylferrocenesulfonate (3)

Cyclic voltammetry

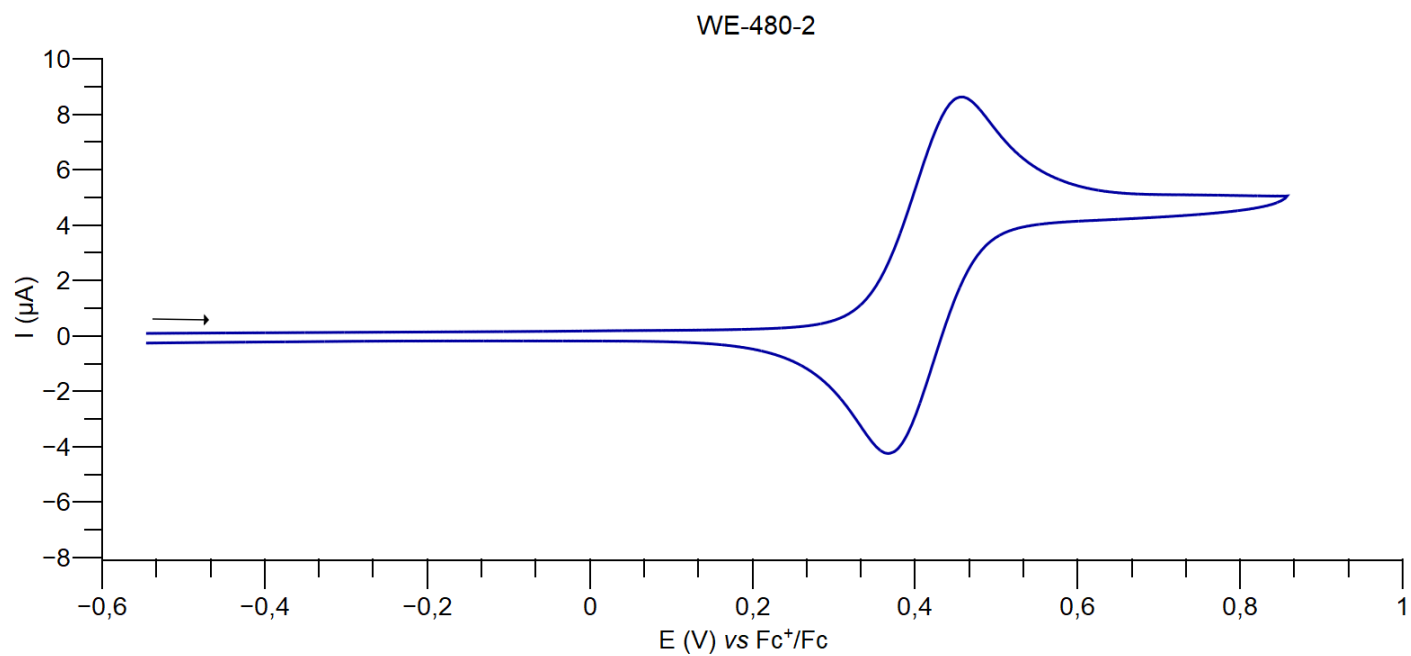


Differential pulse voltammetry

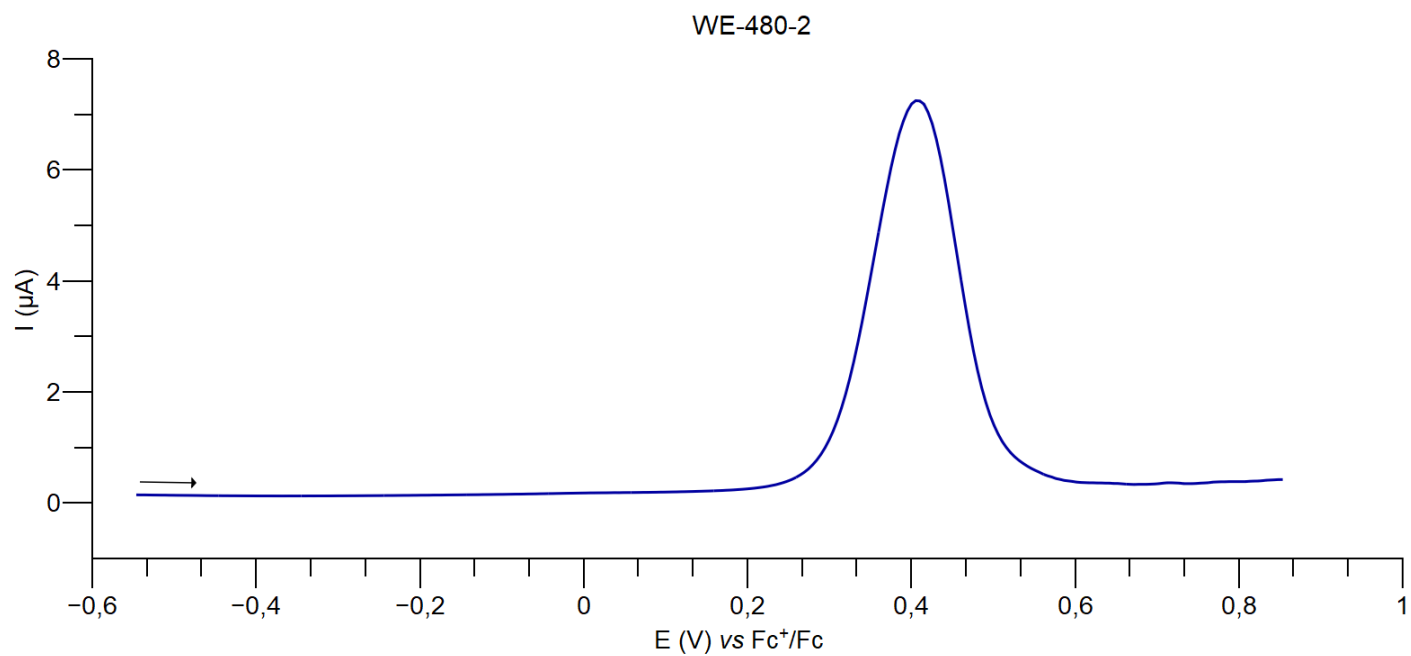


***O*-Isopropyl-2-(trimethylsilyl)ferrocenesulfonate (3)**

Cyclic voltammetry

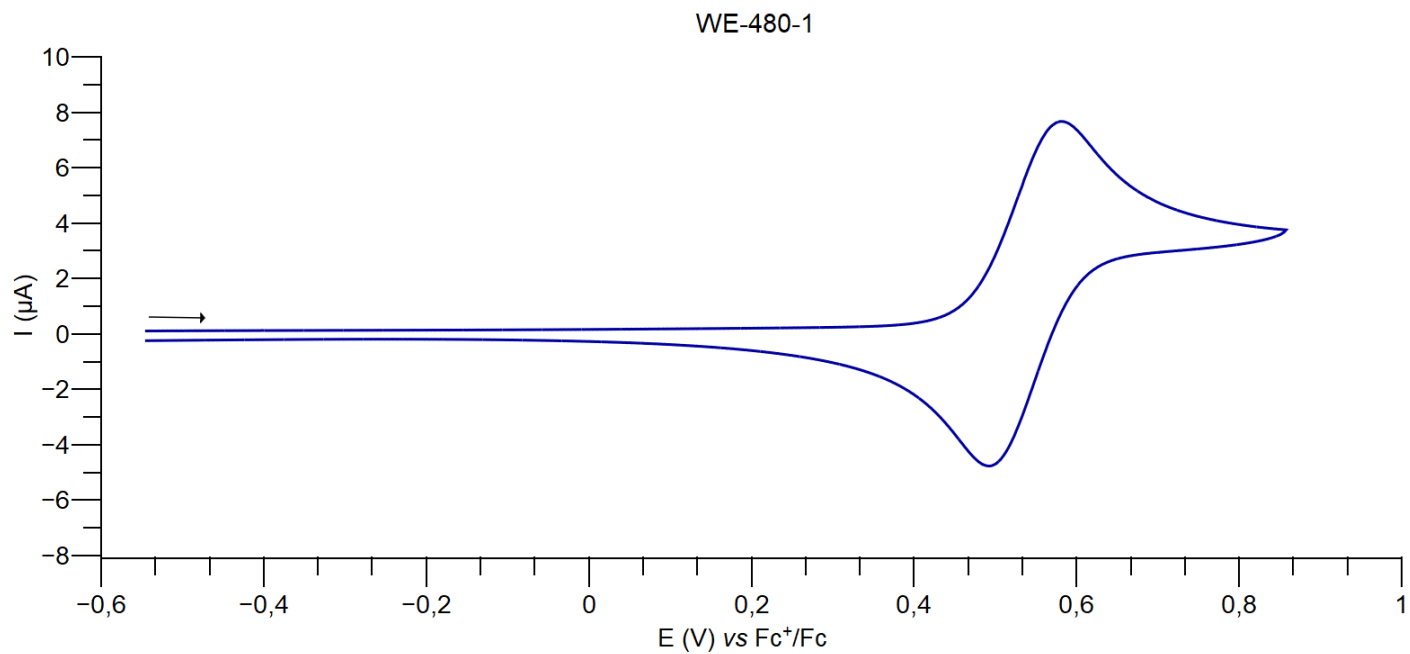


Differential pulse voltammetry

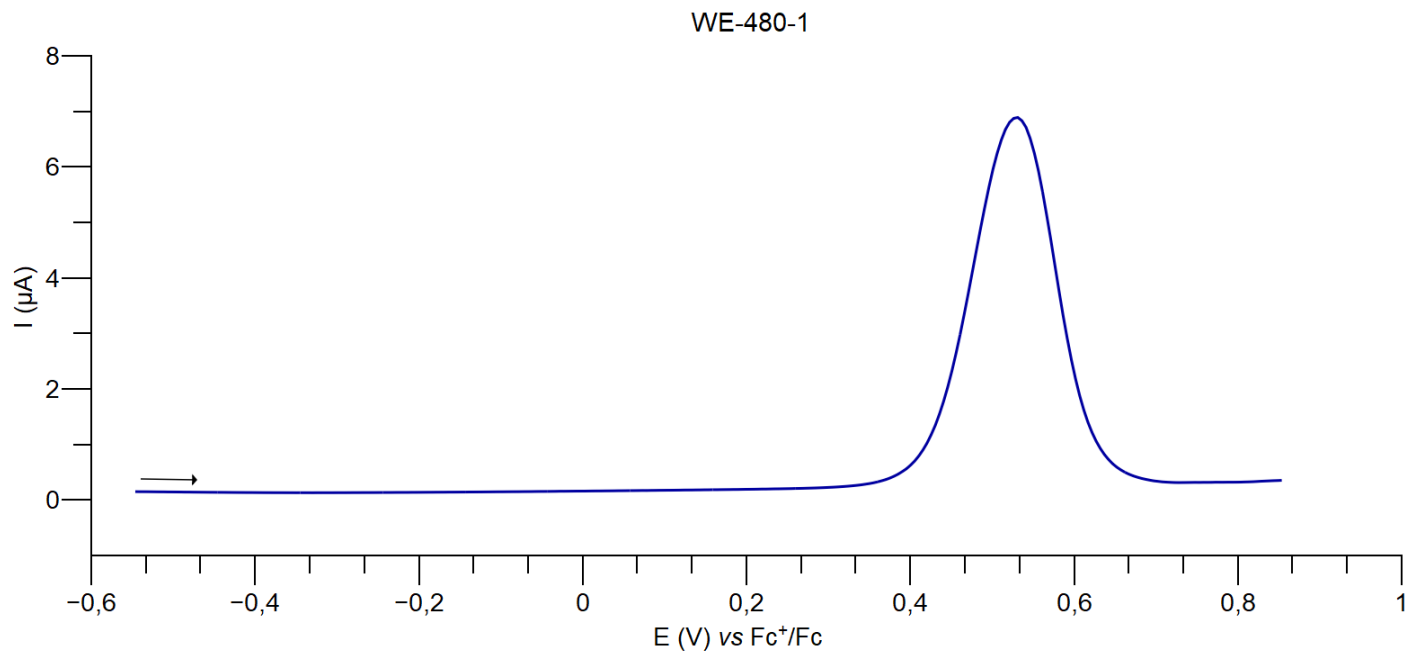


2-Iodo-*O*-isopropyl-5-(trimethylsilyl)ferrocenesulfonate (5)

Cyclic voltammetry

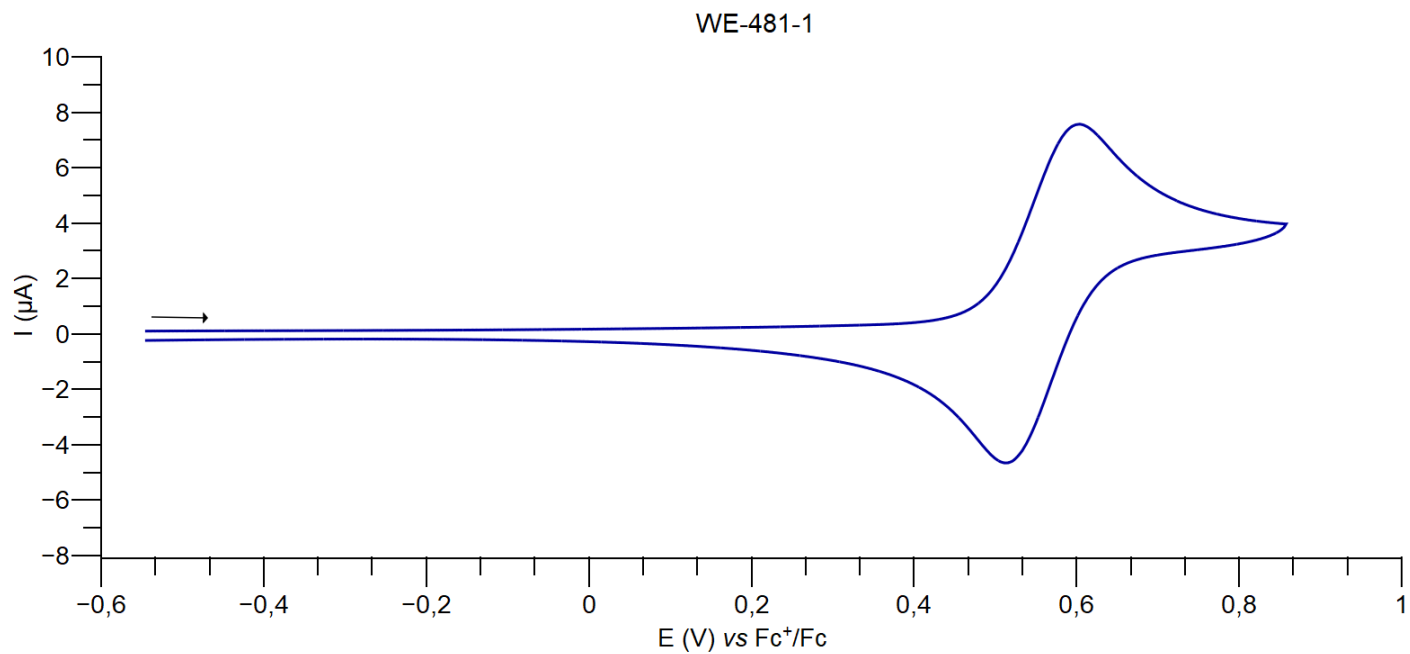


Differential pulse voltammetry

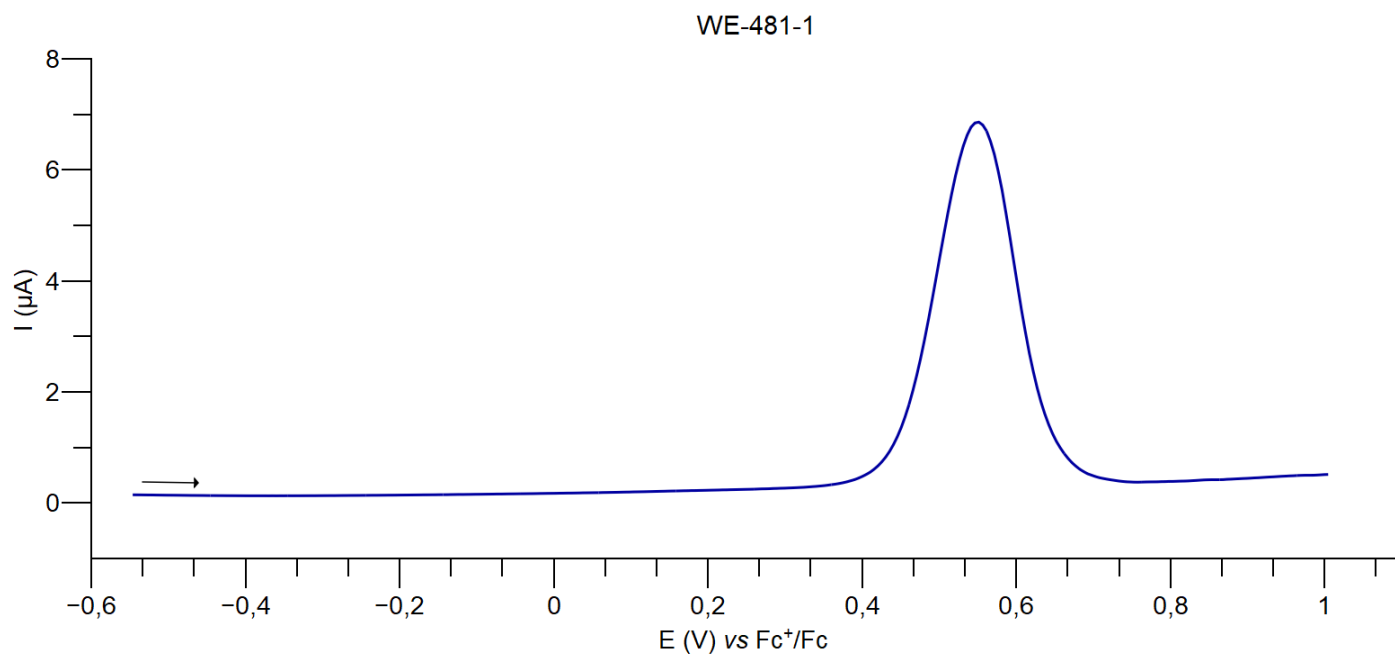


4-Iodo-*O*-isopropyl-2-(trimethylsilyl)ferrocenesulfonate (6)

Cyclic voltammetry

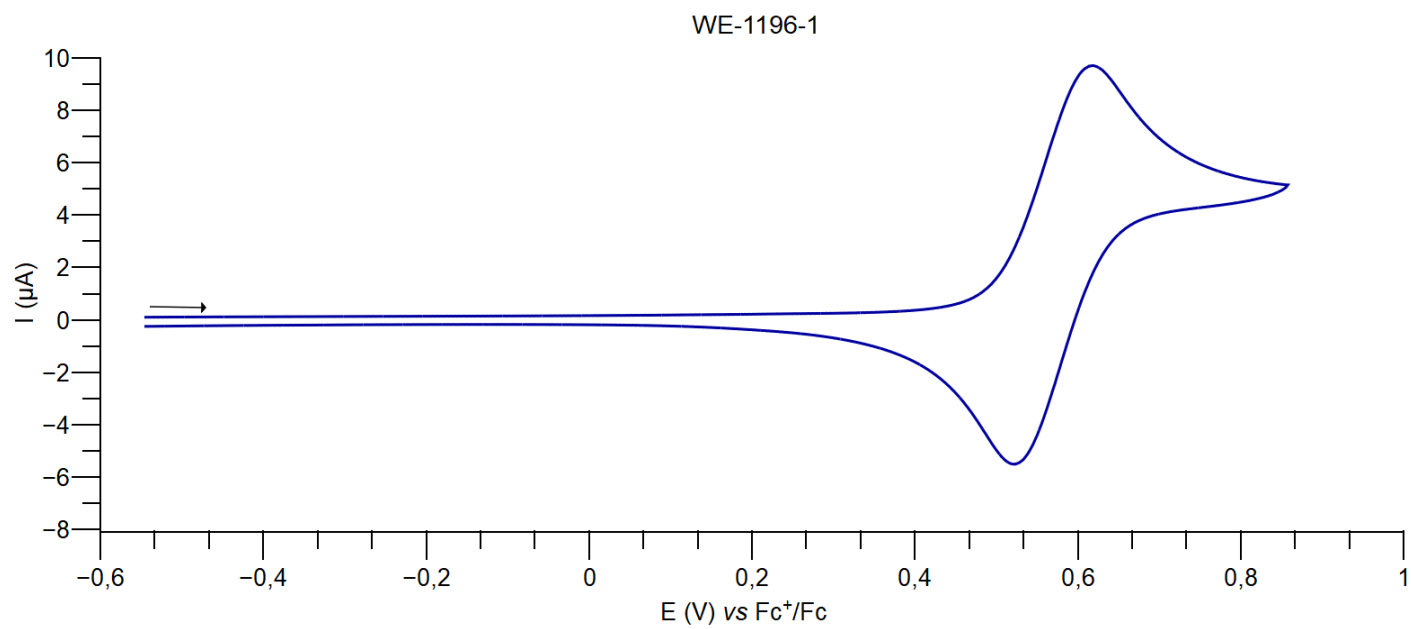


Differential pulse voltammetry

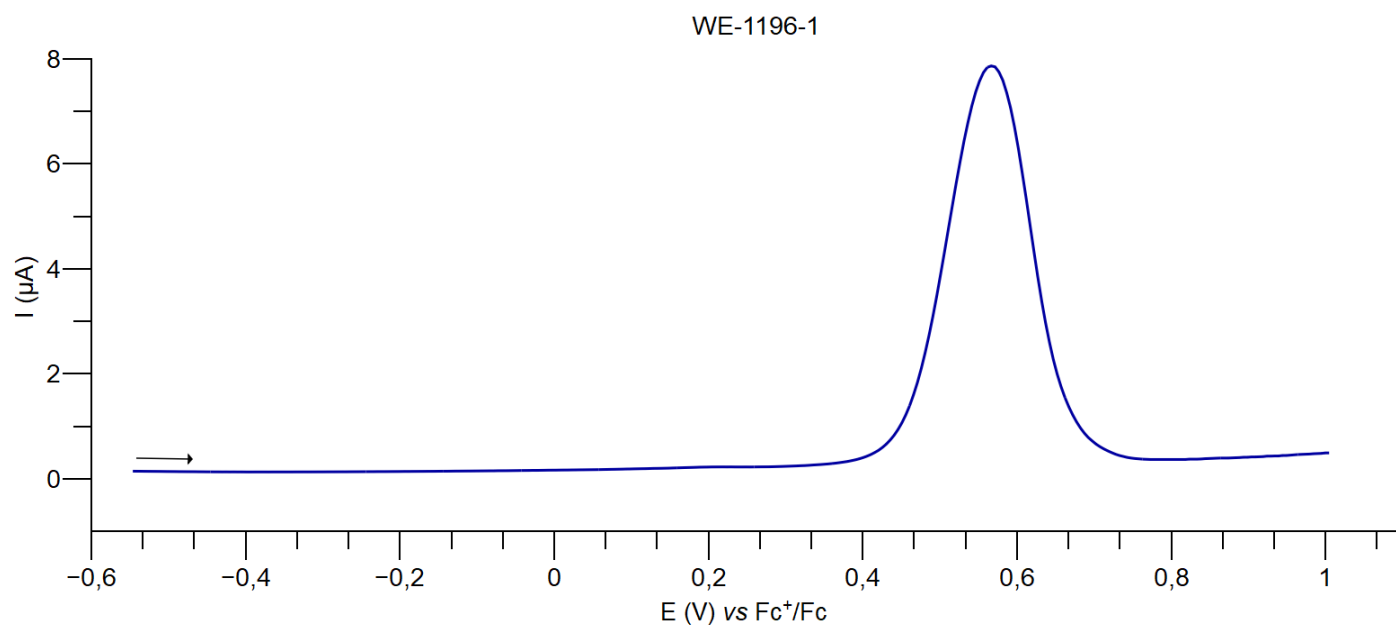


3-Iodo-*O*-isopropylferrocenesulfonate (8)

Cyclic voltammetry

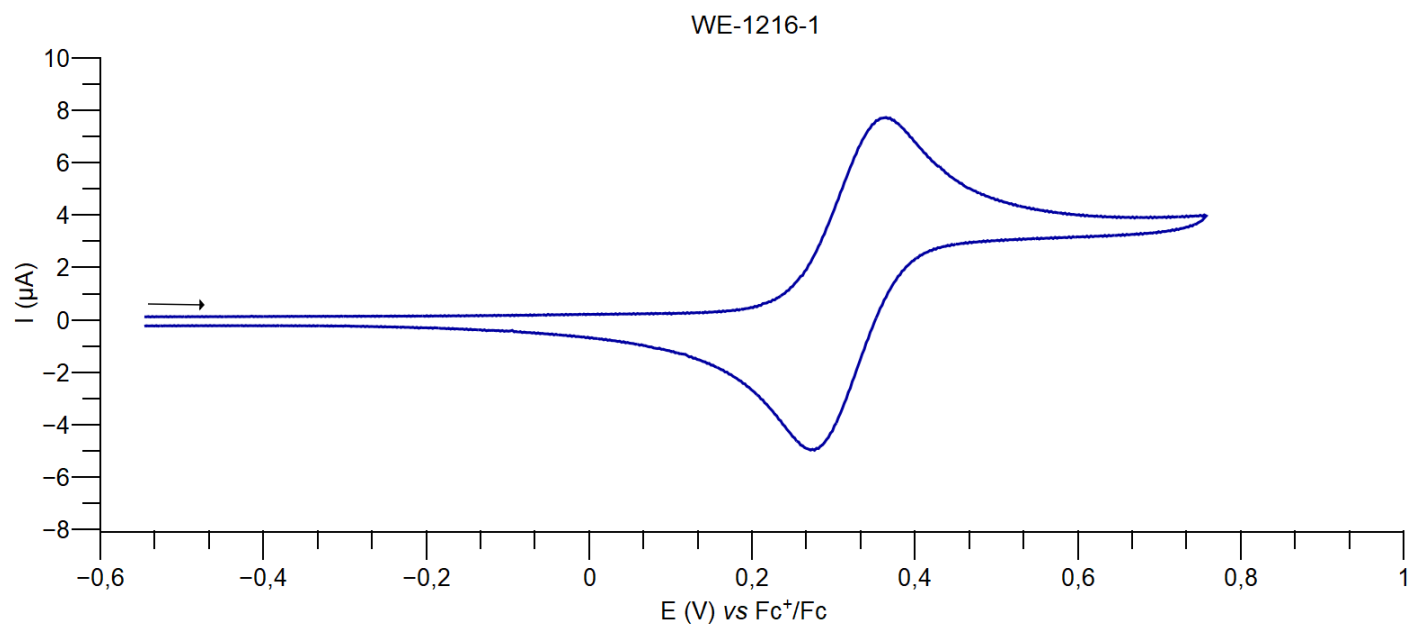


Differential pulse voltammetry

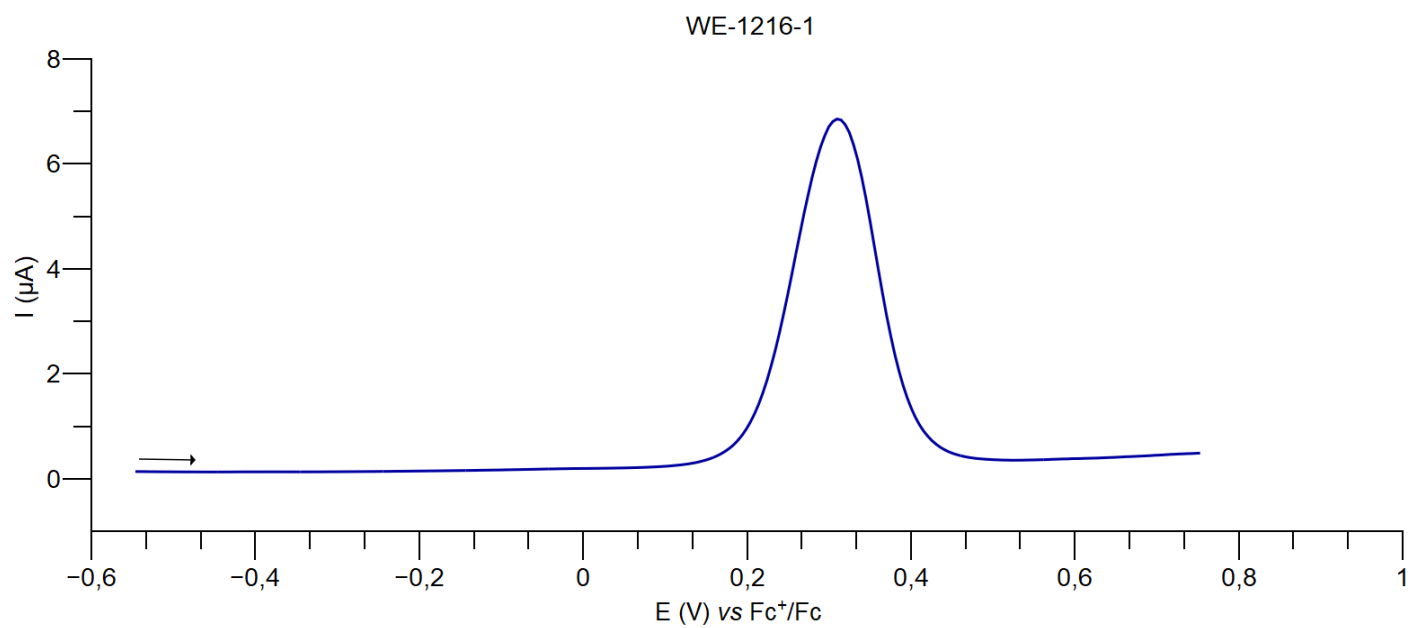


N,N-Dimethylferrocenesulfonamide

Cyclic voltammetry

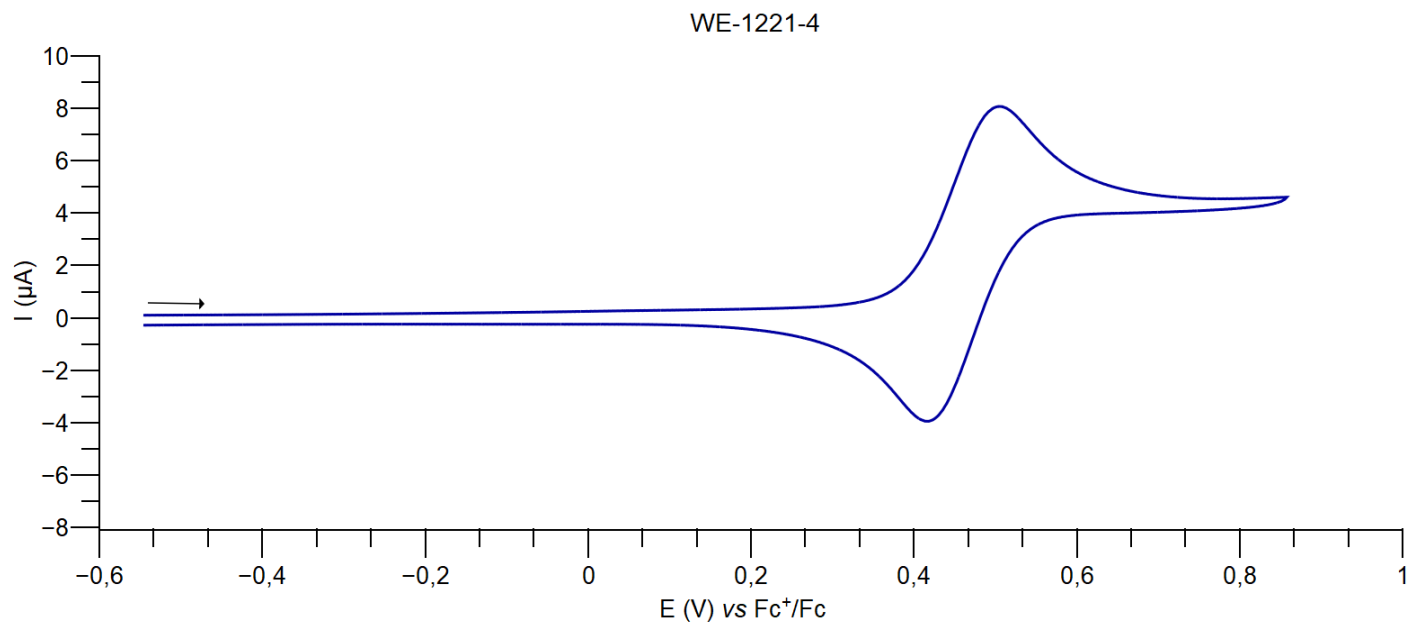


Differential pulse voltammetry

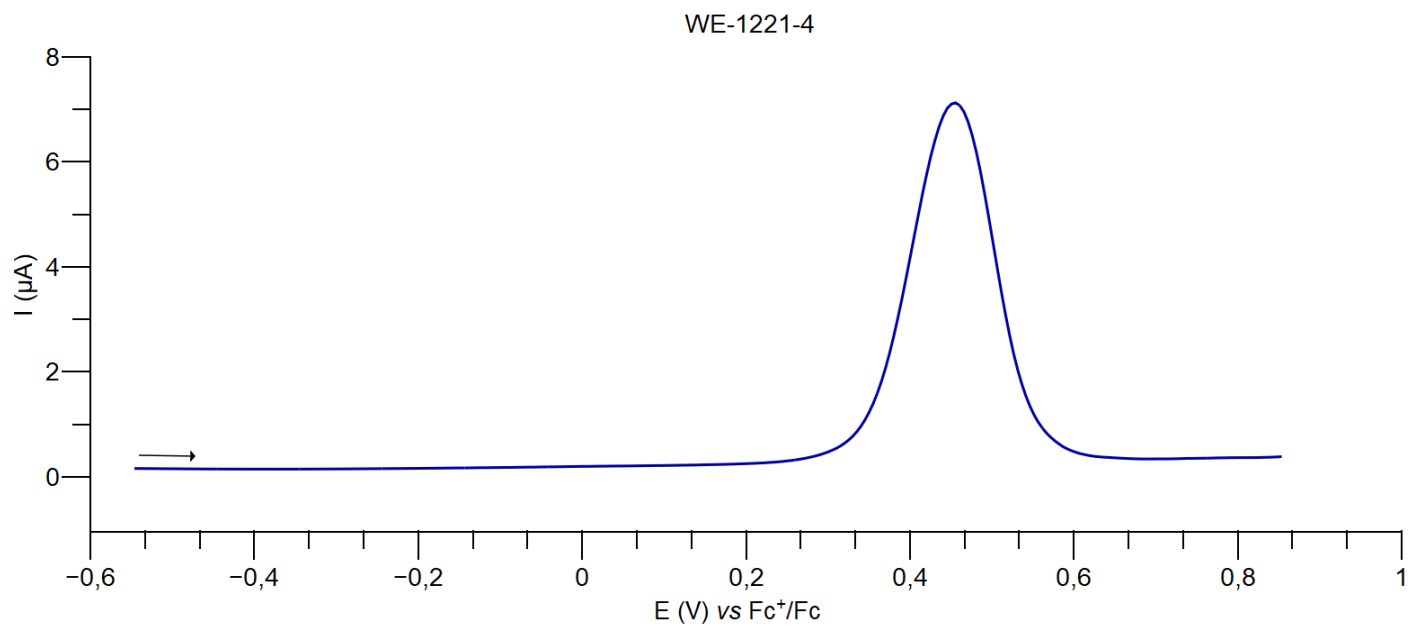


2-Iodo-*N,N*-dimethylferrocenesulfonamide

Cyclic voltammetry

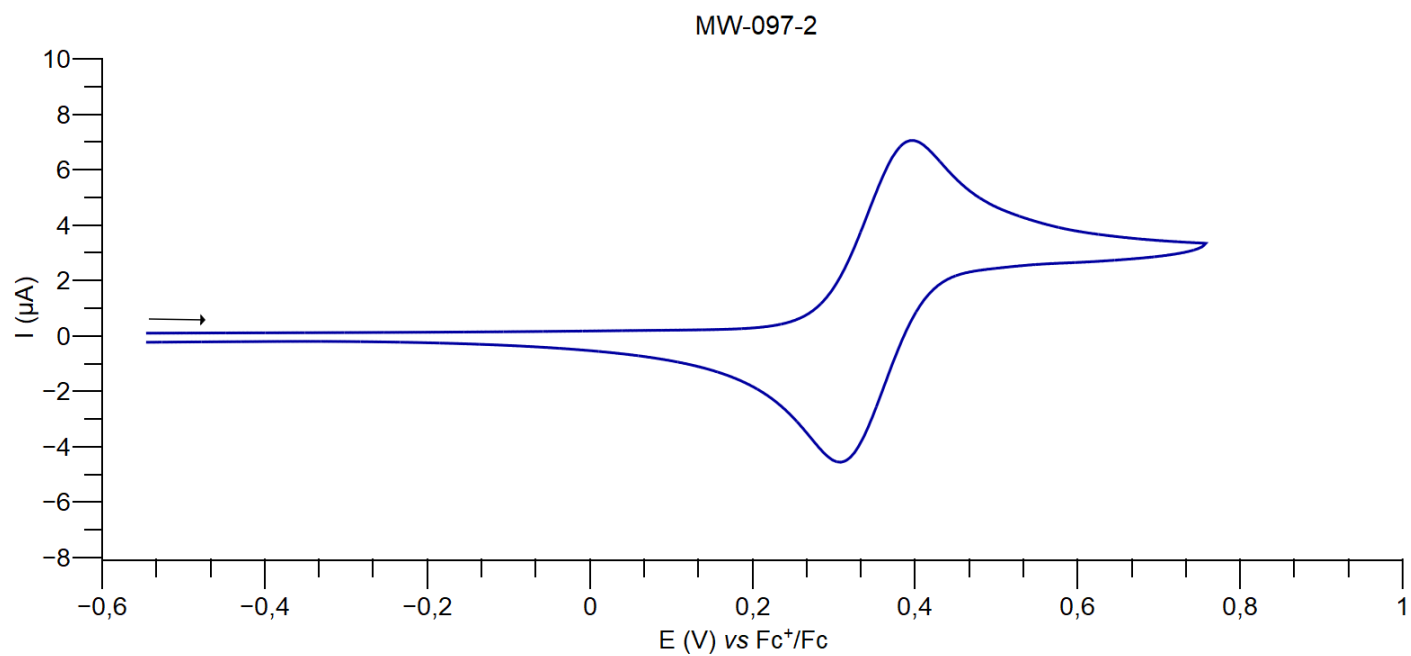


Differential pulse voltammetry

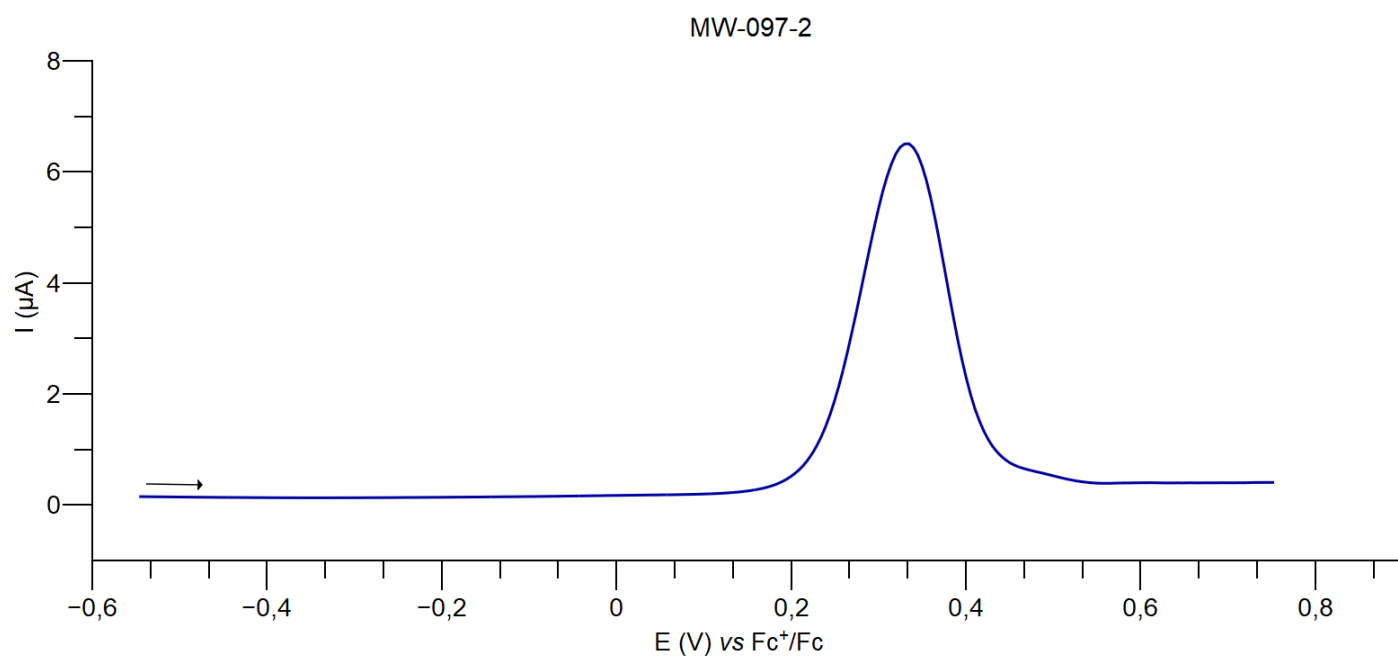


N,N-Dimethyl-2-(trimethylsilyl)ferrocenesulfonamide

Cyclic voltammetry

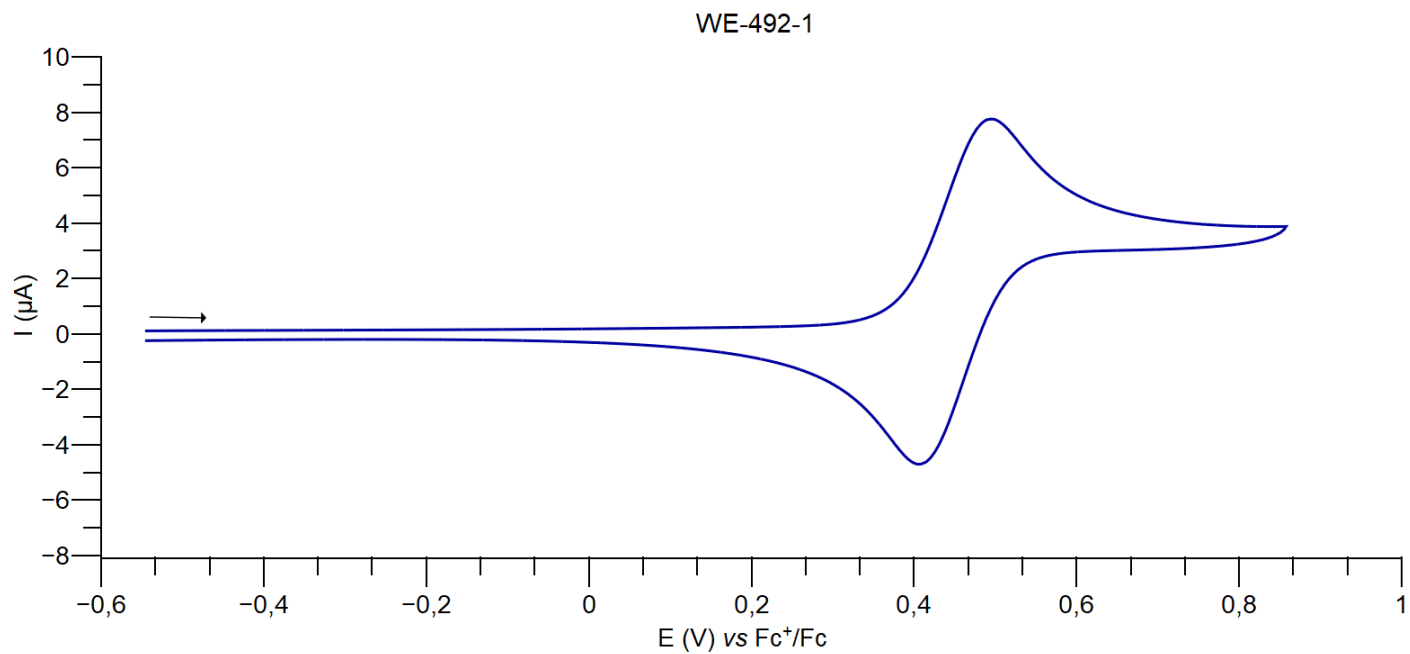


Differential pulse voltammetry

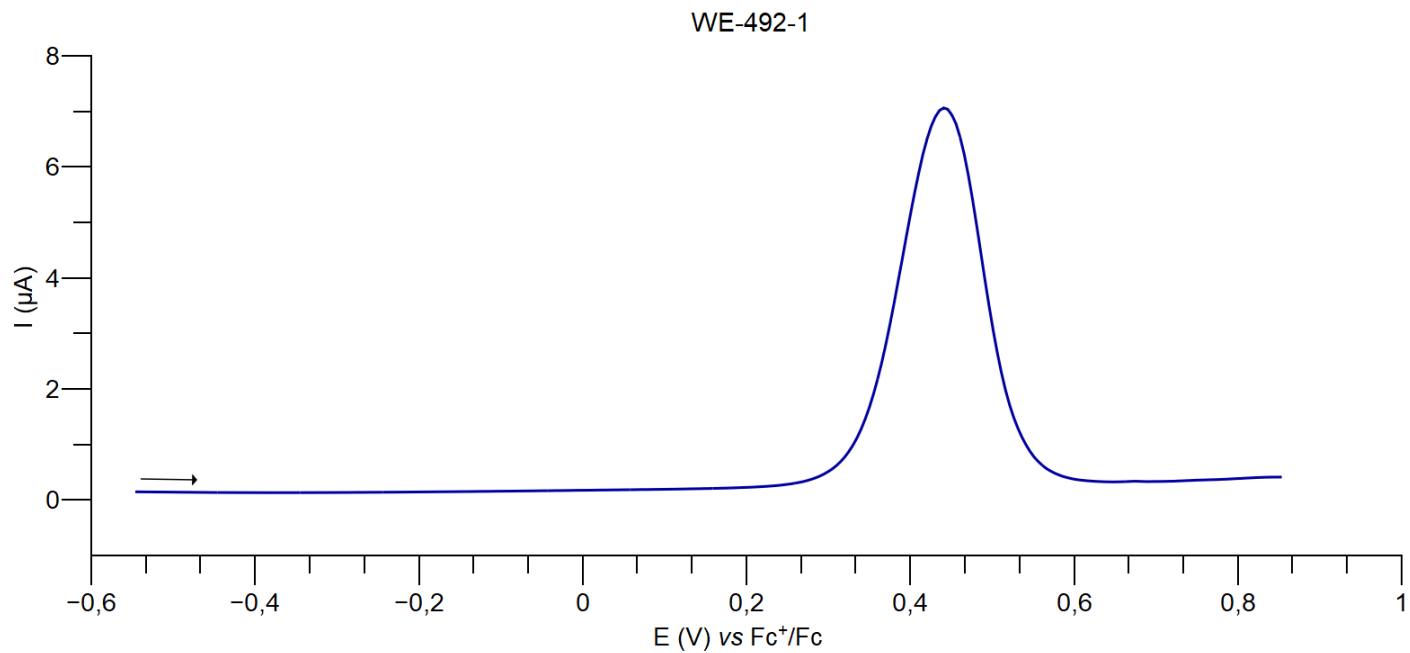


2-Iodo-*N,N*-dimethyl-5-(trimethylsilyl)ferrocenesulfonamide

Cyclic voltammetry

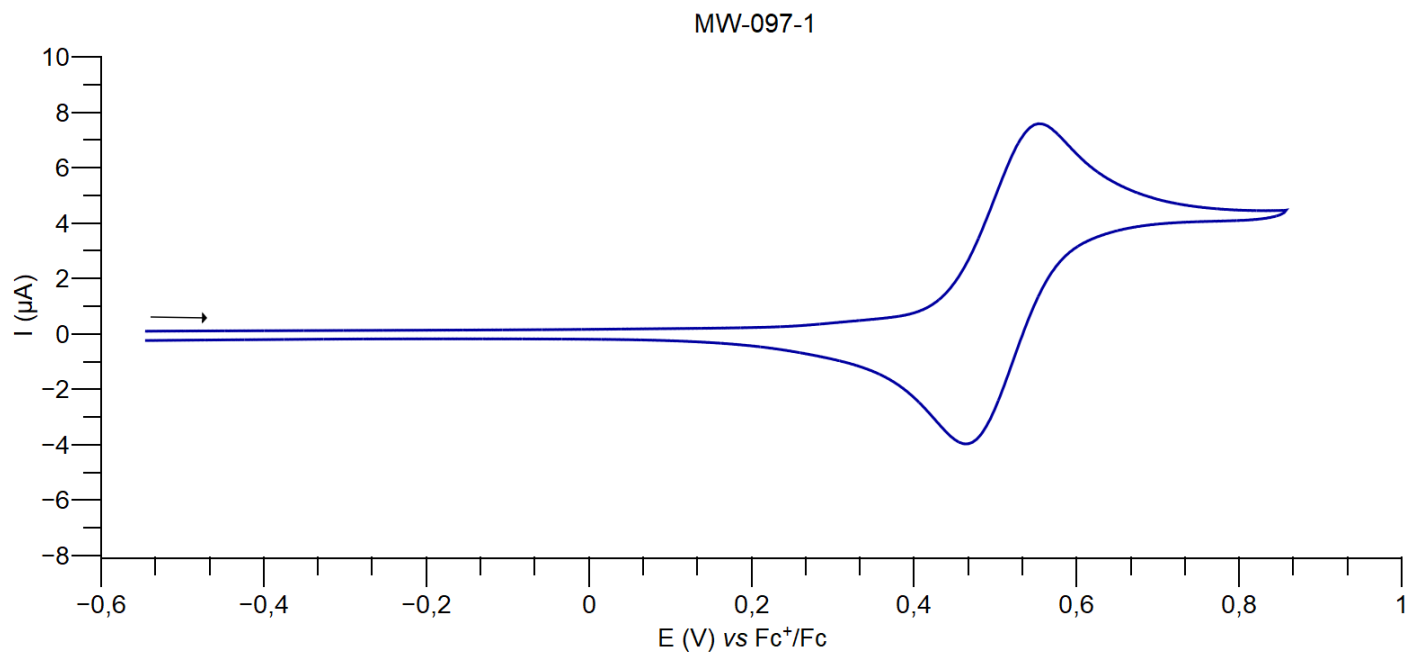


Differential pulse voltammetry

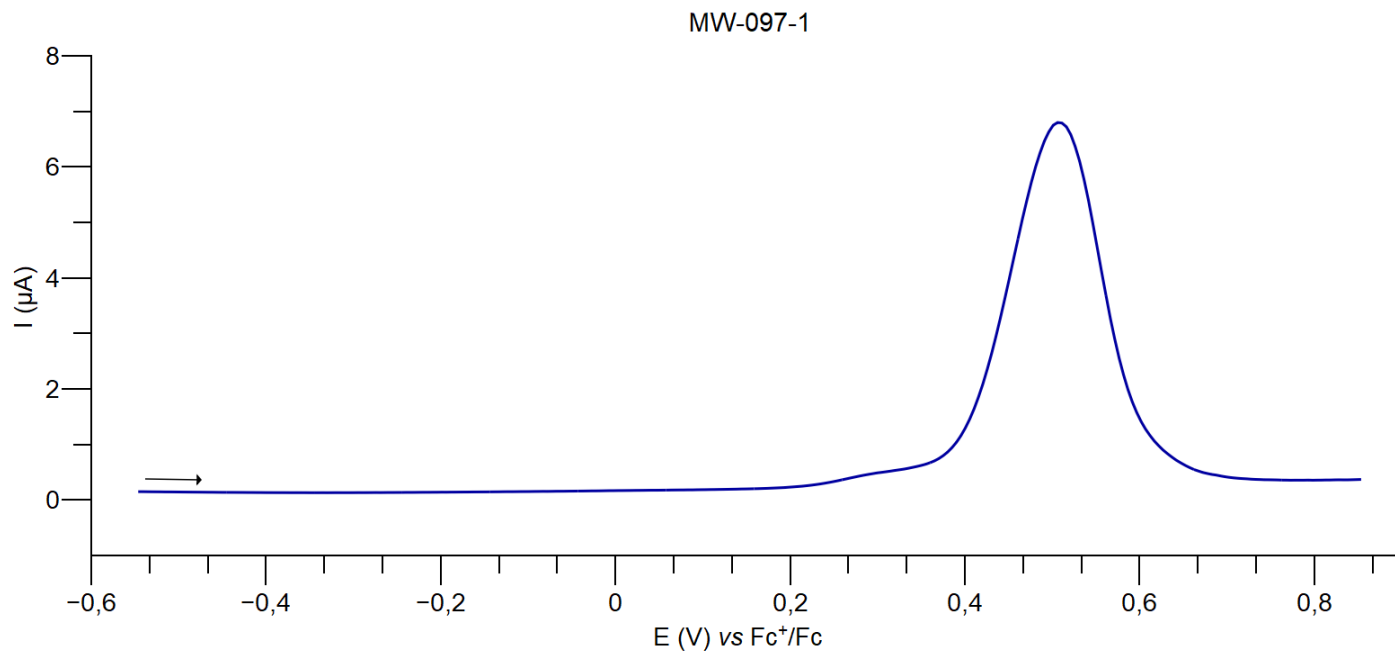


4-Iodo-*N,N*-dimethyl-2-(trimethylsilyl)ferrocenesulfonamide

Cyclic voltammetry

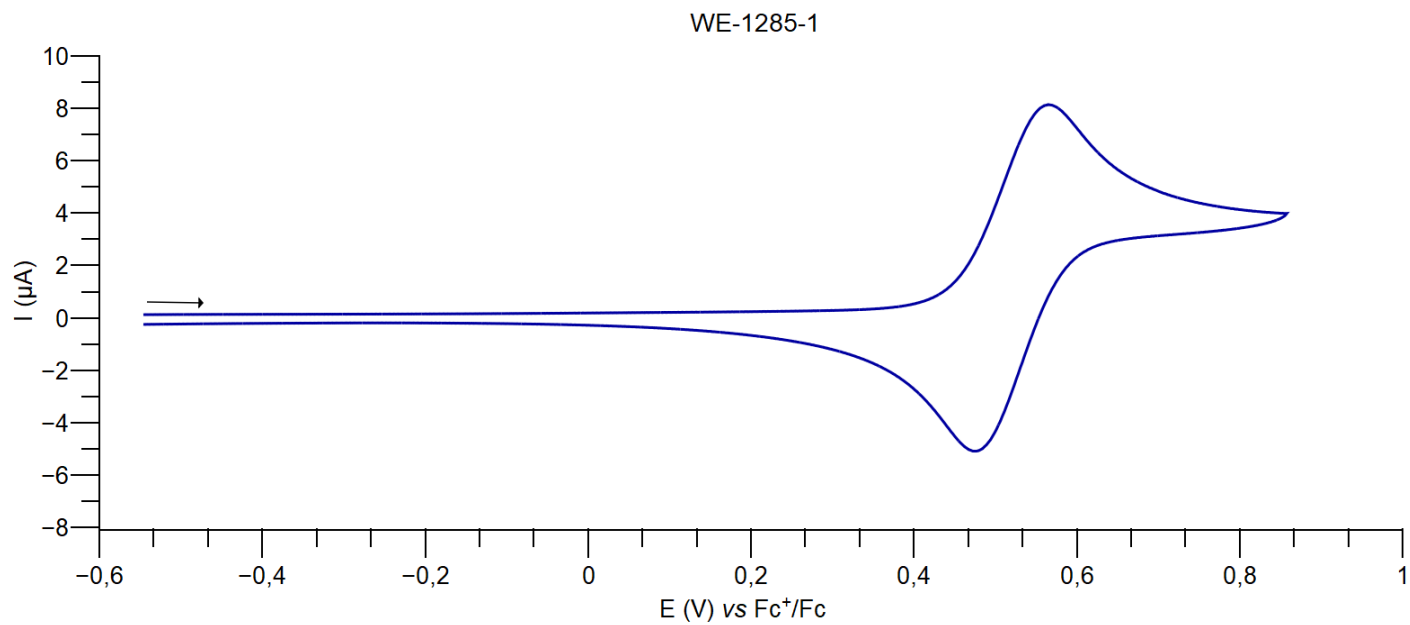


Differential pulse voltammetry

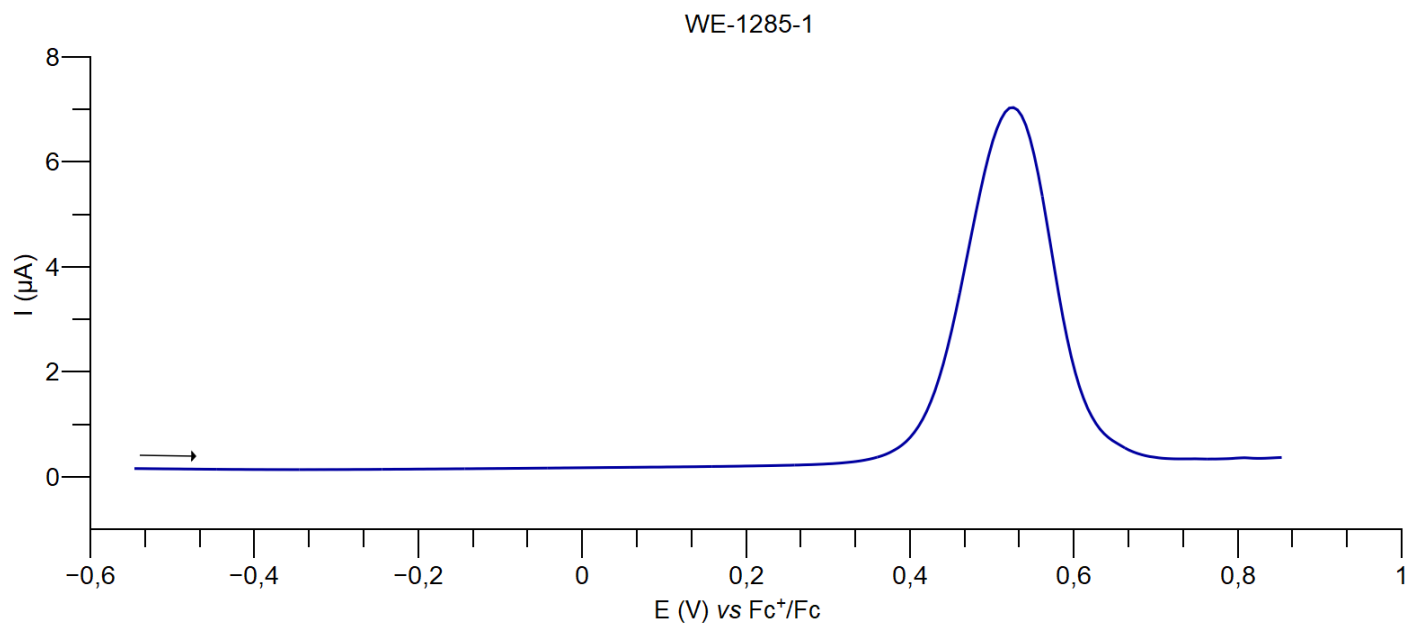


3-Iodo-*N,N*-dimethylferrocenesulfonamide

Cyclic voltammetry

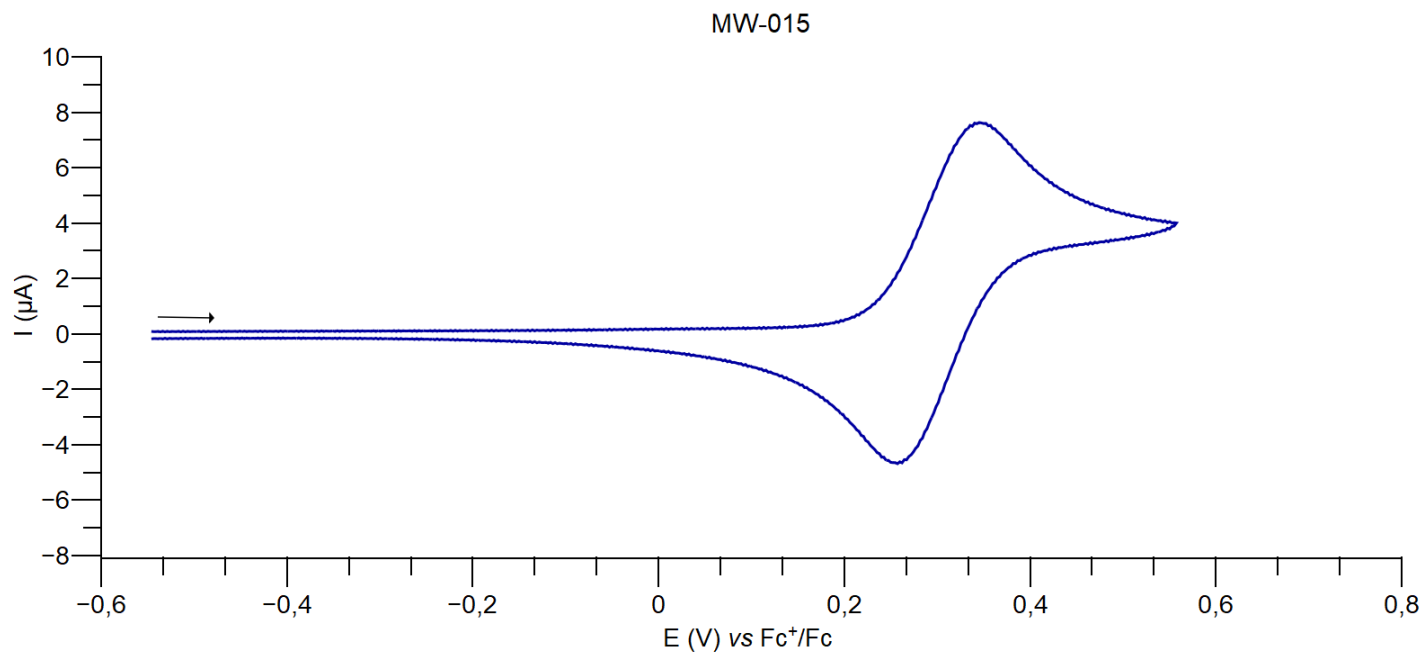


Differential pulse voltammetry

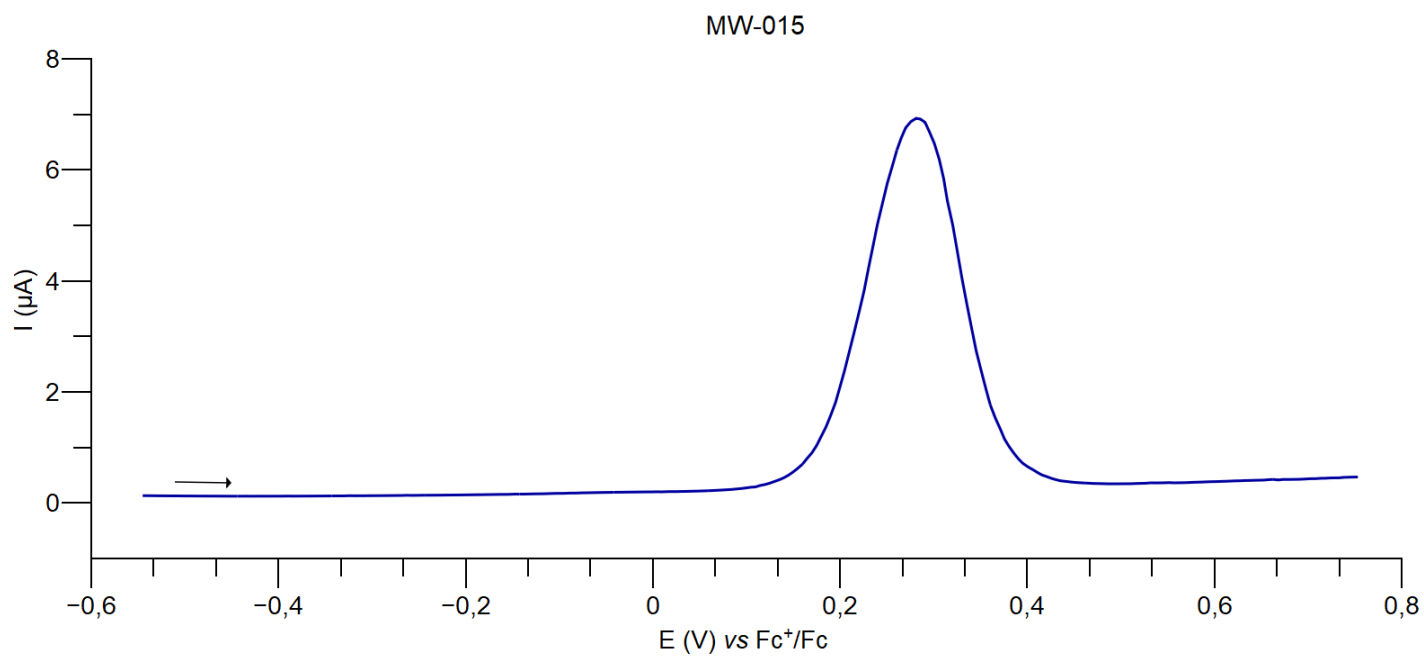


(*N*-pyrrolidino)sulfonylferrocene

Cyclic voltammetry

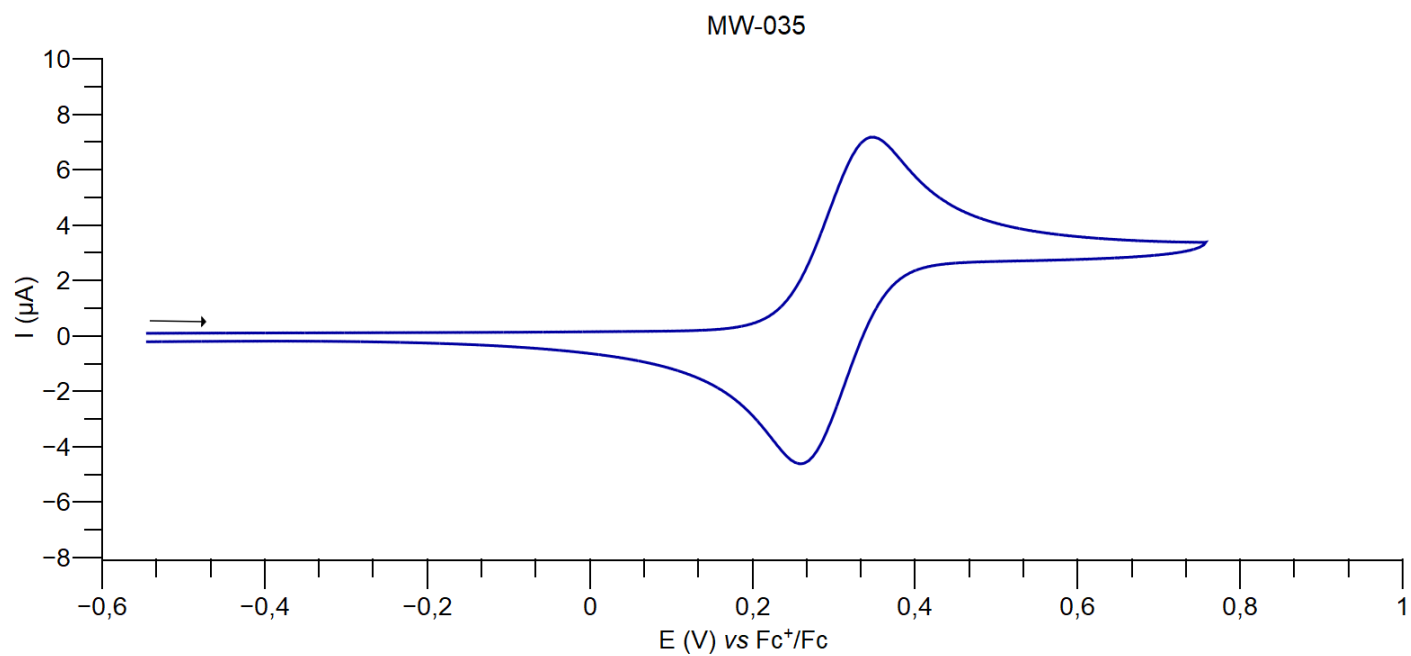


Differential pulse voltammetry

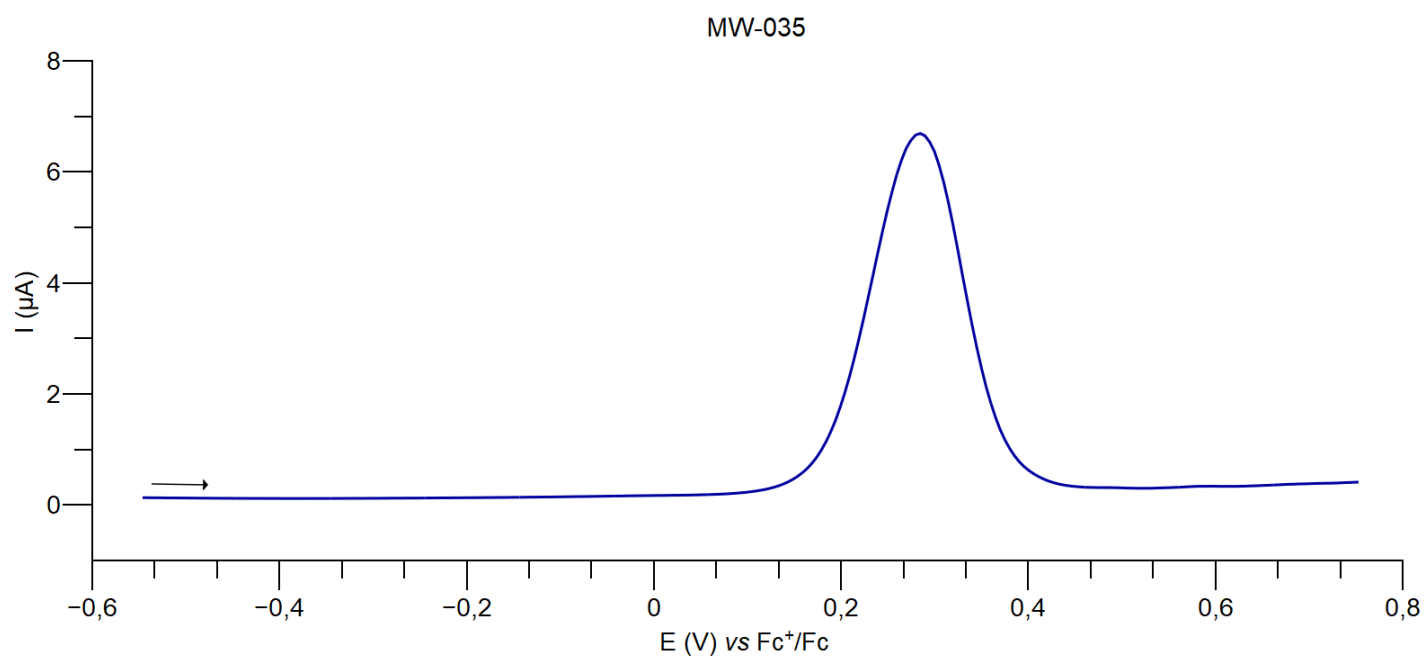


1-(*N*-pyrrolidino)sulfonyl-2-(trimethylsilyl)ferrocene

Cyclic voltammetry




Differential pulse voltammetry



Full tables of electrochemical properties

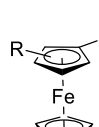
(potentials values relative to FcH/FcH⁺)

Table S1. Electrochemical properties of ferrocenesulfonates.

Substrate	R	Cpd	E_{pa}	E_{pc}	$E_{1/2}$	$i_{pa}/i_{pc}^{[a]}$	$i_{pa}/i_{pc}^{[b]}$	$\Delta E^{[c]}$ (mV)
	H	1	0.48	0.38	0.43	0.85	0.99	90
	2-I	3	0.59	0.50	0.55	0.81	0.94	90
	2-SiMe ₃	4	0.46	0.37	0.41	0.95	1.10	85
	2-I-5-SiMe ₃	5	0.58	0.49	0.53	0.83	0.96	85
	4-I-2-SiMe ₃	6	0.60	0.51	0.55	0.80	0.93	80
	3-I	8	0.62	0.52	0.57	0.83	0.96	90

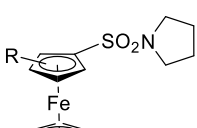
[a] Measured value. [b] Corrected value, taking i_{pa}/i_{pc} for ferrocene (0.86) equal to 1. [c] $E_{pa} - E_{pc}$.

Table S2. Electrochemical properties of *N,N*-dimethylferrocenesulfonamides.

Substrate	R	E_{pa}	E_{pc}	$E_{1/2}$	$i_{pa}/i_{pc}^{[a]}$	$i_{pa}/i_{pc}^{[b]}$	$\Delta E^{[c]}$ (mV)
	H	0.36	0.27	0.31	0.90	1.04	80
	2-I	0.50	0.42	0.45	0.90	1.02	85
	2-SiMe ₃	0.39	0.31	0.33	0.88	1.02	95
	2-I-5-SiMe ₃	0.49	0.41	0.44	0.87	1.01	80
	4-I-2-SiMe ₃	0.55	0.46	0.51	0.90	1.04	85
	3-I	0.56	0.47	0.52	0.84	0.97	90

[a] Measured value. [b] Corrected value, taking i_{pa}/i_{pc} for ferrocene (0.86) equal to 1. [c] $E_{pa} - E_{pc}$.

Table S3. Electrochemical properties of (*N*-pyrrolidino)sulfonylferrocenes.

Substrate	R	E_{pa}	E_{pc}	$E_{1/2}$	$i_{pa}/i_{pc}^{[a]}$	$i_{pa}/i_{pc}^{[b]}$	$\Delta E^{[c]}$ (mV)
	H	0.34	0.25	0.27	0.87	1.01	90
	2-I	-	-	-	-	-	-
	2-SiMe ₃	0.42	0.26	0.28	0.77	0.89	90
	2-I-5-SiMe ₃	-	-	-	-	-	-
	4-I-2-SiMe ₃	-	-	-	-	-	-
	3-I	-	-	-	-	-	-

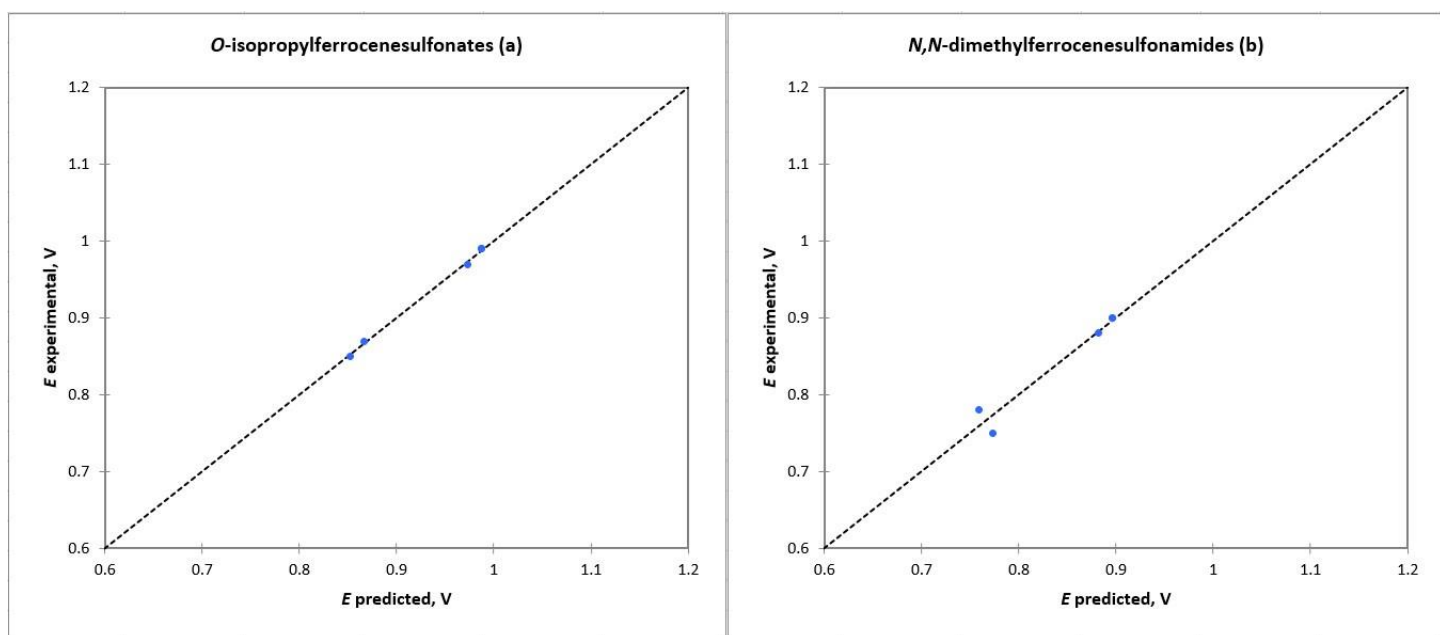
[a] Measured value. [b] Corrected value, taking i_{pa}/i_{pc} for ferrocene (0.86) equal to 1. [c] $E_{pa} - E_{pc}$.

Hammett constant values

Table S4. Hammett constant values¹ tried for description of electrochemical properties.

R	σ_m	σ_p	F	R
H	0.00	0.00	0.00	0.00
I	0.35	0.18	0.42	-0.24
SiMe ₃	-0.04	-0.07	0.01	-0.08

Figure S1. Plot of experimental vs. predicted half-wave potential values for (a) *O*-isopropylferrocenesulfonates and (b) *N,N*-dimethylferrocenesulfonamides



Reference

1. C. Hansch, A. Leo, R. W. Taft, *Chem. Rev.* **1991**, *91*, 165-195..